ROYAL SOCIETY
OF CHEMISTRY

Dalton 2014

Joint Interest Groups Meeting

15-17 April 2014
University of Warwick, UK

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OF CHEMISTRY

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MATERIALS

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Inorganic Chemistry
including bioinorganic chemistry

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Tuesday 15th April

1.30-1.45 **L3** Welcome and Introduction: **David Cole-Hamilton**

1.45-2.30 **Thomas O'Halloran** (*Northwestern*) – Bioinorganic Chemistry Award: “Inorganic Chemistry of Cellular Decision Making Processes: Structure and Dynamics of Transition Metal Receptors”

2.30-3.15 **Richard Layfield** (*Manchester*) – Sir Edward Frankland Fellowship: “Reactive metal-carbon bonds in three-coordinate iron NHC complexes”

3.15-3.40 Tea/Coffee

Room	**L3**	**L4**	**L5**	**B202**
Chair	**Jason Love**	**Debbie Kays**	**Jon Rourke**	**David Evans**
3.40 - 4.00	**Stephen Mansell** *Heriot-Watt University* “Unconventional ligands: Developing the chemistry of N-heterocyclic stannylenes”	**Adi Nako** *Imperial College London* “Weakly Coordinated Zinc & Aluminium σ-Complexes of Copper(I)”	**Adrian Chaplin** *University of Warwick* “Cyclometalation reactions of Rh and Ir NHC complexes: attenuation and reversibility through ligand variation”	**Anne-K Duhme-Klair** *University of York* “Periplasmic binding protein captures low-denticity siderophores”
4.00 - 4.20	**Clare Bakewell** *Imperial College London* “Group 3 and Rare-Earth Phosphasalen Complexes: Iso-selective Initiators for rac-Lactide Ring-Opening Polymerization”	**Ewan Clark** *University of Manchester* “Moving Beyond $B(C_6F_5)_3$: Hydride-selective carbocations in frustrated Lewis pairs”	**Claire McMullin** *Heriot-Watt University* “Does rate limiting C-H activation always entail a kinetic isotope effect?”	**Philip Ash** *University of Oxford* “New insight into the mechanism of NiFe hydrogenases from IR spectroscopy coupled with protein film electrochemistry”
4.20 - 4.40	**Carlo Sambiagio** *University of Leeds* “New ligands for Cu-catalysed aryl ether formation: structure-activity relationship and mechanistic investigation”	**Elliot Lawrence** *University of East Anglia* “An electrochemical study of frustrated Lewis pairs: a metal-free route to hydrogen oxidation”	**Barbara Villa-Marcos** *University of Leicester* “Controlling Selectivity of $C(sp^2)$-H Activation: An experimental and computational study”	**Amanda Hill** *University of East Anglia* “Unveiling the biosynthesis of the H-cluster of [Fe-Fe]-hydrogenase”
4.40 - 5.00	**James Radcliffe** *Durham University* “Investigating the Coordination Chemistry of PNE Ligands with Group VI Metals”	**André Schäfer** *University of Bristol* “Iron-Catalyzed Dehydrocoupling/Dehydrogenation of Amine-Boranes”	**Margot Wenzel** *University of York* “Exploiting the redox chemistry of nitrite species in Pd-catalyzed aerobic oxidation of unactivated $C(sp^3)$-H bonds”	**Carlotta Figliola** *University of Birmingham* “[FeFe]-Hydrogenase synthetic mimics based on peri-substituted dichalcogenides”
5.00 – 5.20	**Michelle Harris** *University College Dublin* “Breaking Hund's Rule in Manganese(III) drives Jahn-Teller and Spin State Ordering	**Owen Metters** *University of Bristol* “Amine-Boronium Cations: Convenient Precursors to Aminoborane Monomers and Polyaminoboranes via their Addition Polymerisation	**Luca Maidich** *University of Sassari* “Synthesis and reactivity of rollover cyclometalated complexes”	**Lars Jeuken** *University of Leeds* “Oxygen Tolerance in Membrane Bound [NiFe]-Hydrogenases”
5.20 - 5.40	**Jonathan Bailey** *University of Bristol* “'Inorganic' Analogues of Arylphosphines”	**Junjuda Unruangsri** *University of Oxford* “Borate and Borane derivatives as CT agents in Group II Immortal Ring-Opening Polymerisation of ε-Caprolactone and rac-Lactide”	**David McKay** *Heriot-Watt University* “Computational Studies of Ruthenium Hydrides as Novel Nucleophiles in C–F and C–Cl bond activation”	**Sam de Visser** *University of Manchester* “Nonheme iron(IV) enzymes: Unusual mechanism and reactivity of wild-type and bioengineered systems”

6.30-7.30 Dinner – Rootes Restaraunt

7.30-10.00 Posters and Wine/Beer/Soft Drinks – Physics and Science Concourses.

Wednesday 16th April

L3 Session Chair: **Peter Tasker**

9.00-9.45 **Theodore Betley** (*Harvard*): “Targeting high-spin clusters for reactivity”

9.45-10.30 **Jennifer Love** (*UBC Vancouver*): “Developing Catalytic Reactions One Step at a Time”

10.30-10.50 **Jonathan Worrall** (University of Essex): “Copper trafficking pathways and enzymes involved in morphological development of Streptomyces lividans”

10.50-11.15 Tea/Coffee

11.15-12.55 Parallel sessions:

Room	**L3**	**L4**	**L5**	**B202**
Chair	**Paddy McGowan**	**Sylvia Draper**	**Mike George**	**Emma Raven**
11.15 - 11.35	**Manfred Bochmann** *University of East Anglia* “Advance in Gold(III) Chemistry: Hydrides, peroxided and olefin complexes”	**Javier Francos** *University of Strathclyde* “Optimisation of a lithium magnesiate for use in the non-cryogenic asymmetric deprotonation of prochiral ketones”	**Peter Tasker** *University of Edinburgh* “Outer-sphere hydrogen-bond buttressing to control the strength of phenolic pyrazole metal extractants”	**Rianne Lord** *University of Leeds* “Metal complexes as potential anti-cancer agents”
11.35 - 11.55	**Adrián Gómez-Suárez** *University of St Andrews* “Application of Digold-Hydroxides in Dual Activation Chemistry”	**Benjamin Day** *University of Manchester* “Towards The Selective Functionalisation of Pentadienylsilanes”	**Simon Higgins** *University of Liverpool* “Redox switching of single molecule junction conductance using $[Co(pyterpy)_2]^{2+}$ and related complexes”	**Isolda Romero-Canelón** *University of Warwick* “Multi-targeted organometallic anticancer complexes with redox mechanisms of action”
11.55 - 12.15	**Charlotte Willans** *University of Leeds* “Copper-N-Heterocyclic Carbenes; Synthesis, Structure and Reactivity”	**Merle Arrowsmith** *University of Bath* “Atom-efficient group 2-mediated cascade assembly of complex heterocycles”	**John Fielden** *University of East Anglia* “$[CoW_{12}O_{40}]^{6-}$: A Long-Lived Metal-to-Polyoxometalate Charge Transfer Chromophore”	**Rebecca Kaner** *University of Warwick* “Triplex helicates: asymmetric self-assembly of potent, selective anticancer compounds”
12.15 - 12.35	**Rebecca Poulten** *University of Bath* “Low Coordinate Ni(I) Complexes Bearing Ring Expanded N-Heterocyclic Carbenes”	**Rebecca Musgrave** *University of Bristol* “Ring-opening reactions of silicon-bridged [1]ferrocenophanes bearing bulky substituents”	**Charlotte Clark** *University of Nottingham* “Dye-sensitized NiO photocathodes for solar devices”	**Neil Bricklebank** *Sheffield Hallam University* “Triphenylphosphonium-conjusgated gold nanoparticles: potential nanocarriers for mitochondria-targeted therapeutics”
12.35 - 12.55	**Bryan Hogan** *University College Dublin* “Metalloporphyrins as active N-heterocyclic carbene (NHC) transfer reagents”	**Gabriela Espinoza Quintero** *University of Oxford* “Chemical reactivity of group 14 $[E_9]^{4-}$ & 15 $[E'_7]^{3-}$ Zintl ions”	**Debabrata Chatterjee** *Durgapur, West Bengal* “Mechanism of Substrate and Oxidant Activation by RuIII(edta) in Mosaics of Homogeneous Catalysis”	

12.55-2.00 Lunch (Rootes Restaurant) and poster browsing

L3 Session Chair: **Peter Sadler**

2.00-2.45 **Paul Walton** (*York*): "Copper-Containing *Lytic Polysaccharide Monooxygenases*: A New Face for Biomass Breakdown"

2.45-3.30 **Rebecca Melen** (*Toronto*), Dalton Young Researcher Award: "Activation of Alkynes with $B(C_6F_5)_3$: Intramolecular cyclisation reactions and rearrangements."

3.30-4.00 Tea/Coffee

4.00-5.00 Parallel sessions:

Room	**L3**	**L4**	**L5**	**B202**
Chair	**Nick Fletcher**	**Richard Layfield**	**Dai Davies**	**Anne-K Duhme-Klair**
4.00 - 4.20	**Byron Truscott** *University of St Andrews* "Bond activation and CO_2 fixation employing an iridium(I) hydroxide"	**Sylvia Draper** *Trinity College Dublin* "New Insight into Heteroatom-nanographenes and their Applications"	**Andrew Marr** *Queen's University Belfast* "Bio- and Organometallic-Catalysis: Quest for the GRAIL"	**Alison Parkin** *University of York* "New Electrochemical Methods for Understanding Biological H_2 Catalysis"
4.20 - 4.40	**Fabio Marchetti** *University of Pisa* "Activation Reactions of Oxygen-Containing Organic Molecules by High Valent Metal Halides of Groups 5-6"	**Jeremy Sloan** *University of Warwick* "Band gap expansion, phase change behaviour and low-voltage induced crystal oscillation in low-dimensional SnSe"	**Barbara Procacci** *University of York* "Ruthenium hydrides pave the way to time-resolved NMR spectroscopy"	**Dimitrios Pantazis** *Max Planck Institute for Chemical Energy Conversion* "The importance of being consistent: Manganese oxidation states in biological water oxidation"
4.40 - 5.00	**Nik Kaltsoyannis** *UCL* "Covalency and bond strength in heavy element compounds from the quantum theory of atoms in molecules"	**Sophie Benjamin** *University of Southampton* "CVD of Thermoelectric Materials from Single Molecule Precursors"	**Patrizia Lorusso** *University of St Andrews* "Ruthenium-catalysed dehydrogenation of methanol"	**Kate Appleby** *University of York* "Optimising SABRE: applications with biologically-relevant substrates"

L3 Session Chair: **Jon Rourke**

5.05-5.50 **Mike George** (*Nottingham*) – Inorganic Reaction Mechanisms Award: "Photochemistry, Spectroscopy and Supercritical Fluids"

6.00-7.00 Section Committee meetings

7.00-7.30 Pre-dinner drinks (The Bar, Rootes Building)

7.30-11.00 Conference Banquet (Panorama Suite, Rootes Building)

Thursday 17th April

L3 Session Chair: **Mike George**

9.15-10.00 **Kit Cummings** (*MIT*), Ludwig Mond Award: "Group 15 Element Triple Bonds and Reactive Intermediates"

10.00-10.45 **Zhenyang Lin** (*Hong Kong University of Science & Technology*): "Boryl Ligands and Their Roles in Transition Metal Catalysed Borylation Reactions"

10.45-11.15 Tea/Coffee

11.15-12.15 Parallel sessions:

Room	**L3**	**L4**	**L5**	**B202**
Chair	**Jose Goicoechea**	**Paul Walton**	**Stuart Macgregor**	**Sam de Visser**
11.15 - 11.35	**David Cole-Hamilton** *University of St. Andrews* "Chemicals from waste bio-oils"	**Sophia Solomon** *University of Cambridge* "Base Induced Rearrangement of Mesityl-Phosphonium Salts"	**Rory Waterman** *University of Vermont* "Expanding α–elimination to organophosphorus and organosilane synthesis"	**Matthew Berwick** *University of Birmingham* "Using de novo Design to Create Novel Lanthanide-Coiled Coil Imaging Agents"
11.35 - 11.55	**Prabhjot Saini** *Imperial College London* "Dinuclear metal catalysts: Improved performance of heterodinuclear mixed catalysts for CO_2–epoxide copolymerization"	**Catherine Weetman** *University of Bath* "Magnesium catalyzed hydroboration of nitriles"	**Stéphanie Dupuy** *St Andrews* "Gold(I) catalyzed protodecarboxylation of (hetero)aromatic carboxylic acids"	**Kenneth Kam-Wing Lo** *City University of Hong Kong* "Functional cellular reagents derived from phosphorescent rhenium(I) and iridium(III) polypyridine complexes"
11.55 - 12.15	**Andrew Russell** *University of Bristol* "Ring-Opening Polymerization of a Strained [3]Nickelocenophane: A Route to Polynickelocenes, a Class of S = 1 Metallopolymers"	**Antonio Martinez-Martinez** *University of Strathclyde* "A Powerful Tool to Override the Classical Directed ortho-Metallation Chemistry: Co-operative Effects Between Magnesium and Alkali Metals"	**Charles Ellul** *University of Leicester* "Controlling Product Selectivity in Rhodium-Catalysed Oxidative Coupling"	**Carole Perry** *Nottingham Trent* "Peptides as versatile tools in the synthesis of metal oxides"

L3 Session Chair: **Richard Layfield**

12.15-13.00 **Ingo Krossing** (*Freiburg*): "Weakly Coordinating Anions: Facilitators for Applied and Fundamental Chemistry"

13.00-13.05 Concluding remarks: **David Cole-Hamilton**

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P2	Bassim Abdulwahaab	Efficient mono- and di-alkylation of glyoxal-bridged tetraazamacrocycles via mechanochemistry
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P5	Siti Aina Mardia Aznan	Supramolecular Metathesis: cation exchange in salts derived from the sulfa-drug, Sulfathiazole
P6	Nada Al Smail	An Oxamide Metal- Organic Framework for High and Selective Uptake of CO_2
P7	Karrar Al-Ameed	Electronic Structure of Mixed-Valent Triangular (μ_3-O)-Pyrazolato-Fe_3 Complexes
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P11	Rhiann Andrew	NHC-based Rhodium Macrocycles: Reactivity and Convergent Syntheses
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P16	Samantha Binding	Synthesis and characterisation of bimetallic, double-decker sandwich compounds with permethylpentalene
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P18	Mickaële Bonneau	New iridium complexes based on bisbenzimidazole ancillary ligand
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P20	Jennifer Burt	Developing Reagents for the Supercritical Fluid Electrodeposition of Tin
P21	Michael Butler	Zirconium-Catalysed C–O Bond Alumination of Benzofuran: A Mechanistic Study
P22	Ian Cade	1,2-Carboboration of Alkynes with Borenium Cations
P23	Kevin Carr	Competition Studies of Ambiphilic Metal-Ligand Assisted C-H Activation
P24	Amanda Catherall	Deposition of Transparent Conducting Oxides by AACVD
P25	Martin Champion	Exploring the co-ordination chemistry of lanthanide iodides with mixed donor crown ether macrocycles
P26	Gan-Zuei Chang	Using in situ ATR-IR spectroelectrochemistry to understand electrocatalytic activation of CO on metallic and enzymatic sites
P27	Yao-Pang Chang	The synthesis of niobium(V) thio- and selenoether complexes and their application in low pressure CVD
P28	Michael Chapman	Construction of an Electrochemical Flow-Cell for the Synthesis of Metal-NHC Catalysts
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P30	Benjamin Clough	New Group 4 Metal-Nitrogen Multiple Bond Chemistry
P31	Laura Cocker	Inducing a breathing phenomenon through ligand ratio control in a series of zinc metal-organic frameworks.
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P33	Richard Collins	Alkaline Earth Borohydrides as Ring-Opening Polymerisation Catalysts
P34	Lee Collins	Di-Amido Carbene Complexes of Copper
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P39	Mateusz Cybulski	Small molecule and C-F bond activation using $Ru(NHC)_2(PPh_3)_2H_2$ complexes
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Inorganic Chemistry of Cellular Decision Making Processes: Structure and Dynamics of Transition Metal Receptors

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All cells must acquire large numbers of transition metals ions for use as essential cofactors in a multitude of metalloenzymes; however, recent studies have shown that dramatic fluctuations in intracellular metal content and/or availability over relatively short time frames can control key biological events. The ensemble of metal concentrations in the cell, i.e., the metallome, is maintained at steady state levels under tight physiological control. Zn(II) ions for instance are found across a large number of tight-binding metalloenzymes as well a significant number of regulatory, trafficking and compartmentalized homeostasis sites where metal-occupancy is transient or responsive to changes in environmental conditions. It is becoming increasingly clear that metal ion movement in and out of these sites regulates key cellular decisions involving cell cycle control, differentiation and development in prokaryotes and eukaryotes alike. The metal-specific receptor sites found in transporter, metallochaperone and metalloregulatory proteins ultimately allow insertion of a metal ion to appropriate intracellular targets or sense changes in metal availability and turn on or off specific genes. The latter sites sense changes in thermodynamically-defined free metal concentrations in the femtomolar range for Zn(II) or the zeptomolar range for Cu(I) and adjust the transcription of genes in a manner that keeps the *cytosolic* concentrations of the free metal ion at vanishing low levels. Recent structural and mechanistic studies of the CueR and Zur proteins reveal novel biophysical mechanisms for transduction of the signal as well as the molecular basis for the remarkable thermodynamic sensitivity of these metal-sensing molecular switches.

While steady-state concentrations of free zinc and copper ions are generally quite low in the mammalian cytosol, this is not necessarily so in other compartments where thermodynamically distinct pools of metal ions can ebb and flow in response to cellular signals. For instance, the developmental progression of the mammalian egg and the first step of embryo formation require a stepwise series of massive zinc fluctuations. A variety of new single cell STEM-EDS/EELS, X-ray fluorescence microscopy methods and fluorescent zinc-specific probes reveal that billions of zinc atoms per cell must undergo dramatic translocations in short time frames, including events known as 'zinc sparks' before the embryo proceeds through its developmental program. We broadly conclude that biological regulatory mechanisms in the egg, embryo and other cells involve key metal-specific receptors as well as wholesale fluctuations in zinc content and activity in subcellular locations. In this sense zinc joins calcium and phosphorous as conductors of information in biological signaling networks.

Reactive metal-carbon bonds in three-coordinate iron NHC complexes

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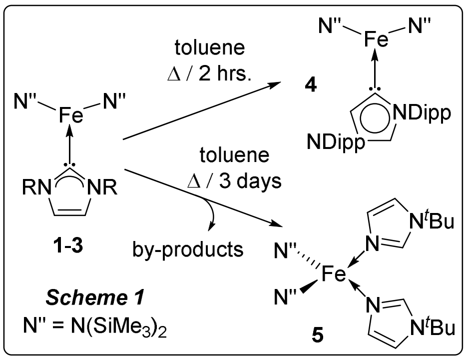
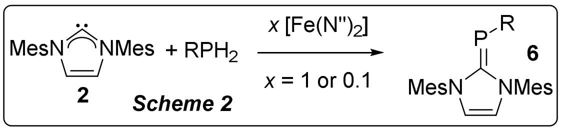
The chemistry of iron with N-heterocyclic carbene (NHC) ligands is under-developed compared to late transition metal NHC chemistry.[1] However, the use of NHC ligands in iron chemistry has recently resulted in eye-catching studies dealing with: the stabilization of novel coordination environments and unusual oxidation states, biomimetic chemistry, and homogeneous catalysis.[2-6]

We recently reported the three-coordinate iron-NHC complexes [(IPr)Fe(N″)$_2$] (**1**), [(IMes)Fe(N″)$_2$] (**2**),[7] and [(I^{t}Bu)Fe(N″)$_2$] (**3**) (Scheme 1), and our initial studies of the reactivity of **1-3** have produced some unexpected results.[8] Simply refluxing **1** in toluene for two hours results in a normal-to-abnormal rearrangement of the NHC, giving [(*a*IPr)Fe(N″)$_2$] (**4**) (Scheme 1). Refluxing **3** in toluene for three days effects a C–H/C–N activation reaction, in which a ^{t}Bu substituent is eliminated from the NHC ligand as isobutene.



Scheme 1
N" = N(SiMe$_3$)$_2$

The non-innocennce of the NHC ligands in **1-3** is further reflected in their reactivity towards E–H acidic substrates. When E = Se, the NHC ligands can either rearrange to their abnormal isomers,[9] or they can display Brønsted basic reactivity towards selenols, providing access to selenium-ligated iron-NHC complexes. In the reactions of **2** with primary phosphines, an unusual C–P ‘cross-coupling’ is observed with stoichiometric iron(II) and also with 10 mol% iron(II), forming the phospha-alkene **6** (Scheme 2).[10] Initial mechanistic studies on the formation of **6** will be presented.



Scheme 2

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Unconventional ligands: Developing the coordination chemistry of *N*-heterocyclic stannylenes

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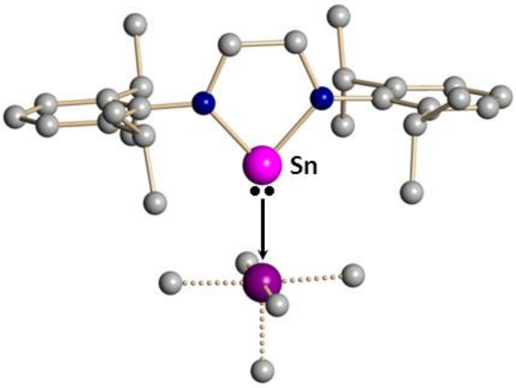
Conventional ligands, such as phosphines, hold a privileged place in organometallic chemistry because they have a proven track record of success in many catalytic and non-catalytic systems. They are used on scales ranging from small vials to huge industrial reactors and their chemistry has been extensively explored. I am interested in developing new ligands for applications in homogeneous catalysis by studying unconventional ligands with unexplored potential. To this end the synthesis and coordination behaviour of *N*-heterocyclic stannylenes (NHSns), heavier group 14 analogues of *N*-heterocyclic carbenes, were explored. Initial studies found NHSns to be easily synthesised and thermally stable species, although they are also highly air- and moisture-sensitive.[1] Further investigations revealed remarkable differences to conventional ligands which highlighted the ability of NHSns to act as bridging ligands, in contrast to the almost exclusively terminal binding seen with conventional ligands.[2]



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Group 3 and Rare-Earth Phosphasalen Complexes: *Iso*-selective Initiators for *rac*-Lactide Ring-Opening Polymerization

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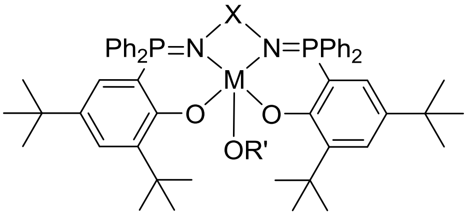
Polylactide, PLA, shows considerable promise as a sustainable replacement for petrochemicals; it is produced by the ring-opening polymerization (ROP) of lactide which is derived from high starch content biomass. The ROP is initiated by Lewis acidic metal alkoxide complexes, control over the rate, molecular weight and stereochemistry is important as it affects the material's properties. Stereocontrol is particularly important as it controls the tacticity of the resulting PLA.

This presentation will describe the synthesis, characterization and polymerization catalysis of Group 3 yttrium phosphasalen complexes, which are able to polymerize *rac*-LA in a fast and highly *iso*-selective fashion ($P_i = 0.86$). Polymerization kinetics, multi-nuclear NMR studies and structure-activity relationships will be presented and used to rationalize the performance characteristics of this new class of catalyst. In particular, the catalysts are compared to the ubiquitous metal salen catalysts: phosphasalen catalysts show superior rates and stereoselectivities.

The synthesis and characterization of other Group 3 and rare-Earth metal phosphasalen complexes will also be described, and their applications as polymerization catalysts compared with the yttrium phosphasalen catalysts. In particular, the differences between the metal centres and the concomitant influence over the catalysis will be described.

Figure 1 – General structure of a phosphasalen metal complex.



Where X = diimine bridge
R = alkyl group
M = Y, Lu, La

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New Ligands for Cu-Catalysed Aryl Ether Formation: Structure-Activity Relationship and Mechanistic Investigation

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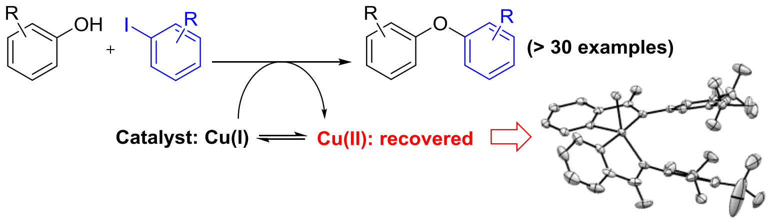
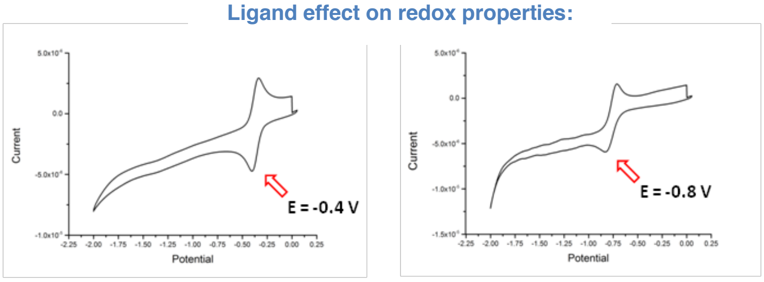
ABSTRACT

Aryl ethers are important motifs in medicinal chemistry, and the use of Cu-catalysed couplings (Ullmann reactions) for their synthesis is a common procedure.[1] Typically, these reactions require neutral or anionic bidentate ligands to work efficiently. However, the role of the ligand is not totally clear yet,[2] and only a few structure-activity relationship studies on families of ligands have been reported.[3] Moreover, several mechanistic studies have been performed on neutral ligands,[4,5] whereas only a few were focused on anionic ligands.[6]

Herein, we report investigations on a new class of anionic ligands for Ullmann ether synthesis under mild conditions, including structure-activity relationship, substrate scope and mechanistic investigations.



Ligand effect on redox properties:



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Investigating the Coordination Chemistry of PNE Ligands with Group VI Metals

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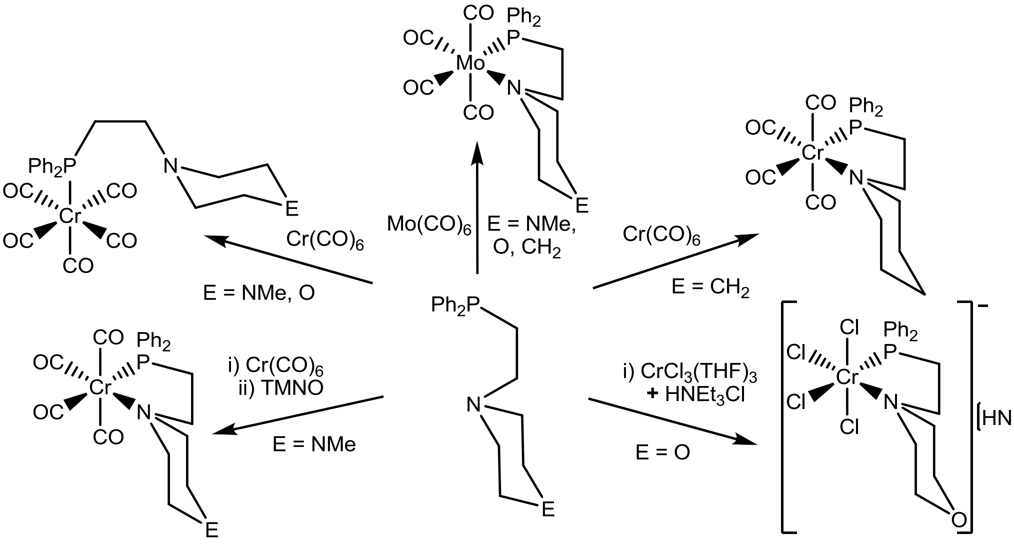
Heteroditopic chelate ligands have found widespread application in catalysis due to their varied structural and coordination chemistry.[1] An important feature of many such unsymmetrical metal scaffolds is their hemi-labile behaviour, *i.e.* the ability to reversibly provide a vacant metal coordination site without complete ligand dissociation.[2] For example, it has been shown that hemi-labile ligands play a key role in selective ethene trimerisation systems based around $Ar_2PN(R)PAr_2$ (Ar = Ph-*o*-OMe) ligands where the *ortho*-OMe group has been shown to bind to chromium in a reversible fashion.[3]



Scheme 1. Chromium and molybdenum complexes of PNE ligands.

This work investigates the use of novel PNE-type ligand systems, which can potentially act as mono-, bi- or tri-dentate metal scaffolds in chromium-based ethene oligomerisation catalysis. A range of PNE ligands have been synthesised using a straightforward base-catalysed Michael addition of vinyl-diphenylphosphine to various heterocyclic secondary amines.[4] The interaction of these PNE ligands with Cr and Mo complexes has been investigated with the ligands having been shown to adopt either $\kappa^1{}_P$ or $\kappa^2{}_{P,N}$ coordination modes. The impact of the E-donor group in catalysis is probed.

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Breaking Hund's Rule in Manganese(III) drives Jahn-Teller and Spin State Ordering

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Spin crossover (SCO) molecules comprise a promising class of compounds for application in memory devices. A hysteretic transition pathway and hence molecular bistability i.e. having two electronic states under the same set of conditions is essential in promoting a memory effect and considerable efforts have been expended to develop systems with wide hysteresis loops close to room temperature. Triggers for SCO include temperature, pressure or light. In contrast to Fe and Co there are few examples of SCO in Mn^{III}. Mn^{III} is a particularly interesting candidate for SCO as it has a pronounced Jahn-Teller (JT) effect in the high spin (HS) state. We have shown the importance of ligand flexibility in promoting Mn^{III} SCO where population of $d_{x^2-y^2}$ on switching to HS requires elasticity in the xy plane. To date this system type has promoted gradual SCO profiles and we have shown that anion modulation and substituent modulation play a pivotal role in in Mn^{III} SCO. We have also reported the first example of a Mn^{III} compound with an abrupt and complete thermal spin transition and opening of an 8 K hysteresis window.[1] We now report here two types of symmetry breaking which has not been observed in the case of Mn^{III}. One driven by the resolving of disorder of the normally passive BPh_4 anion[2] and the other driven by the cation. This occurs through the breaking of hund's rule which drives Jahn-Teller and spin state ordering. The transition also occurs with the presence of a hysteresis loop.

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'Inorganic' Analogues of Arylphosphines.

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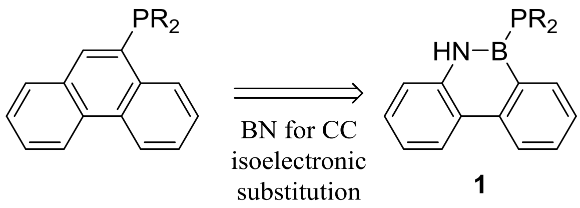
Arylphosphines such as PPh_3 are ubiquitous ligands in coordination chemistry and homogeneous catalysis. The importance of triphenylphosphine is illustrated by the abundance of references relating to it in the literature (~29,000 references in SciFinder).

By replacing C-C units with the isoelectronic B-N unit in the aryl rings of phosphines, we have obtained P-B ligands (**1**) with electronic and catalytic properties different to their all-carbon counterparts.[1] To synthesise these compounds, we developed a silane elimination route (B-Cl + P-Si → P-B + Si-Cl) which has opened the door to many more borylphosphines, including the first example of a tris(boryl)phosphine (**2**).



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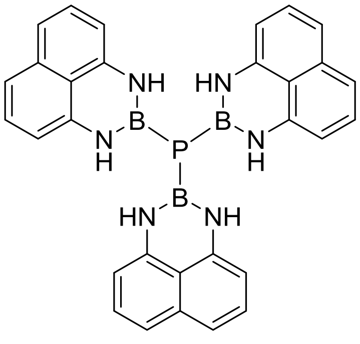
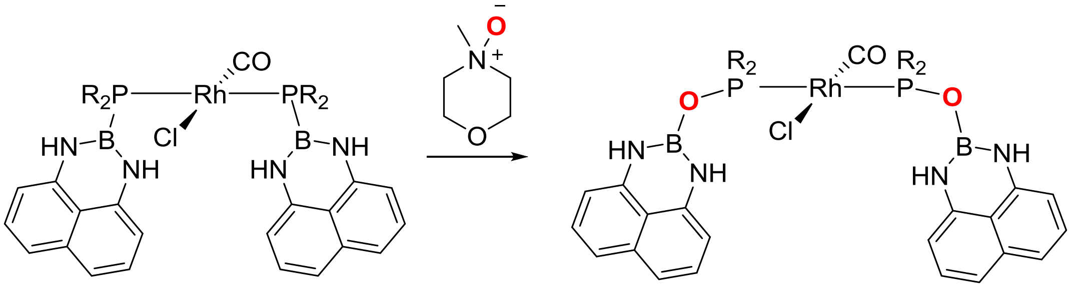


2

Furthermore, we are able to selectively insert an oxygen atom into the P-B bond, effectively converting these P-B phosphine analogues to phosphinite, phosphonite and phosphite P-O-B ligands. This can be done both on- and off-metal.



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Weakly Coordinated Zinc and Aluminium σ-Complexes of Copper(I)

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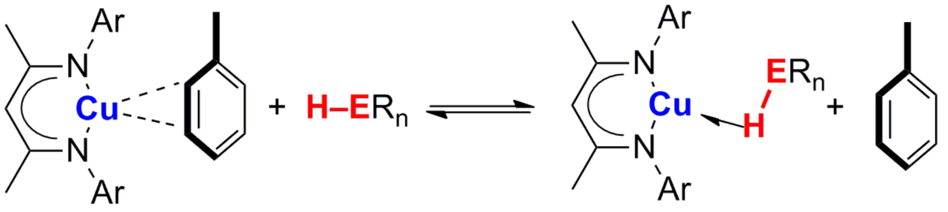
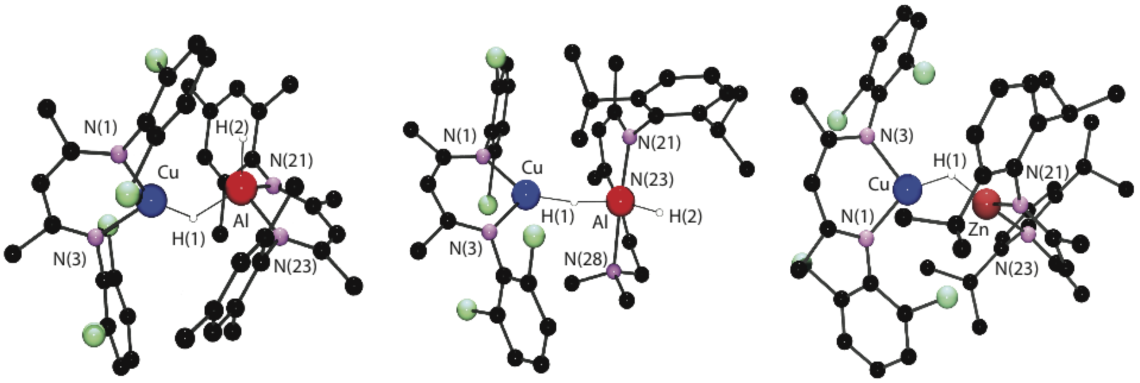
Since the isolation of the first dihydrogen complex by Kubas and coworkers[1] in the mid-1980's research into the field of σ-complexes has been expanding rapidly. σ-Complexes are considered to be important intermediates in catalysis,[2] but despite the use of the coinage metals in a variety of chemical processes, intermolecular σ-complexes of copper are to the best of our knowledge unknown.[3]

We report the synthesis and characterisation of rare examples of intermolecular sigma complexes of Cu(I). The coordination of both Al–H and Zn–H bonds to Cu(I) are reversible reactions which compete with arene complexation in aromatic solvents. These complexes are isolable as crystalline solids in high yields and their synthesis does not require the use of photolysis apparatus. The three complexes have been fully characterised by NMR spectroscopy, CHN analysis, and X-ray crystallography, with two contrasting coordination modes observed in the solid state.





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Moving beyond $B(C_6F_5)_3$: Hydride-selective carbocations in frustrated Lewis pairs

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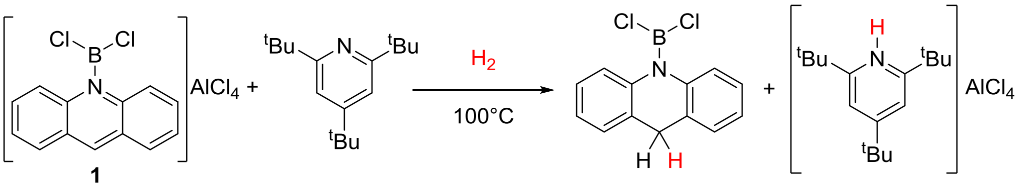
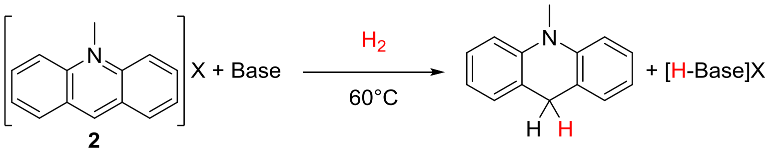
$B(C_6F_5)_3$ and its derivatives have found many uses over the years, perhaps most notably in their efficient activation of dihydrogen when paired with a suitable Lewis base, in the quintessential example of "Frustrated Lewis Pair" (FLP) chemistry.[1] Within our group, the search for alternatives lead us to develop **1**, a borenium cation which activates dihydrogen under FLP conditions but does so not as a boron centred Lewis acid but rather with the hydride accepted at carbon.[2] Computational studies[3] revealed that whilst the hydride ion affinity (HIA) for this species at boron was significant, the HIA at the carbon centre was, unexpectedly, 14 kcalmol^{-1} greater. Calculated HIAs for simple alkylated pyridines and polycyclic nitrogen bases indicated that substituent choice allows for the design of carbon centred Lewis acids with HIAs comparable to or greater than that of $B(C_6F_5)_3$. Herein we report the first successful exploitation of cheap, air and moisture stable, carbocations, **2**, as the Lewis acid components in the FLP activation of dihydrogen. Furthermore, these systems are shown to be viable catalysts for the Lewis acid activation of Si-H bonds for the functionalization of organic feedstocks.[4]





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An electrochemical study of frustrated Lewis pairs: a metal-free route to hydrogen oxidation.

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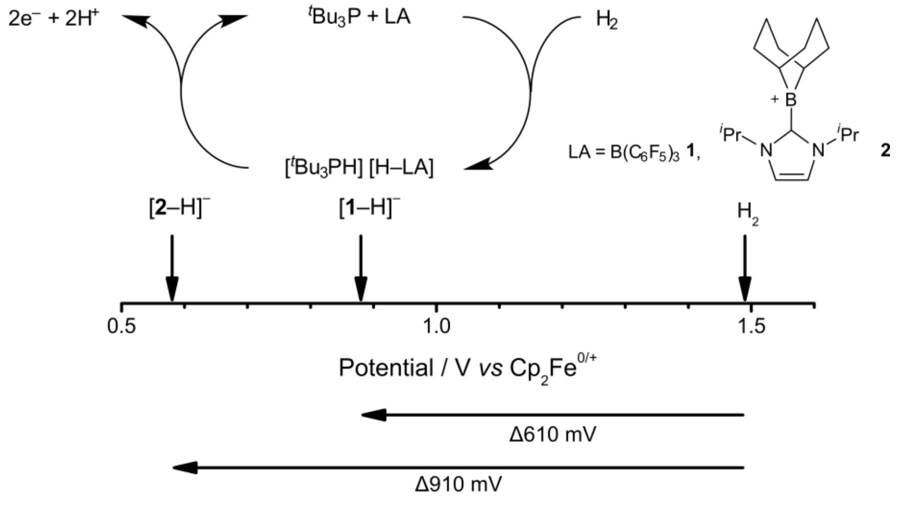
Frustrated Lewis pairs have found many applications in the heterolytic activation of H_2 and subsequent hydrogenation of small molecules through delivery of the resulting proton and hydride equivalents. In this talk we will describe how H_2 can be pre-activated using classical frustrated Lewis pair chemistry and combined with *in situ* non-aqueous electrochemical oxidation of the resulting borohydride. Our approach allows hydrogen to be cleanly converted into two protons and two electrons in situ. Our initial studies focused on the archetypal Lewis acid $B(C_6F_5)_3$ (**1**) combined with the bulky Lewis base ${}^{t}Bu_3P$. This system reduced the overpotential (the required energetic driving force) for non-aqueous H_2 oxidation by up to 610 mV (117.7 kJ mol^{-1}) at a carbon electrode without the use of metal catalysts. However, the ability to recycle the system was limited by decomposition of the Lewis acid via a protolysis process. Since then we have graduated to an N-heterocyclic carbene-stabilized borenium cation (**2**) derived from the 9-borabicyclo[3.3.1]nonane dimer. This has numerous advantages over **1**. The borenium cation (**2**) exhibits faster electrode kinetics and a greater resistance to protolytic decomposition, thus enabling an improved recycling of the system. Most importantly, the new system further gives a further 300 mV reduction in the H_2 oxidation overpotential. This is equivalent to a 269.8 kJmol^{-1} reduction in total activation energy. Such a significant energy reduction opens up routes to the development of non-aqueous hydrogen energy technology.



Iron-Catalyzed Dehydrocoupling/Dehydrogenation of Amine-Boranes

André Schäfer, James R. Vance, Alasdair P. M. Robertson, Kajin Lee, Joshua Turner, George R. Whittell, Ian Manners

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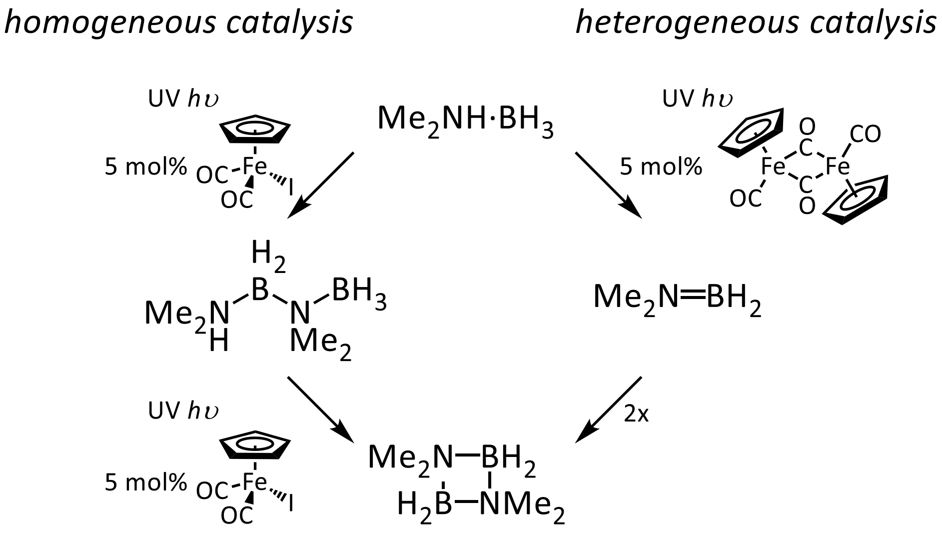
The iron carbonyl complexes, $[Cp(CO)_2Fe]_2$ and $Cp(CO)_2FeI$ were found to be efficient precatalysts for the dehydrocoupling / dehydrogenation of dimethylamine-borane $Me_2N(H){\cdot}BH_3$ to afford the cyclic diborazane $[Me_2N\text{-}BH_2]_2$ upon UV photoirradiation at ambient temperature. *In situ* analysis of the reaction mixtures by ^{11}B NMR spectroscopy indicate that different mechanisms operate in each case. $[Cp(CO)_2Fe]_2$ dehydrocouples $Me_2N(H){\cdot}BH_3$ via the aminoborane $Me_2N{=}BH_2$ which then undergoes a [2+2] cycloaddition to give $[Me_2N\text{-}BH_2]_2$ in an off-metal step. In contrast to this, the reaction with $Cp(CO)_2FeI$ proceeds via the linear diborazane $Me_2N(H){\cdot}BH_2\text{-}NMe_2{\cdot}BH_3$ as the key intermediate, affording $[Me_2N\text{-}BH_2]_2$ in a second metal-catalyzed step. Mechanistic studies indicate that the active catalyst generated from $[Cp(CO)_2Fe]_2$ is heterogeneous in nature and consists of small nanoparticles (≤10 nm). In contrast to this, experimental and DFT studies for the photoactivated precatalyst $Cp(CO)_2FeI$ suggest that the active catalyst formed in this reaction was homogeneous.



J. Am. Chem. Soc. **2014**, (DOI: 10.1021/ja410129j)

Amine-Boronium Cations: Convenient Precursors to Aminoborane Monomers and Polyaminoboranes *via* their Addition Polymerisation

Owen J. Metters, Andy M. Chapman, Alasdair P. M. Robertson, Paul J. Gates, Christopher H. Woodall, Duncan F. Wass* and Ian Manners*

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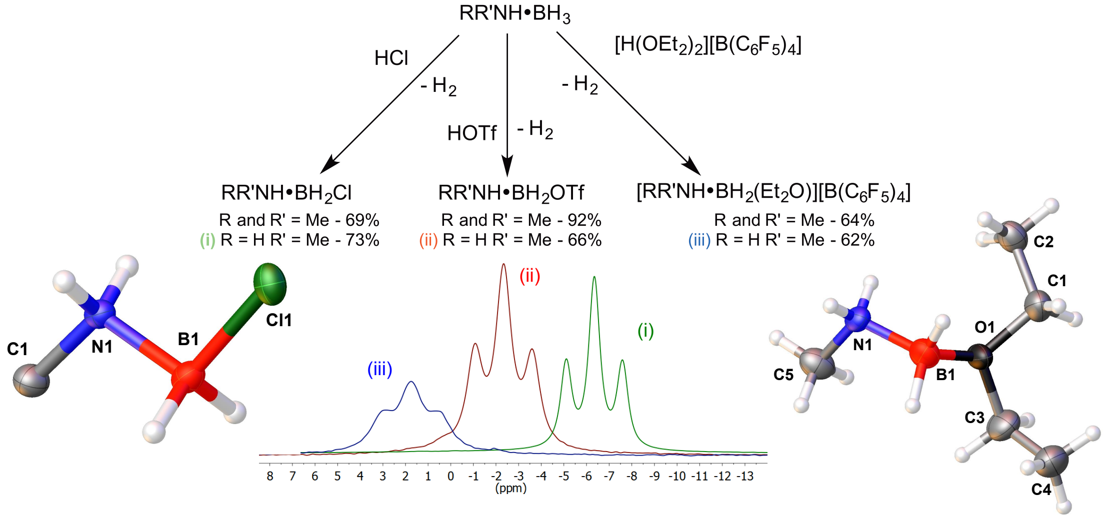
Within the last decade, many methodologies have emerged to facilitate the dehydrocoupling of amine-boranes to yield oligomeric and polymeric B-N species.[1] The majority of this work focuses on the use of transition metal complexes to catalyse dehydrocoupling reactions, with effective metal-free processes proving elusive.

Through stoichiometric reactions of amine-boranes ($RR'NH{\bullet}BH_3$, R=R'=Me and R=H, R'=Me) with Brønsted acids we have isolated and characterised a range of amine-boronium cations with various accompanying anions (Cl^-, $^-OSO_2CF_3$ and $[B(C_6F_5)_4]^-$).



These cations react cleanly with sterically hindered amine bases ($^iPr_2EtN$ or 2,6-di-*tert*butyl pyridine) to yield the expected amine-borane dehydrocoupling products ($[Me_2N\text{-}BH_2]_2$ or $[MeNH\text{-}BH_2]_n$), with the reaction proceeding *via* highly reactive amino-borane intermediates/monomers ($RR'N{=}BH_2$). Trapping reactions and direct observation of such species ($MeNH{=}BH_2$ and $Me_2N{=}BH_2$) by ^{11}B NMR spectroscopy has provided new insight into the transition metal catalysed dehydropolymerization of amine-boranes.[2]

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Borate and Borane derivatives as chain-transfer agents in Group II Immortal Ring-Opening Polymerisation of ε-Caprolactone and *rac*-Lactide

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Immortal Ring-Opening Polymerisation (iROP) has been of great interest over the past decade. The remarkable characteristic of iROP involves the rapid reversible exchange between the growing polymer chains and chain-transfer agents (CTAs), allowing a large number of polymer chains with narrow molecular weights to be produced. The most common CTAs found in the literature are protic species, such as alcohol, water and hydrogen chloride, which sometimes lead to the decomposition of the active, stereoselective metal catalyst.[1,2] Herein, we report the use of external and *in-situ* generated borate derivatives, $B(OBn)_3$, $B(OMe)_3$ and pinacolborane (HBPin) as CTAs in iROP of ε-caprolactone (CL) and *rac*-lactide (LA). These elaborate catalytic systems can yield a variety of end group-capped PCL and PLA in a one-pot polymerisation with no evidence of catalyst decomposition.

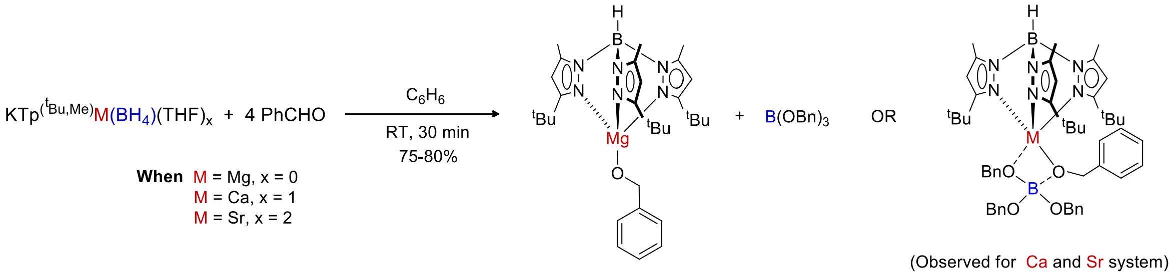

Figure 1. *In-situ* generated Group II pre-catalyst and the borate derivative as CTA.

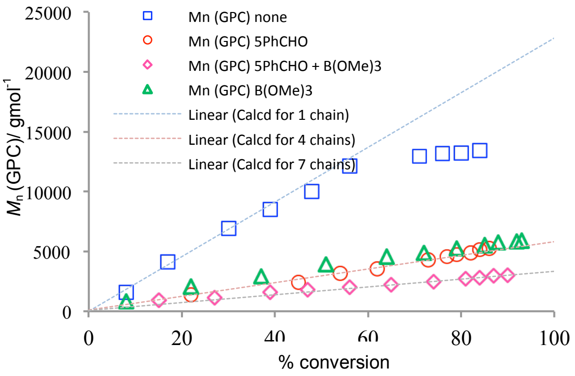

Figure 2. Plots of M_n (GPC) *vs* % conversion of ε-CL ROP using (Tp^{tBu,Me})Mg(BH$_4$) and various additives in THF.

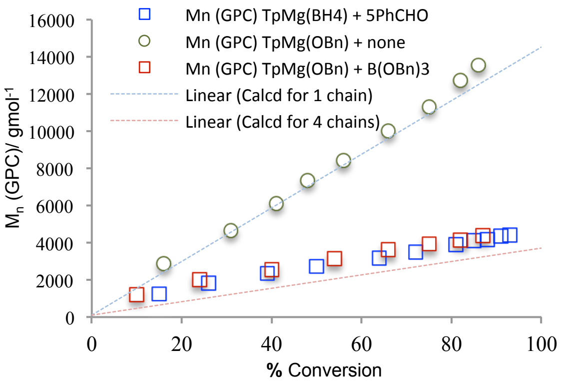

Figure 3. Plots of M_n (GPC) *vs* % conversion of *rac*-LA ROP using (Tp^{tBu,Me})Mg(BH$_4$) and various additives in THF.

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Cyclometalation reactions of rhodium and iridium NHC complexes: attenuation and reversibility through ligand variation

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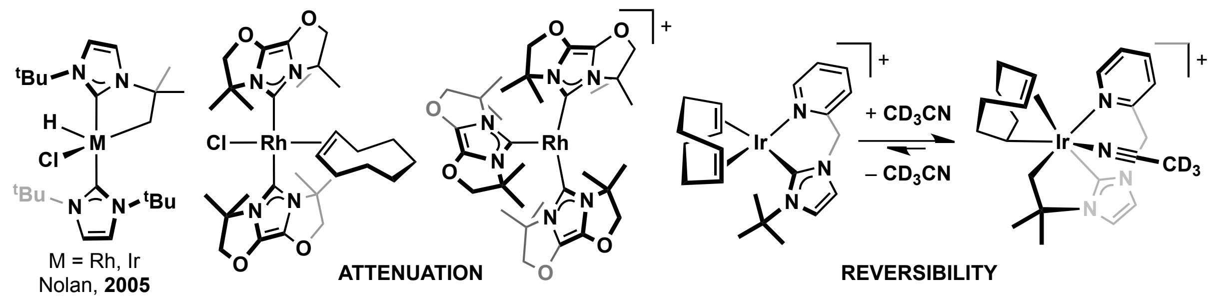
Promoted by the chelate effect, cyclometalation reactions of alkyl and aryl ligand appendages represent a convenient means for achieving the activation of strong and nominally unreactive C–H bonds.[1] With direct applications in organic synthesis and serving as models for the corresponding intermolecular processes, C–H bond cyclometalation reactions are of considerable interest in organometallic chemistry and catalysis. As a consequence of their strong σ-donor characteristics and substituent directionality, N-heterocyclic carbene (NHC) scaffolds are particularly well suited to cyclometalation reactions.[2] However, in applications where spectator roles are intended, intramolecular activation of NHC ligands is unwanted and potentially detrimental.

As part of our ongoing interest in the reaction chemistry of coordinatively unsaturated group 9 transition metal complexes, in this communication we present recent work involving NHC complexes of rhodium and iridium. In particular an interesting example of reversible cyclometalation using a tethered NHC ligand is reported together with the application of Glorius' conformational rigid IBioxMe$_4$ ligand for the isolation of low-coordinate NHC complexes.[3–5]



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Does rate limiting C-H activation always entail a kinetic isotope effect?

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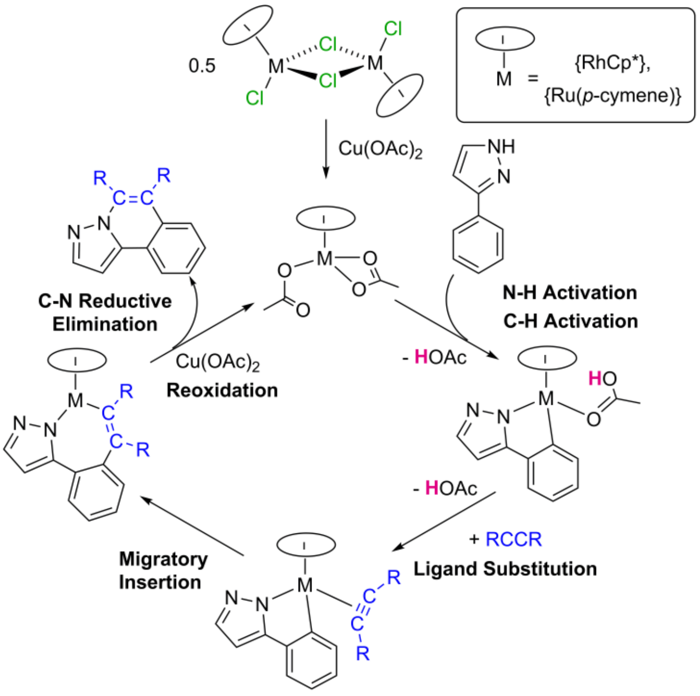
Catalytic C-H functionalization using Rh and Ru catalysts has shown potential as a new route to many desired heterocycles by forming new C-Y bonds (Y = C, N, O). However, current understanding of the mechanisms involved in such reactions is limited - yet key to a rational basis for developing efficient and selective catalytic systems.

The work presented here combines experimental and DFT studies on the efficient coupling of 3-phenylpyrazole with alkynes to form new C-C and C-N bonds, using $[Cp^*RhCl_2]_2$ or $[(p\text{-cymene})RuCl_2]_2$ as catalysts[1] (see Scheme 1).

Experimental studies indicate that with Rh C-H activation is competitive with migratory insertion and a k_H/k_D kinetic isotope effect (KIE) of 2.7 ± 0.5 is determined. In contrast for Ru the k_H/k_D KIE is 1.1 ± 0.2.

DFT studies on the Rh system showed the need to model the full experimental system in the calculations and to incorporate a correction for disperion effects in order to capture the experimental behaviour. With Ru this approach suggested rate-limiting C-H activation. This result can still be consistent with the lack of a KIE due to the two-step nature of the C-H activation process, which involves (i) κ^2-κ^1 acetate displacement and (ii) C-H bond cleavage. For Ru the former step - in which no C-H bond elongation is seen - has the higher lying transition state. This is therefore consistent with a rate limiting C-H activation step that occurs without a significant KIE.



Scheme 1 – C-H functionalisation reaction pathway for 3-phenylpyrazole and an alkyne (RC≡CR) with a [Cp*Rh] or [(*p*-cymene)Ru] catalyst

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[1] A. G. Algarra, W. B. Cross, D. L. Davies, Q. Khamer, S. A. Macgregor, C. L. McMullin and K. Singh, *J. Org. Chem.*, 2014, DOI: 10.1021/jo402592z.

Controlling Selectivity of Csp^2-H Activation: An experimental and computational study.

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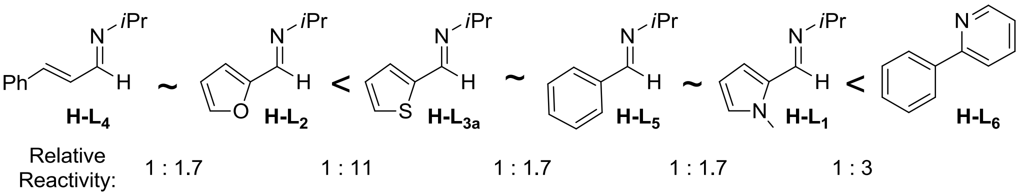
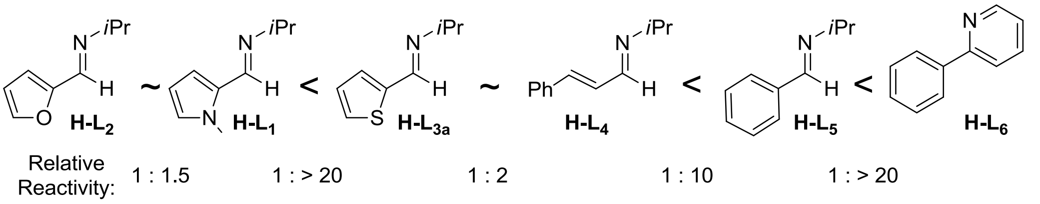
Catalytic C-C bond formation by functionalisation of C-H bonds is a step-economical approach for the synthesis of complex organic molecules. An understanding of the kinetic and thermodynamic selectivity of the C-H activation will facilitate the rational design of more efficient and selective catalysts in the future.

Herein, we present a combination of experimental and computational studies on the relative reactivity towards acetate-assisted C(sp^2)–H activation in a series of imines featuring heterocyclic, vinyl and phenyl substituents at iridium and rhodium. H/D exchange experiments suggest that the selectivity of C–H activation at Ir is determined by kinetic factors while that at Rh is determined by the product thermodynamic stability, leading to a different order of selectivity depending on the metal used. The different reactivity of these substrates with Ir and Rh is well supported by the computational studies. This work provides the foundation for the development of a computational methodology for the design of selective catalysts that involve an AMLA/CMD[1] C-H activation process.

(a) at iridium



(b) at rhodium



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[1] AMLA: Ambiphilic Metal-Ligand Assistance; CMD: Concerted Metalation-Deprotonation.

Exploiting the redox chemistry of nitrite species in Pd-catalyzed aerobic oxidation of unactivated C(sp^3)-H bonds.

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The catalytic and selective C-H bond functionalization of organic substrates is a challenge in synthetic chemistry, especially in the field of unactivated C(sp^3)-H bonds. In a recent paper, Sanford and co-workers described the acetoxylation of C(sp^3)-H bonds using $Pd(OAc)_2$ as catalyst and dioxygen as the terminal oxidant in acetic acid/acetic anhydride.[1] It was found that the addition of $NaNO_3$, a redox co-catalyst, was crucial for effective catalysis, however, its precise role is still not well established. Our group recently described the presence of nitrite impurities in commercial $Pd(OAc)_2$, asking as well the question of its implication (spectator ligand or involved in catalytic processes?).[2] We choose to direct our mechanistic studies on the acetoxylation reaction of 8-Methylquinoline. A series of five new palladacycles containing both the 8-Methylquinoline and nitrate/nitrite ligands have been synthesized, characterised and evaluated as catalyst for the acetoxylation reaction (Figure 1).

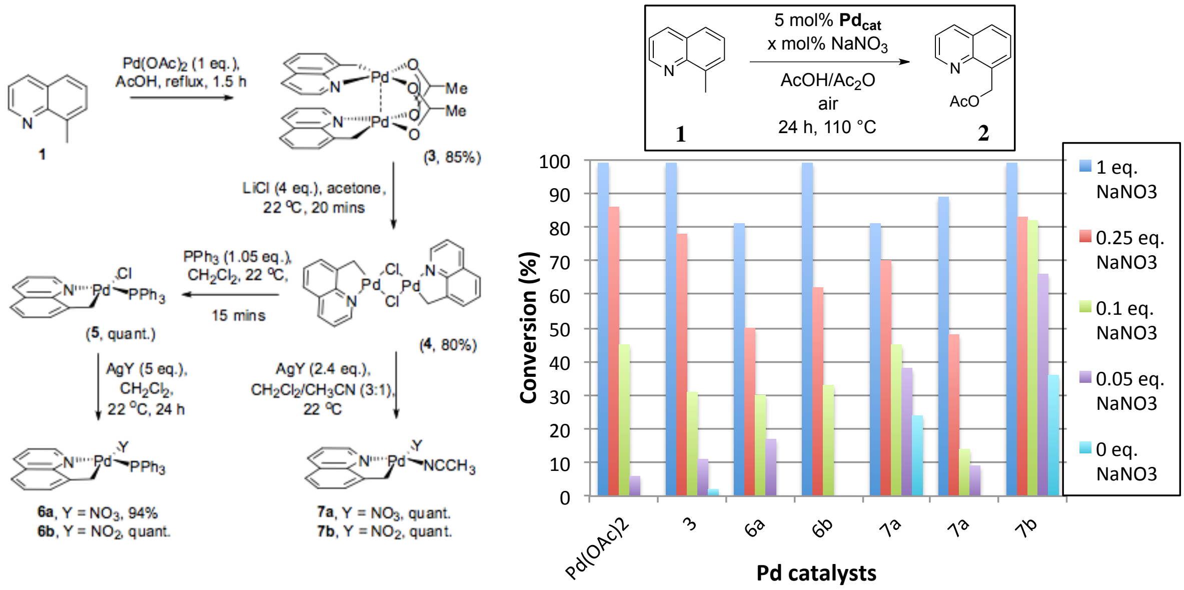

Figure 1: Synthesis and catalytic evaluation of the new palladacycles **3**-**7**

Mechanistic studies of the reaction, isolation of intermediate Pd-species during the catalytic cycle, ^{18}O-labelling experiments and kinetics studies have been performed and will be described.

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Synthesis and reactivity of rollover cyclometalated complexes

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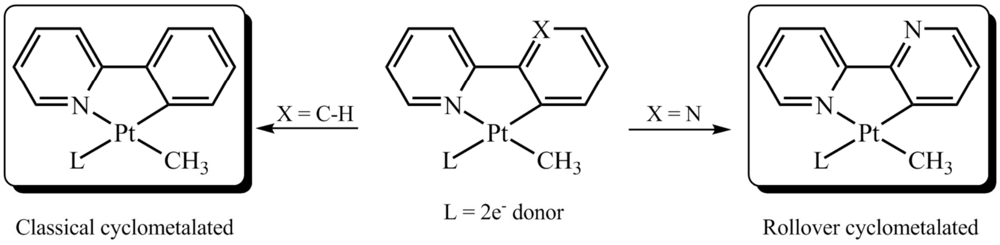
Cyclometalation reactions constitute one of the evergreen fields in synthetic chemistry because of the variety of applications, from substrate functionalization to catalyst production and model for C-H activation.[1] A variation on this theme is rollover cyclometalation where a bidentate donor, such as 2,2'-bipyridine, upon C-H activation leads to a species with a free donor atom that is able to influence the properties, hence the reactivity, of the complex.[2]

We explored the similarities/differences between classical and rollover cyclometalation to check the importance of the second nitrogen donor by comparing suitably substituted 2,2'-bipyridines and 2-phenylpyridines; moreover the properties of the ligands were tuned to investigate the impact of stereoelectronic modification on the C-H activation process.

The reactivity of the newly synthesized cyclometalates having formula [Pt(κ^2-N,C)(CH_3)(L)] (κ^2-N,C = cyclometalated ligand, L = neutral ligand) was tested in different conditions: ligand substitutions, protonolysis, oxidative additions and reductive eliminations.[3] A wide variety of mono and dinuclear complexes was obtained and fully characterized by NMR spectroscopy.

Further insights have been sought from *in silico* experiments using DFT calculations that led to a nice agreement with the chemistry observed.



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Computational Studies of Ruthenium Hydrides as Novel Nucleophiles in C–F and C–Cl bond activation

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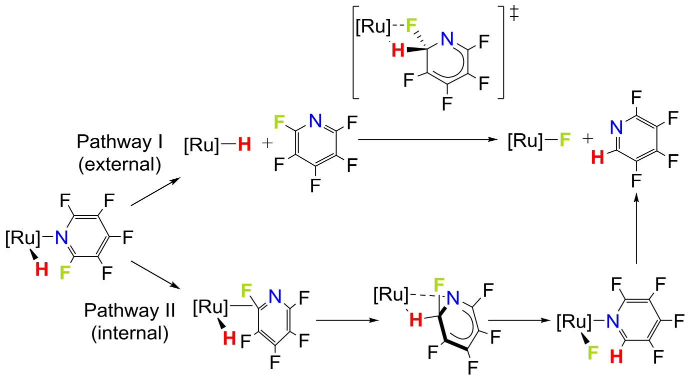
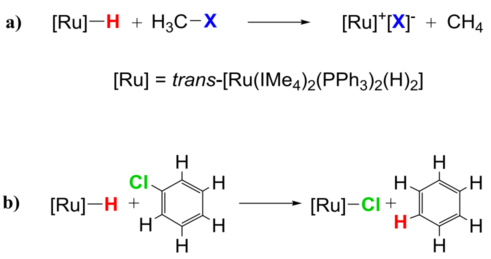
The Ru(II) N-heterocyclic carbene complex, [$Ru(IPr)(PPh_3)_2(CO)(H)_2$], catalyses hydrodefluorination (HDF) of perfluoroaromatics.[1] Previous work with $C_6F_{6-x}H_x$ (x = 0, 1) has shown that HDF proceeds via a novel mechanism involving hydride attack at the arene.[2, 3] Here DFT calculations show the same mechanism is operative in the HDF of pentafluoropyridine (Scheme 1). Thus, Pathway I sees an external Ru–H···C–F hydride attack process, while Pathway II features a stepwise internal process. Moreover the HDF of lower fluorinated fluoropyridines $C_5NF_{5-x}H_x$ (x = 0 – 3) is accessible via the same mechanism.



[Ru] = Ru(IPr)(PPh$_3$)(CO)(H)

Scheme 1



[Ru] = *mer*-[$Ru(PPh_3)_3(H)_2$]

Scheme 2

Further calculations have explored the general ability of Ru-hydrides to act as nucleophiles. For example, *trans*-[$Ru(IMe_4)_2(PPh_3)_2(H)_2$] is computed to undergo facile S_N2 reactions with methyl halides (Scheme 2a) and a hydride attack mechanism is accessible in the C–Cl bond activation of chlorobenzene at *mer*-[$Ru(PPh_3)_3(H)_2(H_2)$] (Scheme 2b). Hydride nucleophilic attack therefore provides an alternative mechanism that may compete with more established processes such as oxidative addition.

1. S. P. Reade, M. F. Mahon and M. K. Whittlesey, *J. Am. Chem. Soc.*, 2009, **131**, 1847.
2. J. A. Panetier, S. A. Macgregor and M. K. Whittlesey, *Angew. Chem. Int. Ed.*, 2011, **50**, 2783.
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4. V. V. Grushin, S. A. Macgregor, D. McKay, H. Samouei, *in prep*.

Periplasmic binding protein captures low-denticity siderophores

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Department of Chemistry, University of York, UK

Microorganisms produce siderophores to acquire essential Fe(III). Whilst the most efficient siderophores are hexadentate, others are only tetradentate but still coordinate to Fe(III) and mediate its uptake. The Fe(III) complexes of hexadentate siderophores and mimics, such as MECAM^{6-}, are coordinatively saturated and interact with their binding proteins through a combination of electrostatic interactions and hydrogen bonding (Figure 1, left) [1].

Tetradentate siderophores, however, can occupy only four of the six coordination sites of octahedral Fe(III). We determined the crystal structures of the Fe(III) complexes of a series of tetradentate siderophores bound to the periplasmic binding protein CeuE of *Campylobacter jejuni* and found that two amino acid side chains coordinate directly to the Fe(III) centre, thus completing its coordination sphere (Figure 1, right) [2]. By displaying this switch in binding mode, CeuE is the first siderophore binding protein to provide structural insights into the binding of both hexadentate and tetradentate siderophores. We propose that the two amino acid residues act as an adaptor that enables the binding protein to capture more than one type of ferric siderophore.

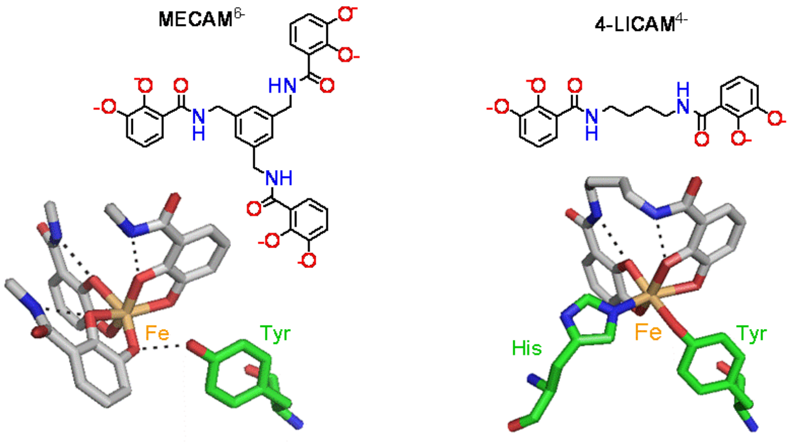

Figure 1: Fe(III) coordinated to the siderophore mimics MECAM^{6-} and 4-LICAM^{4-} (coloured by atom type) with key amino acid residues in the binding pocket of CeuE shown (green carbon atoms).

References:

[1] A. Müller, A. J. Wilkinson, K. S. Wilson, A.-K. Duhme-Klair, *Angew. Chem. Int. Ed.*, **2006**, *45*, 5132.

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New insight into the mechanism of NiFe hydrogenases from IR spectroscopy coupled with protein film electrochemistry

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This talk describes experiments that provide new insight into the mechanism and reactions of nickel-iron hydrogenases - nature's efficient catalysts for oxidation and production of H_2. Metalloenzymes are fascinating to chemists because of their ability to carry out catalysis selectively using cheap, abundant metals. One important technique used in studying redox catalysis by enzymes is the approach known as protein film electrochemistry (PFE) in which the enzyme of interest is immobilised on an electrode and can undergo rapid and direct exchange of electrons with the electrode surface. The enzyme is thus handled as a heterogeneous electrocatalyst, directly comparable to a metal electrode or supported nanoparticle catalyst. The power of this technique in replacing the biological redox chain of an enzyme by direct electron transfer to or from an electrode has spurred the development of electrode configurations designed to allow spectroscopic sampling to be coupled with PFE.[1-3] We have focussed on coupling infrared spectroscopy with direct electrochemical control of hydrogenases adsorbed on a carbon electrode, and describe simultaneous electrocatalytic and *in situ* infrared measurements on *E. coli* hydrogenases. For the first time, these measurements allow states of the active site to be probed under catalytic as well as non-catalytic conditions, correlating active site states with turnover under different solution and potential conditions. These data provide new insight into the catalytic mechanism of H_2 activation by nickel-iron hydrogenases and the approach opens up possibilities for addressing catalytic states of a range of metalloenzymes.

References

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UNVEILING THE BIOSYNTHESIS OF THE H-CLUSTER OF [Fe-Fe]-HYDROGENASE

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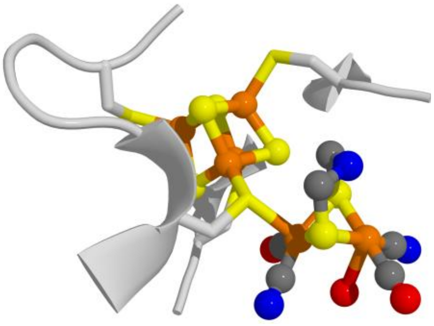
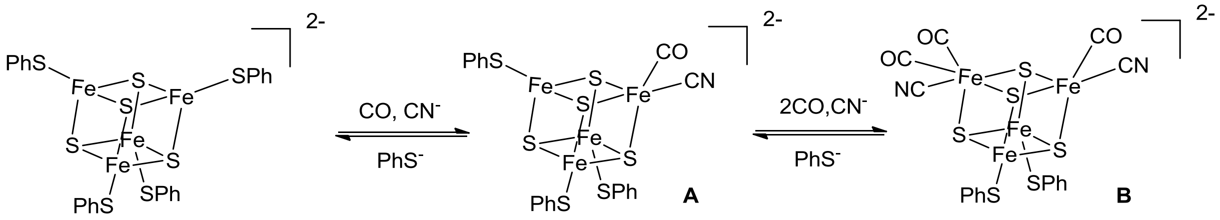


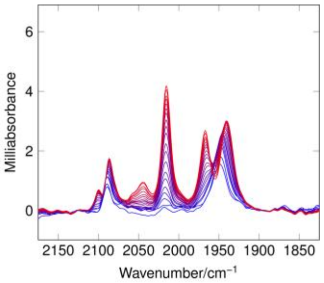
Figure 1 The H-cluster

One of the most remarkable catalysts in biology is the H-cluster of the [FeFe]-hydrogenase, which can catalyse the evolution of hydrogen from water at rates comparable to the precious metal platinum.[1] The structure of the H-cluster is shown in Figure 1, and features a Fe_4S_4 cubane linked to a diiron subsite. Iron-sulfur clusters featuring such Fe_4S_4 centres are ubiquitous in living systems and are perhaps the most ancient of prosthetic groups. The fascinating Fe_2S_2 subsite contains biologically unusual carbon monoxide and cyanide ligands, and is the reactive centre for hydrogen activation.

We have been exploring how such Fe_2S_2 subsites might be assembled. We now show that in the presence of carbon monoxide and cyanide, the Fe(CO)(CN) motif can be generated at synthetic clusters. This provides chemical precedence for synergic binding of CO and CN^-, strongly supporting the proposal that biosynthesis of the subsite originates from Fe_4S_4 cubane precursors.[2,3] The infrared spectrum of our chemical species formed at short time has essentially identical bands to those observed in protein studies recently conducted by Britt, George and coworkers.[2] The identification of these bands as arising from a Fe(CO)(CN) motif is supported by computational simulation. This confirms the spectroscopic fingerprint for both the synthetic molecule and the detected biological intermediate.



	Wavelength/cm^{-1}	
	CO	CN
Protein	1949	2093
Synthetic	1942	2087
Computed	1948	2093



Evolution of the infra-red spectra in the stopped-flow FTIR experiment. At short times (blue) species **A** is detected, at longer times (red) a spectrum assigned to **B** is attained.

¶ Dept Environmental and Earth Sciences, University of Milan Bicocca, Piazza della Scienza 2, 20126 Milano, Italy.

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[FeFe]-Hydrogenase synthetic mimics based on *peri*-substituted dichalcogenides

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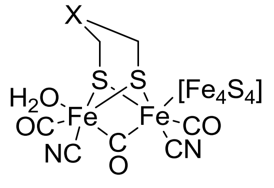
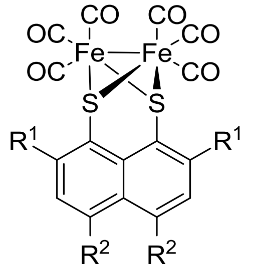
[FeFe]-Hydrogenase plays a central role in microbial energy metabolism, catalysing the reversible interconversion of protons and electrons into molecular hydrogen. The H-cluster is composed of an [Fe_4S_4]-cubane core linked by a cysteinyl residue to a [2Fe2S]-subsite**.** The [Fe_4S_4]-cluster is anchored to the protein by three cysteines and the binuclear metal centre is bridged by a dithiolate ligand with biologically unusual carbonyl and cyanide ligands completing the coordination sphere. [1]

Naphthalene-1,8-dithiolate complexes **1a**-**c** have been previously investigated as [FeFe]-Hydrogenase mimics. [2] The naphthalene backbone provides a three atom spacer between the sulfur atoms as in the active site of the enzyme. Its rigidity should prevent the associative degradation observed for other mimics, [1] and allow considerable variation of steric and electronic properties of complexes.

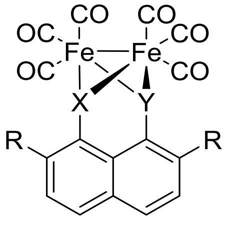


H-cluster
of [FeFe]-hydrogenase

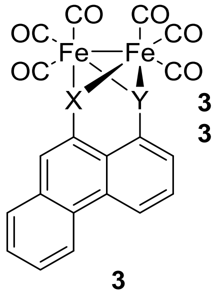


1a R^1, R^2 = H
1b R^1= ^{t}Bu; R^2 = H
1c R^1, R^2 = Cl

We have prepared additional complexes **2a**-**e** based on the naphthalene backbone, which differ in the heteroatoms X and Y and substituents R in the *ortho* positions, and related complexes **3a**-**b** and **4**.



2a R= OMe; X=Y=S
2b R= H; X=Y=Se
2c R= ^{t}Bu; X=Y=Se
2d R= OMe; X=Y=Se
2e R= H; X=S; Y=Se
2f R= ^{t}Bu; X=S; Y=Se



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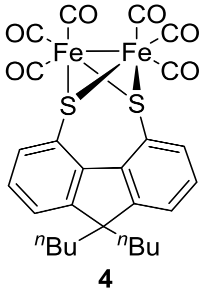
3a X=Y=S
3b X=Y=Se



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Complexes **2a**, **2b**, **2c**, **3** and **4** show reduction potentials ($E_{1/2}$) between 1.5 and 1.4 V, more positive than ligands with saturated linkers, but with enhanced stability upon reduction/oxidation. Upon addition of PTSA an increase in the current intensity of the peak relative to the reduction potential of the [FeFe]-complex was observed, confirming the catalytic activity.

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Title: Oxygen Tolerance in Membrane-Bound [NiFe]-Hydrogenases

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Hydrogenases have been extensively studied for applications in hydrogen-oxygen fuel cells. Their ability to selectively interconvert H_2 to H^+s makes them ideal catalysts for H_2/O_2 biofuel cells. When they are used in conjunction with a selective catalyst for O_2 reduction, like laccase or bilirubin oxidase, it is no longer necessary to separate the anode from the cathode with a gas impermeable membrane as required in Pt based fuel cells. However, the fact that hydrogenases are inactivated by oxidative redox conditions or O_2 has reduced their promise. Membrane-bound [NiFe]-hydrogenases (MBH) are relatively tolerant to oxygen, but anodes coated with water-soluble subcomplexes of MBH are still inactivated under oxidative conditions. Here, we will present electrochemical investigations of the full heterotrimeric MBH of *Ralstonia eutropha* using electrodes modified with planar tethered bilayer lipid membranes (tBLM). Cyclic voltammetry and chronoamperometry experiments show that MBH, in equilibrium with the quinone pool in the tBLM, does not ‘anaerobically’ inactivate under oxidative redox conditions. In aerobic environments, the MBH shows some inactivation by O_2, but only to a small extend and reactivation was found to be fast even under oxidative redox conditions. This significant enhancement in resistance to inactivation will be discussed with respect to molecular mechanism of oxygen tolerance and the oligomeric state of MBH in the lipid membrane.

Title: Nonheme iron(IV) enzymes: Unusual mechanism and reactivity of wild-type and bioengineered systems.

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Abstract. High-valent metal-oxo species are common intermediates in enzymatic processes and have been identified in heme as well as nonheme iron enzymes, where often the catalytic intermediate is an iron(IV)-oxo species.[1] We have performed a series of density functional theory and quantum mechanics/molecular mechanics calculations to establish the properties of the iron(IV)-oxo oxidant of enzymatic and biomimetic model complexes and investigated the chemical properties and reactivity patterns. In particular, we are interested in the effects of ligands, substitution of the metal and environmental perturbations, e.g. hydrogen bonding, that may affect its chemical properties and its potential to act as an active oxidant in a reaction with substrates.[2] These studies show that seemingly minor perturbations to the oxidant through weak/non-covalent interactions may result in major catalytic differences due to their electrostatic effects on orbital occupation. In further studies we focused on several enzymatic nonheme iron enzymes and established the catalytic cycles of AlkB repair enzymes and S-mandelate synthase.[3,4] Finally, computational studies assisted experimental biochemical engineering studies whereby *S*-mandelate synthase was converted into *R*-mandelate synthase, i.e. a full enantioselectivity reversal was established.

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Title: Targeting high-spin clusters for reactivity

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We have ventured to make small molecule activation more kinetically favorable by creating a minimal reaction site capable of effecting multi-electron reactivity. The generation of reactive transition metal clusters has long been sought after to meet this challenge, though preventing strong M–M bond formation and being able to manipulate both the local and ensemble coordination spheres is an unsolved problem. Small molecule activation is already accomplished in nature by a number of metalloenzymes that feature polynuclear transition metal assemblies. Polynuclear metallocofactors in biology (e.g. FeMo-cofactor in nitrogenase, water-oxidation catalyst in photosystem II) extensively use first row transition metal ions that adopt open-shell electronic configurations. The presence of multiple transition metal centers within close proximity to one another enables the complex to efficiently carry out multi-electron redox processes, buttress redox changes within the cluster, and provide multiple coordination sites and modes for substrate binding. The protein superstructure provides the organizational template within which the polymetallic core self-assembles and functions. Thus the challenge towards replicating the function of these metallocofactors is to, in the absence of a protein, generate a modular weak-field ligand scaffold that can proximally accommodate multiple transition metals, allowing the reaction chemistry of clusters as molecular units to be explored. To synthesize open-shell cluster complexes meeting the aforementioned design criteria, we have developed flexible, multinucleating ligands composed of weak-field binding sites to direct the formation of predesigned multinuclear architectures. In addition to synthetic tunability, this directed approach offers the advantage of the ability to probe how the ligand scaffold influences the overall molecular symmetry and electronic structure. My talk will discuss how we: (1) Synthesize ligand platforms capable of proximally binding multiple transition metals; (2) establish the cluster capacity for multi-electron redox chemistry; and (3) demonstrate the clusters' ability to bind and activate small molecule substrates.

Developing Catalytic Reactions One Step at a Time

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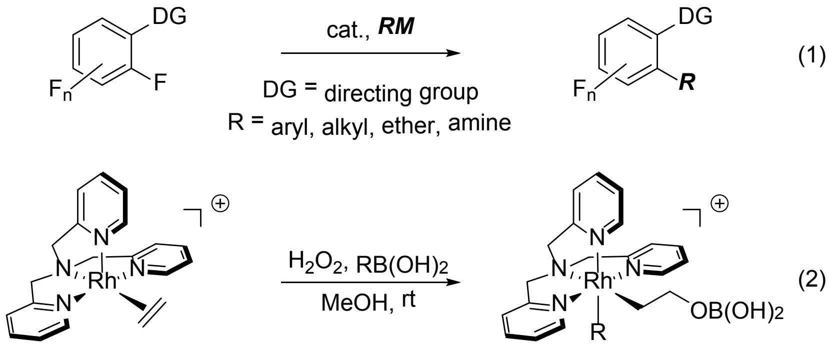
Transition metal catalysts are widely used in the industrial synthesis of pharmaceuticals, materials and fine chemicals. Despite this obvious utility, the factors that control catalyst activity and the individual steps of a catalytic reaction (e.g., oxidative addition, reductive elimination, etc.) are often poorly understood. This knowledge is essential for the design of chemical processes that are highly efficient and generate minimal chemical waste – two key goals in catalysis research that have widespread significance for the development of safe and sustainable chemical processes. My research group explores the reactivity of a number of transition metal complexes with the goal of using the knowledge gained from these studies to develop highly efficient, fundamentally new reactions. Of particular interest is the reactivity of late transition metal-element (M-X, X = C, O, F, S, N, etc) bonds, as these are implicated in a wide variety of catalytic processes. In this lecture, I will discuss our recent progress in metal-catalyzed synthesis of functionalized aryl fluorides (eq 1) and Rh-mediated olefin oxidation reactions (eq 2).



Copper trafficking pathways and enzymes involved in morphological development of *Streptomyces lividans*

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Streptomycetes are soil dwelling bacteria, best known for their production of a large number of compounds that have antibacterial and antifungal properties. Certain streptomycetes display a distinct dependence on the bioavailability of copper to initiate a key development switch in their life cycle. *Streptomyces lividans* is one such strain and is used commercially as a host in biotechnology applications. We have studied using biochemical and structural methods the role of copper ions, cupro-proteins and cupro-enzymes in *S. lividans* and have recently identified a branched extracytoplasmic copper trafficking pathway that under low copper concentrations chaperones copper ions to two cuproenzymes. Genetic manipulation of this trafficking pathway leads to *S. lividans* strains in which their morphology in liquid cultures is altered. In some mutants the morphology can be controlled by addition of very low amounts of copper ions. This leads to a potential opportunity for use of these new strains as improved cell factories for the production and secretion of enzymes.

Advances in Gold(III) Chemistry: Hydrides, Peroxides and Olefin Complexes

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Gold(III) complexes find widespread use in catalytic transformation of alkenes and alkynes. However, whereas Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, was the first transition metal alkene complex, well-defined alkene complexes of the isoelectronic Au(III) systems were unknown. Bis-cyclometallated complexes derived from 2,6-diphenylpyridine show sufficient stability towards reduction to generate Au(III) cations capable of binding olefins. Pincer ligands also provide sufficient stability to allow the isolation of the first gold(III) hydride and an exploration of the chemistry of Au(III) towards oxygen ligands: Hydroxides, oxides, as well as the first examples of gold(III) peroxides, alkylperoxides and hydroperoxides. Most unusually, it can be shown that, unlike its Pt(II) analogues, Au(III) hydroxides can act as oxidising agents, forming gold hydrides in the process. Several of these reactions also lead to remarkably stable Au(II) complexes with an unsupported Au-Au bond, although under photochemicsal conditions disproportionation into an octanuclear $Au(I)_4Au(III)_4$ cluster was observed. The reactions, structures and mechanisms and bond energies will be discussed.

Many of the new gold compounds show interesting photoluminescent properties and allow modulation of the emission wavelength from blue to orange.

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Application of Digold-Hydroxides in Dual Activation Chemistry

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The majority of gold-catalysed transformations take advantage of the exceptional Lewis acidity displayed by gold species to activate C-C multiple bonds, generally alkynes, towards nucleophilic attacks. It has always been assumed that these reactions proceed *via* the interaction of *one* gold centre with *one* substrate molecule. The seminal work published by Toste in 2008 casts doubt upon this assumption. Therein, he proposed that not one, but *two* gold centres could interact with *one* substrate molecule, therefore generating two new kinds of complexes: a) σ,π-digold acetylide and b) *gem*-diaurated species (Figure 1).[1] Studies on the nature of these species have lead to the development of a novel type of gold catalysed transformations that require dual activation of the substrate by the gold catalyst. Mechanistic studies support the proposal that these reactions require the interaction of *two* gold centres with *one* substrate molecule.

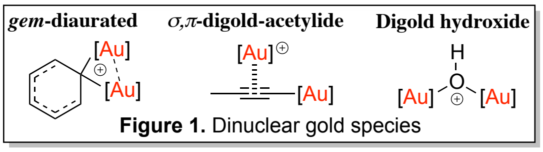
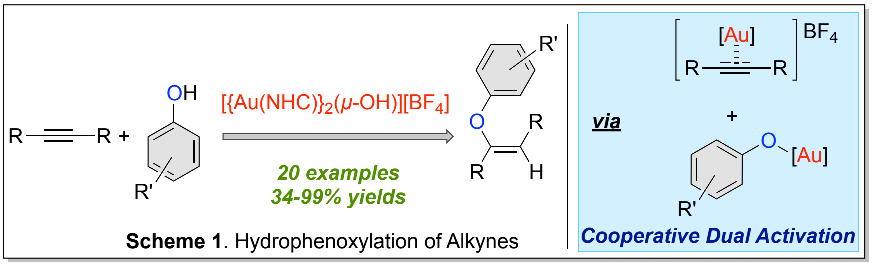


Figure 1. Dinuclear gold species

Our group has contributed to this area with the study of the synthesis and reactivity of a series of diaurated complexes of the formula [{Au(NHC)}$_2$(μ-OH)][BF$_4$] (**1**) (NHC = *N*-heterocyclic carbene). Digold hydroxides **1** can be considered as a combination of Lewis acid [Au(NHC)][BF$_4$] (**2**) and Brønsted base [Au(OH)(NHC)] (**3**). Taking advantage of the bifunctional nature of this species we have been able to access both σ,π-digold acetylide and *gem*-diaurated species (Figure 1).[2] Moreover, we have been able to use this bifunctional nature to develop reactions, such as efficient alkyne hydrophenoxylation protocols, in which *two* gold centres interact with *two* different substrates (Scheme 1).[3]



Scheme 1. Hydrophenoxylation of Alkynes

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Title: Copper-N-Heterocyclic Carbenes; Synthesis, Structure and Reactivity

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Copper-N-heterocyclic carbenes (NHCs) are active in a number of catalytic reactions, including C-H activation, cycloaddition, hydrosilylation, and alkene functionalisation.[1] Preparation of copper-NHCs usually relies on strong bases and the need for strict inert conditions. We have reported a simple and efficient electrochemical procedure to prepare a range of structurally diverse copper(I)-NHC complexes.[2] Following on from this work we have examined pyridyl- and picolyl-substituted NHC ligands in copper(I) and copper(II) chemistry. This has led to an interesting array of different compounds and structures. We have found that the nitrogen substituents are not innocent and direct the pathway that the NHC ligands take (Figure 1).

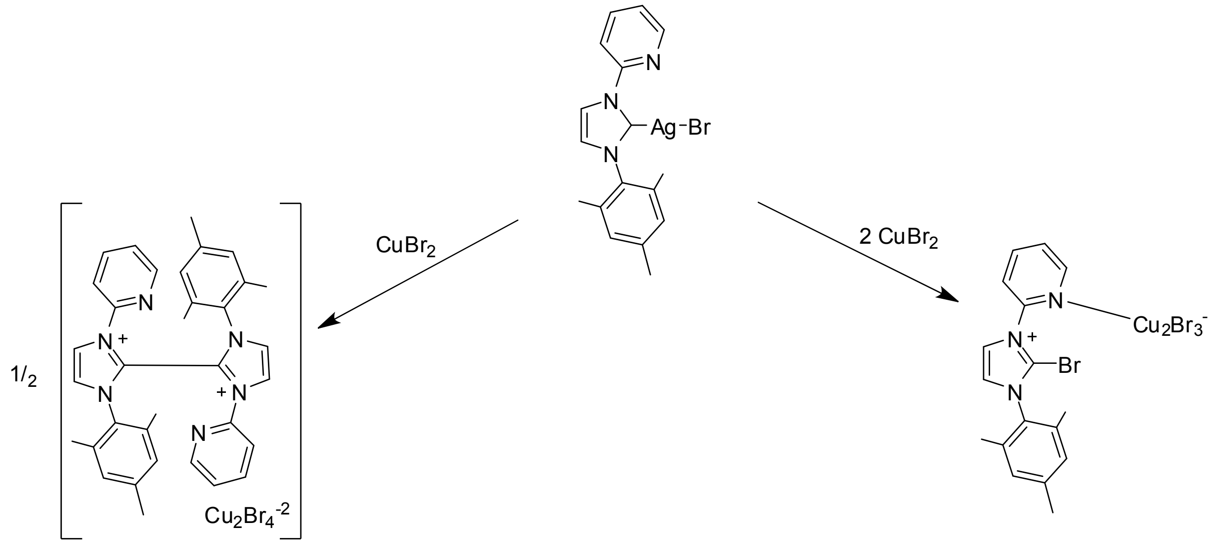

Figure 1: Reaction of silver(I)-NHC complex with different stoichiometries of copper(II)

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Title: Low Coordinate Ni(I) Complexes Bearing Ring Expanded N-Heterocyclic Carbenes

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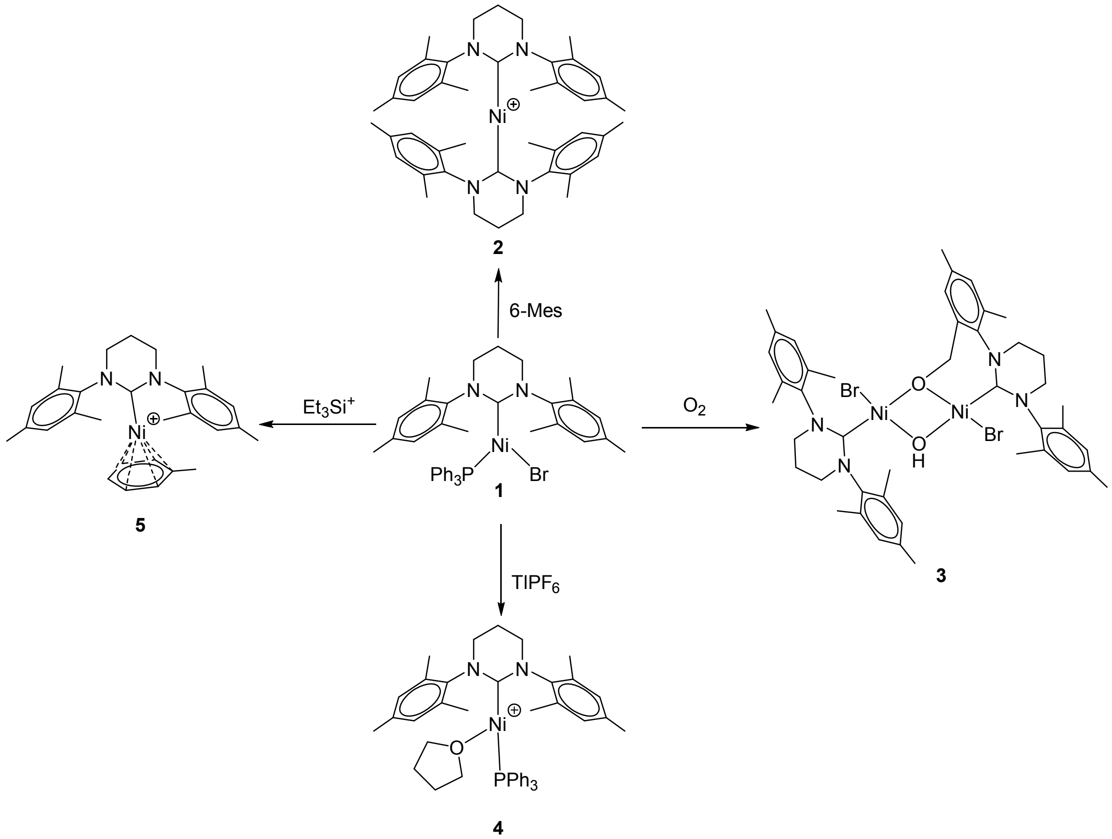
In a series of recent publications[1-3] we have described the use of sterically demanding 6- and 7- membered ring expanded N-heterocyclic carbene (RE NHC) ligands for the preparation of three coordinate Ni(I) species, exemplified by the 6-membered N-mesityl derivative, **1**. In this presentation we will discuss various reactions of **1**, including formation of the magnetically interesting two coordinate Ni(I) cation, $[\mathrm{Ni(6\text{-}Mes)_2}]^+$ **2**, and its Ni(0) analogue $\mathrm{Ni(6\text{-}Mes)_2}$, formation of the Ni(II) C-H hydroxylation product **3** upon activation of O_2 and isolation of low coordinate Ni(I) species (**4** and **5**) formed by abstraction of the halide.



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Metalloporphyrins as active N-heterocyclic carbene (NHC) transfer reagents

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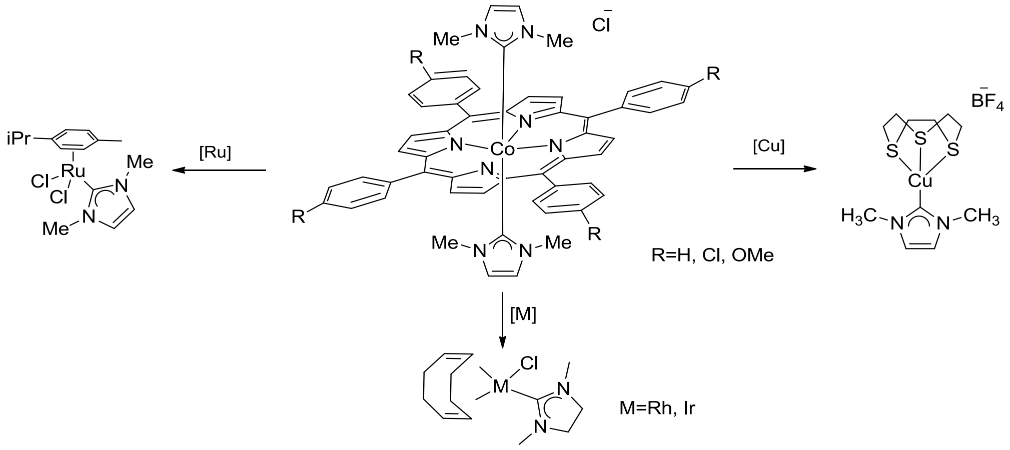
With the growing relevance of NHCs as ligands in transition metal catalysis, the development of new synthetic methods for NHC complex formation has become increasingly important in recent years.[1] An often-used method involves transmetallation of Ag-NHC complexes or related precursors.[2] However, these carbene transfer methods lack for tunability of the carbene transfer reagent.

We have discovered porphyrin Co(III) complexes which contain a labile NHC ligand and which therefore show activity as carbene transfer agents. Modification of the porphyrin ligand and the NHC substituents affects the transfer ability of these porphyrin NHC hybrid systems and induces significant electronic and structural changes at the metal center. This understanding has allowed us to develop optimised conditions and an efficient method of N-heterocyclic carbene ligand transfer to various transition metal centers such a ruthenium(II), copper(I), iridium(I), and rhodium(I).



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Optimisation of a lithium magnesiate for use in the non-cryogenic asymmetric deprotonation of prochiral ketones

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One of the most fundamentally important reactions in modern day synthesis is metallation, which is the replacement of a relatively unreactive C–H bond with a more reactive (more useful) C–metal one.[1] Over the past 60 years, the reagents of choice to carry out such reactions have generally been from the organolithium family, primarily due to their high Brønsted basicity. Unfortunately, most common deprotonations (and particularly enantioselective reactions) employing lithium reagents are carried out employing cryogenic temperatures (often lower than –78°C). This requirement implies an expend of over £250k per annum per batch tonne process, for a process carried out at –40°C.[2] One priority in modern day synthesis is to provide solutions to this problem by designing new metallating reagents that are capable of producing excellent results akin to their lithium counterparts but at temperatures closer to ambient. One strategy which can be employed to enable these reactions to be successful at ambient temperatures involves the employment of bimetallic organometallic reagents [a combination of an alkali metal and a second metal complexes (normally magnesium or zinc)], avoiding undesirable side-reactions with common functional groups and can even also perform chemistry unobtainable by the monometallic reagents on their own.[3]

In this talk, our work detailing the utilisation of lithium magnesiates for the deprotonation of conformationally locked 4-substituted cyclohexanones at *ambient temperature* will be detailed. The levels of enantioselectivity and conversion are significantly enhanced when compared with the values obtained using the respective monometallic amides at ambient temperature.[4]

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Towards The Selective Fuctionalisation of Pentadienylsilanes

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The coordination chemistry of pentadienyl ligands with main group metals remains relatively unexplored in comparison to that of the transition metals[1] and despite the ubiquitous use of s-block pentadienyl reagents in the formation transition metal complexes, structurally characterised examples are rare.[2] This is surprising given that related π-delocalised carbanions such as cyclopentadienyl and allyl are well known for their diverse structures and reactivity.

S-block allyl complexes have found widespread use in organic synthesis however analogous pentadienyl chemistry is much rarer. This is likely due in part to the complex structure-reactivity manifold displayed by the carbanion. Pentadienyl anions can adopt one of three different conformations, namely W, S, and U, each of which can potentially react with electrophiles at one of three different sites, the α-, γ- and ε-carbons (Figure 1). This leads to complications with regio- and stereoselectivity.[3]

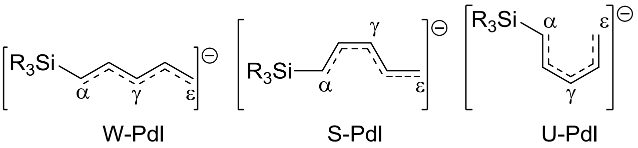

Figure 1

The work presented here explores the coordination chemistry of main group pentadienyl complexes containing donor functionalised silyl groups subsequent reactions with electrophiles.[4]

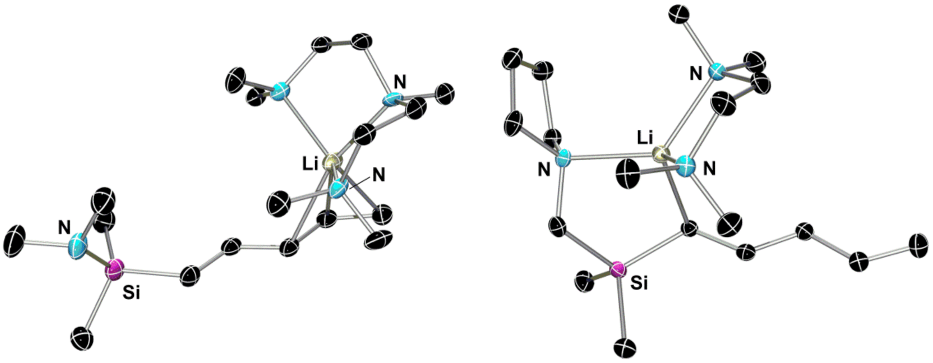

Figure 2

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Atom-efficient group 2-mediated cascade assembly of complex heterocycles

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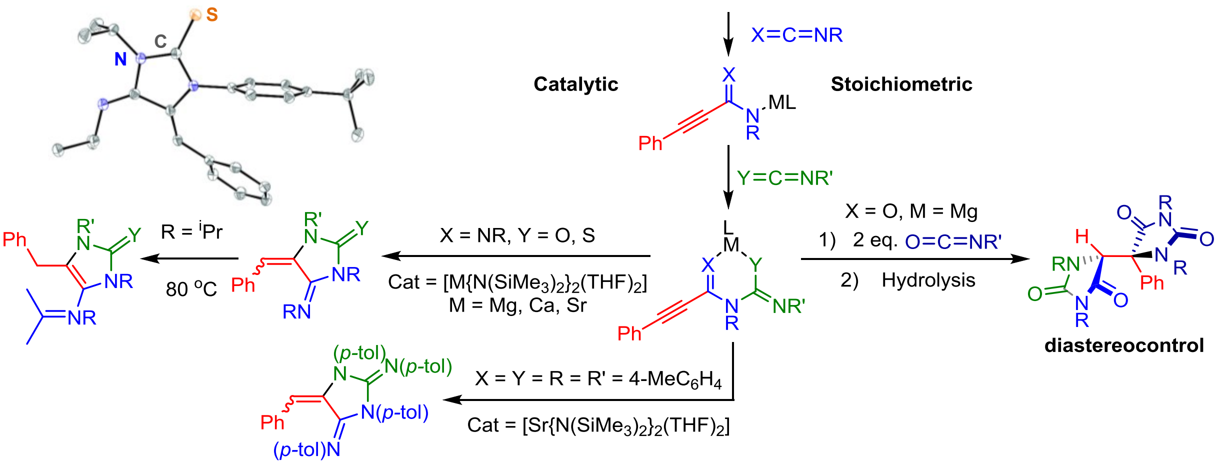
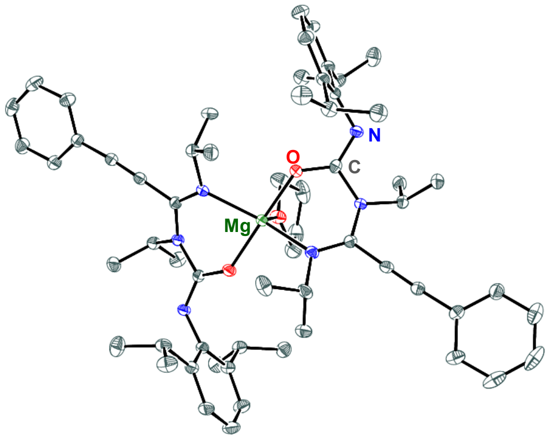
The last decade has seen the rapid expansion of group 2-catalysed transformations, from multiple bond heterofunctionalisation to dehydrocoupling via polymerisation reactions.[1] The vast majority of research in this area has focused on the intramolecular hydroamination of aminoalkenes to yield simple aza-heterocycles. The synthesis of more complex heterocycles of potential biological relevance using well-documented alkaline earth-mediated reactivity is therefore of considerable interest.



On this subject we recently reported the atom-efficient, multicomponent, diastereoselective cascade assembly of bis(imidazolidin-2,4-diones) from isocyanates and phenylacetylene using a stoichiometric amount of commercial Mg(^{n}Bu)$_2$.[2] This cascade-type reactivity, based on cumulene insertion and intramolecular hydroamination pathways has now been extended to the catalytic stepwise synthesis of a wide variety of 4-(phenylethylidene)-5-iminoimidazolidin-2-ones and their thione analogues using the simple group 2 amides precursors [M{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (M = Mg, Ca, Sr).



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Ring-opening reactions of silicon-bridged [1]ferrocenophanes bearing bulky substituents

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Ferrocenophanes and related metallocenophanes make up the broadest class of strained metal-containing rings and have attracted substantial attention in recent years, particularly as a result of their propensity to undergo ring-opening polymerisation (ROP) to yield metal-containing polymers.[1] Sila[1]ferrocenophanes with bulky substiutents such as **1** (Figure 1) are of interest as precursors to reactive ring-opened species such as silyl cations,[2] and polyferrocenylsilanes with controlled tacticity. In this presentation interesting recent results in both areas will be discussed.

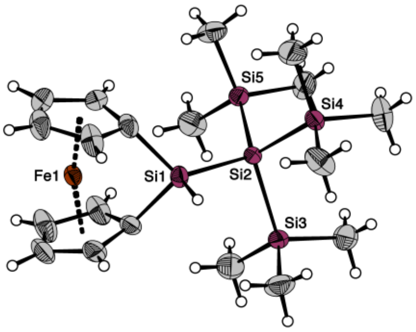

Figure 1. Structure of a $Si(SiMe_3)_3$ substituted sila[1]ferrocenophane (**1**).

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Chemical reactivity of group 14 $[E_9]^{4-}$ & 15 $[E'_7]^{3-}$ Zintl ions

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The coordination chemistry of group 14 and 15 Zintl ions has been extensively studied over the last twenty years.[1] These Zintl ions can be accesed in solution by extraction of binary alloys of the alkali metals and p-block elements into polar non-protic solvents such as ethylenediamine.

Recent studies by our research group have investigated reactions between ethylenediamine solutions of K_4Ge_9 and $[Ru(COD)(\eta^3\text{-}CH_2C(CH_3)CH_2)_2]$ yielding the novel cluster anion $[Ru@Ge_{12}]^{3-}$,[2] or $[Co(mes)_2(PPhEt_2)_2]$ resulting in the isolation of the non-spherical species $[Co_2@Ge_{16}]^{2-}$.

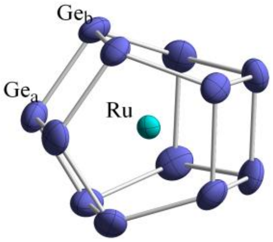

Figure 1: $[Ru@Ge_{12}]^{3-}$.

Currently, we are studying reactions between pyridine solutions of $[E'_7]^{3-}$ (E' = P and As) and different stoichiometries of VCp_2. Reactions with 0.7 equivalents of VCp_2 yield the sandwich complexes $[E'_5VCp]^{x-}$ (E' = P, $x = 1$; E' = As, $x = 1, 2$), whereas with 2.5 equivalents the products are the triple-decker compounds $[As_5V_2Cp_2]^-$ and $[P_6V_2Cp_2]^-$. These novel species have been studied by X-ray crystallography, EPR spectrometry, ESI-MS mass-spectrometry and DFT calculations.

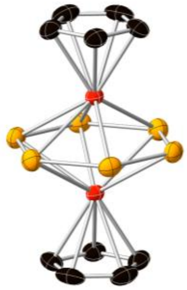

Figure 1: $[P_6V_2Cp_2]^-$

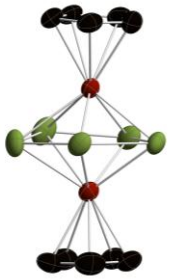

Figure 2: $[As_5V_2Cp_2]^-$

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Outer-sphere hydrogen-bond buttressing to control the strength of phenolic pyrazole metal extractants.

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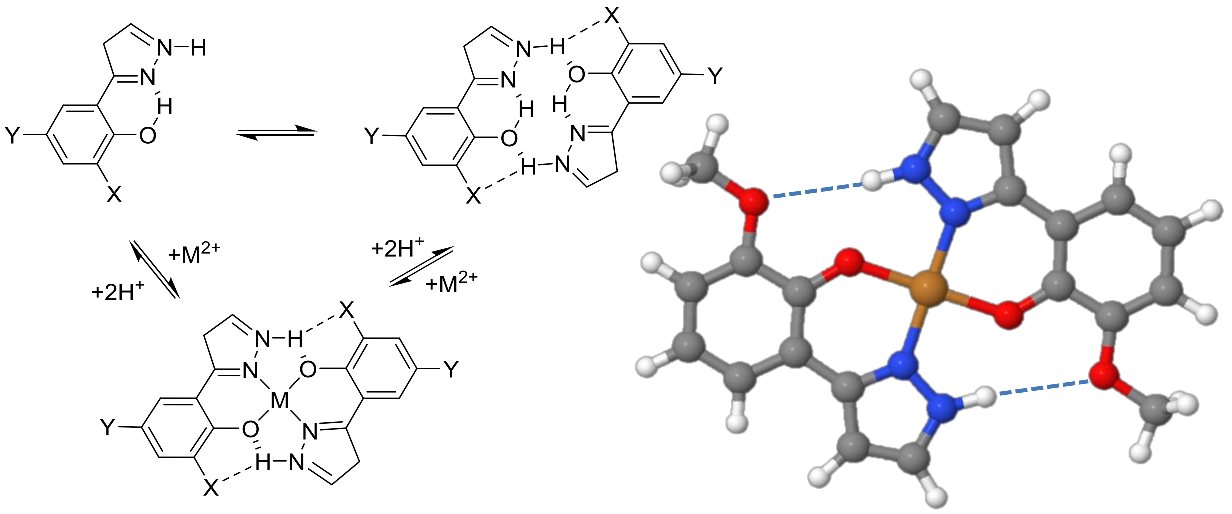
We have shown previously that substitution *ortho* to the OH group in phenolic oxime extractants of the types used in commercial recovery of 25% of the world's copper has a major influence on intramolecular H-bonding and extractant strength.[1] Phenolic pyrazoles have similar H-bonding motifs (below) and the effect of 3-X substitution on their strength as copper extractants has been studied by comparing the calculated energies of formation of the Cu-complexes in the gas phase with results from solvent extraction experiments. X-groups with H-bond acceptor properties could buttress the H-bonding between two ligands and variations of the groups' electron withdrawing/donating properties should also affect the pK_a of the pro-ligand and copper-ligand bond strengths. A comparison of the experimentally observed extractant strengths with calculated energy-minimised structures and the calculated energies of deprotonation and of formation of the copper complexes suggests that the dominant effect of X is on H-bond buttressing.



Inter-ligand H-bonding showing buttressing by 3-X substitution

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Redox switching of single molecule junction conductance using $[Co(pyterpy)_2]^{2+}$ and related complexes (pyterpy = 4'-(pyridin-4-yl)-2,2':6',2''-terpyridine).

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Molecules that undergo a switch in their electrical properties as a result of a reversible external stimulus (*e.g.* redox reaction, photoisomerisation, magnetic field) are of considerable interest in molecular electronics. We previously showed that organic redox groups (4,4'-bipyridinium, pyrrolotetrathiafulvalene) could be incorporated into metal | single molecule | metal junctions,[1-3] and we showed that they underwent structure-dependent changes in junction conductance upon redox switching. We have begun to extend these studies to completely conjugated, rigid redox-active metal complexes using the ligand 4'-(pyridin-4-yl)-2,2':6',2''-terpyridine (pyterpy), previously used by Constable *et al.* as 'extended viologens'.[4] This talk will describe the conductance behavior of the Co(II) complex as a function of redox potential, and compare this with the organic redox systems.

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$[CoW_{12}O_{40}]^{6-}$: A Long-Lived Metal-to-Polyoxometalate Charge Transfer Chromophore

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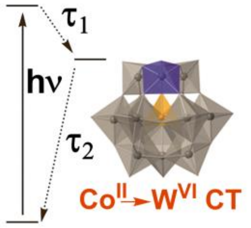

Chromophoric heterobimetallic groups supported on mesoporous substrates are promising alternatives to metal oxide semiconductors, and organic/metallo-organic chromophores in photocatalytic solar fuel production.[1] We are seeking *molecular* analogues of these metal-to-metal charge transfer (MMCT) systems, which combine robustness with the tuneability of organic chromophores. Polyoxometalates (POMs) are excellent candidates because they are oxidatively and thermally stable and can incorporate multiple heterometals. The heterometals can participate in metal-to-polyoxometalate charge transfer (MPCT) transitions,[2] but the photophysical behaviour of such compounds is still little explored. We have studied the excited state dynamics and electronic structure of a family of cobalt-containing Keggin POMs, comprising Co centred $[Co^{II}W_{12}O_{40}]^{6-}$ (**1**) and $[Co^{III}W_{12}O_{40}]^{5-}$ (**2**), Si-centred, Co-substituted $[SiCo^{II}(H_2O)W_{11}O_{39}]^{6-}$ (**3**) and $[SiCo^{III}(H_2O)W_{11}O_{39}]^{5-}$ (**4**), and the dicobalt anion $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$ (**5**). Anion **1**, based on a centrally located tetrahedral Co^{II} atom, undergoes a Co^{II}-to-polytungstate charge transfer upon 400 nm excitation, and at 1.7 ns has a far longer lived excited state than any POM MPCT chromophore studied so far. However, anion **2**, where an octahedral Co^{II} is substituted into the tungstate skeleton, shows a charge transfer lifetime of only 1.3 ps. An intermediate lifetime (150 ps) is seen for the dicobalt species **5**, and short lived, non-CT excited states for the Co^{III} systems **2** and **4**. The long-lifetime of **1** has been rationalized based on the increased ground-to-excited state structural change permitted by the central site, and a putative valence trapped intermediate.

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DYE-SENSITIZED NiO PHOTOCATHODES FOR SOLAR DEVICES

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Efficient dye-sensitized photocathodes offer new opportunities for converting sunlight to storable energy cheaply, sustainably and more efficiently.[1] We are developing dye-sensitized NiO cathodes both for use in dye sensitized solar cells (DSSCs) and for the photo-reduction of protons or water to hydrogen. Tandem DSSCs are a promising modification to existing n-type cells. In these cells a dye sensitized photocathode is used in place of the passive counter electrode, enabling the absorption of a broader range of photons. For the reduction of water several homogenous catalysts have been reported in the literature that utilise a Co-metal centre.[2] We are combining the lessons we have learnt regarding the kinetic and thermodynamic limitations to producing photocurrent and our understanding of photocatalysis in solution to the more challenging problem of using a heterogeneous semiconductor-catalyst system for the splitting of water in which the catalyst is adsorbed onto NiO.

We will report recent results from our investigations into:

- Dynamics of charge transfer in DSSCs. We have used a combination of techniques including photoelectrochemical measurements, DFT calculations and ultrafast Transient Absorption (TA) and Time-Resolved Infrared (TRIR) spectroscopies.[3]

- Splitting of water using Co catalysts. The evolved products are able to be continuously detected by our automated GC rig that utilises an in-flow approach.

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Mechanism of Substrate and Oxidant Activation by Ru^{III}(edta) in Mosaics of Homogeneous Catalysis

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Ru-edta complexes have been extensively studied over the years because they enjoy a combination of unique properties: (a) the number of stable and accessible oxidation states they posses and (b) high lability towards aqua substitution reactions that affords a straight forward synthesis of mixed ligand complexes that has allowed to explore a wide variety of areas including catalysis and bioinorganic applications.[1] In this lecture some recent results of the mechanistic studies achieved by the application of fast kinetic techniques to the reactions of $[Ru^{III}(edta)(H_2O)]^-$ with different oxidants containing an O-O bond that lead to the formation of various catalytically active intermediate species viz. $[Ru^{III}(edta)(OOH)]^{2-}$, $[Ru^{IV}(edta)(OH)]^-$ and $[Ru^{V}(edta)(O)]^-$ are presented, and their effectiveness towards the oxidation of some compounds of biological significance are highlighted.[2,3] Furthermore, various mechanistic aspects of the oxidation of organic substrates catalyzed by the Ru-edta complexes are also covered in this talk.[5-7] The purpose of this talk is to shed light on the detailed mechanistic understanding of Ru(edta) catalyst system for the oxidation of biologically important substrates by H_2O_2. Our results may shed light towards mechanistic understanding of the important biological redox processes carried out by heme oxygenases, such as cytochrome P450, cytochrome c oxidase, peroxidases and catalases, using hydrogen peroxide.

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METAL COMPLEXES AS POTENTIAL ANTI-CANCER AGENTS

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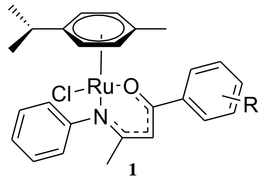
The reducing nature of hypoxic cancer cells means the drugs can potentially be administered in a less active form and reduced *in vivo* potentially increasing the activity.[1, 2] This project builds on previous work and presents a series of novel ruthenium(II) arene complexes primarily incorporating β-ketoiminate ligands (**1**).[3, 4] Comparisons have also been made with the ruthenium β-diketonate complex (**2**) and their iridium(III) Cp* analogues (**3** and **4**).[5, 6] The data presented will include cell line results against a range of carcinomas, with selected compounds tested under both normoxic and hypoxic conditions. Trends will be discussed using hydrolysis studies, the relative hydrophobicities, the degree of single and double strand DNA damage using the Comet Assay, apoptosis studies using flow cytometry and finally thioredoxin reductase inhibition. Results show the (*N,O-*) complexes have the highest activities and the most potential as an anti-cancer agent.



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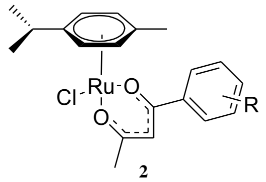

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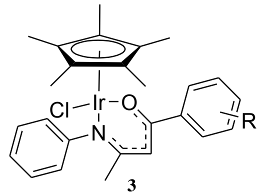

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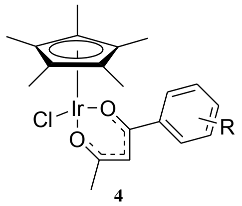

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Multi-targeted organometallic anticancer complexes with redox mechanisms of action

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Cisplatin (CDDP) and its derivatives carboplatin and oxaliplatin are now the most widely used anticancer drugs (>50 % of chemotherapeutic regimes). Their antineoplastic properties rely on interactions with DNA, which in turn activate apoptosis. DNA-targeting for cancer treatment results in a low selectivity approach with consequent side effects and a high incidence of resistance. New generations of metal chemotherapeutics are urgently needed to combat resistance, reduce side-effects and expand the range of treatable cancers. Recent work has demonstrated that organometallic complexes offer this potential.[1]

Chemically tailored ruthenium-, osmium- and iridium-based compounds can outperform CDDP, and most importantly, can exert their activity through non-DNA mechanisms of action (MoAs). Organometallic piano-stool complexes, can target mitochondrial pathways and induce redox effects as part of their MoA.[2] Iridium complexes have the unprecedented ability to generate H_2O_2 by catalytic hydride transfer and to produce superoxide in ovarian cancer cells.[3] Interestingly, the use of low non-toxic doses of the redox modulator L-buthionine sulfoximine can potentiate the activity of ruthenium/osmium and iridium compounds by up to a 16-fold.[1] Co-administration of such modulators opens a ground-breaking possibility of combination therapy for metal-based complexes which has so far been reserved for classical organic drugs. In addition to developing novel therapies for parental cancers, we aim to show that such manipulation of the levels of reactive oxygen species (ROS) may also provide a highly effective strategy for treating CDDP-resistant cancers.

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Triplex helicates; asymmetric self-assembly of potent, selective anticancer compounds

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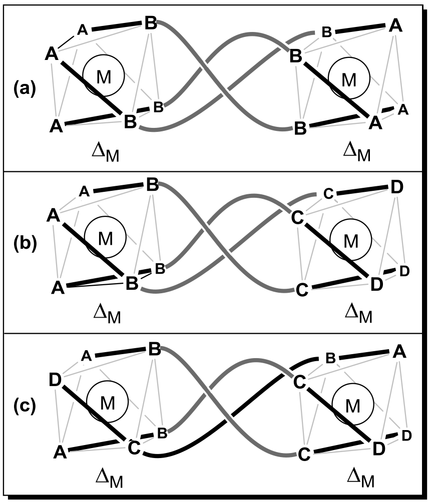

Protein α-helices in nature are key in many interations;[1] however as therapeutic agents they tend to display poor pharmacokinetics and so synthetic mimics are being developed.[2] Bis(bidentate) ligands (**AB**–**BA**) can be self-assembled over a metal scaffold to form helicates[3] **(a)** which are of an appropriate size shape and charge, and some examples bind to biomolecules,[4] but they rarely contain functional groups, form as a racemic mixture which is hard to separate and have high symmetry.[5]

Recently we have developed a new system known as *Flexicates*, which do not rely on the helication principle. These highly symmetric compounds form in an optically pure manner, are water stable, easily functionalised and have shown great potential as both antimicrobial[7] and anticancer agents,[8] with the exact nature of the activity observed dependant on the structure of the ligand.

If however *directional* ligands (**AB→CD**) are employed, Head-to-Head-to-Head [HHH] and Head-to-Head-to-Tail [HHT] configurations are possible.[9] We have recently reported a new [HHH] system which assembles C_3-symmetric homohelical heterobimetallic helicates **(b)** using a chiral directional ligand.[10] Broadly speaking selective self-assembly, such as that required to make the optically pure C_1-symmetric [HHT] helicate, presents a great challenge for (metallo)supramolecular chemistry.

Most excitingly we have devised functional C_1-symmetric [HHT] *triplex helicates* **(c)** using a second carefully designed directional ligand. *Triplex helicates* are found to show exceptional selectivity and activity as anticancer agents, with some very interesting leads to possible modes of action.

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Triphenylphosphonium-conjugated gold nanoparticles: potential nanocarriers for mitochondria-targeted therapeutics.

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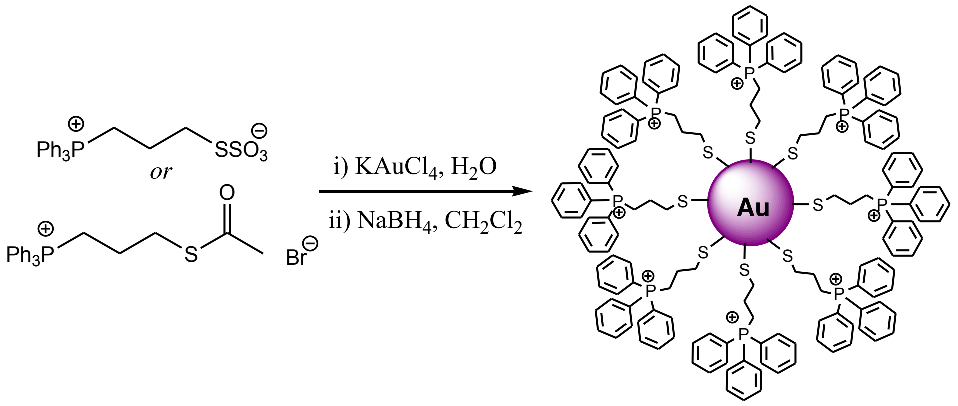
Mitochondria dysfunction is associated with a number of diseases ranging from neurodegenerative disorders, such as Alzheimer's and Parkinson's disease, to diabetes and cancer, and there is increasing awareness of the importance of targeting drugs to this organelle. Lipophilic cations, especially phosphonium species, have been found to be extremely valuable for mitochondria-targeted therapeutics and diagnostics.

We hypothesise that attachment of phosphonium compounds to the surface of gold nanoparticles (AuNPs) would facilitate the absorption of the nanoparticles by cells. With this goal in mind we have synthesised of a series of phosphonioalkylthiosulfate zwitterions and ω-thioacetylalkylphosphonium salts that behave as masked thiolate ligands, in which the thiolate group is 'protected' as a thiosulfate or thioacetate group, respectively. Upon contact with gold surfaces, cleavage of the sulfur–sulfur or sulfur-carbon bonds in the thiosulfate and thioacetate species generates thiolate anions *in situ* leading to water-soluble, cationic, phosphonium-functionalised AuNPs.

The phosphonioalkylthiolate ligands and associated AuNPs have been characterised using X-ray crystallography, XPS, LDI-ToF-MS and ^{31}P NMR spectroscopy. Transmission Electron Microscopy (TEM) revealed the formation of spherical particles with diameters in the range 3 – 5 nm. Furthermore, TEM investigations show that the triphenylphosphonium-conjugated AuNPs are readily taken-up by the mitochondria of PC3 prostate cancer cells.



Copper-Containing *Lytic Polysaccharide Monooxygenases*: A New Face for Biomass Breakdown

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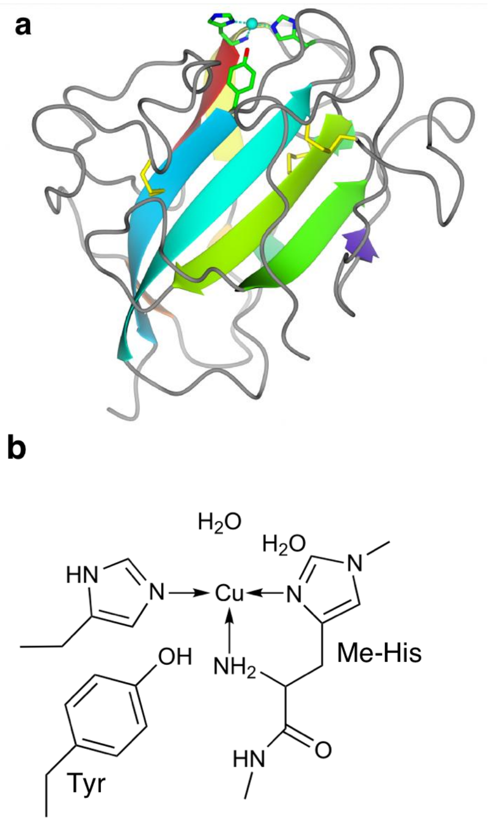
Biopolymers such as cellulose, chitin and diverse marine polysaccharides are widespread and abundant. They offer the potential to become *the* primary feedstocks in the production of biofuels and/or sustainable commodities. Notwithstanding this potential however, the chemical and mechanical resistance of these biopolymers constrains their commercial viability to a significant extent. In this regard the recent discovery of a class of enzymes now known as *lytic polysaccharide mono-oxygenases* (LPMOs) is a breakthrough. Using an oxidative mechanism LPMOs are capable of potentiating the crystalline surfaces of polysaccharides such that they are then tractable to conversion through to sugars and bioethanol. In other words, they allow cellulose to be fermented.Our discovery of LPMOs and their novel copper active site will be described,[1,2] particularly the genomic discovery of LPMOs and their structural and spectroscopic properties (EPR and XANES).[3]

LPMOs have a copper active site that is located near the centre of an extended flat face, where the face is presumed to interact with the crystalline surface of the substrate (**Fig. a**). X-ray crystallographic structural details of the Cu-active site were first fully shown in a cellulose-active fungal LPMO from *Thermoascus aurantiacus* in which a single copper ion is chelated by two nitrogen atoms of the N-terminal histidine (through the NH_2 terminus and an N-atom of the side chain) and a further nitrogen atom of another histidine side chain in an overall T-shaped N_3 configuration coined as the *histidine brace* (**Fig. b**). This active site occurs only in one other known enzyme, *particulate copper methane-monooxygenase*, which carries out the oxidation of methane. The copper *histidine brace* structure is therefore unusual insofar as it appears in enzymes which carry out oxidations with very high activation barriers. The potential reasons for this will also be discussed.[4]



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Activation of Alkynes with $B(C_6F_5)_3$: Intramolecular cyclisation reactions and rearrangements.

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The strong Lewis acid $B(C_6F_5)_3$ has found extensive applications in organic and organometallic chemistry. In recent years, $B(C_6F_5)_3$ has been employed as the Lewis acid component in frustrated Lewis pair (FLP) chemistry.[1] Here we discuss the use of $B(C_6F_5)_3$ to promote intramolecular cyclisation reactions of propargyl amides to generate oxazole (**II**) heterocycles (Figure 1).[2]

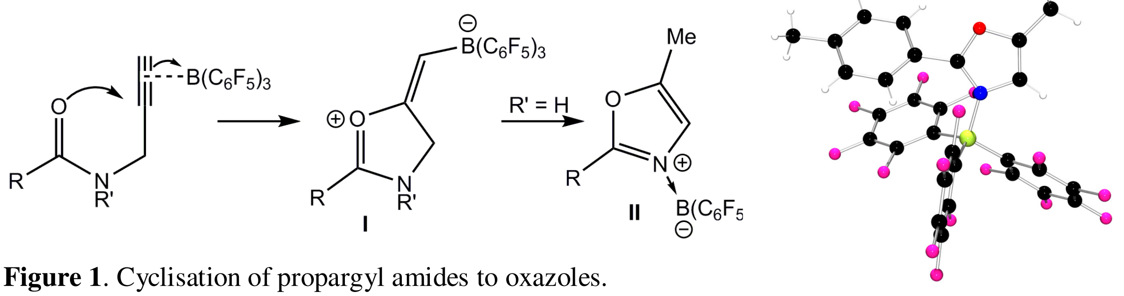

Figure 1. Cyclisation of propargyl amides to oxazoles.

The initial activation of the alkyne π-bond in propargyl esters also permitted us to uncover a novel synthetic route to functionalised allyl-boron compounds which we have subsequently utilised as allylation reagents with aldehydes, opening a new route to highly functionalised organic compounds.[3]

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Bond activation and CO_2 fixation employing an iridium^{I} hydroxide

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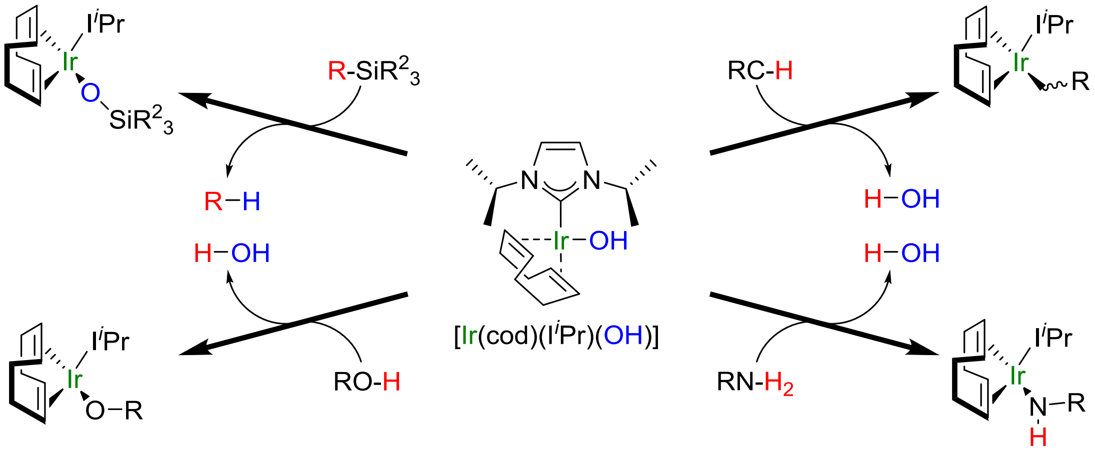
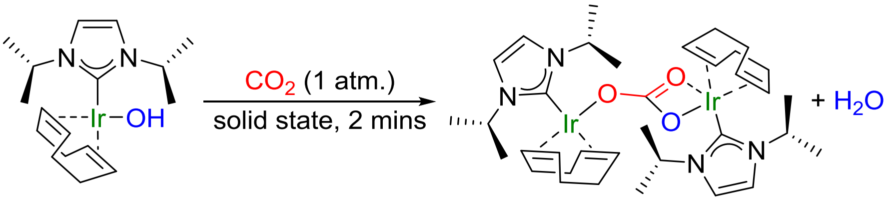
General methods are reported for the preparation of a family of [Ir(cod)(NHC)(OH)] complexes (cod = 1,5-cyclooctadiene, NHC = *N*-heterocyclic carbene). The Ir^{I}-hydroxide motif is shown to be a valuable synthon for bond activation and its activity towards various organic substrates has been explored. The Ir^{I}-hydroxide is able to deprotonate N-H, O-H and C-H bonds to afford valuable organometallic species.



Furthermore, the reactivity of a number of Ir^{I} complexes towards CO_2 is explored using [Ir(cod)(NHC)(OH)] as a key synthon. CO_2 insertion into Ir-O and Ir-N bonds proved facile, yielding a number of Ir^{I}-carbonates and -carbamates. Most importantly, reaction between CO_2 and Ir^{I}-hydroxide led to isolation of the novel complex [{Ir^{I}}$_2$-(μ-κ^1:κ^2-CO_3)] under very mild conditions.



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Activation Reactions of Oxygen-Containing Organic Molecules by High Valent Metal Halides of Groups 5-6

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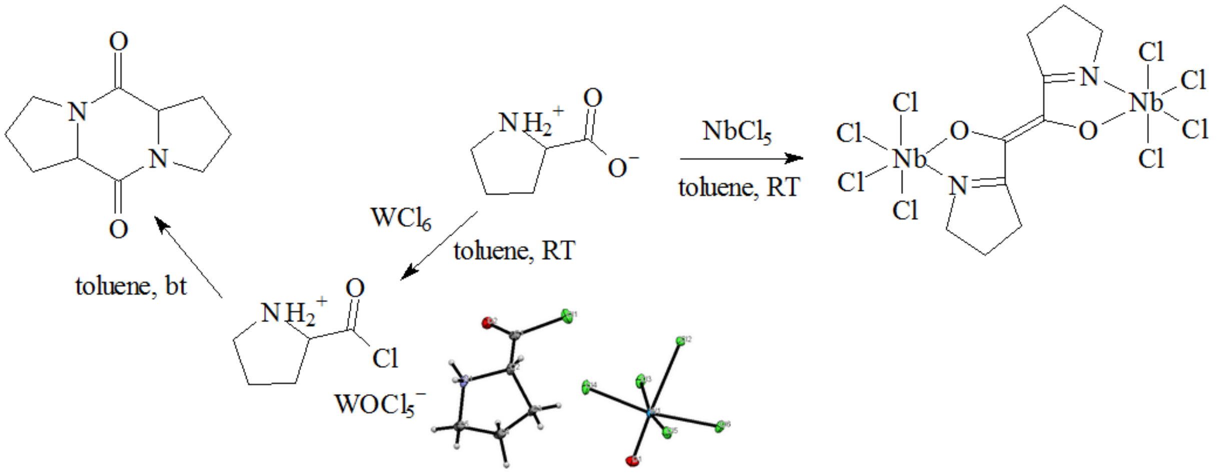
NbF_5, $NbCl_5$ and WCl_6 are commercial non expensive compounds, which have found large application as catalytic precursors in synthetic organic chemistry. However, the direct interactions of such transition metal halides with stoichiometric amounts of organic reactants has been limitedly explored. Our recent, systematic investigation on the chemistry of NbF_5, $NbCl_5$ and WCl_6 with oxygen donors has provided evidences of unusual features: 1) such halides are capable of directing mild conditions transformations, which are not commonly achieved by means of other transition metal compounds;[1] 2) NbX_6^- (X = F, Cl) and $WOCl_5^-$ are easily obtained and may allow the isolation of unstable organic cations.[2] Examples will be provided with particular reference to natural α-aminoacids, such as *L*-proline (see Figure).[3]



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Covalency and bond strength in heavy element compounds from the quantum theory of atoms in molecules

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The extent to which the lanthanides and actinides bond covalently to other elements is of great fundamental interest and also of relevance to, for example, minor actinide partitioning technologies in nuclear waste treatments. Quantum chemistry allows the detailed study of the electronic structure of f element compounds, and provides many different methods for assessing covalency, including partial atomic charges, orbital compositions and spin densities. None of these analysis tools is ideal, however, in part because they are typically not rooted in physical observables. By contrast, the quantum theory of atoms-in-molecules (QTAIM) approach of Bader and co-workers [1] is based on topological analysis of the electron density, lending it a rigour not always associated with other approaches. It can also offer significant insight into chemical bonding.

In the last few years, we have employed the QTAIM extensively to analyse a variety of lanthanide and actinide molecular electron densities [*e.g.* 2-6]. In this presentation I will explore some results from these studies, and in particular discuss the application of the QTAIM to the strength of actinide–element bonds [7].

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New Insight into Heteroatom-Nanographenes and their Applications

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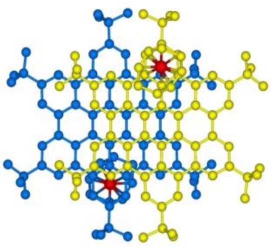
http://chemistry.tcd.ie/staff/people/sd/sylvia.html.



This paper describes the synthetic development of heteroatom-polyaromatic materials and explores their properties in a journey from soluble molecular graphenes to ligands and from opto-electronics to upconversion. Opto-electronic and photovoltaic devices depend at a fundamental level on the interconversion of light and electrical energy. In optoelectronic devices, electrically injected charge-carrier species (electrons and holes) generated in an organic semiconductor recombine to form localised excited states (excitons) which emit light on relaxation. If the HOMO-LUMO gap is 1.5-3.2 eV then the emission is in the visible region (λ 380 – 780 nm) and ideally suited to efficient OLEDs. In photovoltaic systems, excitons are generated on the absorption of light and it is the separation of these species, driven by the attraction of electrons and holes to appropriately charged electrodes, that gives rise to the electrical current. The strong synergies in the processes involved, translate to the design features of the organic components in these two applications and there is growing evidence to suggest a role for graphene-based materials.

This paper explores our investigations into the synthetic processes involved in developing a range of N-doped graphenes. We have examined the effect of methoxy and alkyl and bromo substitution on the oxidative cyclodehydrogenation of a series of heteroatom-doped polyphenylenes such that the resulting systems differ in their degree of N-doping (2, 4 or 6 nitrogen atoms), the number and relative positions their subsitutents and the size of their aromatic platforms. The consequences of these changes and the processes by which occur are examined. They are found to influence CC bond formation on cyclodehydrogenation and the photophysical, electrochemical and supramolecular properties of the resulting ligand materials. In systems with the same comparative aromatic platform the combination of 4N atoms and 6 MeO substituents gives rise to the smallest HOMO-LUMO gap (2.3V) Each system is highly fluorescent with emission quantum yields as high as 53%, lifetimes in the ns region and significant solvatochromism observed. Where MeO are present, there is a new inherent intermolecular order and a marked preference for head-to-tail dimeric stacking in the solid-state.

Band Gap Expansion, Phase Change Behaviour and Low-Voltage Induced Crystal Oscillation in Low-Dimensional SnSe

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In common with rocksalt-type alkali halide phases and also semiconductors such as GeTe and SnTe, SnSe forms all-surface two atom-thick low dimensional crystals when encapsulated within single walled nanotubes (SWNTs) with diameters below ~1.4 nm. Whereas previous Density Functional Theory (DFT) studies indicate that optimised low-dimensional trigonal HgTe changes from a semi-metal to a semi-conductor, low-dimensional SnSe crystals typically undergo band-gap expansion. In slightly wider diameter SWNTs (~1.4-1.6 nm), we observe that three atom thick low dimensional SnSe crystals undergo a previously unobserved form of a shear inversion phase change resulting in two discrete strain states in a section of curved nanotube. Under low-voltage (i.e. 80-100 kV) imaging conditions in a transmission electron microscope, encapsulated SnSe crystals undergo longitudinal and rotational oscillations, possibly as a result of the increase in the inelastic scattering cross-section of the sample at those voltages.[1]

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CVD of Thermoelectric Materials from Single Molecule Precursors

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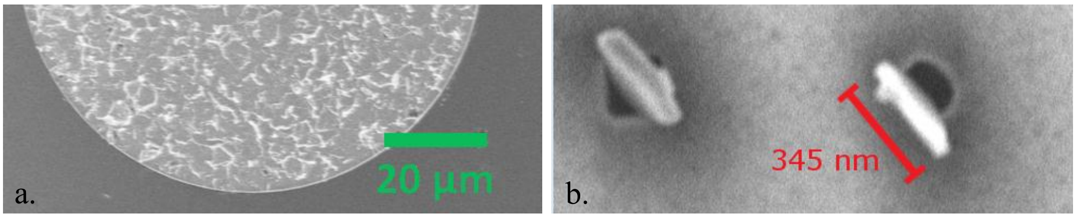
Solid state thermoelectric materials have the potential to provide clean and sustainable sources of electrical power, by exploiting existing temperature gradients in a multitude of everyday environments. The barrier to the widespread adoption of this technology is the low thermoelectric efficiency of the current generation of materials.[1] Group 15 chalcogenides, in particular Bi_2Te_3 and its doped derivatives, are among the most promising of these materials at lower temperatures. It has been demonstrated that nanostructuring materials can lead to a large increase in their theoretical thermoelectric efficiencies.[2]



a. *Film of Bi_2Te_3 crystals lying flat in a micron-scale template;* ***b***. *Single Bi_2Te_3 crystals standing on end in a nano-scale template*

We report a methodology for the deposition of individual nanocrystals of Bi_2Te_3 and Sb_2Te_3 by chemical vapour deposition (CVD). CVD is a low cost and scalable technique, though often requires toxic gases as precursors. A safer and more convenient method is to use a single molecular precursor which contains both the required elements. Synthetic pathways to molecular CVD precursors for Group 15 chalcogenides were investigated. The unusual bismuth telluroether complex $[BiCl_3(Te^nBu_2)_3]$ and the organometallic species $MeSb(Te^nBu)_2$ were synthesised, characterised, and found to be excellent precursors for the CVD of high purity Bi_2Te_3 and Sb_2Te_3 respectively. Thin films of these materials with highly preferred c-axis orientation of the hexagonal crystallites were obtained. Using lithographically patterned substrates, these films can be confined to micron-scale or nano-scale wells creating a patterned array of the material; in wells of below 200 nm single crystals selectively deposit into each well, with the opposite orientation to that observed in larger wells or thin films.

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Bio- and Organometallic-Catalysis: Quest for the GRAIL.

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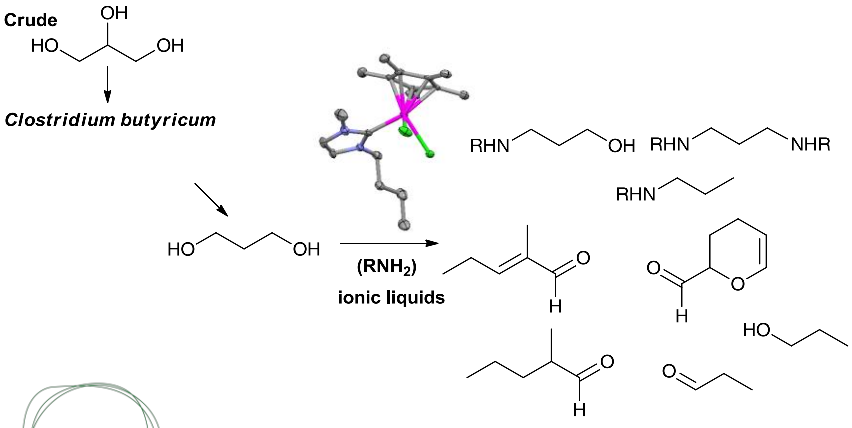
We are combining bio- and chemo-catalytic methods in order to convert biomass waste into chemicals and fuels.[1]

The combination of whole cell biocatalysis and organometallic catalysis enables the transformation of crude bio-renewable feeds into value added chemicals.[2,3] Utilisation of the glycerol by-product from biodiesel manufacture is an important factor in fuel cost. We have shown that the combination of fermentation and hydrogen transfer catalysis can yield a range of chemical products at mild conditions from crude glycerol.[4,5] Task specific ionic liquids facilitate the extraction of products from fermentation broths, and can be tuned to increase the rate of desirable reactions. Ir(III) catalysts with NHC ligands give tunable activity coupled with excellent stability and poison resitance.[5,6]



GRAIL
Glycerol Biorefinery Approach for the Production of High Quality Products of Industrial Value

Project funded by the FP7 of the European Union under the Grant agreement no: 613667.

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Ruthenium hydrides pave the way to time-resolved NMR spectroscopy

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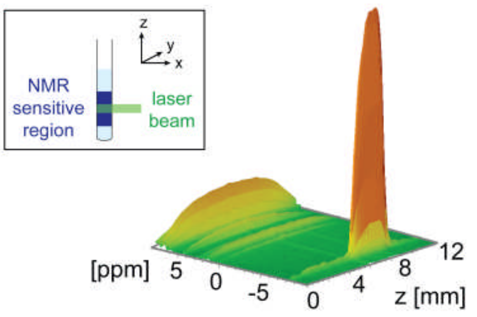
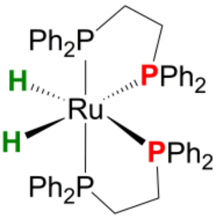
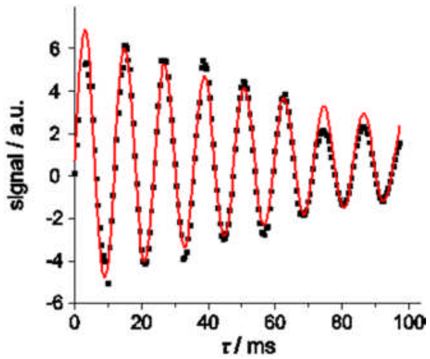
Pump-probe time-resolved techniques have allowed extremely fast chemical reactions to be understood as illustrated by Zewail's seminal studies of femtochemistry.[1] Whilst many probe-methods have been successfully exploited, the nature of their data often provides limited structurally diagnostic information. By contrast, time-resolved NMR spectroscopy could be a powerful tool for providing extensive structural information in multiproduct processes.

Here, we report that the combination of laser pumping with synchronized NMR detection in conjunction with *para*-H_2 induced polarization[2] allows nanomoles of product to be detected on microsecond timescales. By the use of ruthenium dihydride complexes,[3] which photochemically add *p*-H_2, we prepare the products in a hyperpolarized nuclear spin-state which enhances the observed NMR signal. We then investigate the time-evolution of this enhanced NMR signal as a function of the delay, τ, between the laser pump and NMR probe. As a result, an oscillatory behaviour diagnostic of the products' spin topology is observed and the product distribution is readily differentiated by each compound's unique frequency response. In addition, our pump-probe system allows the distinction between thermal and photochemical reactivity by chemical shift mapping. Furthermore, we can diversify secondary reaction pathways as deriving from one-photon/two-ligands *versus* two-photon/two-ligands loss mechanism.



CHEMICAL SHIFT MAP





OSCILLATION OF SPIN-STATE

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Ruthenium-catalysed dehydrogenation of methanol

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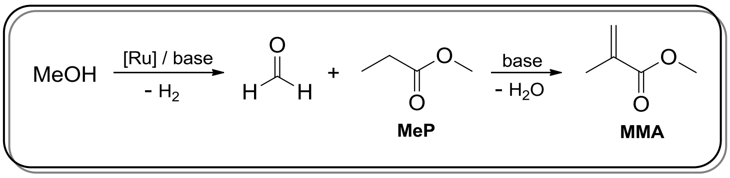
The ALPHA technology is an innovating two-step process for the current large scale production of methyl methacrylate (MMA), involving methoxycarbonylation of ethene to methyl propanoate (MeP) followed by condensation with formaldehyde.[1] As an alternative second step, we investigated the possibility of performing the one-pot α-methylenation of methyl propanoate *via* catalytic dehydrogenation of methanol for the *in situ* production of anhydrous formaldehyde.[2]



We have reported that catalytic hydrogen production, together with the formation of aldehydes, can be achieved from a wide range of alcoholic substrates using the $[RuH_2(X)(PPh_3)_3]$ catalyst (where X = N_2, PPh_3 or H_2) in the presence of a base.[3] This catalytic system is complicated by a number of side reactions including a decarbonylation reaction of the formed formaldehyde which generates a carbonyl complexes such as $[RuH_2(CO)(PPh_3)_3]$ that we also reported to be active as a dehydrogenation catalyst.

In this presentation, we shall focus on the mechanism of dehydrogenation for $[RuH_2(CO)(PPh_3)_3]$ and especially on the experimental determination of kinetic isotope effects (KIEs) for the dehydrogenation and decarbonylation reactions using $[RuH_2(X)(PPh_3)_3]$.[4]

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New Electrochemical Methods for Understanding Biological H_2 Catalysis.

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Redox-metalloenzymes are extremely inspirational catalysts for developing renewable energy technologies. Microbes produce highly efficient and active H_2 enzymes (hydrogenases) to enable them to achieve photosynthetic hydrogen production or to use hydrogen as a fuel. Rather than relying on Pt, hydrogenases contain earth-abundant transition metals at the H_2-reaction centre so they are inspirational 'green energy' systems. Recent studies on both [NiFe]-hydrogenase single site mutants[1,2] and [FeFe]-hydrogenase synthetic analogues[3] have highlighted the essential role that the iron-sulfur electron transfer relay plays in controlling the chemistry at the bimetallic active site. We are developing a new alternating-current electrochemical technique to provide a far more detailed insight into how the kinetics and thermodynamics of electron transfer ultimately tunes enzyme active site chemistry.[4]

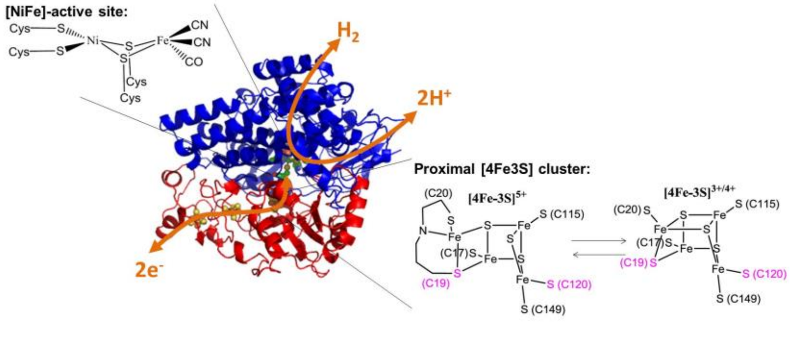

Figure 1: Structure of *Escherichia coli* hydrogenase-1 showing the [NiFe] bimetallic active site and the iron-sulphur cluster 'proximal' to the active site. It is the unusual redox properties of this cluster rather than the active site ligand field that controls O_2-reactivity.

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The importance of being consistent: Manganese oxidation states in biological water oxidation

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A fundamental mechanistic question regarding the splitting of water by photosynthetic organisms is what are the oxidation states of the four manganese ions that comprise the inorganic Mn_4CaO_5 core of the oxygen-evolving complex and how do they change along the catalytic cycle. Two competing paradigms are the so-called “high oxidation state scheme”, where the Mn oxidation states are assumed to reach an all-IV configuration immediately prior to the final O-O bond formation step, and the “low oxidation state scheme” that differs by a total of two metal unpaired electrons, i.e. with Mn oxidation states of III, III, IV, IV in the catalytic step before O_2 evolution. Which scheme is correct? Without a definitive answer to this question, both the atomistic understanding of the mechanism of biological water oxidation and the development of electronic design principles for synthetic manganese-based water oxidizing catalysts will remain elusive.

We address this question through a comparison of the two oxidation state schemes using for the first time a common structural and methodological approach: building upon the most recent crystallographic information on photosystem II, models are constructed and examined for every oxidation state assignment in the first four catalytic states of the oxygen evolving complex. The models are evaluated using extensively benchmarked theoretical methods of proven accuracy against unambiguous state-specific data from EXAFS and especially EPR/ENDOR (ground spin states and ^{55}Mn hyperfine coupling constants). The results demonstrate that the phenomenology of the first four catalytic steps can be readily accommodated within the high oxidation state scheme, by adopting a single structural motif and protonation pattern that evolves smoothly within the catalytic cycle, satisfying all experimental constraints and reproducing all spectroscopic observables. It is impossible to achieve the same spectroscopic consistency with low oxidation state scheme models. The result converge towards a radical-based mechanism for nature’s water oxidizing catalyst.

Optimising SABRE: Applications with biologically-relevant substrates

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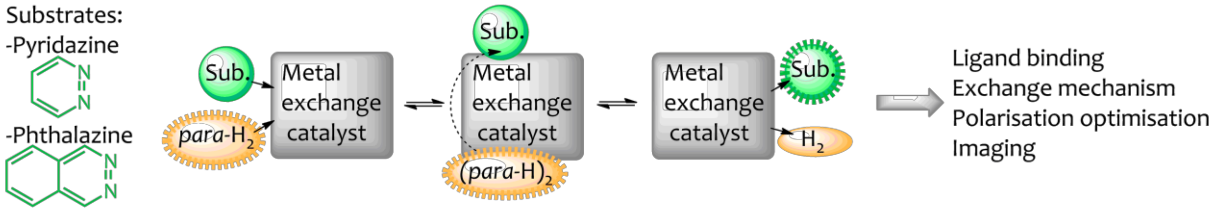
Centre for Hyperpolarisation in Magnetic Resonance, York Science Park, University of York, Heslington, York, United Kingdom, YO10 5NY

Parahydrogen induced polarisation (PHIP) is used to increase the sensitivity of nuclear magnetic resonance (NMR) spectroscopy. The inherent insensitivity of NMR is caused by the very small population difference that exists between the nuclear spin alignments that are probed. *Para*-H_2 is traditionally used to 'overpopulate' (hyperpolarise) specific spin alignments in hydrogenation products and thereby increase NMR sensitivity.

In this study, *para*-H_2 is used to hyperpolarise **pyridazine** and **phthalazine** - two dinitrogen-containing organic substrates, both of which are **biologically-active drug precursors** used in the treatment of cancer and Alzheimer's. The iridium complex [IrCl(COD)(IMes)] reacts with the substrate and *para*-H_2 to form the 'active catalyst', $[IrH_2(IMes)(substrate)_3]Cl$ in these studies. Whilst the substrate is bound to the metal at low-magnetic field, polarisation transfer flows from the *para*-H_2 derived hydride ligands to the substrate, after which it can dissociate from the catalyst. Through the processes of **substrate and *para*-H_2 ligand exchange**, a build-up in concentration of hyperpolarised substrate is achieved in solution. This effect has been termed 'signal amplification by reversible exchange' (SABRE). In this study, SABRE has resulted in the unbound forms of chemically-unchanged pyridazine and phthalazine showing ^{1}H-NMR signal enhancements that exceed 1000-fold.



The aim of this research is to **optimise the efficiency of polarisation transfer** from *para*-H_2 to these substrates. The 'contact time', during which substrate and hydrogen are bound to the iridium-exchange catalyst, can be optimised by altering the rates of substrate and hydrogen ligand exchange. The resulting transition metal complexes of pyridazine and phthalazine are characterised, and shown to undergo **ligand loss as well as 1,2-metallotropic shifts** between the contiguous nitrogen donor atoms. The **ligand exchange mechanism** is elucidated through kinetics and thermodynamic studies using exchange spectroscopy (EXSY) and shown to be dissociative. A strategy to optimise the SABRE effect is detailed.

SABRE promises to be applicable to magnetic resonance imaging (MRI) by enhancing the signal strengths of biologically-important substrates. The potential to use pyridazine and phthalazine-containing drug molecules as hyperpolarised contrast agents will be discussed. This **novel imaging method** could lead to the detection of diseases, like cancer, at earlier stages, which has the potential to save lives.

Photochemistry, Spectroscopy and Supercritical Fluids

Michael W George

School of Chemistry, University of Nottingham, Nottingham NG7 2RD

This lecture will show how the combination of photochemistry and fast spectroscopy in conventional and supercritical fluids is used to shed new light on chemical processes. The aim is introduce each of these approaches and report recent results to show they can be used to contribute to the area of reaction mechanisms following areas particularly using time-resolved IR spectroscopy. Recent results using time- resolved XAFS will also be presented. The lecture will focus on (i) Organometallic Alkane Complexes, Noble Gas Complexes and C-H Activation; (ii) how spin states affect chemical reactivity and (iii) how the use reactions of singlet oxygen ($^1O_2$) in an industrial setting can contribute to the area solar fuels. Although this lecture is primarily centred on inorganic mechanisms, it will also touch focus on other areas using a combination of spectroscopy and supercritical fluids ranging from transportation in Carbon Capture and Storage (CCS) to the production of nanomaterials.

Group 15 Element Triple Bonds and Reactive Intermediates

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http://web.mit.edu/ccclab

We have learned how to make triple bonds between transition metals (molybdenum, niobium) and the group 15 elements nitrogen, phosphorus, and arsenic, using the elements themselves as the source of the triply bonded atom. In the case of nitrogen, this means splitting the strong N-N triple bond of the N_2 molecule, while in the case of phosphorus, it is the P_4 tetrahedron of elemental, molecular phosphorus that is broken down. Considering the dichotomy between triply bonded N on the one hand, and P on the other that prefers to form three single bonds, we set out to synthesize thermal molecular precursors to the P_2 molecule which, due to its high-energy triple bond, we supposed would be a reactive intermediate. Our first approach to generate P_2 was via niobium chemistry, and thereafter we turned to photochemical methods for P_2 generation from white phosphorus in the presence of trapping agents. Currently we are investigating anthracene as a protecting group for the reactive pi bonds of P_2, in what represents an organic synthesis approach to the chemistry of P_2 transfer reactions. Bound up in this investigation was our discovery of new thermal precursors to singlet phosphinidenes (the phosphorus analogs of carbenes) as a further example of a reactive phosphorus intermediate. We are making efforts to characterize both the gas- and solution-phase properties of the key reactive intermediates featured in this work.

Boryl Ligands and Their Roles in Transition Metal Catalysed Borylation Reactions

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Boryl ligands in transition metal boryl complexes play important roles in many catalytic processes including hydroboration, diboration, and other boron addition reactions to unsaturated organics as well as borylation of carbon-halogen and carbon-hydrogen bonds in arenes and alkanes.

In this Talk, we discuss selected aspects of metal boryl (M-BR_2) chemistry pertaining to the role of boryl ligands in various catalytic processes. The exceptionally strong sigma-donor properties of boryl ligands and their related nucleophilic/electrophilic behaviors will be highlighted.

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Chemicals from Waste Bio - Oils

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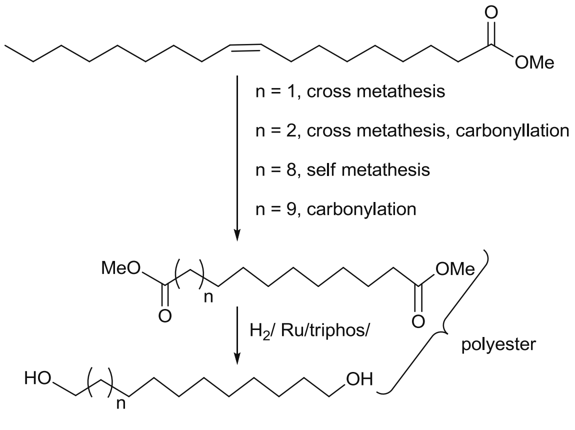
As oil supplies dwindle and the price increases, it is essential to find new ways of making the many chemicals on which the quality of our lives depends. One approach is to use renewable resources which can be grown. However, there is a tension between using land for fuel or chemicals production and the need to use land to produce food for the rapidly increasing world population. One possible solution is to use waste products for the manufacture of chemicals. In this presentation, we shall discuss the conversion of methyl oleate and oleic acid, a major component of *Tall Oil,* a waste from wood processing, into polymer precursors. We shall also discuss the synthesis of a range of important chemicals from cashew nut shell liquid (CNSL), a waste from cashew nut processing.



Scheme1. The formation of a range of α,ω–difunctionalised compounds from methyl oleate using homogeneous catalysis

We shall show how homogeneous carbonylation,[1] metathesis, and reductive amination[2] (see Scheme 1) can be used to make difunctional esters acids, alcohols and amines[1a, 3] for polymer formation[4] (Figure 1).

Since homogeneous catalysts suffer the potential difficulty of product-catalyst separation, we shall show how supported ionic liquid phase SILP) catalysts with carbon dioxide flow (see Figure 1) allow the ready separation of the products from the catalyst, thus overcoming one of the major difficulties associated with scaling up and using homogeneous catalysts commercially. We shall describe our developments on metathesis[5] and other reactions using these systems.

Cashew nut shell liquid contains interesting phenols *meta* substituted with an unsaturated C_{15} chain. We shall described how it can be used to synthesise tse-tse fly attractants, potentially safe detergents, polymer additives, monomers for polymerisation and large ring macrocyclic lactones.[6] (Figure 2.

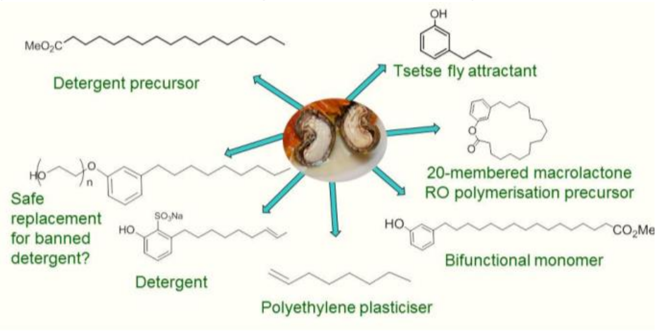


Fig. 2 Chemicals from cashew nut shell liquid

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Dinuclear metal catalysts: Improved performance of heterodinuclear mixed catalysts for CO_2–epoxide copolymerization

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Polymers synthesized from carbon dioxide are attractive as they have the potential to deliver improved sustainability compared to the current petrochemical derived polymers.[1] Copolymerizing epoxides and carbon dioxide can lead to the formation of low molecular weight, di-hydroxyl terminated, polycarbonates or 'polycarbonate polyols' which are important as they can replace polyether polyols used in polyurethane synthesis (textiles, packaging, construction, furniture).[2]

Many catalysts have been synthesized for the copolymerization of epoxides and CO_2, which include metal salen and phorphyrin complexes.[1] However, some of the most active catalysts are homodinuclear metal complexes, but until now heterodinuclear catalysts remain unreported.[1, 3]

This presentation will outline a new *in situ* route to forming a catalyst system consisting of a mixture of homo- and heterodinuclear Zn–Mg complexes and the characterisation techniques used. This catalyst system exhibits significantly higher activity in cyclohexene/CO_2 copolymerization reactions compared to the homodinuclear catalysts alone or in combination. Additionally, this catalyst system still conveys excellent polymerization control even with three different catalysts species present. The system is very robust and also shows promising activity in propylene oxide/CO_2 copolymerization reactions.[3]

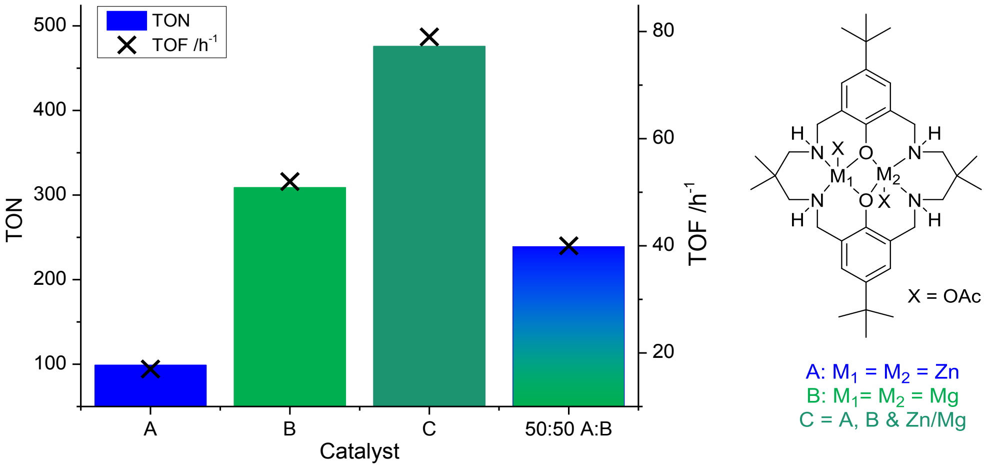

Figure 1: Structure of catalysts and their activity in cyclohexene oxide/ CO_2 copolymerization

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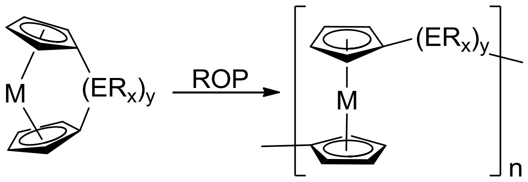
Ring-Opening Polymerization of a Strained [3]Nickelocenophane: A Route to Polynickelocenes, a Class of S = 1Metallopolymers

Baljak, S.; Russell, A. D.; Binding, S. C.; Haddow, M. F.; O'Hare, D.; Manners
University of Bristol

The field of [*n*]metallocenophane chemistry has attracted growing interest since the first example of these strained species was reported in 1960.[1] Significantly, the propensity of strained metallorings (**1**) to undergo ring-opening polymerization (ROP) reactions affords access to polymeric products (**2**) that incorporate metallocene units into the main chain (Scheme 1). The interesting redox, catalytic and magnetic properties of these materials has resulted in their use in a variety of applications.[2]



1 **2**

M = Fe, Ru, Co, **Ni**

Scheme 1. Ring-opening polymerisation of strained [*n*]metallocenophanes

To date, the majority of [*n*]metallocenophane research has focused on the ROP of strained [1]ferrocenophanes, a result of their ease of preparation and ready propensity to undergo ring-opening reactions.[3] However, reports of ROP for strained [*n*]metallocenophanes of late transition metals other than iron are rare.[4] Here we describe the first ROP of a strained [3]nickelocenophane, affording polynickelocene, an interesting class of metallopolymers with a S = 1 monomer unit.[5]

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Base Induced Rearrangement of Mesityl-Phosphonium Salts

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The applications of phosphorus ylides as ligands in inorganic chemistry were first introduced by Schmidbaur.[1] Our interest in this area has recently focused on the triple-deprotonation of the phosphonium salts $[R'P(CH_2R)_3]^+X^-$ (X = a halide ion) to give the ylides of the type $[R'P(CHR)_3]^{2-}$. Previously, we were able to structurally-authenticate the first example of this type of ylide dianion, $[\{PhP(CH_2)_3\}_2(Li\cdot THF)_4]$ (Figure 1).[2] We also showed that the $[PhP(CH_2)_3]^{2-}$ dianion can be transferred, by a metal exchange reaction with $FeBr_2$ to give the unusual hydride complex $[\{PhP(CH_2)_3Fe\}_4(\mu_4\text{-}H)]^-$, composed of a tetrahedron of Fe^{II} atoms with a μ_4-H at the centre of the cluster.[3] However, the reaction of mesityl-phosphonium iodides $[2,4,6\text{-}Me_3C_6H_2PR_3]^+I^-$ (R = Me, Et) with ^{t}BuLi does not result in the anticipated deprotonation of the phosphorus-bonded R-groups. Instead, quantitative 1,3-sigmatropic rearrangement occurs to give the new benzylic phosphonium salts $[(3,5\text{-}Me_2C_6H_3)\text{-}CH_2PR_3]^+I^-$ (R = Me, Et), in which the R_3P group is transferred to an *ortho*-CH_3 group Scheme 1). *In situ* ^{31}P NMR studies show that the reaction is base-activated and stoichiometric with respect to ^{t}BuLi. DFT calculations support the conclusion that the rearrangement is thermodynamically favourable in the gas-phase and in THF and show that it is enthalpically driven.[4]

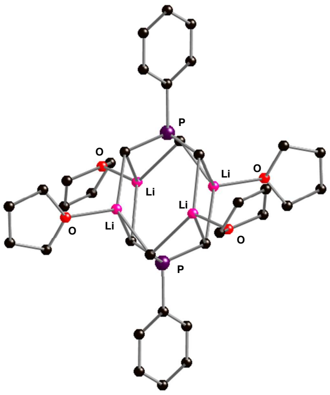
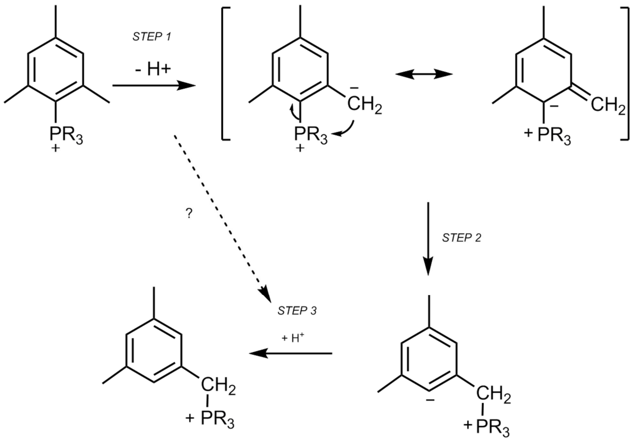


Figure 1



Scheme 1

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Magnesium Catalysed Hydroboration of Nitriles

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As an extension to our previous studies in alkaline earth-mediated borane reduction catalysis,[1,2] we now report that the hydroboration of nitriles with pinacolborane (HBpin) may be catalysed by the β-diketiminato *n*-butyl magnesium complex, $[\mathrm{HC}\{(\mathrm{Me})\mathrm{CN}(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\}_2\mathrm{Mg}n\mathrm{Bu}]$ (**1**). The catalytic reactions have been found to proceed under mild conditions to produce the bis-borylated amine product using 10 mol% catalyst loadings of (**1**). Catalytic turnover is proposed to occur through nitrile insertion into a magnesium hydride bond followed by subsequent Mg-N/B-H σ-bond metathesis to regenerate the active hydride catalyst and the bis-borylated product (Figure 1).

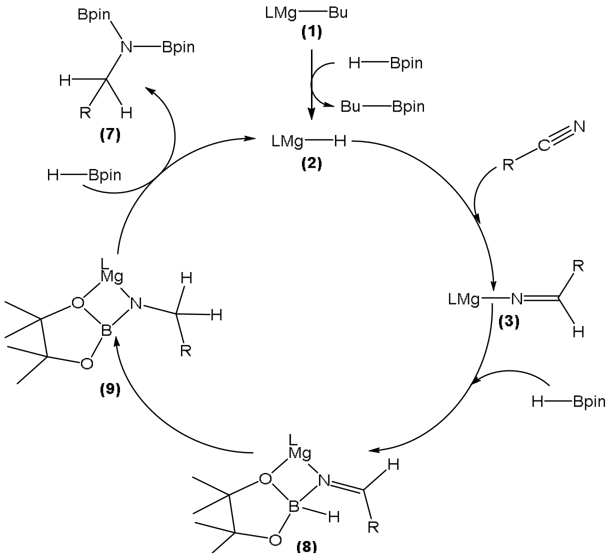

Figure 1. Proposed catalytic cycle for the Mg-mediated hydroboration of nitriles

Mechanistic analyses have shown that the magnesium-catalysed hydroboration of alkyl nitriles displays overall zero order kinetics whereas aryl nitriles conform to an overall first order rate dependence. A Hammett study on the aryl nitriles indicated a change in mechanism whilst moving from electron donating aryl substituents to electron withdrawing groups. Stoichiometric reactivity studies and resultant crystallographic analyses (Figure 2) have enabled the identification of a magnesium borate species, which is proposed as a likely resting state during catalytic turnover.

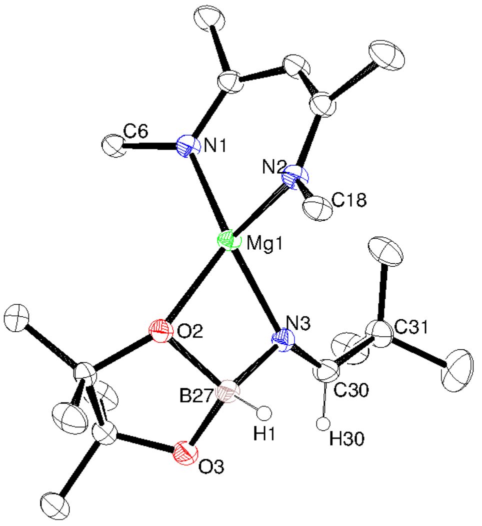

Figure 2. Proposed catalyst resting state during the hydroboration of nitriles catalysed by **1**

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Development of a Powerful Tool to Override the Classical Directed *ortho*-Metallation Chemistry: Co-operative Effects Between Magnesium and Alkali Metals

Antonio J. Martínez-Martínez, David R. Armstrong, Ben J. Fleming, Alan R. Kennedy, Robert E. Mulvey, Stuart D. Robertson, and Charles T. O'Hara*

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Around 95% of pharmaceuticals rely on the use of an organolithium reagent at one point in their synthesis.[1] One of their major uses is in the metallation reaction, which is the conversion of a C-H bond to a more useful C-M bond. In particular, Directed *ortho*-Metallation (D*o*M) is one of the most widely used protocols and is utilised to *ortho*-functionalise aromatic systems. However, organolithiums have some key drawbacks, for example they often exhibit poor functional group tolerance, react with solvents and generally require low temperature reaction conditions.

During the past decade or so, it has been shown that the utilisation of alkali metal magnesiates in synthetic protocols has emerged as a leading alternative to organolithiums reagents in a series of regioselective deprotonations (metal-hydrogen exchange) and metal-halogen exchanges.[2]

This work details the chemistry of certain potassium and sodium magnesiates which exhibit a novel reactivity and selectivity, activating *one* or *two* C–H bonds respectively. Ultimately, the organometallic reagents isolated in these reactions are mixed-metal amide-containing macrocyclic complexes known as *inverse crown* complexes.[3] We have recently reported inverse crown precursors[4] which has allowed us to develop a new general metallation strategy to regioselectively 2,5- and 3,5-dimetallate selected aromatic systems while tolerating a wide range of functional groups without the need for cryogenic temperatures.[5]

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Expaning α elimination to organophosphorus and organosilane synthesis

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After observation of α-arsinidene elimination from triamidoamine-supported zirconium complexes and reports of α-stannylene and -stibinidene elimination from group 4 metallocenes by Tilley, an expansion of the elements that participate in this rare class of deinsertion reactions has been sought. Triamidoamine-supported zirconium complexes have been limited in effecting α elimination for lighter elements using, for example, silanes or phosphines as substrates. However, silanes with π-donating substituents, $RXSiH_2$ (X = NMe_2, Cl, etc), do react with [κ-*N,N,N,N,C*-$(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2$]Zr (**1**) to give $(N_3N)ZrX$ ($N_3N = N(CH_2CH_2NSiMe_3)_3^{3-}$) with evidence of silylene formation. Furthermore, catalytic N–Si dehydrocoupling using triamidoamine-supported zirconium complexes has provided an in situ substrate, $RXSiH_2$, for α-silylene elimination. In select cases, the silylene fragment can be intercepted by an unsaturated organic substrate. Yet more success in organoelement synthesis has been realized recently with the use of iron catalysts. These compounds appear to dehydrocouple phosphines by α-phosphinidene elimination and can engage in catalytic preparation of phospholes from primary phosphines and either alkynes or dienes.

Gold(I)-Catalyzed Protodecarboxylation of (Hetero)Aromatic Carboxylic Acids

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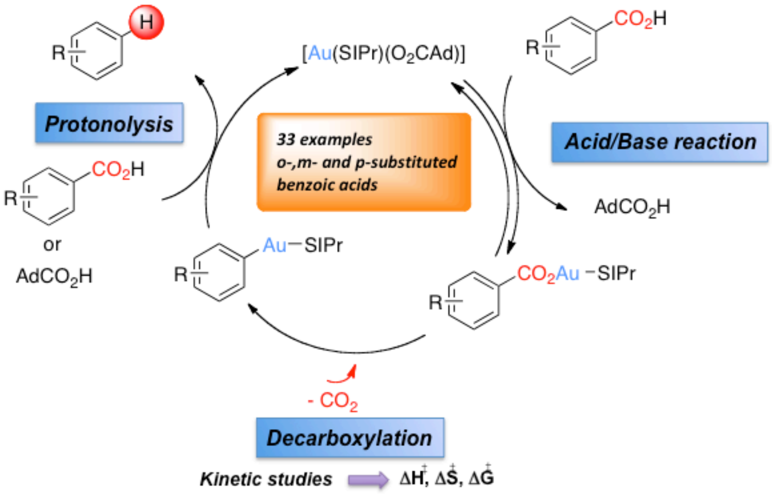
In organic molecules, carboxylic acids are among the most common functionalities. In recent years, this single functionality has been widely used in decarboxylative coupling reactions[1] and as a directing group in transition-metal reactions.[2] For the latter, development of methodologies for the removal of surplus carboxylate groups is of great appeal.[3] Here, we disclose the first protodecarboxylation of (hetero)aromatic carboxylic acids catalyzed by gold.[4] This newly-developed methodology is highly efficient, uses low catalyst loadings and is not limited to *o*-substituted substrates like silver protocols, and has been successfully applied to electron-rich and electron-deficient substrates. Mechanistic studies have been carried out to probe the reaction mechanism. Isolation of key steps and intermediates allowed us to determine rate constantes for the rate-determining step i. e. the extrusion of CO_2 from various substrates. These values allowed access to thermodynamic parameters, which could be compared to previously described systems, to furnish a better understanding of how the substrate structure affects the reactivity.



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Controlling Product Selectivity in Rhodium-Catalysed Oxidative Coupling

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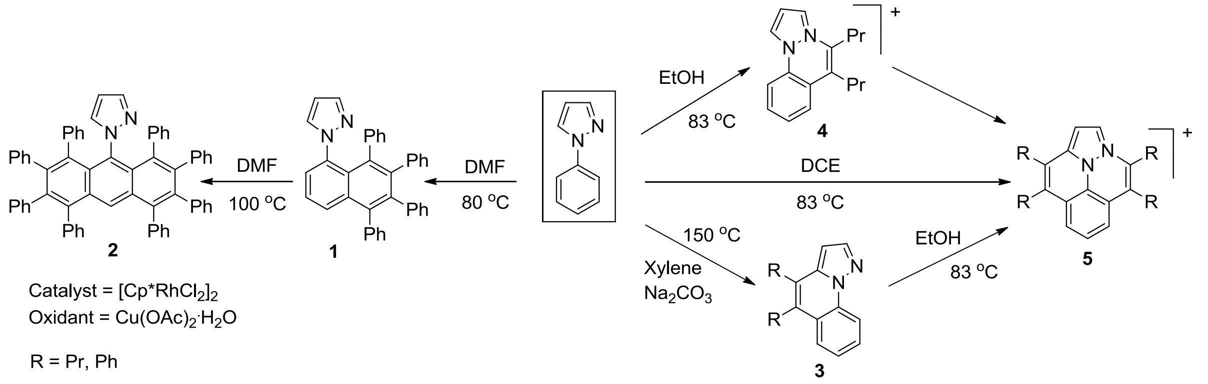
Directed C-H functionalization catalysed by $[Cp^*RhCl_2]_2$ and related derivatives has recently attracted a large amount of interest as a convenient route to value added products.[1] For example, 1-phenylpyrazole has been shown to be a versatile substrate for the oxidative coupling with internal alkynes forming carbocycles (**1**, **2**) or heterocycles (**3**) via C,C coupling.[2]



Additionally, we will demonstrate that C,N coupling is also facile (**4**, **5**). Furthermore, we will highlight that combined experimental and computational studies can led to the elucidation of the mechanism thus enabling the identification of key steps within the catalytic cycle which control product selectivity. Our results suggest that product selectivity is dependent on anion coordination and reductive elimination, enabling rational control over product selectivity by altering the nature of alkyne and reaction conditions.

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Using *de novo* Design to Create Novel Lanthanide-Coiled Coil Imaging Agents

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Figure 1. Model of the 4 different Ln(III) binding sites

A library of peptide sequences have been designed which, in the presence of a trivalent lanthanide ion, Ln(III), have been programmed to spontaneously self-assemble to form a three stranded metallo-coiled coil. An aspartate/asparagine (Asp/Asn) binding site for Ln(III) coordination has been introduced into the hydrophobic core, restricting inner sphere water coordination. The resulting Ln(III) coiled coil is therefore of interest for luminescence applications as O-H vibrations quench Ln(III) emission. Despite having no inner sphere water molecules, we have found that our gadolinium coiled coil, the first to be reported, displays promising magnetic resonance imaging (MRI) contrast agent capabilities.[1,2]

Furthermore, by repositioning the Ln(III) binding site at four different locations along the peptide motif, coiled coils with different stabilities and Ln(III) sites with different coordination environments (Figure 1) can be achieved. Most notably, the number of inner sphere coordinated water molecules is highly sensitive to the location of the binding site, leading to varying photophysical and NMR relaxation properties. This therefore provides an opportunity to tailor the design of these metallo-peptides towards use in either luminescence or MRI applications depending on the choice of binding site and the Ln(III) ion chosen.

MRB, MMB and AFAP thank the School of Chemistry and the University of Birmingham for funding. Some equipment used was obtained through Birmingham Science City with support from Advantage West Midlands (AWM) and European Regional Development fund (ERDF)

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Functional cellular reagents derived from phosphorescent rhenium(I) and iridium(III) polypyridine complexes

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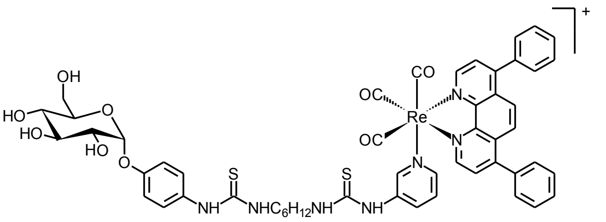
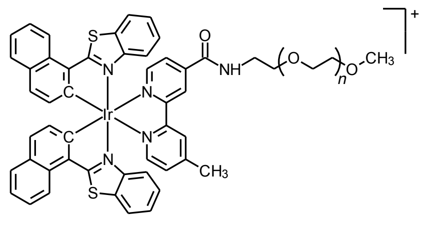
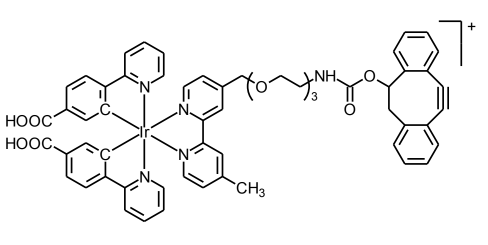
The interesting phosphorescence properties of rhenium(I) and iridium(III) polypyridine complexes have prompted us to develop new biological labels and cellular probes using these complexes. Recently, we have designed new complexes to: (1) study glucose transporters-mediated sugar uptake by cancer cells, (2) develop photocytotoxic agents, (3) label surface-glycans of living cells from a bioorthogonal approach, (4) detect intracellular zinc(II) ion and nitric oxide and (5) identify the intracellular protein targets of these reagents. We have focused on the photophysical and photochemical properties, cytotoxicity, cellular-uptake and intracellular functions of these new complexes.



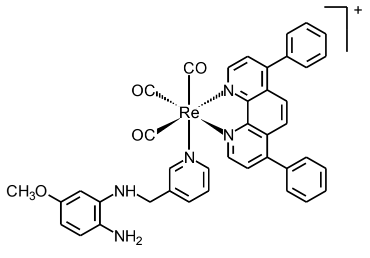
glucose uptake indicator



photocytotoxic agent



bioorthogonal probe



nitric oxide sensor

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Peptides as versatile tools in the synthesis of metal oxides

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Events occurring at the solid/ aqueous interface (i.e. molecular recognition, adsorption, desorption etc.) underpin a variety of technologies used in the biomedical and technological fields. Interactions occurring at interfaces are also used to good effect in Nature where biomolecules are used to guide and control the formation of biominerals. My research group is involved in studies of biomineralization *in vivo* and the transition of mechanistic information learnt from the natural systems to laboratory based reactions. Our aim is to generate new material forms and increase our understanding of the principles by which materials formation *in vitro* can be regulated under environmentally 'green' reaction conditions.

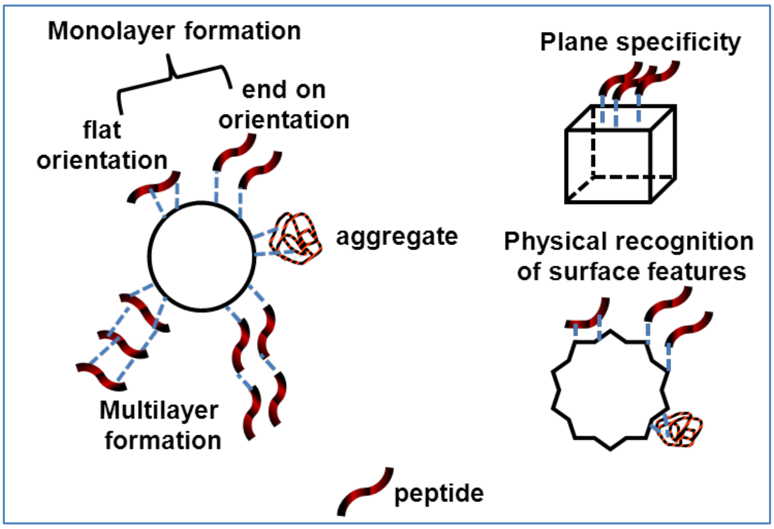
This presentation will use examples from our studies of oxides to showcase what we have learnt about how peptides interact with surfaces thereby regulating mineral formation.

Governing factors

Properties of the peptide sequence (hydropathy, charge, conformation)

Properties of the inorganic surface (physical and chemical)

Environment/media



Weakly Coordinating Anions: Facilitators for Applied and Fundamental Chemistry

Ingo Krossing[a]

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Weakly Coordinating Anions (WCAs): If the surface of a larger, chemically robust anion is terminated by fluorine, its performance as a WCA usually gets better. This is mainly due to the low polarizability of element-fluorine bonds and the capability of fluorine to effectively delocalize the negative charges.

The lecture will focus on the unusual chemistry enabled by the $[Al(OR^F)_4]^-$ (R^F = fluorinated alkoxide) and related types of WCAs.

Cationic Main Group Clusters: We present novel homopolyatomic clusters of the Group 15 or 16 elements, for example Se_{12}-, Se_{19}-complexes or $[P_9]^+$.

Subvalent Group 13 Cations: We devised a route to univalent Ga^+ and In^+ and used them for novel coordination chemistry. We show that chelating ligands like diphosphenes or bipyridines lead to an interesting follow-up chemistry.

Univalent Nickel Cations: Simple, purely organometallic Ni^+ salts are accessible with the $[Al(OR^F)_4]^-$ anion. The road to and chemistry of will be presented.

Organo-Zinc-Salts RZn^+: A facile route to ion-like RZn^+ salts is presented and the preliminary chemistry thereof presented, also in terms of applications for hydroamination.

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