



Dalton Younger Members Event

(DYME@Leeds-2015)

University of Leeds

(Lecture Theatre A, School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, UK, LS2 9JT)

9-10th September 2015



Dalton Transactions **Asynt** 

Dalton Younger Members Event

 UNIVERSITY OF LEEDS

Wednesday 9th September 2015

10:00-11:00	Registration and coffee
Session 1	Heba Abdelgawad (Chair)
11:00-11:05	Welcome
11:05-12:05	Scott Dalgarno (Heriott-Watt University) <i>Plenary speaker</i>
12:05-12:25	Charlotte Rivas (Imperial College London)
12:25-12:45	Simon McAdams (University of Manchester)
12:45-13:00	Nicola Bell (University of Edinburgh)
13:00-14:00	Lunch and poster session
Session 2	Fabrizio Ortu (Chair)
14:00-14:20	Shani Osborne (Birmingham University)
14:20-14:40	Seb Pike (Imperial College London)
14:40-15:00	Kate Appleby (University of York)
15:00-15:30	Coffee and posters
Session 3	Jenni Garden (Chair)
15:30-15:50	Vikki Pritchard (University of Leeds)
15:50-16:10	Melvyn Ansell (University of Sussex)
16:10-16:30	Orlando Santoro (University of St. Andrews)
16:30-17:30	Nigel Pickett (Nanoco, Manchester) <i>Plenary speaker</i>
17:30-18:30	Wine reception
18:30	Conference meal @ The Terrace

School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, UK, LS2 9JT

Contact: Flora Thorp-Greenwood | 0113 34336574 | chmft@leeds.ac.uk

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Thursday 10th September 2015

Session 4	Seb Pike (Chair)
9:00-9:20	Stefano Nuzzo (Trinity College Dublin)
9:20-9:40	Conrad Goodwin (University of Manchester)
9:40-10:00	Sarah Makin (University of Reading)
10:00-10:20	Victoria Greenacre (University of Sussex)
10:20-10:40	Coffee and posters
Session 5	Charlotte Rivas (Chair)
10:40-11:00	Rafal Kulmaczewski (University of Leeds)
11:00-11:20	Laura Dornan (University of Belfast)
11:20-11:40	Alistair MacNair (University of Edinburgh)
11:40-12:00	Julia Sarju (University of York)
12:00-13:00	Lunch and posters
Session 6	Rafal Kulmaczewski (Chair)
13:00-13:20	Jenni Garden (Imperial College London)
13:20-13:40	Luke Wilkinson (University of Sheffield)
13:40-14:00	Callum Benson (University of Cambridge)
14:00-14:20	Jesus Ferrando-Soria (University of Manchester)
14:20-14:50	Coffee and posters
Session 7	Flora Thorp-Greenwood (Chair)
14:50-15:50	Ian Fairlamb (University of York) <i>Plenary speaker</i>
15:50-16:00	Closing remarks and prizes

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Asynt

DUAL-MODAL MR/FLUORESCENT ZINC SENSING PROBES TOWARDS DIABETES IMAGING

Charlotte Rivas^a, Graeme J. Stasiuka, Pauline Chabosseau, Guy A Rutter and Nicholas J. Long,^{*a}

Department of Chemistry, Imperial College London, South Kensington Campus, London, SW7 2AZ ^a, Department of Medicine, Imperial College London, Hammersmith Hospital, London, W12 0NNb.

Email: c.rivas11@ic.ac.uk

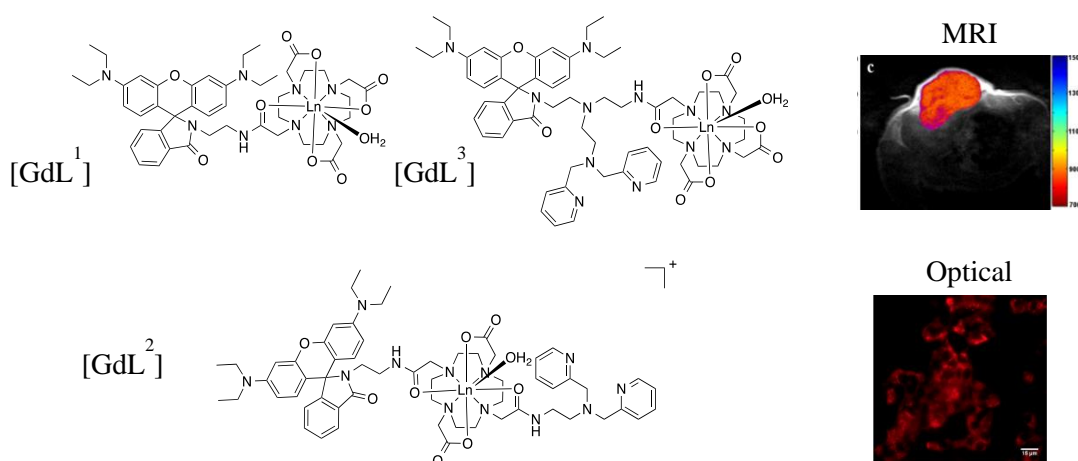


Figure 1: (Left) Dual-modal probes [GdL1], [GdL2] and [GdL3]; (right) T_1 map of BALB/c nude mouse tumour ([GdL1]) and fluorescence microscopy of [GdL3] in INS1 cells.

The detection of zinc intracellularly is becoming increasingly important due to its involvement in a number of biological processes and diseases, in particular, diabetes. It is well known that there is a high concentration of zinc within insulin granules held in pancreatic β -cells.¹ Changes in pancreatic β -cell mass contribute to the development of both type 1 and type 2 diabetes, the underlying mechanisms of which are poorly understood.² As such, the concept of using MR-active probes capable of binding zinc to report on β -cell mass *in vivo* has fast become a field of importance.

We will present our recent work on dual-modal MR/fluorescent contrast agents that show specific binding to zinc. Three novel probes based on rhodamine-DO3A conjugates have been prepared and coordinated to paramagnetic Gd^{3+} and luminescent Eu^{3+} and Tb^{3+} lanthanide ions. The ligands were functionalised to incorporate di-picolylamine (dpa) zinc binding moieties. The biological and chemical properties of the resulting complexes were investigated.

[GdL1] behaves as a dual-modal probe ($r_1 = 3.8 \text{ mM}^{-1}\text{s}^{-1}$, $\lambda_{\text{ex/em}} = 560/580 \text{ nm}$) that displays a switch on of fluorescence in acidic environments. [GdL2] displayed a 31 % increase in r_1 in the presence of Zn^{2+} but showed no fluorescence response to the metal ion.

Finally, [GdL3] displayed an improved relaxivity response to Zn^{2+} ($\sim 50 \%$) as well as a switch on in fluorescence. All probes were assessed *in vitro* with localisation shown to be mitochondrial, cytosolic and lysosomal for [GdL1], [GdL2] and [GdL3] respectively.

1. X. Qian and Z. Xu, *Chem Soc. Rev.* 2015, 44, 4487 – 4493.

2. G. R. Kokil, R. N. Veedu, G. A. Ramm, J. B. Prins and H. S. Parekh, *Chem. Rev.*, 2015, 115, 4719 – 4743.

MULTIMODAL MAGNETIC AND LUMINESCENT NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

Simon McAdams^{*a}, *Paul McNaughter*^a, *David Lewis*^b, *Edward Lewis*^b, *Sarah Haigh*^b, *Paul O'Brien*^{a, b} and *Florian Tuna*^{a, c}

^aSchool of Chemistry, The University of Manchester.

^bSchool of Materials, The University of Manchester, UK.

^cPhoton Science Institute, The University of Manchester, UK.

Email: simon.mcadams@postgrad.manchester.ac.uk

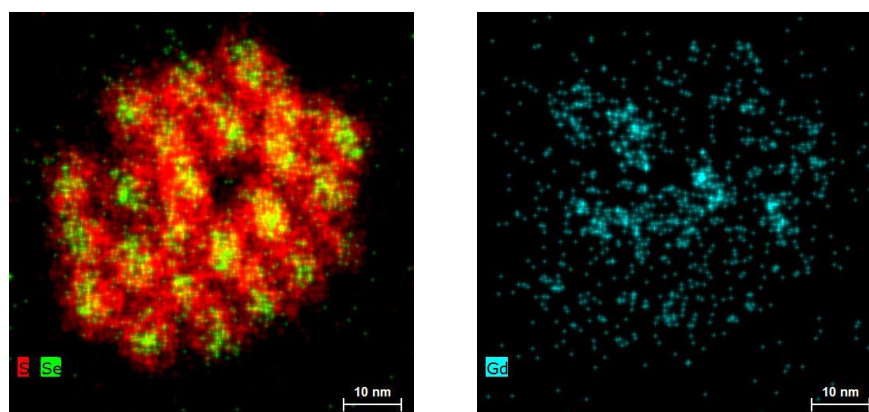


Figure 1: Energy-dispersive X-ray spectroscopy of CdSe/CdS/ZnS quantum dots (a) functionalised with a Gd complex (b).

Dual functioning nanoparticles will likely be key to future imaging, diagnostics, and treatments. Combining magnetic and optically active components would allow both MRI and fluorescent imaging with a single imaging probe. Semiconductor nanocrystals, or ‘quantum dots (QDs)’, are promising fluorescent probes with size-tunable optical properties and high photoluminescent quantum yields. However, QDs typically emit in the visible, and hence lack the tissue penetration of NIR. Conversely, lanthanides, in addition to paramagnetism, have sharp emission bands ranging from the UV to NIR. Modifying QDs with lanthanides would create attractive magnetic and luminescent hybrids well-suited for biomedical applications. Here, we have combined bright CdSe/CdS/ZnS QDs with a paramagnetic Gd complex¹ to form a multimodal hybrid with potential applications in dual MRI-fluorescence imaging (figure 1).

1. Lewis *et al.*, *J. Am. Chem. Soc.*, 2011, *133* (4), pp 1033-1043. DOI: 10.1021/ja109157g.

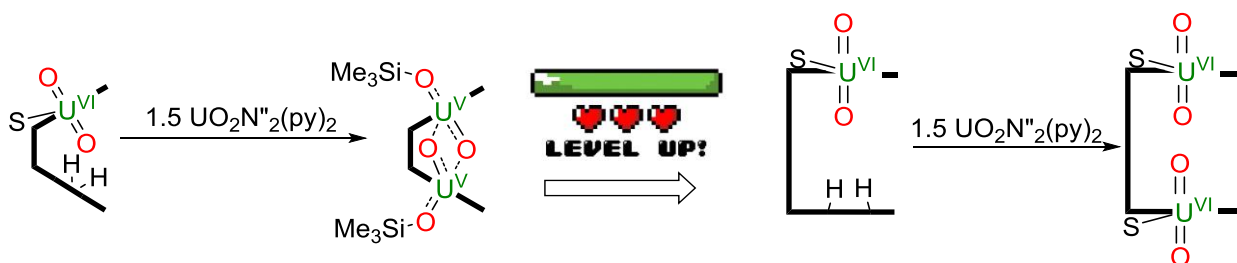
TAKING URANYL PACMAN CHEMISTRY TO THE NEXT LEVEL

Nicola Bell

University of Edinburgh

Email: Nicola.Bell@ed.ac.uk

The strong and covalent O=U=O multiple bonds in the linear uranyl dication $[\text{UO}_2]^{2+}$ are relatively inert with most reactivity of the U(VI) metal occurring around the equatorial plane.¹ However, we have previously shown that encapsulation of $[\text{UO}_2]^{2+}$ within the orthophenylene-linked polypyrrolic Schiff base ‘Pacman’ macrocycle can result in facile reduction of the U(VI) to U(V) and allow silylation and metalation reactivity.² Due to steric constraints two linear uranyl moieties cannot be accommodated within a single orthophenylene-linked ‘Pacman’ ligand; instead a doubly reduced ‘butterfly’ compound with a ‘cis-uranyl’ motif is accessed (Scheme 1).³



Scheme 1: Synthesis of bis-uranyl ‘Pacman’ complexes

Working with our extended anthracenylene-linked macrocycle we have recently developed a synthetic route to both mono- and bis-uranyl complexes the latter of which contains two U(VI) linear trans-dioxo uranyl cations in contrast to the reduced U(V)/U(V) ‘butterfly’ species observed with the orthophenylene-linked macrocycle.⁴

1. Denning, R. G.; Green, J. C.; Hutchings, T. E.; Dallera, C.; Tagliaferri, A.; Giarda, K.; Brookes, N. B.; Braicovich, L. *J. Chem. Phys.* **2002**, *117*, 8008; Vallet, V.; Wahlgren, U.; Grenthe, I. *J. Phys. Chem. A* **2012**, *116*, 12373.
2. Arnold, P. L.; Blake, A. J.; Wilson, C.; Love, J. B. *Inorg. Chem.* **2004**, *43*, 8206; Arnold, P. L.; Patel, D.; Wilson, C.; Love, J. B. *Nature* **2008**, *451*, 315; Arnold, P. L.; Pecharman, A. F.; Hollis, E.; Yahia, A.; Maron, L.; Parsons, S.; Love, J. B. *Nat. Chem.* **2010**, *2*, 1056; Arnold, P. L.; Hollis, E.; Nichol, G. S.; Love, J. B.; Griveau, J.-C.; Caciuffo, R.; Magnani, N.; Maron, L.; Castro, L.; Yahia, A.; Odoh, S. O.; Schreckenbach, G. *J. Am. Chem. Soc.* **2013**, *135*, 3841.
3. Arnold, P. L.; Jones, G. M.; Odoh, S. O.; Schreckenbach, G.; Magnani, N.; Love, J. B. *Nat Chem* **2012**, *4*, 221.
4. [Arnold, P. L.; Jones, G. M.; Pan, Q.-J.; Schreckenbach, G.; Love, J. B. *Dalton Trans.* **2012**, *41*, 6595.

LUMINESCENT RUTHENIUM PROBES FOR COATING NANOPARTICLES: EFFECT OF PROBE DESIGN ON LUMINESCENT PROPERTIES

Shani Osborne

University of Birmingham, School of Chemistry

Email: sao983@student.bham.ac.uk

Nanoscale probes are ideal for monitoring cellular events based on the spatial resolution offered by imaging techniques. We have used labelling approaches to prepare gold nanoparticles coated with luminescent probes, so that the nanoprobe bears the distinct optical signature of the luminescent agent, independent of the particle properties. Such designed

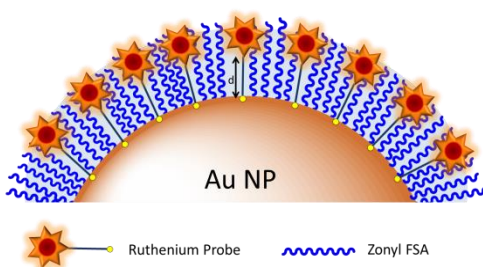


Figure 1: Schematic to show the ruthenium probe and surfactant on the gold nanoparticles. The distance, d , of the probe from the gold surface can be varied

probes offer multimodal detection taking advantage of gold's high electron density, and also lack the blinking effect observed in quantum dots. Our methodology involves attachment of metal probes onto nanoparticles using either fluorinated surfactants or peptides. We have found that the

100 nm gold nanoparticles can be visualized as single particles with conventional confocal luminescence microscopy techniques as single nanoparticles in cancer cells.

The luminescent properties of the metal complex upon binding to the nanoparticle are influenced by the design of the molecule and the surrounding surfactant. We

have been working with ruthenium luminescent probes which have excellent compatibility with confocal fluorescence microscopes available in biochemistry labs and also provide blue visible excitation and luminescence in the red. In this paper we will present the effect of the distance of the luminescent centre from the gold surface on the luminescent properties of the nanoparticle. We have studied their luminescent properties on different size gold nanoparticles.

The change in lifetime of the complex upon attachment to the nanoparticles is analysed to determine the quenching or in some cases enhancement of the excited state.

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2. Lewis DJ, Bruce C, Bohic S, Hammond SP, Arbon D, Pikramenou Z, Kysela B (2010) Nanomedicine 5: 1547.
3. Rogers NJ, Claire S, Harris RM, Farabi S, Zikeli G, Styles IB, Hodges NJ, Pikramenou Z (2014) Chem. Commun. 50: 617.
4. Lewis DJ, Dore V, Rogers NJ, Mole TK, Nash GB, Angeli P, Pikramenou Z (2013) Langmuir 29: 14701.

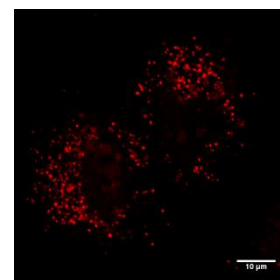


Figure 2: Ruthenium luminescence imaging (shown in red) of individual nanoparticles in A549 lung cancer cells.

PHOSPHINATE CAPPED ZNO NANOPARTICLES (AND CLUSTERS) FOR COMBINATION WITH CU NANOPARTICLES AS CATALYSTS TO HYDROGENATE CO₂ TO METHANOL.

S. D. Pike, A. García-Trenco, E. R. White, M. S. P. Shaffer, C. K. Williams

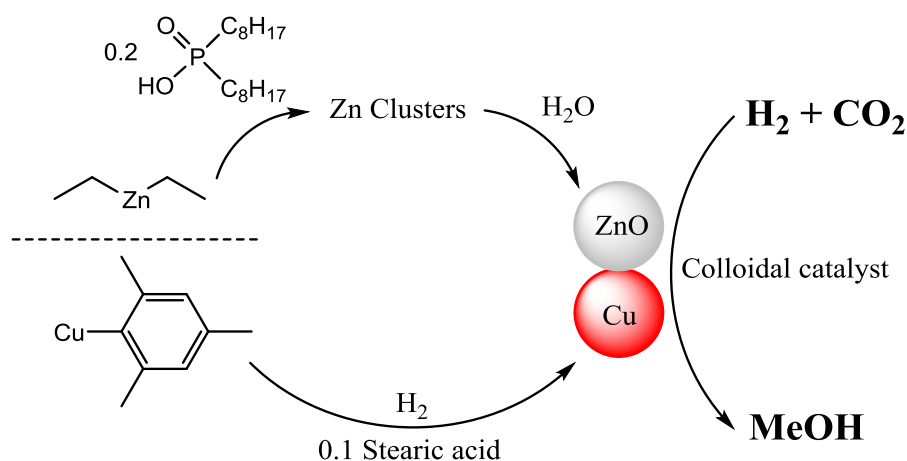
Department of Chemistry, Imperial College London, London, SW7 2AZ, U.K.

Email: s.pike@imperial.ac.uk

Over 40 million tonnes of methanol are produced every year, typically from syn-gas using a heterogeneous CuZnO catalyst.¹ The industrial catalyst has been optimised by enhancing the interface between the small Cu and ZnO particles, this interface is considered to be essential for the formation of catalytically active sites.^{1,2} The hydrogenation of CO₂ to form methanol would represent a more environmentally friendly synthesis, and opens the possibility of using methanol as a sustainable fuel.

The use of organometallic precursors for the formation of Cu and ZnO nanoparticles has been utilised to give small, well defined nanoparticles with a controlled metal:ligand ratio. Phosphinate ligands may stabilise ZnO nanoparticles and are stable themselves under the reducing conditions used in hydrogenation catalysis.³ Utilising ³¹P NMR spectroscopy and X-ray crystallography a series of Zn cluster complexes have been identified during the ZnO synthesis, giving insight into the synthetic process of forming nanoparticles.

A mixture of Cu and ZnO nanoparticles solvated in mesitylene acts as a colloidal catalyst for the hydrogenation of CO₂ to form methanol. The influence of nanoparticle size and of ligand effects has been investigated. The appearance of Zn clusters in post catalysis samples shows the dynamic relationship between nanoparticles and molecular clusters in solution.



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2. Behrens, M. *et al. Science* **2012**, 336, 893.
3. Brown, N. J.; Weiner, J.; Hellgardt, K.; Shaffer, M. S. P.; Williams, C. K. *Chem. Comm.* **2013**, 49, 11074.

UNRAVELLING THE MYSTERIES OF THE PALLADIUM CLUSTER PHASE

Kate Appleby^a, *Simon Duckett*,^{*a} and *Ian Fairlamb*^{*a}

Department of Chemistry, University of York, Heslington, UK.^a
Email: kma507@york.ac.uk

Palladium is incredibly versatile, making it an irreplaceable catalytic metal. The exact nature of the active catalytic species, however, continues to be a matter of debate. It is known that palladium nanoparticles can form from monomers during catalysis, and that monomers can also leach from nanoparticles. Consequently there is evidence to support both homogeneous and heterogeneous catalysis.^{1,2} Despite arguments focussing on these two distinct catalytic phases, it is likely that a short-lived cluster phase contains relevant, active, species however their low abundances make them difficult to identify and characterise. Such clusters can form by leaching from palladium nanoparticles, or by growing from palladium monomers.

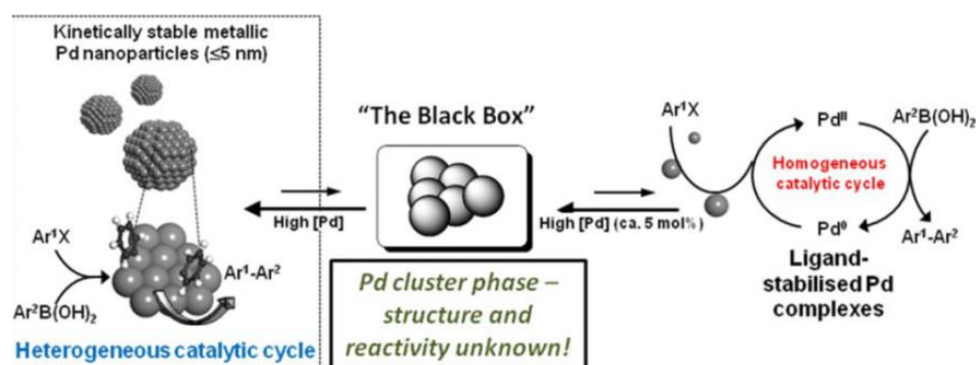


Figure 1: Equilibria between the homogeneous, cluster, and heterogeneous phases of palladium. This work focuses on the synthesis of reactive palladium monomers in order to observe the growth of palladium clusters, on the pathway to palladium nanoparticles. Palladium-catalysed hydrogenation reactions are the focus, and the monomers comprise two stabilising-phosphine ligands and two triflate ligands ($[\text{Pd}(\text{OTf})_2(\text{PR}_3)_2]$).³ The lability of triflate makes these monomers highly reactive in solution, and palladium nanoparticles form on addition of hydrogen, which are observed using transmission electron microscopy. Furthermore, a number of unusual hydride species form on addition of hydrogen, and are characterised using advanced nuclear magnetic resonance spectroscopy methods.

Unusual tri-nuclear palladium species have been identified and characterised. Due to the increasing interest in the use of arsine ligands in palladium catalysis,⁴ the phosphine ligands have been replaced with arsine ligands, and palladium cluster formation has been observed in these species as well. The eventual aim is to use these palladium clusters to catalyse cross-coupling reactions. Such novel coordination complexes and clusters might influence future palladium catalyst design.

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METALLOSUPRAMOLECULAR ARCHITECTURES AS FUNCTIONAL ARCHITECTURES

Victoria E. Pritchard[†], Michael P. Coogan[§], Eli Zysman-Colman[‡], Diego Rota Martir[‡]
and Michael J. Hardie^{*†}

[†]University of Leeds, LS2 1JT, [§]Lancaster University, LA1 4YW, [‡]University of St. Andrews, KY16 9ST

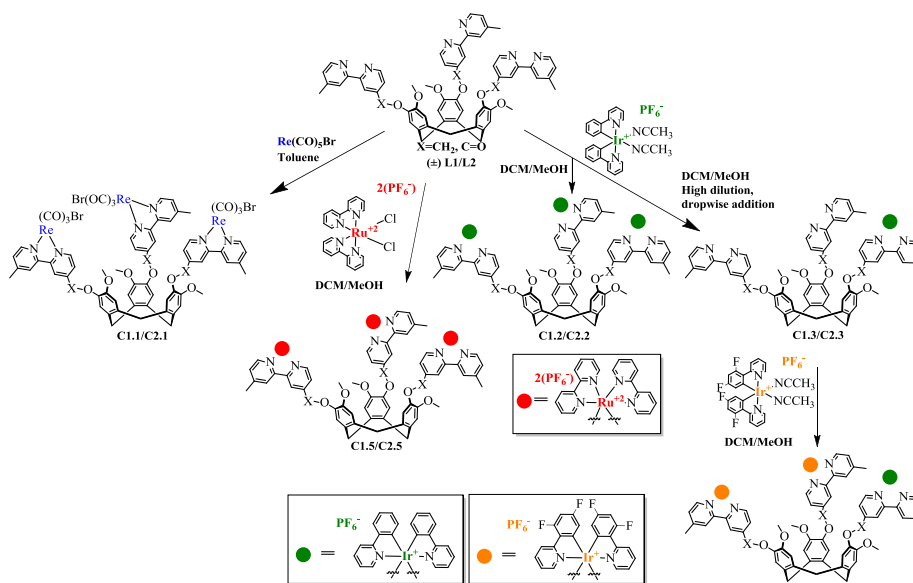
Email: cmvp@leeds.ac.uk

The cyclic trimer, cyclotriguaiacylene, is a rigid, bowl-shaped molecule possessing a hydrophobic cavity. The parent ligand can be functionalised with metal binding groups and subsequently employed in supramolecular self-assembly with an assortment of metal ions to form metallo-cages, MOFs and more complex supramolecular architectures.¹

Interest is now moving towards not only novel supramolecular metallo-cages and assemblies, but functional complexes with host-guest abilities and possible applications in OLED and LEEC formation, catalysis, sensing and cargo-delivery.² The current work revolves around luminescent CTG scaffolds, particularly the d⁶ metals, rhenium(I), ruthenium(II) and iridium(III), and the potential application of these complexes, exploiting their environment dependent *photo*-, and *electro*-luminescence.

The well-known rhenium-bipyridine luminescent motif was the focus; appending bipyridine arms to the CTG core and forming the first *tris*-rhenium CTG based cavitand, **C1.1**.

The first *tris*-iridium CTG species, **C1.2** and **C2.2**, have also been formed, these multi-centred iridium complexes have potential applications as LEECs.³ Through use of a monomeric iridium precursor, and modulation of the stoichiometric ratios of metal-to-ligand, formation of the *mono*-iridium CTG complexes, **C1.3** and **C2.3**, can be achieved also. HR-MS is employed as a diagnostic tool to match the distinctive isotope patterns that these complexes show. The unsaturated iridium complexes, **C1/2.3**, possess vacant binding sites for secondary metallation, leading to the formation of *heteronuclear* or *heteroleptic* complexes, in the case of **C1.4** and **C2.4**.



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SYNTHESIS OF AN $(\text{NHC})_2\text{Pd}(\text{SiMe}_3)_2$ ($\text{NHC} = \text{N}$ -HETEROCYCLIC CARBENE) COMPLEX. CATALYTIC, *CIS*-BIS-SILYLATIONS OF INTERNAL ALKYNES WITH UNACTIVATED DISILANES

Melvyn B. Ansell^a, F. Geoffrey. N. Cloke,^a Oscar Navarro^a and John Spencer^a

University of Sussex^a
Email: ma462@sussex.ac.uk

The transition metal (TM) catalysed regio/stereoselective bis-silylation of alkynes has resulted in the formation of high value organosilicon compounds.¹ Platinum group TM complexes act as stoichiometric/catalytic mediators of this process but are largely limited to the use of strained or activated disilanes.² A vital mechanistic step is the oxidative addition of a disilane to the TM centre. Hexamethyldisilane (HMDS) represents one of the hardest Si-Si bonds to cleave and even stoichiometric examples using platinum group metals are rare. We have accomplished and fully characterised the first oxidative addition of HMDS to a palladium metal centre using a *N*-heterocyclic carbene ligand set.³ The resulting complex, *cis*- $\text{Pd}(\text{ITMe})_2(\text{SiMe}_3)_2$, acts as a pre-catalyst for the bis-silylation of sterically and electronically demanding internal acetylenes using non-activated disilanes at low catalytic loadings.

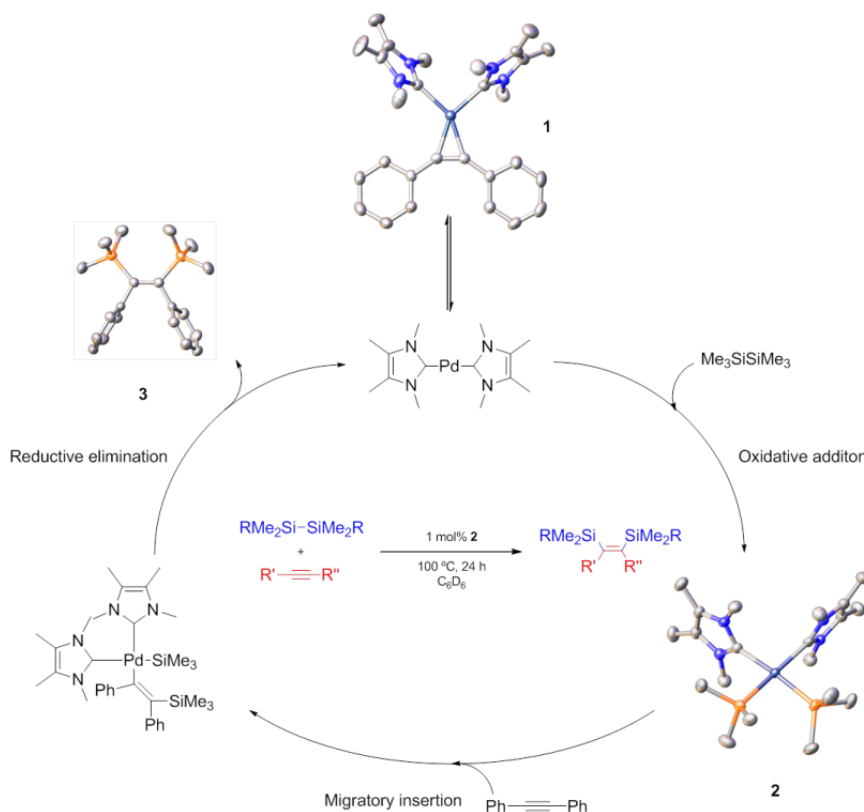


Figure 1: catalytic cycle and general scheme

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3. M. B. Ansell, D. E. Roberts, F. G. N. Cloke, J. Spencer and O. Navarro, *Angew. Chem. Int. Ed.* 2015, **54**, 5578-5582.

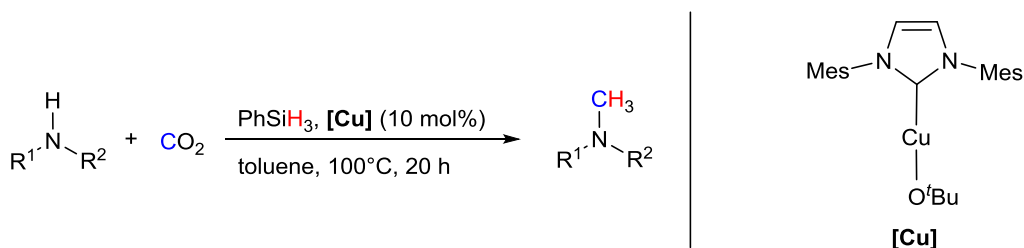
N-HETEROCYCLIC CARBENE COPPER(I) CATALYSED N-METHYLATION OF AMINES USING CO₂

Orlando Santoro

University of St Andrews
Email: Os7@St-andrews.ac.uk

The simple methylation of amines is a well-known transformation in organic chemistry leading to compounds having application in the synthesis of dyes, natural products and fine chemicals. Aside the existing synthetic protocols to achieve this transformation, metal-mediated as well as organocatalysed methodologies based on the use of CO₂ as a reagent have been recently reported.^{1,2} Despite their elegance, all systems suffer from important drawbacks such as expensive catalysts and, in some cases, harsh reaction conditions (P, T). In addition, mechanistic details for this reaction have not been explored yet.

Recently, we have shown that *N*-heterocyclic carbene -Cu(I) complexes can promote direct carboxylation of N-H and C-H bonds using CO₂.³ Based on these observations, the development of the first NHC-Cu catalysed *N*-methylation of amines using CO₂ as C₁ feedstock was undertaken.



The scope of this transformation showed that secondary amines are converted under mild conditions into the desired methylated products while primary amines provide a distribution of products depending on the nature of the substrate. DFT calculations supported by experimental work were carried out in order to elucidate the mechanism of this transformation.

1 a) Cantat and co-workers, *Chem. Sci.*, 2013, **4**, 2127 b) Beller and co-workers, *Angew. Chem. Int. Ed.*, 2013, **52**, 9568. c) Beller and co-workers, *Angew. Chem. Int. Ed.*, 2013, **52**, 12156. d) Leitner and co-workers, *Angew. Chem. Int. Ed.*, 2013, **52**, 9554.

2 a) Cantat and co-workers, *Angew. Chem. Int. Ed.*, 2014, **53**, 12186. b) Dyson and co-workers, *Angew. Chem. Int. Ed.*, 2014, **53**, 12876.

3 Nolan and co-workers, *Angew. Chem. Int. Ed.*, 2010, **49**, 8674.

A COMPREHENSIVE MAGNETIC STUDY OF URANIUM(IV) COMPOUNDS

Stefano Nuzzo^a and Robert James Baker*^a

^a School of Chemistry, Trinity College, Dublin, Dublin 2, Ireland
Email: nuzzos@tcd.ie

Actinide complexes with thiocyanate ligands have received great interest due to their potential in the field of spent nuclear fuel separation.¹ These systems provide a chloride-free extractant for liquid-liquid extraction process used during the separation of actinide and lanthanide fission products and thiocyanate systems were reported to have higher efficiency as extractant ligands than azide or isocyanate systems.²

Herein, we report an extensive study on three high symmetry octathiocyanate uranium(IV) compounds $A_4[U(NCS)_8]$, where $A = Et_4N$, Cs, $^{n}Pr_4N$, $^{n}Bu_4N$. X-ray diffraction shows that the size and the geometry of the counter ion A affect the packing arrangement in the lattice and favor a particular symmetry of the anion $[U(NCS)_8]^{4-}$. Thus the geometry is cubic (O_h) in $[Et_4N]_4[U(NCS)_8]$,³ square antiprismatic (D_{4d}) in $Cs_4[U(NCS)_8]$,⁴ and distorted square antiprismatic (D_4) in $[^{n}Pr_4N]_4[U(NCS)_8]$ and $[^{n}Bu_4N]_4[U(NCS)_8]$.⁵

Unexpectedly this influences significantly the low temperature magnetic behaviour, as demonstrated by SQUID, Figure 1, and specific heat measurements down to 0.3 K. EPR spectroscopy, Figure 2, shows a triplet electronic ground state for $Cs_4[U(NCS)_8]$, which is the first of its kind in U(IV) chemistry. Therefore, magnetism and EPR measurements demonstrate that the geometry around the metal center does significantly influence the crystal field splitting of the 3H_4 state. A computational study at the CASPT2 level has corroborated the experimental results.

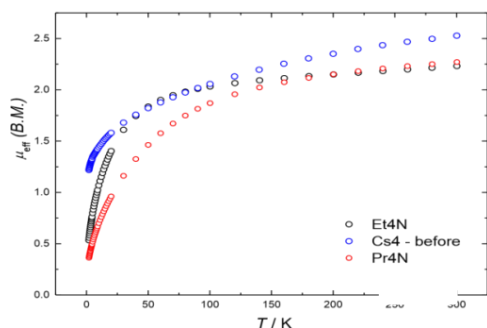


Figure 1: Temperature dependent magnetic susceptibility measurement of $A_4[U(NCS)_8]$. $A = Cs$ (blue); Et_4N (black); Pr_4N (red)

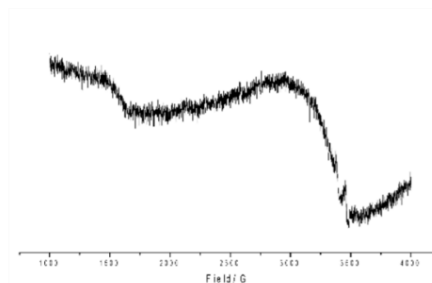


Figure 2: EPR spectrum of $Cs_4[U(NCS)_8]$ (solid state)

1. a) P. K. Khopkar and J. N. Mathur, J. Inorg. Nucl. Chem. 1980, 42, 109; b) F. L. Moore, Anal. Chem., 1964, 36, 2158; c) R. Chiarizia, P. R. Danesi, G. Scibona and L. Magon, J. Inorg. Nucl. Chem., 1973, 35, 3595; d) M. Borkowski, J. Krejzler and S. Siekierski, Radiochim. Acta, 1994, 65, 9
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UNPRECEDENTED F-ELEMENT GEOMETRIES USING SUPER-BULKY LIGANDS

Conrad A. P. Goodwin,^a Ji-Dong Leng,^a Richard E. P. Winpenny,^a William J. Evans,^b & David P. Mills^{*a}

^a School of Chemistry, The University of Manchester, Manchester, M13 9PL, UK.

^b School of Physical Sciences, University of California, Irvine, CA 92697, USA.

Email: conrad.goodwin@postgrad.manchester.ac.uk

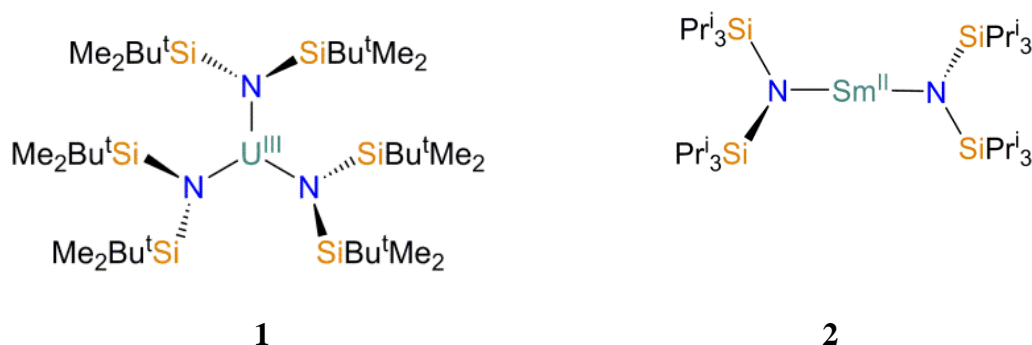


Figure 1. Complexes **1** and **2**.

Investigations into low coordination number (CN) metal complexes are legion as they can exhibit interesting properties, including small molecule activation chemistry¹ 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, $[Sm^{II}\{N(SiPr^i)_2\}_2]$ (**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.

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INFLUENCE OF STRUCTURE DIRECTING AGENTS ON THE CRYSTAL STRUCTURE AND OPTICAL PROPERTIES OF GALLIUM SULPHIDES

Sarah Makin^a, Paz Vaqueiro,^{*a}

#University of Reading^a

Email: s.makin@pgr.reading.ac.uk

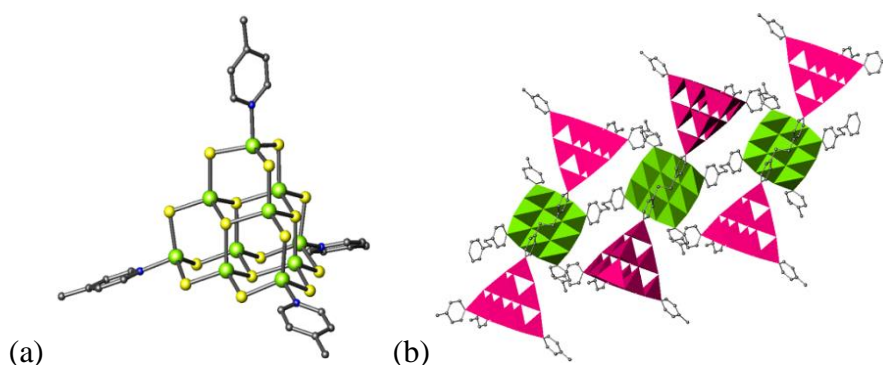


Figure 1(a),(b): A hybrid T3 gallium sulphide supertetrahedron $[\text{Ga}_{10}\text{S}_{16}(\text{NC}_6\text{H}_7)_4]^{2-}$ (a) and view of a structure containing dimers (pink) and cluster chains (green) (b).

Solid-state chalcogenides can be exploited for their semiconducting properties. In framework materials, this could find applications in areas such as photocatalysis. Supertetrahedral clusters are a common building block in main-group metal sulphides.¹ These clusters are tetrahedrally-shaped fragments of the ZnS (sphalerite) structure varying in size; cluster sizes are denoted T_n ,² where n is the number of tetrahedra along the cluster edge. Clusters can link through their corners, forming inorganic networks, or via ditopic organic ligands with nitrogen replacing sulfur at the corner sites.³

Ionothermal synthesis is a relatively new method for the synthesis of frameworks.⁴ Recently, the ionothermal method has been successfully used to synthesise T5 copper-gallium sulphide supertetrahedra.⁵ We have attempted to use the ionic liquids (ILs) 1-butyl-2,3-dimethyl imidazolium tetrafluoroborate [BMMIm][BF₄] and trihexyltetradecyl phosphonium chloride [THTDP]Cl in ionothermal reactions to prepare gallium sulphides. This proved unsuccessful as a number of low-crystallinity powders were obtained. We therefore redirected our attention to using ILs as structure-directing agents (SDAs) for solvothermal synthesis. Here six different structures based on the T3 supertetrahedron $[\text{Ga}_{10}\text{S}_{16}(\text{L})_4]^{2-}$ (where $\text{L} = \text{NC}_6\text{H}_7$ or $\text{N}_2\text{C}_{12}\text{H}_{12}$) are presented. These have been synthesised under solvothermal conditions using the amine 4-methylpyridine (4-MPy) as a solvent, with a range of SDAs: imidazole, 4,4'-trimethylenedipyridine and the ILs [BMMIm][BF₄] and [THTDP]Cl. The effect of the SDA on the structures and on the optical properties, and in particular, on the band gap and charge-transfer effects have been investigated.

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FUNCTIONAL BORON AND PHOSPHORUS LIGANDS: SYNTHESIS, COORDINATION CHEMISTRY AND REACTIVITY

V. K. Greenacre, M. B. Ansell and I. R. Crossley*

Department of Chemistry, University of Sussex, Brighton, UK

Email: V.Greenacre@sussex.ac.uk

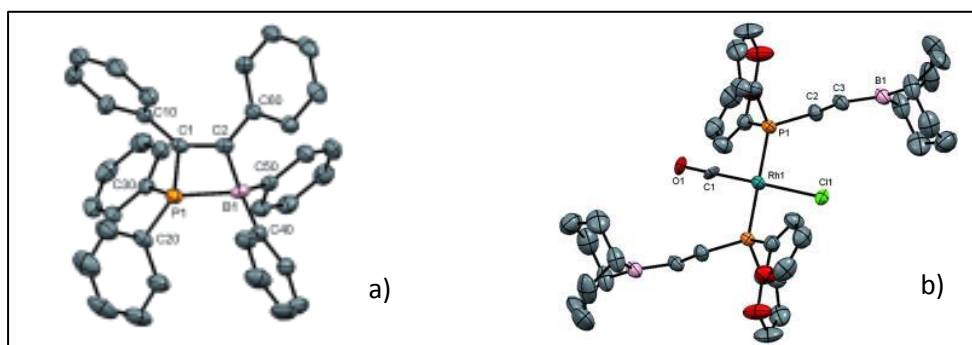


Figure 1a,b: Structure of $\text{Bu}_2\text{BC}(\text{Bu})=\text{C}(\text{Ph})\text{PPh}_2$ (a) and $[\text{Rh}(\text{CO})\{\text{Fu}_2\text{P}(\text{CH}_2)_2\text{BBN}\}_2\text{Cl}]$ (b).

The chemistry of ambiphilic molecules, possessing both Lewis acidic and Lewis basic functionalities such as phosphine-boranes, has experienced a resurgence in interest, in part due to the emergence of Frustrated Lewis Pairs. While Lewis bases are classically based on main group elements, transition metals can also fill this role, as illustrated by recent interest in metal-borane complexes featuring a retrodonative $\text{M} \rightarrow \text{B}$ interaction.

In pursuing this concept, intramolecular systems, in which the acid can be geometrically constrained in proximity to the metal, while precluding adduct formation, are an attractive starting point. To this end, the improved synthesis of unsaturated phosphine-boranes, $\text{Bu}_2\text{BC}(\text{Bu})=\text{C}(\text{Ph})\text{PPh}_2$ (Figure 1a),¹ and the structure, electronic and steric properties of analogous compounds $\text{Et}_2\text{BC}(\text{Et})=\text{C}(\text{Ph})\text{PPh}_2$ and $\text{Ph}_2\text{BC}(\text{Ph})=\text{C}(\text{Ph})\text{PPh}_2$ have been investigated.²

In addition, building on previous work from within the group, the reactivity of saturated pro-ligands containing the mildly Lewis acidic 9-borabicyclo[3.3.1]nonane 9-BBN ligand with a variety of phosphines are presented with the coordination of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{BBN}$ and $\text{Fu}_2\text{PCH}_2\text{CH}_2\text{BBN}$ to a number of group 9 and 10 transition metal centres (Figure 1b).²

These studies and efforts to illustrate useful reactivity will be discussed, along with the pursuit of other functional phosphorus-based ligands.

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UNDERSTANDING AND ENGINEERING FUNCTION IN SWITCHABLE MOLECULAR CRYSTALS

Rafal Kulmaczewski

School of Chemistry, University of Leeds, Leeds, UK.

Email: chmrku@leeds.ac.uk

Octahedral transition metal complexes ($d^4 - d^7$) can be switched between the high spin (HS) and low spin (LS) state by application of temperature, pressure, light, magnetic and electric field.[1] This process is known as spin crossover (SCO). It can be continuous (gradual), when transition occurs over a wide range of stimulus or it can be discontinuous (abrupt), when it takes place over a short range. The abrupt switching between two spin states is a result of cooperativity between the switching centres, and it might result in hysteresis. The cooperativity itself is a function of the crystal lattice and its strength can be attributed to: hydrogen bonding, $\pi - \pi$ interactions and/or van der Waals forces. From the point of view of applications, systems undergoing transition with wide hysteresis loop centered at room temperature are desirable.[2] A recent review relating structure with function in SCO systems outlined that strong cooperativity might be achieved by the increase of mechanical coupling between spin centres.[3] This argument was investigated by targeting the complexes with aromatic moieties in ligand structure in which arene groups can interdigitate in solid state resulting in large surface contact areas and extended $\pi - \pi$ interactions throughout the lattice. As an example, a three types of iron(II) complexes, shown in Figure 1, were structurally and magnetically characterised. Detailed results showing the relationship between crystal packing ($\pi - \pi$ interactions) and magnetic properties will be discussed.

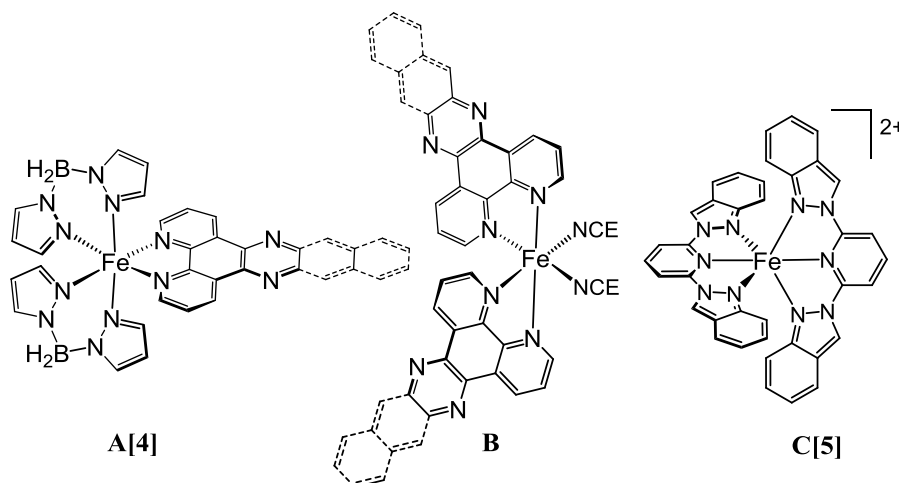


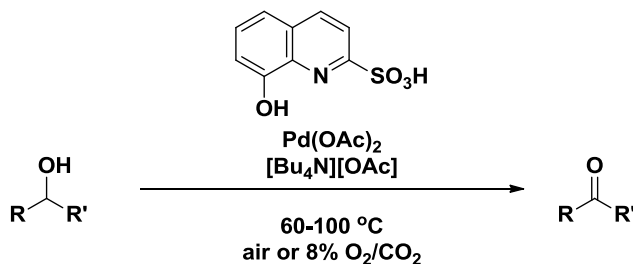
Figure 1 – Fe(II) complex families tested for structure:function relationship.

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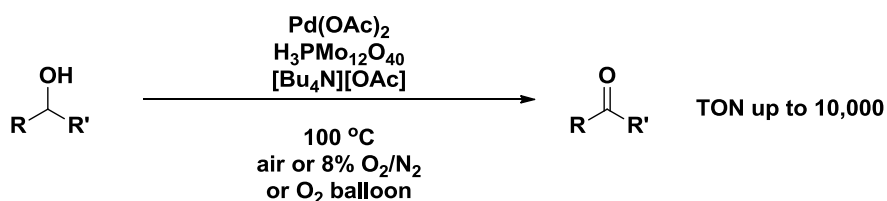
HIGHLY EFFICIENT Pd(II) CATALYST SYSTEMS FOR AEROBIC ALCOHOL OXIDATION

Laura M. Dornan and Mark J. Muldoon*

School of Chemistry and Chemical Engineering, Queen's University Belfast, UK
Email: ldornan05@qub.ac.uk



The oxidation of alcohols to their corresponding carbonyl compounds is an extremely useful transformation however it is rarely exploited in the pharmaceutical and fine chemicals industries due to the problematic methods normally employed.¹ Aerobic oxidation methods are ideal as they use an inexpensive and abundant oxidant without hazardous by-products. Pd(II) has been known as proficient catalyst in aerobic alcohol oxidation but the turnover number (TON) of these systems are often limited due to catalyst deactivation through Pd black formation. Recently we have explored the use of *N,O*-ligated Pd(II) complexes as effective catalysts in aerobic alcohol oxidation and found that the 8-hydroxyquinoline-2-sulfonic acid (HSA) ligand provides high initial turnover frequencies (TOF).² Herein we will discuss the structure and activity of these catalyst systems.



We also examined the use of heteropoly acids as electron transfer mediators in the aerobic oxidation of alcohols and found that a $Pd(OAc)_2/H_3PMo_{12}O_{40}/[Bu_4N][OAc]$ was highly efficient for the oxidation of a range of alcohols with unprecedented turnover. We will discuss the optimization and scope of this system.

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ACTIVATOR-FREE, IRON-CATALYSED FORMAL HYDROGENATIONS AND HYDROBORATIONS

Alistair J. MacNair^a, Stephen Thomas^{*a} and Alan Ironmonger^b

University of Edinburgh, School of Chemistry, Joseph Black Building,
David Brewster Road, Edinburgh, EH9 3FJ^a Research and Development, GlaxoSmithKline,
Gunnelswood Road, Stevenage SG1 2NY^b
Email: stephen.thomas@ed.ac.uk

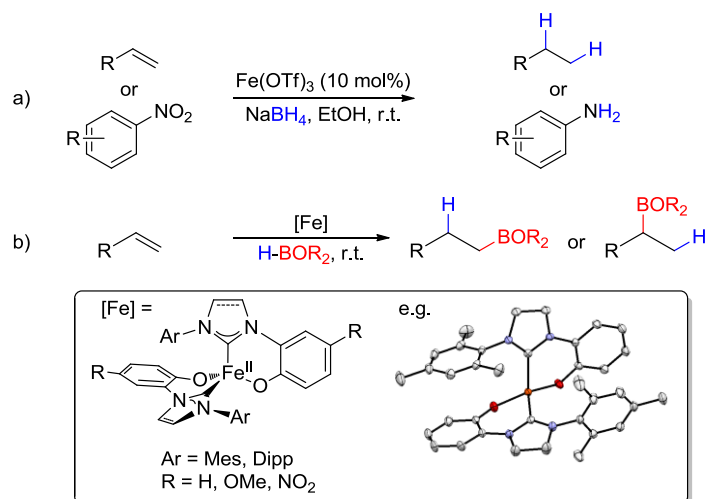


Figure 1: Formal hydrogenations of alkenes and nitro groups (a) and novel iron(II) carbene complexes for the hydroboration of alkenes with tuneable regioselectivity (b).

Transition metal-catalysed hydrogenation and hydrofunctionalisation reactions provide efficient, sustainable methodologies for the manipulation of synthetic handles and the formation of carbon-heteroatom bonds from readily available starting materials providing value-added products.¹ To date, the most powerful iron-catalysed hydrogenation and hydrofunctionalisation reactions have required either preformed iron(0) complexes or iron(II) complexes activated with an organometallic reagent.²

An operationally simple and environmentally benign formal hydrogenation protocol has been developed using a simple iron(III) salt and NaBH₄ in ethanol, under ambient conditions. This reaction has been applied to the formal hydrogenation of terminal alkenes (22 examples, up to 95% yield) and nitro-groups (26 examples, up to 95% yield). Deuterium-labelling studies indicate that this reaction proceeds by an ionic rather than radical mechanism.³

Additionally a series of iron(II) complexes bearing unsymmetric carbene ligands with a chelating phenoxide moiety have been synthesised and characterised. These complexes are catalytically active for the hydroboration of alkene and carbonyl derivatives. Significantly, these complexes do not require external activators to achieve catalytic activity and modification of reaction conditions can lead to dramatic changes in regioselectivity.

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HIGHLY ACTIVE AND SELECTIVE HETERODINUCLEAR CATALYSTS FOR CO₂-EPOXIDE COPOLYMERIZATION

Jennifer A. Garden, Prabhjot K. Saini, Charles Romain, Charlotte K. Williams*

Imperial College London
Email: j.garden@imperial.ac.uk

The copolymerization of CO₂ and epoxides to synthesize polycarbonates (and subsequently polyurethanes) provides a very promising and commercially viable synthetic strategy for adding value to captured CO₂. This copolymerization is critically dependent on the selection of a viable catalyst. Our group have previously reported homodinuclear magnesium and zinc catalysts based upon an ancillary macrocyclic ligand (Fig. 1, **1** and **2**), which operate successfully at 1 bar of CO₂ pressure and show activities amongst the highest reported for this copolymerization.^{1,2}

Detailed kinetic and mechanistic studies have suggested that a heterodinuclear catalyst could exhibit even greater activity, by operating through a cooperative metal-metal mechanism.³ Herein, we report the first examples known in this field of heterodinuclear homogeneous catalysts (Fig. 1, **3**). These catalysts show significantly improved performance metrics compared to the homodinuclear analogues, either alone or in combination.⁴

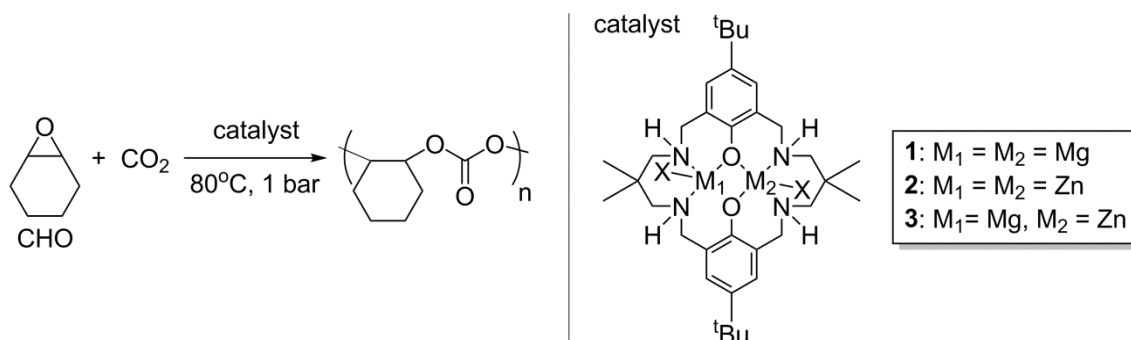


Fig. 1 Application of dinuclear catalysts for CO₂-epoxide copolymerization

The presentation will describe the syntheses and characterizations of new heterodinuclear catalysts, with a particular focus towards magnesium and zinc containing compounds. Application of these catalysts for the efficient and well controlled copolymerization of CO₂-cyclohexene oxide will be described. Notably, such heterodinuclear systems have shown double the activity of homodinuclear magnesium analogues, which themselves are amongst the most active catalysts for CO₂-epoxide copolymerization.

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PROTON COUPLED MIXED VALENCY: MECHANISTIC INSIGHT

Luke A Wilkinson^a, Nathan J Patmore,^{*a} Kevin B Vincent^b and Lee Brown^b

University of Sheffield^a, University of Huddersfield^b

Email: chp11law@sheffield.ac.uk

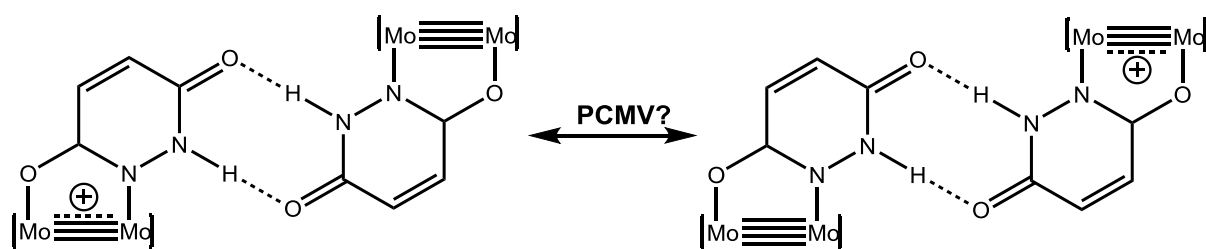


Figure 1: A diagram displaying the mechanistic details of PCMV

Understanding electron transfer processes from a mechanistic point of view is important for understanding many of the complex processes in nature and in the development of molecular electronics.¹ It has now been established that proton-coupled mixed valency (PCMV) is distinct from other forms of mixed valency²⁻⁴ as there is no direct orbital overlap between the donor and acceptor and there does not appear to be a strong Coulombic component to the stabilisation of the mixed valence state. However there is, as yet, no mechanistic understanding of this process. This presentation details our efforts towards the determination of the mechanism for PCMV with techniques such as cyclic voltammetry, EPR spectroscopy, spectroelectrochemical UV/Vis/NIR and IR techniques and DFT calculations. From these studies, it is believed that the mechanism for PCMV has been established (Figure 1).

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P₂N₂ RING SYSTEMS: VERSATILE BUILDING BLOCKS IN ORGANOMETALLIC, MACROCYCLIC AND INORGANIC CHEMISTRY

Callum G.M. Benson^a, Torsten Roth^b, Lutz H. Gade^b, Vladislav Vasilenko^b and Dominic S. Wright,^{*a}

University of Cambridge^a, Universität Heidelberg^b
Email: cgmb3@cam.ac.uk

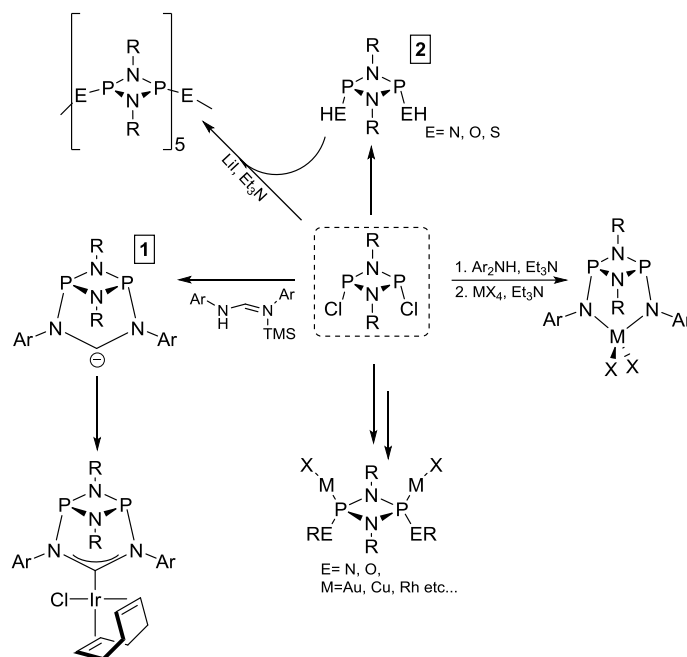


Figure 1: Reactivity scope of $[P(\mu\text{-NR})Cl]_2$ systems showing novel carbenic species (**1**) and bidentate macrocyclic precursors (**2**).

Inorganic rings of the type $[P(\mu\text{-NR})Cl]_2$ are excellent building blocks for a variety of metal coordination complexes and macrocyclic rings. The design of complex ligand systems is facilitated by substitution sites on both the phosphorus and nitrogen atoms. This leads to the possibility of bidentate, monodentate and bimetallic species. Recently, carbene species based on these rings (**1**) have been developed which allow for unparalleled spherical steric bulk when coordinated to a metal centre, as well as chiral control.¹

Substitution at the phosphorus by main group elements also allows for the formation of macrocycle precursors of the type $[P(\mu\text{-NR})E]_2$ ($E = NH_2, O, S, Se$) (**2**). The *cis* configuration of these compounds makes them pre-organised for the formation of large inorganic macrocycles that have potential applications in ion encapsulation and gas storage. The R group on the nitrogen allows for simple modifications that are less accessible in analogous organic macrocycles.

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A CONVERGENT STRATEGY FOR MAKING HYBRID [n]-ROTAXANES (WHERE $n = 3-7$); SUPRAMOLECULAR ARRAYS OF MOLECULAR ELECTRON SPIN QUBITS

Jesus Ferrando-Soria

The University of Manchester, School of Chemistry and Photon Science Institute

Email: jesus.ferrandosoria@manchester.ac.uk

A fully-modular design strategy has been applied to hybrid organic-inorganic [2]- and [3]-rotaxanes, which allows them to be linked into still larger poly-rotaxanes. The ring components are heterometallic octanuclear $[\text{Cr}_7\text{Ni}(\mu\text{-F})_8(\text{O}_2\text{C}^t\text{Bu})_{16}]^-$ coordination cages and the thread components feature a dialkylammonium salt, which templates the formation of the heterometallic ring about the organic axle, and which can also be functionalised to act as a ligand. The chemical versatility of the systems allows us to construct large supramolecular arrays of these heterometallic rings. As the rings have been proposed as qubits for quantum information processing (QIP), the strategy provides a means to bring together many entangled qubits in a controllable manner and suggests a route towards scalable molecular electron spin devices for QIP.