XXV CONFERENCE
ON ORGANOMETALLIC CHEMISTRY

EuCOMC XXV

SEP 4th - 8th 2023

ALCALÁ DE HENARES / MADRID-SPAIN

www.eucomc2023.com

ABSTRACTS BOOK

Universidad de Alcalá

EuChemS
European Chemical Society

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ABSTRACTS

WELCOME

Dear Colleagues and Friends,

The EUCOMC Organizing Committee welcomes you to the **25th EuCOMC Conference on Organometallic Chemistry** in Alcalá de Henares after the on-line edition for the previous EuCOMC meeting.

In this meeting we will celebrate the full diversity of Organometallic Chemistry research in Europe. This event brings together our wide and active European Organometallic Community and is a perfect forum for established and early-career researchers to present their contributions. We have an outstanding selection of invited speakers, as well as a remarkable number of oral presentations reporting innovative and cutting-edge research results. The program also includes flash and poster contributions of the highest quality. We hope that this exciting schedule will promote lively discussions and new networking opportunities.

As part of this meeting, we will also have a dedicated session to celebrate the anniversary of the Nobel Prize awarded to Profs. G. Wilkinson and E. O. Fischer for their pioneering work in Organometallic Chemistry. As part of this, Prof. H. Werner, winner of the first edition of the Fischer-Wilkinson Prize for Organometallic Chemistry, will deliver a Plenary lecture.

On behalf of the Organizing Committee, we hope you enjoy the conference and that it will consolidate and inspire the future of Organometallic Chemistry in Europe and beyond.

Marta E. G. Mosquera

Chair of the Organizing Committee

COMITTEES

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CONFERENCE VENUE

Monday 4th and Friday 8th of September

Rectorate of the University of Alcala (Colegio de San Ildefonso)

This historic building was built between the sixteenth and seventeenth centuries and is the current seat of the rectorate of the University of Alcalá. It is located in the **center of the city** and is easily accessible on foot from almost every hotel in the city. In addition, most city bus lines stop near this building, which is also easily accessible from the central train station of Alcalá de Henares (10-15 min on foot).

Coordinates
40.482746, -3.362950

Transportation (see map)

City bus lines: L1A, L1B, L2, L3, L5, L6, L7, L11
Train station: Alcalá de Henares (central)

Google maps link

https://goo.gl/maps/ar4aeczjY4WAh4oXA

Address
Pl. de San Diego, s/n
28801 Alcalá de Henares
(Spain)

Tuesday 5th, Wednesday 6th and Thursday 7th of September

School of Engineering (Escuela Politécnica Superior)

The School of Engineering building is located on the **outer campus of the University of Alcalá**, which is about 4 km from the city center. This campus focuses on scientific and technological studies. City bus line 2 directly connects the city center with the School. City bus lines 1A, 1B, and 3, as well as some other regional lines, also connect the city to the external campus. The campus has a train station (line C-2) which is located about 15-20 minutes walk from the polytechnic building.

Coordinates
40.513037, -3.348631

Transportation (see map)

City bus lines: L1A, L1B, L2, L3
Train station: Universidad (line C-2)

Google maps link

https://goo.gl/maps/mfLhifmNy2LaPC8A9

Address
Campus Universitario
Ctra. Madrid-Barcelona km, 33,6
28805 Alcalá de Henares,
(Spain)

City map

Escuela Politécnica Superior
(School of Engineering)
Main EuCOMC venue

Science and
Technology Campus

Colegio de San Ildefonso
(Rectorate of the University of Alcala)
Special venue for
Monday 4th and
Friday 8th of September

Historic city center

TRANSPORTATION

TO THE EXTERNAL CAMPUS

Special bus transportation

On September 5, 6 and 7 there will be a special free shuttle bus service from the main hotels in the city to the **School of Engineering** building. The schedule of this service will be adjusted to the start and end of the conference sessions. The following table details the departure schedule for the morning service to the congress venue. Stops will be close to all major hotels in the city (see map of hotels and stops on previous page). Return buses will depart after the end of the daily program, following the same route.

Hotels (see map for numb.)	Nearest bus stop (blue circle on the map)		Bus Departure
1, 2	Plaza Puerta de Aguadores	https://goo.gl/maps/ocY36FyQ1Qm4o7B79	8:15
3, 4, 5	Vía Complutense 34 (access to the Parking San Lucas)	https://goo.gl/maps/C4JgMs1CtQwAthRQ8	8:15
6, 7	Hotel PCM Forum Alcalá	https://goo.gl/maps/NXqVmxRKKxDfZr2F8	8:00
8	Hotel Cisneros	https://goo.gl/maps/GGod1i62WCA56yWk9	8:00
9	Hotel AC Alcalá de Henares	https://goo.gl/maps/rqHJXpp7i4wbso9y5	8:35
10, 11	Glorieta Fernando VII (La Garena - train station)	https://goo.gl/maps/nVgiZ7ENwmgd4uG18	7:50
12, 13	Hotel Ibis budget - Alcalá	https://goo.gl/maps/J6HB2oLDEemNCYED9	8:35

City bus, train and on foot

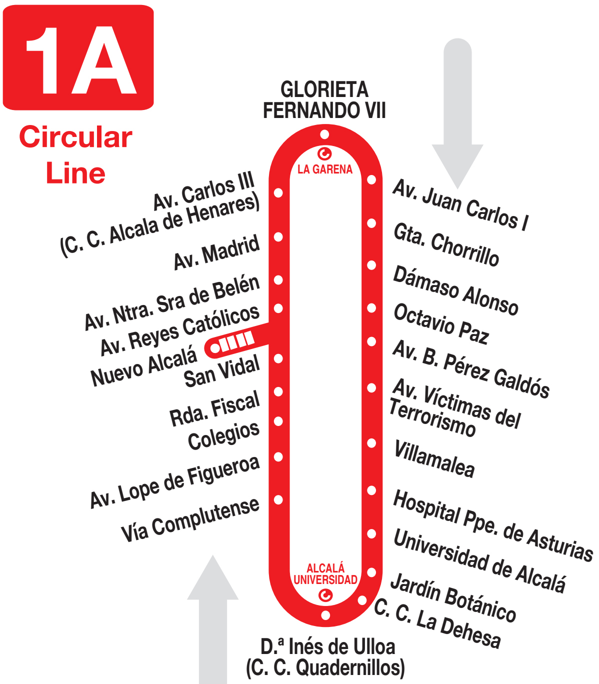
Alcalá de Henares has a modern bus service that connects the different areas of the city. The outer campus of the University of Alcalá, where the School of Engineering is located, is served by four urban bus lines (L1A, L1B, L2 and L3). In addition, several intercity bus lines connect the external campus with the city of Madrid (line 227) and with other points in the region. The external campus train station is connected to Madrid and to the other two stations in the city (Alcalá de Henares - central and La Garena) with commuter trains every 15-30 minutes.

The following table shows the recommended means of public transportation to access the School of Engineering from the most important hotels in the city.

Hotels (see map for numbering)	Recommended public transportation (estimated door-to-door travel time)	Other alternatives
1, 2, 3, 4, 5, 6, 7	City bus L2 (25-40 min, see map)	City bus L1B/L1A, and L3
8	City bus L1B (towards the congress venue), City bus L1A (towards the hotel) (40-60 min)	--
9	City bus L1A (towards the congress venue), City bus L1B (towards the hotel)	Walking (30 - 40 min)
10, 11	**Option 1:** Train line C-2 or C-8 to Universidad (freq. 15-30 min, travel 8 min) -> walk (15-20 min) **Option 2:** Train line C-2, C-7 or C-8 to Alcalá (freq. <10 min, travel 4 min) -> City bus L2 (20-25 min)	City bus L11
12, 13	City bus L1B (towards the congress venue), City bus L1A (towards the hotel) (40-60 min)	Walking (30 min)

CITY BUS INFORMATION

Fares: 1.30 € (single trip, to be paid in cash to the bus driver); 4,20 € (10-trip card, purchase at tobacco shops).



Hours: 6 a.m. to 11:45 p.m., every 15 min.

NEXT BUS ARRIVALS

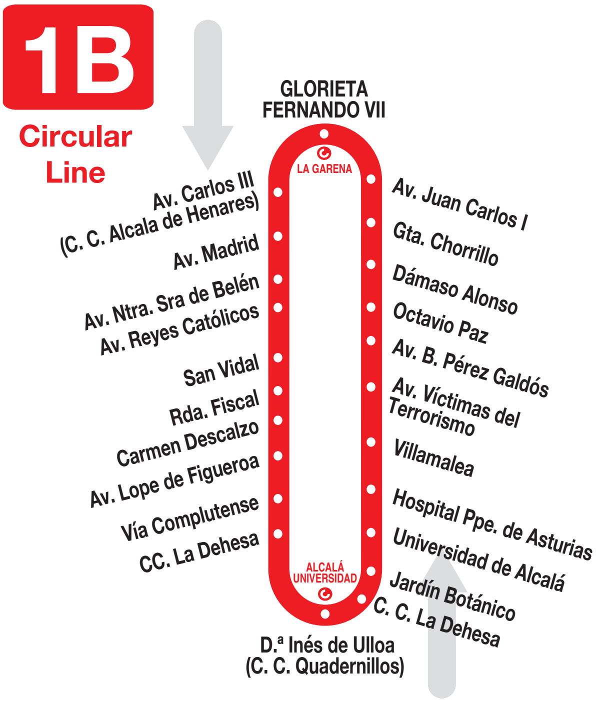
Line 1A

https://moovitapp.com/madrid-21/lines/1a/3418732/4608783/en

NEXT BUS ARRIVALS

Line 1B

https://moovitapp.com/madrid-21/lines/1b/3418733/4608784/en



Hours: 6 a.m. to 11:45 p.m., every 15 min.

Hours: 6 a.m. to 12 p.m., every 15 min.

Line 2 (Sta. Ana -> Universidad)

https://moovitapp.com/madrid-21/lines/2/749958/3287886/en

Line 2 (Universidad ->Sta. Ana)

https://moovitapp.com/madrid-21/lines/2/749958/3287887/en

TRAIN INFORMATION

Fare for trips between train stations in the city of Alcalá de Henares: 1.70 € (single trip). To Madrid: 3.40 € (single trip). Tickets are purchased at the train station.

PRACTICAL INFORMATION

WIFI ACCESS

Free Wifi access is available for all event attendees. Please use the following codes:

Username: EUCOMC
Password: e-UAH-2828

In addition, members of institutions associated to the **Eduroam network** have access to this service in both congress venues.

COFFEES AND LUNCH

There will be a free coffee service during the conference breaks. From Tuesday to Thursday, a free lunch service will be served at noon in the restaurant of the School of Engineering Building.

SOCIAL ACTIVITIES

Guided visit to the historic buildings of the University of Alcalá

Tuesday, 5th September 2023, 19:30 h

The University of Alcalá was founded in 1499 by Cardinal Cisneros, reaching a preeminent place among the Spanish universities during the sixteenth and seventeenth centuries. It subsequently entered a period of decline until 1836, when the government decreed its transfer to Madrid. The current University of Alcalá was re-founded in the 1970s.

In recent years, an important work of rehabilitation of the historical heritage of this university, which was declared a World Heritage Site by UNESCO in 1998, has been carried out. In this guided tour you will be able to see some of the most representative buildings of our University.

Meeting point: Entrance door to the Colegio de San Ildefonso building (Rectorate of the Univ.).

Google maps link

https://goo.gl/maps/N9NqGyTnxxTV4c3i7

Excursions

Wednesday, 6th September 2023, 16:00 h

Visits to the following places have been organized for Wednesday afternoon:

- Winery Finca Rio Negro (Cogolludo, Guadalajara) with wine tasting.
- Prado Museum.

Both visits require prior registration and the payment of a fee of 20,00 € per person. Buses will leave from the door of the Polytechnic building between 16:00 and 16:15 h. The return is scheduled for approximately 20:00 h.

More information

Winery Finca Rio Negro	Museo del Prado
https://www.fincarionegro.com/en/welcome-finca-rio-negro-2019/	https://www.museodelprado.es/en

Gala Dinner

Thursday, 7th September 2023, 20:30 h

The dinner will take place at the Parador de Alcalá de Henares (Calle Colegios, 8. 28804 Alcalá de Henares). All participants who have registered for the dinner will receive a personal invitation to attend the dinner. It is VERY IMPORTANT that you keep it and bring it to the dinner to identify yourselves and to know the chosen menu, meat or fish.

Punctuality is requested

Parador de Alcalá de Henares, Calle Colegios 8, 28804 Alcalá de Henares

Google maps link

https://goo.gl/maps/CkAMJhK6fBcGBkuw5

PROGRAMME

Monday, 4th September 2023

15:00 – 17:30	**Registration**
17:00 – 17:30	**Opening Ceremony**
	Salón de Actos (Colegio de San Ildefonso)
	Chair: Martin Albrecht - University of Bern
17:30 – 18:30	PL1: **Polly L. Arnold** University of California and Berkeley National Laboratory (USA) Transuranic Organometallics
18:30 – 19:00	YPL1: **Mónica H. Pérez-Temprano** Institute of Chemical Research of Catalonia (Spain) Deciphering Mechanisms to Design Better Catalytic Reactions
19:00 – 21:00	**Welcome Reception**

Tuesday, 5th September 2023

	Salón de Actos (School of Engineering)
	Chair: Agustí Lledós - Universitat Autònoma de Barcelona
9:00 – 10:00	PL2: **Christophe Copéret** ETH Zürich (Switzerland) NMR Chemical Shifts Beyond Numbers: From Understanding Electronic Structures to Reactivity Descriptor
10:00 – 10:30	YPL2: **Ruth L. Webster** University of Bath (UK) Mechanistic Insight into Iron(salen) Catalysed Reactions
10:30 – 11:00	**Coffee Break**

Tuesday, 5th September 2023

	Salón de Actos	**Room A4**
	Chair: F. J. Fernández-Álvarez ISQCH-Universidad de Zaragoza	**Chair:** Ana Petronilho ITQB-Universidade Nova de Lisboa
11:00 – 11:30	KN01: **Belén Martín-Matute** Stockholm University (Sweden) Selective Construction Carbon-Heteroatom Bonds Mediated by Cp*Ir(III) Complexes	KN03: **Miquel Costas** Institut de Química Computacional I Catalisi (Spain) Site and Enantioselective Oxidation of Strong C-H Bonds with Bioinspired Catalysts
11:30 – 12:00	KN02: **Martin Kotora** Charles University (Czech Republic) Catalytic Cyclotrimerization Route to [n]Helical Indenofluorenes and Transformations Thereof	KN04: **Bas de Bruin** University of Amsterdam (The Netherlands) Synthetic Applications of Metalloradical Catalysis
12:00 – 12:15	OC01: **Satoshi Takebayashi** Okinawa Institute of Science and Technology (Japan) Synthesis of a 21-electron cobaltocene derivative	OC05: **M. Carmen Nicasio** Universidad de Sevilla (Spain) Bis-phosphine Ni(0) Complexes and Catalytic Applications in Alkyne Cycloaddition Reactions
12:15 – 12:30	OC02: **C. Gunnar Werncke** Philipps-University Marburg (Germany) Isolation of Radical Anions via 3d-Metal Complexation or Cation Encapsulation	OC06: **Miguel Baya** CSIC-Universidad de Zaragoza (Spain) The Trifluoromethyl Silver(III) Moiety as a Platform for Highly Unusual Organometallic Compounds
12:30 – 12:45	OC03: **Max García-Melchor** Trinity College Dublin (Ireland) Towards Catalyst Design and Databases for Molecular OER Catalysis	OC07: **Vincenzo Passarelli** ISQCH, CSIC-Universidad de Zaragoza (Spain) Iridium complexes based on aminophosphano ligands: synthesis and application in catalysis
12:45 – 13:00	OC04: **Jesús M. Martínez-Ilarduya** Universidad de Valladolid (Spain) Problematic Ar^F-Alkynyl Stille Coupling: From Partial Success to Efficient Solutions, via Mechanistic Understanding of the Hidden Complexity	OC08: **Gregori Ujaque** Universitat Autònoma de Barcelona (Spain) Encapsulation and Reactivity Inside Metallocages
13:00 – 14:30	**Lunch**	

Tuesday, 5th September 2023

Salón de Actos (School of Engineering)

Chair: Jesús J. Pérez-Torrente - ISQCH-Universidad de Zaragoza

14:30 – 15:30 PL3: **Alois Fürstner**
Max-Planck-Institut für Kohlenforschung (Germany)
A New Reactivity Paradigm: trans-Hydrogenation, gem-Hydrogenation, and trans-Hydrometalation of Alkynes

15:30 – 16:00 YPL3: **Josep Cornella** EurJIC Lecture
Max-Planck-Institut für Kohlenforschung (Germany)
Tales on Bismuth Redox Catalysis

16:00 – 16:15 OC09: **Axel Straube**
Wiley-VCH GmbH (Germany)
Chemistry Europe - Who We Are and What We Do

16:15 – 16:45 **Coffee Break**

	Salón de Actos	**Room A4**	**Room A1**
	Chair: Terrance Hadlington Tech. Univ. München	**Chair:** Cristina García-Yebra Universidad de Alcalá	**Chair:** Alberto Hernán-Gómez Universidad de Alcalá
16:45 – 17:00	OC10: **Cristina Tubaro** Università degli Studi di Padova (Italy) Catalysis with NHC-Au(I) Complexes in Confined Space: Resorcinarene Capsule and Monolayer Protected Nanoparticles	OC12: **Christina Erken** University of Helsinki (Finland) Elucidating the Catalytic CO_2 Reduction to CO	OC14: **Christopher J. Whiteoak** Universidad de Alcalá (Spain) Exploring the Potential of Catalysts based on the Heavier Group 13 Elements for Cyclic Carbonate Synthesis
17:00 – 17:15	OC11: **Marina Uzelac** University of Bath (UK) A New Family of Alkali-metal Manganates and their Role in Catalysing C-C Bond Formation via Oxidative Homocoupling	OC13: **Ola F. Wendt** Lund University (Sweden) Pincer Iridium Hydride Complexes: Mechanisms for Acceptorless Dehydrogenation of Alcohols	OC15: **Felipe Garcia** Universidad de Oviedo (Spain) Mechanochemical Synthesis of Compounds and Complexes
17:15 – 17:45	FP01-06 **Flash Presentations** Session A	FP07-12 **Flash Presentations** Session B	FP13-17 **Flash Presentations** Session C

17:45 – 19:00 PA01-79: **Poster Session A** and FP01-17: **Flash Poster Session A**

19:00 **End of Scientific Programme**

Tuesday, 5th September 2023

19:30	**Guided visit to the historic buildings of the University of Alcalá.** Meeting point: Entrance door to the Colegio de San Ildefonso building (Rectorate of the Univ.).

Wednesday, 6th September 2023

	Salón de Actos (School of Engineering)	
	Chair: M. Concepción Gimeno - ISQCH - CSIC-Universidad de Zaragoza	
9:00 – 10:00	PL4: **Prof. Angela Casini** Technical University of Munich Gold Chemistry in Water: From Catalysis to Medicine	
	Salón de Actos	**Room A4**
	Chair: Rafael Gómez - Univ. de Alcalá	**Chair:** M. Carmen Nicasio - Univ. de Sevilla
10:00 – 10:30	KN05: **Maria Contel** City University of New York (USA) Gold-based Antibody Drug Conjugates as Targeted Breast Cancer Therapeutic Agents	KN06: **Jun Okuda** RWTH Aachen University (Germany) Dihydrogen Activation by Cationic Hydrides of Alkaline Earth Metals and Zinc
10:30 – 11:00	**Coffee Break**	
11:00 – 11:30	KN07: **Patrick McGowan** University of Leeds (UK) Bis-picolinamide Metal Dihalide Complexes with a cis to trans Isomer Switch, Triggering High Potency and Cancer Cell Selectivity	KN09: **Janusz Lewiński** Warsaw University of Technology (Poland) From Organometallic Molecular Systems to Functional Materials: Solution and Solid-state Methodologies
11:30 – 12:00	KN08: **Sylvestre Bonnet** Leiden University (The Netherlands) In Vivo Metallophilic Self-Assembly of Cyclometalated Metallodrugs for Anticancer Phototherapy	KN10: **Alfonso Grassi** University of Salerno (Italy) Hydroamination of Alkynes Catalyzed by Gold Nanoparticles: A Sustainable and Effective Approach to the Synthesis of N-heterocyclic Compounds
12:00 – 12:15	OC16: **Alice Johnson** Sheffield Hallam University (UK) Gold Carboxylate Complexes as Dual Action Anticancer Agents	OC20: **Fabio Ragaini** Università di Milano (Italy) Mechanistic Studies of the Palladium/Phenanthroline Catalysed Reductive Cyclization of Nitroarenes by CO to give N-Heterocycles

Wednesday, 6th September 2023

12:15 - 12:30	OC17: **Thomas Cailly** Normandie University (France) Gold(I) Mediated Radio-Iododecarboxylation Toward Applications in Nuclear Medicine	OC21: **Esaïe Reusser** Universität Bern (Switzerland) Electronically Flexible Pyridylidene Amide Ligands for Palladium-catalyzed α-arylation of Ketones
12:30 - 12:45	OC18: **Damian Plazuk** University of Lodz (Poland) Synthesis and Biological Activity of Organometallic Hybrids with Selected Tubulin-binding Anticancer Agents	OC22: **Dominik Munz** Saarland University (Germany) Palladium and Gold Nitrenes
12:45 - 13:00	OC19: **Jose Ruiz** Universidad de Murcia (Spain) Ir(III)-coumarin Conjugates as Promising Photosensitizers in Both Normoxia and Hypoxia	OC23: **Jaime Martín** University of Zurich (Switzerland) Unlocking Cyclometalation: A New Entry to Cyclometalated Gold(III) Complexes via Catalytic Rhodium to Gold(III) Transmetalation
13:00 - 14:30	**Lunch**	

	Salón de Actos	**Room A4**
	Chair: Eva Royo - Universidad de Alcalá	**Chair:** Eva Hevia - Universität Bern
14:30 - 15:00	KN11: **M. Concepcion Gimeno** CSIC-Universidad de Zaragoza (Spain) Investigating the Biological Properties of Gold Carbene Complexes	KN12: **Jeanne Crassous** University of Rennes (France) Combining Helicenes with Transition Metals or Lanthanides for Chirality-Related Properties
15:00 - 15:15	OC24: **Ana Petronilho** Instituto de Tecnologia Química e Biológica António Xavier (Portugal) Metal Complexes Bearing Uracil Ligands: Synthesis and Applications	OC28: **Antonio Rodríguez-Delgado** Universidad de Sevilla-CSIC (Spain) Bis(imino)pyridine-based Ligand Reactivity in Main Group Alkyls Complexes
15:15 - 15:30	OC25: **Arkaitz Correa** University of the Basque Country (Spain) C-H Functionalization of Tyr-Containing Peptides	OC29: **Alberto Hernán-Gómez** Universidad de Alcalá (Spain) Titanium (IV) and (III) Bis(O-Phenylenediamido) Compounds: A Story of Structural Variety and CO2 Functionalization

Wednesday, 6th September 2023

15:30 – 15:45	OC26: **Marta Martínez-Alonso** Universidad de Burgos (Spain) The Effect of Antibody Conjugation Over a Cyclometalated Ru(II) Complex as Targeted NIR Photosensitizers for PDT	OC30: **Terrance J. Hadlington** TU Munich (Germany) On the Single-Centre Ambiphile Concept
15:45 – 16:00	OC27: **Laura Rodríguez** Universitat de Barcelona (Spain) Room Temperature Phosphorescence Au(I) and Pt(II) Supramolecular Organometallic Assemblies	OC31: **Meera Mehta** University of Manchester (UK) Phosphorus Clusters in Small Molecule Activation and Catalysis
16:00	**End of Scientific Programme**	
16:00	**Optional Excursions**	

Thursday, 7th September 2023

	Salón de Actos (School of Engineering)
	Chair: Robert Mulvey - University of Strathclyde
9:00 – 10:00	PL5: **Sjoerd Harder** Friedrich-Alexander Universität Erlangen-Nürnberg Low-Valent Alkaline-Earth Metal Complexes for Bond Activation and Catalysis
10:00 – 10:30	YPL4: **Tatiana Besset** CNRS (France) Sustainable Tools to Access Fluorinated Molecules by C-H Bond Functionalization
10:30 – 11:00	**Coffee Break**

	Salón de Actos	**Room A4**
	Chair: Christopher J. Whiteoak - Univ. Alcalá	**Chair:** Laura Rodríguez - Univ. de Barcelona
11:00 – 11:30	KN13: **Aleš Ružička** University of Pardubice (Czech Republic) Cationic Polyhedral Heteroboranes - Fact or Fiction?	KN15: **Elena Fernández** Universidad Rovira i Virgili (Spain) Borylalkyde Copper(I) Species for Selective Electrophilic Trapping in Advanced Synthetic Protocols

Thursday, 7th September 2023

11:30 – 12:00	KN14: **Arjan W. Kleij** Institute of Chemical Research of Catalonia (Spain) Catalytic Creation of Sterically Challenging Stereogenic Centers: Concepts and Mechanistic Insights	KN16: **Mark Crimmin** Imperial College London (UK) Activation of C-H Bonds with Fe-Al Heterometallic Complexes

	Salón de Actos	**Room A4**
12:00 – 12:15	OC32: **Jarl Ivar van der Vlugt** University Oldenburg (Germany) Iron-catalyzed $C(sp^3)$-H Amination	OC36: **Antonio J. Martínez-Martínez** University of Huelva (Spain) Bimetallic Synergy with Low-Valent Group 13 Main Group Systems for Small Molecule Reactivity
12:15 – 12:30	OC33: **Montserrat Gómez** Université Toulouse III – Paul Sabatier (France) Cu(II)-mediated Functionalization of C-H Bonds: Synthesis of Heterocycles and Kinetico-mechanistic Studies	OC37: **Clément Camp** CNRS / CPE-Lyon / UCBL (France) Heterobimetallic Complexes for Cooperative Reactivity
12:30 – 12:45	OC34: **Adrian B. Chaplin** University of Warwick (UK) Stability and C–H Bond Activation Reactions of Palladium(I) and Platinum(I) Metalloradicals: Carbon-to-Metal H-atom Transfer and Cyclometallation by a Radical Rebound Mechanism	OC38: **Govindarajan Ramadoss** Okinawa Institute of Science and Technology Graduate University (Japan) Pt/Main Group Bimetallic Complexes: Small Molecule Activation and Metal-metal Cooperative Transmetalation
12:45 – 13:00	OC35: **Luis F. Sánchez-Barba** Universidad Rey Juan Carlos (Spain) Highly Efficient and Versatile Heterobimetallic Al-M(II) Catalysts for Sustainable Processes	OC39: **Montserrat Diéguez** Universitat Rovira i Virgili (Spain) Synergistic Approaches to Catalyst Design for the Sustainable Production of Challenging Enantioenriched Compounds
13:00 – 14:30	**Lunch**	

Salón de Actos (School of Engineering)

Chair: Jun Okuda - RWTH Aachen University

14:30 – 15:30 PL6: **Manfred Bochmann** ______________________ **Prof. Pascual Royo Session**

University of East Anglia (UK)

Gold(III) Chemistry: Surprise, Intrigue, Mechanisms

Thursday, 7th September 2023

	Salón de Actos	**Room A4**
	Prof. Pascual Royo Session (cont.)	**Chair:** Marta E. G. Mosquera - Univ. de Alcalá
15:30 – 16:00	**KN17: Beatriz Royo** Instituto de Tecnologia Química e Biológica António Xavier (Portugal) The Impact of N-Heterocyclic and Mesoionic Carbenes in Manganese Catalysis	**KN18: Simon Aldridge** University of Oxford (UK) Unleashing New Patterns of Reactivity with Electron Rich Main Group Compounds
16:00 – 16:15	**OC40: Rinaldo Poli** LCC CNRS Toulouse (France) Revisiting $[FeEt_2(bipy)_2]^{n+}$ (n = 0, 1, 2): a Radically New View	**OC41: Miguel A. Huertos** Universidad del País Vasco Chiral-at-Rhodium Complex Bearing Si, N Ligands
16:15 – 16:45	**Coffee Break**	

	Salón de Actos	**Room A4**	**Room A1**
	Chair: Sara Cembellín U. Complutense de Madrid	**Chair:** Juan M. Asensio IFP Energies nouvelles	**Chair:** Marina Uzelac University of Bath
16:45 – 17:00	**OC42: Fabio Juliá** University of Murcia (Spain) Copper-catalysed Amination of Alkyl Iodides Enabled by Halogen-atom Transfer	**OC44: Blanca Martin-Vaca** Université Toulouse 3 Paul Sabatier (France) Metal-Ligand Cooperation with Group 10 Metals and Hydrosilylation	**OC46: Thomas M. Horsley Downie** University of Regensburg (Germany) Copper(I)-Mediated Functionalisation of White Phosphorus
17:00 – 17:15	**OC43: Gabriel Menendez Rodriguez** University of Perugia (Italy) Electrochemical Hydrogen Production Catalysed by Cp*Co(III) Complexes	**OC45: Petr Štěpnička** Charles University (Czech Republic) Hybrid Ferrocene Ligands Combining Phosphine and Stibine Donor Groups	**OC47: Itzel Guerrero-Ríos** UNAM (Mexico) Biomass-derived Substrate Valorisation through Hydrogenation by Hybrid Catalysts
17:15 – 17:45	**FP18-21: Flash Presentations** Session D	**FP22-25: Flash Presentations** Session E	**FP26-29: Flash Presentations** Session F
17:45 – 18:45	**PB01-82: Poster Session B and FP18-29: Flash Poster Session B**		
18:45	**End of Scientific Programme**		
20:30	**Conference Dinner** Parador de Alcalá de Henares, Calle Colegios 8, 28804 Alcalá de Henares		

Friday, 8th September 2023

	Salón de Actos (Colegio de San Ildefonso)
	Chair: Ana C. Albéniz - CINQUIMA-Universidad de Valladolid
9:30 – 10:30	**PL7: Pedro J. Pérez** Universidad de Huelva (Spain) Catalytic and Stoichiometric Carbene and Nitrene Transfer Reactions
10:30 – 10:45	**OC48: Eva Hevia** Universität Bern (Switzerland) Synthesis, Bonding and Catalytic Applications of Homoleptic Tri-Lithium Nickelates
10:45 – 11:00	**OC49: Moritz Malischewski** Freie Universität Berlin (Germany) Tenfold Metalation and Functionalization of Ferrocene
11:00 – 11:15	**OC50: Gema Durá** University of Castilla-La Mancha (Spain) A New Half-sandwich Ir Complex with a pi-extended Ligand as a Potent Photocatalyst in Green Conditions
11:15 – 11:30	**OC51: Jitendra K Bera** IIT Kanpur (India) Asking Ligands to Lend a Hand
11:30 – 12:00	**Coffee Break**
	Chair: Rinaldo Poli - LCC CNRS Toulouse
12:00 – 12:30	**YPL5: Viktoria Däschlein-Gessener** Ruhr-University Bochum (Germany) Ligand Exchange at Carbon in Metalated Ylides: Synthetic Entry to Elusive Species
12:30 – 13:30	**Helmut Werner** ___________ Fischer-Wilkinson Prize for Organometallic Chemistry University of Würzburg (Germany) 50 Years of Organometallic Chemistry: From Sandwiches, Tripeldeckers and Beyond
13:30	**Closing Remarks**
	End of Conference

COMMUNICATIONS INDEX

Plenary Lectures

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— XXV CONFERENCE —
ON ORGANOMETALLIC CHEMISTRY
EuCOMC XXV

ABSTRACTS:
PLENARY LECTURES

PL1

Monday 4th September 17:30

Transuranic Organometallics

Polly L Arnold,[1] Nicholas Katzer,[1] Amy Price,[1] Mikaela Pyrch,[1] David Fiszbein,[1] Rachel Meyer,[1] Dominic Russo,[1] S. Olivia Gunther,[1] Rebecca Abergel,[1] Stefan Minasian,[1] Michal Dutkiewicz,[2] Jason B. Love,[2] Simon Parsons,[2] Roberto Caciuffo,[3] Olaf Walter,[3] Nikolas Kaltsoyannis,[4] Dumitru-Claudiu Sergentu,[5] Jochen Autschbach.[5]

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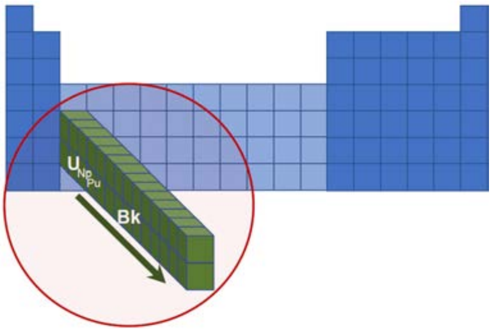
[2]EaStCHEM School of Chemistry, University of Edinburgh, Edinburgh, UK.
[3] European Commission, Joint Research Centre, Directorate G, Karlsruhe Institute of Technology, Germany.
[4] Department of Chemistry, University of Manchester, UK.
[5] Department of Chemistry, University of Buffalo, 732 Natural Sciences Complex, Buffalo, New York, 14260, United States.

Organometallic chemistry has been foundational in developing our knowledge of electronic structure and bonding in the d-block. It should be even more valuable for understanding the more complicated electronic structures and properties of the f-block elements, but the field is only just beginning to take off. This is in part because engineering controls that protect the students and their short-lived, air-sensitive radioactive complexes from each other are essential.

We will present new synthetic work with some of the rarest isotopes in the periodic table, using carbon-centered ligands to stabilize unusual geometries and electronic structures. This includes working at microgram scales in order to isolate the unusual berkelium oxidation state of +4, and using new techniques such as variable high-pressure crystallography for the first time in molecular actinide science to define covalency. Experimental contributions to the 'f-electron challenge' will in the long term improve our ability to manipulate and recycle the energy technology-critical rare earth elements, to use isotopes in medicine, and exotic physics applications such as quantum computing, and to safely handle our civil nuclear waste legacies.



References

1. Reviews: P. L. Arnold, Z. R. Turner *Nature Chem. Rev.* **2017**, *1*, 17; P. L. Arnold, M. S. Dutkiewicz, O. Walter *Chem. Rev.* **2017**, *117*, 11460. P. L. Arnold, M. W. McMullon, J. Rieb, F. E. Kuhn *Angew. Chem., Int. Ed.*, **2015**, *54*, 82.
2. M. S. Dutkiewicz, J. H. Farnaby, C. Apostolidis, E. Colineau, O. Walter, N. Magnani, M.G. Gardiner, J.B. Love, N. Kaltsoyannis, R. Caciuffo *Nat. Chem.* **2016,** *8*, 797.
3. P. L. Arnold, T. Ochiai, F.Y.T. Lam, R. Kelly, M. Seymour, L. Maron *Nat. Chem.* **2020**, *12,* 654.
4. J.J. Shephard, V.E.J. Berryman, T. Ochiai, N. Kaltsoyannis S. Parsons, P.L. Arnold *Nat. Commun.* **2022**, *13*, 5923.

PL2

Tuesday 5th September 09:00

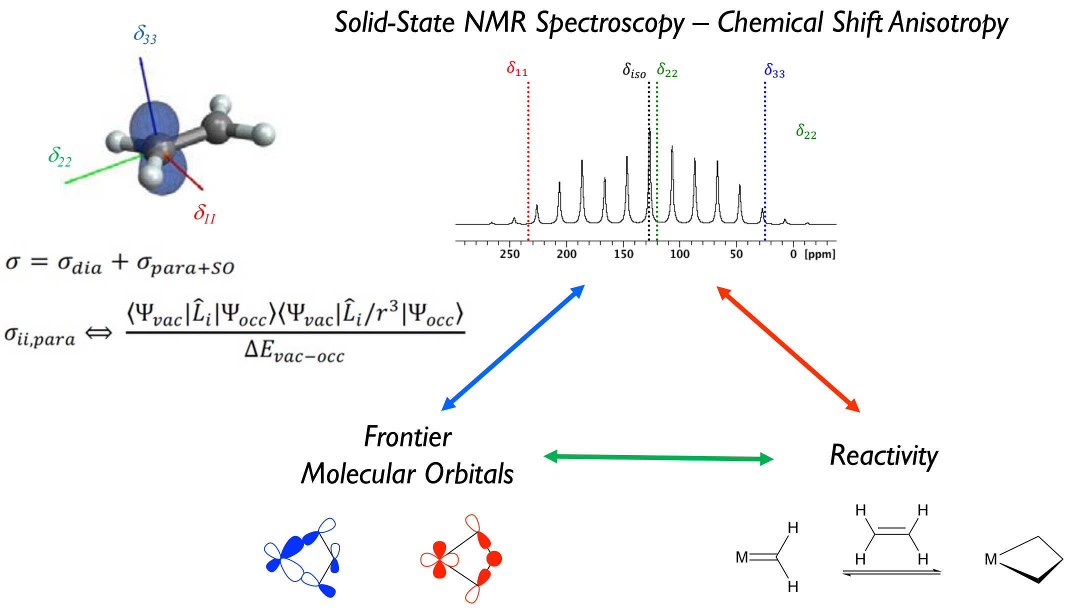
NMR Chemical Shifts Beyond Numbers: From Understanding Electronic Structures to Reactivity Descriptor

Christophe Copéret

Department of Chemistry and Applied Biosciences – ETH Zürich, Switzerland

Chemical shift has been successfully used since the beginning of NMR to identify the signature of molecules (and materials) making NMR an invaluable tool of characterizations. Because of its power to elucidate molecular structure, NMR interpretation is taught at early stage, often in laboratory courses, even before one understands the fundamentals of spectroscopy and their selection rules. We all remember solving organic and inorganic puzzles based on 1D and 2D NMR spectra during our undergraduate (and graduate…) times.[1]

This lecture, targeted for all aficionados of NMR (and those who want to become one), will concentrate on developing a detailed understanding of the origin of NMR chemical shift, and how it can be used to reconstruct the electronic structure of molecules, in particular organometallic intermediates. This lecture will also aim to show that the angular momentum operator has an “ideal” symmetry, that makes NMR a privilege spectroscopic descriptor of reactivity.



$$\sigma = \sigma_{dia} + \sigma_{para+SO}$$

$$\sigma_{ii,para} \Leftrightarrow \frac{\langle \Psi_{vac} | \hat{L}_i | \Psi_{occ} \rangle \langle \Psi_{vac} | \hat{L}_i / r^3 | \Psi_{occ} \rangle}{\Delta E_{vac-occ}}$$

References

1) Spectral identification of organic compounds, Eds. Silverstein, Webster and Kiemle, Wiley&Sons, **2005**.
2) a) Metal Olefin Complexes: Revisiting the Dewar-Chatt-Duncanson Model and Deriving Reactivity Patterns from Carbon-13 NMR Chemical Shift. C. P. Gordon, R. A. Andersen, C. Copéret *Helvetica Chim Acta* **2019**, *102*, e1900151. b) Carbon-13 NMR Chemical Shift: A Descriptor for Electronic Structure and Reactivity of Organometallic Compounds C.P. Gordon, C. Raynaud, R.A. Andersen, C. Copéret, O. Eisenstein, *Acc. Chem. Res.* **2019**, *52*, 2278-2289. c) Nuclear Magnetic Resonance: A Spectroscopic Probe to Understand the Electronic Structure and Reactivity of Molecules and Materials. C. P. Gordon, L. Lätsch, C. Copéret *J. Phys. Chem. Lett.* **2021**, *12*, 2072-2085. d) Classifying and understanding the reactivities of Mo-based alkyne metathesis catalysts from ^{95}Mo NMR chemical shift descriptors. Z. Berkson, L. Lätsch, J. Hillenbrand, A. Fürstner, C. Copéret, *J. Am. Chem. Soc.* **2022**, *144*, 15020–15025.

PL3

Tuesday 5th September 14:30

A New Reactivity Paradigm: *Trans*-hydrogenation, *Gem*-Hydrogenation, and *Trans*-Hydrometalation of Alkynes

Alois Fürstner

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This lecture intends to showcase some unconventional ways of harnessing the reactivity of alkynes via highly selective metal-catalyzed transformations. After a review of our work in the area of triple bond metathesis [1], some unorthodox addition reactions to internal alkynes will be discussed, including metal catalyzed *trans*-hydrogenation, *trans*-hydroboration, *trans*-hydrostannation, *trans*-hydroalkynylation and *trans*-chloroalkynylation, which have little precedent in the literature, if any [2].

Even more perplexing is the ability to transfer both H-atoms of H_2 to one and the same C-atom of a triple bond with concomitant formation of a discrete metal carbene at the adjacent position ("*gem*-hydrogenation") [2]. This entirely new reactivity mode unlocks numerous opportunities for organic synthesis and organometallic chemistry alike, which we have started to explore.

The underlying mechanisms will be discussed in some detail; selected applications to target-oriented synthesis are meant to illustrate the current state of development.

References

[1] A. Fürstner, *J. Am. Chem. Soc*. **2021**, *143*, 15538.
[2] A. Fürstner, *J. Am. Chem. Soc*. **2019**, *141*, 11.

PL4

Wednesday 6th September 09:00

Gold Chemistry in Water: From Catalysis to Medicine

Angela Casini

Chair of Medicinal and Bioinorganic Chemistry, Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85747 Garching, Germany; email: angela.casini@tum.de

Several studies have proven that metal-based compounds can be used to develop new drugs, diagnostic agents, as well as chemical probes to study the molecular mechanisms of diseases. This lecture summarizes recent developments for different families of bioactive organometallic gold compounds including cyclometallated Au(III) and Au(I) N-heterocyclic carbene (NHC) complexes, and provides insights into their reactivity in biological environments. For example, anticancer Au(I) NHCs compounds with caffeine-derived ligands were shown to potently and selectively stabilize G-quadruplexes structures *via* non-covalent interactions. [1] Interestingly, starting from Au(I) NHCs precursors, water soluble gold nanoparticles stabilized by NHC ligands (NHC@AuNPs) have been synthesized by 'bottom-up' approaches and used for catalysis and PTT in cells.[2]

Moreover, organogold complexes have recently emerged as promising tools for bio-orthogonal transformations, endowed with excellent chemoselectivity, compatibility within aqueous reaction medium and fast kinetics of ligand exchange reactions. Recent findings from our group on Au(III)-catalyzed reductive elimination in aqueous media provide the proof-of-concept for the use of cyclometalated Au(III) C^N complexes to achieve efficient modification of proteins through C-atom transfer, enabling chemoproteomic studies (e.g. profiling of cysteine residues) and novel therapeutic approaches.[3] The obtained mechanistic insights have allowed to extend the cross-coupling concept to other substrates, to afford C–P and C–C bond formation under mild conditions,[4-5] relevant to applications of gold compounds in catalysis.

References

[1] D. Wragg, A. de Almeida, R. Bonsignore, S. Leoni, A. Casini, *Angew. Chem. Int. Ed.*, **57**, (2018), 14524.
[2] S. R. Thomas, A. Casini, *Chemistry Eur. J.,* **28**, (2022), e202201575.
[3] C. Schmidt, M. Zollo, R. Bonsignore, A. Casini, S.M. Hacker, *Chem. Commun.*, **58**, **(**2022), 5526.
[4] R. Bonsignore, S. R. Thomas, et al. *Chemistry Eur. J.*, **26**, (2020), 4226.
[5] R. Bonsignore, S. R. Thomas, M. Rigoulet, C. Jandl, A. Pöthig, D. Bourissou, G. Barone, A. Casini, *Chemistry Eur. J.*, **27**, (2021), 14322.

PL5

Thursday 7th September 09:00

Low-Valent Alkaline-Earth Metal Complexes for Bond Activation and Catalysis

Sjoerd Harder

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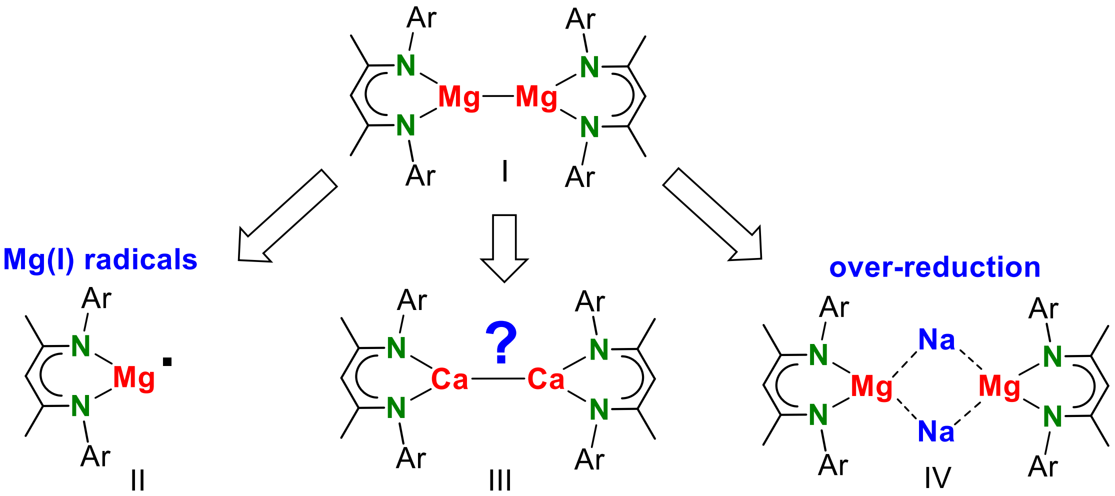
The first Mg(I) complex is a milestone in alkaline-earth metal chemistry (**I**).[1] These versatile reducing agents have numerous advantages. Recent advances in low-valent group 2 metal chemistry include the generation of Mg(I) radicals (**II**), attempts to isolate Ca(I) species (**III**) and over-reduction to formal Mg(0) complexes (**IV**).[2-4]

While **II**-**IV** will be extremely potent reducing agents, the problematic irreversibility of redox reactions makes such complexes unsuitable for catalysis. It is, however, shown that low-valent alkaline-earth metals may play a role in catalysis. The importance of *d*-orbitals for heavier Ca, Sr and Ba metals will be discussed.



References

[1] S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754..

[2] D. Jędrzkiewicz, J. Mai, J. Langer, Z. Mathe, N. Patel, S. DeBeer, S. Harder, *Angew. Chem. Int. Ed.* **2022**, *61*, e202200511.

[3] B. Rösch, T. X. Gentner, J. Langer, C. Färber, J. Eyselein, L. Zhao, C. Ding, G. Frenking, S. Harder, *Science* **2021**, *371*, 1125.

[4] B. Rösch, T. X. Gentner, J. Eyselein, J. Langer, H. Elsen, S. Harder, *Nature* **2021**, *592*, 717.

PL6

Thursday 7th September 14:30

Gold(III) Chemistry:
Surprise, Intrigue, Mechanisms

Manfred Bochmann

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Catalysis by gold has seen a meteoric rise in recent years. While this involves mostly gold(I), the much less well studied complexes of gold(III) are also frequently involved. While catalytically relevant key species and mechanisms are often formulated on the basis of analogies with the chemistry of isoelectronic Pd(II) or Pt(II), this lecture will discuss the different nature of key intermediates in gold(III) chemistry and how gold manages to avoid and bypass well-trodden mechanistic pathways.[1]

References

[1] L. Rocchigiani, M. Bochmann, Recent Advances in Gold(III) Chemistry: Structure, Bonding, Reactivity and Role in Homogeneous Catalysis. *Chem. Rev.* **2021**, *121*, 14, 8364–8451.

PL7

Friday 8th September 09:30

Catalytic and Stoichiometric Carbene and Nitrene Transfer Reactions

Pedro J. Pérez

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Edificio Robert H. Grubbs, Campus de El Carmen, 21007 Huelva, Spain
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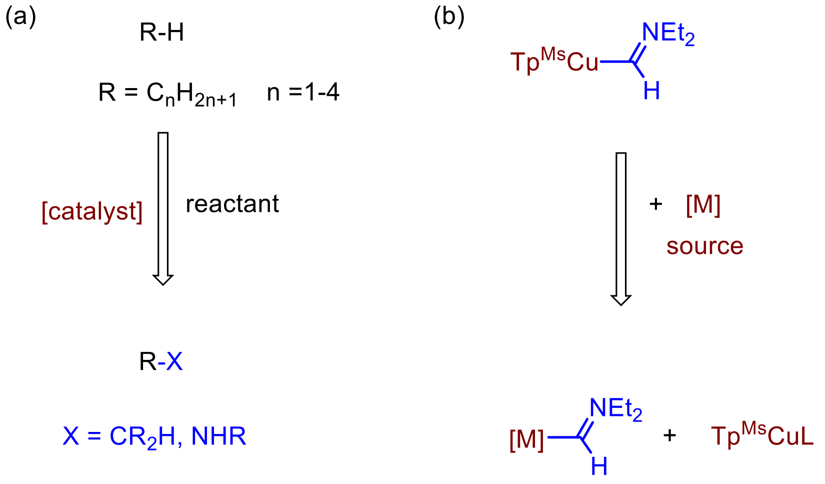
In the context of the functionalization of C-H bonds by processes involving the transfer of carbene or nitrene units, a plethora of substrates have been employed.[1] Among them, examples involving alkanes and, more specifically, the gaseous alkanes C1-C4, are yet reduced. Our group has provided several examples of the functionalization of methane and light alkanes leading to products derived from the formation of C-C and C-N bonds (Scheme, a).[2] The latest results involving the functionalization of such substrates involving carbene and nitrene units will be presented.

In a second approach, we have recently reported the formation of a stable copper-monosubstituted carbene complex upon a decarbonylation process of a diazoacetamide.[3] We have found that this complex is an excellent transmetallating reagent for the aminocarbene ligand, that can be transferred to an array of metal centers (Scheme, b). An account of this stoichiometric carbene transfer process will be also presented.



References

[1] a) He, Y.; Huang, Z.; Wu, K.; Ma, J.; Zhou, Y.-G.; Yu, Z. *Chem. Soc. Rev.* **2022**, *51*, 2759. b) *Transition Metal-Catalyzed Carbene Transformations*; Wang, J. B.; Che, C.-M.; Doyle, M. P., Eds.; Wiley-VCH, 2022. c) Caballero, A.; Díaz-Requejo, M. M.; Pérez, P. J. *Metal-catalyzed oxidation of alkanes to give esters or amines*. In *Catalytic Oxidation in Organic Synthesis*, K. Muñiz, Ed. Science of Synthesis 2017/4.

[2] a) Caballero, A.; Despagnet-Ayoub, E.; Díaz-Requejo, M. M.; Díaz-Rodríguez, A.; González-Nuñez, M. E.; Mello, R.; Muñoz, B. K.; Solo Ojo, W.; Asensio, G.; Etienne, M.; Pérez, P. J. *Science* **2011**, *332*, 835-838. b) Fuentes, M. A.; Gava, R.; Saper, N. I.; Romero, E. A.; Caballero, A.; Hartwig, J. F.; Pérez, P. J. *Angew. Chem. Int. Ed.* **2021**, *133*, 18615-18619.

[3] M. Álvarez, M. Besora, F. Molina, F. Maseras, T. R. Belderrain, P. J. Pérez, *J. Am. Chem. Soc.* **2021**, *143*, 4837-4843.

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ABSTRACTS:
YOUNG PLENARY LECTURES

YPL1
Monday 4th September 18:30

Deciphering Mechanisms to Design Better Catalytic Reactions

Mónica H. Pérez-Temprano

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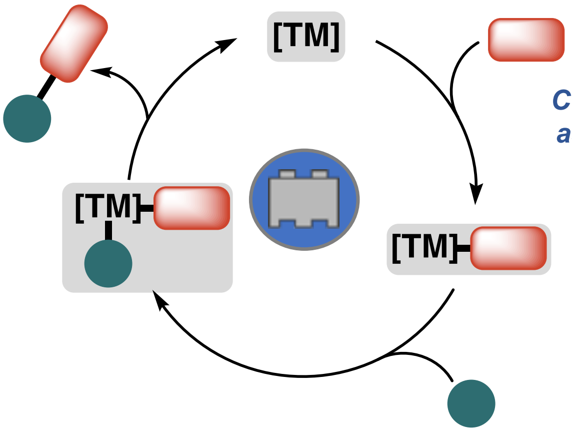
Most reactions set-up in the lab fail.[1] This is one of the biggest problems chemists faces when designing transition metal-catalyzed transformations.[2] This striking situation prompts two key questions: Why do reactions fail? Can failed reactions be used to trigger a paradigm-shift in reaction design?

My group aims to answer these questions placing fundamental understanding at the center of process design. We use mechanistic studies as a powerful tool to facilitate the bottom-up design of more efficient chemical processes.[3] My research program is based on simple, yet usually overlooked, concept: chemical reactions rely on the performance of the reactive intermediates within the catalytic cycles. By capturing these transient species and using them as "knowledge building blocks" (KBBs), we expose the obstacles hindering transition metal-catalyzed transformations efficiency and capitalize on the gathered fundamental knowledge to streamline more resource-efficient transformations. As a proof-of-concept, my group targets chemical transformations catalyzed by cost-effective cobalt complexes.[4]



Capturing Reaction Intermediates as "Knowledge Building Blocks"

✓ ***streamlining the rational design*** *of TM-catalyzed transformations*

✓ ***exploring new reactivity*** *patterns*

References

(1) Zaragoza Dörwald, F. Side Reaction in Organic Synthesis: A guide to Successful Synthesis Design. Wiley- VCH Verlag GmbH&Co. 2005.
(2) Collins, K. D.; Glorius, F. *Nat. Chem.* **2013**, *5*, 597.
(3) Sanjosé-Orduna, J.; Mudarra, A. L.; Martínez de Salinas, S.; Pérez-Temprano, M. H. *ChemSusChem* **2019**, *12*, 2882.
(4) (a) Sanjosé-Orduna, J.; Gallego, D.; Garcia-Roca, A.; Martin, E.; Benet-Buchholz, J.; Pérez-Temprano, M. H. *Angew. Chem. Int. Ed.* **2017**, *56*, 12137. (b) Sanjosé-Orduna, J.; Sarria Toro, J. M.; Pérez-Temprano, M. H. *Angew. Chem. Int. Ed.* **2018**, *57*, 11369. (c) Martínez de Salinas, S.; Sanjosé-Orduna, J.; Odena, C.; Barranco, S.; Benet-Buchholz, J.; Pérez-Temprano, M. H. *Angew. Chem. Int. Ed.* **2020**, *59*, 6298. (d) López-Resano, S.; Martínez de Salinas, S.; Garcés-Pineda, F. A.; Moneo-Corcuera, A.; Galán-Mascarós, J. R.; Maseras, F.; Pérez-Temprano, M. H. *Angew. Chem. Int. Ed.* **2021**, *60*, 11217.

YPL2

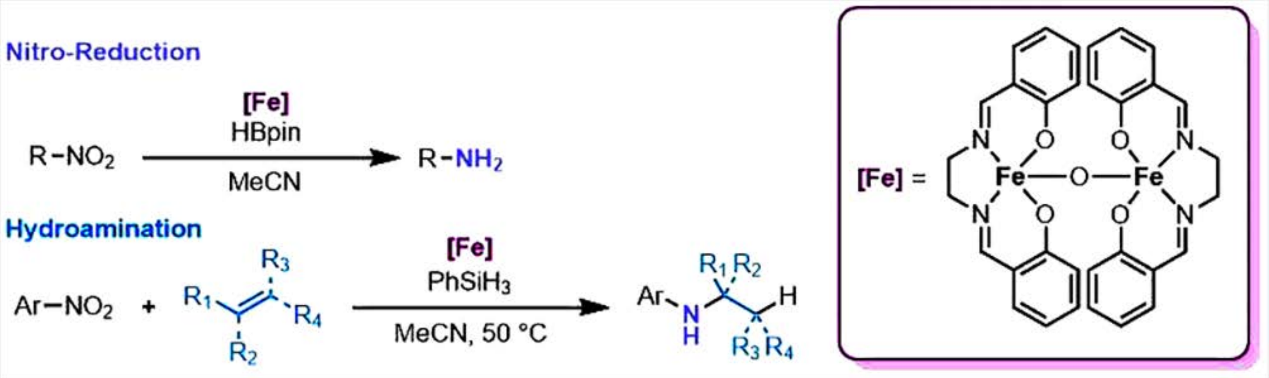
Tuesday 5th September 10:00

Mechanistic Insight Into Iron(Salen) Catalysed Reactions

R. L Webster

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

Iron catalysis offers an attractive alternative to precious metal catalysis due to its abundance and low cost, along with the additional benefits of being a non-toxic and environmentally-benign metal. A large number of transition metal salen complexes have been reported and are capable of mediating several organic transformations.[1] Complexes containing these ligands are highly versatile due to the ligand's modular nature and synthesis scalability.[2] Herein, we report the use of Fe(salen) complexes to yield synthetically important products, for example the reduction of nitro compounds and functionalisation of amines, under mild reaction conditions. This presentation will cover our efforts in mechanistic elucidation.



References

[1] Canali, L.; Sherrington, D. *Chem. Soc. Rev.* 1999, **28**, 85-93.
[2] Gallagher, K. J.; Webster, R. L. *Chem. Commun.* 2014, **50**, 12109-12111.

YPL3

Tuesday 5th September 15:30

Tales on Bismuth Redox Catalysis

Josep Cornella

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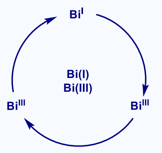
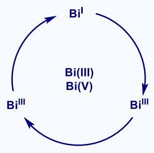
The ability of the bismuth (Bi) to maneuver between different oxidation states in a catalytic redox cycle will be presented. We will show how Bi challenges the current dogmas of main group redox catalysis by emulating canonical organometallic steps of transition metals. A series of Bi complexes capable of revolving between oxidation states Bi(I)/Bi(III) and Bi(III)/Bi(V) have been unlocked and applied in various contexts of catalysis for organic synthesis. For example, capitalizing on the Bi(III)/Bi(V) redox pair, we have developed a catalytic protocol for the C-F, C-O and C-N bond formation. We will show how bismuth is capable of a unique 5-membered reductive elimination step, which differs from the traditional 3-membered of transition metals.

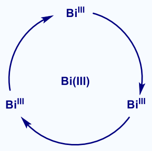
Additionally, we will show how a low-valent redox manifold based on Bi(I)/Bi(III) enabled the reduction of hydrazines and nitro compounds, the catalytic decomposition of the rather inert nitrous oxide (N_2O) and the catalytic hydrodefluorination of $C(sp^2)$-F bonds. In addition, we will show how one-electron pathways are also accessible, thus providing a platform for SET processes capitalizing on the triad Bi(I)/Bi(II)/Bi(III) for organic synthesis. Finally, we will also show how redox-neutral organometallic steps (insertion, transmetallation and ligand exchange) can be merged in a catalytic platform to unlock novel organic transformations. For all methodologies, a combination of rational ligand design with an in depth analysis of all the elementary steps proved crucial to unlock the catalytic properties of such an intriguing element of the periodic table.



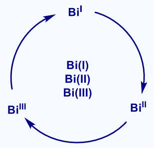
2-electron redox catalysis



2-electron redox catalysis



redox neutral catalysis



1-electron redox processes

Selected References from the group:

[1] For a perspective on Bi Redox Catalysis: *ACS. Catal.* **2022**, *12*, 1382.
[2] For articles about high-valent Bi(III)/Bi(V) redox catalysis: a) *Science*, **2020**, *367*, 313; b) *J. Am. Chem. Soc.* **2020**, *142*, 11382; c) *J. Am. Chem. Soc.* **2022**, *144*, 14489.
[3] For articles about low-valent Bi(I)/Bi(III) Redox Catalysis: *J. Am. Chem. Soc.* **2019**, *141*, 4235; b) *J. Am. Chem. Soc.* **2020**, *142*, 19473; c) *J. Am. Chem. Soc.* **2021**, *143*, 12487.
[4] For articles about Bismuth Redox Neutral Catalysis: *J. Am. Chem. Soc.* **2021**, *143*, 21497.
[5] For articles about Bismuth Radical Redox Chemistry and Catalysis: *J. Am. Chem. Soc.* **2022**, *144*, 36, 16535; b) *J. Am. Chem. Soc.* **2023**, *145*, 10, 5618; c) *ChemRxiv*, **2022**, 10.26434/chemrxiv-2022-dqj5r

YPL4

Thursday 7th September 10:00

Sustainable Tools to Access Fluorinated Molecules by C-H Bond Functionalization

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Organofluorine chemistry is a fascinating research field. Beyond the strong interest that represents fluorinated molecules in materials science, pharmaceuticals and agrochemicals as well as modern drug design,[1] the quest for innovative approaches are still needed to achieve synthetic challenges and to push further the boundaries of knowledge in this appealing research field.[2] Besides, a lot of attention was paid to the development of more sustainable transformations and transition metal catalyzed direct C-H bond functionalization has reshaped the field of organic chemistry over the last decade.[3] In that context, aiming at designing new tools to access original fluorinated molecules, our group developed new approaches based on the combination of organofluorine chemistry and transition metal catalyzed C-H bond functionalization.[4] Moreover, a special attention was paid to the design of original reagents.[5]

References

[1] For selected reviews, see: a) T. Furuya, A. S. Kamlet, T. Ritter, *Nature* **2011**, *473*, 470-477. b) G. Landelle, A. Panossian, S. Pazenok, J.-P. Vors, F. R. Leroux, *Beilstein J. Org. Chem.* **2013**, *9*, 2476-2536. c) T. Besset, T. Poisson, X. Pannecoucke, *Chem. Eur. J.* **2014**, *20*, 16830-16845. d) C. Ni, J. Hu, *Chem. Soc. Rev.* **2016**, *45*, 5441-5454.

[2] For selected reviews, see: a) J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok, H. Liu, *Chem. Rev.* **2014**, *114*, 2432 and references therein. b) M. Inoue, Y. Sumii, N. Shibata, *ACS Omega* **2020**, *5*, 10633-10640.

[3] Special issue on C-H activation, *Chem. Rev.* **2017**, *117*, 8481-9520.

[4] For selected exemples, see: a) H.-Y. Xiong, T. Besset, D. Cahard, X. Pannecoucke, *J. Org. Chem.* **2015**, *80*, 4204-4212. b) Q. Zhao, T. Poisson, X. Pannecoucke, J.-P. Bouillon, T. Besset, *Org. Lett.* **2017**, *19,* 5106-5109. c) M. Barday, R. Blieck, L. Ruyet, T. Besset, *Tetrahedron* **2020**, *76*, 131153. d) L. Ruyet, M. I. Lapuh, V. S. Koshti, T. Földesi, P. Jubault, T. Poisson, Z. Novák, T. Besset, *Chem. Commun.* **2021**, *57*, 6241-6244.

[5] a) H.-Y. Xiong, X. Pannecoucke, T. Besset, *Angew. Chem. Int. Ed.* **2016**, *55*, 13490-13494. b) H.-Y. Xiong, X. Pannecoucke, T. Besset, *Org. Chem. Front.* **2016**, *3*, 620-624. c) E. Carbonnel, X. Pannecoucke, T. Besset, P. Jubault, T. Poisson, *Chem. Commun.* **2018**, *54*, 2491-2493. d) F. Petit-Cancelier, B. François, X. Pannecoucke, S. Couve-Bonnaire, T. Besset, *Adv. Synth. Catal.* **2020**, *362*, 760-764. e) E. Nobile, T. Castanheiro, T. Besset, *Chem. Commun.* **2021**, *57*, 12337-12340.

YPL5

Friday 8th September 12:00

Ligand Exchange at Carbon in Metalated Ylides: Synthetic Entry to Elusive Species

Viktoria H. Gessner[1] and the Gessner Group

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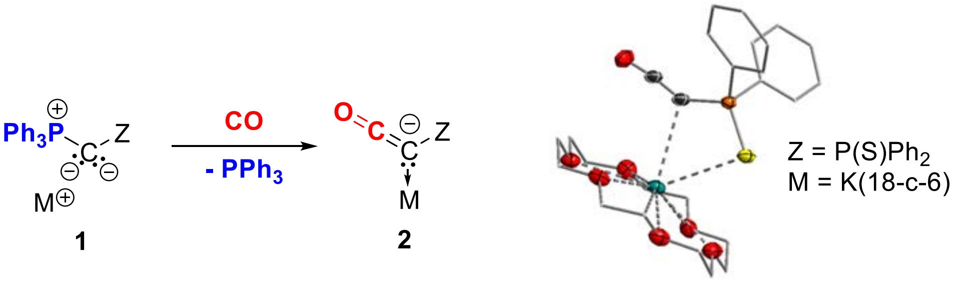
Phosphines are amongst the most important ligands in coordination chemistry and frequently applied in transition metal catalysis. Here, they often are readily displaced by other ligands which subsequently participate in the bond forming step within the catalytic cycle. Recent reports have demonstrated that also ylidic phosphorus compounds such as carbodiphosphoranes[1] - because of their unique electronic structure - can be interpreted as coordination complexes of carbon. However, the synthetic exploitation of this bonding situation to access new compounds via ligand exchange has so far been extremely limited.

In the past years, our group has reported on the synthesis and reactivity of metalated ylides (**1**). Owing to their highly nucleophilic character these compounds turned out to be excellent precursors to access electron-rich phosphines for homogeneous catalysis[2] and to stabilize electron-deficient main group species.[3] Most recently however, we uncovered that metalated ylides also react as coordination complexes of carbon to readily exchange the phosphine substituent by carbon monoxide.[4] This remarkable reactivity provided access to ketenyl anions **2** which long have been regarded as elusive species but proved stable to serve as starting materials to ketenes and related compounds. In this presentation, the ability of metalated ylides to react under displacement of the phosphine by other ligands will be discussed.



References

[1] M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nature Chem.* **2009**, *1*, 295.
[2] S. Lapointe, A. Sarbajna, V. H. Gessner, *Acc. Chem. Res.* **2022**, *55*, 770.
[3] A. Sarbajna, V.S.V.S.N. Swamy, V.H. Gessner, *Chem. Sci.* **2021**, *12*, 2016
[4] M. Jörges+, F. Krischer+, V. H. Gessner, *Science*, **2022**, *378*, 1331.

— XXV CONFERENCE —
ON ORGANOMETALLIC CHEMISTRY

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ABSTRACTS:
KEYNOTE LECTURES

KN01

Tuesday 5th September 11:00

Selective Construction Carbon-Heteroatom Bonds Mediated by Cp*Ir(III) Complexes

Belén Martín-Matute[1]

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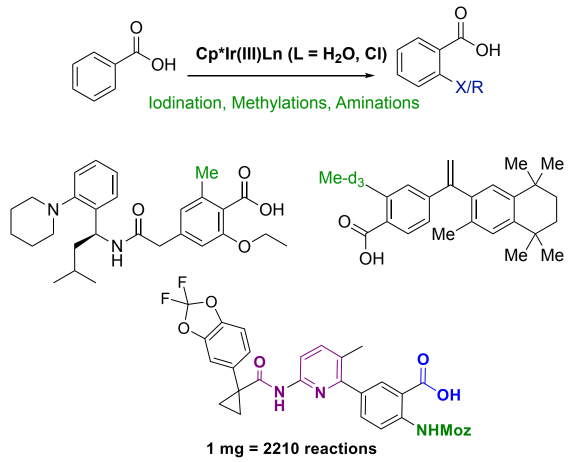
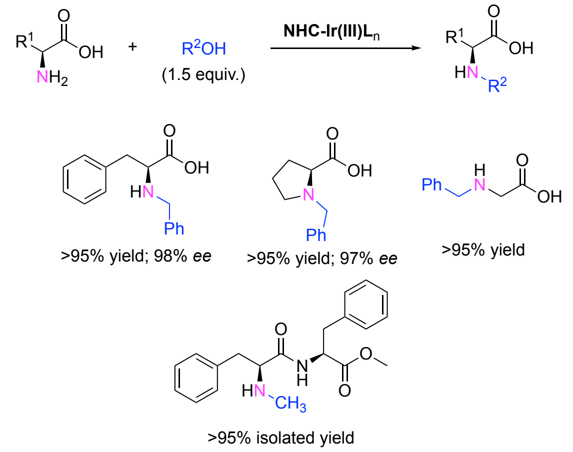
Iridium(III) complexes of the general formula [Cp*Ir(III)] have been used for functionalization or activation of a variety of C-H bonds, resulting in formation of new C-C or C-heteroatom bonds. In the absence of P- or N-based ligands, 1,3-hydride shift / functionalization of allylic alcohols, as well as C-H functionalization of benzoic acids and amides.[1,2] We have also developed Ir(III) complexes with functionalized NHC ligands for the N-alkylation of aliphatic and aromatic amines with alcohols.[3] These reactions have been used for the late-stage functionalization (LSF) of a variety of drug-molecules. Mechanistic investigations will be presented.[1-3]





References

1. Chem. Commun. **2011**, 47, 8331-8333; Angew. Chem. Int. Ed. **2013**, 52, 6273; Chem. Eur. J. **2014**, 20, 10703; ACS Catalysis, **2015**, 5, 708; Chem. Commun. **2017**, 53, 9842; ACS Catal., **2018**, 8, 920; Chem. Eur. J. **2020**, 26, 14978; Nature Commun. **2019**, 10, 524450; iScience **2021**, 24, 102467; JACS Au **2022**, 2, 90.
2. J. Am. Chem. Soc. **2016,** 138, 13408; ACS Catalysis, **2019**, 9, 9134; Org. Lett. **2020**, 22, 4123.
3. *ACS Catalysis* **2015**, *5,* 3704; *Chem* **2022**, *8*, 3302.

KN02

Tuesday 5th September 11:30

Catalytic Cyclotrimerization Route to [n]Helical Indenofluorenes and Transformations Thereof

Martin Kotora

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Helical aromatic compounds constitute an interesting class of molecules that find potential applications in many branches of chemistry. Recently, we have developed a method for the synthesis of [7]- and [9]helical indenofluorenes (bispiroindeno[2,1-*c*]fluorenes) by using a catalytic intramolecular [2+2+2] cyclotrimerization (Figure 1, a and b).[1,2] In the latter case, the course of the reaction strongly depended on reaction conditions used.

Chiral [7]helical indenofluorenes were prepared as well by using enantioselective cyclotrimerization and asymmetric induction was as high as 92% *ee*. All prepared [7]helical Indenofluorenes exhibited high fluorescence in the region of 410-430 nm (Φ_F up to 0.87) and were CPL active (glum ~1×10-3).3

In addition, deposition of a [7]-helical indenofluorene lead to planarization accompanied by skeletal rearrangements leading to formation of various aromatic compounds such as a moth-shape compound (Figure 1, c).[4,5]

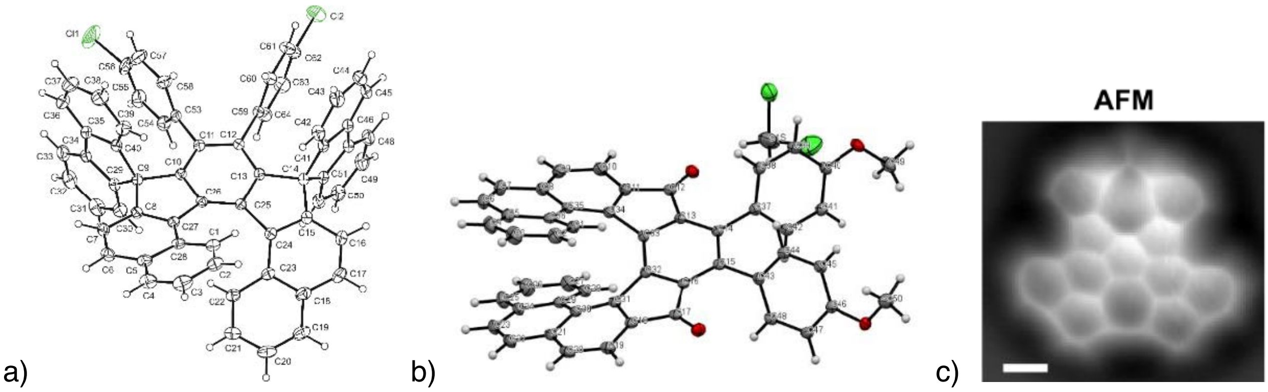

Figure 1. [7]helical indenofluorene (a), [9]helical indenofluorene, and a moth shape compound (c).

References

1. Kaiser, R. P.; Nečas, D.; Cadart, T.; Gyepes, R.; Císařová, I.; Mosinger, J.; Pospíšil, L.; Kotora, M. *Angew. Chem. Int. Ed.* **2019**, *58*, 17169.
2. Cadart, T.; Nečas, D.; Kaiser, R. P.; Favereau, L.; Císařová, I.; Gyepes, R.; Hodačová, J.; Kalíková, K.; Bednárová, L.; Crassous, J.; Kotora, M. *Chem. Eur. J.* **2021**, 27, 11279.
3. Cadart, T.; Gläsel, T.; Císařová, I.; Gyepes, R.; Hapke, M.; Kotora, M. *Chem. Eur. J.* **2023**, 29, accepted.
4. Mendieta-Moreno, J. I.; Mallada, B.; de la Torre, B.; Cadart, T.; Kotora, M.; Jelínek, P. *Angew. Chem. Int. Ed.* **2022**, *61*, e202208010.
5. Mendieta-Moreno, J. I.; Mallada, B.; de la Torre, B.; Cadart, T.; Kotora, M.; Jelínek, P. *Angew. Chem. Int. Ed.* **2022**, *61*, e202208010.

KN03

Tuesday 5th September 11:00

Site and Enantioselective Oxidation of Strong C-H Bonds with Bioinspired Catalysts

Arnau Call,[1] Andrea Palone,[1] Laia Vicens,[1] Marco Galeotti,[1] Marco Cianfanelli,[1]
Giorgio Olivo,[1] Massimo Bietti,[2] Miquel Costas[1]

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Aliphatic C-H oxidation is a very powerful approach to functionalize hydrocarbon skeletons. The main challenge of this reaction is the control of site-selectivity, given the multiple C-H bonds present in any organic molecule.[1] Natural enzymes elegantly solve this problem through the interplay of different interactions that geometrically orient the substrate to expose specific C-H bonds to the active unit, thus overriding intrinsic reactivity patterns.[2] Coordination complexes based on iron and manganese can reproduce fundamental aspects of this chemistry;[3] upon reaction with hydrogen peroxide, high valent metal-oxo species are formed that can engage in C-H oxidation reaction proceeding via short lived radical intermediates. Control of the first and the second coordination sphere of the catalysts can be used to shape the place where the metal-oxo reactive centre attacks the C-H bond, and this translates into site and stereoselective C-H oxidation reactions.[4] Strategies pursued for the design of biologically inspired catalysts based on the manipulation of electronic and steric properties of the catalysts, and incorporation of substrate recognizing units via supramolecular effects will be discussed.[5]

References

1. White, M. C.; Zhao, J. *J. Am. Chem. Soc.* **2018**, *140*, 13988.
2. Vicens, L.; Olivo, G.; Costas, M. *Acs Catal* **2020**, *10*, 8611.
3. Costas, M. Chem. Rec. **2021**, *21*, 4000.
4. Cianfanelli, M.; Besalú-Sala, P.; Olivo, G.; Palone, A.; Vicens, L.; Ribas, X.; Luis, J. M.; Bietti, M.; Costas, M. *J. Am. Chem. Soc.* **2022**, *144(42)*, 19542–19558. b) Vicens, L,; Bietti, M.; Costas, M. *Angew. Chem. Int. Ed.* **2021**, *60*, 4740.
5. a) Vicens, L.; Olivo, G.; Costas, M.: *Angew Chem. Int. Ed.* **2022**, *61*, e202114932. b) Olivo, G.; Capocasa, G.; Ticconi, B.; Lanzalunga, O.; Di Stefano, S.; Costas, M. *Angew. Chem. Int. Ed.* **2020**, *59*, 12703-12708.

KN04

Tuesday 5th September 11:30

Synthetic Applications of Metalloradical Catalysis

Bas de Bruin[1]

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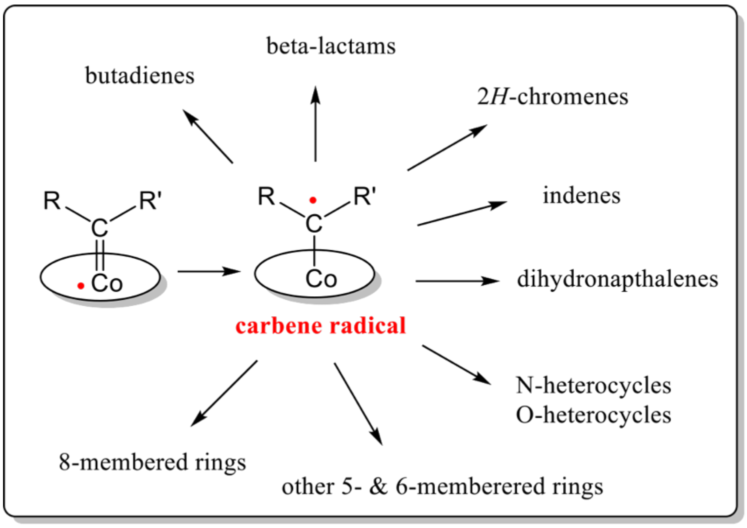
Our understanding and application of organometallic catalysis is predominantly based on closed-shell two-electron reactivity, and consequently traditional synthetic catalysis is primarily based on diamagnetic organometallic complexes undergoing a limited number of elementary steps. Open-shell catalysis offers fascinating new possibilities to steer and control radical-type single-electron transformations. Understanding such reactions aids in the development of entirely new synthetic protocols using sustainable base metal catalysts instead of noble metals. Our group is devoted to developing this field.

In this presentation we focus on C-C bond formation reactions proceeding via "carbene radical" intermediates.[1] These are intrinsically reactive metal-bound carbon centered radicals, useful for catalytic synthesis of a variety of ring compounds and other useful organic building blocks. These reactions have in common that they all proceed via selective radical-type transformations and single-electron elementary steps uncommon in traditional organometallic chemistry. The reactive radical-type intermediates are useful in organic synthesis, and mediate a variety of one-pot catalytic transformation leading to among others 2H-chromenes,[2] indenes, piperidines,[3] dihydronaphtalenes,[4a] butadienes,[4a] dibenzocyclooctenes.[4b,4c] and 1H-2-benzoxocins.[4d] The latter prove to be new molecular switches, which will also be presented.



References

1. (a) Dzik, W.I; Reek, J.N; de Bruin, B., *Chem. Eur. J.* **2008**, *14*, 7594. (b) Dzik, W.I.; Xu, X.; Zhang, X.P.; Reek, J.N.H.; de Bruin, B.; *J. Am. Chem. Soc.* **2010**, *132*, 10891. (c) Goswami, M.; Zhang, X.P, de Bruin, B., *et al. J. Am. Chem. Soc.*, **2015**, *137*, 5468. (d) Epping, R.F.J; Hoeksma, M.M.; Bobylev, E.O.; Mathew, S.; de Bruin, B. Nature Chemistry **2022**, *14*, 550.
2. Paul, N.D.; Mandal, S. Otte, M. Cui. X. Zhang, X.P.; de Bruin, B., *J. Am. Chem. Soc.* **2014**, *136*, 1090.
3. (a) Das, B.G.; Chirila, A.; Tromp, M.; Reek, J.N.H; de Bruin, B., *J. Am. Chem. Soc.* **2016**, *138*, 8968. (b) Lankelma, M.; Olivares, A.M; de Bruin, B. *Chem. Eur. J.* **2019**, *25*, 5658 .
4. a) te Grotenhuis, C.; Das, B.G.; de Bruin, B. *et al.*, *Chemical Science* **2017**, *8*, 8221. b) te Grotenhuis, C.; de Bruin, B. *et al.*, *Angew. Chem. Int. Ed.* **2018**, *57*, 140. c) M. Zhou, B. de Bruin, *et al.*, *Angew. Chem. Int. Ed.* **2020**, *59*, 11073. d) Zhou, M.; de Bruin, B. *et al. J. Am. Chem. Soc.* **2021**, *143,* 20501.

KN05

Wednesday 6th September 10:00

Gold-Based Antibody Drug Conjugates as Targeted Breast Cancer Therapeutic Agents

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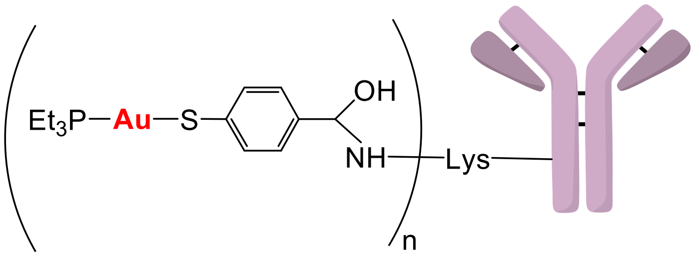
Overexpression of the human epidermal growth factor receptor 2 (HER2) is found in 20-30% of breast cancer tumors (named HER2-positive breast cancers) and is associated with more aggressive onset of disease, higher recurrence rate and increased mortality.[1] Monoclonal antibodies (mAb) like trastuzumab and pertuzumab in combination with chemotherapeutics, are used in the clinic to treat these cancers. However, therapeutic efficacy is limited by the cell death effect that the mAb may generate. Antibody–drug conjugates (ADCs) combine the antigen-targeting specificity of mAbs with the cytotoxic potency of chemotherapeutics. Two ADCs have been approved for the treatment of HER2 positive breast cancers.[2] One disadvantage of ADCs is their high cost due mainly to the linker technology necessary to attach highly cytotoxic payloads, and the synthesis of these payloads (complex organic molecules).

Metal-based ADCs have been overlooked despite there is enormous potential in this area with the resurgence of metal-based drugs as prospective cancer chemotherapeutics.[3,4] Here, I will report on the development and anticancer evaluation of second-generation gold-phosphane- and N-heterocyclic carbene-based antibody drug conjugates attached to anti-HER2 monoclonal antibodies trastuzumab, pertuzumab and engineered thiomab™. I will also describe the results of an efficacy *in vivo* trial (HER2+ breast cancer SKBR3 xenograft model) with novel gold(I)-based ADC (**Tras-2a**) incorporating the monoclonal antibody trastuzumab attached to the Au-PEt_3 motif present in Auranofin, by a very simple linker. Challenges and opportunities in this area for potential clinical traslation will be discussed.



Tras-2a

References

1. Mitri Z, Constantine T, O'Regan R. *Chemother Res. Pract.* **2012**, 2012:743193.
2. Drago, J.Z., Modi, S. & Chandarlapaty, S. *Nat Rev. Clin. Oncol.* ***2021***, **18**, 327–344.
3. Del Solar, V.; Contel, M. *J. Inorg. Biochem.* **2019**, *119*, 110780.
4. Curado, N.; Dewaele-Le Roi, G.; Poty, S.; Lewis, J.S.; Contel, M. *Chem Comm.* **2019**, *55*, 1394–1397.

KN06
Wednesday 6th September 10:00

Dihydrogen Activation by Cationic Hydrides of Alkaline Earth Metals and Zinc

Jun Okuda[1]

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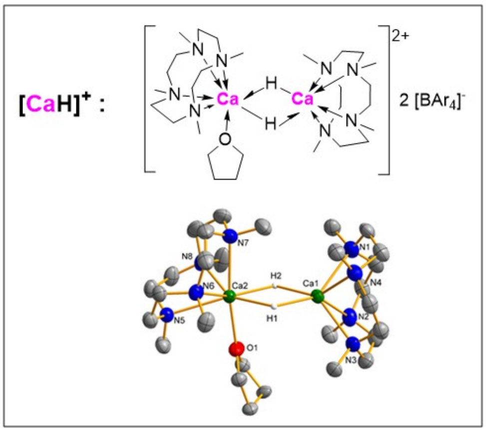
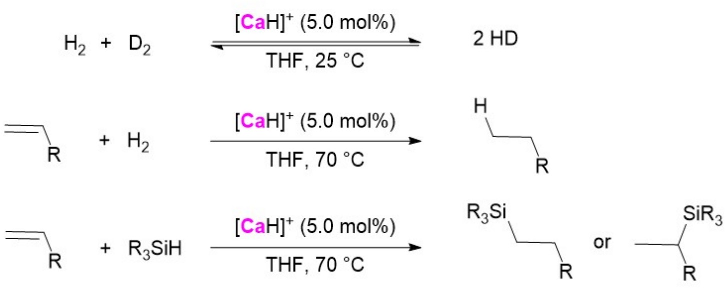
Hydrides of s-, d- and f-block metals are insoluble solid state materials. Currently, hydrides of highly electropositive metals (electronegativity < ≈ 1.6) such as MgH_2, $Ca(BH_4)_2$, and $LaNi_5H_6$ are being considered as hydrogen storage materials to allow reversible hydrogen uptake and release. When solubilized, metal hydrides could also become useful as inexpensive and non-toxic precursors for homogeneous catalysts. By introducing ligands such as CO, phosphines, olefins, and more recently N-heterocyclic carbenes (NHCs), homogeneous hydride catalyst precursors of late transition metals became accessible for synthetic applications. When dealing with highly electropositive metal centers, the use of chelating ligands is preferable, in particular in the context of catalysis to suppress intermolecular ligand exchange reactions. Furthermore, the restriction of ligand dynamics allows to generate stereochemically defined coordination spheres.





We have introduced what we call TACD ligands, derived from the NNNN macrocycle 1,4,7,10-**t**etra**a**za**c**yclo**d**odecane, cyclen, or [12]aneN_4. The neutral L_4-type ligand *N*,*N*',*N*'',*N*'''-methylated cyclen Me_4TACD (Me_4[12]aneN_4) is similar to the crown ether 12-crown-4 but acts as a rather versatile and mostly kinetically inert ancillary ligand for metal ions with different size of the s-, p-, d-, and f-block elements. Cationic molecular hydrides of Group 2, 3, 13 metals as well as of zinc can now be isolated. Owing to their solubility in organic solvents, they have been structurally characterized and found to catalyze reactions such as olefin hydrogenation and hydrosilylation. From the fundamental standpoint of studying the reactivity of electropositive metal hydrides as models for hydrogen storage materials, as efficient hydride nucleophiles, and reductants, molecular hydrides of electropositive metals supported by Me_4TACD and related ligands will be presented.

KN07

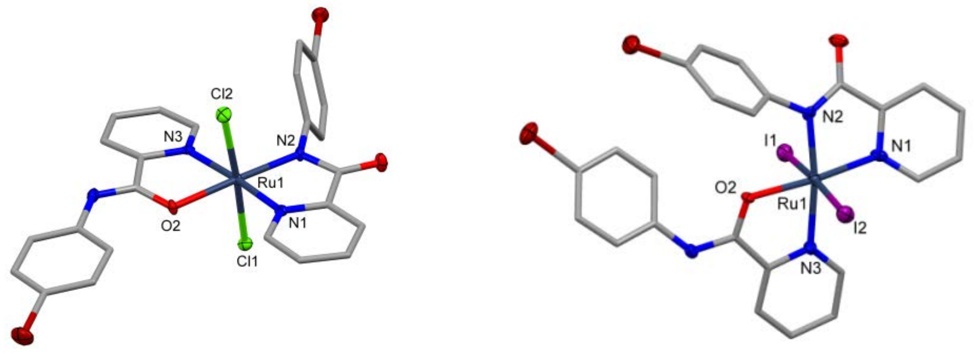
Wednesday 6th September 11:00

Bis-Picolinamide Metal Dihalide Complexes With A *Cis* To *Trans* Isomer Switch, Triggering High Potency And Cancer Cell Selectivity

Patrick C. McGowan,[1] Rianne M. Lord,[2] Aida M. Basri,[1] Roger M. Phillips,[3]
Benjamin Hofmann,[2] Matthew Allison,[1] Pablo Carames-Mendez[1] and Christopher Pask.[1]

[1] School of Chemistry, University of Leeds, Leeds, LS2 9JT, U.K. [2] School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, NR4 7JT, UK. [3] Department of Pharmacy, University of Huddersfield, Huddersfield, HD1 3DH, U.K. email: p.c.mcgowan@leeds.ac.uk; r.lord@uea.ac.uk.

This work presents a strategy to combat the issues with drug formulation by using transition metal group 8 and 9 *trans* complexes. [1-4] The *trans* complexes were synthesised as single isomers with nanomolar potencies against various cancer cell lines, contrary to earlier literature which considered *trans*-Pt complexes to be inactive due to high kinetic instability. Among the complexes studied, a library of *bis*-picolinamide ruthenium(III) dihalide complexes, RuX_2L_2 (X = Cl or I and L = picolinamide) reveal a mixture of *cis* and *trans* isomers for the $RuCl_2L_2$ complexes. Upon changing the halide to iodide, RuI_2L_2, generates exclusively a single *trans* isomer, (**Fig. 1**). Chemosensitivity studies show high cytotoxic activity against human cancer cell lines, with potencies for selected complexes better than cisplatin. The RuI_2L_2 complexes show a substantial increase in cytotoxicity when compared to the $RuCl_2L_2$ complexes, with potencies >8.5-fold (compared to cisplatin) against HT-29 (colon cancer), (**Fig. 1**). Moreover, these complexes are cytotoxic against the A2780cis (cisplatin-resistant ovarian cancer) cell line, with potencies >4-fold (compared to cisplatin). Conclusively, the change in conformers from *cis* to *trans* triggers high *in vitro* cancer cell selectivity with the complexes remaining active under hypoxic conditions.



a) $RuCl_2(4'\text{-}Br)_2$, $IC_{50} = 6.8 \pm 0.3$ μM b) $RuI_2(4'\text{-}Br)_2$, $IC_{50} = 0.8 \pm 0.1$ μM

Fig. 1 Molecular structures of a) $RuCl_2(4'\text{-}Br)_2$ and b) $RuCl_2(4'\text{-}F)_2$ (with 4'-Br = pyridine-2- carboxylic acid (4-bromo-phenyl) amide) with IC_{50} values against HT-29 cells.

References

[1] Allison, M.; Carames-Mendez, P; Pask, C. M.; Phillips, R. M.; Hofmann, B.; Lord, R. M.; McGowan, P. C. *Organometallics.* **2023**, *accepted.* [2] Allison, M.; Carames-Mendez, P; Pask, C. M.; Phillips, R. M.; Lord, R. M.; McGowan, P. C. *Chem. Eur. J.* **2021**, 3737–3744. [3] Lord, R. M.; Zegke, M.; Basri, A. M.; Pask, C. M.; McGowan, P. C., *Inorg. Chem.,* **2021**, 2076–2086. [4] Lord, R. M.; Hebden, A. J.; Pask, C. M.; Henderson; I. R., Allison, S.; Shepherd, S. L.; Phillips; R. M.; McGowan, P. C. *J. Med. Chem.,* **2015**, 58(12), 4940-4953.

KN08

Wednesday 6th September 11:30

In Vivo Metallophilic Self-Assembly of Cyclometalated Metallodrugs for Anticancer Phototherapy

Sylvestre Bonnet[1]

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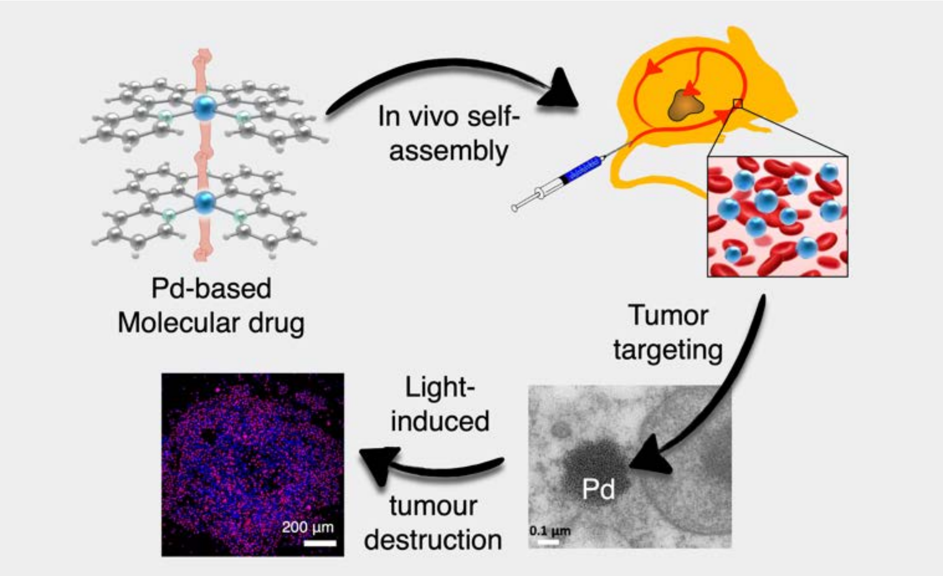
Enhanced passive diffusion is usually considered to be the primary cause of the enhanced cellular uptake of cyclometalated metal-based PDT photosensitizers, because cyclometalation lowers the charge of a metal complex and increases its lipophilicity. However, cyclometalated palladium-based photosensitizers for PDT self-assemble, in aqueous solutions, into soluble supramolecular nanorods. These nanorods formed *via* metallophilic Pd···Pd interaction and π–π stacking, and were stabilized in cell medium by serum proteins, in the absence of which they precipitated. In cell cultures, these protein-stabilized self-assembled nanorods were responsible for the improved cellular uptake of the sensitizers, which took place via endocytosis (i.e., an active uptake pathway). In addition to triggering self-assembly, cyclometalation also led to dramatically enhanced photodynamic properties under visible light irradiation, also in hypoxic cancer cells. Such combination of enhanced cellular penetration and type I photodynamic properties were also observed in multicellular tumor spheroids and in mice tumor xenografts, demonstrating that protein-stabilized nanoaggregation of cyclometalated sensitizer allows efficient cellular uptake also in 3-dimensional tumor models. Overall, serum proteins appear to be a major element in the design of PDT photosensitizers because they strongly influence the size and bioavailability of supramolecular prodrug aggregates, and hence their efficacy in vitro and in vivo.



References

[1] Zhou, Z.-Q., Xiao, M., Ramu, V., Hilgendorf, J., Li, X., Papadopoulou, P., Siegler, M.A., Kros, A., Sun, W., Bonnet, S. *J. Am. Chem. Soc.* **2019**, 142, 10383.

[2] Zhou, Z.-Q., Wang, P., Ramu, V., Zhang, L., Jiang, S., Li, X., Abyar, S., Papadopoulou, P., Shao, Y., Bretin, L., Siegler, M. A., Buda, F., Kros, A., Fan, J., Peng, X., Sun*, W., Bonnet*, S. *Nat. Chem.* **2023**, *in press*.

KN09

Wednesday 6th September 11:00

From Organometallic Molecular Systems to Functional Materials: Solution and Solid-State Methodologies

Janusz Lewiński[1,2]

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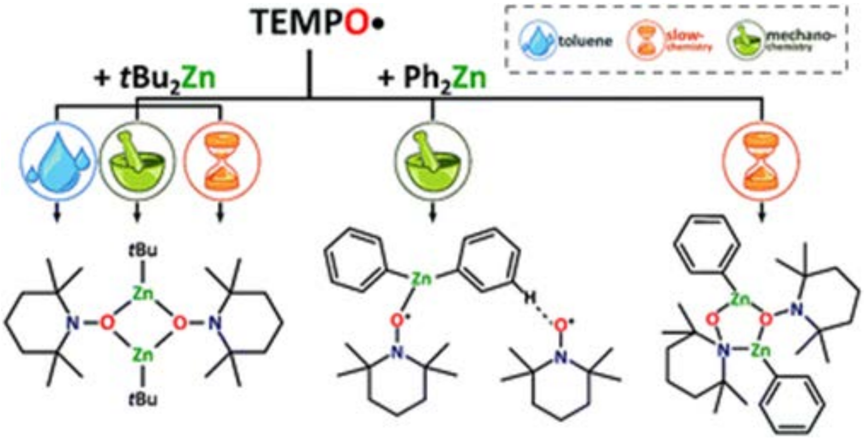
On 15 November 2021 the father of organometallic chemistry in Poland Prof. Stanisław Pasynkiewicz passed away. He was the Chairman of Division of Organometallic Chemistry of the FECS/EuChem for over 25 years (1974 - 2001) and since 2001 the Honorary Chairman. With the aim to honour his seminal contributions to organometallic chemistry, we demonstrate our case studies on the desired evolutions of organometallic compounds using solid-state mechano- and slow-chemistry, melt, and solution approaches.[1-5] Successful attempts to monitor temperature-induced solid-state evolutions of molecular organometallics to semiconductor nanocrystals will be also presented.[6]



Solution-based syntheses are omnipresent in chemistry but are often associated with obvious disadvantages. In the recent decade, solvent-free processes like mechanochemical synthesis driven by mechanical force or slow-chemistry reactions (solid-state transformations occurring without external stimuli) have gained enormous momentum as an alternative approach to synthesize a wide range of molecules and materials.[7] The reactions mediated by grinding or ball-milling avoid the solubility restrictions imposed by insoluble reactants, shorten the synthesis times and offer a number of other advantages. These transformations may be assisted by a melt phase as in some instances the heating caused by mechanical work can lead to localized melting, triggering local chemical reaction. Moreover, while mechanochemistry requires engagement of the mechanical stress, the core concept of emerging slow-chemistry avoids external stimuli but does not exclude acceleration of a reaction rate by the presence of a solvent vapor.

References

1. J. Lewiński, et.al, *Angew. Chem. Int. Ed.* **2010**, 49, 8266.
2. K. Budny-Godlewski, et. al., *Chem. Sci.* **2019**, 10, 7149.
3. K. Budny-Godlewski, et. al., *ChemSusChem* **2021**, 14, 3887.
4. P. Krupiński, et. al., *ACS Sustainable Chem. Eng.* **2021**, 9, 1540.
5. M. Wolska-Pietkiewicz, et. al., *Adv. Funct. Mater.*, **2022**, 2205909.
6. J. Lewiński and coworkers, *Materials Horizons*, **2018**, 5, 905.
7. a) J. Lewiński and coworkers, *Acc. Chem. Res.*, **2019**, 52, 3233; b) F. García, *Chem. Soc. Rev.*, **2019**, 48, 2274.

KN10

Wednesday 6th September 11:30

Hydroamination of Alkynes Catalyzed by Gold Nanoparticles: A Sustainable and Effective Approach to the Synthesis of *N*-Heterocyclic Compounds

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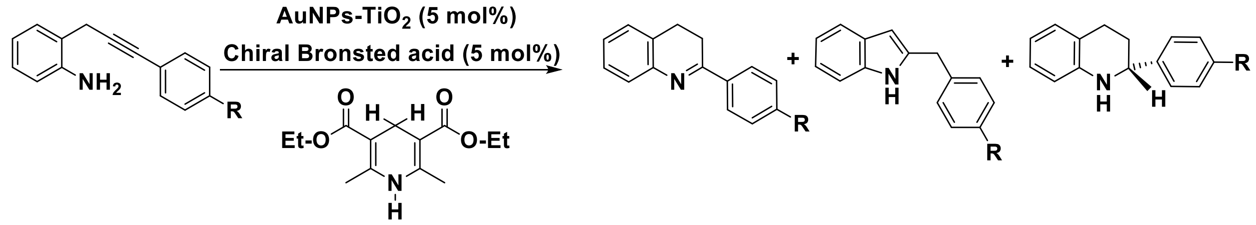
The direct addition of amines to alkynes or olefins is an elegant approach for the synthesis of C-N bonds characterized by 100% atom economy and high efficiency, chemo and stereoselectivity. Thermodynamic and kinetic constraints make hydroamination reaction particularly challenging and the choice of the appropriate metal catalyst is thus critical.[1] Gold Nanoparticles (AuNPs) stabilized by inorganic or organic polymer supports readily catalyze intermolecular hydroamination of a wide range of alkynes with anilines.[2] In this contribution, we report on the *one-pot* hydroamination followed by in situ asymmetric transfer hydrogenation of 2-(2-propynyl)aniline derivatives catalyzed by AuNPs-TiO_2 in the presence of the Hantzsch ester as reductant; this route allows the synthesis of chiral tetrahydroquinolines in moderate to excellent yields with good enantioselectivity. The electronic effect of substituents onto the aryl group of the phenylpropynyl moiety has been investigated to address the reaction pathway toward the *6-endo-dig* (dihydroquinoline) *vs* the *5-exo-dig* (indole) ring closure. The kinetic parameters and isotopic effect have been also studied to shed light on the reaction mechanism.



References

[1] I.P. Beletskaya, C. Najera, M. Yus *Russ. Chem. Rev.* **2020**, *89*, 1074-1114.

[2] A. Dentoni Litta, A. Buonerba, A. Casu, A. Falqui, C. Capacchione, A. Franconetti, H. Garcia, A. Grassi, *J. Catal.* **2021**, *400*, 71-82.

KN11

Wednesday 6th September 14:30

Investigating The Biological Properties Of Gold Carbene Complexes

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Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, E-50009 Zaragoza, Spain.

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During the last few decades, interest in the chemistry of N-Heterocyclic Carbenes (NHC) or Acyclic Diamine Carbenes (ADC) has increased due to their applications in different fields of research such as medicine, catalysis, and materials science. This wide range of applications is a direct consequence of the great functionalization capacity of these compounds, as they are able to modify the substituents of both nitrogen atoms, and consequently, the electronic and steric properties of the final complexes.

These carbenes are excellent σ-donor ligands and form extraordinarily stable gold derivatives. Indeed, NHC-Au(I) species display high cytotoxicity *in vitro* against a variety of human cancer cell lines with different degrees of selectivity. In the search for new alternatives of stable and robust derivatives, not only N-heterocyclic but also N-acyclic carbenes could be explored, and their activity and selectivity compared. The aim of this work is the synthesis of Au(I) complexes with NHC and ADC ligands using different substituents in their structural frameworks that can direct the compounds to specific biological targets. The anticancer activity has been explored, and high selectivity towards tumor cells has been found in the studied complexes.

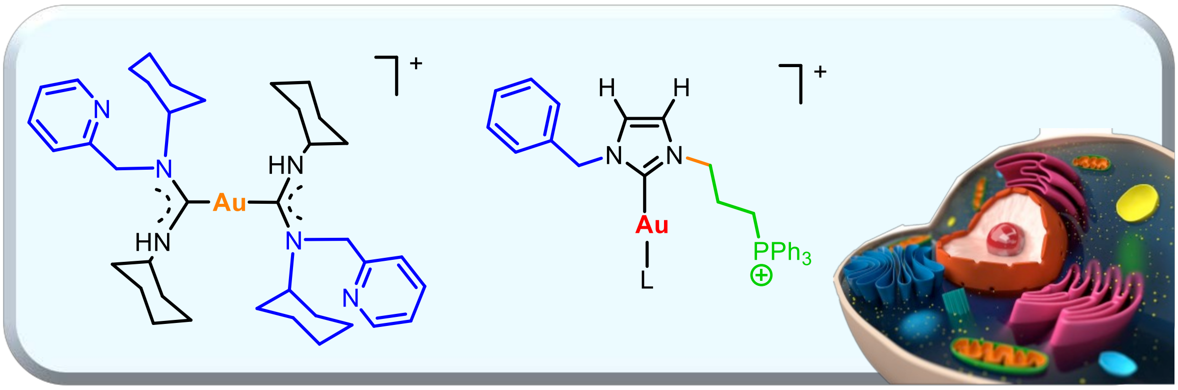

Figure 1. Some of the NAC and NHC gold complexes prepared.

KN12

Wednesday 6th September 14:30

Combining Helicenes With Transition Metals Or Lanthanides For Chirality-Related Properties

Jeanne Crassous

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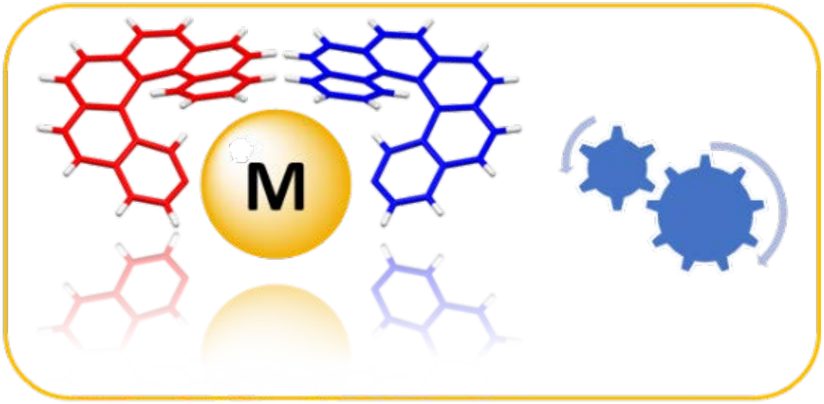
Ortho-fused aromatic rings form helically shaped chiral molecules such as carbo[6]helicenes, that wind in a left-handed (M) or a right-handed (P) sense.[1] The helical topology combined with extended π-conjugation provides helicenes with peculiar properties such as strong photophysical and chiroptical properties (high optical rotation values, intense electronic circular dichroism and circularly polarized emission). The molecular engineering of helicenes using organometallic and coordination chemistries offers a convenient way to tune the properties of these helically shaped π-ligands. Indeed, their combination with transition metals or lanthanides leads to chiral materials with appealing properties (tuneable electronic circular dichroism, circularly polarized phosphorescence, magnetochirality, spin selectivity) for applications in materials science (Circularly Polarized OLEDs, Chiroptical Switches, Spintronics). I will present a set of representative examples.[2]



References

1) a) C. -F. Chen, Y. Shen, *Helicenes Chemistry: From Synthesis to Applications.* Springer, Berlin, **2017**; b) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 1051; c) K. Dhbaibi, L. Favereau, J. Crassous *Chem. Rev.* **2019**, *119*, 8846; d) J. Crassous, I. G. Stará, I. Starý (Eds) *Helicenes - Synthesis, Properties and Applications.* Wiley, **2022**.
2) a) N. Hellou, M. Srebro-Hooper, L. Favereau, F. Zinna, E. Caytan, L. Toupet, V. Dorcet, M. Jean, N. Vanthuyne, J. A. G. Williams, L. Di Bari, J. Autschbach, J. Crassous, *Angew. Chem. Int. Ed.* **2017**, *56*, 8236; b) E. S. Gauthier, L. Abella, N. Hellou, B. Darquié, E. Caytan, T. Roisnel, N. Vanthuyne, L. Favereau, M. Srebro-Hooper, J. A. G. Williams, J. Autschbach, J. Crassous, *Angew. Chem. Int. Ed.* **2020**, *59*, 8394; c) M. Atzori, K. Dhbaibi, H. Douib, M. Grasser, V. Dorcet, I. Breslavetz, K. Paillot, O. Cador, G. L. J. A. Rikken, B. Le Guennic, J. Crassous, F. Pointillart, C. Train, *J. Am. Chem. Soc.* **2021**, *143,* 2671*;* d) K. Dhbaibi, M. Grasser, H. Douib, V. Dorcet, O. Cador, N. Vanthuyne, F. Riobé, O. Maury, S. Guy, Amina Bensalah-Ledoux, B. Baguenard, Geert L. J. A. Rikken, C. Train, B. Le Guennic, M. Atzori, F. Pointillart, J. Crassous, *Angew. Chem. Int. Ed.* **2023**, 62, e202215558.

KN13

Thursday 7th September 11:00

Cationic Polyhedral Heteroboranes - Fact or Fiction?

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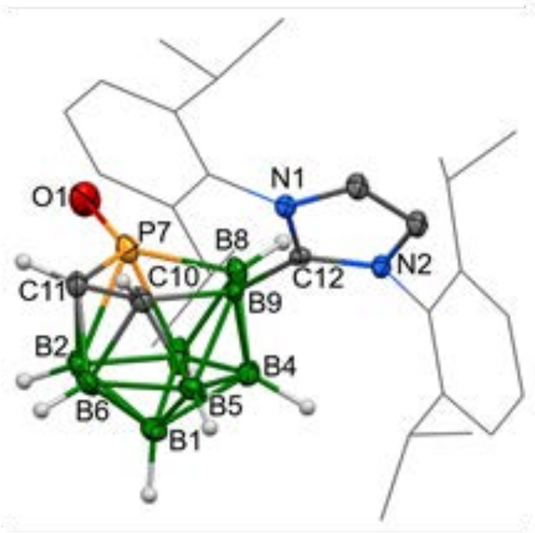
In the hundred-year-history of boron hydrides and their successors (polyhedral boranes, carboranes and other heteroboranes) and derivatives, the number, molecular shape, reactivity and applications of these species have become enormous, thus establishing a self-consistent field of chemistry. Areas of possible applications of these species ranging from energy/hydrogen storage, synthetic organic chemistry, catalysis and medicine to preparation of new materials. Polyhedral boranes and hereroboranes appear almost exclusively as neutral or anionic species, while the cationic ones are protonated at exoskeletal heteroatoms or they are instable. Taking these considerations into account, one could expect that the addition of a strong σ-donor such as NHCs would increase the electron density on those traditionally taken electron-deficient skeletons and stabilise them like in the many cases of low-valent or cationic main-group elements.

Surprisingly enough, the addition of NHCs to 10-vertex *closo* dicarbaborane species followed by subsequent addition of protonation agent produced cationic cages.[1] In this work, we would like to demonstrate the power of NHC donation for stabilization of unusual species. (Scheme 1).



Scheme 1 An example of NHC stabilized compound.

This work was supported by Czech Science Foundation grant nr. 22-03945S.

References

1 J. Vrána, J. Holub, M. A. Samsonov, Z. Růžičková, J. Cvačka, M. L. McKee, J. Fanfrlík, D. Hnyk, A. Růžička, *Nat. Commun.* **2021**, *12*, 4971.

KN14

Thursday 7th September 11:30

Catalytic Creation of Sterically Challenging Stereogenic Centers: Concepts and Mechanistic Insights

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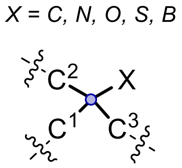
[1] Institute of Chemical Research of Catalonia (ICIQ), the Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 - Tarragona, Spain. E-mail: akleij@iciq.es. [2] Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain

Catalytic asymmetric preparation of compounds featuring quaternary and similarly challenging stereogenic centres remains a highly attractive and rewarding objective in organic synthesis.[1] Often such motifs are found in biologically active substances and natural compounds. We have developed over the years effective methodologies addressing these synthetic targets utilizing either allylic or propargylic substitution reactions to construct new C–C and C–X (X = heteroatom) bonds.[2] Apart from devising such protocols, part of our attention has been on elucidating the principal manifolds that are involved to empower the formation of sterically congested carbon stereocenters.[3] A recent development in the group is the use of base metal catalysis in combination with photo-chemical reduction to enable dual catalysis approaches.[4] This contribution will give an overview of all these activities highlighting the most important achievements.



- *synthetic protocols for 3° and 4° stereocenters*
- *diastereoselective and/or enantioselective*
- *mechanistic analysis and understanding*
- *use of base metal catalysis empowered by Co/Ni*

via allylic/ propargylic chemistry

References

1. (a) Li, C.; Ragab, S. S.; Liu, G.; Tang, W. *Nat. Prod. Rep.* **2020**, *37*, 276; (b) Das, J. P.; Marek, I. *Chem. Commun.* **2011**, *47*, 4593.
2. Some examples: (a) Cai, A.; Guo, W.; Martínez-Rodríguez, L.; Kleij, A. W. *J. Am. Chem. Soc.* **2016**, *138*, 14194; (b) Guo, W.; Kuniyil, R.; Gómez, J. E.; Maseras, F.; Kleij, A. W. *J. Am. Chem. Soc.* **2018**, *140*, 3981; (c) Gómez, J. E.; Cristòfol, À.; Kleij, A. W. *Angew. Chem. Int. Ed.* **2019**, *58*, 3903.
3. Some examples: (a) Hu, L.; Cai, A.; Wu, Z.; Kleij, A. W.; Huang, G. *Angew. Chem. Int. Ed.* **2019**, *58*, 14694; (b) Limburg, B.; Cristòfol, À.; Kleij, A. W. *J. Am. Chem. Soc.* **2022**, *144*, 10912; (c) Garcia-Roca, A.; Pérez-Soto, R.; Stoica, G.; Benet-Buchholz, J.; Maseras, F.; Kleij, A. W. *J. Am. Chem. Soc.* **2023**, *145*, 6442.
4. (a) Cristofol, A.; Limburg, B.; Kleij, A. W. *Angew. Chem. Int. Ed.* **2021**, *60*, 15266; (b) Xue, S.; Cristòfol, À.; Limburg, B.; Zeng, Q.; Kleij, A. W. *ACS Catal.* **2022**, *12*, 3651; (c) Zeng, Q.; Gao, F.; Benet-Buchholz J.; Kleij, A.W. *ACS Catal.* **2023**, *13*, 7514.

KN15

Thursday 7th September 11:00

Borylalkyde Copper(I) Species for Selective Electrophilic Trapping in Advanced Synthetic Protocols

Elena Fernández[1]

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Boron-stabilized carbanions can be considered versatile reagents that have found numerous synthetic applications in advanced synthetic protocols.[1-4] Copper (I) is one of the most reliable counter cation of α-borylcarbanions and the synthesis of borylalkyde copper (I) can be performed via complementary efficient methods. The chemistry of borylalkyde copper (I) show a remarkable diversity and enable many different synthetic routes towards efficient C-C bond formation. The electrophilic trapping of α-boryl carbanions with allyl halides has been extensively studied to control both, the S_N2 and the S_N2' substitution reactions. Alkyl or aryl halides also react smoothly with α-borylcarbanions through S_N2 mechanism, as a new methodology for homologation reactions. Copper catalyzed addition of borylalkyde to vinyl carbonates and vinyl epoxides, proceeds through allylic alkylation with concomitant ring opening. But also, C-C bond formation through ring closing strategies becomes a suitable platform for the preparation of selective borylated cycles. We correlate the selection of the appropriate reactive borylalkyde copper (I) depending on the sought reactivity.

References

[1] N. Miralles, R. J. Maza, E. Fernández, *Adv. Synth. Catal.* **2018**, *360*, 1306.
[2] Ch. Wu, J. B. Wang, *Tetrahedron Lett.* **2018**, *59*, 2128.
[3] R. Nallagonda, K. Padala, A. Masarwa, *Org. Biomol. Chem.* **2018**, *16*, 1050.
[4] N. Kumar, R. R. Reddy, N. Eghbarieh, A. Masarwa, *Chem. Commun.* **2020**, *56*, 13.

KN16

Thursday 7th September 11:30

Activation of C–H Bonds with Fe–Al Heterometallic Complexes

Mark Crimmin,[1] Nikolaus Gorgas,[1] and Benedek Stadler[1]

[1] *Molecular Sciences Research Hub, Imperial College London, White City, London, W12 0BZ, UK,*
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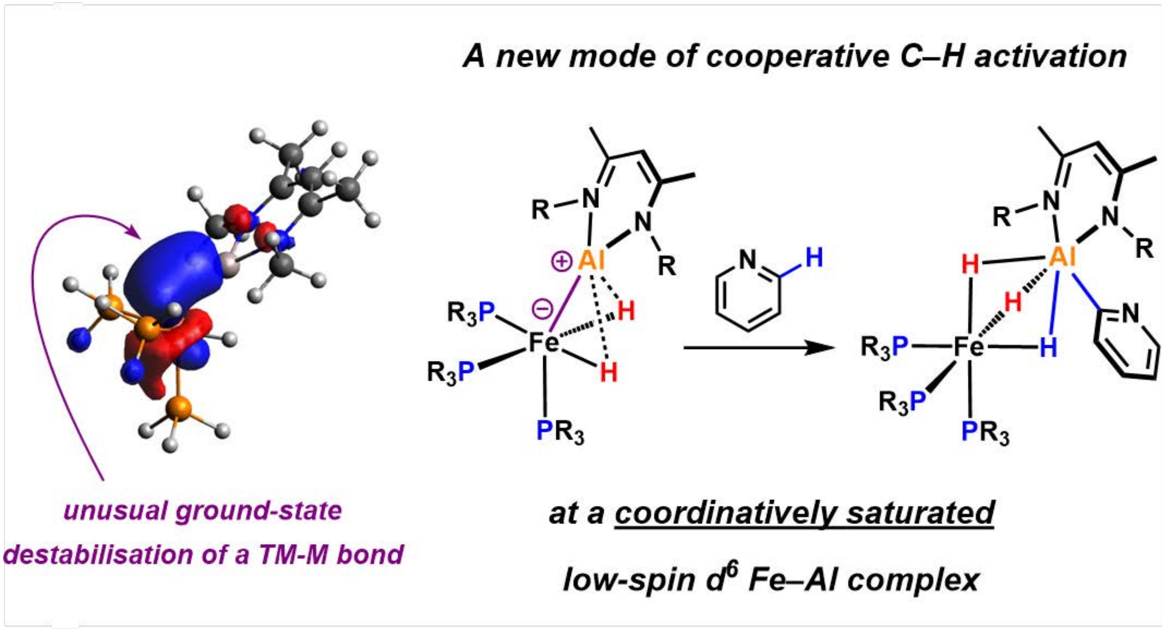
The reactions of transition metal complexes underpin numerous synthetic processes and catalytic transformations. Typically, this reactivity involves the participation of empty and filled molecular orbitals centred on the transition metal. Kinetically stabilised species, such as octahedral low-spin d^6 transition metal complexes, are not expected to participate directly in reactions. However, novel approaches that exploit metal ligand-cooperativity offer an opportunity to challenge this preconception. Here we show that inclusion of an aluminium-based ligand into the coordination sphere of neutral low-spin d^6 iron complex leads to unexpected reactivity. Complexes featuring an unsupported Fe–Al bond can activate the sp^2C–H bonds of pyridines and alkenes,[1-2] along with the sp^3C–H bonds of acetonitrile.[3] Kinetic data and DFT calculations have been used to better understand the mechanisms of these new reactions and the role of Fe–Al cooperativity in bond activation.



A new mode of cooperative C–H activation

unusual ground-state destabilisation of a TM-M bond

at a coordinatively saturated low-spin d^6 Fe–Al complex

References

1. J. Am. Chem. Soc. **2022**, 144, 8770;
2. *Chem. Commun.* **2022**, *58*, 10849;
3. Angew. Chem. Int. Ed. **2023**, 62, e202219212.

KN17

Thursday 7th September 15:30

The Impact of N-Heterocyclic and Mesoionic Carbenes in Manganese Catalysis

Beatriz Royo[1]

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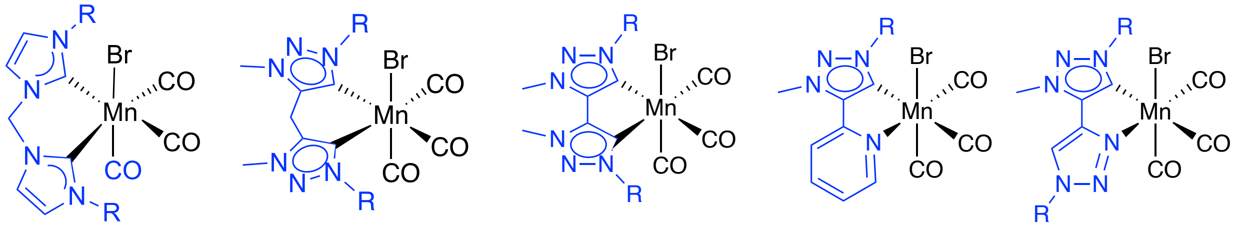
N-Heterocyclic carbenes (NHCs) are solidly established as one of the most versatile ligands in organometallic chemistry and catalysis. Surprisingly, although manganese-NHC complexes are known since the beginning of the 1970s, their application in homogeneous catalysis has remained poorly explored, and its chemistry is limited to imidazolium-derived NHCs.[1] In this seminar, our recent work on manganese with mesoionic carbenes of 1,2,3-triazolylidene type, an interesting subclass of NHCs, will be presented. We will describe the first examples of Mn(I) tricarbonyl complexes with bidentate ligands featuring combinations of pyridine, triazole, and 1,2,3-triazolylidene ligands (Scheme 1). Having these complexes with varying electronic and steric properties, we have investigated their activity in a number of catalytic processes, including hydrosilylation, oxidation, borrowing hydrogen processes, and electrocatalytic reduction of CO_2.[1] The impact of the introduction of imidazolium- and triazolium-derived NHCs in the catalytic efficiency of the Mn complexes will be discussed.



Scheme 1. Mn complexes bearing bidentate NHC ligands

Acknowledgments. We thank FC&T for funding: PTDC/QUI-QIN/0359/2021, MOSTMICRO-ITQB, UIDB/04612/20220 and UIPD/04612/2020, and CERMAX through project 022162.

References

(1) S. Friães, S. Realista, H. Mourão, B. Royo, *Eur. J. Inorg. Chem.* **2022**, (10) e202100884.

KN18

Thursday 7th September 15:30

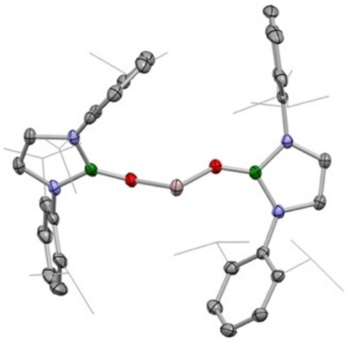
Unleashing New Patterns of Reactivity with Electron Rich Main Group Compounds

Simon Aldridge,[1] Jamie Hicks,[1] Josef T. Boronski,[1] Petra Vasko,[1] Andreas Heilmann,[1] Caitilín McManus,[1] Debotra Sarkar, Agamemnon E. Crumpton.[1]

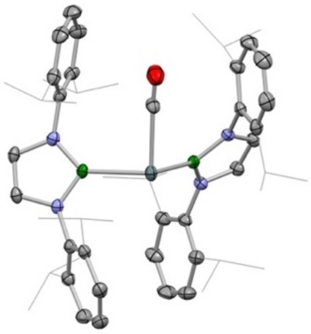
[1] *Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK;* simon.aldridge@chem.ox.ac.uk

Main group compounds capable of carrying out the sorts of small molecule activation processes more often associated with transition metal complexes have become a highly topical area of modern chemistry.[1] *p*-Block systems capable of capturing and cleaving key small molecules such as H_2, ammonia, carbon monoxide and alkenes have been developed, and the applications of some such systems in heavy-metal-free catalysis have started to emerge.

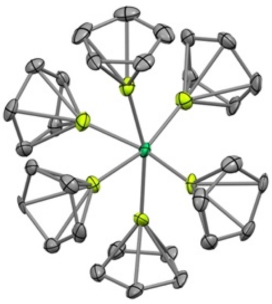
We have been interested in the development of highly electron rich group 13 metal systems (M = Al, Ga, In) which bear a net negative charge and can act in 'umpolung' fashion as nucleophiles towards carbon- and metal-centred electrophiles.[2-5] These aluminyl systems also show highly unusual patterns of small molecule activation chemistry for main group metal systems, e.g. C-H activation of benzene (and other arenes)[2] and CO homologation,[3] together with other modes of reactivity (C-C bond cleavage) which are unprecedented for *any* isolated metal complex.[4] The highly electron rich nature of these group 13 systems can also be exploited in bimetallic compounds, by acting as highly electron releasing metallo-ligands;[5] this chemistry has recently been extended by the advent of Be(I) species,[6] which have the potential to act as even stronger □-donor X-ligands.



[(BorylO)$_2$Al]$^-$



(Boryl)$_2$Sn·CO.



Ni(Berylyl)$_6$

References

[1] See, for example: Power, P. P. *Nature*, **2010**, *463*, 171.
[2] Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. *Nature,* **2018**, *557*, 92.
[3] Heilmann, A. et al. *J. Am. Chem. Soc.*, **2022**, *144*, 12942.
[4] Hicks, J. et al. *J. Am. Chem. Soc.*, **2019**, *141*, 11000.
[5] Hicks, J. et al. *Nature Chem.,* **2019**, *11*, 237.
[6] Boronski, J. T. et al. *Science*, **2023**, in press (publication: 16/06/23).

— XXV CONFERENCE —
ON ORGANOMETALLIC CHEMISTRY

EuCOMC XXV

ABSTRACTS:
ORAL COMMUNICATIONS

OC01

Tuesday 5th September 12:00

Synthesis of a 21-electron cobaltocene derivative

Satoshi Takebayashi[1], Jama Ariai[2], Urs Gellrich[2], Sergey V. Kartashov[3], Robert R. Fayzullin[3], Hyung-Been Kang[1], Takeshi Yamane[4], Kenji Sugisaki[4], and Kazunobu Sato[4]

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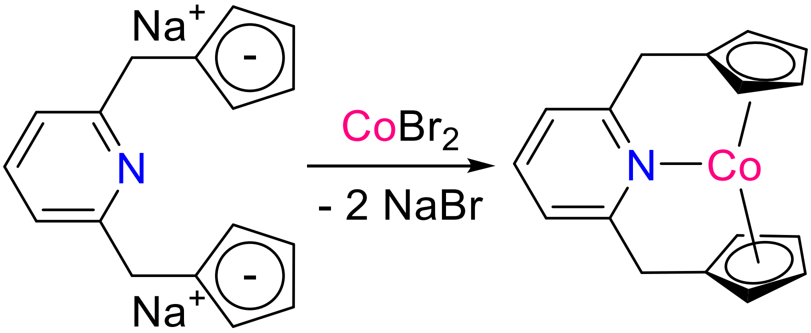
[2]Justus Liebig University Giessen, Giessen, Germany.
[3]Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russian Federation.
[4]Osaka Metropolitan University, Osaka, Japan.

Metallocenes are highly versatile organometallic compounds. The versatility of the metallocenes stems from their ability to stabilize a wide range of formal electron counts. To date, *d*-block metallocenes with electron counts up to 20 have been synthesized and utilized in catalysis, sensing, and other fields. However, *d*- block metallocenes with more than 20-electron counts have remained elusive.[1-3] Synthesis and isolation of such complexes are challenging since metal-carbon bonds in *d*-block metallocenes become weaker upon increasing deviation from the stable 18-electron configuration. Here, we report the first synthesis, isolation, and detailed characterization of a 21-electron cobaltocene derivative. This discovery is based on the ligand design that allows the coordination of a two- electron donor to a 19-electron cobaltocene derivative while maintaining the η^5- coordination mode of two cyclopentadienyl groups, a previously unexplored synthetic approach. Furthermore, we clarified the origin of the stability, redox chemistry, and spin state of the 21-electron cobaltocene derivative.



References

1 Holloway, J. D. L.; Geiger, W. E., *J. Am. Chem. Soc.* **1979,** *101* (8), 2038-2044.

2 Howard, C. G.; Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B., *J. Am. Chem. Soc.* **1984,** *106* (7), 2033-2040.

3 Goodwin, C. A. P. *et al.* *Nat. Chem.* **2021,** *13* (3), 243-248.

OC02

Tuesday 5th September 12:15

Isolation of Radical Anions via 3d-Metal Complexation or Cation Encapsulation

C. Gunnar Werncke[1]

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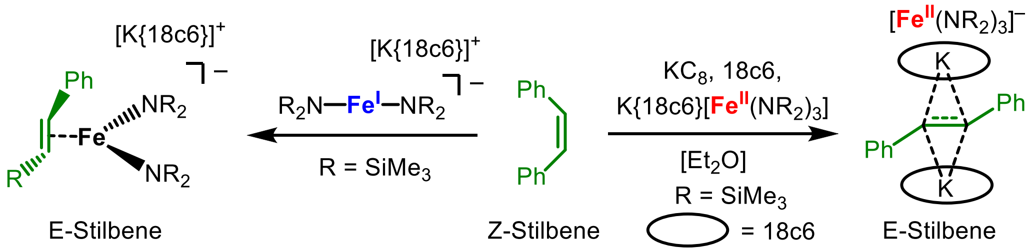
Organic radical anions appear as intermediates in a variety of organic reductions. They are intrinsically unstable due to their ability to react subsequently in a multitude of reaction pathways, such as dimerization, as exploited in pinacol-type coupling reactions. In recent years, organic radical anions have received further attention due to the surge of photoredox catalysis. As such there is a longstanding interest in the physical and chemical behaviour of simple radical anions. Common methods to stabilize or even isolate such species rely on the use of extended aromatic systems or electron withdrawing functional groups, such as carbonyl units, lowering the energy of the involved π* orbitals as well as to disperse of the radical character over a larger π-system. Alternatively, radical anions can be formed in conjunction with low-valent metal centres.

Here we present the interaction of highly reducing linear 3d-metal(I) silylamides (M = Cr – Co) with alkynes,[1] alkenes,[2] aldimines and ketimines.[3] This leads to the observation of rare and unprecedented metal(II) bound radical anions, which subsequently can undergo bond formation and/or rearrangement processes.



Furthermore, isolation of simple organic radical anions is achieved via encapsulation of the radical anion between two K{18-crown-6} cations. It allows for the isolation of the long-time elusive stilbene radical anion.[2]

References

[1] I. Müller, D. Munz, C. G. Werncke, *Inorg. Chem.* **2020**, 59, 9521. [2] G. Sieg, I. Müller, K. Weißer, C. G. Werncke, *Chem. Sci.* **2022**, *3*, 13872. [3] G. Sieg, Q. Pessemesse, S. Reith, S. Yelin, C. Limberg, D. Munz, C. G. Werncke, *Chem. Eur. J.* **2021**, *67*, 16760.

OC03

Tuesday 5th September 12:30

Towards Catalyst Design and Databases for Molecular OER Catalysis

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Despite fossil fuels having brought forth the dawn of civilisation as we know it, they have also left an enduring effect on the Earth's climate. To address this, it is imperative that we devise renewable technologies to decarbonise our economy. For example, one could envision using sunlight to drive (photo)electrochemical water splitting devices to produce H_2, a highly energy-dense fuel when compressed and stored. A major roadblock in realizing this, however, is the lack of affordable and efficient catalysts for the oxygen evolution reaction (OER).

In the first part of this talk I will describe our recent findings which demonstrate that molecular catalysts obey the same OER scaling relations observed for heterogeneous systems, and thereby are constrained to the "overpotential wall" imposed by such relations.[1] In addition, I will discuss how some of the most active complexes reported in the literature can circumvent the overpotential wall, and how this knowledge can be translated into a set of catalyst design principles to accelerate the discovery of "ideal" molecular OER catalysts via high-throughput and machine learning studies.[2]

In the second part of this talk, I will describe our ongoing research efforts in the generation of curated molecular databases to boost molecular discovery. To this aim, we have created a modular platform named *Directed Assembly of Random Transition metal complexes* (DART),[3] which currently allows us to retrieve a subset of over 50,000 monometallic complexes from the Cambridge Structural Database, and to extract and classify unique metal ligands based on their atomic composition, denticity, coordinating atoms, molecular weight, formal charge, etc. Furthermore, DART can assemble novel metal complexes with the desired topology (*e.g.* octahedral) based on a user-specified set of instructions using the user-curated set of unique ligands in an automated fashion. Ultimately, we envisage this automated, modular workflow to accelerate molecular discovery for a broad range of applications, including OER catalysis.

References

[1] Craig, M. J.; Coulter, G. O.; Dolan, E. T.; Soriano-López, J.; Mates-Torres, E.; Schmitt, W.; García-Melchor, M. *Nat. Commun.* **2019**, *10*, 4993; b) Craig, M. J.; García-Melchor, M. *Curr. Opin. Electrochem.* **2022**, *35*, 101044; c) Craig, M. J.; Barda-Chatain, R.; García-Melchor, M. *J. Catal.* **2021**, *393*, 202–206.

[2] Craig, M. J.; García-Melchor, M. *Cell Rep. Phys. Sci.* **2021**, *2*, 100492. b) Craig, M. J.; García-Melchor, M. *Molecules*, **2021**, *26*, 6362.

[3] Sommer, T.; Clarke, C.; Kleuker, F.; García-Melchor, M. Manuscript in preparation.

OC04

Tuesday 5th September 12:45

Problematic Ar^F-Alkynyl Stille Coupling: From Partial Success to Efficient Solutions, *via* Mechanistic Understanding of the Hidden Complexity

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Ana M. Gallego,[1] Max García-Melchor,[2] and Pablo Espinet[1]

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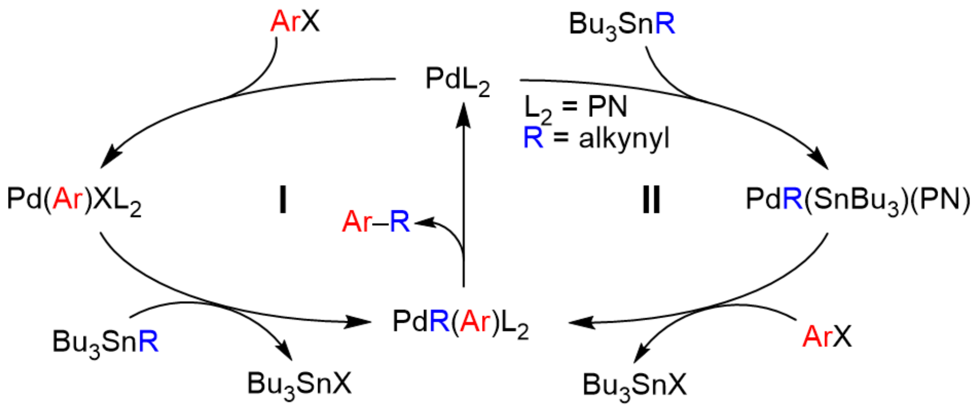
Since its discovery, Stille catalysis has proven to be an excellent method for C-C coupling. The mechanisms of the different steps of the classic cycle (Scheme 1, cycle **I**), namely Ar-X oxidative addition (Ar = aryl), R-$SnBu_3$ transmetalation, and Ar–R reductive elimination, have been thoroughly studied.[1] Remarkably, a variation of the classic Stille pathway, operating specifically for Ar-Alk coupling (Alk = alkynyl) and initiated by oxidative addition of Alk-$SnBu_3$ to Pd^0(PN) (PN = chelating amino-phosphine) was previously proposed in the literature (Scheme 1, cycle **II**).[2]

Herein, using experimental and theoretical information, from kinetic,[3] microkinetic and DFT studies, either in stoichiometric or catalytic conditions, we unambiguously disproved the alternative cycle. The mechanistic knowledge allowed to clarify the reasons behind the initially poor catalytic performance using perhaloaryl groups. The delusive interference of several out-of-cycle Pd-Sn molecular species, that were fully characterized, provokes the catalyst decay and the competitive formation of side-products. Ultimately, the knowledge acquired leads to the rational choice of additives and the subsequent raising of the catalytic results to quantitative yields.[4]



Scheme 1. Classical Stille cycle (**I**), and alternative pathway (**II**) proposed for the aryl-alkynyl coupling, using PN ligands.

References

[**1**] Cordovilla, C.; Bartolomé, C.; Martínez-Ilarduya, J. M.; Espinet, P. *ACS Catal.* **2015**, *5*, 3040–3053.
[**2**] Shirakawa, E.; Yoshida H.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 5177–5180.
[**3**] Gallego, A. M.; Peñas-Defrutos, M. N.; Marcos-Ayuso, G.; Martin-Álvarez, J. M.; Martínez-Ilarduya, J. M.; Espinet, P. *Dalton Trans.* **2020**, *49*, 11336-11345.
[**4**] Marcos-Ayuso, G.; Peñas-Defrutos, M. N.; Gallego, A. M.; García-Melchor, M.; Martínez-Ilarduya, J. M.; Espinet, P. *J. Am. Chem. Soc.*, **2023**, *145*, 527–536.

OC05

Tuesday 5th September 12:00

Bis-Phosphine Ni(0) Complexes and Catalytic Applications in Alkyne Cycloaddition Reactions

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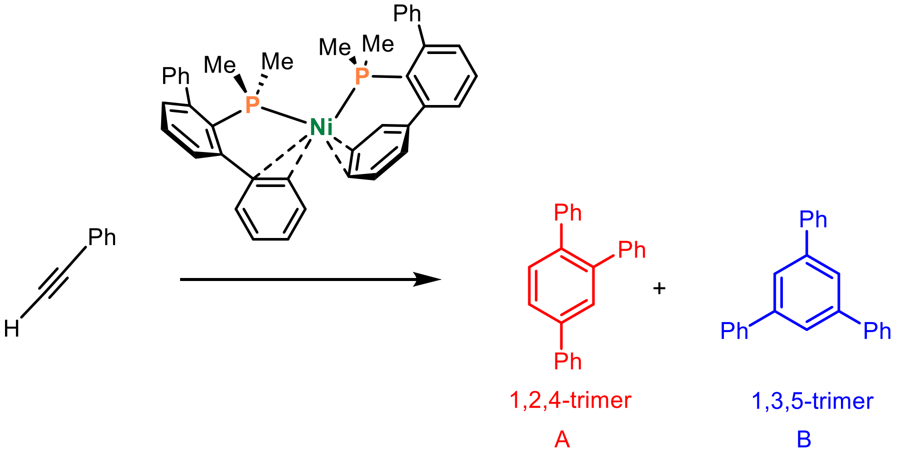
Di-coordinate, zero-valent Ni complexes have attracted widespread attention for their capability to activate unreactive bonds via oxidative addition.[1] On this basis, these species are postulated as intermediates in catalytic transformations that proceed through a M(0)/M(II) pathway, including cross-coupling and C-H activation reactions. Homoleptic and heteroleptic d^{10}-ML_2 complexes of Pd and Pt are known bearing bulky phosphines, N-heterocyclic carbenes (NHCs) and isocyanide ligands are known. However, two-coordinate Ni(0) analogues are rare and instances known are largely restricted to compounds supported by large NHC ligands. This presentation will focus on the use of dialkylterphenyl phosphines[2] as ancillary ligand to stabilize homoleptic NiP_2 complexes[3] and their applications in catalytic transformations involving alkynes as reactants.



References

1) Rama, R.J.; Martín, M.T.; Peloso, R.; Nicasio, M.C. *Adv. Organomet. Chem.* **2020**, *74*, 241.
2) Marín, M.; Moreno, J.J.; Navarro-Gilabert, C.; Álvarez, E.; Maya, C.; Peloso, R.; Nicasio, M.C.; Carmona, E. *Chem. Eur. J.* **2019**, *25*, 260; (b) Marín, M.; Moreno, J.J.; Alcaide, M.M.; Maya, C.; Álvarez, E.; López-Serrano, J.; Campos, J.; Nicasio, M.C.; Carmona, E. *J. Organomet. Chem.* **2019**, *896*, 120.
3) Martín, M.T.; Marín, M.; Rama, R.J.; Álvarez, E.; Maya, C.; Molina, F.; Nicasio, M.C. *Chem. Commun.* **2021**, *57*, 3031.

OC06

Tuesday 5th September 12:15

The Trifluoromethyl Silver(III) Moiety as a Platform for Highly Unusual Organometallic Compounds

Miguel Baya,[1] Daniel Joven-Sancho,[1,2] Luca Demonti,[2] Antonio Martín,[1]
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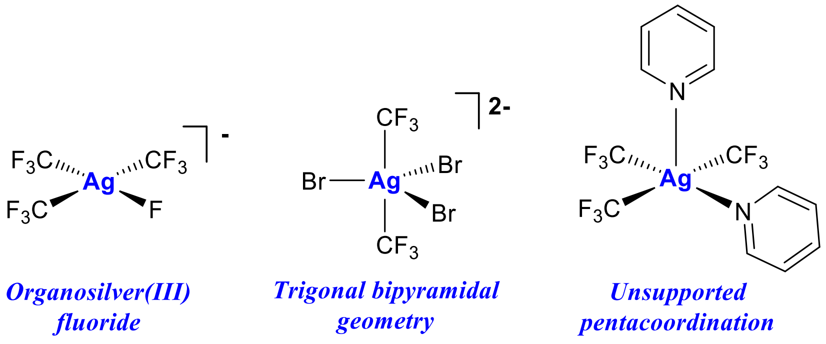
The CF_3 is an optimal ligand for stabilizing complexes in high oxidation states.[1] In recent years we have studied the chemistry of Ag-CF_3 complexes in oxidation state III. We have developed convenient procedures for the synthesis of the homoleptic complex $[Ag^{III}(CF_3)_4]^-$, as well as for a wide series of neutral and anionic derivatives of general formulae $[Ag^{III}(CF_3)_3L]$ and $[Ag^{III}(CF_3)_3X]^-$. Most of them exhibit electronic structures with Ligand Field Inversion, a rare phenomenon that is currently attracting much attention.[2] As a consequence of this singularity, some of the d^8 Ag(III) square-planar complexes show a marked trend to incorporate a fifth ligand in the metal coordination sphere.

In this communication we will provide a summarizing of some of our most outstanding results in trifluoromethyl silver chemistry, including synthesis, properties, and reactivity studies.[3]



Organosilver(III) fluoride

Trigonal bipyramidal geometry

Unsupported pentacoordination

Figure 1. Selection of highly unusual silver(III) complexes to be discussed.

References

[1] M. A. García-Monforte, S. Martínez-Salvador, B. Menjón *Eur. J. Inorg. Chem.* **2012**, 4945.
[2] R. Hoffmann, S. Alvarez, C. Mealli, A. Falceto, T. J. Cahill, III, T. Zeng, G. Manca *Chem. Rev.* **2016**, *116*, 8173.
[3] (a) D. Joven-Sancho, M. Baya, A. Martín, B. Menjón *Chem. Eur. J.* **2018**, *24*, 13098. (b) M. Baya, D. Joven-Sancho, P. J. Alonso, J. Orduna, B. Menjón *Angew. Chem. Int. Ed.* **2019**, *58*, 9954. (c) D. Joven-Sancho, M. Baya, A. Martín, J. Orduna, B. Menjón *Chem. Eur. J.* **2019**, *26*, 4471. (d) D. Joven-Sancho, M. Baya, L. R. Falvello, A. Martín, J. Orduna, B. Menjón *Chem. Eur. J.* **2021**, *27*, 12796. (e) D. Joven-Sancho, M. Baya, A. Martín, J. Orduna, B. Menjón *Angew. Chem. Int. Ed.* **2021**, *60*, 26545. (f) D. Joven-Sancho, L. Demonti, A. Martín, N. Saffon-Merceron, N. Nebra, M. Baya, B. Menjón *Chem. Commun.* **2023** (accepted, DOI: 1039/D3CC00493G).

OC07

Tuesday 5th September 12:30

Iridium complexes based on aminophosphano ligands: synthesis and application in catalysis

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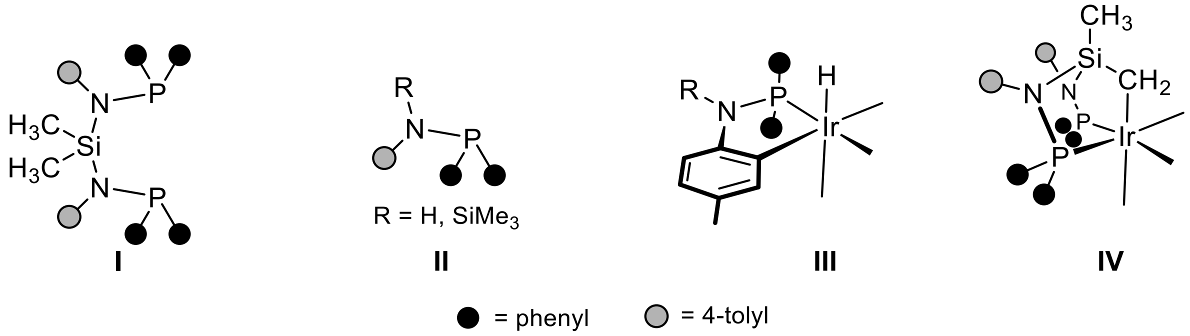
Despite the fact that the modular synthesis of aminophosphano ligands[1] makes them especially attractive and versatile when it comes to tailoring electronic and steric properties of the resulting metal-ligand platforms, they are substantially less explored than related phosphanes or phosphites. On this background, in the last years we have focussed on the design of novel aminophosphano ligands and the study of their coordination chemistry towards rhodium[2] and iridium[3]. Herein, we report on the preparation of a varied family of iridium compounds based on aminophosphanes of formula SiMe$_2${N(4-C$_6$H$_4$CH$_3$)PPh$_2$}$_2$ (**I**) and NR(4-C$_6$H$_4$CH$_3$)PPh$_2$ (R = H, SiMe$_3$) (**II**) showing that a variety of structural motifs can be obtained, including unexpected orthometallated moieties (**III**) or [Ir{κ^3*C,P,P'*-(SiNP–H)}] platforms (**IV**) (Scheme 1).



Scheme 1

Additionally, selected iridium complexes have proved to be effective catalysts for the dehydrogenation of formic acid or the dehydrogenative silylation of alcohols, carboxylic acids and amines. A selection of results will be presented.

References

[1] a) G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane, *J. Chem. Soc.*, 1962, 3984; b) H. H. Sisler and N. L. Smith, *J. Org. Chem.* 1961, **26**, 611, c) 1 W. A. Hart and H. H. Sisler, *Inorg. Chem.*, 1964, **3**, 617.

[2] V. Passarelli and F. Benetollo, *Inorg. Chem.*, 2011, **50**, 9958.

[3] V. Passarelli, J. J. Pérez Torrente, and L. A. Oro, *Inorg. Chem.*, 2014, **53**, 972; *idem*, *Dalton Trans.*, 2015, **44**, 18596; *idem*, *Dalton Trans.*, 2016, **45**, 951; M. Palmese, J. J. Pérez-Torrente, V. Passarelli, *Dalton Trans.*, 2022, **51**, 7142; *idem*, *Dalton Trans.*, 2022, **51**, 12334.

OC08

Tuesday 5th September 12:45

Encapsulation and Reactivity Inside Metallocages

Gregori Ujaque[1], Iker Zapirain,[1] Gantulga Norjmaa,[2] Giuseppe Sciortino[3]

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[3] Present address: Institut Català d'Investigacions Químiques (ICIQ), Tarragona

Metal Organic Cages (MOCs, also known as Supramolecular Organometallic Cages, Coordination Cages or Metallocages) are an exciting area of research with many potential applications in catalysis and molecular recognition.[1] The encapsulation of reactants (host-guest chemistry) can involve distortion of the cavity and displacement of solvent molecules. Modelling such process is quite challenging from computational point of view, however, obtaining a molecular/computational description of the encapsulation should provide valuable insights into the physicochemical properties that guide such process.

When encapsulated molecules are reactants, the reaction rates can significantly increase. Here we will present a multiscale computational investigation on both, the encapsulation as well as the origin of the acceleration rate.[2] Some of the most relevant reactions catalysed by the Raymond's[3] tetrahedral $[Ga_4L_6]^{12-}$ metallocage and the Fujita's octahedral $[Pd_6L_4]^{12+}$ metallocage are investigated.[4] We will evaluate how the nature of the guest, the motion of the metallocage, and the presence of the (encapsulated) solvent affect encapsulation and their reactivity.

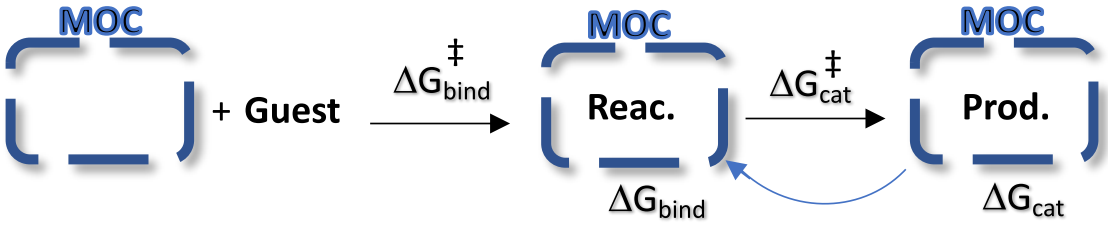

Figure 1. Scheme of encapsulation and catalysis by a molecular host – metallocage.

References

1. Supramolecular Catalysis: New Directions and Developments. Eds. Piet W.N.M. van Leeuwen and Matthieu Raynal. WILEY-VCH GmbH, 2022.
2. (a) G. Norjmaa, J.D. Maréchal, G. Ujaque J. Am. Chem. Soc. 141, (2019) 13114-13123; (b) G. Norjmaa, J.D. Maréchal, G. Ujaque Chem. Eur. J. 26, (2020) 6988-6992. (c) G. Norjmaa, J.D. Maréchal, G. Ujaque Chem. Eur. J. 27, (2021) 6988-6992. (c) G. Norjmaa, J.D. Maréchal, G. Ujaque Chem. Eur. J. 27, (2021) 15973–15980. (d) G. Norjmaa, P. Vidossich, J.D. Maréchal, G. Ujaque J. Chem. Inf. Model. 61, (2021) 4370–4381. (e) G. Norjmaa, F. Himo, J.D. Maréchal, G. Ujaque Chem.Eur. J.2022, e202201792.
3. M. Morimoto S.M. Bierschenk, K.T. Xia, R.G. Bergman, K.N. Raymond, F.D. Toste Nat. Cat. 3 (2020) 969–984.
4. H. Takezawa, M. Fujita Bull. Chem. Soc. Jpn. 94 (2021), 2351–2369.

OC09

Tuesday 5th September 16:00

Chemistry Europe - Who We Are and What We Do

Axel Straube[1]

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Founded in 1995, Chemistry Europe is an association of 16 chemical societies from 15 European countries, representing over 75,000 chemists. It publishes a family of high-quality scholarly chemistry journals, covering a very broad range of disciplines. Its mission is to evaluate, publish, disseminate, and amplify the scientific excellence of chemistry researchers from around the globe in high-quality publications. It supports its members at every stage of their careers as they strive to solve the challenges that impact humankind. In all its work, Chemistry Europe values integrity, openness, diversity, cooperation, and freedom of thought.

The talk will discuss the publishing process from the perspective of the editor. It will touch upon Chemistry Europe as the publishing association behind high-quality scholarly chemistry journals such as *Chemistry – A European Journal*, the *European Journal of Inorganic Chemistry* and *ChemCatChem*, how the Editorial Office works (including what editors look for in manuscripts and what they consider important when evaluating them) and on recent developments in Open Science and Open Access. Questions on scholarly publishing are very welcome!

About the speaker:

Dr. Axel Straube is an Associate Editor for *ChemistryOpen*, *Chemistry–Methods* & *ChemistrySelect* (Wiley-VCH GmbH, Weinheim, Germany). Before joining Wiley-VCH, Axel studied chemistry at Leipzig University (Germany) and Cardiff University (Wales, UK) with a brief placement at Uppsala Universitet and completed his PhD on redox-switchable homogeneous catalysis in the group of Evamarie Hey-Hawkins.

OC10

Tuesday 5th September 16:45

Catalysis With NHC-Au(I) Complexes in Confined Space: Resorcinarene Capsule and Monolayer Protected Nanoparticles

Cristina Tubaro[1], Giovanni Rubello[1], Riccardo Cendron[1], Alessandro Scarso[2], Francesca Bordignon[2], Fabrizio Mancin[1] and Andrea Biffis[1]

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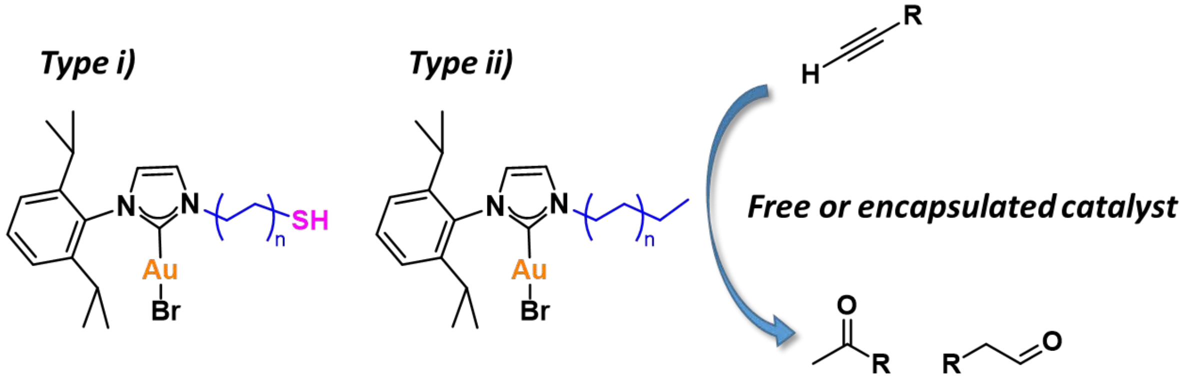
Gold(I) complexes bearing N-heterocyclic carbene ligands (NHCs) are well known homogeneous catalysts for many alkyne transformations.[1] The introduction of transition metal catalysts in a supramolecular system has been demonstrated to be a viable method to enable new catalytic performances compared to traditional homogenous systems, taking advantage from the spatial confinement of the catalyst imparting enzyme-like selectivity (i.e. substrate selectivity, regioselectivity and stereoselectivity).[2] The encapsulation of the commercial NHC-Au(I) complex IPrAuCl within resorcinarene capsule, held together by H-bond network, was investigated a few years ago by some of us. In the hydration of alkynes, the encapsulated catalyst showed interesting substrate selectivity in direct competitive experiments using equimolar amounts of terminal alkynes with similar electronic properties but different sizes and shapes.[3] In this contribution, the synthesis and characterization of two type of NHC-Au(I) complexes, designed to maximize interactions either with monolayer-protected gold nanoparticles (type *i*) or with the resorcinarene capsule (type *ii*) will be presented. Catalytic results in the substrate and product selective hydration reaction of terminal alkynes will also be discussed.



References

1. C.H. Leung, M. Baron, A. Biffis, *Catalysts* **2020**, *10*, 1210.
2. S.H.A.M. Leenders, R. Gramage-Doria, B. de Bruin, J.N.H. Reek, *Chem. Soc. Rev.* **2015**, *44*, 433-448.
3. G. La Sorella, L. Sperni, P. Ballester, G. Strukul, A. Scarso, *Catal. Sci. Technol.*, **2016**, *6*, 6031-6036.

OC11

Tuesday 5th September 17:00

A New Family of Alkali-Metal Manganates and Their Role in Catalysing C-C Bond Formation *via* Oxidative Homocoupling

Marina Uzelac

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Recent advances in mixed-metal chemistry have shown that by pairing metals with different polarities within the same molecule, novel bimetallic (‘ate’) reagents can be prepared which display unique synergic chemical profiles.[1] By incorporating a transition-metal in such system opens the possibility for accessing behaviour uncharacteristic for the main-group metals (e.g. redox chemistry, magnetic properties, catalysis). Relatively inexpensive, toxicologically benign and readily available manganese embodies a great appeal to industry.[2] More importantly, organometallic chemistry of manganese in oxidation state +2 has been shown to be more comparable to that of main-group metals than to d-block metals due to the presence of predominantly ionic Mn-C bonds.[3] While lithium manganates have already shown great promise in organic synthesis specially in C-C bond forming processes,[3-4] their identities and the role of each metal in these transformations remain blurred.

Shedding new light in this area, here we present our recent finding on the rational synthesis and structural elucidation of alkali-metal manganates containing alkyl groups[5] and their applications to promote tandem processes giving access to symmetric bis(aryl)[6] and bis(alkynyl) organic scaffolds.

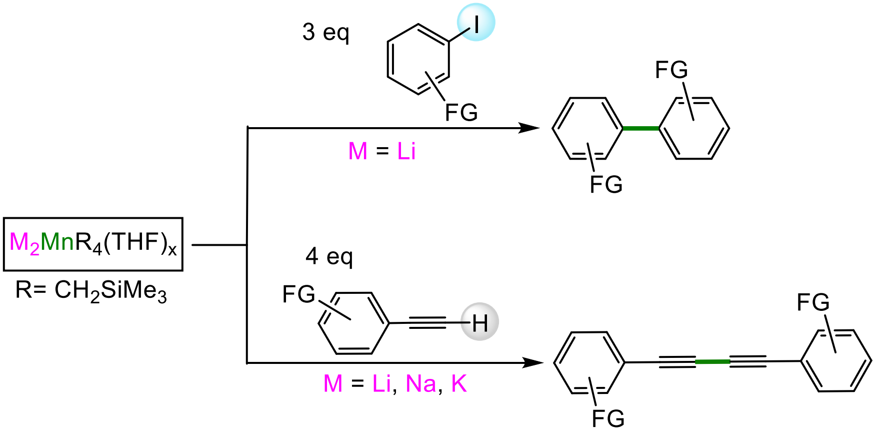

Figure 1. Examples of reactivity of alkali-metal manganates in oxidative homocoupling reactions.

References

[1] R. E. Mulvey, *Acc. Chem. Res.* **2009**, *42*, 743. [2] D. A. Valyaev, G. Lavigne, N. Lugan, *Coord. Chem. Rev.* **2015**, *308*, 191. [3] R. A. Layfield, *Chem. Soc. Rev.* **2008**, *37*, 1098. [4] G. Cahiez, C. Duplais, J. Buendia, *Chem. Rev.* **2009**, *109*, 1434. [5] M. Uzelac, I. Borilovic, M. Amores, T. Cadenbach, A. R. Kennedy, G. Aromí, E. Hevia, *Chem. Eur. J.* **2016**, *22*, 4843. [6] M. Uzelac, P. Mastropierro, M. De Tullio, I. Borilovic, M. Tarres, A. R. Kennedy, G. Aromí, E. Hevia, *Angew. Chem. Int. Ed.* **2021**, *60,* 3247.

OC12

Tuesday 5th September 16:45

Elucidating the Catalytic CO_2 Reduction to CO

Christina Erken[1], Juan Miranda Pizarro[1], Martin Nieger[1], Petra Vasko[1] and Timo Repo[1]

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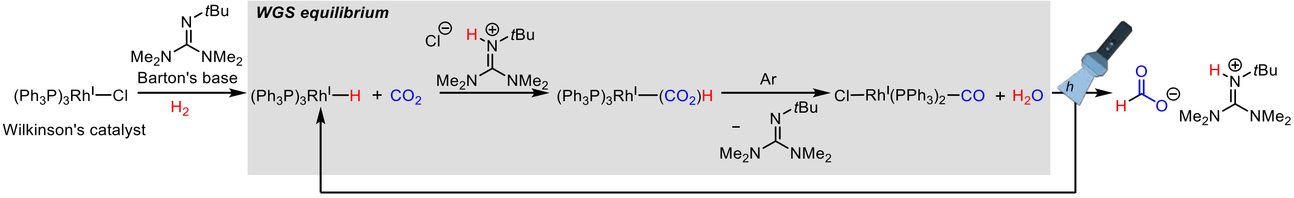
The reverse water gas shift (*r*WGS) reaction is the most promising sustainable CO_2 utilization process with hydrogen to CO and water as by-product.[1] Compared to heterogeneous catalysis, examples in homogeneous catalysis are sparse, but demonstrate the synthesis of highly attractive value-added chemicals i.e. aldehydes, carboxylic acids, amines.[2] However, these are ruthenium-based systems[3], and mechanistic details of this crucial reaction are not truly understood.



Reaction conditions: *in situ* generated $RhH(PPh_3)_3$[4], Barton's base, PPh_3, 0.5 bar CO_2, 0.5 bar H_2, 60 °C, 20 h.

Scheme 1: Rh(I)-monohydride-catalyzed CO_2 insertion step studied in the present work.

Herein, we report a novel Rh(I)-monohydride-catalyzed reduction of CO_2 to CO by assistance of Barton's base. Investigations of the individual mechanistic steps by NMR studies and X-ray analysis reveal the Rh(I)-formate intermediate and *trans*-Rh(I)COCl$(PPh_3)_2$. By using visible light, the Rh(I)-monohydride complex is capable of reducing CO to the formate salt of the base with a comparable activity to the commercial Rh-carbonyl complex. The experimental study is supported with DFT calculations to elucidate the mechanism. It can be applied for other carbonyl compounds (formates) that are transformed to CO and the corresponding alcohol. This study could play an important role in future industrial technologies for producing hydrocarbon fuels or synthesis gas (CO and H_2).

References

[1] M. Aresta et al., An Economy Based on Carbon Dioxide and Water: Potential of Large Scale Carbon Dioxide Utilization, Springer Nature Switzerland AG, Cham, Switzerland, **2019**.

[2] K.-i. Tominaga et al. *J. Chem. Soc., Chem. Commun.* **1993**, 629-631; *Catal. Commun.* **2000**, *1*, 1-3; *J Mol Catal A Chem* **2004**, *220*, 159-164; S. Jääskeläinen et al., *Appl. Catal. A: Gen.* **2003**, *247*, 95–100; L. Wu et al., *Nat. Commun.* **2014**, *5*, 1-6; V. K. Srivastava et al., *Catal. Commun.* **2009**, *10*, 1791–1795.

[3] T. G. Ostapowicz et al. *Eur. J. Inorg. Chem.* **2012**, *2012*, 5632-5641; *Angew. Chem.* **2013**, *125*, 12341-12345.

[4] J. E. Perea-Buceta et al. *Angew. Chem. Int. Ed.* **2015**, *54*, 14321-14325.

OC13

Tuesday 5th September 17:00

Pincer Iridium Hydride Complexes: Mechanisms for Acceptorless Dehydrogenation of Alcohols

Ola F. Wendt

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To enable the large-scale use of hydrogen fuel cells for mobility applications, convenient methods for on-board hydrogen storage and release need to be developed. A promising approach is liquid organic hydrogen carriers (LOHCs), since these are safe, available on a large scale and compatible with existing re-fuelling infrastructure. Usually, LOHC dehydrogenation is carried out in batch-type reactors by transition metals and their complexes and suffers from slow H_2 release kinetics and/or inability to reach high energy density by weight due to low conversion or the need to dilute the reaction mixture.[1] We have developed a system based on a continuous flow reactor in combination with a heterogenized iridium pincer complex which enables a tremendous increase in LOHC dehydrogenation rates.[2] Thus, dehydrogenation of isopropanol allowed unprecedented turnover numbers (TONs up to 1 600 000) and turnover frequencies (TOFs, up to 160 000 h^{-1}), which translates to a productivity of up to 25 $g(H_2)g^{-1}(Ir)min^{-1}$. However, the system suffers from limited stability at the temperatures used and probably higher activities are needed. For a rational approach the reaction mechanism was investigated, and we were able to show that mass transfer is rate-limiting under batch conditions which is one of the factors behind the extremely large rates obtainable in the flow reaction. Overall, a mechanism will be presented that gives a satisfactory quantitative description of the catalytic cycle, such that kinetic curves and reaction order in catalyst can be reproduced.[3] Also, we can show that small variations in ligand structure can give rise to large variations in activity and that there may be different mechanisms (one associative and one dissociative) operating in different temperature regimes.

References

[1] a) Y. Sekine, T. Higo. *Top. Catal.* **2021**, *64*, 470–480. (b) K. Müller, T. Skeledzic, P. Wasserscheid, *Energy Fuels* **2021**, *35*, 10929–10936.

[2] A. V. Polukeev, R. Wallenberg, J. Uhlig, C. P. Hulteberg, O. F. Wendt, *ChemSusChem*, **2022**, e202200085.

[3] A. V. Polukeev, O. Y. Abdelaziz, O. F. Wendt, *Organometallics*, **2022**, *41*, 859-873.

OC14

Tuesday 5th September 16:45

Exploring the Potential of Catalysts based on the Heavier Group 13 Elements for Cyclic Carbonate Synthesis

Christopher J. Whiteoak,[1] Lucía Álvarez-Miguel,[1] Carlos Diéz-Poza,[1] Diego Jaraba Cabrera,[1] Jesús Damián Burgoa,[1] Maria Distressa G. Billacura,[2] Alex Hamilton,[2] Ryan Lewis,[2] Marta E. G. Mosquera[1]

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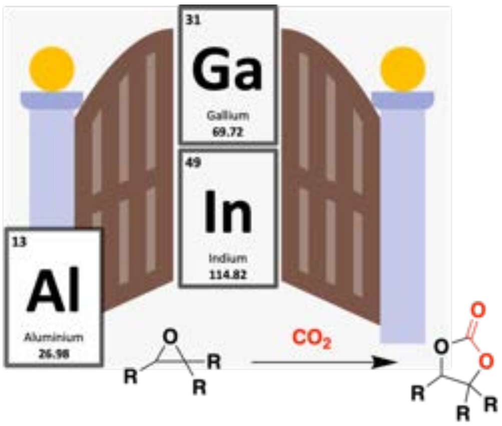
The use of carbon dioxide (CO_2) as a chemical feedstock is attracting significant interest as a result of its low-cost, relative low toxicity and abundance. However, the application of CO_2 is limited by its stability. Reaction with high energy molecules (eg. epoxides) and a catalyst is one approach to its utilisation. In this context, the catalytic coupling of epoxides and CO_2 has been a relative success story with an abundance of catalytic systems reported.[1] One of the key features of many of these catalysts is the involvement of a Lewis acid. The group 13 elements have well established Lewis acid character and it is therefore no surprise that many of the reported catalysts for cyclic carbonate synthesis are based on abundant and cheap aluminium. However, and rather surprisingly, comparatively little attention has been paid to the heavier group 13 elements and this presents an opportunity to study the distinct properties and reactivities of catalysts based on these elements. In this contribution we will present our most recent results on the application of complexes based on the heavier group 13 elements as catalysts for the addition of epoxides to CO_2 to form a wide variety of cyclic carbonates (including, novel bio-derived examples).[2,3]



Acknowledgments. CJW would like to thank the Comunidad de Madrid (Spain) for funding (Programa de Atracción de Talento 2019: Modalidad 1; Award number 2019-T1/AMB-13037, and CM/JIN/2021-018). and the Spanish Government (PID2020-113046RA-I00/AEI/10.13039/501100011033)

References

[1] (a) Pescarmona, P. P. *Curr. Opin. Green Sustain.* **2021**, *29*, 100457; (b) Büttner, H.; Longwitz, L.; Steinbauer, J.; Wulf C.; Werner, T. *Top. Curr. Chem.* **2017**, 375, 50; (c) Martín, C.; Fiorani, G.; Kleij, A. W. *ACS Catal.* **2015**, 5, 1353.

[2] Álvarez-Miguel, L.; Damián Burgoa, J.; Mosquera, M. E. G.; Hamilton, A.; Whiteoak, C. J. *ChemCatChem.* **2021**, *13*, 4099.

[3] Jaraba Cabrera, D.; Lewis, R. D.; Díez-Poza, C.; Álvarez-Miguel, L.; Mosquera, M. E. G.; Hamilton, A.; Whiteoak, C. J., *Dalton Trans.*, **2023**, *52*, 5882.

OC15

Tuesday 5th September 17:00

Mechanochemical Synthesis of Compounds and Complexes

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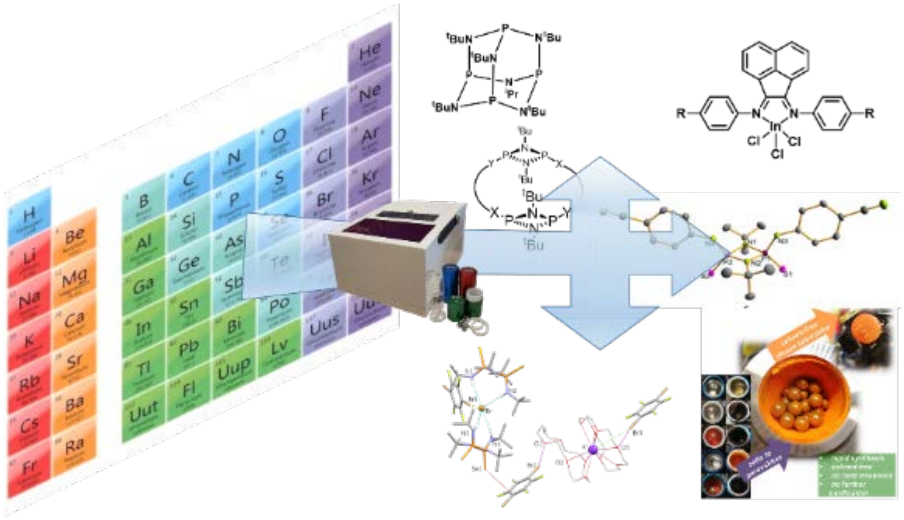
Traditionally, solution-based processes have dominated laboratory set-ups and industrial manufacturing protocols. However, the past decade has seen the renaissance of solid-state synthetic routes, driven by the need for more sustainable chemical processes. Within this context, mechanochemistry (i.e., chemical transformations initiated or sustained by mechanical force) has rapidly evolved from being a laboratory curiosity to a widely applicable synthetic technique that not only enables greener chemical transformations but offers exciting opportunities for the synthesis and screening of molecules and materials.

The talk will focus on the recent developments in reactive mechanochemistry of main group compounds and materials.[1] The novel application of mechanochemistry to the synthesis of phosphorus-nitrogen frameworks – from orthogonal synthesis[3] to "unattainable" molecules[2,3] – will be discussed, followed by their implementation in the rational design of high-order organic-inorganic hybrid multicomponent cocrystals.[4] This will be followed by a brief introduction of the challenges facing the broader adoption of mechanochemistry in industry,[5] with a focus on the upscaled synthesis of metal complexes.[6]



References

1. D. Tan and F. García. Chem. Soc. Rev., 2019, 48, 2274-2292
2. Y. Sim, D. Tan, R. Ganguly, Y. Li, and F. García. Chem. Commun., 2018, 20, 5998-6004
3. X. Shi, K. Xu, J. K. Clegg, R. Ganguly, H. Hirao, T. Friščić, and F. García. Angew. Chem. Int. Ed., 2016, 55, 12736-12740.
4. Z. X. Ng, D. Tan, T. Wei Liang, F. Leon, X.-Y. Shi, Y. Sim, Y. Li, R. Ganguly, Z. Yanli, M. Sharmarke and F. García. Angew. Chem., Int. Ed., 2021, 60, 17481-17490.
5. E. Colacino, V. Isoni, D. Crawford, F. García. Trends in Chem., 2021, 3, 335-339.
6. V. K. Singh, A. Chamberlain-Clay, H. C. Ong, F. León, G. Hum, M. Y. Par, P. Daley-Dee, F. García. ACS Sust. Chem. & Eng., 2021, 9, 1152-116.

OC16

Wednesday 6th September 12:00

Gold Carboxylate Complexes as Dual Action Anticancer Agents

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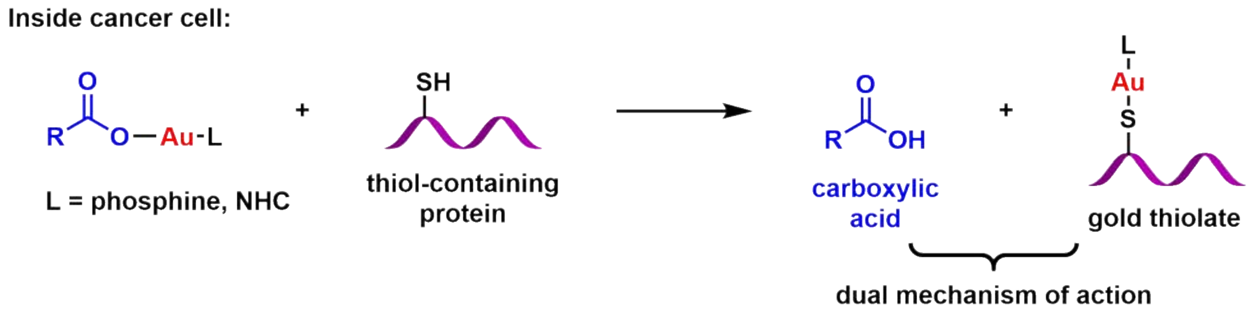
Cancer is currently one of the leading causes of death and has huge social and economic impacts worldwide. The development of new anticancer treatments is therefore vital. The main challenges in this field are the existence of highly resistant cells and the need to be selective for cancer cells over non-cancerous cells. In this context, transition metal complexes offer significant advantages over purely organic compounds due to their chemical and physical diversity and the fine-tuning of steric and electronic properties which can be achieved through subtle changes to ligand architectures. Incorporating a drug molecule as a ligand in a transition metal complex can enhance the solubility and passive cellular uptake, and where the metal is also biologically active can provide a dual-action drug which can circumvent resistance mechanisms.

We have recently found a simple synthetic route to novel gold(I) carboxylate complexes where the gold is bound to the oxygen atom of the carboxylate group. In the presence of intracellular thiols or selenols, the carboxylic acid can be released from the gold centre with the gold binding preferentially to the softer group. When a biologically active carboxylic acid (e.g. an NSAID) is employed, a dual mechanism of action in the cancer cells is observed due to the co-delivery of two active components: carboxylic acid and gold auxiliary ligand unit, allowing more resistant cell lines to be targeted. These gold(I) complexes additionally show enhanced selectivity for cancer cells over non-cancerous cells due to an overexpression of thiol containing compounds in these cells, offering an opportunity to develop effective cancer treatments with reduced side effects.



Scheme 1. Reactivity of gold(I) carboxylate complex in cancer cells

OC17

Wednesday 6th September 12:15

Gold(I) Mediated Radio-Iododecarboxylation toward Applications in Nuclear Medicine

Thomas CAILLY[1,2,3,4], Ahmed AIT KHOUYA[1] and Hugo BLOUX[1]

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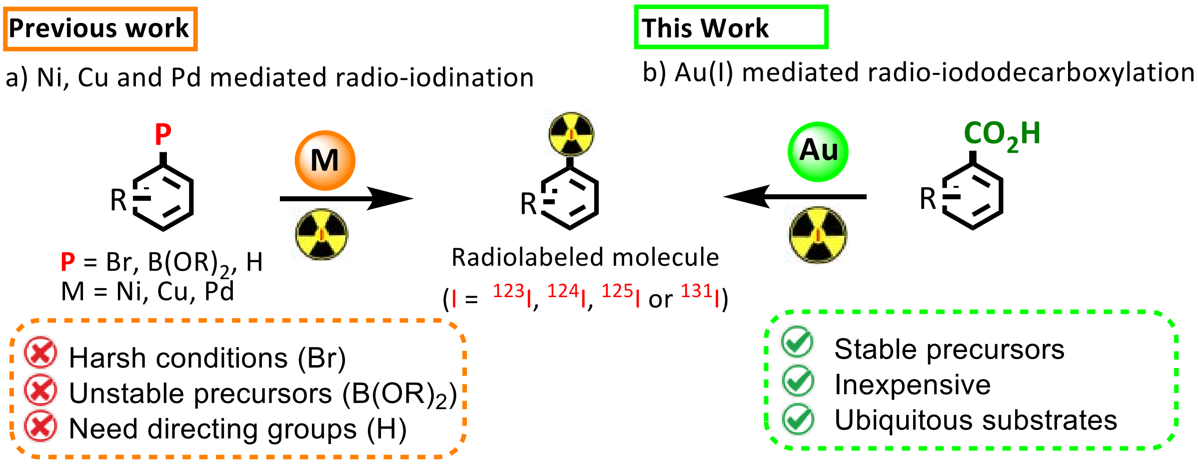
Labelling of (bio)molecules with radioactive isotopes is of high interest to the scientific community, as it strongly impacts the discovery process in life sciences and nuclear medicine. In nuclear medicine, radio-therapeutics for RadioIsotope Therapy (RIT)[1] and radio-tracers for molecular imaging experiments such as Positron Emission Tomography (PET) or Single Photon Emission Computed Tomography (SPECT) have been described.[2] In this context, four iodine radioactive-isotopes can be used, each one with a specific application: ^{123}I and ^{124}I for SPECT and PET imaging respectively, ^{125}I for binding studies, and ^{131}I for radiotherapy.[3] Considering the difficulties and the cost to develop a radiolabeling process, the discovery of efficient synthetic methods is highly desirable. A variety of new transformations mediated by transition metal have been developed in recent years.[4] Inspired by the gold(I) mediated decarboxylation of arene described by Larrosa,[5] our team recently demonstrated that a carboxylic acid function can be used to promote radio-iodination. In this study, we will present the straightforward decarboxylative gold(I) mediated radioiodination, with iodine-125, of a variety of carboxylic acids. Such reactions were performed in different conditions and without the need of purifying the gold organometallic adduct. In addition, to demonstrate the potential of our methodology, we will also present the radio-iodination of known radiotracers or iodinated drugs using the carboxylic acid function as a precursor.



References

[1] *Chem. Rev.* **1999**, *99*, 2269–2292. [2] *Chem. Soc. Rev.* **2011**, *40*, 149–162. [3] *Chem. Soc. Rev.* **2005**, *34*, 153–163. [4] *J. Org. Chem.* **2020**, *85*, 8300–8310. [5] *Adv. Synth. Catal.* **2011**, *353*, 1359–1366.

OC18

Wednesday 6th September 12:30

Synthesis and Biological Activity of Organometallic Hybrids with Selected Tubulin-Binding Anticancer Agents

Damian Plażuk[1], Karolina Rózga[1], Andrzej Błauż[2], Błażej Rychlik[2]

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Tubulin-binding anticancer agents are chemotherapeutic drugs targeting the microtubule network, which is essential for cell division. Microtubules play a crucial role in mitosis, the process by which cells divide and proliferate. By disrupting microtubule formation or function, tubulin-binding agents prevent cancer cells from dividing and ultimately induce cell death. However, the usage of tubulin-disturbing agents is occupied with severe disadvantages, i.e., developing resistance to tubulin-binding agents over time, relatively high toxicity in normal cells, leading to a range of side effects; relatively low selectivity - they can also affect normal cells that are rapidly dividing. Despite these disadvantages, tubulin-binding agents remain an important class of chemotherapeutic drugs with significant clinical efficacy. Nevertheless, developing new antimitotic agents with improved specificity, reduced toxicity, and improved ability to overcome drug resistance is crucial to overcome such disadvantages.[1]

We will present the synthesis and evaluation of the biological activity of new organometallic hybrids with tubulin-binding agents active toward multidrug-resistant cancer cell lines.

Acknowledgment. This study was financially supported by the National Science Centre Poland (NCN) based on decision UMO-2018/29/B/ST5/01736

References

(1) Jackson, J. R.; Patrick, D. R.; Dar, M. M.; Huang, P. S. Targeted anti-mitotic therapies: can we improve on tubulin agents? *Nat. Rev. Cancer* **2007**, *7* (2), 107-117.

OC19

Wednesday 6th September 12:45

Ir(III)-Coumarin Conjugates As Promising Photosensitizers In Both Normoxia And Hypoxia

J. Ruiz,[1] A. Rovira,[2] E. Ortega-Forte,[1] C. Hally,[3] M. Jordà-Redondo,[3] G. Vigueras,[1]
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Photodynamic therapy (PDT) holds great promise as a non-invasive anticancer tool against drug-resistant cancers. However, highly effective, non-toxic and reliable photosensitizers (PSs) with operability under hypoxic conditions remain to be developed. In this context, we have been pioneers in describing a novel class of PDT agents based on the conjugation of a far red-emitting COUPY coumarin[1] to a cyclometalated Ir(III) complex, able to combat both differentiated and tumorigenic cancer stem cells.[2] Herein, we report a family of new Ir(III)-COUPY conjugates with the aim of exploring structure–activity relationships (SARs), specially to investigate how the structural modifications within the COUPY scaffold influence the photophysical, photochemical and biological properties of the resulting PSs, as well as investigating the mechanism of action leading to the formation of type I ROS.[3] Among them, two hit conjugates showed excellent phototherapeutic indexes in cisplatin-resistant A2780cis cancer cells, both in normoxia (≥269) and in hypoxia (≥147).

Acknowledgements. This work was supported by funds from the Spanish Ministerio de Ciencia e Innovación-Agencia Estatal de Investigación (MCI/AEI/10.13039/501100011033) and FEDER funds (projects PID2020-117508RB-I00 and PID2021-122850NB-I00), and Fundación Séneca-CARM (project 21989/PI/22). E.O.-F. thanks AECC (PRDMU19003ORTE).

References

[1] E. Ortega-Forte, A. Rovira, et al. *J. Med. Chem.* **2021**, 64, 17209-17220.
[2] a) V. Novohradsky, A. Rovira, C. Hally, A. Galindo, et al., *Angew. Chem. Int. Ed.* **2019**, 58, 6311-6315; b) V. Novohradsky, et al. *Chem. Eur. J.* **2021**, 27, 8547-8556.
[3] A. Rovira, E. Ortega-Forte, C. Hally, et al. submitted to *J. Med. Chem.* **2023.**

OC20

Wednesday 6th September 12:00

Mechanistic Studies of the Palladium/Phenanthroline Catalysed Reductive Cyclization of Nitroarenes by CO to give *N*-Heterocycles

Fabio Ragaini*[1], Manar Ahmed Fouad[1,2], Doaa R. Ramadan[1,2],
Francesco Ferretti[1] and Chiara Costabile[3]

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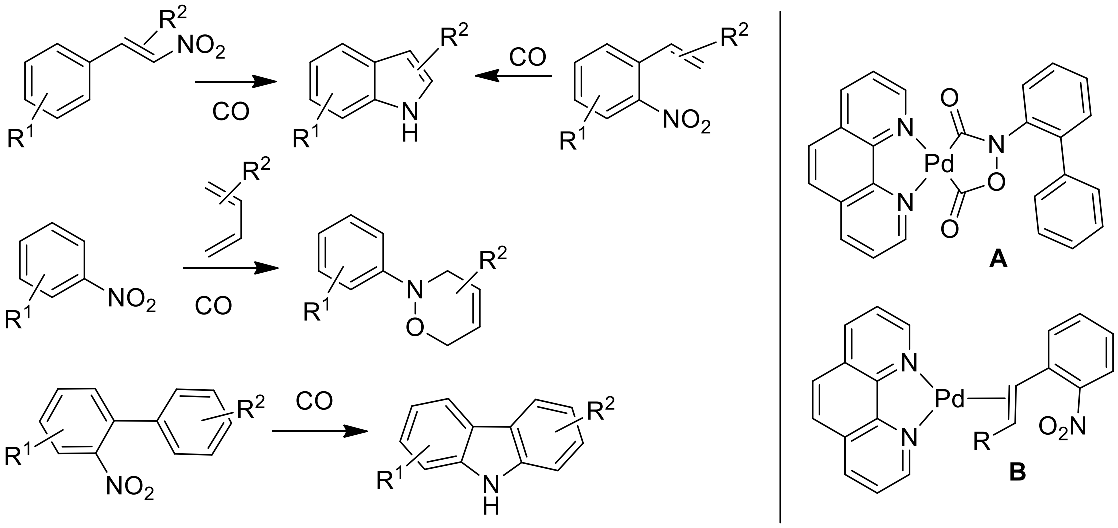
[2] Chemistry Department, Faculty of Science, Alexandria University, P.O. Box 426, Alexandria 21321 (Egypt). [3] Dipartimento di Chimica e Biologia "A. Zambelli", Università di Salerno, V. Giovanni Paolo II, Fisciano (SA) (Italy)

Transition metal catalysed reductive cyclization reactions of suitably substituted nitroarenes to yield heterocycles using pressurized carbon monoxide as a reductant are efficient reactions.[1] In recent years, we have developed the use of phenyl formate as a cheap and non-toxic CO surrogate, which is able to liberate CO under the reaction conditions, thus allowing the same reactions to be performed in a single glass pressure tube. [2-5] (Scheme 1, left side).

However, virtually nothing is known about the mechanism of these reactions. We have thus undertaken an experimental and computational study of the reaction pathways. Two proposed reaction intermediates are shown in Scheme 1.



Scheme 1: Reactions investigated and proposed catalyst resting states

References

[1] F. Ferretti, D. R. Ramadan, F. Ragaini, *ChemCatChem* **2019**, *11*, 4450.
[2] F. Ragaini, F. Ferretti, M. A. Fouad, *Catalysts* **2023**, *13*, 224.
[3] D. R. Ramadan, F. Ferretti, F. Ragaini, *J. Catal.* **2022**, *409*, 41.
[4] M. A. Fouad, F. Ferretti, D. Formenti, F. Milani, F. Ragaini, *Eur. J. Org. Chem.* **2021**, 4876.
[5] M. A. EL-Atawy, D. Formenti, F. Ferretti, F. Ragaini, *ChemCatChem* **2018**, *10*, 4707.

OC21

Wednesday 6th September 12:15

Electronically Flexible Pyridylidene Amide Ligands for Palladium-Catalyzed A-Arylation Of Ketones

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Electronically flexible ligands such as pyridylideneamides (PYAs, Fig. 1A) can vary their degree of donor ability and may stabilize several intermediates of a catalytic cycle.[1] This ligand flexibility is a highly desirable feature in catalytic processes, especially when different oxidation states are involved.[2] In their zwitterionic form, these ligands exhibit strongly donating properties that facilitate oxidative additions on the coordinated metal center. Furthermore, their ease of production, low-cost synthesis and high tunability make them efficient alternatives to carbenes and phosphines. Surprisingly, the potential of such donor-flexible PYA ligands has been poorly investigated in palladium-catalyzed cross-coupling processes. Here we introduce different bidentate pyridyl-PYA ligands coordinated to palladium(II), which afford highly active and robust ketone α-arylation catalysts with unprecedented turnover numbers (TONs) for N-based ligands in this transformation (Fig. 1B).[3] Moreover, we will discuss mechanistic details that emerged from using these well-defined precatalysts.

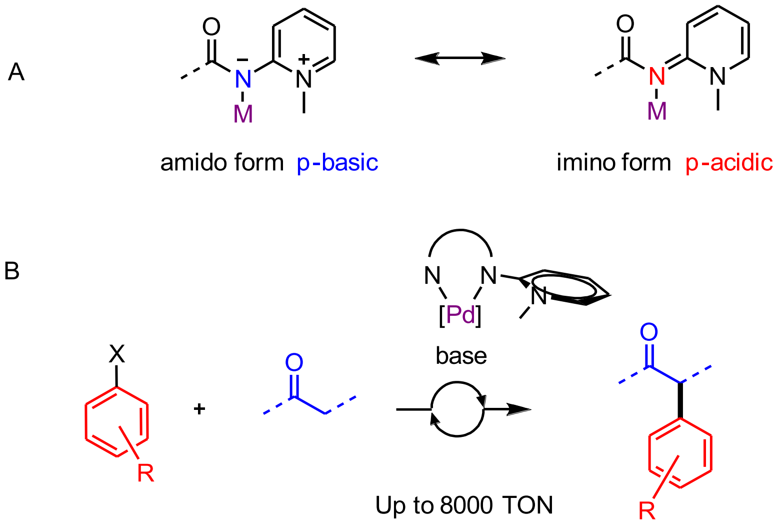

Figure 1. A: Resonance forms of the PYA ligand. B: Schematic representation of a palladium complex containing a pyridyl-pyridylidene amide ligand that is active in the α-arylation of ketones.

References

[1] M. Navarro, L. Mo, H. Müller-Bunz, S. Bernhard, M. Albrecht. *Chem. Eur. J.*, **2016**, 22, 6740-6745.
[2] P. D. W. Boyd, L. J. Wright, M. N. Zafar, *Inorg. Chem.*, **2011**, 50, 10522-10524.
[3] P. Novák, R. Martin, *Curr. Org. Chem.*, **2011**, 15, 3233-3262.

OC22

Wednesday 6th September 12:30

Palladium and Gold Nitrenes

Dominik Munz[1], Kevin Breitwieser, Emiliano Martinez Vollbert

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We reported the isolation of palladium terminal imido complexes with aliphatic, aromatic, as well as sulfonyl substituents.[1,2] The reactivity with nucleophiles such as phosphines and olefins as well as Hydrogen-Atom-Abstraction reactivity suggest that the nitrene character is weak for the latter, yet substantial if not strong for the former. In this talk, I will present on their electronic structure based on – among others – 15N CP-MAS spectra of isotopically enriched congeners, XAS measurements, and quantum chemical calculations.[3] As such, I will elaborate why we understand some of these compounds as singlet-nitrene complexes, which I will put into perspective with a high-valent cobalt terminal imido complex.[4] Further, I will present on our progress with terminal gold imido complexes and report on their C–H amination and H-atom abstraction reactivity with hydrocarbons.[5]

References

[1] A. Grünwald, B. Goswami, K. Breitwieser, B. Morgenstern, M. Gimferrer, F. W. Heinemann, D. M. Momper, C. W. M. Kay, **D. Munz*** *J. Am. Chem. Soc.* **2022**, *144*, 8897.

[2] A. Grünwald, N. Orth, A. Scheurer, A. Pöthig, F. W. Heinemann, D. Munz *Angew. Chem. Int. Ed.* **2018**, *57*, 16228.

[3] K. Breitwieser, T. Schmidt-Räntsch, S. Danes, D. Andrada, K. Ray, S. Schneider, D. Munz *in preparation*.

[4] W. Mao, Z. Zhang, D. Fehn, S. A. V. Jannuzzi, F. W. Heinemann, A. Scheurer, M. van Gastel, S. DeBeer, D. Munz, K. Meyer *in revision.*

[5] E. Martínez Vollbert, S. S. Anjana, D. Munz *in preparation*.

OC23

Wednesday 6th September 12:45

Unlocking Cyclometalation: A New Entry to Cyclometalated Gold(III) Complexes via Catalytic Rhodium to Gold(III) Transmetalation

Jaime Martín,[1] Enrique Gómez-Bengoa,[2] and Cristina Nevado[1]

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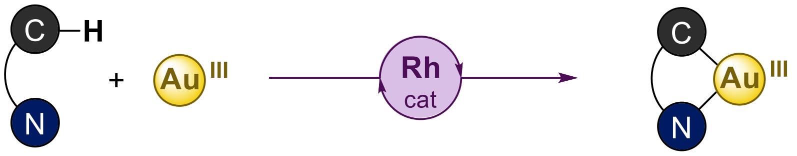
Gold(III) complexes have a significant impact on several fields, including materials science, biomedical research, and catalysis.[1] Despite the strongly oxidizing nature of this metal, bidentate or tridentate ligands can stabilize gold(III) complexes against reduction, making them more durable and robust for translational applications. In this context, cyclometalated gold(III) species containing bidentate (C^N) ligands play a prominent role as tunable photochemical dopants in OLEDs and as antitumoral agents.[2] Unfortunately, only a few strategies tackling their synthesis are available to date. These rely on organomercury reagents, silver salts, or harsh conditions thus severely limiting the functional group compatibility, synthetic efficiency, and applicability of these systems in the abovementioned areas.

To overcome this challenge, we have successfully developed a catalytic, environmentally friendly and redox-neutral approach to synthesize a broad array of cyclometalated (C^N)gold(III) complexes. Our methodology relies on the catalytic Csp^2-H bond activation of 2-aryl-pyridine ligands using a commercially available and stable rhodium complex, followed by an unprecedented Rh-to-Au(III) transmetalation step. Detailed mechanistic investigations using kinetic measurements, control experiments, and DFT calculations revealed a rate-determining stepwise (C-then-N) transmetalation process underlying these transformations.[3]

Catalytic Rhodium to Gold(III) Transmetalation



✓ Catalytic ✓ Environmentally friendly ✓ Mild conditions ✓ Broad scope

✓ No prefunctionalization ✓ 1st Example of **Rh**-to-**Au(III)** transmetalation

✓ Rate-determining, stepwise (first C, then N) ligand transfer

References

Rocchigiani, L.; Bochmann, M. *Chem. Rev.* **2021**, *121*, 8364-8451.
Kumar, R.; Nevado, C. *Angew. Chem. Int. Ed.* **2017**, *56*, 1994-2015.
Martín, J.; Gómez-Bengoa, E.; Genoux, A.; Nevado, C. *Angew. Chem. Int. Ed.* **2022,** e202116755.

OC24

Wednesday 6th September 15:00

Metal Complexes Bearing Uracil Ligands: Synthesis and Applications

Ana Petronilho and Giulia Francescato

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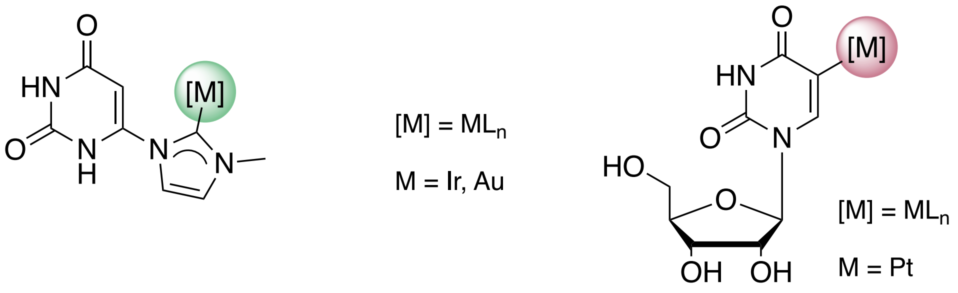
The utilization of ligands based on biologically-relevant compounds has raised interest over the last decade[1]. The main reason for this is the propensity of these ligands to provide access to more sustainable catalysts and/or more selective drugs, due either to a favorable solubility in solvents such as water or a higher biocompatibility inside the cells. We have worked in the development of metal complexes bearing nucleobases as ligands and their application in medicinal chemistry and catalysis[2]. In this regard, we have examined the reactivity of uracil-based betaines. Imidazolium salts functionalized with uracil can be converted into their corresponding betaines in the presence of a base [3].



Scheme 1

We examined the reactivity of these ligand precursors to form metal complexes, using both imidazolium salts and the corresponding betaines. The catalytic activity of these compounds towards the reduction of NAD+ to NADH was evaluated. These results will be discussed in this communication.

References

[1] Hanif, M., Hartinger, C.G., *Future Med. Chem.*, 2018, 615, 10.

[2] Francescato, G., Da Silva, S.M., Leitão, M.I.P.S., Cordeiro, A.G., Giannopoulos, N., Gomes, C.S.B., Pimentel, C., Petronilho, A., *Appl Organomet Chem,* 2022, e6687.

[3] Schmidt, A., Kindermann, M.K., Vainiotalo, P., Nieger, M., *J. Org. Chem.*, 1999, 9499-9506, 64.

OC25

Wednesday 6th September 15:15

C–H Functionalization of Tyr-Containing Peptides

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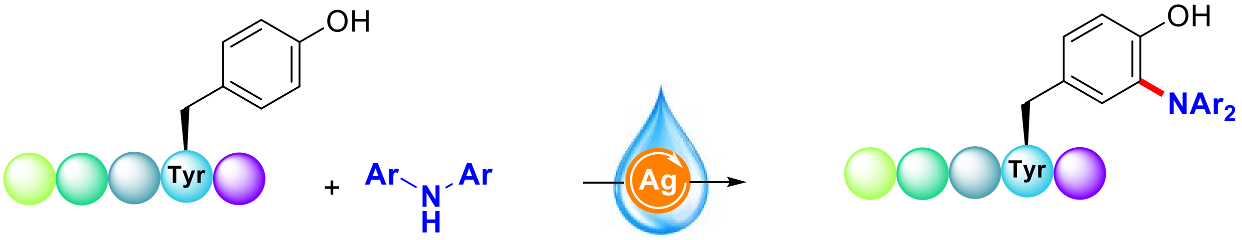
The site-selective chemical modification of biomolecules represents a pressing challenge of capital importance at the forefront of chemical biology and medicinal chemistry. Metal catalysis has recently unlocked new tactics in the field, thereby providing streamlined techniques toward the manipulation of C–H bonds embedded within amino acids and their peptides derived thereof.[1] However, despite the wealth of reports in the field, the modification of tyrosine (Tyr) compounds remains comparatively overlooked.[2] In this communication, we will describe our latest results on the development of reliable late-stage tagging techniques of Tyr-containing peptides following two different approaches: chelation assistance featuring an external directing group[3] and leveraging the innate reactivity of the phenol ring upon radical chemistry. In particular, we are currently studying a practical water-compatible C–H amination of phenol-containing biomolecules.



✓ *Operational simplicity*

✓ *Air and water-tolerant*

✓ *Scalable process (multigram scale)*

✓ *Assembly of peptidomimetics*

Acknowledgements. We are grateful to Ministerio de Ciencia e Innovación (PID2021-122889NB-I00, MCI/AEI/FEDER, UE) and Basque Government (IT1741-22) for financial support.

References

[1] a) H.-R. Tong, B. Li, G. He, G. Chen. *CCS Chem.* **2020**, *2*, 1797; b) B.-B. Zhan, M.-X. Jiang, B.-F. Shi, *Chem. Commun.* **2020**, *56*, 13950.; c) W. Wang, M. M. Lorion, J. Shah, A. R. Kapdi, L. Ackermann, *Angew. Chem. Int. Ed.* **2018**, *57*, 14700; d) M. San Segundo, A. Correa, *Synthesis* **2018**, *50*, 2853.

[2] a) A. Correa, *Eur. J. Inorg. Chem.* **2021**, 2928; b) D. A. Dorta, D. Deniaud, M. Mével, S. G. Gouin, *Chem. Eur. J.* **2020**, *26*, 14257; c) P. A. Szijj, K. A. Kostadinova, R. J. Spears, V. Chudasama, *Org. Biomol. Chem.* **2020**, *18*, 9018.

[3] a) I. Urruzuno, P. Andrade-Sampedro, A. Correa, *Eur. J. Org. Chem.* **2023**, *26*, e20220148; b) P. Andrade-Sampedro, J. M. Matxain, A. Correa, *Adv. Synth. Catal.* **2022**, *364*, 2072; c) I. Urruzuno, P. Andrade-Sampedro, A. Correa, *Org. Lett.* **2021**, *23*, 7279; d) M. San Segundo, A. Correa, *Chem. Sci.* **2020**, *11*, 11531.

OC26

Wednesday 6th September 15:30

The Effect of Antibody Conjugation Over a Cyclometalated Ru(II) Complex as Targeted NIR Photosensitizers for PDT

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Demeubayeva Nurikamal,[4] Vincent Guérineau,[5] Céline Frochot,[4]
Alain C. Jung,[2,3] Christian Gaiddon,[3] and Gilles Gasser[1]

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Currently approved anticancer metal-based drugs are mainly based on platinum, but they usually lack selectivity and cause harmful side effects. Photodynamic therapy (PDT) is an approved medical technique based on the combined action of a photosensitizer (PS), molecular oxygen and light. One of the aims of a PDT PS is to absorb light in the red or NIR region of the spectrum (> 600 nm), so that complexes can be irradiated with low energy. Regarding Ruthenium(II) polypyridyl complexes, they usually absorb in the yellow or orange range, but it is difficult to reach the red region of the spectrum, that is more useful from a therapeutic point of view.

In this work, we present a Ru(II) complex bearing a 2-phenylpyridinate-based ligand that absorbs light up to 700 nm and two cetuximab conjugates with two different conjugation strategies. In the design of the complexes, we used cyclometalation since this strategy lowers the energy of the triplet metal-to-ligand charge transfer state (^{3}MLCT), and therefore, causes a bathochromic shift in the absorption. The biological evaluation of the complex showed high PI values at 740 nm, a NIR wavelength. This means, this complex can cause cell death after light irradiation, but it is innocuous in the dark. However, the Ru-cetuximab bioconjugates show a mild effect, despite being the first examples of ADC (antibody drug conjugates) with cetuximab.

References

1. Karges, J. Angewandte Chemie International Edition **2022**, 61 (5).
2. Huang, H.; Zhang, P.; Yu, B.; Chen, Y.; Wang, J.; Ji, L.; Chao, H. *J Med Chem* **2014**, *57* (21), 8971–8983.
3. Martínez-Alonso, M.; Gasser, G. *Coord Chem Rev* **2021**, *434*, 213736.

OC27

Wednesday 6th September 15:45

Room Temperature Phosphorescence Au(I) and Pt(II) Supramolecular Organometallic Assemblies

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The formation of gold(I) supramolecular aggregates is an important tool from different perspectives. On one hand, the modulation of the possible assemblies with different sizes and shapes starting from single molecules is a challenge for the chemistry community and even more, trying to have a control on it. On the other hand, when our molecules present a chromophore, we can also tune the resulting colors that come upon aggregation.[1]

Regarding this, in the last years we have developed different series of gold and platinum complexes and we have been able to obtain large assemblies that produce very long fibers, rods and vesicles with yellow, green and red emission. Their use in molecular recognition processes have been also explored.[2]

Interestingly, gold(I) and platinum(II) metal centers are heavy atoms and they play an important role on the resulting luminescent properties of both the resulting compounds and assemblies. In fact, it can be observed in most cases phosphorescence emission from a chromophore in the presence of these heavy atoms (Figure 1).

In the last years, we have focused in our group in the development of phosphorescence emitters that emit this type of emission at room temperature.[3] This is an important challenge from different type of applications such as in OLED devices.

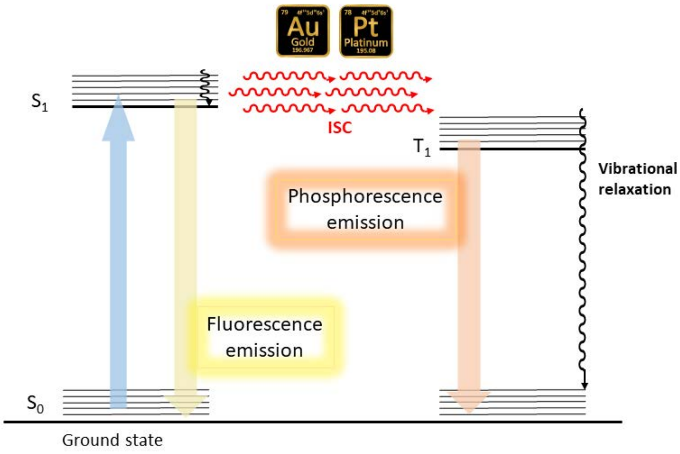

Figure 1. Jablonski diagram exemplifying the heavy atom effect on the emission properties.

References

[1] a) A. Pinto, *et al. Dalton Trans.*, **2017**, 46, 11125; b) E. Aguiló *et al. Dalton Trans.* **2016**, *45*, 7328.

[2] a) E. Aguiló *et al. Inorg. Chem.*, **2018**, 57, 1017; b) A. Lázaro *et al. Inorg. Chem.* **2020**, *59*, 8220; c) A. de Aquino et al. *Chem. Eur. J.* **2021**, *27*, 1810; d) A. Pinto *et al. Inorg. Chem. Front.* **2022**, *9*, 6047; e) A. de Aquino et al. *Dalton Trans.*, **2022**, *51*, 16282; f) A. Lázaro *et al. Inorg. Chem.* **2023**, *62*, 2000; g) G. Romo-Islas *et al. Inorg. Chem. accepted.*

OC28

Wednesday 6th September 15:00

Bis(Imino)Pyridine-Based Ligand Reactivity in Main Group Alkyls Complexes

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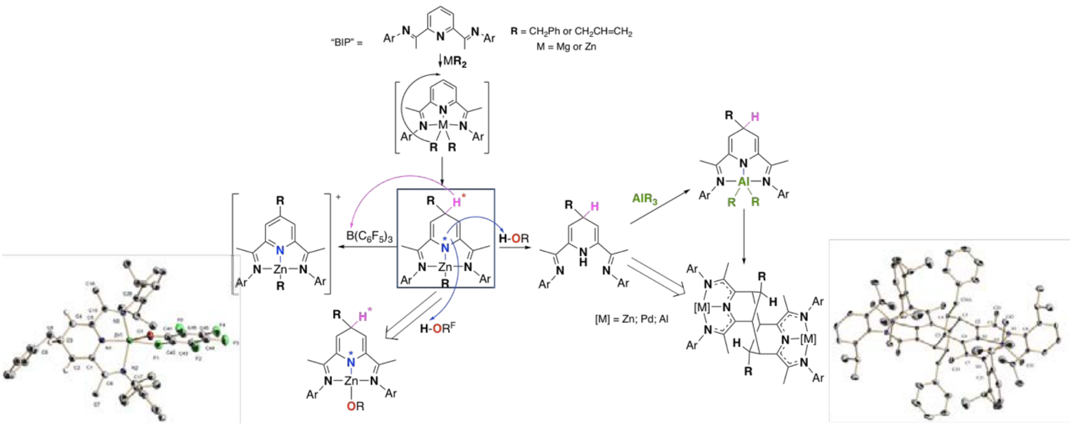
Main-group alkyl complexes of 2,6-bis(imino)pyridine (BIP) ligands conform an interesting combination that has stimulated research from different groups, including ours over the last decades. However, the development of the current knowledge has been very challenging, due to the high reactivity and non-innocent character of BIP-based ligands.[1] Their often-unique transformations provide new opportunities for the discovery of innovative chemistry and a largely unexplored potential for applications in Catalysis.



Recently, we have developed the chemistry of 2,6-(diimino)-dihydropyridinate-alkylzinc complexes (inset, see Scheme). These are formed after reactions of BIP ligands with diorganozinc derivatives ZnR_2, which upon coordination, transfer one of the alkyl groups R to the distal 4-position of the pyridine ring, dearomatizing the ring. Reactivity studies allow discovering that the resultant species contain two reactive sites: (i) the Zn-amide, a strong base that reacts with weak protic acids like alcohols, MeOH releasing the dihydropyridine base; and (ii) a nucleophilic moiety located at the *sp*^{3} 4-C(H)R position of the central ring, a hydride donor when reacting with Lewis acids. The latter transformation brings about the re-aromatization of the heterocycle. This dual behaviuor suggests that BIP-based ligands might act as reversible hydrogen donors, akin to the pyridine-based co-enzymes (e.g., NADH/NAD$^+$), redox exchangers in biological systems. In this presentation, we will disclose details of our most latest advances in this research, detailing the formation of (dihydropyridinate)Zn alkoxides, potentially useful for the activation of organic electrophiles,[2] and the reversible hydrogen transfer from BIP ligands to organo-Al(III) fragments.[3]

References

[1] J. Cámpora, A. Rodríguez-Delgado; P. Palma. σ-Organometallic chemistry with 2,6-Bis(imino)pyridine Ligands: New Pathways to Innovative Pincer Architectures. *in* Pincer Compounds: Chemistry and Applications. pp. 539-586. Elsevier, **2018**. [2] J. M. Delgado, J. Campora, A. Rodríguez-Delgado, *manuscript in preparation* ***2023*** [3] M. Gallardo-Villagrán, J. Cámpora, A. Rodríguez-Delgado *et al. Dalton Trans.* **2019**, *48*, 9104-9116.

OC29

Wednesday 6th September 15:15

Titanium (IV) and (III) Bis(O-Phenylenediamido) Compounds: A Story of Structural Variety and CO_2 Functionalization

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Low-valent early transition metals have shown great promise in the challenging field of small molecule activation.[1] Within group 4, the high reactivity displayed by titanium compounds in low oxidation state is attributed to their strong reductant nature, that at the same time makes difficult their synthesis and handling. Typically, stabilization is achieved by using cyclopentadienyl ligands.[2] Nevertheless, recent advances point to the use of readily tuneable ligands, such as amido fragments, to fully leverage the applications of this metal.[3] In the field of small molecule activation, big efforts are devoted to the functionalization of CO_2, which have led to several examples of reduced titanium species for the stoichiometric activation of CO_2,[4] however the investigations on the catalytic transformation are comparatively scarce.[5]

Being aware of the potential of early transition metals in small molecule activation and the influence of the supporting ligands on their reactivity, herein, we report the structural mapping towards the synthesis of bis(diamido)titanium compounds in oxidation states IV and III. The use of ortho-phenylenediamido ligands as stabilizing fragments results in a wide structural variety of species with different bonding situations and hence different chemical behaviour. Finally, we describe the extraordinary catalytic activity of the prepared Ti(III) compounds in the copolymerization of CO_2 and epoxides under ambient conditions (1 bar) towards the selective formation of polycarbonate in excellent yields.

References

[1] a) E. P. Beaumier, A. J. Pearce, X. Y. See, I. A. Tonks, Nat. Rev. Chem. 2019, 3, 15-34; b) M. Manßen, L. L. Schafer, Chem. Soc. Rev. 2020, 49, 6947-6994.
[2] P. J. Chirik, M. W. Bouwkamp, 4.03 - Complexes of Titanium in Oxidation States 0 to II, in Comprehensive Organometallic Chemistry III, ed. D. M. P. Mingos and R. H. Crabtree, Elsevier, Oxford, 2007, 243–279.
[3] S. Fortier, A. Gomez-Torres, Chem. Commun. 2021, 57, 10292-10316.
[4] K. A Grice, Coord. Chem. Rev. 2017, 226, 78–95.
[5] Y. Wang, Y. Qin, X. Wang, F. Wang, ACS Catal. 2015, 5, 393–396.

OC30

Wednesday 6th September 15:30

On the Single-Centre Ambiphile Concept

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The Renaissance in main group chemistry over recent decades has given us a huge depth in understanding the electronic characteristics of low-valent *p*-block species.[1,2] The importance of developing sustainable chemical technologies, in conjunction with the impressive reactive capacity of the abundant *p*-block elements in non-classical oxidation states, has firmly established this chemistry as a cornerstone in modern synthesis, albeit in a largely fundamental capacity. In taking such species from laboratory curiosities to utility, our research focuses on developing the Single-Centre Ambiphile ligand concept.[3] This concept utilises the ambiphilic frontier orbitals of now well established low-valent group 13 and 14 species, incorporating these elements into chelating ligands and thus forming a bespoke family of non-innocent ligand systems. These have the unique capacity to bind a transition metal centre through a lone electron pair, whilst the same binding centre remains highly Lewis acidic (Fig. 1). This, in turn, promotes nucleophile binding at the ligand centre, even in complexes containing sub-18-electron transition metal centres. This opens a new mechanistic pathway for accessing hitherto unknown bond activation processes, moving towards catalysis. Utilizing Single-Centre Ambiphile ligands, we have shown that stable complexes of Fe^0, Co^0, and Ni^0 are readily accessible, with each transition metal displaying a unique reactive capacity. This is also dependent on the ligand's binding centre (*e.g.* Ge^{II} vs. Sn^{II}), giving a high degree of control over these reactive systems. This and subsequent chemistry of these complexes will be discussed.[3,4,5,6]

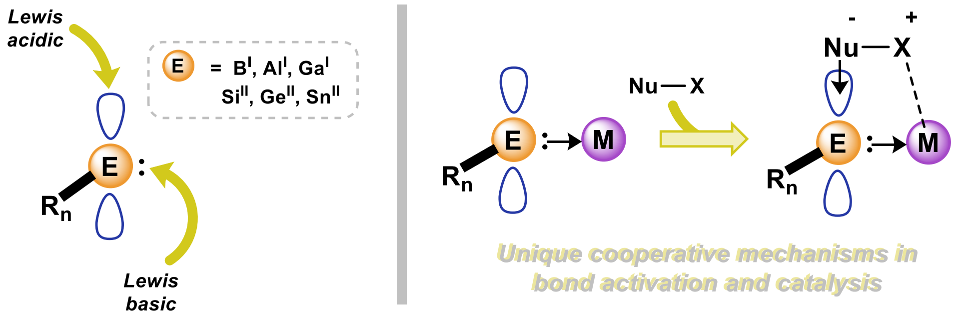

Figure 1. The Single-Centre Ambiphile concept.

References

1. Hadlington, T. J., Driess, M., and Jones, C. *Chem. Soc. Rev.*, **2018**, *47*, 4176.
2. Power, P. P. *Nature*, **2010**, *463*, 171.
3. Keil, P. M., Szilvasi, T., and Hadlington, T. J. *Chem. Sci.*, **2021**, *12*, 5582.
4. Keil, P. M., and Hadlington, T. J. *Angew. Chem.*, **2022**, *134*, e202114143.
5. Keil, P. M., and Hadlington, T. J. *Chem. Commun.* **2022**, *58*, 3011.
6. Keil, P. M., Soyemi, A., Weisser, K., Szilvási, S., Limberg, C., and Hadlington, T. J. *Angew. Chem.* **2023**, e202218141.

OC31

Wednesday 6th September 15:45

Phosphorus Clusters in Small Molecule Activation and Catalysis

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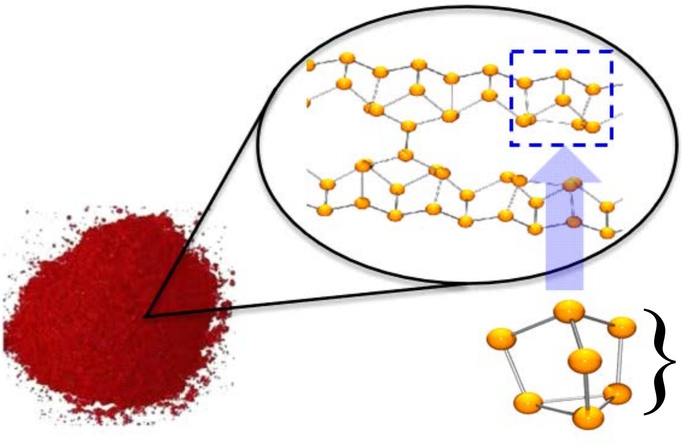
Clusters occupy the space between molecules and bulk solids.[1] Zintl clusters can be thought of as molecular mimics for heterogeneous materials: for example, the structure of $[P_7]^{3-}$ can be viewed as a fragment of red phosphorus,[2] which is an inexpensive and abundant material, albeit a challenging one to study because of its poor solubility. In contrast, $[P_7]$ clusters, especially those that have been functionalized, are soluble in common laboratory solvents, offering a broader range of handles for in situ investigations. An improved understanding of reactivity patterns for $[P_7]$ could be extended to corresponding reactions with materials based on the many allotropes of phosphorus. Here we will discuss small molecule activations and catalysis with $[P_7]$ clusters.[3-6] Most interestingly, we find the first applications of Zintl-base clusters in transition metal-free catalysis.[5,6]



- ☐ transition metal free catalysis
- ☐ CO_2 to methanol
- ☐ hydroboration catalysis

References

1. van IJzendoorn, B.; Mehta, M. *Dalton Trans* **2020**, *49*, 14758–14765.
2. Ruck, M.; Hoppe, D.; Wahl, B.; Simon, P.; Wang, Y.; Seifert G. *Angew. Chem. Int. Ed.* **2005**, *44*, 7616–7619.
3. van IJzendoorn, B.; Vitorica-Yrezabal, I.J.; Whitehead, G.F.S.; Mehta, M. *Chem. Eur. J.* **2021**, *28*, e202103737.
4. Jobbins, W.D.; van IJzendoorn, B.; Vitorica-Yrezabal, I.J.; Whitehead, G.F.S.; Mehta, M. doi.org/10.1039/D2DT04074C.
5. Réant, B.L.L.; van IJzendoorn, B.; Whitehead, G.F.S.; Mehta, M. *Dalton Trans.* **2022**, *51*, 18329–18336.
6. van IJzendoorn, B.; Albawardi, S.F.; Vitorica-Yrezabal, I.J.; Whitehead, G.F.S.; McGrady, J.E.; Mehta, M. *J. Am. Chem. Soc.* **2022**, *144*, 21213–21223.

OC32

Thursday 7th September 12:00

Iron-catalyzed C(*sp*^{3})–H Amination

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The development of efficient methods for the formation of carbon–nitrogen (C–N) bonds is one of the most crucial tasks in chemical synthesis. The installment of C–N bonds by direct functionalization of C(*sp*^{3})–H bonds is a powerful and atom-efficient transformation for chemical synthesis. Although the direct installation of nitrogen into a C(*sp*^{3})–H bond is extremely challenging due to the thermodynamic and kinetic stability of the C(*sp*^{3})–H bond, intra- and intermolecular C(*sp*^{3})–H amination has seen much progress in the past decade. Particularly, intramolecular C(*sp*^{3})–H amination as an atom-economical strategy has found extensive applications for the construction of varieties of important N-heterocycles.

Fe-mediated catalysis has slowly made its way to various important classes of organic chemical transformations, including hydroaddition chemistry and recently also C–H activation, but the Fe-mediated functionalization of aliphatic C(*sp*^{3})-H bonds is still a formidable challenge.

Nitrene (in situ generated) insertion into a C(*sp*^{3})–H bond is an efficient and perhaps the best studied approach for C(*sp*^{3})–N bond formation. In situ generation of a metal-bound nitrene species from readily available aliphatic organoazides, releasing only molecular nitrogen as the side product, followed by selective insertion into a C(*sp*^{3})–H bond would constitute an efficient approach for catalytic C–H amination. Synthesis of *N*-heterocycles via direct C(*sp*^{3})–H amination using aliphatic azide substrates is an appealing strategy, given that *N*-heterocycles are prevailing building blocks in natural products, pharmaceuticals, and functional material.

Herein, we discuss the synthesis and detailed characterization of various iron complexes, with different metal oxidation states, and their catalytic performance in the direct C(*sp*^{3})–H amination of aliphatic azides to *N*-heterocycles.

Research funded by NWO.

OC33

Thursday 7th September 12:15

Cu(II)-Mediated Functionalization Of C–H Bonds: Synthesis of Heterocycles and Kinetico-Mechanistic Studies

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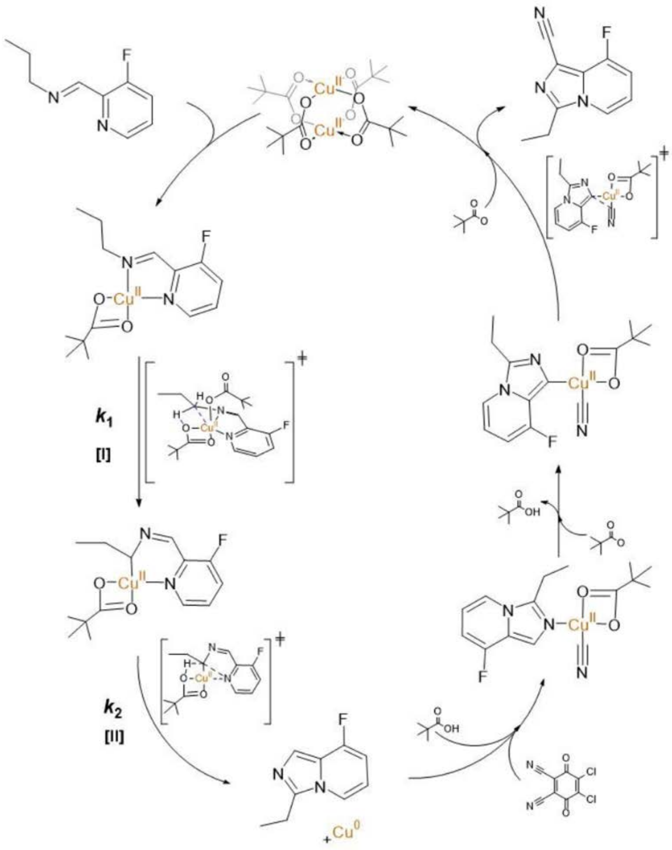

C–H Bond activation represents a highly attractive topic in catalysis leading to valuable transformations. The functionalization of C(sp^3)–H bonds in a selective and efficient manner is especially challenging, in particular using non-noble metals.[1] Copper is an earth-abundant 3d transition metal of relevance in catalysis due to its high functional group tolerance and low toxicity that are key to design C–H sustainable processes by minimizing the generation of wastes.[2] Herein, we focus on the mechanistic studies of a carboxylate-assisted Cu(II)-catalysed relay towards the synthesis of imidazo[1,5-*a*]pyridines encompassing C(sp^3)–H amination and cyclization of aldimines followed by C(sp^2)–H cyanation[3] using operando UV-Vis reaction monitoring coupled to ex-situ analyses.[4] Thus, kinetic studies have been carried out, providing a proof of the elementary steps involved (see Figure). The experimental data obtained is consistent with the formation of a cyclometalated complex **[I]** (***k*$_1$**), *via* a high enthalpy demanding transition state, followed by a C(sp3)–H bond cleavage event **[II]** (***k*$_2$**). Both processes showing a well-defined Eyring behaviour with reasonable values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Further insights on the fast final of C(sp^2)–H cyanation will be presented together with control reactions. These results reveal plausible reaction manifolds for C–H bond activation processes promoted by organometallic copper(II) complexes.

References

1. Pla, D.; Gomez, M., *ACS Catal.* **2016**, *6*, 3537.
2. a) Evano, G.; Blanchard, N.; Toumi, M., *Chem. Rev.* **2008**, *108*, 3054; b) Camats, M.; Pla, D.; Gómez, M., *Nanoscale* **2021**, *13*, 18817.
3. Camats, M.; Favier, I.; Mallet-Ladeira, S.; Pla, D. *et al.*, *Org. Biomol. Chem.* **2022**, *20*, 219.
4. Gonzálvez, M. A.; Williams, C. M.; Martínez, M.; Bernhardt, P. V., *Inorg. Chem.* **2023**, *62*, 4662.

OC34

Thursday 7th September 12:30

Stability and C–H Bond Activation Reactions of Palladium(I) and Platinum(I) Metalloradicals: Carbon-to-Metal H-Atom Transfer and Cyclometallation by a Radical Rebound Mechanism

Tobias Krämer,[1,2] Matthew R. Gyton,[3] Itxaso Bustos,[3,4] Matthew J. G. Sinclair,[3] Sze-yin Tan,[3,5]
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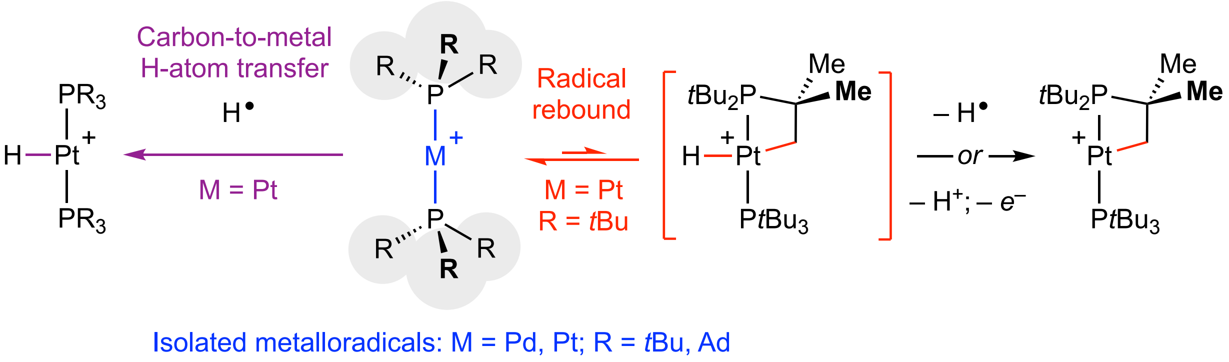
The development of new and more effective methods for enacting the cleavage of C(sp^3)–H bonds is an important facet of contemporary organometallic chemistry, which are most typically realised through concerted oxidative addition to electron rich, low-valent platinum group metals.[1] Reactions that proceed *via* transient 3-centre-2-electron M–H–C adducts and involve +2 changes in the formal oxidation state of the metal (*viz.* ΔOS = +2). Building on our work exploring the chemistry of two coordinate palladium(I) and platinum(I) complexes,[2] we will present mechanistic findings on C(sp^3)–H bond activation reactions mediated by late transition metal metalloradicals where less common radical-based oxidative addition reactions are invoked (*viz.* ΔOS = +1).[3]



References

[1] *Nature* **2002**, *417*, 507–514; *J. Am. Chem. Soc.* **1994**, *116*, 9585–9589; *Inorg. Chem.* **1985**, *24*, 1986–1992.
[2] *Angew. Chem. Int. Ed.* **2016**, *55*, 3754–3757; *Org. Lett.* **2018**, *20*, 5537–5540; *Inorg. Chim. Acta* **2020**, *513*, 119948; *Dalton Trans.* **2022**, *51*, 11617–11619.
[3] J. Porphyrins Phthalocyanines **2004**, 8, 103–110; J. Am. Chem. Soc. **2010**, 132, 73–75; Chem. Eur. J. **2007**, 13, 3386–3405; J. Am. Chem. Soc. **2014**, 136, 3572–3578; *J. Am. Chem. Soc.* **2005**, *127*, 15684–15685.

OC35

Thursday 7th September 12:45

Highly Efficient and Versatile Heterobimetallic Al-M(II) Catalysts for Sustainable Processes

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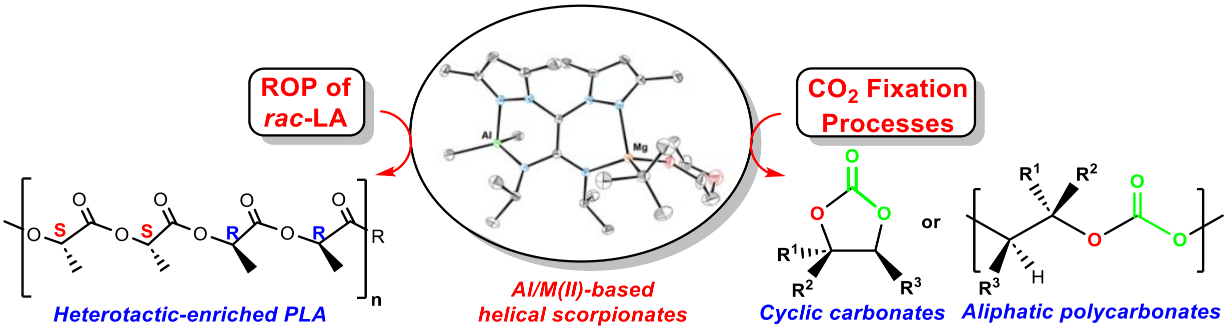
The rational use of natural resources and the efficient management of waste materials represent two of the most critical challenges nowadays for the sustainability of the planet. In this context, the polylactide (PLA), which is annually produced from sustainable resources, and the chemical utilization of waste CO_2 as a C1 platform for the production of valuable chemicals are currently attracting great attention. Consequently, the search of highly efficient and versatile catalytic species for these industrially demanded processes is an urgent demand for their sustainability. We describe here the design of novel heterobimetallic Al-M(II)-based complexes for their use as efficient and versatile catalysts through a synergic intramolecular communication between centres.[1]

We verified their potential utility for the well-controlled ROP of *rac*-LA at 20 °C, reaching an unprecedented TOF value of 2,160 h^{-1} for Al/Mg-based initiators. Very interestingly, these heterobimetallics in combination with an onium salt, led to a very active and selective bicomponent system for CO_2 fixation into five-membered cyclic carbonates, with a wide range of substrate scope, including mono-, di- and sustainable tri-substituted epoxides, under mild and solvent-free conditions. These binary systems also displayed high activity and selectivity for the synthesis of poly(cyclohexenecarbonate) under soft conditions (Scheme 1).



Scheme 1

References

[1] Gruszka, W.; Jennifer A. Garden, J. A.; *Nat. Commun.*, **2021**, *12*, 3252.

OC36

Thursday 7th September 12:00

Bimetallic Synergy with Low-Valent Group 13 Main Group Systems for Small Molecule Reactivity

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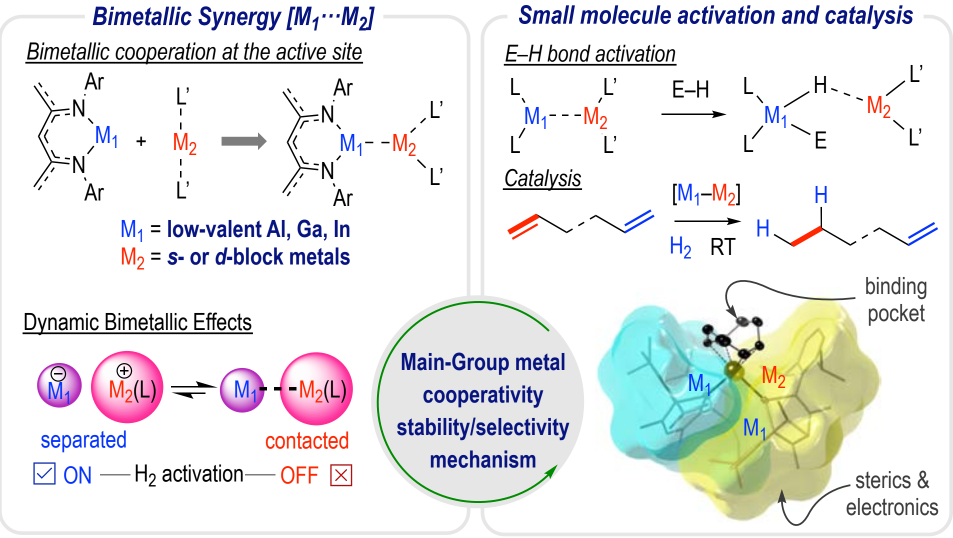
Innovative catalytic methodologies are essential for activating dormant chemical bonds and advancing synthetic chemistry. While transition metals have long been the mainstay of catalysis,[1] main group systems have recently risen as potent alternatives for redox catalysis.[2] Low-valent main-group systems effectively activate small molecules (e.g., H_2 and N_2) and engage in two-electron catalysis.[3]

Our research is focused on creating innovative bimetallic systems employing main group metals, specifically focusing on low-valent group 13 systems. These systems feature unique M···M electronic/structural configurations, fostering reactivity with small molecules (e.g., H^2, olefins, alkynes) and catalysis. We utilize low-valent Al(I), Ga(I), and In(I) species, which showcase distinct bimetallic M···M interactions with s- and d-block metals. This presentation will emphasize our latest advancements in bimetallic group 13 systems (Figure 1) and delve into the activation/catalytic mechanisms associated with their M···M interactions.[4] We will also discuss the potential impact of these findings on the broader field of redox catalysis.



References

[1] a) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals* (7th Ed); Wiley: **2019**. b) M. Beller, C. Bolm, *Transition Metals for Organic Synthesis* (2nd Ed); Wiley: **2004**.
[2] a) C. Weetman, S. Inoue, *ChemCatChem*, **2018**, 4213. b) R. Melen, *Science* **2019**, 363, 479.
[3] a) P.P. Power, Nature **2010**, 463, 171. b) T. Chu, G. I. Nikonov, *Chem. Rev.* **2018**, *118*, 3608. c) T. J. Hadlington, M. Driess, C. Jones, *Chem. Soc. Rev.* **2018**, *47*, 4176. d) B. Rösch, T. X. Gentner, J. Langer, C. Färber, J. Eyselein, L. Zhao, C. Ding, G. Frenking, S. Harder, *Science* **2021**, *371*, 1125.
[4] H. Videa, A. J. Martínez-Martínez, ChemRXiv **2022**, preprint, *Unpublished results.*

OC37

Thursday 7th September 12:15

Heterobimetallic Complexes for Cooperative Reactivity

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One of the current frontiers in organometallic catalysis is to study the combined action of two metal centers to promote novel modes of reactivity, where the two metal centers act in synergy, in order to access a chemistry not possible with monometallic species. The association of electron-rich late metal centers (such as iridium), with Lewis acidic metals (such as Al, Hf, Ta, Th, U) is particularly interesting to create polarized metal-metal pairs presenting original electronic structures,[1-3] and thus potentially novel reactivity. Recently, we have shown that these heterobimetallic species are able to activate carbon dioxide (Fig. 1a)[4] as well as C-H bonds (Fig. 1b)[5–7] in a concerted way on both metal centers, which explains why these bimetallic systems have a catalytic activity largely superior to their monometallic analogues. In this presentation we will describe our latest results in this area of research.

References

1. Escomel, L.; Soulé, N.; Robin, E.; Del Rosal, I.; Maron, L.; Jeanneau, E.; Thieuleux, C.; Camp, C. *Inorg. Chem.* **2022**, *61*, 5715-5730.
2. Lassalle, S.; Petit, J.; Falconer, R. L.; Hérault, V.; Jeanneau, E.; Thieuleux, C.; Camp, C. *Organometallics* **2022**, *41,* 1675-1687.
3. Ye, C. Z.; Del Rosal, I.; Boreen, M.; Ouellette, E. T.; Russo, D. R.; Maron, L.; Arnold, J.; Camp, C. Chem. Sci. **2023**, *asap article.*
4. Escomel, L.; Del Rosal, I.; Maron, L.; Jeanneau, E.; Veyre, L.; Thieuleux, C.; Camp, C. *J. Am. Chem. Soc.* **2021**, *143*, 4844–4856.
5. Lassalle, S.; Jabbour, R.; Schiltz, P.; Berruyer, P.; Todorova, T. K.; Veyre, L.; Gajan, D.; Lesage, A.; Thieuleux, C.; Camp, C. *J. Am. Chem. Soc.* **2019**, *141*, 19321–19335.
6. Del Rosal, I.; Lassalle, S.; Dinoi, C.; Thieuleux, C.; Maron, L.; Camp, C. *Dalton Trans.* **2021**, *50*, 504–510.
7. Escomel, L.; Abbott, D. F.; Mougel, V.; Veyre, L.; Thieuleux, C.; Camp, C. *Chem. Commun.* **2022**, *58*, 8214-8217.

OC38

Thursday 7th September 12:30

Pt/Main Group Bimetallic Complexes: Small Molecule Activation and Metal-Metal Cooperative Transmetalation

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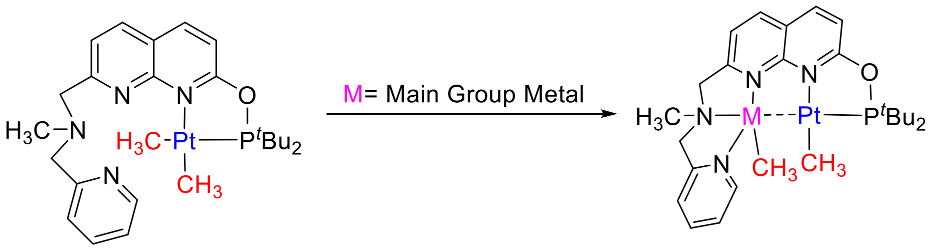
Multimetallic complexes have gained much interest from the synthetic chemistry community, especially bimetallic complexes which feature close metal-metal interaction and have been the subject of current interest due to their vital role in small molecule activation and catalysis. However, the selective synthesis of heterobimetallic complexes still presents a significant challenge, and many research groups rely on the thorough optimization of the ligand design to overcome this issue.[1] Our group focused on the synthesis of unsymmetrical naphthyridine-based bi-nucleating ligands containing distinct coordination sites. Such ligand design allowed us to form selective heterobimetallic complexes via stepwise synthesis. In continuation of that, recently we reported the selective formation of Pt/Cu and Pt/Zn heterobimetallic complexes showing close metal-metal interaction and promoting cooperative small molecule activation (H_2, B-H, Si-H, and C-H).[2] Herein, we report Pt/main group heterobimetallic complexes and their metal-metal cooperative reactivity in the activation of silanes and boranes. We demonstrate how the synergistic interaction plays an important role in metal-metal cooperative small molecule activation, transmetalation, and retrotransmetalation relevant to Stille and Negishi coupling reactions. Computational studies (QTAIM and NBO) also shed light on the nature of the metal-metal interaction.



- * Transmetalation
- * B-H, Si-H, B-F activation

References

1) R. Govindarajan, S. Deolka, J. R. Khusnutdinova, *Chem. Sci.,* **2022**, *13,* 14008.

2) a). S. Deolka, O. Rivada, S. L. Aristizábal, R. R. Fayzullin, S. Pal, K. Nozaki, E. Khaskin, J. R. Khusnutdinova, *Chem.Sci.* **2020**, *11*,5494. b) R. Govindarajan, S. Deolka, E. Khaskin, R. R. Fayzullin, S. Pal, S. Vasylevskyi, J. R. Khusnutdinova, *Chem. Eur. J.* **2022**, e202201639

OC39

Thursday 7th September 12:45

Synergistic Approaches to Catalyst Design for the Sustainable Production of Challenging Enantioenriched Compounds

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Advances in the synthesis of enantioenriched molecules, whether producing new compounds or improving existing methodologies, are made possible by the incessant innovations in asymmetric catalysis.[1] In order to fully exploit the application of asymmetric catalysis, there is a incessant need to broaden the range of substrates undergoing the process with high enantioselectivity, thus making possible to prepare of the most assorted set of chiral compounds possible. The search for a catalyst that can work for new types of substrates is hampered by a lack of data, since most catalytic systems have only been tested with model substrates. To speed up the process it would be very convenient to find catalysts with a broad substrate scope. So, in this context I will present different ways to integrate theoretical calculations into the catalyst design (from guiding it to predictive models going through in silico-based catalyst optimization) for the preparation of challenging enantioenriched compounds.[2] I will also present the progress made on the synthesis of immobilized versions of the catalysts for continuous flow production of these challenging substrates.

References

[1] a) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, **1994**; b) E. N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.) Comprehensive Asymmetric Catalysis, Springer-Verlag, Berlin, **1999**. c) H.-U. Blaser, H.-J. Federsel (Eds.) Asymmetric Catalysis in Industrial Scale: Challenges, Approaches and Solutions, 2nd Ed, Wiley, Weinheim, **2010**. d) T. Akiyama, I. Ojima (Eds.) Catalytic Asymmetric Synthesis, 4th Ed, John Wiley & Sons, Inc., Hoboken, **2022**.

[2] See for instance: a) M. Biosca, J. Saltó, M. Magre, P.-O. Norrby, O. Pàmies, M. Diéguez, *ACS Catal.* **2019**, *9*, 6033; b) J. Faiges, C. Borràs, I. M. Pastor, O. Pàmies, M. Besora, M. Diéguez, *Organometallics* **2021**, *40*, 3424; c) J. Wahlers, J. Margalef, E. Hansen, A. Bayesteh, P. Helquist, M. Diéguez, O. Pàmies, O. Weist, P.-O. Norrby, *Nature Commun.* **2021**, *12*, 6719; d) M. Biosca, P. de la Cruz-Sánchez, J. Faiges, J. Margalef, E. Salomó, A. Riera, X. Verdaguer, J. Ferré, F. Maseras, M. Besora, O. Pàmies, M. Diéguez, *ACS Catal.* **2023**, *13*, 3020.

OC40

Thursday 7th September 16:00

Revisiting $[FeEt_2(Bipy)_2]^{N+}$ (N = 0, 1, 2): A Radically New View

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The diamagnetic complex $[FeEt_2(bipy)_2]$ was first described by Yamamoto *et al.*[1, 2] and used as a butadiene cyclodimerization/polymerization catalyst. In a seminal 1982 report by Kochi *et al.*,[3] its thermal stability and decomposition pathway were shown to strongly depend on the oxidation state: slow at 50°C for $[FeEt_2(bipy)_2]$ complex to selectively yield C_2H_4 and C_2H_6 (disproportionation), faster for $[FeEt_2(bipy)_2]^+$ to yield a mixture of disproportionation and combination (C_4H_{10}), instantaneous for $[FeEt_2(bipy)_2]^{2+}$ to selectively yield C_4H_{10}. The decomposition was proposed to follow a conventional 2-electron β-H elimination/reductive elimination mechanism for the neutral complex, a 1-electron homolytic cleavage for the cationic complex and a 2-electron reductive elimination for the dicationic complex.

We the help of new experiments and DFT calculations, we will show that the parent $[FeEt_2(bipy)_2]$ complex has an unexpected electronic structure and that its “2-electron” disproportionation follows instead a 1-electron radical pathway. The 1-electron homolytic Fe-Et bond cleavage is actually easier for the neutral complex than for its 1-electron oxidation product. These results are an eye-opener on the action of alkyl complexes, particularly for 1st-row transition metals with homolytically weak bonds, in certain metal-catalyzed transformations such as C-C cross-couplings.

References

1. A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida and A. Misono, *J. Am. Chem. Soc.*, 1965, **87**, 4652-4653.
2. A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida and A. Misono, *J. Amer. Chem. Soc.*, 1968, **90**, 1878-1883.
3. W. Lau, J. C. Huffman and J. K. Kochi, *Organometallics*, 1982, **1**, 155-169.

OC41

Thursday 7th September 16:00

Chiral-at-Rhodium Complex Bearing Si,N Ligands

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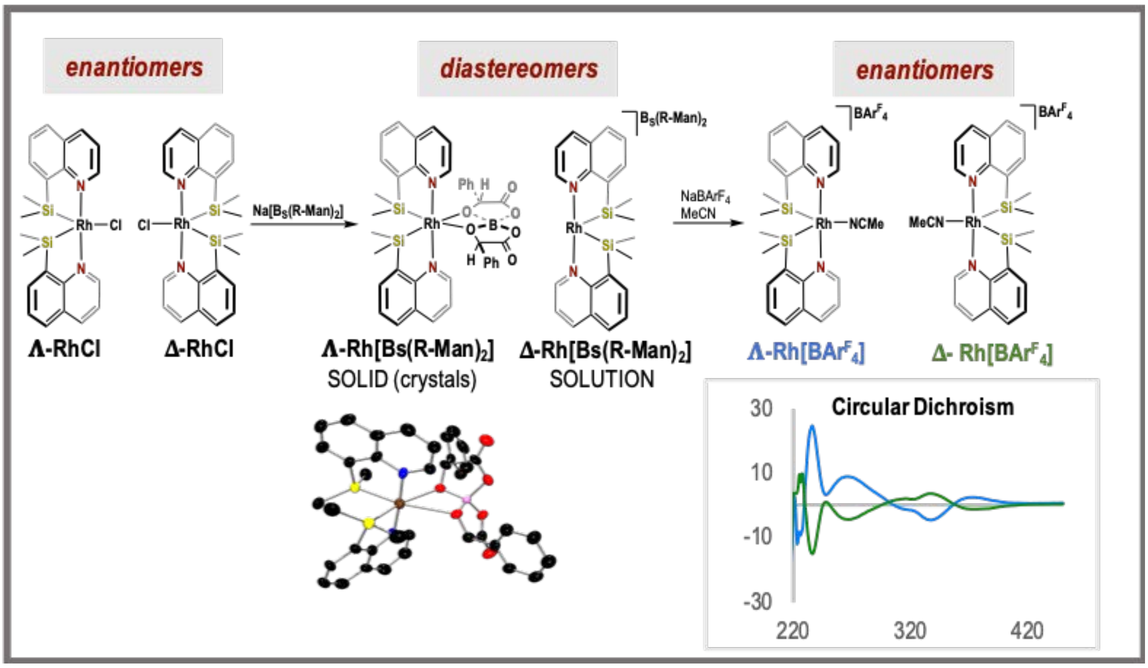
The synthesis of chiral molecules continues to be one of the most important challenges in chemistry with asymmetric catalysis being the most widely used method to achieve this goal. Apart from the well-known catalytic systems with a metal complex and a chiral ligand, there is a less studied approach involving transition metal catalysts without chiral ligands, where the metal center itself is chiral (chiral-at-metal). This field has developed exponentially since 2013 when group of Prof. Eric Meggers started publishing several chiral-at-metal complexes with exceptional properties as electrophilic catalysts.[1,2]

During the last few years, my group has been dealing with the synthesis and resolution of racemic mixtures of rhodium and iridium(III) complexes bearing Si-based bidentate ligands. Herein we report an straightforward protocol for the resolution of a Rh-Si,N complex, which have been used as asymmetric catalyst in the Mukaiyama aldol reaction.



Acknowledgements. PID2019-111281GB-I00 funded by MCIN/AEI/10.13039/501100011033 and IT1741-22 funded by Gobierno Vasco.

References

[1] L-A. Chen, W. Xu, B. Huang, J. Ma, L. Wang, J. Xi, K. Harms, L. Gong, E. Meggers, *J. Am. Chem. Soc.* 2013, *135*, 10598–10601. [2] J. Ma, X. Zhang, S. Luo, E. Meggers, *Nat. Protoc.* 2018, *13*, 605–632.

OC42

Thursday 7th September 16:45

Copper-Catalysed Amination of Alkyl Iodides Enabled by Halogen-Atom Transfer

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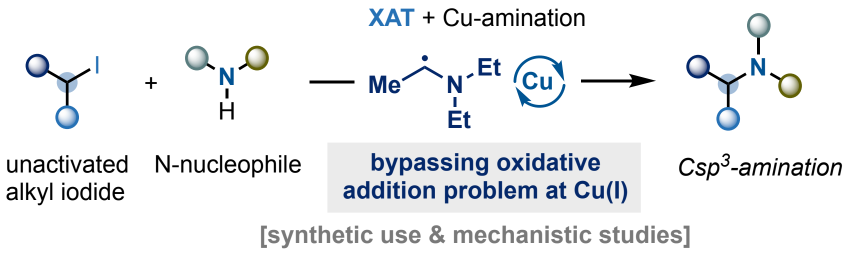
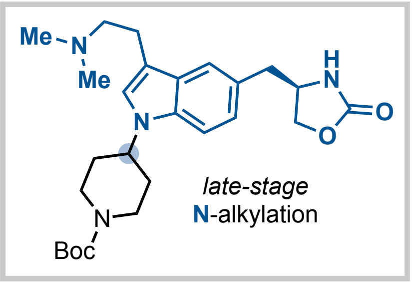
Csp^3–N bonds are widespread in pharmaceuticals and agrochemicals and when approaching their construction, we all immediately think of S$_N$2 chemistry – a cornerstones in organic chemistry education. However, this strategy is only effective if the electrophile is either primary or activated (*e.g.* benzylic, α-carbonyl). S$_N$2 reactions between N-nucleophiles and secondary unactivated alkyl halides are, in fact, very challenging and require forcing conditions that often lead to unwanted E2 elimination. A possible solution would lie on the ability of Cu catalysts to capture C-radicals, which has emerged as a versatile tactic to assemble C–C and C–heteroatom bonds. However, the implementation of this route has been thwarted by *the limited ability of Cu(I) to undergo oxidative addition*,[1] being only efficient when activated alkyl halides are employed.

Capitalizing on the ability of aminoalkyl radicals to activate carbon-halogen bonds,[2] we have developed a general approach for the assembly of Csp^3–N bonds from unactivated alkyl iodides. Here is shown how halogen-atom transfer (XAT) can be recruited to circumvent the otherwise sluggish oxidative addition in Cu(I) resulting in a practical, fast and effective method to aminate alkyl iodides.[3] The utility of the process has been demonstrated by the late-stage N-alkylation of several bioactive molecules and mechanistic studies are provided.





References

[1] G. Evano, N. Blanchard, *Copper-Mediated Cross-Coupling Reactions,* John Wiley, **2014**
[2] T. Constantin, M. Zanini, A. Regni, N. S. Sheikh, F. Juliá and D. Leonori, *Science*, **2020,** *367*, 1021-1026
[3] B. Górski, A.-L. Barthelemy, J. J. Douglas, F. Juliá and D. Leonori, *Nature Catal.*, **2021**, *4,* 623-630

OC43

Thursday 7th September 17:00

Electrochemical Hydrogen Production Catalysed by Cp*Co(III) Complexes

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The development of efficient electrocatalysts for the hydrogen evolution reaction (HER) from water is attracting a lot of interest, in the general framework of finding strategic processes toward renewable fuels. Among different possible electrocatalysts, those based on cobalt have shown very promising performance likely due to their intrinsic oxygen tolerance and efficient proton reduction ability.[1]

Herein, we report the results of an in-depth investigation on the utilization of a large family of water-soluble Cp*Co(III) molecular complexes, bearing bidentate ligand, as HER electrocatalysts in buffered aqueous solutions.[2] Controlled potential electrolysis and rotating ring-disk electrode experiments were performed to disclose Faradaic efficiencies and catalyst stability under neutral pH electrocatalytic conditions. Activity strongly depends on the nature of the bidentate ligand. Remarkable TOF values (up to over 44 000 s^{-1}) are observed. Structure/performance correlations and mechanistic considerations, aimed at explaining the observed catalytic trends, will be discussed.

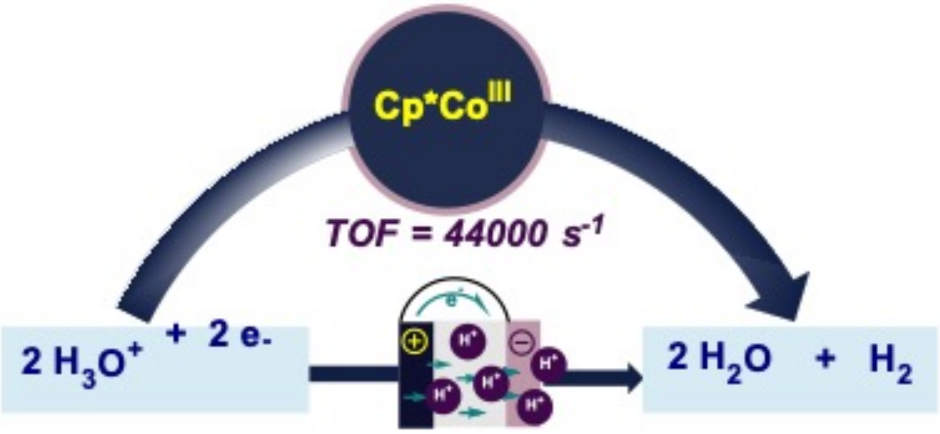

Figure 1. Electrochemical H_2 production catalyzed by a Cp*Co(III) complex.

References

[1] F. Zaccaria *et al. Front. Catal.* 2:892183. doi: 10.3389/fctls.2022.892183.
[2] P. Dahiya et al. *Adv. Synth. Catal.* **2022**,364, 2642–26.

OC44

Thursday 7th September 16:45

Metal-Ligand Cooperation with Group 10 Metals and Hydrosilylation

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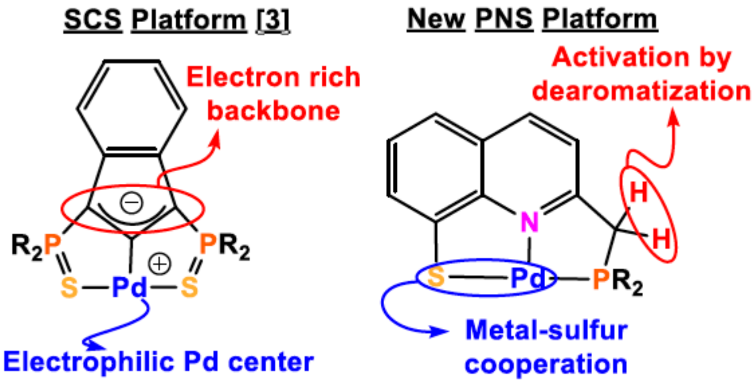
Over the last decade, cooperative effects in transition metal catalysis have attracted increasing interest from the scientific community. In this context, metal/ligand cooperation (MLC), in which one of the ligands participates actively to the activations of the substrates, can be highlighted [1]. In this domain, pincer complexes of transition metals play an important role. One of the most representative models was reported by Milstein [1], based on an aromatization/dearomatization process of a pyridine-based pincer ligand.

Although group 10 metals are widely used in catalysis, they are much less studied in MLC than metals of group 8 and 9 [2]. In this context, our group has reported an indenediide Palladium and Platinium complexes bearing an electron rich backbone [3]. Remarkable results have been obtained in catalytic cyclisation processes involving C-O/C-N & C-C bonds formation.

To further develop MLC with group 10 metals, we are now working on a new platform deriving from the quinoline moiety that can combine two types of non-innocent behavior. The activation can occur either via aromatization/dearomatization of the quinoline moiety or may involve the sulfur atom as described by Ohki & Oestreich [4].



References

[1] Khusnutdinova, J. R.; Milstein, D. *Angew. Chem. Int. Ed.* **2015**, *54*, 12236.

[2] (a) A. Scharf, I. Goldberg, A. Vigalok, *J. Am. Chem. Soc.* **2013**, *135*, 967. (b) A. Scharf, I. Goldberg, A. Vigalok, *Inorg. Chem.* **2014**, *53*, 12.

[3] (a) Monot, J.; Brunel, P.; Kefalidis, C. E.; Espinosa-Jalapa, N. Á.; Maron, L.; Martin-Vaca, B.; Bourissou, D. *Chem. Sci.* **2016**, *3*, 2179. (b) Clerc, A.; Marelli, E.; Adet, N.; Monot, J.; Martin-Vaca, B.; Bourissou, D. *Chem. Sci.* **2021**, *12*, 435.

[4] T. Stahl, K. Müther, Y. Ohki, K. Tatsumi, M. Oestreich, *J. Am. Chem. Soc.* **2013**, *135*, 10978.

OC45

Thursday 7th September 17:00

Hybrid Ferrocene Ligands Combining Phosphine and Stibine Donor Groups

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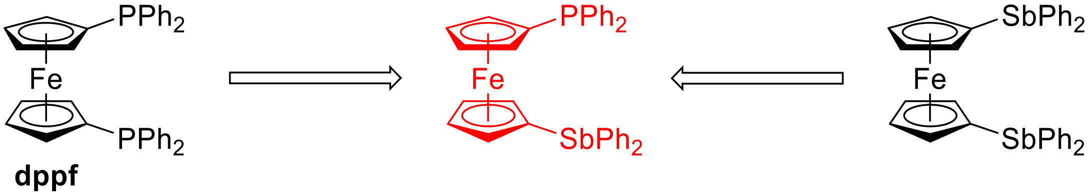
While ligands combining P- and N-donor groups are well established hybrid donor in coordination chemistry and catalysis, those featuring different combinations of pnictogen donor groups remain much less explored. This contribution will focus on the preparation and reactivity of new ferrocene-based ligands with phosphine and stibine donor moieties that are structurally related to the widely studied 1,1′-bis(diphenylphosphino)ferrocene[1] (Scheme 1). These compounds will be shown to exert reactivity that differs from that of P- and P,N-donors, which opens the way to new structures and tailored applications, mainly in coordination chemistry and catalysis, which will also be illustrated.[2]



Scheme 1. Dppf and the analogous ligands with P- and Sb-donor groups.

Financial support. The Czech Science Foundation (project 21-02316S) is acknowledged.

References

1 a) *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, Germany **1995**; b) *Ferrocenes: Ligands, Materials and Biomolecules* (Ed.: P. Štěpnička), Wiley, Chichester, United Kingdom **2008**; c) R. C. J. Atkinson, V. C. Gibson, N. J. Long, *Chem. Soc. Rev.* **2004**, *33*, 313; d) R. Gómez Arrayás, J. Adrio, J. C. Carretero, *Angew. Chem. Int. Ed.* **2006**, *45*, 7674; e) L. Cunningham, A. Benson, P. J Guiry, *Org. Biomol. Chem.* **2020**, *18*, 9329-9370.

2 J. Schulz, J. Antala, I. Císařová, P. Štěpnička, *Dalton Trans.* **2023**, *52*, 1198.

OC46

Thursday 7th September 16:45

Copper(I)-Mediated Functionalisation of White Phosphorus

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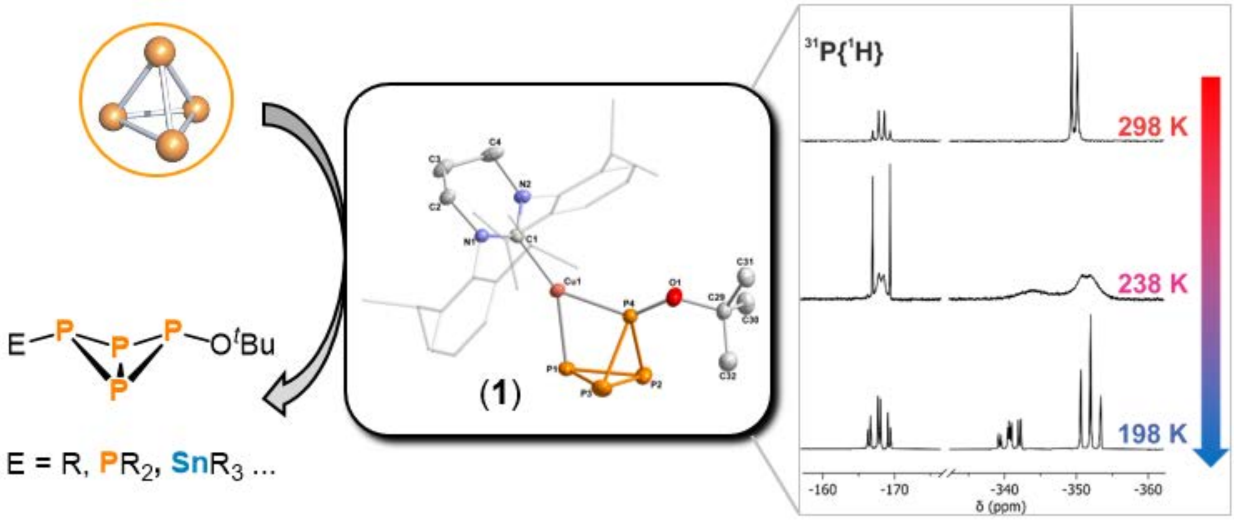
White phosphorus (P_4) remains the key starting material in the synthesis of organophosphorus compounds. Over several decades, the activation of P_4 by organometallic complexes has yielded a myriad of remarkable P_n coordination complexes.[1] However, these generally provide limited opportunity for subsequent functionalisation of the resulting polyphosphorus ligands to yield isolable organophosphorus compounds.

Herein, we present the selective activation of P_4 by an *N*-heterocyclic carbene-supported copper(I) complex to give the 'butterfly' complex **1**. The insertion of the tetrahedron into a metal-element bond affords concurrent functionalisation of the resulting polyphosphido ligand. Characterisation of **1** by single-crystal X-ray diffraction and variable temperature NMR spectroscopy gives insight into the remarkable dynamic behavior of the complex. The reactivity of **1** with a variety of substrates is discussed. Our investigations illustrate a means to access new organophosphorus species derived from P_4 in a convenient manner. Furthermore, recovery of the metal complex for recycling is presented – an important step on the way to establishing efficient metal-mediated routes for the functionalisation of P_4.



References

a) L. Giusti, V. R. Landaeta, M. Vanni, J. A. Kelly, R. Wolf, M. Caporali, *Coord. Chem. Rev.* **2021**, *441*, 213927; b) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236–4256; c) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164–4177; d) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178–4235.

OC47

Thursday 7th September 17:00

Biomass-Derived Substrate Valorisation through Hydrogenation by Hybrid Catalysts

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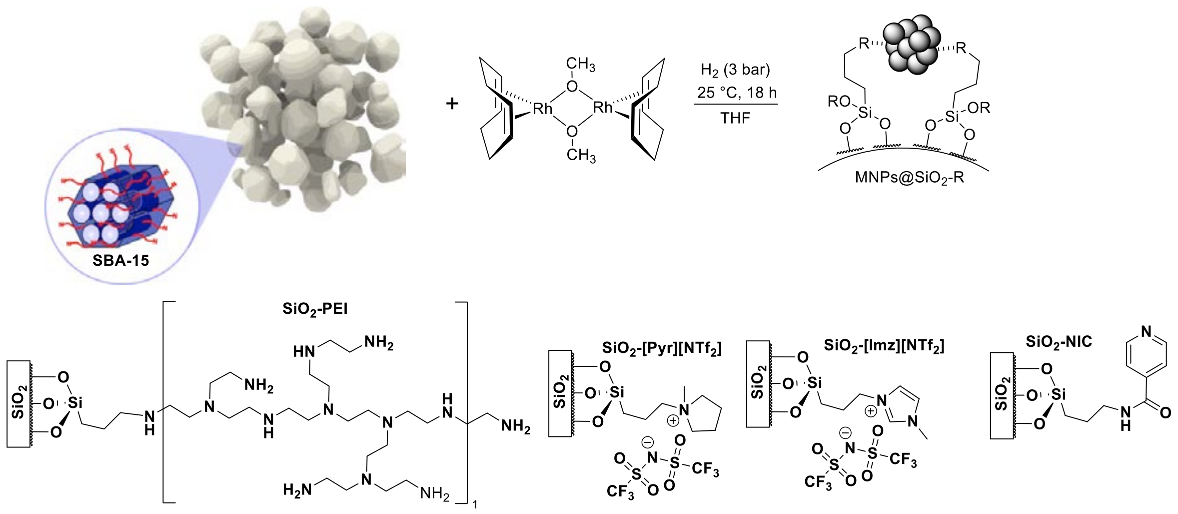
Nowadays the valorisation of Biomass into value-added products could provide society an environmentally friendly solution to cover their needs. Today, few processes are well established in the industry and fewer are metal-based catalysed. The key to applied metal-based catalysts into biomass valorisation require robust catalyst that could be separated from the reactants. Immobilized catalysts,[1-4] in liquid or solid phases, offer several advantages over conventional homogeneous catalysts, including: i) increased thermal and chemical stability: they are less likely to be affected by environmental changes such as temperature, pH, and pressure; ii) increased selectivity: they may be able to catalyse specific reactions more efficiently, in particular those where regio- and stereoselectivity should be controlled; iii) increased cost-effectiveness: there can be used for longer times, so they are more cost-effective in the long run.

The current synthetic routes often require further activation steps that modify the catalyst. Colloidal pre synthesis of metal nanoparticles in combination with silica functionalize afford materials where the surface is homogeneously covered with small RhNPs, and it is not affected after the transformation takes place. Herein we present RhNPs supported in structured silica SBA-15 functionalized with nitrogenated compounds (polyethylenimine or ionic liquids) applied in the valorization of furfural, levulinic acid, phenols, among other substrates.



References

1. A. Serrano-Maldonado, *et. al.*, *Catal. Sci. & Technol*,, **2018**, *8* (17), 4373-4382.
2. K. P. Ramírez-Cuellar, *et. al.*, *Catal. Today*, 2020, 358, 45-50.
3. A. Serrano-Maldonado, *et.al.*, Eur. J. Inorg. Chem., **2020**, *26*, 2506-2511.
4. I. T. Pulido-Díaz, *et. al.*, *Dalton Trans.*, **2021**, *50*, 3289-3298.

OC48

Friday 8th September 10:30

Synthesis, Bonding and Catalytic Applications of Homoleptic Tri-Lithium Nickelates

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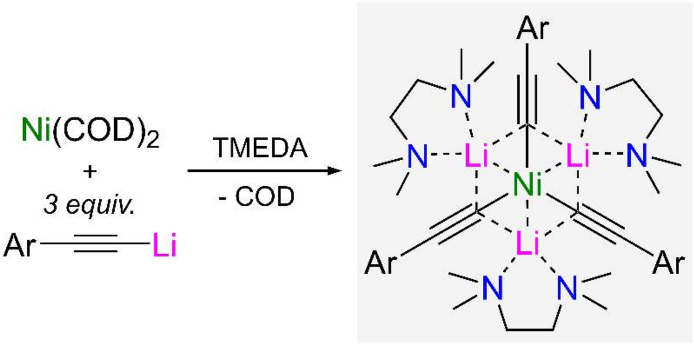
Heterobimetallic nickelates derived from Ni(0)-olefin complexes and polar organometallics were widely studied during the spawn of low-valent organonickel chemistry but remained dormant in the literature for several decades.[1] We have recently demonstrated that nickelates are key intermediates in the Ni-catalysed cross-coupling of aryl ethers, prompting a renewed experimental and theoretical interest into these unique heterobimetallic complexes.[2]

In this presentation, we will unveil the synthesis and structures of homoleptic tri-lithium nickelates which can be readily accessed from $Ni(COD)_2$ and lithium aryl-acetylides.[3] Complementary bonding analysis reveals that despite the apparent Li···Ni interactions observed in the solid-state, that these are repulsive in nature, whilst attractive London dispersion interactions are crucial for facilitating the isolation of such compounds. Mechanistic insights and applications of tri-lithium nickelates in catalytic cross-coupling reactions will also be discussed.[4]



- Synthesis and structure
- Theoretical bonding analysis
- Onward reactivity
- Catalytic cross-coupling

References

1) K. Jonas, C. Krüger. *Angew. Chem. Int. Ed. Engl.,* **1980**, *19*, 520-537.
2) A. M. Borys, E. Hevia. *Angew. Chem. Int. Ed.,* **2021**, *60*, 24659-24667.
3) (a) A. M. Borys, L. A. Malaspina, S. Grabowsky, E. Hevia. *Angew. Chem. Int. Ed.*, **2022**, *61*, e202209797. (b) A. M. Borys, E. Hevia. *Dalton Trans.*, **2023**, *52*, 2098-2105.
4) A. M. Borys, L. Vedani, E. Hevia. Unpublished.

OC49

Friday 8th September 10:45

Tenfold Metalation and Functionalization of Ferrocene

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The tenfold metalation of ferrocene is achieved by reaction with 10 equivalents of mercury butyrate. The resulting permercurated ferrocene $FeC_{10}(HgO_2CC_3H_7)_{10}$ is stable towards air and water and can easily be prepared in gram scale.[1] The substitution of ten anionic carboxylate groups by ten neutral ligands (e.g. L = acetonitrile or tetrahydrothiophene) yields decacationic metallostars $[FeC_{10}(HgL)_{10}]^{10+}$ which can be (electro)chemically oxidized to undecacations.[2]

Bromination of permercurated ferrocene gives access to decabromoferrocene. The corresponding ferrocenium ion is strongly oxidizing ($E_{1/2}$ = 1.1 V vs. Cp_2Fe) and can be prepared via reaction of $FeC_{10}Br_{10}$ with AsF_5 in liquid SO_2.[3]

Reaction of decabromoferrocene with a large excess of tert-butyllithium followed by quenching with dimethylchlorosilane Me_2SiHCl gives a mixture of highly silylated ferrocenes. Interestingly, persilylated ferrocene $FeC_{10}(SiMe_2H)_{10}$ has a purple colour. The decreased HOMO-LUMO gap is a consequence of electronic effects and steric overcrowding.[4]

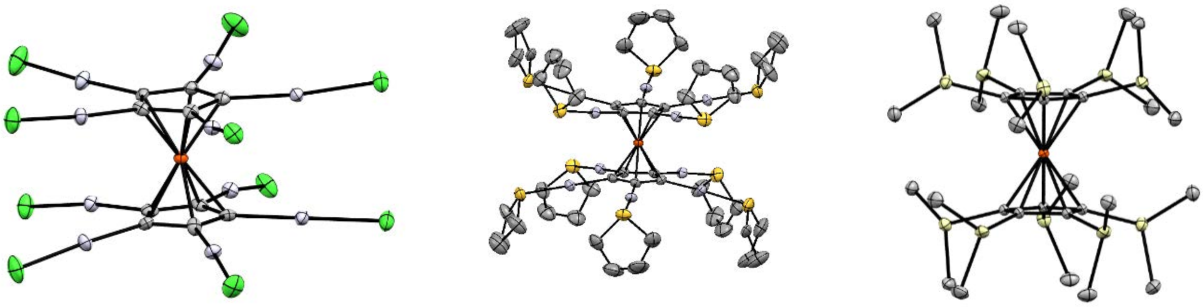

Figure 1. Solid state structures of $FeC_{10}(HgCl)_{10}$ (left), $[FeC_{10}(HgTHT)_{10}][SbF_6]_{10}$ (middle) and $FeC_{10}(SiHMe_2)_{10}$ (right).

References

[1] S. M. Rupf, G. Schröder, R. Sievers, M. Malischewski, *Chem. Eur. J.* **2021**, *27*, 5125-5129.
[2] S. M. Rupf, A. L. Moshtaha, M. Malischewski, *Chem. Sci.* **2023**, *14*, 1132-1137.
[3] S. M. Rupf, I. S. Dimitrova, G.Schröder, M. Malischewski, *Organometallics* **2022**, *41*, 1261–1267.
[4] S. M. Rupf, R. Sievers, P. S. Riemann, M. Reimann, M. Kaupp, C. Fasting, M. Malischewski, *ChemRxiv* **2023**, 10.26434/chemrxiv-2023-538rg

OC50

Friday 8th September 11:00

A New Half-Sandwich Ir Complex with a Pi-Extended Ligand as a Potent Photocatalyst in Green Conditions

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Demand for efficient energy techniques has increased due to growing environmental and energy crises. Photocatalysis is an effective and green technology that can address these problems and it has become a powerful tool in organic synthesis that uses photons as a sustainable source. The photocatalyst can be excited by visible light. From the excited state, the photocatalyst can react with oxygen, generating singlet oxygen or other reactive oxygen species (ROS), which can transform the reactants to products that are not usually obtained by a thermal reaction. The process can reduce the formation of subproducts and decrease the reaction expenses significantly. In this context, we have synthesized half-sandwich Ir(III) complexes with a pi-extended ligand, which have shown an excellent capacity to produce singlet oxygen and other ROS (ϕ=0.99) under visible light. **DFT** studies and **TAS** measurements allow to explain this outstanding behaviour. Complex **1** (Figure 1a) has been explored as photocatalyst in different reactions under mild conditions, at room temperature, under blue light (470 nm) and **air atmosphere.** The complete photooxidation of alkyl or aryl amines into the corresponding imine with **1** at **0.005 mol%** was achieved in 8 h (Figure 1b). Furthermore, at 0.05 mol%, the complete formation of the imines was achieved in 40 min. The photoxidation of thioanisol was tested in similar conditions (Figure 1c), yielding the corresponding sulfoxide as single product in 36 h. Excellent recyclability of **1** was found in the photooxidation of 1,5-dihydroxynaphthalene to yield juglone as similar activity was observed even after **10 cycles**. Complex **1** showed outstanding activity compared with the common photocatalyst [Ru(bpy)$_3$](PF$_6$)$_2$, which achieved only 12% or 0% for benzylamine or thioanisole oxidations, respectively, in similar conditions. Other substrates are being explored and greener conditions are under evaluation such as sun light or water as solvent.

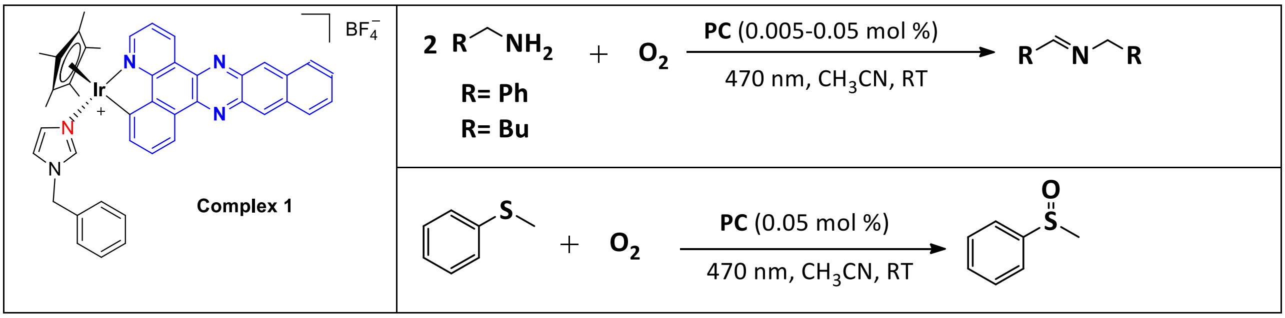

Figure 1. a) Structure of the catalyst. b) Reaction of photooxidation of alkyl or aryl amines. c) photooxidation of thioethers to give sulfoxides.

OC51

Friday 8th September 11:15

Asking Ligands to Lend a Hand

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Two donor modules with different sigma and pi-bonding characteristics in a ligand offer prospect for uniting and managing two electronically disparate substrates on a metal center. In this talk, I will provide an orbital perspective on the origin of ligand electronic asymmetry. A Pd(II)-catalyzed Wacker-type oxidation of terminal olefins to methyl ketones will be taken as a test case to highlight the role of the ligand. Proton/hydride management at the ligand/metal assembly for reductive amination of aldehyde and alkylation of ketones will be discussed. Further, new ligand scaffolds that display metal-ligand cooperation will be disclosed.[1-5]

References

1. ACS Catal., **2022** (DOI:10.1021/acscatal.2c05086).
2. Organometallics **2022**, 41, 1836.
3. ACS Catal., **2020,** 10, 11385.
4. Chem. Eur. J., **2021** (doi.org/10.1002/chem.202101360).
5. Chem. Commun. **2021**, 57, 9204.

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ABSTRACTS:
FLASH PRESENTATIONS

FP01

Tuesday 5th September 17:15 h

Highly Active and Markovnikov-Selective Cobalt-Catalyzed Formation of Ketones from Olefins under Ambient Conditions

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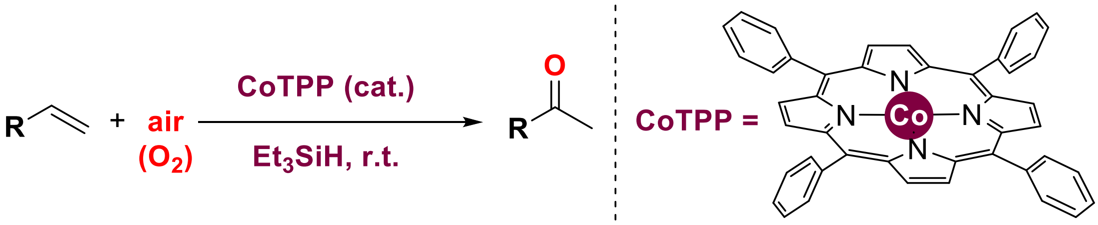
The replacement of palladium catalysts for Wacker-type oxidation of olefins into ketones by first-row transition metals is a relevant approach to searching for more benign protocols.[1] Besides highly sophisticated iron catalysts,[2] all the other first-row transition metal complexes have only led to poor activities and selectivities.[3] Herein, we show that the trivial cobalt-tetraphenylporphyrin complex is a competent catalyst for the oxidation of olefins into ketones with silanes as the hydrogen sources. Importantly, under room temperature and air atmosphere, the reactions were exceedingly fast (<30 minutes) with low catalyst loadings (1 mol%) while keeping excellent chemo- and Markovnikov-selectivity. A kinetic study and in-depth control experiments indicate a mechanism similar to the Mukayama-type hydration of olefins with a change in the last step, which controls the chemoselectivity.



References

[1] P. Rajeshwaran, J. Trouvé, K. Youssef, R. Gramage-Doria, *Angew. Chem. Int. Ed.* **2022**, *61*, e202211016.

[2] (a) G.-Q. Chen, Z.-J. Xu, C.-Y. Zhou, C.-M. Che, *Chem. Commun.* **2011**, *47*, 10963-10965; (b) Y.-D. Du, C.-W. Tse, Z.-J. Xu, Y. Liu, C.-M. Che, *Chem. Commun.* **2014**, *50*, 12669-12672; (c) S. C. Hammer, G. Kubik, E. Watkins, S. Huang, H. Minges, F. H. Arnold, *Science*, **2017**, *358*, 215-218; (d) B. Liu, F. Jin, T. Wang, X. Yuan, W. Han, *Angew. Chem. Int. Ed.* **2017**, *56*, 12712-12717; (e) F. Puls, H.-J. Knölker, *Angew. Chem. Int. Ed.* **2018**, *57*, 1222-1226; (f) F. Puls, P. Linke, O. Kataeva, H.-J. Knölker, *Angew. Chem. Int. Ed.* **2021**, *60*, 14083-14090; (g) T. Schuh, O. Kataeva, H.-J. Knölker, *Chem. Sci.* 2023, 14, 257-265; (h) J. Trouvé, K. Youssef, S. Kasemthaveechok, R. Gramage-Doria, *ACS Catal.* **2023**, *13*, 4421-4432.

[3] Y.-i. Matsushita, T. Matsui, K. Sugamoto, *Chem. Lett.* **1992**, 1381-1384.

FP02

Tuesday 5th September 17:15 h

Exploring new metal-ligand bonding modes using tantalum redox-active ligands complexes

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Miguel Mena [1] and Cristina Santamaría[1]

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Developing new metal-ligand interactions is essential for applied organometallic chemistry as it dictates the reactivity of the generated compounds.[1] This has been notably relevant for compounds of group 5 elements in maximum oxidation state, in which the incorporation of redox-active ligands has made them capable of mediating multielectron processes.[2] In this regard, Orthophenylendiamido (o-PDA) ligands display flexibility in their coordination modes and the possibility of undergoing one or two electron redox processes. Nevertheless, the combination of these ligands with early transition metals has been less investigated.[3]

Herein, we report our studies on the combination of different o-PDA ligands and the fragment $[TaCl_{5-n}(\eta^5\text{-}C_5H_4SiMe_3)_n]$ (n = 0, 1). Through a systematic study, we have achieved control over the binding mode of the o-PDA ligands, which can coordinate through the nitrogen atoms or the central phenylene ring, adopting different electronic structures.

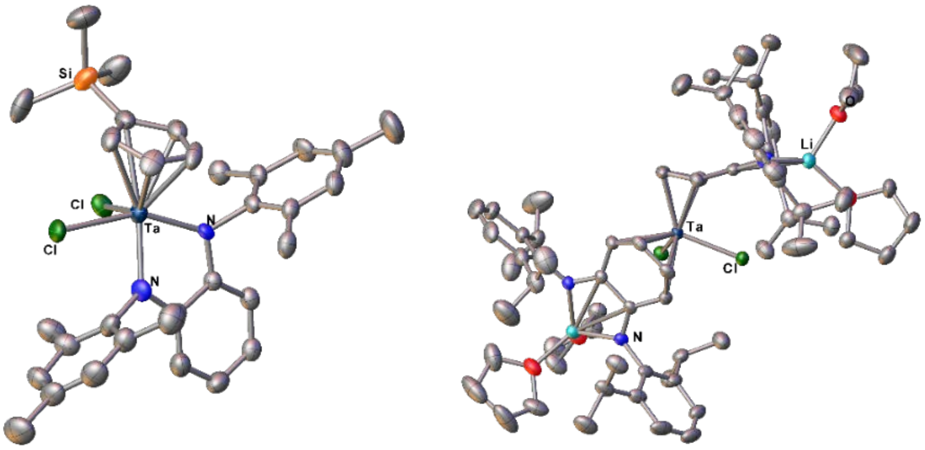

Figure 1. Solid state structures of o-PDA-Ta compounds with two different coordination modes.

References

[1] E.P. Beaumier, I.A. Tonks et al. *Nat. Rev. Chem.* **2019**, 3,15–34.
[2] O.R. Luca, R.H. Crabtree. *Chem. Soc. Rev.* **2013**, 42, 1440-1459.
[3] T. Janes, M. Xu M, D. Song. *Dalton Trans.* **2016**, 45, 10672–10680.

FP03

Tuesday 5th September 17:15 h

Zirconium-mediated C-F bond activation

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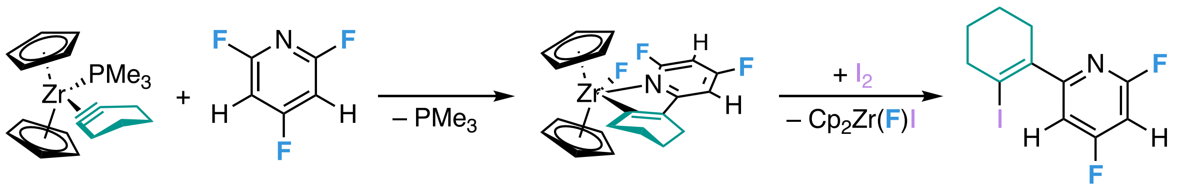
Fluorine-containing organic molecules are found in a wide range of applications. As such, there is a synthetic requirement to develop efficient and selective methods for the incorporation or removal of fluorine on organic compounds. Access to such complex molecules necessitates elaborated synthetic strategies, including transition-metal chemistry based on C–F bond activation. This contribution describes the use of zirconocene derivatives, which are able to activate the strong and inert C–F bond of fluorinated aromatics.[1,2] Complex 1-cyclohexenylmethylzirconocene, $[Cp_2Zr(CH_3)(C_6H_{13})]$, thermally eliminates methane, giving the transient η^2-cyclohexyne intermediate $[Cp_2Zr(\eta^2\text{-}C_6H_{12})]$.[3] The addition of trimethylphosphine (PMe_3) helps stabilise the complex by forming a PMe_3 adduct **A**. We have found that **A** is able to cleave a C–F bond of 2,4,6-trifluoropyridine selectively at the 2-position, forming new Zr–F and C–C bonds (**B**). The fluorinated organometallic ligand formed remains in the coordination sphere of the metal, ready for further functionalisation, but liberation of the free fluorinated organic is possible via I_2 addition (**C**).



A **B** **C**

Regioselective C–F bond activation
1,3-CF addition
C–C coupling
Complex organofluorine compound

Fig. 1 C–F bond activation of 2,4,6-trifluoropyridine assisted by **A**.

In the case of 2,3,5,6-tetrafluoropyridine, C–H bond activation occurs leading to (1-cyclohexenyl)(2,3,5,6-tetrafluoro-4-pyridinyl)zirconocene. In parallel, we have shown that PMe_3 in these systems is highly reactive toward electrophilic fluoropyridines, e.g. pentafluoropyridine, leading to hydrodefluorination and a series of fluoroalkylphosphoranes.

References

[1] Romero, N.; Dufrois, Q.; Crespo, N.; Pujol, A.; Vendier, L.; Etienne, M. *Organometallics,* **2020**, *39*, 2245–2256; [2] Hoyt, M.; Forrest, E.; Bergman, R. G. *J. Am. Chem. Soc.,* **2004**, *126*, 1018–1019; [3] Buchwald, S. L.; Lum, R. T.; Dewan, J. C.; *J. Am. Chem. Soc.*, **1986**, 108, 7441–7442.

FP04

Tuesday 5th September 17:15 h

Copper-Catalyzed Alkane Amidation with Azides as Nitrene Source

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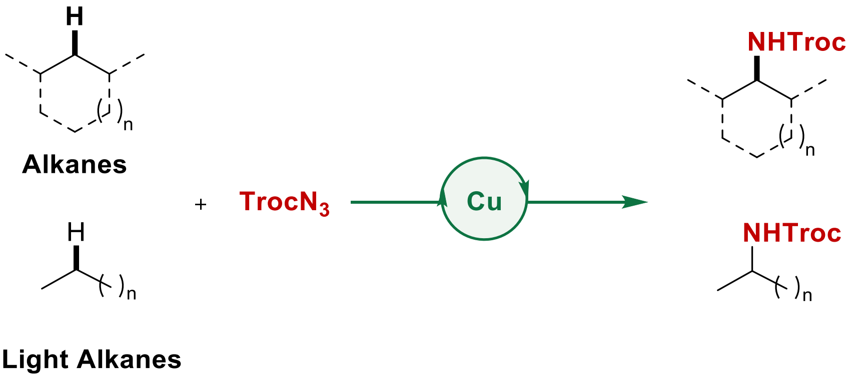
The development of synthetic strategies to convert available raw materials into value-added products is one of the continuous challenges for modern chemistry.[1] Among catalytic methods studied in the last decades, the formation of new C-N bonds via direct functionalization of C-H bonds has emerged as a useful tool toward that end. However, direct and selective amidation of alkanes C_nH_{2n+2}, and especially light (gaseous) alkanes, remains underdeveloped mainly due to their chemical inertness (high bond dissociation energies and low C-H bond polarity).[2]

Our research group has described a series of copper and silver complexes bearing hydrotrispyrazolylborate ligands (Tp^x) as efficient catalysts for amidation of C_{sp3}-H bonds using the nitrene transfer methodology with PhI=NTs as the nitrene source.[3] In this contribution, we report a copper-based catalytic system for the direct carbon-hydrogen bond amidation of such alkanes, including gaseous examples, using 2,2,2-trichloroethyl carbonazidate (N_3Troc).



References

[1] Díaz-Requejo, M. M.; Pérez, P. J. *Chem. Rev.* **2008**, *108*, 3379.

[2] a) Li, Y.; Lei, M.; Gong, L. *Nat. Catal.* **2019**, *2*, 1016. b) Tran, B. L.; Li, B.; Driess, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 2555.c) Lee, J.; Jin, S.; Kim, D.; Hong, S. H.; Chang, S. *J. Am. Chem. Soc.* **2021**, 143, 5191.

[3] a) Fructos, M. R.; Trofimenko, S.; Díaz-Requejo, M. M.; Pérez, P. J. *J. Am. Chem. Soc.* **2006**, *126*, 11784. b) Gómez-Emeterio, B. P.; Urbano, J.; Díaz-Requejo, M. M.; Pérez, P. J. *Organometallics* **2008**, *27*, 4126.

FP05

Tuesday 5th September 17:15 h

Switching the Regioselectivity in the Synthesis of Conjugated Dienes by Mn(I)-Catalyzed C–H Activation

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Pedro Almendros,*[2] Sara Cembellín*[1]

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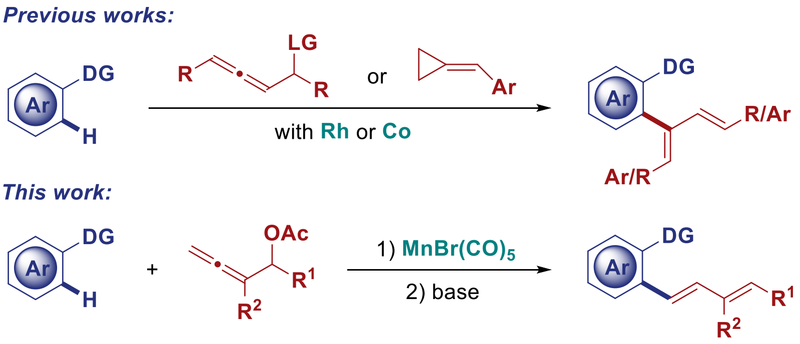
Conjugated dienes are highly interesting motifs for medicinal chemistry, organic synthesis, and polymer industry. These structural units occur in a broad variety of natural products, while some are produced every day in multi-ton scale for the preparation of synthetic rubbers. Due to their importance, it is not surprising to find in the literature a huge number of synthetic routes for the preparation of 1,3-dienes, although most of them still remain some drawbacks.[1]

On the other hand, over the last decade transition metal catalyzed C–H activation has emerged as an environmentally benign and economically attractive tool for organic chemistry.[2] Taking advantage of this strategy, several research groups have used it to synthesize 1,3-dienes, obtaining in all the cases branched products. However, no dienylation has been described to date through Mn-catalyzed C–H activation, despite its significant advantages as the high abundance, low price, low toxicity, and unique reactivity of the metal.

Therefore, in this work we develop a highly selective method to synthesize linear 1,3-dienes via Mn(I)-catalyzed C–H activation of aromatic and heteroaromatic compounds using acetylated allenols as coupling partners (Figure 1). The final compounds were obtained as sole regioisomers with high stereoselectivity and total regioselectivity, which diverts in comparison with the previous works.[3]



Acknowledgements: This work was supported by MCIN/AEI /10.13039/501100011033/FEDER (Projects PID2021-125982OA-I00 and PID2021-122183NB-C21).

References:

[1] a) M. De Paolis, I. Chataigner, J. Maddaluno. *Topics in Current Chemistry* **2012**, *327*, 87–146. b) R. G. Soengas, H. Rodríguez-Solla. *Molecules* **2021**, *26*, 249.
[2] a) T. Dalton, T. Faber, F. Glorius. *ACS Cent. Sci.* **2021**, *7*, 245–261; b) T. Aneeja, M. Neetha, C. M. A. Afsina, G. Anilkumar. *Catal. Sci. Technol.* **2021**, 11, 444–458.
[3] Manuscript in preparation.

FP06

Tuesday 5th September 17:15 h

Li vs Na: Divergent Reaction Patterns between Organo-Lithium and -Sodium Complexes, and Ligand-catalysed Ketone/Aldehyde Methylenation

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Alkali metal alkyl reagents are essential tools in synthetic chemistry. Alkali metal organometallics aggregate in solution and solid-state. The relationship between structure and reactivity has been of great interest for many decades and, in general, by breaking the alkali metal organometallics into smaller aggregates, the reactivity can be increased. The monomeric organosodium complex $[Na(CH_2SiMe_3)(Me_6Tren)]$ (**1**-Na) was found to exhibit a distinct reaction pattern in sharp contrast with its organolithium counterpart $[Li(CH_2SiMe_3)(Me_6Tren)]$ (**1**-Li) (methylenation vs nucleophilic addition) (Figure 1a). Moreover, using **1**-Na as a platform, the versatile reactivity of organosodium complexes depending on their aggregate sizes (monomer vs polymer) and nature of incoming substrates (ketone, aldehyde, amide vs ester) was demonstrated. Based on these observations, ligand-catalysed ketones/aldehyde methylenations were designed using $[NaCH_2SiMe_3]_\infty$ and catalysed by as low as 5 mol% of the Me_6Tren ligand (Figure 1b).[1]

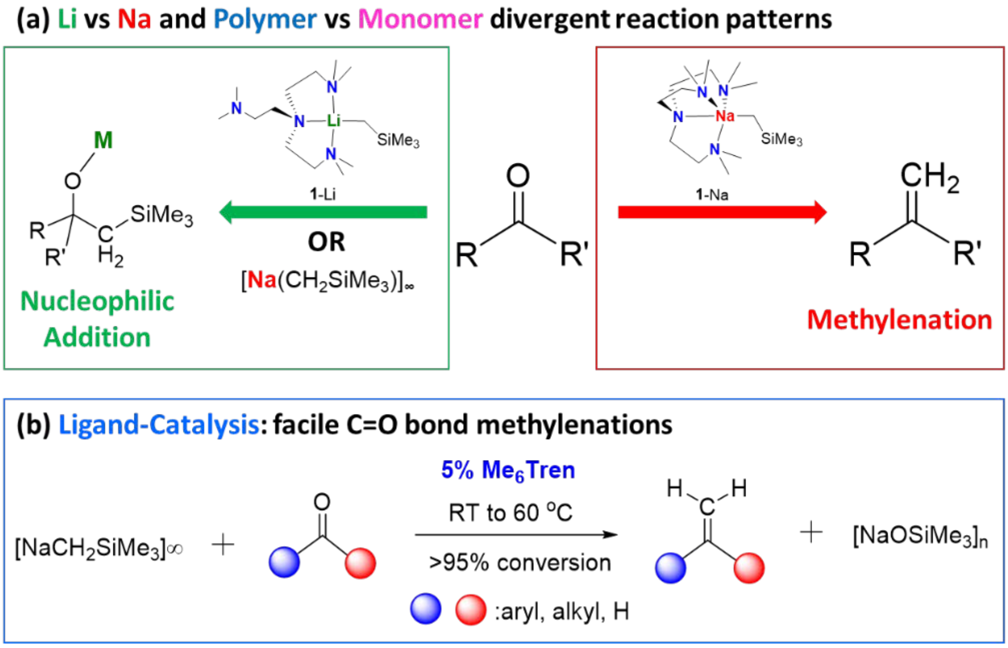

Figure 1: (a) Divergent reaction patterns between organo-sodium and -lithium complexes towards carbonyls; (b) Ligand-catalysed C=O bond methylenation.

References

1. N. Davison, L. Zhang, P. G. Waddell, C. Wills, C. Dixon, S. -X. Hu, C. L. McMullin and E. Lu, *J. Am. Chem. Soc.*, 2023, **145**, 6562.

FP07

Tuesday 5th September 17:15 h

Development of heteroleptic dirhodium(II,II) catalyst precursors toward the hydroformylation and hydroaminomethylation of alkenes

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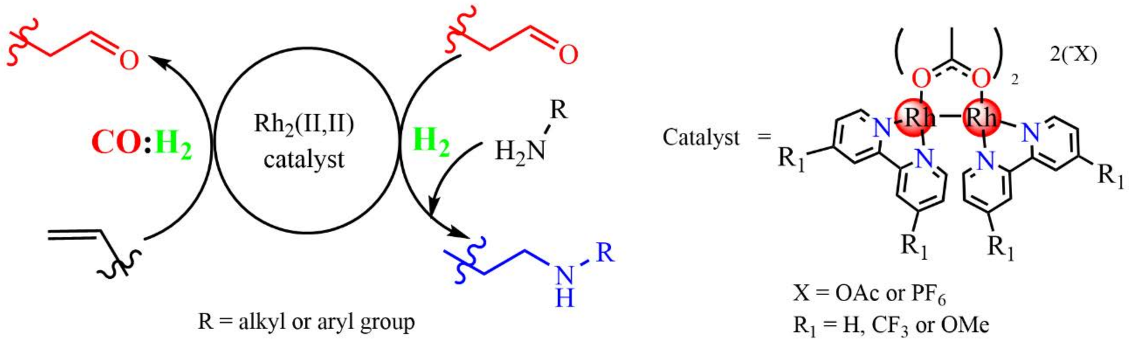
The hydroformylation and hydroaminomethylation reactions provide a straightforward means of accessing high-value precursor chemicals with industrial and pharmaceutical relevance, from low-value alkene substrates.[1]



Scheme 1. Depiction of catalytic reactions expolored with dirhodium(II,II) catalyst precursors.

To this end, the synthesis of six heteroleptic dirhodium(II,II) acetato-bipyridyl chelate complexes containing acetate or hexafluorophosphate counter ions is described. The catalytic performance of the complexes in the hydroformylation of 1-octene, were evaluated and compared to the parent $Rh_2(OAc)_4$ compound previously reported.[2] Axial interaction of the acetate counter ions was found to significantly affect the hydroformylation capabilities of the catalytic system. with A range of cyclic, aromatic and internalized alkene substrates were explored, and efforts regarding the recyclability of catalyst precursor is also described.

Optimization of the reaction conditions through a model hydrogenation reaction was carried out to maximize the target amine yield. The catalyst precursor which produced the highest amine during reaction condition optimization was applied in model hydroaminomethylation reactions of cyclohexene with selected amines. Partial pressure variation of the CO and H_2 components in the reactor atmosphere was carried out to enhance conversion of alkene substrate and chemoselectivity toward the production of secondary or tertiary amine products.

References

1. C. Qian, Q. Zheng, J. Chen, B. Tu and T. Tu, *Green Chem.* 2023, 25, 1368-1379.
2. S. de Doncker, A. Casimiro, I. A. Kotze, S. Ngubane and G. S. Smith, *Inorg. Chem.* 2020, **59**, 12928–12940.

FP08

Tuesday 5th September 17:15 h

Coordination and Reduction of Dioxygen on a Pd(I) Center

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Until recently, mononuclear open-shell Pd(I) complexes have been difficult to access because of their easy dimerization or disproportionation processes, resulting in high instability. Although a few paramagnetic mononuclear palladium(I) complexes have been recently reported,[1-3] their reactivity has not been extensively investigated yet.

Our research group has developed a general method for the preparation of mononuclear palladium(I) complexes of general formula $[Pd^{I}(NHC)_2][PF_6]$. These palladium(I) bis-carbene species coordinate and reduce the O_2 molecule in a temperature-dependent reversible equilibrium. Coordination of O_2 in the presence of either π-donor (Cl^-) or π-acceptor (CO) ligands L readily affords $[Pd^{II}(NHC)_2(L)(\eta^1\text{-}OO^\bullet)]^{+/0}$ species containing a superoxide ligand. The corresponding IPr complexes (**1**, Figure 1) evolve by activation of a C-H bond of the NHC ligand to afford a mixture of a metallacycloperoxide (**2**) and a hydroperoxide complex (**3**). Herein, we report thermodynamic, kinetic, and computational studies on the coordination of dioxygen to the Pd(I) center and the mechanism involved in the intramolecular C-H bond activation and hydrogen transfer.

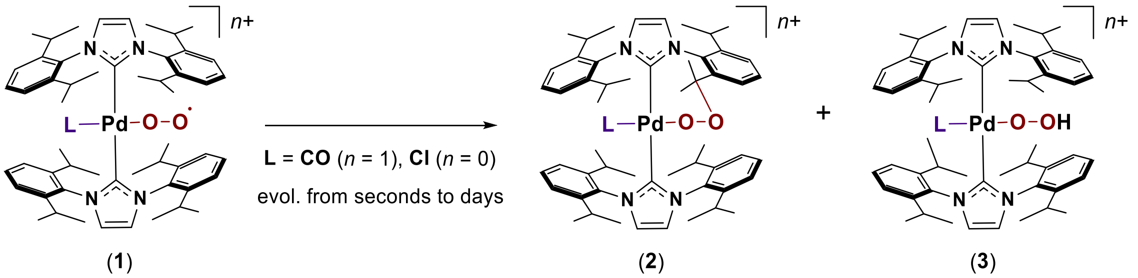

Figure 1.

References

[1] Troadec, T.; Tan, S. Y.; Wedge, C. J.; Rourke, J. P.; Unwin, P. R.; Chaplin, A. B. *Angew Chem Int Ed.* **2016,** *55*, 3754-3757; MacInnis, M. C.; DeMott, J. C.; Zolnhofer, E. M.; Zhou, J.; Meyer, K.; Hughes, R. P.; Ozerov, O. V. *Chem.* **2016,** 1, 902-920.

[2] Liu, J.; Bollmeyer, M. M.; Kim, Y.; Xiao, D.; MacMillan, S. N.; Chen, Q.; Leng, X.; Kim, S. H.; Zhao, L.; Lancaster, K. M.; Deng, L. *J Am Chem Soc.* **2021,** 143, 10751-10759.

[3] Tran, G. N.; Bouley, B. S.; Mirica, L. M. *J Am Chem Soc.* **2022**. 144, 20008-20015.

FP09

Tuesday 5th September 17:15 h

Oxidative addition to a macrocyclic dinickel complex and subsequent unique reactivity

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The catalytic properties of homogenous nickel complexes have been of interest for decades, partly as a cheaper replacement for palladium catalysts, but also due to their expanded range of accessible oxidation states and access to challenging transformations. More recently, interest has been sparked in homogenous bimetallic catalysts and their potential for higher activity, altered selectivity, or novel reactions. However, a challenge in these systems is confirming that the observed activity is due to bimetallic, rather than monometallic, mechanisms. Several examples of powerful dinickel catalysts that operate by bimetallic mechanisms have been uncovered, such as those by Uyeda,[1] Matsubara[2] and Schoenbeck.[3]

This work aims to explore the reactivity of a dinickel(I) complex, $Ni_2(^{tBu}PONNOPONNO)$.[4] The 1,8-naphthyridine backbone has been used in previous studies[1] to hold metal atoms in close proximity, and in this work forms an unusual rigid macrocyclic dinucleating ligand, preventing dissocation into monometallic species and encouraging metal-metal cooperative reactivity.

Oxidative addition studies have shown that alkyl halides are able to add across the Ni–Ni bond to form $Ni_2(\mu\text{-}R)(\mu\text{-}X)(^{tBu}PONNOPONNO)$. However, these species are generally unstable due to two pathways; the first is disproportionation into $Ni_2(\mu\text{-}X)_2(^{tBu}PONNOPONNO)$ and a homocoupled organic product; the second is β-hydride elimination to form an olefin and a dinickel(II) hydride. Both of these pathways reveal the ability of bimetallic systems to subvert traditional reactivity trends and offer the potential for powerful cooperative catalysis.

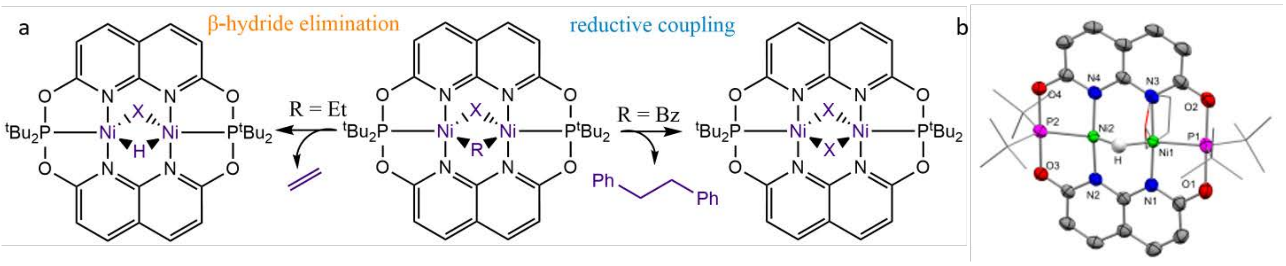

Figure 1. a. Reactivity pathways for $Ni_2(\mu\text{-}R)(\mu\text{-}X)(^{tBu}PONNOPONNO)$. b. Crystal structure of $[Ni_2(\mu\text{-}H)(^{tBu}PONNOPONNO)]BAr^F_4.THF$.

References

1. Uyeda, C., Farley, C. M., *Acc. Chem. Res.* **54**, 3710-3719 (2021).
2. Matsubara, K. et al. *Organometallics* **36**, 255-265 (2017).
3. Dürr, A. B., et al. *Angew. Chem. – Int. Ed.* **56**, 13431-13435 (2017).
4. R., Yu, L-J., Doan, V., Coote, M. L., Colebatch, A. L., *Chem. – Eur. J*, **29**, e202203940 (2023).

FP10

Tuesday 5th September 17:15 h

Trapping of transient base-stabilized arylalumylene: A two-coordinated Al^{I}-complex for deconstruction of aromatic molecules

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Alumylenes (RAl^{I}:) are heavier group 13 analogs of carbenes, where the formal oxidation state of aluminum is +1, generally a highly unstable species to isolate. Recent attempts to stabilize and isolate Al^{I} have seen increasing success by choosing a suitable ligand and stabilizing base.[1]

We have reported here the generation of a transient acyclic, dicoordinate alumylene **2** of the form [LRAl:] (L = neutral Lewis donor), which deconstructs the aromatic solvents benzene and toluene to furnish dialuminum derivatives of pentalene, **4** (Figure 1). When the alumylene is generated in the absence of an aromatic solvent, it undergoes homocoupling, providing a "masked" dialumene (LRAl=AlRL), **5.** This in situ generated arylalumylene (LRAl:) was trapped using an alkyne, generating an aluminacyclopropene, **6.** The regeneration of the alumylene from this masked dialumene is suggested by the reaction of the latter with benzene, again forming the C-C activated product in addition to a C-H activation product. We provide a calculated reaction mechanism that rationalizes these three interconnected pathways.

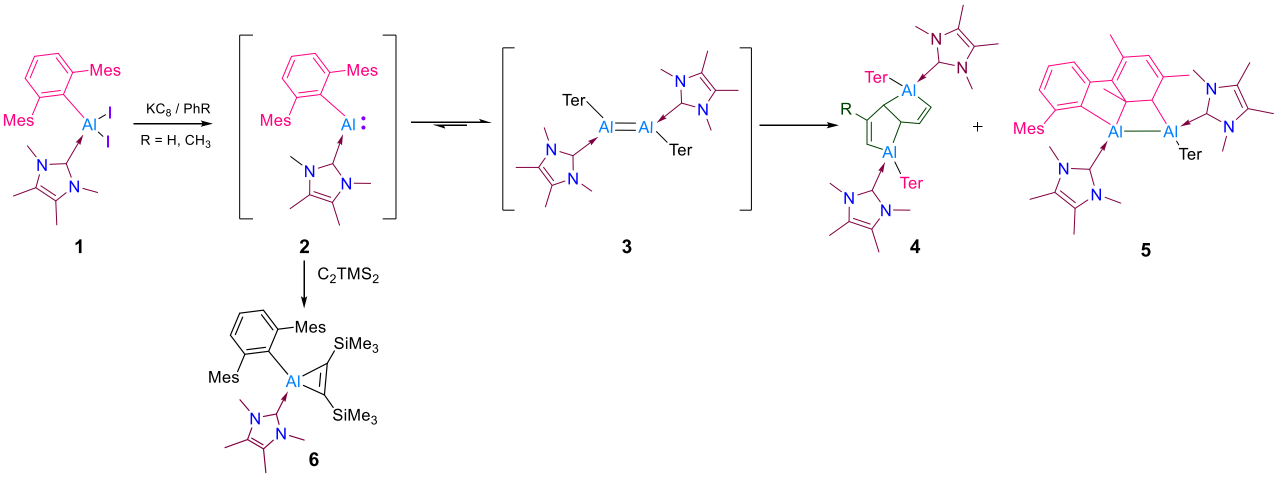

Figure 1. Synthesis of compounds **4**, **5** and **6** from **1** (Ter = 2, 6-Mes-C_6H_3, Mes = 1, 3, 5-Me- C_6H_2).

References

[1] X, Zhang, Y. Mei, L. L. Liu, *Chem. Eur. J.* **2022**, *28*, e202202102. [2] D. Dhara, A. Jayaraman, M. Harterich, H. Braunschweig, *Chem. Sci.* **2022**, *13*, 5631–5638.

[3] D. Dhara, A. Jayaraman, M. Härterich, M. Arrowsmith, M Jürgensen, M. Michel, H. Braunschweig, *Chem. Eur. J.* **2023**, e202300483.

FP11

Tuesday 5th September 17:15 h

Intramolecular Interception of the Remote Position of Vinylcarbene Silver Complex Intermediates by C(sp3)–H Bond Insertion

Àlex Díaz-Jiménez[1], Roger Monreal-Corona,[1] Albert Poater,[1] María Álvarez,[2] Elena Borrego,[2] Pedro J. Pérez,[2] Ana Caballero,[2] Anna Roglans,[1] Anna Pla-Quintana,[1]

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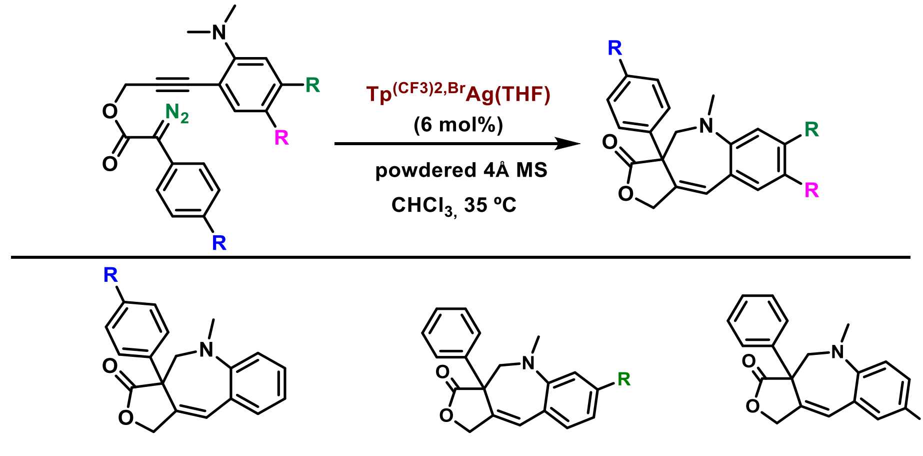
Vinylcarbene metal complexes have become one of the most intriguing subclass of metal carbenes since the pioneering studies by Davies and coworkers in the 90's.[1] Vinylcarbenes display two potential electrophilic sites: the more common carbenic position or the less accessible vinilogous one. Carbene alkyne/methathesis (CAM),[2] has become one of the most powerful tools for *insitu* generation of vinylcarbenes. Starting from an initial carbene, reaction with an alkyne transfers the carbene reactivity to one of the alkyne carbons generating the vinylcarbene which can further react in a cascade manner. Herein we wish to report the first example of a C(sp^3)-H bond insertion into the elusive vinylogous position of a vinyl carbene, promoted by the use of silver catalysis.[3] Building upon a platform developed by Xu and Doyle known to generate a vinyl carbene by a CAM processes,[4] a new family of benzoazepines has been accessed by selective reaction of the vinylogous position with an aliphatic C(sp3)-H bond. Morover, DFT studies unraveled the whole reaction profile including an stepwise C-H insertion mechanism involving a zwitterionic intermediate as the rate determing step of the transformation.



R = H (71 %)
R = Me (57 %)
R = OMe (42 %)
R = Ph (42 %)
R = F (30 %)
R = Br (23 %) at 55 ºC

R = Me (60 %)
R = Cl (69 %)

R = Me (66 %)
R = Cl (58 %)

References

[1] H.M. L. Davies,E. Saikali,T. J. Clark, E.H. Chee,*Tetrahedron Lett.* **1990**, *31*, 6299–6303.[2] C. Pei, C. Zhang,Y. Qian, X. Xu, *Org.Biomol.Chem.* **2018**, *16*, 8677–8685.[3] À. Díaz-Jiménez, R.Monreal-Corona, A. Poater, M. Álvarez, E. Borrego, P.J. Pérez, A. Caballero, A. Roglans, A. Pla-Quintana. *Angew. Chem.Int. Ed.* **2023**, *62*, e202215163.[4] K. Dong, C. Pei, Q. Zeng, H. Wei, M.P. Doyle, X. Xu, *ACSCatal.* **2018**, 8, 9543–9549.

FP12

Tuesday 5th September 17:15 h

RAPTA/heteroscorpionate hybrid ruthenium derivatives for the generation of feasible metallodrugs delivery systems in breast cancer treatment

Elena Domínguez Jurado[1,2], Carlos Alonso Moreno[1,2] Iván Bravo,[1] and Agustín Lara Sánchez[2]

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The modular synthesis of the heteroscoriponate core is explored as a tool for the rapid development of ruthenium-based therapeutic agents. Starting with a series of structurally diverse alcohol-NNO heteroscopionate ligands, a family of RAPTA/heteroscorpionate-hybrid ruthenium derivatives were obtained (RUSCO1-RUSCO5), fully characterized, and evaluated in vitro for antitumoral activity in a series of breast cancer cell lines using UNICAM-1 and cisplatin as metallodrugs control. Through this approach, a bimetallic hybrid RAPTA/heteroscorpionate metallodrug (RUSCO3) was identified as the lead compound of the series with the IC_{50} value range as low as 3–5 µM. Due to the toxicity related to the use of metallodrugs, the lead compound was loaded into lipid-based formulations to improve its effectivity for the treatment of triple-negative breast cancer. Liposomes were prepared by injection and evaporation solvent method. RUSCO3-loaded drug delivery systems displayed optimal hydrodynamic radii with a very low polydispersity index and high encapsulation efficiencies. Formulations showed high stability and sustained release. RUSCO3 formulation improved antiproliferative activity compared to RUSCO3 and support heteroscorpionate ligands for the generation of robust ruthenium-based metallodrugs capable of being encapsulated in nanodevices to assist metallodrugs in a prompt translation to the clinic.

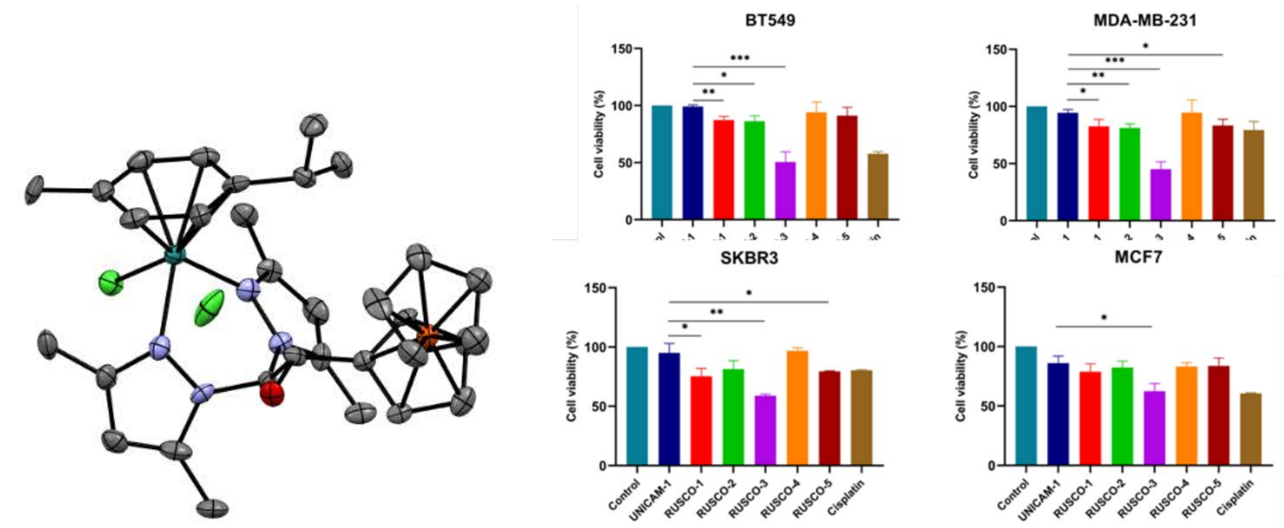

Figure 1. Mercury plot of RUSCO3 and MTT assays in 4 breast cancer cell lines. The values for the statistical analyses are: * $p \leq 0.05$; ** $p \leq 0.01$; *** $p \leq 0.001$.

FP13
Tuesday 5th September 17:15 h

Fully Tin-Coated Coinage Metal Ions: A Pincer Type Bis-stannylene Ligand for Exclusive Tetrahedral Complexation

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The synthesis of a novel bis-stannylene pincer ligand is described,[1] followed by its complexation of coinage metals (Cu^I, Ag^I and Au^I). All coinage metal centres are in tetrahedral coordination environments in the solid state and are exclusively coordinated by four neutral Sn^{II} donors. This was presumed for copper and silver but is rather unusual for gold.[2-3] ^{119}Sn NMR experiments were performed to provide information about their behaviour in solution. All isolated compounds show photoluminescent properties and were investigated at low and elevated temperatures. Compared to the free bis-stannylene ligand, coordination to coinage metals led to an increase in the luminescence intensity and showing broad bands tailing far into the NIR region. The new compounds were investigated in detail through all-electron relativistic density functional theory (DFT) calculations.[4-5]

References

[1] D. Gallego, S. Inoue, B. Blom, M. Driess, *Organometallics* **2014**, *33*, 6885-6897.
[2] J. K. West, G. L. Fondong, B. C. Noll, L. Stahl, *Dalton Trans.* **2013**, *42*, 3835-3842.
[3] R. Jambor, L. Dostál, M. Erben, Z. Růžičková, R. Jirásko, A. Hoffmann, *Organometallics* **2021**, *40*, 783-791.
[4] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs Computational Molecular Science* **2014**, *4*, 91-100.
[5] F. Krätschmer, X. Sun, S. Gillhuber, H. Kucher, Y. J. Franzke, F. Weigend, P. W. Roesky, *Chem. Eur. J.*, *n/a*, e202203583.

FP14

Tuesday 5th September 17:15 h

Unlocking the direct decarboxylation of trifluoroacetates using Iron photocatalysis

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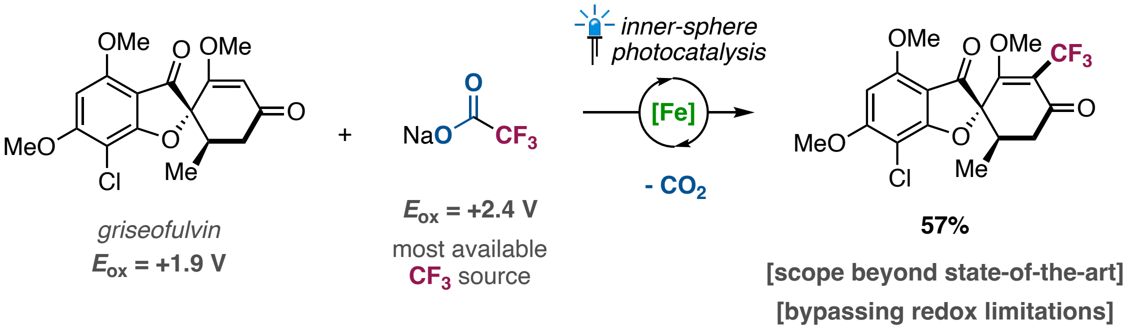
Trifluoroacetates are the most available, stable and inexpensive sources of trifluoromethyl groups (CF_3), which are key substituents in pharmaceuticals and agrochemicals as they improve their biological activity and stability.[1] Despite the extensive research done over the last decades,[2,3] trifluoromethylation reactions still require the use of expensive or toxic reagents. Therefore, the possibility of using trifluoroacetates as CF_3 radical sources would constitute a significant step forward for the development of more sustainable syntheses. However, the generation of CF_3 reactive radicals from trifluoroacetates requires their single-electron oxidation and decarboxylation which is hampered by their extremely high oxidation potential (+2.4V *vs* SCE in MeCN). This represents a major challenge for redox-based methods because of the necessity to pair such elevated oxidation potential under reaction conditions that could be applied to trifluoromethylation reactions. In this work, we unlock the direct photodecarboxylation of trifluoroacetates using an iron photocatalyst that works via an inner-sphere electron transfer pathway, which overcomes thermodynamic redox limitations.[4] Additionally, we have been able to expand our methodology towards the delivery of bromo- and chlorodifluoromethyl groups, which are suitable surrogates to access relevant CF_2H motifs of interest in medicinal chemistry.



We thank MCIN/AEI/10.13039/501100011033 and “ESF Investing in your future” (PID2020-115408GA- I00, PRE2021-099616 and RYC2018-024643-I) for financial support.

References

1) M. Inoue, Y. Sumii, N. Shibata, *ACS Omega* **2020**, *5*, 10633. 2) H. Baguia, G. Evano, *Chem. Eur. J.* **2022**, *28*, 41. 3) R. Britton, V. Gouverneur, JH. Lin, *et al. Nat Rev Methods Primers*, **2021**, *1*, 47. 4) S. Fernández-García, V.O. Chantzakou, F. Juliá-Hernández, *Submitted,* **2023**.

FP15

Tuesday 5th September 17:15 h

From molecular Frustrated Lewis pairs to activation of dihydrogen by Lewis acidic zeolites

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Keywords: Frustrated Lewis pair, Lewis acid, zeolite, N-formylation, CO_2 hydrogenation

Frustrated Lewis pairs (FLPs) are a rapidly expanding group of homogenous hydrogenation catalysts based on sterically hindered Lewis acids (LAs) and Bases [1]. While the original focus of FLPs was on electron deficient boranes as the LAs, examples utilizing Al-, Ga-, Sn-, N- and P-based LAs are known. Nevertheless, most of the compounds suffer from low stability especially in the presence of water. In attempts to overcome this limitation, we studied organometallic tin LAs [2] and aluminium macrocyclic complexes as potential LA components of FLPs in N-formylation reactions of amines with CO_2 and H_2. Coordination, structures and frontier molecular orbitals of these LAs resemble those of Sn^{4+} and Al^{3+} ions within the framework of zeolites. Zeolites are industrially applied microporous silicates with acidic properties, where the LA sites are generated by isomorphous incorporation of hetero-ions such as Al^{3+}, Sn^{4+}, Zr^{4+} or Ti^{4+}[3]. From this perspective, zeolites can be considered single-site heterogeneous catalysts. Herein, we discuss the similarities between homogeneous R_3SnX and aluminium macrocyclic complexes with Al-, Sn- and Zr- substituted beta zeolites and demonstrate that the zeolites can be applied as heterogeneous LA component of FLP hydrogenation catalysts in N-formylation of amines with CO_2 and H_2 . To our knowledge, this is the first time a sole Lewis acidic zeolite has been observed to activate molecular hydrogen, which demonstrates how development of homogenous catalysts can go hand-in-hand with the development of heterogeneous ones.

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References

[1] Stephan, D.W. *J. Am. Chem. Soc.* **2015**, *137*, 10018-10032.
[2] A. Paparakis, R. C. Turnell-Ritson, J. S. Sapsford, A. E. Ashley, M. Hulla, Catal. Sci. Technol. **2023**, *13*, 637–644
[3] Suib, S.L.; Přech, J.; Szaniawska, E.; Čejka, J. *Chem. Rev.* **2023**, *123*, 3, 877–917.

FP16

Tuesday 5th September 17:15 h

How to make substituted pentalenide ligands less exotic

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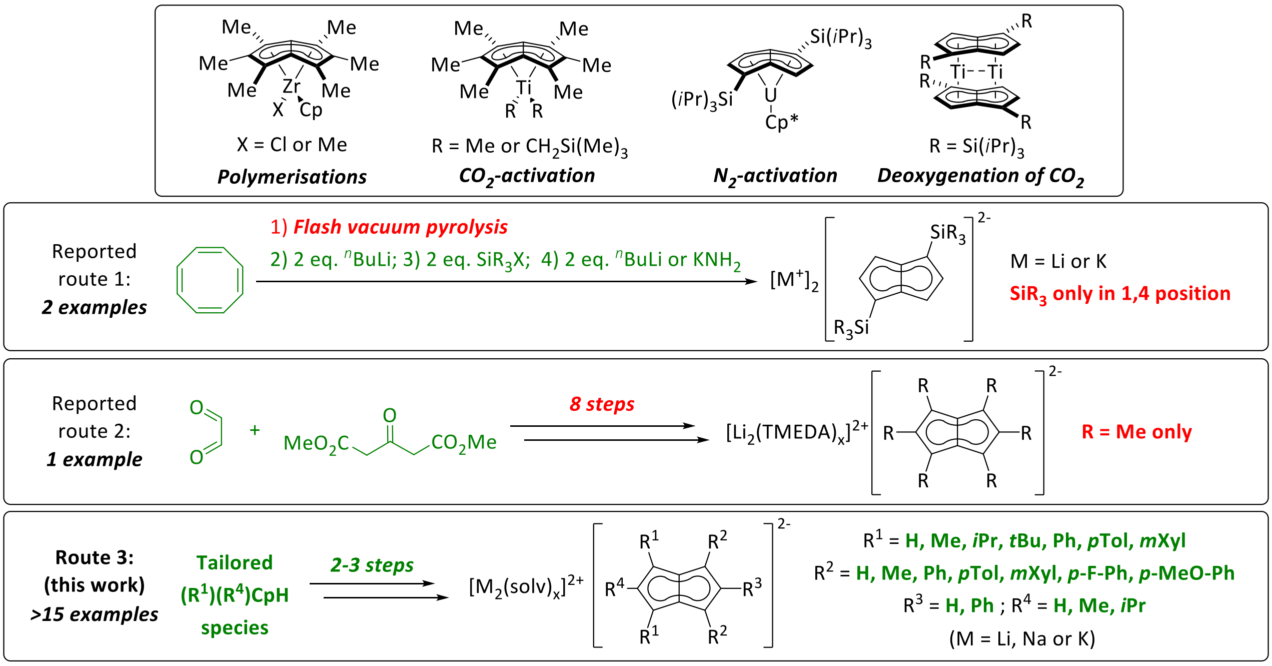
Pentalenide ligands (parent framework **$C_8H_6^{2-}$**; **Pn^{2-}**) have attracted interest in organometallic transition metal chemistry due to their unique coordination properties like the ability of folding around the metal centre and a variety of bonding modes (η^1; η^3; η^5; η^8) paired with ring slippage.[1] Mono- and bimetallic d-block pentalenide complexes have thus found applications in small molecule activation and polymerisation catalysis.[1] However, due to pronounced difficulties of synthesising suitable precursors, organometallic pentalenide chemistry and its applications have been confined to solely three ligands (**$[1,4\text{-SiMe}_3]_2Pn^{2-}$**, **$[1,4\text{-Si}i\text{Pr}_3]_2Pn^{2-}$** and **$Me_6Pn^{2-}$**) over the past 25 years.[1,2] Here we present mild solution phase syntheses that expand our recently reported method for synthesizing **Ph_4Pn^{2-}**,[3,4] with the aim of widening the field of organometallic pentalenide chemistry substantially: The synthesis of tailored pentalenide ligands becomes more accessible and strategies, like electronic tuning or regiospecific substituent implementation, are being introduced for the first time as well.



References

1. F. G. N. Cloke, J. C. Green, A. F. R. Kilpatrick, D. O'Hare, *Coord. Chem. Rev.* 2017, **344**, 238—262.
2. S. M. Boyt, N. A. Jenek, U. Hintermair, *Dalton Trans.* 2019, **48**, 5107—5124.
3. M. Boyt, N. A. Jenek, H. J. Sanderson, G. Kociok-Köhn, U. Hintermair, *Organometallics* 2022, **41**, 211—225.
4. A. Jenek, M. Balschun, S. M. Boyt, U. Hintermair, *J. Org. Chem.*, 2022, 87, 21, 13790–13802.

FP17

Tuesday 5th September 17:15 h

On The Difference in Dehalogenation of Bromoacetic Acids on Ag^0 and Au^0 Surfaces

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Bromoacetic acids are the major disinfection by-products (DBPs) formed in situ along the drinking water treatment. According to the experimental studies, the Ag^0 and Au^0 showed better catalytic activity towards the reductive dehalogenation of bromoacetic acids[1]. Acetic acid (AA) is formed as the final product of dehalogenation on Ag^0, while succinic acid (SA) is obtained on Au^0 for dibromo acetic acid (DBAA) and tribromo acetic acid (TBAA)[2]. An in-depth mechanistic study of reductive dehalogenation is carried out using the DFT methods implemented in the VASP package to study the difference.

The results indicated that the dehalogenation mechanism varies considerably on Ag^0 and Au^0 surfaces. Due to the difference in charge transfer between the surface and the adsorbent, the brominated species are adsorbed more strongly on Au^0 surfaces than that on Ag^0. On Ag^0 the C-Br bond dissociation energy barrier is less than that on Au^0 and the reaction barrier is reduced further with the increase in the Br substitution. AA is formed as the final product while reacting with the adsorbed hydrogens on the surfaces. The presence of hydrogen transfer reagents like BH_4^- is important for the dehalogenation of bromoacetic acids and the absence of either catalyst or BH_4^- results in zero dehalogenation[1,3].According to our calculations, BH_4^- is required to supply adsorbed hydrogen to form the AA. The SA is not formed on the Ag^0 surfaces due to the large activation energy barrier for the dimerization. On Au^0, SA is not formed using MBAA due to the large activation energy barrier for dimerization. The formation of the SA on the Au surface, after the C-Br dissociation from DBAA, is studied. The presence of adsorbed hydrogen on Au^0 surfaces reduces the activation energy barriers of the dimerization reactions without directly interacting with the adsorbents. Unlike the dehalogenation of methyl halides on Ag^0 and Au^0 [4], the presence of negative charge on metal surfaces didn't facilitate the C-Br bond dissociation of bromoacetic acids.

References

1 M. Meistelman, J. Adhikary, A. Burg, D. Shamir, G. Gershinsky, D. Meyerstein and Y. Albo, Ag^0 and Au^0 nanoparticles encapsulated in sol-gel matrices as catalysts in reductive de-halogenation reactions, *Chim. Oggi/Chemistry Today*, 2017, **35**, 23–26.

2 J. Adhikary, D. Meyerstein, V. Marks, M. Meistelman, G. Gershinsky, A. Burg, D. Shamir, H. Kornweitz and Y. Albo, Sol-gel entrapped Au^0- and Ag^0-nanoparticles catalyze reductive de-halogenation of halo-organic compounds by BH_4^-, *Appl. Catal. B Environ.*, 2018, **239**, 450–462.

3 J. Adhikary, M. Meistelman, A. Burg, D. Shamir, D. Meyerstein and Y. Albo, Reductive Dehalogenation of Monobromo- and Tribromoacetic Acid by Sodium Borohydride Catalyzed by Gold Nanoparticles Entrapped in Sol–Gel Matrices Follows Different Pathways, *Eur. J. Inorg. Chem.*, 2017, **2017**, 1510–1515.

4 B. R. Karimadom, D. Meyerstein, A. Mizrahi and H. Kornweitz, On the mechanism of dehalogenation of methyl halides (Br and Cl) on Ag(111) and Au(111) surfaces: A DFT study, *Appl. Surf. Sci.*, 2023, **615**, 156059.

FP18

Thursday 7th September 17:15 h

An efficient Iron N-Heterocyclic carbene molecular complex as electrocatalyst for water oxidation

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Water splitting in molecular hydrogen and oxygen is an important reaction in the panorama of new green energy sources. However, this process is hampered by the energetically demanding water oxidation.[1] The high overpotential requires the use of water oxidation catalysts (WOCs), usually based on expensive metals.[2] In the field of electrocatalysts, cheaper alternatives based on iron provided new systems but they suffered of high overpotentials and low activities.[2,3]

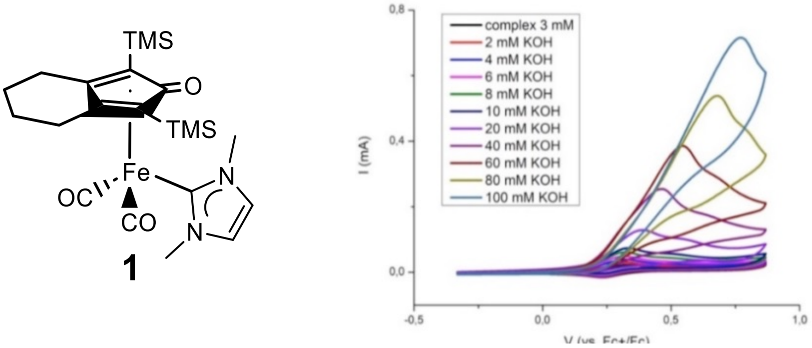

Figure 1. Water oxidation mediated by iron complex **1**.

Lately, our group reported on an iron N-heterocyclic carbene complex **1** (Figure 1) that demonstrated competitive activity and low overpotential under basic conditions.[4] Thanks to DFT calculations on frontier orbitals, EPR measurements and experimental data we spotted a light on the catalytic pathway followed in the reaction.

References

1. J. D. Blakemore, R. H. Crabtree and G. W. Brudvig, *Chem. Rev.*, **2015**, *115*, 12974–13005.
2. Garrido-Barros, P.; Gimbert-Surinach, C.; Matheu, R.; Sala, X.; Llobet, A. *Chem. Soc. Rev.*, **2017**, *46*, 6088.
3. Praneeth, V. K. K.; Kondo, M.; Okamura, M.; Akai, T.; Izu, H.; Masaoka, S. *Chem. Sci.*, **2019**, *10*, 4628.
4. A. Cingolani, I. Gualandi, E. Scavetta, C. Cesari, S.Zacchini, D. Tonelli, V. Zanotti, P. Franchi, M. Lucarini, E. Sicilia, G. Mazzone, D. Nanni and R. Mazzoni, *Catal. Sci Technol.*, **2021**, *11*, 1407-1418.

FP19

Thursday 7th September 17:15 h

Metal Formyl Complexes as Intermediates in Carbon–Carbon Bond Formation

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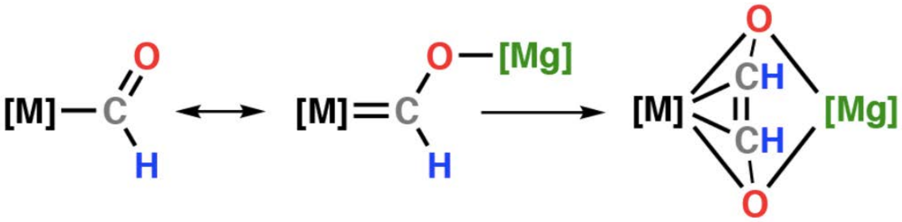

Transition metal formyl complexes are important intermediates in the reduction of carbon monoxide (CO) and carbon dioxide (CO_2).[1] For example, transition metal formyl species have been proposed as key intermediates in the reduction of CO with H_2 to form linear alkanes in the Fischer–Tropsch (F–T) process.[2] Despite their importance, the detailed study of transition metal formyl complexes has been hampered by their low stability.[3] As a result, even the simplest steps involving carbon–carbon bond formation from these intermediates can be ill- defined. Take for example ethenediolate formation from combining two CO and two H^- ligands on a transition metal. This reaction is relevant to F–T type chemistry where metal- bound CO and H^- ligands are prevalent. Several reaction pathways have been proposed over the last 50 years, with an overall understanding of this fundamental chemistry important for the rational design of improved F–T catalysts.[4] In this talk, I discuss efforts to determine the role of metal formyl intermediates in ethenediolate formation through reaction of a series of main-group hydrides with transition metal carbonyl complexes. Metal-formyl and (bis)formyl complexes are explored as key intermediates in carbon–carbon bond formation through a combined synthetic and computational approach.[5]

References

[1] *Coord. Chem. Rev.*, 2011, **255**, 881–898; **[2]** *J. Am. Chem. Soc.*, 1979, **101**, 1589–1591; *J. Am. Chem. Soc.*, 1981, **103**, 6959–6962; **[3]** *J. Am. Chem. Soc.*, 1978, **100**, 7224–7236; **[4]** *Angew. Chem. Int. Ed.*, 2023, e202219203; **[5]** *Chem. Sci.*, 2022, **13**, 6592–6598.

FP20

Thursday 7th September 17:15 h

Strongly Phosphorescent Pt(II) Complexes with Terdentate N^C^C Ligands

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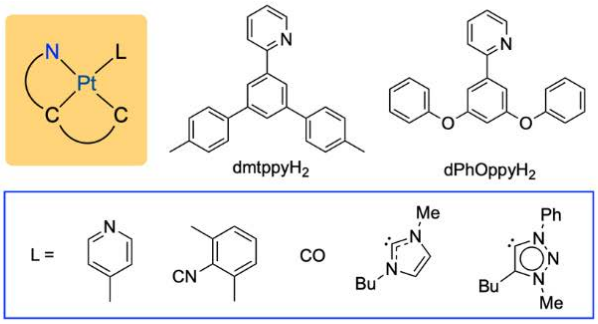
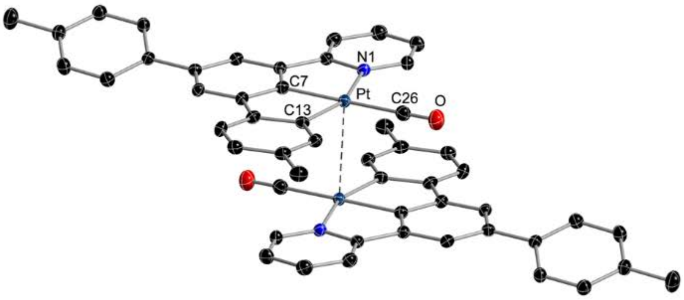
Pt(II) complexes with chelating heterocyclic ligands have been extensively studied due to their extraordinary photophysical and photochemical properties.[1] Among them, those with cyclometalated 2-arylpyridines (N^C) have been by far the most studied, whereas derivatives with terdentate or tetradentate ligands have been developed to achieve increased rigidity and enhanced emission efficiencies. Recently, we have developed a photochemical cyclometalation methodology that has allowed the synthesis of the first Pt(II) complexes with N^C^C ligands through irradiation with visible light at room temperature. The presence of two adjacent, strongly σ-donating C-donor moieties greatly destabilizes deactivating ^{3}MC excited states by inducing a large ligand-field splitting, leading to enhanced luminescence. A series of derivatives of two different N^C^C ligands containing diverse ancillary ligands such as pyridines, N-heterocyclic carbenes, phosphines, CO and isocyanides have been prepared and their photophysical properties are presented. Ancillary ligands play a crucial role on their supramolecular structures and luminescence by enabling different types of molecular aggregation through π-stacking and/or Pt···Pt interactions.





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References

1. Li, K.; Ming Tong, G. S.; Wan, Q.; Cheng, G.; Tong, W.-Y.; Ang, W.-H.; Kwong, W.-L.; Che, C.-M. *Chem. Sci.* **2016**, *7*, 1653–1673.

FP21

Thursday 7th September 17:15 h

Tetrylenes in low-valent TM^0 systems for metal-ligand cooperative small molecule activation and catalysis

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Metal-ligand cooperativity (MLC) has become an increasingly important concept due to its potential ability to achieve challenging catalysis and bond activations, aided by non-innocent ligands.[1] Heavier tetrylenes form a unique class of non-innocent ligand: as so-called Single-Centre Ambiphiles,[3] they possess both a high s-character lone pair of electrons, and a vacant p-orbital. As such, they have the capacity to maintain Lewis acidic properties even while coordinating to a TM center.[2] For this purpose, we have developed a family of bespoke phosphine functionalised tetrylenes, which have the capacity to chelate a TM centre.[4] This readily modifiable ligand system gives access to a range of low-valent tetrylene-TM^0 complexes, which also employ differing ancillary ligands at the TM center.[5][6] Here we discuss their divergent electronic situations, whereby the landscape of ligand modification and complex design allows for the fine tuning of chemical reactivity, for selective ligand-centred or cooperative small molecule activation, and ultimately catalytic alkene functionalisation (Figure 1).

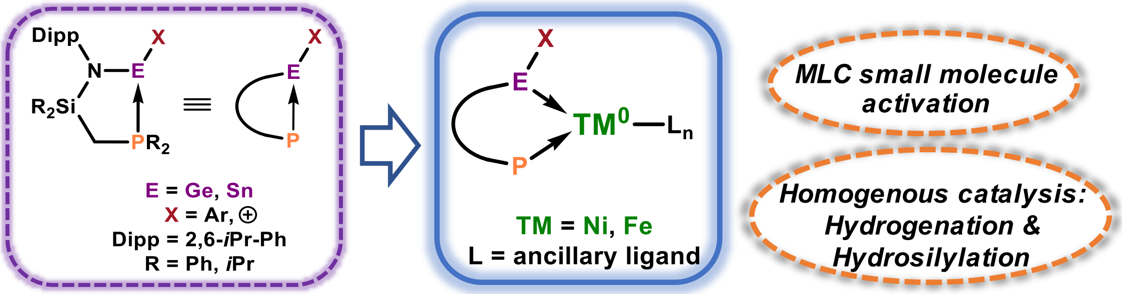

Figure 2. General structure of chelating group 14 element(II) Single-Center ambiphile ligands and corresponding TM^0-complexes including possible further chemistry.

References

[1] J. R. Khusnutdinova, D. Millstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236-12273.
[2] R. J. Somerville, J. Campos, *Eur. J. Inorg. Chem.* **2021**, 3488-3498.
[3] Y. Apeloig, R. Pauncz, M. Karni, W. Steiner, D. Chapman, *Organometallics* **2003**, *22*, 3250-3256.
[4] P. M. Keil, T. Szilvási, T. J. Hadlington, *Chem. Sci.* **2021**, *12*, 5582-5590.
[5] P. M. Keil, T. J. Hadlington, *Angew. Chem. Int. Ed.* **2022**, *61*, e202114143.
[6] P. M. Keil, A. Soyemi, K. Weisser, T. Szilvási, C. Limberg, T. J. Hadlington, *Angew. Chem. Int. Ed.* **2023**, e202218141.

FP22

Thursday 7th September 17:15 h

Synthesis and Reactivity of Transition Metal Stabilized Oligophosphorus Cations

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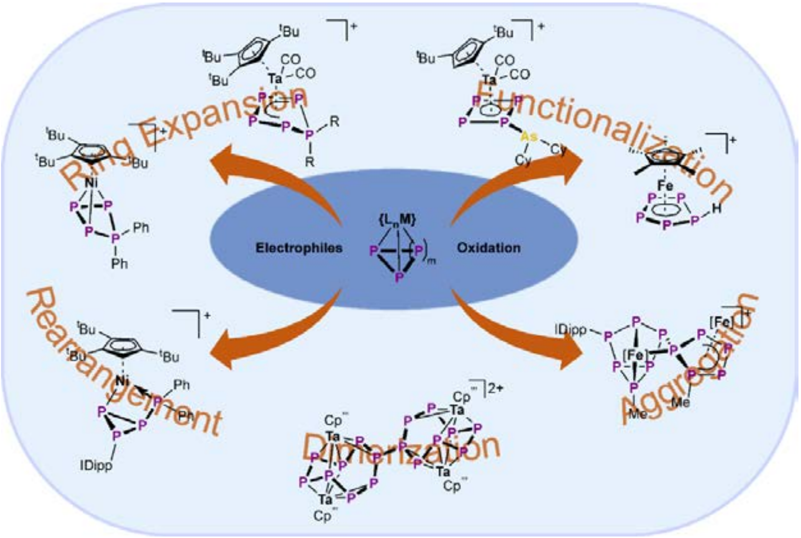
The elements carbon and phosphorus are fundamentally related by both, the diagonal relation in the periodic table, and the isolobal relationship between e. g. the CH fragment and the P atom.[1] Thus, a similar structural wealth as is observed for carbon is expected for oligo- and polyphosphorus species. However, while anionic, neutral and often highly substituted oligo- and polyphosphines are well known, the synthesis and reactivity of cationic oligophosphorus species is only scarcely explored. This contribution explores the diverse reactivity of selected organometallic oligophosphorus (P_n) complexes, a highly promising class of compounds in this regard, both towards oxidation and reactivity towards cationic main group electrophiles. While phosphenium cations insert into small *cyclo*-P_3 and *cyclo*-P_4 ligands[2] yielding the respective ring-expanded species, their heavier congeners, such as arsenium cations undergo addition to the *cyclo*-P_n ligand.[3] Thus, exotic species such as functionalized *cyclo*-P_5R and even the parent pentaphosphole (*cyclo*-P_5H) could be stabilized within the coordination sphere of Fe.[4] In contrast, oxidation of a *cyclo*-P_8 complex yielded an unprecedentedly large P_{16} cation via dimerization.[5] Ongoing studies on these oligophosphorus cations reveal a broad spectrum of reactivity ranging from simple functionalization over rearrangement to complex aggregation reactions and, thus, paving the way towards the access of novel complex oligophosphorus architectures.



References

[1] R. Hoffmann, Angew. Chem. Int. Ed. Engl. **1982**, 21, 711.
[2] C. Riesinger, L. Dütsch, G. Bálazs, M. Bodensteiner, M. Scheer, *Chem. Eur J.* **2020**, *26*, 17165.
[3] C. Riesinger, G. Balázs, M. Seidl, M. Scheer, *Chem. Sci.* **2021**, *12*, 13037.
[4] C. Riesinger, G. Bálazs, M. Bodensteiner, M. Scheer, *Angew, Chem. Int. Ed.* **2020**, *59*, 23879.
[5] C. Riesinger, F. Dielmann, M. Scheer, *Angew. Chem. Int. Ed.* **2023**, e202218828.

FP23

Thursday 7th September 17:15 h

Visible-Light Deaminative Reaction of Primary Amines and Cyanopyridines

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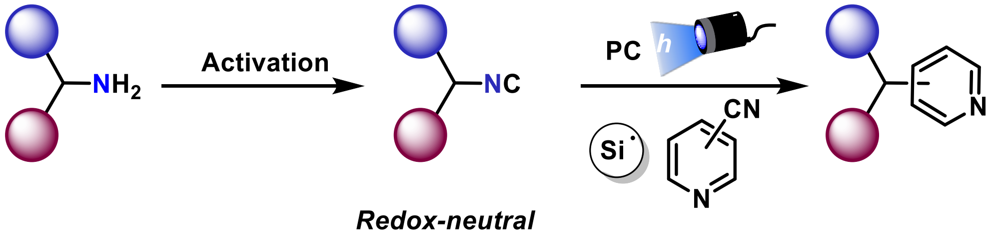
Amines are ubiquitous natural products, pharmaceuticals, polymers and biomolecules. The number of commercial available amines makes them one of the most accessible native functional groups, representing and attractive feedstock for the preparation of functionalized molecules through C-N bond activation.

Amine activation through the formation of pyridinium salts[1] or electron-rich imines[2] has emerge as a tool to promote the C-N bond cleavage. These redox-active amines undergo a single-electron transfer reduction or oxidation under photocatalytic conditions to generate a carbon-centered radical that can be engaged in different carbon-carbon bond forming reactions. Recently, our group described and alternative C-N bond activation using isonitriles as redox-neutral amine derivatives in the deamination process.[3]

Within this context, we have developed a mild and simple protocol for this transformation via isonitrile activation. This process shows a broad scope and functional group tolerance for different types of primary amines with excellent yields.



References

[1] Correia, J. T.; Fernandes, V. A., Matsuo, B. T.; Delgado, J. A. C.; de Souza, W. C.; Paixao, M. W. *Chem. Commun.* **2020**, *56*, 503-514.
[2] Ashley, M. A.; Rovis, T. *J. Am. Chem. Soc.* **2020**, *142*, 18310-18316.
[3] Quirós, I; Martin, M.; Cabrera-Afonso, M.J., Tortosa, M. *Submitted.*

FP24

Thursday 7th September 17:15 h

NHC-CDI betaines as ligands towards Group 13 elements: coordination studies and reactivity

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N-heterocyclic carbene and carbodiimide (NHC-CDIs) betaine adducts are an emerging family of compounds that contain two well-defined moieties with separated charges of opposite sign and exhibit a strongly basic character. These zwitterionic derivatives have provided promising results in the fields of Materials Science[1] or in Coordination Chemistry, as ligands in the stabilization of nanoparticles[2] and in the synthesis of transition and main group metal complexes.[3] Additionally, due to their zwitterionic character and enhanced basicity, NHC-CDIs can be protonated and therefore used as ligand precursors, allowing the formation of unusual cationic complexes by combination with alkyl metal derivatives.

Recently, we have prepared a variety of metal adducts by reaction of the NHC-CDI ligands (L) with aluminum alkyls, AlR_3. Moreover, we have employed the protonated ligands (LH·X; X = BPh_4, $BAr^F{}_4$) to afford novel cationic aluminium complexes, such as $[AlMeL_2]^{2+}$, which displays an atypical pentacoordinated environment with two formal positive charges. Furthermore, we have extended our coordination studies on Group 13 elements to boron, and we have isolated the first Lewis pair of an NHC-CDI with a borane species $[L\cdots{>}B(C_6F_5)_3]$. We are currently exploring the reactivity of these derivatives towards small molecules such as CO_2 or H_2 and in ring opening polymerization processes.

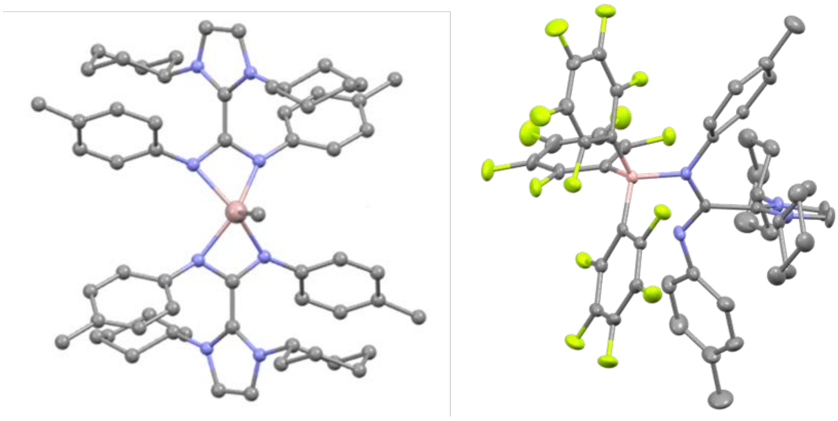

Figure 1. Complex $[AlMeL_2]^{2+}$ (left) and adduct $[B(C_6F_5)_3L]$ (right).

References

[1] J. R. Lamb, C. M. Brown and J. A. Johnson, *Chem. Sci.*, **2021**, 12, 2699.

[2] Martínez-Prieto, L. M.; Cano, I.; Márquez, A.; Baquero, E. A.; Tricard, S.; Cusinato, L.; del Rosal, I.; Poteau, R.; Coppel, Y.; Philippot, K.; Chaudret, B.; Cámpora, J.; van Leeuwen, P. W. N. M, *Chem. Sci.* **2017**, 8, 2931-2941.

[3] D. Sánchez-Roa, T. G. Santiago, M. Fernández-Millán, T. Cuenca, P. Palma, J. Cámpora and M. E. G. Mosquera, *Chem. Commun.*, **2018**, 54, 12586-12589.

FP25

Thursday 7th September 17:15 h

Half-sandwich nickel complexes with aminoacid-based *N*-heterocyclic carbenes: synthesis, reactivity and catalytic activity

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N-Heterocyclic carbenes (NHC) are a family of ligands capable to stabilize metal species. They form robust bonds to metals, due to their outstanding σ-donor coordinative capability, and exert steric protection to the M-C bond through the *N*-substituents.[1] We have synthesized enantiomerically pure complexes of Ni from the imidazolium salt and nickelocene, starting from amino-acids,[2] and obtained single-crystals of some of them. X-Ray diffraction studies show that, apart from the carbene ligand, the Ni complex has an η^5-coordinated cyclopentadienyl. Unlike other complexes found in the bibliography, this type of compounds does not require another counteranion ligand, because of the presence of the chelating carboxylate group of the NHC, which is bounded to the metal center. This structure has also been confirmed by HRMS and appears to be same in solution, according to the NMR data collected.

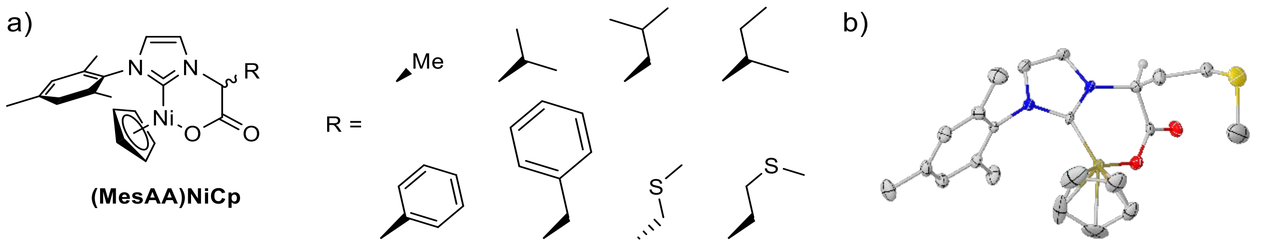

Figure 1. a) Amino acid derived NHC complexes of Ni. b) Solid structure of the complex derived from (*L*)-methionine.

With the cristalographic data it has been measured the burried volume, as one of the characteristic property of the NHC ligands. In addition, we have studied the reactivity of the complexes with MeOTf an thus obtained a complex with a chelating ester or thioether, which are more labile groups than the carboxilate group.

The carboxilate complexes has been also used as catalyst in the hydrosililation of ketones and the hydrothiolation of alquines with interesting results.

References

[1] a) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature* **2014**, 510, 485-496; b) H. V. Huynh. *The Organometallic Chemistry of N-heterocyclic Carbenes*. Wiley-VCH, Hovoken (NJ), **2017**.

[2] a) C. Jahier-Diallo, M. S. T. Morin, P. Queval, M. Rouen, I. Artur, P. Querard, L. Toupet, C. Crévisy, O. Baslé, M. Mauduit, *Chem. Eur. J.* **2015**, 21, 993-997. b) C.D. Abernethy, A.H. Cowley, R.A. Jones, *J. Organomet. Chem.* ***2000***, 596, 3-5.

FP26

Thursday 7th September 17:15 h

Nucleophilic Addition on Coordinated N_2: Fact or Fiction ?

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Nitrogen is a life-sustaining element primarily sourced from the widely available, inexhaustible but commonly non-bioavailable N_2 allotrope. Coordination to transition metals is the way Nature has chosen to achieve the transformation of this abundant but inert molecule: within the active site of the nitrogenase enzymes, an FeS cluster can activate N_2 towards its reduction to NH_3. Taking inspiration thereof, chemists have achieved N_2 activation on metal complexes, culminating in catalytic reduction of N_2 to NH_3 under ambient conditions. The reactivity of N_2-complexes may also extend beyond NH_3 synthesis, with the production of N-containing organic molecules.[1] The large majority of N–C bond formation reactions between coordinated N_2 and an organic substrate relies on its reaction with a C-electrophile. Yet, a unique example of functionalization by a C-nucleophile stands out in the literature and involves the complex $[CpMn(N_2)(CO)_2]$[2] (Figure). Intrigued by this particular reactivity, we have carried out a mechanistic study combining experiment and DFT. We have disclosed a previously undetected intermediate that seems crucial for obtaining an N_2-derived nitrogen-containing compound. Besides, our data suggest that the direct attack of the C-nucleophile (RLi) on coordinated N_2, initially proposed as a key step for N_2 functionalization, is not likely to take place.

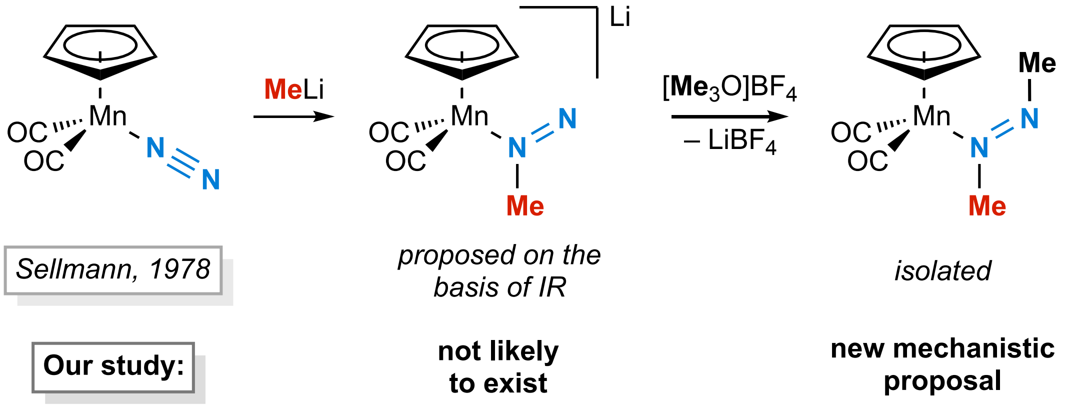

Figure. The unique reactivity of $[CpMn(N_2)(CO)_2]$.

References

1. Kim, S.; Loose, F.; Chirik, P. J. *Chem. Rev.* **2020**, *120*, 5637.
2. Sellmann, D.; Weiss, W. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 269.

FP27
Thursday 7th September 17:15 h

So happy together: metal cooperativity within a preorganized dinickel complex achieves bioinspired thioester synthesis

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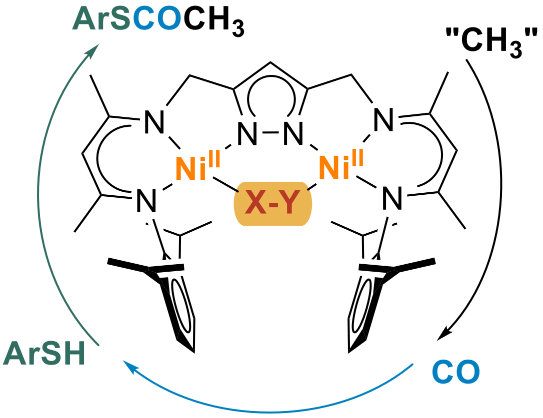
While synthetic approches to thioester synthesis are charachterized by low yields and poor atom economy, nature mediates stepwise anaerobic Coenzyme A acetylation from CO and a methyl source through Acetyl CoA Synthase (ACS)[1]. Synthetic analogues of the the A cluster, the dinickel core structure of ACS, have tried to address unravelled questions of ACS working mechanism i.e the binding events sequence, the involvement of different redox states and the participation of both metals [2]. However, few models have achieved the Ni-mediated conversion of CO, a CH_3^+ equivalent and a thiol into an acetyl thioester still providing scarce elucidation on the enzymatic reaction [3]. Using a preorganized dinickel site based on pyrazolato-bridged bis(ß-diketiminato) ligand [4], herein we report a sequence where methylation precedes CO insertion, starting from a dinickel(I) state, and where all intermediates are stabilized via synergistic interaction with both metal ions. Characterization of the complexes and mechanistic insight will be discussed.



References

[1] Y. Ilina, B. M. Martins, J.-H. Jeoung, H. Dobbek, *Met. Ions Life Sci.* **2020**, *20*, 381-413.

[2] M. Can, F. A. Armstrong, S. W. Ragsdale, *Chem. Rev.* **2014**, *114*, 4149-4174.

[3] (a) G. C. Tucci, R. H. Holm, *J. Am. Chem. Soc.* **1995**,117, 6489-6496; (c) W. G. Dougherty, K. Rangan, M. J. O'Hagan, G. P. A. Yap, C. G. Riordan, *J. Am. Chem. Soc.* **2008**, 130, 13510-13511; T. Matsumoto, M. Ito, M. Kotera, K. Tatsumi, *Dalton Trans.*, **2010**, 39, 2995-2997; (d) B. Horn, C. Limberg, C. Herwig, S. Mebs, *Angew. Chem. Int. Ed.* **2011**, 50, 12621-12625; (e) A. C. Manesis, A. Yerbulekova J. Shearer, H. S. Shafaat, *PNAS,* **2022**, 119, 21230-22119.

[4] D.-H. Manz, P. C. Duan, S. Dechert, S. Demeshko, R. Oswald, M. John, R. A. Mata, F. Meyer, *J. Am.Soc.* **2017**, *139*, 16720-16731.

FP28

Thursday 7th September 17:15 h

Ruthenium (II) and copper(II) carbosilane metallodendrimers as a new therapeutic approach in the fight against cancer

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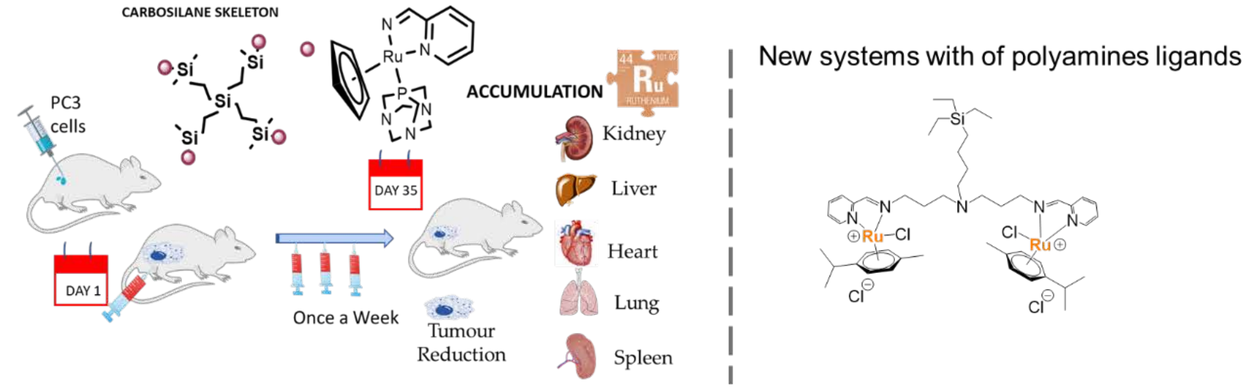
We are focused on the design of carbosilane dendritic systems that contain ruthenium (II) and copper (II) complex in their structure to use them as anticancer agents. So far, the results obtained in different *in-vivo* and *ex-vivo* treatments, against prostate or breast cancer, show how the system with the highest potential is able to inhibit tumor growth by 40% compared to untreated mice.[1-3] We are currently working on the design of new systems that, through the inclusion of polyamines ligands in the dendritic scaffold such as spermine and spermidine, that will provide an increase of the number of metal centers per dendritic generation (multivalency) in the search of better cytotoxic activity. The presence of aliphatic amines could allow the increase of positive charges by reactions of cauterization, particularly in tumor areas where the pH is slightly acid helping to exhibit their antitumoral properties. Besides, the electrostatic interactions and formation of hydrogen bonds between the polyamine chain and the nucleic acid backbone plays a crucial role in the mechanism of metal complex–DNA interaction, allow us to increase the number of metal centers per dendritic molecule.



References

[1] S. Michlewska, M. Maroto, et al. *Dalton Trans.* **2021,** *50* (27), 9500-9511.
[2] N. Sanz del Olmo, M. Maroto-Diaz, et al. *Eur. J. Med. Chem.* **2020,** *207.*
[3] N. Sanz del Olmo, A. M. Bajo, M. et al . *Eur. J. Med. Chem.* **2020,** *199.*

FP29

Thursday 7th September 17:15 h

Effect of glycoconjugation on metastasis related processes mediated by carbohydrate-based metallo drugs

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Lourdes Gude[1] and Eva Royo[1]

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Cancer is the second most frequent cause of death in the world. Research on a variety of metal compounds have demonstrated that the unique properties of metals can be exploited and used for cancer cell-targeted approaches. Within this field, functionalization of drugs with carbohydrates is an anticancer strategy that has gained great interest in recent years [1]. The presence of carbohydrates can improve solubility and selective interactions with carbohydrate-binding proteins involved in cell adhesion, migration, and angiogenesis-related processes, all closely related events to metastasis [2].

On the other hand, polypyridyl compounds such as 1,10-phenanthroline are powerful bidentate metal chelating ligands able to act as DNA intercalators and groove binders. Furthermore, they serve as scaffolds for several potent stabilizers of DNA G-quadruplexes, which are being investigated as potential targets for anticancer drug development [3].

In contrast with other complex carbohydrate functionalization reactions reported, we have used an efficient and stereoselective *N*-glycosylation of 5-amino-1,10-phenanthroline to prepare *N*-(1,10-phenanthrolin-5-yl)-β-glycopyranosylamines [4]. Herein, we report the synthesis and biological studies of novel arene-Ru(II), polypyridyl Ru(II) and palladium(II) compounds containing N-phenanthroline glycosylamine ligands. Effect of the carbohydrate on the biological behaviour of the metalloglycoconjugates have been elucidated by comparison with corresponding metal-aglycones [5].

References

[1] E.C. Calvaresi and P.J. Hergenrother, Chem. Sci. (2013) 4:2319.

[2] A. Franconetti, O. López, J.G. Fernandez-Bolanos, Curr. Med. Chem. (2020), 27(8):1206-1242.

[3] N. S. Ilyinsky, A. M. Varizhuka, A. D. Beniaminova, M. A. Puzanova, A. K. Shchyolkinaa, and D. N. Kaluzhnya, Mol. Biol. (2014) 48:778.

[4] K. Duskova, S. Sierra, M.S. Arias-Pérez, L. Gude, Bioorg. Med. Chem. (2016) 24:33. E. de la Torre-Rubio, L. Muñoz-Moreno, A.M. Bajo, M.S. Arias-Perez, T. Cuenca, L. Gude, E. Royo, J. Inorg. Biochem., (2023), in press.

[5] J. Valladolid, C. Hortigüela, N. Busto, G. Espino, A.M. Rodriguez, J.M. Leal, B.R. Manzano, A. Carbayo, B. García, Dalton Trans., (2014), 2629-2645.

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ABSTRACTS:

POSTER COMMUNICATIONS

PA01

Silver salts as phosphine scavengers and different behavior of nickel and palladium complexes

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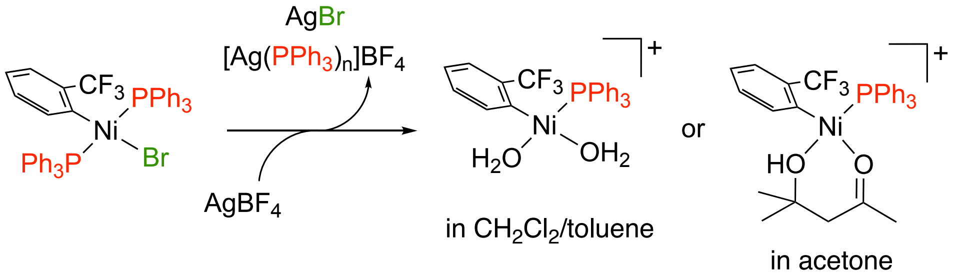
Palladium and nickel complexes are involved in many catalytic transformations. In particular, the need to shift from precious to earth-abundant metals has greatly increased the interest in nickel catalysis.[1] A common activation process of a metal precatalyst is the abstraction of a halide ligand to generate species with an easily available coordination site and silver salts are common reagents for this purpose by formation of insoluble AgX. We describe how silver salts can act as phosphine scavengers, a process concomitant to the halide abstraction when activating a nickel precatalyst.[2] This process affects the identity of the actual active species and the catalyst performance.

The reaction of $[NiArBr(PPh_3)_2]$ with $AgBF_4$ brings about the abstraction of both the halide and phosphine from the nickel center by silver (Scheme 1). Cationic aquo derivatives are formed in CH_2Cl_2/toluene whereas in acetone a complex with a ligand formed the aldol self-condensation of acetone is observed. Phosphine abstraction by silver is less favorable for analogous Pd(II) complexes.



Scheme 1

Acknowledgments: We thank the financial support of the Spanish MICINN (PID2019-111406GB-I00) and the Junta de Castilla y León-FEDER (VA224P20).

References

[1] a) P. Gandeepan, T. Müller, D. Zell, G. Cera, S. Warratz, L. Ackermann, *Chem. Rev.* **2019**, 119, 2192–2452; b) J. Diccianni, Q. Lin, T. Diao, *Acc. Chem. Res.* **2020**, *53*, 906–919.

[2] I. Pérez-Ortega, A. C. Albéniz, *Dalton Trans.* **2023**, *52*, 1425-1432.

PA02

Understanding Ligand Exchange Processes of Ru (II) Piano Stool Complexes to control the Formation of Artificial Metalloenzymes via Dative Anchoring

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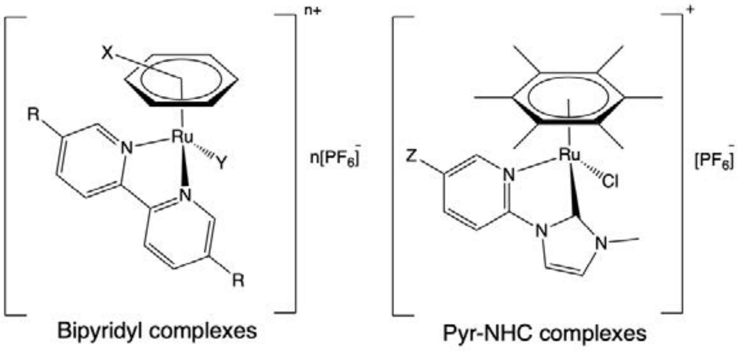
Artificial metalloenzymes (ArMs) are non-natural catalysts that consist of a metallic moiety attached to a protein scaffold. Utilising metals and ligands that are not found in nature yields enzymes for catalysis of new-to-nature reactions.

One approach to ArM design is to exploit direct metal-protein coordination via controlled ligand exchange of a precursor metal complex. Careful control of the ligand sphere of organometallic complexes has allowed us to deliver specific metal fragments to apoproteins to form ArMs. The catalytic activity of the ArM can then be screened and optimised *via* directed evolution campaigns.

Our work aims to understand the ligand exchange processes of Ru (II) piano stool complexes in order to control the formation of protein adducts. Specifically, we are interested in the aquation and ligand exchange reactions of these complexes in the presence of protein. To probe this, a suite of Ru(II) piano stool complexes has been synthesized (**Figure**). The structural and electronic properties of these complexes have been correlated with their reactivity via aquation kinetic experiments, theoretical calculations and X-ray crystallography. We are currently working on expanding the Ru(II) piano stool library to complexes containing coumarin ligands which have been designed to track protein attachment via fluorescence upon metal-coumarin bond cleavage. Systematic attempts to attach the coumarins by varying the coordinating heteroatom has allowed us to study the balance between metal-heteroatom stability and lability.



Symbol	Substituent
R	F, CF_3
X	Ben, HMB
Y	Cl, OH, MeCN, Coumarin
Z	H, F

Figure. General formula for the Ru(II) piano stool complexes studied.

References

Biggs, G. S. *et al. Angew. Chem. Int. Ed.* **60**, 10919–10927 (2021).
Biggs, G. S. *et al. Dalton Trans.* **48**, 6910–6920 (2019).

PA03

A Highly Active Gallium Aminotrisphenolate Catalyst for the Synthesis of Bio-derived Cyclic Carbonates

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Alex Hamilton[2] and Christopher J. Whiteoak[1]

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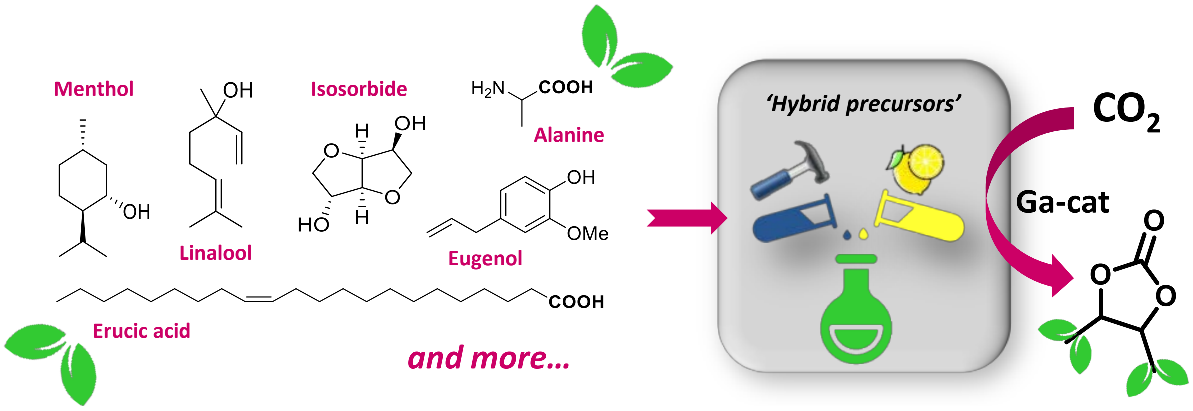
The valorisation of carbon dioxide (CO_2) and its use as a chemical feedstock provides an opportunity for the scientific community to realise a more sustainable economy. To date, a wide range of synthetic applications have emerged to utilise this non-toxic and highly abundant C1 source.[1] One reaction of interest is the atom-efficient coupling of CO_2 and epoxides to form cyclic carbonates (CCs). We recently reported the use of a highly active gallium aminotrisphenolate complex (more active than the corresponding aluminium congener; displaying a TON of up to 344,000 at low catalyst loadings) as catalyst for the synthesis of CCs, at low and elevated temperatures across a wide substrate scope including terminal, internal, multiple, and fully deuterated epoxides.[2] Measurement of the Lewis acidity using the Gutmann-Beckett method provided the experimental proof that the gallium compounds are more Lewis acidic than their aluminium congeners. Further, DFT studies confirmed that the gallium catalysts have lower energetic profiles compared to the aluminium congeners. As part of these studies, AIMD simulations quantified the dynamic behavior of the catalytic systems, highlighting an important increase in fluxionality which helps to explain the increase in catalytic activity. With this catalyst system optimized for common epoxides, we have embarked on transforming naturally occurring compounds into bio-derived epoxides and thereafter, into the corresponding CCs which can be used as sustainable precursors for a range of applications.[3]



References

[1] (a) Kim, C.; Yoo, C.-J.; Oh, H.-S.; Min, B. K.; Lee, U. *J. CO_2 Util.* **2022**, *65*, 102239; (b) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nat. Commun.* **2015**, *6*, 5933.
[2] Álvarez-Miguel, L.; Burgoa, J. D.; Mosquera, M. E. G.; Hamilton, A.; Whiteoak, C. J. *ChemCatChem.* **2021**, *13*, 4099.
[3] Álvarez-Miguel, L.; Mosquera M. E. G.; Whiteoak, C. J. *Org. Biomol. Chem.* **2022**, *20*, 9629.

PA04

Exploring the intramolecular chemistry of iron(V)-oxo-carboxylato species

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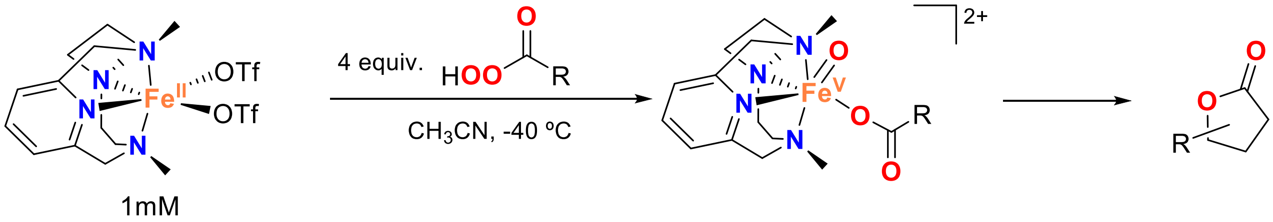
The development of iron(V)-oxo synthetic models that can mimic the reactivity of the iron-oxygenases that are found in nature is an important challenge. Their characterization though, has been hampered due to their high reactivity. It is important to highlight that iron(V)-oxo-carboxylato species have been postulated as the key compounds in the catalytic oxidation of carboxylic acids that leads to the formation of γ-lactones. [1]

In this work, the intramolecular reactivity of an iron(V)-oxo-carboxylato species, $[Fe^V(O)(OC(O)R)(PyNMe_3)]^{2+}$, reported in the QBIS-CAT research group has been studied. [2] It has been observed that both the accumulation of the iron(V)-oxo-carboxylato compound and the formation of the corresponding γ-lactone are affected by the strength of the γ-C-H bond. Moreover, it could be observed that the iron(V)-oxo-carboxylato species is directly related to the formation of the corresponding γ-lactones by following the formation of the lactone along the formation and the decay of the high-valent species. Also, through intra and intermolecular reactivity competition studies, it has been confirmed that the iron(V)-oxo-carboxylato species is directly related to the formation of the γ-lactones. Finally, mechanistic studies are being carried out to gain more insight into the mechanism for the formation of the γ-lactones.



Generation of $[Fe^V(O)(OC(O)R)(PyNMe_3)]^{2+}$ species by reaction of $[Fe^{II}(PyNMe_3)(OTf)_2]$ with different peracids at -40 °C in acetonitrile followed by the γ-lactone formation.

References

[1] M. Cianfanelli, G. Olivo; M. Milan; R. J .M. Klein Gebbink; X. Ribas; M. Bietti; M. Costas. *J. Am. Chem. Soc.* **2020,** *142*, 1584.

[2] J. Serrano-Plana; W. N. Oloo; L. Acosta-Rueda; K. K. Meier; B. Verdejo; E. García-España; M. G. Basallote; E. Münck; L. Que; A. Company; M. Costas. *J. Am. Chem. Soc.* **2015,** *137*, 15833

PA05

Complexes and reactions of ferrocene phosphino-stibine ligand

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While numerous ferrocene compounds with phoshine donor moieties have been reported, the chemistry of ferrocene ligands containing heavier group 15 elements remains nearly unexplored. This contribution focuses on the ligating properties and reactivity of two hybrid phosphino-stibine ligands $R_2PfcSbPh_2$ (R = Cy (**L**^{Cy}), Ph (**L**^{Ph})). The ligands were prepared by metalation of the corresponding 1-bromo-1´-phosphinoferrocene with *n*-BuLi and subsequent reaction with chloro(diphenyl)stibine. The ability of **L**^{Cy} to act as a ligand was probed via its reactions with various transition metal precursors (Ru(II), Rh(III), Pd(II), Pt(II), Au(I)), to which **L**^{Cy} binds in various modes. Further research was focused on the reactivity of compund **L**^{Ph}, specifically on the preparation of chalcogenides $Ph_2P(E)fcSbPh_2$ (E = O, S, Se) and the corresponding stiborane derivatives $Ph_2P(E)fcSbPh_2(O_2C_6Cl_4)$ (E = void, O, S, Se), in which the stiborane center bears tetrachloropyrocatechol substituent, which makes it Lewis acidic and potentially prone to behave as an acceptor of electron pair from the $Ph_2P(E)$ moiety. The presence of this interaction was confirmed by single-crystal X-ray diffraction analysis and $^{31}P\{^1H\}$ NMR spectroscopy only if E = void or O. The nature of this interaction was clarified using computational methods. All substances were characterised by using standard analytical techniques. When possible, the crystal structure was determined.

PA06

High water-soluble PEGylated NHC Ruthenium(II) Complexes for a better biocompatibility of metallodrugs, in the fight against cancer

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Hydrosolubility represents one of the major challenges for the development of new therapeutic agents. Low absorption of drugs usually explains minimum effect in cancer cell lines, triggering the use of higher doses that normally ends up provoking off-target effects and poor selectivity. Therefore, many efforts have been recently made to enhance the solubility of new pharmaceuticals in aqueous solutions. Both physical and chemical modifications have been reported of late which include formation of ionic compounds, reduction of particle size or introduction of hydrosoluble ligands into the pharmaceutical system[1].

Furthermore, since cisplatin was casually discovered in 1963, metallodrugs have been stablished as a good strategy in the fight against cancer. More specifically, ruthenium complexes have demonstrated to have a versatile solution against cancer. Numerous studies dealing with the use of ruthenium complexes have described several interesting effects, including the disruption of vital signaling pathways for the survive of the cell [2], DNA interaction and subsequent suspension of cell cycle [3], and so forth. In this study, we have put in place the interest of PEGylation in the enhancement of the hydrosolubility of metallodrugs by the development of new ruthenium(II) complexes with different polyethylene glycol fragments.

New high water-soluble Ru(II) complexes have been developed with the intention of enhancing the applicability of ruthenium(II) metallodrugs by low doses and thus, better selectivity. Herein, synthesis and characterization are exposed together with first proliferation results realized on both liver and prostate cancer cell lines.

Acknowledgement. This work has been supported by MINECO (Spain, PID2020-112924RB-I00 and CIBER-BBN (Instituto de Salud Carlos III, Spain).

References

1. Savjani, K. T.; Gajjar, A. K.; Savjani, J. K. Drug Solubility: Importance and Enhancement Techniques. ISRN Pharmaceutics 2012, 2012, 195727.
2. Barrios, O.; Sánchez, B. G.; Rodríguez-Prieto, T.; Cano, J.; Bort, A.; Gómez, R.; Díaz-Laviada, I. Alteration of the HIF-1α/VEGF Signaling Pathway and Disruption of the Cell Cycle by Second Generation Carbosilan Dendrimers. Biomacromolecules 2022, 23, 5043-5055.
3. Pavlović, M.; Tadić, A.; Gligorijević, N.; Poljarević, J.; Petrović, T.; Dojčinović, B.; Savić, A.; Radulović, S.; Grgurić-Šipka, S.; Aranđelović, S. Synthesis, chemical characterization, PARP inhibition, DNA binding and cellular uptake of novel ruthenium(II)-arene complexes bearing benzamide derivatives in human breast cancer cells. J. Inorg. Biochem. 2020, 210, 111155.

PA07

Interplay between C-I Coupling, Aryl Scrambling and Isomerization Processes in Au(III) Complexes

Camino Bartolomé,[1] Sara Fernández-Moyano,[1] Guillermo Marcos-Ayuso,[1]
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There are just a few reported cases of aryl scrambling phenomena involving Au(III) complexes. However, they were only detected when strong oxidants come into play and consequently, a deep mechanistic understanding behind this remarkable behaviour is lacking.[1] Interestingly, we recently observed that, in our attempts to obtain (μ-Cl)$_2$[AuRf$_2$]$_2$ (Rf = $C_6F_3Cl_2$-3,5), an unexpected Rf/Cl scrambling occurred upon treating *trans*-[Au^{III}Rf$_2$Cl$_2$]$^-$ with a silver salt.[2]

In this context, ^{19}F NMR monitoring also shows that heating *trans*-[Au^{III}Rf$_2$I$_2$]$^-$ solutions leads to formation of *cis*-[AuRf$_2$I$_2$]$^-$, [AuRf$_3$I]$^-$ and [AuRfI$_3$]$^-$ via kinetic competition between isomerization and Rf/I transmetalation. The system evolution is driven by the easy Rf-I reductive elimination from [AuRfI$_3$]$^-$ (concomitantly forming [AuI$_2$]$^-$), which is faster than any of the Rf–Rf couplings from the coexisting species, hindering the commonly desired and thermodynamically preferred C-C coupling (Figure 1).[3] A simple kinetic model, that proposes both isomerization and transmetalation steps triggered by I$^-$ dissociation, fits satisfactorily the experimental data. DFT calculations further support the ability of iodide to ease the C-X coupling, compared to other halides.

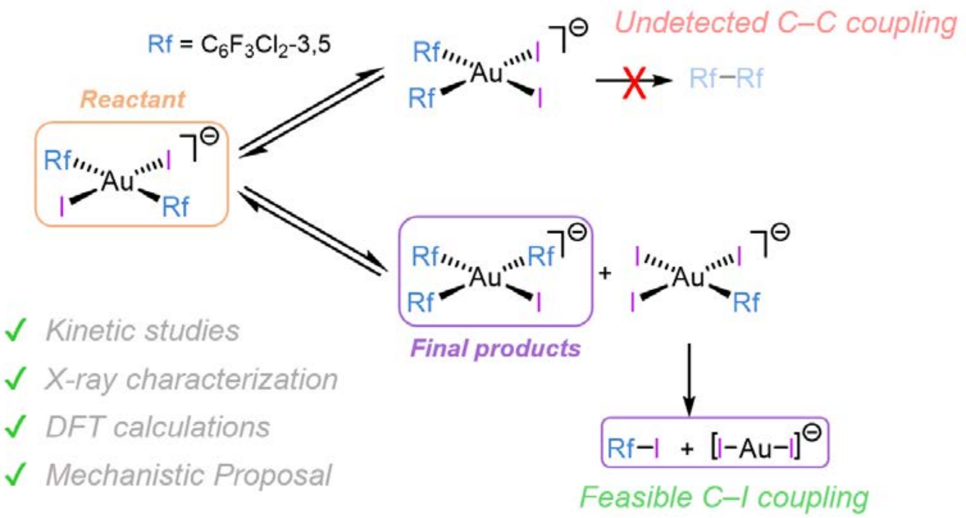

Figure 1. Reactivity of *trans*-[Au^{III}Rf$_2$I$_2$]$^-$ in CDCl$_3$ solution.

References

[**1**] (a) Overton, A. T.; López-de-Luzuriaga, J. M.; Olmos M. E.; Mohamed, A. A. *Organometallics,* **2012**, *31*, 3460–3462. (b) Hofer M.; Nevado, C. *Eur. J. Inorg. Chem.,* **2012**, 1338–1341.
[**2**] Fernández-Moyano, S.; Peñas-Defrutos, M. N.; Bartolomé C.; Espinet, P. *Chem.Commun.,* **2021**, *57*, 125–128.
[**3**] Fernández-Moyano, S.; Marcos-Ayuso, G.; Peñas-Defrutos, M. N.; Bartolomé C.; Espinet, P. *Chem.Commun.,* **2023**, *59*, 1975–1978.

PA08

New Reactivity Patterns and Catalytic Application of Ruthenium(II) Arene Complexes

Lorenzo Biancalana[1], Chiara Saviozzi[1], Lorenzo Bonaldi[1], Roberta Colaiezzi[2], Stefano Zacchini[3], Marco Bortoluzzi[4], Andrea Di Giuseppe[2] and Fabio Marchetti[1]

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[2] *Dipartimento di Scienze Fisiche e Chimiche, Università dell'Aquila, L'Aquila, Italy*
[3] *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Bologna, Italy*
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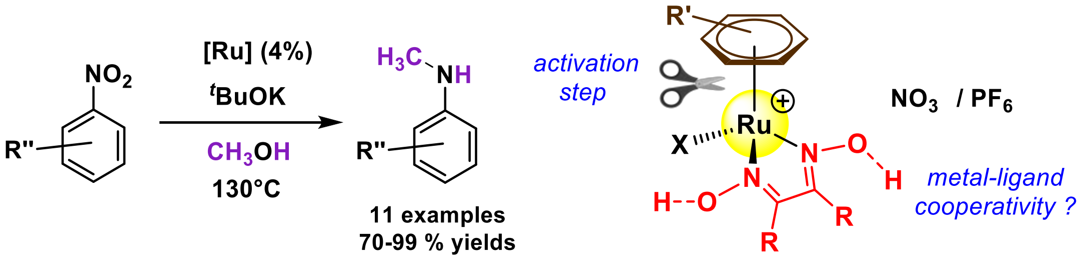
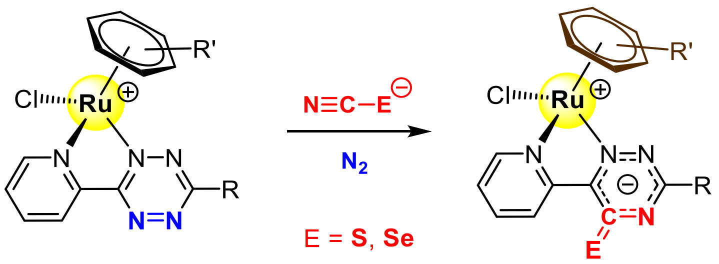
After almost 50 years from their breakthrough discovery,[1] half-sandwich η^6-arene ruthenium(II) complexes still represent an attractive class of compounds for developing new catalysts and to explore new reactivity pathways. Herein we report two recent findings.

The first topic[2] involves novel **dioxime** complexes as effective catalysts for the one-pot transfer hydrogenation and *N*-methylation of nitroarenes, using methanol as solvent, H_2 donor and alkylating agent. The arene plays the unusual(?) role of leaving ligand while while the dioxime ligand is crucial for the selectivity in the hydrogen borrowing step (*N*-methylation).



The second topic[3] deals with the unprecedented reactivity of **1,2,4,5-tetrazines** with chalcogenocyanate anions. The room temperature reaction of pyridyl-tetrazine complexes with stoichiometric amounts of thiocyanate and selenocyanate salts results in the regioselective formation of a rare triazine-chalcogenone heterocycle within a zwitterionic complex.



References

[1] M. A. Bennett, A. K. Smith, J. Chem. Soc., *Dalton Trans.*, **1974**, 233-241. [2] R. Colaiezzi, C. Saviozzi, N. di Nicola, S. Zacchini, G. Pampaloni, M. Crucianelli, F. Marchetti, A. Di Giuseppe, L. Biancalana, *Catal. Sci. Technol.*, **2023**, Adv. Art., DOI:10.1039/D3CY00218G. [3] L. Bonaldi, M. Bortoluzzi, S. Zacchini, G. Pampaloni, F. Marchetti, L. Biancalana, *under revision*.

PA09

Efficient Ir-Catalysts for the Asymmetric Hydrogenation of Challenging Substrates

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Asymmetric catalysis is a widely used approach to fulfill the ever-increasing demand for chiral molecules. From particularly interest, the asymmetric hydrogenation of olefins has emerged as one of the most powerful methodology for the synthesis of these compounds. While the asymmetric hydrogenation of functionalized olefins has been comprehensively studied and can now be considered a mature field, the hydrogenation of unfunctionalized olefins remains a less developed area and the search for more efficient ligands is still needed.[1] Our group has expertise in preparing modular and easy to handle ligand libraries from readily available materials. The design of these ligands have resulted in the development of highly effective catalysts for the asymmetric hydrogenation of a variety of non-chelating olefins with differing geometry, substitution patterns, and levels of functionalization.[2] These air-stable and readily available catalysts provided excellent enantioselectivities (ee's up to 99%) in the asymmetric hydrogenation of several challenging di- and trisubstituted alkenes as well as in the more demanding tetrasubstituted olefins. Moreover, by combining DFT calculations with experimental, we have identified the key factors responsible for enantioselectivity, allowing the rationalization of the most suitable substrates for these catalysts.

References

[1] (a) J. J. Verendel, O. Pam̀ies, M. Dieǵuez, P. G. Andersson, *Chem. Rev.* **2014**, *114*, 2130–2169. (b) C. Margarita, P. G. Andersson, P. G. *J. Am. Chem. Soc.* **2017**, *139*, 1346–1356.

[2] (a) M. Biosca, M. Magre, O. Pàmies, M. Diéguez, *ACS Catal.* **2018**, *8*, 10316–10320. (b) M. Biosca, E. Salomó, P. de la Cruz-Sánchez, A. Riera, X. Verdaguer, O. Pàmies, M. Diéguez, *Org. Lett.* **2019**, *21*, 807–811. (c) M. Biosca, P. de la Cruz-Sánchez, J. Faiges, J. Margalef, E. Salomó, A. Riera, X. Verdaguer, J. Ferré, F. Maseras, M. Besora, O. Pàmies, M. Diéguez, *ACS Catal.* **2023**, *13*, 5, 3020–3035.

PA10

Unravelling the Mechanism of the Guerbet Reaction Catalyzed by a Ruthenium Catalyst: a Synergistic Computational and Experimental Study

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Fabrizio Cavani,[1,2] Fahmi Himo,[3] Ivan Rivalta[1,2,4] and Rita Mazzoni.[1,2]

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The Guerbet reaction promises to provide biofuels alternative to gasoline, by catalytically upgrading (bio)ethanol to higher alcohols. However, this reaction has challenging the scientific community for decades, being its mechanism still far to be fully understood, hampering the development of more efficient catalysts.[1] Our group has recently reported a promising ionic Ruthenium(0) catalyst active for this process in mild conditions and in the presence of a base co-catalyst.[2,3] Here, we report the characterization of the reaction mechanism for the Guerbet reaction catalyzed by a neutral Ru(0) catalyst (**1**), also active in mild conditions. The complex reaction mechanism was elucidated following a synergistic approach involving density functional theory (DFT) calculations, kinetic simulations, and various experimental measurements (see Figure 1), paving the way for the rational design of a new class of catalysts active in the homologation of (bio)ethanol.

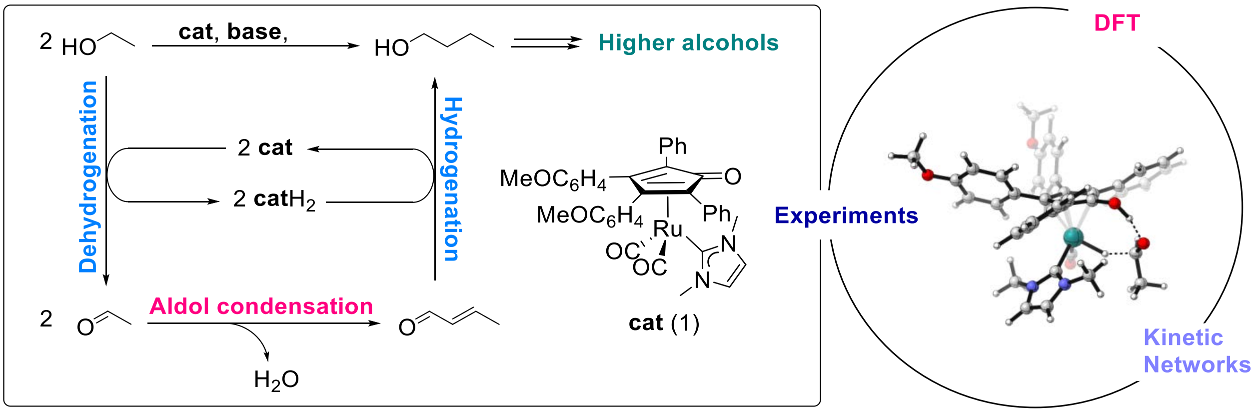

Figure 1. The combined experimental and computational approach for studying the Ru-catalysed Guerbet reaction.

References

[1] Messori, A. *et al. Catal. Today* (2023). doi:https://doi.org/10.1016/j.cattod.2023.01.010.
[2] Mazzoni, R. et al. *ACS Sustain. Chem. Eng.* **7**, 224–237 (2018).
[3] Cesari, C. *et al. J. Catal.* **405**, 47–59 (2022).

PA11

Synthesis, Structure and Properties of Low-Valent Monocyclopentadienylchromium Hydride Complexes

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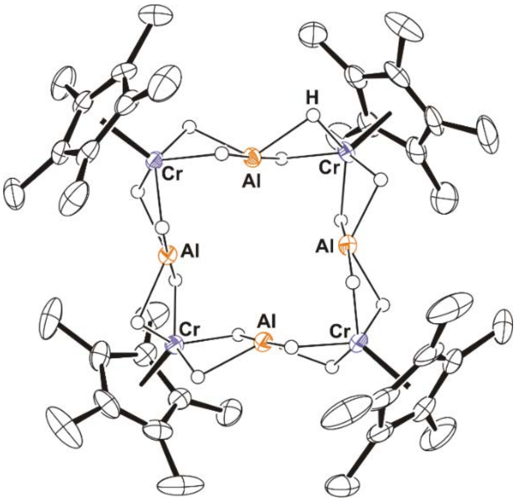
Early transition metal complexes in low oxidation states are highly reducing species with a great number of applications as reagents or promotors for small-molecule activation, such as dinitrogen.[1] Over the last few years we have been involved in the study of the synthesis and reactivity of monocyclopentadienyl compounds of group 4 metals in low oxidation states. For instance, we recently described a series of low-valent titanium complexes stabilized with aluminum/boron hydride fragments.[2] Furthermore, we achieved the conversion of dinitrogen to ammonia under ambient conditions employing [TiCp*Cl$_3$] (Cp* = η^5-C_5Me_5) with Mg and HCl via a mixed-valence polynuclear titanium species.[3]

Based on these results, we have now extended our studies to other early transition metal systems. In this communication, we will present several low-valent chromium species obtained by treatment of the readily available [(CrCp*Cl$_2$)$_2$] and [(CrCp*Cl)$_2$] precursors with a variety of reagents such as $LiBH_4$ and $LiAlH_4$. These reactions lead to polyhydride chromium(II) and chromium(III) complexes (an example is shown in the Figure), some of which show singular structures and bonding interactions.



We thank the Universidad de Alcalá for the financial support of this research (PIUAH22/CC-049 and UAH-GP2022-4) and a predoctoral fellowship (A.C.-M.). J.J. acknowledges the Spanish Structures of Excellence María de Maetzu program through grant MDM-2017-0767.

References

[1] E. P. Beaumier, A. J. Pearce, X. Y. See, I. A. Tonks, *Nat. Rev. Chem.* **2019**, *3*, 15-34.
[2] E. del Horno, J. Jover, M. Mena, A. Pérez-Redondo, C. Yélamos. *Chem. Eur. J.* **2022**, *28*, e202103085.
[3] E. del Horno, J. Jover, M. Mena, A. Pérez-Redondo, C. Yélamos. *Angew. Chem. Int. Ed.* **2022**, e202204544.

PA12

A Versatile and Commercially Available Iron Catalyst Active in Carbene Transfer Reactions

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The development of C-H functionalization reactions catalyzed by non-precious metals is an important aim for gaining sustainability in chemical synthesis. In 1992, Hossain reported the first example of carbene transfer reactions using iron as a catalyst, $[CpFe(CO)_2(THF)]BF_4$.[1] With this as a starting point, over the past decades iron has exhibited promising results in this field.[2]

Our group has previously described a synergy between an iron catalyst, $[Fe(^{F}pda)(THF)]_2$, and a lithium aluminate salt, $Li[Al(OC(CF_3)_3)_4]$. The aforementioned catalyst activates azoesters under mild conditions promoting both intramolecular and intermolecular functionalization of strong Csp^3-H bonds via carbene insertion.[3,4]

During our research we have been able to identify a much simpler and manageable catalyst, $[Fe(acac)_3]$, that, upon previous activation, exhibits superior performance. $[Fe(acac)_3]$ has shown excellent selectivity practically avoiding the formation of “hydride shift” side products. Of important to note is that $[Fe(acac)_3]$ is commercially available, cheap, and air/moisture stable. Finally, $[Fe(acac)_3]$ has proven to be a versatile catalyst achieving good yields in intermolecular C-H insertion and cyclopropanations reactions, and it is also able to access to Buchner ring expansion products generating cycloheptatrienes derivatives.

References

[1] W. J. Seitz, A. K. Saha, M. M. Hossain, *Organometallics* **1993**, *12*, 2604.
[2] C. Damiano, P. Sonzini, E. Gallo, *Chem. Soc. Rev.* **2020**, *49*, 4867.
[3] A. Hernán-Gómez, M. Rodríguez, T. Parella, M. Costas, *Angew. Chem. Int. Ed.* **2019**, *58*, 13904.
[4] M. Rodríguez, G. Font, J. Nadal-Moradell, A. Hernán-Gómez, M. Costas, *Adv. Synth. Catal.* **2020**, *362*, 5116.

PA13

NCP Pincer Iridium Complex: Synthesis, Structure and Reactivity

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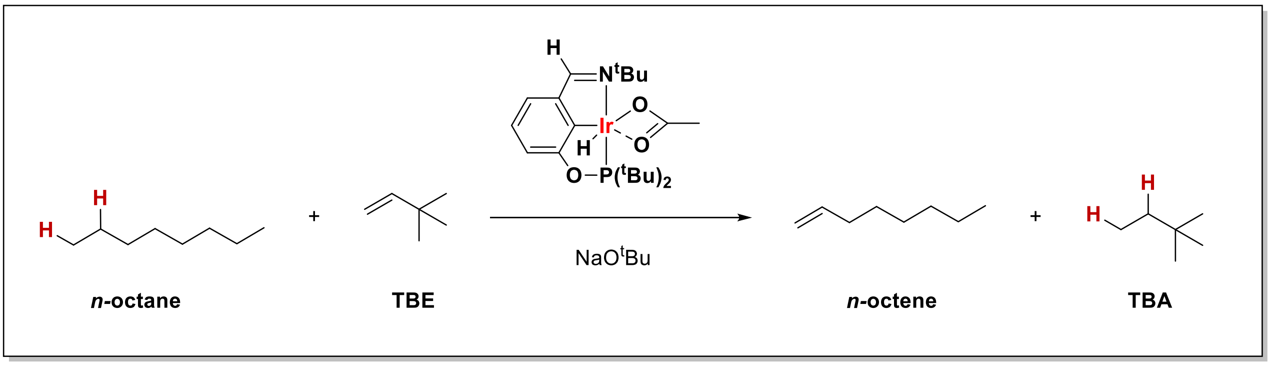
The dehydrogenation of alkanes to obtain olefins is widely studied with different Iridium pincer systems.[1] This reaction holds tremendous potential as the olefins can be subsequently functionalised to various other higher value-added chemicals.[2,3] Herewith, we describe an Iridium complex with an iminophosphinite (NCP) pincer ligand. The synthesis was achieved by metalation of the NCP ligand with $[Ir(cod)OAc]_2$ to obtain the desired [(NCP)Ir(H)(OAc)] complex. The structure of the complex was established by NMR and XRD studies. The crystal structure revealed that the imine group is intact after coordination to the metal centre. The complex contains a vacant coordination site, that could be reacted with CO, to obtain the saturated complex [(NCP)Ir(CO)(H)(OAc)] . The complex was also tested for the transfer dehydrogenation of alkanes using tert-butlylethylene as the H_2 acceptor. It shows catalytic activity, performing reasonably well as a catalyst.



References

[1] A. Kumar.; T.M. Bhatti.; A.S. Goldman. *Chem. Rev.* 2017, 117, 12357–12384.
[2] Jia, X.; Huang, Z. *Nat. Chem.* 2016, 8, 157–161.
[3] Leitch, D. C.; Labinger, J. A.; Bercaw, J. E. *Organometallics* 2014, 33, 3353–3365.

PA14

Tp$_x$Cu(I) complexes as efficient catalysts for the radical aminocyclization of alkenes

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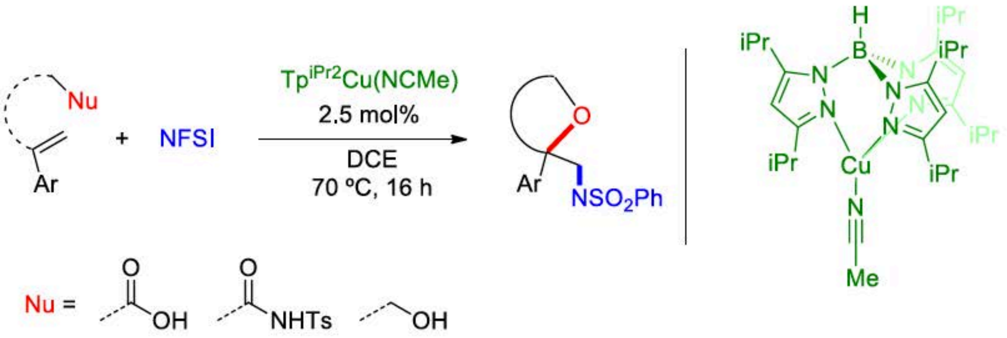
Oxygen- or nitrogen-containing heterocycles are significant molecular scaffolds for bioactive molecules, pharmaceuticals, and natural products.[1] Therefore, great effort has been made to develop convenient and green routes for their synthesis.[2] A particularly interesting approach is the radical aminooxygenation of alkenes. When an electrophilic amino source is used as the oxidant, the reaction shows high chemo- and regioselectivity.[3] For instance Zhang and Qi used this strategy for the copper catalyzed amino lactonization of alkenes with NFSI (*N*-fluorobenzenesulfonimide) as the amino source.[4]

Our group has previously reported the use of Tp^{x}Cu complexes (Tp^x = hydrotrispyrazolylborate ligand) as catalysts in ATRA (atom transfer radical addition) reactions of polyhalogenated compounds to olefins[5] and in the intramolecular C–H activation of *N*-fluorinated amines for the formation of piperidines and pyrrolidines.[6] Based on these precedents, herein we present the results obtained in the synthesis of heterocyclic compounds, in moderate to high yields, by the reaction of a variety of alkenes and NFSI catalyzed by TpxCu complexes (Scheme 1).



Scheme 1. Radical aminooxygenation of alkenes with NFSI catalyzed by Tp^{x}Cu complexes.

References

(1) (a) Karmakar, R.; Pahari, P.; Mal, D. *Chem. Rev.* **2014**, *114*, 6213–6284. (b) Huang, J.-M.; Yokokawa, R.; Yang, C.-S.; Fukuyama, Y. *Tetrahedron Lett.* **2000**, *41*, 6111–6114.
(2) Cossy, J., Ed. Synthesis of Saturated Oxygenated Heterocycles I: 5- and 6-Membered Rings; Springer, 2014.
(3) Muñoz-Molina, J. M.; Belderrain, T. R.; Pérez, P. J. *Synthesis* **2021**, *53*, 51–64.
(4) Xie, J.; Wang, Y.-W.; Qi, L.-W.; Zhang, B. *Org. Lett.* **2017**, 19, 1148–1151.
(5) Muñoz-Molina, J. M.; Belderraín, T. R.; Pérez, P. J. *Inorg. Chem.* **2010**, *49*, 642–645.
(6) Bafaluy, D.; Muñoz-Molina, J. M.; Funes-Ardoiz, I.; Herold, S.; de Aguirre, A. J.; Zhang, H.; Maseras, F.; Belderrain, T. R.; Pérez, P. J.; Muñiz, K. *Angew. Chem. Int. Ed.* **2019**, *58*, 8912–8916.

PA15

Silicon Compounds as Catalysts for Limonene Polymerization

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Conventional petroleum-derived plastics are essential in everyday life. However, it must not be forgotten that their use results in a significant problem for the environment due to their long life cycle and also that petroleum use has led to a geo-economic dependence on some oil-producing countries.[1]

Limonene is a naturally occurring compound belonging to the terpene family, widely found in citrus fruits, particularly orange and lemon peels. It is commonly used as a flavouring agent in food and cosmetic products.[2]

Our research focuses on the polymerization of limonene extracted from orange peel waste, using a cationic silicon compound as the catalytic system. This catalyst is readily prepared from a silicon halide pre-catalyst using silver triflate as the abstracting agent. The cationic nature of the system and the fact that the polymerization proceeds better in polar solvents led us to consider a cationic mechanism for the polymerization. The effect of temperature, pre-catalyst:silver salt ratio, and time has been studied in order to optimize towards the formation of polymers with a high molecular weight. Thus far, oligomers have been obtained and GPC weight analysis has suggested very short chains of only 4 or 5 limonene units. However, these chain lengths make them ideal as plasticizers when mixed with other bio-based polymers.[3] As a result of these initial findings, we are studying the effect on the thermal properties studied by thermal gravimetric analysis (TGA) of the films obtained from mixtures of polylactic acid (PLA) [4] and polylimonene.

Additionally, the known bactericidal properties of the limonene have directed us to study the potential of these polylimonenes. We have observed that these oligomers act as bacterial killers so new properties for the materials obtained could be expected. Further, to confer another property, thiol-ene click chemistry has been used to prepare novel functionalized polymers containing amino groups or a more hydrolysable moiety.

References

[1] Thakur, S.; Chaudhary, J.; Sharma, B.; Verma, A.; Tamulevicius, S.; Thakur, V. K. Sustainability of Bioplastics: Opportunities and Challenges. Current Opinion in Green and Sustainable Chemistry 2018, 13, 68–75.
[2] Ciriminna, R.; Lomeli-Rodriguez, M.; Demma Carà, P.; Lopez-Sanchez, J. A.; Pagliaro, M. Limonene: A Versatile Chemical of the Bioeconomy. Chem. Commun. 2014, 50 (97), 15288–15296.
[3] A. Brito, C.; C. Silvino, A. A Brief Review of the Use of Limonene Derivative as a Promising Monomer in the Synthesis of Biodegradable Polymers. Rev. Virtual Quim. 2021, 13 (4), 1017–1041.
[4] Alam, J.; Alam, M.; Raja, M.; Abduljaleel, Z.; Dass, L. MWCNTs-Reinforced Epoxidized Linseed Oil Plasticized Polylactic Acid Nanocomposite and Its Electroactive Shape Memory Behaviour. IJMS 2014, 15 (11), 19924–19937.

PA16

Molecular Metal Carbonyl Clusters and Nanoclusters for Catalytic Applications

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Metal carbonyl clusters (MCCs) and higher-nuclearity molecular clusters may be viewed as perfectly monodisperse and atomically defined metal nanoparticles. Therefore, nanoclusters (NCs) have recently emerged as a promising class of metal NPs attracting an increasing interest from both a fundamental and applicative point of view. Different chemical and physical properties may arise, and these can find several applications particularly regarding catalysis.

In this framework, heterometallic clusters containing polar metal–metal interactions are attracting interest for the activation of small molecules and catalytic applications. Herein we report some examples including ammonia-borane dehydrogenation by bimetallic Co–M(NHC) and Fe–M(NHC) carbonyl clusters,[1] and heterometallic Ru–M (M = Cu, Ag, and Au) clusters as catalyst precursors for transfer hydrogenation reactions.[2]

Furthermore, we recently reported the synthesis of a series of Ni–Pt Chini-type clusters that may be viewed as random alloy clusters, since their composition can be varied in a continuous way.[3] Then, these compounds have been employed as molecular precursors for the preparation of heterogeneous catalysts based on well-defined finely dispersed nanoparticles supported on TiO_2 for redox reactions (Figure 1), such as 5-hydroxymethylfurfural (HMF) oxidation to 2,5-Furandicarboxylic acid (FDCA).

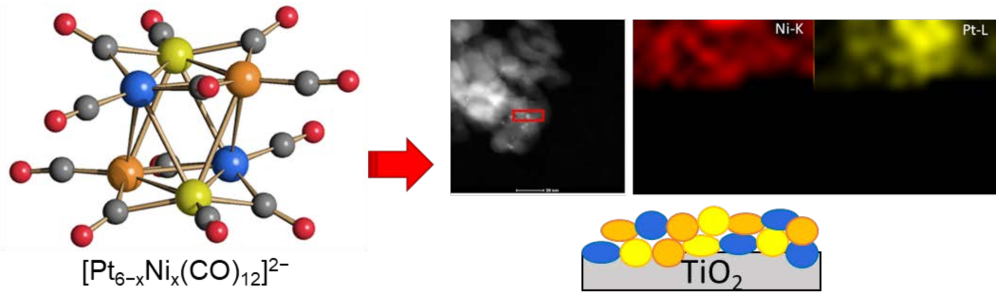

Figure 1. Preparation of PtNi nanoparticles from metal carbonyl clusters.

References

[1] C. Cesari, B. Berti, F. Calcagno, C. Lucarelli, M. Garavelli, R. Mazzoni, I. Rivalta, S. Zacchini, *Organometallics*, **2021**, *40*, 2724.
[2] C. Cesari, M. Bortoluzzi, F. Forti, L. Gubbels, C. Femoni, M. C. Iapalucci, S. Zacchini *Inorg. Chem.* **2022**, *61*, 14726.
[3] C. Cesari, B. Berti, M. Bortoluzzi, C. Femoni, M. C. Iapalucci, S. Zacchini, *Inorg. Chem.* **2021**, *60*, 8811; C. Cesari, B. Berti, M. Bortoluzzi, C. Femoni, T. Funaioli, F. M. Vivaldi, M. C. Iapalucci, S. Zacchini, *Dalton Trans.*, **2023**, *52*, 3623.

PA17

Synthesis and reactivity of ring-expanded N-heterocyclic carbene supported copper(I) p-block compounds

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The addition of p-block element containing functional groups to organic molecules can significantly tune their structure, bonding, and reactivity. In spite of this, the synthesis of transfer agents of these groups are underdeveloped compared to their carbon analogues. Copper(I) catalysis facilitates a plethora of organic transformations, but less work has been conducted in the generation of main group element-element bonded compounds. During this talk we will discuss our work in generating a "p-block" of copper(I) element compounds and their reactivity in both stoichiometric and catalytic transformations.

Employing the use of ring-expanded NHCs (RE-NHCs), we have synthesised a range of ligand supported copper(I) boryl, tetranide, and phosphide compounds from σ-bond metathesis reactions. They generally form linear, two-coordinate monomers and persistently acted as a source of p-block nucleophile which react with organic and inorganic electrophilic substrates generating unique insertion compounds and element-element bonds. The prodigious steric imperative of RE-NHCs allowed for the isolation of reactive intermediates providing mechanistic insights.

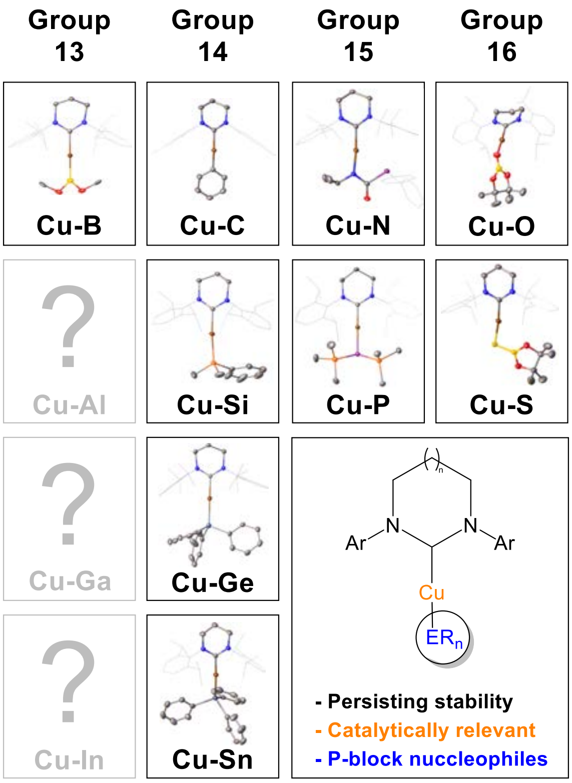

Figure 1. A partial p-block of NHC-supported copper(I) element compounds.

In this talk, we will highlight how through judicious selection of the reactive groups on the p-block element centre, we were able to generate unprecedented copper(I) boryl anions and low coordinate phosphorus compounds.

PA18

Substituted diiminoisoindoles as promising ligands for coordination and organometallic chemistry

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Isoindole and its derivatives already found application in multiple fields of chemistry. Among others use as pharmaceuticals, resistant isoindoline and isoindolinone pigments and building blocks for phthalocyanines can be mentioned.[1] However, their use as ligands in coordination and organometallic chemistry is still poorly explored.

Therefore, we decided to prepare series of isoindole-based protoligands and examine their reactivity with alkali and alkaline earth metals and also with selected transition and post-transition metals. Prepared acyl substituted diiminoisoindoles possess carbonyl group, which allows them typically to form six-member metallacycles as in case of potassium or aluminium. In case of coinage metals and zinc formation of dinuclear complex compounds is observed. Some of the prepared dinuclear complexes even contain remarkable metallophilic interactions.

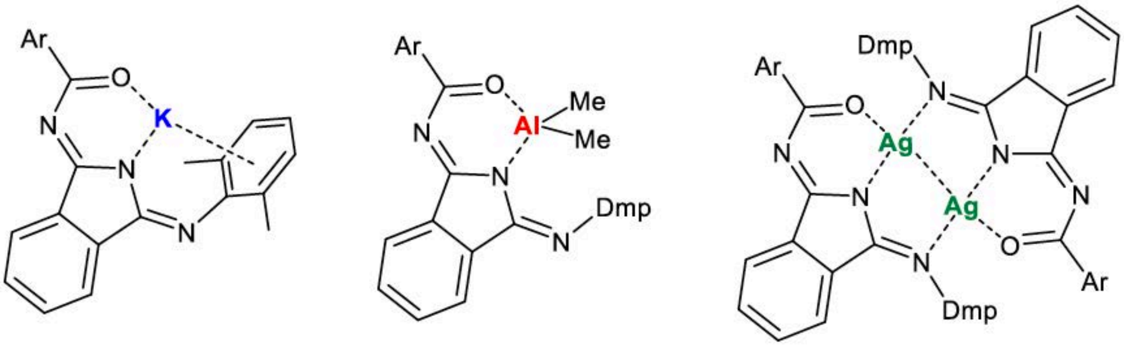

Figure 1. Metallacyclic compounds of diiminoisoindoles.

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References

1 (a) K. Speck and T. Magauer, Beilstein J. Org. Chem., 2013, 9, 2048. (b) W. Herbst, K. Hunger and G. Wilker et al., Azo Pigments. In Industrial Organic Pigments; Wiley, Weinheim, 2004, Vol 3, p 417.

PA19

Directed Exploration of Chemical Space for the Generation of Molecular databases

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The unique properties of molecular complexes have impelled their applications in therapeutics, catalysis, and supramolecular chemistry.[1] Despite their prevalence, rational design of coordination compounds still proves challenging owing to the cost and complexities associated with experimental synthesis. Computational exploration of the vast chemical space that these compounds inhabit provides an opportunity to facilitate and accelerate this design process.

In this presentation we introduce a modular and versatile workflow to enable the generation of bottom-up molecular databases from a library of *ca.* 50,000 ligands extracted from the Cambridge Structural Database (CSD).[2] The workflow includes a method for assigning formal charges to each ligand based on previous work by Duan et al.[3] In addition, a series of filters are implemented to enable the user to target ligand properties of interest, including atomic composition, charge, and coordinating atom types. Novel molecular complexes with the desired topology are then assembled based on a user-specified set of instructions using the user-curated set of unique ligands. Ultimately, we envisage this automated workflow accelerating molecular discovery through applications in high throughput screening.

References

[1] Turel, I. *Molecules*. **(2015)**. *20*(5), 7951–7956.
[2] Sommer, T., Clarke, C., Kleuker, F., García-Melchor, M. Manuscript in preparation.
[3] Duan, C., Ladera, A. J., Liu, J. C.-L., Taylor, M. G., Ariyarathna, I. R., Kulik, H. J. *J. Chem. Theory Comput.*, **(2022),** *18*(8), 4836–4845.

PA20

Towards Phosphorus Cations as Main Group Catalysts

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Dependence on an ever-dwindling supply of transition metals (TMs) for their catalytic ability necessitates research into the development of candidates based on more-abundant elements[1]. Phosphenium cations, divalent phosphorus centres with a positive charge, have been shown to be effective main group catalysts in reactions such as reductions and hydroborations and are of interest for their potential in Frustrated Lewis Pair (FLP) chemistry[2]. The aim of this work is to determine the catalytic viability and potential scope of a number of phosphenium cations through the synthesis and subsequent analysis of catalytic candidates, with the view to provide viable alternatives to their well-established and widely employed TM counterparts.

Bis(arylimino)acenaphthene (Ar-BIAN, Figure 1 left) ligands are rigid, redox noninnocent diimines. Insertion of phosphorus into the ligand through reaction with phosphorus trihalides and subsequent anion exchange affords the isolated phosphenium cation (Figure 1 right)[3]. These are elements of a particular subset of phosphenium cations refered to as N-heterocyclic phosphenium cations (NHPs) characterised by the formation of a 5-member aromatic ring.

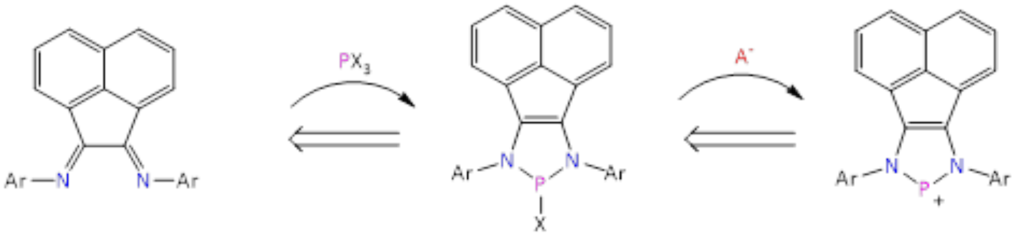

Figure 1: Insertion of phosphorus centre into bis(arylimino)acenaphthene (Ar-BIAN) ligands and isolation of the phosphenium cation.

In this project the Ar-BIAN ligands were synthesised, phosphenium cations isolated and their reactivity against a number of substrates was investigated. It is hoped that this work will add to the library of existing phosphenium cations, as well as provide the reactivity studies required for the determination of their catalytic viability.

References

[1] C. Wilkins, R. L. Melen, *Coord. Chem. Rev.* **2016**, *324*, 123-139
[2] D.W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306–316.
[3] J.W. Dube, G.J. Farrar, E. L. Norton, K.L.S. Szekely, B.F.T. Cooper, C.L.B. Macdonald, *Organometallics* **2009** *28* (15), 4377-4384.

PA21

Iridium-Cp* Complexes bearing Chelating Ligands: Catalytic Applications

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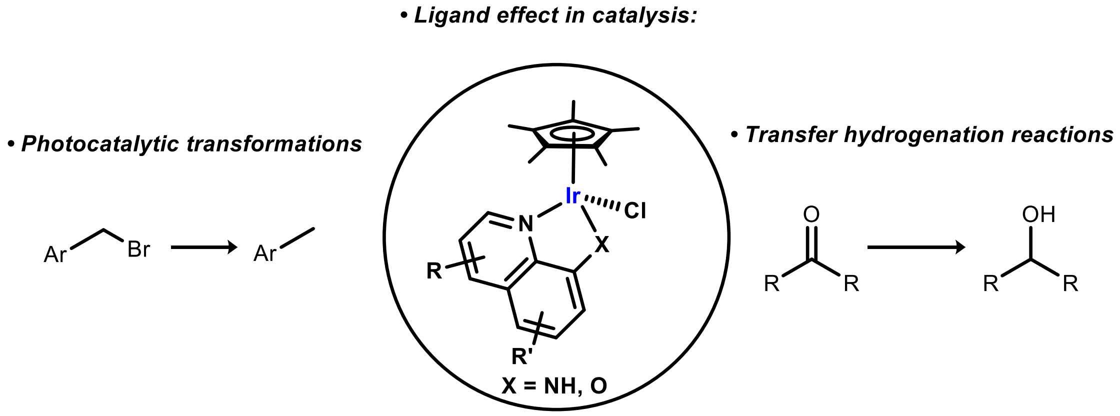
Iridium complexes have been shown to be excellent catalysts for a wide variety of classical homogenous catalytic processes and photocatalytic transformations.[1,2] In this area, piano-stool IrCp*-derivatives have been widely employed in organometallic catalysis but have attracted much less attention as photocatalysts. In our search for new and more efficient photocatalysts, we have studied the photocatalytic potential of such species.

In this communication, we present the synthesis and full characterization of complexes of formula [Ir(Cp*)(LX)Cl] where LX is a chelating ligand derived from hydroxy-and aminoquinolines.[3] The ligand effect in the photocatalytic reactivity of the complexes as well as in traditional homogeneous catalysis will be discussed.



References

[1]. Iridium Complexes in Organic Synthesis, 2008; Ed: L. Oro and C. Claver, Wiley-VCH

[2]. Teegardin, K.; Day, J. I.; Chan, J.; Weaver, J., Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations. *Org. Process Res. Dev.* **2016,** *20*, 1156-1163.

[3]. Hong, S. Y.; Park, Y.; Hwang, Y.; Kim, Y. B.; Baik, M.-H.; Chang, S., Selective formation of γ-lactams via C–H amidation enabled by tailored iridium catalysts. *Science* **2018,** *359*, 1016.

PA22

Group 13 aminobisphenolate pyridyl complexes as catalysts for the synthesis of cyclic carbonates

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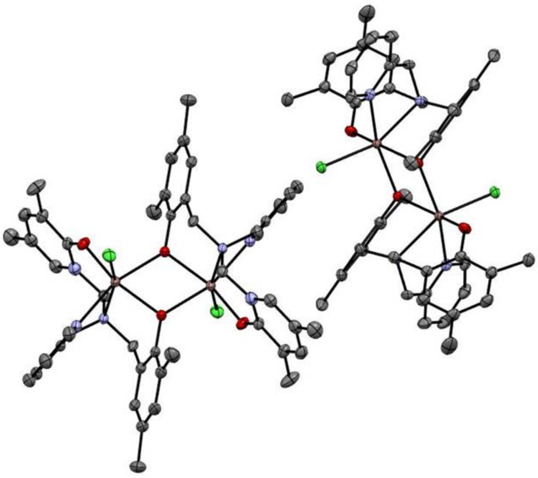
Carbon dioxide is the largest component of the emitted greenhouse gases, and the global CO_2 emissions increase generated by humans, contribute to the global climate change. But also, carbon dioxide can be considered as a nontoxic, abundant, low-cost, and renewable resource.[1] Nevertheless, the presence of two covalent double bonds in the structure of CO_2 makes this molecule thermodynamically stable and kinetically inert.[2]

In our group we are focused in the design of catalysts for the formation of cyclocarbonates from epoxides and CO_2. In this type of reactions Aluminium has been widely used as catalyst but the use of Ga or In complexes has been poorly explored.[3] Recently, we have reported a highly active Ga catalyst based on tris(3,5-dimethyl-2-oxidaneyl)benzyl)amine ligand. In this work we extended the studies to the N,N-Bis(2-hydroxy-3,5-dimethylbenzyl)-N-(2-pyridylmethyl)amine ligand. Hence, we prepared new group 13 compounds with a halogen ligand completing the coordination sphere of the metal. All of them show a good activity in mild conditions (60°C, 1 bar CO_2 pressure).



References

[1] Q. Liu, L. Wu, R. Jackstell, M. Beller, Nat. Commun. 2015, 6, 5933.

[2] T. Sakakura, J.C. Choi, H. Yasuda, Chem. Rev. **2007**, 107,2365–2387.

[3] (a) D. Prasad et al, Catalysis Reviews. **2022**, 64, 2, 356-443; (b) L. Álvarez-Miguel, J. Damián Burgoa, M. E. G. Mosquera, A. Hamilton, C. J. Whiteoak, *ChemCatChem*. **2021**, 13, 4099-4110.

PA23

Zn(II) based carbosilane metallodendrons as potential candidates for the topical treatment of bacterial infections

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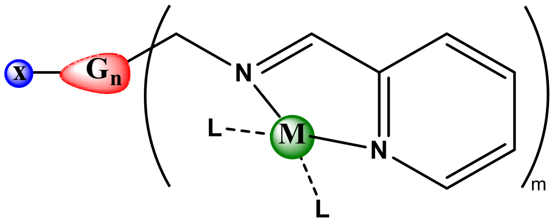
Metallodendrimers are making their own way as promising strategies in the biomedical field, since these nanometric-sized molecules combine, in a single molecule, the properties of the dendrimers with those of the transition metals, adding the features of their multivalence and nanoscopic size[1]. In particular, carbosilane metallodendrimers and metallodendrons comprising iminopyridine ligands bound to Ru(II) or Cu(II) have shown significant antitumor and antibacterial activity[2].

This project focuses in the synthesis and characterization of different iminopyridine-decorated carbosilane metallodendrons, suitable for the coordination of Zn(II) metal centers. These bifunctional systems present multiple metal complexes at the periphery and an additional moiety in the focal point, available for post-functionalization purposes. This study evaluates the impact of different metal counterions, and the multivalency through techniques such as NMR, IR, or elemental analysis. Synthesis, structural characterization, and antibacterial activity of all compounds is reported. Finally, selected compounds were formulated as cream and their diffusion through skin-mimicking membranes was performed, to evaluate their potential as antibacterial agent candidates for topical treatments.



n=1; m=2
n=2; m=4
n=3; m=8

M = Zn(II); L=Cl,NO_3, H_3CCOO

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References

(1) Sanz del Olmo, et al. Metallodendrimers as a Promising Tool in the Biomedical Field: An Overview. *Advances in Organometallic Chemistry* **2020**, *74*, 1–52

(2) Carloni, R., et al. . Elaborated Study of Cu(II) Carbosilane Metallodendrimers Bearing Substituted Iminopyridine Moieties as Antitumor Agents. *Eur J Med Chem* **2021**, *215*, 113292

PA24

A Systematic Study of Group 13 Compounds based on Salphen ligands as Catalysts for Cyclic Carbonate Synthesis

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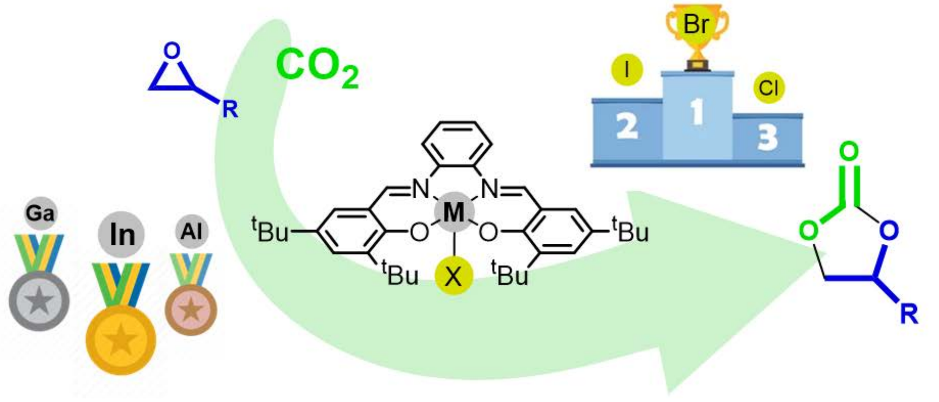
The synthesis of cyclic carbonates through the atom efficient coupling of epoxides to carbon dioxide (CO_2) presents an interesting application of CO_2 as a C1 reagent. Over recent years, a large number of catalysts have been reported, focusing on readily prepared ligands, for example, Salphens[1] and aminotrisphenols.[2] Regarding group 13 metals, it is notable that most reports have focused on the use of aluminium-based compounds likely because of the well-established Lewis acidity and its cost. However, little attention has been paid to the use of heavier group elements (gallium and indium).



This work studies the synthesis of aluminium, gallium and indium salphen compounds with variation of the halide ligand, and explores the potential of the compounds obtained as catalysts for the synthesis of cyclic carbonates. The effects of changing the metal centre and halogen on the structure and catalysis show unexpected trends which are discussed and fully supported through a complete DFT study.

References

[1] (a) Wu, X.; North, M.; *ChemSusChem* **2017**, *10*, 74-78; (b) Castro-Osma, J. A.; North, M.; Wu, X.; *Chem. Eur. J.* **2016**, *22*, 2100-2107; (c) Castro-Osma, J. A.; Lamb, K. J.; North, M.; *ACS Catal.* **2016**, *6*, 5012-5025.
[2] Alvarez-Miguel, L.; Damian Burgoa, J.; Mosquera, M. E. G.; Hamilton, A.; Whiteoak, C. J.; *ChemCatChem* **2021**, *13*, 4099-4110.

PA25

Boron-copper 1,3-rearrangement: the new concept behind the boryl migration from C(sp^2) in alkenyl boranes to C(sp^3)

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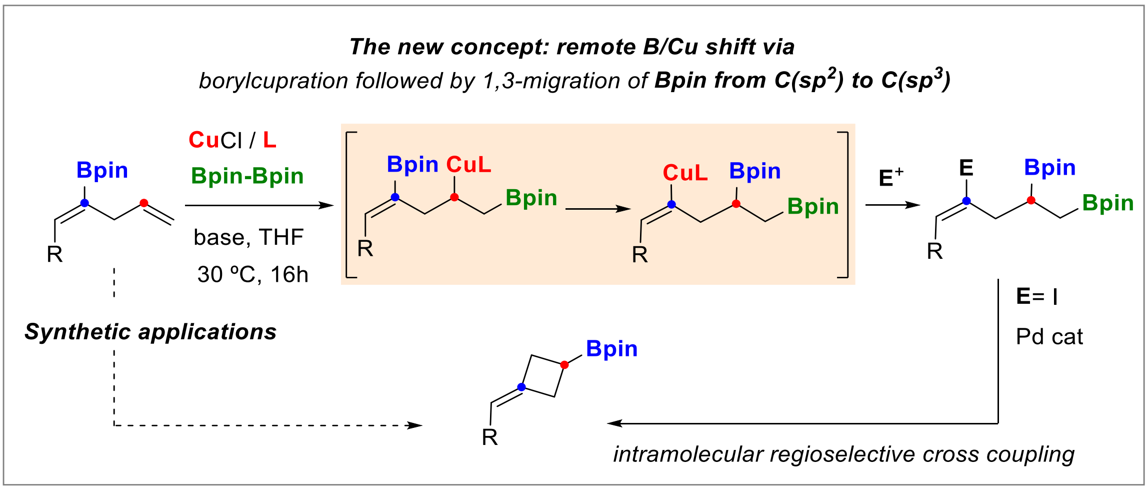
Herein, we describe a regioselective borylcupration of borylated skipped (Z)-dienes that generates diborylated alkyl copper species which are involved in an intramolecular stereospecific B/Cu 1,3-rearrangement by migration of Bpin moiety from C(sp^2) to C(sp^3)[1]. Mechanistic studies suggested the formation of a 4-membered boracycle intermediate and a moderate free-energy barrier (19.4 kcal·mol^{-1})[2].

This unprecedented carbon-to-carbon boryl migration takes place stereospecificity around the alkene, leading to subsequent stereoselective electrophilic trapping. Finally, the utility of these novel homoallyl diborated products is demonstrated by using palladium-catalyzed regioselective intramolecular cross-coupling to synthesize alkylidenecyclobutanes. These highly strained, yet stable, molecules are commonly found in biologically active natural products[3].



References

1 A. Holownia, Ch. N. Apte, A. K. Yudin, *Chem.Sci.* **2021**, *12*, 5346.

2 R. J. Maza, J. Royes, J. J. Carbó, E. Fernández, *Chem. Commun.,* **2020**, *56*, 5973.

3 a) A. Brandi, S. Cicchi, F. M. Cordero, A. Goti, *Chem. Rev.* **2014**, *114*, 7317; b) F. Wang, S. Yu, X. Li, *Chem. Soc. Rev.* **2016**, *45*, 6462.

PA26

Zwitterionic-type ligand-coated zinc oxide quantum dots engineered by the organometallic approach

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The nanocrystalline wurtzite core of zinc oxide quantum dots (ZnO QDs) is the essential element of this semiconductor nanomaterial. No less important is the outer organic stabilising shell. The nanoparticle morphology and structure/composition significantly impact the physiochemistry properties and allow further functionalisation.

The presented results continue research to obtain high-quality ZnO QDs by controlled hydrolysis and oxidation of organometallic precursors [1,2]. In the first crucial step, the synthetic procedure assumes the formation of an organozinc complex from a dialkylzinc compound and an appropriate organic ligand. In this case, the ligand is a zwitterionic compound classified as an amphoteric surfactant. Finally, luminescent ZnO QDs are obtained with a core diameter in the so-called "quantum-size regime" range by exposing the reaction mixture to air. The obtained nanoparticles form stable colloidal solutions in a wide range of organic solvents.

One of the materials was successfully tested as an electron transport layer in a perovskite photovoltaic cell, obtaining a record-breaking solar energy conversion factor for this type of construction. Also, earlier ZnO QDs from our team were tested in the same role in perovskite photovoltaic cells, achieving high efficiency and stability during work [3,4].

References

[1] M. Terlecki, M. Wolska-Pietkiewicz, G. De Paëpe, J. Lewiński et al., *Advanced Functional Materials*, **2021**, 49, 2105318.
[2] M. Wolska-Pietkiewicz, M. Jędrzejewska, J. Wielgórska, J. Lewiński et al., *Chemical Engineering Journal*, **2023**, 455, 140497.
[3] R.D. Chavan, M. Wolska-Pietkiewicz, M. Jędrzejewska, C.K. Hong, J. Lewiński et al., *Advanced Functional Materials*, **2022**, 2205909.
[4] R. Runjhun, E. A. Alharbi, Z. Drużyński, M. Wolska-Pietkiewicz, M. Graetzel, J. Lewiński et al., *Journal of the American Chemical Society*, **2023** (under revision).

PA27

Stabilization of Reactive Main Group Compounds by Carbanionic Ligand

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Strong donor phosphines have been synonymous with high efficiency and selectivity in many catalysis reactions such as hydrogenation reactions, C-C and C-X bond formation reactions.[1] Recently, our group reported on ylide-substituted phosphines (YPhos) where a ylide moiety is directly bound to the phosphorus centre leading to increased donor strengths and excellent catalytic activities in a series of gold and palladium catalyzed reactions.[2] We herein extend the idea that the presence of a carbanion directly attached to the phosphorous center would be pushing the limits of phosphine donation. In literature there are very few phosphine ligands with anionic moieties such as isolated reports by Stradiotto[3] and Lavallo[4]. Herein we report the design, synthesis and systematic study of carbanionic phosphines with stabilizing substituents and we examine the impact of deprotonation on the donor strength and use them as ligands for the synthesis of main group compounds.[5]

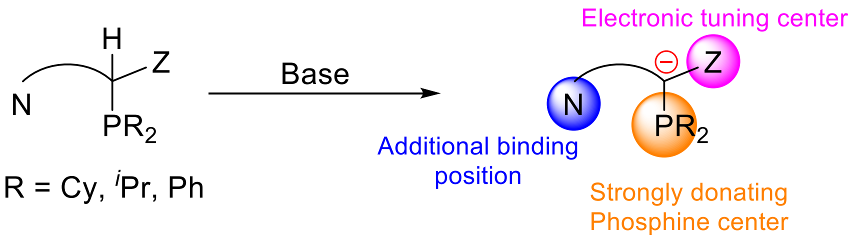

Figure 1. Basic ligand design principle

References

1. a) Torborg, C.; Beller, M. *Adv. Synth. Catal.* **2009**, *351*, 3027; b) Schlummer, B.; Scholz, U. *Adv. Synth. Catal.* **2004**, *346*, 1599; c) Farina, V. *Adv. Synth. Catal*. **2004**, *346*, 1553; d) Ager, D. J.; de Vries, A. H. M.; de Vries, H. G. *Chem. Soc. Rev*. **2012**, *41*, 3340.
2. Lapointe, S.; Sarbajna, A.; Gessner V. H. *Acc. Chem. Res*. **2022**, *55*, 770-782.
3. Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618-5619.
4. Lavallo, V.; Wright II, J. H.; Tham, F. S.; Quinlivan, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 3172-3176.
5. Zur, J.-A.; Schmidt, M.; Feichtner, K.-S.; Duari, P.; Löffler, J.; Scherpf, T.; Gessner, V.H. *Angew. Chem., Int. Ed.* **2022**, 61, e202203950.

PA28

Ruthenium (II) NHC Complexes in Transfer Hydrogenation

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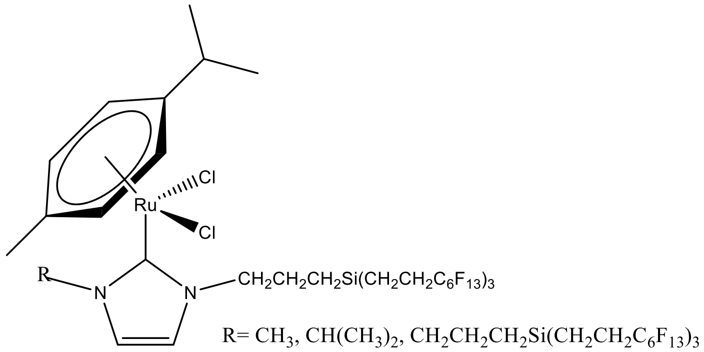
Ru(II)-N-heterocyclic carbene complexes containing three or six fluorous ponytails were prepared. All of these ruthenium complexes were characterized by HRMS, EA and multinuclear NMR spectroscopy. Fluorophilicity (*f*) of fluorinated NHC transition metal complexes were determined by their partition coefficients (*P*) in the standard solvent system (perfluoro)methylcyclohexane/toluene. The Tolman electronic parametr of fluorinated NHC was deteremined by FTIR.



The use of fluorous compounds in catalysis is well known for highly efficient recycling of catalysts. Therefore, the catalytic activity of ruthenium biphasic catalysts was investigated. The catalysts were used in the transfer hydrogenation of cyclohexanone.[1,2]

The fluorous catalysts were recovered at the end of the reaction at room temperature after settling by liquid/liquid separation. The adsorption (physisorption) of the fluorous catalysts on a solid fluorous substrate such as fluorous silica was also investigated.[3]

References

1. Gladysz, J.A.; Curran, D.P.; Horváth I. T. (Eds.) *Handbook of Fluorous Chemistry*; John Wiley & Sons; **2004**, ISBN: 352730617X.
2. Lundgren, R. J., Rankin, M. A., McDonald R., Schatte G., Stradiotto M.; *Angewandte Chem. Int. Ed.*; **2007**, 46, 4732-4735, doi: 10.1002/anie.200700345.
3. Vincent J-M.; *Biphasic Chemistry and The Solvent Case* John Wiley & Sons, **2020**, doi: 10.1002/9781119695080.ch2.

PA29

Understanding Metal-Support Interactions on Cu Catalyzed Atom Transfer Reactions using Immobilized Cu Phenanthroline Complexes

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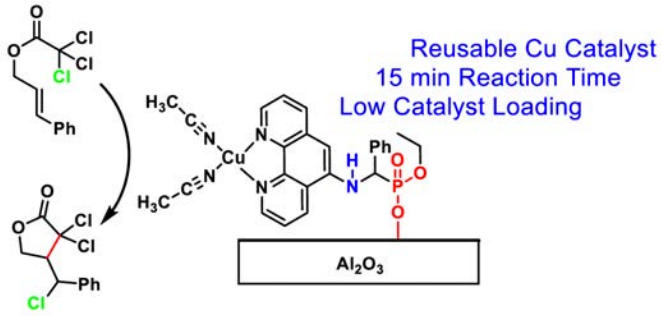
Strong Metal-Support Interactions (SMSIs) occur in supported metal catalysts in heterogeneous catalysis when both the metal and the support (usually a metal oxide) play an intimate role in catalysis (usually through direct bonding with the substrates). Such metal supports are known to occur for many different heterogeneously catalyzed reactions. However, the origins of such metal support interactions are often not well understood. This is partially due to the chemically ill-definde nature of the catalyst surfaces, making it difficult to identify specific metal support interactions spectroscopically.

One technique that has been very successful in understanding heterogeneously catalyzed active sites is Molecular Heterogeneous Catalysis (MHC) in which well defined organometallic complexes are immobilized onto metal oxide surfaces through linker groups. This has traditionally been used to heterogenize organometallic catalysts for use in flow reactions and for easy separation from reaction media. However, what is also possible with this technique is to examine the effect that a nearby surface (and its functionality) has on the chemical reactivity of these catalytically active complexes (when compared to non-immobilized species). Here we report the effect of surface immobilization on the catalytic chemistry of Cu Phenantholine complexes for atom transfer radical cyclizations (ATRC).

Using a simple two-step procedure involving no noble metals, we were able to install a-aminophosphonate esters onto the backbone of phenanthroline. The phosphonate group could then be immobilized on metal oxides in order to heterogenize the ATRC catalyst. Immobilization of phosphonated phenanthroline ligands followed by complexation with either Cu(I) or Cu(II) salts yields immobilized complexes that are active for ATRC reactions. The immobilization works best on Al_2O_3 while SiO_2 gives reduced Cu loadings.

Comparison of the reactivity of the homogeneous complexes versus the immobilized catalysts yields some interesting insights into the metal support interaction of these catalysts. For example, cyclization of trichloroacetate and trichloroacetamide substrates with both the heterogeneous and homogeneous versions occurs extremely rapidly (catalyst loadings as low as 1 mol%, reaction times as short as 15 min). However, the immobilized complexes seem to be more selective for the desired cyclized product than the homogeneous complexes, consistently giving yields greater than 90%. Moreover, this catalyst can be used repeatedly with no decay of selectivity and only slight activity decreases. Additionally, both the Cu(I) and Cu(II) salts can be used with no adverse effects to catalysis. All this suggests that immobilization results in improved catalysis, presumably due to an effect of the surface. Plausible mechanisms of this favorable metal-support interaction are discussed.



Reusable Cu Catalyst
15 min Reaction Time
Low Catalyst Loading

PA30

Highly Stable α,α- Diimine Silver(I) Catalysts that Incorporate CO_2 into Alkynes Frameworks

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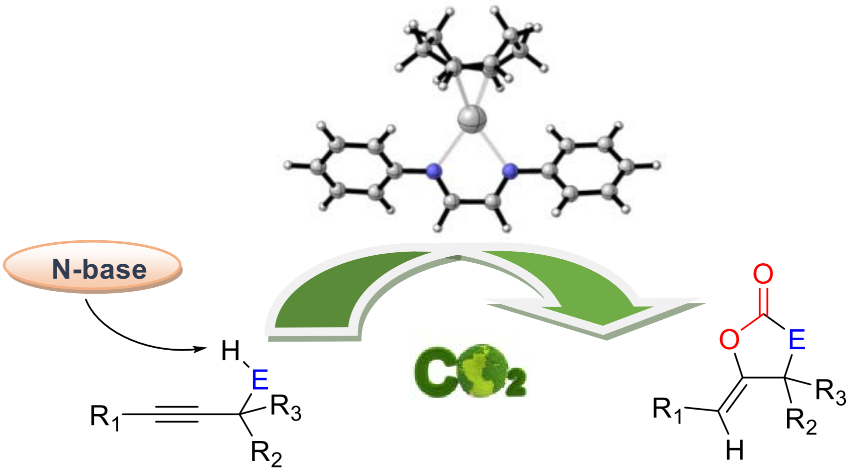
Carbon dioxide is a potentially valuable and highly accessible C1 feedstock. However, the application of this ubiquitous gas in industrial processes is comparably limited due to thermodynamic restraints and general inertness towards C-activation. This work addresses the development of novel room temperature stable cationic silver(I) complexes supported by *N,N'*-chelating α,α-diimines, that demonstrate high alkynophilicity. These complexes are highly efficient in incorporating CO_2 into organic alkynes frameworks,[2,3] affording cyclic carbonates and carbamates under mild conditions. The unusual high stability of these silver(I) pre-catalysts was accomplished by employing a η^2:η^2-chelating cis-cyclo-octadiene which was predicted through DFT calculations and compared to the corresponding Cu(I) and Au(I) analogues. The ability of these novel α,α-diimines silver(I) complexes to catalyse the incorporation of CO_2 into a propargylic alcohols/amines and the subsequent cyclisation was evaluated using a variety of terminal and internal alkynes substrates was evaluated in the presence of different non-nucleophilic nitrogen bases. All reactions were performed at 25 °C under 1 to 6 bars of CO_2 pressure affording the corresponding α-alkylidene cyclic products, which are employed as precursors for drugs and polymers. This family of catalysts shows high conversion at atmospheric CO_2 pressure, using 1-5 mol% catalyst loading. The reaction pathway proved was fully modelled with DFT/solvent corrections, showing the deprotonation of the propargyl alcohols or amines as the rate limiting step.



E= O or NH R_1= H or aryl R_2 and R_3= alkyl or aryl

Acknowledgments: This research was funded by SSPC, SFI /Science Foundation Ireland) Research Centre for Pharmaceuticals. We thank ICHEC for access to high level computational resources.

References

[1] Yamada, W.; Sugawara, Y.; Cheng, H.M.; Taketo Ikeno, T.; Yamada, T. *Eur. J. Org. Chem.* ***2007****, 2604–2607.*
[2] Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. *Chem. Lett.* ***2009****, 38, 786-787*

PA31

From a nanoparticular solid-state material to molecular organo-f-element-polyarsenides

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For group 15 Zintl ions, the research on molecular coordination compounds is heavily focused on phosphorus and transition metals or main group elements, which can be ascribed to the availability of the molecular and soluble phosphorus allotrope P_4.[1] The heavier congener As_4 is inconvenient to synthesize and highly prone to decompose into gray arsenic. With the synthesis of As^0_{nano}, we have presented an approach to this issue that allows the stoichiometric usage of an elemental As source. The activation of As^0_{nano} by the application of different reducing agents from f-element and main group chemistry was recently reported.[2] In this study, we report a new pathway towards organo-f-element arsenic Zintl ions by combining the solid-state material As^0_{nano} with the high redox potentials of molecular non-classical divalent lanthanide compounds.[3]

The non-classical divalent lanthanide three electron reducing agents **A** and four electron reducing agents **B** (Fig. 1) were employed for the activation of As^0_{nano}.

On the one hand, the clean formation of an As_7^{3-} Zintl anion with a nortricyclic structure in **1** (Fig. 2) is observed by using the 3-electron reducing agents **A(La)** and **A(Ce)**. On the other hand, the formation the As_{14}^{4-} Zintl species **2** as sole isolable product is seen by applying the 4-electron reducing agent **B(Nd)** at elevated temperature. Compound **2** represents the largest known organo-lanthanide-polyarsenides to date. In between these boundaries, mixtures of various compounds with a polyarsenide as central motif were obtained (Compounds **3** and **4** with **B(Nd)**). These results show that the formation of sophisticated structures directly out of nanoscale gray arsenic, which is a kind of polymer, is a complex process with various intermediates. Only careful tuning of the reaction conditions and the use of an optimized reducing agent leads to isolable and unprecedented products.

In summary, we have demonstrated that the solid state material As^0_{nano} can be activated via 3- and 4-electron reducing agents of the early non-classical divalent lanthanides to obtain a variety of new molecular organo-lanthanide-polyarsenides. This significantly extends the bridge from solid-state gray arsenic to molecular f-element polyarsenides, contributing to a better understanding of the formation and properties of such polyarsenide materials.

Acknowledgments. We are grateful to the Deutsche Forschungsgemeinschaft (DFG) (No. 266153560, Ro 2008/17-2) and to the Fonds der Chemischen Industrie (102431) for financial support.

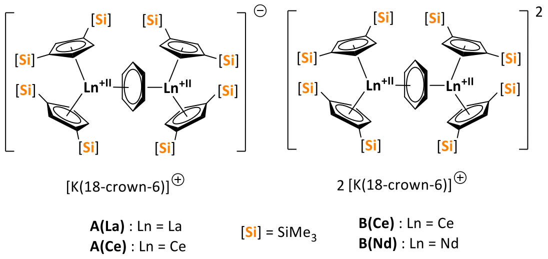

Fig 2. Three- (**A(La)**, **A(Ce)**) and four- (**B(Ce)**, **B(Nd)**) electron reducing agents, featuring non-classical divalent lanthanides ([Si] = $SiMe_3$).[4]

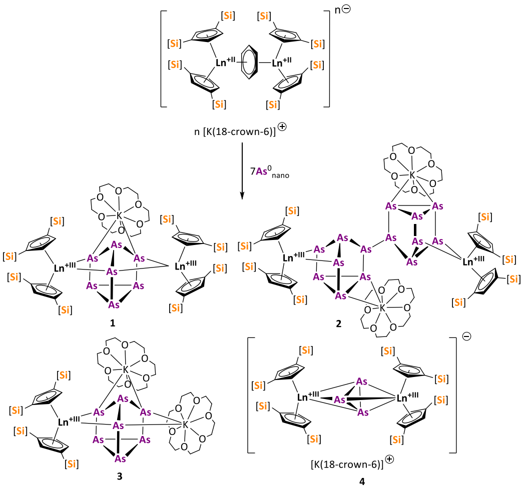

Fig 2. Overview of the variety of synthesized polyarsenides ([Si] = $SiMe_3$).

References

[1] (a) Scheer M. *et al.*, *Chem. Rev.*, **110**, 4236-4256, 2010; (b) Peruzzini M. *et al.*, *Chem. Rev.*, **110**, 4178-4235, 2010; (c) Cummins C. *et al.*, *Chem. Rev.*, **110**, 4164-4177, 2010. [2] (a) Roesky P. W. *et al.*, *Angew. Chem. Int. Ed.*, **58**, 4386-4389, 2019; (b) Roesky P. W. *et al.*, *Chem. Commun.*, **57**, 5503-5506, 2021; (c) Zhu C. *et al.*, *CCS Chem.*, **3**, 3268–3276, 2021. [3] Roesky P. W. *et al.*, *Chem. Sci.*, 2022. [4] (a) Evans W. J. *et al.*, *Organometallics*, **37**, 3322-3331, 2018; (b) Roesky P. W. *et al.*, *Chem. Eur. J*, **27**, 7862-7871, 2021.

PA32

Activation of White Phosphorus by Co–Zn Complexes: Access to P_4 Sandwich Compounds

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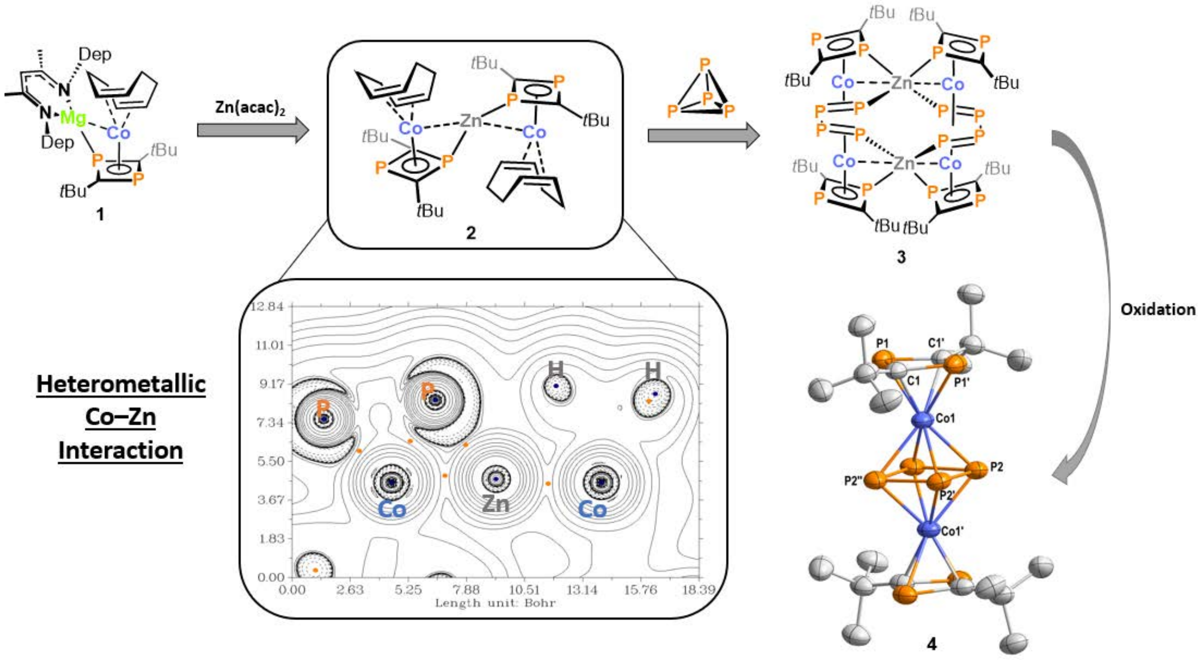
White phosphorus (P_4) is a key starting material for the preparation of phosphorus-rich transition metal complexes.[1] However, generation of reactive polyphosphido ligands is often challenging. One approach is to use two electronically different elements for the cooperative activation of P_4. Using this strategy, we recently synthesized complexes $[(\eta^4\text{-}t\text{Bu}_2\text{C}_2\text{P}_2)_2\text{Co}_2(\mu,\eta^5{:}\eta^5\text{-P}_4\text{Tt})]$ [Tt = Sn, Pb] containing unusual heavy cyclopentadienide analogues TtP_4^{2-}.[2]

Here, we describe the activation of P_4 by novel heteronuclear Co–Zn complexes. The Zn^{2+} complex **2** showing weak, covalent metal-metal interactions, which is readily accessible by salt metathesis of the known magnesium salt **1**[3] with $Zn(acac)_2$. Reaction of **2** with P_4 affords the dimeric complex **3** with butadiene-type catena-P_4 ligands. A stepwise mechanism for the formation of **3** is proposed based on ^{31}P NMR monitoring studies and the isolation of reaction intermediates. Chemical oxidation of **3** generates the remarkable phosphorus-rich sandwich complex **4**, featuring a *cyclo*-P_4 middledeck.



References

[1] L. Giusti, V. R. Landaeta, M. Vanni, J. A. Kelly, R. Wolf, M. Caporali, *Coord. Chem. Rev.* **2021**, 441, 213927.
[2] J. A. Kelly, V. Streitferdt, M. Dimitrova, F. F. Westermair, R. M. Gschwind, R. J. Berger, R. Wolf, *J. Am. Chem. Soc.* **2022**, 144, 44, 20434 – 20441.
[3] J. A. Kelly, J. Gramüller, R. M. Gschwind, R. Wolf, *Dalton Trans.* **2021**, 50, 13985-13992.

PA33

Organometallic polypyrazolylborate complexes: New Strategies

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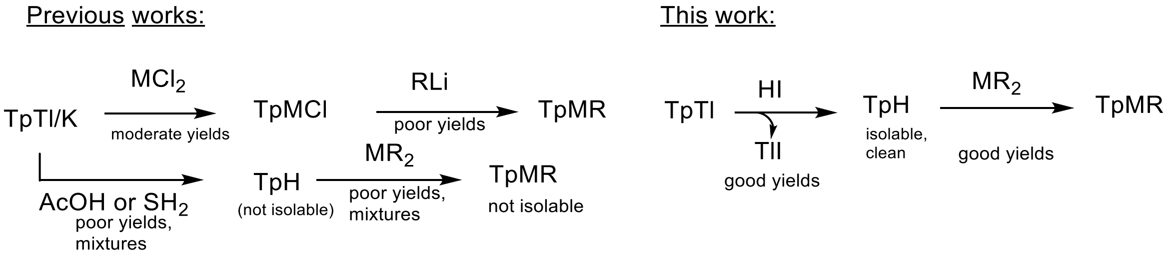
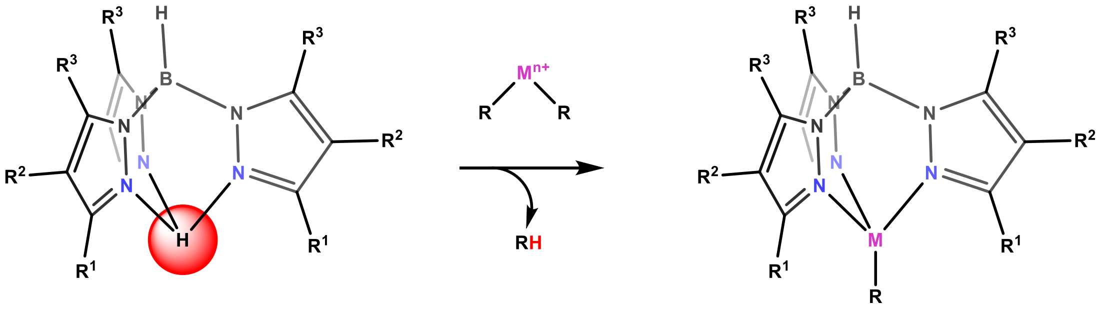
Polypyrazolylborates have been a topic of active research since their discovery in the 1960s by S. Trofimenko, having different applications in organometallic chemistry, coordination chemistry and polymeric materials.[1] In earlier attempts to make trispyrazolylborate organometallic compounds (TpMR), thallium and potassium precursors (TpTl/TpK) were shown to react with a metal halide before being treated with organolithium compounds. The obtainment of protonated polypyrazolylborates as intermediates (TpH) in the way to TpMR compounds was suggested as an alternative method. However, the methods reported in literature are inefficient and tedious, TpH intermediates were not isolable, and TpMR derivatives were obtained impure and with low yields.[2],[3]



Here, we offer a highly effective approach for producing pure TpH precursors in high yields. These pure isolated TpH derivatives react cleanly with distinct alkylmetal derivatives through alkane elimination to form organometallic complexes with good yields. These new organometallic complexes are active catalyst precursors.[4],[5],[6]



References

[1] Pettinari, C. et. al. *Adv. Organomet. Chem.* **2016**, *65*, 175
[2] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *87*, 3170
[3] Cheng, J. et. al. *Angew. Chem.* **2008**, *120*, 26.
[4] Kauffmann, T. et. al. *Chem. Ber.* **1992**, *125*, 163.
[5] Blackwell, J. *Can. J. Chem.* **1997***, 75,* 702.
[6] Uchiyama, M et al. *J. Am. Chem. Soc.* **2004**, *126*, 8755.

PA34

New approach to ring-opening polymerization through Pd-catalyzed C–C bond cleavage

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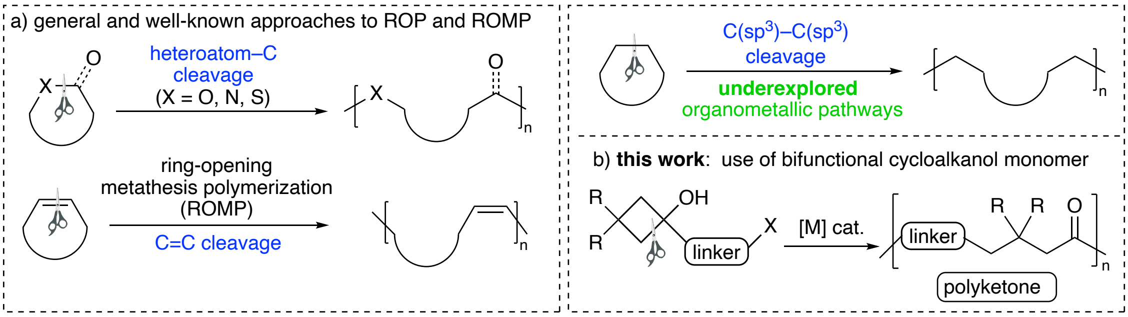
The synthesis of polymeric materials through ring-opening polymerization (ROP) strategies has been widely studied in the last years, remaining as a key research topic given the great versatility of the polymers delivered by such methods. So far, the ROP routes have been mainly focused on the use of cyclic monomers in which a C–heteroatom bond is cleaved during the polymerization reaction (a, Scheme 1).[1] The availability of ROP methods that make use of C–C cleavage is much more restricted, and they are centered on the splitting of C=C bonds (ring-opening metathesis polymerization, ROMP) by TM-catalysts (a, Scheme 1).[2] Given our interest in TM-catalyzed C–C cleavage,[3] we have now developed a new approach to ROP based on the ability of Pd to perform C(sp^3)–C(sp^3) bond splitting through a beta-carbon elimination process in a conveniently designed bifunctional cycloalkanol monomer (b, Scheme 1). Thus, this novel strategy represents a new avenue of research for ROP, allowing the synthesis of polyketones with substitution patterns that would be difficult to obtain through the usual CO/ethylene copolymerization route employed previously in the literature.



Scheme 1. Previously reported and new Pd-catalyzed path for ROP.

References

[1] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147–6176. [2] S. Sutthasupa, M. Shiotsuki, F. Sanda, *Polym. J.* **2010**, *42*, 905–915. [3] (a) H. Azizollahi, V. P. Mehta, J. A. García-López, *Chem. Commun.* **2019**, *55*, 10281–10284. (b) M. Pérez-Gómez, P. Herrera-Ramírez, D. Bautista, I. Saura-Llamas, J. A. García-López, *Organometallics* **2022**, *41*, 649-658.

PA35

A Phenolate-Carbene Supported High-Valent Fe–O Intermediate Derived From Dioxygen

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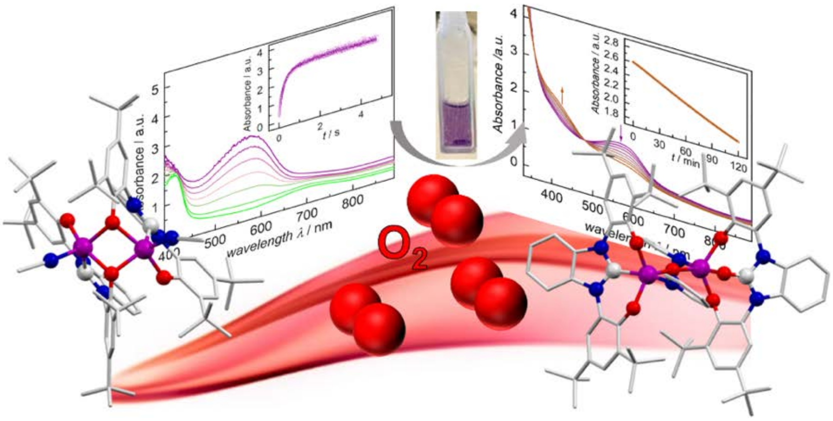
Soluble methane monooxygenases utilize dioxygen to transform methane into methanol by breaking the 105 kcal/mol C–H bond.[1,2] Recently, porphyrin-like tetracarbene macrocycles broadened the scope of suitable ligands in the biomimetic chemistry of Fe-mediated O_2 activation.[3,4] The dimeric iron(II) complex $[Fe(OCO)(MeCN)]_2$ (**1**), supported by the bis-phenolate carbene (OCO) ligand, was synthesized and characterized by single-crystal X-ray diffraction analysis, a variety of spectroscopic methods, and magnetization measurements. In solution, at room temperature, **1** activates O_2 to yield the asymmetric, μ-oxo-bridged [(OCO)Fe(μ-O)Fe(O(C=O)O)] (**2**). In **2**, one of the Fe–C bonds was oxidized by one of the O_2 oxygen atoms, while the other bridges to two Fe units. At –80 °C, a purple intermediate **3** (λ_{max} = 570 nm) is observed. Spectroscopic studies indicate iron(III) sites with one phenoxyl radical on each ligand. The absence of O–O vibrations in the resonance Raman spectrum of **3** suggests a symmetric diamond core structure $[\{(OCO^{\cdot})Fe\}_2(\mu\text{-}O)_2]$ in **3**.



References

[1] Jasniewski, A. J.; Que, L., Jr., *Chem. Rev.* **2018**, *118* (5), 2554-2592.
[2] Zhang, X. P.; Chandra, A.; Lee, Y. M.; Cao, R.; Ray, K.; Nam, W., *Chem. Soc. Rev.* **2021**, *50* (8), 4804-4811.
[3] Hohenberger, J.; Ray, K.; Meyer, K., *Nat. Commun.* **2012**, *3*, 720-733.
[4] Schlachta, T. P.; Kühn, F. E., *Chem. Soc. Rev.* **2023**, *52,* 2238-2277.

PA36

Regio- and Enantioselective Ni-Catalyzed Synthesis of Branched 1,5-Dienes featuring a Quaternary Stereogenic Center

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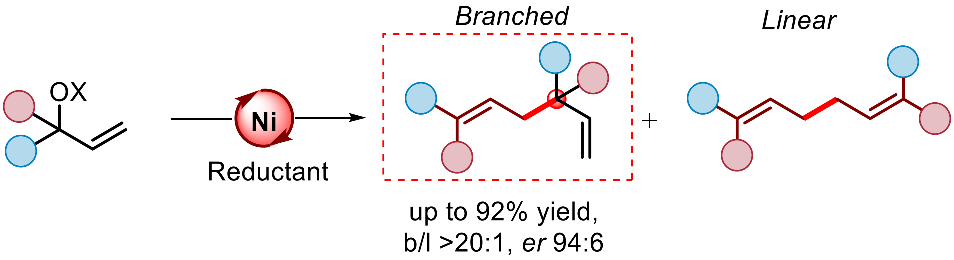
Asymmetric synthesis of quaternary stereogenic centers remains a highly important and very challenging objective in organic synthesis.[1] Chiral 1,5-dienes featuring such stereocenters represent important building blocks in organic synthesis and are also found in many biologically active substances and naturally occurring terpenes.[2] In this study, we report a highly regio- and enantioselective nickel-catalyzed reductive homoallylic cross-coupling process providing access to chiral 1,5-dienes in good yields. The developed methodology reflects an atypical preference for the formation of branched regioisomers (>20:1) in a sterically challenging allylic substitution event and furnishes the products with enantiomeric ratios of up to 94:6. Mechanistic investigations indicate the involvement of several low-valent η^3- or η^1-allyl Ni intermediates in two kinetic regimes, and the beneficial role of divalent Zn is additionally demonstrated.



- Generation of all carbon quaternary carbon center
- High regio- and enantioselective process
- Isolation of key Ni-intermediates
- Mechanistic study depicts presence of two regimes of catalysis

References

[1] (a) Li, C.; Ragab, S. S.; Liu, G.; Tang, W. *Nat. Prod. Rep.* **2020**, *37*, 276; (b) Das, J. P.; Marek, I. *Chem. Commun.* **2011**, *47*, 4593.
[2] (a) Breitmaier, E. Terpenes, Flavors, Fragrances, Pharmaca, Pheromones, *Wiley-VCH*, *Weinheim*, **2006**; (b) Dewick, P. M. Medicinal Natural Products: A Biosynthetic Approach, *Wiley*, *Chichester*, **2002**.

PA37

The electronic structure of atomically-precise Pt(0) clusters from solid-state ^{195}Pt NMR

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Atomically-precise metal clusters show unique properties which make them appealing for the preparation of optical devices and for biomedical applications. Furthermore, some of these species are proposed to be catalytically active for the activation of small molecules and for selective transformations of organics. As such, they provide fundamental knowledge on the bonding and reactivity of complex systems.[1]

Common characterization techniques of metal clusters involve mass spectrometry, optical and X-ray spectroscopies.[2,3] While these tools can describe a system in its totality, they only provide an averaged information of the different metal sites. Conversely, solid-state NMR (ss-NMR) spectra encode information on the electronic structure of a specific nucleus, as the shape and orientation of the chemical shift (shielding) tensor (CST) is strictly related to its valence orbitals (fMOs).[4]

In this work, we show how ^{195}Pt ss-NMR can be used to understand the bonding situation of metal nuclei in a library of $Pt_n(0)$ species with different nuclearity (n= 1 to 5) and connectivity.[5] ss-NMR can be therefore applied as a general tool to distinguish among the metal sites of clusters. Additionally, the analysis of the CST of a nucleus in a cluster can provide information on its local electronics and environment (Figure 1).

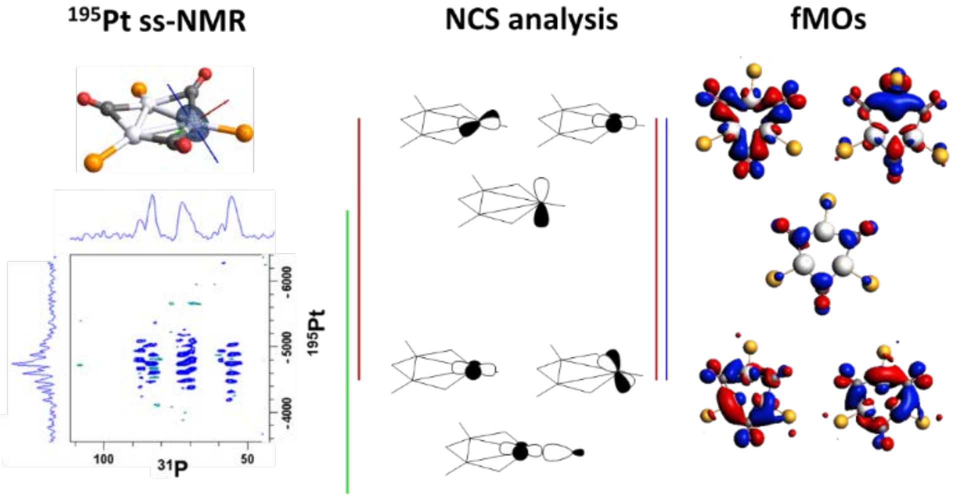

Figure 1: Investigation of a $Pt_3(CO)_3(PR_3)_3$ cluster: $^{31}P\{^{195}Pt\}$ ss-NMR, CST and MOs responsible for the (de)shielding.

References

(1) Chakraborty, I.; Pradeep, T. *Chem. Rev.* **2017**, *117* (12).
(2) Joshi, C. P.; et.al, . *J.Am.Chem.Soc.* **2015**, *137* (36).
(3) Zhang, B.; et. al., *ChemCatChem* **2018**, *10* (23).
(4) Venkatesh, A.; Gioffrè, et. al., *J.Am.Chem.Soc.* **2022**, *144* (30).
(5) Chatt, J.; Chini, P. *J. Chem. Soc. Inorg. Phys. Theor.* **1970**, (0).

PA38

Synthesis, Properties, and Reactivity of a Linear NHC-Based Chromium(I) Silylamide

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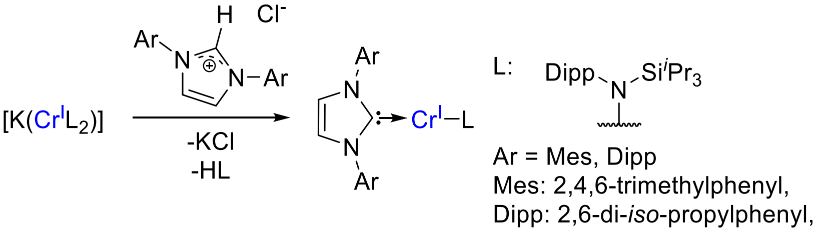
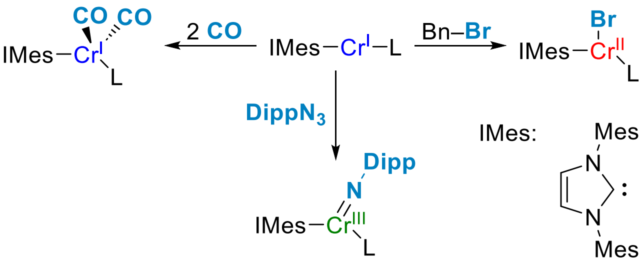
Linear open-shell metal complexes have recently attracted interest as the presence of a low-valent, low-coordinate metal ion is prospective of unique magnetic and chemical properties.[1-3] In this regard heteroleptic NHC based metal(I) complexes of the type [NHC(M^{I})L] of iron and cobalt (L: anionic ligand) have exhibited remarkable activity in bond activation catalysis.[4,5]

Herein we describe the first examples of heteroleptic NHC-based complexes bearing two-coordinate chromium(I) ions (Scheme 1). These are obtained from the reaction of a linear homoleptic chromium(I) bis(silylamide) complex and the imidazolium salt of the respective NHC ligand; and were subsequently analyzed for their physical properties.[6]



Scheme 1: Synthesis of heteroleptic, quasilinear, NHC bearing chromium(I) complexes.

Initial studies on the reactivity of [(IMes)Cr^{I}L] lead to the formation of a four-coordinate chromium dicarbonyl complex in presence of CO. A trigonal chromium(II) bromide was observed with benzyl bromide, and the first three-coordinate chromium(III) imide was synthesized with DippN$_3$ (Scheme 2).



Scheme 1: Reactivity of the linear complex [(IMes)Cr^{I}L] towards CO, BnBr and DippN$_3$.

References

[1] P. P. Power, *Chem. Rev.* **2012**, *112*, 3482.
[2] L. J. Taylor, D. L. Kays, *Dalton Trans.* **2019**, *48*, 12365.
[3] S. Roy, K. C. Mondal, H. W. Roesky, *Acc. Chem. Res.* **2016**, *49*, 357.
[4] R. J. Witzke, D. Hait, K. Chakarawet, M. Head-Gordon, T. D. Tilley, *ACS Catal.* **2020**, *10*, 7800.
[5] Y. Dong, M. I. Lipschutz, R. J. Witzke, J. A. Panetier, T. D. Tilley, *ACS Catal.* **2021**, *11*, 11160.
[6] A. Gonzalez, T.-Y. Chen, S. Demeshko, F. Meyer, C. G. Werncke, *Organometallics*

PA39

6-(6-Methyl-1,2,4,5-tetrazine-3-yl)-2,2‘-bipyridine: A N-donor ligand for the separation of lanthanides(III) and actinides(III)

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For lanthanide / actinide separation, the novel *N*-donor ligand 6-(6-methyl-1,2,4,5-tetrazine-3-yl)-2,2‘-bipyridine (MTB) is showcased. First the ligand synthesis is described, followed by its complexation of lanthanides. Finally the ligand is tested as an extraction agent for trivalent actinide cations over lanthanides.[1]

The reaction of MTB with $[Ln(NO_3)_3(H_2O)_6]$(Ln = Sm, Eu, Gd) results in $[Ln(MTB)(NO_3)_3MeCN]$(Ln = Sm, Eu, Gd).

The three isostructural lanthanides compounds were synthesized and fully characterized. Solid-state structures of MTB and the respective complexes were established by single-crystal X-ray diffraction. Time resolved laser fluorescence spectroscopy (TRLFS) studies were performed with Cm(III) by using MTB as a ligand and the complexation kinetic is comparable to the structurally similar ligand C5-hemi-BTP[2] and *n*Pr-tetrazine.[3] Cm(III) is observed to form 1:1, 1:2 and 1:3 complexes.

References

[1] G. Greif, P. Weßling, P. J. Panak, P. W. Roesky, unpublished results.

[2] A. Bremer, A. Geist, P. J. Panak*, Dalton Trans.* **2012**, *41*, 7582

[3] B. B. Beele, E. Rüdiger, F. Schwörer, U. Müllich, A. Geist, P. J. Panak, *Dalton Trans.* **2013**, *42*, 12139-12147.

PA40

Understanding Heterometallic Cooperativity using Predesigned Model Systems for Ring opening Copolymerization of Epoxides with CO_2

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The product of ring opening copolymerization (ROCOP) of epoxides with CO_2 i.e., alternating polycarbonates have strong potential as sustainable replacements for petrochemicals with their properties spanning plastics, elastomers, fibres, resins, foams, coatings, adhesives, and self-assembled nanostructures. Since the discovery of the first catalytic system (in 1969 by Inoue and co-workers)[1] for the alternating copolymerization of propylene oxide (PO) and CO_2, a significant amount of research has been directed toward the development of catalysts of improved activity and selectivity.[2] Among the plethora of homogeneous catalytic systems, zinc complexes in particular bimetallic zinc catalysts have attracted widespread attention due to the cooperative effect. Investigations of the heterometallic cooperativity in catalytic ROCOP of epoxides with CO_2 offer promising strategies to improve catalyst performance.[3] However, the understanding of structure-activity trends and reactivity patterns is very crucial for future catalyst design.

As a part of our study on the activation of heterocyclic monomers by the organometallic complexes,[4] keeping in mind the heterometallic cooperativity we have synthesized the heterometallic model systems to clearly demonstrate the role of different metal centres in the catalytic ROCOP of epoxides with CO_2. The key intermediates into the catalytic cycles have been successfully isolated and structurally characterized. These studies not only provide the substantial evidence to the suppositional intermediates but also guides the future catalyst development for the heterometallic ring opening copolymerization.

References

1. Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci. Part B Polym. Lett.* **1969**, *7*, 287–292.
2. a) Cao, H.; Liu, S.; Wang, X. *Green Chemical Engineering* **2022**, *3*, 111–124; b) Mbabazi, R.; Wendt, O. F.; Allan Nyanzi, S.; Naziriwo, B.; Tebandeke, E. *Results Chem.* **2022**, *4*, 100542; c) Kozak, C. M.; Ambrose, K.; Anderson, T. S. *Coord. Chem. Rev.* **2018**, *376*, 565–587.
3. a) Diment, W. T.; Lindeboom, W.; Fiorentini, F.; Deacy, A. C.; Williams, C. K. *Acc. Chem. Res.* **2022**, *55*, 1997–2010; b) Gruszka, W.; Garden, J. A. *Nat. Commun.* **2021**, *12*, 3252.
4. a) Bury, W.; Justyniak, I.; Prochowicz, D.; Wróbel, Z.; Lewiński, J. *Chem. Commun.* **2012**, *48*, 7362; b) Lewiński, J.; Horeglad, P.; Wójcik, K.; Justyniak, I. *Organometallics* **2005**, *24*, 4588–4593; c) Lewiński, J.; Zachara, J.; Horeglad, P.; Glinka, D.; Lipkowski, J.; Justyniak, I. *Inorg. Chem.* **2001**, *40*, 6086–6087.

PA41

Reactivity of a Carbazolyl Bromosilylene towards Carbodiimides

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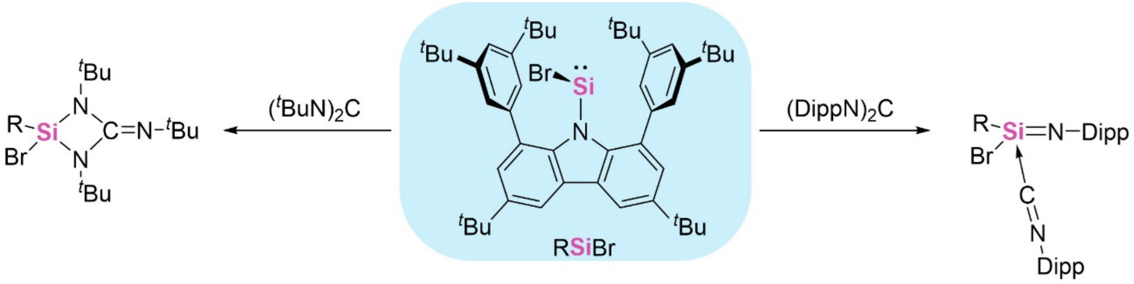
Silylenes are known to react with unsaturated substrates such as alkenes, nitriles or carbonyls.[1] Most of the silylenes involved in these reactivity studies are base-stabilised tricoordinated species, which are readily accessible. In the course of reactivity studies concerning the dicoordinated carbazolyl bromosilylene RSiBr,[2] we probed its behaviour towards carbodiimides in order to elucidate the differences in reactivity compared to tricoordinated silylenes. While with $(^tBuN)_2C$ a guanidinate-type compound is obtained, the reaction with $(DippN)_2C$ yields a donor-stabilised silaimine. Thus, the steric parameters of the carbodiimide allow control over the addition reaction. The latter was further investigated in terms of its cycloaddition chemistry.



Scheme 1: Reactivity of RSiBr towards $(^tBuN)_2C$ and $(DippN)_2C$ (Dipp = 2,6-Diisopropylphenyl).

References

[1] L. Wang, Y. Li, Z. Li, M. Kira, *Coord. Chem. Rev.* **2022**, *457*, 214413.
[2] A. Hinz, *Angew. Chem. Int. Ed.* **2020**, *59*, 19065–19069.

PA42

Comparative study of the efficiency of various mono- or bimetallic reagents for the functionalization of heterocycles: towards the synthesis of fused heteroaryl-lactones

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Nature encompasses a myriad of natural substances that contain heterocycles within their molecular structures. These compounds play a fundamental role in chemistry and hold undeniable importance in various fields such as the pharmaceutical industry, materials science, and organic synthesis.

In the course of our research, our primary objective was to investigate and enhance the efficiency and selectivity of three distinct pathways for the metalation of halogeno-heterocycles using lithium, magnesium, and lithium magnesiate reagents. Following the metalation step, an electrophilic trapping and subsequent cyclization step are performed.

This study presents a significant challenge as it aims to facilitate the development of an efficient new methodology and strategy for the one-pot synthesis of heteroaryl-lactones. Its main purpose is to compare and evaluate these metalation routes, offering valuable insights into their respective advantages and limitations.

PA43

Interplay between Tridentate Pincer Molybdenum Catalysts and SmI_2 in Ammonia Synthesis

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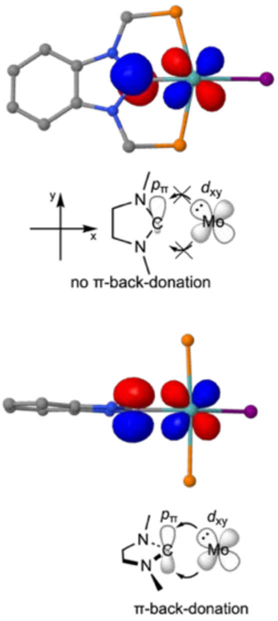
The Haber-Bosch ammonia process combines dinitrogen and hydrogen under harsh reaction conditions.[1] In contrast, Nature's ammonia process, catalyzed by nitrogenase enzymes, is fast under ambient conditions even though a relatively stable and little acidic proton source (water) is used.[2] For decades, researchers have used these enzymes, containing V, Fe, or Mo ions in the active site, as inspiration when developing homogenous transition-metal-based catalysts for nitrogen fixation. Recently, these efforts have resulted in the first examples of water-based ammonia synthesis at enzymatic rates using man-made catalysts.[3] The stunning activities are thought to derive in part from efficient proton-coupled electron transfer (PCET) from the combination of the chemical reductant, SmI_2, and water,[3] although no mechanistic studies of this transfer exist. The catalytic activities also vary dramatically between the different Mo-based catalyst complexes, but little is known about the origins of these variations.

To uncover both the role of the Sm reductant and the factors promoting catalytic activity, we here use density functional theory (DFT) calculations to investigate a series of Mo complexes bearing variations over the tridentate ligand design ubiquitous in the nitrogen-fixation catalysts. Using a thoroughly validated computational model including spin-orbit coupling effects for Sm,[4] we investigate, for the first time, the interplay between the Mo catalyst and the Sm reductant. We find the rate-determining step to be that of a proton-coupled electron transfer to a d^2 Mo(IV) nitrido species, consistent with experimental observations.[3] The key to achieving a low barrier for this step is to interlock, in the tridentate ligand, a potent π-acceptor so that it cannot π-back-bond with Mo(IV)'s d_{xy} lone pair (Figure 1a). Thus, a too stable Mo(IV) nitrido intermediate (Figure 1b) is avoided at the same time as a the interlocked π-acceptor helps stabilize the product of the PCET, a d^3 Mo(III) imido intermediate.



(1a)

(1b)

Figure 1. (1a) Interlocking of the π-acceptor such that it is incapable of π-back-bonding, resulting in high catalyst activity. (1b) π-back bonding resulting in a stable Mo(IV) nitrido species and, thus, reduced catalyst activity.

References

(1) Service, R. F. Liquid Sunshine. *Science* **2018**, *361*, 120–123.

(2) Burgess, B. K.; Lowe, D. J. Mechanism of Molybdenum Nitrogenase. *Chem. Rev.* **1996**, *96*, 2983–3012.

(3) Ashida, Y.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. Molybdenum-Catalysed Ammonia Production with Samarium Diiodide and Alcohols or Water. *Nature* **2019**, *568*, 536–540.

(4) Himmelstrup, J.; Jensen, V. R. Enabling Molecular-Level Computational Description of Redox and Proton-Coupled Electron Transfer Reactions of Samarium Diiodide. *J. Phys. Chem. A.* **Article ASAP**. **2023**. DOI: 10.1021/acs.jpca.3c00418

PA44

Non-palindromic pincer complexes based on donor-substituted biphenyls

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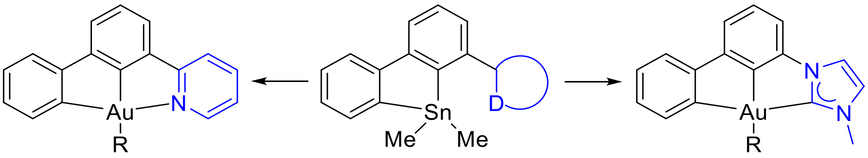
We present new synthetic strategies for the preparation of pyridine and imidazole substituted 2,2'-dihalo biphenyls.[1] These structures are pre-ligands suitable for the preparation of respective stannoles. This stannole can successfully be transmetalated to K[$AuCl_4$] forming non-palindromic [(C^C^D)Au^{III}] pincer complexes featuring a lateral pyridine (D=N) or *N*-heterocyclic carbene (NHC, D=C') donor. The latter is the first report on a pincer complex with two formally anionic sp^2 and one carbene carbon donor.



Scheme 3: Preparation of non-palindromic (C^C^D)Au^{III} complexes. D: Donor.

The [(C^C^D)Au^{III}] complexes show intense phosphorescence in solution at room temperature. Besides the Au^{III} pincer complexes, a highly luminescent non-palindromic Pd^{II} pincer complex could be synthesized *via* double oxidative addition with the (C^C^N) ligand.[2,3] Another pre-ligand bearing a dicyclohexyl phosphine donor could be synthesized. Its complexes of Pt^{II} as well as Pd^{II} emit similar green phosphorescence particularly efficiently in the solid state. The most fascinating photophysical feature, however, is a direct singlet-triplet ($S_0 \rightarrow T_1$) excitation of this phosphorescence in the spectral window between the emission and major singlet-singlet UV absorption. The $S_0 \rightarrow T_1$ excitation spectra show a rich vibronic pattern, which is especially pronounced for the solid samples at cryogenic temperatures.

References

[1] W. Feuerstein, C. Holzer, X. Gui, L. Neumeier, W. Klopper, F. Breher, *Chem. Eur. J.* **2020**, *26*, 17156–17164.
[2] W. Feuerstein, F. Breher, *Chem. Commun.* **2020**, *56*, 12589–12592.
[3] W. Feuerstein, F. Breher, *Dalton Trans.* **2021**, *50*, 9754-9767

PA45

Reversible Assembly of Quadruple-Decker Gallium Coordination Structures

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Following the pioneering work of Cram, Lehn, and Pedersen, supramolecular chemistry has emerged as a cornerstone in the field of chemistry.[1] Supramolecular self-assembled coordination hosts, which mimic enzyme active sites, have attracted interest in organometallic chemistry and catalysis due to their unique reactivity, rate enhancements, and product selectivity, surpassing conventional chemical systems.[2] These characteristics are reminiscent of enzymatic catalysis.[3]

In this communication, we will showcase novel supramolecular coordination self-assembled quadruple-decker structures utilizing gallium. These supramolecular arrays display reversible assembly and disassembly processes, which we have examined in relation to organometallic interactions and molecular recognition during their supramolecular formation, employing NMR and hydrodynamic studies in solution.[4]

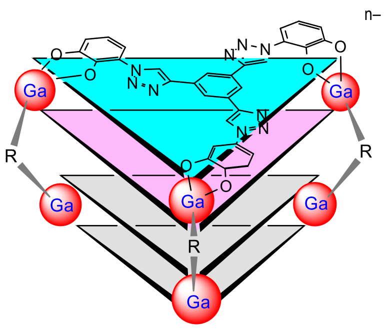

Figure 1. Quadruple-decker coordination gallium supramolecular structures.

References

[1] D. J. Cram, *Angew. Chem. Int. Ed.* **1988**, *27*, 1009-1020.
[2] a) M. Morimoto, S. M. Bierschenk, K. T. Xia, R. G. Bergman, K. N. Raymond, F. D. Toste, *Nat. Catal.* **2020**, *3*, 969-984; b) J. Meeuwissen, J. N. H. Reek, *Nature Chem.* **2010**, *2*, 615-621; c) Z. J. Wang, K. N. Clary, R. G. Bergman, K. N. Raymond, F. D. Toste, *Nature Chem.* **2013**, *5*, 100-103.
[3] D. M. Kaphan, M. D. Levin, R. G. Bergman, K. N. Raymond, F. D. Toste, *Science* **2015**, *350*, 1235.
[4] Manuscript in preparation.

PA46

Synthesis of Optically Pure Aminoacids Bearing Cyclic Carbonates using a Gallium Catalyst

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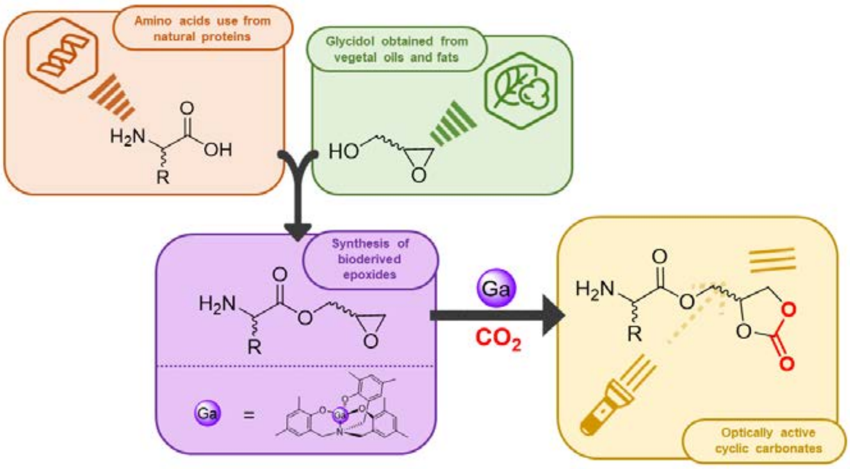
Interest in carbon dioxide (CO_2) storage and utilization has recently increased exponentially due to it being one of the main causes of climate change. CO_2 has found use as a renewable, cheap and non-toxic C_1 feedstock. Indeed, it is already used for the synthesis of methanol, carboxylic acids, ureas and cyclic carbonates amongst other value-added products.[1] Cyclic carbonate synthesis through the coupling of CO_2 and epoxides is an atom-efficient alternative to the traditional synthesis of these compounds, which uses highly toxic phosgene. Considering the inert nature of the CO_2 molecule, harsh conditions are needed for its activation, this has led to scientists designing catalyst systems that promote the reaction. In our case, we have developed a highly active gallium catalyst, and this has been recently reported.[2] Due to the limited natural abundance of epoxides, it has been necessary to develop synthetic methods to modify biomolecules in order to obtain bioderived epoxides that can be used to produce bioderived cyclic carbonates. In this context, amino acids can be used as natural, cheap and optically active biomolecules, whereby the desired epoxide can be included through the esterification of the carboxylic group with glycidol as a source of a potentially bioderived epoxide. Using this approach, a variety of bioderived epoxides have been synthesized using optically pure substrates, obtaining optically active cyclic carbonates after the insertion of CO_2 with high yields. This contribution describes our most recent results arising from this project.



References

[1] (a) Kim, C.; Yoo, C.-J.; Oh, H.-S.; Min, B. K.; Lee, U. *J. CO_2 Util.* **2022**, *65*, 102239; (b) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nat. Commun.* **2015**, *6*, 5933.

[2] Álvarez-Miguel, L.; Damián Burgoa, J.; Mosquera, M. E. G.; Hamilton, A.; Whiteoak, C. J. *ChemCatChem.* **2021**, *13*, 4099-4110.

PA47

Pattern recognition analysis of structural parameters of some metal complexes with substituted benzimidazole derivatives

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The pattern recognition analysis of the structural parameters of the synthesized metal complexes with potential pesticide activity was carried out applying hierarchical cluster analysis (HCA) based on Ward's algorithm and Euclidean distances. The set of nine analysed compounds included three cobalt(II), three zinc(II) and three copper(II) benzimidazole complexes (general formula: $[CuLCl_2(H_2O)]$, $[CoL_2Cl_2]$, $[ZnL_2Cl_2]$) that were shown to have antibacterial activity towards *Erwinia amylovora* and *Pectobacterium carotovorum*, well-known plant pathogens (Podunavac-Kuzmanović et al, 1999). The HCA was carried out on the data set of structural properties of the complexes including lipophilicity parameter (LogP), stretching energy, bending energy, stretch-bend energy, torsion energy, non-1.4 VDW parameter, 1.4 VDW parameter, dipole-dipole interactions, total energy, Balaban index, cluster count, molecular topological index, polar surface area, sum of valence degrees and Wiener index. In the space of the analysed variables, the copper(II) complexes are placed in the separate cluster and are significantly different from the others since they are monoligand benzimidazole complexes and their molecules are smaller than others from the series. In the second cluster there can be found other complexes of zinc(II) and cobalt(II). In this cluster, the complexes of zinc(II) and cobalt(II) with chlorine atom in meta position of the benzene core of the ligand are separated from the others. Observing their microbiological activity data, it can be noticed that these two compounds possess similar activity (among highest) probably induced by their structural specificity. The obtained results of HCA indicate that the copper(II)-benzimidazole complexes significantly stand out from the rest of the analysed compounds in terms of the considered molecular properties.

Acknowledgement. The present research is financed in the framework of the project "Molecular engineering and chemometric tools: Towards safer and greener future" financed by the Provincial Secretariat for Higher Education and Scientific Research of AP Vojvodina (Project No. 142-451-3095/2022-01/01).

References

Podunavac-Kuzmanović, S.; Leovac, V.M.; Perišić-Janjić, N.U.; Rogan, J.; Balaž, J. *J. Serb. Chem. Soc.* 1999, 64 (5-6), 381-388.

PA48

Transition metal free ketene formation from carbon monoxide via isolable ketenyl anions

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The activation of carbon monoxide through the use of main group compounds continues to pose a challenge.[1] Despite the initial report of such an activation, only a limited number of additional instances have been reported.[2-5] In general, ambiphilic reagents are needed which are capable of efficiently donating electron density into the LUMO of carbon monoxide while accepting electron density in a vacant orbital. Recently, we described a different mechanism that employs phosphorus ylides to form a stable ketenyl anion ($[Ph_2P(S)\text{-}C{=}C{=}O]^-$) *via* elimination of the phosphine when treated with carbon monoxide.[6] By this means, we were able to use CO as a C1 building block with excellent yields, without the need for any transition metals. These ketenyl anions possess an electronic structure that lies between a prototypical ketene ($H_2C{=}C{=}O$) and ethynol ($HC{\equiv}C\text{-}OH$). Nevertheless, they react selectively with electrophiles at the carbon atom, providing access to a range of substituted ketenes and related compounds.

Herein, we report the detailed gram-scale synthesis of our first synthesized ketenyl anion. We present our initial steps and successes in this field, as well as novel reactivities and reaction products.

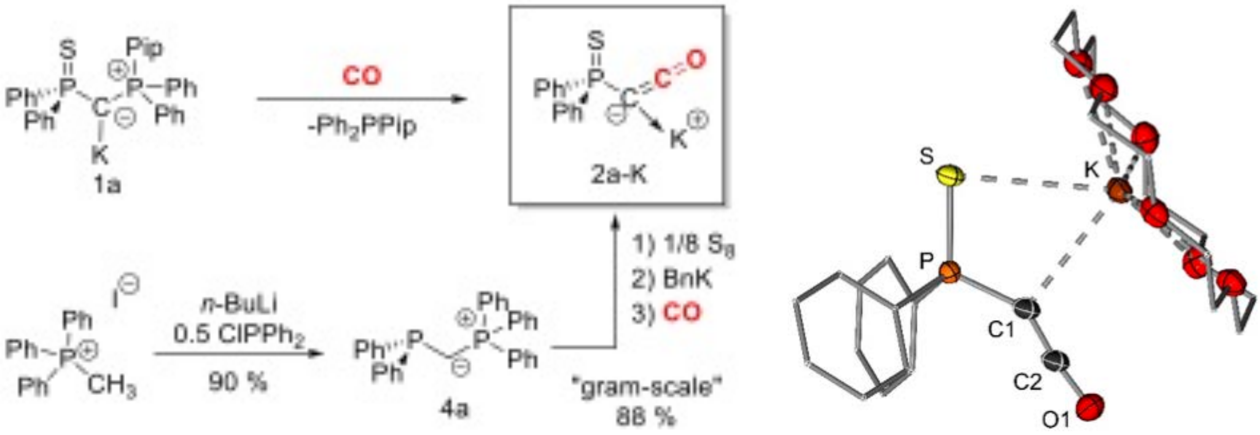

Figure 1: Left: reaction scheme for the possible reactions of metalated ylides and carbon monoxide with the desired ketenyl anion. Right: Structure of the reported ketenyl anion with 18-crown-6.

References

[1] P. P. Power, *Nature*, **2010**, *463*, 171.
[2] H. Braunschweig, R. D. Dewhurst, F. Hupp, M. Nutz, K. Radacki, C. W. Tate, A. Vargas, Q. Ye, *Nature*, **2015**, 327.
[3] D. Reiter, C. Holzner, A. Porzelt, P. Frisch, S. Inoue, *Nat. Chem.*, **2020**, *12*, 1131.
[4] M. Xu, T. Wang, Z.-W. Qu, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.*, **2020**, *60*, 25281.
[5] T. J. Hadlington, T. Szilvási, *Nat. Commun.*, **2022**, *13*, 461.
[6] M. Jörges, F. Krischer, V. H. Gessner, *Science*, **2022**, *378*, 1331.

PA49

Alkali-Metal-Alkoxide Powered Zincation of Fluoroarenes Employing Zinc Bis-Amide $Zn(TMP)_2$

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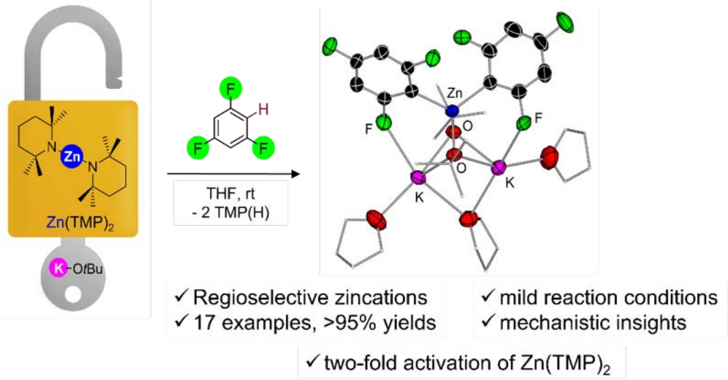
The unique activating effects of alkali-metal alkoxides when added to other s-block organometallics is a well-established phenomenon in polar organometallic chemistry.[1] Typified by the LIC-KOR (Lochmann-Schlosser) superbase, combining potassium *tert*-butoxide with *n*-butyllithium greatly enhances the metalation capabilities of this mixture when compared to those of their monometallic counterparts.[2,3] Extending these reactivity enhancement effects beyond group 1 organometallics, our group has recently demonstrated the ability of alkali-metal alkoxides to activate dialky magnesium or zinc reagents towards metal halogen exchange reactions of bromo and iodoarenes. Mechanistic studies indicate that these special behaviors can be attributed to the formation of more reactive mixed-metal mixed-aggregate complexes. [4–6]

Building on this work, we have recently developed a new bimetallic base which allows for the direct zincation of a broad range of aromatic substrates.[7] By combining the Zn amide $Zn(TMP)_2$ (TMP = 2,2,6,6-Tetramethylpiperidide) with two equivalents of KO*t*Bu effective zincation of sensitive substrates such as 1,3,5-trifluorobenzene can be achieved while operating at room temperature (see Figure). Trapping of key reaction intermediates and NMR monitoring of the reactions have uncovered the close interplay between the different components of this bimetallic mixture to facilitate the success of the Zn-H exchange reaction and the stability of the metalated intermediates. Showcasing its metalating power, this bimetallic KO*t*Bu/$Zn(TMP)_2$ partnership, can even effect benzylic zincation of toluene and benzene at room temperature.[7]



✓ Regioselective zincations
✓ 17 examples, >95% yields
✓ mild reaction conditions
✓ mechanistic insights
✓ two-fold activation of $Zn(TMP)_2$

References

[1] L. J. Bole, E. Hevia, *Nat. Synth.* **2022**, *1*, 195–202.
[2] M. Schlosser, *J. Organomet. Chem.* **1967**, *8*, 9–16.
[3] M. Schlosser, *Angew. Chem. Int. Ed.* **2005**, *44*, 376–393.
[4] M. Balkenhohl, D. S. Ziegler, A. Desaintjean, L. J. Bole, A. R. Kennedy, E. Hevia, P. Knochel, *Angew. Chem. Int. Ed.* **2019**, *58*, 12898–12902.
[5] L. J. Bole, N. R. Judge, E. Hevia, *Angew. Chem. Int. Ed.* **2021**, *60*, 7626–7631.
[6] N. R. Judge, L. J. Bole, E. Hevia, *Chem. Eur. J.* **2022**, e202104164.
[7] N. R. Judge, E. Hevia, *Angew. Chem. Int. Ed.* **2023**, 62, e202303099.

PA50

Unveiling the Unprecidented Class of Homoatomic Group 13 σ-Complexes

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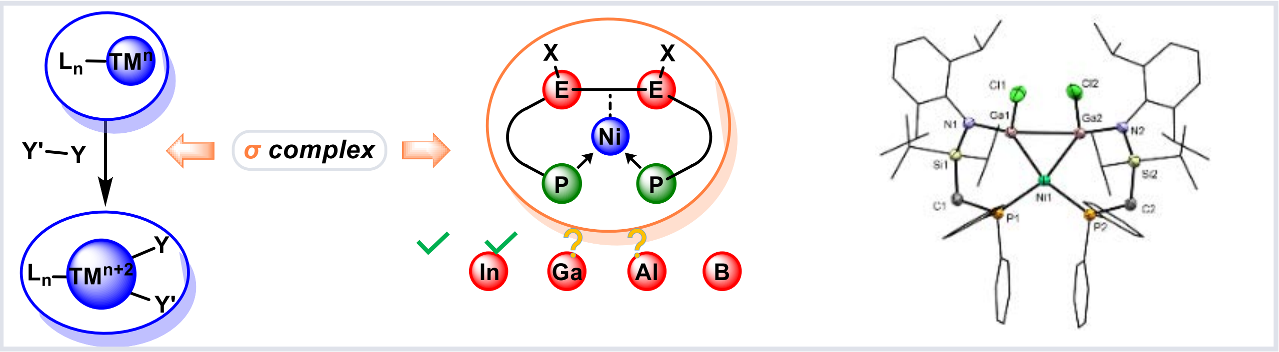
Progress only comes through understanding! For chemical reactivity bond activation is vital. When it comes to bond activation processes, oxidative addition to a Transition Metal (**TM**) center is one of the most powerful transformations, at play in countless catalysis systems.[1] Therein, *σ*-complexes are crucial intermediates. Still, aside from dihydrogen, carbon, and silicon, no stable homonuclear *σ*-complexes are known.[2] A broader understanding of homonuclear *σ*-complexes thus remains elusive – expanding this compound class, to develop an understanding of their fromation and electronic nature, is of undisputeable importance.[1] This work tackles these challenges, in establishing hitherto unknown homoatomic group 13 *σ*-bond **TM** complexes. This gives direct insights into kinetic and mechanistic aspects of the oxidative addition chemistry of homoatomic **E**-**E** bonds (**E** = **B**-**In**), and allows for the observation of otherwise 'hidden' processes, *e.g.* disproportionation. This is driven by our isolation of the first examples of η²-(**In**-**In**)-**Ni** and η²-(**Ga**-**Ga**)-**Ni**/**Pd** *σ*-complexes, forming the basis for the exploration of the full family of homoatomic group 13 *σ*-complexes. The formation of these complexes is determined by ligand design, supported by intra-molecular phosphine chelation using our in-house developed ligand systems. Since **TM** catalyzed *σ*-bond functionalization processes typically proceed *via σ*-complexes, insights into the structure, electronics, and reactivity of this compound class forms an important cornerstone for developing future catalytic processes. As such, this works aims to lay a new foundation of fundamental knowledge, helping us to tackle some of the greatest issues we face in catalysis today.

Homoatomic σ complexes



References

1] R. N. Perutz, S. Sabo-Etienne, A. S. Weller, *Angew. Chem. Int. Ed.* **2022**, *61*, e202111462.
[2] P. Gualco, A. Amgoune, K. Miqueu, S. Ladeira, D. Bourissou, *J. Am. Chem. Soc.* **2011**, *133*, 4257-4259.

PA51

QSAR analysis of antibacterial activity of tetrahedral metal(II)-benzimidazole complexes towards *Erwinia amylovora* and *Pectobacterium carotovorum*

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The present study is focused on the quantitative structure-activity relationship (QSAR) analysis of antibacterial activity of tetrahedral copper(II), zinc(II) and cobalt(II) complexes with benzimidazole derivatives towards *Erwinia amylovora* and *Pectobacterium carotovorum* (previously known as *Erwinia carotovora* subsp. *carotovora*) as well-known plant pathogens. The general structures of the analysed compounds are the following: $[CuLCl_2(H_2O)]$, $[CoL_2Cl_2]$, $[ZnL_2Cl_2]$, where L presents different benzimidazole derivatives as ligands. The synthesis and microbiological analysis of the complexes were performed earlier (Podunavac-Kuzmanović et al, 1999). The synthesized complexes possess significant antibacterial activity towards aforementioned plant pathogens and can be considered to be potential pesticide candidates. The established QSAR models are based on linear relationships and correlate inhibition zone diameter (mm) with specific molecular descriptors. The molecular descriptors were calculated using ChemBio3D Ultra 13.0 software based on 3D molecular structures that were previously subjected to the energy minimization procedure applying MM2 method. The QSAR analysis pointed out the significant influence of lipophilicity (logP), stretch energy and total energy on antibacterial activity of the analysed complexes. The obtained QSARs have narrow applicability domain and they are aimed for prediction of antibacterial activity of structurally similar benzimidazole-metal complexes towards *Erwinia amylovora* and *Pectobacterium carotovorum*. They can be considered to be guidelines for design of new complexes with higher antibacterial activity towards aforementioned microorganisms.

Acknowledgement. The present research is financed in the framework of the project “Molecular engineering and chemometric tools: Towards safer and greener future” financed by the Provincial Secretariat for Higher Education and Scientific Research of AP Vojvodina (Project No. 142-451-3095/2022-01/01).

References

Podunavac-Kuzmanović, S.; Leovac, V.M.; Perišić-Janjić, N.U.; Rogan, J.; Balaž, J. *J. Serb. Chem. Soc.* 1999, 64 (5-6), 381-388.

PA52

Group 1 and 2 Tetraphenyl-pentalenides for Lanthanide Transmetalation

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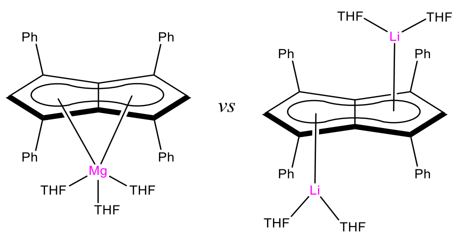
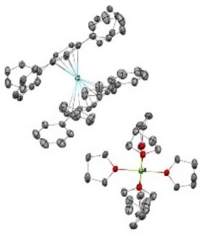
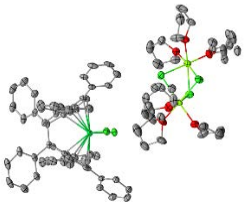
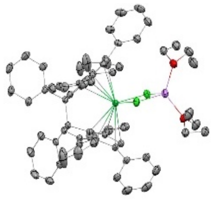
Ligand systems exhibiting strong binding and flexible coordination abilities are of great interest in organometallic chemistry. Among a plethora of such ligands, π- anionic cyclopentadienide (Cp^-) and its divers derivatives are the most widely employed. The bicyclic pentalenide (Pn^{2-}) is an interesting extension of the Cp^- system which can offer strong η^8, syn/anti-η^5/η^5, η^5/η^3, or η^3/η^3 binding modes to Lewis acidic metal centers.[1] Despite these attractive features the use of pentalenides in coordination chemistry remains sparse, mainly due to synthetic difficulties. We recently reported a facile and high-yielding solution phase synthesis of 1,3,4,6-tetraphenyl-dihydropentalene (H_2Ph_4Pn) and investigated its deprotonative metalation with a range of group 1 bases (Li/K/Na) to afford the first examples of arylated homo and hetero bimetallic pentalenides.[2] The use of group 2 bases (Mg) for the double deprotonation to access the Pn^{2-} salts has also been explored. Much like Cp^- chemistry, the synthesized group 1 and 2 Pn^{2-} salts can be used for transmetallation to d and f-block elements.

Organometallic f-block chemistry has attracted increased attention due to the presence of large f orbitals that often result in multiple spin states which are sensitive to ligand effects, leading to applications in catalysis, redox chemistry, photochemistry, magnetochemistry and material science.[3] Here we present our recent work on the behaviour of group 1 and group 2 pentalenide towards lanthanide coordination. $Li_2[Ph_4Pn]$ and $Mg[Ph_4Pn]$ have been investigated for transmatellation using $Y(HMDS)_3$, YCl_3 and $YbCl_3$. To draw the comparison, a systematic analysis of all the performed reactions has been carried out using multinuclear NMR spectroscopy (^1H, ^7Li, ^{13}C, HSQC). The molecular structures of $[Mg(THF)_6][Y(Ph_4Pn)_2]_2$, $[Mg(THF)_3Cl_3][Yb(Ph_4Pn_2)Cl_2]$ and heterometallic (Yb/Li)Pn and (Y/Mg)Pn complexes has been determined by X-ray crystallography.









References

[1] S. M. Boyt , N. A. Jenek , U. Hintermair, *Dalton Trans.* 2019, 48, 5107-512.

[2] S. M. Boyt, N. A. Jenek, H. J. Sanderson, G. Kociok-Köhn, and U. Hintermair, *Organometallics* 2022, **41**, 211–225.

[3] J. H. Farnaby, T. Chowdhury, S. J. Horsewill, B. Wilson, F. Jaroschik, *Coord. Chem. Rev.* 2021, **437***,* 213830-213913.

PA53

Synthesis of highly fluorinated *N*-Heterocyclic Carbene and evaluation of catalytic activity of copper complexes

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N-Heterocyclic carbenes (NHCs) are one of the most important ligands in organometallic chemistry and transition metal catalysis.[1] While various molecular designs have been reported to enhance the electron-donating ability of NHCs, there are few reports on controlling the electron-donating ability of NHCs by the introduction of electron-withdrawing groups.[2],[3],[4]

In this study, we designed a 1*H*-1,2,3-triazol-5-ylidene ligand bearing six number of trifluoromethyl groups. In this presentation, we will report on the synthetic methods for copper complexes with this ligand and their catalytic functions. Moreover, to evaluate the coordination ability of the carbene, rhodium-carbonyl complexes with this ligand were synthesized and the Tolman electrical parameters (TEP) were investigated. These results reveal the unique properties of NHC ligands with numerous fluorine substituents.

References

[1] Albrecht, M. *et al. Chem. Rev.* **2018**, 118, 9493-9586.
[2] Togni, A. *et. al. Organometallics.* **2015**, 34, 1384–1395.
[3] Ananikov, V. *et al. Dalton Trans.* **2022**, 51, 9843-9856.
[4] Morales-Morales,D. *et al.* *New J. Chem.* **2022**, 46, 16789-16800.

PA54

Silyl Substituted Low Oxidation State Aluminium Complexes: Al^{I} vs. Al^{II}

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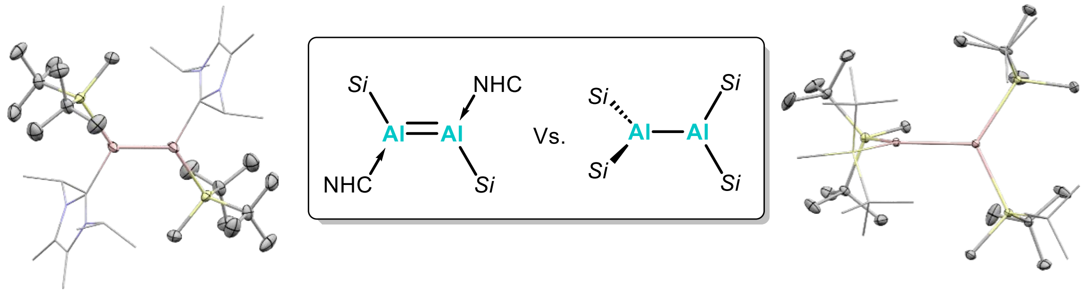
There has been a shift in contemporary chemical research towards utilising highly abundant elements for reactions generally in the remit of precious metals, allowing for more sustainable chemistry, with aluminium being a prime candidate. Trivalent Al compounds have seen a wealth of uses in processes such as Ziegler-Natta polymerisation and Friedel-Crafts alkylation.[1] Conversely, the reactivity and bonding in low oxidation state aluminium complexes is much less prevalent but has seen tremendous growth in recent times.

Our group has had great success utilising silyl-based ligands in the stabilisation of novel main group compounds, including the double bonded dialumene (Al^{I}=Al^{I}), which has been shown to be effective in "transition-metal"-like reactivity, such as in bond activation and catalysis.[2] Our interests have turned to other low oxidation state, homodiatomic aluminium species, such as dialanes (Al^{II}-Al^{II}), although they have been known for decades, their chemistry is underexplored. The synthesis and reactivity of new Al^{II} compounds will be presented and compared to previously reported low oxidation state aluminium compounds.



References

[1] (a) Boor, J. Jr.; *Zeigler-Natta catalysts and polymerizations*; Academic Press Inc.: New York, **1979**; (b) Olah, G. A.; *Friedel-Crafts and Related Reactions*; Wiley: New York, **1963**.

[2] (a) Bag, P.; Porzelt, A.; Altmann, P. J.; Inoue, S.; *J. Am.Chem.Soc.*, **2017**, *139*, 14384; (b) Weetman, C.; Porzelt, A.; Bag, P.; Hanusch, F.; Inoue, S.; *Chem. Sci.*, **2020**, *11*, 4817; (c) Weetman, C.; Bag., P.; Szilvási, T.; Jandl, C.; Inoue, S.; *Angew. Chem. Int. Ed.*, **2019**, *58*, 10961; (d) Xu, H.; Kostenko, A.; Weetman, C.; Fujimori, S.; Inoue, S.; *Angew. Chem. Int. Ed.*, **2023**, *62*, e203316021.

PA55

d(CH$_2$P(*i*Pr)$_2$)abB–Bpin – An Unsymmetrical Diborane(4) as a Versatile PBP Pincer Complex Precursor

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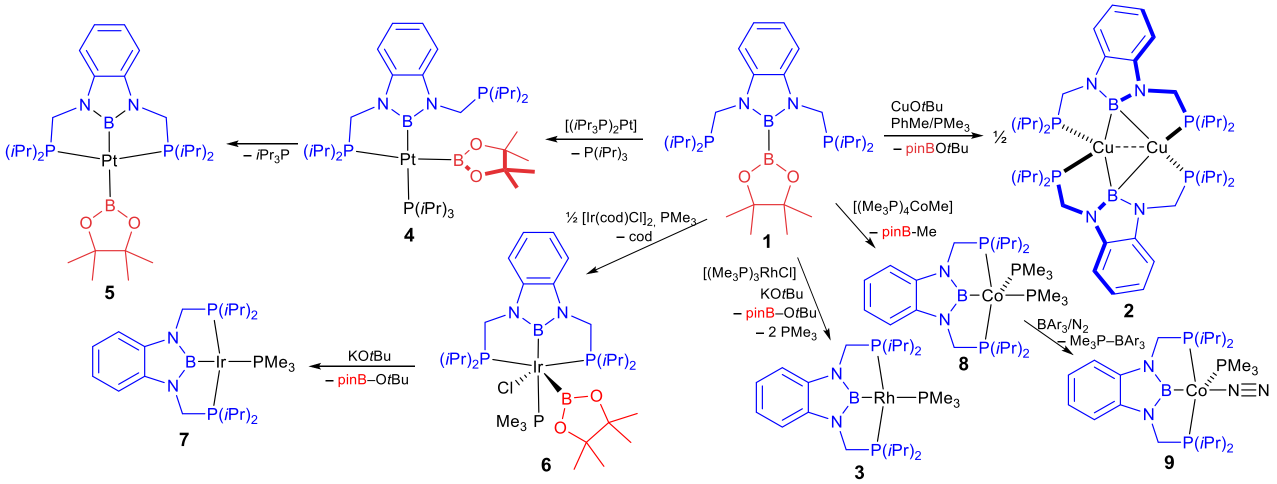
PBP pincer ligands, comprising one boryl ligand and two phosphine ligands within a pincer ligand framework, have first been report in 2009 by *Nozaki*, *Yamashita* and co-workers.[1] This type of ligand has since than been explored with respect to their coordination chemistry with various transition metals as well as with respect to potential applications in divers catalytic and stoichiometric processes.[2] However, their further development of PBP pincer complexes is hampered by its exclusive synthetic accessibility *via* an oxidative addition of a B–H precursor. To broaden the accessible PBP pincer complexes we recently developed an unsymmetrical diborane(4), d(CH$_2$P(*i*Pr)$_2$)abB–Bpin (**1**), as a versatile PBP ligand precursor. Reacting *via* σ bond metathesis, as exemplified by its copper (**2**) and rhodium (**3**) complexes and, alternatively, *via* oxidative addition, as exemplified by the *bis*-boryl platinum (**4**, **5**) and iridium (**6**, **7**) complexes as well as the PBP cobalt (**8**, **9**) boryl complex, this diborane is an ideal precursor for so far inaccessible PBP pincer complexes.[3,4] The talk will address the synthesis of PBP pincer complexes via the diborane d(CH$_2$P(*i*Pr)$_2$)abB–Bpin (**1**) and their structural and chemical properties, as well as their fundamental reactivity.



Scheme: Formation of PBP boryl complexes from a diborane(4) precoursor.

References

[1] Y. Segawa, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 9201. [2] For recent examples: P. Ríos, J. Borge, F. Fernández de Córdova, G. Sciortino, A. Lledós, A. Rodríguez, *Chem. Sci.* **2021**, *12*, 2540. F. Fang, J. Chang, J. Zhang, X. Chen, *Organometallics* **2021**, *40*, 3825. F. W. Seidel, K. Nozaki, *Angew. Chem. Int. Ed.* **2022**, *61*, e202111691. M.-M. Xue, J. Chang, J. Zhang, X. Chen, *Dalton Trans.* **2022**, *51*, 2304. [3] P. M. Rutz, J. Grunenberg, C. Kleeberg, *Organometallics* **2022**, *41*, 3044. [4] P. M. Rutz, J. Grunenberg, C. Kleeberg, *in preparation*.

PA56

Lithium Aluminium Hydride and Metallic Iron: A Powerful Team in Alkene and Arene Hydrogenation Catalysis

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$LiAlH_4$ is a bulk reagent for reduction of ketones and imines. Although generally used in stoichiometric quantities, recently it was shown to be a catalyst for the hydrogenation of imines under H_2 atmosphere.[1]

We report that addition of metallic iron drastically boosts the reducing power of $LiAlH_4$.[2] Stoichiometric or catalytic use of $LiAlH_4/Fe^0$ mixtures enables reduction of alkenes and even arenes, partially under mild conditions (2.5 mol% $LiAlH_4$/Fe, 25-150 °C, 1-50 bar H_2). The iron was activated by metal vapour synthesis and is itself hardly active in hydrogenation catalysis.

The actual catalyst is Fe^0 and the decomposition product of $LiAlH_4$, presumably Al^0. A mixture of Fe^0 and $Al(iBu)_3$ was found to be an even better catalyst.

References

[1] H. Elsen, C. Färber, G. Ballmann, S. Harder, *Angew. Chem. Int. Ed.* **2018**, *130*, 7156–7160.
[2] C. Knüpfer, C. Färber, J. Langer, S. Harder, *Angew. Chem. Int. Ed.* **2023**, e202219016.

PA57

Direct Cross Coupling of Potassium Organyls with Aryl Halides Enabled by YPhos-Palladium Catalysts

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Organolithium reagents have been the state of the art for many applications in the field of synthetic chemistry, which can be attributed to their accessibility, high solubility in hydrocarbons, and relatively high basicity.[1] [2] In recent years however, researchers have been looking beyond lithium in a surge for more sustainable alternatives, due to its low earth abundance.[3] Recent studies have shown remarkable applicability of sodium- and potassium organyls in synthetic chemistry.[4] [5]

The direct cross coupling of alkali-metal organyls has early been described for lithium by Murahashi, and later more generalized by Feringa.[6] Also, the coupling of organosodium reagents has been reported, but no examples with potassium organyls are known in literature until to date.[5] Herein we present the first protocol for a successful direct cross-coupling of organopotassium compounds with aryl halides using an easily accessible YPhos-palladium catalyst. This efficient procedure is realized due to the fast oxidative addition enabled by our YPhos ligands and requires no further additives.[7]

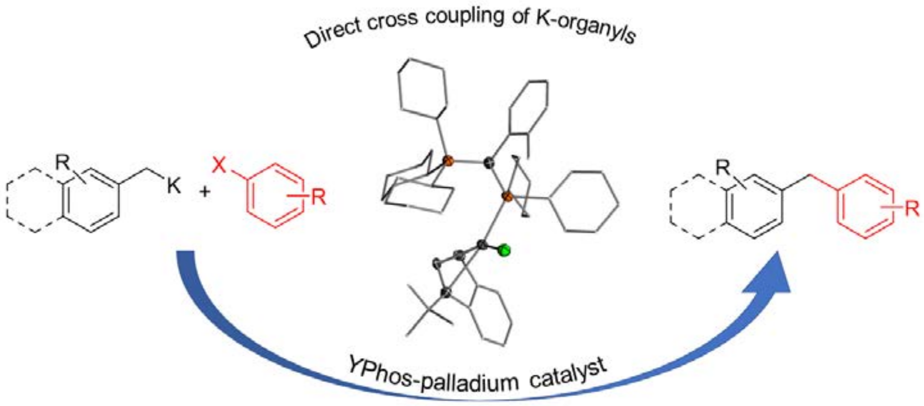

Figure 1. General scheme of the direct cross-coupling of potassium organyls with aryl halides using a YPhos-Pd catalyst.

References

[1] U. Wietelmann and J. Klett, *Z. Anorg. Allg. Chem.,* **2018**, *644*, 194-204.
[2] R. E. Mulvey , S. D. Robertson, *Angew. Chem. Int. Ed.,* **2013**, *52*, 11470-11487.
[3] J. M. Tarascon, *Nat. Chem.,* **2010**, *2*, 510.
[4] D. E. Anderson, A. Tortajada , E. Hevia, *Angew. Chem. Int. Ed.,* **2023**, *62*, e202218498.
[5] S. Asako, H. Nakajima , K. Takai, *Nat. Catal.,* **2019**, *2*, 297-303.
[6] S. Hazra, C. C. C. J. Seechurn, S. Handa , T. J. Colacot, *ACS. Catal.,* **2021**, *21*, 13188-13202.
[7] T. Scherpf, H. Steinert, A. Großjohann, K. Dilchert, J. Tappen, I. Rodstein , V. H. Gessner, *Angew. Chem. Int. Ed.,* **2020**, *59*, 20596-20603.

PA58

Ecotoxicology and environmental parameters of monobenzimidazole copper(II) and dibenzimidazole cobalt(II) complexes as potential pesticides

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Significant number of benzimidazole derivatives possesses considerable antifungal, antibacterial and antiviral activity. Taking into account that some benzimidazoles express antibacterial activity towards certain causative agents of infectious diseases in plants, for example *Erwinia amylovora*, their potential application in agriculture as pesticides should be considered. The series of three tetrahedral copper(II)-based monobenzimidazole (general formula: $[CuLCl_2(H_2O)]$) and three cobalt(II)-based dibenzimidazole (general formula: $[CoL_2Cl_2]$) complexes was synthesized (Podunavac-Kuzmanović et al, 1999). Since they expressed significant antibacterial activity and their potential application as pesticides was suggested, in the present study the estimation of their ecotoxicology and environmental parameters was done based on VegaNIC-1.0.8 program. Based on Benigni-Bossa mutagenicity model, the synthesized complexes are non-mutagens, however some of them are considered potential carcinogens (the complexes that possess halogens (Cl and F) in the ligand structure). The copper(II)-complexes have the lowest IC_{50} values for fathead minnow (*Pimephales promelas*) for 96h and *Daphnia magna* after 48h which makes them more toxic for aquatic species than the cobalt(II)-complexes. Also, based on read-across prediction it was estimated that the copper(II)-complexes have higher bioconcentration factors (BCF) than cobalt(II)-complexes. Also, lower lipophilicity (higher water solubility) of copper(II)-complexes may significantly influence their toxicity for aquatic species and limit or dispute their practical utilization as pesticides.

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References

Podunavac-Kuzmanović, S.; Leovac, V.M.; Perišić-Janjić, N.U.; Rogan, J.; Balaž, J. *J. Serb. Chem. Soc.* 1999, 64 (5-6), 381-388.

PA59

Development and Homo-Coupling of Base-Stabilized Bis-Phosphinidenes

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Chelating bis-phosphines have long been a valuable ligand class for transition-metal complexes. Phosphinidenes, which can be isolated as base-stabilized P^I compounds, hold two lone pairs of electrons at their P-center, which gives them a unique ability to bind two metal centers at the P-atom. Bis-phosphinidenes combine the chelating effect of bis-phosphines with characteristics of phosphinidenes, leading to the formation of a new highly electron rich ligand class. So far, only two bis-phosphinidene ligands are known. The first was reported in 2020 by Hadlington et al. featuring a xanthene-backbone,[1] followed by a ferrocene-supported derivative in 2021 from Inoue et al.[2] To further expand the scope of this unique ligand class, synthesis of a new family of bis-phosphinidenes has been targeted. Expanding to derivatives of the known xanthene-supported system, we have been able to access the ^{t}Bu-modified derivative, as well as the benzofuran derivative (Fig. 1a). These give important changes in the solubility and bite-angle of the ligand scaffolds, respectively. Spectroscopic methods indicate the formation of bis-phosphinidenes, with characteristic ^{31}P NMR resonances between δ = -70 and -90 ppm. Importantly, xanthene-derived bis-phosphinidenes undergo a remarkable Ni-templated P-P coupling reaction when combined with Ni(cod)$_2$, forming unprecedented low-valent P-P macrocycles (Fig. 1b). The same reaction for the benzofuran system leads to intractable mixtures, indicative of the importance in the bite-angle of developed bis-phosphinidenes in this coupling process.

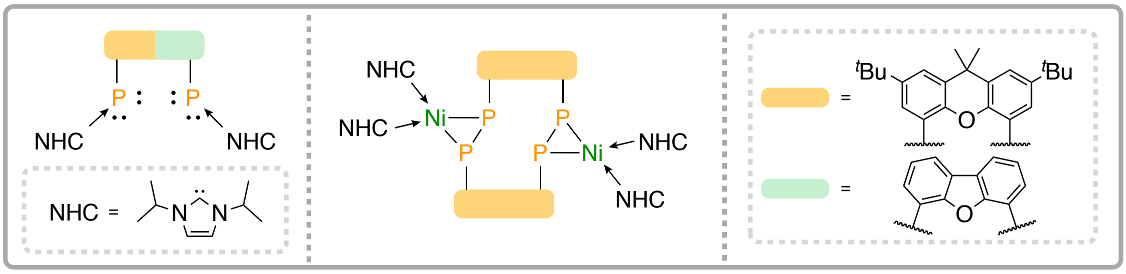

Fig. 1: Schematic representation of **a)** NHC-stabilised bis-phosphinidenes, and **b)** P-P macrocycle from Ni-templated P-P coupling reaction of bis-phosphinidenes.

References

[1] T. J. Hadlington, A. Kostenko, M. Driess, *Chem. – Eur. J.* **2021**, *27*, 2476–2482.
[2] R. Baierl, A. Kostenko, F. Hanusch, S. Inoue, *Dalton Trans.* **2021**, *50*, 14842–14848.

PA60

Role of a ferrocenyl group in chemoselectivity of cross Rauhut-Currier reaction

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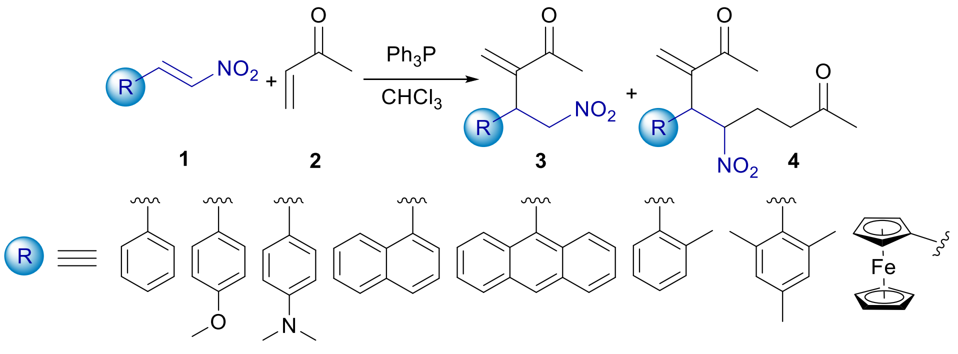
A cross Rauhut-Currier (CR) reaction provides a new carbon-carbon bond formation between electron-deficient alkenes (Michael acceptors) in the presence of a nucleophilic catalyst (Lewis bases).[1,2] This reaction yields multifunctional compounds that are used for further synthetic transformation.[2] The chemoselectivity of the CR reaction was studied employing β-substituted nitroalkenes **1** and methyl vinyl ketone (**2**) in the presence of triphenylphosphine. The RC coupling between **1** and **2** gave a product mixture identified as RC adduct **3** and **4** (Scheme). There is observed that the chemoselectivity of the reaction improves with an increase of electron-donating properties of the substituent at the β-position of nitroalkene **1**. Therefore, the study showed that the reaction efficiency directly depends on the electronic and steric properties of substituents at the β-position of nitroalkenes and the strong electron-donating bulky ferrocenyl group at the β-position certainly contributes to a more chemoselective protocol. Employing 1-ferrocenyl-2-nitroethylene in the RC reaction ensured only **3** in high yield (92%). This research could contribute to overcoming typical challenges related to nitroalkenes: instability, limited selectivity, and low reaction efficiency.



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References

1. C. E. Aroyan, A. Dermenci, S. J. Miller, *Tetrahedron* 2009, 65, 4069–4084.
2. P. Xie, Y. Huang, *Eur. J. Org. Chem.* 2013, 6213–6226.

PA61

Addressing the Challenges of Asymmetric Hydrogenation of Exocyclic Benzofused-Based Alkenes with New Ir-P,N Catalysts

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Metal-catalyzed asymmetric hydrogenation is a powerful and sustainable method for preparing chiral compounds due to its perfect atom economy.[1] However, most catalysts are only tested with benchmark substrates, eluding challenging ones that would yield to more appealing compounds, such as exocyclic olefins with a benzofused five/six-membered ring motif, whose hydrogenation products are present in pharmaceutical natural products and key bioactive drug intermediates.

Compared to the considerable number of reports about the reduction of unfunctionalized acyclic and endocyclic olefins, the reduction of unfunctionalized exocyclic olefins is underdeveloped. Only the Ir/In-BiphPHOX catalyst has been reported to have high catalytic performance for a range of exocyclic benzofused five-membered olefins (93-98% ee).[2] However, the enantioselectivity was lower in the reduction of the parent benzofused six-membered olefin (75% ee). Additionally, the reaction required an additive and a specific solvent (*o*-xylene), moving away from the commonly used solvents in Ir-catalyzed asymmetric hydrogenation. The difficulty in the reduction of this type of benzofused five/six-membered olefins is even more evident if we consider that PHOX, which are the most successful ligands for Ir-catalyzed hydrogenation, did not work. Herein, we present a new and simple chiral phosphine-triazole ligand for the asymmetric Ir-catalyzed hydrogenation of exocyclic benzofused alkenes.[3] Overcoming previous limitations, the new catalytic system can successfully hydrogenate a series of exocyclic olefins bearing a benzofused five- and six-membered ring motif (ee's up to 99%). The catalyst tolerates well the presence of several substituents and substitution patterns at both aromatic rings. Mechanistic studies explain the origin of this exceptional high catalytic performance.

References

[1] J. J. Verendel, O. Pàmies, M. Diéguez, P. G. Andersson, *Chem. Rev.* **2014**, *114*, 2130-2169 and references therein.

[2] J. Xia, G. Yang, R. Zhuge, Y. Liu, W. Zhang, *Chem. Eur. J.* **2016***, 22,* 18354-18357.

[3] M. Biosca, P. de la Cruz-Sánchez, D. Tarr, P. Llanes, E. A. Karlsson, J. Margalef, O. Pàmies, M. A. Pericàs, M. Diéguez, *Adv. Synth. Catal.* **2023**, *365*, 167-177.

PA62

Irrecoverable diminish of NAD+ in a hypoxic glioblastoma cell line by photo-activated NAMPT inhibitor

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Photo-activated chemotherapy agents show a promising ability to be activated not only in normoxic cells but also in hypoxic cells. Thereby, they form a new branch of targeted anticancer agents with potentially lower systemic side effects. Here we report a study of the photo-activated NAMP inhibitor Ru-STF31 in the glioblastoma cancer cell line U87 cultured in normoxia (21% O_2)and hypoxia (<1%, O_2). Ru-STF31 has significantly higher toxicity and solubility than the commercially available NAMPT inhibitor STF-31, and it could significantly decrease NAD$^+$ levels in hypoxic cells due to the synergistic effect between free STF31 and Ru-aqua complexes.

PA63

Gold (I) mediated radio-iododecarboxylation toward applications in nuclear medicine

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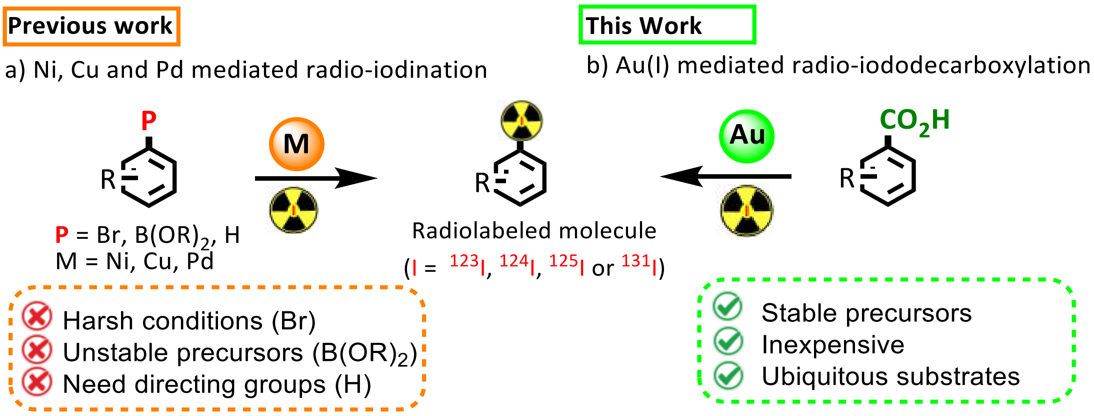
Labelling of (bio)molecules with radioactive isotopes is of high interest to the scientific community, as it strongly impacts the discovery process in life sciences and nuclear medicine. In nuclear medicine, radio-therapeutics for RadioIsotope Therapy (RIT)[1] and radio-tracers for molecular imaging experiments such as Positron Emission Tomography (PET) or Single Photon Emission Computed Tomography (SPECT) have been described.[2] In this context, four iodine radioactive-isotopes can be used, each one with a specific application: ^{123}I and ^{124}I for SPECT and PET imaging respectively, ^{125}I for binding studies, and ^{131}I for radiotherapy.[3] Considering the difficulties and the cost to develop a radiolabeling process, the discovery of efficient synthetic methods is highly desirable. A variety of new transformations mediated by transition metal (Ni, Cu and Pd) have been developed in recent years.[4] Inspired by the gold(I) mediated decarboxylation of arene described by Larrosa,[5] our team recently demonstrated that a carboxylic acid function can be used to promote radio-iodination. In this study, we will present the straightforward decarboxylative gold(I) mediated radioiodination of a variety of carboxylic acids. Such reactions were performed in different conditions and without the need of purifying the gold organometallic adduct. In addition, to demonstrate the potential of our methodology, we will also present the radio-iodination of known radiotracers or iodinated drugs using the carboxylic acid function as a precursor.



References

[1] *Chem. Rev.* **1999**, 99, 2269–2292. [2] *Chem. Soc. Rev.* **2011**, 40, 149–162. [3] *Chem. Soc. Rev.* **2005**, 34, 153–163. [4] *J. Org. Chem.* **2020**, 85, 8300–8310. [5] *Adv. Synth. Catal.* **2011**, 353, 1359–1366.

PA64

Design, synthesis, docking and mechanistic studies of new thiazolyl/thiazolidinylpyrimidine-2,4-dione antiproliferative agents

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We synthesis and biological evaluation of a new series of 3a-l and 5a-e. The structures of the new compounds were confirmed. The antiproliferative activity of 3a-l and 5a-e was evaluated against four human cancer cell lines where the compounds showed promising activity.

3a-l

a: $R = R^1 = Ph$
b: $R = 4\text{-}CH_3Ph$, $R^1 = Ph$
c: $R = 3\text{-}CH_3OPh$, $R^1 = Ph$
d: $R = CH_2Ph$, $R^1 = Ph$
e: $R = CH_3$, $R^1 = Ph$
f: $R = CH_2\text{-}CH{=}CH_2$, $R^1 = Ph$
g: $R = Ph$, $R^1 = CH_3$
h: $R = 4\text{-}CH_3Ph$, $R^1 = CH_3$
i: $R = 3\text{-}CH_3OPh$, $R^1 = CH_3$
j: $R = CH_2Ph$, $R^1 = CH_3$
k: $R = R^1 = CH_3$
l: $R = CH_2\text{-}CH{=}CH_2$, $R^1 = CH_3$

5a-e

5a: $R = Ph$
5b: $= 3\text{-}CH_3OPh$
5c: $= CH_2Ph$
5d: $= CH_3$
5e: $= CH_2\text{-}CH{=}CH_2$

PA65

Screening of the synthesis route on the structural, magnetic and magnetocaloric properties of $La_{0.6}Ca_{0.2}Ba_{0.2}MnO_3$ manganite: A comparison between solid-solid state process and a combination polyol process and Spark Plasma Sintering

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$La_{0.6}Ca_{0.2}Ba_{0.2}MnO_3$ ceramics are prepared by an original route, combining soft chemistry and Spark Plasma Sintering, within a few minutes at 700 °C and by the solid-state reaction at high temperatureswith an annealing temperature of 1200 °C. We have studied the leverage of the powder synthesismethod on the structural, morphological, magnetic and magnetocaloric properties of the samples. X-ray diffraction analysis using Rietveld refinement revealed that our materials crystallize in the rhombohedral system with R3-c space group for the sample prepared by the Polyol-Spark Plasma Sintering method and in the orthorhombic structure with Pbnm space group for the sample synthesized by the solid-state reaction. Magnetization measurements versus temperature under magnetic applied field of 0.05 T show a paramagnetic-ferromagnetic phase transition for both samples. The Arrott plots reveal that ours materials undergo a second-order phase transition. The maximum values of the magnetic entropy change ($-\Delta S_{max\ M}$) under the magnetic field change of 5 T are 2.4 and 4.7 J/kg K for $La_{0.6}Ca_{0.2}Ba_{0.2}MnO_3$ synthesized by using solid-state reaction and Polyol-Spark Plasma Sintering methods respectively. The highest value of the relative cooling power RCP is found to be 244 J/kg for the Polyol-Spark Plasma Sintering sample under 5 T. These results are interesting enough and suggest that the Polyol-Spark Plasma Sintering synthesis method is a feasible route to prepare high quality perovskite material for magnetic cooling application.

Keywords: Manganites, Preparation methods, Magnetization, Magnetocaloric effect

PA66

A Missing Piece- The Isolation of a Cyclodiphosphadiazenium Ion

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Pioneers of main group chemistry sought to produce novel chemical reactivity through the creation of new and abnormal bonding environments. Research in the last two decades, in particular surrounding Frustrated Lewis Pairs has enabled *p*-block centers to perform chemistry only thought possible for transition metals[1]. 1-Chloro-cyclodiphosphadiazenium ions were first reported by Cowley in a detailed NMR spectroscopy study[2] and examined more extensively by Burford.[3-4] The highly strained 4 membered ring system and unusual electronics made this family of compounds prototypical examples of an unusual phosphorus bonding environments. To date, Schulz is the only one to report X-ray crystal structures for cyclodiphosphadiazenium ions.[5-6] However, the structures exhibit a high level of disorder within the ring and uncertainty around the true phosphorus bonding environment.

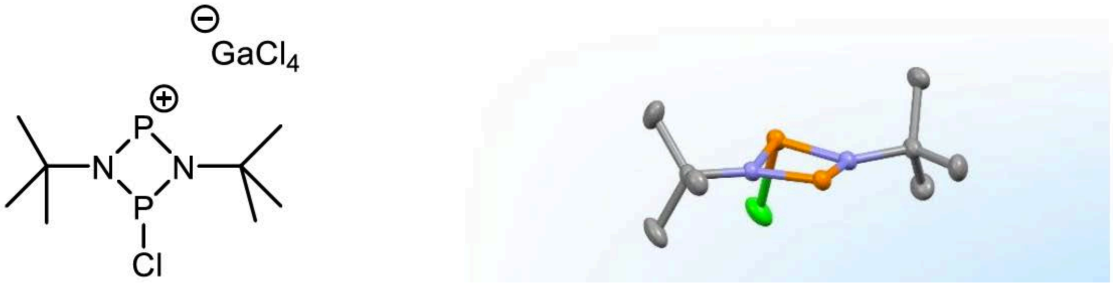

Figure 1 Chemical structure (left) and X-ray crystal structure (right) for 1-chloro-2,4-ditertbutyl- cyclodiphosphadiazenium ion.

This work reports the X-ray crystal structure for 1-Chloro-2,4-ditertbutyl-cyclodiphosphadiazenium tetragalliumate (Figure 1). This is the third of its kind and the only without disorder within the cationic species, filling in a piece which has been missing for the last 40 years. The Lewis acidity was assessed experimentally using the Gutman Beckett[7] method determining the compound to be a superacid with a Lewis acidity of 113% relative to $B(C_6F_5)_3$. The absence of disorder within the structure has enabled the first detailed and experimentally supported computational study in to this elusive family of compounds.

References

1. Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006,** *314* (5802), 1124-1126.
2. Cowley, A.; Lattman, M.; Wilburn, J., *Inorg. Chem.* **1981,** *20* (9), 2916-2919.
3. Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Lumsden, M.; Macdonald, C. L.; McDonald, R.; Phillips, A. D.; Ragogna, P. J.; Schurko, R. W. *J. Am. Chem. Soc.* **2002,** *124* (47), 14012-14013.
4. Burford, N.; Conroy, K. D.; Landry, J. C.; Ragogna, P. J.; Ferguson, M. J.; McDonald, R.. *Inorg. Chem.* **2004,** *43* (26), 8245-8251.
5. Michalik, D.; Schulz, A.; Villinger, A.; Weding, N., A cationic cyclic phosphorus (III) azide. *Angew. Chem. Int. Edit.* **2008,** *47* (34), 6465-6468.
6. Kuzora, R.; Schulz, A.; Villinger, A.; Wustrack, R., *.Dalton. Trans.* **2009,** (42), 9304-9311.
7. Beckett, M. A.; Strickland, G. C.; Holland, J. R.; Varma, K. S. *Polymer* **1996,** *37* (20), 4629-4631.

PA67

Redox-Transmetalation and Associated Bimetallics Based on an Al/Zn System

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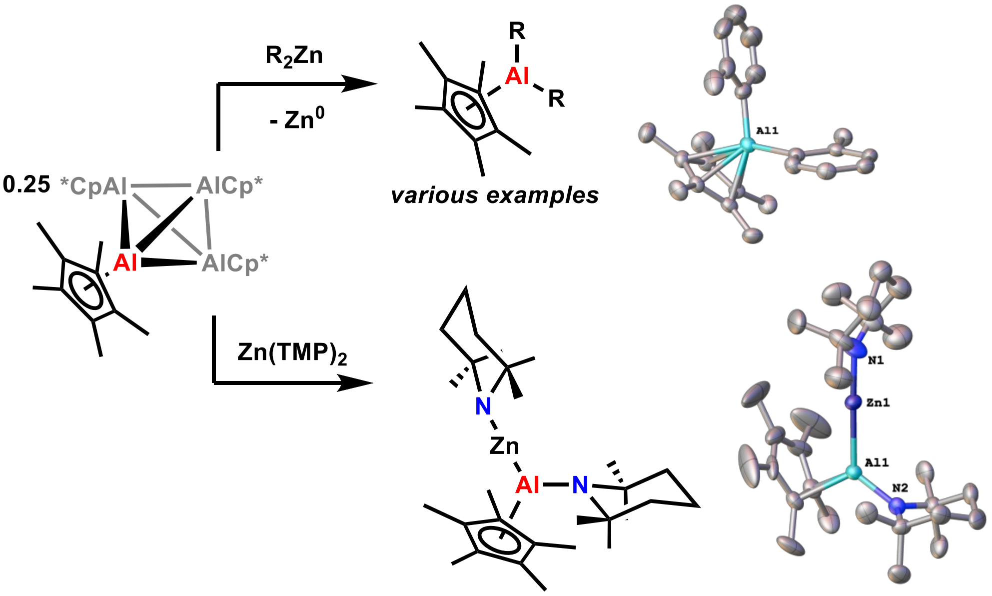
In the last decade, the chemistry of low-valent aluminum has significantly aroused the interest of many different groups around the globe.[1] As the chemistry of group13 low-valents has evolved, it was also put into context of bimetallics. So does the deft combination of aluminyl precursor and metallic partner yield various combinations of compounds which contain a metal-metal bond. The unsupportive nature of these bonds facilitates unique reactivity. A recent breakthrough is for instance the nucleophilic behaviour of beryllium across an [Al]-[Be] bond.[2] To establish such metal-metal bonds, however, usually requires large, bulky ligands to kinetically stabilize these systems.



In our group, we are currently interested in downsizing ligand bulk which would e.g., be promising for the formation of main-group oligomers and multiple bond activations. Therefore, we currently investigate the reactivity of $[AlCp^*]_4$ towards various small organometallics and homoleptic complexes of small molecules. Here, we demonstrate the reactivity towards diorgano-zinc compounds (=ZnR_2) as well as $ZnTMP_2$. In case of ZnR_2 we could observe the selective transfer of "AlCp*" forming $AlCp^*R_2$ *via* reductive transmetalation. The use of bis amide $ZnTMP_2$, however, gives rise to the formation of a compound with an exceptionally short, rarely[3] observed Al-Zn bond of 239.2(3) pm. We are currently having a look into the reactivity of such simpler systems.

References

[1] see e.g. *Chem. Sci.*, **2020**, *11*, 6942-6956, *Chem. Commun.*, **2023**, *59*, 503-519; *ChemCatChem*, **2018**, *10*, 4213-4228. [2] *JACS.* **2023**, 145, 8, 4408–4413. [3] *ACIE.* **2021,** *60(41)*, 22301-22306.; *Chem. Sci.,* **2018***, 9,* 2348–2356; *Chem. Commun.* **2022,** *58*, 10091–10094; *Inorg. Chem..* **2018***, 9,* 2348–2356.

PA68

Gaseous CO-free Palladium-Catalyzed Reductive cyclization reactions of nitroarenes: An Endless story!

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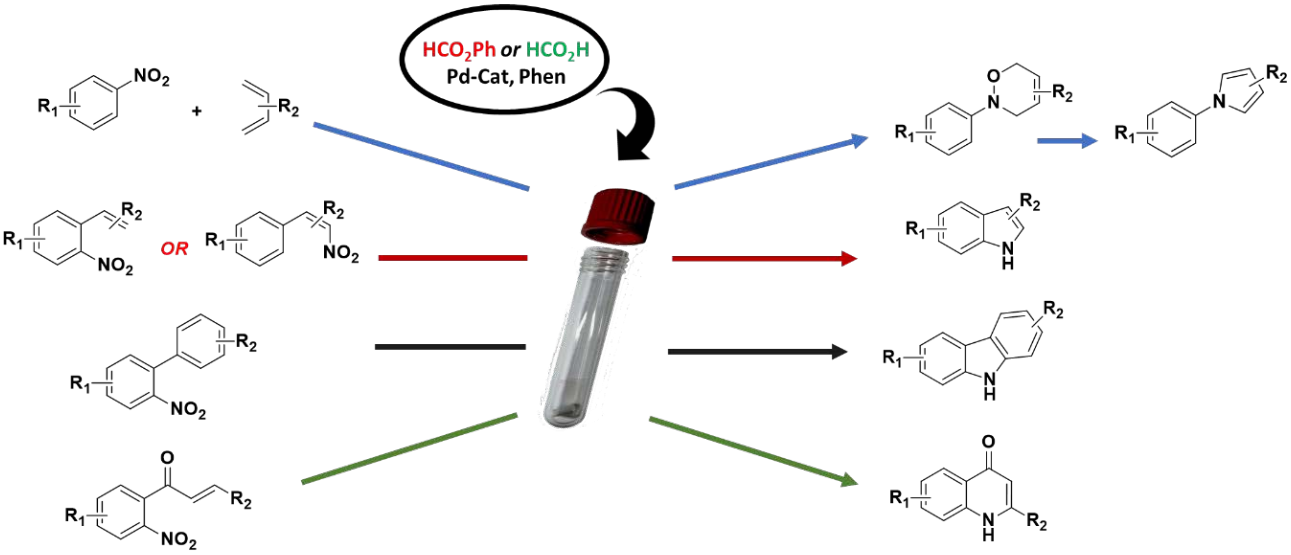
The reductive cyclization reaction of nitroarenes to produce *N*-heterocycles has been investigated for more than four decades using CO as a cheap reductant, but it is still a fascinating area for research and advancements.[1-2] However, using toxic CO gas is accompanied by many disadvantages. Therefore, our group has pioneered the use of phenyl formate [3-6] and formic acid [7] as cheap, affordable, efficient and safe *in-situ* CO surrogates for the reductive cyclization of various nitroarenes (**Scheme 1**). Notably, in most cases, the isolated yield of the desired heterocycle was higher than those previously obtained for the same reaction when gaseous CO had been employed, which indicates that the use of these surrogates should not necessarily be considered a second choice when the use of CO gas is not possible. A cheap thick-walled glass "pressure tube" can be used instead of less-available autoclaves.



Scheme 1. Synthesis of different *N*-heterocycles from nitroarenes.

References

[1] C. Crotti, S. Cenini, B. Rindone, S. Tollari, F. Demartin, *J. Chem. Soc. Chem. Commun.* **1986**, *10*, 784.
[2] F. Ferretti, D. R. Ramadan, F. Ragaini, *ChemCatChem* **2019**, *11*, 4450.
[3] M. A. EL-Atawy, D. Formenti, F. Ferretti, F. Ragaini, *ChemCatChem* **2018**, *10*, 4707.
[4] M. A. Fouad, F. Ferretti, D. Formenti, F. Milani, F. Ragaini, *Eur. J. Org. Chem.* **2021**, 4876.
[5] F. Ferretti, M. A. Fouad, F. Ragaini, *Catalysts* **2022**, *12*, 106.
[6] D. R. Ramadan, F. Ferretti, F. Ragaini, *J. Catal.* **2022**, *409*, 41.
[7] M. A. Fouad, F. Ferretti, F. Ragaini, *J. Org. Chem.* **2023**, *in press*.

PA69

Bis-Triazolylidenes of Mn and Re and Their Application in N-Alkylation of Amines with Alcohols

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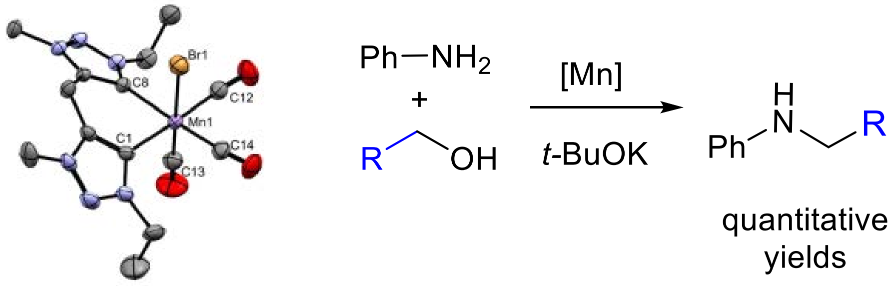
In recent years, the development of catalysts based on inexpensive first-row transition metals has become a central topic in catalysis. In particular, the field of manganese catalysis has attracted a great deal of attention from the scientific community. As a consequence of the intensive research, significant advances in this area have been achieved.[1] Most of the best performing Mn catalysts contain electron-rich phosphine ligands, that are in general air and moisture sensitive, toxic and difficult to prepare. The rational design of phosphine-free Mn complexes with improved activity is a great challenge. Herein, we describe the synthesis of a new family of air-stable Mn and Re complexes bearing bidentate bis(1,2,3-triazol-5-ylidene) ligands (bis-trz) with the general formula *fac*-[Mn(bis-trz)(CO_3)Br], containing a methylene-linker or a direct link between the two trz moieties. All complexes have been applied in the N-alkylation of amines with alcohols. The Mn complex bearing a bis-trz with a CH_2-linker between the two trz fragments was shown to be a highly efficient catalyst, affording the corresponding amine in 92% yield in the presence of a low base loading (*t*-BuOK, 0.1 equiv.).[2]



Scheme 1. N-Alkylation of amines with alcohols catalysed by a Mn(bis-trz) complex.

Acknowledgments: We thank FC&T for funding: PhD grant SFRH/BD/131955/2017 (S.F.), PTDC/QUI-QIN/0359/2021, MOSTMICRO-ITQB, UIDB/04612/20220 and UIPD/04612/2020, and CERMAX through project 022162.

References

1. D. Valyaev, G. Lavigne, N. Lugan, *Coord. Chem. Rev.*, **2016**, *308*, 191-235.
2. S. Friães, C. S. B. Gomes, B. Royo, *Organometallics* **2023**, DOI: 10.1021/acs.organomet.3c00046

PA70

Mesoionic Carbenes of Molybdenum(0) as Catalysts for Acceptorless Dehydrogenative Coupling Reactions

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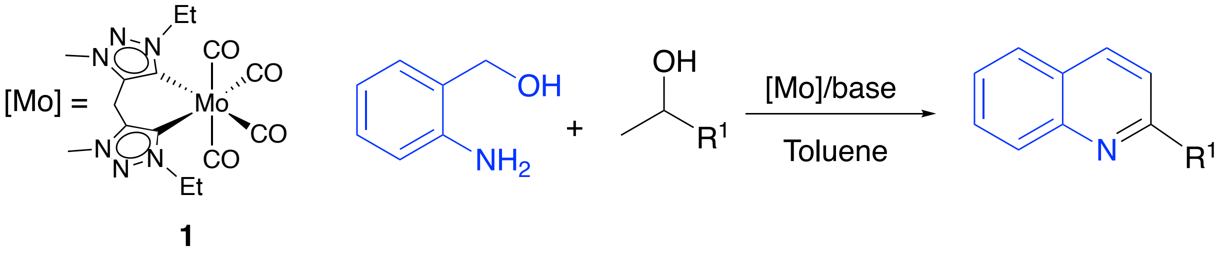
Mesoionic carbenes of the 1,2,3-triazolylidene type (trz) have become popular ligands in organometallic chemistry owing to their strong donor properties and their modular synthesis.[1] Their transition metal complexes have shown excellent activities in a wide variety of catalytic reactions, e.g. water oxidation, and transfer hydrogenation. Up to date, the chemistry of 1,2,3-triazol-5-ylidenes (trz) with molybdenum has remained poorly developed, and application of these complexes in catalysis is limited to few examples. In continuation with our interest in developing phosphine-free catalytic systems with inexpensive metals,[2] we report here a new family of bis-triazolylidene molybdenum(0) complexes and their application in the synthesis of quinolines through acceptorless dehydrogenative coupling reactions (ADC) (Scheme 1). We have disclosed the excellent catalytic activity of complex **1** for the synthesis of a wide variety of substituted quinolines from 2-aminobenzylalcohols and readily available secondary alcohols. Interestingly, we have observed that variation of the substituents at the triazolylidene ring of complexes [Mo(CO)$_4$(bis-trz)] has a significative impact in the catalytic efficiency of their Mo complexes.



Scheme 1. Synthesis of substituted quinolines mediated by a Mo(0)-trz complex

Acknowledgments: We thank FC&T for funding: PTDC/QUI-QIN/0359/2021, MOSTMICRO-ITQB, UIDB/04612/20220 and UIPD/04612/2020, and CERMAX through project 022162.

References

(1) G. Guisado-Barrios, M. Soleilhavoup, G. Bertrand, Acc. Chem. Res. **2018**, 51, 3236-3244.
(2) S. Friães, S. Realista, H. Mourão, B. Royo, *Eur. J. Inorg. Chem.* **2022**, (10) e202100884.

PA71

Cu(I)-catalyzed synthesis of fluorinated alcohols from alkenes and ketones: DFT studies

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Fluorinated alcohols are a class of organic compounds containing one or more fluorine atoms in their molecular structure. These fluorinated species have a wide range of applications due to their unique properties, and are used in electronics, textiles, *etc.*[1] The preparation of fluorinated alcohols from alkenes and symmetric ketones can be carried out following a copper(I)-catalyzed hydroboration/nucleophilic substitution sequence similar to that proposed by Nielsen and Skrydstrup.[2]

The reaction has been computationally explored to propose a plausible mechanism and the effect of each substrate, in terms of their electron donating ability, has been investigated. The obtained results indicate that the combination of electron-rich alkenes and electron-poor ketones produce the lowest activation barriers, in agreement with the nature of the rate-limiting step of reaction, thus providing a way to prepare fluorinated tertiary alcohols from simple reactants.

References

[1] S. Khaksar, S. M Vahdat, M. Gholizadeh, S. M. Talesh, *J. Fluor. Chem.* **2012**, *136*, 8–11.
[2] M. Juhl, S. L. R. Laursen, Y. Huang, D. U. Nielsen, K. Daasbjerg, T. Skrydstrup, *ACS Catal.* **2017**, *7*, 1392–1396.

PA72

Nickel-based catalyst supported on natural clay synthesis and characterization. Application in the reaction of the dry reforming of methane

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The search for efficient, less expensive and ecological materials for the dry reforming of methane is in perpetual evolution. Indeed, researchers are constantly trying to develop catalysts based on Nickel, a metal with a catalytic activity comparable to that of heavy metals but which is much cheaper due to its abundance in nature. However, Nickel-based catalysts suffer from rapid deactivation caused by Coke deposition and particle sintering at high temperatures and therefore significant loss of active phase. In addition, the large particles promote the deposition of coke which blocks the active sites. To remedy this problem, the researchers are trying to modulate the physicochemical properties of the catalyst by dispersing the active phase on catalytic supports having a sufficient specific surface and by adding promoters to have adequate surface properties. In this work, we were interested in the development of a catalyst based on Nickel supported on natural clay. The material was characterized by X-ray fluorescence, X-ray diffraction (XRD), programmed reduction temperature TPR-H2, BET surface analyzer and was then tested in the dry methane reforming reaction under a reaction mixture of $20CH_4/20CO_2/60He$ and $40CH_4$-$40CO_2$-20He with a total gas flow of 100mL/min in a range of temperatures going from 700°C to 850°C with a step of 50°C/2H and a heating rate of 5°C/min. the spent catalyst was characterized by Raman and SEM.

Keywords: Dry reforming of methane- Nickel based catalysts- Natural Clay.

PA73

Pitfalls on the way to enylenes stabilized by a silyl-bridged bis-amides; Explanation of strange reactivity of lithium precursors

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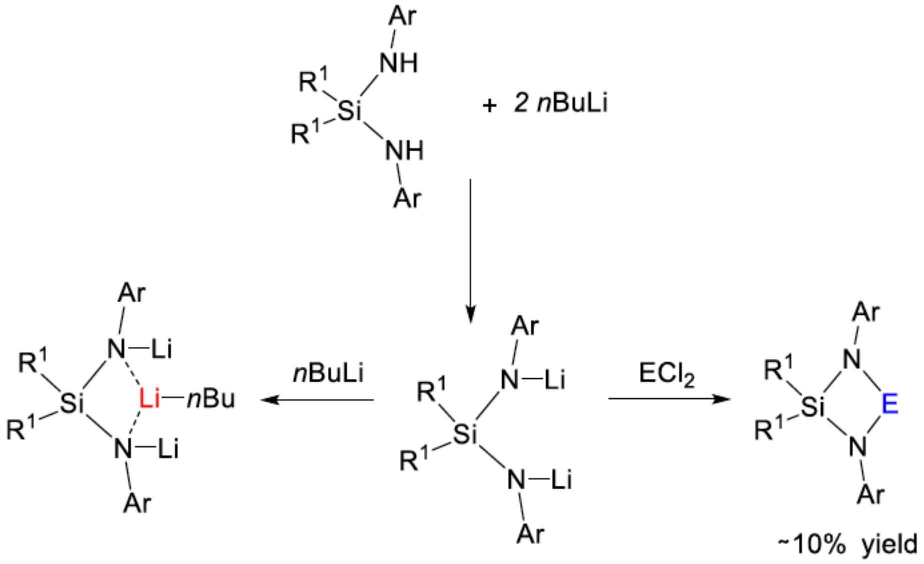
Bulky bis(amido)silyls are known as suitable protoligands for stabilization of enylenes since 1975, in which Veith prepared the first such a stanylene. His work was further extended to germylene and silylene species.[1]

In our group series of new sterically demanding bis(amido)silyls were prepared. These protoligands were further used in the preparation of enylenes by their deprotonation with *n*-BuLi and subsequent reaction with ECl_2. During the search for optimal reaction conditions and causes of low reaction yields, it was found that the addition of deprotonating agent leads not only to double deprotonation but also to subsequent formation of an adduct with a molecule of deprotonating agent such as *n*-BuLi or MeLi.

Considering the fact that this behaviour has not yet been described in the literature, the investigation of this phenomenon and the targeted synthesis of these compounds, their characterization and a follow-up reactivity is crucial for our further research.



This work was supported by Czech Science Foundation (reg. No. 21-02964S).

References

1. M. Veith, Adv. Organomet. Chem., 1990, 31, 269 – 300.

PA74

Heterometallic complexes: a versatile tool for the preparation of doped semiconductor quantum dots

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Heterometallic complexes have drawn considerable attention in organometallic chemistry over the past decades, mainly due to their intriguing properties arising from the cooperation and potential synergy of two metal centers. Nowadays, the preparation of these compounds is often directed towards catalytic applications, mainly in polymerization and organic transformations. Very recently these systems, in particular zinc-based heterometallic complexes (i.a. Zn-Li, Zn-Mg), have been considered as promising precursors for functional materials, e.g. metal organic frameworks (MOFs)[1] or intentionally doped semiconductor zinc oxide (ZnO) nanomaterials.[2] However, the synthetic approach for the preparation of ZnO nanomaterials, in particular ZnO quantum dots (ZnO QDs), from heterometallic precursors with defined chemical composition and desired properties has not been fully explored and remains highly undeveloped. In this vein, we took up the challenge to design and obtain zinc-based heterometallic complexes using organometallic approach. The presented study draws from a wide experience of our research group in the synthesis of alkylzinc complexes incorporating various organic ligands (e.g. carboxylates) and their transformation to high-quality semiconductor ZnO QDs.[3] We introduce an organometallic route to doped ZnO QDs by exploiting novel heterometallic complexes supported by monoanionic organic ligands.

The research demonstrates a rational design and in-depth characterization of high-quality, colloidal, intentionally doped nanomaterials with desired properties and emerges as an attractive alternative to classical wet-chemical (e.g. sol-gel)[4] methods. Moreover, the study opens up new paths for smart design of functional materials for specific applications, including optoelectronics or photocatalysis.

References

1. A.A. Sapianik, M. Kiskin, K.A. Kovalenko, D.G. Samsonenko, D.N. Dybtsev, N. Audebrand, Y. Sun V.P. Fedin, *Dalton Trans.* **2019**, 11, 3676-3686.
2. S. Jana, Y. Aksu, M. Driess, *Dalton Trans*. **2009**, 1516–1521.
3. Wolska-Pietkiewicz, M.; Tokarska, K.; Wojewódzka, A.; Wójcik, K.; Chwojnowska, E.; Grzonka, J.; Cywiński, P. J.; Chudy, M.; Lewiński, J. *Sci. Rep.* **2019**, 9, 18071.
4. Meulenkamp, E. A. *J. Phys. Chem. B* **1998**, 102, 5566–5572.

PA75

Coordination Chemistry of Formazanate towards Alkaline-Earth Metal Compounds

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In the past two decades, the chemistry of formazanates has gained increasing attention; however, the exploration of alkaline-earth metals within this field has been largely neglected.[1] Here we present the synthesis and characterization of several alkaline-earth metal complexes supported by formazanates.[2,3] Interestingly, depending on the size of the central metal ions, the coordination mode of the formazanate ligand varies, including symmetrical “close” and unsymmetrical "open" coordination modes. Furthermore, the reaction of a solvent-free bis(formazanate) Mg complex with CO_2 was investigated, which resulted in stoichiometric insertion of CO_2 into one of the four Mg-N bonds. Remarkably, the insertion reaction was found to be reversible, depending on thermolysis or treatment with THF, as supported by DFT calculations. This discovery represents the first example of reversible CO_2 uptake by a s-block coordination compound. Additionally, we evaluated the catalytic activities of the heavier alkaline-earth metal compounds in the hydroboration of carbonyl compounds and the hydrophosphination of styrenes. Among the compounds tested, the formazanate Ba amide exhibited the highest catalytic efficiency. Overall, our findings shed light on the coordination chemistry of formazanates with alkaline-earth metals and demonstrate their potential for reversible CO_2 capture as well as catalytic applications in important organic transformations.

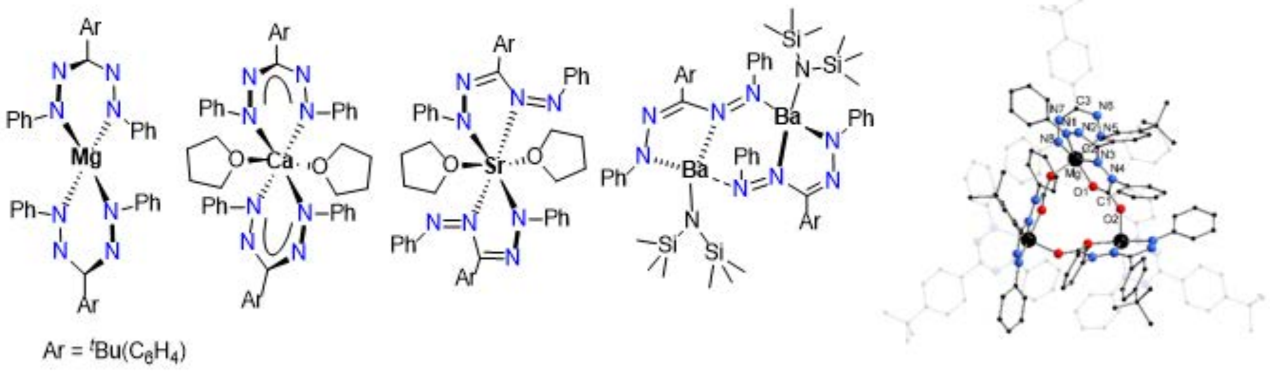

Figure 1. (**a**) Different configurations of formazanate alkaline-earth metal compounds; (**b**) the first formazanate carbamato compound.

References

1. J. B. Gilroy and E. Otten, *Chem. Soc. Rev.*, 2020, **49**, 85-113.
2. D. Jin, X. Sun, A. Hinz and P. W. Roesky, *CCS Chemistry*, 2023, **5**, 1277-1284.
3. D. Jin, X. Sun and P. W. Roesky, *Organometallics*, 2023, in press.

PA76

Efficient routes to elusives tetramethylalumoxanes

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Dedicated to Professor Stanisław Pasynkiewicz in recognition of his outstanding contribution to the chemistry alumoxanes

The chemistry of alumoxanes has been under investigation over the last few decades. Alumoxanes are attracting attention as highly active catalysts or co-catalysts as a result of their importance for the polymerization of a wide range of organic monomers, and initial studies into these systems trace back to the end of the 1950s.[1] Strikingly, the first structurally authenticated tetraalkylalumoxane [$(tBu_2AlOAltBu_2)_2$] and its Lewis acid/base adduct with pyridine [$tBu_2(py)AlOAltBu_2(py)$] was reported by Barron only in 1993.[2] Pasynkiewicz and co-workers extensively studied solution structures of methylalumoxanes, however the exact composition and structure of alumoxanes featuring shortchain alkyl substituents have ramainded not entirely clear until now.[3,4]

Herein, we report on the synthesis and structure characterization of tetramethylalumoxanes derived through direct hydrolysis of Me_3Al or the alkylation of carboxylic acids. In addition, their catalytic activity in the ring-opennig of heterocyclic monomers will be demonstrated.

References

1. a) K. Ziegler, *Angew. Chem.* **1956**, 68,721; b) R. O. Colclough, *J. Polym. Sci.* **1959**, 34, 178.
2. M. R. Mason, J. M. Smith, S. G. Bott, A. R. Barron, *J. Am. Chem. Soc.* **1993**, 115, 4971.
3. For review, see: S. Pasynkiewicz, *Polyhedron* **1990**, 9, 429.
4. S. Collins, A. Joshi, M. Linnolahti, *Chem. Eur. J.*, **2021**, 27, 15460.

PA77

T-shaped TM^0 complexes with cationic tetrylenes: Observation of L/Z ligand duality and their use in hydrogenation catalysis

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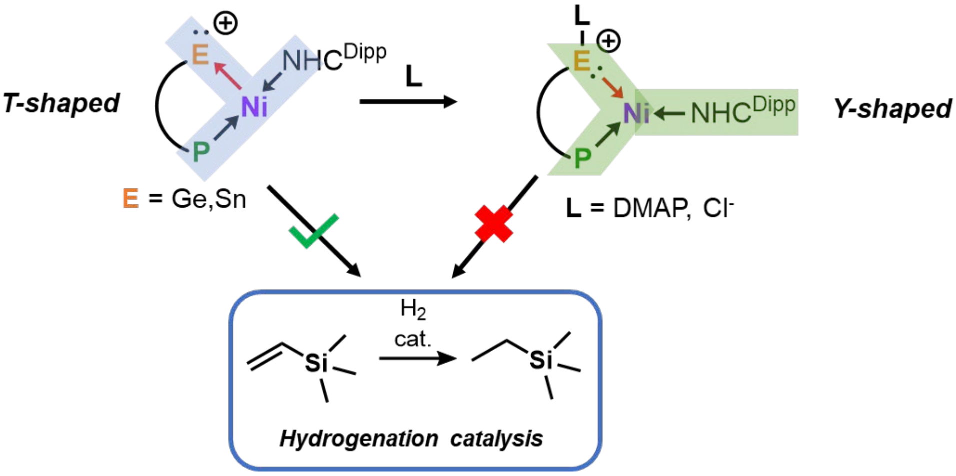
With growing awareness of environmental pollution and climate change, there is increasing interest in finding novel and innovative compounds containing abundant transition metals (**TM**s), such as nickel, iron and cobalt, to replace expensive **TM**s like platinum in catalysis or small molecule activation. In addition to different metals, ligand design also plays a crucial role in determining reactivity.[1] In our group, we are developing non-innocent ligand systems which exploit the amphiphilic nature of tetryliumylidenes, as 'Single-Centre Ambiphile' ligands. These cationic **Ge**^{II} and **Sn**^{II} systems, which can actively participate in reactions whilst bound to a **TM**, exhibit extraordinary electronic properties. The [**E**^{II}]$^+$ centres in these ligands not only act as σ-donors due to a free electron pair, but can also behave as strong Lewis acids due to their vacant p-orbitals.[2-3] Our own efforts combine the tetryliumylidenes with a chelating phosphine-flanked amido scaffold, leading to geometrically constrained systems in which Lewis acidic character is amplified. This allows for the formation of a remarkable class of T-shaped **E**^{II}-**Ni^0** complexes, in which this Lewis acidic character drives Z-type ligand formation at **E**^{II}, bound to the electron donating **Ni**. These compounds show interesting reactivities towards incoming nucleophiles: the direct observation of Z/L-type ligand duality could be made through coordination of N-bases to the germanium centre, with a concomitant switch from a Z-type to an L-type ligand. Further, T-shaped **Ni^0** complexes are shown to be active catalysts for alkene hydrogenation. These can be 'switched off' by the addition of N-donor ligands, forming the basis for a potential new class of switchable ligands in the tetryliumylidenes.



References

[1] R. J. Somerville, J. Campos, *Eur. J. Inorg. Chem.* **2021**, *2021*, 3488-3498.
[2] P. M. Keil, T. J. Hadlington, *Angew. Chem. Int. Ed.* **2022**, *61*, e202114143.
[3] T. J. Hadlington, M. Driess, C. Jones, *Chem. Soc. Rev.* **2018**, *47*, 4176-4197.

PA78

Catalyst-free dipolar cycloaddition of 1-ferrocenyl-2-nitroethene - pathway to novel pyrazolopyrazolones with ferrocene

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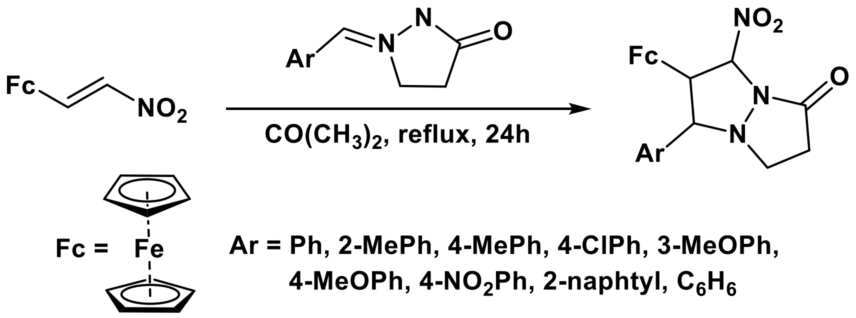
Synthesis of dinitrogen fused heterocycles such as pyrazolopyrazolones represent attractive research area in organic chemistry since they are frequent structural fragments of numerous biologically active compounds. These heterocycles have been investigated as antibacterial, anti-Alzheimer, anti-inflammatory and antipyretic agents. On the other hand, it is well known that implementing the ferrocene moiety in the molecular structure can increase the bioactivity of some compounds. For this reason, we devoted ourselves to exploration of new pathways for synthesis of this type of molecules.[1]

The most suitable way for synthesis of such heterocycles is based on dipolar cycloaddition of azomethine imines. In this research, we investigated dipolar cycloaddition of ferrocene containing nitroolefin with different azomethine imines. Usage of 1-ferrocenyl-2-nitroethene as dipolarophile was explored. To establish the most sustainable method, we tried to achieve conditions for catalyst free reaction, so we refluxed the mixture of nitroolefin with azomethine imine in acetone for 24h. This way, series of novel pyrazolopyrazolones with ferrocene was successfully synthesized in moderate yield (up to 70%) and all compounds were characterized by spectroscopic techniques (^{1}H NMR, ^{13}C NMR and IR). Also, some of the synthesized compounds were suitable for the crystallographic examination.



Acknowledgements: Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant no. 451-03-47/2023-01/ 200122).

References

[1] J. Bugarinovic et al., Journal of Inorganic Biochemistry 189 (2018) 134–142, and references cited within.

PA79

Photoinduced perfluoroethylation mediated by cobalt complexes supported by naphthyridine ligands

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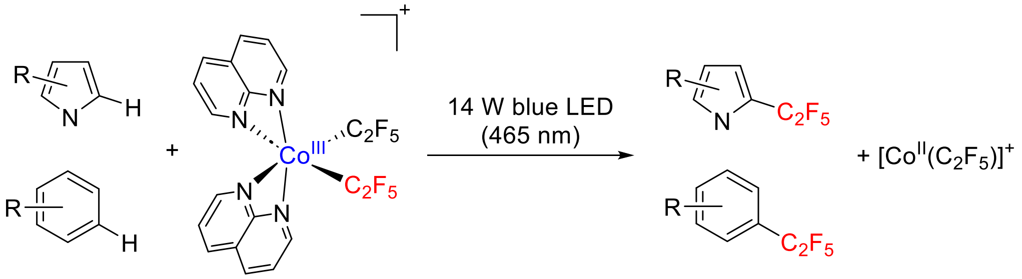
Incorporating fluoroalkyl groups into drug molecules has attracted great attention recently as a powerful tool to modulate metabolic stability and biological activity of pharmaceuticals. While radical trifluoromethylation mediated by first-row transition metal has been widely applied in medicinal chemistry, the analogous strategy to introduce pentafluoroethyl or longer-chain fluoroalkyl group is relatively less explored, even though longer perfluoroalkyl chains may cause a significant change in steric demand, dipole moment and lipophilicity.[1] Among the base metals, nickel has emerged as a powerful, cheap alternative to precious second and third-row transition metals for radical perfluoroalkylation.[2] Cobalt complexes, on the other hand, have gained less attention since they are considered relatively less active in trifluoromethylation than nickel complexes.

In this work, we reported a new series of cobalt(III) and cobalt(II) perfluoroethyl complexes supported by simple naphthyridine-based ligands. Under blue LED irradiation, these complexes undergo facile Co-C_2F_5 bond homolysis and release a C_2F_5 radical, which can be trapped by TEMPO radical trap. Selective, monoperfluoroethylation of arenes and heteroarenes mediated by cobalt(III) complexes was observed under blue light irradiation, while cobalt(II) complexes were unreactive. Catalytic C(sp^2)-H perfluoroethylation with perfluoroethyl Acid Togni reagent catalyzed by cobalt(III) complexes has also demonstrated the potential for catalytic applications, albeit moderate yields were observed and the reactivity was limited to electron-rich arenes.



1) B. Linclau et al., *J. Med. Chem.* **2018**, *61, 23*, 10602. 2) a) N. Nebra et al., *Angew. Chem. Int. Ed.* **2017**, *56*, 12898. b) D. A. Vivic et al., *Angew. Chem. Int. Ed.* **2021**, *60*, 18162. c) E. Khaskin et al. *Chem. Sci.*, **2022**, *13*, 12971.

PB01

Photocatalytic oxidation of benzylamine and thioanisole by two biscyclometalated Ir(III) complexes

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Visible light photocatalysis is a growing strategy due to environmental crisis. It consist on the use of visible light to produce new C-C, C-heteroatom or other bonds with higher efficiency and selectivity.[1] In this work, two new biscyclometalated Ir(III) complexes with two different π-expansive ligands derived from benzo[*h*]quinoline have been prepared and their photocatalytic activity in the oxidation of benzylamine and thioanisole has been explored (Figure 1).

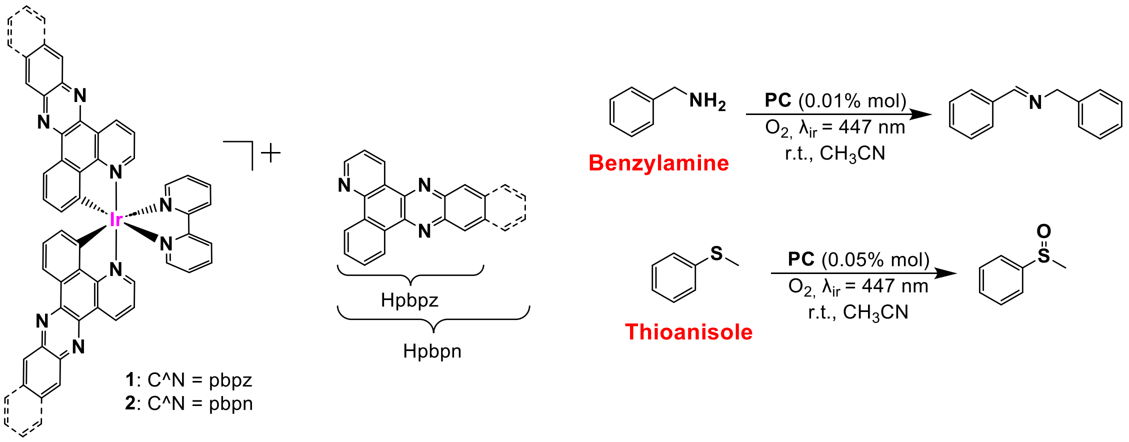

Figure 1. Structure of the photocatalysts and photocatalytic reactions explored in this work.

Both complexes have shown high $^1O_2$ generation ($\phi_\Delta = 0.41$ and 0.91 for **1** and **2** respectively) under blue light irradiation. As $^1O_2$ can induce some oxidative reactions, complexes **1** and **2** were studied in different photocatalytic oxidations. Complex **2** exhibited very high activity in the oxidative coupling of benzylamine under mild conditions (0.01% mol of photocatalyst, PC, room temperature, $\lambda_{ir} = 447$ nm, 1 atm of O_2), achieving the complete photooxidation at 2 h. Complex **1** exhibited lower activity (86%), according to its lower ϕ_Δ. The photocatalytic activity in the oxidation of thioanisole was also explored, obtaining the total conversion with complex **2** at 0.05% mol and 24 h and reaching the 95% of selectivity to the sulfoxide. The oxidation mechanism and other challenging oxidations are being explored.

References

[1] X.-K. Huang, L.-P. Li, H.-Y. Zhou, M.-F. Xiong, J.-Y. Fan, B.-H. Ye, *Inorg. Chem.* **2022**, 61, 51, 20834–20847.

PB02

Catalytic Transfer Hydrogenation of Glucose to Sorbitol and of Furfural to Furfuryl Alcohol by an air stable Ru(II) precatalyst in water/toluene biphasic medium

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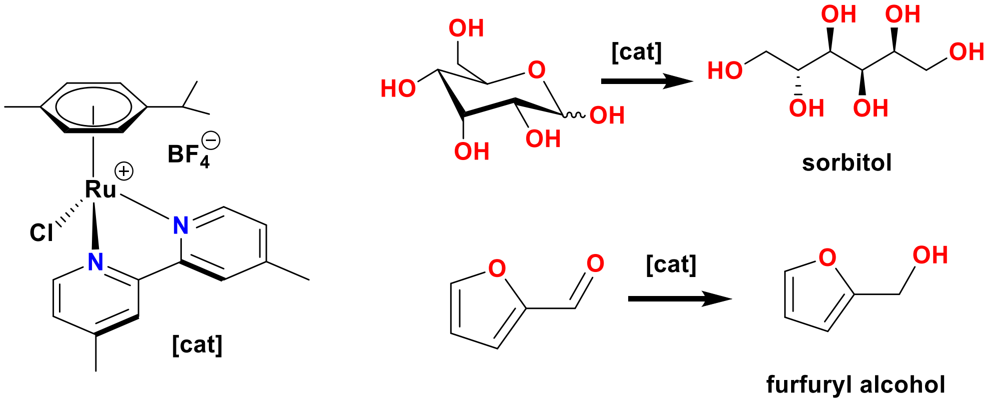
The valorisation of different biomass fractions to chemicals is now a days receiving notable attention due to environmental benefits and also to the possibility of producing a wide variety of chemicals difficult to be obtained from other sources [1]. In this context we show in this work the transformation of furfural to furfuryl alcohol and of glucose to sorbitol by catalytic transfer hydrogenation (CTH) [2]. Furfural (FF) is one of the top value-added chemicals derived from biomass and it is considered a renewable source of C5 molecules, some of which have important added value. More specifically, furfuryl alcohol (FA) is a key precursor for the manufacture of foundry resins, furan fiber-reinforced plastics, lubricants, drugs, fragrances and pesticides. On the other hand, sorbitol is considered one of the most promising biomass-based platform products. Several products can be obtained from sorbitol after aqueous-phase reforming as methanol, alkanes, and biofuels.

CTH has also been explored in the reduction of these substrates although reported results are scarce, compared to hydrogenation, and evidence a low performance in terms of alcohol productivity. We show excellent results in this transformation using formic acid as hydrogen source and a simple and stable organometallic ruthenium compound in water/toluene biphasic medium.



References

[1] J. He, H. Li, A. Riisager, S. Yang, ChemCatChem **2018**,10, 430–43.
[2] M. Ruiz-Castañeda, L. Santos, B. R. Manzano, G. Espino, F. A. Jalón, Eur. J. Inorg. Chem. **2021**, 1358–1372.

PB03

Stabilizing Group 13/14 Compounds by a Iminophosphinoyl-Substituted Yldiide

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Reactive main group compounds such as low-valent or cationic species have received intense research interest in the past years due to their unique structures and reactivities, above all their propensity to act as transition metal mimics.[1] The isolation of such electron-deficient compounds requires a careful molecular design which usually involves the use of sterically demanding and electron-donating substituents. Like amino substituents phosphorus ylides can act as powerful donor ligands with an enhanced π-electron donating ability which can be used to synthesize electron-rich phosphines for applications in homogeneous catalysis.[2] Likewise, they are suitable for stabilizing electron-deficient group 13/14 compounds.[3] Our group has reported the gram-scale syntheses yldiides, which exhibited diverse structures and provide convenient access to ylide-functionalized compounds.[4] Herein, we report on an iminophosphinoyl-substituted yldiide, its structure and application for stabilizing low-valent group 13/14 compounds.

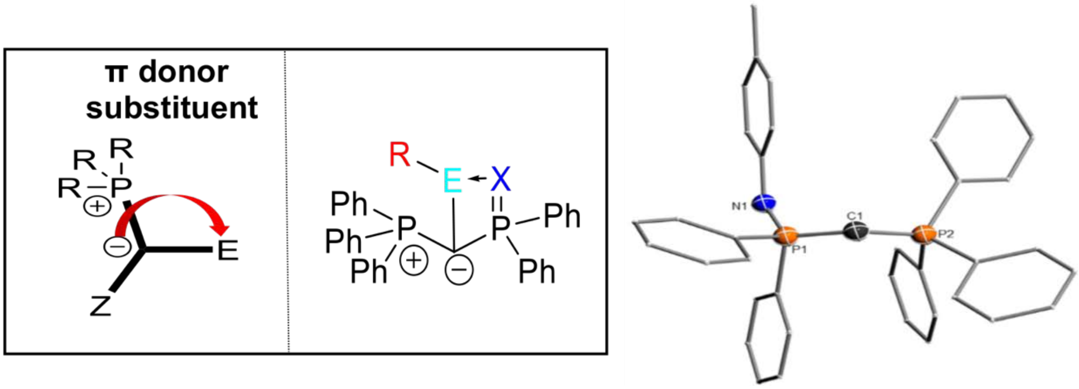

Figure 1. Basic representation of iminophosphinoyl-substituted yldiide.

References

1. R. C. Fischer and P.P. Power, *Chem. Rev.*, **2010**, 110, 7, 3877–3923.
2. S. Lapointe, A. Sarbajna, and V.H. Gessner, *Acc. Chem. Res.* **2022**, 55, 5, 770–7822.
3. a) T. Scherpf, R. Wirth, S. Molitor, K.-S. Feichtner, V. H. Gessner, *Angew. Chem.Int. Ed.* **2015**, 54, 8542. b) C. Mohapatra, L. Scharf, T. Scherpf, B. Mallick, K.-S.Feichtner, C. Schwarz, V. H. Gessner, *Angew. Chem. Int. Ed.*, **2019**, 58, 7459.
4. a) C. Schwarz, L. T. Scharf, T. Scherpf, J. Weismann, V. H. Gessner, *Chem. Eur. J.***2019**, 25, 2793.b) M. Jörges, A. Kroll, L. Kelling, R. Gauld, B. Mallick, S. M. Huber, V. H. Gessner *ChemistryOpen* **2021,** 10, 1089–1094

PB04

N-Formylation of Amines with H_2 and CO_2 Catalysed by Aluminum Porphyrin Complex

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N-formylation of amines with CO_2 and H_2 is catalyzed by aluminum porphyrin complexes. Dihydrogen is activated by frustrated Lewis Pair (FLP) with the amine acting as the base and subsequently, reductive amination of CO_2 is achieved. Water is generated as the byproduct of the reaction, which demonstrates high water stability and tolerance of the Al-porphyrin-based FLPs.

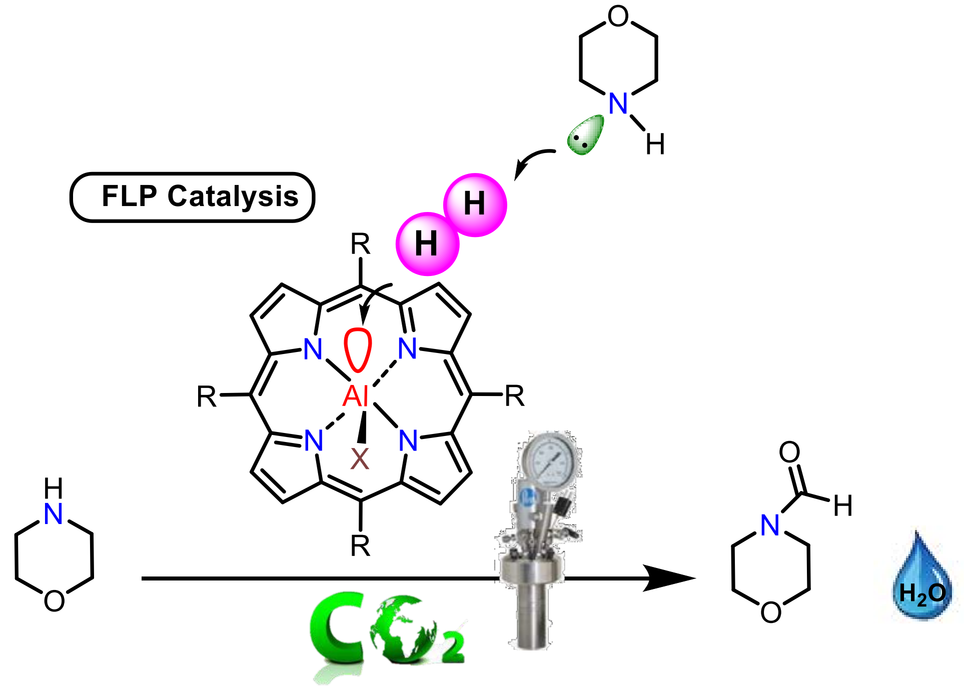

Figure 1. *N*-formylation of morpholine with CO_2 and H_2 catalyzed by aluminum porphyrins

PB05

CO_2-based polymeric materials using chloride indium catalysts

Agustín Lara-Sánchez,*[1] Felipe de la Cruz Martínez,[1] Marc Martínez de Sarasa Buchaca,[1]
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During the last few decades, the depletion of fossil fuels and the requirement for a circular economy have driven the scientific and industrial community to search for greener and more sustainable catalytic processes to synthesize high value-added chemicals and polymers. In this context, the ring-opening copolymerization (ROCOP) of renewable-based substrates such as carbon dioxide (CO_2), epoxides and cyclic esters, has emerged as an attractive and versatile synthetic route to afford polymeric materials with desired properties. Although a wide range of metal catalysts has been reported for the synthesis of polycarbonates, polyesters and terpolymers via ROCOP, the use of indium complexes has hardly been explored for this synthetic approach.[1]

In this contribution, we report the use of bimetallic chloride indium complexes as catalysts for the copolymerization processes of cyclohexene oxide, CO_2 and *L*-lactide under mild reaction conditions (Figure 1). The catalysts displayed good catalytic activity and excellent selectivity towards the preparation of poly(cyclohexene carbonate) at one bar CO_2 pressure in the absence of a co-catalyst. Additionally, poly(lactide-co-cyclohexene carbonate) copolymers were obtained via one-pot route without the use of a co-catalyst. The degree of incorporation of CO_2 can be easily modulated by changing the CO_2 pressure and the monomer feed, resulting in copolymers with different thermal properties.[1]

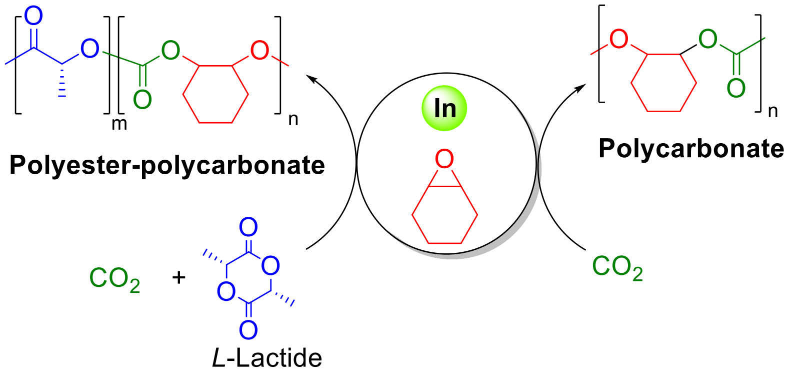

Figure 1

References

[1] M. Martínez de Sarasa Buchaca, F. de la Cruz-Martínez, L. F. Sánchez-Barba, J. Tejeda, A. M. Rodríguez, J. A. Castro-Osma, A. Lara-Sánchez, *Dalton Trans.*, **2023**, *52*, 3482.

PB06

Synthesis and Characterization of Cobalt(II) and Palladium(II) Complexes Leading to Development of Cyclic Olefin Polymer (COP)

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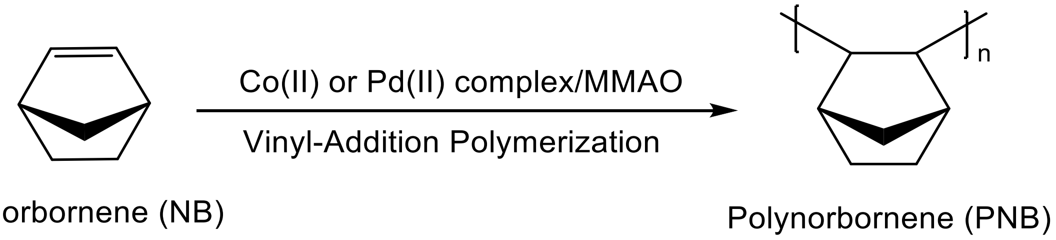
We have sythesized and characterized Co(II) and Pd(II) complexes with several Shiff base related ligands to develop cyclic olefin copolymer (COP). Specifically, Co(II) complexes **[L_NCoCl_2]** (L_N = L_A and L_B) where L_A is (*E*)-*N*^{1},*N*^{1}-dimethyl-*N*^{2}-(pyridin-2-ylmethylene)ethane-1,2-diamine and L_B is (*E*)-*N*^{1},*N*^{1}-dimethyl-*N*^{2}-(thiophen-2-ylmethylene)ethane-1,2-diamine, and Pd(II) complexes **[L_MPdCl_2]** (L_M = L_C and L_D) where L_C is (*E*)-3-methoxy-*N*-(quinolin-2-ylmethylene)propan-1-amine and L_D is (*E*)-*N*-(pyridin-2-ylmethylene)hexan-1-amine have been synthesized and structurally characterized. X-ray diffraction analysis revealed distorted square planar geometry for two Pd(II) complexes, a distorted trigonal bipyramidal geometry for **[L_ACoCl_2]**, and a distorted tetrahedral geometry for **[L_BCoCl_2]**. It was shown that catalytic system of **[L_NCoCl_2]** or **[L_MPdCl_2]**/MMAO (Modified methyl aluminoxane) can effectively catalyze vinyl addition polymerization of cyclic olefin such as norbornene with over 90% conversion.



PB07

Synthesis and coordination behavior of a hybrid ferrocene phosphinoamidine ligand

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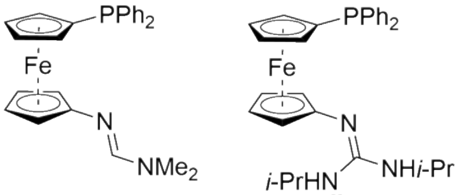
The aim of this contribution is to disclose the optimized synthesis and coordination behavior of a new hybrid ferrocene phosphinoamidine ***I***, which further extends the library of the known heteroannulary functionalized ferrocene phosphines decorated with a polar basic tag as a potential donor moiety (analogous guanidine ***II***)[1]. Coordination properties were studied in reactions with Pd(II) precursors and half-sandwich complexes of the remaining triad elements. The newly prepared compounds were studied comprehensively by means of NMR and IR spectroscopy, mass spectrometry, elemental analysis and, in some cases, XRD crystallography.



I ***II***

Figure 1. Structure of phosphinoamidine ***I*** and analogous guanidine ***II***

The ligand was obtained by reacting primary ferrocene phosphinoamine[2] with dimethylformamide-dimethylacetal. The need for phosphine group protection by borane adduct formation was also evaluated. Depending on stoichiometry, reacting ***I*** with $[PdCl_2(MeCN)_2]$ furnished complexes $[PdCl_2($***I***$\text{-}\kappa^2P,N)]$ and *trans*-$[PdCl_2($***I***$\text{-}\kappa P)_2]$. The ligand was further reacted with half-sandwich dimeric precursors of Ru(II) and Rh(II), giving the corresponding κ*P*-species, which were further converted into P,N-chelated complexes *via* halogen abstraction.

This work was financially supported by GA ČR 23-06718S.

References

1) Bárta O, Císařová I., Štěpnička P.: Dalton Trans. *50*, 14662 (2021).
2) Škoch. K, Císařová I., Schulz J., Siemeling U., Štěpnička P.: Dalton Trans. *46*, 10339 (2017)

PB08

Cascade Transformation of Carbon Dioxide and Alkyne-1,*n*-diols into Densely Substituted Cyclic Carbonates

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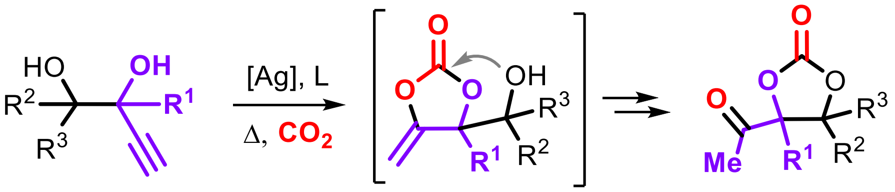
A new Ag-promoted cascade process has been developed that involves the use of alkyne-1,*n*-diols as modular substrates which can be coupled with CO_2 to the formation of a wide range of cyclic carbonates (see Figure).[1] In situ IR studies, control experiments, and DFT analysis of this manifold revealed the intermediacy of an α-alkylidene carbonate that is intercepted by an intramolecular alcohol (pro)nucleophile. The protocol is characterized by operational simplicity, excellent scope, and mild reaction conditions. The synthetic potential of this conceptually attractive CO_2 transformation is demonstrated in the preparation of larger ring carbonates and their thermal rearrangement to sterically crowded, five-membered fused carbonate products.



References

[1] Li, X.; Villar-Yánez, A.; Bo, C.; Kleij, A. W. et al. *ACS Catal.* **2022**, *12*, 2854-2860.

PB09

Novel cyclometalated iridium(III) complexes with functionalized benzimidazole derivatives as potential photodynamic agents in chemotherapy

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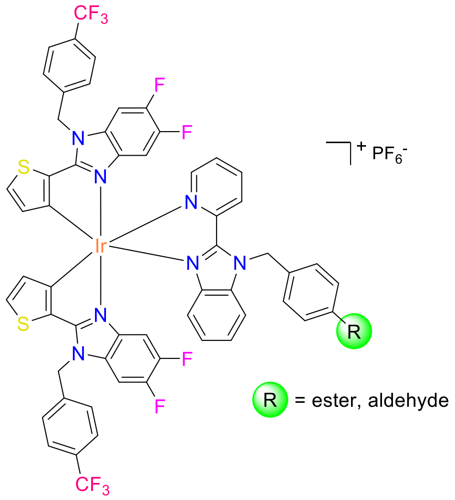
Nowadays the major drawbacks in chemotherapy, derived from acquired resistance of tumoral cells and adverse side effects related to the administration of the classic antitumoral drugs, urge the research to develop new anticancer drugs with novel mechanisms of activity and therapeutic modalities, such as photodynamic therapy (PDT). This strategy consists in the photoactivation of a drug that induces cellular death by generating highly cytotoxic reactive oxygen species (ROS). In this sense, cyclometalated complexes postulate as very interesting photodynamic agents since they exhibit great photophysical and photochemical properties. [1] We have prepared new cyclometalated iridium(III) complexes derived from ester- and aldehyde-functionalized benzimidazoles. The presence of ester and aldehyde groups can generate ROS upon light irradiation, and they can be useful handles for further functionalization with many molecules of high biological interest. [2]



Acknowledgements: The authors would like to thank for the funds received from the Spanish Ministerio de Ciencia e Innovación-Agencia Estatal de Investigación (MCI/AEI/10.13039/501100011033) and FEDER (PID2021-122850NB-I00). A. Linero is also thankful to the University of Murcia for its predoctoral fund (100159/2021).

References

[1] Madec, H.; Figueiredo, F.; Cariou, K.; Roland, S.; Sollogoub, M.; Gasser, G. *Chem. Sci.* **2023**, *14*, 409-442.
[2] Novohradsky, V.; Zamora, A.; Grandioso, A.; Brabec, V.; Ruiz, J.; Marchán, V. *Chem. Commun.* **2017**, *53*, 5523-5526.

PB10

Solvent-free Birch Reductions and Benzene C-H Activation/C-C Coupling mediated by a Room-Temperature Stable Electride (RoSE)

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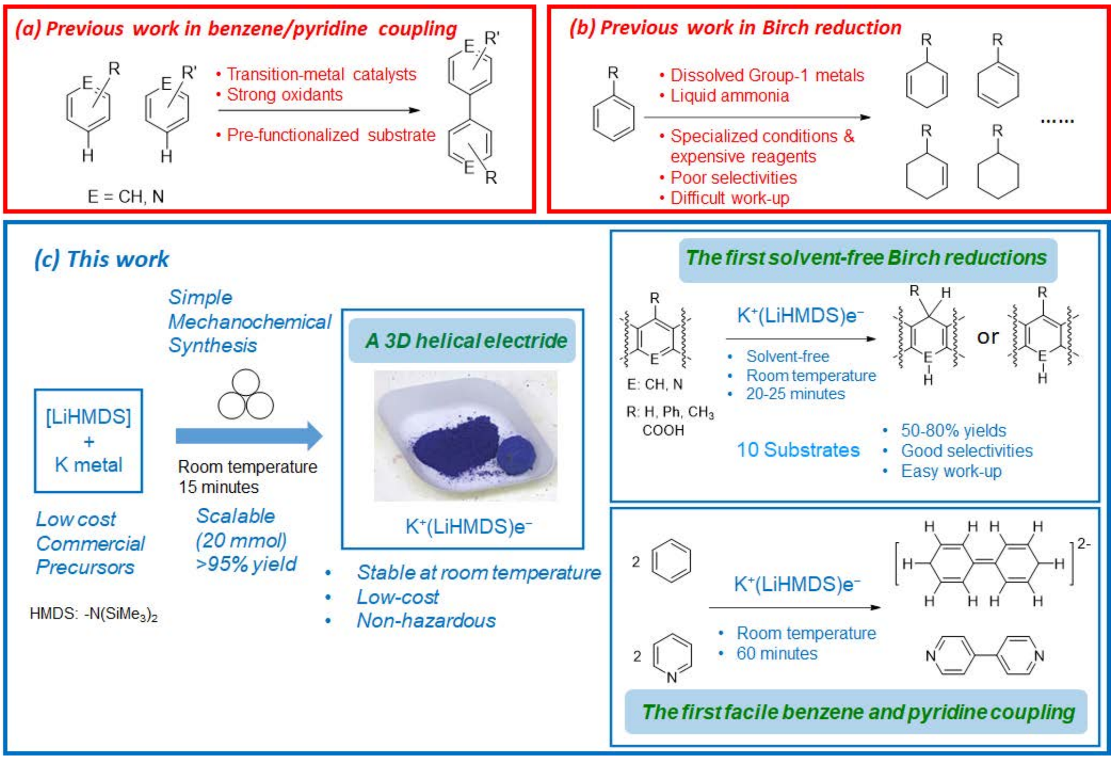
Birch reduction [1] and benzene C–H activation/C–C coupling [2] are essential tools for converting arene feedstock into value-added organic compounds and to build complex molecules. However, state-of-the-art methods require hazardous reagents (e.g., Group-1 metal-liquid ammonia, solvated electrons, strong oxidants), harsh conditions (e.g., high temperatures, long reaction time), expensive and/or specialized reagents/catalysts (e.g., precious metals), and last but not least, petrochemical-derived organic solvents. In 2023, we reported an accessible and scalable Room-temperature Stable Electride (RoSE), namely K$^+$(LiHMDS)e$^-$ (1) (HMDS: N(SiMe$_3$)$_2$), which mediated the first solvent-free Birch reductions and facile benzene C–H activation and C–C coupling. Herein we would like to present the breakthrough and its very recent updates.



References

[1] Parikh, A.; Parikh, H.; Parikh K. Chapter 18. Birch reduction. in: Name Reactions in Organic Synthesis. Foundation Books, **2006**: 69-72; [2] Lv, F.; Yao, Z. -J. *Sci. China Chem.* **2017**; *60*, 701-720; [3] Lu, E. and co-workers, *Chem* **2023**, *9,* 579-591.

PB11

Tripodal Modifications of a Common β-Diketiminate Framework Accessed via Lithium Intermediates

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Inserting three classes of isoelectronic small molecule, namely isocyanates, isothiocyanates and carbodiimides into the γ-carbon backbone position of the common 2,6-diisopropylphenyl-β-methyldiketiminate [NacNac(Dipp,Me)] molecule generates a new family of tripodal, proligands. Adding to the known variations of β-diketiminates, where denticity has been extended via side arms, these new tripodal diamine variations provide the additional benefit of blocking the nucleophilic γ-carbon site from unwanted reactivity.[1,2,3,4] Herein, we report several variations of these new proligands characterized by X-ray crystallography and present a diversity of monomeric, dimeric and tetrameric structures that are adopted by their corresponding lithiated intermediates. The diamine nature of these modified NacNac species presents opportunities for a new class of bimetallic ligand system, as well as the potential for further ligand extension.

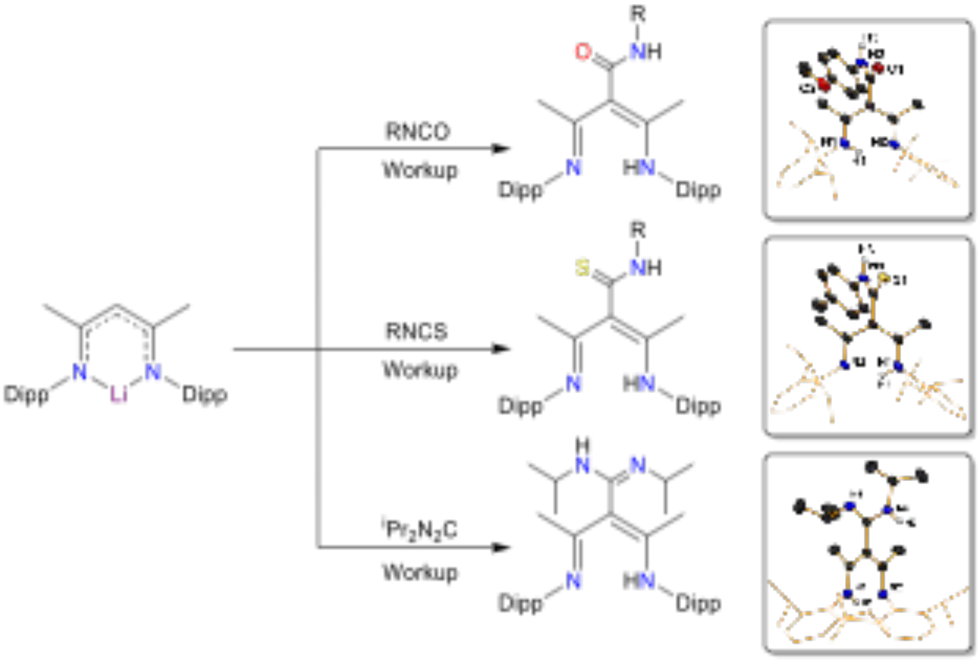

Figure 1. Synthesis of tripodal proligands presented in this work

References

(1) Zhu, X., Wang, Z., Zha, L., Zhang, Y., Qi, Y., Yuan, Q., Zhou, S., Wang, S. *Organometallics,* **2022**, 41, 1087-1098.
(2) Pahar, S., Swamy, V. S. V. S. N., Das, T., Gonnade, R. G., Vanka, K., Sen, S. S., *Chem. Commun.*, **2020**, *56*, 11871–11874.
(3) Gao, H., Su, J., Xu, P., Xu, X., *Org. Chem. Front.,* **2017**, *5*, 59-63.
(4) Camp, C., Arnold, J., *Dalton Trans.* **2016**, *45*, 14462–14498.

PB12

Snapshots of sequential polyphosphide rearrangement upon metallatetrylene addition

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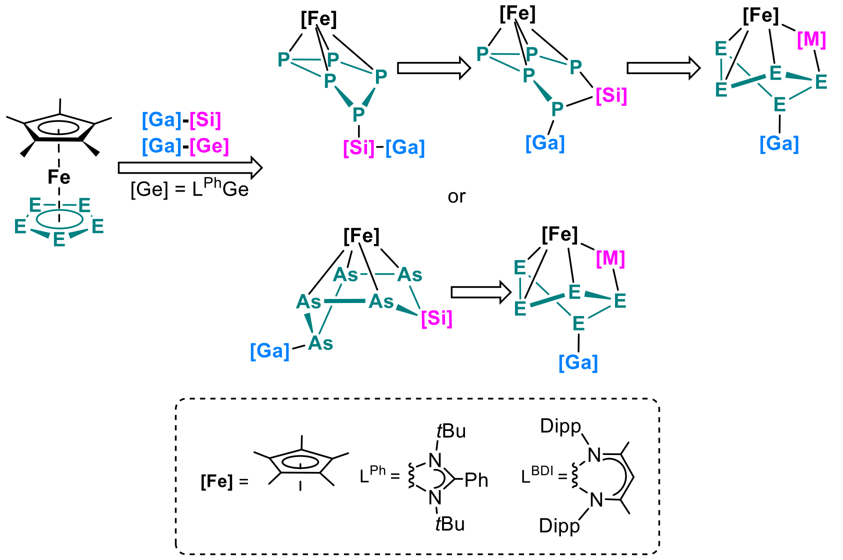
Insertion and functionalization of gallasilylenes [L^{Ph}Si–Ga(Cl)L^{BDI}] (L^{Ph} = PhC(N*t*Bu)$_2$; L^{BDI} = [{2,6-iPr$_2$C$_6$H$_3$NCMe}$_2$CH]) into the *cyclo*-E$_5$ rings of [Cp*Fe(^{5}-E$_5$)] (Cp* = ^{5}-C$_5$Me$_5$; E = P, As) are reported. Reactions of [Cp*Fe(^{5}-E$_5$)] with gallasilylene result in E–E/Si–Ga bond cleavage and the insertion of the silylene in the *cyclo*-E$_5$ rings. [(L^{Ph}Si-Ga(Cl)L^{BDI}){(^{4}-P$_5$)FeCp*}], in which the Si atom binds to the bent *cyclo*-P$_5$ ring, was identified as a reaction intermediate. The ring-expansion products are stable at room temperature, while isomerization occurred at higher temperature, and the silylene moiety further migrates to the Fe atom, forming the corresponding ring-construction isomers. Furthermore, reaction of [Cp*Fe(^{5}-As$_5$)] with the heavier gallagermylene [L^{Ph}Ge–Ga(Cl)L^{BDI}] was also investigated. All the isolated complexes represent rare examples of mixed group 13/14 iron polypnictogenides, which could only be synthesized by taking advantage of the cooperativity of the gallatetrylenes featuring low-valent Si(II) or Ge(II) and Lewis acidic Ga(III) units/entities.

Cooperative transformation by binuclear mixed group 13/14 tetrylenes



Consecutive isomerization through migration of [Si] moiety: Highly selective!

PB13

Copper-catalyzed intramolecular cyclization of alkynylazobenzenes for the synthesis of 2*H*-indazoles

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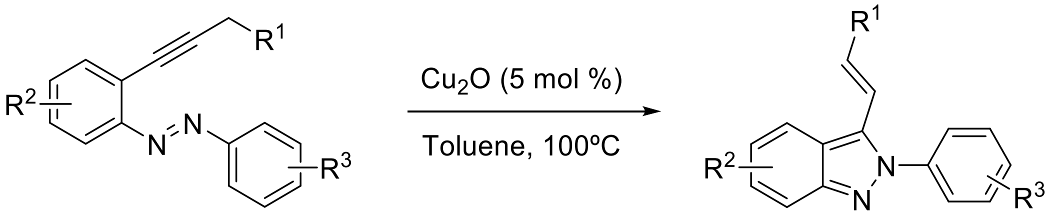
Indazoles are a crucial group of heterocycles that find applications in various fields,[1] including pharmaceuticals, where they form the core of several drug molecules, such as Niraparib and Pazopanib, used for treating ovarian and renal cancer. However, the synthesis of 2*H*-indazoles has been challenging compared to 1*H*-indazoles, and only a limited number of approaches for the regioselective synthesis of N-substituted indazoles have been reported.[2] Therefore, there is a need for new and selective methods for preparing 2*H*-indazoles.

In this communication, we present a copper-catalyzed intramolecular cyclization of alkynylazobenzenes for the efficient synthesis of 3-substituted N-aryl 2*H*-indazoles. Using copper oxide (I) as catalyst, we achieve good yields of the products in short reaction times. Our approach offers a new and useful strategy for the synthesis of 2*H*-indazoles with potential applications in drug discovery and materials science.



Acknowledgements. We are grateful to Comunidad de Madrid Research Talent Attraction Program (2018-T1/IND-10054 and 2022-5A/IND-24227) and University of Alcalá (CCG20/CC-009 and PIUAH21/CC-003) for financial support.

References

[1] S. Mal, U. Malik, M. Mahapatra, A. Mishra, D. Pal. And S. K. Paidesetty, S. K. *Drug Dev. Res.* **2022**, *83*, 1469–1504.
[2] N. Cankařová, J. Hlaváč, V. Krchňák, *Org. Prep. Proced. Int.* **2010**, *42*, 433–465.

PB14

Synthesis of Silylamines Catalyzed by Iridium (III) Complexes

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The catalytic silylation of amines is a straightforward method to prepare silylamines, which have been used as reactants in several organic synthetic processes. In particular, our interest on this chemistry lies in its application to trap CO_2 in the form of silylcarbamates. These type of carbamates have been employed as synthons for the preparation of ureas.[1,2]

Here, we show the synthesis and characterization of new iridium catalytic precursors with the monoanionic bidentate (4,8-dimethyl-quinoline-2-yloxy) dimethysilyl (NSi^{DMQ}) ligand. We have also studied the activity of these new complexes as catalysts for the dehydrogenative silylation of amines using tertiary hydrosilanes. We have discovered that the presence of the Lewis acid, $B(C_6F_5)_3$, increases notably the catalytic activity. Experimental and DFT studies to understand the mechanism of the reaction are ongoing (Figure 1).

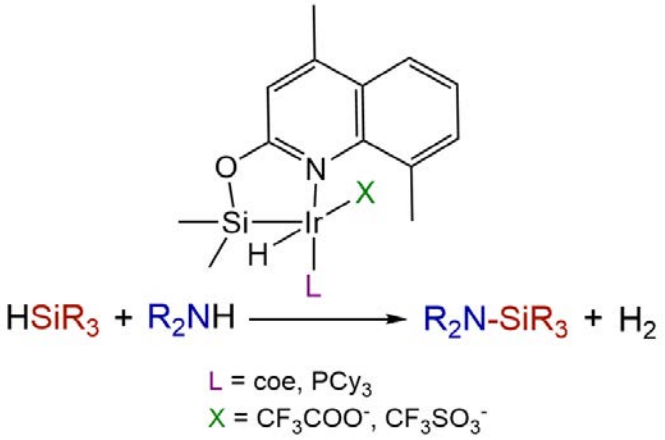

Figure 1. Reaction of secondary amines and tertiary hydrosilanes in presence of Iridium catalysts.

References

[1] Verma, V.; Koperniku, A.; Edwards, P.M. and Schafer, L.L. *Chem. Commun.*, **2022**, *58*, 9174-9189.
[2] Julian, A.; Polo, V.; Jaseer, E. A.; Fernández-Alvarez, F. J. and Oro, L. A. *ChemCatChem*, **2015**, *7*, 3895-3902.

PB15

Direct conversion of C1–C6 alkanes into trifluoromethyl derivatives

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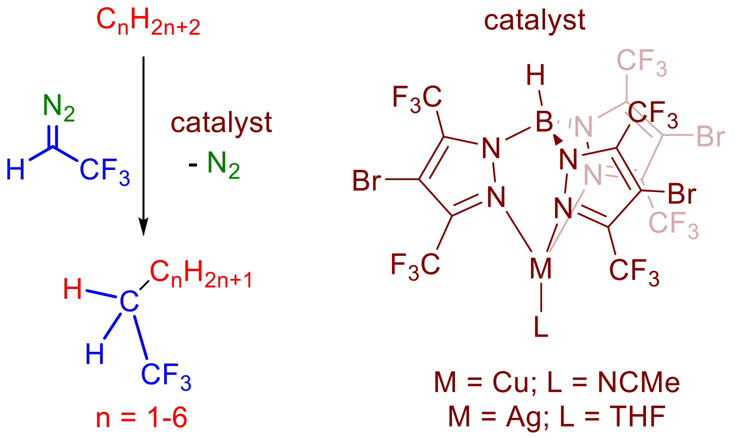
The incorporation of a CF_3 unit to an organic molecule is considered a powerful tool because its drastic changes in physical and chemical properties.[1] A variety of strategies have been developed to introduce the CF_3 group in a wide variety of substrates by different mechanistic approaches.[2] However, the direct conversion of alkanes C_nH_{2n+2} (lacking any polar or activating group) into products containing that CF_3 moiety is still a challenge. In this context, the metal-catalyzed carbene insertion into the C–H bonds of hydrocarbons has been achieved with excellent regioselectivity, even with gaseous alkanes as substrates.[3] Herein we describe the use of copper- and silver-based catalysts for such transformation, in which alkanes C_nH_{2n+2}, can be directly converted into trifluorocarbons $C_{n+1}H_{2n+3}CF_3$ for n = 1 (methane) to n = 6 (hexane). The complexes $Tp^{(CF3)2,Br}ML$ (M = Cu, Ag; L = NCMe, THF) promotes the catalytic functionalization of the C–H bonds of these hydrocarbons upon inserting the $:CHCF_3$ carbene unit from 2,2,2-trifluoromethyldiazoethane (CF_3CHN_2, TFMDE). These results constitute the first example of the direct conversion of gaseous alkanes into fluoroalkanes, opening a new way in the area of the functionalization of the challenging C–H bonds of alkanes.



References

[1] *Chem. Rev.* **2016**, *116*, 422–518. [2] *Alkane C–H Activation by Single-Site Metal Catalysis;* P. J. Pérez, Ed. Springer: Dordrecht, **2012**. [3] a) *Chem. Rev.* **2015**, *115*, 683–730; b) *Chem. Rev.* **2015**, *115*, 650–682.

PB16

Copper Catalyzed Synthesis of Chiral γ-Amino Alcohols from Alkynyl Oxetanes

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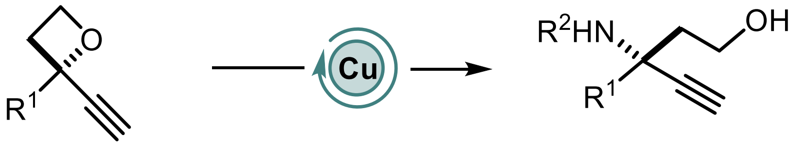

- high atom-economy
- functionalized γ-amino-alcohols
- versatile enantio-enriched BBs

The synthesis of compounds featuring quaternary stereocenters represents one of the most demanding tasks in organic synthesis due to the large steric repulsion present in congested carbon centers.[1] Although γ-amino alcohol fragments are present in a multitude of pharmaceutical and intermediates for natural product synthesis (e.g. benzo[1,4]oxazepines and benzo[1,4]diazepines), enantioselective approaches for the preparation of such targets comprising quaternary stereocenters has remained largely unexplored.[2,3]

Here we present a simple, scalable, and attractive method for the enantioselective synthesis of γ-amino alcohols having quaternary stereocenters. Enantioselective Cu-catalyzed ring opening amination of oxetanes is demonstrated to provide access to these compounds in high yields. These functional propargylic compounds are illustrated to be suitable and versatile synthons for the preparation of a series of biological importance intermediates such as β-unnatural amino acids.

References

1 J. Feng, M. Holmes, M. J. Krische, *Chem. Rev.* **2017**, *117*, 12564.
2 V. A. Palchykov, A. A. Gaponov, in *Advances in Heterocyclic Chemistry*, Elsevier, **2020**, pp. 285.
3 K. W. Quasdorf, L. E. Overman, *Nature* **2014**, *516*, 181.

PB17

Hetero-Trimetallic Low-Valent *s*-Block Chemistry

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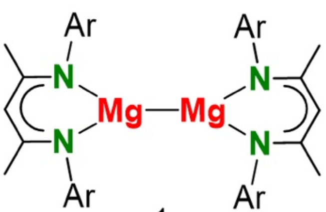
Since Jones‘ milestone discovery of bimetallic Mg(I) complexes (*e.g.* **1**), low-valent group 2 metal chemistry is a prime research area [1]. Attempts to isolate a mononuclear Mg(I) radical with a superbulky β-diketiminate ligand culminated in a first sodium magnesyl complex (**2**) featuring a Mg-Na bond [2]. While low-valent complexes with a Ca-Ca bond are still elusive, calculations predict the stability of Mg-Ca bound complexes. Attempted isolation led to a first hetero-trimetallic low-valent *s*-block metal complex of which we describe synthesis, structure and preliminary reactivity.



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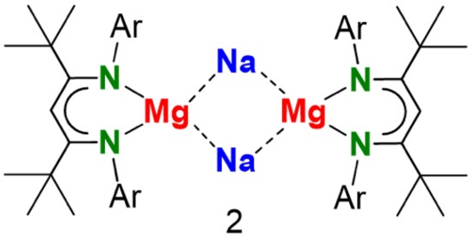

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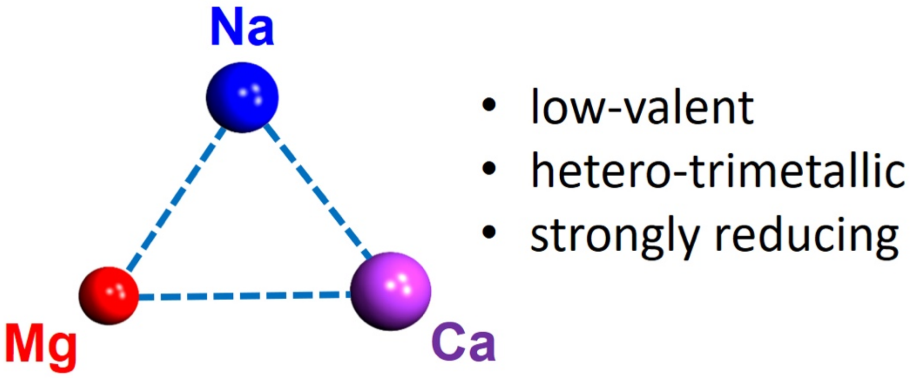

References

[1] S. P. Green, C. Jones, A. Stasch, *Science* **2007**, 318, 1754.
[2] B. Rösch, T.X. Gentner, J. Eyselein, J. Langer, H. Elsen, S. Harder, *Nature* **2021,** *592*, 717.

PB18

Gold(III)-catalyzed C_{sp3}-H and C_{sp2}-H functionalization by carbene insertion

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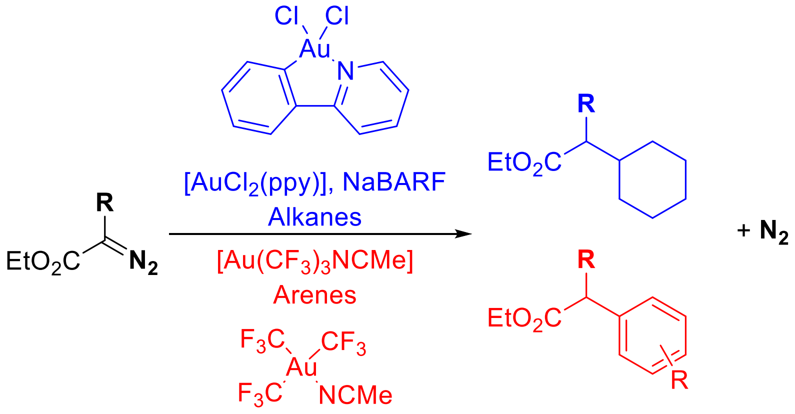
The use of gold in homogenous catalysis continues expanding nowadays.[1] Most of the catalytic systems are based on Au(I) albeit Au(III) catalysts are gaining interest.[2] We have previously reported the use of (NHC)AuX_3 complexes as catalysts for the transfer of carbene groups from diazo compounds, where the ancillary ligand is monodentate.[3] We have now turned our attention to the use of a bidentate ancillary ligand in order to check the effect of such change in the catalytic outcome. In this contribution we present the results obtained with Au(III) complexes bearing phenylpyridine (ppy) and tris(trifluoromethyl)acetonitrile on the functionalization of Csp^3-H and Csp^2-H bonds by carbene insertion from diazocompounds.



References

1) Meera G.; Rohit, K. R.; Susan Treesa, G. S.; Anilkumar, G. Advances and Prospects in Gold-Catalyzed C–H Activation. *Asian J. Org. Chem.*, **2020**, *9,* 144–161
2) Rocchigiani, L.; Bochmann, M. Recent Advances in Gold(III) Chemistry: Structure, Bonding, Reactivity, and Role in Homogeneous Catalysis. *Chem. Rev.*, **2021**, *121*, 8364–8451.
3) Rivilla, I.; Gómez-Emeterio, P.; Fructos, M. R.; Díaz-Requejo, M. M.; Pérez, P. J. Exclusive Aromatic vs Aliphatic C–H Bond Functionalization by Carbene Insertion with Gold-Based Catalysts. *Organometallics*, **2011**, *30*, 2855-2860.

PB19

Aluminium Phenoxoimines as Active Catalysts for Cyclic Esters Ring-Opening Copolymerization

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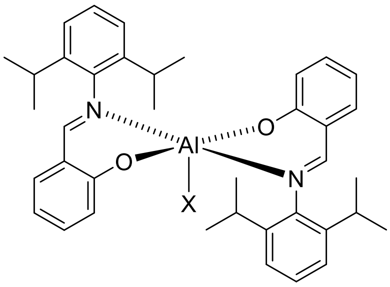
Nowadays the industry produces millions of tons of plastic per year. These plastics come from non-renewable fossil resources and have long life cycles, which is causing a high impact on the environment. As a result, alternatives that use more sustainable processes and respect the environment are being searched for. In this context, bioplastics stands out due to their renewable origin and their biodegradablility in specific conditions.[1]

This work aims to produce bioplastics like poly-*L*-actide (PLLA) that could offer advanced properties. As such, PLLA can show piezoelectricity which gives this material a high added value, and enables applications in biomedicine or electronics. However, the difficult processability of this polymer and the low flexibility affects its piezoelectric properties, so new strategies should be developed to improve those properties and eliminate the limitations. A possible solution is the combination of different cyclic esters as monomers.[2] Therefore, this work reports the synthesis of copolymers mixing poly-*L*-lactide with either poly-*p*-dioxanone (PLLA-PPDO) or poly-δ-valerolactone (PLLA-PVL) that could offer advanced properties. Aluminium phenoxoimine compounds have been used as catalysts for the ring opening copolymerization (ROCOP) (figure 1). These aluminium compounds have proven to be active in ROP reactions of cyclic esters, while showing good control of the polymerization stereochemistry, achieving highly isotactic copolymers. [3]



X = Me , Cl

Figure 1.

References

[1] A. Di Bartolo, G. Infurna, N.T. Dintcheva. *Polymers,* **2021**, 13, 1229.
[2] J. Yin, Q. Zhao, Y. Shein, B. He. *Journal of Applied Polymer Science*, **2022**, 139.
[3] F.M. García-Valle, V. Tabernero, T. Cuenca, M.E.G. Mosquera, J. Cano, S. Milione. *Organometallics*, **2018**, 37, 837.

PB20

Monofunctional platinum(II) complexes bearing *p*-ferrocenylaniline: synthesis, characterization and anticancer activity

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Bifunctional platinum complexes such as cisplatin, carboplatin and oxaliplatin are well known anticancer drugs as they form intrastrand adducts with the DNA. However, their drawbacks show the need for alternative compounds which present a higher antitumor activity and less side effects than bifunctional derivatives.[1] Thus, the incorporation of a metallocene in its structure, such as ferrocene, can help to overcome Pt(II) complexes side effects because of its wide bioactivity and the synergistic effect of the different metal sites.[2]

In this communication we present the synthesis of new monofunctional Pt(II) complexes bearing *p*-ferrocenylaniline as a ligand. These compounds were obtained with high yields via ligand substitution reactions from the bifunctional Pt(II) complexes. Different silver salts were used to evaluate their effect.[3] The compounds were characterized using multinuclear (^{1}H, ^{13}C and ^{195}Pt) NMR, IR spectroscopy, mass spectrometry and single-crystal X-ray analysis. In addition, ^{1}H NMR stability studies in DMSO were carried out. The electrochemical behaviour of the ferrocene precursors and the monofunctional complexes was examined by cyclic (CV) and square wave (SWV) voltammetries.

Finally, the antiproliferative behavior of the heterometallic complexes was studied. Their biological activity was checked on different cancer cell lines and a non-cancer cell line, comparing the results to the antitumoral drug cisplatin.

References

(1) L. Ma, L. Li, G. Zhu. *Inorg. Chem. Front.* **2022**, *9*, 2424-2453.
(2) M. Patra, G. Gasser. *Nat. Rev. Chem.* **2017**, *1*, 1-12.
(3) T. C. Johnstone, S. J. Lippard. *J. Am. Chem. Soc.* **2014**, *136*, 2126-2134.

PB21

Synthesis and biological activity of glycoconjugated Pd(II) and Pt(II) complexes based on extended planar aromatic ligands

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Pd(II) compounds represent an alternative to classical Pt(II) derivatives, and adequately tuned with the appropriated ligands, they can display better cytotoxicity and selectivity to cancer cells than their Pt counterparts [1]. On the other hand, there is a growing interest in designing, synthesizing, and evaluating the biological functions and potential therapeutic applications of molecules that recognize DNA and or/RNA quadruplexes. In this context, organic polypyridyl compounds such as 1,10-phenanthroline have served as scaffolds for several potent stabilizers of DNA G-quadruplexes [2]. Sugars can add important features in this regard: they not only can favor G4 interactions and give rise to significant differences in the affinity for a quadruplex target[3], but they can act as recognition domains themselves. Furthermore, concerning cancer diseases, it is well-recognized that carbohydrate-binding protein interactions are involved in a variety of metastasis-related events. All these reasons prompt us to prepare and evaluate glycoconjugated Pd and Pt compounds based on the 1,10-phenanthroline moiety. Herein, we report the synthesis, characterization and some interesting biological properties of palladium and platinum complexes containing *N*-(1,10-phenanthroline-5-yl)- and N-4-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenyl-glycopyranosylamine ligands.

References

[1]. Brabec V. et al, Coord. Chem. Rev., 351, 2017, 2-31; Scattolin T. et al, Cell reports in Physical Science, 2, 2021, 100446.
[2]. Neidle, S. in Therapeutic applications of Quadruplex Nucleic Acids, Academic Press, 2012.
[3]. P. Gratal; M.S. Arias-Pérez; L. Gude. Bioorganic Chemistry 2022, 125, 105851.

PB22

Reactivity of Ketenyl Anions towards Carbonyl Compounds

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The use of CO as C1 building block and its transformation into carbonyl containing organic compounds by transition metals are well known and used in large scale processes such as the Fisher-Tropsch, Monsanto and Cativa process.[1] In contrast, there are very limited reports on the activation of CO by main group compounds, albeit the past years have produced impressive examples of carbonyl complexes or coupling products of the s- and p-block elements.[2] Nevertheless, the application of such compounds in the synthesis of high-value compounds is practically untouched. Recently our group reported on the activation of CO by metallated ylides which leads to the formation of isolable ketenyl anions by displacement of a phosphine by CO.[3] These ketenyl anions showed versatile reactivity and enabled the facile access of ketenes as well as several other carbonyl containing compounds. Herein, we present the synthesis and isolation of a phosphinoyl substituted ketenyl anion and the reactivity of ketenyl anions toward different carbonyl compounds.

Scheme 1. Synthesis of phosphinoyl substituted ketenyl anion

References

1. a) A. Y. Khodakov, W. Chu, P. Fongarland, *Chem. Rev.* **2007**, *107*, 1692-1744; b) P. M. Maitlis, A. Haynes, G. J. Sunley, M. J. Howard, *J. Chem. Soc.*, *Dalton Trans*. **1996**, *11*, 2187-2196.
2. a) H. Braunschweig, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, I. Krummenacher, J. Mies, A. K. Phukan, A. Vargas, *Nat. Chem.* **2013**, *5*, 1025-1028; b) D. Reiter, R. Holzner, A. Porzelt,
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PB23

Solvent-controlled C–H Metalation via Fe/Co Amides

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Heterobimetallic systems utilising the cooperativity of a highly polar alkali-metal amide and a less polar metal amide (*e.g.*, Al, Zn, Fe) have emerged as a powerful class of reagents for the selective deprotonation of arenes.[1] Previously we reported the bimetallic partnership between [Na(HMDS)] and $[M(HMDS)_2]$ (M = Fe^{II} or Co^{II}, HMDS = hexamethyldisilazide) and explained why the deprotonative metalation of pentafluorobenzene does not proceed experimentally with neither Na nor M amides alone.[2] In this oral communication, I will present our recent discovery of controlled metalation activity via improved monometallic Co and Fe systems utilising an amide ligand 2,2,6,6-tetramethylpiperidine (TMP) with higher basicity. An unexpected, solvent-controlled reaction pathway leading to different bisaryl products will be conveyed during the presentation, together with the key roles of the Co and Fe centres in the reactivity observed experimentally (Fig. 1a).[3] In addition, I will shed light on the unique effect of the solvent-metal interaction via activation strain analysis and microkinetic modelling.[4] Overall, these novel monometallic systems offer a path to direct regioselective C–H metalations at room temperature, affording the desired metalation product in quantitative yields.

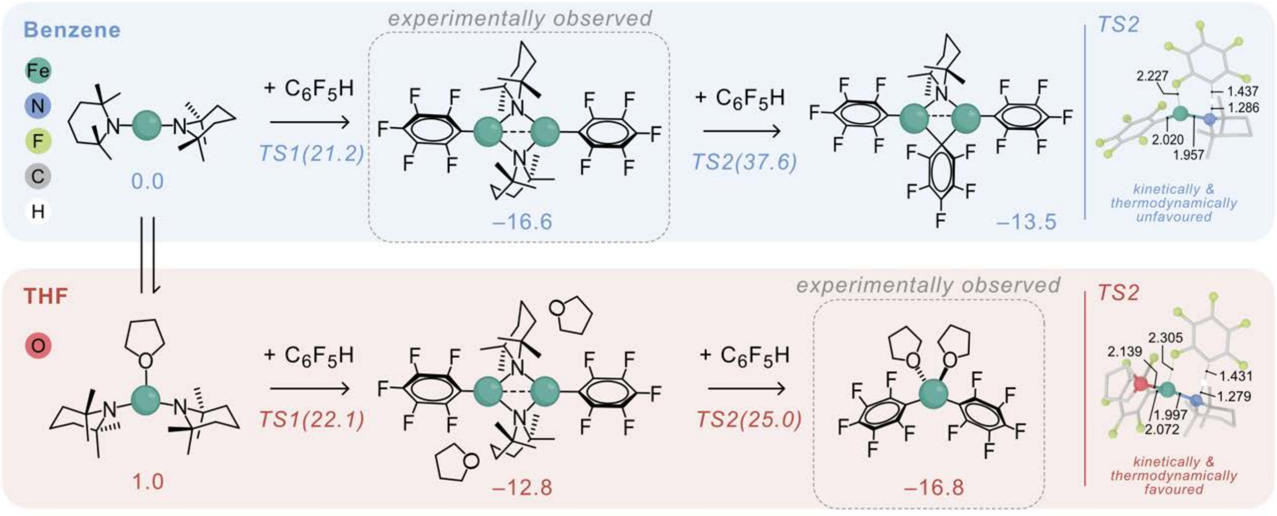

Figure 1. C–H metalation of C_6F_5H with $[Fe(TMP)_2]$ complex in different solvents.

References

[1] S. D. Robertson, M. Uzelac, R. E. Mulvey, *Chem. Rev.* **2019**, *119*, 8332.
[2] a) L. Maddock, M. Mu, A. R. Kennedy, M. García-Melchor, E. Hevia, *Angew. Chem. Int. Ed.* **2021**, *60*, 15296; b) A. Logallo, M. Mu, M. García-Melchor, E. Hevia, *Angew. Chem. Int. Ed.* **2022**, *61*, e202213246.
[3] M. Mu, L. Maddock, A. Logallo, Marconi N. P-D. E. Hevia, M. García-Melchor, *Manuscript in preparation.*

PB24

Afterglow Properties of Coumarin-Phosphine-Based Coinage Metal Complexes

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Afterglow properties are widely investigated among inorganic phosphors or organic molecules. However, the lifetimes of coinage metal complexes in the literature are usually in the range of milliseconds to microseconds.[1] In order to enhance the lifetime of the excited states of metal complexes to seconds timescale, a coumarin functionalized aminodiphosphine was designed and has been introduced as a bidentate ligand in coinage metal chemistry. Copper and silver complexes of different nuclearities were synthesized by using this ligand. A hybrid nature of the ligand resulted in compounds with rich photophysical properties. The properties include a sole coumarin-based blue fluorescence in solution at room temperature, and green phosphorescence at low temperatures which dominates the spectra of the metal complexes. The green phosphorescence of metal complexes shows an unusually long decay time along with high quantum efficiency. Additionally, a red phosphorescence, was observed for the trinuclear complexes at low temperature. The second-long phosphorescence and the red emission were not observed for the ligand and hence, are a result of the coordination to coinage metals. The excited states of these molecules were investigated by quantum chemical calculations and femtosecond transient absorption spectroscopy.[2]

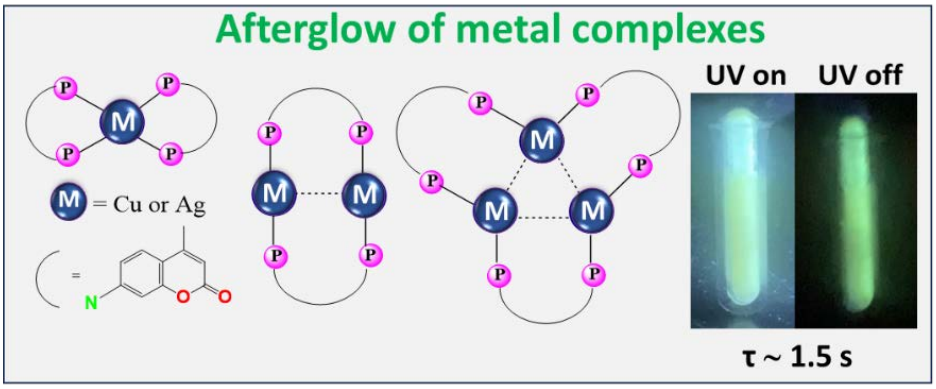

Figure 1: An overview of the metal complexes of different nuclearites and their afterglow emission

References

[1] V. W.-W. Yam, K. K.-W. Lo, *Chem. Soc. Rev.* **1999**, *28*, 323-334. [2] V. R. Naina, A. K. Singh, P. Rauthe, S. Lebedkin, M. T. Gamer, M. M. Kappes, A.-N. Unterreiner and P. W. Roesky, *Chem. - Eur. J.*, 2023, **2023**, e202300497.

PB25

Titanium Complexes Bearing a Tripodal Ligand as Catalysts for Polymerisation of Bio-based Monomers

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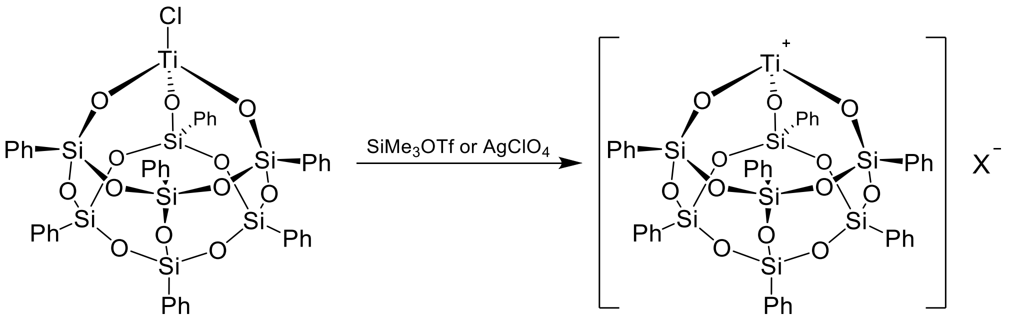
Herein we describe the use of different titanium complexes with a tripodal ligand as catalysts for the generation of biopolymers from biobased monomers. Recently in our Research Group, titanium complexes have been synthesized with a new tripodal ligand cyclopentadienyl-silsesquioxane and used as effective catalysts in oxidation and polymerisation processes [1].

In view of these results, it was proposed to employ different silsesquioxane titanium complexes in polymerisation of terpenoids as bio-based materials. We have mainly used limonene oxide, which is obtained by oxidation of limonene, a natural terpene extracted from citric fruit peels [2]. To increase the electrophilic character of the titanium atom, we prepared different cationic complexes corresponding with the general formula $[Ti(Ph_7Si_7O_{12}\text{-}\kappa^3O_3)]^+X^-$ (X^- = TfO^-, **2a**; ClO_4^-, **2b**), as illustrated in the scheme **1**. In these cases, it was not necessary to use an additional nucleophilic agent contrary to what happens when the neutral chlorinated precursor is used as catalyst, $[Ti(Ph_7Si_7O_{12}\text{-}\kappa^3O_3)Cl]$ (**1**).



(**1**)

X^- = TfO^-, **2a**; ClO_4^- , **2b**

Scheme 1

The reaction of these catalyst with limonene oxide give rise to polylimonene oxide (PLO) of low molecular weight, probably due to chain transfer side reactions. However, these PLO oligomers can be used as potential additive when blended with other polymers to improve their physical properties [3].

References

[1] Ventura, M. et al, *Eur. J. Inorg. Chem*, **2016**, *17*, 2843-2849
[2] Tabernero, V. et al, *Sust. Chem.* **2021,** *2* (3), 467-492
[3] Sessini, V. et al. *Polymer* **2020,** *210*, 123003.

PB26

Towards the rational design of polymetallic Ir(III) polypyridyl complexes based on benzimidazole scaffolds: synthesis, structures, photophysical properties and photocytotoxicity

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Photodynamic therapy (PDT) has emerged as a promising clinical treatment for solid tumors due to its non-invasive nature and spatiotemporal selectivity. However, the poor water solubility, weak photostability, and limited tissue penetration of most photosensitizers (PSs) have hindered their success. To overcome these challenges, organometallic complexes have been utilized, taking advantage of the heavy atom effect to induce fast singlet to triplet intersystem crossing (ISC), generating high $^1O_2$ yields. Furthermore, metal-complexes offer easy chemical modification and improved photostability compared to their organic counterparts. Among these, Ir(III) complexes have gained attention as potential PDT PSs due to their unique emission spectrum and good membrane permeability.

This presentation describes the impact of nuclearity and ligand field on the biological activity of Ir(III) polypyridyl complexes via photodynamic therapy (PDT). In pursuit of this goal, we synthesized novel benzimidazole-based cyclometalated Ir(III) complexes and evaluated their photophysical and electrochemical properties. The complexes displayed two absorption bands at approximately 300 and 400 nm and exhibited intense phosphorescent emission in the green and orange regions. The stability of the complexes in solution, both in the dark and under light, was confirmed using DMEM and PBS. The increased charge of the examined complexes improved their solubility in aqueous media, which is a desirable feature for PSs. The electrochemical properties of the complexes suggested reduction processes. Additionally, DFT and TDDFT calculations provide insight into the electronic and steric properties of the complexes.

References

1. Kar, B., Das, U., Roy, N., & Paira, P. *Coord Chem Rev.* **2023**, *474*, 214860.
2. Gasser, G., *Photodiagnosis Photodyn Ther.* **2023**, 41, 103373.

PB27

Visible-Light-Mediated Regioselective Chlorosulfonylation of Acrylamides

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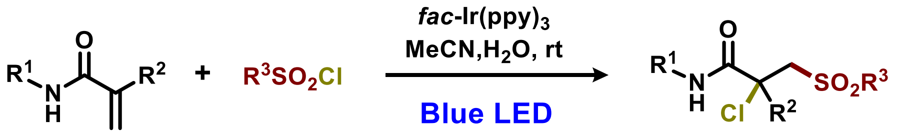
Sulfonyl group-containing compounds have gained significance in medicinal chemistry as therapeutic agents due to their binding affinity towards human receptors. Various research studies have explored the potential of these compounds in the treatment of human diseases such as central nervous system pathologies, Alzheimer´s, and HIV.[1,2] To synthesize these sulfonyl derivatives, novel methodologies have been developed, including the difunctionalization of alkenes via radical processes.[3]

In this communication, we present a one-step chlorosulfonylation of N-arylacrylamides via a regioselective photo-catalytic redox process. The reaction is compatible with a broad range of substrates and results in the formation of acyclic α-chlorosulfonylamides with a quaternary center in moderate to good yields.



21 to >99% yields
23 examples

Acknowledgements. We are grateful to Comunidad de Madrid Research Talent Attraction Program (2018-T1/IND-10054 and 2020-T2/BMD-20391), Investigo Program of European Union NextGenerationEU (46-UAH-INV) and Universidad de Alcalá (CCG20/CC-009, PIUAH21/CC-003 and predoctoral contract for G.G.O.) for financial support.

References

[1] Matviitsuk, A.; Panger, J. L.; Denmark, S. E. *Angew. Chem. Int. Ed.* **2020**, 59, 19796.
[2] Chen, X.; Parveen, S.; Zhang, S.; Yang, Y.; Zhu, C. *Curr. Med. Chem.* **2012**, 19, 3578.
[3] MacMillan, K. S.; Naidoo, J.; Liang, J.; Melito, L.; Williams, N. S.; Morlock, L.; Huntington, P. J.; Estill, S. J.; Longgood, J.; Becker, G. L.; McKnight, S. L. *J. Am. Chem. Soc.* **2011**, 133, 1428.

PB28

Optimization and Upscaling of Ylide-Substituted Phosphines (Yphos)

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Due to their easy synthesis and tunable electronic and steric properties, phosphines are frequently used as ligands in homogeneous catalysis. Particularly, strong electron donating phosphines such as P(tBu)3 are of special interest, such as for applications in palladium-catalysed coupling reactions. Our group has recently reported on the class of ylide-substituted phosphines and their application in catalysis [1-4]. Due to the strong electron-donating ability of the ylide moiety, these phosphines exhibit enhanced donor strength than “classical” phosphines and hence enable new transformations. Herein, we present the synthesis of a series of ylide-substituted phosphines and demonstrate that they can be upscaled without a mayor loss in yields. Batches of more than 50g are easily possible, still giving decent yields in few synthesis steps.

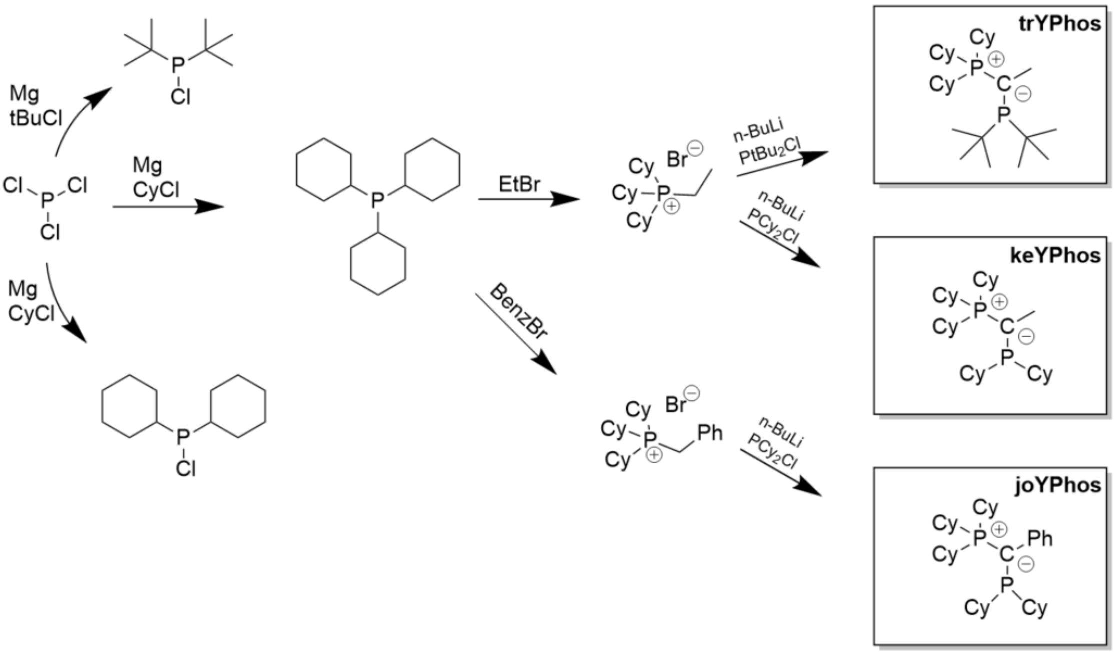

Figure 1. General scheme of the synthesis of YPhos ligands

References

[1] S. Lapointe, A. Sarbajna, V. H. Gessner, *Acc. Chem. Res.* ***2022**, 55, 5, 770–782.*

[2] L. T. Scharf, I. Rodstein, M. Schmidt, T. Scherpf, and V. H. Gessner, *ACS Catal.* ***2020**, 10, 2, 999–1009.*

[3] J. Tappen, I. Rodstein, K. McGuire, A. Großjohann, J. Löffler, T. Scherpf, V, H. Gessner, *Chem. Eur. J.* ***2020**, 26, 4281-4288.*

[4] P. Weber, T. Scherpf, I. Rodstein, D. Lichte, L. T. Scharf, L. J. Gooßen, V. H. Gessner, *Angew. Chem. Int. Ed.*, ***2019**, 58, 3203-3207.*

PB29

Synthesis and catalytic properties of cyclopalladated azobenzenes under mechanochemical conditions

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Ligand-directed C–H bond activation with $Pd(OAc)_2$ is one of the most commonly used synthetic methods to obtain cyclopalladated compounds.[1] Recently, the strong effect of acidic additives on C–H bond activation and functionalization reactions has been reported.[2] While the synthesis of palladacycles and mechanism of cyclopalladation reactions in solution are widely established, solid-state synthetic methods and mechanistic studies of mechanochemical C–H bond activation are still in the early stages.[3] In the last decade, mechanochemistry has emerged as a sustainable and environmentally friendly alternative to solution-based protocols for cross-coupling reactions, significantly reducing reaction times and providing access to new products that are unattainable in solution.[4] Although palladacycles are one of the most commonly used palladium catalysts for cross-coupling reactions, their use as catalysts in solid-state reactions is nonexistent.

In this work, we present a rapid and straightforward mechanochemical procedure for the synthesis of a series of phosphine-free mono- and dicyclopalladated azobenzenes bearing different anionic ligands. *In situ* Raman monitoring of the reactions revealed a strong influence of the organic acids used on the reaction time. At the same time, NMR spectroscopy and diffraction methods were employed to characterize the newly obtained compounds. To investigate the catalytic potential of the prepared palladacycles, a solid-state Suzuki-Miyaura reaction of 4-bromoazobenzene and phenylboronic acid was performed, and the results were compared with those obtained for the reaction catalyzed by commercial palladium catalysts.

References

[1] J. Dupont, M. Pfeffer, Palladacycles: Synthesis, Characterization and Applications, Wiley, Weinheim, Germany, 2008.

[2] J. Váňa, J. Bartáček, J. Hanusek, J. Roithová, M. Sedlák, *J. Org. Chem.* **84** (2019) 12746-12754.

[3] A. Bjelopetrović, S. Lukin, I. Halasz, K. Užarević, I. Đilović, D. Barišić, A. Budimir, M. Juribašić Kulcsár, M. Ćurić, *Chem. Eur. J.* **24** (2018) 10672–10682.

[4] T. Seo, N. Toyoshima, K. Kubota, H. Ito, *J. Am. Chem. Soc.* **143** (2021) 6165–6175.

PB30

Asymmetric cycloaddition reactions. The role of the metal

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Over the last decades, the fruitfulness of the metal-allyl chemistry has been crucial in the preparation of many enantioenriched synthons and natural products.[1] In this context, interceptive asymmetric allylic substitution has become a powerful alternative for the preparation of carbo- and heterocyclic backbones.[2] Mechanistically, most of the examples reported proceeds via a first nucleophilic attack of the metal-zwitterionic species to the dipolarophile followed by the nucleophilic attack of the dipolarophile to the metal-allyl fragment. In this context we will present our latest developments in the use of Pd- and Co-allyl chemistry for the preparation of chiral carbo- and heterocyclic compounds containing multiple stereogenic centers. Special attention will be given to discuss how the nature of the cycle formed can be affected by the ligand used and the nature of the metal employed.

References

[1] For recent reviews, see: a) J. Qu, G. Helmchen, *Acc. Chem. Res.* **2017**, *50*, 2539; b) K. Spielmann, G. Niel, R. M. de Figueiredo, J.-M. Campagne, *Chem. Soc. Rev.* **2018**, *47*, 1159; c) O. Pàmies, J. Margalef, S. Cañellas, J. James, E. Judge, P. J. Guiry, C. Moberg, J.-E. Bäckvall, A. Pfaltz, M. A. Pericàs, M. Diéguez, *Chem. Rev.* **2021**, *121*, 4373; d) L. Süsse, B. M. Stoltz, *Chem. Rev.* **2021**, *121*, 4084.

[2] P. de la Cruz-Sánchez, O. Pàmies, *Adv. Catal.* **2021**, *69*, 103.

PB31

Synthesis of mononuclear Strontium Complexes with ethereal and β-diketonato ligands

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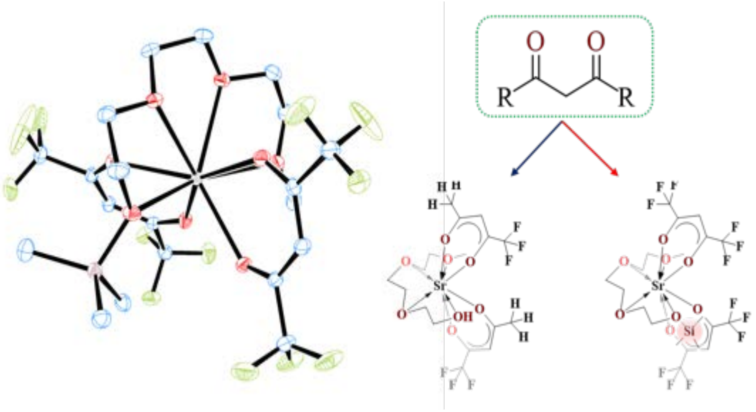
Alkaline earth (group 2) metal compounds have numerous uses, including as magnetoresistive materials, precursors for thin-film growth, and materials for dynamic random-access memory (DRAM). Strontium complexes play a key role in the semiconductor industry because they are used to fabricate thin films containing metal oxides. Among the various ways to deposit thin films, metal-organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) have possibility such as large–area growth, delicate composition control and high film uniformity. Because the application of alkali metals to these depositions requires highly volatile properties, our group's study has focused on design strontium complex with volatile and stability at high temperature. [1-2]

In this study, we tried the development of strontium complexes using β-diketonate ligands, such as tfac, acac, tmhd, and hfac, and ethereal groups, such as tmgeH, todH, and meeH ligands. The etherial ligands of the intermediates $[Sr(tmge)(btsa)]_2$ (1) and $[Sr(tod)(btsa)]_2$ (2) are synthesized and take up an acidic proton from the methylene of β-diketone to afford new complexes ($Sr(\beta\text{-diketonate})_2(ROH)$, ROH = tmgeH or todH). Interestingly, when hfacH was used as the β-diketone, the hydroxyl hydrogen atom of ROH in intermediate compound was substituted by trimethylsilyl from HMDS, which was produced by the reaction of **1** or **2** with hfacH and existed as a by-product in solution. The complexes 1-12 were synthesized via controlled substitution reactions using strontium(II) bis(bis(trimethylsillyl amide)·2DME. Synthesized strontium complexes were fully characterized by single crystal XRD analysis, H - NMR, elemental analysis, and thermal stability was analyzed by TGA.



References

[1] D. L. Schulz, T. J. Marks, Adv. Mater. **1994**, *6*, 719.
[2] S. M. George, B. K. Park, C. G. Kim,*and T. M. Chung, Eur. J Inorg. Chem. **2014**, 2002–2010.

PB32

Development of a new method for the synthesis of polyketones via Pd-catalyzed C-C bond cleavage

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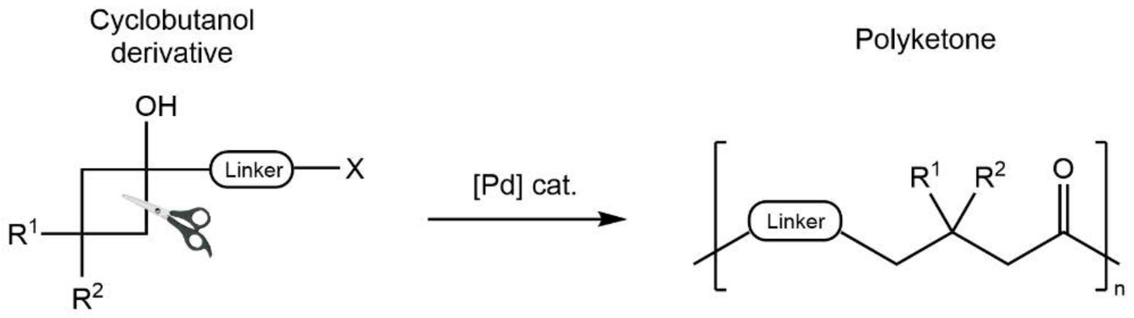
During the last years, some of the most studied polymerization processes have been those based on the opening of cyclic monomers (ROP).[1] However, they are mainly based on the cleavage of C-heteroatom bonds present in heterocycles like lactides and epoxides, or in the use of cyclic alkenes where a C=C bond undergoes a TM-catalyzed metathesis process.[2] Existing polymerization methods through ROP via $C(sp^3)$-$C(sp^3)$ bond cleavage (an structural moiety present in the majority of organic molecules) are much more limited and the mechanisms by which they occur have cationic, anionic or radical nature; which might complicate the control of various properties of the obtained polymer.[3] The use of cyclobutanols derivatives where a $C(sp^3)$-$C(sp^3)$ single bond cleavage is produced by a palladium-catalyzed beta-carbon elimination has been described for obtaining complex heterocycles.[4] In this work, we report the use of cyclobutanols derivatives as monomers for the synthesis of polyketones through a beta-carbon elimination and C-C single bond cleavage, catalyzed by organometallic palladium intermediates.



✓ A new method for polyketones synthesis

✓ $C(sp^3)$-$C(sp^3)$ bond cleavage

✓ Mechanism through organometallic intermediates

References

[1] Kamber, N.E.; Jeong, W.; Waymouth, R.M.; Pratt, R.C.; Lohmeijer, B. G. G.; Hedrick, J.L. *Chem. Rev.* **2007**, *107*, 5813-5840. [2] Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147-6176. Martinez, H.; Ren, N.; Matta, M.E.; Hillmyer, M.A. *Polym. Chem.* **2014**, *5*, 3507-3532. [3] Dubois, P.; Coulembier, O.; Raquez, J.M. *Handbook of Ring-Opening Polymerization*. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2009. [4] Pérez-Gómez, M.; Herrera-Ramírez, P.; Bautista, D.; Saura-Llamas, I.; García-López, J.A. *Organometallics* **2022**, *41*, 649-658.

PB33

DFT-guided understanding of the experimental trends in agostic interaction strength and hydrogenating activity of Fe^{II}(CCC) species

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Agostic interactions were observed in the bound mesityl group in a series of iron compounds bearing a bis(NHC) pincer CCC ligand. The L ligand on the [(CCC)Fe^{II}Mes(L)] (**1-L**) complexes influences the strength of the agostic interaction and is manifested in the upfield shift of the ^{1}H NMR agostic signal. The nature of the interaction was analysed by DFT calculations (Figure 1a), allowing for the experimental trend to be rationalized.[1] Interestingly, [(CCC)Fe(SiR$_3$)(L)(N$_2$)] (**2**) compounds can be obtained by reaction of **1** with various silanes. The nature of the silyl group has a clear impact in the speciation behavior of **2** derivatives upon reaction with H$_2$. This is intimately related with the observed activity as precatalysts for styrene hydrogenation (Figure 1b).[2] In both cases, theorethical analysis constitutes a powerful predictive tool to impel the rational design of new complexes maximising certain desired properties.

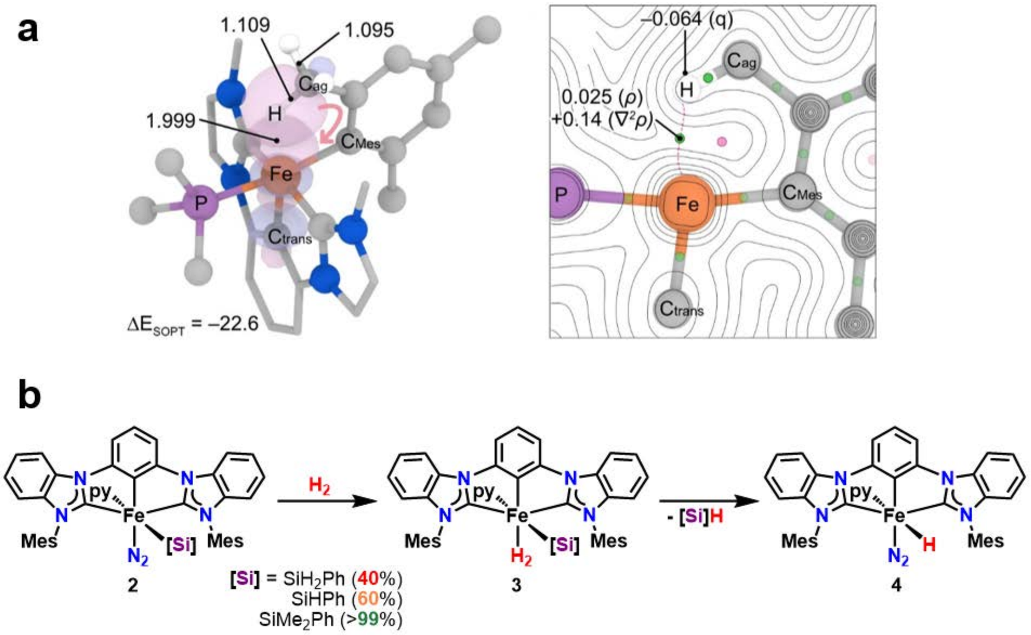

Figure 1. a) NBO and QTAIM analyses on the agostic interaction of **1-PMe$_3$**. b) Sequence of intermediates detected in the reaction of complexes [(CCC)Fe(SiR$_3$)py(N$_2$)] (**2**) with H$_2$. Experimental results (%) for styrene hydrogenation with different silyl groups.

References

[**1**] Nájera, D. C.; Peñas-Defrutos, M. N.; García-Melchor, M.; Fout, A. R. *Chem. Commun.* **2022**, *58*, 9626.
[**2**] Nájera, D. C.; Peñas-Defrutos, M. N.; García-Melchor, M.; Fout, A. R. *Manuscript in preparation.*

PB34

Zirconium and Hafnium Hydrido Complexes Supported by the Pentamethylcyclopentadienyl Ligand

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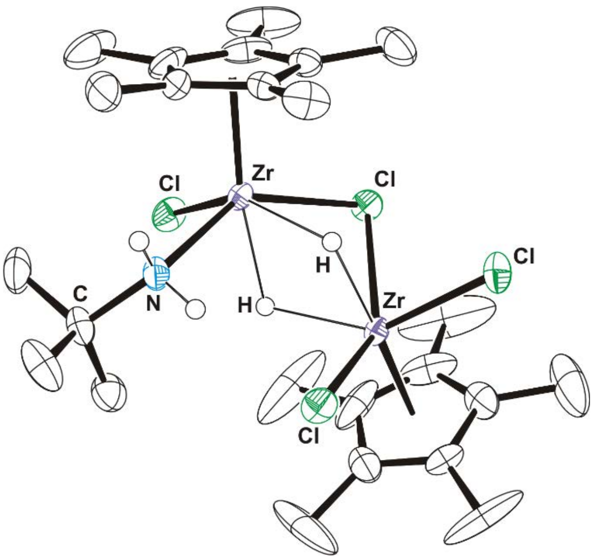
Early transition metal hydrido complexes are relevant due to their implication on the activation processes of small molecules, such as dinitrogen.[1] In this context, our research group has synthesized a series of hydrido derivatives containing group 4 elements using different hydrido sources, such as dihydrogen, $LiEH_4$ (E = B, Al), BH_3(thf) or amine-borane adducts. The hydrido systems attained exhibit interesting properties, remarkable structures and novel bonding schemes.[2]

In this communication, we will describe the synthesis, structure and properties of several half-sandwich zirconium and hafnium hydrido complexes, which were obtained by treatment of (pentamethylcyclopentadienyl)metal alkyl and amido compounds with amine-borane adducts NHR_2BH_3 (R_2 = H_2, Me_2, H*t*Bu). The reactions involve the formation of amidoborane ligands (NR_2BH_3) with M···H-B interactions which readily undergo β-hydride elimination to give hydride functions. For instance, the Figure shows the dinuclear zirconium species isolated from the reaction of $[Zr(\eta^5\text{-}C_5Me_5)Cl_2(NMe_2)]$ with NH_2*t*$BuBH_3$.



We are grateful to Universidad de Alcalá for financial support (UAH-GP2022-4 and PIUAH22/CC-049) and a fellowship (M.G.). J.T. thanks the Programa Investigo-Comunidad de Madrid for a contract Next Generation EU.

References

[1] T. Shima, Q. Zhuo, Z. Hou, *Coord. Chem. Rev.* **2022**, *472*, 214766.

[2] (a) M. Greño, M. Mena, A. Pérez-Redondo, C. Yélamos, *Dalton Trans.* **2017**, *46*, 5138-5142. (b) E. del Horno, J. Jover, M. Mena, A. Pérez-Redondo, C. Yélamos, *Chem. Eur. J.* **2022**, *28*, e202103085. (c) A. Calvo-Molina, E. del Horno, J. Jover, A. Pérez-Redondo, C. Yélamos, R. Zapata, *Organometallics* **2023**, *42*, 10.1021/acs.organomet.2c00580.

PB35

Synthesis of fluorinated aziridines via copper-mediatenitrene transfer

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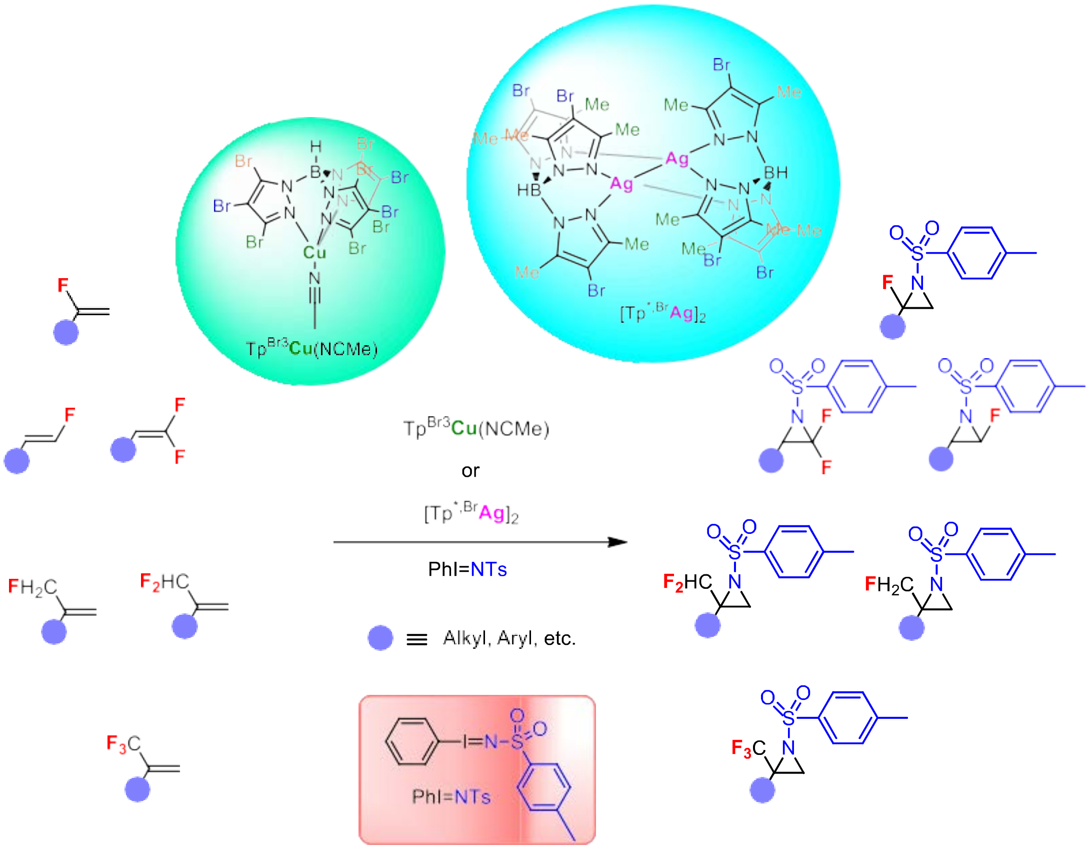
Our research group has long experience in nitrene transfer reactions to substrates of different nature, using copper and silver complexes with hydrotrispyrazolyl borate-type ligands (Tp^X) and leading to compounds with a new C-N bond.[1,2] These catalytic systems are especially active for olefinaziridination.

The catalytic synthesis of fluorinated aziridines still represents nowadays amajor challenge, since methods relying on classic nitrene transfer reactions to fluorinated olefins are scarcely reported.[3] In this communication, we present the use of Cu and Ag-based catalysts for the conversion of fluorinated olefins into fluorinated aziridines, with a noticeable efficiency compared with previous reported examples.



References

[1] Rodríguez, M. R.; Díaz-Requejo, M. M.; Pérez, P. J. *Synlett* **2021**, 32, 763-774.

[2] Caballero, A.; Díaz-Requejo, M. M.; Pérez, P. J. *Metal-Catalyzed Oxidation of Alkanes to Give Esters or Amines*, Science of Synthesis: Catalytic Oxidation in Organic Synthesis. Ed. Muñiz, K., **2018**, Chap. 3.

[3] Guo, Y.; Pei, C.; Jana, S.; Koenings, R. M. *ACS Catal.* **2021**, 11, 337-342.

PB36

Electrochemical bioactivity estimation of ferrocene-containing pyrrolidines

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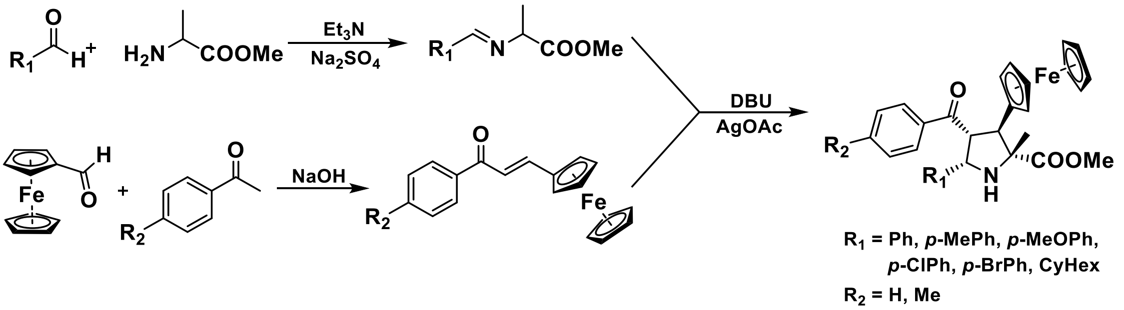
Herein we report the synthesis and electrochemical bioactivity estimation of twelve ferrocene-containing pyrrolidines. The rapid synthetic procedure was carried out under mild conditions, using [3+2] dipolar cycloaddition of azomethine ylides to ferrocenic chalcone-like derivatives (previously prepared from ferrocenecarboxaldehyde). Coordination of the Ag^+ to anion proved to be a key step in the dipole formation. The steric bulkiness of the substrates played a crucial role in limiting the yields (up to 53%) and stereochemistry of ferrocene derivatives.

Electrochemical studies (cyclic voltammetry – CV and differential pulse voltammetry – DPV) revealed that all compounds exhibit a quasi-reversible, diffusion-controlled one-electron oxidation process originating from ferrocene moiety. The DNA-binding study showed moderate interactions with obtained pyrrolidines, mostly of the electrostatic type, between positive ferrocenium ion and negatively charged phosphates of DNA. The presence of the interactions was confirmed by calculations of the diffusion coefficients, binding constants, and the size of the binding sites. DFT calculations and molecular docking studies certified the electrostatic nature of the interactions, probably slightly assisted by hydrogen bonding and weak hydrophobic interactions. The molecular docking analysis disclosed that the products are probably positioned into the major groove of nucleic acid.



Acknowledgments: Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No 451-03-47/2023-01/200122)

References

M. Pešić et al., J. Electrochem. Soc. 167 (2020) 025502, and references cited within

PB37

Small molecule activation by open-shell transition metal complexes

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Small molecule activation is an important field of study ultimately aimed to obtain value-added commodities from simple and abundant entities. One approach to small molecule activation is the use of open-shell paramagnetic complexes which can activate small molecules (such as O_2, N_2, H_2, CO_2) through single-electron events. Thus, the ability of the paramagnetic center to undergo redox reactions can facilitate the breaking of bonds in these molecules[1] and lead to productive catalytic cycles. Although this is highly common in Earth-abundant first-row transition metal complexes, their heavier analogues almost always operate throw two-electron events in closed-shell structures, while their paramagnetic chemistry is comparatively underdeveloped.

In this work, we have synthesized different paramagnetic organometallic complexes, most of them based on precious 2nd and 3rd row metals and explored their reactivity in the field of small molecule activation and catalysis. When possible, we have compared the catalytic activity of these complexes to that of their diamagnetic counterparts.

References

[1] N. Hidalgo, J. J. Moreno, I. García-Rubio, J. Campos, *Angew. Chem. Int. Ed.* **2022**, 61, e202206831

PB38

Pharmacokinetic properties of tetraligand complexes of cobalt(II) and zinc(II) with benzimidazole derivatives

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The main aim of the present study is to estimate pharmacokinetic properties (absorption, distribution, metabolism and excretion – ADME) of six synthesized tetrahedral cobalt(II) and zinc(II) complexes with benzimidazole derivatives as ligands. This estimation is quite important considering the potential application of the synthesized complexes as pesticides with antibacterial activity towards plant pathogens *Erwinia amylovora* and *Pectobacterium carotovorum* (Podunavac-Kuzmanović et al, 1999). The pharmacokinetic behaviour of these compounds in human organism should be estimated considering the fact that pesticides often end up in food products. The synthesized tetraligand complexes have the following general formulae: $[CoCl_2L_2]$ and $[ZnCl_2L_2]$, where L represents benzimidazole derivatives. The analysis was carried out applying SwissADME online program. The obtained results indicate that the synthesized complexes possess low water solubility (classified as poorly soluble) and high lipophilicity (WlogP > 5). The results show that the synthesized complexes have high gastrointestinal absorption and are considered to be a good P-glycoprotein substrates. Some of them are cytochrome P450 inhibitors and have good skin permeation. Also, 5 out of 6 synthesized complexes are not able to penetrate through blood-brain barrier. For all of the studied complexes the synthetic accessibility score is estimated to be around 4 meaning that the synthesis of the complexes is somewhat easy. Considering the obtained results, it can be suggested that the synthesized compounds could express certain influence on human organism through skin and gastrointestinal tract, as well as through the inhibition of some crucial enzymes, however further investigations are needed.

Acknowledgement. The present research is financed in the framework of the project “Molecular engineering and chemometric tools: Towards safer and greener future” financed by the Provincial Secretariat for Higher Education and Scientific Research of AP Vojvodina (Project No. 142-451-3095/2022-01/01).

References

Podunavac-Kuzmanović, S.; Leovac, V.M.; Perišić-Janjić, N.U.; Rogan, J.; Balaž, J. *J. Serb. Chem. Soc.* 1999, 64 (5-6), 381-388.

PB39

One Pot Tandem Conversion of Fructose to 2,5-diformylfuran by Silica-amino polymer-polyoxometalate Nanocomposites

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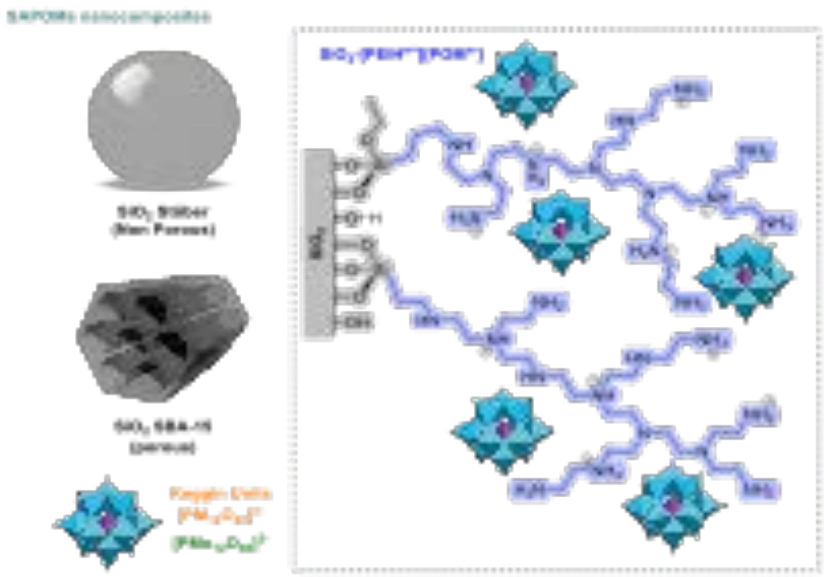
The fructose valorization has been an active area of research due to the increasing demand for renewable and sustainable energy sources.[1] Polyoxometalates (POMs) are a class of inorganic compounds that contain metal oxide clusters. They have attracted attention as catalysts for a variety of chemical reactions, including the valorization of fructose.[2] In this study, a novel silica-aminopolymer-polyoxometalate (SAPOMs) nanocomposite catalyst was developed for the dehydration of fructose to 5-hydroxymethylfurfural (HMF) and the posterior oxidation to 2,5-diformylfuran (DFF). Two silica supports were synthesized and modified with covalently grafted polyethyleneimine (PEI). Then, POM $H_3PMo_{12}O_{40}$ were immobilized onto the surface. The synthesized nanocomposite catalyst was characterized by various techniques, including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), solid NMR, among other techniques. The results showed that the POMs were successfully immobilized onto the surface of the modified silica, and the nanocomposite catalyst exhibited high thermal stability, good reusability, and remarkable catalytic activity towards fructose dehydration-oxidation to HMF and DFF. The HMF yield reached 85% after 0.5 hours of reaction at 150 °C and the DFF yield reached 50 % after 5 hours of reaction in one-pot synthesis. Moreover, the catalyst showed a high selectivity towards HMF and DFF with negligible formation of side products. Overall, the silica-amino polymer-POM nanocomposite catalyst is a promising candidate for fructose valorization towards sustainable energy sources.



References

(1) Zhang, Z.; Song, J.; Han, B. *Chem. Rev.* **2017**, *117* (10), 6834–6880.
(2) Liu, D.; Chen, B.; Li, J.; Lin, Z.; Li, P.; Zhen, N.; Chi, Y.; Hu, C.. *Inorg. Chem.* **2021**, *60* (6), 3909–3916.

PB40

Manganese-Catalyzed Synthesis of Imines

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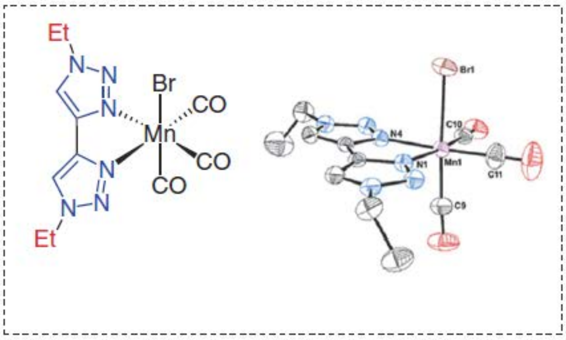
Imines are important intermediates in organic chemistry, widely used in natural products and medicinal chemistry. Their synthesis requires in general harsh conditions and the use of toxic reagents. Therefore, developing a sustainable and environmentally friendly method for producing imines from renewable and low-cost substrates is highly desirable.[1] In this work, a new family of bench-stable manganese(I) complexes containing bidentate triazole ligands, were used to mediate the acceptorless dehydrogenative coupling of alcohols with amines to form a wide variety of imines in excellent yields (up to 99%).[2] Mn-based complexes **3** and **4** proved to be highly efficient and versatile catalysts, allowing for the first time the preparation of several imines containing N-based heterocycles (Scheme 1).

- 28 examples
- up to 99% yield
- anilines and *N*-heterocyclic amines
- compatible with EWG and EDG



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References

[1] Cui, X.; Li, W.; Junge, K.; Fei, Z.; Beller, M.; Dyson, P. J., *Angew. Chemie – Int. Ed.,* 59 (2020) 7501-7507.**[2]** Raydan, D.; Friães, S.; Viduedo, N.; Santos, A. S.; Gomes, C. S. B.; Royo, B.; Marques, A. M. B. *Synlett.,* 33 (2022) 1290-1294

PB41

Alkali metal-based catalysts for the production and chemical recycling of polyesters under mild conditions

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Nowadays the development of bioplastics, especially the production of biodegradable polymers, have gained considerable attention as an environmentally friendly alternative to traditional oil-based plastics.

Polylactic acid (PLA) or polycaprolactone (PCL) are well-known bioplastics due to their good compatibility and mechanical properties for food-packaging or biomedical applications.[1] The most usual synthetic pathway to produce this type of polymers is by the Ring-Opening Polymerization (ROP) of the corresponding cyclic ester. Metallic complexes exhibit a great ability to exert a high control over the ROP process to give polymers with high molecular weight and adequate polydispersities. Recently, in our group, we have developed potassium-based catalysts which are highly active for this type of polymerization.[2]

In this work, potassium and sodium complexes have been employed as catalysts for the control over the polymerization of cyclic esters to produce polymers with defined properties. These alkali metals stand out due to their abundance, non-toxicity and biocompatibility. Furthermore, value-added products have been obtained by the alcoholysis of polyesters, using our catalytic system under mild conditions. This efficient method allows to close the life cycle of these polymers, generating useful chemicals, or even giving the initial monomer which can lead to the production of a new material with the same properties as the original one.[3]

References

[1] Y. Zhu, C. Romain, C.K. Williams. *Nature*, **2016**, *540*, 354-362.

[2] (a) M. Fernandez-Millán, M.E.G. Mosquera *et al. Organometallics*, **2020**, *39*, 2278-2286. (b) C. Rentero, M.E.G. Mosquera *et al.* Polymers, **2022**, *14*, 2982.

[3] (a) L.A. Román-Ramírez, J. Wood *et al. ACS Catalysis*, **2019**, *9*, 409-416. (b) J. Stewart, M.D. Jones et al. *RSC Advances*, **2022**, *12*, 1416.

PB42

Preparation of P,N-donor Ferrocene Ligands by Negishi Cross-Coupling

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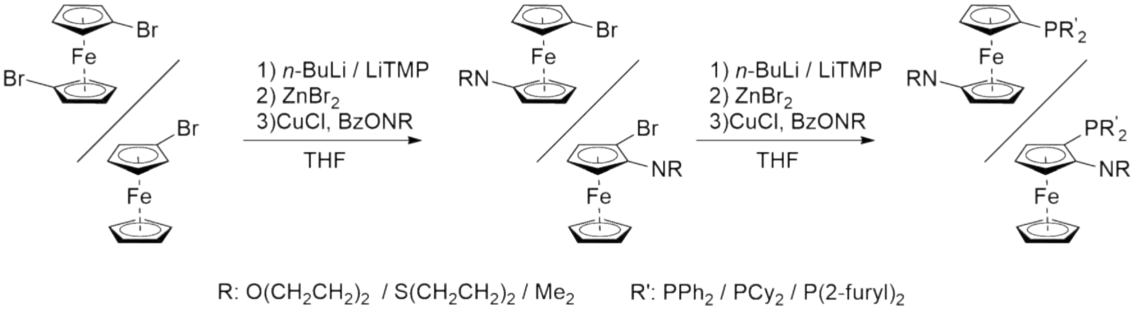
P,N-donor ligands form a varied family of compounds with wide applications in homogeneous catalysis. These ligands capitalize on the geometrical features of the backbone to which the donor groups are attached and on the difference in hardness of the donor groups. Ferrocene moiety offers unique geometrical features and flexibility, which have proven advantageous for diverse catalytic reactions.[1] In addition, the chemical stability of ferrocene makes it possible to use various common synthetic methods like cross-coupling reactions to prepare new derivatives. Utilizing Negishi cross-coupling[2] offers a new general procedure for the preparation of P,N-donor ferrocene ligands. This contribution will describe a series of P,N-donor ferrocene ligands prepared in this manner. Gold(I) complexes of the synthesized ligands were further employed in the gold-catalyzed cyclization of *N*-propargylbenzamide and in the oxidative cyclization of phenylacetylene.



References

1. (a) Carrol, M. P.; Guiry, P. J. *Chem. Soc. Rev.* **2014**, *43*, 819-833. (b) Noël, T.; Eycken, J. V. *Green Process. Synth.* **2013**, *2*, 297-309.
2. Berman, A. M.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 5680-5681.

PB43

Efficient alcohol oxidation with novel manganese(III) complexes with bis(phenolate)-NHC ligands

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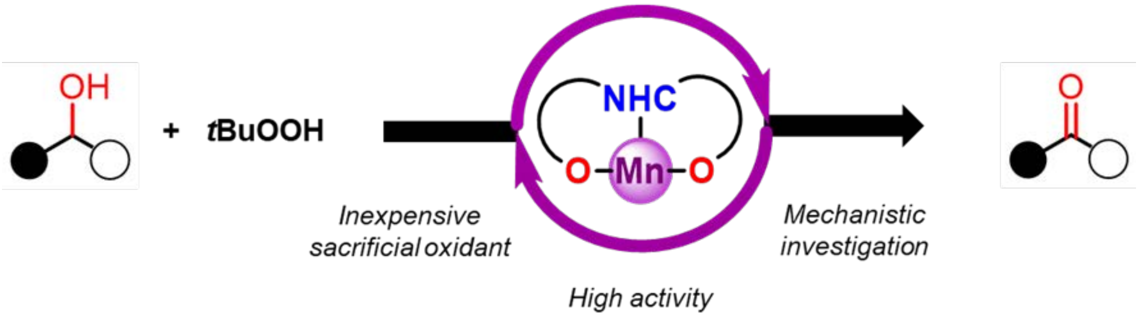
Oxidation chemistry plays a critical role in the synthesis of pharmaceuticals and value-added products, such as perfumes. A catalytic approach based on Earth-abundant metal complexes and cheap oxidants such as peroxides currently represents the most attractive strategy to perform this transformation.[1] Our group recently prepared a new class of N-heterocyclic carbene ligands bearing phenolate moieties and their corresponding metal complexes, investigating the potential benefit of the electronic flexibility of the carbene fragment in catalytic applications involving redox events.[2,3] Here, we decorated imidazole- and triazole-derived carbenes with phenolate substituents[4,5] to access Mn(III) complexes, which efficiently catalyze the oxidation of alcohols in the presence of *t*BuOOH as terminal oxidant. In addition, we will present the versatility of the catalytic system and mechanistic investigations in order to disclose the nature of the active species.



References

[1] C. Miao, X.-X. Li, Y.-M. Lee, C. Xia, Y. Wang, W. Nam, W. Sun, *Chem. Sci.* **2017**, *8*, 7476–7482.
[2] S. Bertini, M. Rahaman, A. Dutta, P. Schollhammer, A. V. Rudnev, F. Gloaguen, P. Broekmann, M. Albrecht, *Green Chem.* **2021**, *23*, 3365–3373.
[3] W. Stroek, M. Keilwerth, D. M. Pividori, K. Meyer, M. Albrecht, *J. Am. Chem. Soc.* **2021**, *143*, 20157–20165.
[4] E. Borré, G. Dahm, A. Aliprandi, M. Mauro, S. Dagorne, S. Bellemin-Laponnaz, *Organometallics* **2014**, *33*, 4374–4384.
[5] M. Baltrun, F. A. Watt, R. Schoch, C. Wölper, A. G. Neuba, S. Hohloch, *Dalton Trans.* **2019**, *48*, 14611–14625.

PB44

Gold(III) Porphyrin-Metallacages as Bioactive Materials

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Self-assembled metallacages are emerging promising supramolecular systems that have shown potential in different fields of chemistry, including as versatile platforms for biomedical applications, such as drug delivery, tumor therapy, bioimaging and biosensing.[1] Such 3-dimensional metal-containing assemblies possess cavities that can accommodate various guest molecules (e.g. anti-cancer drugs, imaging agents). By the correct design of the ligands and exploiting the predictable and well-defined coordination geometries of transition metal ions, the cage's size and its chemical-physical properties can be tuned for promoting specific host-guest interactions.[1]

Herein, we report the first gold(III) porphyrin-based self-assembled metallacage (AuCg), and explore its potential as a bioactive agent in comparison to previously reported Zn-containing (ZnCg) and free-base (H_2Cg) analogs.[2] The new system has consistently shown superior biomedical properties when compared with the analogues. In detail, we evaluated the application of these systems as photosensitizers for the photodynamic treatment of melanoma *in vitro*. We prove that AuCg presents selective photoactivation contrasting with the acute toxicity shown by ZnCg and H_2Cg in the absence of luminous stimulus. Moreover, the photoactivity of AuCg can be enhanced by the encapsulation of therapeutic guests (Figure 1), allowing a combinatory photo- and chemotherapy approach. Furthermore, we observed excellent G4 stabilization properties of AuCg using DNA melting experiments. These important properties are exclusive of the gold-containing cage system revealing the importance of the "golden touch" for the bioactivity of AuCg.

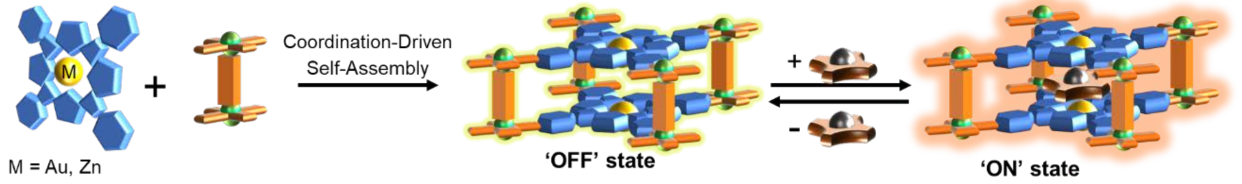

Figure 1. Coordination-driven self-assembly of porphyrin metallacages and reporting of host encapsulation.

References

[1] G. Moreno-Alcántar, A. Casini, FEBS Lett., **597**, 191 (2023)
[2] A M. Gallardo-Villagrán, L. Paulus, J. L. Charissoux, D. Y. Leger, P. Vergne-Salle, B. Therrien, B. Liagre, Dalt. Trans. **51**, 9673 (2022)

PB45

Deep-Blue and near-IR Carbene-Metal-Amide Molecular Design for Application in Energy Efficient OLEDs

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Two-coordinate coinage metal complexes with linear geometry L–Metal–X (L = carbene, M = Cu(I), Ag(I), Au(I) and X = anionic ligand) have recently emerged as a new class of strongly photoemissive materials – Carbene Metal Amides (CMA).[1-5] Their effectiveness is based on a combination of the ligands with a complementary donor and acceptor properties resulting in unity luminescence quantum yields and short excited state lifetimes at room temperature (<1 µs). Varied temperature experiments support thermally activated delayed fluorescence (TADF) process with very low activation energy barriers (ca. 20 meV). Although the coinage metal atoms make only small contributions to HOMOs and LUMOs, the sufficient spin-orbit coupling between the low-lying excited states allows to reduce the excited state lifetimes down to 200 ns for the very deep-blue CMA emitters (420 nm, 100% photoluminescence quantum yield, PLQY). This is five-fold shorter compared to benchmark iridium emitters that enabled fabrication of the deep-blue CMA OLED with significantly improved device lifetime (LT_{50} from several minutes to hours). We will also discuss the molecular design concepts (variations in electronic properties of the carbene and anionic ligands) to realize bright near-UV (down to 390 nm) and near-IR (up to 900 nm) CMA materials with proof-of-concept OLED devices to demonstrate the applied potential of this work within and beyond of the visible spectrum range.

References

(1) *Science*. **2017**, *356*, 159–163; (2) *Nature Commun.*, **2020**, *11*, 1758; (3) *Chem. Sci.*, **2020**, *11*, 435–446. (4) *Adv. Opt. Mater.*, **2022**, 2200312. (5) *Chem. Mater.*, **2022**, *34(16)*, 7526–7542

PB46

A new family of cyclometalated Ir(III) complexes as promising phototherapeutic agents

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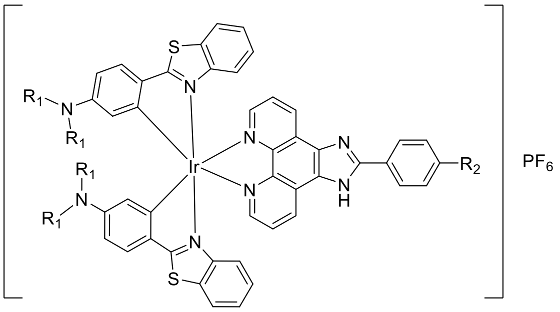
Photodynamic therapy (PDT) is one of the most promising treatments against cancer, because it acts in a selective way leading cancer cells to cell death through the generation of reactive oxygen species (ROS) or/and singlet oxygen ($^1O_2$)[1]. In 2022, our research group reported octahedral Ir(III) complexes bearing phenanthroline-based N^N ligands. Some of them showed photoactivity against cervical cancer cells (HeLa cells), so they open a route to obtain new potential photosensitizers[2]. In this study, a new family of cyclometallated Ir(III) complexes of stoichiometry $[Ir(C^{\wedge}N)_2(N^{\wedge}N)]PF_6$ (**Figure 1**) has been synthesized, using functionalized 2-phenyl imidazole-[1,10]phenanthroline as N^N ligand, and a deprotonated benzothiazole derivated as C^N ligand.



R_1= phenyl
R_2= H, F, NO_2, NPh_2

Figure 1: Chemical structure of the new Ir(III) complexes.

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References

[1] T.C. Pham, V.N. Nguyen, Y. Choi, S. Lee, J. Yoon, *Chem.Rev.* **2021**, *121*, 13454-13619.
[2] N. Busto, G. Vigueras, N. Cutillas, B. García, J. Ruiz, *Dalton. Trans.* **2022**, *51,* 9653–9663.

PB47

Homogeneous hydrogenation of esters using commercially available Gusev catalysts

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Ester hydrogenation is widely used in the manufacture of pharmaceuticals, detergents, cosmetics, flavours and fragrances.[1] The Gusev catalysts are a homogeneous option for ester hydrogenation.[2] JM have an exclusive license to two homogeneous Ru catalysts for the reduction of esters to alcohols for application in fine chemicals and fatty alcohol synthesis. Key characteristics are:

- high chemoselectivity for ester hydrogenation (eg. C=C retention)
- high activity (10,000 – 100,000/1) under basic conditions
- mild conditions – low T (30 – 90C) and P (5 – 50 bar)

The results of in-house R & D at JM will be presented showing examples which demonstrate the potential of this emerging and commercially relevant technology.

At low enough catalyst loadings the cost contribution of this hydrogenation process becomes competitive with more traditional stoichiometric hydride reagents. Non-qualified advantages include reduced waste disposal costs, improved safety & sustainability and process simplification.[3]

References

[1] S. Werkmeister, K. Junge, M. Beller, *Org. Process Res. Dev.* **2014**, 18, 289

[2] D. Spasyuk, S. Smith, D. G. Gusev, *Angew. Chem. Int. Ed.* **2013**, 52, 2538

[3] A. Zanotti-Gerosa, D. Grainger, L. Todd, G. Grasa, L. Milner, E. Boddie, L. Browne, I. Egerton, L. Wong, *Chimica Oggi Catalysis & Biocatalysis*, **2019**, 37 (4), 10

PB48

Platinum and Gold complexes of TPA derivatives with hydrophilic and hydrophobic side-chains

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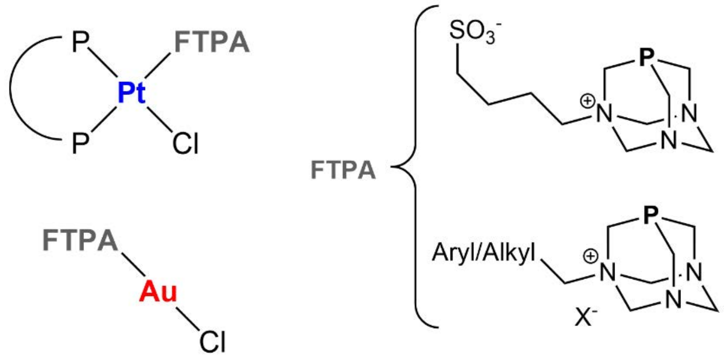
Among the monodentate phosphine ligands, TPA (1,3,5-triaza-7-phosphaadamantane) is characterized by a cage-like structure with a small cone angle (103°) and nitrogen atoms which can be involved in further functionalization. This makes TPA and its derivatives attractive ligands for organometallic synthesis and catalysis [1]. Considering the huge variety of reactions catalysed by platinum(II) and gold(I) phosphine complexes [2], we synthesized their complexes with some N-functionalized TPA derivatives (FTPA) bearing either ionic hydrophilic or long alkyl hydrophobic side chains (Figure). The complexes were characterized and studied as pre-catalysts in model reactions, such as the hydration of alkynes and oxidation of ketones.



Acknowledgements: the authors wish to thank Fondazione CaRiPaRo for funding the project Ricerca Scientifica di Eccellenza 2018 "Selective catalysis in supramolecular confined spaces (SELECT)".

References

[1] Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M., Coord. Chem. Rev. 2004, 248, 955-993. [2] Michelin, R.A.; Sgarbossa, P.; Scarso, A.; Strukul, G. Coord. Chem. Rev. 2010, 254, 6465-660; Li, Z.; Brouwer, C.; He, C., Chem. Rev. 2008, 108, 3239-3265.

PB49

Mechanistic investigations on the copper catalysed borylation of *p*-Me-Phenylacetylene

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Since their introduction by Miyaura *et al.* Copper catalysed borylation reactions with diboranes(4) as reagents have become a well-established type of functionalisation reactions.[1]

The mechanistic understanding of these reactions is based mostly on extensive studies by Sadighi *et al.*[2] Using as model catalyst IDippCu-Bpin they fully retraced the catalytic cycle in a series of stoichiometric reactions. This study as well as theoretical studies by Marder and Lin *et al.* are the basis of the current understanding of copper catalysed borylations.[3]

The model system used by Sadighi *et al.* is not universally applicable, in particular as sterically less demanding catalysts, as often employed, are generally not well described by the model catalyst, IDippCu-Bpin, used.

Inspired by Sadighi's studies we therefore set out to study the borylation of alkynes and α,β-unsaturated carbonyls. Here we present first results employing a sterically less demanding model system including I*t*BuCu-O*t*Bu as precatalyst, B_2pin_2, *p*-Me-Phenylacetylene as substrate and *i*PrOH or MeOH as additives. This system is compared to the analogous system with the sterically more demanding IDippCu-O*t*Bu as precatalyst.

The role of each component of the reaction as well as each step of the catalytic cycle is elucidated by stoichiometric reactions monitored by NMR spectroscopy as well as by isolation and characterization of the respective products and intermediates.

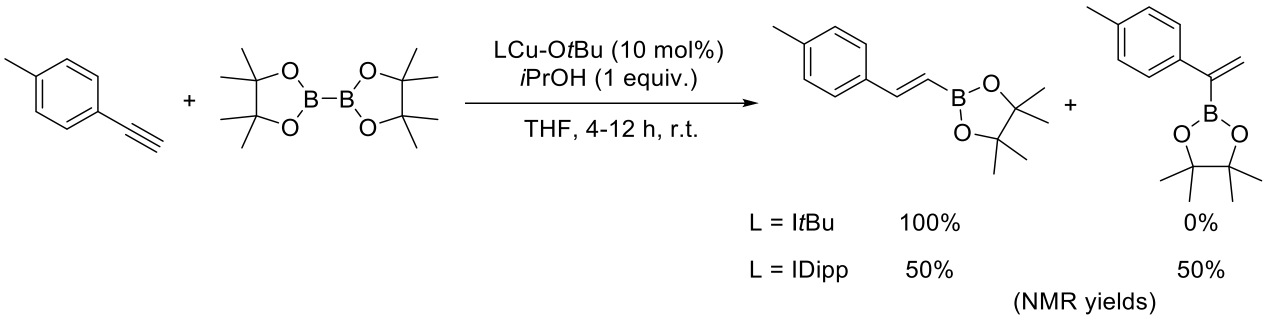

Figure 1: Copper catalysed borylation of p-Me-Phenylacetylene – the model system employed in this study.

References

[1] K. Takahashi, T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2001**, *625*, 47.

[2] a) D. S. Laitar, P. Müller, J. P. Sadighi, *J. Am. Chem. Soc.* **2005**, *127*, 17196; b) D. S. Laitar, E. Y. Tsui, J. P. Sadighi, *J. Am. Chem. Soc.* **2006**, *128*, 11036.

[3] a) H. Zhao, Z. Lin, T. B. Marder, *J. Am. Chem. Soc.* **2006**, *128*, 15637; b) H. Zhao, L. Dang, T. B. Marder, Z. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 5586; c) C. Kleeberg, L. Dang, Z. Lin, T. B. Marder, *Angew. Chem.* **2009**, *121*, 5454.

PB50

Synthesis of Bimetallic Rh_2 Half-Baguette Complexes from a Novel Magnesium Pentalenide

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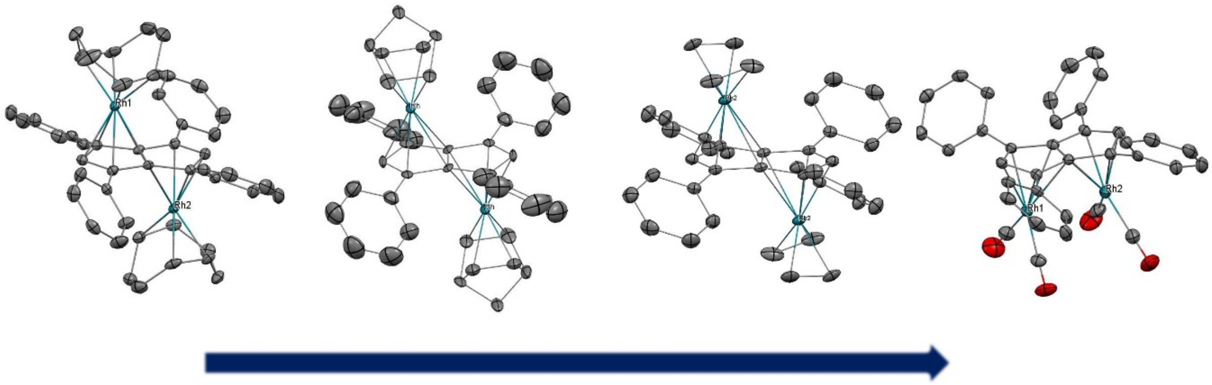
Pentalenide (**Pn^{2-}**, $C_8H_6^{2-}$) is the bicyclic analogue of the cyclopentadienyl anion. However, compared to the ubiquitous use of its’ monocyclic relative, the organometallic chemistry of pentalenide is underexplored and has predominantly been restricted to the 1,4-disilylated and permethylated frameworks of Cloke and O’Hare, respectively.[1] The lack of research into pentalenide chemistry can be attributed to the limitations in accessing suitable precursors.[2]

Recently we have reported a straightforward synthesis of a stable tetraphenyl-dihydropentalene and its deprotonation behaviour towards a range of group 1 bases.[3] Building upon this work, attention has turned to the hitherto unexplored alkaline earth chemistry of pentalenides. The deprotonative metalation of 1,3,4,6-Ph_4PnH_2 with dialkylmagnesium yielded the first known group 2 pentalenide salt in good yield, where the choice of solvent influences the structure of pentalenide formed.

Subsequent transmetalations with a range of Rh(I) precursors, with decreasing auxiliary ligand size, has led to the formation of a series of novel homobimetallic Rh(I) pentalenide complexes. The reactivity of a carbonyl complex towards chemical oxidation and substitution by a range of P-donor ligands has been explored.



Decreasing Steric Bulk

References

1. Cloke, F. G. N.; Green, J. C.; Kilpatrick, A. F. R.; O’Hare, D. *Coord. Chem. Rev.*, **2017**, 344, 238-262
2. Boyt, S. M.; Jenek, N. A.; Hintermair, U. *Dalton Trans.*, **2019**, 48, 5107-5124
3. Boyt, S. M.; Jenek, N. A.; Sanderson H. J.; Kociok-Köhn, G.; Hintermair, U. *Organometallics*, **2022**, 41, 211-225

PB51

New cyclometalated osmium(II) complexes as anticancer agents

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Osmium is a member of the platinum group of metals, but its complexes have been far less explored so far for cancer treatment than those based on platinum or ruthenium. However, given the clinical success of ruthenium complexes, which entered and progressed into clinical trials, research efforts have been directed towards investigating the therapeutic properties of osmium complexes.

In this communication we present new cyclometalated Os(II) complexes of the type [Os(C^N)(N^N)$_2$]OTf. The C^N ligand is based on a benzimidazole backbone, which is widely used as pharmacophore and has exhibited good (photo)biological results in ruthenium analogs. Importantly, some substitutions have also been introduced on the aryl group of the C^N ligand to modulate their electronic and biological properties. 2,2′-bipyridine (bpy) and dipyrido[3,2-d:2',3'-f]quinoxaline (dpq) were chosen as N^N ancillary ligands because their implications in the light-activated metal complexes [1]. The new compounds are kinetically inert and absorb a full-wavelength range of visible light. The antiproliferative activity of the new osmium(II) compounds has been performed in a panel of seven human cancer and two noncancerous cell lines under dark conditions and for selected cell lines also after green light irradiation. The mechanism of antiproliferative action of complexes has also been investigated and, under dark conditions, the Os(II) complexes are able to activate the endoplasmic reticulum stress pathway in cancer cells and disrupt calcium homeostasis.

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References

[1] F. J. Ballester; E. Ortega; D. Bautista, M. D. Santana, J. Ruiz, Chem. Commun., 2020, *56*, 10301-10304.

PB52

Isolation and the reactivity of an acyclic-monomeric aluminyl

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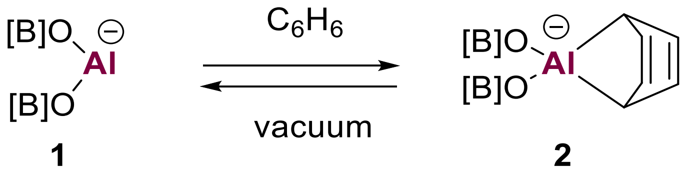
Molding compounds derived from the abundant lighter p-block elements (e.g., Al, Si, etc.) through molecular design to interact with industrially relevant molecules in a 'Transition Metal like' fashion represents an exciting fundamental chemical challenge offering very high potential rewards.[1] Aluminium is the most abundant metal in the Earth's crust by mass. Recently, low valent aluminium compounds, possessing a nucleophilic Al center with an anionic charge, namely the aluminyl anion ($[R_2Al:]^-M^+$), which are in the +I oxidation state, with comparatively small HOMO-LUMO gaps, showed promising activity in potentially mimicking the ambiphilic reactivity of transition metals.[2] For example, ([(NON)AlK]$_2$, enabled the first single-site C–H oxidative addition of benzene by a main-group metal, and its corresponding monomeric counterpart [(NON)AlK] has shown the unprecedented reversible C–C bond activation of benzene.[2a, 2b] Moreover, exploiting the extreme nucleophilicity of Al(I) in aluminyls, a diverse range of small molecules (e.g., H_2, CO_2, N_2O, P_4, and RN_3, etc.) have been activated, leading to the formation of reactive Al–E bonds (E = H, O, N).[2a, 2b] Typically, these aluminyls are stabilized by N/N, N/C, C/C based di-anionic chelating ligand system. Apart from these examples, an acyclic bis amido aluminyl $K_2[Al\{N(Dipp)SiMe_3\}_2]_2$ is reported, recently, which exists as a dimer.[2c] To the best of our knowledge a charge separated monomeric-acyclic aluminyl is still unknown.

With a view to targeting an isolable monomeric-acyclic aluminyl, we envisaged need for more strongly π-donating ligands which would potentially lead to a wider HOMO–LUMO gap on the basis of LUMO destabilization (ligand-to-Al π donation) and HOMO stabilization (high electronegativity of adjacent atom of Al). Herein we present the first example of a monomeric-acyclic aluminyl **1**, stabilized by bis-boryloxy ligands. Notably compound **1** activate a diverse range of small molecules (e.g., CO, CO_2, N_2O, P_4), including the reversible two electron reduction of benzene.



References

[1] a) C. Weetman, S. Inoue, *ChemCatChem* **2018**, *10*, 4213-4228; b) P. P. Power, *Nature* **2010**, *463*, 171-177.

[2] a) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed* **2021**, *60*, 1702-1713; b) M. P. Coles, M. J. Evans, *Chem. Commun.* **2023**, *59*, 503-519; c) R. A. Jackson, A. J. R. Matthews, P. Vasko, M. F. Mahon, J. Hicks, D. J. Liptrot, *Chem. Commun.* **2023**, *59*, 5277-5280.

PB53

Synthesis of Fluorinated Aluminium Complexes

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The longstanding dominance of transition metal complexes in catalysis is attributed to their facile interconversion between oxidation states.[1] However, the focus has recently shifted towards main group chemistry and catalysis, specifically within the s and p-block metals.[2] Chelating and pincer-type ligands have become crucial in stabilizing dinuclear M(I)-M(I) and mononuclear M(I) main group metal species, such as reduced Mg(I)-Mg(I) complexes[3] and nucleophilic Al(I) anions.[4] These advancements have unlocked new avenues in main-group metal chemistry, enabling the discovery of unconventional main-group metal species with distinct electronic and stereochemical properties, ultimately contributing to developing innovative reactivities and catalytic systems.

We present the synthesis of a series of novel Al complexes featuring fluorinated chelating ligands (Figure 1),[5] which hold potential as precursors for main group-mediated transformations and catalysis. Our communication will discuss the synthesis, characterization, stability and applications of these highly electrophilic Al complexes.

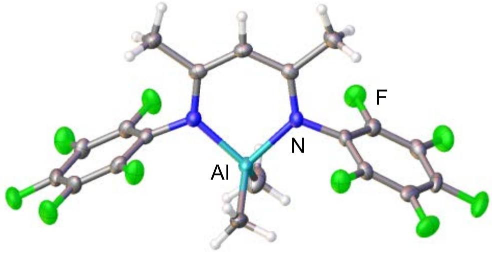

Figure 1. Fluorinated organoaluminium complexes.

References

1 R. H. Crabtree, The Organometallic Chemistry of the Transition Metals (7th Ed); Wiley: **2019**.
2 R. L. Melen, *Science* **2019**, 363, 479.
3 S. P. Green, C. Jones, A. Stasch. *Science* **2007**, 318, 1754
4 J Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* ***2021**,* 60, 1702-1713.
5 Unpublished results, manuscript in preparation.

PB54

Engineering PHB via Ring-opening polymerization of β-butyrolactone using Al-based catalysts

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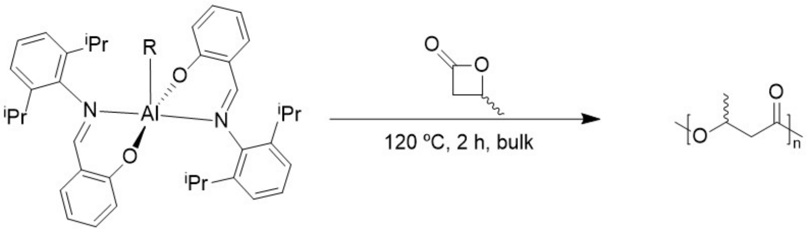
Poly(3-hydroxybutyrate) (PHB) is a polymer produced naturally by bacteria under unbalanced growth conditions as intracellular carbon and energy reserves. This natural PHB is a highly isotactic semicrystalline thermoplastic material with a T_g and T_m of approximately 5 °C and 180 °C, respectively, showing properties comparable to those of isotactic polypropylene such as good resistance to ultraviolet light between others [1]. Furthermore, its applications are limited by its poor processability and rigidity due to its high crystalline degree (around 70%) as well as due to its high production costs.

Alternatively, ring-opening polymerization (ROP) of β-butyrolactone (*β*-BL) using metal-based catalysts has provided an alternative route to obtain this biodegradable polyester, allowing PHB with different molecular weights, narrow polydispersity, as well as different stereoregularity [2]. Among metal-based catalysts, we have reported that aluminum complexes are very active in ROP of β-butyrolactone [3].

In this work, we have exptended the studies and the catalytic ROP of *β*-BL have been optimized using two different diphenoxyimine five-coordinated aluminum complexes in order to fabricate high value polymers for different applications.



1: X = CH_3
2: X = Cl

In particular, low molecular weight PHB has been proposed as biodegradable additive for bacterial PHB while high molecular weight PHB has been processed by electrospinning to study its piezoelectric properties.

References

1. E. D. Cross *et al. J. Polym. Sci. A Polym. Chem.* 2013, 51: 1137-1146.
2. J. Brichmoser *et al. Organometallics* 2023, 10.1021/acs.organomet.2c00624; J. Bruckmoser *et al. JACS* 2023, 10.1021/jacs.3c02348
3. F. M. García-Valle *et al. Organometallics* 2018, 37, 837–840.

PB55

Synthesis and Catalysis of Planar-Chiral Ferrocene-Based NHC Copper Complexes

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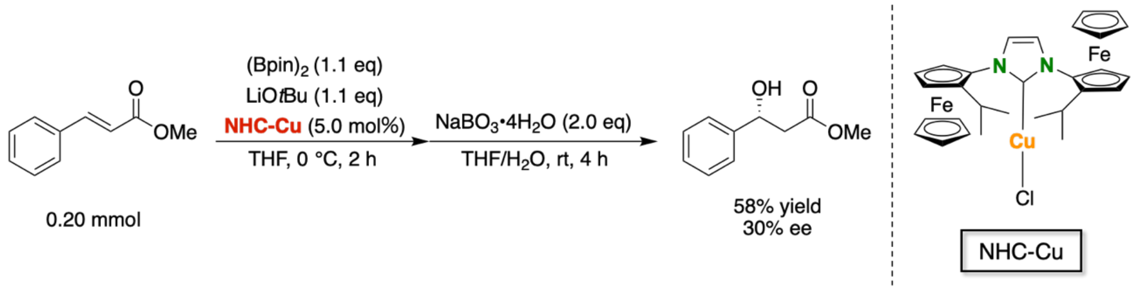
Planar-chiral ferrocene based phosphines are established as privileged ligands and their transition metal catalysts are effective in asymmetric organic synthetic reactions.[1] On the other hand, limited examples of planar-chiral ferrocene based N-Heterocyclic carbenes (NHCs) have been reported, although chiral NHC have often been used in asymmetric reactions.[2] We have previously demonstrated that planar chiral ferrocenyl triazolylidene metal complexes are effective catalyst in asymmetric reactions, where the ferrocenyl triazolylidene ligand works as bulky (%V_{bur} = 42.2) and strong electron-donor (TEP = 2044 cm^{-1}).[3] However, synthetic protocol for the triazolylidene ligand is long (more than 10 steps from starting Ugi's amine) and difficult, so the more simple method for the preparation of planar chiral ferrocene based NHC ligands should be required.

In this study, we would like to propose *ortho*-isopropyl-substituted planar chiral ferrocene based NHC ligand which can be prepared shorter and simple protocol from Ugi's amine. We have achieved to synthesize and characterization N-planar chiral ferrocenyl imidazolylidene ligand; the electronic and steric properties of the ligand was revealed to have strong electron-donating ability (TEP = 2043 cm^{-1}) and high steric bulk (%V_{bur} = 48.0). We prepared its Cu complex and examine its catalysis in the asymmetric borylation of methyl cinnamate with bis(pinacolato)diboron.



References

[1] For a review, P. J. Guiry, *et. al., Org. Biomol. Chem.*, **2020**, *18*, 9329.
[2] S.-i. Fukuzawa, *et. al., Chem. Commun.*, **2018**, *54*, 2110.
[3] S.-i. Fukuzawa, *et. al., Dalton Trans.*, **2020**, *49*, 17578.

PB56

Catalytic nitrene transfer reaction to alkenyl boronates:
Introducing the borylaziridines

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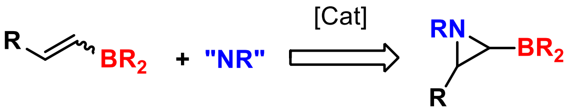
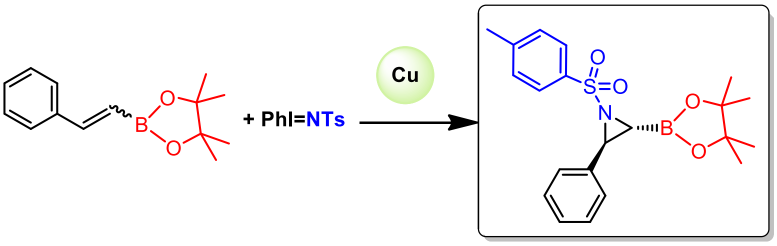
Organoboron derivatives constitute a family of compounds with continuing interest due to the versatility of the borane group to be replaced by other groups in the construction of complex molecules.[1] Our research group has developed different active catalytic systems based on copper and silver for nitrene transfer reactions to substrates of different nature, upon generating C-N bonds in several types of compounds.[2] In the context of the largely developed aziridination reaction, we have learnt that the catalytic nitrene transfer to alkenyl boronates is yet unknown.



We have faced that target aiming at converting alkenyl boronates into borylaziridines by metal-catalyzed nitrene transfer reactions. The catalytic activity of different metal sources towards the aziridination has been studied, the $BpmCu(NCMe)_2PF_6$ complex providing the best conversions, using PhI=NTs as the nitrene source. The scope and conditions will be discussed in this contribution.



References

[1] Contemporary Boron Chemistry; Davidson, M., Hughes, A. K., Marder, T. B., Wade, K., Eds.; RSC. Cambridge, 2000.
[2] a) Rodríguez, M. R.; Díaz-Requejo, M. M.; Pérez, P. J. *Synlett* **2021**, 32, 763-774 b) Caballero,A.; Díaz-Requejo, M. M.; Pérez, P. J. *Metal-Catalyzed Oxidation of Alkanes to Give Esters or Amines*, Science of Synthesis: Catalytic Oxidation in Organic Synthesis. Ed. Muñiz, K., **2018**, Chap. 3.

PB57

A general database of 50,000 ligands extracted from the Cambridge Structural Database

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Molecular databases are an invaluable tool for theoretical and experimental chemists alike. Besides offering easy access to physical properties, they are the foundation for many high-throughput screening and machine learning studies with applications for catalyst discovery and drug design, among many others.[1]

In this work we present a publicly available database of *ca.* 50,000 different ligands, extracted from 160,000 monometallic transition metal complexes from the Cambridge Structural Database.[2] Each ligand has associated various features such as 3D structure, denticity, coordinating atoms or previously bound metals (see Figure 1). Furthermore, we have computed the formal charge of each ligand using a self-consistent method inspired by previous work,[3] showing excellent accuracy on a benchmark dataset. We expect this ligand database to be a useful tool for a broad community of researchers in organometallic chemistry.

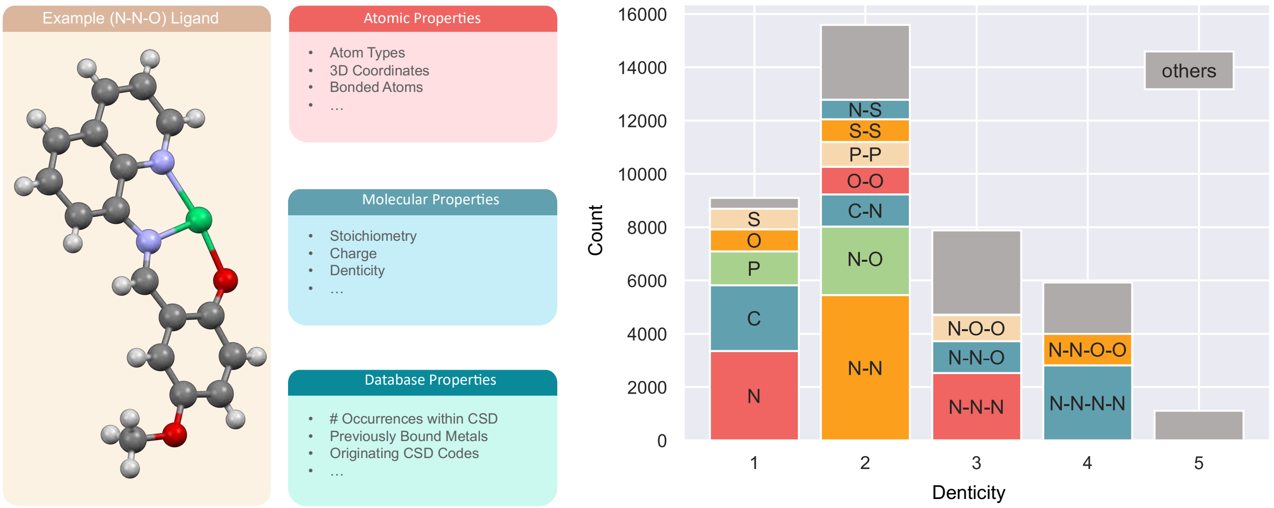

Figure 1. a) An example of a ligand with the metal center (green) displayed for visibility. Each ligand is associated with various properties shown to the right. b) A histogram of the ligand denticities in the database up to a denticity of 5. The colored sections indicate the donating elements.

References

[1] Sodhi, R. K., Paul, S. *Canc Therapy & Oncol Int J.* **(2019)**, 14(2): 555883.

[2] The Cambridge Structural Database, C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Cryst.* **(2016)**, B72, 171-179.

[3] Duan, C., Ladera, A. J., Liu, J. C.-L., Taylor, M. G., Ariyarathna, I. R., Kulik, H. J. *J. Chem. Theory Comput.* **(2022)**, *18*(8), 4836–4845.

[4] Sommer, T., Clarke, C., Kleuker, F., García-Melchor, M. *Manuscript in preparation.*

PB58

Synthesis and biomedical applications of Ruthenium (II)-NHC chelate complexes

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Several metallodrugs have been explored in cancer treatment since the discovery of cis-platinum in 1963. Ruthenium (II) complexes have been widely studied as anticancer drugs, but their activity depends on their facility to penetrate cells [1]. The structure of the stabilizing ligands of the ruthenium complex is crucial to ensure a good hydrophilic/lipophilic balance and therefore secure the internalization of the ruthenium complex.

In this study we have synthetized different families of dendrimers as ligands containing NHC-L chelates in order to stabilize metal ions. We propose a lipophilic carbosilane core leading ruthenium complexes into cells and therefore, enhanced their biological activity. Furthermore, dendrimers allow to introduce several ruthenium complexes in the same molecule enhancing the biological activity due to multivalence [2]. The antioxidant properties and cytotoxicity in prostate cancer cells (PC3) of these metallodrugs have been studied.

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References

[1]. Oscar A. Lenis Rojas; Sandra Cordeiro; Pedro V. Baptista; Alexandra R. Fernandes. Half-sandwich Ru(II) N-heterocyclic carbene complexes in anticancer drug design. Journal of Inorganic Biochemistry, 245, 2023,112255.

[2]. Fuentes-Paniagua, E.; Sánchez-Nieves, J.; Hernández-Ros, J. M.; Fernández-Ezequiel, A.; Soliveri, J.; Copa-Patiño, J.L.; Gómez, R.; de la Mata, F. J., RSC Adv. 2016, 6, 7022-7029.

PB59

Copper-catalyzed strain-release driven homoallylation reactions

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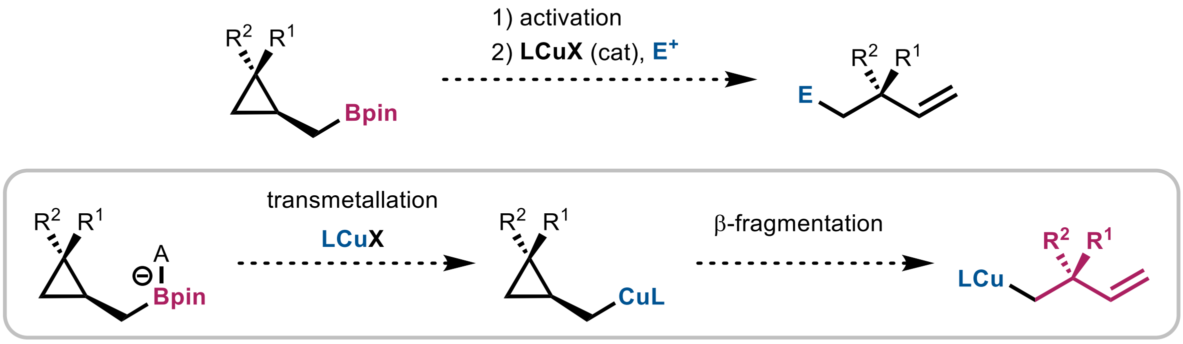
The selective carbon-carbon bond cleavage of three-membered rings has become a powerful approach to reveal sp^3-stereocenters in acyclic systems.[1] A few years ago, our group reported the copper-catalyzed enantioselective desymmetrization of cyclopropenes to prepare enantiomerically enriched cyclopropyl boronates.[2] These synthetic intermediates undergo efficiently a Matteson homologation to provide cyclopropylmethyl boronic esters with a quaternary stereocenter. In line with our interest in exploring novel transformations of alkyl boronic esters promoted by boron-copper transmetallation, we envision that cyclopropylmethyl boronic esters could be efficient precursors of homoallylic copper species via transmetallation followed by selective β-fragmentation to form the energetically favored primary organometallic derivative. Trapping the homoallylic copper species with different electrophiles in a catalytic fashion would provide a powerful tool to prepare functionalized homoallylic derivatives. In this communication we will present our efforts towards this goal.



Keywords: boronic esters, copper catalysis, ring opening

References

[1] Cohen, Y.; Cohen, A.; Marek, I. *Chem. Rev.* **2021**, 121, 1, 140.
[2] A. Parra, L. Amenós, M. Guisán-Ceinos, A. López, J. L. Garcia-Ruano, M. Tortosa *J. Am. Chem. Soc.* **2014**, 136, 15833-15836.

PB60

Small Molecule Activation Promoted by a Low-Valent Calcium Synthon

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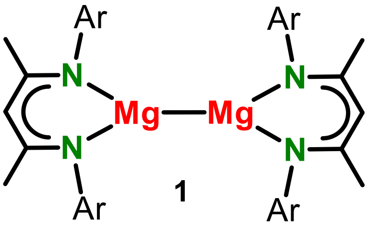
In 2007, Jones and coworkers isolated the first low-valent Mg(I) complexes with a direct Mg–Mg bond (**1**) [1]. These proved to be versatile non-toxic reducing agents [2]. Attempts to obtain similar low-valent complexes for Ca (**2**) led to N_2 reduction [3]. The resulting N_2-complex complex acts as a highly potent reducing agent, releasing N_2 and 2*e*. We compare the scope and reactivity of this Ca(I) synthon with that of low-valent Mg(I) complexes.



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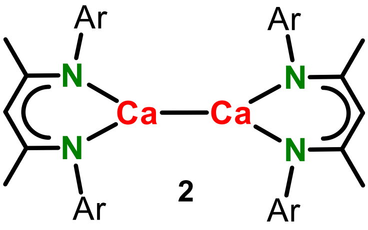

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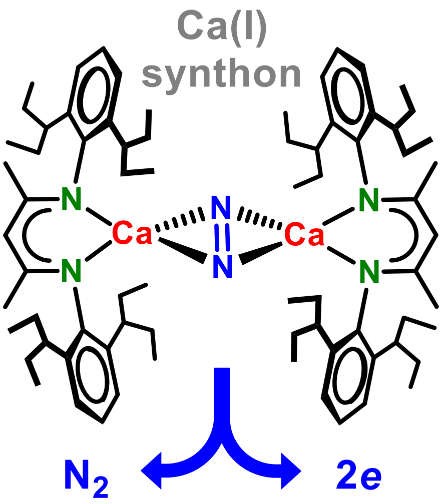

References

[1] S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754–1757.

[2] C. Jones, *Nat. Rev. Chem.* **2017**, *1*, 0059.

[3] B. Rösch, T. X. Gentner, J. Langer, C. Färber, J. Eyselein, L. Zhao, C. Ding, G. Frenking, S. Harder, *Science* **2021**, *371*, 1125–1128.

PB61

Tailoring Sodium Organometallic Reagents for Arene Functionalisation

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Organosodium compounds have attracted the attention of the scientific community in recent years as an alternative to widely used organolithium reagents.[1] Lithium alkyls and amides reside at the front of organometallic synthesis as key players in countless transformations, owing to their availability, substantial stability and solubility in hydrocarbon solvents.[2] However, these desirable traits are often pitfalls of heavier alkali-metal organometallics, meaning that their applications have remained underexplored. While recent reports have hinted at the untapped potential of these reagents,[3] the constitution of the organometallic intermediates that operate in these reactions has been overlooked, missing an opportunity to tackle their high reactivity and improve their poor solubility.

Filling this gap in the knowledge, the preparation of organosodium compounds soluble in hydrocarbon solvents and the isolation and characterization of reactive sodium organometallic intermediates in the solid state and in solution by X-Ray crystallography and ^{1}H DOSY (Diffusion Ordered SpectroscopY) have allowed the development of new protocols for the functionalisation of organic molecules. Our efforts have been focused on selective deprotonative metalation reactions of synthetically attractive arenes, providing access to the selective functionalization of these scaffolds, including the borylation[5] and the perdeuteration of aromatic scaffolds,[6] and the aroylation of toluene derivatives via selective benzylic metalation.[7] The reactivity and/or selectivity obtained with organosodium compounds was different to the one with its lithium analogues, opening new vistas in the use of polar organometallic reagents for the functionalization of organic molecules.

References

[1] P. B. De, S. Asako, L. Ilies, *Synthesis* **2021**, *53*, 3180–3192.
[2] Lithium Compounds in Organic Synthesis – From Fundamentals to Applications, (Eds.:R. Luisi and V. Capriati), Wiley-VCH, Weinheim **2014**
[3] S. Asako, H. Nakajima, K. Takai, *Nat Catal* **2019**, *2*, 297–303.
[4] H. J. Reich, *Chem. Rev.* **2013**, *113*, 7130–7178.
[5] L. J. Bole, A. Tortajada, E. Hevia *Angew. Chem. Int. Ed.* **2022**, *61*, e202204262.
[6] A. Tortajada, E. Hevia *J. Am. Chem. Soc.* **2022**, *144*, 20237–20242.
[7] D.E. Anderson, A. Tortajada, E. Hevia *Angew. Chem. Int. Ed.* **2023**, *62*, e202218498.

PB62

Alkynyl cyclic carbonates as 1,3-enyne surrogates in photoredox / cobalt-catalyzed reductive coupling

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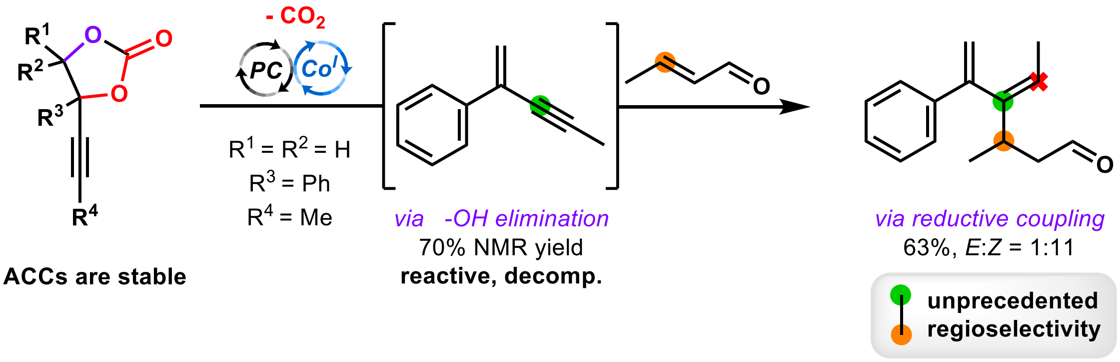

1,3-Enynes are important and versatile building blocks in organic synthesis as they are prone to be transformed into allene and 1,3-butadiene products. However, compared to simple alkynes they are more reactive and thus difficult to handle, whereas regioselective additions are challenging. Herein we present a dual Co/photoredox-catalyzed approach that utilizes modular and stable Alkynyl Cyclic Carbonates (ACCs) to generate in situ 1,3-enynes, which can be intercepted by crotonaldehyde in a novel reductive cross-coupling reaction. The double bond of the conjugated enyne intermediate is formed by a β-OH elimination step and remains inert in the presence of aldehyde reactants.[1,2] However, under reductive reaction conditions the triple bond is favoured to undergo a Co-promoted formal hydroalkylation. Furthermore, this unprecedented stereo- and regioselective coupling reaction of 1,3-enynes is in contrast to the typical reactivity of internal alkynes[3-5] that selectively provide the β-regioisomer.

References

[1] Xue, S.; Cristòfol, À.; Limburg, B.; Zeng, Q.; Kleij, A. W. *ACS Catal.* **2022**, *12*, 3651–3659. **[2]** Cristòfol, À.; Limburg, B.; Kleij, A. W. *Angew. Chem. Int. Ed.* **2021**, *60*, 15266–15270. **[3]** Cui, K.; Li, Y.-L.; Li, G.; Xia, J.-B. *J. Am. Chem. Soc.* **2022**, *144*, 23001. **[4]** Holmes, M.; Schwartz, L. A.; Krische, M. J. *Chem. Rev.* **2018**, *118*, 6026. **[5]** Chang, H.-T.; Jayanth, T. T.; Wang, C.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **2007**, *129*, 12032.

PB63

Iridium mediated chemical and electrochemical NADH regeneration

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The NADH cofactor is a high-energy redox mediator successfully employed in many biological processes catalysed by oxidoreductase enzymes. Owing to its high cost, the regeneration of NADH starting from economical starting materials, through chemical or electrochemical catalytic processes, is highly desirable. Previous studies showed that IrCp* complexes efficiently and selectively reduce NAD$^+$ to its biologically active form (1,4-NADH) using formate or phosphite as hydride donors .[1,2] It was also showed that Rh-organometallic complexes can act as molecular redox mediators for the indirect regeneration of NADH with relevant advantages in terms of selectivity with respect to the direct reduction of NAD$^+$ on the electrode surface. [3]

In this study we report the synthesis and complete characterization (in solution by multinuclear and multidimensional NMR spectroscopy and in the solid state through single-crystal X-Ray diffraction) of new Cp*Ir complexes, bearing N,N-type ancillary ligands, and their application to the selective NADH regeneration. The novel catalysts show extremely high activity for the chemical regeneration of NADH using formate and phosphite as hydride donors (TOF approaching 5000 h^{-1}). On the other hand, they successfully act as redox mediator in the electrochemical reduction of NAD$^+$ (Figure 1).

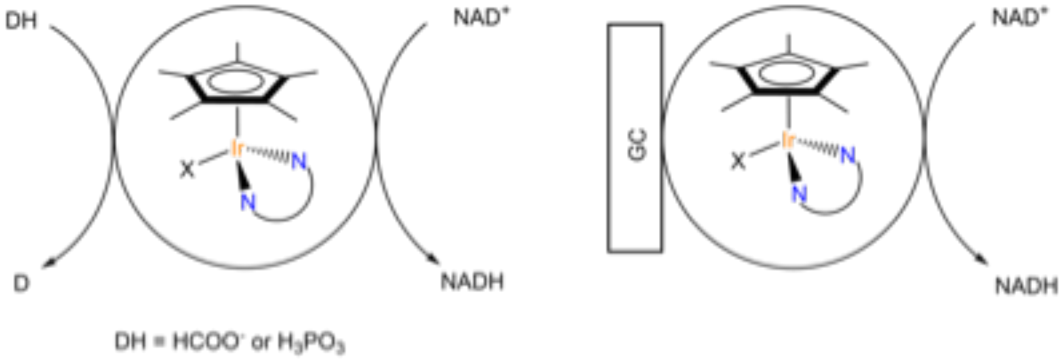

Figure 1. Chemical and electrochemical Ir mediated NADH regeneration.

References

[1] L. Tensi *et al.*, *ACS Catal.* **2020**, *10*, 7945–7949.
[2] A. Bucci et al., ACS Catal. **2017**, 7, 7788–7796
[3] F. Hollmann et al., Angew. Chem. Int. Ed. **2001**, 40, 169-171

PB64

Coinage Metal Bis(amidinate) Complexes as Building Blocks for Self-assembled One-Dimensional Coordination Polymers

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A newly designed pyridyl functionalized amidinate ligand $[\{PyC{\equiv}CC(NDipp)_2\}Li(thf)_2]_n$ was used to synthesize a series of coinage metal bis-amidinate complexes $[\{PyC{\equiv}CC(NDipp)_2\}_2M_2]$(M = Cu, Ag, Au) with fully supported metallophilic interactions.[1] These metalloligands were then used as building blocks for the synthesis of one-dimensional heterobimetallic coordination polymers using different connectors via self-assembly. More precisely, these compounds were treated with $[Zn(hfac)_2]$ and $[M'(acac)_2]$ to yield one-dimensional heterobimetallic chains in the solid state. Therby two different coordination geometrys were obtained based on the used linker. The three coordination polymers $[\{PyC{\equiv}CC(NDipp)_2\}_2M_2][Zn(hfac)_2]$ (M = Cu, Ag, Au), exhibit a zigzag shape in the solid state, by cis configuration of the successive pyridyl units at the zinc atom. By usage of $[M'(acac)_2]$ (M' = Co, Ni) as linker linear linear scaffold in the solid state was observed. The two pyridyl moieties occupy trans-position within the coordination polyhedral formed by the Co and Ni atoms. The calculated packing coefficients with solvent molecules of the zig zag polymer $[\{PyC{\equiv}CC(NDipp)_2\}_2Cu_2][Zn(hfac)_2]$ is 62.6 %, and a hypothetical packing density, in which only the polymeric backbones and not the intercalated solvent molecules are considered in the calculation, is 42.6 %.[2] The calculated packing coefficients with solvent molecules of both linear polymers $[\{PyC{\equiv}CC(NDipp)_2\}_2Cu_2][M'(acac)_2]$ (M' = Co, Ni) are 66.3% and 60%,[2] respectively, and are thus slightly increased compared to the zig zag compound. A hypothetical packing density, in which only the polymeric backbones and not the intercalated solvent molecules are considered in the calculation, is 54.6% and 54.9%.[2] This suggests far less solvent accessible voids in linear packing compared to zig zag.

References

[1] C. Uhlmann, T. J. Feuerstein, M. T. Gamer and P. W. Roesky, Chem. Eur. J. *n/a*, e202300289.

[2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr. **2009**, *42*, 339-341.

PB65

Ullmann coupling reactions on gold nanoparticles

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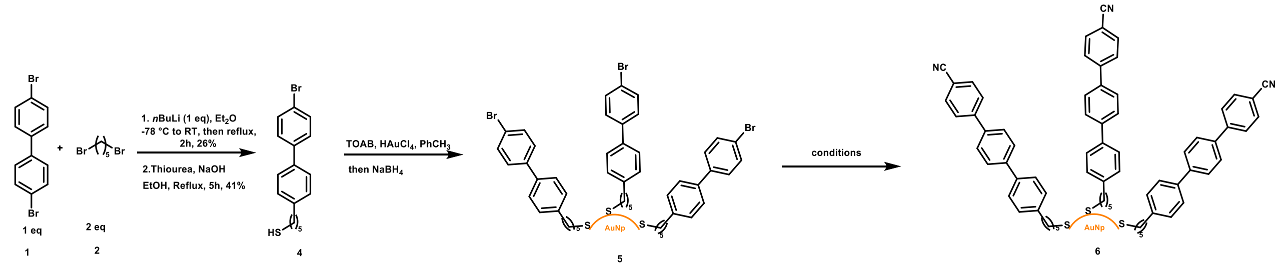
The Ullmann reaction is one of the oldest coupling reactions. Besides its widespread use, it has been posed with many disadvantages, such as poor functional group tolerance, harsh reaction conditions, as well as poor selectivity towards heterocoupled products.[1] Most of these aforementioned demerits have been surmounted with appropriate ligands and catalysts, with the exception of clear selectivity between the homocoupled product and the heterocoupled product.[1] In some cases, the former reaction tends to be faster than the latter, resulting to an appreciable yield of the homocoupled product in Ullmann reactions. Previous work in our collaborative research group has shown that, adsorbing coupling partners to a 2-D Au (111) surface will enable these molecules to be oriented in a manner that they can be dragged and dropped, using a CO-functionalized tip of an Atomic Force Microscope (AFM).[2] With this technique, organic molecules which hitherto, remained elusive by on-surface synthesis became selectively accessible. Nevertheless, this method is limited to single molecules and not suitable for bulk material synthesis. In a quest to access functionalized hybrid materials in a selective manner, we devised a novel Ullmann reaction on thiol-functionalized gold nanoparticles.

We chose 4,4-dibromobiphenyl **1**, as a model compound due to its similaritude with the terphenyl units used in our previous on-surface studies.[2] A functional group interconversion of **1** gave rise to **4**. Reaction of **4** with $HAuCl_4$ using the Brust-Schiffrin approach furnished the surface assembled monolayers on the nanoparticles, thereby, setting up the system for an Ullmann reaction with 4-bromobenzonitrile. It is noteworthy to mention that, selectivity towards heterocoupled product was possible due to the orientation of the ligands on the nanoparticles, enabling a proximity for the coupling partner with no proximity for a homocoupled reaction.



References

[1] J. Jiang, L. Du, Y. Ding, *MROC* **2020**, *17*, 26.
[2] Q. Zhong, A. Ihle, S. Ahles, H. A. Wegner, A. Schirmeisen, D. Ebeling, *Nature chemistry* **2021**, *13*, 1133.

PB66

Tuning the photoreactivity of 5(4*H*)-thiazolones with Lewis acids (BF_3): synthesis of cyclobutanes [2+2] *vs* dihydropyranothiazoles [4+2]

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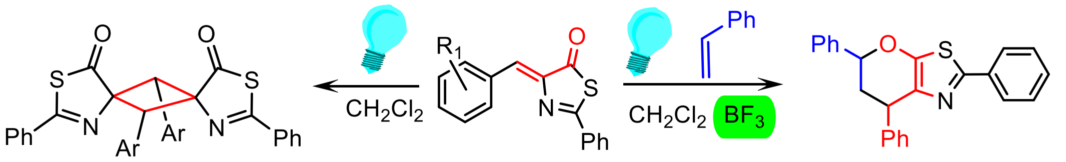
The use of light as a reagent in organic synthesis is experiencing an exponential development due to its particular characteristics. The involvement of excited states of high energy and different electronic distribution allows access to alternative synthetic routes and new reaction products. This reactivity can be modulated using the same strategies than in the ground state. In this respect, it is known that the introduction of a Lewis acid changes the orientation and selectivity of photochemical processes.[1]

In this contribution it is described how the blue light irradiation of thiazolones in the absence of Lewis acids (Figure, left part) occurs via [2+2] photocycloaddition to give cyclobutanes derived from truxillic acid.[2] This reactivity radically changes in the presence of a Lewis acid (BF_3) to lead to the formation of 6,7-dihydro-5*H*-pyrano[3,2-*d*]thiazoles (Figure, right) by [4+2] oxa-Diels Alder photocyclization of inverse electron demand between thiazolones and styrene. An explanation based on the mechanism, determined by DFT, is also presented. The novelty of this reaction lies in the fact that it is promoted by light, not thermally, and that it had never been described, not even thermally, for 5(4*H*)-thiazolones.



No Lewis acid
[2+2]-photocycloaddition

Lewis acid BF_3
[4+2]-oxa Diels Alder of inverse electron demand

References

1 Lewis, F. D.; Howard, D. K.; Oxman, J. D. Lewis Acid Catalysis of Coumarin Photodimerization. *J. Am. Chem. Soc.* **1983**, *105*, 3344–3345.

2 Sierra, S.; Dalmau, D.; Higuera, S.; Cortés, D.; Crespo, O.; Jimenez, A. I.; Pop, A.; Silvestru, C.; Urriolabeitia, E.P. Reactivity of (Z)-4-Aryliden-5(4*H*)-thiazolones: [2+2]-Photocycloaddition, Ring-Opening Reactions, and Influence of the Lewis Acid BF_3. *J. Org. Chem.* **2021**, *86*, 12119-12140.

PB67

Synthesis of ferrocene derivatives with condensed heterocycles by C-H activation

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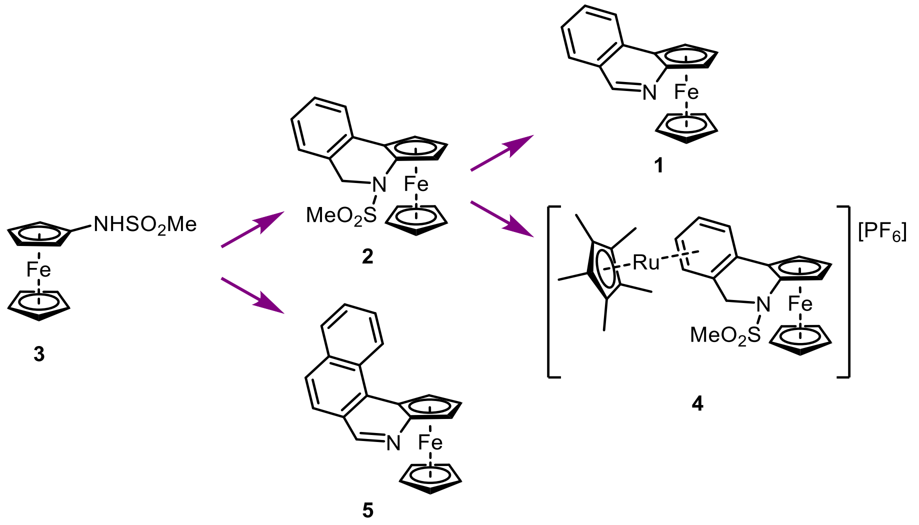
This study contributes to the less explored group of compounds, namely annelated ferrocenes with condensed nitrogen heterocycles, wherein the ferrocene moiety provides planar chirality and redox properties. The nitrogen can serve as a donor site and, hence, can open a way to applications of these compounds as ligands in transition metal catalysis.[1]

The starting compound, [(methylsulfonyl)amino]ferrocene (**3**) was prepared by a three step procedure from commercially available bromferrocene. Cascade nucleophilic substitution/C–H activation/aromatization did not provide the desired annelated ferroceno[c]isochinoline **1**. However, optimization of the individual reaction steps, enabled the synthesis this compound **1** in 67% yield.

Intermediate **2** was further used to prepare cationic ruthenium complex **4**, wherein it coordinates *via* its benzene ring. Analogous complex of compound **1** could not be prepared. Derivative **5** with additional ortho-condensed benzene ring was also prepared using an optimized procedure.



References

1 Bernardo, O.; González-Pelayo, S.; López, L. A. *Eur. J. Inorg. Chem.* e202100911 (2022).

PB68

Alkali Metal Gallyl Complexes: Synthesis, Structure, and Computational Studies

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New principles and reactivities have marked the resurgence of main-group chemistry and catalysis in the s and p-block elements.[1] Tailor-made chelating ligands have facilitated the stabilisation of low-valent group 13 M(I) species, such as neutral Al(I) and Ga(I) compounds.[2] The isolation of an aluminyl Al(I) anion has led to a nucleophilic aluminium centre with unprecedented reactivity in activating strong chemical bonds.[3] This discovery has opened new avenues in bimetallic chemistry, where alkali metals are crucial in stabilising low-valent anions.

In this communication, we will discuss our recent advancements in stabilising, isolating, and characterising a series of alkali metal gallyl complexes using NMR and X-ray crystallography. We have also investigated the nature of interactions in these heterobimetallic systems through DFT calculations, which correlate well with the experimental data obtained.[4]

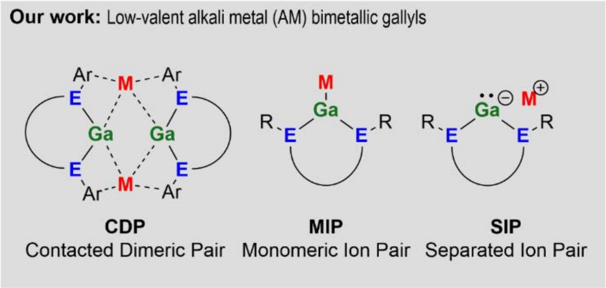

Figure 1. Low-valent alkali metal bimetallic gallyl systems.

References

[1] R. L. Melen, *Science* **2019**, 363, 479. [2] a) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, 111, 354-396. b) P. W. Roesky, *Dalton Trans.* **2009**, 1887-1893. [3] a) T. X. Gentner, M. J. Evans, A. R. Kennedy, S. E. Neale, C. L. McMullin, M. P. Coles, R. E. Mulvey, *Chem. Commun,* **2022**, 58, 1390-1393. b) M. J. Evans, M. D. Anker, C. L. McMullin, S. E. Neale, M. P. Coles, *Angew. Chem. Int. Ed.* **2021**, 133, 22463-22466. c) C. Weetman, S. Inoue, *ChemCatChem*, **2018**, 10, 4213-4228. d) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldrige, *Angew. Chem. Int. Ed.* **2021**, 60,1702-1713. [4] *Manuscript in preparation*.

PB69

Cationic Cyclopentadienyl-Silsesquioxane Titanium (IV) Complexes as Lewis Acid Activators for Polymerization of Biobased Monomers

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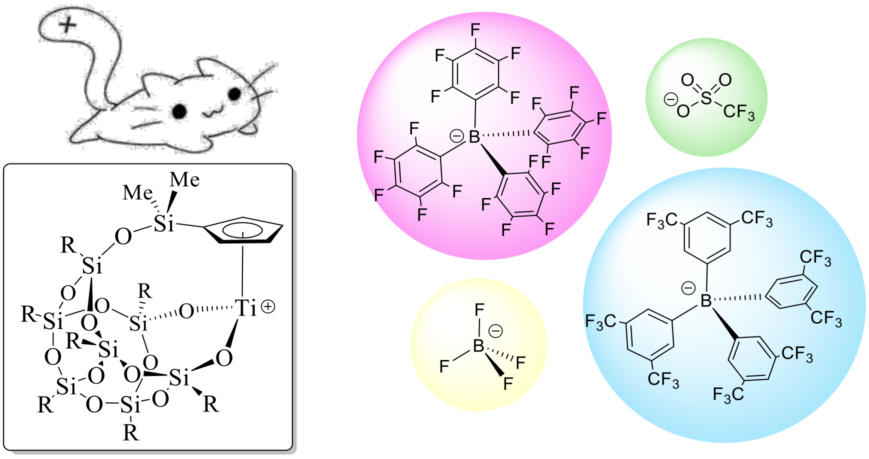
Recently we reported a family of titanium complexes bearing a cyclopentadienyl-silsesquioxane ligand. These complexes have shown a remarkable catalytic activity in oxidation reactions using as oxidant aqueous H_2O_2 (1-4), because of the hydrophobic pocket that the cyclopentadienyl-silsesquioxane ligand generates around the titanium atom. Currently, such complexes are being studied as catalysts for polymerization of different biobased substrates.

In this work, we report the synthesis and study of the Lewis acidity of a series of cationic complexes derived from $[Ti(\eta^5\text{-}C_5H_4SiMe_2OPh_7Si_7O_{11}\text{-}\kappa^2O_2)Cl]$ (**1**). As the selection of a suitable non-coordination anion is a critical factor to controlling the Lewis acidity of the titanium centre and, therefore, the polymerization activity of these complexes, the triflate anion and different borates, with different steric and electronic properties, have been chosen as counterion to reach the proposed target. Thus, complexes of general formula $[Ti(\eta^5\text{-}C_5H_4SiMe_2OPh_7Si_7O_{11}\text{-}\kappa^2O_2)]^+X^-$ {X = SO_3CF_3 (**2**); $B(C_6F_5)_4$ (**3**); BF_4 (**4**); $B(C_6H_3\text{-}3,5\text{-}CF_3)_4$ (**5**)} have been prepared through an abstraction reaction of the chlorine atom. Additionally, we describe different decomposition pathways of these complexes as well as their effectiveness in polymerization of different biobased monomers.



References

1. L. Postigo, M. Ventura, T. Cuenca, G. Jiménez, B. Royo. Catal. Sci. Technol., 2015, 5, 320-324
2. M. Mateos; J. Vinueza; M.E.G. Mosquera; V. Tabernero; T. Cuenca; G. Jiménez. Inorg. Chim. Acta, 2020, 501, 119275
3. M. Ventura, M.E.G. Mosquera; T. Cuenca, B. Royo, G. Jiménez. Inorg. Chem. 2012, 51, 6345.
4. M. Ventura, V. Tabernero, T. Cuenca, B. Royo, G. Jiménez, Eur. J. Inorg. Chem. 2016, 2843.

PB70

Synthesis and characterization of BPI alkali metal complexes in three redox states

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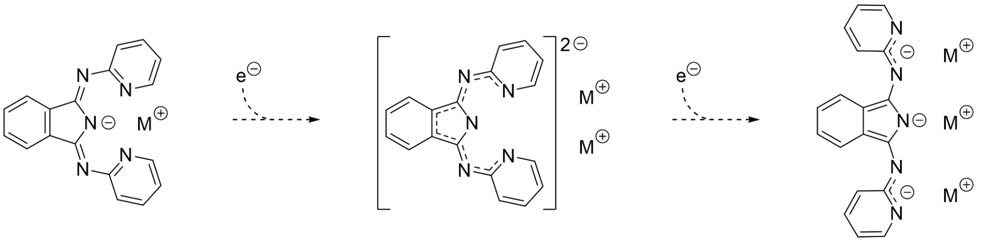
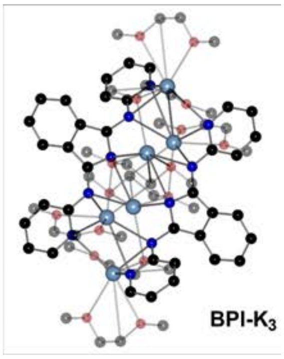
Non-innocent ligands (NILs) like bis(pyridylimino) isoindoline (BPI) play crucial roles in coordination chemistry,[1] biochemistry,[2] catalysis[3] and material sciences.[4][5] Investigating the isolated redox states of NILs is inevitable for understanding their redox-activity and fine-tune properties of corresponding metal complexes. Fundamental studies on the coordination behavior and redox states of the sole BPI ligand are not presented until today which is suggested to hamper further applications of the title compounds. This work reports on the isolation of alkali metal complexes of BPI in three different redox states and their investigation by means of NMR or EPR spectroscopy as well as cyclovoltammetry and SC-XRD. The latter revealed the connection between bond orders in the ligand scaffold and its oxidation state. Furthermore, the so far unreported trianionic state of BPI was reported. This divulges an unprecedented bis(amidinato)isoindolide coordination mode which was reversibly accessible after reduction through the lowered C=N bond order as supported by NMR spectroscopy and DFT calculations.



BPI^{1-} **BPI^{2-}** **BPI^{3-}**

M = Li, Na or K

CV ↔ redox potentials ✓
EPR ↔ BPI radical characterization ✓
XRD ↔ bond length alteration ✓



References

[1] J. I. van der Vlugt in *Topics in Organometallic Chemistry*, Springer Berlin Heidelberg, Berlin, Heidelberg, **2020**.
[2] T. Benkó, D. Lukács, M. Li, J. S. Pap, *Environ Chem Lett* **2022**, *20*, 3657.
[3] M. Kumar, S. Ahmad, A. Ali, *Russ. J. Inorg. Chem.* **2022**, *67*, 1573.
[4] D. M. D'Alessandro *et al.*, *Coord. Chem. Rev.* **2021**, *439*, 213891.
[5] R. Csonka, G. Speier, J. Kaizer, *RSC Adv.* **2015**, *5*, 18401.

PB71

Cationic and Electrophilic functionalization of a Hexaphosphabenzene ligand complex

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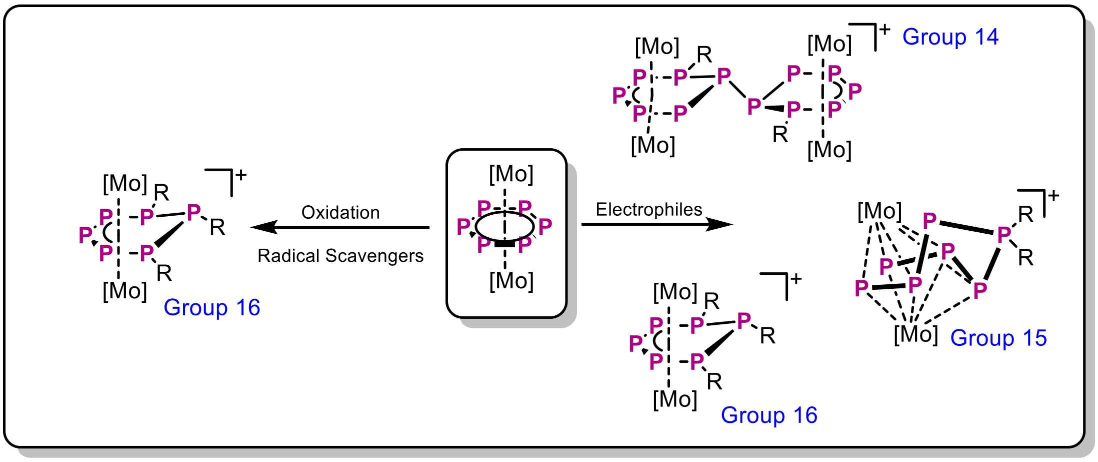
Carbon-based aromatic compounds with the general formula C_nH_n are not only a universal substance class in organic chemistry but are also prominent ligands in organometallic chemistry. In contrast to free benzene, benzene ligands, coordinated to transition metal fragments show a reduced tendency to electrophilic aromatic substitutions, which is caused by the significantly reduced π-electron density.[1] Compared to the organic benzene, the isolobal hexaphospha-benzene ligand shows similar structural features. However, very little is known about its reactivity and its tendency towards electrophilic or cationic functionalization.[2] This contribution explores the reactivity of such a hexaphospha-benzene containing transition-metal complex as the inorganic analog of the ubiquitous benzene ligand towards oxidation as well as electrophilic functionalization with main group electrophiles and radical scavengers. While functionalization of smaller polyphosphorus complexes typically lead to mono-functionalized or ring-inserted products,[3] ongoing research on the reactivity of this *cyclo*-P_6 moiety also reveals the possibility of multiple substitutions to take place. The selectivity of these reactions can be decisively modified by the choice of main group electrophile. Our approach enables the targeted and selective synthesis of novel cationic polyphosphorus complexes, which bridge the gap between the reactivity of organic and inorganic aromatic systems.



References

[1] a) H. P. Fritz, E. O. Fischer, *Z. Naturforsch. B* **1957**, *12*, 67–68; b) V. Graves, J. J. Lagowski, *Inorg. Chem.* **1976**, *15*, 577–586.

[2] A. Garbagnati, M. Seidl, G. Balazs, M. Scheer, *Chem. Eur. J.* **2022**, e202200669.

[3] a) C. Riesinger, G. Balázs, M. Seidl, M. Scheer, *Chem. Sci.* **2021**, *12*, 13037–13044; b) C. Riesinger, L. Dütsch, G. Balázs, M. Bodensteiner, M. Scheer, *Chem. Eur. J.* **2020**, *26*, 17165–17170; c) C. Riesinger, G. Balázs, M. Bodensteiner, M. Scheer, *Angew. Chem. Int. Ed.* **2020**, *59*, 23879–23884.

PB72

Precatalyst Association of Palladium Hydrides for Enyne Cycloisomerization

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In the fine-chemical industry, catalyst systems are used that consist of multiple components that must be combined in a specific way to generate the active catalyst species. Such association of the pre-catalyst species is therefore necessary to make the active catalyst, as is demonstrated in the seemingly simple example of the Pd-Zipper reaction.[1] However, if the association of the pre-catalyst species is disfavored, reaction rates will be low, and selectivity problems may arise.

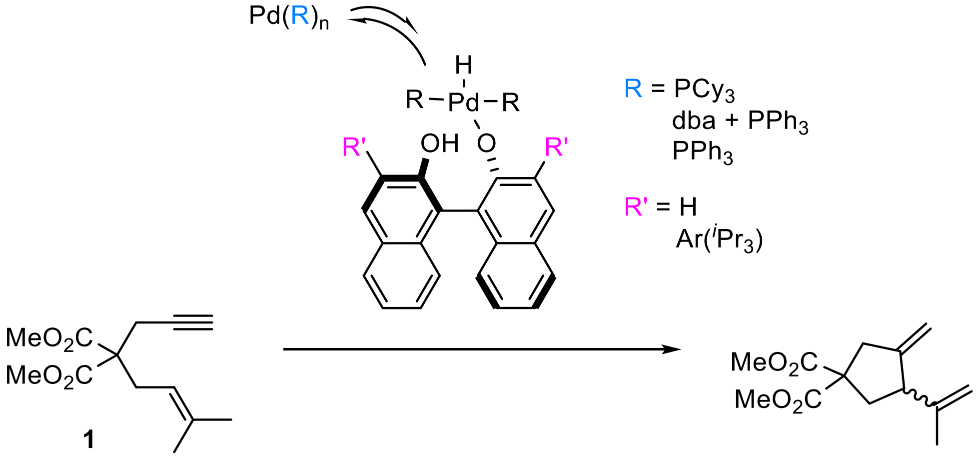

Figure 1: Scheme of Precatalyst euqilibrium for enyne cycloisomerization.

In this study, we investigated the use of $Pd(PCy_3)_2$ in combination with chiral alcohols such as BINOL and its derivative phosphoric acid as pre-catalyst components. We measured the equilibrium constants of the oxidative addition to produce the active Pd-H species for various BINOL derivatives using solution NMR measurements. These catalyst systems are capable of enantioselective cyclization of substrate **1** which are measured as a function of sterics, acidity, solvent, concentration, and temperatures. The catalytic activity of these systems increases with increasing acid/alcohol concentration.

References

[1] a) B. M. Trost, *J. Am. Chem. Soc.* **1991**, *113*, 701; b) I. Watson, D. Toste, *Chem. Sci.* **2012**, *3*, 2899.
[2] S. Maier, D. P. Estes, Organometallics **2021**, 40, 11, 1751–1757.

PB73

Investigation of the Donor Properties of κ^{6}N Donor Ligands Based on Their Lanthanide Complexes

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The lanthanides complexes (Ln = Y, La, Sm, Lu, Ce) of several κ^{6}N podant ligands have been synthetized and characterized. Structural properties of the complexes have been investigated by X-ray diffraction in the solid state and by advanced NMR measurements techniques in solution. To estimate the donor capabilities of the presented ligands experimental comparison study have been done by cyclic voltammetry as well absorption experiments using the cerium complexes and by analyse of ^{89}Y NMR shifts of the different yttrium complexes. In order to obtain a multidimensional picture all experiments where corroborate by state-of-the-art quantum chemical techniques. Finally, competition studies have been carried out to investigated the correlation with donor properties and selectivity. Studies have been analysed by ^{1}H- and ^{31}P NMR spectroscopy.

PB74

Stereoselective Three-Component Allylic Alkylation enabled by Dual Photoredox/Ni Catalysis

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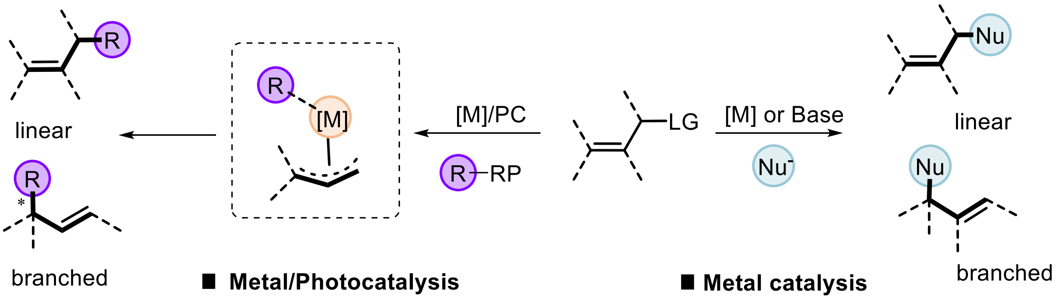
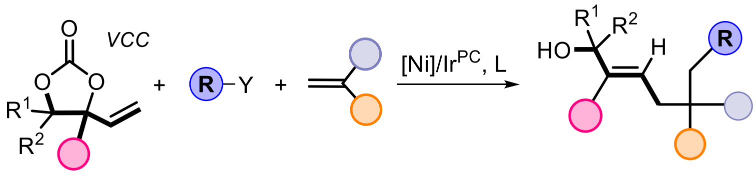
Existing strategies for allylic alkylation



Our work: dual photoredox/Ni catalyzed stereoselective 3CR



Excellent regio- and stereocontrol
41 examples, E/Z typically >95:5
Elaborate quaternary carbon centers
Use of 1°, 2° and 3° radicals
Extendable to other allylic substrates

A rare regio- and stereoselective three-component allylic alkylation enabled by dual Ni/photoredox catalysis has been developed. Our approach allows for rapid access to multi-functional allylic alcohols with congested/functional stereocenters from a wide range of allylic precursors, vinyl compounds and primary, secondary and tertiary alkyl radicals. This new three-component, photo-mediated catalytic process expands the use of vinyl cyclic carbonates affording a variety of elaborative stereo-defined building blocks with excellent synthetic potential.[1][2]

References

[1] (a) Trost, B. M. *Acc. Chem. Res.* **1996**, *29*, 355–364. (b) Rao, W.; Chan, P. W. H. *Org. Biomol. Chem.* **2008**, *6*, 2426–2433. (b) Bandini, M.; Eichholzer, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 9533 –9537. (c) Huang, H.-M.; Bellotti, P.; Glorius, F. *Chem. Soc. Rev.* **2020**, *49*, 6186-6197.

[2] (a) Matsui, J. K.; Gutiérrez-Bonet, I.; Rotella, M.; Alam, R.; Gutierrez, O.; Molander, G. A. *Angew. Chem. Int. Ed.* **2018**, *57*, 15847–15851. (b) Zhang, H.-H.; Tang, M.; Zhao, J.-J.; Song, C.; Yu, S. *J. Am. Chem. Soc.* **2021**, *143*, 12836–12846.

PB75

Strain-driven ring expansion of silicon heterocycles

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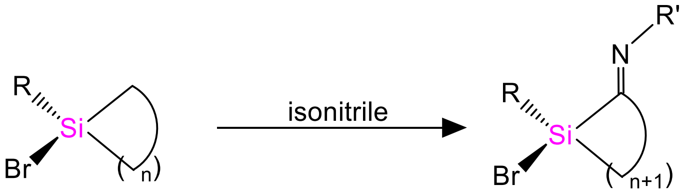
The investigation of organosilicon cyclic compounds has become an intensively researched topic in the last decades.[1-3] These heterocycles are not only used as pharmaceuticals or industrial chemicals,[4] but they can also be suitable starting materials for highly reactive molecules such as silylenes[1,2,4] or silenes.[5,6] We studied the reactivity of the base-free bromosilylene [(Cbz)SiBr] (Cbz = 1,8-bis(3,5-di-*tert*-butyl-phenyl)-3,6-di-*tert*-butyl-carbazolyl)[7] towards alkenes and alkynes and observed [2+1] addition reactions. In distinction to such reactions observed with base-stabilised silylenes, these small silicon heterocycles were then treated with 2,6-dimethylphenylisonitrile (Figure 1) to induce ring expansion reactions.



R' = 2,6-dimethylphenyl

Figure 1: Ring expansion of small silicon heterocycles with 2,6-dimethylphenylisonitrile.

References

[1] D. Seyferth, D. C. Annarelli, S. C. Vick, *J. Organomet. Chem.* **1984**, *272*, 123–139.
[2] M. Ishikawa, A. Naka, J. Ohshita, *Asian J. Org. Chem* **2015**, *4*, 1192–1209.
[3] R. R. Aysin, L. A. Leites, S. S. Bukalov, *Organometallics* **2020**, *39*, 2749–2762.
[4] J. Huang, F. Liu, X. Wu, J. Q. Chen, J. Wu, *Org. Chem. Front.* **2022**, *9*, 2840–2855.
[5] K. K. Milnes, M. C. Jennings, K. M. Baines, *J. Am. Chem. Soc.* **2006**, *128*, 2491–2501.
[6] L. E. Gusel'nikov, N. S. Nametkin, V. M. Vdovin, *Acc. Chem. Res.* **1975**, *8*, 18–25.
[7] A. Hinz, *Chem. Eur. J.* **2019**, *25*, 3267–3271.

PB76

Tin catalysed reductive coupling of CO_2 to amines in the presence of H_2

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Reductive coupling reactions of amines to CO_2 in the presence of H_2 can be efficiently catalysed by Sn/N 'Frustrated Lewis Pairs' (FLPs). Sn/N FLPs, like traditional main group CO_2 to amine reductive coupling catalysts, which are usually comprised of an inorganic salt, ionic liquid, or Lewis base along with a silane or borane, have the advantage of being highly selective for CO_2 reduction over other reducible functional groups. This leads to selective formation of value-added products such as N-formamides which contain alkene, ester, alcohol, and carboxylic acid functionalities. Since H_2 is the source of hydride this circumvents the need for an auxiliary hydride source, like a silane, which saves the production of siloxane/silanol waste which other main group systems suffer from. However, Sn/N do suffer drawbacks such as being unable to formylate primary amines and not being able to compete with transition metals complexes in terms of turnover frequency due to H_2 activation being much slower. This led to the development of Lewis basic solvent systems, which typically quench FLP reactivity, that can act as 1) a Lewis base to enhance the rate of hydrogen activation and 2) a scaffold which can preferentially be formylated and transfer formylate 'difficult to formylate' amines. Both factors have led to Sn/N FLPs having comparable turnover frequencies than Ruthenium and Palladium at similar pressures for the synthesis of azoles. Eventually, the studies on these FLPs will allow us to move away from using rare, toxic, and expensive transition metals to cheaper more renewable main group elements for the process.

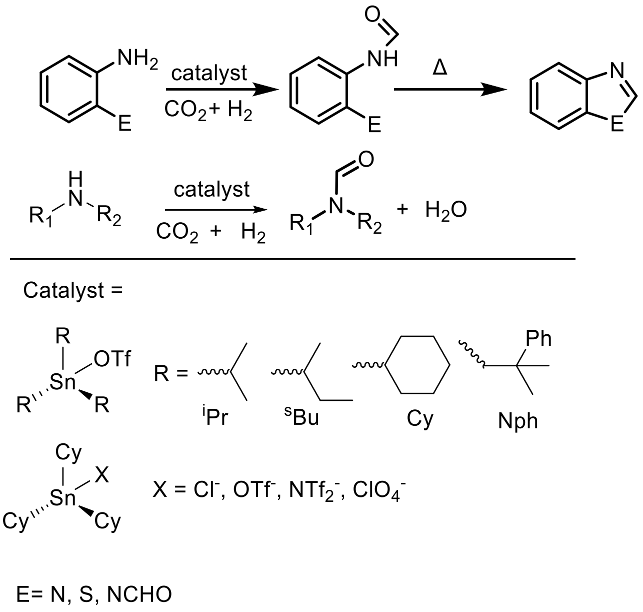

Figure 1: Examples of tin catalysed reductive coupling reactions of CO_2 and amines in the presence of H_2.

PB77

Reactivity of rhodium(I) PNNYP-pincer complexes: small changes with big consequences

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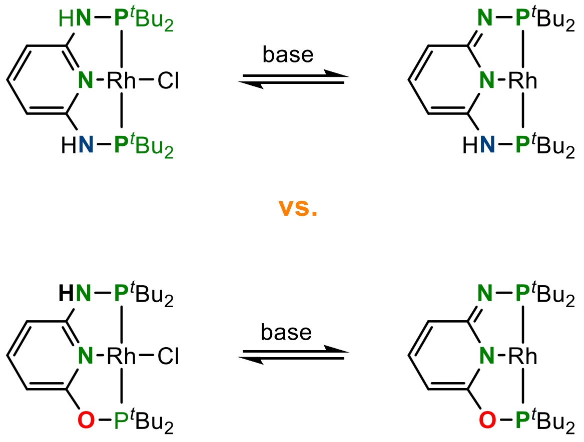
Two Rh PNNYP type pincer complexes were synthesized. On the on hand, the symmetric [Rh(PNNNP)Cl] complex (Y = NH) established by Huang and co-workers [1] and on the other side the asymmetric [Rh(PNNOP)Cl] complex (Y = O). They only differ on one linker group from the pyridine backbone to the phosphine ligand handle. However, this small change in ligand design causes a notable change in reactivity.



not stable in solution
over time or *in vacuo*

stable in solution at r.t.
over several days and
vacuum stable

Both complexes undergo a dearomatization process, in the presence of a base, which is known for pyridine-based pincer ligands.[2] The change from one NH to O in the linker group of the ligand affects the stability of the dearomatized product. The resulting consequences on their reactivity are shown on selected examples. The differences in structure, stability and reactivity are confirmed by NMR, IR and XRD studies.

References

[1] Y. Wang, B. Zheng, Y. Pan, C. Pan, L. He, K.-W. Huang, *Dalton Transactions* **2015**, *44*, 15111-15115.

[2] A. Sacco, G. Vasapollo, C. F. Nobile, A. Piergiovanni, M. A. Pellinghelli, M. Lanfranchi, *Journal of Organometallic Chemistry* **1988**, *356*, 397-409.

PB78

Introducing the Perfluorinated Cp* Ligand into Coordination Chemistry

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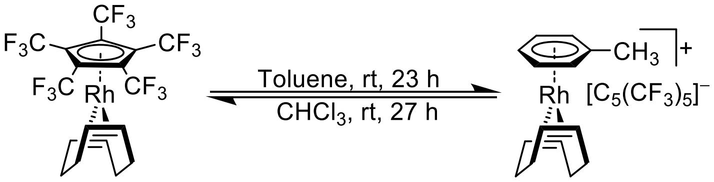
The perfluorinated Cp* anion $[C_5(CF_3)_5]^-$ was first synthesized by Lemal in 1980 but so far resisted all coordination attempts due to its low basicity.[1] Recently, we succeeded in the preparation of its first complex $[Rh(C_5(CF_3)_5)(COD)]$.[2,3] Quantum-chemical calculations reveal the significantly lowered π-donor ability of $[C_5(CF_3)_5]^-$ in comparison to $[C_5(CH_3)_5]^-$. As a consequence of the weaker M-Cp bond strength, the $[C_5(CF_3)_5]^-$ ligand is remarkably labile towards substitution. For example, toluene is able to quantitatively displace the $[C_5(CF_3)_5]^-$ ligand, converting it into a weakly coordinating anion. Interestingly, the reaction is reversible in $CHCl_3$ (Scheme 1). Furthermore, a similar reactivity is observed between $[Rh(C_5(CF_3)_5)(COD)]$ and fluorinated pyridines.[4]



Scheme 1. Equilibrium reaction between $[Rh(C_5(CF_3)_5)(COD)]$ and toluene.

The high acidity of $HC_5(CF_3)_5$ also allows to prepare the corresponding salts containing reactive cations, e.g. $[Ph_3C]^+$, $[Cp_2Fe]^+$ and $[N(C_6H_4Br)_3]^+$ as well as group 11 complexes $[M(C_5(CF_3)_5)({}^tBu_3P)]$ (M = Cu, Ag, Au).[5,6]

References

[1] E. D. Laganis, D. M. Lemal, *J. Am. Chem. Soc.* **1980**, *102*, 6633-6634.
[2] R. Sievers, M. Sellin, S. M. Rupf, J. Parche, M. Malischewski, *Angew. Chem. Int. Ed.* **2022**, *61*, e202211147.
[3] R. Sievers, J. Parche, N. G. Kub, M. Malischewski, *Synlett* **2023**, DOI: 10.1055/s-0042-1751426.
[4] J. Parche, S. M. Rupf, R. Sievers, M. Malischewski, *submitted.*
[5] R. Sievers, M. Malischewski, *manuscript in preparation.*
[6] R. Sievers, M. Malischewski, *manuscript in preparation.*

PB79

Group 13 organometallics: beyond the classical coordination modes

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Group 13 organometallic complexes are of fundamental and practical importance due to their structural diversity and a significant number of reported applications. Hence, attempts to gain an in-depth understanding of the multi-faceted chemistry of Group 13 organometallics are essential for the development of derived new reagents, catalysts and building units for modern functional materials.[1] Particularly, both the reactivity of octet-compliant compounds and the bonding in electron-rich hypervalent molecules are still a topic of constant debate.[2] A large number of studies have been directed to the better understanding of the factors controlling the formation and stability of higher coordinate Group 13 complexes. However, none of them offers a comprehensive view on this subject. Furthermore, non-covalent interactions could have play a significant role in the properties of the title organometallic compounds. Those interactions are common and influential forces that affect the primary and secondary coordination spheres as various second-sphere interactions often operate in concert with the primary donor-acceptor bonds and can lead to complexities in the structure of metal complexes, stabilize reactive species or lower activation barriers.

In this work, we focused on the reactivity of previously synthesized derivatives of model alkylaluminium or alkylgallium complexes supported by (O, X)-type anionic chelate ligands (X = N or S) towards various Lewis bases of different nature (incl. steric and electronic properties). Our studies lead to the formation of a number of oligonuclear alkylaluminium or alkylgallium complexes of different molecular structures. The resulting compounds were fully characterized using spectroscopic techniques (including Diffusion-Ordered) and, if possible, single crystal X-ray diffraction studies.

References

[1] Wei, Y.; Wang, S.; Zhou, S. *Dalt. Trans.*, **2016**, *45* (11), 4471–4485.
[2] Terlecki, M.; Justyniak, I.; Prochowicz, D.; Lewiński, J. *Eur. J. Inorg. Chem.*, **2020**, 119–127.

PB80

Group 13 organometallic carboxylates as molecular building units of supramolecular assemblies

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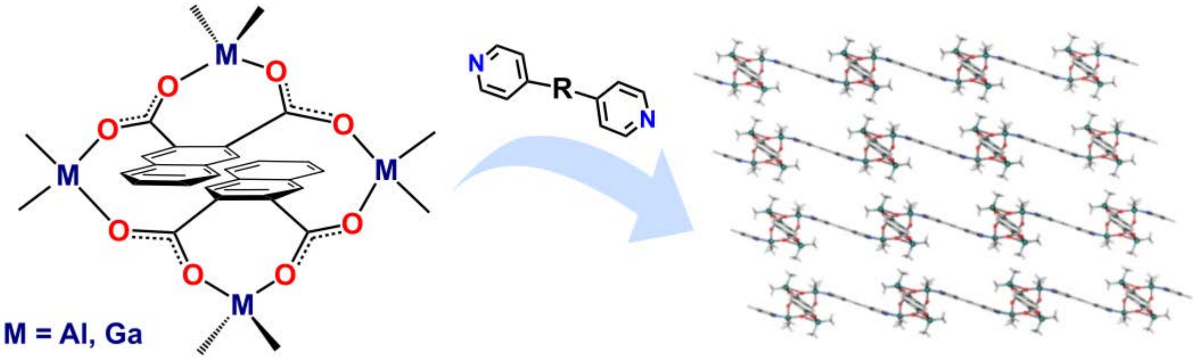
Group 13 organometallic complexes exhibit interesting multi-faceted chemistry, which constantly plays important role in the development of new reagents and catalytic systems as well as molecular building blocks for modern functional materials. In the course of our comprehensive studies on the factors controlling the structure and reactivity of organometallic compounds, we introduced the concept of *dormant Lewis acidity* to rationalize the tendency of octet-compliant Group 13 complexes with highly polarized bonds in the metal coordination sphere to form higher coordinated adducts with a wide range of neutral donor ligands.[1] Herein, we apply this concept to multinuclear organometallic carboxylates, as so-called *dormant poly-Lewis acids*, to rationally construct new supramolecular assemblies based on model macrocyclic $[(Me_2M)_2(OOCArCOO)]_2$ (M = Al, Ga) building units.[2] The results emphasize the important role of noncovalent interactions in the character of formed adducts with various pyridine and bipyridine neutral Lewis bases, demonstrating how subtle changes in organic backbones of both carboxylate ligand and linkers can dramatically affect the molecular and supramolecular structures of the studied assemblies.



References

[1] I. Justyniak, D. Prochowicz, A. Tulewicz, W. Bury, P. Goś, J. Lewiński, *Dalton Trans.* **2017**, *46*, 669.
[2] M. Terlecki, I. Justyniak, D. Prochowicz, J. Lewiński, *Eur. J. Inorg. Chem.* **2020**, *2020*, 119.

PB81

(Hetero)bimetallic Main Group Metal Complexes of Dianionic Nitrogen-Rich Guanidinate Ligand

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Guanidinates are popular *N*-chelating donor ligands in the coordination and organometallic chemistry of almost the whole periodic table. Successful use of, mostly anionic, both transition and main group metal guanidinates in various catalytic processes, materials science, and other chemical transformations has been reported. The contrasting scarcity of dianionic/dinuclear guanidinate complexes in the literature makes this topic of high interest. Great configurability of the central CN_3 moiety in terms of steric/electronic contributions opens the door for suitable expansion of the π-electron conjugated skeleton and possible accomodation of two (or more) metal atoms.[1]

Our chosen nitrogen-rich scaffold engages in six-membered triazametallacycles, unusual for guanidinates, as well as expected four-membered κ^2-bidentate chelates, and their combinations (**Figure 1** – left), showing electronic flexibility and versatility in the coordination of a range of elements. Moreover, the environment of the coordinated metal atoms can be further refined by careful substituent design (**Figure 1** – right). The nature of the coordinated atoms and the respective relationship between the two metal centres was therefore studied in detail.

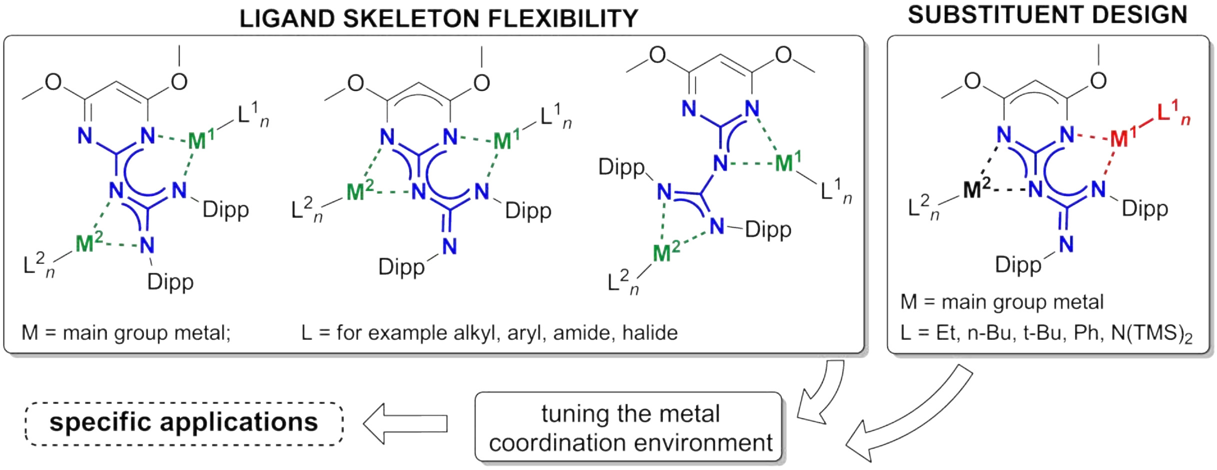

Figure 1: Combined approach for obtaining bimetallic guanidinate complexes.

This work was supported by the Czech Science Foundation (No. 21-02964S).

References

1 (a) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*(1), 91; (b) Jones, C. *Coord. Chem. Rev.* **2010**, *254*, 1273; (c) Edelmann, F. T. *Adv. Organomet. Chem.* **2013**, *61*, 55. (d) Carrillo-Hermosilla, F.; Fernández-Galán, R.; Ramos, A.; Elorriaga, D. *Molecules* **2022**, *27*, 5962.

PB82

Ring-opening polymerization of functionalized aliphatic bicyclic carbonates

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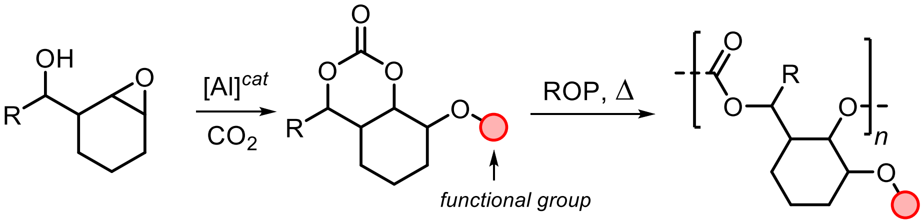
Polymers are a class of important materials for consumer and industrial applications. However, they also can create serious environmental issues due to incorrect disposal and microplastic formation in our eco-systems. So, there is a need to develop degradable polymers that combine the easy modulation of their mechanical and thermal properties, and are easily recyclable. Here we demonstrate that Al-catalysis can be applied towards a wide range of functional bicyclic carbonate monomers,[1] which after ring-opening polymerization afford novel types of CO_2-based polycarbonates[2] with predefined functional sites. These functionalities allow for further modifications, and are chemically degradable under mild reaction conditions.



References

[1] Qiao, C.; W. Shi, Brandolese, A.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Kleij, A. W. *Angew. Chem. Int. Ed.* **2022**, *61*, e202205053.
[2] Grignard, B.; Gennen, S.; Jerome, C.; Kleij, A. W.; Detrembleur, C. *Chem. Soc. Rev.* **2019**, 48, 4466.

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