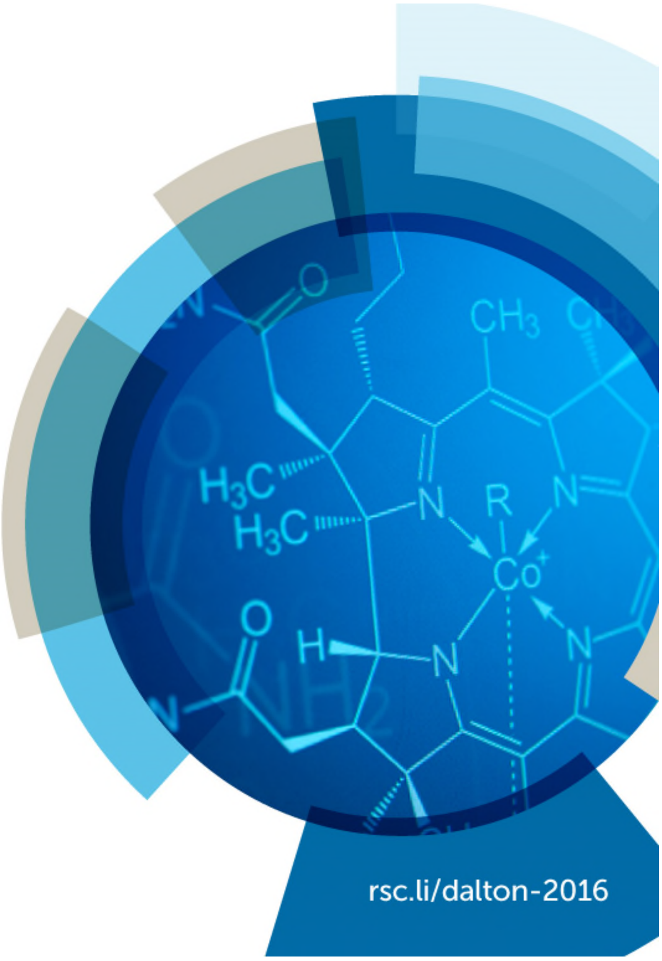
ROYAL SOCIETY OF CHEMISTRY

Dalton 2016

Joint Interest Groups Meeting



29-31 March 2016
University of Warwick, UK

rsc.li/dalton-2016

Programme and Oral Abstracts

Dalton 2016 Sponsors

ROYAL SOCIETY
OF CHEMISTRY

Dalton
Transactions

NETZSCH

WARWICK
Global
Research
Priorities

MATERIALS

GPE
SCIENTIFIC LIMITED

STREM UK & EIRE
CHEMICALS UK LTD
Supporting Research for Improved Quality of Life

Metal Catalysts for Organic Synthesis;
Phosphorus Ligands & Compounds;
MOCVD, CVD & ALD Precursors;
Nanomaterials

www.strem.co.uk

KNF

5+5+5 at Dalton 2016

The 5+5+5 competition was designed to initiate new collaborations, by bringing together teams of three inorganic chemistry researchers based in Canada, US and the UK (one in each country). The five winning teams will attend and present at Dalton 2016. The 'Headline' 5+5+5 session will feature speakers from each team, who will each present the intended synergies of their team, as well as their own science. The two other members of each team will present within the Interest Group parallel sessions.

Engagement

Dominic McDonald (Programme Manager for Outreach, RSC)

Challenging Attitudes: Engaging the Public with Chemistry

The Public Attitudes to Chemistry research which was published in June 2015 was the first ever national study of what people think about chemistry, chemists and chemicals. Dom will present some of the key findings, invite you to explore the ways that they confirm or challenge our assumptions, and ask how this new information changes the way that we reach out to different audiences.

Sarah Newton

European Young Chemists' Network

The European Young Chemists' Network. EYCN is the younger members division of the European Association for Chemical and Molecular Sciences (EuCheMS). Every chemist under 35 within the EuCheMS framework is part of EYCN.

Publishing your chemical sciences research

Dr Andrew Shore, Editor of *Dalton Transactions*, will present an overview on how to get your research published in scientific journals and share hints and tips to help you through the publication process involved at the Royal Society of Chemistry. He will also talk about publication ethics, how you can promote your own work and the evolving Open Access landscape. At the end of the presentation there will be an open Q & A "Ask the Editor" session.

Twitter users:
please use #Dalton2016 to tweet about the meeting

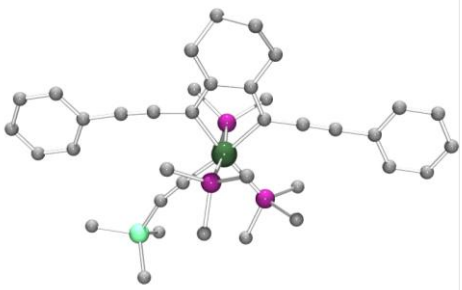
The oral abstracts appear in the following order:
Plenary Lectures/Prize Winner Lectures
5+5+5 Lectures
Coordination Chemistry
Main Group
Reaction Mechanisms
Inorganic Biochemistry
Solid State
Poster abstracts available at http://www2.warwick.ac.uk/fac/sci/chemistry/news/events/dalton2016/

Synthesis and Photophysical Properties Rhodacycles Formed via Unusual Diyne Couplings

Todd B. Marder
Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074-Würzburg, Germany. e-mail: todd.marder@uni-wuerzburg.de

---

Metallacycles featuring bipyridine or 2-phenylpyridine and related ligands have been of much recent interest due to their photophysical properties, triplet emissions, and thus various applications including OLEDs. However, relatively few studies of the the photophysical properties of all-carbon dibenzometallacyclopentadiene analogues were reported and none had appeared on simple metallacyclopentadienes before our work. The talk will address unusual high-yield coupling reactions of diynes at rhodium(I) centres, and the interesting photophysical (fluorescence or phosphorescence) behaviour of the highly luminescent metallacyclic products of such reactions.



References

1. J. P. Rourke, A. S. Batsanov, J. A. K. Howard, T. B. Marder, *Chem. Commun.*, 2001, 2626.
2. A. Steffen, M. G. Tay, A. S. Batsanov, J.A. K. Howard, A. Beeby, K. Q. Vuong, X.-Z. Sun, M. W. George, T. B. Marder, *Angew. Chem. Int. Ed.*, 2010, **49**, 2349.
3. A. Steffen, R. M. Ward, W. D. Jones, T. B. Marder, *Coord. Chem. Rev.*, 2010, **254**, 1950.
4. A. Steffen, R. M. Ward, M. G. Tay, R. M. Edkins, F. Seeler, M. van Leeuwen, L.-O. Pålsson, A. Beeby, A. S. Batsanov, J. A. K. Howard, T. B. Marder, *Chem. Eur. J.*, 2014, **20**, 3652.
5. A. Steffen, K. Costuas, A. Boucekkine, M.-H. Thibault, A. Beeby, A. S. Batsanov, A. Charaf-Eddin, D. Jacquemin, J.-F. Halet, T. B. Marder, *Inorg. Chem.*, 2014, **55**, 7055.

Title: Using Ligand Design and Donor-acceptor Stabilization to Access New Bonding Modes and Functional Nanodimensional Materials.

Eric Rivard, Anindya Swarnakar, Melanie Lui and Christian Hering-Junghans
Department of Chemistry, University of Alberta, 11227 Saskatchewan Dr., Edmonton, Alberta, Canada T6G 2G2; e-mail: erivard@ualberta.ca

---

Over the past few years, our group has advanced the concept of donor-acceptor stabilization, whereby reactive entities such as the parent inorganic methylenes (EH_2; E = Si, Ge and/or Sn,[1] ethylenes (H_2EEH_2)[2] or iminoborane HBNH[3] have been trapped in between a Lewis base and a Lewis acid. In this presentation, recent developments in this field will be discussed including the use of these complexes to afford nanodimensional materials with useful properties (e.g. luminescence) under mild conditions.[4]

1) (a) E. Rivard, *Dalton Trans.* 2014, **43**, 8577. (b) E. Rivard, *Chem. Soc. Rev.* 2016, DOI: 10.1039/c5sc00365b

2) S. M. I. Al-Rafia, M. R. Momeni, M. J. Ferguson, R. McDonald, A. Brown and E. Rivard, *Organometallics* 2013, **32**, 6658 and reference therein.

3) A. K. Swarnakar, C. Hering-Junghans, K. Nagata, M. J. Ferguson, R. McDonald, N. Tokitoh, and E. Rivard, *Angew. Chem., Int. Ed.* 2015, **54**, 10666.

4) T. P. Purkait, A. K. Swarnakar, G. De Los Reyes, F. A. Hegmann, E. Rivard, and J. G. C. Veinot, *Nanoscale*, 2015, **7**, 2241.

Synthetic single-site iron nitrogenases

Jonas C. Peters (jpeters@caltech.edu)
Bren Professor of Chemistry, Division of Chemistry and Chemical Engineering,
California Institute of Technology

Nitrogen reduction to NH_3 is a requisite transformation for life. While it is widely appreciated that the Fe-rich cofactors of nitrogenase enzymes facilitate this transformation, how they do so remains poorly understood. A central element of debate has been the site(s) of dinitrogen coordination and reduction. The synthetic inorganic community placed an early emphasis on Mo because Mo was thought to be an essential element of nitrogenases, and because pioneering work by Chatt and his coworkers established that well-defined Mo model complexes could mediate the stoichiometric conversion of coordinated N_2 to NH_3. Catalytic N_2-to-NH_3 conversion was later demonstrated using a molecular Mo catalyst by Schrock.

It is known, however, that Fe is the only transition metal essential to all nitrogenases, and recent biochemical and spectroscopic data have implicated Fe as the likely site of N_2 binding in FeMo-co. These observations motivate a search for functional Fe catalysts. In this talk, I will discuss a tris(phosphine)borane supported Fe complex that catalyzes the reduction of N_2 to NH_3, wherein >40% of the H^+/e^- equivalents are delivered to N_2. This catalytically functional model system establishes that a single Fe site may be capable of stabilizing the various N_xH_y ligands generated en route to NH_3 formation. Geometric flexibility at Fe imparted by a hemi-labile axial donor may be critical for catalysis, and the interstitial C-atom recently assigned in the nitrogenase cofactor may serve a similar hemi-labile role. To further build on this idea, I will discuss more recent data for various Fe complexes aimed at improving the catalysis and providing new mechanistic data that is pertinent to the catalysis.

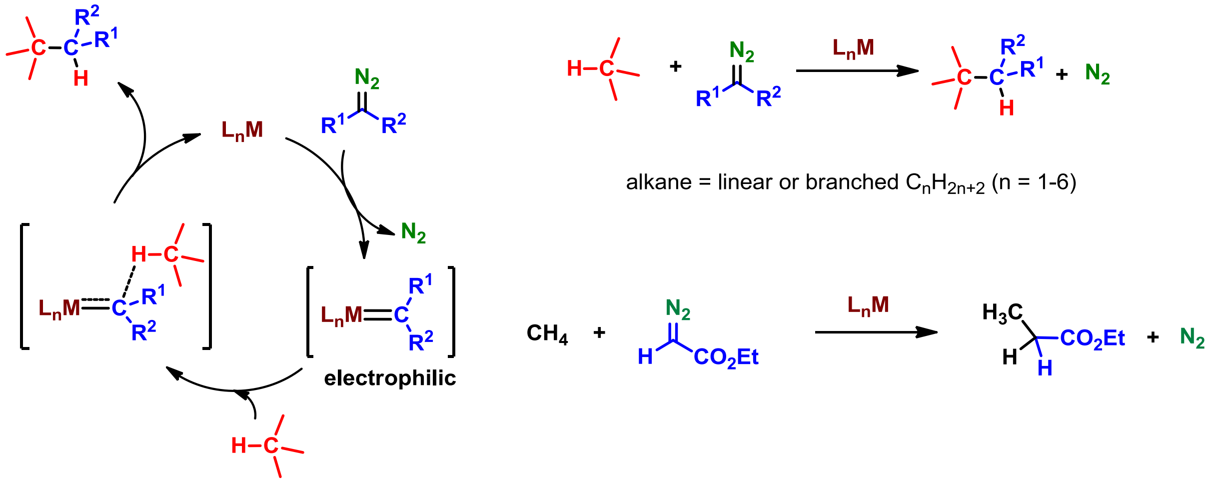
Title: Overcoming the alkane inertness toward C-H functionalization

Pedro J. Pérez

Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO- Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, 21007, Huelva (Spain). e-mail:perez@dqcm.uhu.es

The metal-catalyzed diazocompound decomposition and subsequent carbene transfer to organic substrates constitutes a powerful tool in organic synthesis.[1] It takes place through the formation of a transient metallocarbene intermediate (Scheme) that acts as an electrophile and therefore reacts with an added nucleophile transferring the carbene moiety. The strategy has been applied in the last decades with success to a variety of substrates. Among them, saturated bonds such as C-H entities have also been employed, albeit their low nucleophilicity have precluded its general functionalization.[2]

In this contribution the development of group 11 metal-based catalysts, based on a rational design model, for the catalytic functionalization of unreactive alkanes C_nH_{2n+2} is presented. It contains a perspective of the overall process that has led to the ultimate conversion of methane into ethyl propionate using ethyl diazoacetate as the carbene source.[3] In addition, a study on the relative reactivity of a series of C-H bonds of alkanes will also be presented.



---

[1] (*a*) M. P. Doyle, R. Duffy, M. Ratnikov and L. Zhou, *Chem. Rev.,* 2010, **110**, 704-724; (*b*) M. P. Doyle, M. A. McKervey and T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley & Sons: New York, 1998**.**

[2] A. Caballero, M. M. Díaz-Requejo, M. R. Fructos, A. Olmos, J. Urbano and P. J. Pérez, *Dalton Trans*, 2015, **44**, 20295.

[3] A. Caballero, E. Despagnet-Ayoub, M. M. Díaz-Requejo, A. Díaz-Rodríguez, M. E. González-Núñez, R. Mello, B. K. Muñoz, W. Solo Ojo, G. Asensio, M. Etienne and P. J. Pérez, *Science*, 2011, **332**, 835.

Polar and Magnetic Oxides in the $A_2BB'O_6$-Type Corundum Derivatives

Martha Greenblatt

Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey,
610 Taylor Road, Piscataway, NJ 08854, USA
greenbla@rci.rutgers.edu

Polar and magnetic oxides are fundamentally and technically of great importance, but difficult to prepare. Recently, the corundum-derived $A_2BB'O_6$ oxides with unusually small A-site cations attracted much interest.[1-4] The crystal structure of $A_2BB'O_6$ allows the incorporation of strong magnetic transition metal ions on all cation sites for magnetic and potentially multiferroic, or magnetoelectric behavior. Therefore, it appeared promising to design room-temperature polar ferri- or ferro-magnets by composition modulation of $A_2BB'O_6$ phases. So far, we have successfully prepared a series of polar and magnetic oxides in this corundum-derived family via high pressure and temperature syntheses, and systematically investigated the relationship between the crystal, magnetic, electronic structure and physical properties. The discovery of polar $LiNbO_3$-type ($R3c$) Mn_2FeMO_6 (M = Nb, Ta)[1] predicted new polar structures with second-order Jahn-Teller distorted ions (such as Nb^{5+} and Ta^{5+}, d^0) at the B'-site and small ions at the A-site of $A_2BB'O_6$, which has been confirmed by the preparation of Zn_2FeTaO_6.[2] In the Ni_3TeO_6-type ($R3$) ferrimagnetic semiconductor Mn_2FeMoO_6 ($T_C \sim 340$ K),[3] the structure polarization is, for the first time, found to be stabilized by the spin structure at high pressure, while at ambient pressure, a new spin structure with lower energy state induces an unusually low-temperature (~400 - 550 K) cationic rearrangement, providing a new mechanism to tune the physical properties at the atomic-scale under mild conditions in bulk oxides. In polar ferromagnetic Mn_2FeWO_6 with the Ni_3TeO_6-type structure the charge and size difference between Fe^{2+} and W^{6+} leads to a fully ordered Fe/W lattice .[4] These findings open a new path to design polar and potentially multifunctional useful materials.

References

1. Li, M.-R.; Walker, D.; Retuerto, M.; Sarkar, T.; Hadermann, J.; Stephens, P. W.; Croft, M.; Ignatov, A.; Grams, C. P.; Hemberger, J.; Nowik, I.; Halasyamani, P. S.; Tran, T. T.; Mukherjee, S.; Dasgupta, T. S.; Greenblatt, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 8406.
2. Li, M.-R.; Stephens, P. W.; Retuerto, M.; Sarkar, T.; Grams, C. P.; Hemberger, J.; Croft, M. C.; Walker, D.; Greenblatt, M. *J. Am. Chem. Soc.* **2014**, *136*, 8508.
3. Li, M.-R.; Retuerto, M.; Walker, D.; Sarkar, T.; Stephens, P. W.; Mukherjee, S.; Dasgupta, T. S.; Hodges, J. P.; Croft, M.; Grams, C. P.; Hemberger, J.; Sánchez-Benítez, J.; Huq, A.; Saouma, F. O.; Jang, J. I.; Greenblatt, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 10774.
4. Li, M.-R.; Croft, M.; Stephens, Peter, W.; Ye, M.; Vanderbilt, D.; Retuerto, M.; Deng, Z.; Grams, Christoph P.; Hemberger, J.; Hadermann, J.; Li, W.-M.; Jin, C-Q.; Saouma, F. O.; Jang, J. I.; Akamatsu, H., Gopalan, V; Walker, D; Greenblatt, M. *Adv. Mater.* **2015**,*27, 2177.*

Collaborating with the Pharmaceutical Industry – views of a middle man!

Dr Christopher Barnard

Johnson Matthey. chris.barnard@yahoo.co.uk

Until recently I worked for Johnson Matthey plc on a number of projects directed towards the pharmaceutical industry, both in developing active ingredients (APIs) and in providing new catalysts for improved synthesis. In the former area, the majority of the work related to platinum compounds for anti-cancer use and I will describe some of the history of this interesting story that began over 50 years ago. The use of palladium catalysis has played a major part in the increased efficiency of the synthesis of organic small molecule APIs and this is the second topic that I will address from the point of view of developing academic research for application in the pharmaceutical industry.

Sustainable manufacturing of functional materials

Claire J. Carmalt

Department of Chemistry, 20 Gordon Street, University College London, London WC1H 0AJ.

A range of precursors have been developed for the deposition of main group oxides, in particular Ga_2O_3, In_2O_3 and $Ga_xIn_{2-x}O_3$. The synthesis, structures, thermal properties and of a range of gallium and indium bis-β-ketoiminate complexes have been reported. Synthesis is possible via various routes, affording products of high purity in good yields. Of particular note is the successful stabilisation of rare gallium hydride species. Chemical vapour deposition (CVD) studies show the potential for this class of compounds for application in metal oxide thin film deposition.Films were grown via aerosol assisted AACVD which uses a liquid-gas aerosol to transport soluble precursors to a heated substrate. Compared to conventional CVD, the AACVD method uses aerosol droplets to transport precursors, with the aid of inert carrier gases. Therefore, in AACVD volatility is no longer crucial and this allows for a wider choice of precursors being available for use and can lead to high quality films at low cost.[1] The functional properties of the films have been investigated, including their use as transparent conducting oxides and photocatalysts.

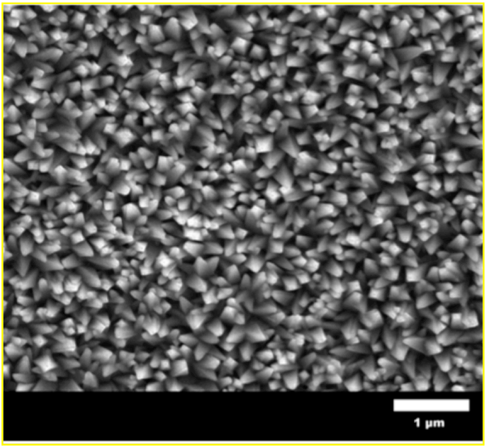


Fig. 1. TiO_2:SnO_2 film deposited by AACVD

Current research involves developing processes and resources towards sustainable and inexpensive high quality TCO films on float glass using AACVD. In particular replacement materials for Indium Tin Oxide (ITO) and F-doped Tin Oxide (FTO) are being developed. These materials are used in low-e window coatings (>£5B pa), computers, phones and photovoltaic devices. The current electronics market alone is worth in excess of £0.9 Trillion and every tablet PC uses ca 3g of tin. Indium is listed as a critical element- available in limited amounts often in unstable geopolitical areas. Tin metal has had the biggest rise in price of any metal consecutively in the last four years (valued at >£30K per ton) and indium is seen as one of the most difficult to source elements. We have been developing sustainable upscaled routes to TCO materials from precursors containing earth abundant elements (titanium, aluminium, zinc) with equivalent or better figures of merit to existing TCOs.

1. C. E. Knapp, C. J. Carmalt, *Chem. Soc. Rev.*, 2016, DOI: 10.1039/C5CS00651A

Chemistry and Education: Representation in the Teaching of John Dalton

Rachel Dunn.

Department of Philosophy & Foundation Centre, Durham University, UK. Email: r.l.dunn@durham.ac.uk

---

In this paper I will discuss representation in nineteenth-century chemistry through the life and career of Quaker chemist John Dalton (1766-1844). Though he is famous for proposing the model that modern scientists use to understand the structure of the atom he spent the majority of his life as a teacher. After a brief biography, I will unpack Dalton's time as a teacher and how he used visual culture in his pedagogy. By setting my discussion in the context of his teaching, I will explore the changing demographic of Dalton's private pupils and his work teaching chemistry to medical students.

The focus of the talk will be on the design and implementation of Dalton's atomic symbols. I will first examine the individual symbols presented in *A New System of Chemical Philosophy* (1808-1827) and attempt to categorize them according to design. The discussion will then shift to the two-dimensional representations of compounds Dalton drew using his individual symbols. In creating these compounds he assumed the simplest possible formulae, e.g. water as a binary compound, OH, rather than, as we now know, H_2O. Essentially, Dalton had to make assumptions as to the numbers of atoms that combined to form each compound. I will examine the ways in which he manipulated the symbols, looking at his spatial arrangements to suggest he was one of the earliest stereochemists. In doing this, the posters and handbills he employed as pedagogic tools will be presented. Finally, I will draw conclusions to show that his visual thinking was apparent in his symbols.

MECHANISMS OPERATING IN MOLECULAR WATER OXIDATION CATALYSIS

Antoni Llobet

Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, Avinguda Països Catalans 16, E-43007 Tarragona, Spain.
Departament de Química Universitat Autònoma de Barcelona, Cerdanyola del Vallès, E-08193 Barcelona, Spain.
E-mail: allobet@iciq.es)
http://www.iciq.org/research/research_group/prof-antoni-llobet/

Abstract

The replacement of fossil fuels by a clean and renewable energy source is one of the most urgent and challenging issues our society is facing today, which is why intense research is devoted to this topic recently. Nature has been using sunlight as the primary energy input to oxidize water and generate carbohydrates (a solar fuel) for over a billion years. Inspired, but not constrained, by nature, artificial systems[1] can be designed to capture light and oxidize water and reduce protons or other organic compounds to generate useful chemical fuels. In this context this contribution will present a variety of molecular water oxidation catalysts based on first row and second row transition metal complexes, and the different pathways through which they operate will be explored and discussed.[2]

References

[1] Berardi, S.; Drouet, S.; Francàs, L.; Gimbert-Suriñach, C.; Guttentag, M.; Richmond, C.; Stoll, T.; Llobet, A. *Chem. Soc. Rev.*, **2014**, *43*, 7501-7519.
[2] (a) Neudeck, S.; Maji, S.; López, I.; Meyer, S.; Meyer, F.; Llobet, A. *J. Am. Chem. Soc*. **2014**, *136*, 24-27. (b) López, I.; Ertem, M. Z.; Maji, S.; Benet-Buchholz, J.; Keidel, A.; Kuhlmann, U.; Hildebrandt, P.; Cramer, C. J.; Batista, V. S.; Llobet, A. *Angew. Chem. Int. Ed.* **2014**, *53*, 205-210. (c) Garrido-Barros, P.; Funes-Ardoiz, I.; Drouet, S.; Benet-Buchholz, J.; Maseras, F.; Llobet, A. *J. Am. Chem. Soc.* **2015**, *137*(21)*,* 6758-6761. (d) Matheu, R.; Ertem, M.Z.; Benet-Buchholz, J.; Coronado, E.; Batista, V. S.; Sala, X.; Llobet, A. *J. Am. Chem. Soc.* **2015**, *137*(33)*,* 10786-10795

Modified tetrapyrroles: incarcerating a Goblin and a Devil

Dr Martin Warren

University of Kent

m.j.warren@kent.ac.uk

Many of the fundamental respiration processes on which living systems depend rely on essential roles played by modified tetrapyrroles, whose members represent a molecular fraternity that have been dubbed the pigments of life. This group includes the hemes, chlorophylls, vitamin B12, siroheme, heme *d*1 and coenzyme F430, molecules that are defined not only by their macrocyclic architecture and colour but also by the presence of specific, centrally chelated, metal ions such as Fe, Mg, Co and Ni. These metallo-prosthetic groups are made along an intricate, branched, biosynthetic pathway requiring upwards of thirty enzymes and often involving many highly unstable intermediates. Their construction also has to be coordinated with the availability of the particular metal ion and thus regulatory metal circuits must be involved to ensure procurement, delivery and insertion. Recent advances stemming from the identification of some of the components involved in the biogenesis of these tetrapyrrole chassis has provided us with new insights into how this takes place. More specifically, we have focussed our attention on how cobalt and nickel are incorporated into vitamin B12 and coenzyme F430. Of course, the elemental names for cobalt and nickel are derived from German miner mythology reflecting the mischievous role of either a goblin (kobold) or devil (old Nick) in complicating their extraction from the appropriate ores. So, what is so special about the corrin and corphin frameworks that they have been selected as biological homes for these metals to tame their malevolent tendencies and allow their biochemical exploitation?

Photo-Uncaging of Small Molecule Bioregulators from Metal Complexes

Peter C. Ford
Department of Chemistry and Biochemistry, University of California, Santa Barbara

The gaseous molecules nitric oxide and carbon monoxide are important regulators of many functions in mammalian and human physiology. For examples, NO is a regulator of blood pressure, while NO and CO both have key roles in wound healing and inflammation. This presentation will discuss ongoing studies to design new photochemically activated NO and CO releasing moieties (photoNORMs and photoCORMs, respectively) that deliver such bioactive small molecules (BSMs) to specific biological targets.

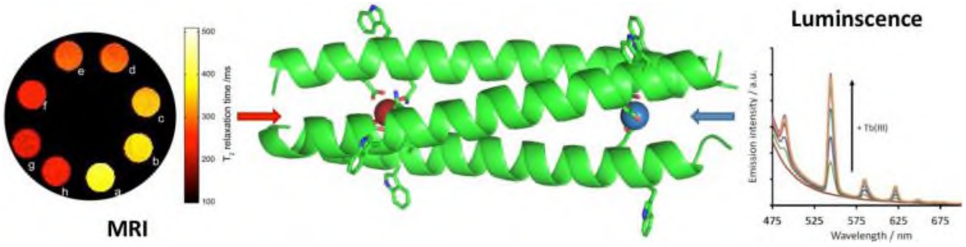
Inorganic Biochemistry Discussion Group Young Investigator Award Lecture

Advancing metalloprotein design for new functions and applications

Anna F. A. Peacock, Louise N. Slope, Matthew R. Berwick, Sarah L. Newton,
Anbu Sellamuthu, Oliver J. Daubney, Luca Salassa and Melanie M. Britton
School of Chemistry, University of Birmingham, Edgbaston, B15 2TT,
UK. a.f.a.peacock@bham.ac.uk

De novo designed miniature protein scaffolds, such as the coiled coil, offer exciting opportunities for metal ion coordination.[1] Not surprisingly due to the protein like nature of the scaffold, the large majority of *de novo* metallocoiled coil examples have focussed their efforts on mimicking the active sites of native metalloenzymes. Our approach is to instead to use these artificial proteins as novel ligands for the coordination of xeno metals, with no known biological role, with the view to developing functional systems for valuable applications beyond the scope of nature.

We recently reported the design of the first gadolinium coiled coil, which displayed promise as a potential MRI contrast agent.[2,3] We have since interrogated the coordination of various lanthanide ions to our coiled coils and have for the first time shown that we can selectively discriminate between Ln(III) ions based on size. As a result we have now designed coiled coils capable of binding two different Ln(III) ions selectively to two different sites (see Figure), and at a defined distance from one another. The opportunities this affords and the potential applications of this new class of lanthanide coiled coils, will be discussed.



Generous financial support from The University of Birmingham, the School of Chemistry and EU COST action CM1105 is acknowledged.

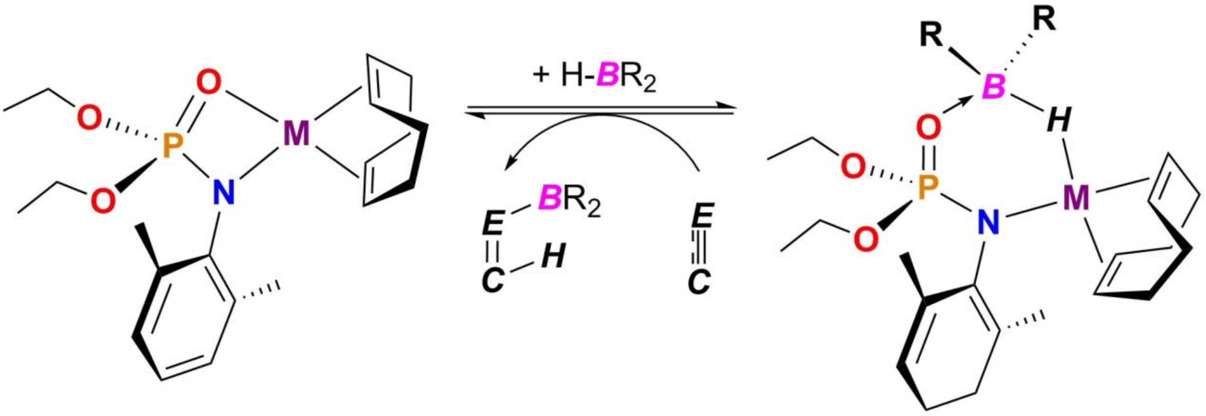
References

1. A. F. A. Peacock, Cur. Opin. Chem. Biol. 17 (2013) 934-939.
2. M. R. Berwick *et al.*, J. Am. Chem. Soc. 136 (2014) 1166-1169.
3. M. R. Berwick *et al.*, Chem. Sci. 7 (2016) 2207-2216.

N,O-chelates becoming unhinged. New perspectives in metal-ligand cooperativity.

Marcus W. Drover, Jennifer Love, Laurel L. Schafer
Department of Chemistry, University of British Columbia
Email: schafer@chem.ubc.ca, Telephone: (604) 822-9264

The synthesis, characterization, and reactivity of N,O-chelated amidate and phosphoramidate complexes of rhodium and iridium will be discussed. These complexes are hemilabile in solution, allowing for E-H (E = B, C, Si) bond capture and/or subsequent activation (depending on the nature of E). We have found that these ligands allow for cooperative metal-ligand E-H bond activation, allowing for controlled product release in the presence of an unsaturated substrate. Recent advances in the characterization of such intermediates, including E-H agostic complexes, as well as efforts to render such processes catalytic will be presented.



Metal Catalyzed Amine– and Phosphine–Borane Dehydropolymerisation. Control Through Catalyst Design.

Andrew S. Weller

Department of Chemistry, University of Oxford, Oxford, UK.

The catalysed dehydrocoupling of amine–boranes (and phosphine boranes) potentially allows for the production of B–N (or B–P) oligomeric or polymeric materials via dehydropolymerisation. Such main–group polymers of empirical formula $(ERHBH_2)_x$, (E = N, P) are (valence)isoelectronic with technologically pervasive polyolefins, and are virtually unexplored. In addition, the development of routes for the construction of E–E' (E = p–block element) bonds by catalytic routes lags significantly behind those used for the construction of C–E or C–C bonds. Despite the significant potential for these new materials, the mechanism for, and control of, their construction remains generally ill–defined when compared to analogous olefin polymerisation or other C–C bond forming processes. This talk will outline the development, by mechanism–led design, of well–defined catalysts for the dehydropolymerisation of amine–boranes and phosphine–boranes. Through this it will be shown that new catalysts can be designed that have the potential to deliver new polyaminoboranes “to order” in terms of controlled molecular weight.

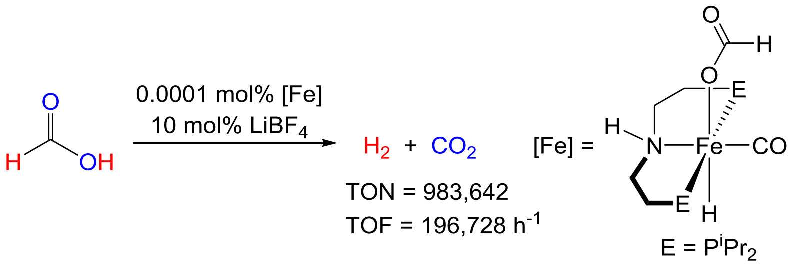
Pincer Supported Iron Complexes for the Reversible Hydrogenation of CO_2 to Formic Acid and Methanol.

Nilay Hazari[a] and Wesley H. Bersnkoetter[b]

[a]*Department of Chemistry, Yale University, P. O. Box 208107, New Haven, Connecticut, 06520, USA. E-mail: nilay.hazari@yale.edu*
[b]*Department of Chemistry, University of Missouri, Chemistry Bldg Rm 243, 601 S. College Ave, Columbia, Missouri, 65211, USA.*

Given the steady decline in the world's fossil fuel reserves and the potential environmental consequences of continued fossil fuel use, there is considerable interest in the utilization of alternative carbon sources. Carbon dioxide is a particularly attractive feedstock owing to its high abundance, low cost and toxicity, and relative ease of transport. Formic acid and methanol are especially promising targets for the catalytic conversion of carbon dioxide. Both are valuable commodity chemicals, which are synthesized on a large scale, and could be used as materials for chemical hydrogen storage.

In this presentation the development of a series of pincer supported iron complexes for the catalytic hydrogenation of carbon dioxide to formic acid and methanol and the dehydrogenation of formic acid and methanol will be described. Initially the synthesis and characterization of a family of unusual pincer supported iron complexes will be reported. The catalytic activity of these species for formic acid and methanol dehydrogenation will be discussed and the important role that Lewis Acids play in facilitating this process will be described. Finally, the process for formic acid and methanol dehydrogenation will be compared to that for carbon dioxide hydrogenation.

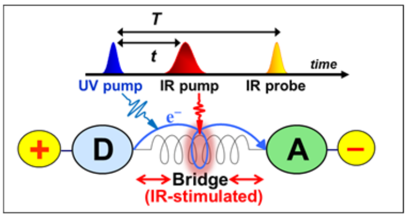


Ultrafast Photoinduced Charge Transfer in Metal Chromophores: towards directing photochemical pathways with bond-specific IR-excitation

Milan Delor,[a] Paul Scattergood,[a,c] Igor Sazanovich,[a,b] Theo Keane,[a] Anthony Meijer,[a]
Anthony Parker,[b] Mike Towrie,[b] Julia Weinstein[a]*

[a] *Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK*
[b] *Central Laser Facility, Rutherford Appleton Laboratory, STFC, OX11 0QX, UK*
[c] *Department of Chemical Sciences, University of Huddersfield, UK*
e-mail: Julia.Weinstein@Sheffield.ac.uk

The photochemically driven electron transfer (ET), one of the simplest chemical reactions known, is a fascinating target to attempt optical control of chemical reactions. The nuclear-electronic (vibronic) interactions are one of the major factors in directing ET, and potentially offer a mechanism of influencing ET reactions.[1] In solution, perturbing vibronic coupling is challenging due to fast vibrational relaxation.



Transition metal Donor-Bridge-Acceptor (DBA) complexes which can be constructed in a “modular” fashion, offer a versatile test-bed for investigating such effects. To perturb vibronic coupling in the excited state, we apply ultrafast Transient 2-Dimensional Infrared (T-2DIR) spectroscopy, where electronic excitation is followed by vibrational excitation.

We show that the outcome of a light-induced ET reaction can be radically altered by mode-specific IR excitation of vibrations which are coupled to the ET pathway. This effect is demonstrated on covalent DBA triads, build around trans-Pt(II)-acetylide motifs. Selective excitation of bridge-localised vibrations leads to control of charge separation, up to a complete switching off of the charge separation pathway.[2,3] Analysis of the behavior of several DBA systems with varied thermodynamic and electronic factors of electron transfer, yields preliminary criteria necessary to achieve such an effect.

These studies add to a growing body of evidence of the possibility to control photoinduced charge transfer by modulating vibronic coupling,[1,4] and directing photoinduced reactions.

We thank the EPSRC, STFC, and the University of Sheffield for support.

[1] Xiao D., Skourtis S.S., Rubtsov I.V., Beratan D.N. *Nano Lett.* **2009,** 1818;
Rubtsov I.V., Beratan D.N. *et al*, *Dalton Trans.*, **2015**, 8609.
[2] Delor M., Scattergood P., Sazanovich I., Parker A.W., Greetham G.M., Meijer A., Towrie M., Weinstein J.A., *Science*, **2014**, 1492;
[3] Delor, M. *et al.*, *Nat. Chem.* **2015**, 689.
[4] Sukegawa, J. *et al. Nat. Chem.* **2014**, 899.

Rhenium complexes and conducting metallopolymers for electrocatalytic CO_2 reduction

Yawei Liang, Lauren Lytwak, Bradley J. Holliday

Department of Chemistry, The University of Texas at Austin, 105 E. 24th St., Stop A5300, Austin, TX 78712-0165, USA. E-mail: bholliday@cm.utexas.edu; Fax: +1 512-471-8648; Tel: +1 512-471-8491

Diimine rhenium(I) tricarbonyl complexes are well known as phosphorescent emitters and electro- and photocatalysts for the reduction of carbon dioxide to carbon monoxide. Conducting metallopolymers containing this rhenium diimine moiety should not only retain the photoluminescent and catalytic properties of rhenium diimine complexes but also gain the conductivity, thin film processability, and mechanical flexibility typical of conjugated conducting polymers. A series of facial tricarbonyl rhenium(I) diimine-type monomers and corresponding metallopolymers have been prepared. The dinitrogen donor ligand is a bidentate diimine-type derivative, such as 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), or dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz), or a trinitrogen *bis*(pyrazolyl)pyridine (BPP) ligand that behaves as a bidentate chelate. Appended to the ligands are 3,4-ethylenedioxythiophenes (EDOTs), a thiophene derivative, for electropolymerization of the metal complexes. UV-Vis absorption and emission spectroscopy studies of the monomers under a variety of conditions indicate that visible light emission originates from triplet ligand-centered (^{3}LC) $\pi \rightarrow \pi^*$ and triplet metal-to-ligand charge transfer (^{3}MLCT) excited states. Although red-shifted absorbance is observed for the metallopolymers, upon excitation at λ_{max} of absorption, no emission was detected. In addition to visible phosphorescent emission, both the rhenium-containing monomers and metallopolymers show electrocatalytic activity towards the reduction of carbon dioxide to carbon monoxide.

Controlling Optical Properties of Conjugated Oligomers Using Metal and Main Group Chemistry

Michael O. Wolf, Peter Christensen, Yang Cao

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada, mwolf@chem.ubc.ca

---

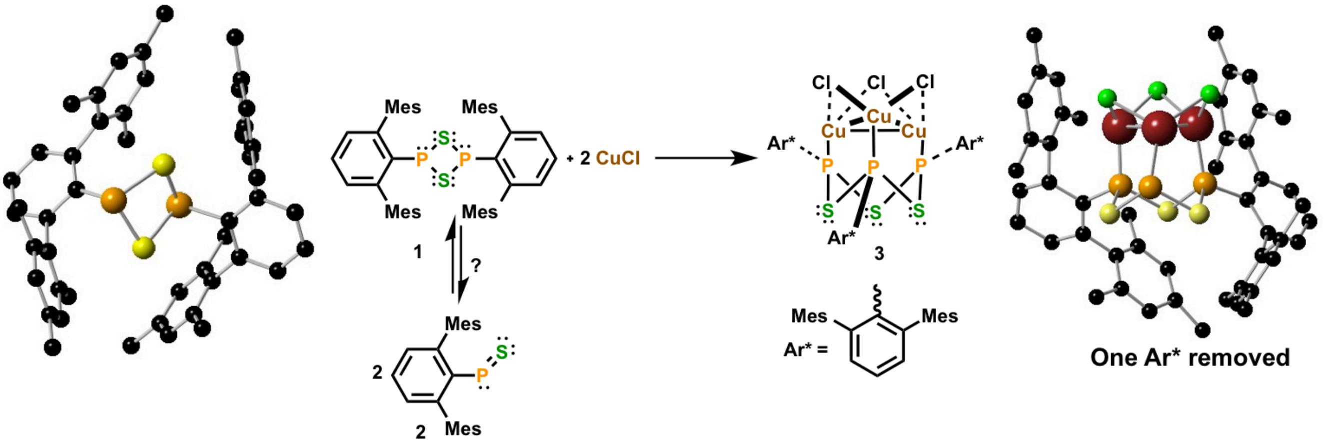
Conjugated oligomers are of interest for a broad range of applications including solar cells, chemical sensors, molecular switching and catalysis. Many of these applications are dependent on the optical properties of the materials, including absorption and emission properties, excited state charge separation and energy transfer. Thiophene-based conjugated materials in which conjugated oligomers are combined with light-absorbing metal-complexes and main-group elements, that give rise to enhanced photofunctional behavior will be described. The photophysical properties of these novel compounds will be discussed, along with possible applications in optics.

Four-membered pnictogen-chalcogen rings: Synthesis and chemistry.

Cameron M.E. Graham, Tylor Pritchard and Paul J. Ragogna
The University of Western Ontario, London, ON, Canada, N6A 5B7; pragogna@uwo.ca

---

There has been a long-standing interest in heterocyclic chemistry since the realization that molecular structures can adopt ring formations. Heterocycle development can have an organic or inorganic “flavor” with the inorganic side often working to substitute carbon for an inorganic element. Over the decades there has been extensive development of inorganic rings, but compact systems like $[Ch_4]^{2+}$ or those with Pn_2Ch_2 cores (related *via* the isolobal analogy, e.g. **1**; Pn = P, As, Sb, Bi; Ch = S, Se, Te;) have received very little attention. These inorganic rings could yield inroads to fundamentally relevant aromatic compounds, polycations, ligands and/or internal Lewis acid/base pairs provided one considers the appropriate use of sterics and electronics. Given our past interest in pnictogen and chalcogen chemistry, we are taking on the challenge of understanding these synthetic targets. The sysntesis of compact $(RPn)_2Ch_2$ rings will be presented as well as some of their onwards chemistry that underscores the presence of low coordinate pnictogen centres (e.g. **2**). Their coordination chemistry with the coinage metals will also be highlighted (e.g. **3**)



Representative references:

1. He, G.; Shynkaruk, O.; Lui, M. W.; Rivard, E. *Chem. Rev.* **2014**, *114*.
2. Velian, A.; Nava, M.; Temprado, M.; Zhou, Y.; Field, R. W.; Cummins, C. C. *J. Am. Chem. Soc.* **2014**, *54*, 13586.
3. Hering-Junghans, C.; Rivard, E. *Angew. Chem., Int. Ed.* **2015**, *54*, 10077.
4. Cameron, T. S.; Dionne, I.; Jenkins, H. D. B.; Parsons, S.; Passmore, J.; Roobottom, H. K. *Inorg. Chem.* **2000**, *39* 2042.
5. Passmore, J.; Sutherland, G.; White, P. S. *J. Chem. Soc. Chem. Commun.* **1980**, 330.

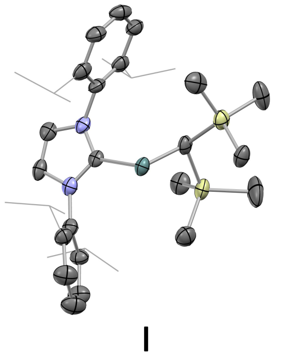
Bond Activation by Highly Reactive Low-valent Germanium Complexes

Arnab Rit and Simon Aldridge*
Inorganic Chemistry laboratory, South Parks Road, Oxford, UK. OX1 3QR.
Simon.Aldridge@chem.ox.ac.uk

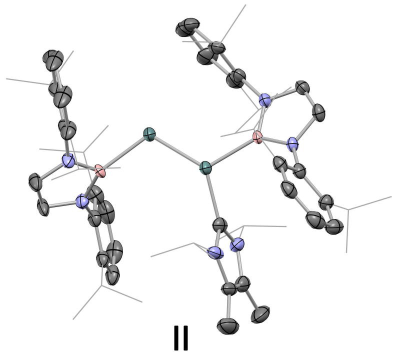
Small molecule capture and activation by low-valent Main Group systems has been an area of great interest in recent years, not least with a view to developing the sorts of catalytic bond modification processes long thought to be the preserve of 'Noble' Transition Metals. A number of Group 14 systems – notably heavier analogues of carbenes and alkynes have been implicated in such chemistry, for example in capturing/activating alkenes, CO, dihydrogen etc.

With E-H bond activation in mind, tuning the HOMO-LUMO gap either by appropriate selection of ancillary ligands, or by variation in the net charge is critical to providing metal systems with sufficient intrinsic reactivity. In recent work we have been targeting a number of germylene and related complexes for oxidative bond activation.

These include two-coordinate cationic systems of the type $[L(R)Ge:]^+$ (e.g. **I**)[1] which are shown to possess narrow HOMO-LUMO gaps (< 200 kJ mol^{-1}) and which can be used to access Ge=E multiple bonds via oxidation. Neutral systems featuring extremely strong σ-donor boryl ligands as ancillary substituents have also been examined (e.g. **II**), and feature elevated HOMO energies and high reactivity towards E-H bonds (E = H, B, N, Si).



I



II

(1) A. Rit, R. Tirfoin and S. Aldridge, *Angew. Chem. Int. Ed.*, *2016*, **55**, 378-382

Chelating Ligands Incorporating Reactive N-Heterocyclic Phosphenium Cations

Christine M. Thomas, Mark W. Bezpalko, Deirdra A. Evers-McGregor
Brandeis University, 415 South Street, Waltham, MA USA 02454, thomasc@brandeis.edu

---

The exploration of the coordination chemistry of N-heterocyclic phosphenium cations (NHPs) has been hampered by their electrophilic nature, which only favors coordination to very electron-rich metals and renders them susceptibile to nucleophilic attack. One strategy to expand the coordination chemistry of NHPs is to incorporate them into chelating ligand frameworks in which additional donor functionalities enforce metal coordination and impart stability. An N-heterocyclic phosphenium heterocycle has been incorporated into the central position of a tridentate disphosphine pincer ligand. Upon exploring the coordination chemistry of the NHP-diphosphine ligand with electron-rich rich transition metal fragments including Pd^0, Pt^0, Ni^0, and Co^{-I}, it was found that the rigidity of the tridentate ligand led to unusual binding properties. The enforced coplanarity of the N-bound aryl rings dramatically effects the electronic structure of the NHP^+ cation and stabilizes a reduced NHP^- state in which two electrons have been transferred from the metal precursor to the NHP phosphorus atom, as evident by a pyramidal geometry about phosphorus. Replacement of one phosphine sidearm with a freely rotating N-aryl group was explored to probe the importance of the rigidity and coplanarity of the N-aryl rings in promoting the unusual behavior of the NHP. When incorporated into a bidentate ligand with just one phosphine sidearm, the NHP exclusively adopts a rigorously planar geometry about the NHP phosphorus. The coordination chemistry of the bi- and tri-dentate NHP-containing ligands with Pd, Pt, Ni, and Co will be discussed.

Towards Borylation Reactions in Aqueous Medium

Webster L. Santos, Amanda K. Nelson, Cheryl L. Peck, and S. Brandon Thorpe
Department of Chemistry, Virginia Tech, Blacksburg, VA 24061. santosw@vt.edu

---

Organoboron compounds serve as important intermediates in the synthesis of complex molecules, pharmaceuticals, and material science. Transition metal-catalyzed cross-coupling of boronic acids and esters, i.e. Suzuki-Miyaura cross-coupling reaction, provides a convenient route to construct difficult C—C bonds. Although methods for organoboron syntheses have advanced significantly in the past few decades, the protocols require harsh reaction conditions and use organic solvents. Surprisingly, borylation methods in aqueous medium are scarce. In this presentation, we will report the development of copper-catalyzed borylation of activated alkenes, alkynes, and allenes in aqueous medium. Further, we will discuss our mechanistic understanding of regio- and chemoselective transfer of diboron reagents onto carbon-carbon multiple bonds.

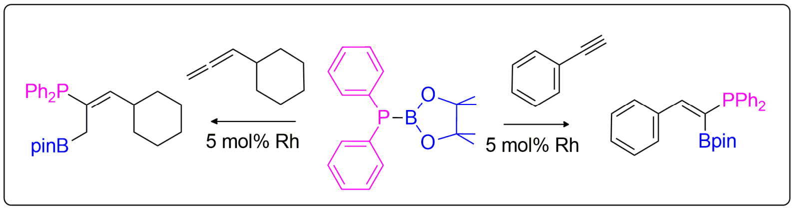
To B-E or not to B-E? Developing the Phosphinoboration Reaction

Stephen J. Geier,[†] Christopher M. Vogels,[†] Simon Doherty,[‡] Stephen A. Westcott[†]

[†]*Department of Chemistry and Biochemistry, Mount Allison University, Sackville, NB E4L 1G8, Canada*

[‡] *NUCAT, School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, England*

Over the past two decades, the transition metal catalysed addition of boron-element (B-E, where E = H, B, Sn, Si, etc) bonds to unsaturated compounds has received a considerable amount of attention. Given the intensity of interest in the reactivity of B-E bonds it is somewhat surprising that relatively little is known about the analogous addition chemistry of compounds containing single B-E bonds where E is phosphorus. The corresponding phosphinoboration would introduce a P-C bond and a reactive B-C bond that could be further elaborated to provide access to a host of useful structural motifs and, in this regard, is a worthy target. The synthesis of phosphinoboronate esters containing a single P-B bond is reported herein, together with reactivity studies towards a range of organic substrates. We also discuss the transition metal catalysed phosphinoboration of C-C multiple bonds in which P-C and B-C bonds are formed in a single step; allenes react *via* a highly regioselective 1,2-addition while terminal alkynes give products where both P and B groups have added to the same carbon atom.



Understanding the Selectivity of Ir-Catalysed Arene C-H Borylation

Patrick Steel

Department of Chemistry, University of Durham, Durham, DH1 3LE

Organoboronic acids and esters are a class of compounds of great importance in organic synthesis and material science with a growing role in medicinal chemistry / chemical biology. They represent ideal reagents being, non-toxic, tolerant to air and water, stable in the absence of a catalyst, and react under mild conditions in a diverse range of transformations. Organoboronic acids and esters are a class of compounds of great importance in organic synthesis and material science with a growing role in medicinal chemistry / chemical biology. They represent ideal reagents being, non-toxic, tolerant to air and water, stable in the absence of a catalyst, and react under mild conditions. Given these attributes boronic acids can be regarded as environmentally friendly (green) reagents. However such a label masks difficulties both in preparation and use. Traditionally, boronic acids are generated via the reaction of air & moisture sensitive organolithium or Grignard reagents with a trialkylborate followed by hydrolysis or transesterification. However, this restricts the scope of the reaction to substrates free of reactive functional groups, or adds costly protection/deprotection steps.. Over the last decade, the direct C-H borylation of aromatic C-H bonds catalysed by tris boryl iridium complexes has become the method for the synthesis of aromatic boronic acids. No substrate pre-activation is required, the reaction occurs under mild conditions with relatively low loadings of Ir and gives excellent yields of the corresponding aryl and heteroaryl boronates. Moreover, the regiochemistry of the C-H borylation step is dominated by steric effects and, with unsubstituted arenes, suffers from poor selectivity. This presentation will discuss our attempts to understand this selectivity and develop synthetic strategies for the more important basic heterocycles of relevance to the agrochemical / pharmaceutical industry not being well tolerated.

"Gold-finger" domains formation: implications for the use of gold compounds in therapy

Angela Casini

School of Chemistry, Cardiff University, Park Place, CF103AT Cardiff, United Kingdom

Email: casinia@cardiff.ac.uk.

Gold-based compounds have raised attention in recent years as new promising experimental anticancer agents.[1] Among the possible pharmacological targets for cytotoxic gold complexes, zinc finger (ZF) proteins occupy an important place, being involved in a wide range of functions in DNA repairing, recognition, transcription, replication, apoptosis and metabolism. All of these processes are essential for cell growth and development, having direct implications in health and disease. Therefore, ZFs are frequently recognized as possible medicinal targets.[2]

Determining the structural changes induced by the substitution of Zn2+ ions with Au^{+}/Au^{3+} ions in ZFs, and correlating them to possible inhibition properties is fundamental to the understanding of the mechanism of action of gold-based cytotoxic agents at a molecular level. Thus, we investigated the reactivity of gold complexes with different ZF domains via different techniques, including high-resolution mass spectrometry, UV-Vis absorption spectroscopy and quantum mechanics/molecular mechanics among others.[3,4]

The obtained results support a model whereby displacement of zinc from the ZF peptide by gold ions leads to decreased protein activity, and to formation of the so-called ''gold-finger'' (GF) domain. The influence of both the gold oxidation state and the ZF coordination sphere in GF formation provided useful insights into the possible design of new gold complexes targeting specific ZF motifs.

References

1) B. Bertrand, A. Casini, Dalton Trans., 2014, 43, 4209.

2) F. Mendes, M. Groessl, A. A. Nazarov, Y. O. Tsybin, G. Sava, I. Santos, P. J. Dyson, A. Casini, J. Med. Chem. 2011, 54, 2196.

3) U. A. Laskay, C. Garino, Y. O. Tsybin, L. Salassa, A. Casini, Chem.Comm. 2015, 51, 1612.

4) A. Jacques, C. Lebrun, A. Casini A, I. Kieffer, O. Proux, J.M. Latour, O. Sénèque, Inorg Chem. 2015, 54, 4104.

Speciation is central for the mode of action of metal-based drugs

Debbie C. Crans

Dept. Chemistry and Cell and Molecular Chemistry, Colorado State University, Fort Collins, CO, 80523, USA, email: Debbie.Crans@Colostate.Edu

---

Most of the metal-based drugs currently in the clinics or metal based diagnostics and radiopharmaceuticals are coordination complexes[1]. Because most coordination complexes are inherently labile each of these systems will be distributed over a range of species determined by the case-by-case conditions[2-3]. The speciation of these drugs is therefore generally complex. Some examples of metallodrugs presented here forms several species in physiological conditions, and their overall pharmacological response is derived from the combination of such species[4]. The consequences of the stability and speciation have deep impact on the action of these drugs because the pharmacokinetics may not follow a simple one-component distribution model if uptake of the different metal-containing species varies[4]. The consequences of speciation will be discussed for anticancer and antidiabetic agents. Studies of compound efficacy and uptake is generally accompanied by measurements of metal content identifying the need for methods for quantitative analysis, as well as to study speciation[5]. A range of different drugs will be discussed from therapeutic platinum- (anticancer) and vanadium-based drugs (antidiabetic) to metal-based diagnostics and radiopharmaceuticals. The consideration of the simple speciation curves[2-3] when put in context of biological studies takes on different levels of complexities[4-5]. Importantly, the properties of compounds can be implemented by appropriate formulation and, because, the choice of drug formulation may influence the mode of action of the drug[4].

[1] N.P.E. Barry and P.J. Sadler *Chem. Commun*. 2013,49:5106-31.

[2] C.F. Baes, Jr. and R.E. Mesmer “The Hydrolysis of Cations” John Wiley & Sons, Inc. New York 1976.

[3] D.C. Crans, K.A.Woll, K. Prusinskas, M.D. Johnson, E. Norkus *Inorg. Chem*. **2013**, 52:12162-75

[4] G.R. Willsky, K. Halvorson, M.E. Godzala III< L-H Chi, M. Most, P. Kaszynski, D.C. Crans, A.B. Goldfine and P.J. Kostnyniak *Metallomics,* **2013**, 5:1491-1502.

[5] C.F. Harrington and A. Taylor *J. Pharmaceutical Biomed. Anal.* **2015**, 106:210-17

Targeting Small-Molecules to Treat Alzheimer's Disease

Tim Storr
Simon Fraser University, Department of Chemistry, Burnaby, BC, V5A 1S6, Canada
(tim_storr@sfu.ca)

Alzheimer's disease (AD) is a progressive neurodegenerative disorder initially affecting brain regions involved in learning and memory, eventually resulting in death. It is estimated that approximately 44 million people worldwide suffer from AD, and these numbers are expected to increase sharply in the next 20 years.[1] We and others are currently studying the role of excess metal ions in the development of neurodegenerative diseases such as AD.[2-4] AD is characterized by the formation of amyloid-beta (Aβ) plaques and neurofibrillary tangles in the brain. Aβ plaques are insoluble extracellular deposits of the Aβ peptide, and the aggregation and toxicity of this peptide is increased in the presence of dysregulated metal ions (Cu, Fe, and Zn). Cu and Fe have been shown to be redox-active when bound to Aβ, and form toxic reactive oxygen species (ROS) in the presence of dioxygen. The use of multifunctional molecules that limit peptide aggregation, sequester metal ions, and minimize the production of toxic ROS is a practical therapeutic strategy. New molecules are being tested for efficacy in a number of disease-relevant assays and an overview of recent findings will be presented. We are also investigating the utility of pre-formed metal complexes to modulate Aβ peptide aggregation processes. These metal complexes can be tuned to interact with the Aβ peptide and reduce toxicity in a neuronal cell model.[5] In addition, a sub-set of these compounds can act as catalytic antioxidants under certain conditions. This multidisciplinary research aims to improve our understanding of the etiology of metal overload diseases, and offer new avenues for treatment of AD.

(1) *World Alzheimer Report* 2015.
(2) Lim, M. H. et al. *Acc. Chem. Res.* **2014**, *47*, 2475.
(3) Jones, M. R.; Service, E. L.; Thompson, J. R.; Wang, M. C. P.; Kimsey, I. J.; DeToma, A. S.; Ramamoorthy, A.; Lim, M. H.; Storr, T. *Metallomics* **2012**, *4*, 910.
(4) Scott, L. E.; Orvig, C. *Chem. Rev.* **2009**, *109*, 4885.
(5) Jones, M. R.; Mu, C. H.; Wang, M. C. P.; Webb, M. I.; Walsby, C. J.; Storr, T. *Metallomics* **2015**, *7*, 129.

Organometallic chemistry in the solid state: isolating a sigma-pentane compound

F. Mark Chadwick, Andrew S. Weller

Department of Chemistry, University of Oxford, Mansfield Road, Oxford, OX1 3TA.

Transition metal σ-alkane complexes are when an alkane binds to a metal centre only through a 3-centre-2-electron M···H–C interaction. The formation of such species is posited to be the key step in the catalytic cycle for C-H activation processes.[1] Characterized examples however are elusive due to i) alkanes being extremely weak nucleophiles and ii) the local steric bulk of the alkane itself. Because of these factors, examples of complexes involving σ-alkane interactions tend to be serendipitous[2] or short-lived, generally characterised only using fast, time-resolved techniques at low temperature.[3] Recently we reported the first rational, solid-state synthesis of such a species.[4] The success of our route was due to the exploitation of a single-crystal to single-crystal transformation. Taking a crystalline sample of suitable cationic rhodium bis-alkene species (supported by a bidentate phosphine), hydrogen could be added to form the desired σ-alkane complex (Fig. 1). Though the first example was unstable we have recently extended this work to synthesize a particularly stable example.[5]

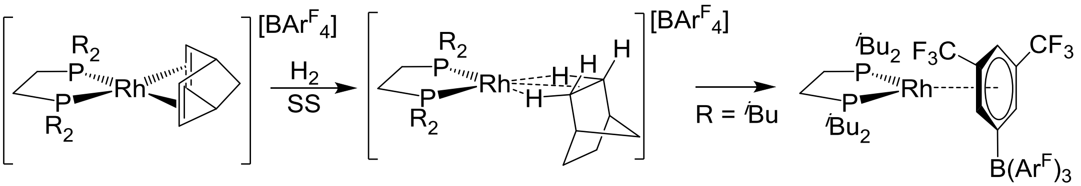


Figure 1. The synthesis of previous examples of σ-alkane complexes. R = Cy, ^{i}Bu; Cy = C_6H_{11}, Ar^F = (3,5-CF_3)-C_6H_3.

However norbornane is an alkane with no known uses, as such a more relevant alkane was targeted, that of the lightest, liquid alkane – pentane. In this presentation we will report the synthesis and characterization of the first pentane compound in the solid state (Fig. 2). The species $[\{(Cy)_2PCH_2CH_2(C_6H_{11})_2\}Rh\{2,4\text{-}\eta^2{:}\eta^2\text{-}C_5H_{12}\}][BAr^F_4]$ was characterised using X-ray crystallography, solid state NMR and computational techniques.

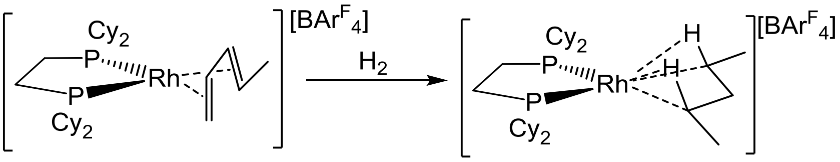


Figure 2. The solid-state synthesis of an organometallic complex of pentane.

References

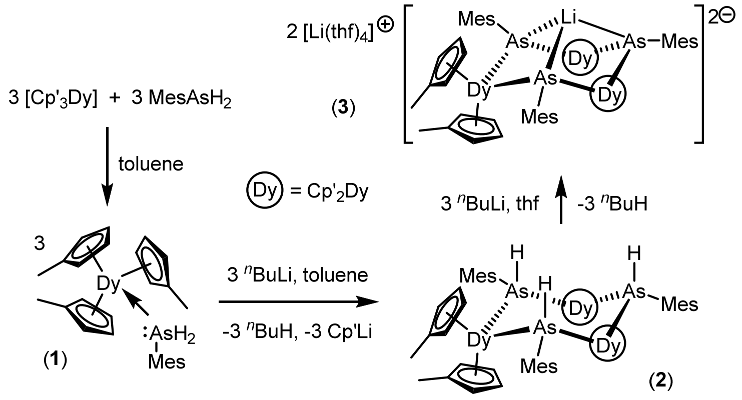
1. Perez, P. J., *Alkane C-H activation by single-site metal catalysis; Springer: New York,* 2012; p. 269. **2.a)** Evans, D. R.; Drovetskaya, T.; Bau, R.; Reed, C. A.; Boyd, P. D. W. *J. Am. Chem. Soc.* 1997, *119*, 3633–3634; **b)** Castro-Rodriguez, I.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* 2003, *125*, 15734–15735; **c)** Andreychuk, N. R.; Emslie, D. J. H. *Angew. Chem. Int. Ed. Engl.* 2013, *52*, 1696–1699.**3.a)** Cowan, A.; George, M. *Coord. Chem. Rev.* 2008, *252*, 2504–2511; **b)** Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* 1998, *120*, 9953–9954; **c)** Bernskoetter, W. H.; Schauer, C. K.; Goldberg, K. I.; Brookhart, M. *Science* 2009, *326*, 553–556; **d)** Walter, M. D.; White, P. S.; Schauer, C. K.; Brookhart, M. *J. Am. Chem. Soc.* 2013, *135*, 15933–15947 **4.** Pike, S. D.; Thompson, A. L.; Algarra, A. G.; Apperley, D. C.; Macgregor, S. A.; Weller, A. S. *Science* 2012, *337*, 1648–1651 **5.** Pike, S. D.; Chadwick, F. M.; Rees, N. H.; Scott, M. P.; Weller, A. S.; Krämer, T.; Macgregor, S. A. *J. Am. Chem. Soc.* 2014, *137*, 820–833.

Magneto-Structural Correlations in Dysprosium Single-Molecule Magnets.

Thomas Pugh and Richard A. Layfield*
School of Chemistry, The University of Manchester, Oxford Road, M13 9PL, U.K.
Thomas.Pugh@manchester.ac.uk.

Single-molecule magnets (SMMs) are discrete molecular nano-magnets that, unlike bulk magnets, retain magnetization in ways that do not rely on long range magnetic ordering. SMMs offer unique properties with potential applications in device materials.[1] Our group has pioneered the use of organometallic chemistry in single-molecule magnetism,[2] focusing on developing unconventional ligand environments containing heavier p-block donor atoms.

We now report a synthetic route to rare-earth complexes of monoanionic pnictide $[R_2E]^-$ (**2**) and dianionic pnictinidene $[RE]^{2-}$ (**3**) ligands (E = P,[3] As,[4,5] Sb[6]), with the dianionic ligands being unprecedented in rare-earth chemistry with E = As and Sb (Scheme 1). We have found that varying the pnictogen donor atom in **1-3** produces systematic changes in the SMM properties, which has allowed substantial increases in the anisotropy barrier to be targeted, and a general design model for *bis*(cyclopentadienyl)-dysprosium SMMs to be developed.



Scheme 1. Synthesis of complexes **1-3** (E = P, As, Sb; Ln = Dy, Y).

1. W. Wernsdorfer *et al.*, *Nat. Mater.*, **2008**, *7*, 179; *Science*, **2014**, *344*, 1135.
2. R. A. Layfield, *Organometallics*, **2014**, *33*, 1084; *Chem. Rev.*, **2013**, *113*, 5110.
3. T. Pugh and R. A. Layfield *et al.*, *Nat. Commun.*, **2015**, *6*, 7492.
4. T. Pugh, A. Kerridge, R. A. Layfield, *Angew. Chem. Int. Ed.*, **2015**, *54*, 4255.
5. T. Pugh, R. A. Layfield *et al.*, *Chem. Sci.*, **2016**, *7*, 2128.
6. T. Pugh, N. F. Chilton, R. A. Layfield, manuscript in preparation.

Reexamining Oxidation States in Transition Metal π-complexes: Implications for Reactivity

Addison N. Desnoyer, Shirin Behyan, Jennifer A. Love, and Pierre Kennepohl
Department of Chemistry, The University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada. email: pierre@chem.ubc.ca

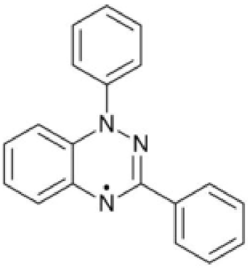
---

Spectroscopic and computational data investigations of a rhodium ethylene precursor to the formation of 2-rhoda(III)oxetanes is best described as a rhodium(III) metallacyclopropane rather than a Rh(I) olefin adduct as previously described. X-ray absorption spectroscopy clearly demonstrates a change in oxidation state at rhodium following ligand coordination with tris(2-pyridylmethyl)amine. Both NMR and density functional theory studies suggest a high energy barrier to rotation of the coordinated ethylene, which is attributed to large geometric and electronic reorganization resulting from the loss of π-backbonding. The mechanism of formation of 2-rhoda(III)oxetanes is reevaluated based on the electronic description of the initial olefin complex and it is shown that H_2O_2 performs ligand-centred oxidation of the C_2H_4 fragment (rather than metal oxidation). The broader implications of these findings are discussed within the context of metal π-complexes in general and their reactivity.

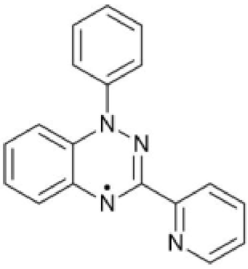
Synthesis and characterization of a new air stable 1,2,4-triazinyl radical and its coordination complexes

Ian Morgan, Akseli Mansikkamäki and Heikki M. Tuononen
Department of Chemistry, P.O. Box 35, University of Jyväskylä, Jyväskylä, FI-40014, Finland.
heikki.m.tuononen@jyu.fi

A benzo-1,2,4-triazinyl radical **1** synthesized by Blatter in 1968[1] has been dubbed 'indefinitely stable' in air.[2] Surprisingly few structural modifications have been performed to this system in the 35 years since its synthesis. Alteration of the structure to afford **2** has now been performed creating a bidentate coordination environment while retaining the stability of the radical in air. Full characterization of **2** has been published along with its successful coordination to a copper(II) centre.[3] Further coordination attempts with a variety of paramagnetic *d*-block metal ions have been executed, yielding new metal-radical complexes in different stoichiometry and crystal environments.[4] Density functional theory calculations and magnetic measurements have been used to elucidate the nature of metal-radical interactions in these systems.



1



2

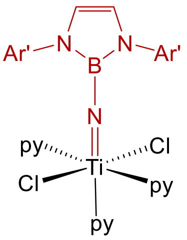
[1] H. M. Blatter, H. Lukaszewski *Tetrahedron Lett.* **1968**, *9*, 2701. [2] P. A. Koutentis, D. Lo Re *Synthesis* **2010**, 2075. [3] I. S. Morgan, A. Peuronen, M. H. Hänninen, R. Reed, R. Clérac, H. M. Tuononen *Inorg. Chem.* **2014**, *53*, 33. [4] I. S. Morgan, A. Mansikkamäki, G. A. Zissimou, P. A. Koutentis, M. Rouzières, R. Clérac, H. M. Tuononen *Chem. − Eur. J.* **2015**, *21*, 15843.

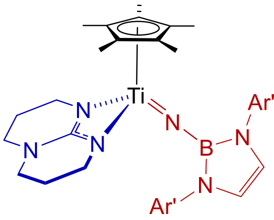
Synthesis and reactivity of titanium borylimido compounds

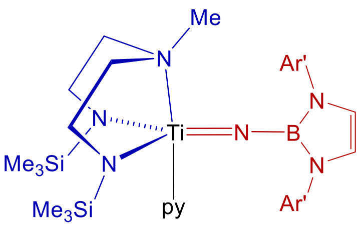
Benjamin A. Clough and Philip Mountford*
Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, OX1 3TA, U.K.
benjamin.clough@chem.ox.ac.uk

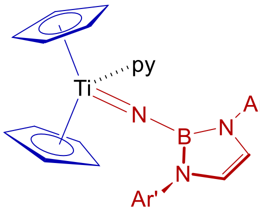
The chemistry of metal–nitrogen multiple bonds has been an area of considerable interest to researchers for over 20 years.[1] In particular, the synthesis and small molecule reactivity of Group 4 imido and hydrazido complexes, (L)M=NR and (L)M=NNR$_2$, have been extensively studied within this research group, and by others.[2]

In contrast, only a handful of examples of the related transition metal borylimides, (L)M=NBR$_2$, have been reported to date,[3] with no established synthetic route and no established reactivity. We here present the first systematic pursuit of borylimido complexes, namely of titanium, using the borylamine H$_2$NB(NAr'CH)$_2$ (Ar' = 2,6-C$_6$H$_3$^{i}Pr$_2$). To this end, we report two novel routes into titanium borylimido chemistry, and the subsequent installation of a varied range of supporting ligand sets.









Our desire to discover new C–N or C–B bond-forming reactions has now prompted us to carry out the first reactivity studies of the borylimido functional group. The results of the reactivity of these complexes with heteroallenes (CO$_2$, CS$_2$) and terminal alkynes will be reported here.

References

[1] For example: *Acc. Chem. Res.*, **2005**, *38*, 955; *Acc. Chem. Res.*, **2005**, *38*, 839; *J. Am. Chem. Soc.*, **2001**, *123*, 2923.
[2] For example: *Organometallics*, **2011**, *30*, 1182; *J. Am. Chem. Soc.*, **2004**, *126*, 1794; *Organometallics*, **2009**, *28*, 4747.
[3] *Polyhedron*, **1993**, *12*, 1061; *Z. Anorg. Allg. Chem.*, **2003**, *629*, 744; *Angew. Chem. Int. Ed. Engl.*, **2002**, *41*, 3709-3712; *J. Am. Chem. Soc.*, **2014**, *136*, 8197; *J. Am. Chem. Soc.*, **2015**, *137*, 10140.

Thorium(III) Small Molecule Activation Chemistry

Alasdair Formanuik, Fabrizio Ortu, Reece Beekmeyer, Andrew Kerridge, Ana-Maria Ariciu,
Floriana Tuna, Melissa A. Denecke, Ivan Pidchenko, Eric J. L. McInnes and David P. Mills*
School of Chemistry, The University of Manchester. Email: david.mills@manchester.ac.uk.

The small molecule activation chemistry of U(III) complexes has flourished in recent years,[1] whilst the corresponding Th(III) chemistry is underdeveloped.[2] This is surprising given that the calculated Th(IV)→Th(III) standard reduction potential (E^{Θ} –3.7 V) is far greater than its U(IV)→U(III) counterpart (E^{Θ} –0.6 V);[3] therefore a rich small molecule activation chemistry of Th(III) complexes can be anticipated.

We have started our investigations by studying the reactivity of Lappert's Th(III) complex, $[\mathrm{Th(Cp'')_3}]$ (**1**, Cp″ = $\{\mathrm{C_5H_3(SiMe_3)_2}\text{-}1,3\}^-$)[4] towards selected substrates. We found that **1** reacts with white phosphorus to give $[\{\mathrm{Th(Cp'')_3}\}_2(\mu\text{-}\eta^1\!:\!\eta^1\text{-}\mathrm{P_4})]$ (**2**), which exhibits a novel cyclo-P_4 binding mode (Figure 1).[5] The U(III) homologue of **1**, $[\mathrm{U(Cp'')_3}]$, does not activate P_4, and we have observed such divergent reactivity profiles for a wide range of small molecules and organic substrates. Our current progress in these studies will be presented here.

We thank The University of Manchester, the EPSRC and the Nuclear FiRST DTC for funding.

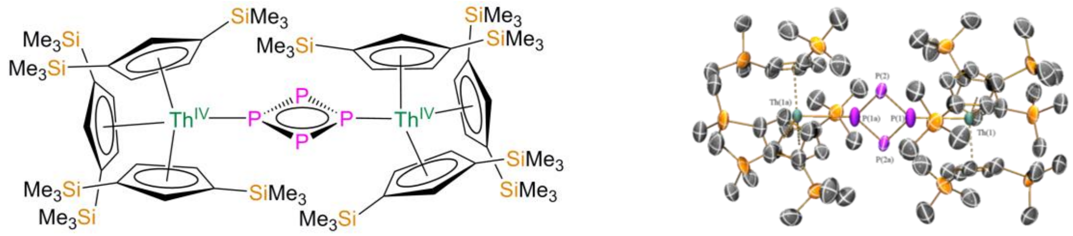


Figure 1. The cyclo-P_4 complex, **2**.

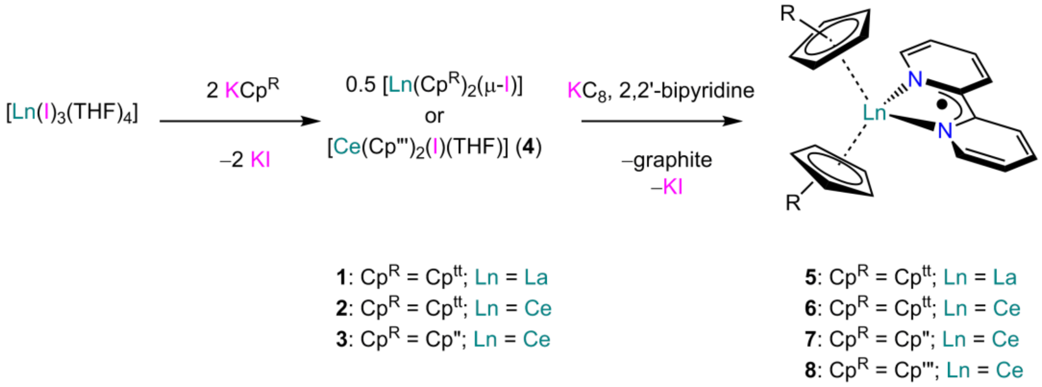
1. H. S. La Pierre and K. Meyer, *Prog. Inorg. Chem.*, 2014, **58**, 303.
2. R. R. Langeslay, J. R. Walensky, J. W. Ziller and W. J. Evans, *Inorg. Chem.*, 2014, **53**, 8455, and references cited therein.
3. L. J. Nugent, R. D. Baybarz, J. L. Burnett and J. L. Ryan, *J. Phys. Chem.*, 1973, **77**, 1528.
4. P. C. Blake, M. F. Lappert, J. L. Atwood and H. Zhang, *Chem. Commun.*, 1986, 1148.
5. A. Formanuik, F. Ortu, R. Beekmeyer, A. Kerridge, R. W. Adams and D. P. Mills, *Dalton Trans.*, 2016, **45**, 2390.

Synthetic, Physical and Theoretical Investigation of Lanthanide-Radical Complexes

Fabrizio Ortu, Jingjing Liu, Nicholas F. Chilton and David P. Mills

School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, UK.

Lanthanide (Ln) complexes containing non-innocent ligands have been widely studied for their interesting properties and potential applications.[1] In particular, Ln complexes containing bipyridyl radicals have been shown to possess remarkable physicochemical properties,[2] the true nature of which is yet to be fully unravelled. Herein we present the synthesis of a family of early lanthanide complexes of formula $[\mathrm{Ln(Cp^{R})_2(bipy^{\cdot -})}]$, obtained *via* reduction of heteroleptic cyclopentadienyl Ln complexes[3] with $\mathrm{KC_8}$ in the presence of 2,2'-bipyridine (see Scheme 1). The chemical and physical properties of these complexes have been thoroughly investigated, including an unprecedented in-depth theoretical analysis.[4]



Scheme 1. Synthesis of $[\mathrm{Ln(Cp^{R})_2(bipy^{\cdot -})}]$ complexes

References

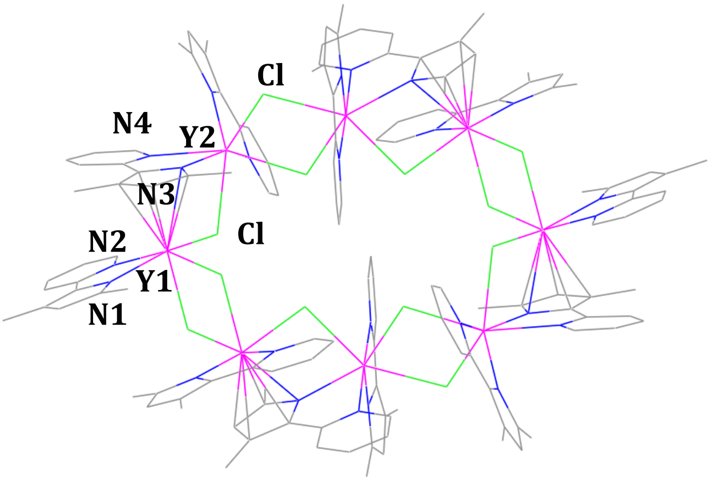
1. a) G. Poneti, G. Bernot, L. Bogani, A. Caneschi, R. Sessoli, W. Wernsdorfer, D. Gatteschi, *Chem. Commun.*, 2007, 1807-1809; b) J. D. Rinehart, M. Fang, W. J. Evans, J. R. Long, *Nature Chem.*, 2011, **3**, 538-542.
2. a) W. J. Evans, D. K. Drummond, *J. Am. Chem. Soc.*, 1989, **111**, 3329-3335; c) G. Nocton, W. W. Lukens, C. H. Booth, S. S. Rozenel, S. A. Medling, L. Maron, R. A. Andersen, *J. Am. Chem. Soc.*, 2014, **136**, 8626-8461.
3. F. Ortu, J. M. Fowler, M. Burton, A. Formanuik, D. P. Mills, *New. J. Chem.*, 2015, **39**, 7633-7639.
4. F. Ortu, J. Liu, M. Burton, J. M. Fowler, A. Formanuik, M.-E. Boulon, N. F. Chilton, D. P. Mills, *manuscript submitted*.

Title: Multi-metallic f-element complexes with redox-active ligands.

Joy H. Farnaby,* James R. Hickson, Kelsey V. Mills, Pippa K. Mitchell, Frederik Eiler, Andrew J. P. White and Nicholas J. Long.

*Department of Chemistry, Imperial College London, South Kensington Campus, LONDON, SW7 2AZ, UK, * e-mail: j.farnaby@imperial.ac.uk*

Multi-metallic materials, which combine either different f-element metals or f-metals with transition metals have great potential applications in energy materials science. Organometallic lanthanide and actinide complexes display single molecule magnet behavior and the best bulk magnets are multi-metallic and f-element containing (e.g. $Nd_2Fe_{14}B$). Our research has targeted several redox-active ligand frameworks to develop f-element multi-metallic chemistry: 1,10-phenanthroline derived ligands and substituted pyridylpyrrolides. We have explored a variety of synthetic routes to lanthanide and Ln/Group IV metal complexes containing 1,10-phenanthroline dione and also extended this chemistry to imidazole phenanthroline apended ferrocenes to synthesise Fe/Ln complexes for molecular electronics. The synthesis and reduction chemistry of lanthanide clusters containing redox-active ligands will also be presented, for example the chemistry of the $Y_8Cl_{12}L_{12}$ cluster below (L = 3,5,-dimethyl pyridylpyrrolide).



Steric Control of Redox Events in Organo-Uranium Chemistry.

Nikolaos Tsoureas and F. Geoffrey N. Cloke

School of Life Sciences, Division of Chemistry, University of Sussex, Falmer, Brighton, BN1 9QJ; nt85@sussex.ac.uk.

The use of well-defined molecular complexes of uranium has heralded new examples of chemical reactivity, especially in the topical field of small molecule activation.[1] For instance, in our laboratory we have shown the efficacy of organo-uranium complexes in promoting the reductive activation of CO and CO_2, and in particular the importance of the steric environment around the U(III) centre in controlling C-C bond formation.[2] Here we present further work underlining the influence of sterics in manipulating the oxidation state of the uranium centre, and resulting to the isolation of terminal oxo and nitride U(V) complexes (Figure 1).

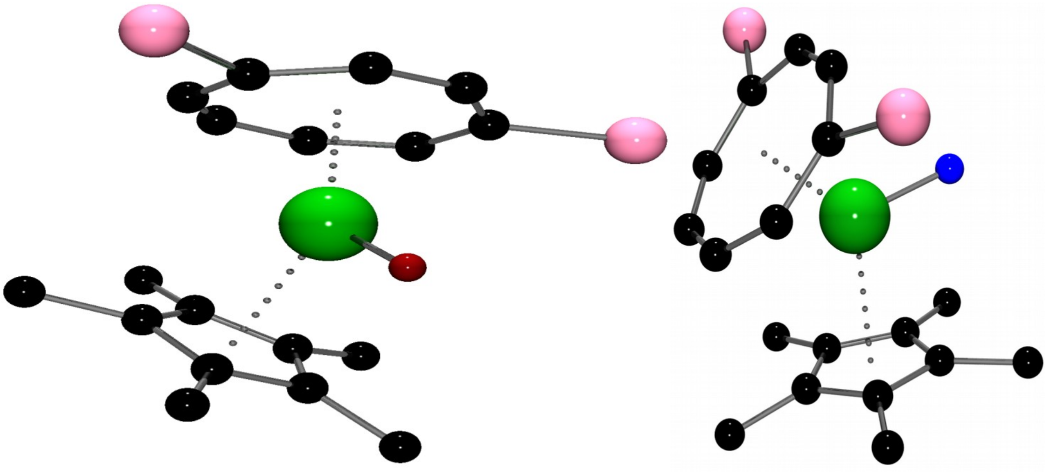


Figure 1 Mixed sandwich U(V) terminal oxo (left) and terminal nitride (right; Na counter-cation omitted for clarity) complexes.

1 a) Stephen T. Liddle, *Angew. Chem. Int. Ed.,* **2015,** *54,* 8604. b) P. L. Arnold, *Chem. Commun.*, **2011,** *47,* 9005. c) M. Ephritikhine, *Organometallics,* **2013,** *32,* 2464. d) H. S. La Pierre and K. Meyer, *Prog. Inorg. Chem.,* **2014,** *58,* 303.

2 a) N. Tsoureas, O.T. Summerscales, F.G.N. Cloke, and S.M. Roe *Organometallics*, **2013**, *32*, 1353. b) N. Tsoureas, L. Castro, A. F. R. Kilpatrick, F. Geoffey N. Cloke and L. Maron *Chem. Sci.,* **2014,** *5,* 3777.

Linear, branched and cyclic $Ru(dppe)_2(-C{\equiv}C-)_2$ systems for molecular electronics

L. E. Wilson,[a] M.S.Inkpen,[b] T. Albrecht[a] and N. J. Long[a*]

[a]*Imperial College London, Department of Chemistry, London, SW7 2AZ, UK.*
[b]*Columbia University, Department of Applied Physics and Department of Chemistry, New York, NY 10027, USA.*

Complex geometries for molecular wires may hold the key to advancing the capabilities of single molecular electronics. Theoretical and physical studies have shown that branched systems can increase the conductance of a molecular electronics system by a factor greater than 2, due to conductive interference. Our work aims to test this experimentally using large complex systems.[1, 2]

Building on our previous work,[3] we have produced robust and repeatable routes to a series of linear, branched and cyclic organometallic molecular wires with several binding groups (Figure 1). *Trans*-$Ru(-C{\equiv}C-R)_2(dppe)_2$ centres are incorporated into these designs as effective HOMO conductors that allow redox control.[4] Thorough investigation of these molecules through cyclic voltammetry and scanning tunnelling microscopy (STM) have probed the effects of interference, metal connectivity and redox properties on the conductance of these systems. The presentation will feature these results and latest data.

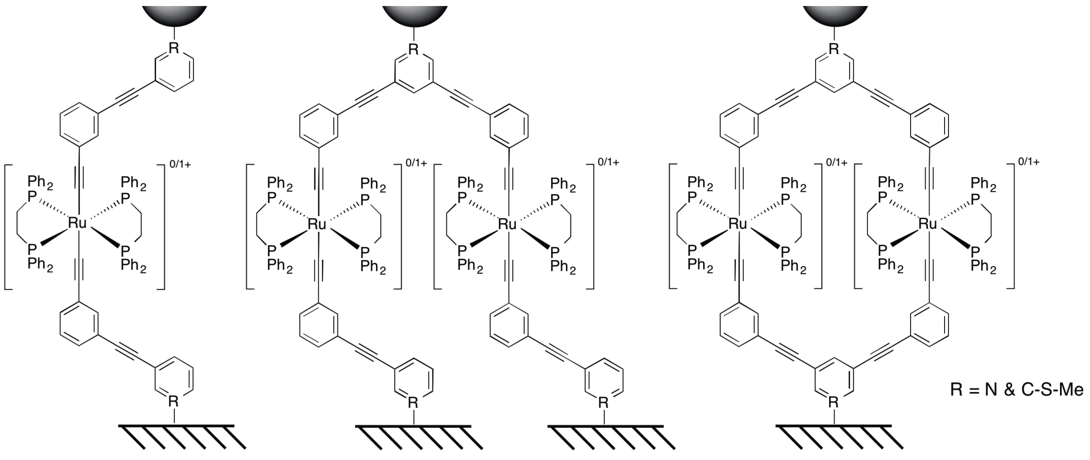


Figure 1: Organometallic molecular wires synthesised and studied within this work.

1. M. Magoga, C. Joachim, *Phys. Rev. B,* **1990**, *59,* 16011.
2. H. Vazquez, R. Skouta, S. Schneebeli, M. Kamenetska, R. Breslow, L. Venkataraman, M.S. Hybertsen, *Nat. Nanotechnol,* **2012**, *7,* 663.
3. M.S. Inkpen, T. Albrecht, N.J. Long, *Organometallics.* **2013**, *32*, 6053.
4. F.B. Meng, Y.M Hervault, L. Norel, K. Costuas, C. Van Dyck, V. Geskin, J. Cornil, H.H. Hng, S. Rigaut, X.D. Chen, *Chem. Sci.* **2012**, *3,* 3113

Reverse Alchemy: Turning Gold into a Transition Metal

Andrew Fensham-Smith, Prof. Paul Pringle, Dr. Chris Russell
School of Chemistry, University of Bristol, Cantock's Close, BS8 1TH
Chris.Russell@bristol.ac.uk

Gold catalysis is currently experiencing huge growth, and gold complexes have shown remarkable selectivity and conversion in a variety of complex transformations. Classical gold(I) cationic complexes almost exclusively adopt linear 2-coordinate environments. We have sought to develop ligands which force gold to adopt higher coordinations and/or 'unusual' coordination geometries, eliciting novel electronic and steric properties. We have developed a rapid and efficient synthesis of cationic bipyridine gold(I) alkene complexes from commercially available materials. Using this synthesis, we have been able to characterise a variety of derivatives of this type (figure 1).

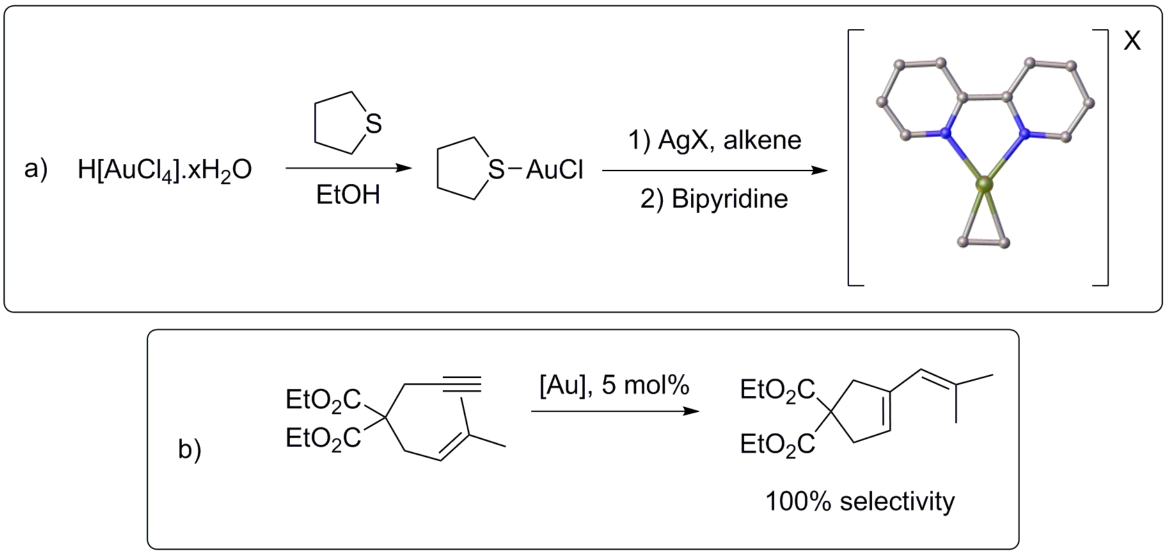


Figure 1. (a) Synthesis of bipyridine-gold(I)-alkene complexes; (b) Ene-yne cycloisomerisation

Gold(I) typically acts as a soft lewis acid, though in this complex significant back-donation occurs.[1] The NMR spectroscopy and bond lengthening in this class of compound is more akin to homoleptic platinum(0) alkene.[2] Herein, we report on a new synthesis and reactivity of these compounds, as well as some initial results of ene-yne cycloisomerisation catalysis.

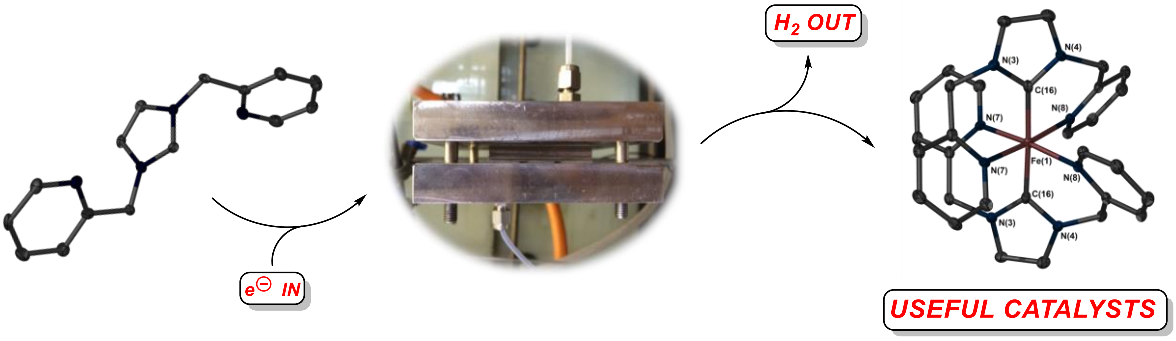
1. Cinellu, M. A.; Minghetti, G.; Cocco, F.; Stoccoro, S.; Zucca, A.; Manassero, M.; Arca, M., *Dalton Transactions* **2006,** (48), 5703-5716.
2. Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A., *J. Chem. Soc., Chem. Commun.* **1975,** (11), 449-451.

An Electrochemical Flow-Reactor for the Synthesis of Organometallic Complexes.

Michael R. Chapman, Prof Nikil Kapur, Dr Charlotte E. Willans, Dr Bao N. Nguyen.
Institute of Process Research and Development (iPRD), School of Chemistry, University of Leeds, LS2 9JT, United Kingdom.
E-mail: cmmrc@leeds.ac.uk

Developed by Arduengo over two decades ago, the notion of employing *N*-heterocyclic carbenes (NHCs) as ancillary ligands for transition metal-based catalysts has been refined such that they now present all required attributes for broad application – typically offering high return over their phosphine rivals (*e.g.* enhanced thermal stability and greater tunability).[1] Despite these advances, a number of drawbacks currently exist with traditional methods of metal-NHC preparation, notably when considering such complexes for industrial use. The pre-requisite for strongly basic/strictly inert conditions within current syntheses largely limits the scope of suitable substrate for metal-NHC complexation.[2] Complementary routes include transmetallation of a carbenic moiety from a basic metal oxide (*e.g.* Ag_2O),[3] leading to the accumulation of metal salt byproducts.

In light of these challenges, the design, construction and optimisation of an innovative electrochemical flow-reactor has been developed which circumvents such issues. The electrochemical approach, which has been published in *Chemical Communications*,[4,5] provides a clean and atom economical route to metal-NHCs as a result of: (i) no external reagents are required, (ii) a simple evaporative work-up and (iii) only H_2 gas byproduct.



References: 1. Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361-363. 2. Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39-91. 3. Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251* (5+6), 642-670. 4. Lake, B. R. M.; Bullough, E. K.; Williams, T. J.; Whitwood, A. C.; Little, M. A.; Willans, C. E. *Chem. Commun.* **2012**, *48* (40), 4887-4889. 5. Chapman, M. R.; Shafi, Y. M.; Kapur, N.; Nguyen, B. N.; Willans, C. E. *Chem. Commun.* **2015**, *51* (7), 1282-1284.

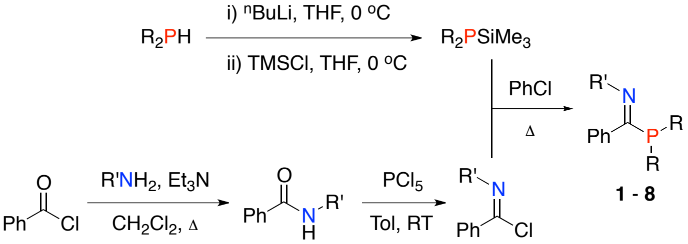
Highly selective ethylene trimerisation/tetramerisation using PCN ligands.

James. E. Radcliffe,[a] Andrei S. Batsanov,[a] David M. Smith,[b] John A. Scott,[b] Martin J. Hanton,[b] and Philip W. Dyer*,[a]

[a] *Centre for Sustainable Chemical Processes, Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK. Email: p.w.dyer@durham.ac.uk*

[b] *Sasol Technology UK, Ltd., Purdie Building, North Haugh, St Andrews, Fife, KY16 9ST, UK.*

Selective ethylene oligomerisation catalysis has attracted considerable interest over the past fifteen years, with tri- and tetra-merisation to commercially important 1-hexene and 1-octene being especially significant.[1-4] Here, we describe a modular synthetic route to κ^2-P,N 1-phosphanyl methanimine (PCN) ligands **1-8** (Scheme 1) and their implementation in ethylene oligomerisation catalysis.[5]



1: R = Ph, R' = *o*-Xyl
2: R = Ph, R' = Dipp
3: R = 2-OMe-C$_6$H$_4$, R' = *o*-Xyl
4: R = 2-OMe-C$_6$H$_4$, R' = Dipp
5: R = ^{i}Pr, R' = *o*-Xyl
6: R = ^{i}Pr, R' = Dipp
7: R = ^{t}Bu, R' = *o*-Xyl
8: R = ^{t}Bu, R' = Dipp

Scheme 1 Convergent, modular synthesis of PCN ligands.[5]

In combination with chromium salts and an activator, PCN metal scaffolds **1-8** promote selective oligomerisation of ethylene to 1-hexene and 1-octene with high activity (≤2800 kg gCr^{-1} h^{-1}). Notably, an exceptionally high liquid fraction selectivity to saleable products (1-hexene + 1-octene) is observed (>95%), making these some of the most selective systems known.[1-5] Furthermore, a potent ligand structure dependence is observed, such that selectivity can be varied from pure trimerization through to mixed tri-/tetra-merisation with a 1-octene:1-hexene (OTH) ratio of 1.7.[5] All of the systems examined have catalyst lifetimes in the range 1−3 h, essential for potentially economic commercial operation.

References:

1 J. T. Dixon, M. J. Green, F. M. Hess and D. H. Morgan, *J. Organomet. Chem.*, 2004, **689**, 3641.

2 D. S. McGuinness, *Chem. Rev.*, 2011, **111**, 2321.

3 T. Agapie, *Coord. Chem. Rev.*, 2011, **255**, 861.

4 P. W. N. M. van Leeuwen, N. D. Clément and M. J. L. Tschan, *Coord. Chem. Rev.*, 2011, **255**, 1499.

5 J. E. Radcliffe, A. S. Batsanov, D. M. Smith, P. W. Dyer and M. J. Hanton, *ACS Catal.*, 2015, **5**, 7095.

Proton-Coupled Mixed Valency in Hydrogen Bonded Dimers.

K. B. Vincent, L. A. Wilkinson, L. Brown, A. J. H. M. Meijer, N. J. Patmore

University of Huddersfield, Department of Chemical Sciences, Huddersfield, HD1 3DH, UK, k.b.vincent@hud.ac.uk.

The study of organometallic mixed valence systems has achieved much attention over recent decades with potential applications in photochromic systems[1] and molecular electronics.[2] In contrast to the typical, conjugated D-B-A architecture we present here a novel class of systems where metal-bridge-metal systems are prepared by exploiting self-complimentary hydrogen bonding functionality of the ligand to form dimeric species.[3] Electrochemical analyses of these hydrogen bonded dimers show that in non-coordinating solvents thermodynamic stability of the mono-cation is observed, resulting in two consecutive one-electron oxidations. Conversely, electrochemistry in coordinating solvents gives a single redox process. Further results from EPR spectroscopy and IR spectroelectrochemistry have shown that timescale for this process is slower than slower than 10^9 s^{-1}, while in the UV-vis NIR spectroelectrochemistry no IVCT band is observed, as would be expected in classic MV systems. In trying to understand the mechanism for PCMV we have probed the possible mechanisms by DFT and results show that ET is directly related to the proton coordinate in what can be considered a dipole induced electron self-exchange mechanism (see, Figure 1). These results are further supported by studies on systems where the nature of the bridging ligand has been augmented with electron donating / withdrawing substituents.

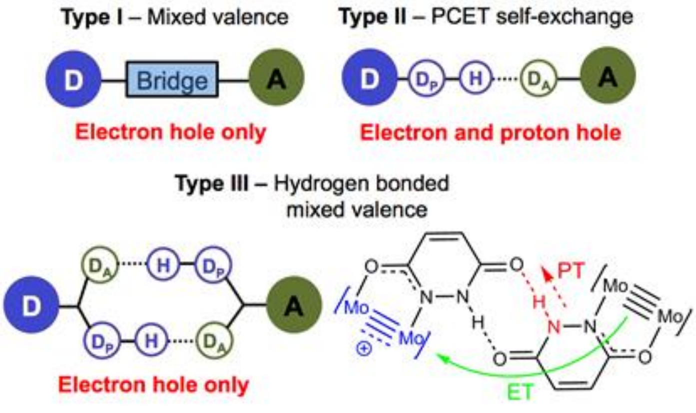


Figure 1: Proposed mechanism for proton-coupled mixed-valency

1. R. Sakamoto. et al. *Chem. Eur. J.* 2008, **14**, 6978
2. P.J. Low. *Dalton Trans*. 2005 2821
3. N. J. Patmore. et al, *J. Am. Chem. Soc*., 2013, **135**, 1723. L. A. Wilkinson; L. McNeill; P. Scattergood,; N. J. Patmore. *Inorg. Chem*., 2013, **52**, 9683. Wilkinson, L. A.; Vincent, K. B.; Meijer, A. J. H. M.; Patmore, N. J., *Chem. Commun.* 2016, **52**, 100.

New *tris*(hydroxypyridinone) chelators for ^{68}Ga PET imaging

Cinzia Imberti [a], Michelle T. Ma[a], Brett M. Paterson[a], Jennifer D. Young[a], Vincenzo Abbate[b], Robert C. Hider[b] Philip J. Blower [a]

[a]*KCL, Division of Imaging Sciences and Biomedical Engineering, St Thomas' Hospital, London;* [b]*KCL, Institute of Pharmaceutical Science,150 Stamford Street, London.*

---

^{68}Ga-based PET imaging agents are gaining increasing interest because of the suitable decay profile of ^{68}Ga ($t_{½}$=68 min, 90% β^+ yield) and its availability from a long-lived generator. Most of the $^{68}Ga^{3+}$ ligands in use to date are based on macrocyclic chelators, whose typical radiolabelling conditions (high temperature, pH ≤ 5) are not ideal for sensitive bioconjugates. In contrast, the acyclic *tris*(hydroxypyridinone) chelator H_3THP^1 efficiently binds $^{68}Ga^{3+}$ under mild conditions[1] and radiolabeled peptide derivatives effectively target tumours *in vivo*.[2] However, persistent retention of such derivatives in non-target tissue suggests that modification of the chelator –to increase its hydrophilicity and water solubility- would improve biodistribution of the radiotracers.

Herein we report the synthesis of a second generation *tris*(hydroxypyridinone) chelator, H_3THP^2, where the N-methyl group in the hydroxypyridinone unit has been replaced by hydrogen. H_3THP^2 coordinates $^{68}Ga^{3+}$under mild conditions and at low ligand concentration, achieving quantitative radiochemical yield and high specific activity. The resulting complex [^{68}Ga(THP^2)] displays vastly improved water solubility compared to [^{68}Ga(THP^1)] and was shown to be the preferential product in competition studies featuring both ligands.

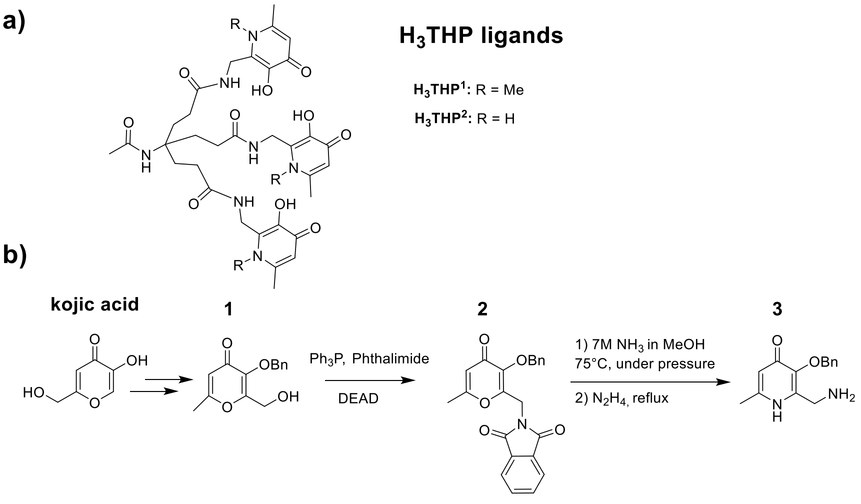


Figure 1 a) Chemical structures of H_3THP ligands. **b)** New synthetic route for the hydroxypyridinone precursor **3**. Compound **1** was synthesized in 4 steps from Kojic acid following literature procedures[1].

1) Berry D.J et al., *Chemical Communications***, 2011**, 47**,** 7068, **2)** Ma, M.T, Imberti, C. et al., *Bioconjugate Chemistry*, **2016**, 27 (2), 309.

Design of Copper and Gold Carbene Complexes for Fabrication of Highly Efficient Organic Light-Emitting Diodes

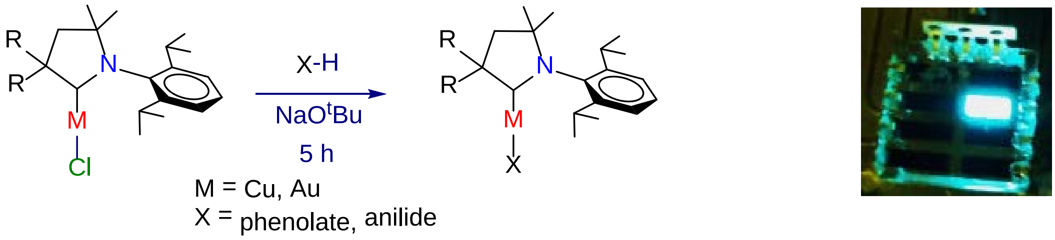
A.S. Romanov,[a] D. Di,[b] D. Credgington,[b] M. Bochmann[a]

[a] *School of Chemistry, University of East Anglia, Earlham Road, Norwich, NR4 7TJ, UK; E-mail: asromanov5@gmail.com*

[b] *Department of Physics, Cavendish Laboratory, Cambridge University, Cambridge CB3 0HE, UK*

A number of coinage metal carbene complexes have been shown to give rise to photoluminescent compounds, especially copper based complexes which are particularly attractive since copper is inexpensive and abundant. At the same time a clever choice of the ligands is important for successful incorporation of coinage metal complexes into organic light-emitting diodes (OLEDs) to achieve high efficiency and brightness.

We report here highly efficient synthesis of Cyclic (alkyl)(amino)carbenes (CAACs) copper and gold complexes with phenolate and amide ligands (Scheme 1).[1] All complexes are stable (up to 260°C) and display intense photoluminescence which is important for fabrication of OLEDs. Electrochemistry allowed us to probe the energies of the frontier orbitals for all complexes and identify the promising candidates for use in OLED. We developed very bright OLED based on (CAAC)M(carbazolate) complexes with brightness (up to 12500 cd/m^2) at maximum efficiency which far exceeds that necessary for display applications. Such a bright OLED allows us to use low voltage (5-6 V) to achieve optimal lighting characteristics which are currently used in LCD (200-300 cd/m^2) and HDTV (450-1000 cd/m^2) display technology.



Scheme 1. General synthetic scheme for the preparation of amide and phenolate complexes. Inset shows operation of OLED based on (CAAC)Au(carbazolate).

---

[1] Romanov, A. S.; Bochmann, M. *Organometallics* **2015**, *34*, 2439−2454.

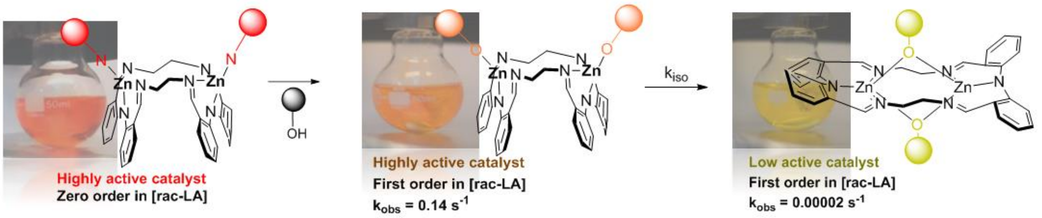
Structure-Activity Relationships for Macrocyclic Dinuclear Zinc Complexes for Polymerization: Importance of the Catalyst Structure.

Arnaud Thevenon [†], Charles Romain [†], Michael Bennington [‡], Hannah Davidson [‡], Sally Brooker [‡], Charlotte K. Williams*[†].

[†] *Department of Chemistry, Imperial College London, London, SW7 2AZ, United Kingdom*

[‡] *Department of Chemistry, University of Otago, Dunedin 9054, New Zealand*

Developing new catalysts for racemic lactide (rac-LA) ring opening polymerization (ROP) is important to understand the key features controlling the production of the bio-degradable polymer and to improve its physical chemical properties. Our focus has been to investigate zinc catalysts and recently, we reported dizinc bis(ethyl) macrocycle pre-catalysts which showed good rates in rac-LA ROP.[1] One limitation was that an induction period was observed due to the slow reaction of the Zn-Et with alcohol sources to generate the active alkoxide initiator. Here, new di-zinc bis(amido) pre-catalysts are synthesised, and are shown to rapidly form alkoxide complexes upon addition of alcohol. The structure-activity relationships of two di-Zn bis(amido) macrocycles, differing in ring sizes, and their corresponding alkoxides are explored.



Scheme 1 Dependence of the catalyst structures on catalytic performance.

The activity of the series is remarkably high, being more than an order of magnitude higher than the other known zinc catalyst under comparable conditions (Scheme 1).[2] The catalysts are highly tolerant and maintain high activity even under high rac-LA loadings (≤ 50,000 equiv. vs. 1 equiv. of catalyst). The catalysts show high levels of control affording aliphatic polyesters with controlled molecular weights and narrow dispersities. Catalyst comparisons reveal that the structure of the complex exerts a strong effect on the rate of the polymerization (Scheme 1). There is a positive effect of two metal centres being in close proximity (~4.8 Å) and the catalysts are significantly better when coordinated by the macrocycle compared to other ligand structures.

[1] Romain, C.; Bennington, M. S.; White, A. J. P.; Williams, C. K.; Brooker, S., *Inorg. Chem.* **2015**, *54* (24), 11842, [2] Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G.; Hillmyer, M. A.; Tolman, W. B., *J. Am. Chem. Soc.* **2003,** *125* (37), 11350.

Field-induced slow magnetic relaxation in a mononuclear Mn(III) complex: An ambient and high pressure study.

G. A. Craig,[a] C. H. Woodall,[b] J. J. Marbey,[c] S. Hill,[c] O. Roubeau,[d] S. C. McKellar,[b] M. R. Probert,[e] K. V. Kamenev,[b] S. A. Moggach,[b] E. K. Brechin,[b] S. Parsons,[b] and M. Murrie[a]

[a]*WestCHEM, School of Chemistry, University of Glasgow, Glasgow, UK*

[b]*EaStCHEM, School of Chemistry, and Centre for Science at Extreme Conditions, University of Edinburgh, Edinburgh, UK*

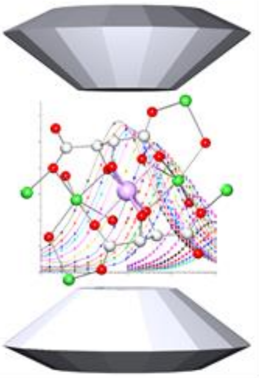
[c]*Department of Physics and NHMFL, Florida State University, Tallahassee, FL, USA*

[d]*Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC and Universidad de Zaragoza, Plaza San Francisco, Zaragoza, Spain*

[e]*School of Chemistry, Newcastle University, Newcastle-upon-Tyne, UK*

gavin.craig@glasgow.ac.uk

Slow relaxation of magnetisation of a single ion in a suitable ligand field,[1] and high pressure studies of metal complexes[2] are hot topics in coordination chemistry. The former uses synthetic chemistry to achieve large magnetic anisotropy: sometimes an order of magnitude beyond that observed in polynuclear assemblies.[3] The latter have shown that pressure can flip the orientation of Jahn-Teller axes.[4] Herein, we describe the magnetic anisotropy and field-induced slow relaxation of magnetisation observed in the compound $Na_5[Mn(L\text{-}tart)_2]\cdot 12H_2O$ (**1**, L-tart = L-tartrate).[5] The effect of hydrostatic pressure on the structure and magnetic properties of **1** will be detailed, revealing an unusual role played by the alkali metal ions.[6]



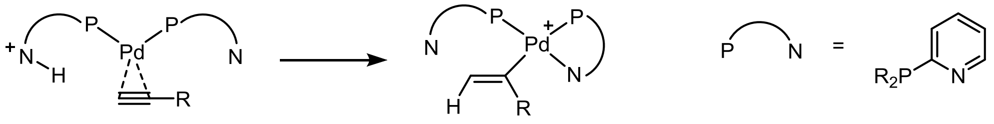
1 G. A. Craig, M. Murrie, *Chem. Soc. Rev.*, **2015**, *44*, 2135. 2 J. P. Tidey, H. L. S. Wong, M. Schroder, A. J. Blake, *Coord. Chem. Rev.*, **2014**, *277*, 187. 3 S. Gomez-Coca, E. Cremades, N. Aliaga-Alcalde, E. Ruiz, *Inorg. Chem.*, **2014**, *53*, 676. 4 P. Parois, S. A. Moggach, J. Sanchez-Benitez, K. V. Kamenev, A. R. Lennie, J. E. Warren, E. K. Brechin, S. Parsons, M. Murrie, *Chem. Commun.*, **2010**, *46*, 1881. 5 G. A. Craig, J. J. Marbey, S. Hill, O. Roubeau, S. Parsons, M. Murrie, *Inorg. Chem.*, **2015**, *54*, 13. 6 G. A. Craig, C. H. Woodall, S. C. McKellar, M. R. Probert, K. V. Kamenev, S. A. Moggach, E. K. Brechin, S. Parsons, M. Murrie, *Dalton Trans.*, **2015**, *44*, 18324.

“Proton shuttling” Pyridylphosphines for Methoxycarbonylation

Timothy A. Shuttleworth, Paul G. Pringle.

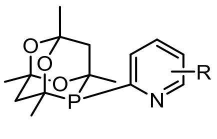
University of Bristol, Timothy.Shuttleworth@bristol.ac.uk.

The palladium-catalysed methoxycarbonylation of alkenes or alkynes is an atom efficient pathway to transform cheap, abundant starting materials into complex organic molecules and platform chemicals.[1] For example, the commercialisation of Lucite’s “Alpha process”, a two stage, high yielding synthesis of MMA, is arguably the most important recent application of homogeneous organometallic catalysis to commodity chemicals manufacture.[2] Drent *et al.* showed that pyridylphosphines produce the most active and selective Pd-catalysts for alkyne methoxycarbonylation,[1] and attributed this to two facets of the ligand: its ability to act as a “proton shuttle” between the bulk media and the metal centre and its hemilability, which acts to stabilise the catalyst (Scheme 1).



Scheme 1. Pyridylphosphines assisting the metal during catalysis.

We have investigated the catalytic potential of the pyridylphosphines CgPPy^R, (where Py^R = R-substituted pyridyl and CgP = 6-phospha-2,4,8-trioxa-1,3,5,7-tetramethyladamant-6-yl). Complexes of mono- and bidentate ligands containing CgP donors have been shown to be excellent catalysts for a range of reactions, including methoxycarbonylation.[3] By variation of the R substituents on the pyridine ring, it should be possible to measure the catalytic properties of the complexes of CgPPy^R as a function of the basicity of the pyridine.



CgPPy^R

The preparation of a range of crystalline, air-stable CgPPy^R ligands has been readily achieved. These ligands have been applied to the Pd-catalysed methoxycarbonylation of phenylacetylene and the results are interpreted by reference to their coordination chemistry, which has shown their potential for hemilabile behaviour and protonation during catalysis.

---

[1] Crawford, L.; Cole-Hamilton, D. J.; Bühl, M. *Organometallics* **2015**, *34*, 438–449 and references therein.

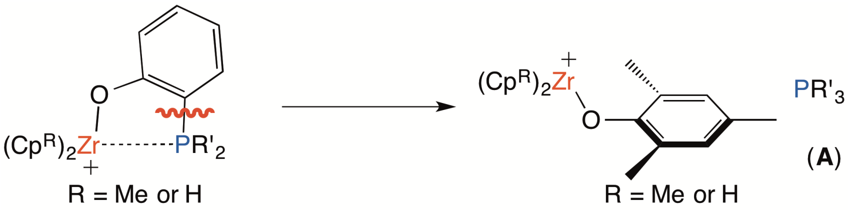
[2] Tooze, R. P.; Eastham, G. R.; Whiston, K.; Wang, X. L. *World Patent* **1996**, WO/1996/019434.

[3] Pringle, P. G.; Smith, M. B. in *Phosphorus(III) ligands in Homogeneous Catalysis: Design and Synthesis*; Kamer, P. C. J.; van Leeuwen, P. W. N. M., Eds.; John Wiley & Sons, 2012.

Advances in Transition Metal Frustrated Lewis Pair Chemistry

Owen J Metters, Duncan F. Wass, Ian Manners
University of Bristol, Cantock's Close, Bristol, UK, BS8 1TS

Recent work in the Wass group has focussed on the development of novel *intra*molecular frustrated Lewis pair (FLP) systems containing transition metal (Zr(IV), Ti(III) and Ti(IV)) fragments. These systems have been shown to be highly reactive towards small molecules (e.g. CO_2, H_2, ethers), and also competent catalysts for the dehydrocoupling of amine-boranes.[1] Modifications to these current systems have led us to synthesise a range of *inter*molecular FLPs containing the analogous transition metal fragments (**A**).



These intermolecular systems (**A**) demonstrate reactivity towards small molecules similar to that of their intramolecular counterparts, however the absence of the aryl tether provides easy access to a wider range of Lewis bases, allowing us to explore the effect of varying phosphine sterics and electronics on FLP reactivity.

The intramolecular nature of these systems also permits more facile exploration of reaction mechanisms; allowing separation of the roles of the Lewis acidic and basic moieties. This methodology has been applied to elucidate the mechanism of FLP catalysed imine hydrogenation and amine-borane dehydrocoupling reactions.

[1] (a) Chapman, A. M.; Haddow, M. F.; Wass, D. F., *J. Am. Chem. Soc.,* **2011**, *133*, 18463, (b) Chapman, A. M.; Haddow, M. F.; Wass, D. F., *J. Am. Chem. Soc.,* **2011**, *133,* 8826 (c) Chapman, A. M.; Wass, D. F; *Dalton Trans.,* **2012**, *41*, 9067

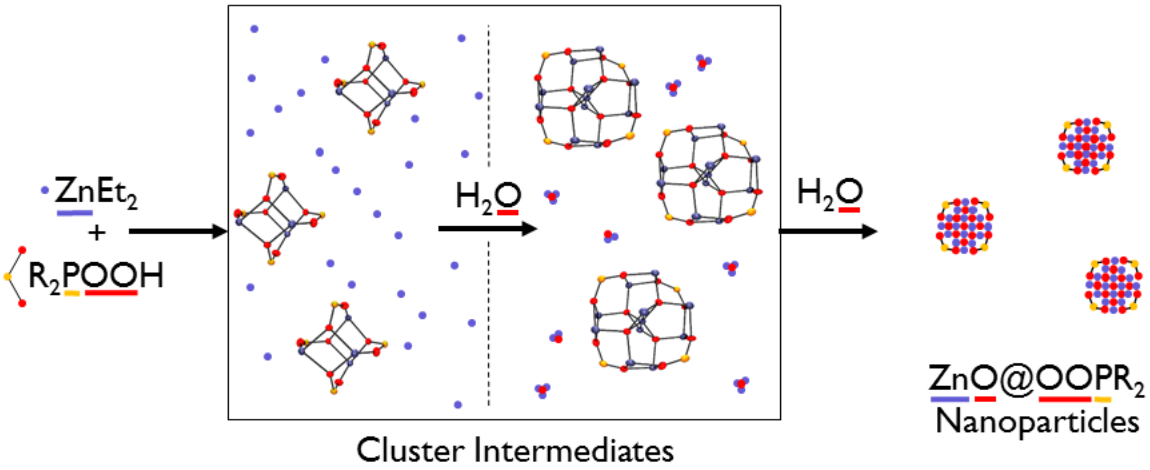
[2] Metters, O. J.; Forrest, S. J. K.; Wass, D. F.; Manners, I.; *J. Am. Chem. Soc.*, **2016**, *138*, 1994

In-situ identification of well-defined zinc cluster molecules during the synthesis of functional ZnO nanoparticles

S. D. Pike, M. S. P. Shaffer, C. K. Williams
Imperial College London, Department of Chemistry, London, SW7 2AZ, U.K.

e-mail: s.pike@imperial.ac.uk

ZnO nanoparticles are used in many contexts including photo-electronic devices, catalysis[1] and photoactive antimicrobial surfaces.[2] This report presents the synthesis of small ZnO nanoparticles (2-4 nm) supported by dioctylphosphinate ligands by the controlled hydrolysis of $ZnEt_2$. In-situ monitoring of the reaction using ^{31}P NMR spectroscopy reveals a series of phosphinate ligated Zn clusters which are formed during the synthesis and act as precursors to ZnO. Analogous clusters using diphenylphosphinate ligands were prepared and fully characterised, including by X-ray crystallography, to reveal the structures of these clusters. The clusters (including a $Zn_{11}Et_{10}O_4L_4$ structure) represent the growing ZnO core as organometallic fragments react with water, and are closely inter-related by a series of equilibria. The results shed new light on nanoparticle synthesis, in particular with respect to an equilibrating reaction mixture and the distribution of ligands during the formation of nanoparticles.



The applications of the ZnO nanoparticles are also explored, especially for use as colloidal catalysts (in combination with Cu nanoparticles) for the hydrogenation of CO_2 to form methanol, and the use of ZnO impregnated polymer films as antibacterial surfaces.

References

(1) Brown, N. J.; Weiner, J.; Hellgardt, K.; Shaffer, M. S. P.; Williams, C. K. *Chem. Commun.* **2013**, *49*, 11074.
(2) Noimark, S.; Weiner, J.; Noor, N.; Allan, E.; Williams, C. K.; Shaffer, M. S. P.; Parkin, I. P. *Adv. Funct. Mater.* **2015**, *25*, 1367.

Novel Precursors for deposition of ZrO_2

Amanda Catherall, Prof. Michael Hill

Department of Chemistry, University of Bath. Email: a.catherall@bath.ac.uk

Interest in ZrO_2 has increased vastly in recent years due to its unique properties such as; high melting point, chemical inertness, high refractive index, wide band gap (> 5 eV), high dielectric constant ($\kappa \sim 18$), low thermal conductivity and high electrical resistivity. These properties give it a wide range of applications which include: optical filters, wear-resistant coatings, thermal barrier coatings and gate dielectrics.

There are numerous reports in the literature of ZrO_2 thin films deposited by a variety of different methods, such as; reactive sputtering, spray pyrolysis, atomic layer deposition (ALD) and chemical vapour deposition (CVD). Sputtering and ALD, however, require high vacuum systems which in turn require specialised equipment and expensive processing costs. A modified CVD technique, aerosol assisted CVD (AACVD) has many advantages over other deposition techniques, the major ones being that it does not require expensive equipment and can provide a large deposition area. This technique differs from conventional CVD techniques as it delivers the precursor to the substrate in aerosol droplets and, therefore, eliminates the need for highly volatile precursors.

There are a number of reports of ZrO_2 deposited by AACVD. In these reports, however, the films are deposited from β-diketonate complexes which results in a high carbon contamination in the films.[1-5] Reported herein is a synthetic approach to suitable AACVD precursors for the deposition of ZrO_2 without any impurities in the film. The complexes will be analysed by NMR and X-ray crystallography (Figure 1) and the decomposition will be analysed by TGA. The deposited films will be analysed by pXRD, SEM, AFM and XPS.

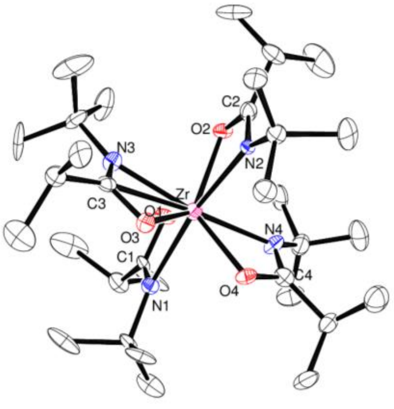


Figure 1 Crystal structure of a homoleptic zirconium amidate

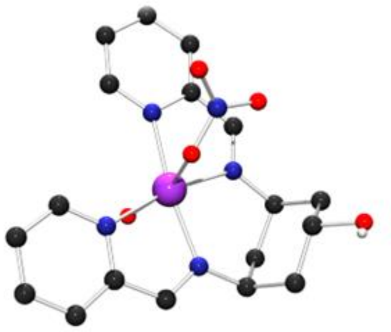
---

1 Wang, H. B.; Xia, C. R.; Meng, G. Y.; Peng, D. K. *Materials Letters* **2000**, *44*, 23.
2 Ramírez, E. B.; Huanosta, A.; Sebastian, J. P.; Huerta, L.; Ortiz, A.; Alonso, J. C. *J Mater Sci* **2007**, *42*, 901.
3 Ortiz, A.; Alonso, J. C.; Haro-Poniatowski, E. *Journal of Elec Materi* **2005**, *34*, 150.
4 Song, H.; Xia, C.; Jiang, Y.; Meng, G.; Peng, D. *Materials Letters* **2003**, *57*, 3833.
5 Jiang, Y.; Gao, J.; Liu, M.; Wang, Y.; Meng, G. *Solid State Ionics* **2007**, *177*, 3405

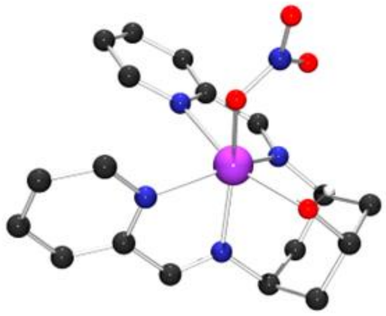
Bis-Iminopyridine based Hydrogen Evolution Catalysts with Coordinating and Non-Coordinating Proton Relays

Simon N. Child, H. El Moll and John Fielden
School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, UK.
E-mail: John.Fielden@uea.ac.uk

Metalloenzymes achieve efficient proton reduction, through substrate-activating secondary coordination spheres and relays that funnel protons and electrons to their active sites.[1] We are developing bio-inspired modular catalytic systems using *bis*-iminopyridine derivatives of 1,3,5-substituted cyclohexanes as ligands.



1



2

1st row transition metal complexes of related N_4 chelators are competent electrocatalysts for H_2 production at moderate pH,[2] but in our case, the rigid cyclohexane backbone allows us to fix the location of a pendant base[3] (proton relay) in relation to the metal, depending on the geometry (*cis* or *trans*) of the ligand. Here we will discuss the influence of these geometries on hydrogen evolution in cobalt(II) complexes, where the cyclohexane based ligand places a hydroxyl 'relay' group in either a proximal, coordinating (*cis* geometry, **1**) or distal, non-coordinating (*trans* geometry, **2**) location relative to the cobalt centre. We will also show preliminary results for related complexes of Ni and Mn.

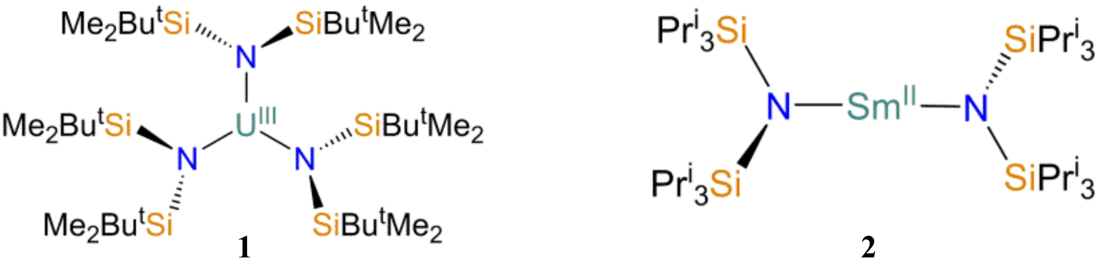
[1] C. Pickett and C. Tard, *Chem. Rev.* 2009, **109**, 2245.

[2] B. D. Stubbert, J. C. Peters and H. B. Gray, *J. Am. Chem. Soc.* 2011, **133**, 18070.

[3] A. D. Wilson, R. H. Newell, M. J. Mc.Nevin, J. T. Muckerman, M. R. DuBois and D. L. Dubois, *J. Am. Chem. Soc.* 2006, **128**, 358

UNPRECEDENTED F-ELEMENT GEOMETRIES USING SUPER-BULKY LIGANDS

Conrad A. P. Goodwin,[a] Nicholas F. Chilton,[a] William J. Evans,[b] David P. Mills*[a]
Email: david.mills@manchester.ac.uk
[a] *School of Chemistry, The University of Manchester, Manchester, M13 9PL, UK*
[b] *School of Physical Sciences, University of California, Irvine, CA 92697, USA*



1 **2**

Figure 1. Complexes **1** and **2**.

Investigations into low coordination number (CN) metal complexes are legion as they can exhibit interesting properties, including small molecule activation chemistry[1] and single molecule magnet (SMM) behaviour.[2] f-Block metal centres prefer high CNs, therefore sterically demanding ligands are required to prevent oligomerisation. Bulky monodentate amides have been frequently utilised, such as the bulky silylamide $\{N(SiMe_3)_2\}^-$ (N″), which has provided landmark low CN f-element complexes such as $[U^{III}(N'')_3]$.[3]

We have recently developed a series of group 1 silylamide transfer agents, $[K\{N(SiR_3)(SiR'_3)\}]$ (SiR_3, SiR'_3 = $SiMe_3$, $SiBu^tMe_2$, $SiPr^i_3$), that are more sterically demanding than N″.[4] We are currently investigating their utility in the preparation of low CN f-element complexes. In preliminary studies, we have prepared:

1) The first trigonal planar actinide complex, $[U^{III}\{N(SiMe_2Bu^t)_2\}_3]$ (**1**).[5] This complex has been compared to $[U^{III}(N'')_3]$, which is trigonal pyramidal, to gauge how changes in geometry affect magnetic properties and reactivity profiles of U^{III} complexes.
2) The first near-linear f-element complex, $[Sm^{II}\{N(SiPr^i_3)_2\}_2]$ (**2**).[6] We have used this complex as a model to prepare a series of near-linear lanthanide complexes with interesting physical properties, and we have embarked on a full reactivity study of this series.

References

1. C. C. Lu, K. Meyer, *Eur. J. Inorg. Chem.* **2013**, 3731–3732 and references cited therein.
2. *Molecular Nanomagnets*, D. Gatteschi, R. Sessoli, J. Villain, OUP, Oxford, **2006**.
3. R. A. Andersen, *Inorg. Chem.* **1979**, *18*, 1507.
4. C. A. P. Goodwin, K. C. Joslin, S. M. Lockyer, A. Formanuik, G. A. Morris, F. Ortu, I. J. Yrezabal-Vitorica and D. P. Mills, *Organometallics*, **2015**, *34*, 2314.
5. C. A. P. Goodwin, F. Tuna, E. J. L. McInnes, S. T. Liddle, J. McMaster, I. J. Vitorica-Yrezabal, D. P. Mills, *Chem. Eur. J.* **2014**, *20*, 14579.
6. N. F. Chilton, C. A. P. Goodwin, D. P. Mills, R. E. P. Winpenny, *Chem. Commun.* **2015**, *51*, 101.
7. C. A. P. Goodwin, N. F. Chilton, G. F. Vettese, E. M. Pineda, I. F. Crose, J. W. Ziller, W. J. Evans and D. P. Mills, *Manuscript in preparation.*

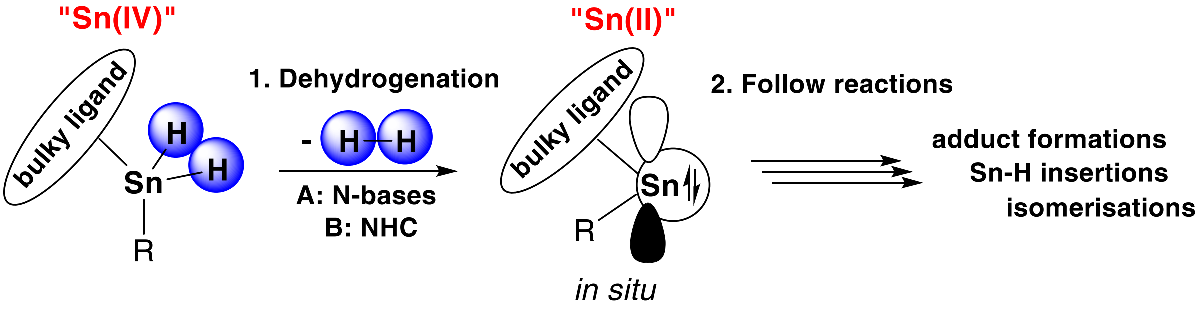
Organotin(IV) di- and trihydrides as precursors for low-oxidation state organotin chemistry by dihydrogen release.

Christian P. Sindlinger[†‡], Lars Wesemann[†*].

† Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen,
‡ Department of Chemistry, University of Oxford, christian.sindlinger@chem.ox.ac.uk

Compared to organotin monohydrides the chemistry of organotin di- and trihydrides has been scarcely investigated. The release of dihydrogen or a synthetic equivalent from Sn(IV) hydrides offers a clean, salt-free reduction reaction route toward the generation of the highly reactive organotin(II) compounds.[1a-c] We investigated selective dehydrogenations of bulky aryl substituted organotin di- and trihydrides applying a catalytic (**A**, see scheme) and a stoichiometric (**B**) approach to *in situ* form stannylenes and organotin(II) hydrides.[1d,e] Depending on the conditions, in controllable follow reactions, clean access to tin-tin dehydrocoupling products or a variety of low-oxidation state tin compounds or their monomeric base-adducts is realized. Effects of variation of the ligand bulk, stoichiometry and donor strength of the dehydrogenation agent have been studied in detail. The obtained low-oxidation state tin(II) species are promising precursors for further derivatization *e.g.* in coordination chemistry.

First results for the applicability of the general concept as well as recent attempts to understand the dehydrogenation processes will be presented.[2]



References:

[1] (a) X. Fu, W.P. Neumann, *J. Organomet. Chem.* **1984**, C5. (b) N. R. Neale, T. D. Tilley *J. Am. Chem. Soc.*, **2002**, *124*, 3802. (c) C. P. Sindlinger, L. Wesemann, *Chem. Sci*, **2014** *5*, 2739; (d) B. E: Eichler, P. P. Power, *J. Am. Chem. Soc* **2000**, *122*, 8785; (e) E. Rivard et al, *J. Am. Chem. Soc* **2007**, *129*, 16197. [2] (a) C. P. Sindlinger et al., *Chem. Sci* **2015**, *6*, 4737. (b) C. P. Sindlinger et al., *Chem. Eur. J.* **2016**, *accepted for publication.*

Synthesis and reactivity of phosphinidene boranes

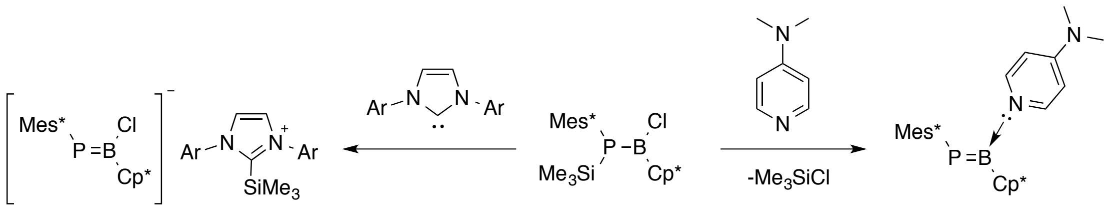
Amy N. Price and Michael J. Cowley*

michael.cowley@ed.ac.uk

EaStChem School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, EH9 3FJ, United Kingdom

Phosphinidene boranes, RP=BR, are the heavier homologues of the widely studied imino-boranes, RN=BR. In contrast to the imino-boranes, few examples are known and those that do exist are generally stabilized by coordination of Lewis acids or bases to the phosphorus or boron centres respectively.[1–3] Nevertheless, the reactivity of the as-yet-unknown uncoordinated phosphinidene-boranes, especially given recent progress in the chemistry of the isoelectronic group 14 alkyne analogues, is of high interest.

We have recently embarked upon a project designed to prepare the first acid/base-free phosphinidene boranes, and here report some preliminary results, including a new high-yielding route to base-stabilised phosphinidene boranes. For example, treatment of the functional phosphino-borane **1** with a range of Lewis bases (e.g. DMAP) results in the formation of base-stabilized phosphinidene boranes such as **2**, whilst reactions with larger NHCs lead to desilylation to form **3**. We will present details of the synthesis, structure and reactivity of these compounds and related species.



3 **1** **2**

Mes* = 2,4,6-trimethylphenyl
Ar = 2,6-dimethylphenyl

Figure 1. Reactivity of the functional phosphinoborane **1.**

Acknowledgements: We gratefully acknowledge the University of Edinburgh and the European commission (Marie Curie CIG to MC) for funding.

References:

[1] G. Linti, H. Nöth, K. Polborn, R. T. Paine, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 682–684.

[2] E. Rivard, W. A. Merrill, J. C. Fettinger, P. P. Power, *Chem. Commun.* **2006**, 3800–2.

[3] E. Rivard, W. A. Merrill, J. C. Fettinger, R. Wolf, G. H. Spikes, P. P. Power, *Inorg. Chem.* **2007**, *46*, 2971–8

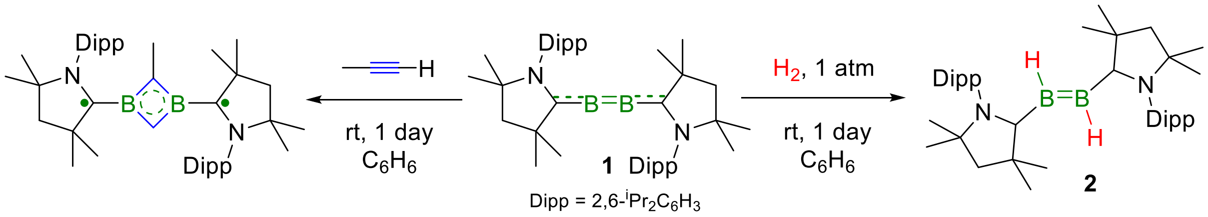
Small molecule activation by CAAC-stabilised low-valent boron species

Dr. Merle Arrowsmith, Julian Böhnke, Dr. Mehmet Ali Celik, Prof. Holger Braunschweig*
Universität Würzburg, 97070, Germany, merle.arrowsmith@uni-wuerzburg.de

---

Owing to their increased σ-donor and π-acceptor properties in comparison to normal N-heterocyclic carbenes (NHCs), cyclic alkyl(amino)carbenes (CAACs) have proven particularly suited to stabilising low oxidation state main group species by reducing build-up of electron density on the main group atom through delocalisation into the empty p-orbital of the carbene center.[1]

Taking advantage of these electronic properties our group recently isolated the linear diborabutatriene, [(CAAC)$\cdots$B=B$\cdots$(CAAC)] (**1**), in which the valence electrons are shared over the entire C-B-B-C unit.[2] Unlike its diboryne counterpart [(IDipp)B≡B(IDipp)] (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene)[3] **1** selectively reacted with molecular hydrogen to form the corresponding 1,2-dihydrodiborene (**2**), representing the first uncatalyzed H_2 activation by an apolar second row multiple bond. Herein we describe the unusual reactivity of compounds **1** and **2** towards small molecules, such as CO[4] and terminal acetylenes. DFT calculations afford insights into reaction mechanisms and the electronic structure of the new boron-containing products.



References

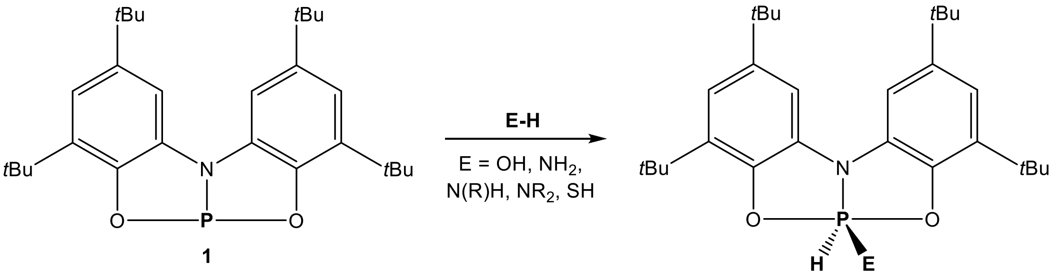
1. M. Soleilhavoup, G. Bertrand, *Acc. Chem. Res.* **2015**, *48*, 256-266.
2. J. Böhnke, H. Braunschweig, W. C. Ewing, C. Hörl, T. Kramer, I. Krummenacher, J. Mies, A. Vargas, *Angew. Chem. Int. Ed.* **2014**, *53*, 9082-9085.
3. H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420-1422.
4. J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, J. Mies, *Angew. Chem. Int. Ed.* **2015**, *54*, 13801-13805.

Small Molecule Activation at a Geometry-Constrained Phosphorus Centre

Thomas P. Robinson, Daniel M. De Rosa, Claire Williams, Simon Aldridge and Jose M. Goicoechea*
University of Oxford
Thomas.Robinson@chem.ox.ac.uk

The activation and catalytic transformation of small molecules has long been considered the domain of precious transition metals, for which low crustal abundance, high cost and toxicity are discouraging factors. Consequently there has been much interest in the development of main-group species that are able to "mimic" this behaviour, with a number of systems now shown to activate highly challenging small molecules including dihydrogen and ammonia.[1]

Recent studies have demonstrated the application of geometry-constraining chelating ligands to synthesise phosphorus(III) compounds that facilitate the oxidative addition of polarised E-H bonds (E = O and N).[2-6] We have developed this chemistry by investigating a *N*,*N*-bis-(2-phenoxide)amide supported phosphorus system (**1**) (Scheme 1).[7] This species is highly reactive towards the oxidative addition of a range of small molecule substrates, most notably water and ammonia, which pose significant challenges for transition metal complexes.



Scheme 1

The ambiphilic nature of **1** has also been demonstrated by exploring the contrasting reactivity towards both electrophilic and nucleophilic substrates. The results from these studies provide a valuable insight towards the mechanism of small molecule activation by **1** and pave the way for new reaction pathways.

References:

[1] P.P. Power, *Nature* **2010**, *463*, 171. [2] A. J. Arduengo III, C. A. Stewart, F. Davidson, D. A. Dixon, J. Y. Becker, S. A. Culley, M. B. Mizen, *J. Am. Chem. Soc.* **1987**, *109*, 627. [3] S. M. McCarthy, Y. –C. Lin, D. Devarajan, J. W. Chang, H. P. Yennawar, R. M. Rioux, D. H. Ess, A. T. Radosevich, *J. Am. Chem. Soc.* **2014**, *136*, 4640. [4] N. L. Dunn, M. Ha, A. T. Radosevich, *J. Am. Chem. Soc.* **2012**, *134*, 11330. [5] W. Zhao, S. M. McCarthy, T. Y. Lai, H. P. Yennawar, A. T. Radosevich, *J. Am. Chem. Soc.* **2014**, *136*, 17634. [6] J. Cui, Y. Li, R. Ganguly, A. Inthirarajah, H. Hirao, R. Kinjo, *J. Am. Chem. Soc.* **2014**, *136*, 16764. [7] T. P. Robinson, D. M. De Rosa, S. Aldridge, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2015**, 54, 13758.

Nitrogen-rich complexes of *p*-block elements: Highly endothermic polytetrazolates and polyazides

R. Campbell, B. F. Crozier, L. James, Z. Smallwood, P. Portius
Department of Chemistry, The University of Sheffield, Brook Hill, S3 7HF, UK;
p.portius@sheffield.ac.uk

Our aim is to stabilise and control the reactivity of N-rich coordination compounds. Upon decomposition, N-rich compounds generate mainly N_2 - ideal for smokeless, CO_2-free, “green” energetic materials as replacement for conventional propellants, explosives & pyrotechnics.[1] Low barriers toward decomposition pose major challenges in their preparation and characterisation. Here we discuss $E(Y)_n$ complexes with E = group 13, 14 or 15 coordination centre in low or high oxidation state, Y = N-rich ligand, n = 2-6. We apply synthetic methods novel to energetic chemistry, which involves a combination of hypercoordination, bulky counterions, and ligand exchanges, to achieve the synthesis and isolation of new classes of complexes as candidates for efficient & controllable energy storage.[4] These include Lewis base adducts,[3,6] homoleptic azido complexes,[2,5] covalent, binary azides $E(N_3)_n$,[3] the first homoleptic *p*-block element tetrazolates $E(T)_6^{2-}$ and $E(T)_3^{-}$ (E = Si - Sn, $T = N_4CH$, Fig. 1). These complexes have a unique chemistry – reactions with nitriles and phosphines afford unusual *poly*(tetrazolato) and *poly*(phosphiniminato) complexes. Syntheses, reactivity, structures, and thermal and spectroscopic properties of the new species, including the application of fast time-resolved IR spectroscopy to study photoreactivity, will be described.

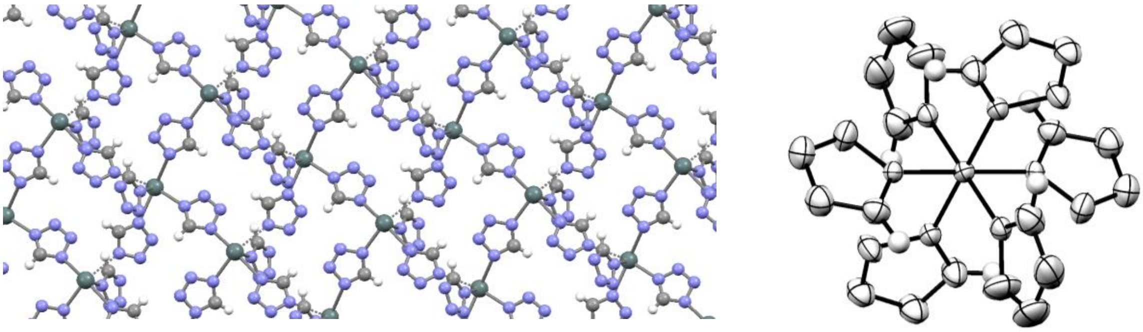


Figure 1 Tetrazole-based N-rich coordination networks and complexes: left $\{Sn(CHN_4)_3^{-}\}_\infty$ (blue N, turquois Sn, white H), right $[Si(\kappa\text{-}N(1)\text{-}N_4CH)_6]^{2-}$(thermal ellipsoid plot, 50%).

1) G. Steinhauser, T. M. Klapoetke *Angew. Chem.* **2008**, *47*, 3330; 2) P. Portius, P. W. Fowler et al. *Inorg. Chem.* **2008**, *47*, 12004; 3) P. Portius, A. C. Filippou et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 8013; 4) M. Davis, P. Portius *Coord. Chem. Rev.* **2013**, *257*, 1011; 5) B. Peerless, T. Keane et al. *Chem. Commun.* **2015**, *51*, 7435; 6) R. M. Campbell, M. Davis, M. Fazakerley, P. Portius *Chemistry-Eur. J.* **2015**, *21*, 16898.

Ruthenaphosphaalkenyls – their structure and ambiphilic reactivity.

Victoria K. Greenacre, Ian R. Crossley*.

Department of Chemistry, University of Sussex, Falmer, Brighton, BN1 9QJ.

Organometallic complexes with low-coordinate phosphorus centres are commonly studied as direct analogues of carbon based systems, with the addition of the phosphorus lone pair allowing for further reactivity.

We have been interested in expanding the variety of systems resulting from the hydroruthenation of phosphaalkynes, such as $P\equiv C^tBu$, reported by Hill *et al.* in 1996.[1] To this end, work has been undertaken towards developing new phosphaalkynes of the form $P\equiv CSiMe_2R$.[3,4] The ruthenaphosphaalkenyls $[Ru\{P{=}CH(SiMe_2R)\}Cl(CO)(PPh_3)_2]$ are prepared in high yield from the corresponding phosphaalkynes ($P\equiv CSiMe_3$, $P\equiv CSiMe_2Ph$, $P\equiv CSiMe_2Tol$).[2,3] The first solid-state structural data of these ruthenaphosphaalkenyls have been complemented by DFT studies of the precedent $[Ru(P{=}CH^tBu)Cl(CO)(PPh_3)_2)]$.[1]

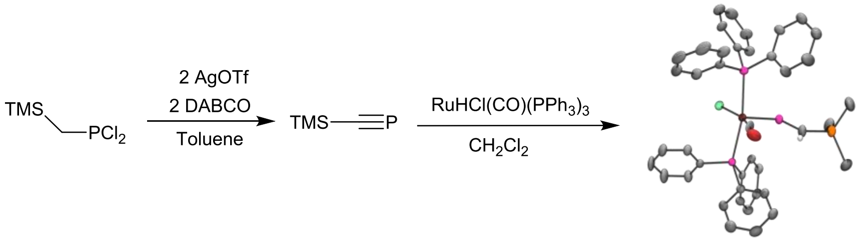


Figure 1: Synthesis and structure of $[RuCl(CO)(PPh_3)_2(P{=}CHSiMe_3)]$.

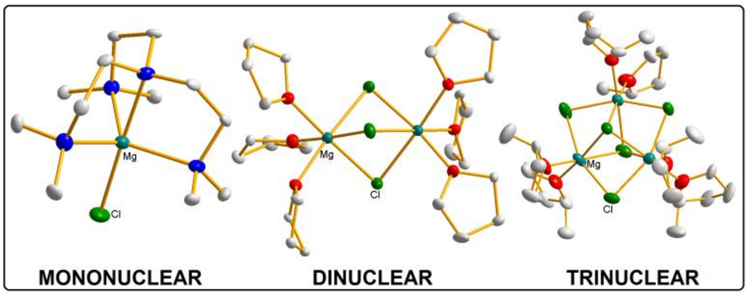
While the silyl systems mimic the previously reported propensity toward electrophilic addition shown by $Ru\{P{=}CH(^tBu)\}Cl(CO)(PPh_3)_2]$,[1] we have also elucidated novel reactivity towards nucleophilic pyrazolates, resulting in the facile formation of η^1,η^2-chelated pyrazolylphosphaalkene complexes. The presence of the silyl group also appears to modify the reactivity compared to that previously demonstrated for $[Ru\{P{=}CH(^tBu)\}Cl(CO)(PPh_3)_2]$;[1] recent reactivity studies and results will be discussed.

1. R. B. Bedford, A. F. Hill, C. Jones, *Angew. Chem. Int. Ed. Engl.* 1996, ***35***, 547.
2. N. Trathen, V. K. Greenacre, I. R. Crossley, and S. M. Roe, *Organometallics*, 2013, **32**, 2501-2504.
3. V. K. Greenacre, N. Trathen and I. R. Crossley, *Organometallics*, 2015, **34**, 2533-254.
4. C. E. Averre, M. P. Coles, I. R. Crossley, I.J. Day, *Dalton Trans*. 2012, ***41***, 278.

Donor Controlled Cation Aggregation in Magnesium Aluminates for Rechargeable Battery Electrolytes

Etienne V. Brouillet, [a] Alan R. Kennedy, [a] Konrad Koszinowski, [a] Ross McLellan, [a]
Robert E. Mulvey [a] and Stuart D. Robertson* [a]
a. Dept of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL
b. Institut für Organische und Biomolekular Chemie, Georg August Universität Göttingen, 37077, Germany
e.brouillet@strath.ac.uk ; stuart.d.robertson@strath.ac.uk

Magnesium is currently receiving widespread attention as a potential replacement for lithium in the field of rechargeable batteries, due in part to its greater natural abundance (and hence lower cost), its higher volumetric capacity and its high reduction potential.[1] Unfortunately, simple binary Mg salts present unsurmountable problems, however a magnesium aluminate modification shows considerable promise as electrolytic material.[2] The cationic magnesium moiety of these magnesium organohaloaluminates typically takes the thermodynamically favourable dinuclear $[Mg_2Cl_3]^+$ form in the solid-state although other oligomeric forms have been proposed to participate in the mechanism.[3] Our studies have revealed that judicious choice of Lewis donor allows the deliberate synthesis and isolation of these postulated mononuclear $[MgCl]^+$ and trinuclear $[Mg_3Cl_5]^+$ modifications, forming a comparable series with a common aluminate anion $[(\text{Dipp})(\text{Me}_3\text{Si})\text{NAlCl}_3]^-$ suitable for probing the effect of cation oligomerization on performance. By pre-forming the Al-N bond prior to introduction of the Mg source, a consistently reproducible protocol has been obtained. Solution state analysis by NMR spectroscopy and Electrospray Ionisation Mass Spectrometry (ESI-MS) has been utilized to study the equilibrium processes between the different aggregation states.

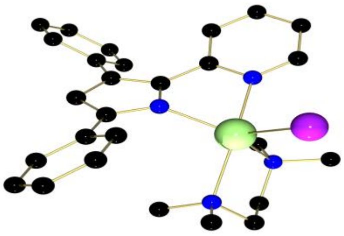


[1] J. Muldoon, C. B. Bucur and T. Gregory, *Chem. Rev.*, **2014**, *114*, 11683-11720; [2] H. D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour and D. Aurbach, *Energy Environ. Sci*., **2013**, *6*, 2265-2279; [3] T. Liu, J. T. Cox, D. Hu, X. Deng, J. Hu, M. Y. Hu, J. Xiao, Y. Shao, K. Tang and J. Liu, *Chem. Commun*., **2015**, *51*, 2312-2315.

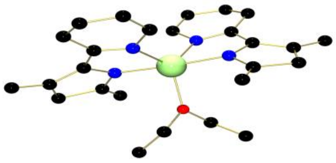
The Stabilisation of Magnesium Complexes using Sterically Demanding N-Donor Ligands

Alexander C. A. Ried and Deborah L. Kays*
School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK.
pcxacr@nottingham.ac.uk; deborah.kays@nottingham.ac.uk

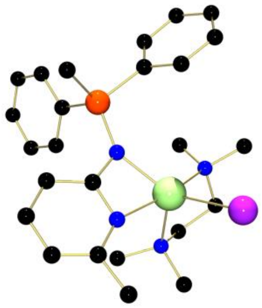
In the recent decades, alkaline earth (Ae) metal chemistry beyond the well-known Grignard reagents has seen renewed attention.[1] Thermodynamically labile species previously believed to be inaccessible under standard conditions have been synthesised employing sterically demanding *N*-based ligands such as *β*-diketiminates,[2a] guanidinates,[2b] *α*-diiminates[2c], *β*-diiminates.[2d] Whilst landmark discoveries such as subvalent Mg^{I}-Mg^{I} complexes have challenged our understanding of Ae chemistry, Group II complexes have also proven their propensity in catalysing a wealth of reactions.[3] Within our group, a variety of sterically demanding N-based ligands have been synthesised and studied towards their ability to stabilise Ae species *e.g.* pyrrolepyridinato complexes **I** and **II**. The ability of a picolamine-derived Hauser base (**III)** to catalyse the selective formation of dimeric borazane has been demonstrated. We are currently exploring similar bulky ligand systems and investigating the reactivity of their complexes.



I



II



III

References

1. a) M. Westerhausen *et al.*, *Chem. Eur. J.*, 2007, **13**, 6292; b) M. Westerhausen *et al.*, *Eur. J. Inorg. Chem.*, 2010, **2**, 197; c) K. Ruhlandt-Senge *et al.*, *Eur. J. Inorg. Chem.*, 2002, 2761.
2. a) C. Jones *et al.*, *Science*, 2007, **318**, 1754; b) G. J. Moxey, A. J. Blake, W. Lewis and D. L. Kays, *Eur. J. Inorg. Chem.*, 2015, **2015**, 5892–5902; c) X.-J. Yang *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 4210; d) S. Harder *et al.*, *Inorg. Chem.*, 2009, **48**, 11257.
3. S. Harder, *Chem. Rev.*, 2010, **110**, 3852–76; G. M. Barrett, M. R. Crimmin, M. S. Hill and P. a. Procopiou, *Proc. R. Soc. A Math. Phys. Eng. Sci.*, 2010, **466**, 927–963.

Coordination chemistry of s-block cations with soft donor macrocycles

Martin J. D. Champion, William Levason, David Pugh, Jamie M. Purkis and Gillian Reid
University of Southampton, Highfield, Southampton, SO17 1BJ. d.c.pugh@soton.ac.uk

---

The s-block elements form hard metal cations which have a high affinity for electronegative O-donor ligands; coordination complexes with other neutral and soft donor ligands are very rare. This is in part because most s-block salts have high lattice energies and very limited solubilities in organic media; especially solvents which do not contain O-donor groups.

We have been using the $[BAr^F]^-$ anion (tetrakis{3,5-bis(trifluoromethyl)phenyl}borate) as a method of increasing the solubility of “naked” s-block cations in low dielectric media, principally CH_2Cl_2.[1] This enabled us to isolate several unusual coordination complexes of the alkali metal cations, including sandwich complexes of Na^+ and K^+ with aza-macrocycles[2] and homoleptic thioether coordination at Na^+ using 1,4,7,10,13,16,19,22-octathiacyclotetracosane (Fig. 1).[3]

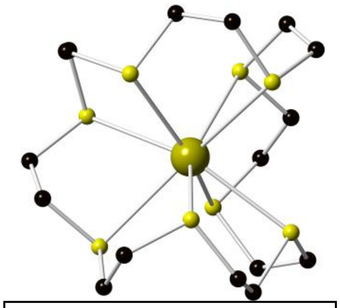


Figure 1: representation of the $[Na([24]aneS_8)]^+$ cation.

The results presented today are from our recent investigations into the coordination of mixed-donor oxa/thia and oxa/selena macrocycles to the s-block cations.[4] Coordination is observed to all of the stable s-block elements bar Be (and Rb/Cs for selenoethers). Complexes of the heavier Group 1 elements are 1D chain polymers where significant M–F interactions with the “weakly-coordinating” $[BAr^F]^-$ anions form the bridges between metal centres. In contrast, complexes of the Group 2 elements are discrete dications which show no interactions with the $[BAr^F]^-$ anions (Fig. 2). These compounds form a series of rare examples where soft thio- and selenoether moieties coordinate to the hard s-block cations.

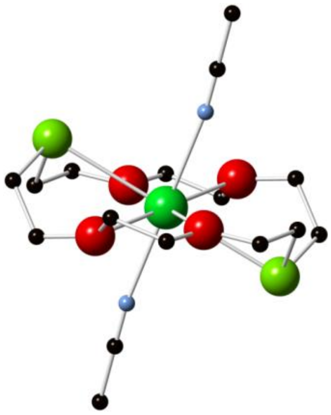


Figure 2: representation of $[Sr([18]aneO_4Se_2)(MeCN)_2]^{2+}$

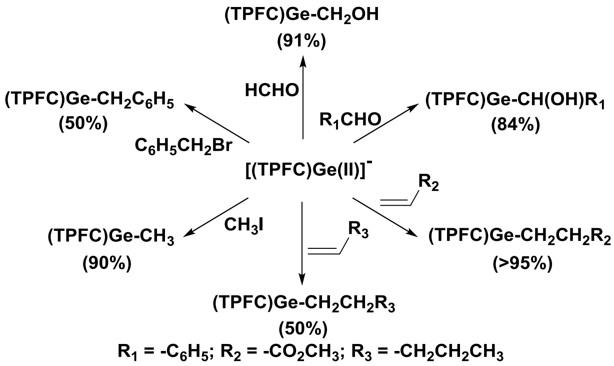
The highly soluble $[BAr^F]^-$ salts are key to this chemistry: they allow reactions to take place in non-competing, low dielectric solvents, revealing a rich new area of the coordination chemistry of s-block cations with soft donor ligands.

1) The SCFED project (www.scfed.net) is a multidisciplinary collaboration of British universities investigating the fundamental and applied aspects of supercritical fluids.
2a) Everett, M. *et al. Chem. Commun.*, **2014**, *50*, 5843. (b) Dyke, J. M. *et al.*, *Dalton Trans.*, **2015**, *44*, 13853.
3) Champion, M. J. D. *et al. Inorg. Chem.*, **2015**, *54*, 2497.
4) Champion, M. J. D. *et al. Dalton Trans.*, **2015**, *44*, 18748.

Synthesis and Reactivity Studies of Corrole Germanium Anion, Radical and Cation

Huayi Fang,[†] Shengfa Ye,[†] Xuefeng Fu[‡]
[†]*Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany. huayi.fang@cec.mpg.de*
[‡]*Peking University, Beijing 100871, China. fuxf@pku.edu.cn*

The synthesis and reactivity studies of carbon anions, radicals and cations have been receiving intense attention for decades. However, relative researches about its heavier congeners (Si, Ge, Sn, Pb) are still limited. We synthesized the corrole germanium anion, radical and cation using tris(pentafluorophenyl)corrole (TPFC) germanium hydride as the starting material and explored their reactivities toward small molecules: (a) In the presence of base, the (TPFC)Ge-H could be deprotonated thus producing the $[(TPFC)Ge(II)]^-$ anion. $[(TPFC)Ge(II)]^-$ was a strong nucleophile and could react with series of small molecules such as aldehydes, olefins and alkyl halides to produce α-hydroxy alkyl and alkyl complexes (**Fig. 1**). (b) $[(TPFC)Ge(III)]^\bullet$ was generated by the visible light irradiation of (TPFC)Ge(TEMPO) and it was found to be capable of the E-H (E=N, O) bond activation (**Fig. 2**). (c) $[(TPFC)Ge(IV)]^+$ was synthesized by the reaction of (TPFC)Ge-H with $[Ph_3C]^+$ and its reactivities toward benzene, ethylene and cyclopropane were also studied (**Fig. 3**).



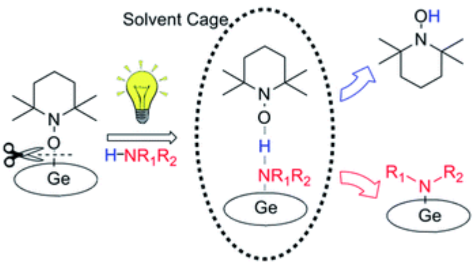


Fig. 1 Reactivity of $[(TPFC)Ge(II)]^-$ anion. **Fig. 2** Reactivity of $[(TPFC)Ge(III)]^\bullet$ radical.

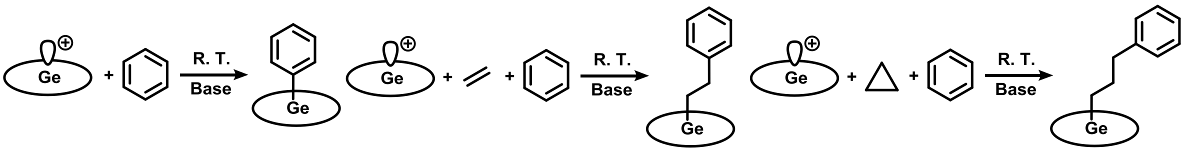


Fig. 3 Reactivity of $[(TPFC)Ge(IV)]^+$ cation

Stable *N*-Heterocyclic Carbenes with a 1,1'-Ferrocenediyl Backbone and Their Heavier Homologues

Clemens Bruhn, Christian Färber, Robin Guthardt, Michael Leibold, Jan Oetzel, Alex R. Petrov, Nadine Weyer and Ulrich Siemeling
Institute of Chemistry, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

N-Heterocyclic carbenes (NHCs)[1] are extremely valuable as nucleophilic organocatalysts. They are widely applied as ligands in transition-metal catalysed reactions, where they are known as particularly potent σ-donors. They are commonly viewed as workhorses exhibiting reliable, but undramatic, chemical behaviour. We recently demonstrated that a stable ferrocene-based NHC (Fig. 1, left) is able to add ammonia, methyl acrylate, *tert*-butyl isocyanide and carbon monoxide under mild conditions.[2] Such small-molecule activation reactions are typical of (alkyl)(amino)carbenes, but were completely unprecedented for diaminocarbenes.[3] In view of the surprising reactivity of this ferrocene-based NHC, which is due to its ambiphilic nature,[4] we surmised that its heavier homologues (Fig. 1, right), too, can be expected to show exceptional chemical behaviour. We have succeeded in the synthesis and structural characterisation of a range of corresponding germylenes, stannylenes and plumbylenes, with the experimental challenges increasing from Ge to Pb in this series. We have been able to obtain a persistent silylenoid and are still hot on the heels of stable or persistent silylenes.

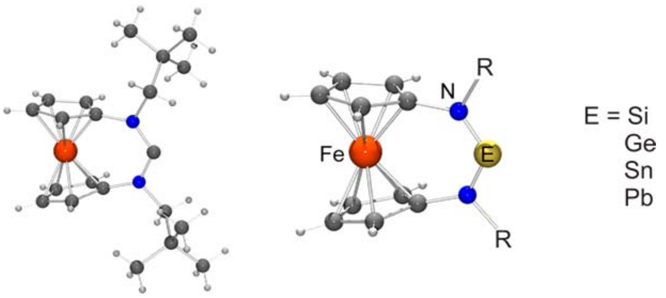


Figure 1. A stable ferrocene-based NHC (XRD result, left) and its heavier homologues (right).

[1] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485.

[2] a) A. R. Petrov, A. Derheim, J. Oetzel, M. Leibold, C. Bruhn, S. Scheerer, S. Oßwald, R. F. Winter, U. Siemeling, *Inorg. Chem.* **2015**, *54*, 6657; b) U. Siemeling, C. Färber, C. Bruhn, M. Leibold, D. Selent, W. Baumann, M. von Hopffgarten, C. Goedecke, G. Frenking, *Chem. Sci.* **2010**, *1*, 697.

[3] D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389.

[4] C. Goedecke, M. Leibold, U. Siemeling, G. Frenking, *J. Am. Chem. Soc.* **2011**, *133*, 3557.

Synthesis and reactivity of fluorenyl-tethered N-heterocyclic stannylenes

M. Roselló-Merino and S. M. Mansell*

Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK. Email: S.Mansell@hw.ac.uk

---

Conventionally, homogeneous catalysts consist of only one type of supporting ligand. Combining different ligands at the same metal centre has the potential to generate further progress by accessing a better mixture of ligand properties. Tethered ligands are excellent candidates for designing the next generation of homogeneous catalyst as they combine two different ligand classes into one chelating ligand.[1] We are interested in combining the unique properties of N-heterocyclic stannylenes (NHSns),[2] the tin analogues of N-heterocyclic carbenes (NHCs), with conventional ligand motifs in order to explore new modes of reactivity such as: 1. Hemilability of the stannylene moiety facilitating bond activation chemistry at the transition metal centre, 2. Bridging binding modes promoting multi-metallic complexes, and 3. Increased complex stability and improved product selectivity facilitated by the presence of a tether. Our recent work exploring the synthesis and reactivity of these new fluorenyl-tethered NHSn ligands will be presented (Figure 1).[3]

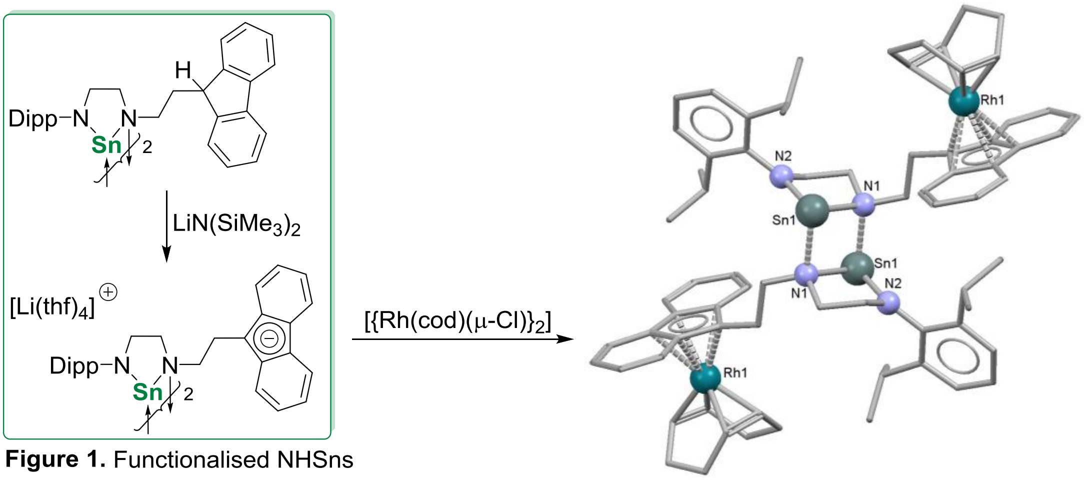


Figure 1. Functionalised NHSns

1. a) H. Butenschön, *Chem. Rev.* **2000**, *100*, 1527; b) U. Siemeling, *Chem. Rev.* **2000**, *100*, 1495.

2 a) S. M. Mansell, C. A. Russell and D. F. Wass, *Inorg. Chem.* **2008**, *47*, 11367; b) S. M. Mansell, R. H. Herber, I. Nowik, D. H. Ross, C. A. Russell and D. F. Wass, *Inorg. Chem.* **2011**, *50*, 2252.

3. M. Roselló-Merino and S. M. Mansell, *Dalton Trans.*, **2016**, DOI: 10.1039/C5DT04060D

Hydroboration of unsaturated C-C bonds using an iron complex

Maialen Espinal-Viguri, Callum Woof, Ruth L. Webster.

Department of Chemistry, University of Bath, BA2 7AY, United Kingdom.

Hydroboration, the addition of a hydrogen-boron bond to C-C, C-N, and C-O double bonds, is a very useful transformation in organic chemistry yielding organoboron compounds which react with different reagents to afford valuable products such as amines, alcohols, alkyl halides, etc.[1]

Herein we report the hydroboration of different unsaturated C-C bonds with an iron precatalyst bearing a β-diketaminate ligand (Figure 1). This transformation is carried out with 100% conversion, between 25-60 ºC, with an extensive scope of substrates and without the need for an activator such as a base or reductant. Kinetic studies suggest that the reaction is first order in HBpin (pinacolborane), alkene and catalyst.

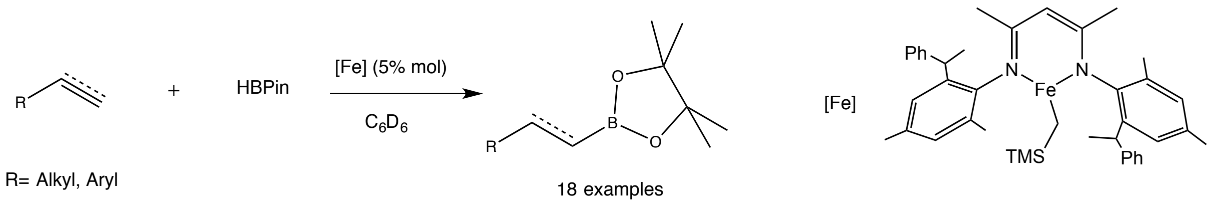


Figure 1. General hydroboration reaction

---

[1] See for example: *Science of Synthesis, Multicomponent Reactions*, **2014**, *2*, 345; S. Huang, Y. Xie, S. Wu, M. Jia, J. Wang, W. Xu, H. Fang, *Current Organic Synthesis*, **2013**, *10*(5), 683; L. Zhang, Z. Huang, *Synlett.*, **2013**, *24*(14), 1745; *Hydroboration and Organic Synthesis*, Ranjit S. Dhillon, *Ed*. Springer-Verlag Berlin Heidelberg, **2007**.

Tuning the Optical and Electronic Properties of Boron-Containing Electron-Acceptor Groups

Robert M. Edkins,[1,2] **Zuolun Zhang**,[2,3] **Todd B. Marder**[2]

[1] *Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, United Kingdom*

[2] *Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97078 Würzburg, Germany*

[3] *State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China*

The strong π-accepting ability of three-coordinate boron is exemplified by the $BMes_2$ (Mes = mesityl) group,[1] wherein steric crowding by the two mesityl moieties prevents hydrolysis, affording air-stable compounds. Following our predictions,[2a] work by Yamaguchi[2b,c] and our earlier collaboration with Jäkle,[3] we report herein the chemistry and photophysics of boron compounds containing FMes groups (FMes = fluoromesityl = 2,4,6-$(CF_3)_3C_6H_2$). Using the $B(FMes)_2$ group, we have observed large reduction-potential shifts of up to 1 V, relative to $B(Mes)_2$ analogues, and have synthesized donor-acceptor compounds exhibiting aggregation-induced emission, turn-on fluoride sensing, and large Stokes shifts of over 10,000 cm^{-1}.[4]

However, the emission of these compounds is strongly quenched in polar solvents, which led us to develop alternative boron-containing groups that allow finer electronic tuning while maintaining strong emission.[5] With luminescence quantum yields of up to 0.96, these are some of the most efficient red-emitting organoboron chromophores to-date. The observed emission properties are rationalized based on a combined spectroscopic and theoretical study, including a TD-DFT study of the TICT excited-states of some archetypal $B(FMes)_2$ compounds. Furthermore, we report the use of the FMes group to stabilize boroles,[6] which may find use as electron-transporting materials in optoelectronic devices.

[**1**] Entwistle, C. D.; Marder, T. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2927-2931 [**2**] (a) Weber, L.; Werner, V.; Fox, M. A.; Marder, T. B.; Schwedler, S.; Brockhinke, A.; Stammler, H.-G.; Neumann, B. *Dalton Trans.* **2009,** 1339-1351; (b) Wang, J.; Wang, Y.; Taniguchi, T.; Yamaguchi, S.; Irle, S. *J. Phys. Chem. A* **2012**, *116*, 1151-1158; (c) Taniguchi, T.; Wang, J.; Irle S.; Yamaguchi, S. *Dalton Trans.* **2013**, *42*, 620-624. [**3**] Yin, X. D.; Chen, J. W.; Lalancette, R. A.; Marder, T. B.; Jäkle, F. *Angew. Chem. Int. Ed.* **2014**, *53*, 9761-9765. [**4**] Zhang, Z.; Edkins, R. M.; Nitsch, J.; Fucke, K.; Steffen, A.; Longobardi, L. E.; Stephan, D. W.; Lambert, C.; Marder, T. B. *Chem. Sci.* **2015**, *6*, 177-190. [**5**] Zhang, Z.; Edkins, R. M.; Nitsch, J.; Fucke, K.; Eichhorn, A.; Steffen, A.; Meier, M.; Wang, Y.; Marder, T. B. *Chem. Eur. J.* **2015**, *21*, 5922-5927. [**6**] Zhang, Z.; Edkins, R. M.; Haehnel, M.; Wehner, M.; Eichhorn, A.; Mailänder, L.; Meier, M.; Brand, J.; Brede, F.; Müller-Buschbaum, K.; Braunschweig, H.; Marder, T. B. *Chem. Sci.* **2015**, *6*, 5922-5927.

Modelling Organometallic Structure and Reactivity in the Solid State

Stuart A. Macgregor and Tobias Kraemer

Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK; email: S.A.Macgregor@hw.ac.uk

---

The standard approach to computing organometallic structure and reactivity has been to employ isolated molecular species as models and to compute structural and thermodynamic properties in what is essentially a vacuum. Environmental effects, such as solvation or dispersion, are then taken into account via subsequent energy corrections, which when applied to reactants, transition states, intermediates and products allow a computed reaction profile to be developed.

This approach has proven to be very successful,[1] but care must be taken to recognize situations where the environment plays a more direct role in determining the properties of the system. An example is the solid-state organometallic chemistry being developed by the Weller group, where solid-gas reactivity is being exploited to study normally transient alkane σ-complexes in the crystalline state.[2-4]

This presentation will describe our on-going efforts to develop reliable computational models and protocols for the study of $[(R_2PCH_2CH_2PR_2)Rh(\sigma\text{-alkane})][BArF_4]$ complexes (R = ^{i}Bu, Cy; alkane = norbornane, pentane; $Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$). While some properties (cation geometry and electronic structure) can be reliably computed based on the isolated cation, others (^{1}H NMR chemical shifts, isomer preferences and fluxionality) cannot. In such cases an approach that includes the solid-state environment explicitly in the calculation is necessary.

References

1. L. Perrin, K. J. T. Carr, D. McKay, C. L. McMullin, S. A. Macgregor and O. Eisenstein, *Struct. Bond.* **2016** in the press, DOI: 10.1007/430_2015_176.
2. S. D. Pike, A. L. Thompson, A. G. Algarra, D. C. Apperley, S. A. Macgregor, and A. S. Weller, *Science* **2012**, *337*, 1648.
3. S. D. Pike, F. M. Chadwick, N. H. Rees, M. P. Scott, A. S. Weller, T. Krämer, and S. A. Macgregor *J. Am. Chem. Soc.* **2015**, *137*, 820.
4. F. M. Chadwick, N. H. Rees, A. S. Weller, T. Krämer, M. Iannuzzi, S. A. Macgregor *Angew. Chem. Int. Ed.* **2016** in the press, DOI: 10.1002/anie.201511269.

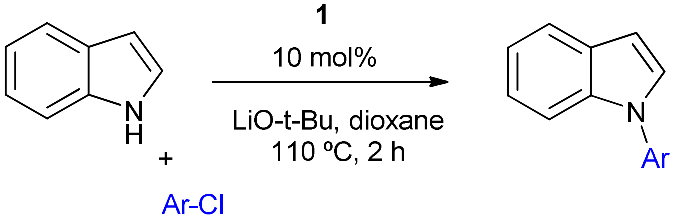
Mechanistic Study of C-N Bond Formation Reaction Catalysed By a NHC-Nickel(0) Complex

Authors. Silvia G. Rull,[a] Manuel R. Fructos,[a] M. Carmen Nicasio*[,b] and Tomás R. Belderrain*[,a]

[a]*Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO- Centro de Investigación en Química Sostenible, and Departamento de Química, Universidad de Huelva, 21007, Huelva (Spain) Fax:(+34)959219942. trodri@dqcm.uhu.es*

[b]*Departamento de Química Inorgánica, Universidad de Sevilla, Aptdo 1203, 41071 Sevilla, Spain*

Over the last decade the number of examples of C-N coupling reactions catalyzed by nickel complexes has increased significantly.[1] Recently, our group initiated a new research line focused on the development of single-component nickel(0) catalysts for C-N bond couplings. Thus, we reported the use of Ni(0) complex [(IPr)Ni(styrene)$_2$] [IPr= 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], **1**, as efficient catalyst in the reaction of aryl tosylates with cyclic secondary amines and anilines,[2] and aromatic chlorides with indoles and carbazoles (Scheme 1).[3] Here, we describe a mechanistic study of latter coupling reactions catalyzed by **1**, with experimental details about the different intermediates involved in the catalytic cycle.



Scheme 1. Reaction of indole and phenyl chloride catalyzed by **1**.

---

[1] (a) V. Ritleng, M. Henrion and M. J. Chetcuti, *ACS Catal.*, 2016, **6**, 890–906; (b) M. Marín, R. J. Rama and M. C. Nicasio, *Chem. Rec.* accepted.

[2] M. J. Iglesias, J. F. Blandez, M. R. Fructos, A. Prieto, E. Álvarez, T. R. Belderrain and M. C. Nicasio, *Organometallics* 2012, **31**, 6312–6316.

[3] S. G. Rull, J. F. Blandez, Manuel R. Fructos, Tomás R. Belderrain and M. Carmen Nicasio, *Adv. Synth. Catal.* 2015, **357**, 907 –911.

Cationic Rearrangements in Polysilanes - Subtle Capture of Intermediates

Lena Albers[a], Thomas Müller[b]*

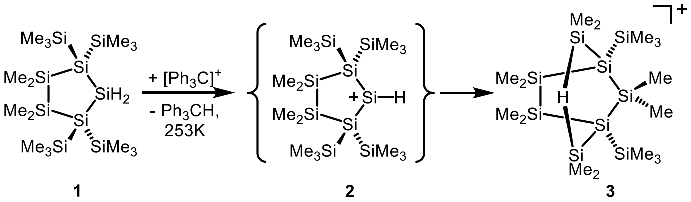
Lena.albers@uni-oldenburg.de

a) School of Chemistry, University of Edinburgh, UK

b) Institute of Chemistry, Carl von Ossietzky University Oldenburg, Germany

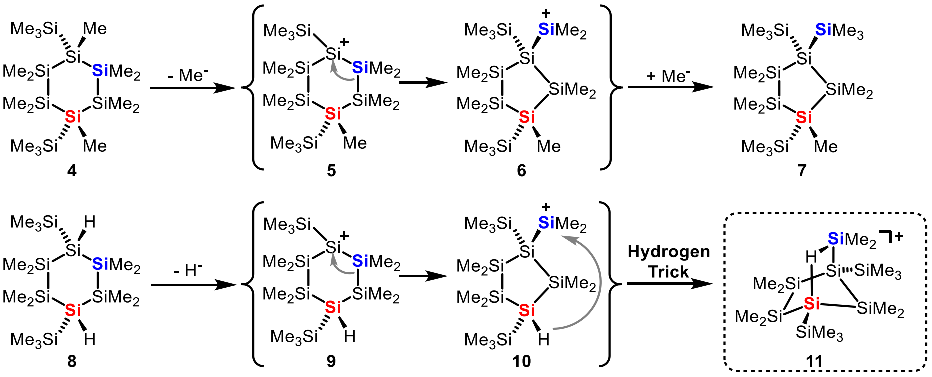
---

We will describe our attempts to prepare the secondary silylium ion **2** and its surprising rearrangement reaction leading to the intramolecular hydrogen-bridged silyl cation **3**. As the main driving force for the rearrangement reaction, we identified the formation of the 2e3c Si - H - Si linkage in cation **3**.[1-3]



We will demonstrate that the targeted formation of this type of intramolecular Si - H - Si bridge can be used for the stabilisation and verification of cationic intermediates in the skeletal rearrangement processes of oligosilanylsilyl cations.

Exemplarily, we investigated the Lewis acid-catalysed rearrangement of cyclohexasilane **4** to give silylcyclopentasilanes **7**.[4] We used the hydrogen-substituted analogue **8** to define the position of the initial positively charged atom by hydride transfer reaction **9** and trapped one of the two postulated silyl cationic intermediates **10** in the form of its Si - H - Si bridged analogue **11**.



Acknowledgements: This work was supported by the ERA-chemistry program (DFG-Mu1440/8-1, FWF-I00669). The Royal Society is thanked for funding (Newton Fellowship).

[1] T. Müller, in *Struct. Bond.*, Ed.: D. Scheschkewitz, Springer, Berlin, **2014**, Vol. *155*, pp. 107. [2] T. Müller, in *Science of Synthesis Knowledge Updates*, Ed.: M. Oestreich, Thieme Verlag, Stuttgart, **2013**, Vol. *3*, pp. 1. [3] A. Schäfer, M. Reißmann, A. Schäfer, M. Schmidtmann, T. Müller, *Chem. Eur. J.* **2014**, *20*, 9381. [4] M. Ishikawa, M. Watanabe, J. Iyoda, H. Ikeda, M. Kumada, *Organometallics* **1982**, *1*, 317.

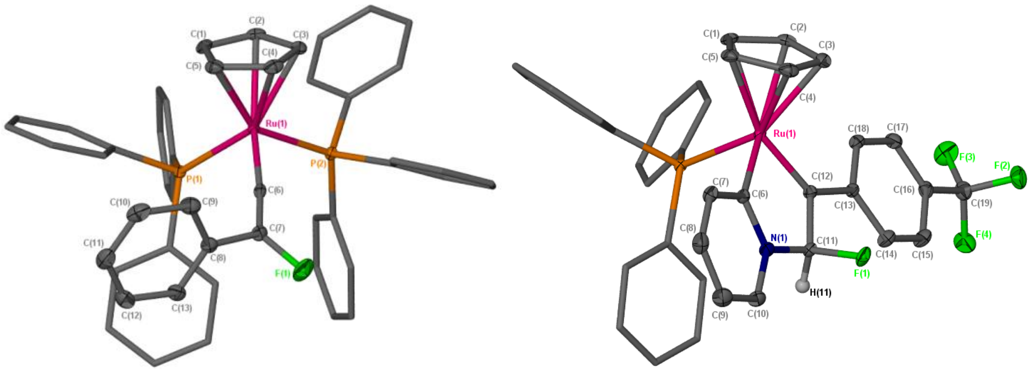
Outer-Sphere Electrophilic Fluorination (OSEF) of Organometallic Fragments

Lucy Milner, Dr Jason Lynam, Dr John Slattery
Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK
lm856@york.ac.uk, jason.lynam@york.ac.uk, john.slattery@york.ac.uk

---

Organofluorine chemistry plays a crucial role in pharmaceuticals, agrochemicals, materials science and medical imaging, with fluorine incorporation enhancing metabolic stability, bioavailability and lipophilicity.[1] However, regio- and stereoselective fluorination remains challenging and current research is focussed on new and highly selective fluorination methodologies which operate under mild conditions with high functional-group tolerance.

We have recently demonstrated the electrophilic fluorination of both ruthenium acetylide and pyridylidene complexes.[2],[3] These reactions achieve rapid, quantitative C-F bond formation under mild conditions with 100 % regio- and stereoselectivity from non-activated substrates.



Scheme 1: Fluorinated vinylidene complex **1** and fluorinated pyridylidene complex **2**

Using this methodology, we have prepared the first mononuclear fluorovinylidene complexes, **1**, and are currently exploring their reactivity in stoichiometric and catalytic reactions.[3] Protio- analogues of **1** are important intermediates in a plethora of catalytic systems, therefore the fluoro-analogues offer the potential to produce novel, fluorinated organic compounds.

Both experimental and computational investigations will be presented and indicate a unique fluorination mechanism, in which the C-F bond forms directly at the coordinated ligand with no metal-fluoride intermediate – Outer-Sphere Electrophilic Fluorination (OSEF).[2],[3]

References: [1] T. Liang *et al*, *Angew. Chem. Int. Ed.*, 2013, **52**, 8214; [2] L. M. Milner *et al*, *J. Am. Chem. Soc.*, 2015, **137**, 10753; [3] L. M. Milner *et al*, *Dalton Trans.*, 2016, **45**, 1717

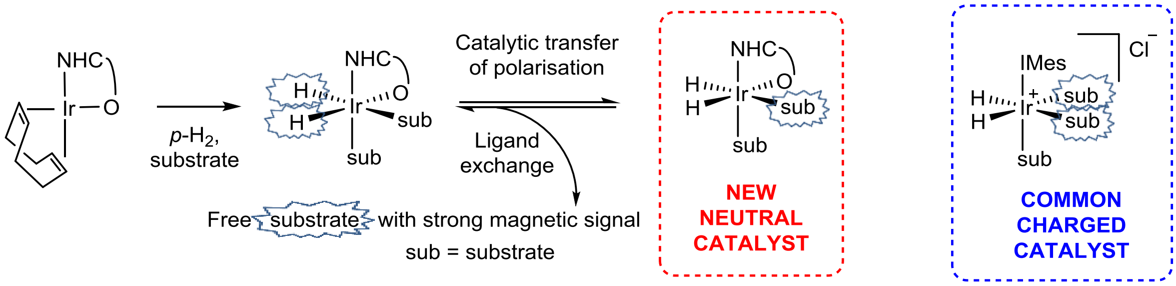
Enhancing NMR: Development of Efficient Polarisation Transfer Catalysts

A. J. Ruddlesden, R. E. Mewis and S. B. Duckett

Centre for Hyperpolarisation in Magnetic Resonance (CHyM), York Science Park, University of York, Heslington, York, YO10 5NY, UK

Nuclear Magnetic Resonance (NMR) is a widely used spectroscopic technique that relies on the intrinsic magnetic properties of nuclei such as hydrogen. It identifies their molecular arrangement, according to their chemical environment, thus allowing structural assignment. Its medical equivalent, Magnetic Resonance Imaging (MRI), provides a non-invasive route to collect anatomical images that aid in clinical diagnosis. In these measurements, slightly more nuclei align with the applied field compared to against it and the weak signal that is observed arises from this small population difference. Routes that artificially increase this population difference could greatly improve the sensitivity of both NMR and MRI.

Signal Amplification By Reversible Exchange (SABRE) is one such route that involves the catalytic transfer of polarisation from *para*hydrogen (*p*-H_2) to a substrate at low magnetic field, using a polarisation transfer catalyst. This rapidly creates the large population difference that is required and leads to so-called hyperpolarised substrate molecules in solution that remain chemically unchanged but become highly visible.



The optimisation and diversification of this approach requires synthesis and development of new catalysts. Commonly the catalysts are charged species, showing high activity in polar solvents such as methanol. These results demonstrate how a wider solvent tolerance can be achieved using neutral catalysts, whilst also facilitating signal enhancement of molecules that are not accessible in methanol. Key intermediates are characterised and the mechanism of catalysis, involving substrate and hydrogen exchange has been studied. Molecules such as nicotine, nicotinamide and tryptamine have shown increased signal intensities. This paves the way to develop more sensitive applications for NMR analysis and MRI contrast agents.

A. J. Ruddlesden, R. E. Mewis, G. G. R. Green, A. C. Whitwood and S. B. Duckett, *Organometallics*, 2015, **34**, 2997

Studies towards Pt-catalyzed activation of methane

Eric G. Bowes, Shrinwantu Pal, Jennifer A. Love

Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, V6T 1Z1, jenlove@chem.ubc.ca

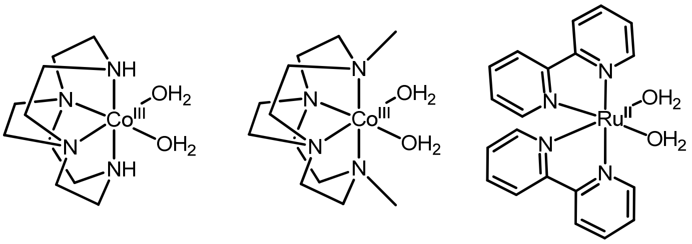
Homogeneous selective C-H functionalization of hydrocarbons is one of the grand challenges of organometallic chemistry. Unsaturated Pt^{II} and Pt^{IV} complexes are considered as critical intermediates in both established and proposed processes for methane functionalization and their intermediacy has been demonstrated in stoichiometric C-H activation and reductive elimination. Building on this knowledge and our own studies of Pt-catalyzed C-X functionalization, we envisioned a possible catalytic system for hydrocarbon functionalization. In this proposed catalytic cycle, a neutral Pt^{II} dimethyl species could undergo oxidative addition of a Csp^2-X bond to form a Pt^{IV} trihydrocarbyl complex. At present, such a process is only possible by tethering the aryl group to the ligand scaffold. Halide abstraction would a generate cationic 5-coordinate complex. Based on the work of Goldberg and coworkers, formation of this species should allow for reductive elimination to occur, releasing the functionalized product and an unsaturated Pt^{II} centre. Complexes of this type are well-known to activate hydrocarbons, including methane, through coordination of the C-H bond to the vacant site of the unsaturated Pt^{II} centre, followed by oxidative addition to form a transient hydrido Pt^{IV} intermediate. Concomitant deprotonation in the presence of a base would lead to regeneration of the original neutral Pt^{II} dimethyl complex.

Selectivity for Csp^2-Csp^3 reductive elimination is essential to the realization of this process. Herein we report both examples of selective Csp^2-Csp^3 and Csp^3-Csp^3 reductive elimination from trihydrocarbyl Pt^{IV} complexes differing in their ligand scaffolds. We demonstrate, through a comparative experimental and theoretical study, that the unexpected selectivity for Csp^3-Csp^3 reductive elimination observed is governed by the rigidity and coordination geometry of the Csp^2 group. These results will be discussed in the context of our efforts towards catalytic hydrocarbon activation.

Kinetico-mechanistic studies on substitution reactions on Co^{III} and Ru^{II} complexes with nucleosides and nucleotides at physiological pH

Marta Vázquez and Manuel Martínez
Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica,
Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona.
manel.martinez@qi.ub.es

The interaction of metal complexes with biomolecules has been established as significant for many biologically relevant processes; the reactivity of *cis*-$[Pt(NH_3)_2Cl_2]$ being the most studied example for evident reasons. It is clear that in aqueous solution, and at pH close to neutrality, aqua/hydroxo complexes should be dominant in the absence of any other ligands. In all cases, the existence of two substitution active positions in *cis* has been found to be preferred for the interaction and activation of some of these significant ligands.



Here we present the study of the substitution mechanism actuating on the Co^{III} and Ru^{II} t_{2g}^{6} inert complexes, shown in the Figure, with some nucleosides and nucleotides.

The reactivity substitution patterns indicate the extreme significance of hydroxo-bridged species for the Co^{III} complexes capable of using conjugate-base substitution pathways.[1-3] In all cases, the importance of outer-sphere complexation results in a rather specific sequential reactivity for some of the ligands used. This fact shows the importance of this type of studies for the wider understanding of the interaction of metal complexes with significant molecules. For the less acidic Ru^{II} complex,[4] no hydroxo-bridged species are observed, but the coordination of thymidine units to the $\{Ru^{II}(bpy)_2\}$ core results in a dramatic involvement of the chelating bipyridine ligand in a fluxional process.

Acknowledgements. Financial support from the Spanish Ministerio de Economía y Competitividad (project CTQ2015-65707-C2-1) is acknowledged.

1.- M. G. Basallote, M. Martínez, and M. Vázquez, *Dalton Trans.*, **2014**, *43*, 11048-11058.
2.- M. Martínez and M. Vázquez, *Inorg.Chem.*, **2015**, *54,* 4972-4980.
3.- M. Vázquez, M. Font-Bardía, and M. Martínez, *Dalton Trans.*, **2015**, *44,* 18643-18655.
4.- M. Vázquez and M. Martínez, *Unpublished results,* **2016.**

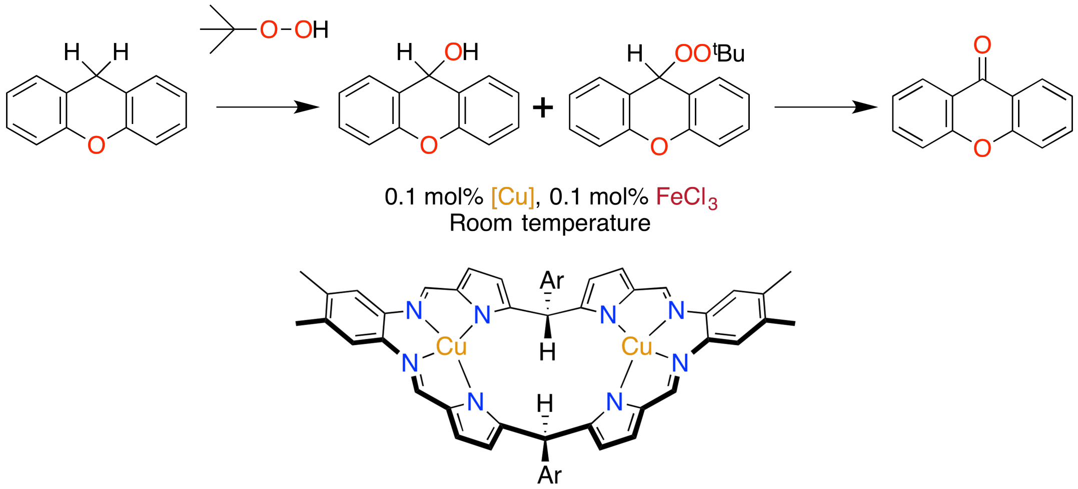
Earth-abundant mixed-metal systems for hydrocarbon oxidation catalysis

James R. Pankhurst, Massimiliano Curcio and Jason B. Love

EaStCHEM School of Chemistry, The University of Edinburgh, J.R.Pankhurst@sms.ed.ac.uk

Selective oxidation of hydrocarbon bonds is both synthetically useful and important to industrial processes. Earth-abundant metal ions such as Cu(II) and Fe(III) are known to act as catalysts for oxidation reactions,[1] and are preferable over other stoichiometric oxidants such as Cr(VI) and Mn(VIII) due to their low cost and toxicity.

Binuclear complexes of Schiff-base macrocycles are good candidates for oxidation catalysis, as the rigid ligand framework provides a reactive cleft between the two metal centres that can bind and activate small molecule substrates.[2] We have recently reported the synthesis of binuclear Cu(II) macrocycles of different geometries,[3] and this talk presents their application to catalysis, using peroxides as oxidants. At elevated temperatures and low loadings, these complexes exhibit high activities (TOF ~ 1000 h^{-1}), but are prone to inhibition/decomposition. We have discovered that the addition of $FeCl_3$ enables this reaction to proceed at room temperature without arresting, and have carried out a detailed kinetic investigation to ascertain the role of Fe(III).



---

[1] L. Que Jr, W.B. Tolman, *Nature*, 2008, **455**, 333;

[2] A.M.J. Devoille, J.B. Love, *Dalton Trans.*, 2012, **41**, 65;

[3] J.R. Pankhurst, T. Cadenbach, D. Betz, C. Finn, J.B. Love, *Dalton Trans.*, 2015, **44**, 2066.

Polymer Immobilised Ionic Liquid Phase (PIILP) Stabilised Pd-Nanoparticles: Synthesis and Applications in Catalysis

E.A. Abood[a,b], S. Doherty[a], J. G. Knight[a], Ian J. S. Fairlamb[c]

aNUCAT, School of Chemistry, Bedson Building, Newcastle University, Newcastle Upon Tyne, NE1 7RU, bPolymer Research Centre ,

University of Basrah, Basrah, Iraq,

cDepartment of Chemistry, University of York, Heslington, York, YO10 5DD, UK

a.b.abood@newcastle.ac.uk

The Doherty group has recently been exploring the concept of Polymer Immobilised Ionic Liquid Phase (PIILP) catalysis, in which the ionic liquid is immobilised in the form of a cation decorated polymer.[1-4] This project has developed imidazolium-based heteroatom-modified Polymer Immobilised Ionic Liquids (PIILs) that can immobilise and stabilise Pd-nanoparticles and been investigating whether the number and type of heteroatom influence catalyst performance. Preliminary studies revealed that PdNPs generated *in situ* by reduction of $PdCl_4$@NH_2-PIILP or $PdCl_4$@PPh_2-PIILP are highly active catalysts for the Suzuki-Miyaura cross-coupling between aryl bromides and boronic acids in a 1:1 mixture of ethanol/water. In a comparative study, Pd^0@PPh_2-PIILP generated by reduction of $PdCl_4$@PPh_2-PIILP with hydrogen, also gave good conversions under mild conditions; the corresponding TONs matched those obtained with catalyst generated *in situ.* In stark contrast the corresponding pre-reduced amino-decorated polymer immobilised ionic liquid stabilised palladium nanoparticles, Pd^0@NH_2-PIILP, were completely inactive. Kinetic studies, reaction dilution experiments, mercury poisoning, and catalyst loading studies have been employed to investigate the difference between the performance of pre-reduced PdNPs and those generated *in situ*. The PdNP@PIILP systems have been characterised by a range of techniques including solid state NMR spectroscopy, SEM, TEM, XRD, XPS and BET analysis. A parallel project has been evaluating the efficacy of the same catalyst for the selective hydrogenation of α,β-unsaturated esters with the aim of identifying potential candidates for the catalytic transformation of biomass derived substrates. Preliminary studies have shown that Pd^0@PPh_2-PIILP catalyses the hydrogenation of trans-cinnamaldehyde in water with high selectivity for reduction of the C=C double bond to afford dihydrocinnamaldehyde in near quantitative yield, under mild conditions and in short reaction times.

---

[1] S. Doherty, J. G. Knight, M. A. Carroll, J. R. Ellison, S. J. Hobson, S. Stevens, C. Hardacre and P. Goodrich, *Green Chem.*, 2015, **17**, 1559-1571.

[2] S. Doherty, J. G. Knight, J. R. Ellison, P. Goodrich, L. Hall, C. Hardacre, M. J. Muldoon, S. Park, A. Ribeiro, C. A. N. de Castro, M. J. Lourenço and P. Davey, *Green Chem.*, 2014, **16**, 1470-1479.

[3] S. Doherty, J. G. Knight, J. R. Ellison, D. Weekes, R. W. Harrington, C. Hardacre and H. Manyar, *Green Chemistry*, 2012, **14**, 925.

[4] S. Doherty, J. G. Knight, A. Clement and J. R. Ellison, *Catal. Sci. & Technol.* **2016** manuscript submitted for publication.

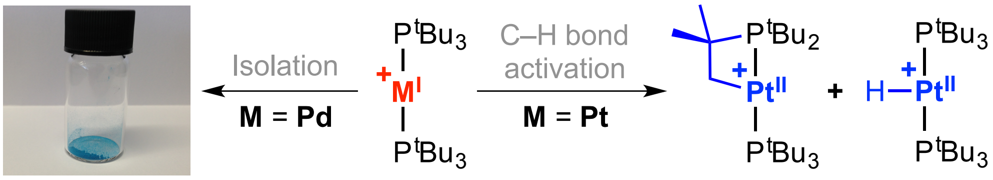
Preparation and reactivity of $[M(P^tBu_3)_2]^+$ (M = Pd, Pt)

Thibault Troadec, Sze-yin Tan, C. J. Wedge, Jonathan P. Rourke, Patrick R. Unwin and Adrian B. Chaplin*

University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, United Kingdom.

E-mail: a.b.chaplin@warwick.ac.uk | Twitter: @chaplinlab

Over the past few decades a rich variety of chemistry has emerged based on the reactions of complexes of palladium and platinum in the 0 and +II formal oxidation states, epitomised by the omnipresence of palladium catalysed cross-coupling reactions in contemporary organic chemistry. In contrast, the organometallic chemistry of well-defined complexes of these elements bearing formal +I oxidation states is much less established and well-defined examples are largely limited to unstable or dinuclear species with distinct metal–metal bonds.[1] With a view to isolating well-defined mononuclear complexes of metals bearing a +I oxidation state relevant to catalysis, our recent work involving the one-electron oxidation of widely used and commercially available zero-valent complexes $[M(P^tBu_3)_2]$ (M = Pd; Pt) will be presented.[2] While the resulting Pd(I) derivative was readily isolated from solution and fully characterised, the heavier congener promotes C–H bond homolysis and 14 VE Pt(II) complexes $[Pt(P^tBu_2CMe_2CH_2)(P^tBu_3)]^+$ and $[Pt(P^tBu_3)_2H]^+$ are produced instead.



References

1. Selected examples of mononuclear complexes: F. Armbruster, T. Augenstein, P. Oña-Burgos and F. Breher, *Chem. Eur. J.*, 2013, **19**, 17899; R. Palmans, D. B. MacQueen, C. G. Pierpont and A. J. Frank, *J. Am. Chem. Soc.*, 1996, **118**, 12647.
2. T. Troadec, S.-Y. Tan, C. J. Wedge, J. P. Rourke, P. R. Unwin and A. B. Chaplin, *Angew. Chem. Int. Ed.*, 2016, **55**, 3754.

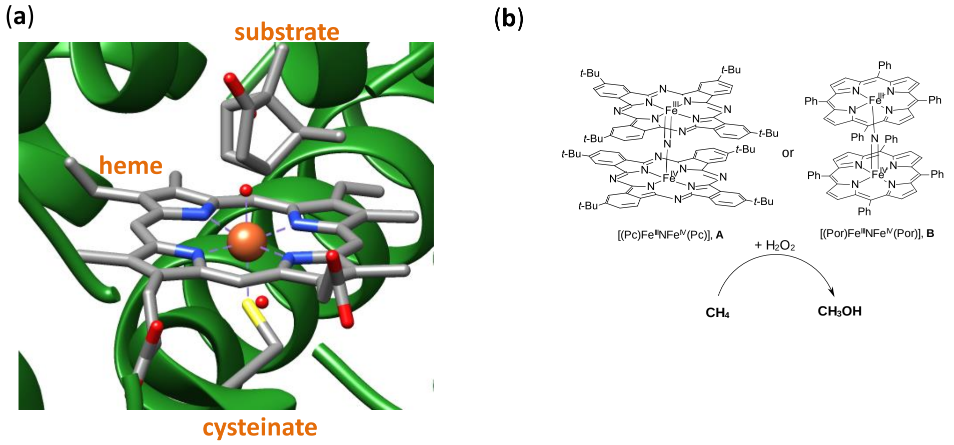
Why are μ-nitrido bridged diiron(IV)-oxo porphyrins able to hydroxylate methane but mononuclear iron(IV)-oxo porphyrins not?

Sam P. de Visser

Manchester Institute of Biotechnology and School of Chemical Engineering and Analytical Science,
131 Princess Street, Manchester M1 7DN, United Kingdom

Abstract:

Cytochrome P450 enzymes are versatile oxidants in nature that hydroxylate a large range of substrates. Interestingly, despite their high efficiency and broad substrate range, they do not hydroxylate methane due to the strength of the C–H bond that needs to be broken. μ-Nitrido bridged diiron porphyrins and Phthalocyanines, by contrast, are able to oxidize some of the strongest C–H bonds in nature, and even the one in methane. The origin of their catalytic efficiency is poorly understood and, in order to gain insight into the structural and electronic features of this chemical system, we performed a detailed and systematic computational study into their chemical properties and reactivities. In this presentation, I will compare the structure and reactivity of cytochrome P450 Compound I and μ-nitrido bridged diiron porphyrins and Phthalocyanines. The calculations show the latter to react with methane with very low reaction barriers and a rate determining hydrogen atom abstraction step. Furthermore, the μ-nitrido bridged diiron porphyrin and phthalocyanine complexes react with a free energy of activation that is more than 10 kcal mol^{-1} lower in energy than, for instance, that is found for cytochrome P450 Compound I, which is known to be one of the most efficient C–H hydroxylating agents in Nature. We have analyzed the electronic configuration of reactants and transition states in detail and have identified the key properties of the oxidants that lead to this rate enhancement. The differences in catalytic activity and the origins of the reactivity differences will be explained and highlight the key factors that contribute to the reactivity enhancement.



References:

1. M. G. Quesne, D. Senthilnathan, D. Singh, D. Kumar, P. Maldivi, A. B. Sorokin and S. P. de Visser, *submitted for publication*.

Title: Reaction Mechanism of Cytochrome P450 Peroxygenase-Regioselectivity towards Biofuel Production.

Abayomi S. Faponle, Matthew G. Quesne, and Sam P. de Visser

Manchester Institute of Biotechnology and School of Chemical Engineering and Analytical Science, The University of Manchester, 131 Princess Street, Manchester M1 7DN, United Kingdom. abayomi.faponle@manchester.ac.uk

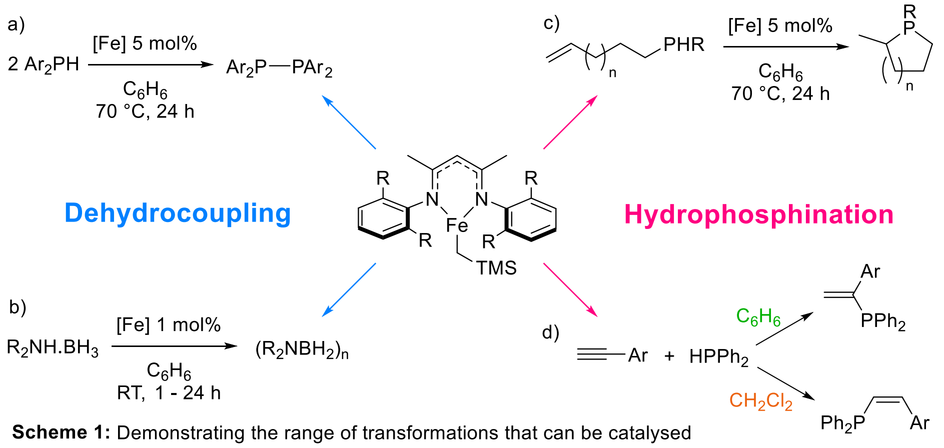
The abstract. The cytochromes P450 are heme based monooxygenases or peroxygenases involved in vital reaction processes for human health. A recently described P450 peroxygenase, OleT$_{JE}$, converts long chain fatty acids to terminal olefins and as such may have biotechnological relevance in biodiesel production. The reaction, however, produces significant amounts of α- and β-hydroxylation by-products and their origin are poorly understood. In this work we elucidate through a QM/MM study on the bifurcation pathways how the three possible products are generated and show how the enzyme can be further engineered for optimum desaturase activity. The studies show that the polarity and the solvent accessibility of the substrate in the binding pocket destabilize the OH rebound pathways and kinetically enable a thermodynamically otherwise unfavorable decarboxylation reaction. The origins of the bifurcation pathways are analyzed with valence bond models and highlight the differences in reaction mechanism.

Exploring the rich chemistry of iron (II) β-diketiminate complexes: from dehydrocoupling to hydrofunctionalisation

Nathan T. Coles, Maialen Espinal-Viguri, Andrew K. King, Ruth L. Webster*

Department of Chemistry, University of Bath, Bath, UK. BA2 7AY.
r.l.webster@bath.ac.uk

The stoichiometric reactivity of β-diketiminate complexes is well reported in the literature,[1] indeed the β-diketiminate pro-ligand has proven to be a work-horse of catalysis when utilised with a wide range of metals. However, the catalytic competency of iron β-diketiminate complexes is not well explored[2] and, as a result, an area of interest for our research group is the development of catalytic competency with iron β-diketiminate complexes. We have already shown that they are proficient catalysts for the dehydrocoupling (DHC) of phosphines (Scheme 1a)[3] and have extended the reactivity to phosphine-borane and amine-borane DHC (Scheme 1b), demonstrating that the system is competitive with seminal work using iron with these substrates.[4]



Scheme 1: Demonstrating the range of transformations that can be catalysed by Fe(II) β-diketiminate complexes.

In the presence of an olefin, a switch in reactivity takes place and hydrophosphination dominates. Intriguingly, a change in solvent results in a vast change in reactivity (Scheme 1d). Our synthetic studies along with mechanistic insights will be discussed.

References 1) P. L. Holland *et al. Dalton Trans.* **2015**, *44*, 16654. 2a) V. C. Gibson *et al. J. Chem. Soc., Dalton Trans.* **2002**, 4321; b) P. L. Holland *et al. J. Am. Chem. Soc.* **2005**, *127*, 7857; c) J. Hannedouche *et al. Angew. Chem. Int. Ed.* **2014**, *53*, 4930. 3) R. L. Webster *et al. Chem. Eur. J.* **2015**, *21*, 15960. 4) I. Manners *et al. Dalton Trans.* **2008**, 2732; b) I. Manners *et al. Chem. Eur. J.* **2011**, *15*, 4099; c) I. Manners *et al. J. Am. Chem. Soc.* **2014**, *136*, 3048; d) I. Manners *et al. Angew. Chem. Int. Ed.* **2015**, *54*, 4836.

Probing the Magnetic and Photophysical Properties of Manganese(III) and Iron(III) Spin Switches.

A.Barker,[a] B. Gildea,[a] Y. Ortin,[a] A.J. Fitzpatrick,[a] H. Müller-Bunz,[a] G. G. Morgan*[a]
School of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland.
andrew.barker@ucdconnect.ie

Thermal spin state switching in some transition metal complexes of iron, manganese and cobalt have been widely studied, with a strong focus on the magnetic properties.[1] [2] Of equal importance are the photophysical properties in both the solid state and in solution, in some instances it can lead to long lived excited states in crystalline samples.[3] This is termed Light Induced Excited Spin State Trapping (LIESST). The LIESST mechanism of Fe(II) (d^6), whereby 2 electrons are excited and spin flipped by a single photon, has been extensively debated in recent years. [4] [5] Much less studied is the LIESST mechanism in Fe(III) (d^5).[6] [7] The phenomenon is unknown in Mn(III) (d^4) and Co(II) (d^7). We present here recent magnetic and photophysical properties of some manganese(III) and iron(III) spin crossover and rationalise the difference between them.

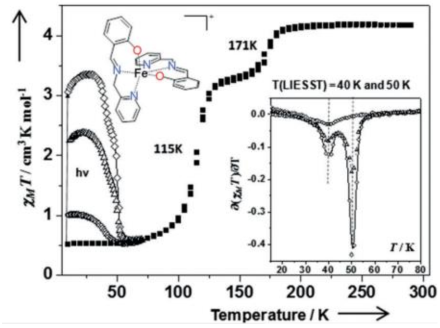


Figure: X_mT versus T for (1 ; ■), showing the LIESST effect on the complex at 10k. Thermal relaxation after (○) irradiation at 647.1nm during 2 h, irradiation at 830 nm during 3 h (△) and 12 h (◇). Structure of the complex cation is shown above the plot. The first derivative in the insert shows a double step relaxation curve. Tranition temperatures are indicated.

1. P. Gutlich, A. Gaspar. Y. Garcia. *Beilstein J. Org. Chem.* 2013, **9,** 342–391
2. M. A. Halcrow, *Chem. Soc. Rev*. 2011, **40**, 4119-4142
3. A. Hauser. *Top. Curr. Chem.* 2004, **234,** 155-198.
4. G. Auböck, M. Chergui. *Nature Chemistry.* 2014, **7,** 629-633.
5. W. Zhang, R. Alonso-Mori, U. Bergmann, C. Bressler, M. Chollet, A. Galler, W. Gawelda, R.G. Hadt, R.W Hartsock, T. Kroll, K.S Kjær, K. Kubicek, H.T. Lemke, H. W. Liang, D.A Meyer, M.M Nielsen, C. Purser, J.S. Robinson, E.I. Solomon, Z. Sun, D. Sokaras, D.B. van Driel, G. Vanko, T-C. Weng, D. Zhu, K. J. Gaffney, *Nature*, 2014, **509**, 345-348.
6. K. D. Murnaghan, C. Carbonera, L. Toupet, M. Griffin, M. M. Dîrtu, C. Desplanches, Y. Garcia, E. Collet, J. –F. Létard, G. G. Morgan, *Chem. Eur. J.*, 2014, **20**, 5613-5618.
7. R. Bertoni, M. Lorenc, J. Laisney, A. Tissot, A. Moréac, S. F. Matar, M. L. BOILLOT, E.Collet, *J. Mater. Chem. C*. 2015.

Proton-pumping and hydrogen oxidation in respiration

Mengqiu Li[1], Valentin Radu[1], Roman Tuma[1], Stefan Frielingsdorf[2], Oliver Lenz[2], Nikos Hatzakis[3], Lars J. C. Jeuken[1]

[1] *the Astbury Centre, School of Biomedical Sciences and School of Molecular and Cellular Biology, University of Leeds, Leeds LS2 9JT, United Kingdom*

[2]*Institut für Chemie, Sekretariat PC14, Technische Universität Berlin, 10623 Berlin, Germany*

[3]*Department of Chemistry, Nano-Science Center and Lundbeck Foundation Center for Biomembranes in Nanomedicine, University of Copenhagen, 2100, Copenhagen, Denmark.*

Bioelectrochemistry has been extremely valuable in elucidating the catalytic mechanism of respiratory redox enzymes, although in almost all cases only globular enzymes or subcomplexes have been investigated. The relative lack of bioelectrochemical studies of membrane proteins are due to their amphiphilic nature, which make them difficult to handle experimentally, especially in sensitive electrochemical experiments where proteins are prone to denaturation on the electrode surface. By modifying ultra-flat electrode surfaces with so-called tethered bilayer lipid membranes (tBLMs) or intact vesicles, supramolecular platforms can be constructed that enable the electrochemical characterisation of membrane-bound redox enzymes. In this presentation, two examples will be discussed in which membrane-modified electrodes have elucidated respiratory processes. In the first example, a membrane-bound [NiFe]-hydrogenases (MBH), which has been extensively studied for applications in hydrogen−oxygen fuel cells, was incorporated in a tBLM. Analysis shows that MBH is more resistive towards oxidative inactivation than previous results with water-soluble subcomplexes have suggested, which we propose is due to the fact that MBH is in a more native-like environment in the tBLM. In the second example, a heme-copper oxidase (HCO) is incorporated in intact vesicles on the electrode surface to create a single-enzyme platform that monitors proton pumping by this enzyme. This single-enzyme study reveals that cytochrome *bo*$_3$ from *Escherichia coli*, an HCO closely homologous to Complex IV in human mitochondria, can enter a rare, long-lifetime leak state during which proton flow is reversed.

Differences in inhibition of NiFe hydrogenases studied by protein film infrared electrochemistry.

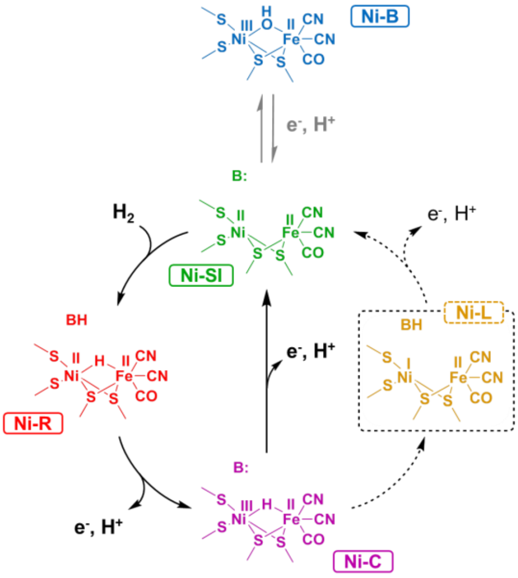
Philip A. Ash,[1] Ricardo Hidalgo,[1] Min-Wen Chung,[1] Nathan Coutard,[1] Eleanor Hall,[1] Oliver Lenz,[2] Kylie A. Vincent[1,*].

[1]*University of Oxford, Department of Chemistry, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, UK.*

[2]*Technische Universität Berlin, Institut für Chemie, PC14, Berlin, Germany.*

philip.ash@chem.ox.ac.uk; kylie.vincent@chem.ox.ac.uk

A nickel-iron catalytic site, incorporating iron coordinated by biologically unusual CO and CN^- ligands, is common to hydrogenases having various biological roles. The Ni is linked to Fe^{II} *via* two bridging cysteine thiolates in addition to coordination by two terminal cysteine ligands.[1] During catalysis the Ni cycles through formal oxidation states of III and II, and there is growing evidence for involvement of a Ni^{I} intermediate.[2] Despite the existence of a common active site NiFe hydrogenases display a range of sensitivities to small molecules such as O_2 or CO. The difference in sensitivity to attack by O_2 has been explained with reference to the availability of electrons from a unusual proximal iron-sulfur cluster,[3] which also affects the rate of recovery upon reductive reactivation.[4] Here we use the novel technique protein film infrared electrochemistry (PFIRE)[2c] to probe the concentration of NiFe active site states under steady-state turnover conditions for hydrogenases with a range of sensitivities to O_2 and CO. Based on these data we postulate that the sensitivity of NiFe hydrogenases toward inhibition is also influenced by the availability of the Ni-SI state.



References

1 - Lubitz, W. *et al.*, *Chem. Rev.* **2014**, *114* (8), 4081.
2 - (a) Tai, H. *et al.*, *Angew. Chem., Int. Ed. Engl.* **2014,** *53*, 13817; (b) Greene, B. L. *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 4558; (c) Hidalgo, R. *et al.*, *Angew. Chem., Int. Ed.* **2015**, *54*, 7110.
3 – Shomura, Y. et al., *Nature*, **2011**, *479*, 253-256.
4 – Radu, V. *et al.*, *Chem. Commun.* **2016**, *52*, 2632-2635.

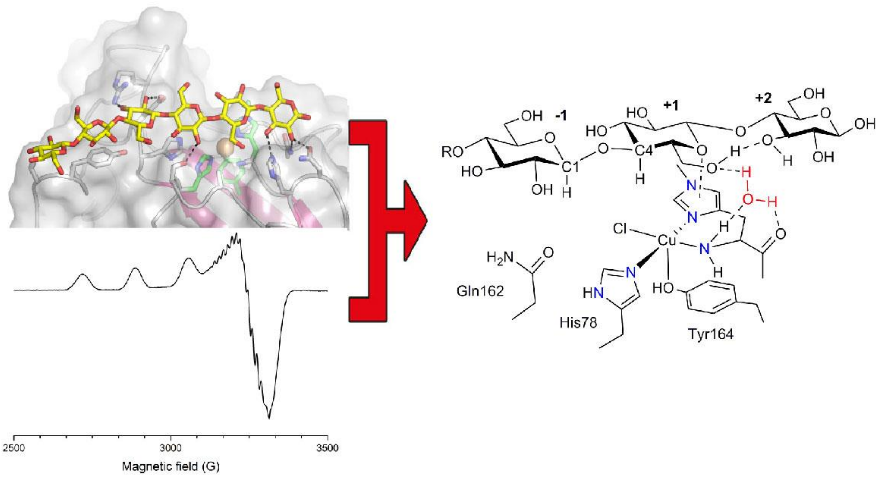
The molecular basis of polysaccharide cleavage by lytic polysaccharide monooxygenases

Luisa Ciano, Kristian E. H. Frandsen, Thomas J. Simmons, Paul Dupree, Jens-Christian N. Poulsen, Glyn R. Hemsworth, Esther M. Johnston, Morten Tovborg, Katja S. Johansen, Pernille von Freiesleben, Laurence Marmuse, Sébastien Fort, Sylvain Cottaz, Hugues Driguez, Bernard Henrissat, Nicolas Lenfant, Floriana Tuna, Amgalanbaatar Baldansuren, Gideon J. Davies, Leila Lo Leggio and Paul H. Walton

Department of Chemistry, University of York, York, UK. Email:luisa.ciano@york.ac.uk

---

The effective use of biomass is crucial in addressing the global need for sustainable energy sources. However, polysaccharides are highly recalcitrant to degradation, a major challenge in their utilisation for the production of biofuel. Lytic polysaccharide monooxygenases (LPMOs) are copper-containing enzymes which break down polysaccharide chains *via* an oxidative mechanism in the presence of a reducing agent and molecular oxygen,[1,2] thus boosting the action of classic enzymatic cocktails for industrial polysaccharide degradation. We report a detailed structural, kinetic and spectroscopic investigation of an oligosaccharide-active LPMO from the AA9 family. We have obtained the first crystal structures of an LPMO bound to cellohexaose and cellotriose in both the Cu(I) and Cu(II) redox states, which reveal important insights into substrate binding to the enzyme. These data, combined with the first solution kinetic measurements and electron paramagnetic resonance spectroscopy, lead to new mechanistic understanding of the LPMOs, key for their effective utilisation in biomass degradation.[3]



References: 1. R. J. Quinlan *et al.*, *PNAS*, 2011, **108**, 15079; 2. G. Vaaje-Kolstad *et al.*, *Science*, 2010, **330**, 219; 3. K. E. H. Frandsen *et al.*, *Nature Chem. Biol.*, 2016, DOI: 10.1038/nchembio.2029

New platinum oxadiazoline complexes with antiproliferative properties.

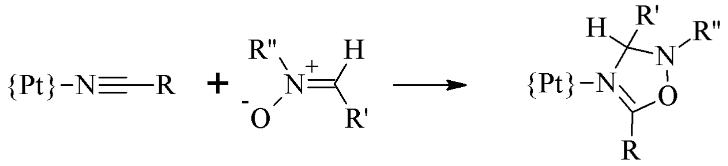
G. Wagner,[a] S. Sieste,[b] I. Lifinchev,[b] N. Stein,[b] J. Dempfle,[b] A. Marchant[c]

[a]: *Department of Natural Sciences, University of Chester, Thornton Science Park, Pool Lane, Ince, Chester, CH2 4NU, UK.*

[b]: *Inorganic Chemistry, University of Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany.*

[c]: *Chemical Sciences, FHMS, University of Surrey, Guildford, Surrey, GU2 7XH, UK.*

Cancer therapy of solid tumours relies heavily on the use of platinum based drugs, namely the globally approved cytotoxic Pt(II) compounds cisplatin, carboplatin and oxaliplatin. Despite their significant therapeutic success there are strong limitations due to the severe side effects experienced by the patients and the occurrence of acquired and intrinsic resistance.[1] Because of this, much effort has gone into the design of improved drugs over the past decades. We found that Pt oxadiazoline complexes show substantial *in vitro* antiproliferative activity, in cisplatin- and carboplatin-sensitive and -resistant human cancer cell lines.[2] These complexes are easily accessible by cycloaddition of nitrones to Pt-coordinated nitriles, as shown below. This synthetic route is potentially suited for a combinatorial chemistry approach and easily allows for a variation of substituents R to R'' in a wide range.



Herein, we describe the design principles, synthesis and characterization as well as the chemical reactivity and a cytotoxicity assessment of a series of Pt(IV) and Pt(II) complexes of the general formula *trans*-[$PtCl_4$(oxadiazoline)(L)], *trans*-[$PtCl_2$(oxadiazoline)(L)] and *cis*-[$PtCl_2$(oxadiazoline)(L)], where L is another oxadiazoline, nitrile, pyridine, imidazole, amine or sulfoxide.[3]

References:

[1] L. R. Kendall, N. P. Farrell, Platinum-Based Drugs in Cancer Therapy, Humana Press, NJ, **2000**.

[2] H. M. Coley, J. Sarju, G. Wagner, *J. Med. Chem.*, **2008**, *51*, 135.

[3] (a) G. Wagner, A. J. L. Pombeiro, V. Yu. Kukushkin, *J. Am. Chem. Soc.*, **2000**, *122*, 3106. (b) G. Wagner, M. Haukka, J. R. Fraústo da Silva, A. J. L. Pombeiro, V. Yu. Kukushkin, *Inorg. Chem.*, **2001**, *40*, 264. (c) G. Wagner, M. Haukka**,** *J. Chem. Soc.,Dalton Trans.*, **2001**, 2690. (d) J. Sarju, J. Arbour, J. Sayer, B. Rohrmoser, W. Scherer, G. Wagner, *Dalton Trans.*, **2008,** 5302. (e) G. Wagner, A. Marchant, J. Sayer, Dalton Trans., 39, **2010**, 7747.

A Study into Anticancer Pyridylphosphinate Metal Complexes[1]

James W. Walton

Department of Chemistry, Durham University, Lower Mountjoy, South Road, Durham DH1 3LE
james.walton@durham.ac.uk

The development of new drugs for the treatment of cancers is an important area of chemical research. In this area, inorganic metal complexes have several advantages over purely organic species including: a variety of metal geometries and coordination numbers, allowing access to intricate 3-dimensional structures; numerous metal oxidation states, allowing redox-activated drugs; tuneable ligands to vary sterics and electronics about the metal centre; exchangeable ligands, for *in situ* activation and binding to biomolecules; simple and modular syntheses, allowing rapid determination of structure to activity relationships.

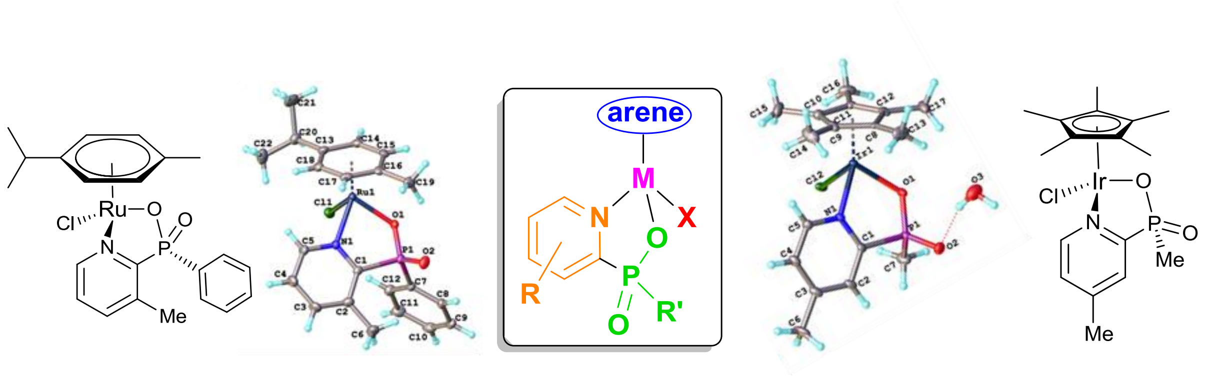


Fig 1

We present the synthesis and anticancer properties of a series of 25 new pseudo-octahedral metal complexes (Ru, Os, Rh, Ir). Each complex incorporates a pyridylphosphinate ligand (Fig 1), along with a monodentate halide and a capping η^6-bound aromatic ligand. Solid-state structural analyses of two complexes (Fig 1) reveal intriguing conformational diastereoselectivity. Aqueous behaviour has been investigated, with respect to hydrolysis of the metal–halide bond and pK_a of the resultant aqua complexes. Toxicity was measured *in vitro* against non-small cell lung carcinoma H460 cells, with the most potent Ir complexes reporting IC_{50} values around 50 μM. Binding studies with selected amino acids and nucleobases provide a rationale for the variation in toxicity observed within the series. Finally, an investigation into the ability of the chelating amino acid L-His to displace the phosphinate O–metal bond shows the potential for phosphinate complexes to act as prodrugs that can be activated *in cellulo*.

Reference

1.Jasmine M. Cross, Natalie Gallagher, Jason H. Gill, Mohit Jain, Archibald W. McNeillis, Kimberley Rockley, Fiona H. Tscherny, Natasha J. Wirszycz, Dmitry S. Yufit, and James W. Walton*, *Dalton Trans.*, 2016, *Under Review*

Piano-stool complexes for cancer treatment: exploiting redox mechanisms

Isolda Romero-Canelón and Peter J. Sadler

Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL UK

Platinum-based complexes are the most widely used chemotherapeutics, nonetheless there is a major unmet clinical need for new treatments that expand the range of treatable cancers and overcome inherent and acquired platinum resistance. This has stimulated the research for potential antineoplastic drugs based on other transition metals. Organometallic 'piano-stool' complexes of Ru^{II}, Os^{II}, and Ir^{III} in particular, can be designed to allow fine tuning of their physical and chemical properties with consequent optimization of biological activity.

Importantly, organo- Ru^{II}, Os^{II}, and Ir^{III} complexes can exert their activity through non-DNA mechanisms of action as they can target mitochondrial pathways and induce redox (both oxidative and reductive) stress. Iridium complexes for example, have an unprecedented ability to generate H_2O_2 by catalytic hydride transfer and to produce superoxide in ovarian cancer cells,[1] while ruthenium complexes can catalyse transfer hydrogenation in cancer cells[2] and osmium complexes can exploit mutations in the genes for mitochondrial proteins in the electron transport chain.[3] In addition to providing novel therapies for parental cancers, manipulation of the cellular levels of reactive oxygen species (ROS) may also provide a highly effective strategy for treating Pt-resistant cancers.

Acknowledgements

Financial support by ERC (247450, 324594), The Wellcome Trust (46782), Science City (AWM and ERDF), and EPSRC is gratefully acknowledged, as well as EC COST Action CM1105 for stimulating discussions

References

1. Z. Liu, I. Romero-Canelón, B. Qamar, J. M. Hearn, A. Habtemariam, N. P. E. Barry, A. M. Pizarro, G. J. Clarkson, and P. J. Sadler, *Angew. Chem. Int. Ed.*, **2014**, *53,* 3941–3946.
2. J. J. Soldevila-Barreda, I. Romero-Canelón, A. Habtemariam, and P. J. Sadler, *Nat. Commun.*, **2015**, *6,* 6582 doi: 10.1038/ncomms7582.
3. J. M. Hearn, I. Romero-Canelón, A. F. Munro, Y. Fu, A. M. Pizarro, M. J. Garnett, U. McDermont, N. O. Carragher, and P. J. Sadler, *PNAS,* **2015**, *112,* E3800-E3805.

Monitoring conformational changes of Zur, a Zn(II) metalloregulatory protein from *Synechococcus* sp. WH8102

Amira Z. Ksibe[1], Branko Rihtman[2], Rahman Rahmanpour[1], James P. Barnett, David J. Scanlan[2], and Claudia A. Blindauer[1]

[1]*Department of Chemistry and* [2]*School of Life Sciences, University of Warwick, UK*

Email: A.Ksibe@warwick.ac.uk

Acquisition and homeostasis of the micronutrient zinc by marine microorganisms is of key importance, given the erratic nutrient supply of oceanic ecosystems, and their global role in the biogeochemical cycling of elements.

Research on Zur (zinc-uptake regulator) proteins, zinc-sensing proteins that mediate responses to zinc deprivation, has burgeoned in the past decade.[1-3] Like other Fur family proteins, Zur proteins are homodimeric and have two or three metal sites per monomer. One of these sites is a Cys_4 structural site, whilst at least one other is the crucial sensory site. Binding to the latter is kinetically labile, and Zn(II) can easily be released and re-bound.[2,4,5]

Zur proteins are predicted in the genomes of marine cyanobacteria, but no representative has so far been characterised experimentally. Zinc-binding residues in the sensory sites of Zur proteins from other bacteria are not conserved in the sequences of cyanobacterial Zur. Therefore, we set out to characterise the predicted Zur protein from *Synechococcus* sp. WH8102, an open-ocean cyanobacterium belonging to subcluster 5.1 A, Clade III of marine *Synechococcus*,[6] a genus playing a key role in global carbon cycling and being an important oceanic primary producer.

The *synw_2401* gene was cloned and its product, the predicted Zur protein, was recombinantly expressed in *E. coli* and characterised by ICP-OES, native electrospray mass spectrometry and 2D $^1H,^{15}N$ NMR spectroscopy. Zur was isolated as a mixture of monomers and homodimers with 2.07±0.2 Zn(II) ions per monomer. However, treating the protein with the strong Zn(II) chelating agent EDTA yielded preparations with 0.9±0.3 Zn(II) ions per monomer. In addition, incubation with EDTA shifted the monomer/dimer equilibrium toward the monomeric state and affected the folding of the protein. Adding back Zn(II) to the Zn_1Zur species generated preparations with 1.9 ± 0.4 Zn(II) per monomer, and NMR and ESI-MS spectra that were comparable to those of the freshly isolated protein, demonstrating the reversibility of zinc removal.

We gratefully acknowledge financial support from the University of Warwick, Birmingham Science City Advanced Materials 2, and Homs University.

(1) Lucarelli, D.; Russo, S.; Garman, E.; Milano, A.; Meyer-Klaucke, W.; Pohl, E. *J. Biol. Chem.* **2007**, *282*, 9914-9922.

(2) Shin, J.-H.; Jung, H. J.; An, Y. J.; Cho, Y.-B.; Cha, S.-S.; Roe, J.-H. *PNAS* **2011**, *108*, 5045-5050.

(3) Gilston, B. A.; Wang, S.; Marcus, M. D.; Canalizo-Hernández, M. A.; Swindell, E. P.; Xue, Y.; Mondragón, A.; O'Halloran, T. V. *PLoS.* **2014**.

(4) Althaus, E. W.; Outten, C. E.; Olson, K. E.; Cao, H.; O'Halloran, T. V. *Biochemist.* **1999**, *38*, 6559-6569.

(5) D'Autréaux, B.; Pecqueur, L.; Gonzalez de Peredo, A.; Diederix, R. E.; Caux-Thang, C.; Tabet, L.; Bersch, B.; Forest, E.; Michaud-Soret, I. **2007**, *46*, 1329-1342.

(6) Scanlan, D. J.; Ostrowski, M.; Mazard, S.; Dufresne, A.; Garczarek, L.; Hess, W. R.; Post, A. F.; Hagemann, M.; Paulsen, I.; Partensky, F. *Microbiol. Mol. Biol. Rev.* **2009**, *73*, 249-299.

Iron Sulfur cluster nitrosylation mechanism in NsrR: mechanisms of nitrosylation in an NO regulatory protein

Authors: Erin Dodd[†], Philip Ash[‡], Kylie Vincent[‡], Nick Le Brun[†]

Royal Society Newton International Fellow, University of East Anglia

[†]*University of East Anglia, School of Chemistry;* [‡]*University of Oxford, Department of Chemistry*

e.dodd@uea.ac.uk

The interplay of signalling molecules such as nitric oxide is a fascinating way in which proteins mediate biological pathways and respond to their environment. Iron-sulfur cluster proteins are exceptionally tuneable chemical catalysts that, as one of many roles they play, are implicated in biological responses to nitrosative stress. Biological NO response is important in applications as diverse as soil science and disease treatment. Both isolated protein and synthetic model iron-sulfur clusters are extremely sensitive to nitrosylation, tending towards complete multi-step reaction and cluster degradation in instants, but biological systems are able to stop at partial nitrosylation and even repair nitrosylated clusters. NsrR, a [4Fe4S] protein found in many bacteria, is a regulator of response to nitrosative stress through a pathway initiated by cluster nitrosylation. With an approach that uses both NsrR and a synthetic model compound which mimics the cluster ligand environment, this work intends to align the investigation of model clusters with the investigation of the real protein, particularly through expansion of a novel technique of ATR infrared spectroscopy to observe nitrosylated intermediates of NsrR and similar proteins. Direct observation of mechanistic intermediates in the cluster nitrosylation reaction allows insight into how nature controls this important signal response pathway.

A Ferritin Optimized for Iron Oxidation not Storage

Justin Bradley[1], Stephanie Pfaffen[2], Raz Abdulqadir[1], Marlo Firme[2], Geoffrey Moore[1], Nick Le Brun[1] and Michael Murphy[1]

[1] Centre for Molecular and Structural Biochemistry, School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, [2] Department of Microbiology and Immunology, University of British Columbia, Vancouver, BC, V6T 1Z3, Canada

Email: Justin.Bradley@uea.ac.uk

Ferritins constitute a superfamily of iron storage and detoxification proteins found in all domains of life[1]. Considerable structural and mechanistic diversity exists within this superfamily. Prokaryotic and plant ferritins are 24meric homo-polymers in which each (H-chain) subunit contains a catalytic centre, the ferroxidase centre, for iron oxidation. Mammalian ferritins are typically hetero-polymers composed of H-chain subunits together with L-chains lacking a catalytic centre. The ferroxidase centre couples iron oxidation to the reduction of either oxygen or peroxide and binds a minimum of two ferrous ions to accomplish this. The ferroxidase centres of prokaryotic ferritins are distinct in that they contain a third iron site, site C. The role of this third iron ion in mineralisation is unclear and may well vary between organisms[2].

The ferritin isolated from the eukaryotic marine pennate diatom *Pseudo-nitzschia multiseries* (PmFTN) is unusual in that it is a homo-polymer in which the ferroxidase centre contains a site C[3]. Here we show by a combination of site directed mutagenesis, X-ray crystallography and spectrophotometrically monitored iron uptake kinetics that the third iron site in this protein limits the rate at which oxidised iron is released from the ferroxidase centre into the central cavity of the protein. The unusually rapid iron oxidation and slow iron mineralisation rates observed for PmFTN are suggestive of an iron buffering role rather than or in addition to the long term storage more commonly associated with ferritins.

1 Andrews, S. C. *Biochim Biophys Acta* **1800**, (2010) 691-705

2 Bradley, J. M., Moore, G. R., Le Brun, N. E. *J Biol Inorg Chem* **19**, (2014) 775-85

3 Pfaffen, S., Abdulqadir, R., Le Brun, N. E., Murphy, M. E. *J Biol Chem* **288**, (2013) 14917-25

Combining Inorganic Medicinal Chemistry and Nanotechnology

Nicolas P. E. Barry

Department of Chemistry, University of Warwick, CV4 7AL Coventry, UK.

N.Barry@warwick.ac.uk

Inorganic medicinal chemistry is in the early days of its development, although there are now a significant number of clinical trials involving metal compounds, or other agents which interfere with metabolic pathways for metals, both for therapy and for diagnosis. However, a number of challenges in inorganic medicinal chemistry remain to be overcome, such as for example, tumour-targeting and reduction of side effects. Nanotechnology, which has been defined as the engineering and manufacturing of materials at the atomic and molecular scale, offers unique tools for developing safer and more effective medicines, and provides several potential advantages for drug formulation and delivery.

In this presentation, I will discuss the design of metallated particles combining unusual ligands (carboranes), precious metals and polymers,[1] and their applications in medicinal[2] and nanomaterials[3] chemistry.

References

1. N. P. E. Barry, *et al.*, *Faraday Discuss.*, **2014**, *175*, 229.
2. I. Romero-Canelon, *et al.*, *J. Organomet. Chem.*, **2015**, *796*, 17-25
3. A. Pitto-Barry, P. J. Sadler, N. P. E. Barry, *Chem. Commun.*, **2016**, *DOI: 10.1039/C5CC09564F.*

Acknowledgments

I thank the Leverhulme Trust (Early Career Fellowship No. ECF-2013-414).

Functionalised Microbubbles for Dual-Modal Cancer Imaging

B. I. Harriss[1], M. Braga[2,3], J. Hernandez-Gil[1], L. Carroll[2], M-X. Tang[3], E. Aboagye[2], N. J. Long[1*]

[1] Dept. of Chemistry, Imperial College London. (*b.harriss13@imperial.ac.uk*, *n.long@imperial.ac.uk*)
[2] Dept. of Surgery and Cancer, Hammersmith Hospital, Imperial College London.
[3] Dept. of Bioengineering, Imperial College London.

Contrast agents are used in molecular imaging to aid in the visualisation of medical conditions. Dual-modal imaging agents aim to improve the information obtained by combining the strengths of multiple imaging modalities into one probe. Microbubbles are phospholipid-stabilised bubbles around 3 μm in diameter and are used as contrast agents in ultrasound imaging. Due to their large surface area, microbubbles provide an ideal platform for further functionalization with imaging and targeting moieties. This project aims to add moieties that allow for Positron-Emission-Tomography (PET) and cancer targeting in addition to other combinations and functionality.

Phospholipids have been successfully modified and fully characterised with a fluorescent moiety (Figure 1), a cancer targeting peptide and a chelate to allow for ^{68}Ga radiolabeling. This can also allow for gadolinium chelation and MRI imaging.

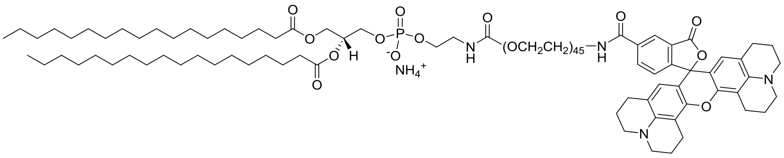


Figure 1: Structure of a phospholipid modified with a fluorescent moiety.

Modified phospholipids have been successfully incorporated into microbubbles and ^{68}Ga labelled, examples of which are given in Figure 2. *In vitro* work has shown that these microbubbles target cancerous cells selectively and work has begun to visualise these microbubbles *in vivo*, whilst an improved generation of phospholipids are being developed.

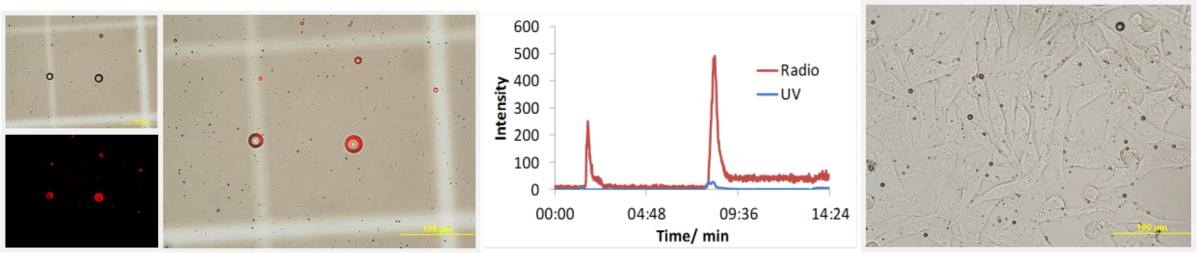


Figure 2: Left: Images of microbubbles under white light, with laser excitation and the merged combination, proving incorporation of modified lipids into microbubbles; middle: HPLC trace of a ^{68}Ga labelled phospholipid; right: microbubbles adhered to cancerous cells.

Copper(II) macrocyclic metal complexes for enhanced protein binding: biological activity and *in vivo* imaging

Benjamin P. Burke[1], Cecilia S. Miranda[1], Gonçalo S. Clemente[1], Shubhanchi Nigam[1], Juozas Domarkas[1], Rhiannon E. Lee[1], James A.Thompson[1], Thomas D'Huys[2], Dominique Schols[2], Chris Cawthorne[1], Stephen J. Archibald[1]

[1]Department of Chemistry and Positron Emission Tomography Research Centre, University of Hull, Cottingham Road, Hul, HU6 7RX; [2]Rega Institute for Medical Research, KU Leuven, Leuven, Belgium.

Metal containing drugs are ideal for disruption of the chemokine receptor signalling, as these cell surface proteins have a high density of negatively charged surface residues including aspartates and glutamates that can form coordinate bonds with metal ions.[1] Our aim is to produce and validate metal complexes that have high in vivo stability and can be used in both therapeutic and diagnostic applications.[2]

Chemokine receptors are involved in cell signalling and implicated in diseases including atherosclerosis, asthma, rheumatoid arthritis, HIV infection and cancer. We have targeted the CXCR4 chemokine receptor using configurationally restricted macrocyclic metal complexes of first row transition metals (copper(II), zinc(II) and nickel(II)) and demonstrated an improved binding profile with the protein (interaction strength and residence time) for these rigid molecules.[2] Enhanced blocking of intracellular signal transduction is observed in comparison to purely organic antagonists.

The copper(II) compounds have been validated both in vitro and in vivo.[3] We have observed that the compounds are stable and well tolerated. Configurationally restricted bimetallic complexes of copper(II) and their biological properties were investigated in a series of assays to fully understand the impact on cancer cells.[3] The receptor targeting compounds can also be used in medical imaging studies when radiolabelled with the copper-64 radioisotope for positron emission tomography (PET) imaging. We have validated this approach for tumour imaging. The radiochemistry has been optimised and in vivo studies carried out.

This research work applies basic chemical principles to design strong coordination bond interactions (in terms of geometry and electron arrangement) and hence optimizes protein binding. The novel compounds give a significant increase in biological activity and bind to target in vivo.

References

(1) Smith, R.; Archibald S. J. In *Comprehensive Inorganic Chemistry II*, Volume 3,Chapter 3.22, **2013**, 661-682.

(2) Khan, A.; Nicholson, G; Greenman, J.; Madden, L.; McRobbie, G.; Pannecouque, C., De Clercq, E.; Ullom, R.; Maples, D. L.; Maples, R. L.; Silversides, J. D.; Hubin, T. J.; Archibald, S. J. *J. Am.Chem. Soc.*, **2009**, *131*, 3416-3417

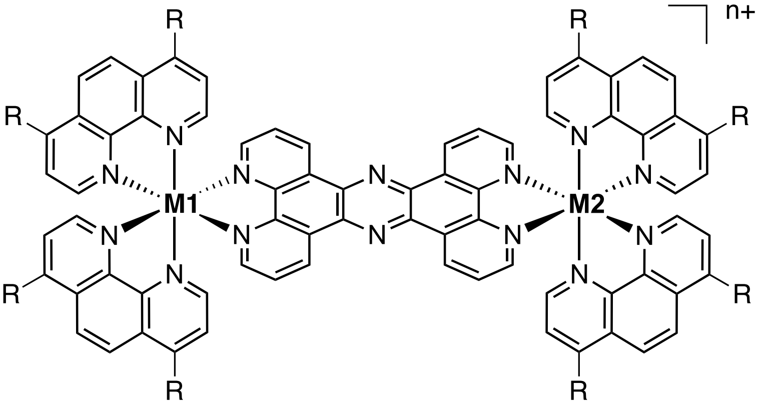
(3) J. Panneerselvam, J. Jin, M. Shanker, J. Lauderdale, J. Bates, Q. Wang, T. J. Hubin, S. J. Archibald, R. Ramesh *Plos One* **2015,** 10, (3).

Multifunctional bioprobes.

Jim A THOMAS

Depart of Chemistry, University of Sheffield, S3 7HF, UK (james.thomas@shef.ac.uk).

Polypyridyl complexes of d^6-metal ions can interact reversibly with DNA with high binding affinities.. Although such complexes offer potential as *in cellulo* probes for luminescence microscopy, poor cellular uptake by live cells generally restricts the use of many such systems.



In recent studies we have developed a series of complexes incorporating Ru^{II}, Os^{II}, and Ir^{III} centres –Scheme 1 - that are taken up by live eukaryotic and prokaryotic cells where they bind to specific biomolecules.[1-5] These complexes function as multifunctional probes imaging intracellular structures and biomolecules through a number of different high-resolution microscopy techniques, including conventional and time-domain optical microscopy [6] and transmission electron microscopy.[3] The diastereoselective interaction of these complexes with biomolecules has also been explored.[7,8]

References

1 M. R. Gill, *et al*, *Nat Chem*, **2009**, *1*, 662.

2 M. R. Gill, *et al. Chem. Sci.*, **2013**, *4*, 4512.

3 A. Wragg, *et al, Chem. Commun.*, **2014**, *50*, 14494. *(Front Cover*).

4 A. Wragg, *et al* , *Chem. Eur. J.*, **2014**, 20, 14004.

5 A. Wragg, *et al, Chem. Eur. J.*, **2015**, *21*, 11865.

6 E. Baggaley, *et al*, *Angew. Chem. Int. Ed.*, **2014**, *53*, 3367–3371 (*Front Cover*).

7. T. Wilson, *et al*, *J. Med. Chem.*, 2013, **56**, 8674–8683.

8. C. Glover, N Green, J A Thomas, in preparation.

Enhancing Stability and Reactivity of Zr Metal-Organic Frameworks.

Dr Ross S. Forgan

WestCHEM School of Chemistry, University of Glasgow, Joseph Black Building,University Avenue, Glasgow, G12 8QQ, UK. E-mail: Ross.Forgan@glasgow.ac.uk;

The mechanical stabilities of metal-organic frameworks (MOFs) – network structures of metal ion(s) or clusters connected by organic linkers – have been relatively understudied in comparison to their chemical stabilities. We will report a novel synthetic method to prepare diffraction quality single crystals of Zr^{4+} and Hf^{4+} dicarboxylate MOFs (the so-called UiO-66 series) whose chemical stabilities are well established, but whose syntheses remain troublesome.[1] Access to single crystals has allowed us to carry out a comprehensive study of their mechanical stabilities by high pressure single crystal X-ray diffraction, nanoindentation and theory, and we shall detail the effects of linker substitution on stability and flexibility.[2]

We will demonstrate that the chemical and mechanical stabilities of these Zr MOFs facilitate quantitative postsynthetic halogenation across integral unsaturated C-C bonds in a single-crystal to single-crystal manner, including an examination of the stereoselective nature of the transformations utilising crystal structures of halogenated MOFs, as well as the potential application of the MOFs for chemisorptive sequestration of iodine. [3] Finally, we will show that postsynthetic modification can be used to modulate the mechanical compliance of the MOFs, potentially tuning their flexibility through chemical reaction.[4]

1. R. J. Marshall, C. L. Hobday, C. F. Murphie, S. L. Griffin, C. A. Morrison, S. A. Moggach and R. S. Forgan, *J. Mater. Chem. A*, **2016**, DOI: 10.1039/C5TA10401G.
2. C. L. Hobday, R. J. Marshall, C. F. Murphie, J. Sotelo, T. Richards, D. Allan, T. Düren, F. –X. Coudert, R. S. Forgan, C. A. Morrison, S. A. Moggach and T. D. Bennett, *Angew. Chem. Int. Ed.* **2016**, *55*, 2401–2405.
3. R. J. Marshall, S. L. Griffin, C. Wilson and R. S. Forgan, *J. Am. Chem. Soc.* **2015**, *137*, 9527–9530; R. J. Marshall, S. L. Griffin, C. Wilson and R. S. Forgan, *Chem. Eur J.* **2016**, DOI: 10.1002/chem.201505185.
4. R. J. Marshall, T. Richards, C. L. Hobday, C. F. Murphie, C. Wilson, S. Moggach, T. D. Bennett and R. S. Forgan, *Dalton Trans.* **2016**, DOI: 10.1039/C5DT03178H.

Graphene and graphene based materials for hydrogen storage

Simon Champet[1], Agata Godula-Jopek[2], Duncan Gregory[1]

[1] *WestCHEM, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK.*

[2] *Airbus Group Innovations, TX6, Willy-Messerschmitt-Straße 1, 81663 Ottobrunn, Germany and Institute of Chemical Engineering, Polish Academy of Sciences, 44100 Gliwice, Poland*

s.champet.1@research.gla.ac.uk

Hydrogen fuel cells can provide an elegant solution to the challenge of generating electrical power without emissions. Efficient hydrogen storage however is one factor preventing the immediate wider use of fuel cells, particularly in terms of mobile applications. In order to unlock this limitation, new approaches to storage are required but to date no system meets all the requirements. Our study focuses on whether graphene-based materials can fulfill their predicted potential as hydrogen stores. Graphene, a one-atom-thick planar sheet of sp^2-bonded carbon atoms, is densely packed in a two-dimensional (2D) honeycomb crystal lattice. It can be wrapped into zero-dimensional (0D) fullerenes, rolled into one-dimensional (1D) carbon nanotubes, or stacked into three-dimensional (3D) graphite[1]. Due to its abundance and intrinsic properties, carbon-based materials are light, relatively cheap and easily recyclable materials.

State of the art graphene-based materials should theoretically achieve the US Department of Energy (DoE) criteria for automotive hydrogen storage (system: 7.5 wt. %.; 0.07 kg H_2 L^{-1} and $ 266 kg^{-1} H_2 while H_2 itself costs 2-4 USD/gge at the pump)[2, 3]. Numerous calculations predict a great potential for graphene-based materials as a superior storage material. With a high specific surface area (pristine graphene has theoretical specific surface area of 2630 m^2g^{-1}); light metal decorated graphene is particularly highlighted by theorists as being able to match hydrogen storage requirements[4, 5]. Such material should indeed have a gravimetric density of *ca*. 10 wt.%[4].

Our investigation aims to address the challenges proposed by theoretical chemists to produce and assess such compounds. To date very few experimental studies of hydrogen storage in graphene and derivatives have been reported. Here we present our approach towards synthesizing such graphene based materials and our preliminary results as we test whether experiment can validate the predictions of computational theory (Fig. 1). Specific surface area enhancement, metal deposition and surface modifications are mainly characterized via nitrogen isotherm adsorption (e.g. BET model), XRD, scanning electronic microscopy and EDX analyses. We focus as well on nanoconfinement and graphene 3D structures[6] via graphene oxide synthesis[7]. Hydrogen uptake assessments are performed using intelligent gravimetric analysis (IGA) and pressure-composition-temperature (PCT) gravimetric and volumetric instruments respectively.

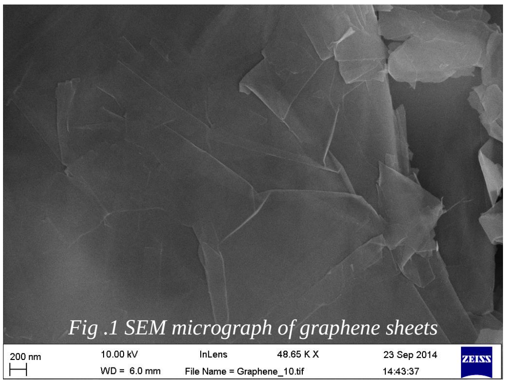


Fig .1 SEM micrograph of graphene sheets

References:

[1] *Graphene: Properties, Preparation, Characterization and Devices*, 2014, Woodhead Publishing, ISBN: 978-0-85709-508-4

[2] *US DoE: http://energy.gov/sites/prod/files/2014/02/f8/hstt_roadmap_june2013.pdf*

[3] *High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery,* Yang et al., *Chem.Soc.Rev*., 2010, 39, 656–675

[4] *Prospects for hydrogen storage in graphene,* Tozzini and Pellegrini, *Phys. Chem. Chem. Phys.*, 2013, 15,80

[5] *Hydrogen storage in porous graphene with Al decoration,* Ao et al., *International journal of hydrogen energy,* 2014, 39, 16244-16251

[6] *Self-Assembled Graphene Hydrogel via a one-Step Hydrothermal Process,* Yuxi Xu et al., *ACSNano*, 2010, *Vol.4, No.7, 4324–4330*

[7] *Improved Synthesis of Graphene Oxide,* Daniela C. Marcano et al., *ACSNano*, 2010, Vol4, No.8, 4806–4814

Solvothermal Synthesis of Novel Oxothio Germanates

John D. Lampkin, Anthony V. Powell, Ann M. Chippindale

University of Reading, Email: j.lampkin@pgr.reading.ac.uk,

We describe the first synthesis and structural characterisation of materials containing oxothio germanate(IV) units. Four discrete oxothio germanate structures have been prepared from GeO_2 under solvothermal conditions: (**1**) $[Co(tren)_2]_2[Ge_4O_6S_4]$, (**2**) $[(Co(tren))_2\ \mu\text{-}tren][Ge_4O_6S_4]$, (**3**) $[Co(deta)_2]_2[Ge_4O_6S_4]_2$ and (**4**) $[Co(deta)_2]_4[Ge_9O_{14}S_8]$, (where tren = tris-2(aminoethyl)-amine and deta = diethylenetriamine). Structures (**1**) - (**3**) contain the same T2 supertetrahedral sulphur-capped adamantane units, $[Ge_4O_6S_4]^{4-}$. In compounds (**1**) and **(3)**, charge balancing is provided by $[Co(tren)_2]^{2+}$ and $[Co(deta)_2]^{2+}$ complexes, respectively. The counter ion in compound (**2**) is unusual and consists of two trigonal bipyramidal Co(tren) complexes bridged *via* a third tren molecule (Figure 1a). The bridging tren molecule has an uncoordinated $(CH_2)_2NH_2$ group within hydrogen bonding (NH•••S) distance of the T2 cluster. Compound (**4**) contains a novel discrete germanate unit in which two T2 supertetrahedral units fuse through a GeO_4^{4-} bridge (Figure 1b), with charge balancing being achieved by $Co(deta)_2$ complexes, as seen in (**3**). To our knowledge, this is the first observation of this inorganic structural building block.

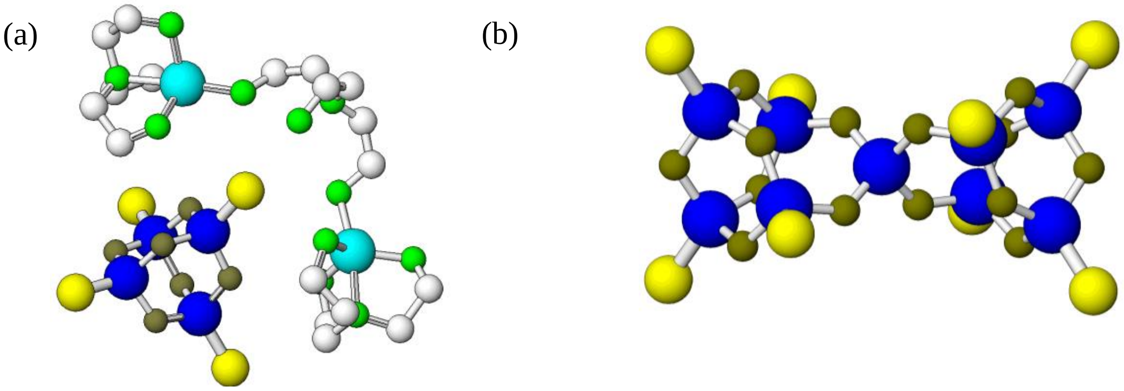


Figure 1: (a) The asymmetric unit in (**2**) and (b) the $[Ge_9O_{14}S_8]^{8-}$ unit in (**4**). Key: blue, Ge; khaki, O; yellow, S; cyan, Co; green, N; white, C. Hydrogen atoms have been omitted for clarity.