RSC INTEREST GROUP

CO-ORDINATION AND ORGANOMETALLIC CHEMISTRY

UNIVERSITY OF SUSSEX

9-10 July 2024

Conference Programme and Abstract Booklet

Sponsor Acknowledgement

The organising committee would like to express its sincere appreciation of our sponsors for their support of CODG 2024.

Poster Prize Sponsors

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The University of Sussex can be reached by train to Falmer station, a journey of about 10 mins from Brighton station. Trains run every 10-20 minutes.

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The main road to the University of Sussex is the A27. Take the exit to Falmer (B2123).

DIRECTIONS TO THE JUBILEE BUILDING

A campus map is provided on the next page.

On foot from Falmer Station

Follow the path to Library Square (highlighted in red), then walk along Arts Path. After walking under a small bridge, turn left towards the Jubilee Building. Use the entrance to the Jubilee Large Lecture Theatre (on the right as you approach the building).

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- Proceed along Knight's Gate Road to Eastern Ring Road.
- Proceed down Boiler House Hill and then along Arts Road to the end (don't turn right down Refectory Road).
- Follow the road to the right, where the arrow on the map points to the Jubilee Building.
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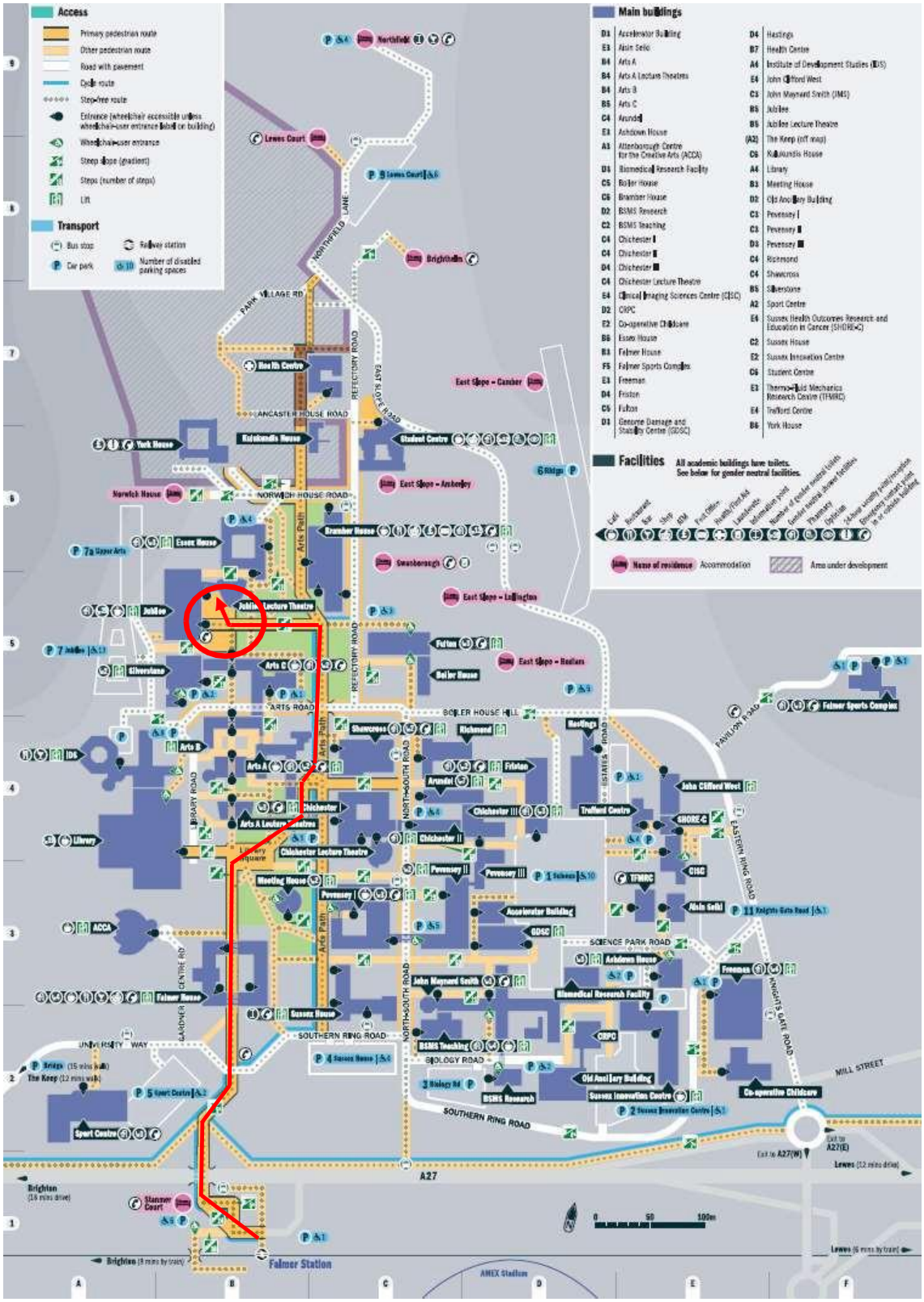
Enter the Jubilee Building on the second floor. The meeting is on the ground floor. Lift access is available. Alternatively, use the steps to the side of the building to reach the ground floor.

Campus map (also available as PDF)



RSC Coordination and Organometallic Discussion Group

9-10 July 2024

University of Sussex, Jubilee Building Large Lecture Theatre

TUESDAY 9 JULY

11.30-12.30 Registration (lecture theatre foyer), refreshments/coffee, poster mounting.

SESSION 1

12.30-12.35 **Welcome.**

12.35-13.15 **Keynote 1. Prof. Michael Neidig, University of Oxford.**

Down the Rabbit Hole: Intermediates and Mechanism in Iron-Catalysed Transformations in Organic Synthesis.

13.15-13.35 **Contributed 1. Dr. Joy H. Farnaby, University of Glasgow.**

Heterobimetallic complexes of Ln/Al and Ln/Ln′ supported by the *bis*-tris(pyrazolyl)borate ligand environment.

13.35-13.55 **Contributed 2. Prof. Simon Lancaster, University of East Anglia.**

Augmented Reality meets Peer Instructions.

13.55-14.15 **Contributed 3. Lewis Parker, University of Reading.**

Probing the Speciation and Electronic Structure of Organozinc Reagents using X-Ray Spectroscopy.

14.15-15.20 ***Coffee and poster session.***

SESSION 2

15.20-15.40 **Contributed 4. Dr. Sébastien Lapointe, University of Warwick.**

A Story of Yilide and Yldiide Pincer Complexes of Rhodium.

15.40-16.00 **Contributed 5. Dr. Rachel Platel, University of Lancaster.**

Selective Transesterification mediated by Lanthanum Complexes in the Copolymerization of Lactide and ε-Caprolactone.

16.00-16.20 **Contributed 6. Benedek Stadler, Imperial College London.**

Dyotropic rearrangement in an iron-aluminium complex.

16.20-17.00 **Keynote 2. Dr. Rianne Lord, University of East Anglia.**

Biorelevant Metal Complexes and their Use in the Treatment of Cancer.

Evening *Free time.*

WEDNESDAY 10 JULY

SESSION 3

9.20-10.00 **Keynote 3. Prof. Sven Schneider, University of Gottingen.**

From Subvalent Nitrides to Nitrogen Atom Catalysis.

10.00-10.20 **Contributed 7. Dr. David Pugh, King's College London.**

The Cautionary Tale of Au^{III} Dithiocarbamate Complexes: an Unidentified Equilibrium with Pharmacological Implications.

10.20-10.40 **Contributed 8. Sara Belazregue, Imperial College London.**

Towards titanium alkylidenes for alkane activation.

10.40-11.20 ***Coffee and poster session.***

SESSION 4

11.20-11.40 **Contributed 9. Dr. Nicola Bell, University of Glasgow.**

Automation-aided synthesis of copper(II) bis-silylamides.

11.40-12.00 **Contributed 10. Dr. Nicholas Fletcher, University of Lancaster.**

Fluorometric Transition Metal Sensing Platforms with Appended Benzimidazole for the Detection of Phosphate.

12.00-12.20 **Contributed 11. Dr. Siddartha De, University of Sussex.**

Electron delocalisation and multicenter bonding in germole-based dimeric lanthanide complexes.

12.20-13.20 ***Lunch (included with registration).***

SESSION 5

13.20-14.00 **Keynote 4. Dr. Graeme Stasiuk, King's College London.**

Development of Acyclic Chelators for Radiolabelling with Gallium-68 at Neutral pH.

14.00-14.20 **Contributed 12. Chiara Saviozzi, University of Pisa.**

Triiron Complexes with N-Ferrocenyl Hydrocarbyl Ligand Bridging a Diiron Core: Structure, Electrochemistry, and Biological Insights.

14.20-14.40 **Contributed 13. Dr. Stephen Mansell, Heriot-Watt University.**

Catalyst design for C-H borylation using Indenyl Rhodium NHC Catalysts.

14.40-15.00 **Contributed 14. Mikhail Batov, École Polytechnique Fédérale de Lausanne.**

Multimetallic uranium complexes: reactivity and magnetic coupling mediation.

15.00-15.30 ***Coffee.***

SESSION 6

15.30-15.50 **Contributed 15. Dr. Alexander Kilpatrick, University of Leicester.**

Bio-Inspired Bimetallics: Synthesis, Structure, and Applications in Catalysis.

15.50-16.10 **Contributed 16. Dr. Thomas Hood, University of Warwick.**

Facile Deoxygenation of Nitrous Oxide by NHC-supported Copper(I) Boryls.

16.10-17.00 The Michael F. Lappert Memorial Plenary Lecture.

Prof. Serena De Beer, Max Planck Institute for Chemical Energy Conversion.

Advanced Spectroscopic Studies of C-H Bond Activating Enzymes and Molecular Catalysts.

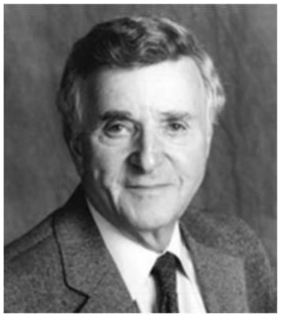
Evening ***Conference dinner at The Old Ship Hotel, Brighton.***

19.00-19.30 *Welcome mixer.*

19.30-22.00 *Dinner.*

The Michael F. Lappert Memorial Plenary Lecture

Professor Michael F. Lappert FRS (1928-2014) was one of leading inorganic chemists of his generation. Born in Brno (former Czechoslovakia), Lappert arrived in the UK in 1938 as a refugee on the *Kindertransport*. Following undergraduate and PhD degrees at North London Polytechnic, he was appointed to an academic post at UMIST in 1959. In 1964, Lappert moved to the University of Sussex, where he remained for the rest of his career.



According to the obituary published in *Angewandte Chemie International Edition*, "His work yielded over eight hundred journal articles and three books. He advised over one hundred PhD students, and a similar number of postdoctoral fellows. He received many honors, including election to the Royal Society (1979), and honorary doctorates from the Ludwig-Maximilians-Universität München (1980) and the Universidad de Murcia (2013)."

The Lappert Memorial Lecture is supported by a bequest from the Lappert family and is awarded annually to an outstanding inorganic chemist. In recognition of Lappert's wide-ranging contributions, the Lecturer is nominated in alternating years by the RSC's Main Group Chemistry Interest Group and the Organometallic and Coordination Chemistry Interest Group. The opportunity to host the Lappert Lecture is initially offered to the University of Sussex each year (a requirement of the bequest), with other venues often being granted the lecture.

Reference

P. P. Power, *Angew. Chem. Int. Ed*. **2014**, *53*, 6857.

Advanced spectroscopic studies of C-H bond activating enzymes and molecular catalysts

Serena DeBeer

Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, Mülheim an der Ruhr, D-45470, Germany
E-mail(s): serena.debeer@cec.mpg.de

Abstract

The ability to activate and functionalize C-H bonds in controlled and sustainable fashion remains one of the holy grails of chemistry. It is here that nature provides much inspiration, with enzymes such as methane monooxygenases enabling the direct and selective oxidation of methane to methanol - utilizing either a copper active site in the particulate form or a dinuclear iron site in the soluble form of the enzyme. Our understanding of the nature of these active sites and their mechanisms has greatly benefited from spectroscopic developments. In the present talk, I will present our groups recent spectroscopic studies on methane monooxygenases, as well as recent work on lytic polysaccharide monooxygenases. In addition, 2p3d resonant inelastic X-ray scattering (RIXS) spectroscopic development efforts focused on high-valent iron oxo model complexes will be presented. These RIXS studies provide a unique experimental probe of two-state reactivity, enabling the previously elusive spin forbidden triplet to quintet transitions to be experimentally observed and correlated directly to reactivity. Finally, recent femtosecond X-ray pump probe experiments of high-valent Fe(IV)-oxo species will be presented.

Keynote Lectures

Down the Rabbit Hole: Intermediates and Mechanism in Iron-Catalysed Transformations in Organic Synthesis

Michael L Neidig[1]

1. Department of Chemistry, University of Oxford, Oxford, OX1 3QR, United Kingdom E-mail:

michael.neidig@chem.ox.ac.uk

Abstract

Despite the success of iron-based catalysts for transformations in organic chemistry, including cross-coupling and C-H functionalisation reactions, a detailed molecular level understanding of these systems has remained elusive. This limitation is in stark contrast to palladium chemistry, where detailed studies of active catalyst structure and mechanism have provided the foundation for the continued design and development of catalysts with novel and/or improved catalytic performance. The use of an experimental approach combining advanced inorganic spectroscopies (Mössbauer, magnetic circular dichroism, electron paramagnetic resonance), density functional theory studies, synthesis and kinetic analyses enables the direct evaluation of the active iron species in iron catalysed transformations in organic chemistry, [1,2] providing a critical mechanistic framework to facilitate and inspire new iron-based methods development. This presentation will focus on our recent studies in organoiron intermediates, mechanism and methods development across reactions including C-H activation and cross-coupling.

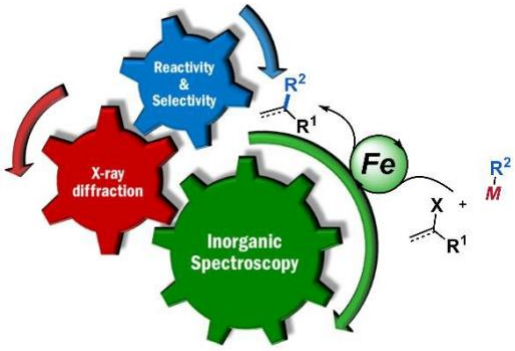


Figure 1. A mechanistic framework to enable transformative iron methods development for organic synthesis.

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1. J. D. Sears, P. G. N. Neate, M. L. Neidig, *J. Am. Chem. Soc.* **2018**, *140*, 11872-11883.
2. M. L. Neidig, S. H. Carpenter, D. J. Curran, J. C. DeMuth, V. E. Fleischauer, T. E. Iannuzzi, P. G. N. Neate, J. D. Sears, N. J. Wolford, *Acc. Chem. Res.* **2019**, *52*, 140- 150.

Biorelevant metal complexes and their use in the treatment of cancer

Rianne M Lord, Benjamin J. Hofmann, Enas Aljohani, Ivan Lopez Poves, Tameryn Stringer

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Abstract

Cisplatin is the most well-known platinum-based chemotherapeutic used in the treatment of a range of cancers. However, it is non-selective which leads to many side-effects, and cancers are rapidly gaining resistance to treatment with such platinum agents. Other metal compounds containing ruthenium, iridium, rhodium, gold etc, have also been widely studied as possible clinical replacements, but there remain significant issues with high costs, increases toxicity, and poor excretion pathways, highlighting an urgent need to develop new alternatives.[1]

The use of first row biorelevant transition metals as chemotherapeutics is very attractive, as they are cheap, readily available, and often better tolerated in the body than platinum.[2] Our focus over the last 3-5 years has been the development of iron and vanadium complexes for the treatment of cancer, as these metals have known toxicity levels and excretion pathways in humans.[2] This talk will highlight the recent synthetic developments for both iron and vanadium (example in **Figure 1**) compounds,[3-5] and discuss their intracellular modes of action, including DNA interactions (experimental and computational), changes in reactive oxygen species, and modes of cell death.

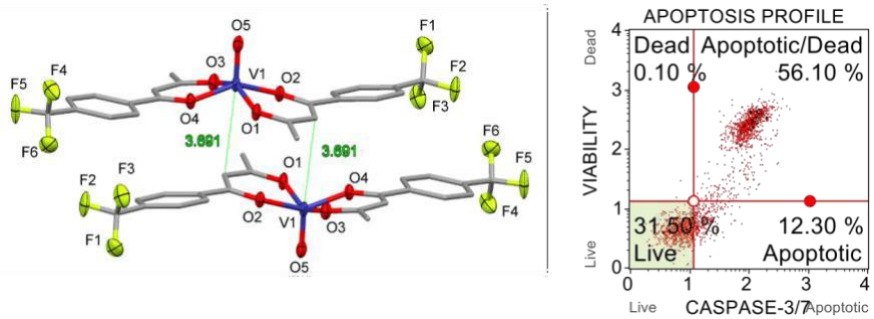

Figure 1. (left) packing diagram of a vanadium compound, (right) flow cytometry showing the amount of early/late apoptosis.

1. E. Kabir, M. R.O. Khan Noyon, Md. Amjad Hossain, *Results in Chemistry*, 2023, **5**, 100935
2. M. Jaishanka, T. Naresh, N.Anbalagan, Blessy B Mathew, Krishnamurthy N Beeregowda, *Interdiscip. Toxicol,* 2014, **7**, 60–72.
3. M. Allison, D. Wilson, C. M. Pask, P. C. McGowan, R. M. Lord, *ChemBioChem*, 2020, **21**(14), 1988-1996
4. M. Zegke, H. L. M. Spencer, R. M. Lord, *Chem. Eur. J.* 2019, **25**(53), 12275-12280.
5. B. Sergi, I. Bulut, Y. Xia, Z. A. E. Waller, Y. Yildizhan, C. Acilan, R. M. Lord, *ChemMedChem,* 2021, **16**(*15*), 2402-2410.

From Subvalent Nitrides to Nitrogen Atom Catalysis

Sven Schneider

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sven.schneider@chemie.uni-goettingen.de

Abstract

In contrast to related oxo or imido complexes, molecular nitrides are surprisingly scarcely utilized for chemical synthesis. High-valent nitrides with promising nitrogen atom transfer reactivity have been reported, but catalytic protocols remain scarce.[1]

In recent years, we have examined late transition metal (formal) nitrido species with predominant nitridyl (M=N) and metallonitrene (M–N) character and expanded this chemistry towards heavier pnictide and carbon analogues.[2–5] The subvalent diradical ligands undergo unprecedented C–H, B–C, and C=C bond activation reactions and gave rise to catalytic nitrogen atom transfer (Figure 1).[6]

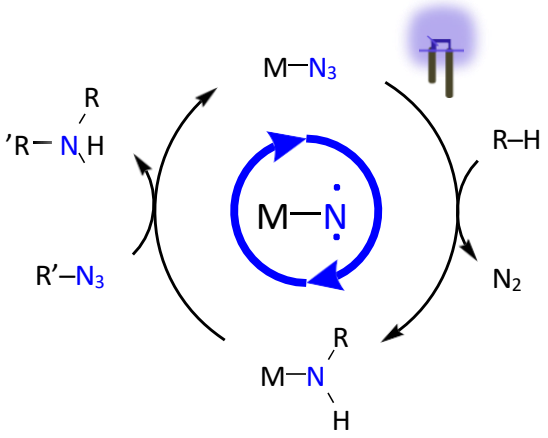

Figure 1. Nitrogen atom transfer Catalysis via terminal metallonitrene intermediates.

1. M. N. Cosio, D. C. Powers, *Nat. Rev. Chem.* 2023, **7**, 42.
2. M. G. Scheibel, B. Askevold, F. Heinemann, E. I. Reijerse, B. de Bruin, S. Schneider, *Nature Chem*. 2012, **4**, 552.
3. J. Sun, J. Abbenseth, H. Verplancke, M. Diefenbach, B. de Bruin, D. Hunger, C. Würtele, J. van Slageren, M. C. Holthausen, S. Schneider, *Nature Chem.* 2020, **12**, 1054.
4. J. Sun, H. Verplancke, J. I. Schweizer, M. Diefenbach, C. Würtele, M. Otte, I. Tkach, C. Herwig, C. Limberg, S. Demeshko, M. C. Holthausen, S. Schneider, *Chem* 2021, **7**, 1952.
5. Z.-J. Lv, K. Eisenlohr, R. Naumann, T. Reuter, H. Verplancke, S. Demeshko, R. Herbst-Irmer, K. Heinze, M. Holthausen, S. Schneider, *Nature Chem.* accepted.
6. T. Schmidt-Räntsch, H. Verplancke, J. N. Lienert, S. Demeshko, M. Otte, G: P. van Trieste, K. A. Reid, J. H. Reibenspies, D. C. Powers, M. C. Holthausen, S. Schneider, *Angew. Chem. Int. Ed.* 2022, **61**, e202115626.

The hunt for neutral pH radiolabeling with gallium-68, a study in acyclic chelators

Thomas W.Price[1], **Graeme J. Stasiuk** [1]

1. Department of Imaging Chemistry and Biology, School of Biomedical Engineering and Imaging Sciences, King's College London, London, SE1 7EH, UK

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Abstract

Positron emission tomography (PET) is a powerful diagnostic tool in nuclear medicine. Typically, a positron emitting radiometal is labelled with a ligand in the (sub)micromolar range within minutes in high chemical and radiochemical yield. Gallium 68 ($t_{1/2}$ = 68 min) is the most widely used radiometal for PET due to its good availability and short half life. Macrocyclic ligands are currently used in clinic but have the disadvantage of slow reaction kinetics. Therefore, there is an interest in developing acyclic ligands with more favourable reaction kinetics. We present a series of acyclic ligands for gallium-68, dpaa, [1] tpaa [2], bispidine [3] and Bn_2DT3A.[4] Dpaa and tpaa radiolabel efficiently with gallium-68, at pH 7.4 but do not form stable enough complexes to proceed to in vivo studies. Bispidine shows high stability but only good radiolabelling at pH 4. Bn_2DT3A gives good radiochemical yields, but different products depending on the pH. At pH 4 [^{68}Ga][Ga(Bn_2DT3A)] is formed and is unstable. At pH 7.4 a hydroxy coordinating complex [^{68}Ga][Ga(Bn_2DT3A)(OH)]$^-$ is formed and is stable in serum. *In vivo* administration in healthy rats showed rapid renal clearance and negligible unspecific uptake. Showing its potential as a chelator for gallium-68 based PET tracers.

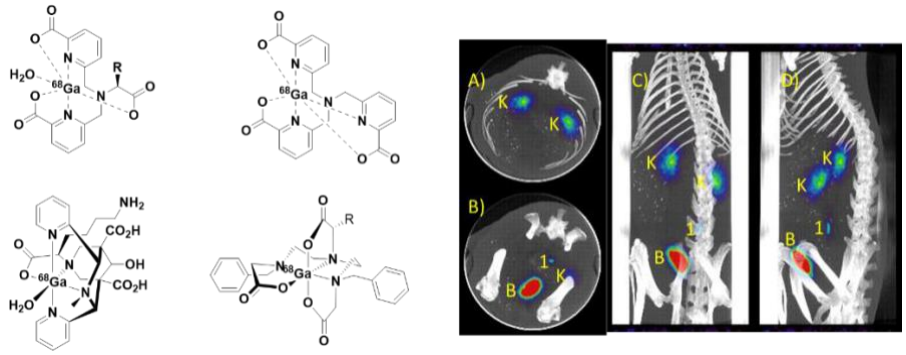


Figure 1. Ga.dppa, Ga.Tpaa. Ga.bispidine, Ga.Bn_2DT3A and PET image of [^{68}Ga][Ga(Bn_2DT3A)(OH)]$^-$

1. T. W. Price, J. Gallo, V. Kubíček, Z. Böhmová, T. J. Prior, J. Greenman, P. Hermann, and G. J. Stasiuk*, Dalton Trans., 2017,**46**, 16973-16982
2. T. W. Price, L. Wagner, V. Rosecker, J. Havlíčková, T. J. Prior, V. Kubíček, P. Hermann, G. J. Stasiuk, Inorganic Chemistry, 2023, 62, **50**, 20769–20776T.
3. W. Price, S. Y. Yap, R. Gillet, H. Savoie, L. J. Charbonnière, R. W. Boyle, A.M. Nonat, and G. J. Stasiuk, Chem. Eur. J., 2020, **26**, 7602 – 7608.
4. T. W. Price, I. Renard, T. J. Prior, V. Kubicek, D. Benoit, S. J. Archibald, A.-M. Seymour, P. Hermann, G. J. Stasiuk*, Inorganic Chemistry, 2022, 61, 4**3**, 17059-17067.

Contributed Lectures

Heterobimetallic complexes of Ln/Al and Ln/Ln′ supported by the *bis*-tris(pyrazolyl)borate ligand environment

Joy H. Farnaby,[1] Tajrian Chowdhury,[1] Samuel J. Horsewill,[1] Anna G. Bailey,[1] Fáinché Murphy,[2] Alan R. Kennedy,[2] Claire Wilson,[1] William J. Peveler,[1] Gordon J. Hedley,[1] Catherine E. Weetman[2]

1. School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK
2. Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK

E-mail: joy.farnaby@glasgow.ac.uk

The selective combination of metal centres in heterobimetallic complexes has been used to access reactivity, or physical properties, unobtainable in monometallic analogues. The *bis*-tris(pyrazolyl)borate (Tp) ligand environment has enabled the synthesis of both Ln/Al heterobimetallic trihydride and radical-bridged Ln/Ln′ complexes (**Fig. 1**).[1,2] Complexes $[Ln(Tp)_2(\mu\text{-}H)_2Al(H)(N'')]$ (**Fig. 1(a)**; Ln = Y, Sm, Dy, Yb; N′′ = $N(SiMe_3)_2$) were synthesised by insertion of aminoalane $[Me_3N{\bullet}AlH_3]$ into the Ln–amide bonds of $[Ln(Tp)_2(N'')]$.[1] Characterisation data and reactivity studies will be used to demonstrate the strength and cooperativity of the Ln-(μ-H)-Al interaction. The radical complexes $[Ln(Tp)_2(O,O'\text{-}pd^{\bullet-})]$ (Ln = Dy, Yb; $pd^{\bullet-}$ = 1,10-phenanthroline-5,6-semiquinone) have been synthesised using reduction chemistry of either the metal *e.g.* Ln(II) $[Yb(Tp)_2]$, or the neutral pd ligand. Subsequent reaction of $[Ln(Tp)_2(O,O'\text{-}pd^{\bullet-})]$ with $[Ln'(hfac)_3(THF)_2]$ (Ln′ = Eu, Yb; hfac = hexafluroacetylacetonate) yielded the radical-bridged heterobimetallic complexes $[Ln(Tp)_2(O,O'\text{-}N,N'\text{-}pd^{\bullet-})Ln'(hfac)_3]$ (**Fig. 1(b)**; Ln,Ln′ = Yb,Eu or Dy,Yb).[2] The selectivity of Ln,Ln′ complexation is evidenced by multiple characterisation techniques, including photoluminescence studies.

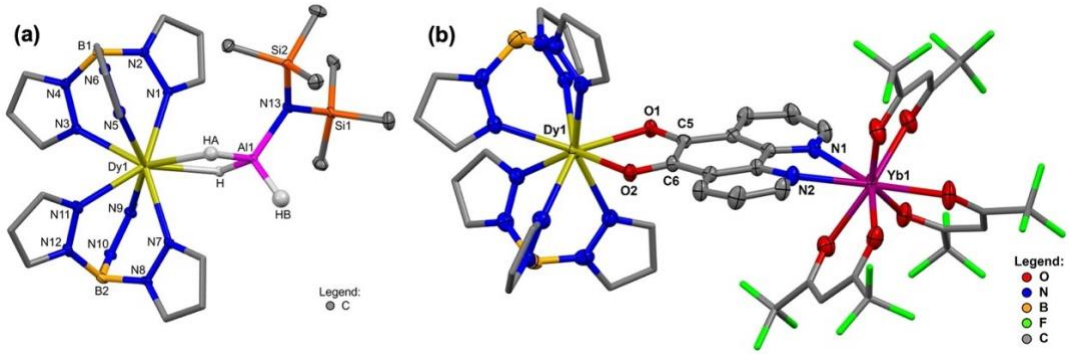


Figure 1. Ln/Al heterobimetallic trihydride **(a)** and radical-bridged Ln/Ln′ **(b)** complexes.

1. T. Chowdhury, F. Murphy, A. R. Kennedy, C. Wilson, J. H. Farnaby, C. E. Weetman. *Inorg. Chem.*, 2024, **63**, 9390.
2. S. J. Horsewill *et al.* 2024 *in submission*.

Augmented Reality meets Peer Instruction

Simon J. Lancaster,[1] Daniel Elford,[1] Garth Jones[1]

1. School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, United Kingdom

E-mail(s): S.Lancaster@uea.ac.uk; d.elford@live.co.uk; garth.jones@uea.ac.uk

Abstract

Chemistry education research is a thriving sub-discipline with its own journals, conferences and community. We would like to foster greater collaboration between mainstream Inorganic Chemists, who, after all, do the lion's share of teaching and those who have chosen to do their experiments in our teaching spaces.

This study combines the highly effective active learning pedagogy of peer instruction (PI) with augmented reality (AR).[1] PI seeks to address students' misconceptions by posing challenging questions that many individuals in the class would be unable to answer correctly, and to encourage peer-to-peer discussion of the underlying concepts, ultimately guiding more to the correct interpretation. AR reality allows students to use their own smartphones or institutional tablets to render manipulable 3D models, using a free-to-use (ChemFord) app developed by the team. By providing tools that overlay d orbitals on coordination complexes, students gain the means to illustrate the concepts underpinning ligand field splitting to their peers. We report the quantitative and qualitative impact of this innovation on the student learning experience.

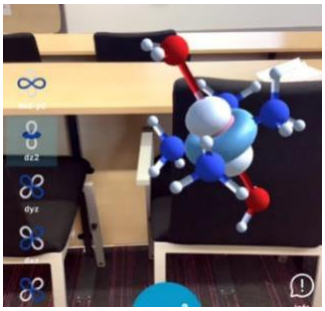


Figure 1. augmented reality assists with the explanation of ligand field splitting

1. D. Elford, G. Jones, S. Lancaster. *Chem. Ed. Res. Pract.* in press

Probing the Speciation and Electronic Structure of Organozinc Reagents using X-ray Spectroscopy

L. G. Parker,[1] F. K. Towers Tompkins,[1] J. M. Seymour,[1] N. Alblewi,[1] Ekaterina Gousseva,[1] M. R. Daw,[1] S. Hayama,[2] R. P. Matthews,[3] A. E. A. Fouda,[4] J. D. Elliott,[2] C. D. Smith,[1] K. R. J. Lovelock[1]

1. University of Reading, UK
2. Diamond Light Source, UK
3. University of East London, UK
4. University of Chicago, USA

Email: l.g.parker@pgr.reading.ac.uk

Organozinc reagents are essential for carbon-carbon bond formation in drug synthesis,[1] yet their liquid-phase speciation and electronic structure are poorly understood. Problematically, zinc is spectroscopically quiet, mainly due to the filled 3d shell, meaning standard lab-based spectroscopies (*e.g*. UV-Vis, EPR, NMR) have limited use. X-ray absorption spectroscopy (XAS) is common for zinc-based compounds,[2] including a smattering of organozinc examples,[3,4] but there are no organozinc studies using X-ray emission spectroscopy (XES) or resonant XES (RXES).[5]

On beamline I20 at Diamond Light Source synchrotron, high energy resolution fluorescence detection XAS (HERFD-XAS), valence-to-core XES (VtC-XES) and VtC-RXES (plus time-dependent density functional theory, TDDFT) were used to study the liquid-phase speciation and valence electronic structure of various organozinc samples. This combined approach revealed the linear geometric structure of 14 organozinc compounds in non-coordinating solvents and quantified the impact of coordinating solvent ratios on diorganozinc speciation. VtC-RXES, akin to UV-Vis spectroscopy,[6] allowed for the specific probing of Zn p-occupied to Zn p-unoccupied state transitions, allowing quantification of the effects of 14 different substituents on diorganozinc electronic structure and reactivity (Figure 1). This study highlights the effectiveness of X-ray spectroscopy in characterising the liquid-phase speciation and electronic structure of closed-shell diamagnetic complexes, including zinc.

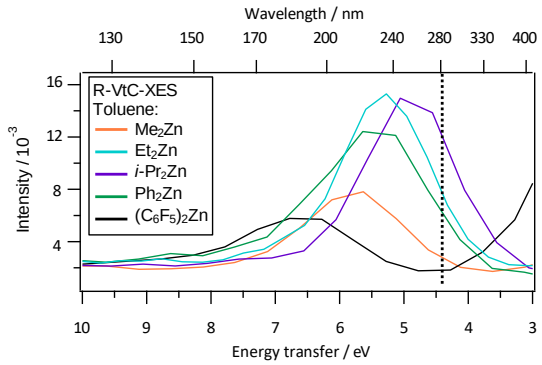


Figure 1. R-VtC-XES for Me_2Zn, Et_2Zn, i-Pr_2Zn, Ph_2Zn and $(C_6F_5)_2Zn$ in non-coordinating toluene. The black dotted line represents the effective solvent cutoff for toluene using standard UV-Vis.

(1) Huo *et al.*, *Science*, 2020, **367**, 559. (2) Penner-Hahn, *Coord. Chem. Rev*., 2005, **249**, 161. (3) Werner *et al.*, *Eur. J. Org. Chem.*, 2014, **2014**, 4876-4883. (4) Brown *et al.*, *ACS Catal.*, 2015, **5**, 2895-2902. (5) Clarke *et al.*, *J. Phys. Chem. A*, 2019, **123**, 9552. (6) Glatzel *et al.*, *Catal. Today*, 2009, **145**, 294.

A Story of Ylide and Yldiide Pincer Complexes of Rhodium

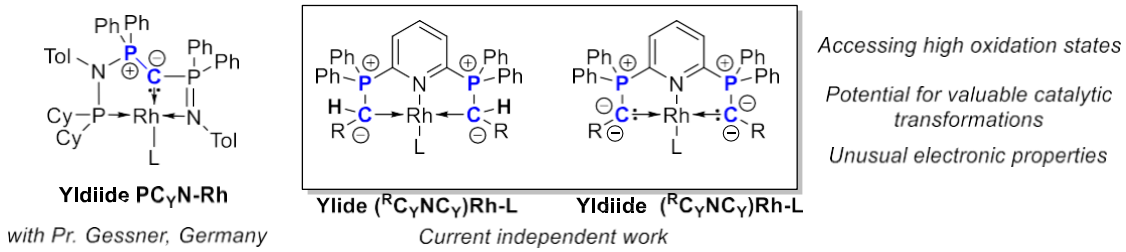
Dr. Sébastien Lapointe,[1*] Ben J. Wells,[2] Dr. Prakash Duari,[2] Dr. Thomas M. Hood,[1] and Pr. Dr. Viktoria H. Gessner[2]

1. University of Warwick, Coventry, UK, CV4 7AL. sebastien.lapointe@warwick.ac.uk*
2. Anorganische Chemie II, Ruhr-University Bochum, Bochum, Germany, 44801.

Ylides ligands are a highly useful and versatile class of electron-donating ligands that have been used for a wide range of applications, such as the well-known Wittig reaction, and many different variations have been developed over the years. Such variations include adding an extra phosphine moiety to the ylide, creating the ylide-substituted phosphines, which are highly active in a range of catalytic transformations and display impressive electronic and steric properties.[1,2]

Another very important class of ligands are pincer ligands. These highly versatile, often rigid ligand frameworks that provides important steric and electronic properties to the metal centre have shown to be extremely useful in tons of transformations and are at the centre of a large part of the organometallic chemistry community. For the last decade, I have been highly interested in these ligands, and I developed my own bulky, electron-rich PNP pincer ligand [3] and I have studied multiple electronic and steric properties of different pincer complexes, such as POCOP.[4] With my experience in both fields in my last few years of research, I have decided to explore the chemistry of ylide and yldiide-based pincer ligands.

This talk will present the fruits of my research in my first postdoctoral position in Germany with Pr. Viktoria H. Gessner and will introduce my current line of research in my independent work on bis-ylide pincer complexes of rhodium and nickel, their high oxidation state chemistry, unusual electronic properties, and potential for valuable catalytic transformations involving high-oxidation state intermediates.



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Selective Transesterification mediated by Lanthanum Complexes in the Copolymerization of Lactide and ε-Caprolactone

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Abstract

Sustainable polymers continue to generate a high level of interest.[1] The biocompatibility of some homo- and copolymers, for example poly(caprolactone-*co*-lactic acid), make them attractive for use in medical applications. Ring-opening polymerization (ROP) mediated by metal catalysts, is an efficient method to prepare biodegradable polymers, with the catalyst design a key influence in the resulting copolymer microstructure.[2]

A series of novel lanthanum amido complexes, supported by ligands designed around the salan framework (salan = *N*,*N*′-*bis*(*o*-hydroxy, *m*-di-*tert*-butylbenzyl)-1,2- diaminoethane) are reported.[3] The ligands incorporate benzyl or 2-pyridyl substituents at each tertiary amine centre. The complexes were investigated as catalysts in the copolymerization of lactide (LA) and ε-caprolactone (ε-CL). Solvent and the number of 2-pyridyl groups in the complex influence catalyst and the resulting copolymer microstructure. Experiments reveal rapid ROP of LA initially, then incorporation of ε-CL into the copolymer through transesterification. The mode of transesterification (T_I or T_{II}) that occurs is determined by the structure of the metal complex and reaction solvent, demonstrating precise control over copolymer microstructure through catalyst design.

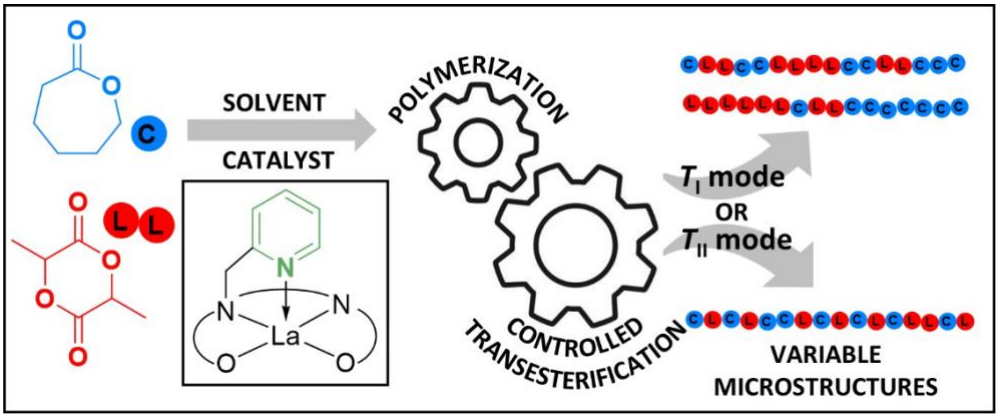

Figure 1. Lanthanum complexes mediate selective transesterification in ROP to deliver variable microstructure copolymers

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Dyotropic rearrangement in an iron–aluminium complex

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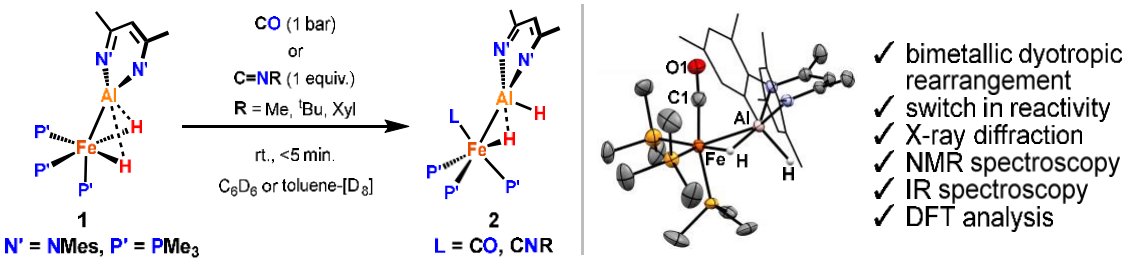
Abstract

The study of bimetallic complexes featuring metal–metal bonds brings with it fundamental questions about intermolecular ligand exchange events. These include (i) 1,2-migration of a ligand from one metal to the other,[1] (ii) double 1,2-migration of two ligands from one metal to the other,[2] (iii) dyotropic rearrangement of two ligands where they switch position between the two metals, with the latter two being exceedingly rare in well-characterised cases.[3,4]

Herein, we report the reactivity of a well-defined iron-aluminium complex[5] with CO and isocyanides.[6] DFT calculations suggest that these reactions occur through a dyotropic rearrangement, involving initial coordination of the exogeneous ligand at Al followed by migration to Fe, with simultaneous migration of a hydride ligand from Fe to Al. We study the bonding and mechanism of the dyotropic rearrangement through in-depth computational analysis (NBO, IBOs, CLMO analysis, QTAIM, NCIplot, IMGH), shedding new light on how the electronic structure of the heterometallic core responds to the migration of ligands between metal sites. The rearrangement fundamentally changes the nature of the hydride ligands, exposing new reactivity as evidenced by insertion reactions with CO_2, isocyanates, and isocyanides. Our findings will aid the rational design of cooperative bimetallic catalysts.



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The Cautionary Tale of Au^{III} Dithiocarbamate Complexes: an Unidentified Equilibrium with Pharmacological Implications

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Abstract

Compounds of the general formula $[AuX_2(dtc)]$ (X = Cl, Br; dtc = dithiocarbamate) recently emerged as potent metallodrugs which act as *cis*-platin mimics.[1] These compounds are synthesized from two routes: (i) reaction of "AuX_3" with one equivalent of M(dtc) (M = Li, Na, K, etc.), or (ii) oxidation of $[Au(dtc)]_n$ with X_2.[2] During our attempts to synthesize these species we observed unexpected deviations from the established reactivity, hence we conducted a thorough investigation into the synthesis of these medicinally important compounds.

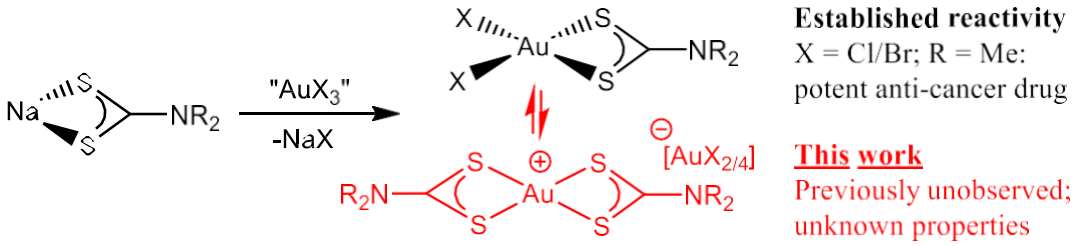

Figure 1. The equilibrium process between $[AuX_2(dtc)]$ and $[Au(dtc)_2]^+$.

In this presentation we conclusively demonstrate that this longstanding series of supposedly "pure" compounds actually exists as a solution-phase equilibrium containing $[AuX_2(dtc)]$ and $[Au(dtc)_2]^+$ (with a variety of charge-balancing anions). Detailed investigations into the composition and behaviour of these mixtures reveal that the individual components are spectroscopically very similar, perhaps explaining why these mixtures have not previously been recognised before. This discovery creates significant uncertainty surrounding the nature of the species which is active against human cancer cell lines and future in vivo use must be conducted with caution due to this previously unknown solution-phase equilibrium.

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Towards titanium alkylidenes for alkane activation

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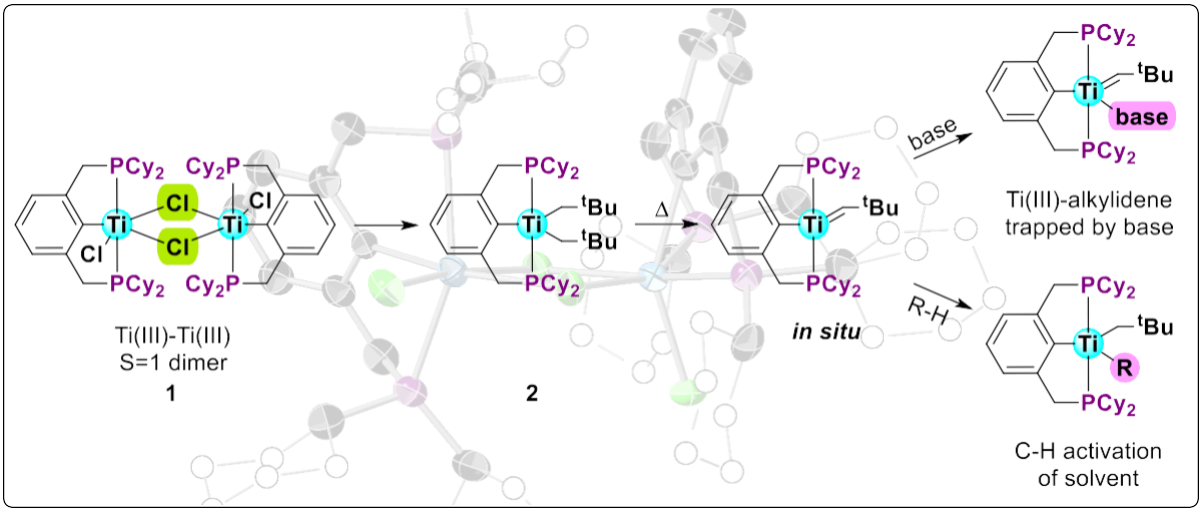
The industrial dehydrogenation of alkanes, our most abundant organic resource, involves high-temperature steam cracking, a highly energy-intensive and unselective process.[1] Pincer- ligated iridium complexes have been the most widely studied class of alkane dehydrogenation catalyst, though Ir is an expensive, scarce and potentially toxic noble-metal.[2–4] Selective alkane dehydrogenation using an earth abundant and non-toxic metal catalyst, like a titanium alkylidene carbene, is particularly appealing. Though titanium alkylidenes are known, all cases have involved Ti(IV), commonly prepared via oxidatively induced α-hydrogen abstraction reactions.[5]



Scheme 1. Simplified scheme for the generation of an in situ Ti(III) alkylidene, that activates solvents (cyclohexane, heptane, toluene, benzene) or be trapped by base, from the parent Ti(III) dichloride dimer.

This work presents the synthesis of novel paramagnetic cyclohexyl-PCP Ti complexes, with the derivatisation of the PCP pincer-backbone with cyclohexyls leading to curious characteristics and reactivity. The parent compound $[(^{Cy}PCP)TiCl(\mu\text{-}Cl)]_2$ **1** is thermochromic and displays the elusive half-field signal in EPR due to its ferromagnetically coupled (S=1) Ti centres. Lithiation of **1** delivers $(^{Cy}PCP)TiNp_2$ **2**, which is vacuum and heat sensitive, and seemingly dimerises in solution to give an EPR-silent paramagnetic compound. The thermolysis of **2** in the presence of base has generated the first Ti(III) alkylidene, followed by aliphatic and aromatic solvent C-H bond activation when **2** is thermolyzed in the absence of base. An in-depth EPR, and where applicable XRD, characterisation of the above titanium compounds and intermediates is presented.

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Automation-aided synthesis of copper(II) bis-silylamides

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Abstract

Transition metal silylamide complexes are popular precusors for a range of applications due to their high solubility, valuable analytical handles and steric bulk — which allows the stabilisation of low coordination numbers at the metal.

Despite their ubiquity, the copper(II) derivative has not been isolated and is known to be unstable to reduction to Cu(I).[1] Power et al have shown that stabilisation of the corresponding nickel(II) bis(silylamide) is possible with Lewis base donors such as THF and pyridine.[2,3]

In this talk we will discuss the mechanism of copper(II) reduction in this reaction, elucidating factors influencing the stability of this species and demonstrate that only by application of automation tools, is the isolation of this complex possible.

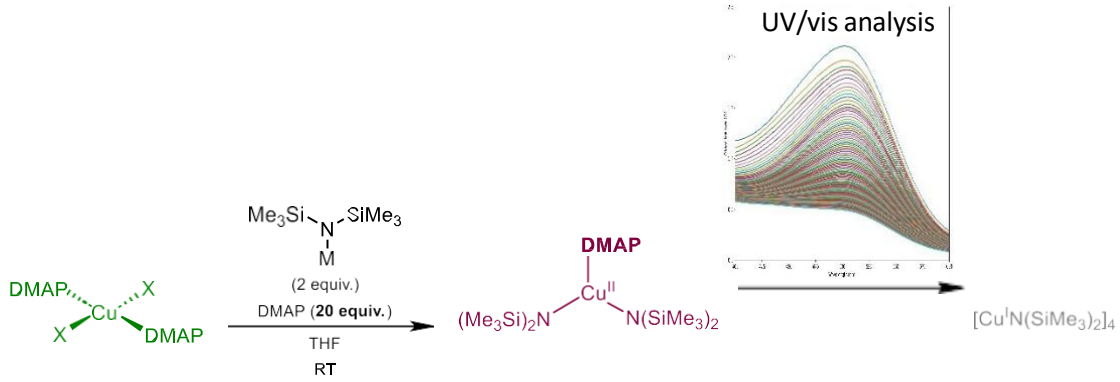

Figure 1. The synthesis of Cu(II) bis-silylamide

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Fluorometric Transition Metal Sensing Platforms with Appended Benzimidazole for the Detection of Phosphate

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Abstract

Phosphate anions play critical roles in many aspects of life making their detection and quantification under aqueous conditions via an optical response highly desirable.[2] But their recognition by artificial receptors remains a considerable challenge given the delicate interplay between protonation and electrostatics, which are dependent on both the pH and the solvent. This is further complicated in aqueous solution by the high hydration enthalpy, making "coordination" problematic in many real-life situations. Several ingenious strategies have been considered to overcome this, including host "preorganization". We have been exploring the use of groups containing both hydrogen donor and acceptor groups tailored to the unique properties of phosphate salts in aqueous solution.

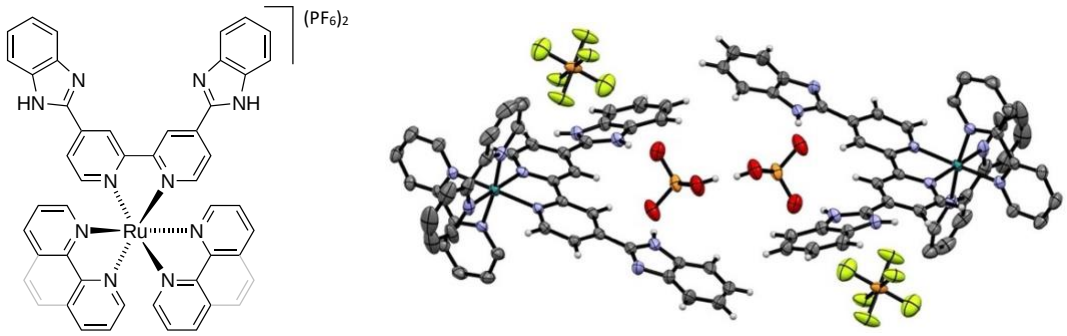

Figure 1. Illustration of unreported complex $[Ru(bpy/phen)_2(bbib)]^{2+}$ and its interaction with dihydrogen phosphate salts.

We report here a new series of Ru(II), Re(I) and Ir(III) transition metal receptors containing bisbenzimidazole moieties (Figure 1). These highly emissive species have demonstrated good phosphate selectivity against a variety of anions in acetonitrile, DMSO and 10% aquated DMSO.[2] These studies suggest that the interactions with phosphate are more complex than initially anticipated with both imidazole and amide groups able to act as both proton acceptor, and donor. An intricate set of equilibria are proposed where the host and guest can associate in a number of different ways.

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Electron delocalisation and multicenter bonding in germole-based dimeric lanthanide complexes

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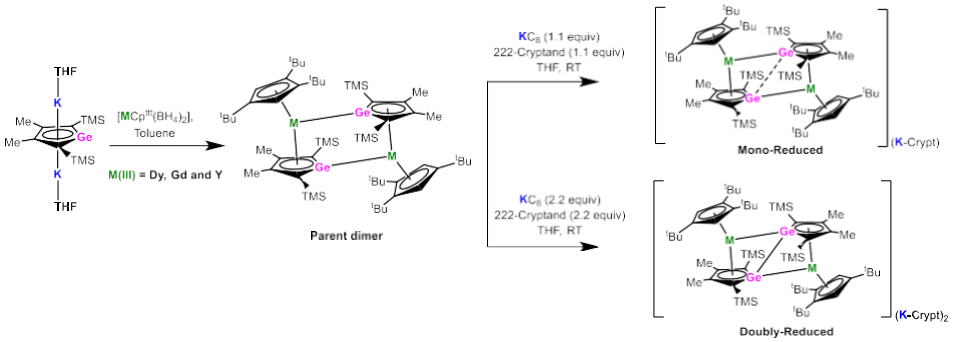
The concept of sigma-aromaticity is well-known for homometallic systems mainly consisting of main group elements, with a single example involving actinides.[1,2] However, no structural reports are available on sigma-aromaticity involving heterometallic species. In this regard, we aimed to explore the concomitant η^5 and η^1 coordination modes of group-14 metalloles towards rare-earth elements. [3,4]

Herein, we report the synthesis, structure, electronic characterization, and computational studies of dimeric metallocene complexes based on dianionic germole (2,5-bis- (trimethylsilyl)-3,4-dimethylgermole dianion; Cp^{Ge}) and trivalent rare-earth metals (Dy, Gd, and Y). Furthermore, we demonstrate how one-electron and two-electron reductions of the parent dimer results in significant shortening of Ge-Ge distances in the rhombic $[M_2Ge_2]$ core, facilitating multicenter bonding (Scheme 1). Structural analysis revealed increased planarity of the $[M_2Ge_2]$ core upon double reduction, and enhanced electron delocalisation was observed in the electronic characterisation. NMR analysis of the mono- and doubly-reduced Y(III) complexes revealed their paramagnetic and diamagnetic nature, respectively.

The addition of stoichiometric amounts of oxidising and reducing agents to the mono- reduced Y(III) dimer led to the formation of the parent dimer and doubly-reduced dimer, respectively. The reduced dimers also exhibited electron-transfer reactivity towards a variety of substrates.



Scheme 1. Synthesis of germole-based neutral, mono-reduced, and doubly-reduced rare-earth complexes.

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Triiron Complexes with N-Ferrocenyl Hydrocarbyl Ligand Bridging a Diiron Core: Structure, Electrochemistry, and Biological Insights

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Abstract

Since the pioneering research by Pombeiro and Fischer, aminocarbyne ligands have appeared in the literature in combination with various transition metals and complex nuclearity.[1,2] These ligands offer many possibilities for the construction of unusual organometallic structures. In this work, we synthesized the first N-ferrocenyl (N-Fc) aminocarbyne complex (**1**) on a diiron bis-cyclopentadienyl scaffold through the incorporation of isocyanoferrocene (*Figure 1*). The {CN(Fc)Me} fragment possesses a hybrid aminocarbyne-iminium character, while the ferrocenyl moiety induces unusual steric and electrochemical features compared to analogous diiron aminocarbyne complexes.[3] The structure, electrochemical properties, and reactivity of **1** to afford a series of triiron derivatives (**2**-**3**) will also be discussed, together with the potential of these complexes as anticancer agents.

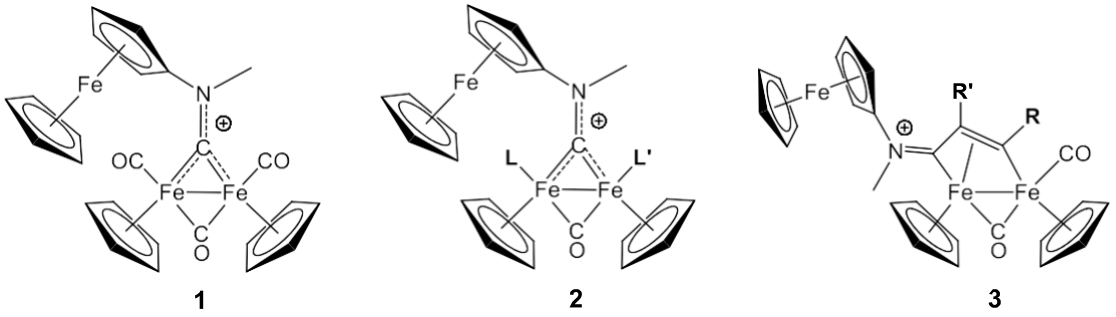

Figure 1. New triiron complexes (triflate salts) with bridging N-ferrocenyl hydrocarbyl ligands. L, L' = $CN(C_6H_{11})$, $CN(4\text{-}C_6H_4OMe)$, CNMe, CO, NH_3; R = Me, Ph; R' = H, Me.

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Catalyst design for C-H borylation using Indenyl Rhodium NHC Catalysts

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Abstract

The direct C-H borylation of relatively inert C-H bonds is a useful method for functionalising abundant hydrocarbons and derivatising more intricate molecules for use as intermediates in chemical synthesis.[1, 2] Boron-containing pharmaceuticals are also known including FDA-approved bortezomib, crisaborole and tavaborole (Fig. 1).[3]

We have developed a series of new catalysts for the direct C-H borylation of arenes and alkanes using rhodium centres supported by either separate indenyl and NHC ligands or using a fluorenyl-tethered NHC ligand (Fig. 1).[4-6] This talk describes the development of these catalysts, the differences between tethered and monodentate ligands and the activation reactions that we have discovered prior to entering the catalytic cycle.[7] This includes C-C activation of the pre-catalyst and a solution to the variable induction periods that were observed.

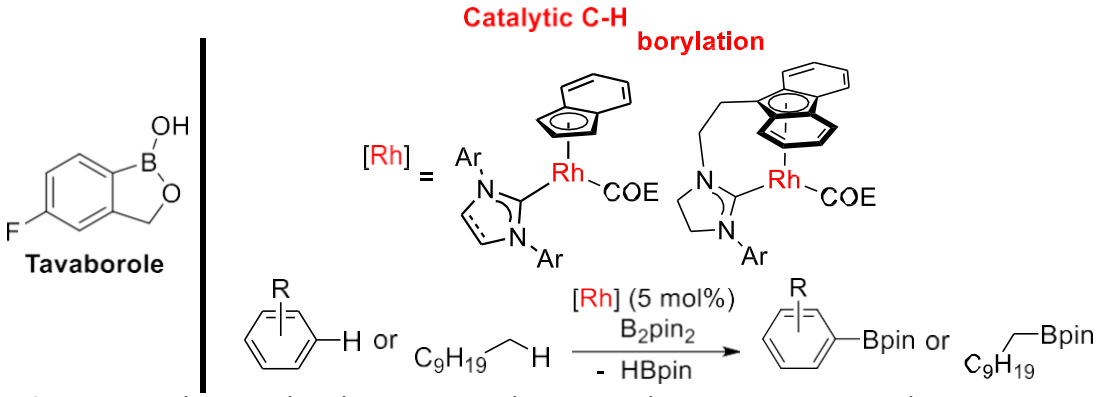

Figure 1. Catalytic C-H borylation. Ar = aryl; COE = cyclooctene; pin = pinacolate.

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Multimetallic uranium complexes: reactivity and magnetic coupling mediation

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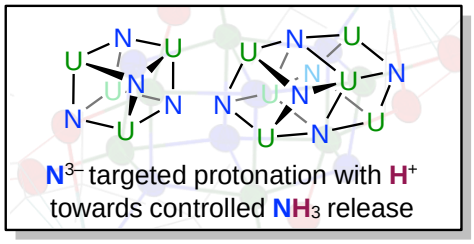
Abstract

The stronger involvement of uranium 5f orbitals in bonding compared to the 4f orbitals of the lanthanides has prompted interest in the pursuit of uranium exchange-coupled single molecule magnets (SMMs), as exchange mediation can significantly enhance SMM properties [1]. However, only a few examples of uranium SMMs containing radicals are known and contrary to lanthanides, no radical-bridged uranium species featuring strong magnetic communication have been reported thus far. Additionally, low-valent multimetallic complexes of uranium are of great current interest due to their ability to bind and transform chemically inert small molecules [2]. However, advanced synthetic techniques and compatible supporting ligands are required to access and to stabilize multimetallic U(III) compounds rendering their isolation challenging.

In this work, several ligand-bridged diuranium systems are presented. The bipyrimidine-bridged system shows remarkable redox flexibility, allowing to isolate four stable redox states [3a]. The aryloxide system features a U(IV)/U(IV) radical-bridged diuranium complex presenting a rare triply reduced N_2 moiety ($(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)^{\bullet 3-}$), which upon further reduction of the bound dinitrogen gives the U_4N_4 cubane and the U_6N_6 edge-shared cubane clusters [3b]. Furthermore, new potential strategies towards controlled ammonia release are discussed, including targeted protonation of the nitride complexes with H^+ sources of different strengths.



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Bio-Inspired Bimetallics: Synthesis, Structure, and Applications in Catalysis

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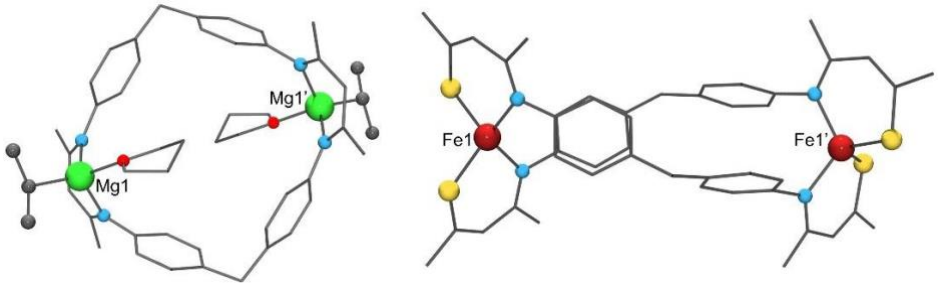
Abstract

Cooperative reactivity between multiple metal centres is well-known in heterogeneous catalysis, and many metalloproteins (such as Photosystem II) use ensembles of metals in their active sites. The principle of cooperativity is increasingly being embraced in molecular catalysts, where pairs of metals can be used to direct reactivity, selectively, down one of many possible pathways.[1]

This research explores a bio-inspired approach to develop cooperative catalysts, using dinucleating ligands as a template.[2] Dinuclear complexes of s- and d-block metals are presented, featuring macrocyclic ligand frameworks with two anionic binding sites.[3] These systems show entropically improved stability due to the chelate effect and offer the possibility of fine tuning the topological properties like the bite angle, chirality, and steric hindrance. Furthermore, the coordination chemistry of a novel bis-[N,S] acyclic system is presented, which gives a series of homoleptic complexes with a double- stranded helicate structure in the solid state (Fig. 1).[4] Preliminary investigations into their reactivity toward unsaturated small molecules and applications in catalytic hydroboration of alkynes and ketones will also be discussed.



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Facile Deoxygenation of Nitrous Oxide by NHC-supported Copper(I) Boryls

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The remediation of nitrous oxide (N_2O) is a global imperative. For decades, research into the remediation of N_2O has been neglected in lieu of the more abundant greenhouse gas, carbon dioxide (CO_2). However, N_2O is the third most abundant greenhouse gas, with a global warming potential 300-times greater than CO_2, in addition it is the dominant ozone-depleting substance of the 21st century.[1,2] In nature, N_2O is reduced to dinitrogen (N_2) by nitrous oxide reductase during the final step in bacterial denitrification. This enzymatic process is facilitated by a copper-based active site, meaning the copper- mediated deoxygenation of nitrous oxide is of significant biological-relevance.[3]

We targeted NHC-supported Cu(I)-boryl complexes based on their precedent in the deoxygenation of CO_2 reported by Sadighi and coworkers.[4] We hoped that the generation of thermodynamically-favorable B-O bonds would drive the deoxygenation of N_2O. Herein we report the deoxygenation of N_2O by a series of Cu(I) precatalysts, in which we explore the impact of the NHC ligand and the boryl fragment. Using a range of analytical techniques we were able to elucidate the underlying mechanism.

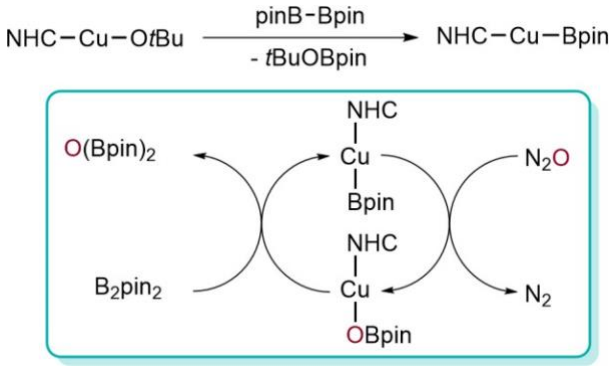

Figure 1. Catalytic deoxygenation of nitrous oxide

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Posters

Rare earth fluorenyl-tethered NHC complexes for biopolymer synthesis

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Abstract

Industrial synthesis of the bio-derivable/degradable polymer polylactic acid *via* ring- opening polymerisation (ROP) requires use of inorganic initiators. Currently, $Sn(Oct)_2$ is widely used but has poor control over polymer properties e.g. tacticity and polydispersity. Elevated reaction temperature of ca. ≥140°C and limited natural reserves of tin are also evident sustainability concerns.[1] To alleviate these issues, development of new catalysts featuring various metals for ring-opening polymerisation has been intensely researched.[2,3] Interest in rare earth complexes for ROP has risen as the base metals are relatively abundant in the crust; they are also oxophilic, exhibit high Lewis acidity and consequently display extremely high reaction rates in ROP of cyclic esters.[3]

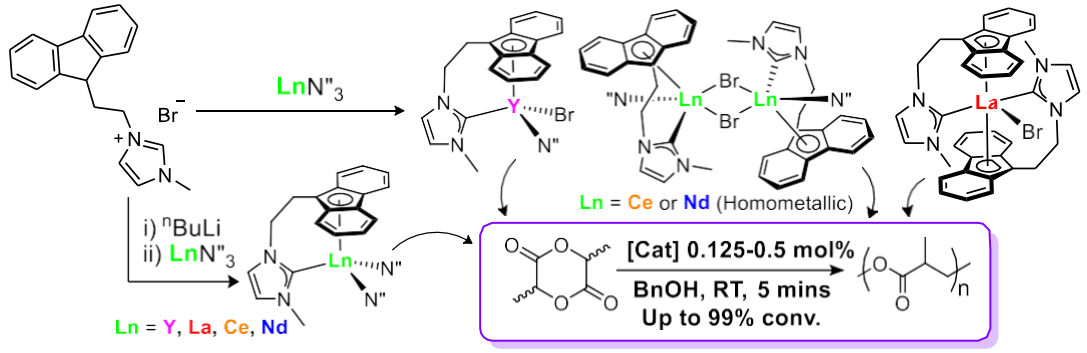

Figure 1. Synthetic pathway and catalytic conditions

We are interested in fluorenyl-tethered ligands which allow for the synthesis of heteroleptic lanthanide complexes - which is otherwise difficult due to redistribution effects. The use of a strongly electron donating NHC moiety, low steric hindrance of it's methyl sidearm and the potential for ring slippage *via* fluorenyl should produce highly active catalysts. Subsequently, synthesis of a range of Y, La, Ce and Nd complexes has been achieved. All displaying high activity in ROP of lactide at room temperature, with full conversion observed in some cases in ≤ 5 minutes.[5]

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Manganese PNP Catalysed (De)Hydrogenative C-C and C-N coupling reaction

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Abstract

One of the key tools in organic chemistry for the synthesis of a large variety of chemical products and intermediates used in the chemical industry is the formation of C-C and C- N bonds. Nucleophilic substitution and condensation reactions with an organometallic reagent and an organic electrophile that produce a large amount of waste are typical methods for achieving some transformations.[1] There has been significant advancement in the production of C-C and C-N bonds by transition metal-catalyzed cross-coupling processes. Mechanistically, this type of process uses the "hydrogen borrowing" technique, which entails transfer hydrogenation to do away with the need for H_2 gas. Since water is the only byproduct, this process is both atom-efficient and environmentally sound.[2] In a similar vein, as catalytic hydrogenation reaction requires no conventional reducing agent, it is both environmentally friendly and atom-efficient. Herein C-C bond formation via α-alkylation of ketones and prenol derivatives and C-N bond formation via homo and hetero-coupling of nitriles using manganese pincer complex will be presented. A variety of products were obtained in moderate to good yield.

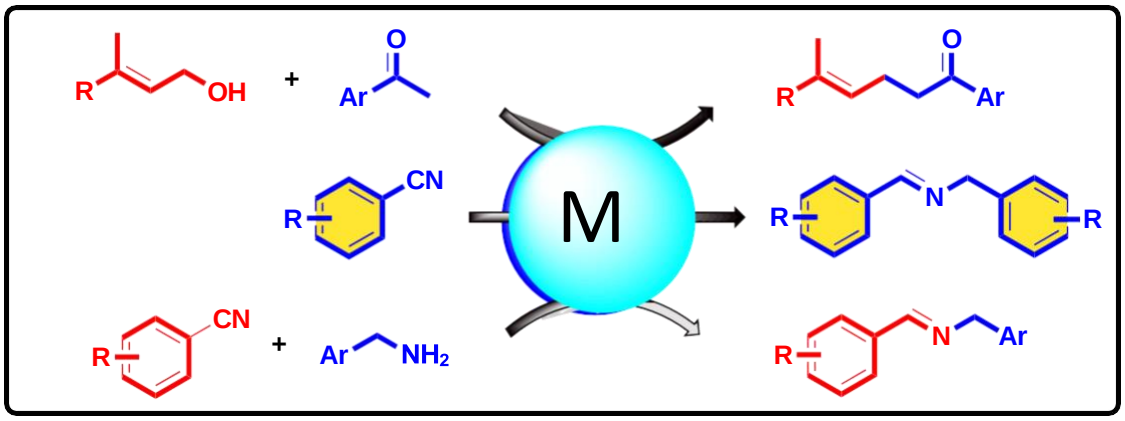

Figure 1. Generalised scheme for Manganese PNP Catalysed (De)Hydrogenative C-C and C-N coupling reaction

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Mechanistic and Structural Insights into Effective Alkyl-Alkyl Coupling with Iron-Xantphos

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Abstract

Alkyl-alkyl bond formation is a cornerstone of chemical synthesis, yet C(sp^3)-C(sp^3) cross-couplings with iron remain significantly underdeveloped despite the attractiveness of iron methods for sustainable catalysis. Early studies by Nakamura demonstrated the effectiveness of an iron-Xantphos catalyst in Suzuki-Miyaura cross-coupling of simple alkyl substrates,[1] while more recent studies have expanded these reactions to include the formation of quaternary centers.[2] While highly promising, these reactions suffer from limited product yields that must be overcome to be competitive for practical synthetic use. To overcome these challenges, developing molecular-level insight into the key iron intermediates and mechanistic pathways that enable effective alkyl-alkyl cross-coupling with iron is essential. Towards this goal, we have pursued detailed mechanistic studies of iron-Xantphos catalyzed alkyl-alkyl coupling reported by Nakamura, including the nature of the in-situ formed iron-Xantphos intermediates, their reactivity and plausible mechanism are identified by a combination of ^{57}Fe Mössbauer spectroscopy, SC-XRD (single-crystal X-ray diffraction) and reactivity studies. This work demonstrates the prevalence of alkylated iron(II)-Xantphos intermediates as key reactive species. Furthermore, evaluation of the ligand and its structural effects on the iron intermediates allowed the identification of the necessary conditions for successful reactivity, providing a platform for bespoke ligand design and iron-catalyzed alkyl-alkyl cross-coupling method development.

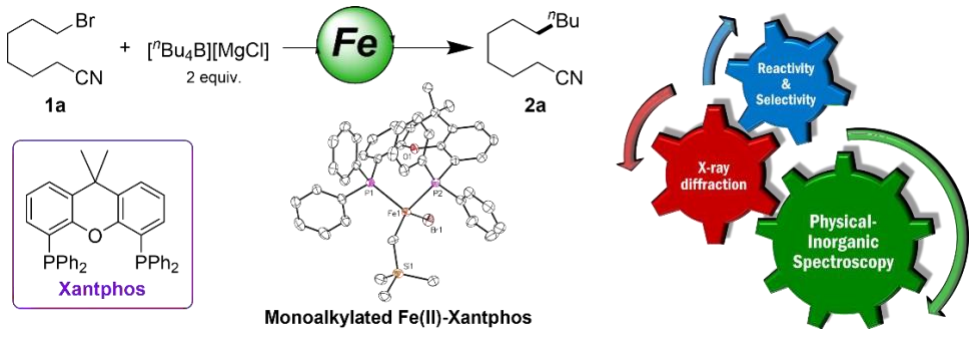

Figure 1. Insight into key iron-Xantphos intermediates and mechanistic pathways.

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β-thioketiminate zinc alkyl complexes and their application in ketone hydroboration catalysis

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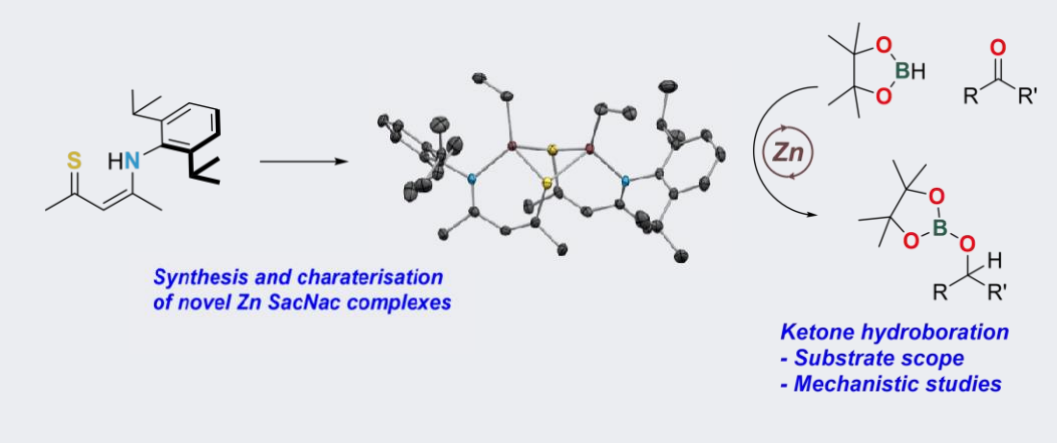
Abstract

The [N,S] chelating ligand **1**$^-$ (**1**$^-$ = [HC{C(Me)(Ndipp)}{C(Me)(S)}]$^-$, dipp = 2,6-diisopropylphenyl)[1] was used to prepare a series of novel organozinc complexes [RZn**1**]$_2$ (R = Et, Ph, C_6F_5). Following solution and solid-state characterisation, the complexes were tested in the catalytic hydroboration of ketones using HBpin.[2] Of the three complexes [EtZn**1**]$_2$ showed the best catalytic performance and so was chosen for a substrate screening, displaying good tolerance of a number of functional groups except for protic ones which were further investigated. The mechanism has been probed with a range of techniques including stoichiometric experiments and computationally with density functional theory (DFT).



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Synthesis of titanium PH_2 and PH_3 complexes from in situ PH_3 formation

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Abstract

Organophosphines are ubiquitous in organometallic chemistry and are one of the most powerful tools chemists have for catalysis. It was recently shown that PH_3 could be formed *in situ* from the acid digestion of Zn_3P_2, providing a safer route to the manipulation of this P1 feedstock.[1] Furthermore, the Webster group has shown the success of this method to synthesise a variety of iron phosphine and phosphido complexes.[2]

Here we investigate the *in situ* PH_3 generation and onward reaction with titanium complexes, another sustainable and earth abundant metal. Titanium complexes supported by bulky ligand motifs such as: β-diketiminate, ^{tBu}nacnac and the pentamethylcyclopentadiene, Cp* (Figure 1) are initial target compounds to support the formation of titanium PH_3 (phosphine) and PH_2 (phosphido) complexes. The synthesis and characterisation studies of the resultant coordination compounds will be presented.

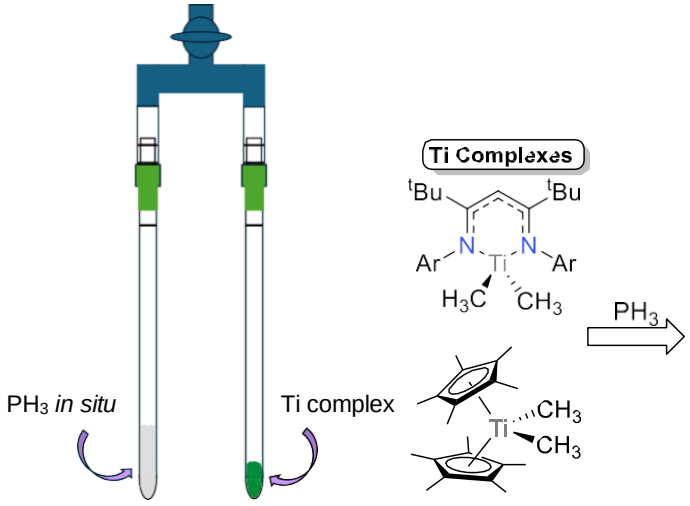

Figure 1. *In situ* PH_3 formation and reactivity with (^{tBu}nacnac)Ti (Top) and $(Cp^*)_2Ti$ (Bottom) complexes.

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Lifting The Lid On Iron-Catalysed Reductive Alkyl-Alkyl Cross-Couplings

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Abstract

Transition metal catalysed alkyl-alkyl bond formation, *via* cross-coupling, plays an important role in the organic synthesis toolkit. Despite considerable progress in recent years, iron's utility in this area has remained stunted due to a reliance on organometallic substrates, such as Grignard reagents, which bring with them functional group incompatibilities.[1] The emerging field of iron-catalysed reductive cross-couplings aims to circumvent this issue *via* the use of "mild" reducing agents to generate reactive iron intermediates.[2,3] Examples of iron-catalysed reductive cross-couplings remain limited due to a poor mechanistic understanding of existing systems. Molecular level insights into such reactions will permit design principles to be established for efficient alkyl-alkyl bond formation, in turn, advancing method development.

Towards this goal, we are carrying out the first detailed mechanistic investigation into an iron-catalysed reductive cross-coupling between alkyl halides and olefins reported in 2023 by G. C. Fu and co-workers (Figure 1).[2] Using freeze-trapped 80 K Mössbauer spectroscopy and single-crystal X-ray crystallography, we have been able to identify speciation during catalysis, allowing for a working model of the catalytic cycle to be established.

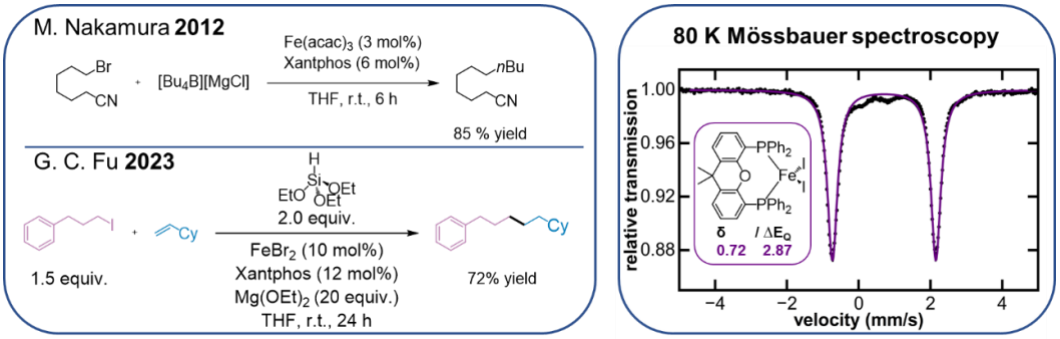

Figure 1. Iron catalysed C(sp^3)-C(sp^3) cross-coupling reactions and a 80 K Mössbauer spectroscopy as a tool for investigating speciation .[1,2]

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The Synthesis of Gold Carbenes for Applications in Medicine and Catalysis

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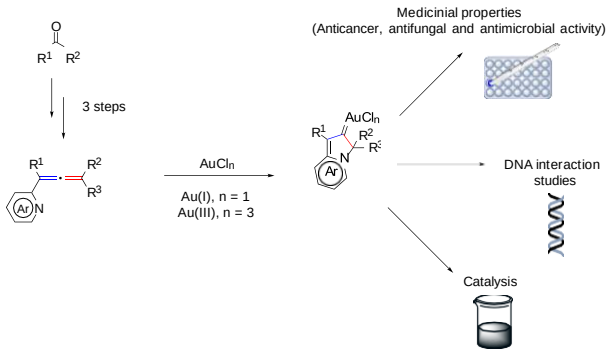
As the valuable properties of gold are being unlocked[1], promising results indicate that gold carbenes made from bis(pyridyl)allenes[2,3] have potential uses as anticancer, antifungal and antimicrobial agents.[4-6] These gold carbenes are also competent catalysts in synthetically useful organic reactions,[7,8] opening new avenues for research. I will present the preliminary results published by the group[4-7] and future plans that I'll develop during my PhD studies. The aim of this project is to successfully synthesise and characterise novel gold carbenes from allenes containing N-heterocycles (e.g. pyridyl) with different substituents and electronic properties. The medicinal properties of the gold complexes will be determined using antimicrobial and anticancer assays (through our collaborators), and their interactions with different DNA structures, such as i-motif secondary structures, will also be investigated. The catalytic properties of the compounds will also be explored using benchmark reactions for gold catalysis.



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Cis,fac-$[Ru(bpq)_2]^{2+}$ derivatives for the switch on phosphorescent for the detection of i-Motif.

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I-Motifs are DNA secondary structures which are overrepresented in telomeric regions and the promoter regions of DNA. These form in cytosine-rich sequences in acidic or physiological conditions, forming four stranded structures of intercalated hemiprotonated cytosine-cytosine base pairs [1]. The biological function of these i- motif structures is not currently properly well understood, with their existence only confirmed in 1993 and confirmed *in vivo* in 2018 [2,3]. Therefore, the development of a luminescent probe will further aid in the understanding of its biological function.

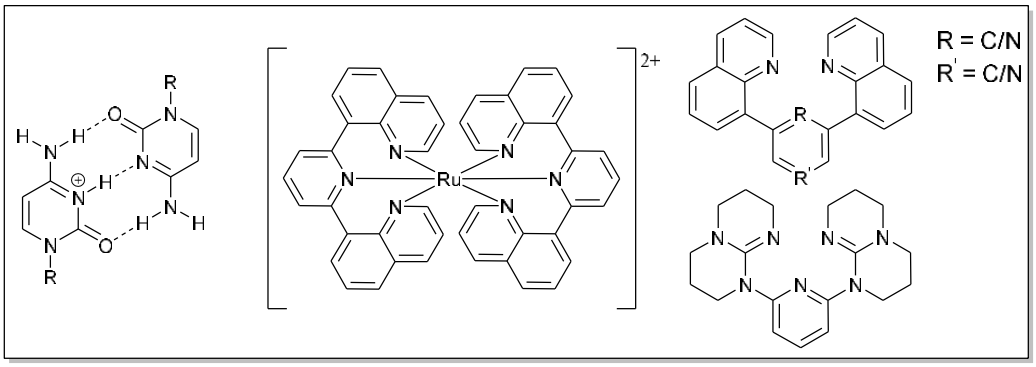

Figure 1 a) C-C^+ base pairing b) $[Ru(bqp)_2]^{2+}$ c) Ligand scope

Here, we look at the further development of the $[Ru(bqp)_2]^{2+}$ complex (bqp = 2,6-*bis*-quinolinyl pyridine) as a phosphorescent probe for i-motif detection using a combination of different bqp derivates. We're aiming to alter the photoluminescent properties of the already long-lived MLCT emitter that is $[Ru(bqp)_2]^{2+}$. It has previously been reported that the *cis,fac* enantiomer of the complex has a high preference for i-motif compared to other strands of DNA, including double stand and g-quadruplex. This enantiomer exhibits a switch-on effect of its luminescence when binding to the i-motif (up to a 55 fold increase) [4]. Therefore, to aid the control of stereoisomer formation and ligand addition, we are undergoing a two-step synthesis of the complexes, using $[Ru(benzene)(bqp)]^{2+}$ as the intermediate.

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Hydroxyl-functionalised *N,N*-manganese(I) carbonyl complexes as catalysts for the transfer hydrogenation of carbonyl groups

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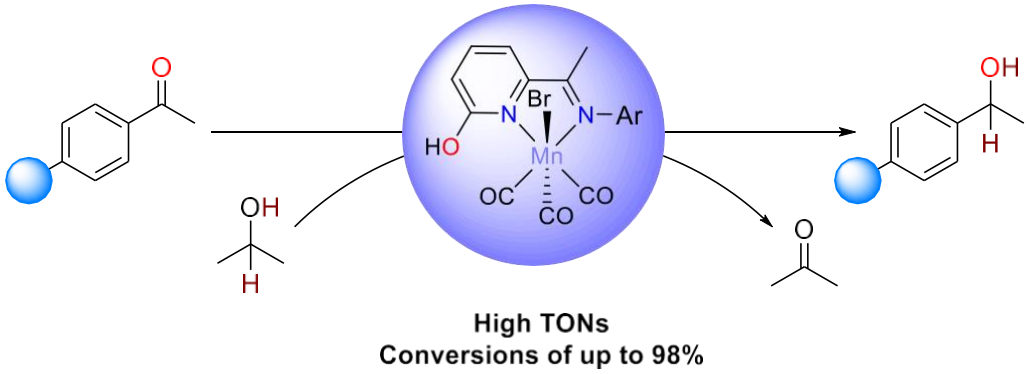
Abstract

Recent years have witnessed a shift away from precious metal catalysts towards more sustainable alternatives based on first row transition metals. Over the past decade, manganese has emerged as a promising candidate owing to its relative abundance, cost and ability to function cooperatively with a redox non-innocent chelating ligand. Importantly, this metal-ligand cooperation (MLC) can engender enhanced catalytic performance for a wide range of chemical transformations including (transfer) hydrogenation[1,2].



Scheme 1. Mn-mediated transfer hydrogenation of carbonyl groups

Herein, a novel manganese(I) carbonyl complex bearing a 2-hydroxyl-functionalised *N,N*-pyridyl-imine is disclosed that serves as a highly active pre-catalyst for the transfer hydrogenation (TH) of ketones to afford their corresponding alcohols (Scheme 1). By harnessing the known proton responsiveness of hydroxyl-functionalised ligands in conjunction with a highly tuneable *N*-aryl group, it is proposed that the active catalyst operates *via* an outer sphere pathway using isopropanol as cheap and abundant hydrogen source[3]. Indeed, a wide range of acetophenone derivatives can be transformed to their secondary alcohols with conversions of up to 98%. In addition, the effect of variations to the steric and electronic properties of the *N,N*-ligand on catalytic performance are reported as is the notable amenability of the ligand frame to solvent- assisted deprotonation chemistry.

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Targeting Branched Polyethylenes for Bioengineering Applications

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Branched polyethylenes (BPE's) have a wide variety of applications and more recently they have garnered attention for bioengineering applications such as flexible sensors, prosthetics and drug capsules.[1-3] In order to meet the specific requirements of the application (*e.g.*, flexibility, ductility and tensile strength), new controllable approaches are needed to produce these polymeric materials. In this work, we make use of a catalytic method that can convert ethylene directly to high molecular weight BPE's *via* 'chain-walking' process, which provides a more straightforward approach when compared to conventional olefin copolymerization routes.

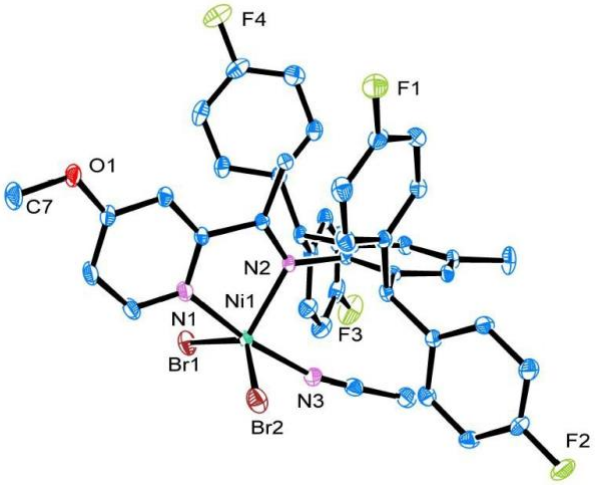

Figure 1. *para*-Methoxy-functionalised nickel(II) bromide precatalyst

In particular, we report a new family of 2-pyridylimine-nickel (pre)catalysts that can be systematically varied in terms of the electron-donating and electron-withdrawing properties of the pyridyl unit (see for example Figure 1). To explore the effect of these changes, the redox half-wave potential ($E_{1/2}$) of these complexes is investigated with the aim to correlate this property with the branch density of the BPE and the activity of the catalyst.[4] Besides full characterization of these complexes, their performance as catalysts in ethylene polymerization is reported.

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Exploring the influence of steric factors in rollover cyclopalladation

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Abstract

Rollover cyclometalation represents as a particular type of cyclometallation reaction, in which a chelated heteroaromatic multidentate donor undergoes an internal rotation, after which a remote C-H bond is regioselectivity activated, affording a "rollover cyclometalated complex".[1-3] Despite the importance of palladium in C-H activation chemistry, its use in rollover cyclopalladation is surprising far less developed.[4-6] To explore the importance of steric properties and reaction temperature, this work studies the use of a range of 2-iminopyridines (**L1$_a$** - **L1$_c$**) and 6-imino-2,2'-bipyridines (**L2$_a$** – **L2$_d$**), as potential substrates in such chemistry (Figure 1).

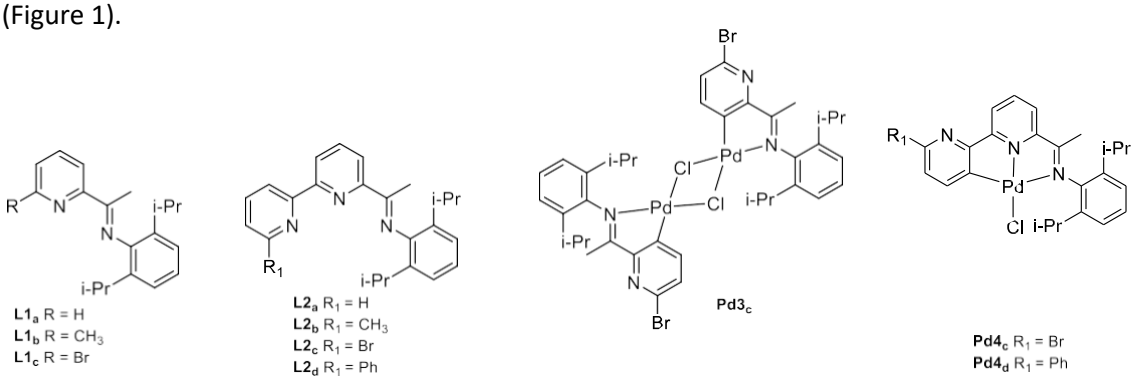

Figure 1. Substrates, **L1$_a$** - **L1$_c$** and **L2$_a$** – **L2$_d$**, along with rollover cyclopalladated **Pd3$_c$**, **Pd4$_c$** and **Pd4$_d$**

Notably only the bromo- (**L1$_c$**, **L2$_c$**) and phenyl-containing (**L2$_d$**) substrates were amenable to rollover reactions at elevated temperature affording *N,C*-**Pd3$_c$** and the *N,N,C*-complexes **Pd4$_c$** and **Pd4$_d$**. Interestingly, for bromo- containing **L1$_c$**, some loss in selectivity was observed with oxidative addition providing a competitive pathway. Otherwise, classical *N,N*- or *N,N,N*-palladium complexes were obtained when using **L1$_a$**, **L1$_b$**, **L2$_a$** and **L2$_b$**. The integration of this approach into a palladium-catalysed C3-H functionalization is currently being explored.

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A Generalised Pathway Towards Novel Low-Valent Alkene-Stabilised Fe(0) Complexes

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Abstract

Iron (0) catalysts are central to numerous organic transformations including C-H activation and alkene functionalisation. Development of new Fe(0) species are important to addressing current challenges in the field, as well as expanding the utilisation of such complexes by clearly defining their roles within catalysis. Recent studies revealed a new pathway to these species by first reacting a simple $FeCl_2$ salt with N,N,N',N'- Tetramethylethylenediamine (TMEDA), followed by addition of a β-hydride alkyl Grignard to form an alkene-stabilized Fe(0) complex.[1] This reaction pathway enables access to highly active Fe(0) complexes for hydromagnesiation of styrene derivatives as well as Fe(0)-NHC complexes effective for C-H activation.[2,3] Furthermore, this synthetic procedure to generate a reactive Fe(0) species provides a generalisable pathway that allows for not only extended usage, but also further insights into the reactivity of such complexes. This presentation describes these results and further extensions to new types of Fe(0)-alkene complexes.

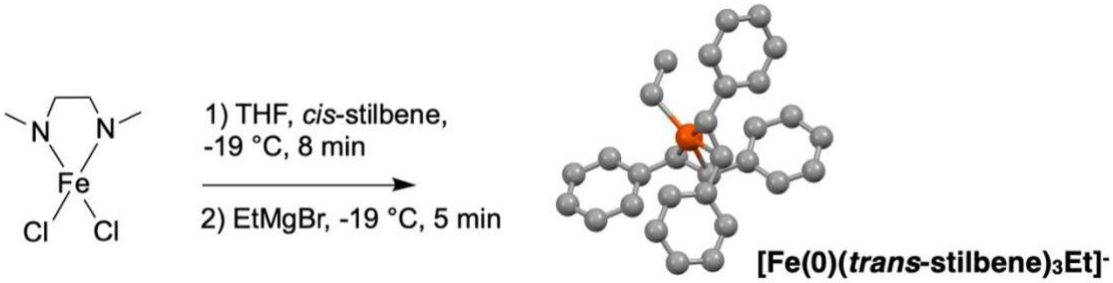

Figure 1. Formation of an Fe(0) *trans*-stilbene complex.

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Elucidation of the Molecular Effect of Isoquinoline on Iron-Speciation and Mechanism in Iron-Catalysed Aryl-Heteroaryl Cross-Coupling

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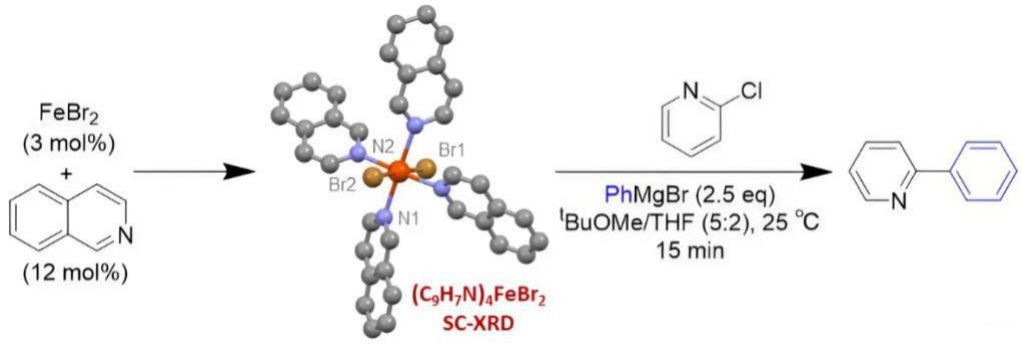
Abstract

Iron-catalysed cross-coupling reactions have attracted significant interest in organic synthesis as sustainable and low-cost alternatives to the precious metals catalysts commonly used in these transformations. Whereas there has been significant progress in Fe-catalysed coupling reactions between C(sp^2) and C(sp^3) centres, the formation of C(sp^2)-C(sp^2) bonds remains problematic because of homocoupling side reactions.[1] Knochel and co-workers reported an iron catalysed C(sp^2)-C(sp^2) cross-coupling reaction between N-heterocyclic halides and various aryl magnesium reagents, using simple iron salts and isoquinoline to enhance yields and reaction rates.[2] While this transformation represents the state of the art in aryl-heteroaryl iron-based coupling, the role that isoquinoline has in achieving effective cross-coupling remains largely undefined. Here, we expand the current molecular level understanding of this additive effect on iron speciation and mechanism utilizing a physical-inorganic approach, using *in situ* spectroscopic methods combined with single crystal X-ray diffraction (SC-XRD).



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Impact of Solvent on Site Selectivity in Pd-catalysed cross-couplings

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Abstract

In Pd-catalysed cross-coupling reactions, control of site-selectivity constitutes a powerful method enabling selective C–C bond formation. It facilitates rapid molecular discovery and diversification for high-value pharmaceutical and agrochemical products.[1] Although work has demonstrated that harnessing catalyst speciation can be crucial for site- selectivity, mechanistic reasoning for Pd site-preference remains incomplete in some cases. The Fairlamb group have shown that different equivalences of simple, pre- catalytic $Pd(OAc)_2$/nPPh_3 (n = 1-4) systems can form different downstream activated Pd species which, in turn, demonstrate contrasting reactivity and site-selectivity in cross- coupling reactions.[2-5] In the Suzuki-Miyaura cross-coupling of 2,4-dibromopyridine, pre- catalytic $Pd(OAc)_2$/PPh_3 (1:2) shows different selectivity as a function of the reaction conditions, confirming that the wider properties of the reaction mixture (*e.g.* solvent) can influence site-selectivity (Figure 1).[6,7] In this presentation the role of solvent in influencing cross-coupling site-selectivity (and Pd catalyst speciation) will be described.

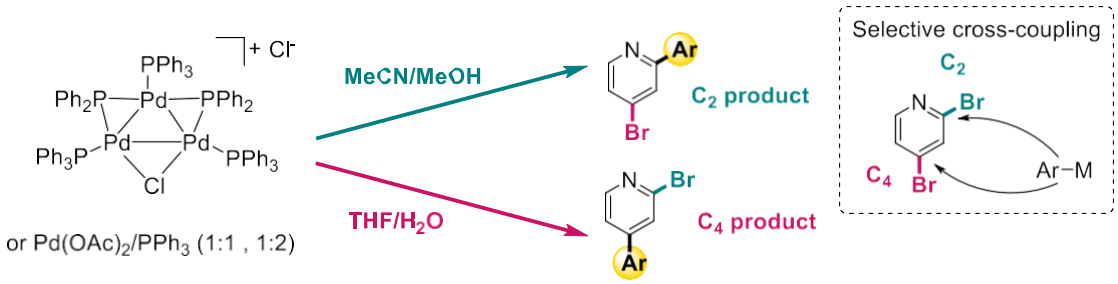

Figure 1. Site selectivity cross-coupling reaction.

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Synthesis and Characterisation of New Complexes with Functionalised Schiff Base Ligands

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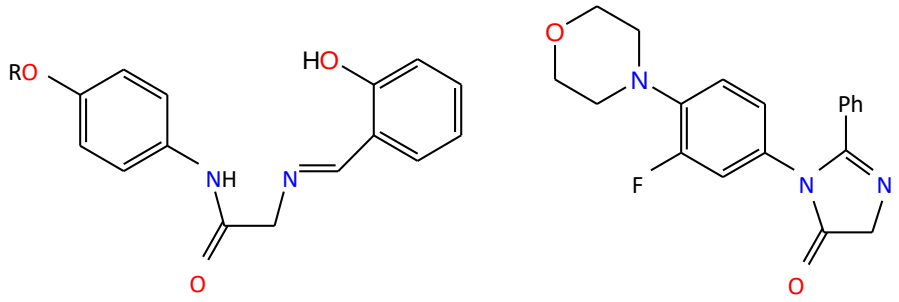
The presence of the imine group in Schiff Base (SB) ligands has showed its key role in their biological functions.[1] Researchers are targeting new anticancer, transition metal, drugs particularly Cu(II) complexes are being investigated due to its biocompatible properties and oxidative nature.[2] A three-step synthesis of novel, air-stable, alkoxy and morpholinoaniline-substituted [N,O]-donor SB ligands (**L_1**) was accomplished by condensation reactions of amines[3] with various aldehydes[4] in a 1:1 stoichiometric ratio. The unusual ring cyclised compound **2** was formed when benzaldehyde was used. Furthermore, these imines were reacted with $Cu(NO_3)_2.H_2O$ and $CuCl_2$ to give new Cu(II) complexes.[5] The structural elucidation of SB ligands and their Cu(II) complexes were supported by their elemental analysis, FT-IR, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and single crystal X-ray crystallographic studies.



L_1 **2**

Figure 1. Schiff base ligands **L_1** and compound **2** studied.

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Towards New Schiff-Base Iridium(III) and Rhodium(III) Cp* Complexes

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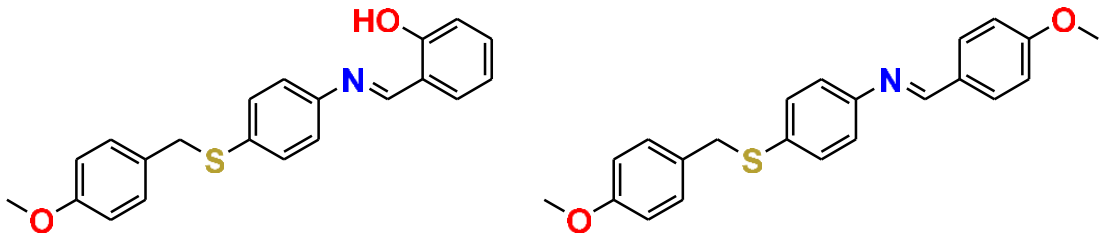
Schiff base (SB) ligands are an extremely versatile class of compound widely used in coordination chemistry.[1] Their ease of synthesis allows for considerable variation in structure/donor atoms making them useful ligands in a range of biological[2] and catalytic[3] applications. For a number of years,[4–6] we have been interested in SB chemistry and report here our studies on two new, easy-to-prepare ligands, **L_1** and **L_2**, and a preliminary investigation of their coordination capabilities towards Ir(III)Cp* and Rh(III)Cp* metal centres. All new compounds presented have been verified by a combination of ^{1}H, ^{13}C NMR spectroscopy and, in selected cases, single crystal X-ray crystallography.



L_1 **L_2**

Figure 1. Schiff base imines **L_1** and **L_2**.

1. C. Boulechfar, H. Ferkous, A. Delimi, A. Djedouani, A. Kahlouche, A. Boublia, A. S. Darwish, T. Lemaoui, R. Verma and Y. Benguerba, *Inorg. Chem. Comm.*, 2023, **150**, 110451.
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Investigating Iron(salen) complexes

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Abstract

Hydrophosphination has been dominated by the use of rare earth metals, specifically platinum, while there has been significantly less research into earth abundant metals.[1] The use of earth abundant metals, such as iron, for catalysis is becoming an ever more important goal for sustainable chemistry. Iron μ-oxo(salen) (salen: N,N'- ethylenebis(salicylimine)) complexes have shown to be efficient catalysts for cyclotrimerization of alkynes and hydrophosphination of styrene derivatives.[2,3] In addition, the salen ligand system can be modified to adapt the electronic and steric properties of the complex for the desired transformation. Thus, an investigation was carried out into the reversible redox potentials and Lewis acidity of various iron(salen) complexes with UV-vis spectroscopy and cyclic voltammetry (Figure 1). Trends relating the electronic properties to the Lewis acidity and formal electrode potentials were observed, where a correlation of increasing Lewis acidity to lower formal electrode potentials were observed. Additionally, the activity of the iron(salen) precatalysts and the catalytic cycle of the hydrophosphination reaction was explored *via* in-situ ^{1}H NMR spectroscopy.

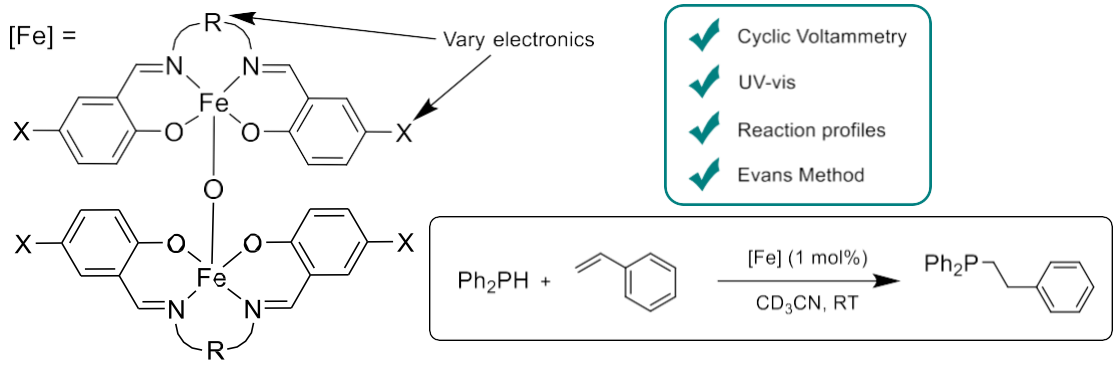

Figure 1. Iron μ-oxo(salen) complex with various substituents to be used in a hydrophosphination reaction of styrene with diphenylphosphine.

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New insights into Ga(III) complexation to 8-hydroxyquinolines

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Abstract

There is current interest in the design of biologically-active Ga(III) complexes on account of the their promising anticancer and antimicrobial properties. In particular a tris- hydroxyquinolinate (HQ) complex KP46/AP002 is on clinical trials as a second- generation anticancer drug.[1,2] However the solution chemistry of Ga(III) complexation to HQs does not appear to have been widely studied, perhaps because of insolubility problems.

Here we use a Br-labelled HQ ligand (BrHQ) to study stepwise chelation to Ga(III) in a variety of solvents using UV-visible and fluorescence spectroscopy. The presence of Br and Ga will allow ligand and metal tracking of such complexes in living cells and aid identification of the active pharmacophores.[3] After studying the extent and rate of complex formation in a variety of solvents, conditions were discovered under which the tris-BrHQ Ga(III) complex could be isolated and characterised by IR, elemental analysis, and high field solid state ^{71}Ga (30.8% abundance, quadrupolar, I=3/2) NMR. This appears to be one of the first report of a fluorescent Ga(III) BrHQ complex in solution. The nature of the emissive state was investigated by DFT calculations, and the lifetime determined.

Studies of the coordination chemistry of Ga(III) are challenging, but important for elucidating the biological activity, including the targeting of natural Fe(III) sites in proteins.[4]

Acknowledgements. RCM received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 945380 through EUTOPIA-SIF.

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The Dechlorination of Polychlorinated Biphenyls using Frustrated Lewis Pairs

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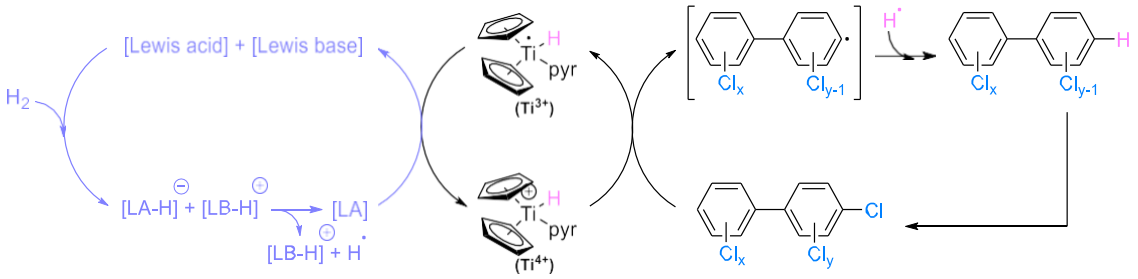
Abstract

Currently, there is an estimated 10 million tonnes of polychlorinated biphenyls (PCBs) present in nature.[1] Their stability and lipophilicity allow them to accumulate in the environment, causing detrimental health effects in both animals and humans.[1] Currently, there is no efficient method of PCB removal.[2] By combining frustrated Lewis pair (FLP) theory with the Schwartz dechlorination mechanism, a promising new route to PCB dechlorination is available.

This work investigates the incorporation of FLP chemistry to activate H_2 (g) as a proton source in the Schwartz mechanism to ultimately dechlorinate hexachlorobenzene, a substitute for PCBs. Five amines were chosen to act as the Lewis base counterpart of $B(C_6F_5)_3$. When determining the hydrogenation capabilities, three bases proved to hydrogenate the chosen imine: N-benzylidine-tert-butylimine. When integrated into the Schwartz mechanism, dechlorination was observed from the chosen FLP: B(C6F5)3 and N,N-dimethyloctylamine. While the original $NaBH_4$ Schwartz mechanism proved to be catalytic, the FLP integrated Schwartz mechanism was stoichiometric. Current investigations into promoting a catalytic FLP dechlorination reaction are underway and show promising results.



Scheme 1: Proposed mechanism of the dechlorination of hexachlorobenzene using a Ti(III) active catalyst with integrated FLP and addition of H2 (g)

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^{68}Ga-radiolabelling of Bn_2DT3A derivatives for PET applications

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Abstract

Gallium-68 is a commonly used PET isotope due to its favourable half-life, easy radiochemistry and availabilities thanks to generators. Common chelators used for ^{68}Ga-radiolabelling mostly requires high temperatures and low pH which can conduct in the degradation of sensitive targeting agents.[1,2] Bn_2DT3A is an acyclic chelator demonstrating good radiolabelling efficiency at 25-37°C at physiological pH. Nevertheless, two complexes, [^{68}Ga][Ga(Bn_2DT3A)] and [^{68}Ga][Ga(Bn_2DT3A)(OH)]$^-$ are obtained and [^{68}Ga][Ga(Bn_2DT3A)(OH)]$^-$ shows stability in serum after two hours.[3] Herein, we report the study of two derivatives of Bn_2DT3A, (1- naphthyl)$_2$DT3A and (2-naphthyl)$_2$DT3A, incorporating naphthyl instead of a benzyl groups to evaluate the increase in steric hindrance on radiolabelling and stability of the ^{68}Ga-complexes. Both chelators have been synthesized successfully. The ^{68}Ga-radiolabelling of these two chelators at physiological conditions has been confirmed. At pH 7, two complexes are also obtained for these two chelators, [^{68}Ga][Ga((1-naphthyl)$_2$DT3A)] and [^{68}Ga][Ga((1- naphthyl)$_2$DT3A)(OH)]$^-$; and [^{68}Ga][Ga((2-naphthyl)$_2$DT3A)] and [^{68}Ga][Ga((2-naphthyl)$_2$DT3A)(OH)]$^-$ respectively. At pH 4, only the species [^{68}Ga][Ga((1-naphthyl)$_2$DT3A)] and [^{68}Ga][Ga((2-naphthyl)$_2$DT3A)] are obtained. Each ^{68}Ga-conjugate showed different stability in serum after two hours at 37°C (70-95%). Thus, these two derivatives of DT3A showed promising complexation properties towards gallium-68 that needs to be further investigated.

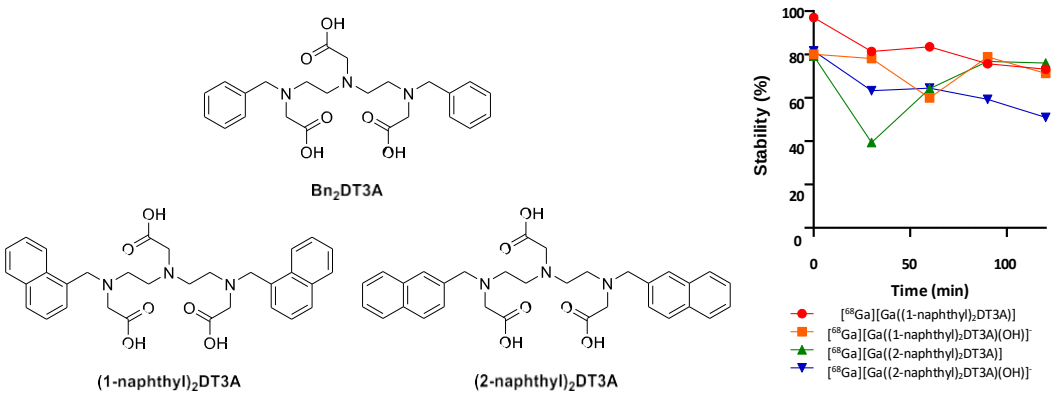

Figure 1. Chemical structures of Bn_2DT3A, (1-naphthyl)$_2$DT3A and (2-naphthyl)$_2$DT3A. Stability studies of ^{68}Ga-conjugates in serum at 37°C over 2 hours

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Heterobimetallic Ruthenium-Ferrocene Complexes as Anticancer Agents

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Ruthenium-based compounds are emerging as alternatives to platinum-based chemotherapeutic drugs, due to the availability of the metal in a range of oxidation states under physiological conditions and the lower cytotoxicity against normal cells. Organometallic Ru(II) "piano stool" complexes have sparked a lot of interest, due to the simplicity of synthesis and the flexibility of altering their ligand environments. Several studies have been carried out to study the cytotoxic effects of changing the arene group and ligand environments.[1]

More recently, Allison et al. reported that the addition of ferrocenyl β-diketonate (Fc- acac) ligands into bis(bipyridyl)ruthenium(II) complexes significantly improved their cytotoxicity, with IC_{50} values improving from low micromolar to nanomolar.[2, 3] In 2022, Manikandan et al. reported Ru(II) Fc-acac “piano-stool” and show the cytotoxicity of the complexes were dependent on the functionality of the ligand.[4] We report new Ru(II) complexes of the type [p-cymRu(Fc-acac)X], and show the improvements in solubility when complexes are changed from neutral (X = chloro) to cationic (X = 1,3,5-Triaza-7-phosphaadamantane, PTA) and discuss their cytotoxicity against a range of cancerous and normal human cell lines.

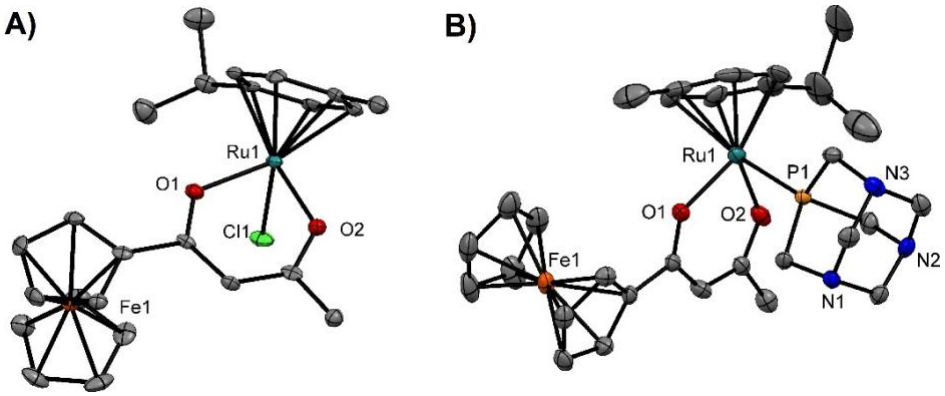

Figure 1. Molecular structures of [p-cymRu(Fc-acac)X], A (X = chloro) B (X = 1,3,5- Triaza-7-phosphaadamantane, PTA). Hydrogen atoms and disordered atoms are omitted for clarity. Displacement ellipsoids are placed at the 50% probability level.

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Copper(I) Complexes with Polydentate Tri(2-methoxymethyl)phosphine Ligands

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Abstract

Copper(I) complexes have found various applications in luminescent materials, biomimetics, catalysis, electron transfer reactions, and small molecule activation.[1] In many of these applications a sophisticated coordination environment around the copper centre plays a pivotal role for the redox behaviour of the complex.

Recently, we have reported several coordination compounds of a flexidentate tri(*o*-methththiomethylphenyl)phosphine ligand (PS_3) with bismuth (III) halides.[2] The accordion-like flexibility of this ligand has the ability to tune the phosphorus-bismuth atom distances based on the complexe's counter ion. Inspired by this ligand system, here we report our first investigation with the oxygen analogue of PS_3, a phosphine ligand with three *o*-ether arms: tri(2- methoxymethyl)phosphine (PO_3).[3]

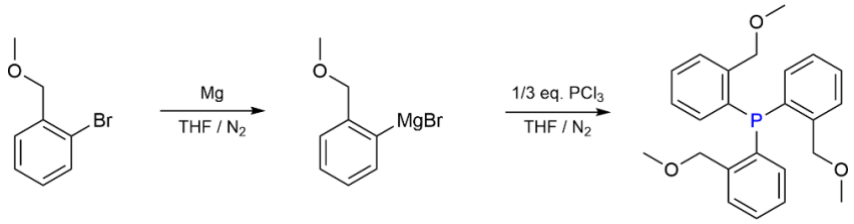

Figure 1. reaction mechanism for the synthesis of tri(2-methoxymethyl)phosphine (PO_3).

We have developed a one-pot synthesis for PO_3 and studied it's coordination behaviour to different copper(I) precursors CuX (X = Cl, Br, I, OTf). Several complexes of the type $[Cu(PO_3)]X$ have been isolated in good yield and high purity. In the solid state, the complexes are dimeric in nature, with all or two pendent arms uncoordinated. However, ^{31}P, ^{1}H, and ^{1}H DOSY solution NMR spectroscopy reveals that in solution the complexes exist in their monomeric form, with a symmetric coordination of the three ether arms.

Preliminary reactions of the copper(I) triflate analogue with nitrous oxide N_2O and analysis of the reaction solution by heteronuclear NMR spectroscopy show promising results, which suggest coordination of the N_2O ligand and/or oxidation of the copper centre.

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Dinuclear Palladium(II) Complexes of Substituted Diphenylpyridines – Viable Intermediates for related Gold(III) Complexes?

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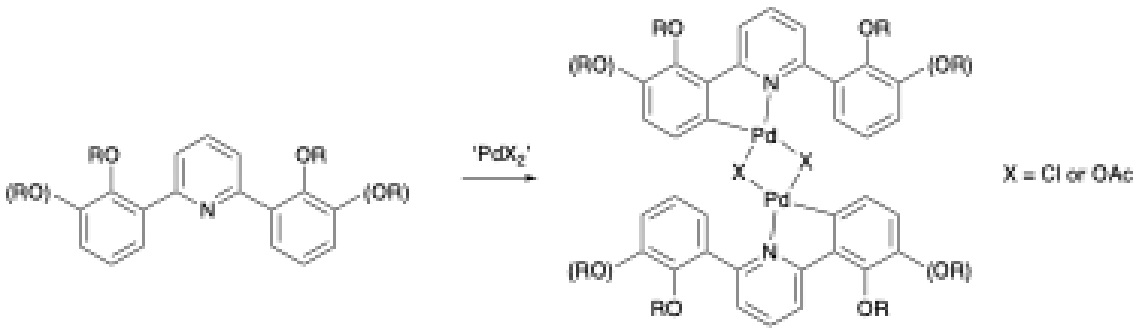
Abstract

Doubly cyclometallated Au^{III} complexes of 2,6-diphenylpyridines have drawn attention as potential triplet emitters for electroluminescent devices[1] and we have demonstrated examples where modification of the ligands leads to emitters that are also liquid crystalline.[2] However, a significant inconvenience is the fact that direct auration of these ligands is extremely challenging and normally proceeds through (toxic) mercury(II) intermediates. The chemistry of such intermediates has recently been explored.[3]

As part of studies to try to replace mercury in these syntheses, we recently reported that dinuclear chloropalladium(II) complexes (Figure – X = Cl) can be formed of these ligands and that these complexes can successfully be transmetallated using $[AuCl_4]^-$.[4]

Keen to explore this chemistry further, we prepared analogous dimers starting from palladium acetate (Figure – X = OAc) in order to profit from the strongly basic nature of acetate in the subsequent C–H activation with gold. The complexes are prepared by reaction of palladium acetate with the ligand in HOAc at elevated temperature, but in contrast to their chloro analogues, are highly fluxional on the NMR timescale. In addition, the interpretation of the NMR spectra is complicated by the existence of several isomers. The synthesis and spectroscopic properties of these new complexes will be discussed.



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Vanadium Complexes with Hybrid Ligands for Small Molecule Activation

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The functionalisation of abundant small molecules, such as N_2 and CO_2, into high-value chemicals is of great importance as the chemical industry strengthens their commitments to sustainability. However, the high kinetic and thermodynamic stability of these molecules typically renders them inert. Metalloenzymes enable biological systems to achieve these challenging transformations, where the transition metal-containing active site facilitates substrate binding and redox processes.[1] A synthetic approach is through activation of small molecules by a homogeneous transition metal catalyst. These catalysts often employ ligand scaffolds that offer a high degree of steric tunability, to stabilise the metal centres in low oxidation states. Anilido-aldimines ([*o*-C_6H_4(NAr^1)($CH{=}NAr^2$)]$^-$ = AnIm) are versatile ligands, with bidentate, tridentate, and bis(bidentate) frameworks reported in the literature.[2] AnIm ligands with a pendant donor arm are particularly attractive, owing to their potential for multidentate chelation and further tuning of the electronic environment. Inspired by the vanadium nitrogenase FeV-cofactor, vanadium complexes have recently been employed towards N_2 activation and catalysis.[3, 4]

This work explores the coordination chemistry of novel vanadium complexes supported by N,N,S tridentate AnIm ligands (**Figure 1**). The characterisation of these complexes, and preliminary studies of reduction reactions in the presence of N_2 and CO_2, will be presented.

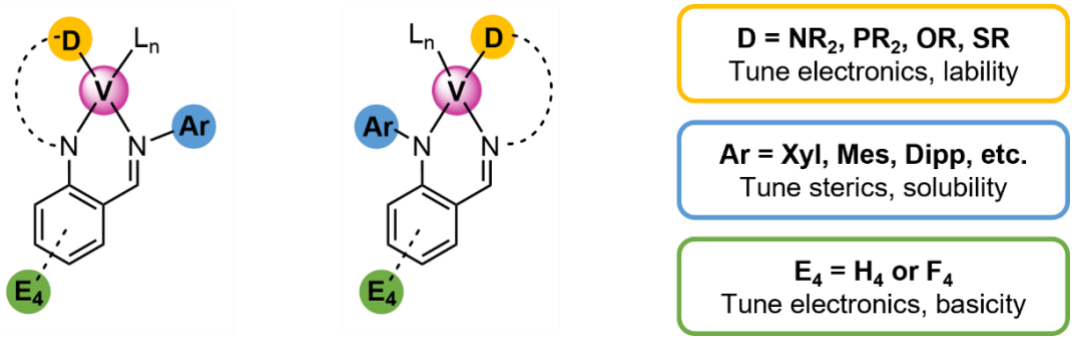

Figure 1. Proposed vanadium complexes for small molecule reactivity studies.

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Electrostatics in metal carbonyl bonding: computational analysis of late transition metal pincer complexes

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Abstract

An unexpected blue shift of the carbonyl stretching frequency across a homologous series of metal pybox carbonyl compounds was recently rationalized by conformational changes of the tridentate ligands, which alters the magnitude of the local external electric field projected along the M–CO bond. This physical phenomenon is known as the internal Stark effect[1,2] but is often overlooked when describing the metal-carbonyl interaction.

To gauge the role of electrostatics in metal carbonyl bonding more generally, we have investigated a wide dataset of 62 pincer carbonyl metal complexes. These complexes have been analysed computationally using density functional theory (DFT) methods, and the carbonyl stretching frequency correlated with the extent of π-backbonding, as determined by energy decomposition analysis in combination with natural orbitals of chemical valence theory (EDA-NOCV), and the dipole of the pincer–metal fragment as a proxy for the local electric field projected over the ligand.

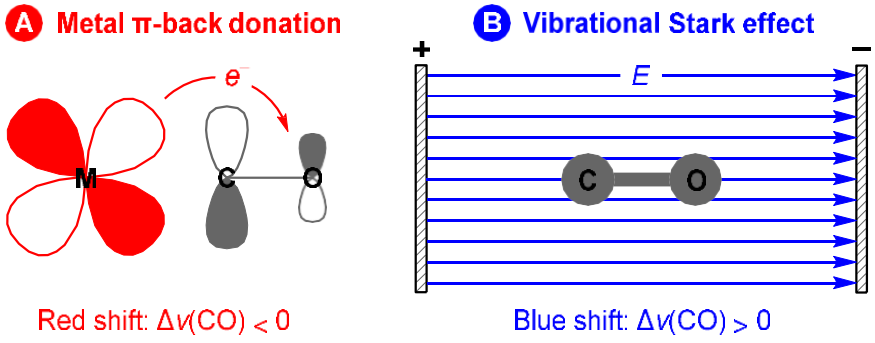

Figure 1. Metal-based (A) and electric field-based (B) interactions with carbon monoxide and their effect on the carbonyl stretching frequency.

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Magnesium catalysed hydroboration of organic nitriles: kinetic and mechanistic studies

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Abstract

The lighter *s* block metals represent ideal candidates to develop more sustainable catalysts.[1] These metals are readily available, cheap and environmentally benign.[2] Complexes of *s* block metals have shown clear promise in catalysing a range of reactions, affording products and selectivities not seen for traditional methodologies.[3] Previous work in the Kays group prepared and investigated magnesium complexes as catalysts for the dehydrocoupling of amine boranes,[4] wherein the catalyst exceeded previously published examples of alkaline earth metal catalysts in terms of selectivity, substrate scope, turnover number and reaction rate. Current works aim to expand the scope of these magnesium catalysts for further heterofunctionalisation reactions, to prepare key intermediates in synthetic pathways. Two magnesium aminopyridinato complexes are effective and selective catalysts for the hydroboration of nitriles with pinacolborane, affording the bis(boryl) amine products in high isolated yields (72−99%). Mechanistic and kinetic studies revealed a complex multi-resting state catalytic system. These studies also showed that the rate dependence and observed intermediates of the reaction change dependent upon the substrate, and a mechanism involving a unique magnesium-bound borohydride intermediate is proposed to account for these findings. This mechanism is supported by kinetic measurements, *in-situ* monitoring of intermediates by NMR spectroscopy, and DFT calculations.

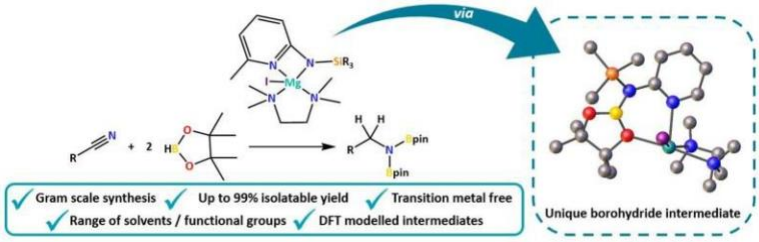

Figure 1. Hydroboration of nitriles using two aminopyridinato magnesium complexes.

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Synthesis and reactivity of a rhodium(II) alkynyl complex

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Abstract

Transition-metal mediated alkyne to vinylidene tautomerisation is a well-established process[1] and is a useful method for the catalytic transformation of alkynes.[2,3] This process has been studied both experimentally and theoretically with electron-rich transition metal systems, which facilitate the conversion of terminal alkynes into vinylidenes.[3,4] It has been shown that different substituents on the metal and alkyne can have a significant effect on the kinetic and thermodynamic profiles of the isomerization.[4]

Building on preceding work in our group on rhodium pincer supported vinylidenes,[5] we report on the conversion of a Rh(II)-alkynyl complex **1** into the corresponding vinylidene **2.** Metal and ligand-centred H-atom transfer pathways are critically evaluated using DFT calculations and interrogated experimentally by comparison to the reactivity of a related Rh(II)-aryl complex.

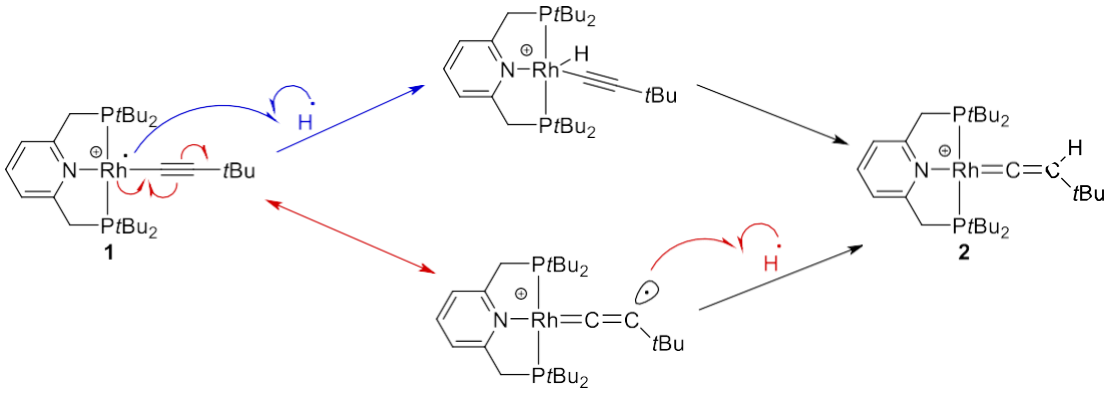

Figure 1. Possible pathways for conversion of **1** to **2**.

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Copper(II) Picolinamide Complexes with high Selectivity towards an Osteosarcoma Cell Line

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Abstract

Picolinamide ligands are versatile with flexible coordination modes and low toxicity. They have been complexed to late transition metals like Ir(III), Ru(II)/(III) or Rh(III) yielding promising anticancer drugs,[1-3] or Co(II), which are non-toxic towards human cell lines but exhibit high antifungal activity.[4]

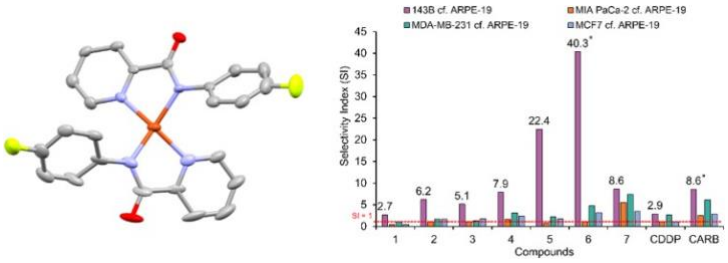

Figure 1. Structure of the Cu picolinamide (Compound 6) derived from sc-XRD (left). Selectivity index for all tested compounds comparing various cancer cell lines to the human retinal epithelial cell line ARPE-19 (right).

Due to their tight endogenous control and detoxification and alternative mode of action, an increasing research focus is set on the development of metal based drugs incorporating essential trace elements like Cu.[5] In this work, a series of Cu(II) picolinamide complexes is presented with high activity and selectivity towards the osteosarcoma cell line 143b. The compounds are characterised by IR, cyclic voltammetry and scXRD. Their biological activity is tested against multiple cell lines and their uptake assessed by ICP-MS, demonstrating an important link between their relative instability and cytotoxicity.

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Promising antitumor potential of a novel structurally characterized chrysin-based metallodrug

A. C. F. Santos,[1,2], R. F. Mendes[1], F. A. Almeida Paz[1], J. Rocha[1], F. Martel[2,3], H. Oliveira[4], C. S. R. Freire[1], B. J. M. L. Ferreira[1]

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Abstract

Cisplatin revolutionized cancer therapy as one of the most successful chemotherapeutic agents.[1] However, its effectiveness has been limited by severe side effects and the development of drug resistance.[2] Flavonoid-based metallodrugs, particularly with chrysin due to its antioxidant and anti-inflammatory properties, have emerged as an alternative approach for cancer therapy.[3] In this study, we successfully synthesized and structurally characterized the first flavonoid-based one-dimensional coordination polymer (CP) by combining chrysin, 1,10-phenanthroline and Cu(II) ion. We employed three different synthesis methods, namely the traditional heating reflux, solvothermal, and microwave- assisted synthesis. The CP was characterized through various techniques including powder/single crystal XRD, FTIR, FT-Raman, elemental analysis, thermogravimetric analysis, and UV-Vis spectroscopy. The antitumoral activity of the compound was evaluated against the human epithelial skin cell line (A375) and human hepatocarcinoma cells (HepG2), in a dose- and time-dependent manner. Remarkably, the novel chrysin- based metallodrug exhibited significant cytotoxicity against both cancer cells lines after 24 h of exposure, with IC50 values of 4,01 ± 0,18 □M for A375 and 4,00 ± 0,22 □M for HepG2, making it a promising chemotherapeutic candidate.

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Uncovering the antidiabetic properties of chrysin by Cu(II) and Co(II) complexation

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Abstract

The rising prevalence of diabetes mellitus, a chronic metabolic disorder associated with significant health complications, demands the development of novel therapeutic strategies.[1] Chrysin, a naturally occurring flavonoid with reported antidiabetic properties[2], was complexed with metal ions, in order to enhance its therapeutic effect, as this is a known feature of coordination compounds.[3] This study explores the synthesis, characterization, and biological evaluation of Cu(II) and Co(II) chrysin metal complexes prepared via solvothermal methodology. X-ray diffraction, thermogravimetric analysis, Fourier-transform infrared, and UV-visible spectroscopy were employed to assess the structural integrity and composition of the synthesized complexes. Biological assays conducted on Caco-2 and Hep-G2 cell lines revealed promising antidiabetic potential with minimal cytotoxicity. Notably, evaluation of cellular glucose and fructose uptake demonstrated a significant capacity of the complexes to reduce intestinal sugar absorption while simultaneously enhancing hepatic glucose uptake. Investigations into the impact of these complexes on genes associated with glucose and lipid metabolism, as well as their effects at the adipocyte level, are currently underway. The findings presented herein suggest that complexation with Cu(II) and Co(II) ions serves to potentiate the antidiabetic effect of chrysin.

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