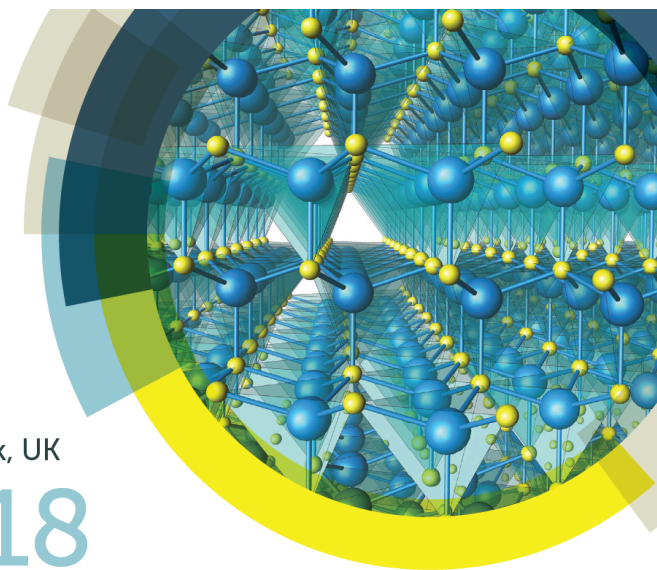




3-5 April 2018, University of Warwick, UK

# Dalton 2018



## PROGRAMME AND ORAL ABSTRACTS



**#Dalton2018**



The Dalton2018 organisation committee would like to thank our generous sponsors for supporting the event

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Programme

**Tuesday 3<sup>rd</sup> April**

1330-1345 Oculus OC1.05 Welcome and Introduction: **Emma Raven**

1345-1430 Inorganic Mechanisms Award 2017

**Robert Morris** (*University of Toronto*) Mechanisms of the H<sub>2</sub>- and transfer hydrogenation of polar bonds catalyzed by iron group hydrides

1430-1515 Coordination and Organometallic Discussion Group Plenary Lecture, Session Chair: **Jason Love** (Edinburgh)

**Connie Lu** (*University of Minnesota*) Innovating bimetallic active sites for small-molecule catalysis

1515-1540 Tea/Coffee

## Parallel Session 1

	Coordination & Organometallic and Dalton Trans Editorial Board	Coordination & Organometallic	Main Group	Reaction Mechanisms	Inorganic Biochemistry	Coordination & Organometallic
Room	OC1.05 (500)	OC0.03 (250)	OC0.02 (100)	OC0.04 (80)	OC1.06 (60)	OC0.01 (60)
Chair	Graeme Hogarth	Patrick McGowan	Michael Cowley	Alison Parkin	Claudia Blindauer	Joy Farnaby
1540-1600	<b>John Arnold</b> <i>UC Berkeley</i> New Catalytic & Stoichiometric Reactivity Promoted by Early Transition Metals	<b>James Hickson</b> <i>Imperial College London</i> Synthesis and characterisation of rare earth-transition metal heterometallic complexes with a redox-active bridging ligand	<b>Nicola Oldroyd</b> <i>University of Bristol</i> General, metal-free routes to polyphosphinoboranes	<b>Samuel de Visser</b> <i>University of Manchester</i> A novel mechanism for aldehyde deformationylation by a side-on manganese(III)-peroxo complex	<b>Pablo Carames-Mendez</b> <i>University of Leeds</i> Breaking the rules, trans-dihalide ruthenium complexes as anticancer agents	<b>Megan Seymour</b> <i>University of Edinburgh</i> Uranium-mediated small molecule activation
1600-1620	<b>Marina Uzelac</b> <i>University of Strathclyde</i> New C-C bond forming strategies mediated by alkali metal manganates	<b>Key Burrows</b> <i>University of Leeds</i> The influence of chirality on the spin states on Fe(II) pybox derivatives	<b>Rachel Kahan</b> <i>University of Manchester</i> Novel routes to B-doped polycyclic aromatic hydrocarbons	<b>Anders Hammarback</b> <i>University of York</i> Understanding the mechanism of Mn-catalysed C-H Bond functionalisation using time-resolved IR spectroscopy (TRIR)	<b>Rianne Lord</b> <i>University of Bradford</i> Organometallic iridium complexes: highly cytotoxic and selective towards colorectal cancer	<b>Samantha Apps</b> <i>Imperial College London</i> Dinitrogen activation of molybdenum(O) N-triphos complexes
1620-1640	<b>Guo-Xin Jin</b> <i>Fudan University</i> Organometallic macrocycles, cages and their application	<b>Andreas Berkefeld</b> <i>Eberhard Karls Universität Tübingen</i> Structure-property relationship of radical-ligand complex near-infrared chromophores of platinum	<b>Merle Arrowsmith</b> <i>Julius-Maximilians-Universität Würzburg</i> From borylene to diborene and back again: towards a bora-Wanzlick equilibrium?	<b>Antonio Martinez-Martinez</b> <i>University of Oxford</i> Valorisation of light hydrocarbons: solid-state molecular organometallic catalytic nanoreactors (SMOM-cat)	<b>Samya Banerjee</b> <i>University of Warwick</i> Activation of Cp* rings in rhodium(III) anticancer complexes	<b>Robin Perutz</b> <i>University of York</i> Self-complementary nickel halides enable intermolecular halogen bonds
1640-1700	<b>Richard Knighton</b> <i>University of Warwick</i> Solution, solid-state, and computational analysis of agostic interactions in a coherent set of low coordinate Rh(III) and Ir(III) complexes	<b>Rebekah Hailes</b> <i>University of Bristol</i> Synthesis and magnetic properties of polytickelocenes with different main chain spacers	<b>Nicholas Phillips</b> <i>Imperial College London</i> Bespoke dihydridoborane reagents: tuning the environment at boron through hemilabile ligation	<b>Nathan Coles</b> <i>University of Bath</i> Iron catalysed transfer hydrogenation and regioselective deuteration reactions	<b>Isolda Romero-Canelon</b> <i>University of Birmingham</i> Chemical modulation of cellular redox balance for cancer treatment	<b>Sophie Benjamin</b> <i>Nottingham Trent University</i> Pd(II) complexes of Lewis amphoteric halosulfides: stoichiometry matters
1700-1720	<b>Thomas Rookes</b> <i>University of Manchester</i> Novel heavy pnictide complexes of U and Th	<b>Sabrina Khoo</b> <i>Nanyang Technological University, Singapore</i> B-H bond activation by an amidinate-stabilized amidosilylene: non-innocent amidinate ligand	<b>Roy Waterman</b> <i>University of Vermont</i> Polymerization of arsine boranes and pyrolysis to boron arsenide	<b>Martin Wills</b> <i>University of Warwick</i> Synthesis and catalytic applications of cyclopentadienyl iron tricarbonyl complexes	<b>Gabriele Agonigi</b> <i>University of Pisa</i> Reactivity of diron complexes with a bridging amino-alkylidene ligand, and cytotoxicity results	<b>Samantha Lau</b> <i>Imperial College London</i> Tunable binding of dinitrogen to a series of M•Ru (M = Mg, Al, Zn) heterobimetallic complexes
1720-1740	<b>Matthew Leech</b> <i>University of Sussex</i> Escaping obscurity: transition metal cyaphides	<b>Nikolas Kaltsoyannis</b> <i>University of Manchester</i> Very high spin ground states in Matryoshka actinide nanoclusters	<b>Yashar Soltani</b> <i>Cardiff University</i> Stoichiometric and catalytic C-C and C-H bond formation with B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> via cationic intermediates	<b>Zoë Turner</b> <i>University of Oxford</i> Evidence for a new mechanism of ethylene polymerisation	<b>Graeme Stasiuk</b> <i>University of Hull</i> Synthesis and validation of a multimodal PET/fluorescence Zn sensing probe as potential imaging agents for prostate cancer	<b>Bradley Cowie</b> <i>University of Edinburgh</i> Reduction, fusion and oxo-group abstraction reactions of the uranyl ion

1830-1930 Dinner – Rootes Restaurant

1930-2200 Posters and Wine/Beer/Soft Drinks

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**Programme**

**Wednesday 4<sup>th</sup> April**

**Lecture Theatre Oculus OC1.05, Session Chair: Nick Le Brun (UEA)**

0900-0945 Inorganic Biochemistry Discussion Group Plenary Lecture

**Kara Bren** (University of Rochester)

A metallopeptide mimic of hydrogenase and nitrite reductase

0945-1030 Main Group Chemistry Plenary Lecture

**Evamarie Hey-Hawkins** (University of Leipzig)

Phosphorus meets carborane

1030-1055 Tea/Coffee

## Parallel Session 2

	Coordination & Organometallic and Dalton Trans Editorial Board	Reaction Mechanisms	Main Group	Inorganic Biochemistry	Main Group
Room	OC1.05 (500)	OC0.03 (250)	OC0.02 (100)	OC0.04 (80)	OC0.01 (60)
Chair	David Mills	Mark Muldoon	Michael Ingleson	Peter Sadler	Stuart Robertson
1055-1115	<b>Masahiro Yamashita</b> <i>Tohoku University</i> Quantum molecular spintronics based on single-molecule magnets: single-molecule memory, spin qubits, and Rabi rotation at RT	<b>Paul Hayes</b> <i>University of Lethbridge</i> Rhodium mediated deoxygenerative metallthesis of CO	<b>Claire Bakewell</b> <i>Imperial College London</i> Reactions of fluoroalkenes with an Al(I) complex	<b>Alevtina Mikhaylina</b> <i>University of Warwick</i> Bacterial metallothioneins that respond to Zn limitation	<b>Richard Procter</b> <i>University of Manchester</i> A zinc catalysed $Csp^2-Csp^3$ Suzuki-Miyaura cross-coupling reaction
1115-1135	<b>Laurence Kershaw Cook</b> <i>University of Bath</i> Insights into crystal design – polymorphism and phase dependent spin-state switching	<b>James Walton</b> <i>Durham University</i> Catalytic reaction of organometallic ruthenium complexes	<b>Rosalyn Falconer</b> <i>University of Edinburgh</i> Aluminium hydrides stabilised by mixed NP donor ligands	<b>Oliver Daubney</b> <i>University of Birmingham</i> Misbehaving lanthanide binding sites in designed peptide trimers	<b>Andrew Wilson</b> <i>University of Bath</i> Reactivity of a solvent-free calcium hydride
1135-1155	<b>Martina Mazzanti</b> <i>Ecole Polytechnique Fédérale Lausanne</i> Small molecule activation by multimetallic uranium complexes	<b>Lewis Hall</b> <i>University of York</i> Mechanistic understanding and novel applications of outer-sphere electrophilic fluorination	<b>Lucy Brown</b> <i>Queen's University Belfast</i> The structure of frustrated Lewis pairs in ionic liquids vs. molecular solvents	<b>Amanda Jarvis</b> <i>University of Edinburgh</i> Enzyme activity by design: an artificial rhodium hydrolase	<b>Felipe Garcia</b> <i>Nanyang Technological University</i> Mechanochemical synthesis of main compound and complexes
1155-1215	<b>William Blackaby</b> <i>University of Bath</i> Synthesis and characterisation of low-coordinate Ni(I) complexes for magnetic applications and small molecule activation	<b>Bryan Ward</b> <i>Imperial College London</i> Magnesium-mediated $sp^3C-F$ and $sp^3C-F$ bond activation	<b>Petra Vasko</b> <i>University of Oxford</i> Hydroboration of alkynes by an FLP: unexpected bond activation and mechanistic studies	<b>Agnieszka Mierek-Admaska</b> <i>University of Warwick</i> The role of seed-specific type 4 metallothionein in <i>Brassica napus</i> seeds	<b>Ajay Venugopal</b> <i>Indian Institute of Science Education and Research Thiruvananthapuram</i> Distinct reactivity of cationic Mg and Zn alkyls
1215-1235	<b>Wolfgang Tremel</b> <i>Johannes Gutenberg Universität Mainz</i> Applications of inorganic nanoparticle enzyme mimics	<b>Mark Dowsett</b> <i>University of York</i> Capacitance assisted sustainable electrochemical carbon dioxide capture and mineralisation	<b>Ewan Clark</b> <i>University of Kent</i> Phosphonium cations – exploring overlooked catalytic potential	<b>Justin Bradley</b> <i>University of East Anglia</i> Unprecedented iron-oxygen reactivity in a ferritin	<b>Alex Pajler</b> <i>University of Cambridge</i> How does changing the bridgehead affect the properties of tripodall ligands?

## 1235-1345 Lunch (Rootes Restaurant) and poster browsing

## OC1.05 Session Chair: Jose Goicoechea (Oxford)

1345-1430 Bioinorganic Chemistry Award 2017

Thomas Ward (University of Basel)

1430-1515 Michael Lappert Memorial Lecturer 2018

Francois Gabbai (Texas A &amp; M)

1515-1545 Tea/Coffee

Exploiting the non-innocence of antimony ligands in organometallic catalysis

Artificial metalloenzymes: challenges and opportunities

## Parallel Session 3

Room	Coordination & Organometallic	Main Group and Dalton Trans Editorial Board	General Interest Mixer	Reaction Mechanisms	Inorganic Biochemistry
Chair	<b>John Fielden</b>	<b>Ian Crossley</b>	<b>Rebecca Melen</b>	<b>Ulrich Hintermair</b>	<b>Rianne Lord</b>
1545-1605	<b>Stephen Mansell</b> <i>Heriot-Watt University</i> Applying phosphinophosphinite ligands to catalysis	<b>Stephen Richards</b> <i>University of Southampton</i> Molecular precursors for the growth of M <sub>2</sub> E <sub>3</sub> (M = Sn, Bi; E = Se, Te) thin film thermoelectric materials by low pressure chemical vapour deposition	<b>Alexander Hinz</b> <i>University of Oxford</i> Limitations of steric bulk: towards phospho-gemynes and phospho-stannynes	<b>Cei Provis-Evans</b> <i>University of Bath</i> Iron catalysed alkyne trimerisation at room temperature	<b>Luca Ronconi</b> <i>National University of Ireland Galway</i> A "sweet approach" to the targeted anticancer chemotherapy: Au-based glycoconjugates
1605-1625	<b>Marcel Philipp Lücke</b> <i>Technische Universität Berlin</i> Bis(silylenyl)-substituted ferrocene-stabilized η <sup>6</sup> -arene Fe(0) complexes: synthesis, structure and catalytic application	<b>Frank Tamborino</b> <i>University of Oxford</i> A general synthetic approach towards heavier group 15/16 cyanate homologues $Pr=C=Ch$ (Pr = P, As; Ch = S, Se).	<b>Richard Layfield</b> <i>University of Manchester</i> Lanthanide SMMs: life beyond the venerable cyclopentadienyl ligand	<b>Sebastian Pike</b> <i>University of Cambridge</i> Titanium-oxo clusters: photoactive materials at the molecular scale	<b>Jonathan Robson</b> <i>Imperial College London</i> Ruthenium(II) complexes for in vitro and ex vivo sensing of carbon monoxide
1625-1645	<b>Pau Farràs</b> <i>NUI Galway</i> Strategies to improve stability and efficiency for solar chemicals production	<b>Chantal Mustoe</b> <i>University of British Columbia</i> Charge transfer in halogen bonds	<b>Warren Piers</b> <i>University of Calgary</i> Synthesis and reactivity of PC <sup>carbonyl</sup> <sub>2</sub> complexes of first row transition metals	<b>James Barwick-Silk</b> <i>University of Oxford</i> Mechanistic understanding of a selective, non-decarbonylating Rh catalyst for the hydroacylation of β-amido aldehydes	<b>Stuart Archer</b> <i>University of Sheffield</i> Photoinduced guanine oxidation in telomeres by dinuclear Ru(II) polypyridyl complexes
1645-1705	<b>Patrick McGowan</b> <i>University of Leeds</i> Cu-catalysed aryl ether formation and the "caesium effect"	<b>Vadapalli Chandrasekhar</b> <i>Tata Institute of Fundamental Research Hyderabad</i> Synthesis and reactivity of compounds containing Si=N, Si=P or P=P motifs	<b>Mark Muldoon</b> <i>Queen's University Belfast</i> New mechanistic insights into Pd(II) catalysed oxidation of alkenes	<b>Muhammad Adnan Asghar</b> <i>University of Education, Lahore</i> Exploration of hybrid phase transition materials and study of their NLO properties	<b>Nick Le Brun</b> <i>University of East Anglia</i> The mechanism of iron sensing by the iron-sulfur cluster regulator RirA

## OC1.05 Session Chair: Samuel De Visser (Manchester)

1710-1755 Homogeneous Catalysis Award 2017

Syuzanna Harutyunyan (University of Groningen)

1800-1900 Section Committee meetings

1900-1930 Pre-dinner drinks (The Slate)

1930-2300 Conference Banquet (The Slate)

Lewis acids promoted copper catalyzed synthesis of functional molecules

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Programme

**Thursday 5<sup>th</sup> April**

**OC1.05** Session Chair: **Michael Hill** (Bath)

0915-1000 Harrison Meldola Award 2017

**Mark Crimmin** (Imperial College London)

Carbon–hydrogen bond activation with intermetallic complexes

1000-1045 Centenary Prize 2017

**Odile Eisenstein** (*University of Montpellier*)

Analyzing reaction in transition metal species: is there an alternative to energy?

1045-1115 Tea/Coffee



## Parallel Session 4

	Coordination & Organometallic and Dalton Trans Editorial Board	Main Group	Reaction Mechanisms and Dalton Trans Editorial Board	Inorganic Biochemistry	Publishing in Science
Room	OC1.05 (500)	OC0.03 (250)	OC0.02 (100)	OC0.04 (80)	OC0.01 (60)
Chair	Stephen Mansell	David Liprot	Martin Willis	Michelle Ma	
1115-1135	<b>David Mills</b> <i>University of Manchester</i> Molecular magnetic hysteresis at 60 K in dysprosocenium	<b>Martin Stanford</b> <i>University of Edinburgh</i> Disilene vs silylsilylene: substituted analogues of the Si <sup>+</sup> H <sub>4</sub> rearrangement	<b>Ulrich Hintermaier</b> <i>University of Bath</i> Watching catalysts at work: H transfer reactions investigated with real-time high resolution FlowNMR spectroscopy	<b>Charlotte Eling</b> <i>University of Hull</i> Dual-modal SERS/fluorescence AuNP probe for mitochondrial imaging	<b>Andrew Shore</b> <i>Royal Society of Chemistry</i> Publishing your inorganic chemistry research with the Royal Society of Chemistry
1135-1155	<b>Ryan Kerr</b> <i>University of Edinburgh</i> Cerium-NH <sub>2</sub> C complexes for the activation of CO <sub>2</sub> and polymerisation of bio-renewable monomers	<b>Joshua Sapsford</b> <i>Imperial College London</i> Beyond boranes: achieving moisture-tolerant Frustrated Lewis Pair catalysis with stannylum Lewis acids	<b>Sascha Ott</b> <i>Uppsala University</i> Phosphaalkenes are key intermediates in the reductive cross-coupling of aldehydes to alkenes	<b>Adam Smith</b> <i>Imperial College London</i> Lipophilic and cationic gallium-68 chelates for imaging mitochondrial function	
1155-1215	<b>Nils Metzler-Noite</b> <i>Ruhr-Universität Bochum</i> Click chemistry for the synthesis of metal-peptide bioconjugates	<b>Haoyu Niu</b> <i>University of Oxford</i> Coordination chemistry and reactivity of the heavier group 14 elements with bulky anionic guanidinato ligands	<b>Luca Rocchigiani</b> <i>University of East Anglia</i> Au(III) hydrides: unexpected interplay of cis- and trans-influence on stability, insertion reactivity and NMR chemical shifts	<b>Jim Thomas</b> <i>University of Sheffield</i> Targeting biomolecules with self-assembled photoactive Ru(II)-based metallomacrocycles	

OC1.05 Session Chair: **Andrew Weller** (Oxford)

1215-1300 Inorganic Reaction Mechanisms Group Plenary Lecture

**Mahdi Abu-Omar** (UC Santa Barbara)

Mechanistic Studies of Sustainable Catalysis

1300-1305 Concluding remarks: **Emma Raven**

## Plenary Speakers at Dalton2018

### RSC Prize winners



Inorganic Mechanisms Award 2017

**Robert Morris** (*University of Toronto*)

*Awarded for the mechanisms of hydrogen activation and catalytic hydrogenation and asymmetric hydrogenation reactions.*

Bioinorganic Chemistry Award 2017

**Thomas Ward** (*University of Basel*)



*Awarded for the development of artificial metalloenzymes which have allowed a systematic investigation of second coordination sphere interactions in catalysis, ultimately leading to the implementation of new-to-nature catalysis in vivo.*



Homogeneous Catalysis Award 2017

**Syuzanna Harutyunyan** (*University of Groningen*)

*Awarded for pioneering work on asymmetric synthesis, establishing an entirely new role for Cu(I)-based catalysts and the use of Lewis acid and Grignard reagent combinations.*

Harrison Meldola Memorial Prize 2017

**Mark Crimmin** (*Imperial College London*)



*Awarded for his research in the area of organometallic and main group chemistry, particularly for developing new types of heterobimetallic complexes.*



Centenary Prize 2017

**Odile Eisenstein** (*University of Montpellier*)

*Awarded for seminal contributions to the theoretical understanding of transition metal complexes and the successful prediction of unknown properties and pathways.*

## Interest Group plenaries

Michael Lappert Memorial Lecturer 2018



**François Gabbai** (Texas A & M)

*Fundamental synthetic inorganic chemistry centred on electrophilic and/or Lewis acidic molecules with a special focus on the discovery of novel structures and bonding modes. Currently studying the design of boron-, antimony- and tellurium-containing Lewis acids as water compatible receptors for small anions.*



**Connie Lu** (University of Minnesota)

*Seeks to develop homogeneous catalysts for converting abundant small molecules, such as N<sub>2</sub> and CO<sub>2</sub>, into useful chemical feedstocks, such as ammonia and methanol. Current projects include building new bonds between 3d elements and constructing new conformationally flexible diphosphines for applications in catalysis.*

**Kara Bren** (University of Rochester)



*Currently investigating metalloprotein structure and function, and engineering metalloproteins for applications in energy conversion. Other projects include the application of manganese porphyrins as low toxicity MRI contrast agents and studying cytochrome c folding.*



**Evamarie Hey-Hawkins** (University of Leipzig)

*Research is focused on several diverse themes including: transition metal complexes and their application in catalysis and materials science; organophosphorus compounds; biologically active boron compounds (reagents for boron-neutron capture therapy (tumour therapy); and, enzyme inhibitors (inflammation, progression of cancer).*

**Mahdi Abu-Omar** (UC Santa Barbara)



*Specialises in catalysis, renewable energy and bioinspired chemistry. A common theme in all areas is catalyst design. Current projects include: conversion of biomass to high-value chemicals, synthesis of renewable polymers and materials from lignin; and, performing highly regioselective olefin oligomerisation catalysis.*

## Sir Geoffrey Wilkinson Dalton Poster Competition

The Geoffrey Wilkinson Foundation will sponsor the annual Dalton Poster competition at Dalton2018. The poster competition is divided into two parts: one for postgraduates and one for postdoctoral researchers. The winner of each section will receive a bursary to attend an international conference of their choice, and there will also be runner-up prizes.

Poster	Forename	Surname	Title of contribution
P1	Gemma	Adams	Rhodium complexes of POP-type ligands: towards controlled, metal-catalysed, amine-borane dehydropolymerisation
P2	Ahmed	Ahmed	Relationship between ligand spin states and spin state in a family of Fe(II) complexes
P3	Lamia	Alharthi	Synthesis, characterization and detailed bio-interaction study of ruthenium complexes supported by salicylaldimine and PTA ligands
P4	Ana	Almeida	Design of de novo coiled coils as ligands for catalysis
P5	Amira	Am	The kinetics and modelling studies of the adsorption phenomenon by a natural rock
P6	Hessah	Althani	Novel derivatives of the NHC-silver antibiotics candidate SBC3
P7	Matthew	Andrews	Developing Ni(II) catalysts for copolymerisation
P8	Rebecca	Andrews	Synthesis and characterisation of iron-magnesium heterobimetallic complexes.
P9	Vincent	Annibale	Lewis acid-catalysed dehydrocoupling of phosphines and silanes
P10	Jaseer	Antholinda	Iridium-NSiN catalyzed CO <sub>2</sub> hydrosilylation processes: tuning the activity and selectivity
P11	Gregory	Baker	Developing heterobimetallic hydrides for selective hydrogenation catalysis
P12	Christopher	Bamforth	Developing radical-bridged lanthanide/transition metal heterometallics utilising a redox-active ligand.
P13	Robert	Bannister	Investigating the effects of group V elements: metal chalcogenide trichloride thioether complexes
P14	Robina	Begum	Silver nanoparticles loaded polymer microgels for catalytic reduction of Malachite Green
P15	Sophie	Bennett	Copper centre biogenesis in the nitrous oxide reductase of <i>Paracoccus denitrificans</i>
P16	Troy	Bennett	Ferrocene based molecular wires for quantum interference enhanced thermoelectrics
P17	Daniel	Berry	Noyori in flow: monitoring asymmetric transfer hydrogenation in real-time using FlowNMR spectroscopy
P18	Sayan	Bhattacharya	Arsenic contamination in groundwater, agricultural soil and subsequent bioaccumulation in rice in Bengal Delta
P19	George	Biggs	The use of <sup>19</sup> F NMR to determine how ruthenium(II) arene complexes interact with proteins
P20	Anna	Booth	Bidentate ligands for <sup>18</sup> F chelation
P21	Andryj	Borys	Main-group heterocyclic radicals: new magnetic organic materials
P22	Stuart	Boyt	Synthesis of substituted dihydropentalenes for organometallic pentalenide complexes
P23	Giulio	Bresciani	Synthesis of cyclic organic carbonates from CO <sub>2</sub> and epoxides at ambient conditions using iron <i>N,N</i> -dialkylcarbamates.
P24	Hannah	Bridgewater	Mechanism of action of novel organometallic osmium anticancer complexes
P25	Rachael	Broomfield-Tagg	Real-time monitoring of a Suzuki-Miyaura cross-coupling reaction by multi-nuclear FlowNMR spectroscopy
P26	Etienne	Brouillet	Synthetic organometallic approach to chloro-free electrolytes for rechargeable magnesium batteries
P27	Ryan	Brown	Palladium-catalysed alumination of C-O bonds of furans
P28	Jean-Charles	Buffet	Chiral group 4 cyclopentadienyl complexes for polymerisation
P29	Alex	Bukvic	The coordination chemistry of light alkanes using solid-state molecular organometallic catalysts (SMOM-Cat)
P30	Jamie	Cadge	Facile oxidative addition to Au(I) at sp, sp <sup>2</sup> and sp <sup>3</sup> centres
P31	Alexa	Caise	Catalytic reduction of C=O bonds by group 13 catalysts: inner sphere vs outer sphere mechanisms
P32	Pablo	Carames-Mendez	Selective synthesis of trans-dihalide ruthenium complexes as anticancer agents
P33	Jamie	Carden	Utilising microwave irradiation as an enabling technology for tris(3,4,5-trifluorophenyl)borane catalysed hydroboration
P34	Qien	Chen	Synthesis and reactivity of rare-earth phosphoethynolates
P35	Wenyi	Chen	Palladium-catalyzed transformation of C-F into C-Al bonds

P36	Florian	Chotard	Atom transfer radical addition catalysed by ruthenium-arene complexes bearing a hybrid phosphine-diene ligand
P37	George	Clarke	Automation of chemical synthesis utilising robotic systems
P38	Mitchell	Clarke	Development of high contrast multimodal imaging agents
P39	Thomas	Clough	A novel series of zinc-sensing NIR fluorescent dyes
P40	Greg	Coates	Magnesium-mediated coupling of $sp^3$ C-F and $sp^2$ -F Bonds
P41	Annie	Colebatch	Tris(2-pyridyl) ligands bearing main group bridgeheads
P42	Nathan	Coles	Base metal catalysed double hydrophosphination of activated alkynes
P43	Christopher	Collins	Methods for probe structure based composition prediction
P44	Richard	Collins	Lanthanide-transition metal organometallics of fundamental interest and as single-molecule magnets
P45	Saul	Cooper	Tripodal <i>N</i> -centred phosphine ligands towards $^{99m}\text{Tc}$ and $^{188}\text{Re}$ radiopharmaceutical formulation
P46	Omar	Coughlin	Lewis acidic properties of neutral and cationic organoantimony(V) compounds
P47	James	Coverdale	In-cell asymmetric transfer hydrogenation: a highly selective approach for targeting cancer cells
P48	Caroline	Davies	Metal-organic structures in the Cambridge Structural Database (CSD)
P49	Peter	De'Ath	Dual metal binding of a functionalised 1,10-phenanthroline-5-amine
P50	Dinh Cao Hun	Do	A $\beta$ -diketiminato stabilised chlorosilylene: access to silicon analogues of classical organic systems
P51	Oliver	Driscoll	Earth-abundant metals for catalysis
P52	James	Durrant	Lanthanide cyclobutadiene chemistry
P53	Oumaima	Eddine	Influence of chemical composition on morphology and mechanical properties of glass fibers based on natural phosphate and clay minerals
P54	Felicia	Ejiah	Synthesis, characterization, antiseptic and antibacterial potentials of cobalt(II) Schiff base metal complexes
P55	Jack	Emerson-King	Rotaxane synthesis exploiting the M(I)/M(III) redox couple
P56	Kieren	Evans	Comparing the reactivity of monodentate/tethered <i>N</i> -heterocyclic carbenes and stannylenes
P57	Peter	Evans	Rearrangement of a diphosphasilylene
P58	Nada	Al Hamad	Synthesis and biological evaluation of phosphine-silver compounds as novel resistance-breaking antibiotics
P59	Andrew	Faben	Synthesis and characterisation of quadruply bonded dirhenium complexes.
P60	Erica	Faria	A simple route to phosphinecarboxamides: reactivity of the $\text{PCO}^-$ anion towards amino acids and amines
P61	Zahoor Hussain	Farooqi	Organic-inorganic hybrid nanoparticles for catalytic application
P62	Valerio	Fasano	Water-tolerance of $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{BPh}_3$ in reductive aminations
P63	Isabelle	Fernandes	Synthesis and characterisation of new, thermally stable alkene and alkyne Au(III) biphenyl complexes
P64	John	Fielden	Revealing DNA's secret structures: towards ruthenium-based i-motif specific phosphorescent probes
P65	Kerry	Flanagan	Synthesis of single source tin chalcogenide precursors
P66	M. Angeles	Fuentes	Phosphine/borane frustrated Lewis pairs chemistry with xanthene scaffolds.
P67	Samantha	Furfari	Investigating the substituents effects of trans alkynyl-cyaphide complexes
P68	Sudhakar	Ganta	Cavity containing metallogel: dye removal from water
P69	Martí	Garçon	Novel Pd-Mg intermetallic complexes: structural snapshots of the addition of Mg-H Bonds to Pd
P70	Nestor	Garcia Villalta	Ir (III) (bis-NHCs) complexes and their application in methanolysis and hydrolysis of silanes
P71	Hollie	Garwood	Catalytic applications of rhodium complexes for bond activation processes: Masters students' projects in the Weller group
P72	Peter	Gawne	Cell labelling and liposome tracking with $^{52}\text{Mn}$ using positron emission tomography.
P73	Maureen	Georges	Group 4 permethylpentalene complexes for cyclic ester polymerisation
P74	Oliver	Glenister	Charge transfer between hydrogen bonded ruthenium complexes
P75	Conrad	Goodwin	Heavy lanthanide metallocenium cations: electronic insights

P76	Christopher	Goult	Exploring the bonding of transition metal vinylidene complexes by solid-state NMR spectroscopy.
P77	Victoria	Greenacre	Trialkylstibene complexes of the Group XIII halides: synthesis, properties, and trends
P78	Matthew	Gyton	Rhodium(III) and iridium(III) complexes of a NHC-based macrocycle: synthesis and reactivity.
P79	Lewis	Hall	Stable fluoroalkynes via outer-sphere electrophilic fluorination
P80	Jonathan	Hall	Catalytic hydrodehalogenation using well-defined Ni(I) complexes
P81	Chris	Hawes	Influencing structure and function through guest exchange in fluorescent coordination polymers and metallogels
P82	Andreas	Heilmann	Small molecule reactivity of nucleophilic aluminium complexes
P83	Alexander	Hicken	Selective reduction of CO <sub>2</sub> with heterobimetallic gold-copper hydride complexes
P84	Jamie	Hicks	Nucleophilic aluminium: highly selective oxidative cleavage of C-H bonds in unactivated arenes at a main group metal centre
P85	Thomas	Hood	Synthesis of phosphine- based macrocyclic pincer ligands
P86	Thomas	Hooper	Palladium catalysed C-H bond aluminatation
P87	Samuel	Horsewill	Synthesis and electronic structure of 4f-3d coordination complexes bridged by a redox-active ligand.
P88	Chloe	Howells	Investigating benzimidazole-based fluorophores for their biological activity
P89	Ingebjorg	Hungnes	Towards <sup>99m</sup> Tc-labelled bioconjugated molecular SPECT imaging agents: BMA as a bifunctional diphosphine chelator
P90	Jamie	Hunter	Understanding how ionic liquids recover rare-earth elements
P91	Hasan Tanvir	Imam	Investigating the role of methionine in the design of artificial metalloenzymes: hydroformylation and metal binding
P92	Jerome	Innocent	Development of nickel oxide ALD precursors
P93	Garrett	Jackson	Exploiting non-covalent interactions in catalysis using pyrenylphosphines
P94	Martin	Jakoobi	Iridium duo in action – breaking C=C bonds in arenes
P95	Alice	Johnson	Synthesis of propargyl functionalised NHC gold complexes with biological and luminescent properties
P96	Corey	Jones	Making a MOF: how does your (crystal) garden grow?
P97	Mohanrao	Kalapaneni	Photoluminescence studies of Eu <sup>3+</sup> in Ba <sub>3</sub> Zn <sub>3</sub> TeP <sub>2</sub> O <sub>14</sub> , under the influence of high energy photon (NUV/Blue) of electromagnetic spectrum of light
P98	Manmeet	Kaur	Effect of nickel decoration on hydrogen storage performance of graphitic carbon nitride
P99	Sophie	Kendall-Price	Single NiFe hydrogenase crystals in well-defined redox states: combined electrochemical control and infrared microspectroscopic imaging
P100	Sabrina	Khoo	Cobaltosilylene with rhombic Si <sub>2</sub> Co <sub>2</sub> ring: synthesis and catalysis
P101	Michelle	Kinnon	Development of platelet specific imaging agent
P102	Alastair	Knights	High molar mass P-disubstituted polyphosphinoboranes via olefin hydrophosphination
P103	Richard Yuze	Kong	Heterobimetallic aluminylene complexes
P104	Pavel	Koroteev	Structural diversity of new transition metal cymantrenecarboxylates
P105	Pavel	Koroteev	Two novel series of 3d-3d'-4f-complexes with organometallic ligands
P106	Jessica	Lamb	Asymmetric group 4 metallocenes as polymerisation catalysts
P107	Nina	Leeb	Proton-shuttling in phosphoramidate assisted alkyne activation
P108	Pannee	Leeladee	Facile synthesis of vitamin B12-grafted silica nanoparticles for targeted delivery of cisplatin
P109	Baptiste	Leforestier	Synthesis and coordination chemistry of macrocyclic phosphine-based pincer ligands
P110	Madeleine	Levis	Synthesis, reactivity and electronics of the first trans- alkyl cyaphide complex
P111	Jingjing	Liu	Small molecule activation of thorium(III) complexes
P112	Ying Kai	Loh	Trapping a highly electrophilic germacarbonate
P113	Kevin	Lovelock	Experimental valence electronic structure of metal complexes in solution
P114	Cailean	Macleod	An investigation into 1,1-dithiolate Co(II) complexes
P115	Robert	Mangan	Low valent germanium cations for small molecule activation
P116	Strachan	McCormick	Cationic niobium complexes for renewable polyester synthesis
P117	Sarah	McDougall	Towards spin-crossover single-molecule magnets

P118	Jake	McGuire	Late transition metal bis(dithiolene) complexes for quantum computation
P119	Thomas	McGuire	The synthesis of borylated iminophospharanes
P120	Alasdair	McKay	Solid state Molecular OrganoMetallics (SMOM): synthesis, mobility and reactivity of a simple cyclic alkane $\sigma$ -complex
P121	Mina	Meseha	Transition metal/metal phosphides for the electrochemical reduction of $\text{CO}_2/\text{H}^+$
P122	Christopher	Miles	Exploiting non-covalent interactions in catalysis using pyrenylphosphophines
P123	Krishna	Mistry	Pt(0) monocarbonyl complexes for small molecule activation
P124	Fatiha	Moughaoui	Production of activated carbon using Moroccan sugarcane bagasse chemical and adsorption properties
P125	Louis	Morris	Organometallic polymers <i>via</i> alkaline earth-catalysed dehydrocoupling
P126	David	Moulding	Investigating the coordination chemistry of uranyl with bulky alkylsilylamide ligands
P127	Chantal	Mustoe	XAS and halogen bonds
P128	Samuel	Neale	Mechanistic studies into iron-catalysed transfer hydrogenation using amines and boranes
P129	Hannah	Nicholas	A new family of lanthanide bis(silyl)amide complexes
P130	Hao-Che	Niu	A novel phosphazane-derived macrocycle
P131	Georgia	Orton	Towards [FeFe] hydrogenase enzyme biomimics with redox active ligands for $\text{H}_2$ oxidation
P132	Fabrizio	Ortu	Isotopically enriched dysprosium(III) single molecule magnets
P133	Darren	Ould	Investigating the structure and reactivity of arsoles and phospholes
P134	Samuel	Page	Palladium catalysed transfer hydrogenations of biogenic acids
P135	Gemma	Parker	Nickel-templated synthesis of a [2]catenane
P136	Vijay	Parmar	Towards high-temperature single-molecule magnets
P137	Kyle	Pearce	Phosphametacyclophanes: toward reliable syntheses and predictable structural features
P138	Anne-Frederique	Pecharman	Easy access to nucleophilic boron
P139	Andrew	Peel	Isomerism in lithium amidocuprates: contrasts in reactivity towards aromatic reagents
P140	Jingying	Peng	Manganese(III)-catalysed homo-coupling of arylboronic acids
P141	Jack	Pike	Transformations of $\pi$ -arene ruthenium complexes
P142	Akkharadet	Piyasaengthong	Photochemical investigations of a $\pi$ -arene ruthenium complex with amino acid residues
P143	Victoria	Pollard	Its Al in the design: heteroleptic aluminium amides as homogeneous catalysts for hydroboration
P144	Amy	Price	Phosphaborenes: accessible reagents for P-B/C-C isosteres of cyclobutene and benzene
P145	Thomas	Price	Tripodal ligands for rapid chelation of gallium-68 at neutral pH
P146	Patrick	Proehm	Novelties in polyhalide chemistry
P147	David	Pugh	Tetraalkoxysilanes as (overlooked) reagents for direct amidation.
P148	Sebastian Yongsen	Quek	A 'stable' end-on superoxocopper(II) complex
P149	James	Radcliffe	Selective 3,4-Hydroboration of $\alpha,\beta$ -unsaturated esters using NHC-boranes
P150	Nasir	Rajabi	DFT study of heterobimetallic complexes derived from the e-deficient Ru-H complex, $[\text{Ru}(\text{IPr})_2(\text{CO})\text{H}]^+$
P151	Benjamin	Reant	Synthetic routes to low coordinate bis(silyl)amide Sm(III) complexes
P152	Feriel	Rekhroukh	Palladium catalysed C-F functionalisation of 1,3-difluorobenzene
P153	Alexander	Romanov	First linear silver complexes to give efficient organic light-emitting diodes
P154	Luca	Rocchigiani	Elusive gold(III) intermediates and how to catch them: the nature of Au(III) $p$ -alkyne and aryl complexes
P155	Cameron	Royle	Towards heterobimetallic catalysts: synthesis and reactivity of a novel mixed amido/carbene ligand system
P156	Max	Savage	Catalytic applications of rhodium complexes for bond activation processes
P157	Dennis	Schoenemann	Selective functionalisation of asymmetric phosph(V)azane dimers
P158	Roy	Schreiber	Self-assembly through noncovalent preorganization of reactants: explaining the formation of a polyfluoroxometalate
P159	Neil	Scott	Is there a role for Pd clusters in Pd-catalyzed arylcyanation?

P160	Sachin	Shah	Fabrication of hollow and porous iron oxide nanotubes from plant virus
P161	Namrah	Shahid	Pyrene functionalised organometallics as catalysts
P162	Stephanie	Sheppard	Functionalisation of cyclic ferrocene systems for molecular electronics
P163	Huayun	Shi	Photoactive platinum anticancer complexes
P164	Matt	Sinclair	Exploring the organometallic chemistry of mononuclear palladium(I)
P165	Frances	Singer	Electrochemical ring-opening during transition metal NHC complex synthesis
P166	Maya	Singer Hobbs	New bimetallic complexes for aerobic oxidation catalysis
P167	Jonathan	Slaughter	The reactivity of methylaluminium compounds with esters
P168	Hualong	Song	Highly stereoselective formation of asymmetric triazole-containing metallohelices
P169	Anastasia	Spearing-Ewyn	Exploring rhodium "PONOP" pincer complexes for amine-borane dehydrogenation
P170	Rachel	Steen	Selective activation of alkynes through cumulene intermediates
P171	Melissa	Stewart	WhiB-like proteins and their Fe-S dependent protein-protein interactions
P172	Caroline	Storey	Switching the regioselectivity of terminal alkyne coupling reactions using macrocyclic ligands
P173	Pattira	Suktanarak	Stability enhancement of copper(I) complexes for application in ascorbic acid detection
P174	Mark	Sullivan	Synthesis of polyesters catalysed by hemi-labile aluminium catalysts
P175	Matthew	Surman	Single-source precursors for $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> thin-films
P176	Alexander	Tansell	MIRIAM and the MOF
P177	Emily	Taylor	The preparation of ZnSe thin films via AACVD
P178	Oliver	Townrow	Base metals in unusual geometries, stabilised by a multidentate phenoxide ligand
P179	Khanittha	Walajjai	H <sub>2</sub> evolution catalyzed by cobalt complexes: electrocatalytic activities of cobalt(III) hydride complexes based on P,N-chelating ligands
P180	Rory	Waterman	P-C forming catalysis with iron
P181	Jessica	Waters	Dehydrocoupling of main group systems
P182	Luke	Wilkinson	Synthesis and coordination chemistry of cyanoferrocenes
P183	Thomas	Williams	Group 4 permethylindenyl constrained geometry complexes for ethylene polymerisation
P184	Dan	Wilson	An isolable phosphoethynolborane and its reactivity
P185	Dan	Wise	Cytotoxic ruthenium-diphosphine complexes
P186	Thomas	Wood	Catalytic applications of rhodium complexes for bond activation processes
P187	Callum	Woof	Iron-catalysed isomerisation of alkenes - examining reactivity & mechanism through synthesis, spectroscopy & DFT
P188	Christopher	Wright	Layered double hydroxides as effective catalyst supports
P189	Joseph	Wright	Ferracyclic Fe(II) complexes releasing carbon monoxide: photoCORMs in the dark
P190	Stephen	Yap	Polyacrylamide nanoparticles: a conjugatable platform for use in the diagnosis and treatment of cancer
P191	Callum	Yeardley	An introduction to nickel amide chemistry with potential for application in C-H activation chemistry
P192	Jiawen	Zhang	Reactions of biologically-relevant iron sulfur clusters with carbon monoxide studied by IR spectroelectrochemistry
P193	Xueer	Zhou	Low valent group 14 cations stabilised by tethered NHC ligands
P194	Richard	Knighton	Combining electronic and steric effects to generate hindered propargylic alcohols in high enantiomeric excess



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## **Publishing your chemical sciences research**

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



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# LECTURE ABSTRACTS

The oral abstracts appear in the following order:

- Plenary Lectures/Prize Lectures
- Dalton Transaction Editorial Board Lectures
- Coordination and Organometallic Chemistry
- Main Group Chemistry
- Inorganic Reaction Mechanisms
- Inorganic Biochemistry

Poster abstracts are available at

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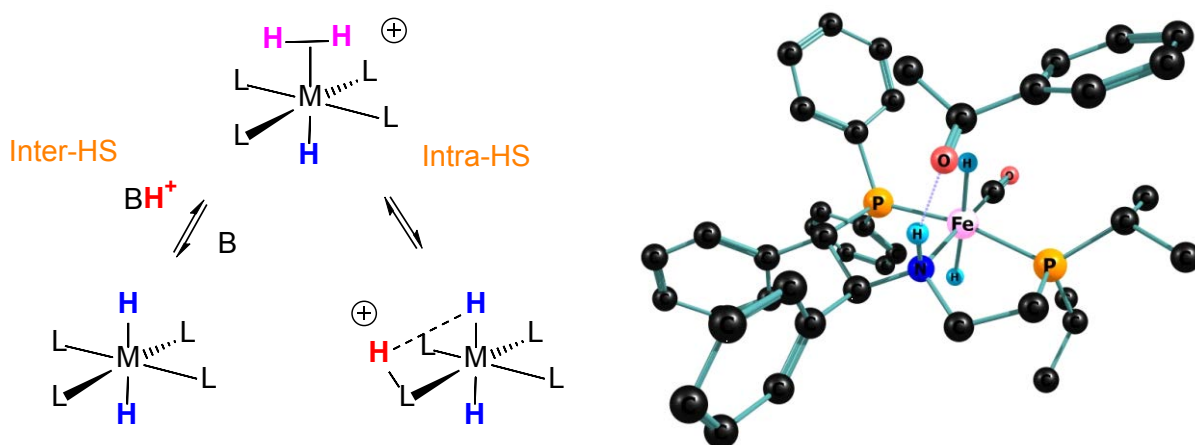
# Mechanisms of the H<sub>2</sub>- and transfer hydrogenation of polar bonds catalyzed by iron group hydrides

Robert H. Morris

*Department of Chemistry, University of Toronto rmorris@chem.utoronto.ca*

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This lecture will review our studies of hydrogenation processes. It commences with establishing thermodynamics and mechanisms of the heterolytic splitting (HS) of dihydrogen (e.g. Inter-HS and Intra-HS as below). Dihydrogen splitting is a common reaction found in industrial catalytic processes for the production of bulk chemicals, pharmaceuticals and other fine chemicals and in nature's hydrogenases. Our discovery of dihydrogen complexes of the iron group elements and metal hydrides acting as a hydrogen bond acceptors led to studies of Noyori's ligand-assisted asymmetric ketone hydrogenation catalyzed by ruthenium complexes in order to find out if these hydride-based phenomena are important in the mechanism. Transferring the knowledge gained to the field of iron-based catalysis, we developed the first highly active catalysts for both asymmetric transfer hydrogenation and H<sub>2</sub>-hydrogenation of prochiral ketones and imines to valuable non racemic alcohols and amines. This involves the synthesis of new ligand platforms where inexpensive enantiopure diamines or amino alcohols are used to make chelating phosphorus, nitrogen or N-heterocyclic carbene ligands. The optimization of catalytic activity are aided by experimental and DFT-based mechanistic investigations. The iron catalysts produced are of commercial interest because of their green, sustainable nature.



S. A. M. Smith, P. O. Lagaditis, A. Lüpke, A. J. Lough and R. H. Morris, *Chem. Eur. J.*, 2017, **23**, 7212; R. H. Morris, *Chem. Record* **2016**, *16*, 2644; *Chem. Rev.* **2016**, *116*, 8588; *Acc. Chem. Res.* **2015**, *48*, 1494.

## **Innovating Bimetallic Active Sites for Small-Molecule Catalysis.**

Connie C. Lu, Ryan C. Cammarota, Matthew V. Vollmer, Sai Puneet Desai, Jing Xie,  
Jinygun Ye, Laura Gagliardi  
*University of Minnesota, clu@umn.edu.*

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Discovering a catalyst that is perfectly tailored for a specific reaction is like finding a needle in a haystack. To optimize catalyst discovery, we investigate readily modifiable catalyst systems, for which small changes in structure or property can tune reactivity and/or selectivity. Multimetallic clusters are attractive systems to develop because their electronic properties and reactivity should depend on both the number and composition of the individual metals. The key challenge is to assemble uniform and well-defined multimetallic active sites in molecules and on solid supports. Often, scrambling, agglomeration, and/or other dynamic processes diminish uniformity of metal sites, giving away to complex catalyst speciations that are ill understood.

We have been developing first-row bimetallic complexes for catalysis, where using non-precious metals is sensible from economical and sustainability standpoints. The synergistic combination of different metals could generate hybrid “metals” with original properties and/or unique reactivities. We have investigated pairings of a late transition metal with a Lewis acidic main group ion to tune catalytic activity in activating small molecules, including H<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>. We have also developed the capability to precisely engineer bimetallic active sites on a robust MOF support, where the control over nuclearity and composition are pre-programmed into a bimetallic precursor complex. In both homogeneous and heterogeneous catalysis, the supporting metal plays a pivotal role and can be used to promote both activity and selectivity.

## **A Metallopeptide Mimic of Hydrogenase and Nitrite Reductase**

Kara L. Bren, Yixing Guo, Banu Kandemir, Saikat Chakraborty, Jesse Stroka

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Metalloenzymes that catalyse multi-electron, multi-proton reactions often have complex structures and multiple redox-active metal ion cofactors. These metal ions facilitate bond-breaking and bond-making steps as well as substrate binding and electron transfer.

Metalloenzymes also feature pathways for delivering protons to the active site at the appropriate  $pK_a$ . In this work, we are mimicking the activity of two such metalloenzymes with a simple metallopeptide, the water-soluble cobalt complex of Gly-Gly-His (CoGGH). CoGGH features a redox-active metal ion and a peptide ligand with protonatable sites, raising the possibility of proton-coupled electron transfer by this system. In this talk, the activity of CoGGH as a catalyst for two reactions relevant to energy and the environment will be described. First, CoGGH mimics the activity of hydrogenase by reducing aqueous protons to hydrogen near neutral pH. CoGGH performs this reaction as an electrocatalyst with an overpotential  $\sim 600$  mV, a faradaic efficiency exceeding 90%, and minimal sensitivity to oxygen. Ongoing mechanistic studies reveal the importance of proton-coupled electron transfer involving a Gly amine in this reaction, as well as the important role of buffer in proton delivery. The ability of CoGGH to facilitate the storage of light energy as  $H_2$  is illustrated by pairing the metallopeptide with a photosensitizer to yield a turnover number of  $\sim 1000$  with respect to catalyst. The second catalytic reaction of CoGGH to be described is the six-electron, eight-proton reduction of nitrite to ammonium. In nature, this reaction is catalysed by cytochrome *c* nitrite reductase as part of the global nitrogen cycle. Controlled potential electrolysis of CoGGH and nitrite at pH 7.2 generates ammonium with a faradaic efficiency of 90%. Ongoing efforts to elucidate catalytic mechanism and to understand the relationship between catalyst structure and function will be presented.

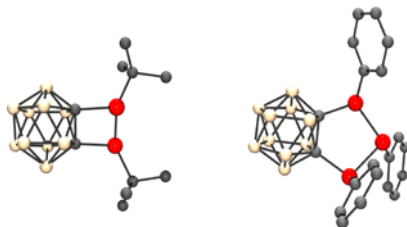
## Phosphorus Meets Carborane

Evamarie Hey-Hawkins, Peter Coburger, Jan Schulz

*Institute of Inorganic Chemistry, Leipzig University, Germany; hey@uni-leipzig.de*

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Carboranyl derivatives which contain phosphorus-based substituents (phosphines, phosphites, phosphonates, etc.) can be employed as (chiral) ligands in catalysis<sup>1</sup> or in medical areas<sup>2</sup>. Furthermore, the carboranyl backbone also allows the targeted synthesis of four- and five-membered phosphorus-containing heterocycles having endocyclic P–P bonds, which are difficult to obtain via other routes.<sup>3</sup> In this presentation, 1,2-bisphosphanyl-substituted *ortho*-carboranes, the precursors for 1,2-diphosphetanes and 1,2,3-triphospholanes<sup>4</sup>, and other carboranyl-substituted heterocycles will be discussed.<sup>5</sup> Especially, 1,2-P-alkynyl-substituted *ortho*-carborane derivatives are highly attractive target molecules due to the additional functionality of the C≡C triple bond.<sup>6</sup> Furthermore, the synthesis of related carboranyl-based heterocycles and following reactions (redox reactions, ring-opening reactions, etc.)<sup>7</sup> will also be presented



Carborane-substituted 1,2-diphosphetane (left) and 1,2,3-triphospholane (right). Hydrogen atoms are omitted.

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- <sup>1</sup> S. Bauer, E. Hey-Hawkins, Phosphorus-Substituted Carbaboranes in Catalysis, Ch. 22, in: *Boron Science, New Technologies and Applications*, ed. N. S. Hosmane, CRC Press: Boca Raton, FL, USA, **2011**, 513-559; S. Bauer, I. Maulana, P. Coburger, S. Tschirschwitz, P. Lönnecke, M. B. Sárosi, R. Frank, E. Hey-Hawkins, *ChemistrySelect* **2017**, 2, 7407.
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  - <sup>4</sup> A. Kreienbrink, S. Heinicke, Thi Thuy Duong Pham, R. Frank, P. Lönnecke, E. Hey-Hawkins, *Chem. Europ. J.* **2014**, 20, 1434.
  - <sup>5</sup> A. Kreienbrink, M. B. Sárosi, E. G. Rys, E. Hey-Hawkins, *Angew. Chem. Int. Ed.* **2011**, 50, 4701.
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## Artificial Metalloenzymes: Challenges and Opportunities

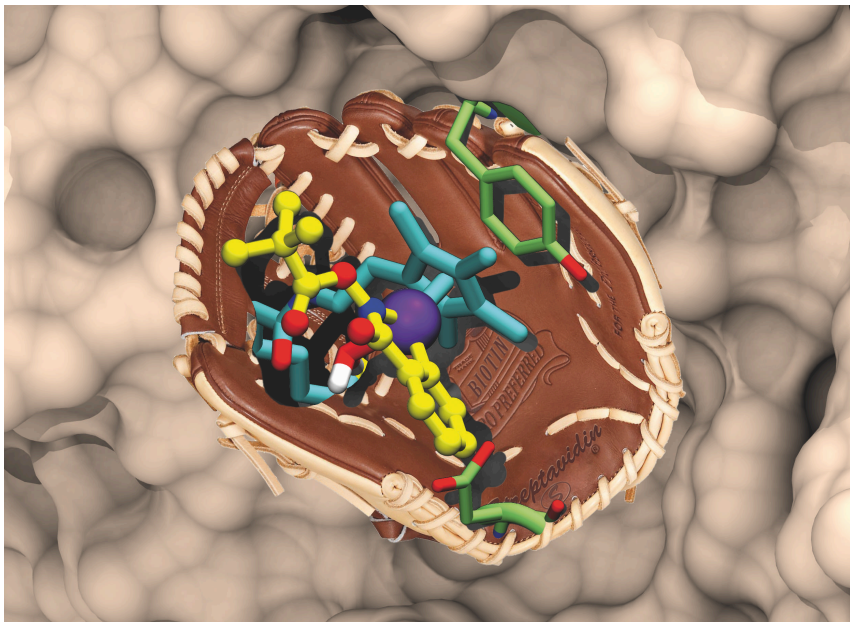
Thomas R. Ward

University of Basel, Switzerland. [thomas.ward@unibas.ch](mailto:thomas.ward@unibas.ch)

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Artificial metalloenzymes (ArMs) result from the incorporation of a catalyst precursor within a host protein, see Scheme. To engineer such ArMs, we have relied on various cofactor- anchoring strategies including: dative-, covalent- and supramolecular interactions. The resulting hybrid catalysts display features that are reminiscent of both homogeneous catalysts and enzymes. The optimization of the catalytic performance is achieved by combining both chemical- and genetic means. The versatility of these strategies will be illustrated with selected examples covering various host proteins, anchoring strategies and reactions including: (transfer)-hydrogenation, cross-coupling, C–H activation, dihydroxylation, Michael addition, olefin metathesis etc.<sup>1</sup>

With the aim of integrating artificial metalloenzymes *in vivo*, the second part of the talk will present our efforts to combine ArMs with natural enzymes to mimic essential features of the metabolism including: cascade reactions, up- and cross-regulation. Having identified the critical metabolites leading to ArM's inhibition *in cellulo*, our efforts towards performing catalysis in the periplasm of *E. coli* will be highlighted.<sup>2</sup>



**Scheme.** Anchoring a catalyst precursor (ball & stick representation) within a host protein (baseball glove) affords an artificial metalloenzyme. The catalytic performance of the resulting hybrid catalyst can be optimized by chemo-genetic means: variation of the nature and position of the cofactor (turquoise stick representation) and mutation of amino acid residues (green stick representation).

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## Exploiting the non-innocence of antimony ligands in organometallic catalysis.

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Thank you Although often regarded as heavy phosphine analogues, stibines behave as non-innocent ligands and display an unusual reactivity even when ligated to transition metals (M). This reactivity comes to light in their ability to undergo oxidation reactions without dissociation of the coordinated transition metal. This oxidation induces the formation of a M →Sb interaction resulting in a drastic Lewis acidity increase at the transition metal center.<sup>[1-3]</sup> Using a family of gold stibine derivatives, we will demonstrate that such coordinated-stibine oxidation reactions can be used to afford potent hydroamination catalysts.<sup>[4-6]</sup> Stibines are also non-innocent from a coordination point of view and can readily bind hard anions such as fluoride, without dissociation from the transition metal center.<sup>[7]</sup> This anion binding events convert the antimony atom into a more strongly donating ligand, leading to an increase of electron density at the metal center.<sup>[8]</sup> In this presentation, we will explain that this process can be exploited in reverse as a means to increase the electrophilic character of the transition metal center. This approach will be illustrated by the chemistry of a series of antimony platinum complexes and their conversion into active electrophilic hydroarylation and enyne cyclisation catalysts via antimony-centered anion abstraction reactions.<sup>[9]</sup>

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## Lewis acids promoted copper catalyzed synthesis of functional molecules

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Our research program<sup>1-5</sup> is aimed at the development of novel catalysis concepts for asymmetric synthesis of chiral functional molecules. In 2011 we introduced an entirely new role for Cu(I)-based catalysts, facilitating highly enantioselective carbon-carbon bond forming reactions between organometallics and enolisable carbonyl as well as imine compounds. Following this initial discovery, we established Cu(I)-catalysis, in combination with Lewis acids/Grignard reagent, as a powerful tool to tackle the reactivity of inherently unreactive substrates for carbon-carbon bond forming reactions. In this lecture I will focus on how we can use these concepts to access highly demanded and valuable chiral heteroarenes and amides, as well as tertiary alcohols and amines, in catalytic and enantioselective fashion.

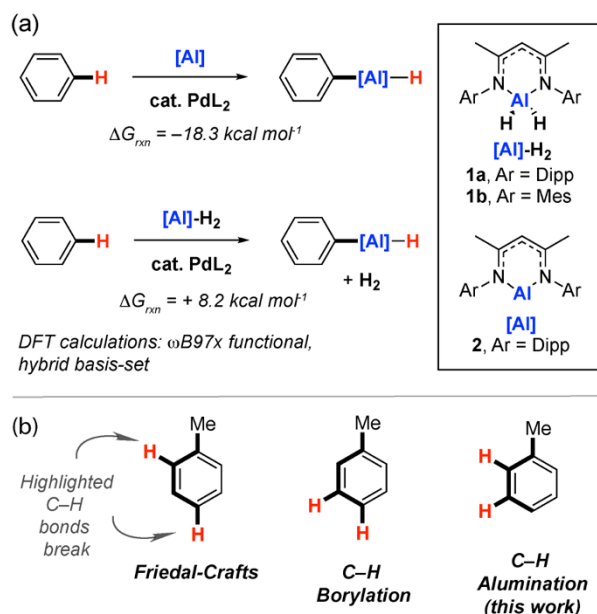
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## Carbon–Hydrogen Bond Activation with Intermetallic Complexes

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Once unimaginable, catalytic methods that selectively break C–H bonds in organic molecules are now considered indispensable in synthesis. The activation and functionalisation of inert C–H bonds in hydrocarbons from oil refineries, such as benzene, toluene and xylenes, is arguably one of the most challenging facets of this field.<sup>1-2</sup> We recently discovered some unusual Pd–Al intermetallic complexes capable of breaking the C–H bond of benzene at 25 °C.<sup>3</sup> Here we present the catalytic C–H alumination of benzene, toluene and xylenes using both Al(I) and Al(III) dihydride reagents (Figure – a).



Remarkably these reactions proceed primarily with *ortho*- and *meta*-selectivity, indicative of a new mode of regiocontrol that is complementary to both C–H borylation and Friedel-Crafts methodology (Figure – b). Preliminary mechanistic analysis suggests that C–H activation is the rate-limiting and selectivity determining step and that weak dispersion forces between the ligands and substrate determine the regiochemistry of C–H functionalisation.

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**Analyzing reaction in transition metal species:  
is there an alternative to energy ?**

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Theoretical chemists have analysed reaction mechanism by calculating energy profiles. This method, fundamentally appropriate for discussing reaction mechanisms, is also associated with interpretations based on the electronic properties of the species, which are themselves constructed from their molecular orbitals. In this presentation, we show how NMR chemical shifts can be also easily derived from molecular orbitals and thus can be used as indicators for reactivity. These facts will be illustrated by discussing metal alkylidene and metal alkyl complexes and associated reactions (olefin metathesis and  $\alpha$ -H abstraction, respectively).

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## **Mechanistic Studies of Sustainable Catalysis**

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Catalysis is one of the fundamental principles of sustainable chemistry. Catalysts improve reaction kinetics, selectivity, and efficiency. The field of catalyst design is both science-based as well as an art. The promise of rational catalyst design remains a challenge, albeit recent advances in constructing volcano plots for heterogeneous catalysts has been hailed as a major breakthrough. Understanding mechanisms of catalytic reactions is still the chemist's best tool to unravel and control molecular reactivity. This lecture will describe kinetics and mechanistic insights for a few transition metal systems spanning bioinorganic and organometallic chemistry to illustrate common themes but to also show limits of kinetics.

Iron porphyrin catalysts were found to mimic chlorite dismutase activity in transforming chlorite to innocuous chloride and dioxygen, a rare O-O bond forming reaction. Mechanistic insight from kinetics, isotope labelling, and computational studies led to new transformations upon changing the metal centre and further introducing secondary sphere interactions. Factors controlling atom transfer versus electron transfer were revealed.

DeOxyDeHydration (DODH) of biomass derived molecules is an attractive synthetic strategy for making renewable chemicals. Homogeneous organometallic oxorhenium complexes and nanoparticles are effective DODH catalysts. Study of their kinetics and mechanism has led to hetero-bimetallic systems envisaged for coupling C-H activation with biomass deoxygenation. Mechanistic lesson from Re-Ir and Re-Pt bimetallic systems eventually guided us to novel reaction chemistry on a single Pt site that can achieve catalytic arene coupling via C-H activation.

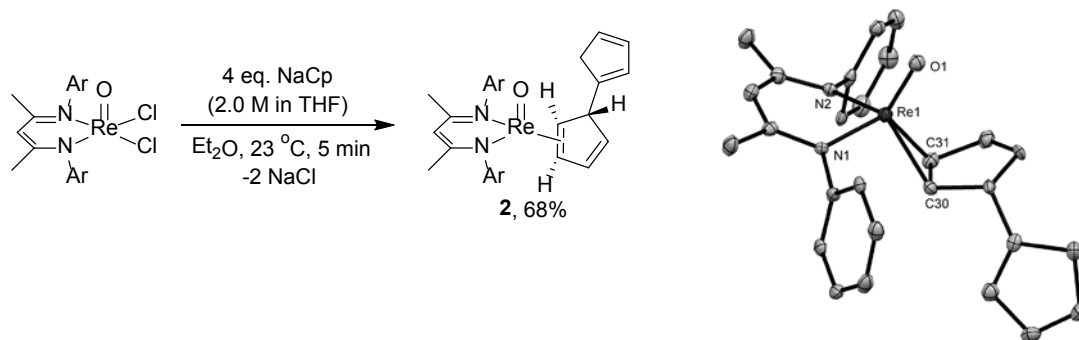
# New Catalytic & Stoichiometric Reactivity Promoted by Early Transition Metals

Trevor Lohrey, Jessica Ziegler, Robert G. Bergman & John Arnold

*Department of Chemistry, University of California, Berkeley, CA 94720-1460*

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Transition metal oxo and imido complexes have been a long-standing area of research due to their highly variable reactivity and their implication in numerous catalytic and enzymatic transformations. This presentation will focus on our recent work with new derivatives from group 5 and 7 metals, such as the unusual, highly reactive Re oxo-olefin species shown below.



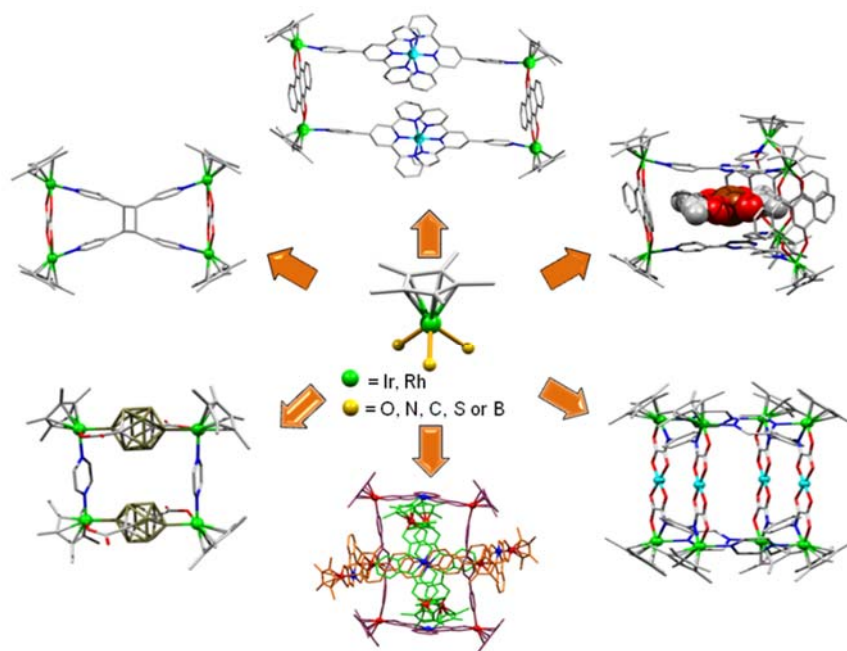
# Organometallic Macrocycles, Cages and Their Application

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The construction of new inorganic and organometallic macrocycles and cages with interesting structural features and technologically useful functions have been topics of intense study with considerable potential.<sup>1</sup> One of the chief motivating factors to growth in this field is the development of new, functional and tunable donor building blocks that can bridge transition metals. Ideal building blocks should be easily accessible, exhibit high affinities toward transition metals, and possess facial coordination sites can undergo exchange reactions with various ligands. Half-sandwich transition metal complexes (Cp\*<sub>2</sub>M, Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) are useful model compounds in which one hemisphere of the coordination shell is blocked by the voluminous Cp\* rings. In the protected space below the Cp\* ligands, various bidentate or tridentate ligands can be accommodated.



Motivated by interest in supramolecular chemistry with organometallic half-sandwich complexes, we have initiated a new approach for preparing organometallic macrocycles via C-H and B-H activations with Terephthalate and dicarboxylate carborane.<sup>2</sup> We report herein an efficient method for synthesizing molecular macrocycles of half-sandwich iridium and rhodium complexes via C-H and B-H activation directed multicomponent self-assembly under mild condition.<sup>3</sup>

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# Quantum Molecular Spintronics Based on Single-Molecule Magnets: Single-Molecule Memory, Spin Qubits, and Rabi Nutation at RT.

Masahiro Yamashita

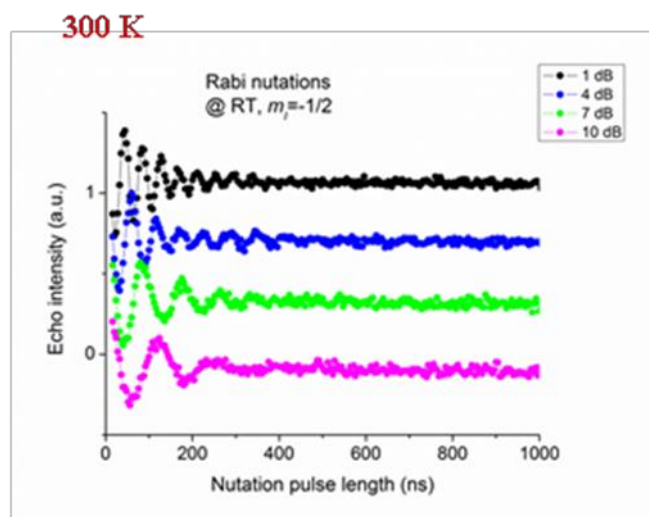
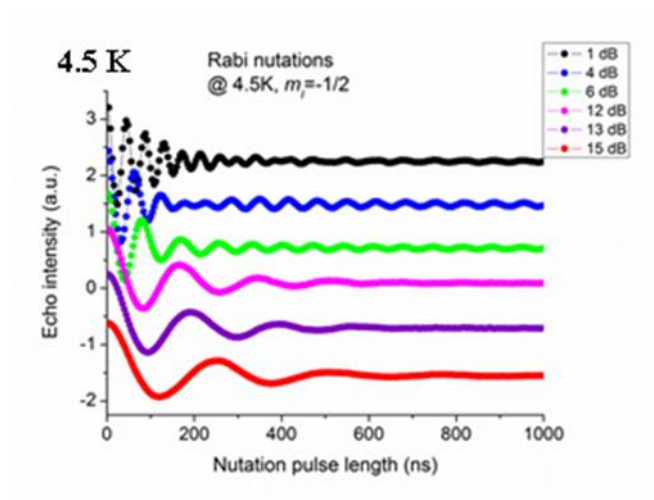
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Spintronics, based on the freedoms of the charge, spin, and orbital of the electron, is a key technology in the 21<sup>st</sup> century. Magnetic random access memory (MRAM), which uses giant magnetoresistance (GMR) or tunneling magnetoresistance (TMR), have several advantages over conventional systems, such as nonvolatile information storage, high operation speeds on the order of nanoseconds, high storage densities, and low power consumption. Although bulk or classical magnets composed of transition metal ions are normally used, in our study, we use single-molecule magnets (SMMs) to overcome “Moore’s Limitation”. SMMs undergo slow magnetic relaxation due to the double-well potential, defined as  $|D|S^2$ , and quantum tunneling, making them excellent materials for quantum computers and high density memory storage devices. I will talk single-molecule memory, spin qubit, and Rabi nutation at RT. Finally, I will talk the SMMs encapsulated into Single-Wall Carbon Nano Tube (SWCNT) to realize the new spintronics.

We usually use the double-decker phthalocyaninato Tb(III) SMM (TbPc2) as a single-molecule memory. On Au(111) substrate, we sublimated TbPc2. Then, by tunneling magnetoresistance (TMR) using STM tip with one Co atom, we have succeeded to put the spin up and down on TbPc2 and read them.

As for the quantum computer, we synthesized 0 ~ 3 dimensional V(TCPP) compounds. In the 3-D compounds, we have realized spin qubit and observed Rabi nutation even at RT. due to the rigid lattice as shown in the right.

As for the new quantum molecular spintronics, we have succeeded to encapsulate some SMMs into the single-wall carbon nano tube (SWCNT). The SMMs behaviors have been



improved by the encapsulation into SWCNT.

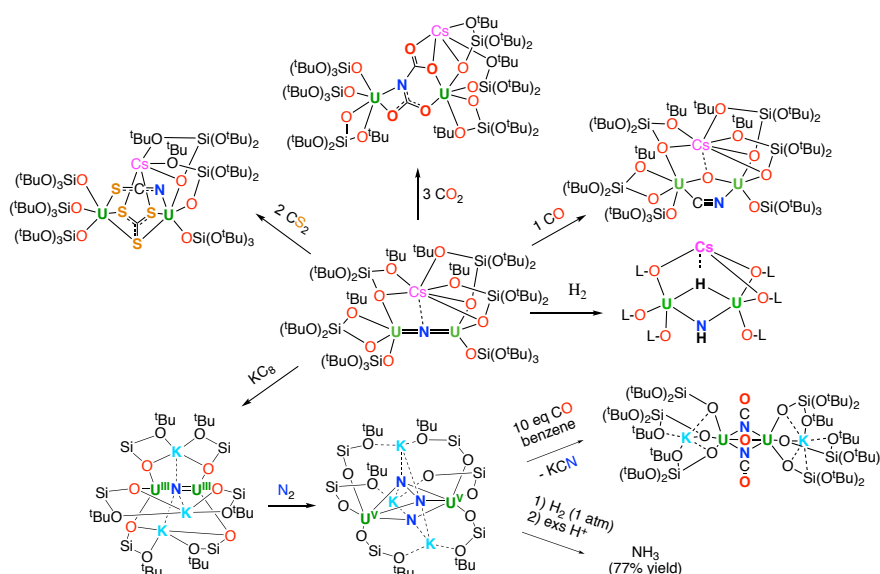


# Small Molecule Activation by Multimetallic Uranium Complexes

Marinella Mazzanti, Marta Falcone, Lucile Chatelain, Luciano Barluzzi

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Siloxide-supported multimetallic complexes of f-elements were found to promote the facile transformation of largely available small molecules such as CO, CO<sub>2</sub> and N<sub>2</sub>. *Tert*-butoxysiloxides are very effective ligands in supporting the reactivity of low valent f elements with small molecules because of their polynucleating nature and multiple binding modes. Moreover, these ligands provided a facile access to multimetallic nitride bridged uranium complexes. Uranium nitrides are attractive candidates for stoichiometric and catalytic small molecule transformation and for N-transfer reactions that are key steps in the construction of value-added chemical compounds. We showed that the multimetallic nitride bridged diuranium(IV) complex Cs{(μ-N)[U(OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>2</sub>}, **1**, easily reacts with CO<sub>2</sub>, CS<sub>2</sub> and CO, H<sub>2</sub>, promoting the formation of N-C or N-H bonds affording diverse N-functionalized products (Figure 1). The high reactivity of complex **1** is confirmed by its ability to cleave one of the strongest bonds in nature, the carbon oxygen bond in carbon monoxide, leading to the oxo/cyanide complex, **4**. Furthermore, we showed that the metal centers in **1** can be further reduced leading to a multimetallic K<sub>3</sub>UNU nitride bridged diuranium(III) complex, **5** which shows extraordinary reactivity towards dinitrogen and CO. An overview of small molecule activation and transformation by multimetallic complexes of uranium will be presented.



**Figure 1.** Nucleophilic reactivity of a siloxide-supported nitride-bridged di-uranium(IV) complex with H<sub>2</sub>, CS<sub>2</sub>, CO<sub>2</sub> and CO and dinitrogen reduction and functionalization by a nitride-bridged di-uranium(III) analogue.

## Applications of inorganic nanoparticle enzyme mimics.

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The ambitious goal of biomimetic chemistry to emulate the structural and functional aspects of natural enzymes. Nature has served as a source of inspiration for “designing” functional (supra)molecular enzyme models, “artificial enzymes”, and much effort has been invested in the synthesis of (supra)molecular models that are more stable and cost efficient compared to their natural counterparts. Although functions of enzymes are governed by the enzyme dynamics, an enzyme is typically much larger than its substrate and the reaction environment it exposes is so different from the surrounding solvent that it may be considered a solid catalyst. The radii of enzymes and nanoparticles are comparable to nanometer-sized cellular features, and the interactions of enzymes and nanoparticles with soluble molecules have comparable strength.

In addition, nanoparticles are highly reactive, they are stabilized in solution with ligands, surfactants, or polymers and their activity and selectivity are determined by characteristics such as size and structure of the facets they expose. The most active particles in catalysis have diameters of a few nanometers, i.e. they contain only a few hundred atoms. Their reactivity may even be higher than that of enzymes, because *any* surface site can be catalytically active, whereas enzymes have only a single binding site, although with exceptional. Therefore, enzyme mimetic catalysis with nanoparticles has been successful in cases, where small species (peroxides, superoxides or sulfites) are involved and steric demands play only a minor role for the specificity of the reaction.

Different from most enzymes nanoparticle mimics can also operate in non-aqueous systems, and they are readily available by cost-efficient synthesis up to industrial-scale. Of all nanoparticles discussed, vanadium oxide, cerium oxide, copper hydroxide, iron oxide and molybdenum oxide nanoparticles showed catalytic activities and stabilities comparable or superior to those of natural enzymes. We highlight recent progress in the field of enzymatically active inorganic nanomaterials and illustrate new applications in antifouling, wound healing, water and gas purification, or fiber staining.

## Lanthanide SMMs: Life Beyond the Venerable Cyclopentadienyl Ligand

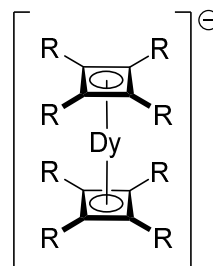
Benjamin M. Day, Fu-Sheng Guo and Richard A. Layfield\*

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Single-molecule magnets (SMMs) are coordination compounds that display magnetic memory effects.<sup>1</sup> We have a particular interest in metallocene SMMs based on dysprosium, and, over the years, we have reported a few examples of such materials.<sup>2</sup> Our work has shown that the [Cp]<sup>-</sup> ligands provide a strong axial crystal field that enhances the magnetic anisotropy of Dy<sup>3+</sup>, leading us to propose that a cation of the type [Cp<sub>2</sub>Dy]<sup>+</sup> should be an interesting synthetic target.<sup>3</sup> Thus, we and others have described the SMM properties of [Dy(Cp<sup>ttt</sup>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Cp<sup>ttt</sup> = 1,2,4-tritertbutylcyclopentadienyl), which displays a record magnetic blocking temperature of 60 K.<sup>4</sup>

Having established the design principles required to optimize the SMM properties of dysprosium sandwich complexes, we now turn our attention to the cyclobutadienide ligand, i.e. [Cb]<sup>2-</sup>. Surprisingly, there were, hitherto, no lanthanide complexes of [Cb]<sup>2-</sup> ligands, hence investigations of such materials furnish an opportunity for fundamental advances in lanthanide organometallic chemistry. In addition, the greater formal charge and the four-fold symmetry provided by the [Cb]<sup>2-</sup> ligand provide a new strategy for the development of SMMs, such as the complex illustrated above. Our initial results on such systems will be described.<sup>5</sup>



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# Synthesis and Reactivity of PC<sub>carbene</sub>P Complexes of First Row Transition

## Metals

Authors. Warren E. Piers, Etienne A. LaPierre, Marissa L. Clapson, Chris Gendy and Benjamin Gelfand

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Controlled activation of small molecules by base metal systems is a key challenge in modern organometallic chemistry. One possible solution to this challenge is the design of ligand fields that actively participate in substrate activation through ligand non-innocence,<sup>1</sup> or metal-ligand cooperation.<sup>2</sup> Recently, we have reported a Ni(II) PC<sub>carbene</sub>P pincer ligand complex, featuring a nucleophilic Schrock-type central donor, capable of activating a wide variety of H-X bonds through metal-ligand cooperation across the Ni=C double bond.<sup>3-4</sup> Modification of the ligand framework has allowed for the synthesis of a family of cationic Ni(II) PC<sub>carbene</sub>P complexes in which the polarity of the carbene is reversed. Preliminary reactivity studies reveal complementary small molecule reactivity to the previously reported Schrock-type system, dominated by the electrophilicity of the *umpolung* nickel-carbene bond. Further, modification of the ligand framework has also led to the isolation of a related cobalt PC<sub>carbene</sub>P complex, and investigations into the electronic structure and reactivity of this complex are currently underway.

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# Synthesis and Reactivity of Compounds Containing Si=N, Si=P or P=P

## Motifs

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## Abstract

Compounds containing multiple bonds between main-group elements can be kinetically stabilized by the use of appropriate sterically encumbered groups on the main-group elements. Apart from the novelty of their synthesis and structure such compounds also have considerable promise in new reactivity which is not accessible from other systems. In this regard, hetero-element compounds containing Si=N or Si=P are of interest because of the electronegativity differences between Si and N or P. Such electronegativity difference can result in unusual reactivity including the possibility of small molecule activation. We discuss, herein, the synthesis and structural characterization of new Si=N and Si=P compounds.<sup>1,2</sup> These compounds were prepared by a direct synthetic route involving dehydrohalogenation across a Si-N/Si-P bond from Si(IV) precursors. These compounds are characterized by the presence of a Si-H motif. The Si=N analogue shows an interesting addition of H<sub>2</sub>O across the multiple bond. We also discuss the reactivity of a P=P system and on NHC-CAAC triazaalkenes in three different oxidation states.<sup>3</sup>

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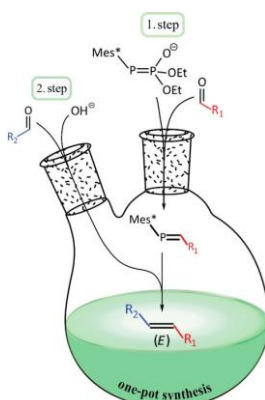
# Phosphaalkenes are Key Intermediates in the Reductive Cross-Coupling of Aldehydes to Alkenes

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The only general method for the reductive coupling of carbonyl compounds to alkenes is the McMurry coupling where low-valent Ti reagents reduce carbonyl substrates in a heterogeneous radical reaction. The McMurry coupling is often described as “tricky”, requiring heating in high boiling solvents for extended periods of time, and the cross coupling of two carbonyl compounds to selectively form unsymmetrical alkenes is not possible.

We have recently reported an alternative, one-pot protocol for the reductive cross-coupling of aldehydes to alkenes.<sup>1</sup> In this proof-of-concept study, a first aldehyde is converted to a phosphaalkene intermediate in a phosphorus version of the Horner-Wadsworth-Emmons (HWE) reaction. This phosphaalkene is then converted to a phosphine oxide, which under basic conditions reacts with a second aldehyde to afford *E*-alkenes (see Figure). The methodology is superior to the McMurry coupling in that it proceeds at room temperature within minutes, without transition metals, and, most importantly, give rise exclusively to unsymmetrical alkenes.



In this presentation, latest and unpublished improvements of the reaction's substrate scope will be disclosed, together with works to control *E*- and *Z*-selectivity in the reductive aldehyde coupling. All modifications are rationally designed and based on a detailed mechanistic understanding of the chemistry of low-coordinate phosphorus compounds.

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## Click Chemistry for the Synthesis of Metal-Peptide Bioconjugates

Nils Metzler-Nolte

*Inorganic Chemistry I – Bioinorganic Chemistry, Ruhr-University Bochum, 44801 Bochum, Germany; Email: [nils.metzler-nolte@rub.de](mailto:nils.metzler-nolte@rub.de); WWW: [www.chemie.rub.de/ac1](http://www.chemie.rub.de/ac1).*

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Our group uses the unique spectroscopic and chemical properties of organometallic complexes for the detection and modification of bioactive peptides and other biomedical applications. The experimental challenge is to identify suitable air- and water stable organometallic compounds with the desired properties, and to devise or adapt methods for the mild, biocompatible synthesis of bioconjugates with these metal complexes.

In our work, several different classes of metal complexes were successfully used in solid phase peptide synthesis (SPPS) techniques and subsequently for biomedical applications. Compounds used in our group include, *inter alia*, metallocenes, third-generation tris(pyrazolyl)borate (Tp') complexes, metal carbonyls, and metal complexes of functionalized N-heterocyclic carbenes (NHCs). Peptides used were derived from sequences known for enhanced and / or cell-type specific uptake (e.g. TAT peptides or octreotate), for intra-cellular delivery (such as nuclear or mitochondrial localization),<sup>[1]</sup> or for G-protein coupled receptor ligands. As a mild, biocompatible method the Cu-catalyzed azide-alkyne cycloaddition (Cu-AAC, often described as the prototypical "click" reaction) has been proven to be tremendously useful. I will show how this reaction can be applied to attach metal complexes to virtually any position of the peptide. While N-terminal functionalization is conceptually most easily realized, unnatural amino acids have to be utilized for amino-acid selective side chain functionalization. Finally, C-terminal derivatization with metal complexes is most difficult to achieve and to this end, a new linker has been developed in our group, the so-called Silyl-Alkyne Modifying (SAM) linker.<sup>[2]</sup> Applications of these metal-peptide conjugates for targeted drugs and the study of mechanisms of action for metal-based drug candidates will be presented.<sup>[3, 4]</sup>

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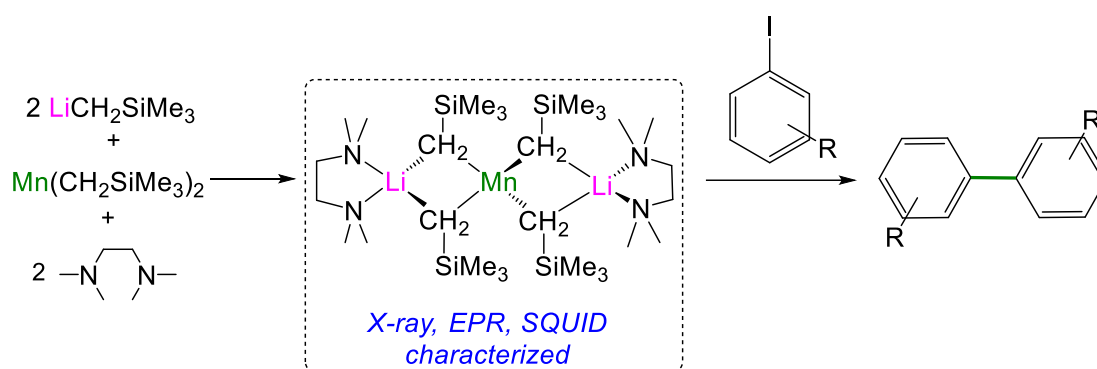
## New C-C Bond Forming Strategies Mediated by Alkali-Metal Manganates

Marina Uzelac, Marco De Tullio, Pasquale Mastropierro and Eva Hevia

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

Shedding new light in this area, here we present our recent finding on the rational synthesis and structural elucidation of alkali-metal manganates containing alkyl groups<sup>[5]</sup> and their applications to promote tandem processes which combine sequential direct Mn-I exchange with a homocoupling step to access symmetric bis(aryl) organic scaffolds.



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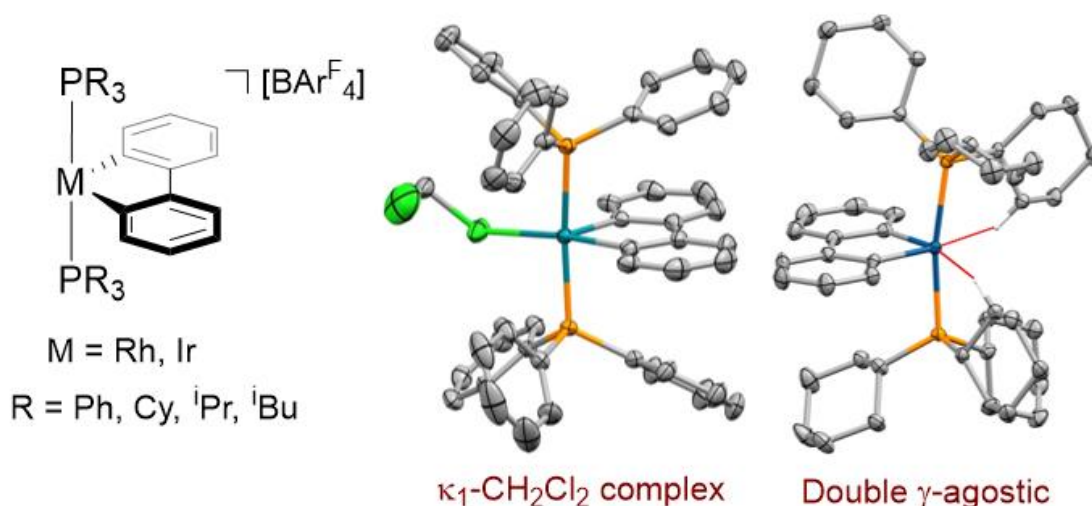


## Solution, solid-state, and computational analysis of agostic interactions in a coherent set of low-coordinate rhodium(III) and iridium(III) complexes

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The preparation of a homologous series of low-coordinate complexes of the general formula  $[M(2,2'\text{-biphenyl})(PR_3)] [BAr^F_4]$  ( $M = Rh, Ir$ ;  $R = Ph, Cy, ^iPr, ^iBu$ ) is described.<sup>1</sup> The structural features these formally 14VE species have been extensively studied using solution (VT  $^1H$  and  $^{31}P$  NMR spectroscopy), solid-state (single-crystal X-ray crystallography), and computational methods (DFT-based NBO and QTAIM analysis). Using this data, the extent of M–H–C bonding has been systematically evaluated and structure-property relationships established for variation of the phosphine and constituent metal centre. The effect of crystal packing on the agostic interactions has also been investigated through using a combination of crystal engineering and variable temperature measurements ( $M = Rh, Ir$ ;  $R = Cy$ ; solvate =  $CH_2Cl_2$ , 1,2-difluorobenzene;  $T = 25, 150$  K).



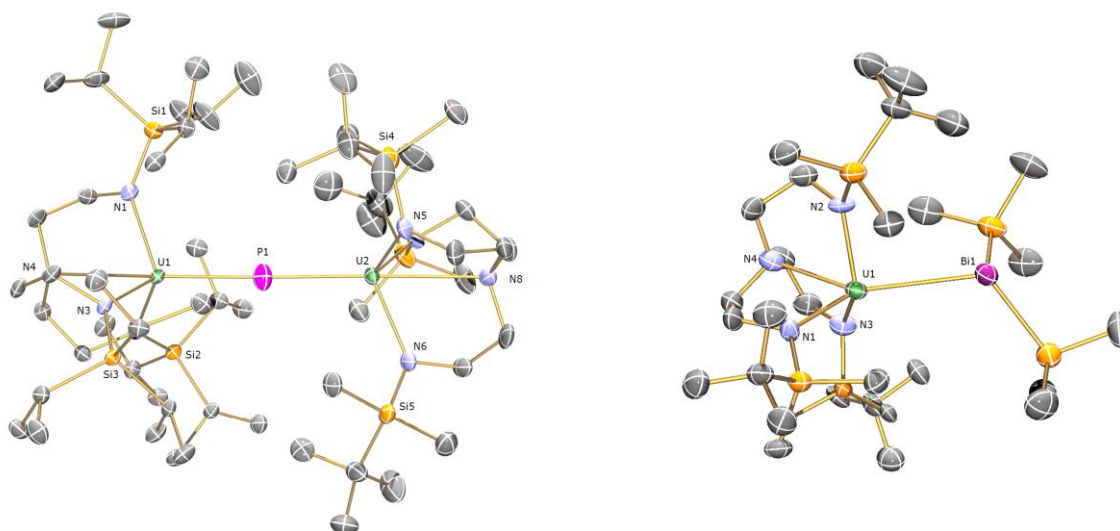
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## Novel Heavy Pnictide Complexes of Uranium and Thorium

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There remain few areas of the periodic table where new element-element bonds can regularly be discovered. However, the actinides remain a fecund period in this regard. Even for the naturally occurring and relatively abundant actinides, uranium and thorium, there remain fundamental actinide-element linkages that have become conspicuous in their absence. The isolation and characterisation of these fundamental linkages can inform us about the chemical characteristics and reactivity of the actinides allowing us to probe and refine periodic trends and provide vital benchmarks for theoretical models of these heavy elements.



In this talk we discuss recent studies of organometallic complexes that exhibit bonds between uranium and thorium and the heavy pnictides (P, As, Sb and Bi), including the first example of a uranium-phosphido complex outside of matrix isolation, the first examples of uranium- and thorium-antimony bonds of any kind and the heaviest crystallographically characterised pairing of any two elements in the form of the first example of a uranium-bismuth bond. Spectroscopic, magnetic, crystallographic and computational data will be presented to provide a detailed description of this previously unexplored class of compounds.

*Angew. Chem. Int. Ed.* **2018**, 57, 1332 – 1336.

*Angew. Chem. Int. Ed.* **2017**, 56, 10495 – 10500.

## Escaping Obscurity: Transition Metal Cyaphides

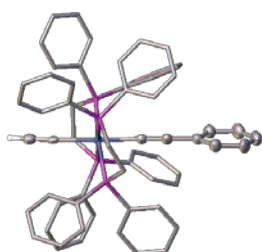
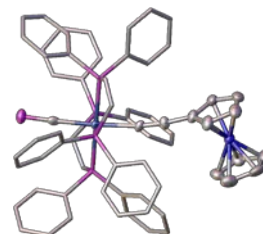
Matthew C. Leech, Ian R. Crossley

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The cyanide ion ( $\text{C}\equiv\text{N}^-$ ) is, alongside the acetylide fragment ( $\text{C}\equiv\text{CH}$ ), one of the most ubiquitous and widely exploited ligands in organometallic chemistry. In contrast, their phosphorus counterpart cyaphide ( $\text{C}\equiv\text{P}$ ) has proven to be an elusive moiety, having never been isolated as a discrete salt, and examples of it ligated to a transition metal centre are rare.<sup>1-5</sup>

Recently, the facile synthesis of transition metal complexes featuring ligated cyaphide has been reported, formed through base induced desilylative rearrangement of the  $\eta^1$ -phosphaalkyne complexes  $\text{trans-}[\text{Ru}(\text{P}\equiv\text{CSiR}_3)(\text{dppf})_2(\text{R}')]^+$  [ $\text{R} = \text{Ph, Me; R}' = \text{H, alkyne}$ ].<sup>2,3</sup> Consequently, it is now possible to furnish a library of mono- and multi-metallic phosphaalkyne and cyaphide complexes with ease.



Comprehensive investigations within the group have demonstrated that cyaphide is indeed a “carbon copy”.<sup>6</sup> In addition, the first instance of multiple  $\text{C}\equiv\text{P}$  units incorporated into conjugated, redox-active bimetallic systems, has been achieved, allowing studies into the influence of this elusive moiety.<sup>5</sup>

The synthesis and study of mono- and multi-metallic transition metal cyaphide complexes, in conjunction with recent developments, will be described.

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# Synthesis and Characterisation of Rare Earth-Transition Metal Heterometallic Complexes with a Redox-Active Bridging Ligand.

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The use of organometallic building blocks for the controlled synthesis of complex molecular or nano-structured materials is an important area of research. The distinct properties observed in molecular materials *vs.* bulk materials represent an opportunity to develop future materials and technologies. Elements with f-electrons are particularly exciting in the scope of their applications. Our interest is in development of f-element systems that allow for the engineering of cooperativity between mixed metal centres.

We have used a redox-active bridging ligand with multiple and selective binding sites as the template for a general and modular synthetic route to d-f or f-f' complexes (Figure 1). The neutral complexes [M(hfac)<sub>3</sub>(N,N'-pd)] (M = Y, Sc, Gd. pd = 1,10-phenanthroline-5,6-dione) have been prepared in 2 steps from M<sub>2</sub>O<sub>3</sub> in excellent yields, and fully characterised. These complexes undergo one or two electron reduction processes to form, [Ln(hfac)<sub>3</sub>(N,N'-O,O'-pd)MCp<sub>2</sub>] (M = Cr, V), [Ln(hfac)<sub>3</sub>(N,N'-O,O'-pd)VCp<sub>2</sub>]<sup>+</sup>[Cl]<sup>-</sup> and [CoCp<sub>2</sub>]<sup>+</sup>[Ln(hfac)<sub>3</sub>(N,N'-O,O'-pd)]<sup>-</sup>. We have used IR, UV-vis-NIR and EPR spectroscopies in combination with XRD and DFT to understand the electronic structure of these bimetallic complexes. Preliminary data on using Ln(II) as reducing agents and efforts to synthesise higher nuclearity complexes, will also be presented.

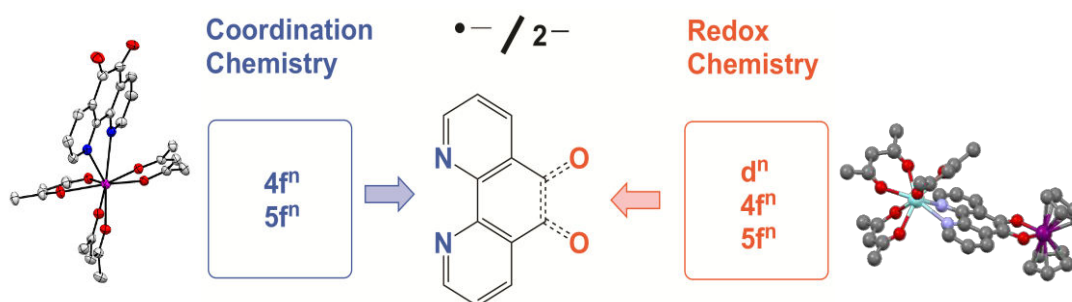


Figure 1. Modular synthesis of heterometallic pd complexes

## The influence of chirality on the spin states on iron (II) pybox derivatives

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Spin-crossover (SCO), a transition between the low-spin and high-spin state of some  $d^4$ - $d^7$  transition metal complexes, can be triggered by an external physical or chemical stimuli. Iron (II) complexes with six nitrogen donor atoms show a prominent shift between a fully diamagnetic low-spin state and a paramagnetic high-spin state; this shift can be tracked to report on the SCO behaviour of the complex.<sup>1</sup>

The interplay between spin-crossover and chirality has been little explored until recently, and it is this relationship which is investigated in this work. Successful combination of these properties could lead to functional non-linear optical materials.<sup>2</sup>

To investigate, a series of homochiral (Fig. 1a) and heterochiral (Fig. 1b) iron (II) complexes bearing pybox ligands were prepared and their solid state and solution phase properties investigated. These data indicate that interactions between the substituents present in the X position dictate the spin-crossover behaviour of the complex, a result supported by Density Functional Theory calculations.

The solution phase magnetic susceptibility data (Fig. 1c) indicate that the high-spin state of the homochiral phenyl-substituted complex is stabilised with respect to the heterochiral complex. This proves, for the first time, that chirality can impact spin-crossover behaviour.

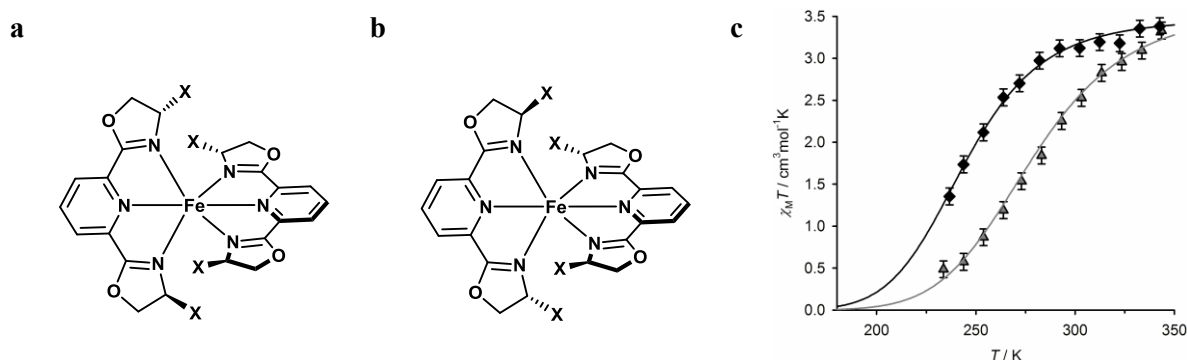


Figure 1 - General structure of a) homochiral complexes and b) heterochiral complexes.  $X = \text{H, Me, Ph, } i\text{Pr}$ . c) Solution phase magnetic susceptibility for homochiral (black) and heterochiral (grey)  $[\text{Fe}(\text{pybox})_2]^{2+}$  complexes bearing phenyl substituents.

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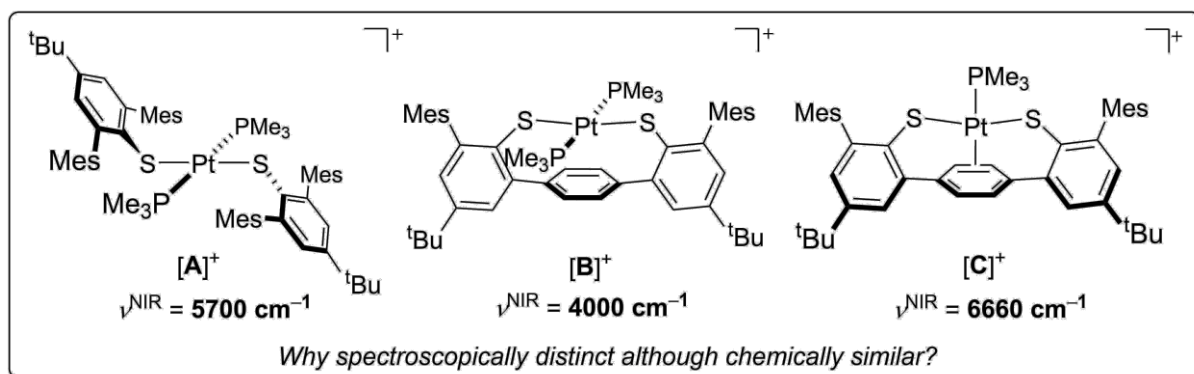
## Structure-property relationship of radical-ligand complex near-infrared chromophores of platinum.

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Transition-metal complexes of radical ligands can exhibit low-energy electronic transitions in the near-infrared (NIR) spectral region.<sup>[1]</sup> NIR band energy and intensity sensitively depend on the degree of electronic coupling of the chromophore. Using the example of open-shell complexes derived from platinum and mono- and multidentate thiophenol ligands, this contribution will present a conceptually different approach toward spectroscopically distinct NIR chromophore systems.<sup>[2]</sup>



The presentation will address the following questions. What is the locus of oxidation in the above series of structures **A**, **B** and **C**? Why do the energies of electronic transitions  $\nu^{\text{NIR}}$  differ substantially although the chemical structures of the series **A-C** are similar? What effect do co-ligands **L** have on the electronic structures and spectroscopic properties? How do these findings fit the context of the chemistry of radical-ligand complexes of the transition-metals? References.

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# Synthesis and Magnetic Properties of Polynickelocenes with Different Main Chain Spacers

Rebekah L. N. Hailes<sup>1\*</sup>, Rebecca A. Musgrave<sup>1</sup>, Alexander F. R. Kilpatrick<sup>2</sup>, Andrew D. Russell<sup>1</sup>, George R. Whittell<sup>1</sup>, Dermot O'Hare<sup>2</sup>, and Ian Manners<sup>1†</sup>

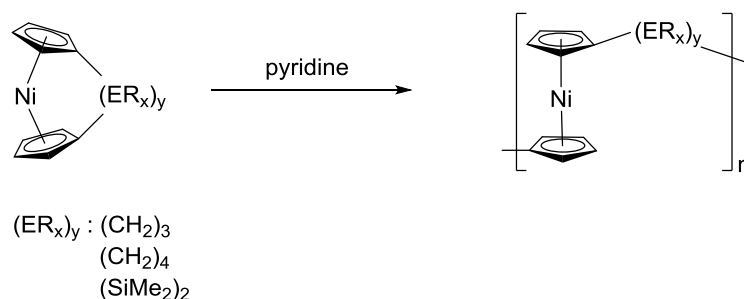
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Metal-containing polymers (metallopolymers), in which the inherent functionality of metal centres is combined with the facile processing typical of organic polymers, have long been regarded as a desirable target. Currently, the only reported polynickelocene is formed as a mixture of cyclic and linear components by the spontaneous ring-opening polymerisation of tricarba[3]nickelocenophane in pyridine (or other polar organic solvents).<sup>1</sup> Containing  $S = 1$  centres, above 28 K the polynickelocene was found to behave as a simple paramagnet according to the Curie-Weiss law, with significant antiferromagnetic spin-spin interactions.<sup>2</sup> The generality of the synthetic approach has now been applied to describe the ring-opening polymerisation of tricarba[4]nickelocenophane and disila[2]nickelocenophane to yield predominantly insoluble homopolymers, that act as paramagnets above 50 K, but deviate to show interesting magnetic behaviour at low temperatures.



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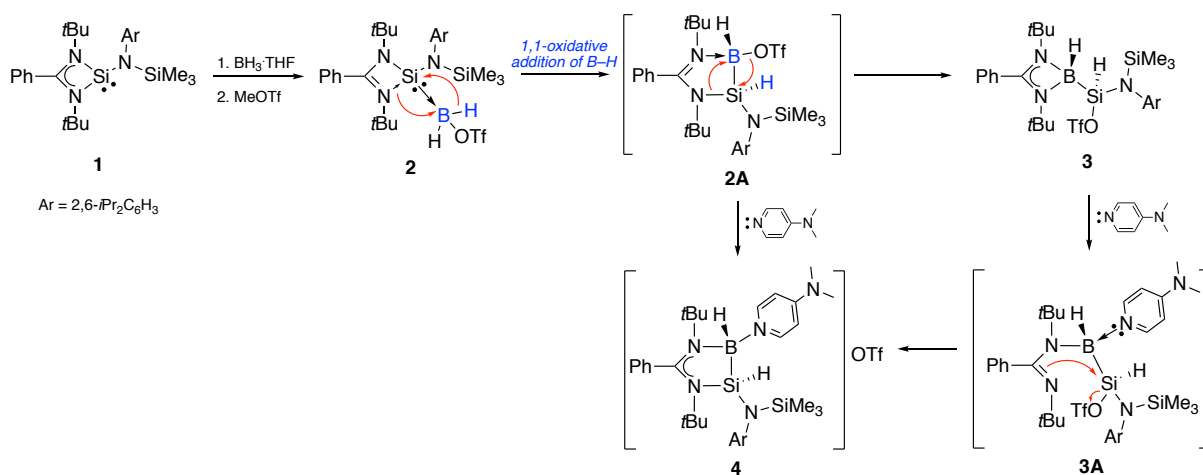
# B-H Bond Activation by an Amidinate-Stabilized Amidosilylene: Non-Innocent Amidinate Ligand

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B-H bond activation by a singlet carbene and its heavier analogue is a synthetic challenge associated with high B-H bond dissociation energy which is generally unaffected by substituent effects. Additionally, borane prefers to use its vacant p orbital, instead of B-H  $\sigma^*$  orbital, to accept electrons, while B-H  $\sigma$  orbital is a poor donor. To date, no examples of B-H bond activation by *N*-heterocyclic silylenes (NHSis) were reported, predictably due to their weak nucleophilicity. Herein, we describe the first B-H bond activation of boranes by an amidinato amidosilylene (**1**) via 1,1-oxidative addition on the Si(II) center (Scheme 1).<sup>1</sup> Mechanistic studies show that **2A**, bearing a non-innocent amidinate ligand, is a key intermediate in the reaction sequence.<sup>1</sup>



Scheme 1. B-H bond activation by amidinato amidosilylene **1**.

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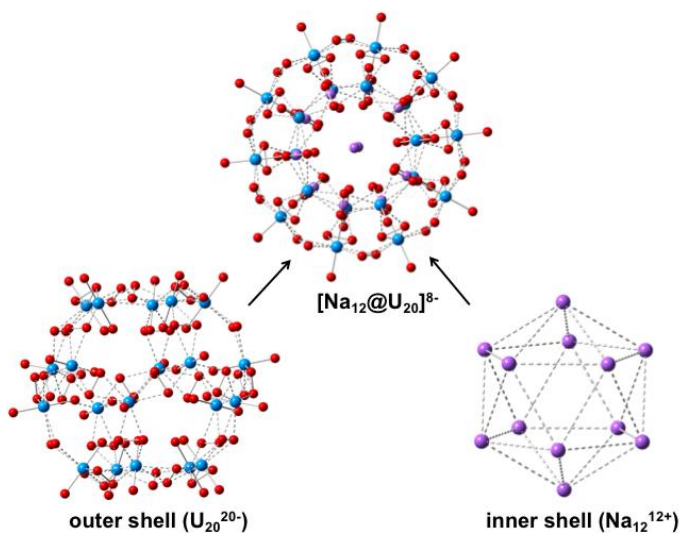
# Very High Spin Ground States in Matryoshka Actinide Nanoclusters

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Inspired by the experimentally synthesized  $\text{Na}_{12}@[(\text{UO}_2)(\text{O}_2)_{1.5}]_{20}^{8-}$  (“ $\text{Na}_{12}@U_{20}$ ”) cluster (Figure 1), we have used density functional theory to explore computationally the substitution of the Na cations by many other metals.<sup>1</sup> Six other  $M_{12}@U_{20}$  systems are found to be stable ( $M = \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Ag}^+, \text{Mg}^{2+}, \text{Fe}^{2+}$ ). For three of these ( $\text{Mg}^{2+}, \text{Ag}^+$  and  $\text{Na}^+$ ), the cluster can support a group 16 dianion at its center, forming a new type of Matryoshka (“Russian Doll”) actinide nanocluster  $E@M_{12}@U_{20}$  ( $E = \text{S}^{2-}, \text{Se}^{2-}, \text{Te}^{2-}$  and  $\text{Po}^{2-}$ ). These systems have 3-shell, onion-like geometries with nearly perfect  $I_h$  symmetry. Seeking to create clusters with very high-spin ground states, we have replaced  $M$  by  $\text{Mn}^{2+}$  and  $U_{20}$  by  $\text{Np}_{20}$  and  $\text{Pu}_{20}$ , generating clusters with maximum possible  $S$  values of  $80/2$  and  $100/2$  respectively. Only in the presence of a central  $\text{S}^{2-}$ , however, are these electronic configurations the most stable; the novel Matryoshka Pu nanocluster  $\text{S}@Mn_{12}@Pu_{20}$  is predicted to have the highest ground state spin yet reported for a molecular cluster.



**Figure 1** Ball and stick representation of  $[\text{Na}_{12}@U_{20}]^{8-}$  and its breakdown into outer shell  $U_{20}^{20-}$  and inner shell  $\text{Na}_{12}^{12+}$  fragments. Uranium atoms in blue, oxygen atoms in red and sodium atoms in purple.

1 H. Hu, N. Kaltsoyannis, *Chem. Eu. J.*, **2018**, *24*, 347.

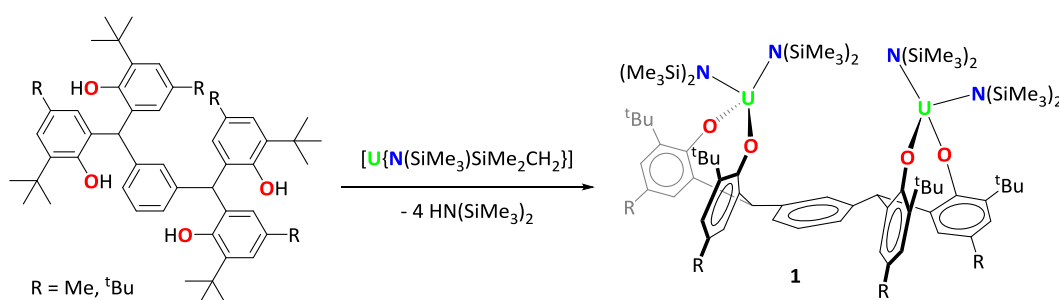
## Uranium-mediated small molecule activation

M. Seymour, J. A. L. Wells, T. Ochiai and P. L. Arnold\*

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Seminal studies have demonstrated that the U<sup>III</sup>/U<sup>IV</sup> redox couple is a powerful tool for reductive activation. This single-electron redox activity is cumulative, allowing multi-electron redox chemistry when multiple uranium centres are present. Currently, uranium mediated activation of small molecules such as CO<sub>2</sub>, CO and N<sub>2</sub> is achieved almost exclusively when two separate monometallic complexes are combined around a substrate.<sup>1-3</sup> It follows that molecules with two reducing U centres pre-arranged in a single molecule should be even more powerful tools for activation and potential catalytic transformations. The recent reduction of N<sub>2</sub> to NH<sub>3</sub> by Mazzanti and co-workers is powerful evidence of this.<sup>4</sup>

New ligand systems capable of supporting multiple U centres are therefore of considerable interest.<sup>5</sup> We recently reported the use of an arene-bridged tetraphenol ligand to isolate the first compounds containing two discrete U<sup>IV</sup> centres in a single molecule: [U<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>4</sub>(L)], **1**.<sup>6</sup> **1** and its analogues possess a geometry pre-organised for small molecule binding and an easily accessible reduction potential. Initial results suggest that these complexes act as powerful catalysts for small molecule transformations under reducing conditions. The reductive activation of N<sub>2</sub>, CO, and related small molecules will be presented.



**Figure 1** Synthesis of **1** via protonolysis of H<sub>4</sub>L.

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## Dinitrogen activation of molybdenum(0) N-triphos complexes

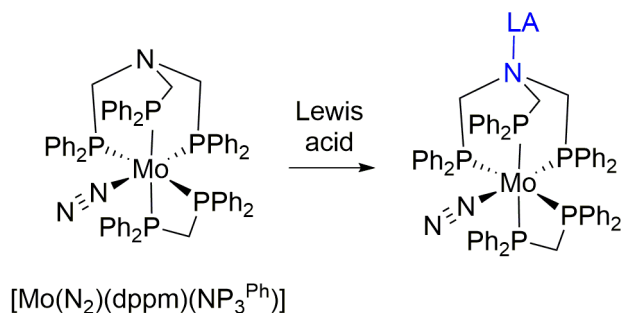
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Department of Chemistry, Imperial College London, London SW7 2AZ, UK

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Facially capping tripodal phosphine ligands (triphos) have recently resurfaced as effective ligands for a range of catalytic transformations.<sup>1</sup> The nitrogen-centred derivative, N-triphos, is particularly advantageous due to its ease of synthesis and tunability of steric and electronic properties at the phosphine substituents. Our group has previously studied the coordination chemistry of N-triphos ligands,<sup>2-4</sup> and we are now investigating the preparation of metal-dinitrogen N-triphos complexes as potential catalysts for ambient nitrogen fixation.

The synthesis and reactivity of a series of molybdenum(0) dinitrogen complexes bearing the N-triphos ligand will be presented, showing varying coordination modes of N-triphos for different phosphine substituents: increasing steric bulk results in bidentate N-triphos coordination, and increasing the electron donating ability increases dinitrogen activation. The reactivity of one such complex,  $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ , with Lewis acids is reported, showing unusual formation of transition metal Lewis adduct complexes at the apical N-triphos nitrogen centre (figure 1).<sup>5</sup>



**Figure 1.** Lewis acid reactivity of an N-triphos dinitrogen complex

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## Self-complementary nickel halides enable intermolecular halogen bonds

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Square-planar nickel halides provide a test-bed for quantifying the ability of halide ligands to form halogen bonds and hydrogen bonds. We have determined the energetics of binding in



solution<sup>1,2</sup> by <sup>19</sup>F NMR spectroscopy and shown that nickel fluorides form some of the strongest known H-bonds between neutral molecules,<sup>2</sup> and also form strong halogen bonds with IC<sub>6</sub>F<sub>5</sub>.<sup>1</sup> Following the discovery of an H-bonded chain in a nickel fluoride, we designed self-complementary molecules that form halogen-bonded chains (Fig. 1). This design has enabled us to compare the structures of a series of nickel halides with C–I⋯X–Ni intermolecular halogen bonds (X = F, Cl, Br, I), examining the effects of regiochemistry, temperature and crystalline environment on their structures.<sup>3</sup> The nickel fluoride shown in Fig. 1 exhibited unique characteristics with a linear chain (Fig. 2) and the shortest halogen bond distance (23% reduction in length compared to the sum of the van der Waals radii). Moreover, we could compare the effect of halogen bonding of nickel fluorides in solution and solid state by use of <sup>19</sup>F MAS-NMR spectroscopy.<sup>3</sup> The results demonstrate the potential of fluoride ligands for formation of halogen bonds in supramolecular structures.

Figure 1. Self-complementary molecules

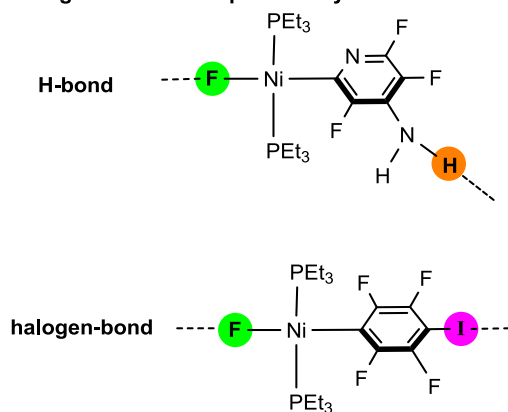
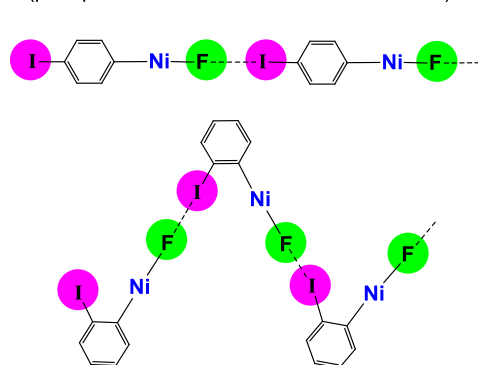


Figure 2. Supramolecular halogen-bonded chains (phosphines and aromatic fluorines omitted)



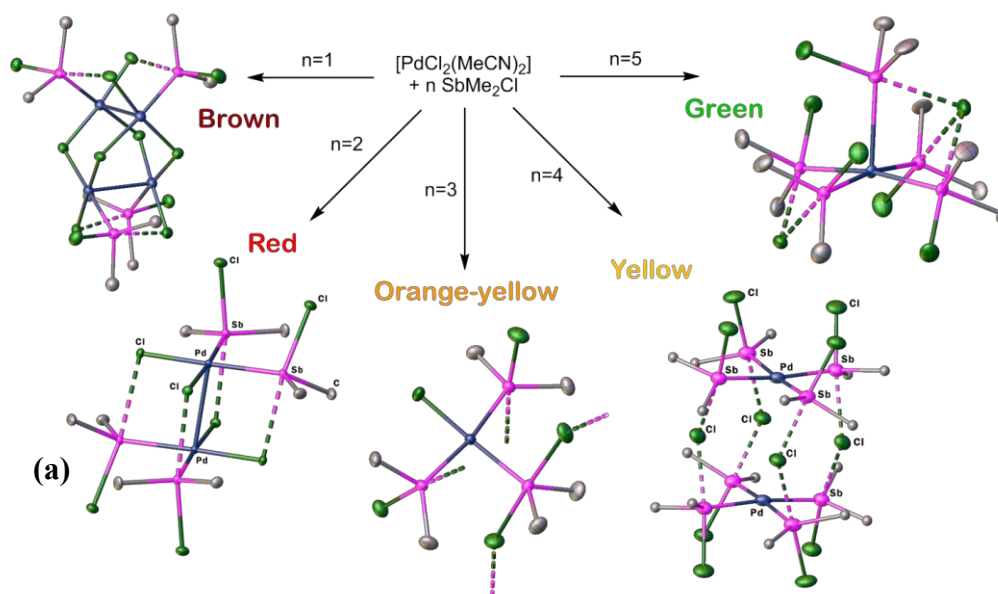
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## Pd(II) complexes of Lewis amphoteric halostibines: stoichiometry matters

Andrew Jolleys, Sophie L. Benjamin

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Halostibines of the form  $\text{SbMe}_2\text{X}$  are notable for their Lewis amphotericism; they readily act as Lewis bases, ligating transition metal centres, but often simultaneously form secondary interactions with nearby donor atoms.<sup>1</sup> We have recently studied  $[\text{PdCl}_2(\text{SbClMe}_2)_2]_2$  (**a**), a dimer which is held together by ligand-ligand (Sb---Cl) interactions. Treatment of this complex with MeLi results in the formation of an unusual Pd(0) tetramer featuring the only known example of unsupported triple bridging behaviour by a pnictine ligand,  $[\text{Pd}_4(\mu_3\text{-SbMe}_3)_4(\text{SbMe}_3)_4]$ .<sup>2</sup> The synthesis of **a** requires combination of  $\text{SbClMe}_2$  with the metal precursor in a 2:1 ratio. By altering this ratio, five different coordination complexes have been prepared, which can be distinguished by their different colours and crystal structures (see figure), and are described by the general formula  $\text{Pd}(\text{SbClMe}_2)_n\text{Cl}_2$  ( $n = 1\text{-}5$ ).



The solid state structures of these unusual complexes include monomeric, dimeric, tetrameric and polymeric examples. All of the complexes exhibit secondary Sb---Cl bonding between chloride ligands or anions and the coordinated  $\text{SbClMe}_2$  ligands which direct these structures.

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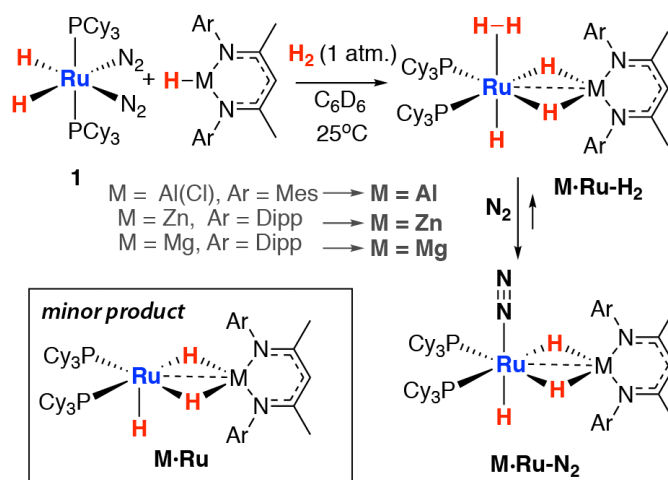
# Tuneable Binding of Dinitrogen to a Series of M•Ru (M = Mg, Al, Zn) Heterobimetallic Complexes

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Investigation into the co-ordination of N<sub>2</sub> at transition metal centres provides an insight into dinitrogen fixation.<sup>1</sup> Changing the nature of the ligands around the transition metal centre can influence the acceptance of electron density from the filled  $\sigma$ -orbital of dinitrogen to a vacant d-orbital at the transition metal as well as the corresponding back donation from the metal to the  $\pi^*$ -antibonding orbitals of N<sub>2</sub>. This in turn allows for tuneable degree of activation of the dinitrogen ligand.<sup>2</sup> Here we report a series of dinitrogen and dihydrogen M•Ru (M = Al, Zn, Mg) heterobimetallic complexes (Scheme 1).



Scheme 1. Preparation of dihydrogen and dinitrogen complex of a series of heterobimetallic hydrides

For the M•Ru-N<sub>2</sub> heterobimetallic complexes, the lowering of the  $\nu_{\text{N}=\text{N}}$  stretching frequencies is observed from changing the main group metal from Al < Zn < Mg. The subtle, but tuneable, effect on N<sub>2</sub> binding is rationalised by considered the main group fragment as a specialised ligand which influences energy of the frontier molecular orbitals of the ruthenium fragment.<sup>3,4</sup>

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## Reduction, fusion and oxo-group abstraction reactions of the uranyl ion

Dr Bradley E. Cowie, Prof. Jason B. Love and Prof. Polly L. Arnold

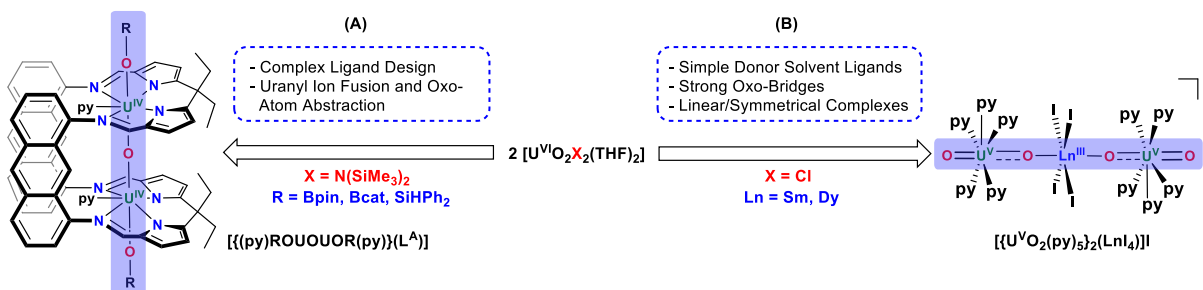
*EaStCHEM School of Chemistry, The University of Edinburgh, Edinburgh, UK*

The oxo-groups of the uranyl ion,  $[\text{UO}_2]^{2+}$ , are traditionally thought to be chemically robust,<sup>1</sup> yet new reactions such as reductive functionalisation and oxo-atom abstraction are becoming increasingly apparent and, in part, reliant on the design of ligands to control coordination geometries and oxidation states.<sup>2</sup> In this work, we highlight two separate but convergent approaches to accessing new uranyl oxo-group chemistry.

By positioning two, co-linear uranyl(VI) ions within a single macrocyclic Pacman ligand,<sup>3</sup> reactions with boranes or silanes result in the formation of new uranyl-derived, linear  $[\text{OUOUO}]^{4+}$  structural types by uranyl ion fusion and oxo-atom abstraction (Scheme 1A). In these reactions, the proximity of the uranium centres is important to allow formation of the single oxo-bridge, and is controlled by the ligand framework.<sup>4</sup>

Alternatively, uranyl reduction and the formation of new linearly functionalised uranyl motifs such as  $[(\text{py})_5\text{OUO-LnL}_4\text{-OUO}(\text{py})_5]^+$  ( $\text{Ln} = \text{Sm}, \text{Dy}$ ) occurs in the absence of spatially directing ligands (Scheme 1B). The use of a suitably coordinating solvent (pyridine) eliminates the requirement for designed ligand systems and, depending on the stoichiometry and solvent choice, highly symmetrical complexes with strong, linear oxo-group bridges are obtained.<sup>5</sup>

The reaction pathways outlined here represent new strategies for uranyl ion reduction and functionalisation, and the synthesis and characterisation of the newly prepared uranyl compounds will be presented.



**Scheme 1.** Uranyl(VI) ion reductive functionalisation utilising: (A) a ligand design that enforces co-linear positioning of the uranyl ions, enabling uranyl ion fusion and oxo-atom abstraction, or (B) a suitably coordinating solvent to satisfy the uranyl coordination sphere.

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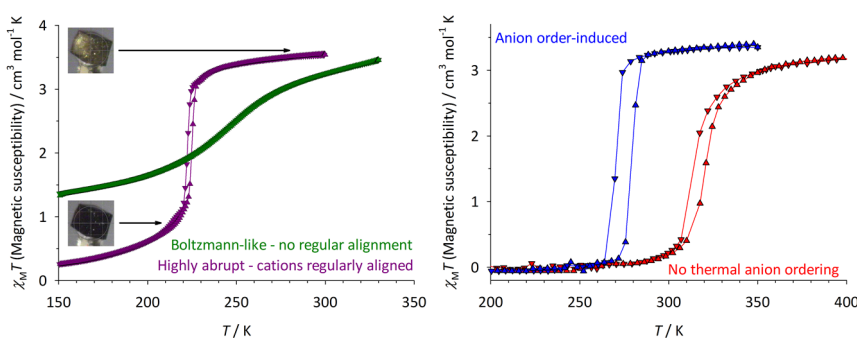
## Insights into crystal design – polymorphism and phase dependent spin-state switching

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Spin-crossover (SCO) materials have received substantial interest recently as the change in spin-state is intrinsically coupled to significant modulation of electrical resistance and optical and magnetic properties. This bestows upon them relevance towards biomedical imaging, as molecular and nanoscale temperature and pressure sensors and as electrically addressable units for display technology.<sup>1</sup> The main challenges associated with the acquisition of the ideal SCO material – wide hysteresis spanning room temperature, high stability and processability – are primarily matters of synthetic feasibility and crystal engineering. An understanding at the level necessary to design a material from first principles meeting such criteria has yet to be met.



We have used a combined computational-spectroscopic screening approach, wherein it is possible to tune the electronic nature of the metal coordination sphere to requirement. In the crystal, structure-shape correlations are generally applied to aid in the prediction of how molecules pack.<sup>2</sup> However, this is still met with several complications due to seemingly fickle occurrences of polymorphism, solvate inclusion and spontaneous ion/solvent ordering. Such phenomena often have profound effects on the spin-state preference for any given metal ion, and drastically alter the behaviour, robustness and stability of the material in question

We present here a series of investigations into the effects of both order-disorder changes and polymorphism on the spin-state switching profiles of structurally related molecular iron(II) crystals, how such effects govern abruptness – that is the rate of SCO propagation through the lattice – and how this consequently manifests in the widths of hysteresis loops or lack thereof.

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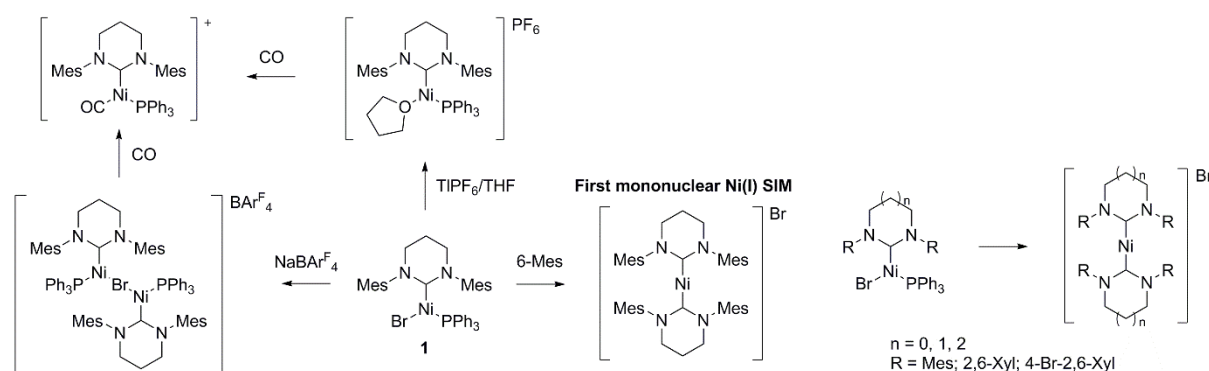
## Synthesis and characterisation of low-coordinate Ni(I) complexes for magnetic applications and small molecule activation.

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Five-membered ring N-heterocyclic carbenes (NHCs) are well established ligands in transition metal chemistry, often producing novel complexes which display superior activity in catalytic transformations when compared to their phosphine analogues. The ability to vary the nature of the N-substituents and the use of larger, ring expanded six-, seven- and eight-membered NHCs (RE-NHCs) gives rise to a whole range of under-explored carbenes, each providing different electronic and steric effects towards the metal centre. It was proposed that increasing the size of the ring could afford greater steric stabilisation of metal centres of low coordination number, and as a result this could lead to complexes in unusual oxidation states.

Hence, we have used these RE-NHCs to prepare a range of new low coordinate Ni(I) complexes that show interesting stoichiometric, catalytic and magnetic properties.<sup>1-5</sup> Figure 1 shows some highlights of this work, where compound **1** has primarily been the starting point for much of the project. Analogues of **1** have also been prepared, then used as a synthon for synthesis of the corresponding two coordinate complexes, with studies into the impact on magnetism performance currently ongoing. This presentation will cover work on the synthesis and characterisation of a range of new two and three coordinate Ni(I) species, using a variety of techniques including X-ray crystallography, EPR spectroscopy, DFT and magnetic susceptibility measurements.



**Figure 1.** Scheme showing interesting reactivity of **1** (left). Reactions with analogues of **1** (right).

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# Applying Phosphinophosphinine Ligands to Catalysis

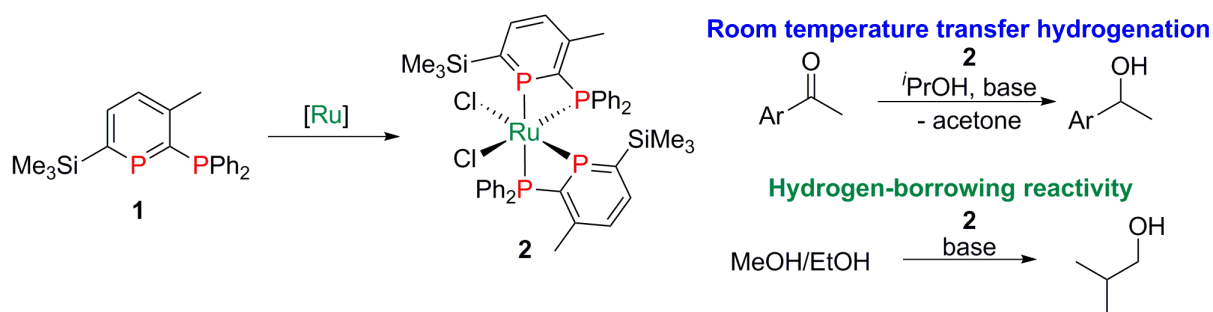
Stephen M. Mansell\* and Robert J. Newland

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Homogeneous catalysis has been the most important application of over 60 years of research into organometallic chemistry. Our research is focussed on how we can harness new aspects of main group chemistry in the development of better homogeneous catalysts. To do this, we are developing catalysts that incorporate unconventional ligands that can offer different pathways for catalysis, including: metal-ligand cooperation, exploitation of small bite-angles<sup>1</sup> and other ligand properties that are difficult to access with conventional ligands.<sup>2</sup>

2-Phosphinophosphinines (**1**) are bidentate ligands that include a phosphine substituent attached to a phosphinine donor (the phosphorus analogue of pyridine).<sup>3</sup> We have recently described the first structurally authenticated example of a chelating 2-phosphinophosphinine (**2**), and this Ru complex was successfully applied to the transfer hydrogenation of acetophenones.<sup>4</sup> In addition, **2** acted as a competent precatalyst in the hydrogen-borrowing upgrading of MeOH/EtOH to isobutanol, an ‘advanced biofuel’ of recent interest because it is more compatible with current engine technologies.<sup>4</sup> We have also studied the ligand properties and coordination chemistry of **1** with group 6 metals, including its application in Cr catalysed ethylene oligomerization,<sup>5</sup> demonstrating additional catalytic applications for these unusual ligands.



**Scheme 1.** Catalysis with a chelating Ru-phosphinophosphinine complex

## References

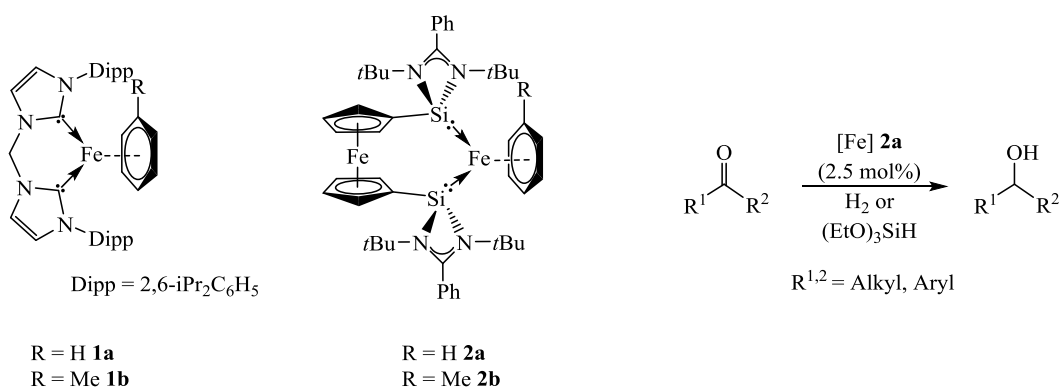
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# Bis(silylenyl)-substituted ferrocene-stabilized $\eta^6$ -arene iron(0) complexes: synthesis, structure and catalytic application

Marcel-Philip Luecke, D. Porwal, A. Kostenko, Y. Zhou, S. Yao, M. Keck, C. Limberg, M. Oestereich and M. Driess.

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In recent years, iron-based catalysts have gained considerable attention as alternative to traditional catalysts based on noble and toxic metals (i.e. Rh, Ir, Ru, Pd, Pt etc.) due to its great abundance, low-cost and low toxicity.<sup>[1]</sup> Following the isolation of the first bis(N-heterocyclic carbene)-stabilized Fe(0)  $\eta^6$ -arene complexes (**1a**, **1b**) and their application in catalytic amide reduction,<sup>[2]</sup> we were highly interested in the isolation of the corresponding bis(N-heterocyclic silylene) complexes. Herein, we report the first bis(silylene)  $\eta^6$ -arene Fe(0) complexes **2a** and **2b** which are stabilized by a bis(silylenyl)ferrocene chelate ligand and bearing benzene (**2a**) and toluene (**2b**) as ligands attached to the Fe(0) site.<sup>[3]</sup> **2a** is the first example of a silylene-iron complex as highly active precatalyst in catalytic hydrogenation reactions. In this contribution the synthesis, characterization (<sup>57</sup>Fe-Mössbauer-Spectroscopy, DFT-Calculations, single-crystal XRD) and the catalytic application of **2a** as a precatalyst in the hydrosilylation and hydrogenation of ketones will be discussed.



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## Title: Strategies to improve stability and efficiency for solar chemicals production.

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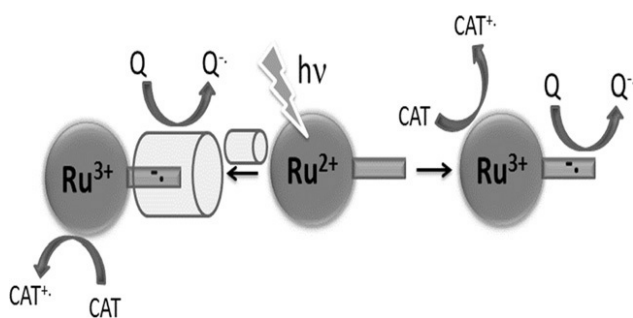
[pau.farras@nuigalway.ie](mailto:pau.farras@nuigalway.ie); <sup>b</sup>*School for Natural & Environmental Sciences, Newcastle*

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The merge of molecular and materials systems in a single device is leading to excellent results in photoelectrochemical water splitting and carbon dioxide reduction. The flexibility of molecular building blocks opens the doors to multiple design iterations to obtain the desired properties of the molecules, either for light harvesting or for catalytic steps. As in the natural system, molecules could also be used to transport electrons from one place to the other, issue still not considered in artificial devices. On the other hand, materials have shown great stability and, of course, is the preferred option for its ease to be implemented at the industrial scale. In this work, I will present two different strategies used to enhance the stability of molecular systems with promising results in the areas of water oxidation [1] and carbon dioxide reduction [2]. In each study, a full characterization of all thermodynamic and kinetic processes is achieved leading to a better understanding of the device.



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## Cu-Catalysed Aryl Ether Formation and the “Caesium Effect”

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<sup>1</sup> *iPRD, School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK*

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Aryl ethers are important motifs in medicinal chemistry and the use of copper catalysed couplings (Ullmann reactions) for their synthesis is a common procedure (Fig. 1).<sup>[1]</sup> Typically, these reactions require simple neutral or anionic bidentate ligands to work efficiently. However, the role of the ligand in these reactions is not totally understood.<sup>[1]</sup>

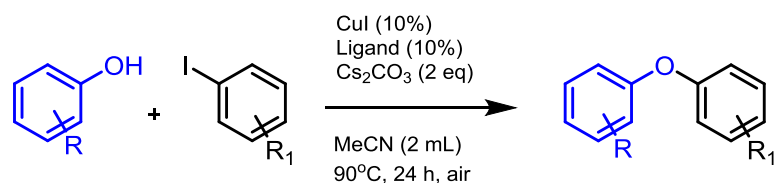


Fig. 1: Cu catalyzed Aryl Ether Formation (Ullmann Coupling)

Using picolinamide ligands and a Cu source, interesting catalytic results were obtained using sterically hindered phenols (Fig 1), which are normally difficult substrates in Ullmann couplings.<sup>[2-3]</sup> Preliminary mechanistic investigation shows that the effect of different ligands may be related to their influence on the redox properties of the copper atom and the effect of the caesium base was also significant.

The term “Caesium Effect” has often been used to describe the better performance of Cs salts when compared to other alkaline metals salts, as bases in organic transformations. Recent theoretical studies on metal-catalysed transformations, showed a more direct involvement of the Cs ion in reaction intermediates or transition states is actually possible (Fig. 2a).<sup>[4]</sup> During our studies on the Ullmann ether Cu-catalysed cross coupling reactions, we obtained the first complex involving a Cu-I-Cs interaction (Fig. 2b).<sup>[5]</sup> The structure of this complex and its activity in catalysis supports the hypothesis of direct involvement of Cs in reaction intermediates.<sup>[5]</sup>

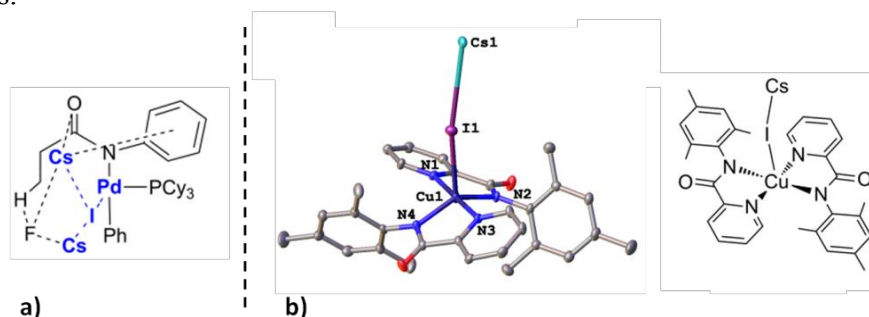


Fig. 2: a) Theoretical Pd-I-Cs intermediate in C-H activation; b) Experimental Cu-I-Cs interaction

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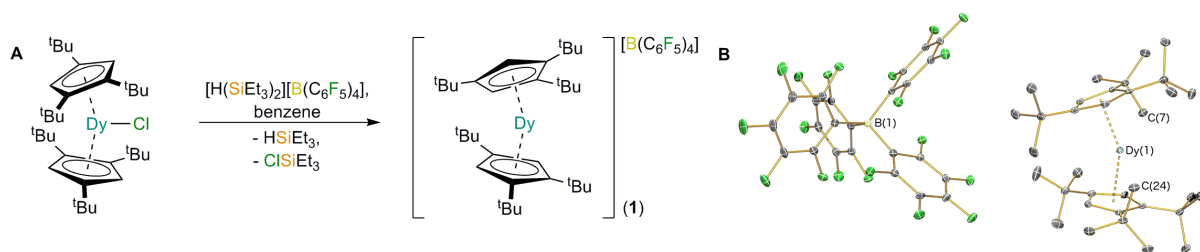
## Molecular magnetic hysteresis at 60 K in dysprosocenium

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Single molecule magnets (SMMs) display magnetic hysteresis of molecular origin – a magnetic memory effect and a prerequisite of data storage – and lanthanide examples have exhibited this phenomenon at the highest temperatures to date.<sup>1</sup> However, in nearly 25 years since the landmark discovery of SMMs hysteresis temperatures have only increased from 4 K to ~14 K (using a consistent magnetic field sweep rate of *ca.* 20 Oe s<sup>-1</sup>). We have recently reported a hexa-*tert*-butyldysprosocenium complex, [Dy(Cp<sup>ttt</sup>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] [**1**; Cp<sup>ttt</sup> = {C<sub>5</sub>H<sub>2</sub><sup>t</sup>Bu<sub>3</sub>-1,2,4}; <sup>t</sup>Bu = C(CH<sub>3</sub>)<sub>3</sub>], which shows magnetic hysteresis up to 60 K at 22 Oe s<sup>-1</sup>.<sup>2</sup> Guo *et al.* have also reported the synthesis and magnetic data of **1**.<sup>3</sup> *Ab initio* spin dynamics demonstrate that magnetic relaxation at high temperatures is due to local molecular vibrations, and thus indicate that with judicious molecular design, magnetic data storage in single molecules at temperatures above liquid nitrogen may become possible.<sup>2</sup> Herein, we present our latest progress in the synthesis and analysis of isolated lanthanocenium cations, using the new methodology that we have pioneered.<sup>2,4</sup>



**Figure 1.** (A) Synthesis and (B) molecular structure of **1**.

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# Cerium-NHC complexes for the activation of CO<sub>2</sub> and polymerisation of biorenewable monomers

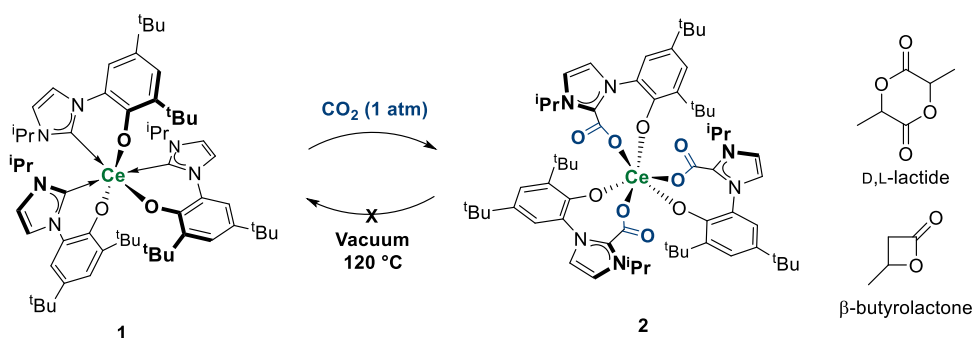
R. W. F. Kerr,<sup>a,b</sup> C. Weetman,<sup>a</sup> S. R. Docherty,<sup>a</sup> S. K. Raman,<sup>c</sup> C. K. Williams,<sup>c</sup> A. D. Smith,<sup>b\*</sup> P. L. Arnold<sup>a\*</sup>

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Since their isolation by Arduengo in 1991,<sup>1</sup> N-heterocyclic carbenes (NHCs) have become ubiquitous as standalone organocatalysts<sup>2</sup> and ligands in organometallic chemistry.<sup>3</sup> As they only bind weakly to rare-earth metal cations, the Arnold group has shown that alkoxy-tethered NHC ligands can exploit NHC hemilability, using Lewis pair reactivity to capture CO<sub>2</sub> and initiate (co-)polymerisation reactions.<sup>4,5,6</sup>

Here, we present the new cerium aryloxy-tethered NHC complex **1** and its reactions with carbon dioxide, a cheap earth-abundant greenhouse gas, producing isolable complex **2**. We will show its potential for catalytic CO<sub>2</sub> functionalisation via further reactivity with Lewis acids and organometallic nucleophiles. Related reactions with other molecules isoelectronic to CO<sub>2</sub> including isocyanates and ketenes will also be shown. Lastly, complex **1** mediates the polymerisation of D,L-lactide with exceedingly high TOF (up to 54600 h<sup>-1</sup>) and is a capable initiator to convert the more challenging monomer, β-butyrolactone into biodegradable polymers.



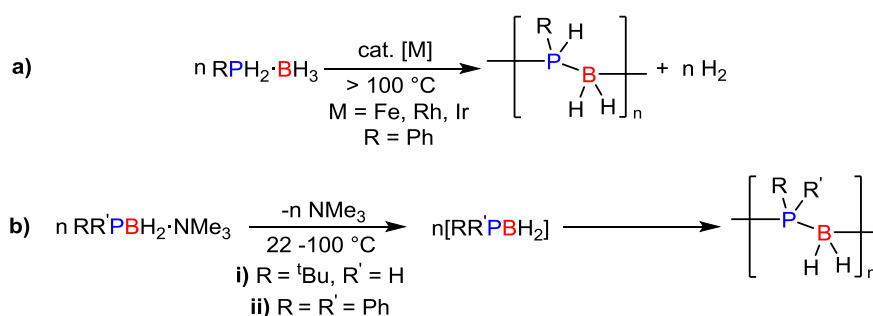
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# General, metal-free routes to polyphosphinoboranes

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The synthesis of high molecular weight P-*monosubstituted* polyphosphinoboranes has been previously achieved through either metal-catalyzed dehydrocoupling of phosphine-borane monomers,<sup>1</sup> or a metal-free route involving thermolysis of an amine-stabilized phosphinoborane (Scheme 1).<sup>2</sup> Both of these routes only give oligomeric P-*disubstituted* derivatives which are the most desirable in terms of potential utility.



**Scheme 1.** Current methods of synthesizing polyphosphinoboranes.

Ambient temperature dehydrocoupling methods that operate for both primary and secondary phosphine-boranes to give the corresponding high molecular weight polymers remain an open challenge. This talk will discuss our very recent progress in this area using main group dehydrocoupling agents, including mechanistic insights and characterisation of novel polymeric materials.

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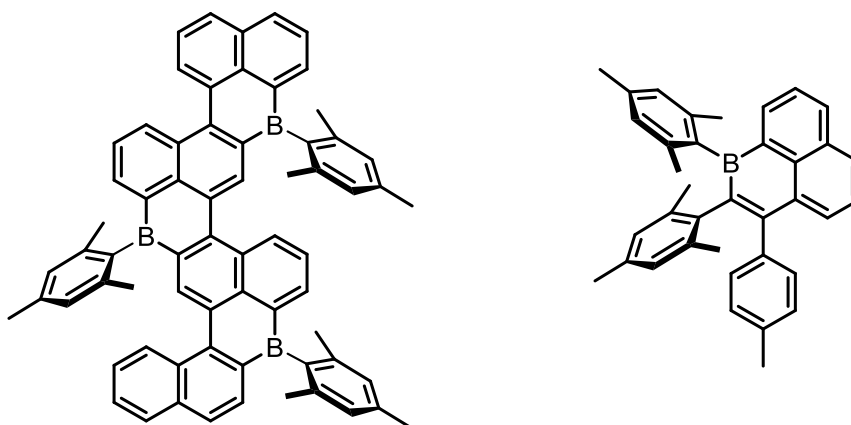


## Novel Routes to B-doped Polycyclic Aromatic Hydrocarbons

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The inclusion of boron atoms into polyaromatic hydrocarbons (PAHs) generates electron deficient PAHs that are isoelectronic to carbocationic PAHs. B-doped PAHs have potential in organic electronics (as ambipolar semi-conductors) and electrocatalysis.<sup>1-2</sup> However, there are currently few simple and/or modular routes to B-doped PAHs in contrast to the methods available to form B-E (with a direct B-E bond, E = N or O) doped PAHs.<sup>3</sup> To assess the potential of B-doped, multiply B-doped and B,E-doped PAHs (without a direct B-E bond),<sup>4</sup> new synthetic routes are required. We have combined alkyne borylative cyclisation and intramolecular electrophilic borylation to prepare a series of multiply B-doped and B,N-doped PAHs.<sup>5</sup> Furthermore, during these studies we discovered a simple route to B-doped phenalenes.<sup>6</sup> These are the first only boron doped phenalenes (to the best of our knowledge) and functionalisation with bulky aryls enables formation of a persistent boron radical.



**Figure 1** A B<sub>3</sub>-doped PAH (left) and a B-doped phenalene (right).

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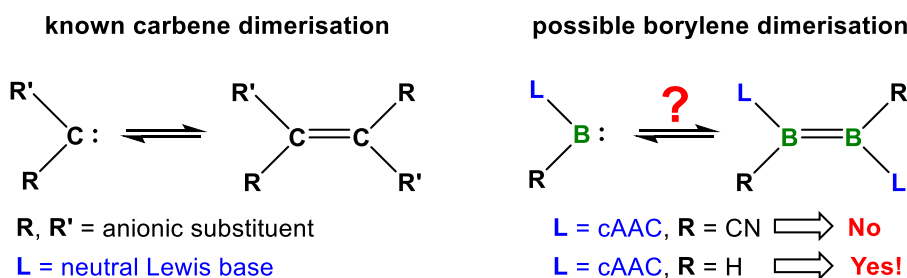
# From Borylene to Diborene and Back Again: Towards a Bora-Wanzlick Equilibrium?

Dr. Merle Arrowsmith, Prof. Dr. Holger Braunschweig\*

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First reported in 2007,<sup>1</sup> doubly base-stabilised diborenes (LRB=BRL, R = anionic substituent, L = neutral Lewis base)<sup>2</sup> can be regarded as the B-B bonded dimers of dicoordinate [LRB:] borylenes. While the dimerisation of [R<sub>2</sub>C:] carbenes is a well-known reaction in organic chemistry<sup>3</sup> and a similar dimerisation process has been observed for [R<sub>2</sub>Si:] silylenes,<sup>4</sup> this process is still unknown for isoelectronic borylenes. Since [LRB:] species are kinetically unstable due to their two empty orbitals, our research has focused on doubly base-stabilised [LL'RB:] borylenes,<sup>5,6</sup> in which L' is sufficiently labile to transiently generate and study the chemistry of the [LRB:] borylene. We have recently shown that, despite a large overlap in reactivity, our [(cAAC)(CN)B:] borylene synthon (cAAC = cyclic (alkyl)(amino)carbene),<sup>6</sup> does not interconvert with its diborene relative.<sup>7</sup> We now present the first example of a [(cAAC)HB:] parent borylene synthon which dimerises to its dihydrodiborene, while the latter can be converted back to a monomeric parent borylene.



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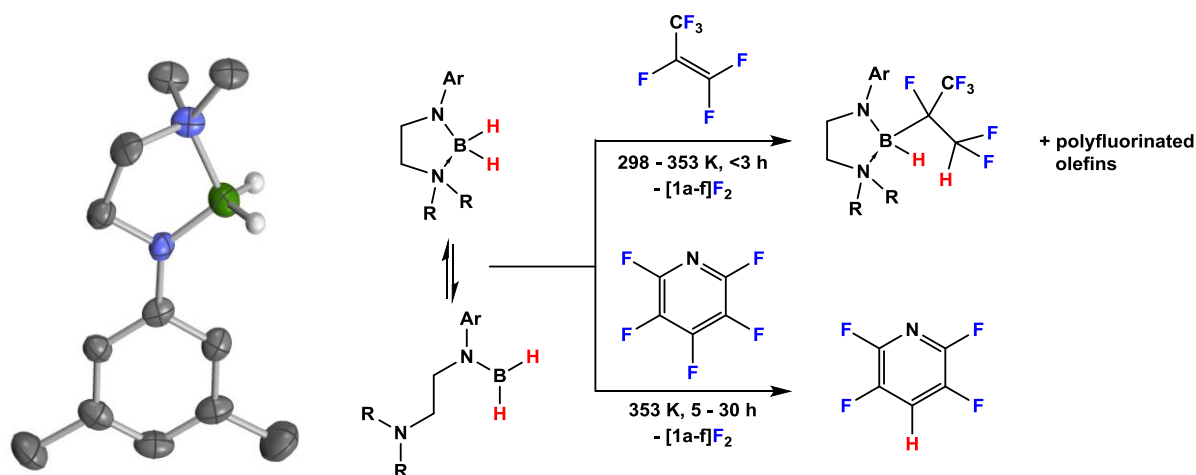
# Bespoke dihydridoborane reagents: tuning the environment at boron through hemilabile ligation

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Monohydridoborane reagents pinacolborane (HBpin) and catecholborane (HBcat) have found wide application in modern synthetic chemistry as selective reducing and hydroboration agents.<sup>1</sup> Due to the  $\pi$ -basic alkoxy- and aryloxy- substituents, they are found to be much less reactive than the parent  $\text{BH}_3$ . Despite the broad and growing applications of monohydridoborane reagents, the preparation and exploitation of dihydridoborane reagents remains somewhat neglected.<sup>2</sup>

Here, we present of a series of four-coordinate dihydridoborane compounds supported by monoanionic *N,N*-chelating ligands (Figure 1). Reactions with pentafluoropyridine and hexafluoropropene proceed uncatalyzed to give both hydroboration and hydrodefluorination products under mild conditions (<1 atm.; 298-353 K). Tuning the steric and electronic structure of the dihydroborane significantly affects the product distribution. These observations can be rationalised in terms of the ease of ligand-dissociation leading to generation of the active three-coordinate borane species.



**Figure 1:** Hydroboration and hydrodefluorination chemistry with dihydridoboranes  $[\mathbf{1a-f}]H_2$  {R = Me, Ar = Ph (**1a**), 3,5-Xyl (**1b**), Mes (**1c**); R =  $-(CH_2)_5-$ , Ar = Ph (**1d**), 3,5-Xyl (**1e**), Mes (**1f**)}

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## Polymerization of Arsine Boranes and Pyrolysis to Boron Arsenide

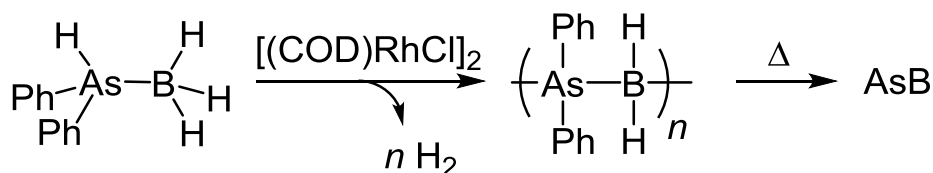
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Dehydropolymerization of  $\text{Ph}_2\text{AsHBH}_3$  is facile with  $[(\text{COD})\text{RhCl}]_2$  to give hydrogen and polymers greater than 30,000 Da as measured by GPC and dynamic light scattering. Under thermal or photochemical conditions,  $\text{Ph}_2\text{AsHBH}_3$  dehydrocouples to arsenic-borane rings (e.g.,  $(\text{AsPh}_2\text{BH}_2)_n$ ,  $n = 4$  or 6) as primary products. As an aside, Lewis acids were identified as facile catalysts for the dehydrocoupling of arsines during the synthesis of arsine boranes (e.g.,  $\text{Ph}_2\text{AsH}$  reacts with catalytic Lewis acid to give  $\text{Ph}_4\text{As}_2$  and  $\text{H}_2$ ). Primary arsine-boranes undergo similar reactivity. Poly(arsine borane) smoothly decomposes under low-temperature pyrolysis to afford boron arsenide as determined by MAS  $^{11}\text{B}$  NMR spectroscopy and powder X-ray diffraction. TGA analysis and NMR spectroscopy indicate complete elimination of carbonaceous products in pyrolysis reactions, suggesting a new, low-energy route to boron arsenide.

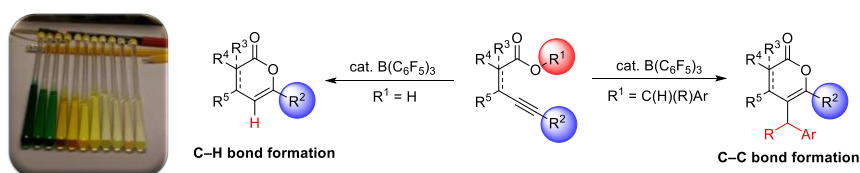


# Stoichiometric and Catalytic C–C and C–H Bond Formation with $B(C_6F_5)_3$ via Cationic Intermediates

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Functionalised heterocycles are key components in many natural products and synthetic pharmaceuticals. Therefore Lewis-Acid catalysed addition of hetero-atoms across unsaturated carbon-carbon bonds has been the target of several studies, in order to create biologically active compounds such as highly functionalised oxazoles.<sup>1–3</sup>



Scheme 1:  $B(C_6F_5)_3$  catalysed cyclization of alkynyl acids and esters<sup>4</sup>

Fluorinated triarylboranes have proven to be powerful catalysts in many catalytic reactions, such as cyclisations, hydrosilylations and hydroborations.<sup>3,5,6</sup> The scope of the  $B(C_6F_5)_3$ -catalysed carbo-oxycarbonylation with various alkynyl acids and esters was examined, and results showed the products to be unsaturated 6-membered heterocyclic species, and that the reactions can be achieved both stoichiometrically and catalytically in mild conditions.<sup>4</sup>

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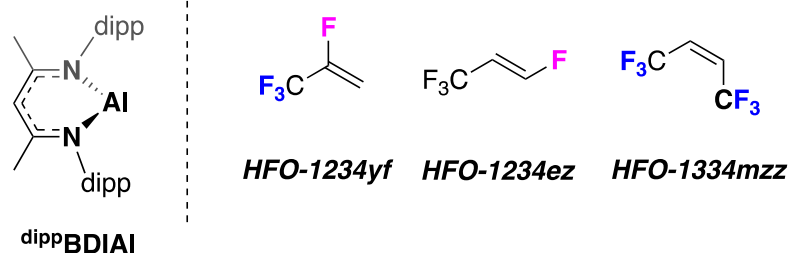
## Reactions of Fluoroalkenes with an Aluminium(I) Complex

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In 2015, the European Union committed to reduce and replace gaseous hydrofluorocarbons (HFCs), which are commonly used as refrigerants and aerosols [1]. Hydrofluoroolefins (HFOs) are now being billed as next generation refrigerants and are being marketed as direct replacements for HFCs. Whilst HFOs possess significantly lower global warming potentials than HFCs, questions have been raised about their long term environmental impact. We are interested in transforming strong carbon–fluorine (C–F) bonds, such as those found in HFOs, into polar C–X (where X = Mg, Al, B etc.) bonds, creating functional building blocks for use in further synthesis [2].



Here we show how a series of industrially relevant fluoroalkenes react with a monomeric Al(I) complex (**dippBDIAI**) [2, 3]. **dippBDIAI** is shown to be a potent 2-electron reducing agent, resulting in the facile bond activation of both  $sp^2$  and  $sp^3$  C–F bonds, forming an array of well-defined organoaluminium products. Mechanistic studies show that two mechanisms are likely in operation: Oxidative addition of the C–F bond to **dippBDIAI** occurs with retention of alkene stereochemistry, while stepwise formation and decomposition of a metallocyclopropane intermediate occurs with inversion of alkene stereochemistry. To demonstrate the synthetic feasibility of metallocyclopropane formation, we have isolated the first example of an aluminium metallocyclopropane, formed by the oxidative addition of an alkene to **dippBDIAI**. Remarkably, complex formation is shown to be reversible and reductive elimination of the alkene occurs at high temperature (333 K).

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## Aluminium Hydrides Stabilised by Mixed NP Donor Ligands

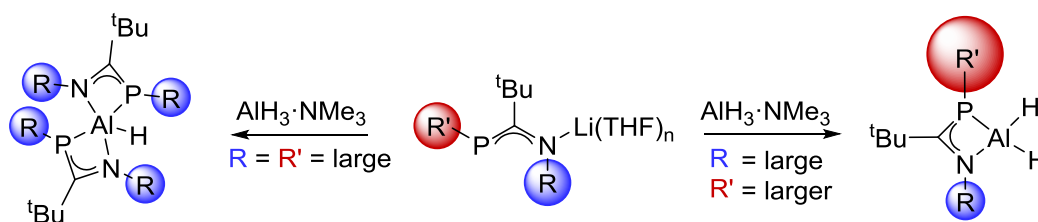
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We recently reported that the simple aluminium hydride reagents  $\text{LiAlH}_4$  and  ${}^i\text{Bu}_2\text{AlH}$  efficiently catalyse the hydroboration of alkenes and alkynes.<sup>1</sup> The prospect of developing further aluminium hydride based transformations is a promising one and for that reason we are interested in the development of aluminium hydride species in other ligand environments.

Amidinate ligands have been widely used in main group chemistry, including that of aluminium.<sup>2</sup> Conversely, their mixed-donor NP analogues, phosphamidinates, are less well explored.<sup>3</sup> We have synthesised phosphamidinate ligands with large substituents on both N and P and explored their coordination chemistry with aluminium hydrides.



We have also prepared aluminium hydrides with amido-phosphine ligands. We will present further details concerning the synthesis, structure, and reactivity of these compounds.

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# The Structure of Frustrated Lewis Pairs in Ionic Liquids vs. Molecular Solvents

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Frustrated Lewis pairs (FLPs) are combinations of Lewis acids and Lewis bases in which steric repulsions between the bulky components prevents adduct formation, firstly described by Stephan *et al.* in 2006.<sup>1</sup> They represent elegant systems capable of metal-free hydrogen activation, in a manner formerly associated exclusively with transition metals.<sup>2</sup> Interestingly, although hydrogen doesn't interact with either the acid or base components in isolation, it forms an adduct with both components in an FLP solution. The kinetics of H<sub>2</sub> activation suggest a bimolecular reaction, which has led to the concept that an **encounter complex** pre-forms, whereby the acid and base pair are held together by Van der Waals forces, and the H<sub>2</sub> molecule interacts with this 'complex'. Formation of FLP encounter complexes is supported by computational studies and some spectroscopic evidence, but simple NMR studies do not show the adduct formation.<sup>3</sup>

In this contribution, the neutron scattering data (Figure 1) illustrates a P-B distance of 10.5 Å, indicative of an encounter complex present in solution. These are the first studies of FLPs by neutron scattering, and the first comparative studies of FLPs structure in ionic liquids vs. molecular solvents. Neutron scattering investigations have been complemented by multinuclear NMR spectroscopy. Differences

were detected when comparing encounter complexes in both environments, suggesting that the use of ionic liquids may offer improved kinetics for catalysis with FLPs.

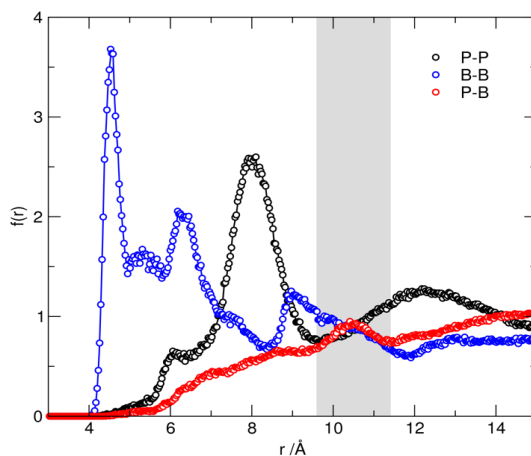


Figure 1. pRDF data from EPSR modelling of <sup>t</sup>Bu<sub>3</sub>P:B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> FLP solutions in benzene showing P-P (black), B-B (blue) and P-B (red) correlations. The small peak in the hetero P-B correlation at 10.5 Å is indicative of association at the encounter complex contact length.

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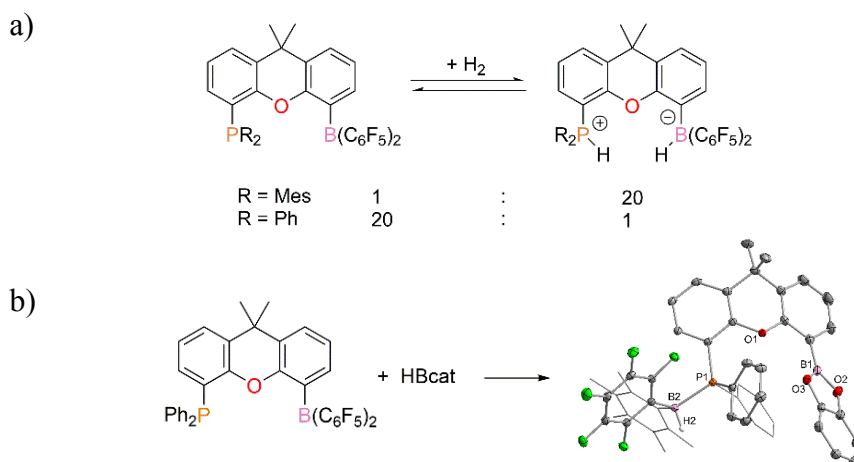


# Hydroboration of Alkynes by an FLP: Unexpected Bond Activation and Mechanistic Studies

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The combination of a Lewis acid and a Lewis base, either as separate molecules or constrained into a single entity, is called a frustrated Lewis pair, FLP. Recently, these compounds have been shown to exhibit remarkable reactivity, for example, in the capture and activation of small molecules and as “metal-free” catalysts in hydrogenation reactions.<sup>1</sup> To facilitate this behaviour, it is imperative that the donor ( $R_3P:$ ) and acceptor ( $BR'_3$ ) sites of the FLP do not form a coordinative bond, but are able to polarize the target chemical bond to the point of heterolytic cleavage (Fig. 1a). However, the drawbacks of using FLPs as catalysts have been the requirement for high catalyst loadings and low turnover numbers. To this end, our group developed an FLP based on a dimethylxanthene backbone (**1**, Fig. 1a), which can reversibly activate  $H_2$  and perform catalytic dehydrocoupling of amine-boranes in ambient conditions.<sup>2</sup> In view of these results, we were interested in extending our studies to the hydroboration of alkynes. In this contribution, we discuss the reactivity of **1** towards selected boranes (HBpin and HBcat), which results in a migration of the  $B(C_6F_5)_2$  group via C-B/B-H metathesis (Fig. 1b). The relevance of this result to the mechanism of FLP catalysed hydroboration reactions of terminal alkynes is discussed.



**Figure 1.** a) Example of reversible binding of  $H_2$  by FLPs b) Reaction of FLP **1** with catecholborane.

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# Phosphenium Cations – Exploring Overlooked Catalytic Potential

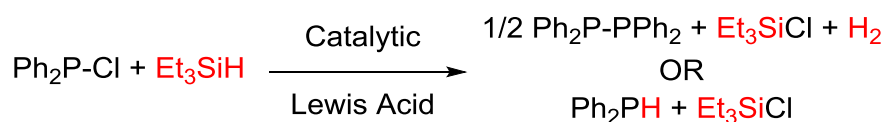
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The possibilities of metal free catalysis revealed by Frustrated Lewis Pair<sup>1</sup> chemistry have attracted a great deal of research, with much emphasis on expanding the scope of the chemistry beyond the boron-based systems for which it was first discovered. A number of Lewis acids based on phosphorus have been shown to be suitable for FLP formation, as well as the heavier pnictogens, but in all cases these are formed based on the +5 oxidation state – e.g. phosphonium<sup>2</sup> or stibonium<sup>3</sup> cations.

Nevertheless, phosphacations derived from P(III) systems (phosphenium cations) are well known, and famed for their very high reactivity and Lewis acidity.<sup>4</sup> Here, we report some observations on the stabilisation of simple phosphenium cations with phosphorus Lewis bases, and explore the role of phosphenium ions in Lewis acid catalysed reduction of P-X. The selective formation of either P-P or P-H bonds can be achieved under mild conditions, and shows remarkable Lewis acid and substrate-substituent dependence which has allowed insight into the mechanisms and pathways involved.



*Catalysis via Phosphenium Intermediates*

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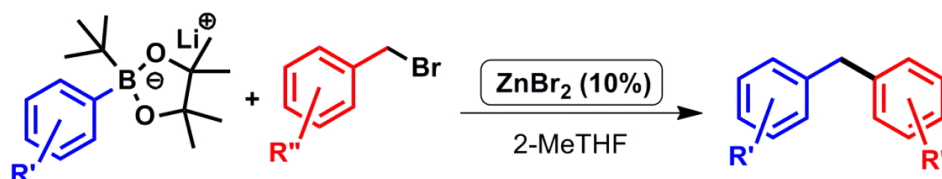
<sup>4</sup> Slattery, J. M.; Hussein, S.; *Dalton Trans.*; 2012; 41; 1808.

## A Zinc catalysed Csp<sup>2</sup>-Csp<sup>3</sup> Suzuki-Miyaura cross-coupling reaction.

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Suzuki-Miyaura cross coupling  
Cheap, low toxicity catalyst  
No ligand required

The Suzuki-Miyaura cross coupling reaction is a powerful and versatile synthetic reaction, forming a new C-C bond by coupling an organoboron nucleophile with an organic electrophile.<sup>1</sup> Since its discovery in the 1970s it has become increasingly important – including in industrial applications, particularly pharmaceuticals synthesis. The most common catalysts are based on palladium or nickel compounds.<sup>2</sup> Replacement of these with low toxicity, inexpensive metals with less supply chain risk would be highly attractive, and significant progress has been achieved using Fe and Cu catalysts.<sup>3,4</sup> Zinc is cheap and has low toxicity, however it is most commonly utilised as a stoichiometric reagent requiring transition metal catalysis (eg. Negishi coupling).<sup>5</sup>

Recently, we have shown the capability of simple zinc salts to effectively catalyse the coupling of aryl-borate reagents with benzyl halides, with high selectivity for hetero-coupling and high yields.<sup>6</sup> This talk will describe the scope and initial mechanistic insight into this reaction, which to the best of our knowledge represents the first example of a zinc catalysed Suzuki-Miyaura cross coupling protocol.

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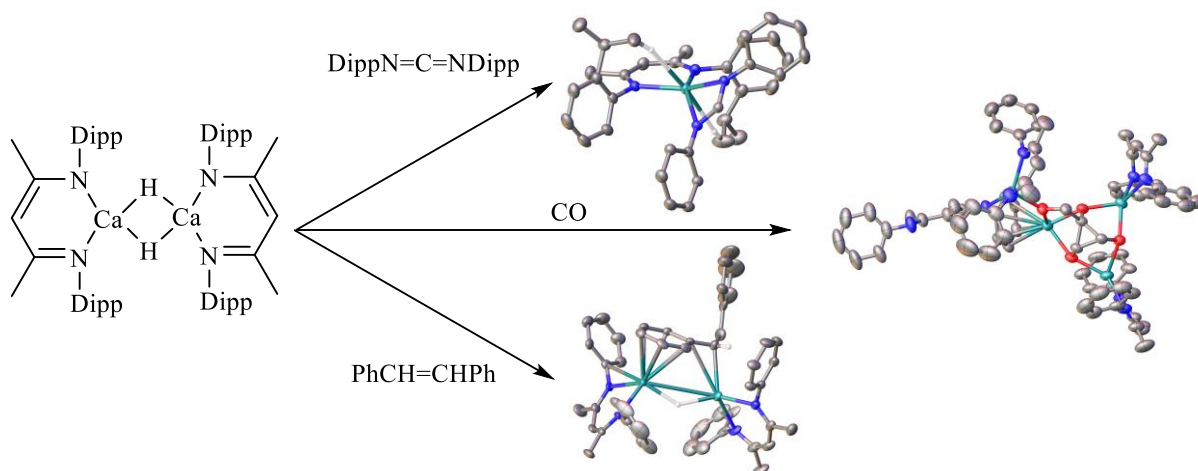
## Reactivity of a Solvent-Free Calcium Hydride.

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In contrast to its lighter congener, magnesium, the chemistry of heteroleptic calcium hydrides is underdeveloped as a consequence of the increased propensity to undergo Schlenk-type redistribution, which typically renders any controlled onward reactivity obsolete. There are however, a handful of isolated heteroleptic calcium hydrides,<sup>[1]</sup> of which Harder's THF solvated hydride has displayed controlled onward reactivity adding across unsaturated (C=O and C=N) bonds and activated alkenes (C=C).<sup>[2]</sup>

We report the synthesis of a solvent-free heteroleptic calcium hydride which, on first inspection, displays similar reactivity to Harder's hydride; adding across C=N bonds of carbodiimides, reductively coupling C=O and adding across activated C=C bonds as illustrated in Figure 1.



**Figure 1:** Reactivity of a solvent free heteroleptic calcium hydride.

In addition to activated alkenes, unprecedented addition across unactivated alkenes affording the first heteroleptic calcium n-alkyls is described along with the extraordinary nucleophilic reactivity of the calcium alkyls towards deuterated benzene.<sup>[3]</sup>

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## Mechanochemical Synthesis of Main Compound and Complexes.

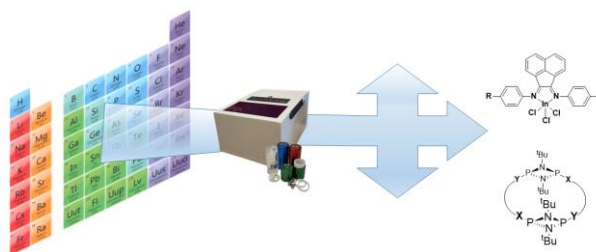
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Mechanochemical syntheses are chemical transformations induced by mechanical means, such as compression, shear and friction.<sup>1</sup> In recent years, there has been an increasing interest in “greener” synthetic methods with less solvent, higher yields, and shorter reaction times being especially appealing to the fine chemicals and inorganic catalyst industries.<sup>2</sup> Mechanochemical approaches present a sustainable route towards the synthesis of inorganic materials and have been widely applied in the synthesis of poorly soluble metal oxides,<sup>3</sup> ceramics, alloys and have increasingly been adopted in modern fields such as nanomaterials.<sup>4</sup> In our studies, we demonstrate that main group compounds and complexes are readily accessible through a mechanochemical milling approach. The synthetic methodology reported herein not only bypasses the use of large solvent quantities and transition metal reagents for ligand synthesis, but also reduces reaction times dramatically.<sup>5-8</sup>



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## Distinct Reactivity of Cationic Magnesium and Zinc Alkyls

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Organometallic chemistry of magnesium and zinc has witnessed several structural and chemical similarities. However, owing to the difference in electronegativity as well as atomic radii, their chemistry can prove to be diverse. We have observed that the  $\beta$ -CH bond in the cationic  $[(\text{Me}_6\text{TREN})\text{MgBu}]^+$  (**1**) can be heterolytically cleaved and the resulting hydride can be used for the reduction of electrophiles. The reactivity of the  $\beta$ -CH bond is very much dependent on the nature of the solvent. While  $[(\text{Me}_6\text{TREN})\text{ZnEt}]^+$  (**2**) is not a potential hydride donor, a reactive cationic terminal zinc hydride  $[(\text{Me}_6\text{TREN})\text{ZnH}]^+$  (**3**) can be prepared from the former. Reactivity of  $[(\text{Me}_6\text{TREN})\text{ZnH}]^+$  (**3**) with electrophiles like  $\text{CO}_2$ , ketones, carbodiimides and other Lewis acids have been explored.

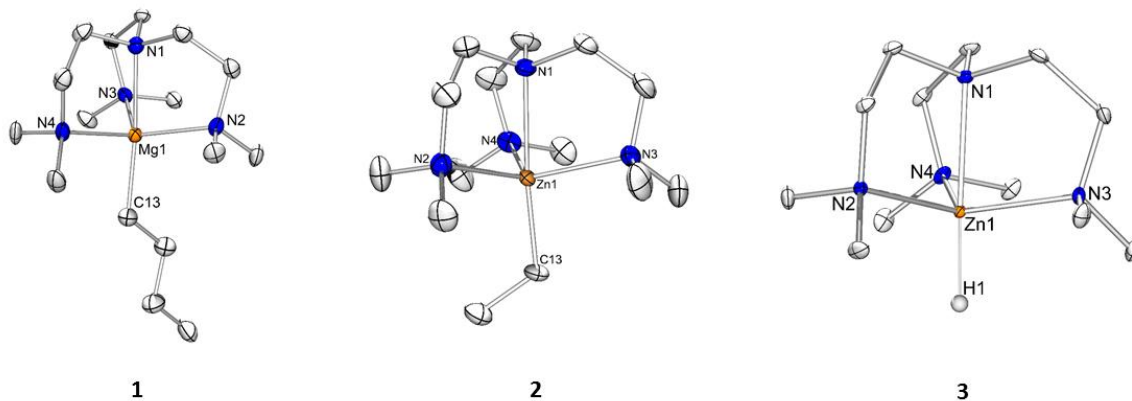


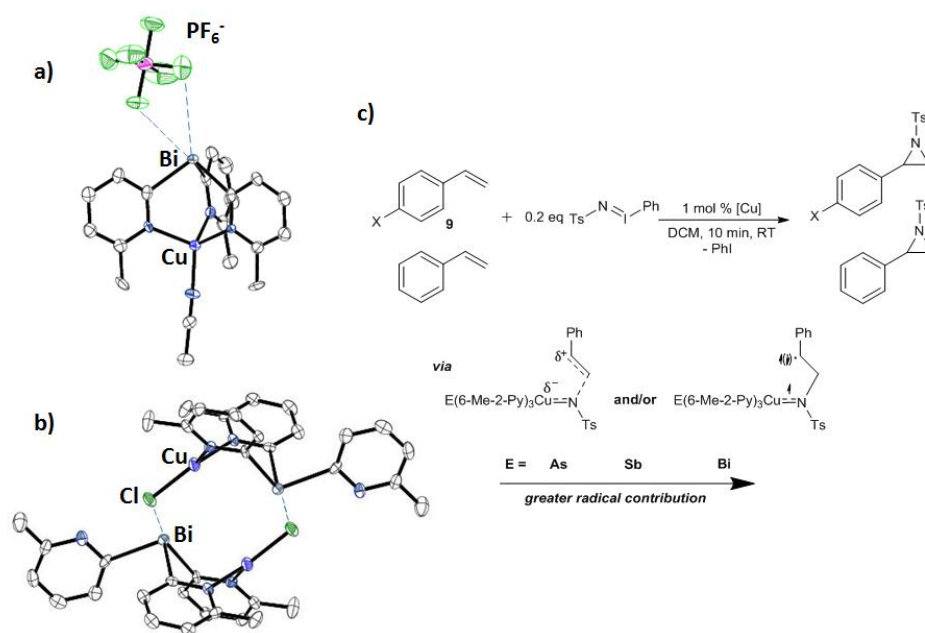
Figure: Solid structure of cationic magnesium and zinc alkyls and hydride.

## How Does Changing the Bridgehead Affect the Properties of Tripodal Ligands?

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Although a multitude of studies have explored the coordination chemistry of classical tripodal ligands containing a range of main group bridgehead atoms or groups, there has been no clear answer to the question of how underlying periodic trends affect ligand character and reactivity within a single ligand family. In addition to standard steric and electronic modification of the organic groups themselves, this issue is of key importance in the design and tuning of tripodal ligands for applications in catalysis. A case in point is the extensive family of neutral tris-2-pyridyl ligands  $E(2\text{-py})_3$  (e.g.,  $E = \text{B-Ph, C-R, N, P}$ ), which are closely related to archetypal tris-pyrazolyl borates. With the new 6-methyl substituted ligands  $E(6\text{-Me-2-py})_3$  ( $E = \text{As, Sb, Bi}$ ) in hand, we have been able to assess the effects of bridgehead modification alone on descending a single group in the periodic table. We show that the primary influence on coordination behaviour is the increasing Lewis acidity of the bridgehead atom as Group 15 is descended, which not only modulates the electron density on the pyridyl donor groups but also introduces the potential for anion selective coordination behavior. Ultimately this can have dramatic influences of the catalytic properties of a coordinated metal centre.



**Figure 1:** a)/b) Anion selective coordination behavior of Bi(6-Me-2-py)<sub>3</sub> c) Bridgehead induced aziridination mechanism shift of [E(6-Me-2-py)<sub>3</sub>CuCH<sub>3</sub>CN]PF<sub>6</sub>

## Molecular precursors for the growth of $M_2E_3$ ( $M = Sb, Bi; E = Se, Te$ ) thin film thermoelectric materials by low pressure chemical vapour deposition

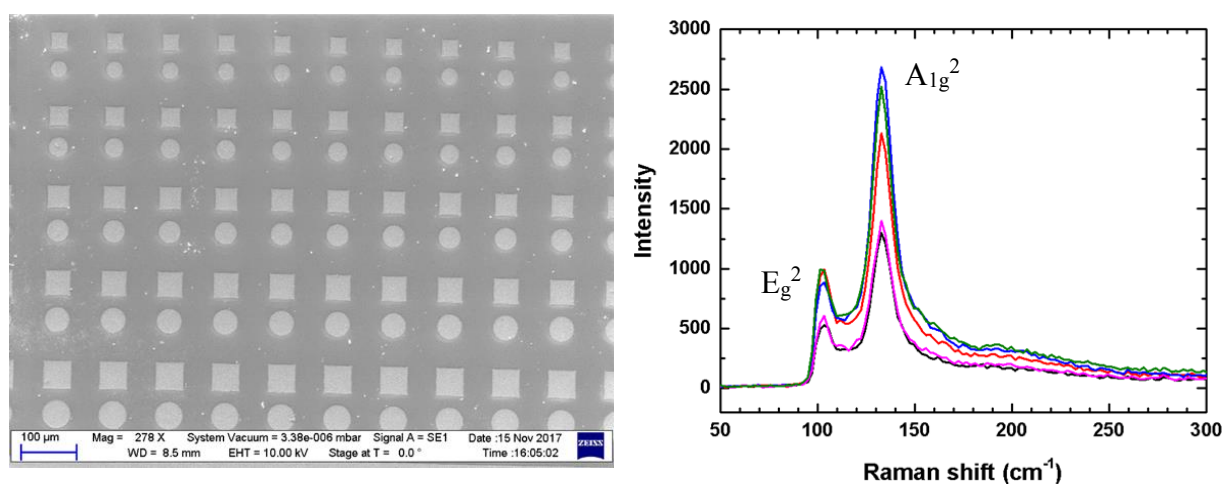
S. L. Benjamin<sup>a</sup>, C. H. de Groot<sup>b</sup>, C. Gurnani<sup>a</sup>, R. Huang<sup>b</sup>, S. L. Hawken<sup>a</sup>, A. L. Hector<sup>a</sup>, W. Levason<sup>a</sup>, G. Reid<sup>a</sup> and S. P. Richards<sup>a</sup>

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Materials of the type  $M_2E_3$  ( $M = Sb, Bi; E = Se, Te$ ) are of interest as thermoelectric materials for energy generation and cooling applications, and as topological insulators<sup>1</sup>. Thermoelectric generators are devices where n- and p-type (doped) semiconducting materials are connected such that they are electrically in series and thermally in parallel, which convert a temperature gradient across that device into electrical energy.  $Bi_2Te_3$  is the archetypical thermoelectric material for near room temperature applications<sup>2</sup>, with thin films of  $Bi_2Te_3$  being of particular interest from both enhanced device performance<sup>3</sup> and materials efficiency standpoints.

We present here our work in the development of molecular precursors for the low pressure chemical vapour deposition of binary  $M_2E_3$  ( $M = Sb, Bi; E = Se, Te$ ) phases, the materials characterisation of thin films, area selective depositions onto regions of photo-lithographically patterned substrates, and results from thermoelectric functionality measurements undertaken.



**Figure:** (L) Substrate selectivity of  $Bi_2Te_3$  for  $Ti_xN_y$  vs  $SiO_2$  on a photo-lithographically patterned substrate, (R) Raman spectra recorded from various locations of a  $Bi_2Te_3$  sample.

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# A General Synthetic Approach Towards Heavier Group 15/16 Cyanate

## Homologues $Pn=C=Ch^-$ ( $Pn = P, As$ ; $Ch = S, Se$ ).

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The 2-phosphaethynolate anion ( $PCO^-$ ) was first reported in 1992 and the 2-arsaethynolate ( $AsCO^-$ ) in 2016.<sup>[1]</sup> Improved synthetic access to  $PCO^-$  has recently sparked systematic investigations into the chemistry of this anion and led to the facile synthesis of its heavier group 16 homologue  $PCS^-$ .<sup>[2]</sup> Heavier homologues of the cyanate ion are valence isoelectronic to a number of small molecules such as  $O=C=O$ ,  $O=C=S$ ,  $F-C\equiv P$ , and the series  $N=C=Ch^-$  ( $Ch = O-Te$ ). They are thus of greatest interest for the investigation of principal electronic states, and bonding modes of combined period 2, 3 and, 4 elements.

Here we report on a general synthetic approach towards  $PCS^-$ ,  $AsCS^-$ ,  $PCSe^-$ , and  $AsCSe^-$  and explore the chemistry of these fundamental new ions. The compounds were characterised by single crystal X-ray diffraction and spectroscopic measurements.

Crystal structures of  $[Na(18\text{-crown-}6)(THF)_2]X$  ( $X = PCS^-$ ,  $AsCS^-$ ,  $PCSe^-$ , and  $AsCSe^-$ ) allow for the thorough analysis of bond metrics and serve as model systems for

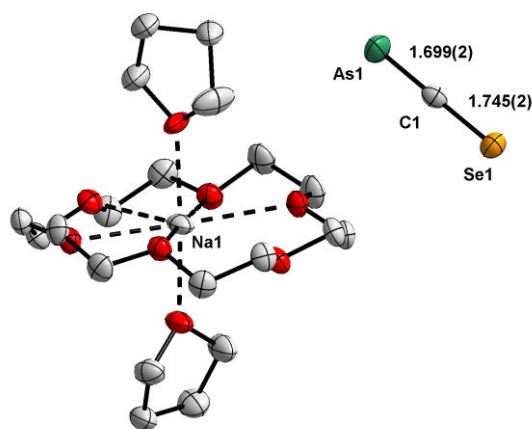


Figure 1: Single crystal X-ray structure of  $[Na(18\text{-crown-}6)(THF)_2]AsCSe$ .

quantum mechanical calculations. We show that the charge distribution is fundamentally different from their lighter homologues  $PCO^-$  and  $AsCO^-$  and, on this basis, discuss the implications on their reactivities.

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## Charge Transfer in Halogen Bonds

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At its simplest, chemical bonding involves a combination of two dominant contributions: direct electrostatics (ionic) and electron sharing (covalent). The relative importance of these contributors has been the subject of significant study in primary (intramolecular) chemical interactions. For example, the relevance and importance of covalent contributions has been a primary focus of transition metal chemistry for decades. For weaker secondary chemical interactions such as hydrogen bonding (HB) and halogen bonding (XB), the prevailing view in the literature is that electrostatic interactions are so dominant that covalent contributions are negligible. A notable exception is that of so-called symmetric hydrogen bonds, which exhibit large covalent contributions.

With X-ray Absorption Spectroscopy (XAS), we have provided the first direct experimental evidence of covalency in weak secondary interactions, specifically in HB and XB systems. From such studies, we observe that XB exhibit a significantly higher degree of covalency compared with HB counterparts of similar bond strength<sup>1</sup>. Notably, the degree of covalency in certain XBs is equivalent to that observed in transition metal halides. Our studies provide information of the electronic changes that occur in both the charge donor and charge acceptor in model systems, affording us a unique experimental view of these weak interactions. We also demonstrate the importance of covalent contributions in XBs by showing the effect of covalency in the electron transfer properties in XB-modified dye sensitised solar cells. These results lead us to conclude that XBs should more generally be classified as coordinate bonds (and thus identified using an arrow) to distinguish them from significantly less covalent HBs and other weak interactions.

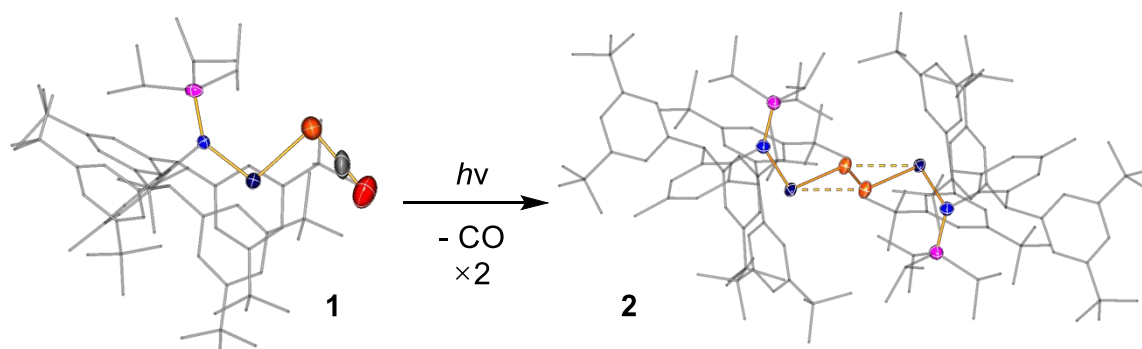
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## Limitations of Steric Bulk: Towards Phospha-Germynes and Phospha-Stannynes.

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The use of sterically bulky ligands has been critical in the stabilisation of unusual structural motifs which violate the double bond rule. Since Lappert's discovery of the first distannene, many landmark examples such as West's disilene, Yoshifuji's diphosphene, Tokitoh's dipnictenes, Sekiguchi's disilyne and Power's alkyne analogues have been reported.<sup>[1]</sup> More recently, Jones and co-workers have exploited bulky [bis(benzhydryl)aryl](silyl)amides as substituents, allowing for the stabilisation of monomeric germanium hydrides and unsupported covalent bonds between main group elements and transition metals such as manganese and magnesium.<sup>[2]</sup>



We envisaged the synthesis of nitrile analogs (R–GeP, R–SnP) stabilised by only one of the Jones-type amido substituents via photolysis of the corresponding phosphaketenes R–GePCO and R–SnPCO (**1**). Amongst other products, the formation of germylenyl- and stannylenyl-substituted diphosphenes (**2**) was observed. Further enhancement of the steric bulk allowed the prevention of dimerisation of R–GeP and R–SnP, but the heavy nitrile analogues could not yet be observed, as the substituent was subject to Si–C and C–H bond activations.

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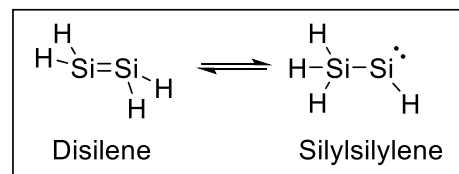
## Disilene vs Silylsilylene: Substituted Analogues of the Si<sub>2</sub>H<sub>4</sub> Rearrangement

Martin W. Stanford, Gary S. Nichol and Michael J. Cowley\*

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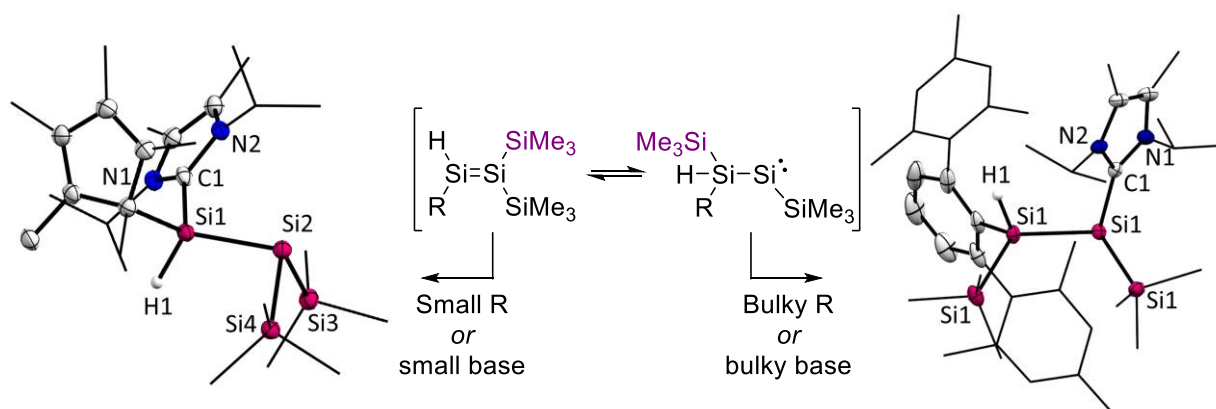
Martin.Stanford@ed.ac.uk

The equilibrium between parent disilene (H<sub>2</sub>Si=SiH<sub>2</sub>) and silylsilylene (H<sub>3</sub>Si-SiH) has been studied extensively both theoretically<sup>1</sup> and at 10 K in an argon matrix<sup>2</sup> due to its importance as an intermediate in the chemical vapour deposition of silicon for electronics.



This equilibrium has been implicated in the rearrangements of disilenes at ambient and elevated temperatures, but has not directly been observed for isolable molecular disilenes.<sup>3</sup> In order to further investigate this process, we sought a facile method for the preparation of substituted disilenes bearing a single hydride substituent that may undergo this transformation.

Here we present a novel route to asymmetrically substituted disilenes. Taking advantage of substituents and coordinating bases with a range of steric parameters, we are able to observe and control the rearrangement of disilenes to isolable silylsilylenes. Despite the presence of a hydride, migration of the trimethylsilyl group is strongly preferred. We present further details of the equilibrium and the synthesis, structures and reactivity of isolated compounds.<sup>4</sup>



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# Beyond Boranes: Achieving Moisture-Tolerant Frustrated Lewis Pair Catalysis With Stannylum Lewis Acids

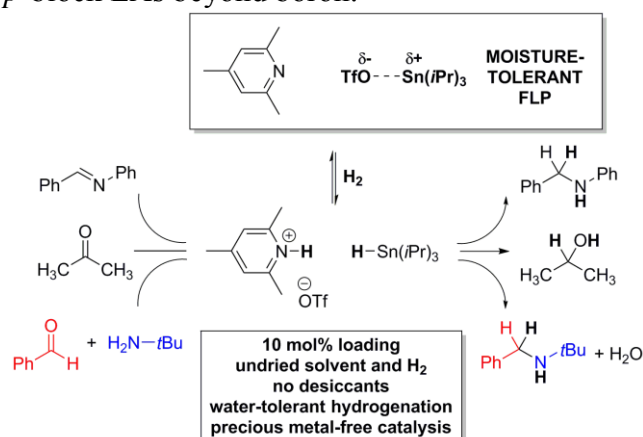
Joshua S. Sapsford, Dr Daniel J. Scott, Dr Andrew E. Ashley

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Frustrated Lewis pairs (FLPs) provide an attractive alternative to precious metal hydrogenation catalysts, which are costly and becoming increasingly scarce. Bulky Lewis acids (LAs) and bases (LBs) which fail to form expected classical adducts, can open up new combined reactivity such as the heterolytic cleavage of H<sub>2</sub>.<sup>1</sup> Triarylboranes (Ar<sub>3</sub>B) derived from the ubiquitous B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> dominate FLP research, as targets for new LAs. These typically form highly Brønsted acidic adducts with H<sub>2</sub>O that are deprotonated (and deactivated) by the LBs required to effect H<sub>2</sub> cleavage. Consequently, the vast majority of FLP catalytic protocols require H<sub>2</sub>O-free conditions; a key barrier to their mainstream adoption.

Due to these limitations, we are instead investigating [R<sub>3</sub>Sn]<sup>+</sup> LAs. Sn, as a heavier *p*-block element, is ‘softer’ and less oxophilic than B, forming weaker and less acidic adducts with H<sub>2</sub>O. Recently, we reported that *i*Pr<sub>3</sub>SnOTf (a surrogate for [*i*Pr<sub>3</sub>Sn]<sup>+</sup>) activates H<sub>2</sub> with 2,4,6-collidine (fig. 1).<sup>2</sup> This FLP is readily applicable as a catalyst for imine and carbonyl hydrogenation, using undried commercial solvents and H<sub>2</sub>.

This presentation will address how simply changing the LA element led rapidly to water-tolerant hydrogenation protocols that present substantial challenges for Ar<sub>3</sub>B, particularly for reductive amination,<sup>3</sup> and highlight potential advances that could be discovered using the relatively unexplored *p*-block LAs beyond boron.



**Figure 1:** FLP-mediated H<sub>2</sub> activation using *i*Pr<sub>3</sub>SnOTf with hydrogenation substrate examples

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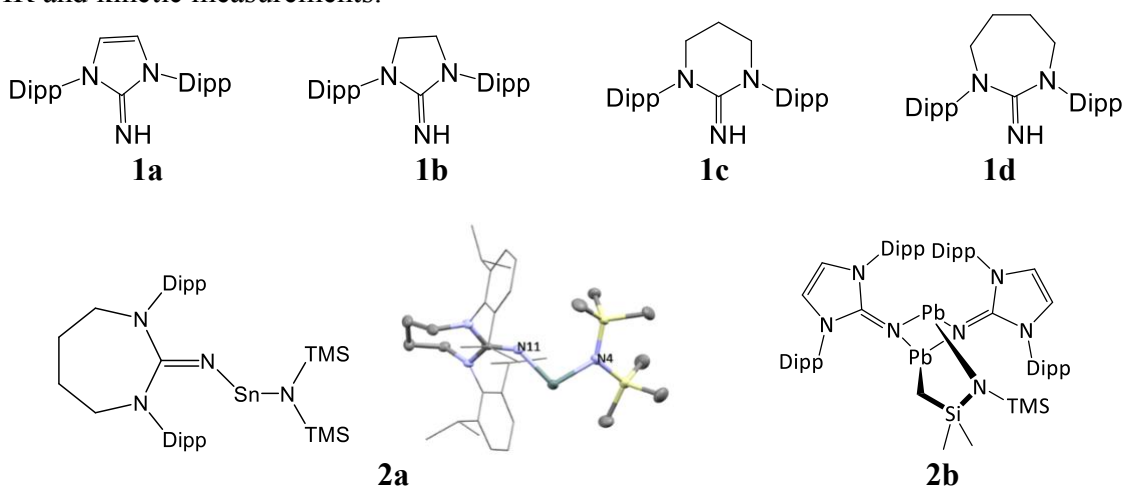
# Coordination Chemistry and Reactivity of the Heavier Group 14 Elements with Bulky Anionic Guanidinato Ligands

H. NIU, E. KOLYCHEV, T. HOOD, P. LÖWE, M. KEMP, S. ALDRIDGE

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Strongly electron donating ligands of the guanidinate family - pioneered by Tamm, Inoue and Rivard - have proved to be highly effective at stabilising reactive transition metal, f-metal and main group systems.<sup>1-3</sup> In recent work we have synthesized two novel ligands to further extend the guanidinato family: **1c** (6-DippNH) and **1d** (7-DippNH) are ring-expanded analogues of the previously reported **1a** (5-DippNH) and **1b** (4-DippNH).<sup>1,4</sup> These ring-expanded derivatives can be accessed via a number of synthetic routes: e.g. directly from cyanogen bromide, via the free carbene and Me<sub>3</sub>SiN<sub>3</sub> or from amidine dibromide and NH<sub>3</sub>.

DFT calculations reveal more strongly  $\sigma$ - and  $\pi$ - donating capabilities compared to their 5-membered ring counterparts, and we therefore set out to investigate their coordination chemistry, targeting unsaturated group 14 systems capable of E-H bond activation. These studies include a range of unsymmetrical and symmetrical group 14 compounds such as Sn(N(SiMe<sub>3</sub>)<sub>2</sub>)(n-DippN), where  $n = 5, 6,$  and  $7$ , which have been characterised by <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectroscopy and in the case of the  $n = 7$  system (**2a**) by X-ray crystallography. In the case of lead, the related system Pb((N(SiMe<sub>3</sub>)<sub>2</sub>)(IDippN)), is shown to be labile, being converted into plumblyenoid **2b** by heating to 90°C for 24 hours. This conversion serves as a very rare example of C-H activation at a heavier group 14 metal centre. Mechanistic possibilities for this activation process have been probed by DFT studies, <sup>207</sup>Pb NMR and kinetic measurements.



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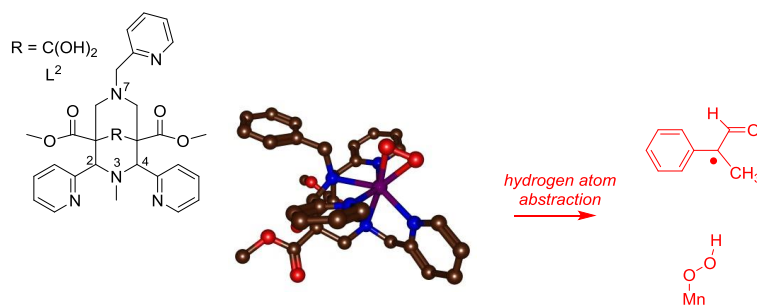
## Title: A novel mechanism for aldehyde deformylation by a side-on manganese(III)-peroxo complex.

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Metalloenzymes have major functions in biology, ranging from biosynthesis to biodegradation of compounds. The most abundant transition metals in Nature and consequently most frequently seen in enzymes are iron, copper and manganese. The latter takes part in strong oxidizing complexes including Photosystem II and superoxide dismutase. How the  $Mn_4O_5Ca$  cluster in Photosystem II binds and converts water molecules into  $O_2$  remains a mystery; therefore biomimetic models have been developed to gain insight on manganese reactivity. In this presentation, I will show recent results<sup>1,2</sup> on the characterization and reactivity of a side-on manganese(III)-peroxo complex with aldehydes. Thus, our recent work<sup>1,2</sup> established a novel mechanism that starts with a hydrogen atom abstraction from the  $\alpha$ -position of substrate. The mechanism was confirmed with kinetic isotope effect studies but also substrate analogues that lacked the transferrable hydrogen atom. A series of computational (density functional theory) studies proposed a new mechanism starting with hydrogen atom abstraction and followed by a keto-enol tautomerization prior to a nucleophilic reaction mechanism. The experimental trends and observations were rationalized with thermochemical cycles and valence bond schemes.



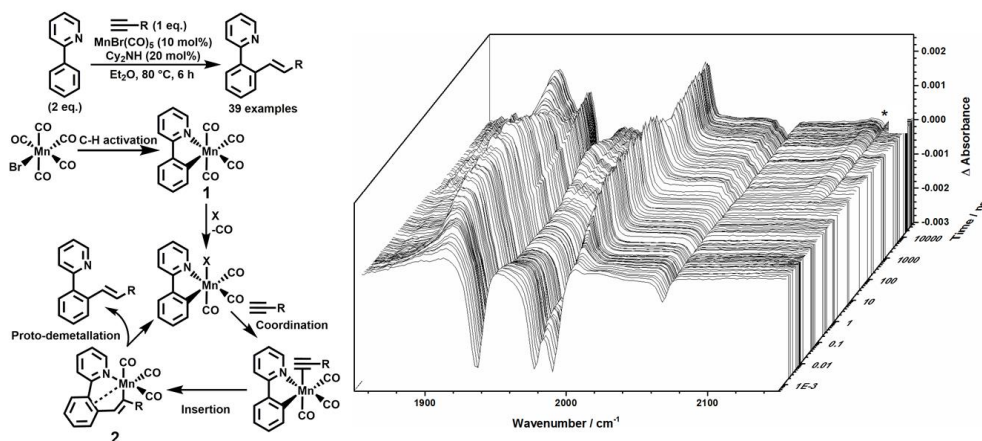
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# Understanding the Mechanism of Mn-Catalysed C–H Bond Functionalisation Using Time-Resolved IR Spectroscopy (TRIR)

L. Anders Hammarback, Ian P. Clark, Igor V. Sazanovich, Michael Towrie, Alan Robinson, Ian J. S. Fairlamb\*, Jason M. Lynam\*.

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Manganese is a versatile, earth abundant first row transition metal, with significant potential for utilisation as a catalyst in chemical synthesis. Recent advances in Mn(I)-catalysed C–H bond functionalisation reactions have provided synthetically useful methodologies that previously was limited to the platinum group metals. Wang and co-workers reported the alkenylation of 2-phenylpyridines with various alkynes using  $\text{MnBr}(\text{CO})_5$  as the precatalyst.<sup>1</sup> The proposed mechanism includes initial cyclometallation and subsequent insertion of the alkyne. The mechanism of this and related reactions has not been studied in-depth. Previous work in York includes characterisation of the 7-membered intermediate (**2**) of a structurally related 2-pyrone derivative, formed by alkyne insertion.<sup>2</sup>



Ultrafast time-resolved IR spectroscopy (TRIR) has been used to observe the C–C bond forming step of the catalytic cycle over the fs to ms timescale. The initial Mn-complex (**1**) is activated by irradiation and the metal carbonyls provide excellent handles to monitor the changes that occur at manganese following initial CO loss. TRIR allowed for the observation of solvent coordination, subsequent displacement by the alkyne and alkyne insertion into the Mn–C bond. Studies have been performed on a series of Mn-complexes and unsaturated substrates, such as alkynes, acrylates and isocyanates.

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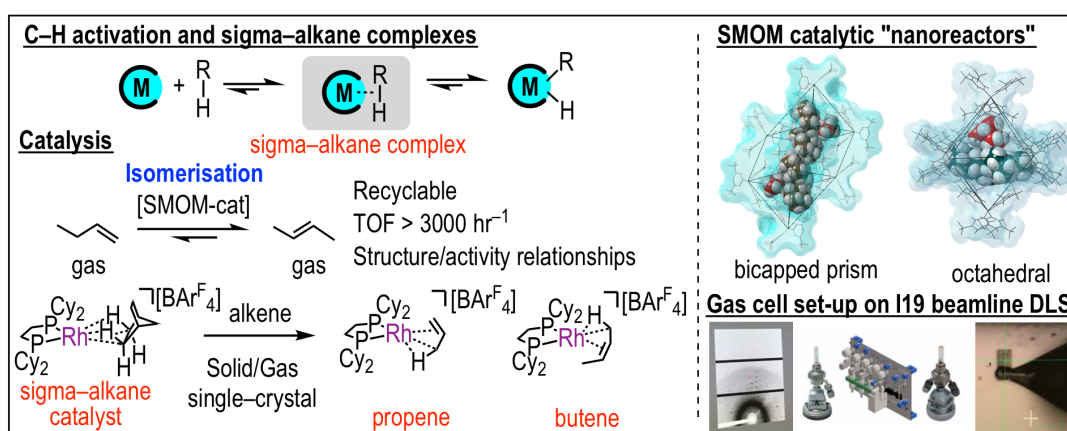
# Valorisation of Light Hydrocarbons: Solid-State Molecular Organometallic Catalytic Nanoreactors (SMOM-cat)

Antonio J. Martínez-Martínez,<sup>a</sup> Alasdair I. McKay,<sup>a</sup> Mark Warren,<sup>b</sup>

Stuart A. Macgregor<sup>c</sup> and Andrew S. Weller<sup>a</sup>

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Low-temperature catalytic processes for the valorisation of light hydrocarbons (alkanes, alkenes) are desirable methods for the production of valuable chemical building blocks such as aromatics and high-value olefins.<sup>1</sup> Although a variety of systems have been developed (e.g. dehydrogenation, isomerisation), heterogeneous methods that operate with a low energy demand and high selectivity represent a real challenge in catalysis. In this context, C–H bond activation processes using solid-state molecular organometallics (SMOM) via solid/gas transformations offer new opportunities that harness the benefits of discrete molecular species placed in a well-defined solid-state environment.<sup>2</sup> We describe here our latest advances on the use of rhodium  $\sigma$ -alkane and alkene catalysts that behave as “molecular nanoreactors”<sup>3</sup> for alkene isomerisation processes at room temperature, low pressure and with high recyclability. The influence of the bite angle of the supporting phosphine and anion identity upon the rate of isomerisation is reported, alongside the structure of the active catalyst determined using *in-situ* single-crystal to single-crystal synthetic techniques.<sup>4</sup> This approach provides unique opportunities in heterogeneous catalysis to precisely control and interrogate the active site.



**Figure 1.** Solid-State Molecular Organometallic catalysis (SMOM-cat).

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## Iron catalysed transfer hydrogenation and regioselective deuteration reactions

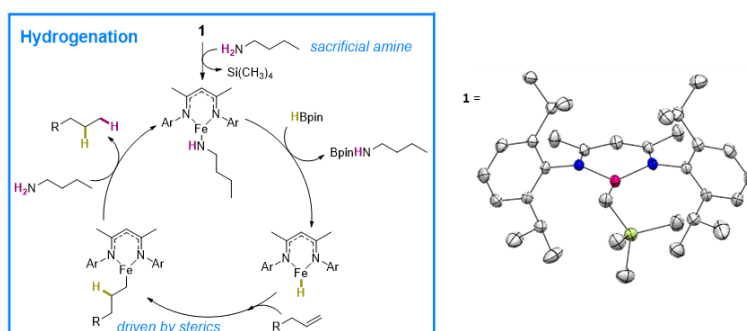
M. Espinal-Viguri,<sup>a</sup> N.T.Coles,<sup>a</sup> S. Neale,<sup>b</sup> R.L. Webster,<sup>a</sup> S. A. MacGregor<sup>b</sup>

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There are very few examples of transfer hydrogenation (TH) of alkenes using iron based catalysts. However, there are numerous examples of TH of imines and ketones, with a notable example showcased by Morris *et al.*<sup>1</sup>

Work by Burke *et al* has shown that ammonia borane has the potential to hydrogenate imines and highly activated alkenes without a metal present, with site selective deuteration being shown to be possible.<sup>2,3</sup> Other work in the literature by Westcott<sup>4</sup> and Liu<sup>5</sup> have shown that amines and boranes can be used with metals to perform hydrogenation of alkenes and alkynes respectively.

Following on from work on hydroboration<sup>6</sup> and hydrophosphination<sup>7</sup> within the group we looked to combine the protic and hydridic character of amines and pinacol borane to hydrogenate a range of alkenes and alkynes. Deuteration reactions lead to regioselective deuteration for several substrates. The results from the synthetic studies will be presented along with a proposed mechanistic cycle from our combined mechanistic/computational studies.



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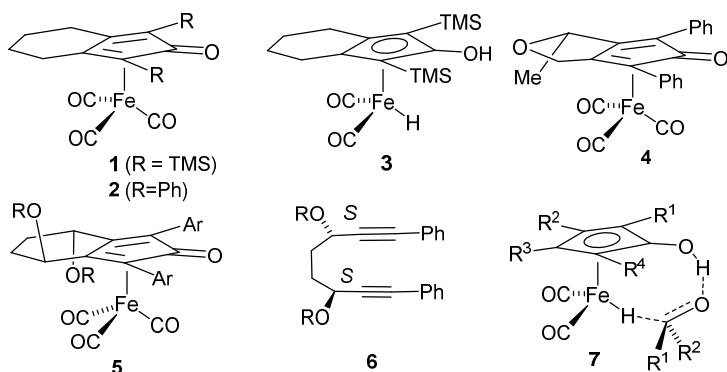
## Title: Synthesis and Catalytic Applications of Cyclopentadienyl Iron Tricarbonyl Complexes.

Authors. Roy Hodgkinson, Alessandro Del Grosso, Alexander E. Chamberlain, Guy J Clarkson and Martin Wills.

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Cyclopentadienyl iron tricarbonyl complexes, of typical structures **1** and **2**, can be prepared readily through the cyclisation of a dialkyne with  $\text{Fe}(\text{CO})_5$ . They have recently found applications as precatalysts (of the active species of general structure **3**) for a range of hydrogen-transfer reactions. In this talk, the synthesis and synthetic applications of a range of such complexes, including asymmetric derivatives **4** and **5** (prepared from **6**), will be described. The complexes have proved to be effective catalysts for alcohol oxidation,<sup>1</sup> ketone reduction<sup>2-5</sup> (believed to be through the concerted mechanism shown in **7**) and ‘hydrogen borrowing’ reactions<sup>6,7</sup> whereby a C-N bond is formed from an alcohol and an amine. Our efforts at enantioselective catalysis of ketone reduction using an asymmetric derivative of a cyclopentadienyl iron tricarbonyl complex will also be described in this presentation.



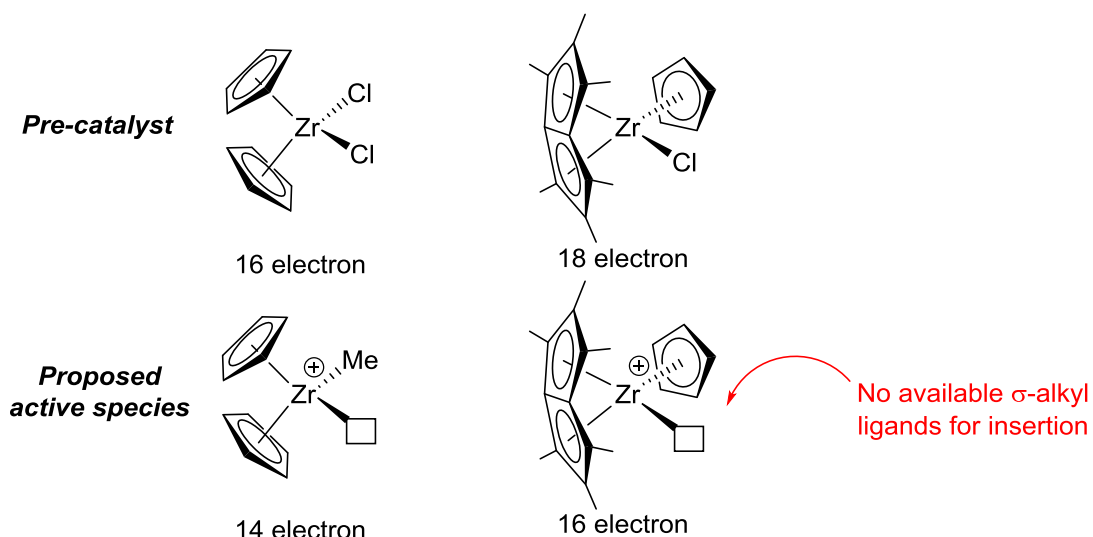
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## Evidence for a new mechanism of ethylene polymerisation.

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Homogeneous ethylene polymerisation with the group 4 bent metallocene derivatives  $\text{Cp}_2\text{MX}_2$  ( $\text{Cp} = [\text{C}_5\text{H}_5]$ ) has been demonstrated to operate *via* a coordination-insertion mechanism, with a 14 electron cationic alkyl complex  $[\text{Cp}_2\text{M}(\text{alkyl})]^+$  as the active species.<sup>1</sup> We have recently reported the related pentalene complexes  $\text{Pn}^*\text{MX}_2$  ( $\text{Pn}^* = [\text{C}_8\text{Me}_6]^{2-}$ ,  $\text{X} = \text{Cl}$ ,  $\text{Cp}$  or alkyl) which are active for ethylene polymerisation ( $\text{M} = \text{Zr}$ , activity up to  $4486 \text{ kg}_{\text{PE}}\text{mol}_{\text{M}}^{-1}\text{h}^{-1}\text{bar}^{-1}$ ) and produce high molecular weight polyethylene.<sup>2, 3</sup> Unusually, these complexes are all 18 electron, saturated species and do not behave as typical coordination-insertion catalysts (Figure 1).



**Figure 1** A structural analogy between  $\text{Cp}_2\text{MX}_2$  bent metallocenes and  $\text{Pn}^*\text{MX}_2$  pentalene complexes.

Herein, we describe our studies to probe the mechanism of ethylene polymerisation with these pentalene complexes through the synthesis of catalytic intermediates and model complexes, and characterisation of the resultant polymer. These studies lead us to propose a new mechanism for polymerisation which generates high molecular weight polyethylene.

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# Rhodium Mediated Deoxygenative Metathesis of CO

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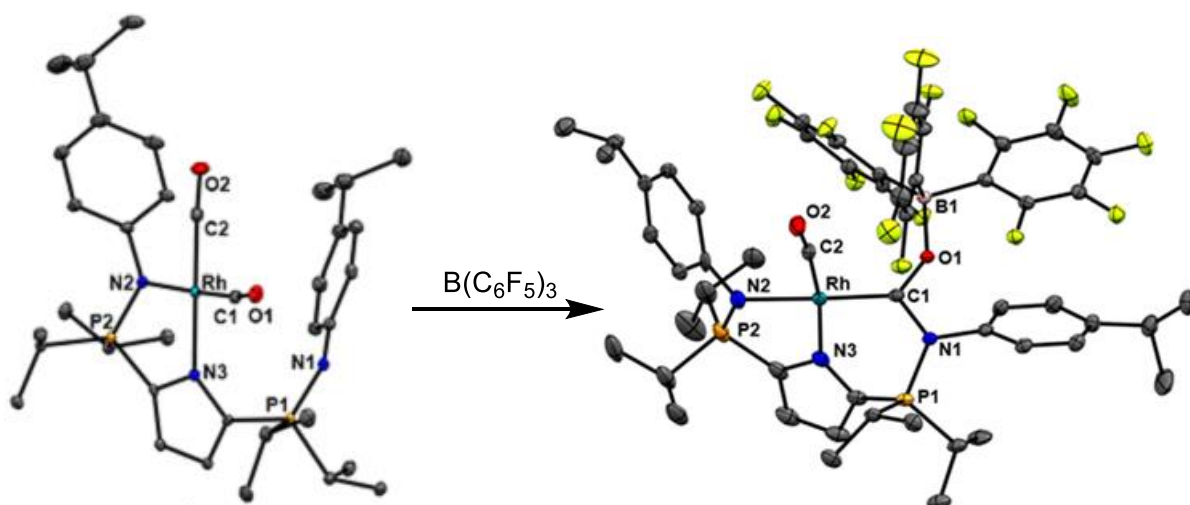
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In an attempt to prepare low-coordinate, 14-electron rhodium species capable of participating in various bond activation processes relevant to industrially important catalytic transformations, several organorhodium complexes supported by an *NNN*-pyrrole-based pincer ligand were synthesized.<sup>1</sup>  $^{\text{Ph}}\text{LRh}(\text{COE})$  ( $^{\text{Ph}}\text{L} = 2,5\text{-[}^i\text{Pr}_2\text{P=N(4-}^i\text{PrC}_6\text{H}_4\text{)]}_2\text{N(C}_4\text{H}_2\text{)}^-$ ) reacts readily with a wide array of small molecules, including silanes, alkynes, CO and phosphines. Upon reaction with  $\text{H}_2$ , an unusual dinuclear rhodium species, which mediates the catalytic hydrogenation of numerous unsaturated hydrocarbons, was identified. A rhodium dicarbonyl complex supported by a related scaffold ( $^i\text{PrLRh}(\text{CO})_2$ ), along with  $\text{B}(\text{C}_6\text{F}_5)_3$ , cooperatively functionalizes CO. Unlike other systems, CO activation is reversible and conversion to a value-added organic product ( $\text{ArN}\equiv\text{C}:\rightarrow\text{B}(\text{C}_6\text{F}_5)_3$ ) does not require stoichiometric addition of harsh reducing agents, such as  $\text{KC}_8$ . Accordingly, this chemistry moves us closer to sustainable alternatives to the Fischer-Tropsch process.



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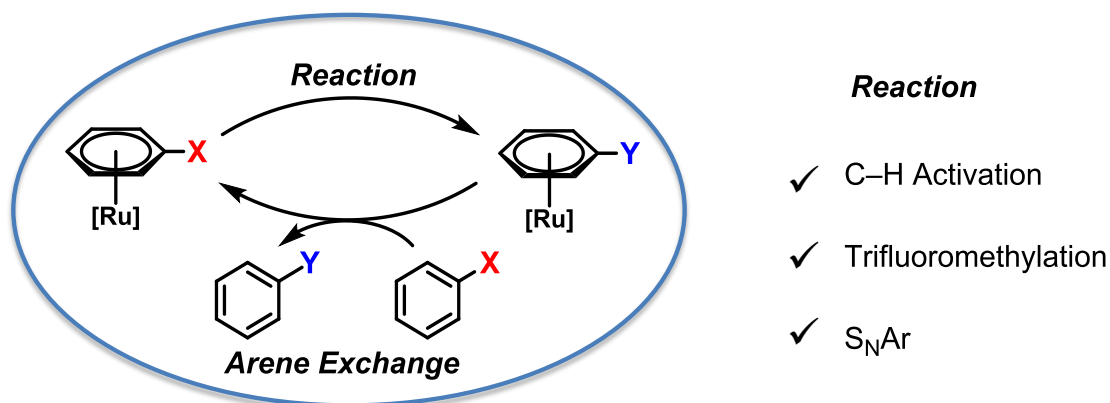
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## Catalytic Reaction of Organometallic Ruthenium Complexes

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$\eta^6$ -Coordination of aromatic molecules to transition metals alters the reactivity of the bound arene. Typically this  $\eta^6$ -coordination will increase the electrophilicity of the arene and stabilise negatively charged reaction intermediates. Since beginning our independent research group in 2014, we have been studying reactions of  $[(\eta^6\text{-arene})\text{RuCp}]^+$  complexes. We will present successful  $\text{S}_{\text{N}}\text{Ar}$ ,<sup>1</sup> C–H activation<sup>2</sup> and trifluoromethylation<sup>3</sup> reactions based on the mechanism shown below.



While  $\eta^6$ -coordination gives access to exciting new reaction of arenes, the requirement for stoichiometric metal is a drawback. To address this issue, our research also focusses on reactions that are catalytic in the activating metal fragment. Following reaction of  $\eta^6$ -bound arenes, exchange between the bound product and starting material will lead to catalytic systems (Figure). To achieve this, we need an understanding of the mechanism of arene exchange. We have recently reported a catalytic  $\text{S}_{\text{N}}\text{Ar}$  process<sup>1</sup> and have shown that C–H activation<sup>2</sup> and trifluoromethylation<sup>3</sup> can proceed with recovery of the activating Ru fragment. This research has great potential to allow late-stage modification of arenes for application in drug discovery, as well as developing fundamental understanding of organometallic Ru complexes.

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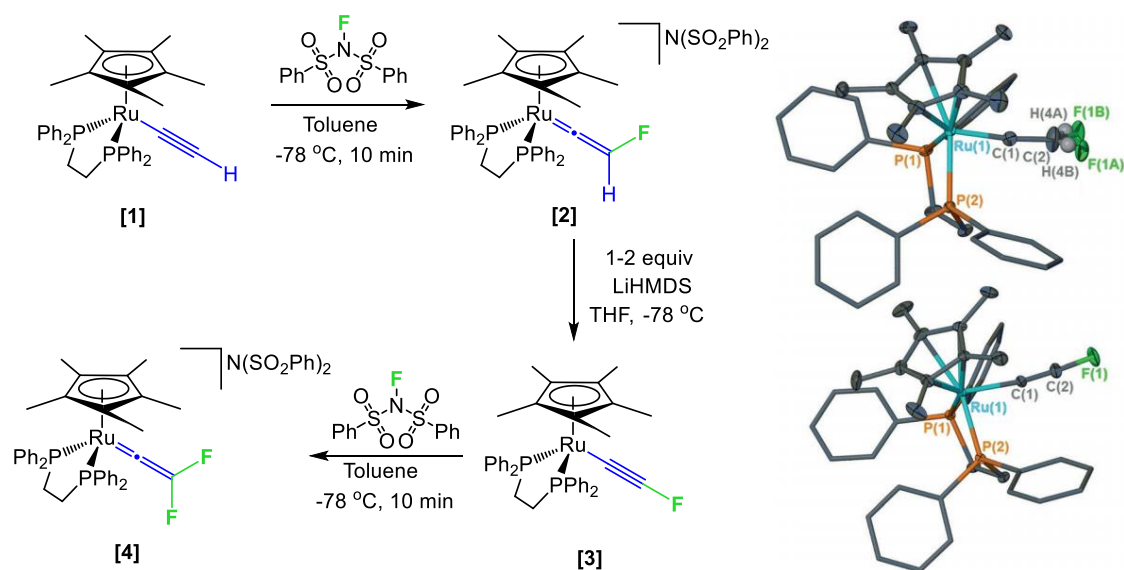
## Stable Fluoroalkynes via Outer-Sphere Electrophilic Fluorination.

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Incorporation of fluorine has become a powerful tool in the pharmaceutical and agrochemical sectors due to its biologically significant properties. Metal-mediated fluorination strategies have become increasingly important in this area in recent years.<sup>1</sup> We have recently uncovered a novel mechanism for metal-mediated C-F bond formation, Outer Sphere Electrophilic Fluorination (OSEF).<sup>2</sup>

This allows the rapid, selective synthesis of fluorinated vinylidene complexes, e.g. [2] and [4].<sup>3</sup> The potential for fluorinated vinylidene ligands to afford novel, fluorinated organic compounds have been investigated. However, OSEF also has significant potential in the synthesis of novel organometallic complexes.



Utilising the OSEF strategy has granted access to the first structurally characterised fluoroalkynes (e.g. [3]), which are remarkably stable compared to the rare and highly reactive organic fluoroalkynes.<sup>4</sup> The synthesis, structure and bonding in these species will be presented. Additionally, the contrasting reactivity observed between different fluorinating agents towards ruthenium acetylide complexes will be discussed.

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## Magnesium-Mediated $sp^2C-F$ and $sp^3C-F$ Bond Activation.

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The activation of strong carbon–fluorine bonds remains a key academic and industrial challenge that is motivated by the prevalence of fluorine-containing molecules in pharmaceutical, agricultural and materials industries. Through a combined experimental and computational (DFT) approach, we have successfully characterised the mechanisms of  $sp^2C-F$  and  $sp^3C-F$  bond activation using low-valent magnesium dimers.<sup>1,2</sup>  $sp^2C-F$  bond activation proceeds via a concerted nucleophilic aromatic substitution-like pathway. This transition state is facilitated by stabilising  $Mg \cdots F_{ortho}$  interactions that, in combination with known trends in C–F and C–M bond strengths in fluoroarenes, provide an explanation for the experimentally determined regiochemistry.<sup>3</sup> Conversely, magnesium-mediated  $sp^3C-F$  bond activation proceeds via an unprecedented front-side nucleophilic attack mechanism involving a highly organized transition state. Calculations have demonstrated that electron density from the Mg–Mg bond populates the  $\sigma^*C-F$  bond in this transition state. In a concerted, asynchronous process the reacting carbon centre adopts carbanionic character during C–F bond activation, which migrates to the most electropositive magnesium centre.<sup>4</sup>

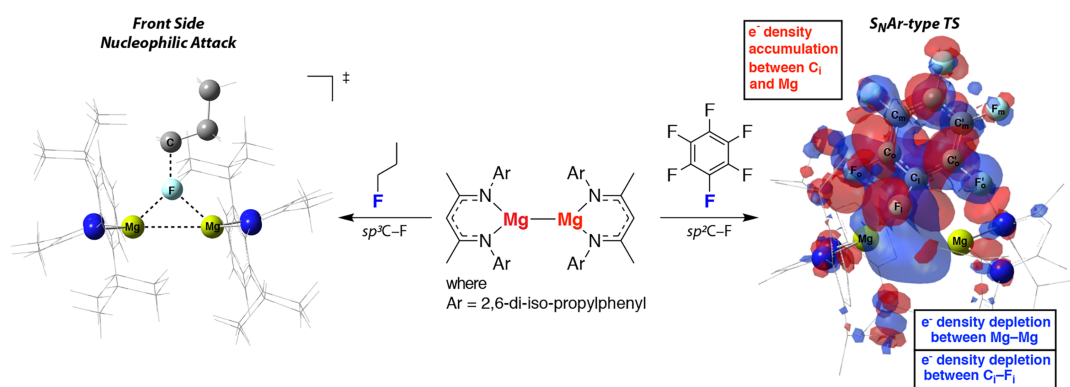


Figure 1.  $sp^2C-F$  and  $sp^3C-F$  bond activation transition states.

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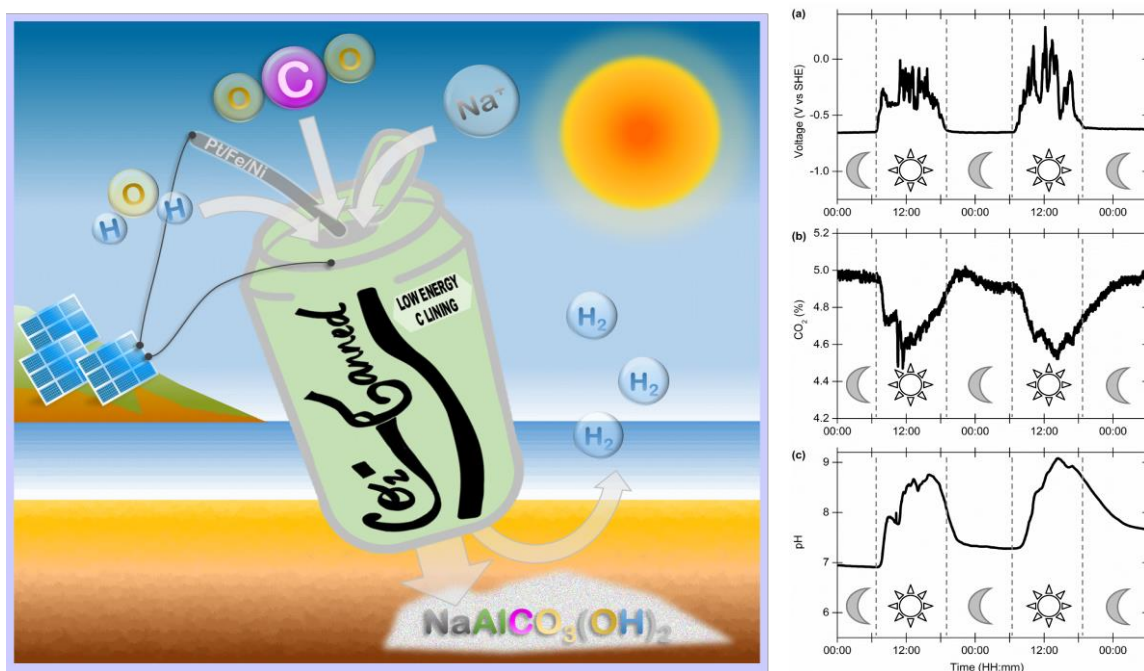


# Capacitance Assisted Sustainable Electrochemical Carbon Dioxide Capture and Mineralisation

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An electrochemical cell comprising a novel dual-component graphite and Earth-crust abundant metal anode, a hydrogen producing cathode and an aqueous sodium chloride electrolyte has been constructed and used for carbon dioxide mineralisation. Under an atmosphere of 5% carbon dioxide in nitrogen, the cell exhibited both capacitive and oxidative electrochemistry at the anode. The graphite acted as a supercapacitive reagent concentrator, pumping carbon dioxide into aqueous solution as hydrogen carbonate. Without the capacitance exhibited by the graphite, the amount of carbon dioxide captured was reduced by over 60%. Simultaneous oxidation of the anodic metal generated cations which reacted with the hydrogen carbonate to give mineralised carbon dioxide. Whilst conventional electrochemical carbon dioxide reduction requires hydrogen, this cell generates hydrogen at the cathode when performing carbon capture. Carbon capture can be achieved in a highly sustainable manner using scrap metal within the anode, seawater as the electrolyte, an industrially-relevant gas stream and a solar panel as an effectively zero-carbon energy source.



Lamb, Dowsett *et al.*, *ChemSusChem*, **2018**, *11*, 137-148

(VIP paper, highlighted by Xie *et al.*, *Chem*, **2018**, *4*, 24-26)

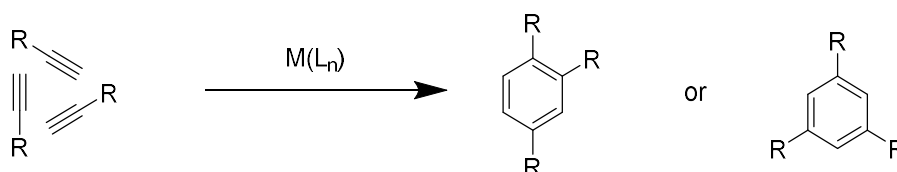
## Iron Catalysed Alkyne Trimerisation at Room Temperature

C. B. Provis-Evans<sup>a</sup>, V. Krewald<sup>a</sup>, E. A. C. Emanuelsson<sup>b</sup>, R. L. Webster<sup>a\*</sup>

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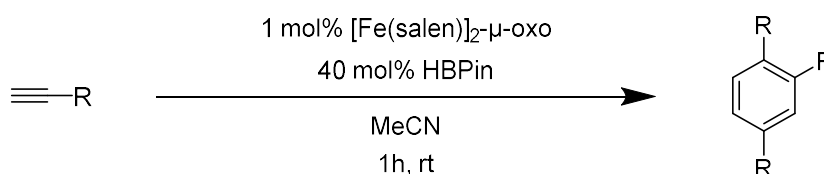
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The [2+2+2] cyclotrimerisation (CT) of alkynes has been known since the discovery of benzene formation from acetylene at high temperature and pressure in 1866.<sup>1</sup> The dream of a more practical methodology for this atom efficient reaction has been pursued since, notably in the discovery of a milder catalytic route by Reppe et al. in 1948.<sup>2</sup> However, problems remain in the lack of regioselectivity (Fig 1.) and in the cost and scarcity of many of the transition metal catalysts required for these methodologies.<sup>3</sup>



**Figure 1: Catalytic CT of terminal alkynes forms both 1,2,4 or 1,3,5 substituted products, dependent on a variety of factors. Selectivity challenging to control.**

A general, regioselective and green procedure has been designed and optimised. This involves earth abundant and air stable iron salen- $\mu$ -oxo catalyst with sub-stoichiometric pinacol borane, which together selectively trimerise a wide variety of terminal alkynes to form products with a 1,2,4 substitution pattern. The reaction delivers good to excellent isolated yields within 1 hour at room temperature (Fig. 2) and is tolerant to a wide variety of substituted aryl and propiolates. Under more forcing conditions, it is also possible to trimerise pyridyl acetylenes. Synthetic scope and mechanistic insight will be presented. Further computational work to elucidate the nature of the catalytic species is underway.



**Figure 1: Catalytic CT of terminal alkynes forms both 1,2,4 or 1,3,5 substituted products, dependent on a variety of factors. Selectivity challenging to control.**

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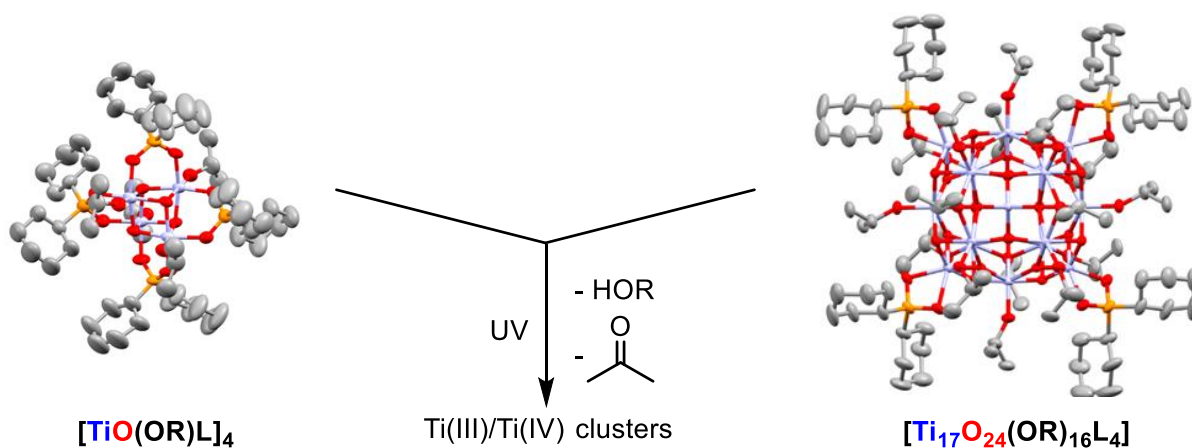
## Titanium-Oxo Clusters: Photoactive Materials at the Molecular Scale.

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Metal-oxide materials find applications in photovoltaic devices, heterogeneous catalysts, antibacterial surfaces, and even self-cleaning windows. Many of these applications arise from the ability of metal-oxides to absorb UV or visible light, allowing promotion of valence band electrons into the empty conduction band. This presentation will demonstrate that this ability may also occur in well-defined titanium-oxo clusters, despite their small size and molecular nature.<sup>1, 2</sup> As these molecular clusters decrease in size quantum confinement effects occur,<sup>3</sup> with the clusters requiring higher energy UV irradiation to become photoreduced.



**Figure 1.** Photoreduction of Titanium-oxo clusters. L = phosphinate

The mechanism of photoreduction is probed by spectroscopic methods and mixed valent Ti(III)/Ti(IV)-oxo clusters are identified and characterised using X-ray crystallography. Subsequent re-oxidation under air is also investigated. Such a process allows the detailed mechanism of photoreduction to be explored in atomically precise molecules, shining light on materials chemistry by using molecular techniques and investigating photocatalytic processes.

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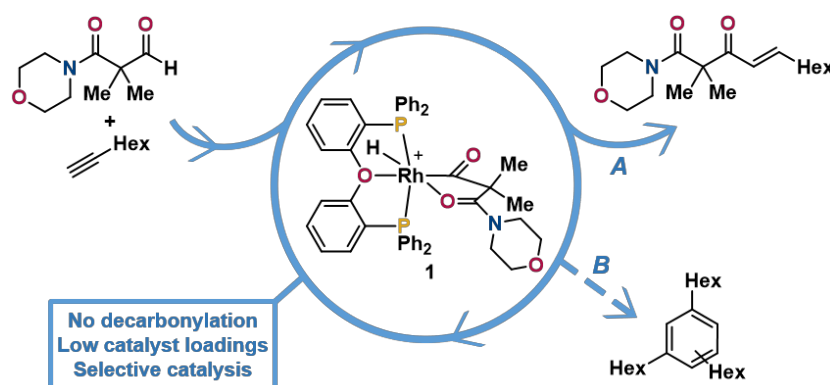
# Mechanistic understanding of a Selective, Non-Decarbonylating Rhodium Catalyst for the Hydroacylation of $\beta$ -Amido Aldehydes

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Rhodium-catalyzed hydroacylation is the 100% atom economic C-C bond forming reaction between an aldehyde and an alkene/alkyne. The development of a general reaction has the potential to be a transformative reaction in organic synthesis, providing a new synthetic disconnection for molecule design.<sup>1</sup> An unsolved problem in rhodium-catalyzed hydroacylation is irreversible catalyst decomposition due to reductive decarbonylation. To suppress this side reaction, a limited number of aldehydes possessing strongly co-ordinating tethering groups including phenolates, thioethers and anilines have been used.<sup>2,3</sup> Nevertheless decarbonylation still occurs, often leading to high catalytic loadings and non-recyclable conditions. Recently we have reported the remarkably general hydroacylation of weakly co-ordinating  $\beta$ -amido aldehydes to create synthetically valuable  $\beta$ -amido ketones and enones.<sup>4</sup> This contribution discusses how a  $[\text{Rh}(\text{DPEPhos})(\text{acylhydride})][\text{BAr}^{\text{F}}_4]$  catalyst (**1**) has been developed that does not decompose by reductive decarbonylation but instead by an off-cycle cyclotrimerization reaction (**B**). Detailed mechanistic understanding has led to optimized conditions that are selective for hydroacylation (**A**) and avoid catalyst decomposition, enabling reactions on large scale with low catalyst loadings.



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## Exploration of Hybrid Phase Transition Materials and study of their NLO Properties

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Temperature-induced solid-to-solid reversible multifunctional phase transition materials have captured renowned interest owing to their future applications in switchable dielectric, sensing, ferroelectric, optoelectronic, signal processing and data storage devices. Among these, above room temperature ferroelectric and solid state nonlinear optical (NLO) materials have attracted great interest due to their possible practical applications. Strategically, we introduced highly flexible, branched and cyclic amines to construct smart phase transition materials. These amines are believed to be potential candidate due to their inherent architectural flexibility with diversified molecular configurations. Herein, we would like to report three room temperature novel molecular switch materials including tri-*n*-ethylammonium Picrate (**1**), [(C<sub>6</sub>H<sub>14</sub>)NH<sub>2</sub>]<sub>3</sub>•SbBr<sub>5</sub> (**2**) and [(C<sub>5</sub>H<sub>11</sub>)NH<sub>2</sub>]<sub>2</sub>•ZnCl<sub>4</sub> (**3**). These materials exhibit excellent switchable NLO (0.8 to 3.0 times than KDP) and dielectric properties. In addition, cause of switching behaviour of **1** and **3** predominantly thought to be originated from order-disorder transformations of the cations. Interestingly, a clear conformational change from twist-chair structure of seven-member ring (RTP) to strictly planer (HTP) one is the cause of this high temperature NLO switch phase transition in **2**. The solution evaporation and hydrothermal treatments have been utilized to fabricate these materials. The structural, thermal, dielectric, optical and mechanistic studies of synthesized materials have been thoroughly studied by using different techniques, such as variable temperature single crystal analysis, variable

temperature PXRD, differential scanning calorimetry (DSC), TG-DTA, second harmonic generation (SHG), dielectric measurements, etc. All these results help in understanding of NLO properties in hybrid materials together with structure-property relationships and open a new way to design and assemble novel phase transition materials.

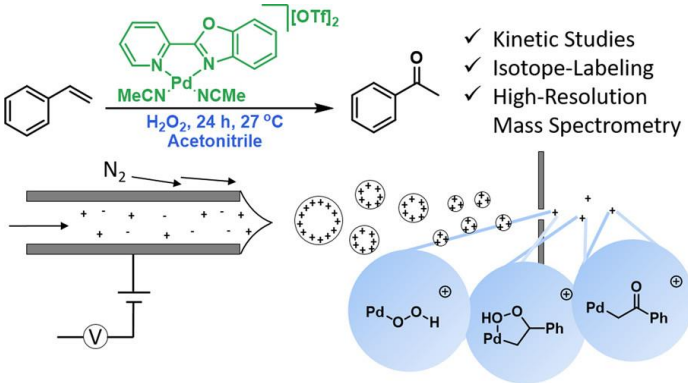
## New Mechanistic Insights into Pd(II) Catalysed Oxidation of Alkenes

Laura M. Dornan,<sup>1,2</sup> Katherine L. Walker,<sup>2</sup> Richard N. Zare,<sup>2</sup> Robert M. Waymouth,<sup>2</sup> Matthew Blair,<sup>1</sup> Clare Brown<sup>1</sup> Meadhbh Murray-Williams<sup>1</sup> and Mark J. Muldoon<sup>1</sup>

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The performance of many oxidation reactions lags decades behind other areas of catalysis and there is the need to develop more sustainable catalytic methods. The oxidation of an alkene to a ketone is a valuable transformation and is a key reaction in the synthesis of many fine chemicals, agrichemicals and pharmaceuticals. Although the “Wacker Process” is a text-book example of industrial chemistry, when the substrate is changed from ethylene to a higher olefin, significant challenges arise. So called “Wacker-Tsuji” type conditions are used for longer chain olefins, however the performance of these reactions is not sufficient for larger scale application. We are interested in developing new catalysts, which use peroxides<sup>1,2</sup> as the oxidant or can exploit O<sub>2</sub> directly (*i.e.* without the need for redox active co-catalysts).<sup>3</sup> Perhaps surprisingly, there are still important unanswered mechanistic questions for these reactions. Developing a detailed understanding of these reactions is key to developing next generation catalysts which have superior performance. We will discuss our recent mechanistic explorations, which have involved kinetic studies, isotope labelling and *in situ* high-resolution mass spectrometry.<sup>2</sup>



- ✓ Kinetic Studies
- ✓ Isotope-Labelling
- ✓ High-Resolution Mass Spectrometry

*Reproduced from Ref 2*

This programme of study is ongoing, however we have already obtained new insights into the complex and intertwined mechanisms for these reactions. We will also discuss how we are exploiting such mechanistic knowledge to develop new catalysts for both peroxide (H<sub>2</sub>O<sub>2</sub> and TBHP) and aerobic mediated Wacker-type reactions.

<sup>1</sup> Q. Cao, D.S. Bailie, R. Fu and M.J. Muldoon, *Green Chem.*, **2015**, 17, 2750.

<sup>2</sup> K. L. Walker, L. M. Dornan, R. N. Zare, R. M. Waymouth, and M. J. Muldoon, *J. Am. Chem. Soc.*, **2017**, 139, 12495.

<sup>3</sup> H. Chai, Q. Cao, L. M. Dornan, N. L. Hughes, C. L. Brown, P. Nockemann, J. Li and M.J. Muldoon, *Eur. J. Inorg. Chem.*, **2017**, 5604.

# Watching Catalysts at Work: Hydrogen Transfer Reactions Investigated with Real-time High Resolution FlowNMR Spectroscopy

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The development and optimization of homogeneous catalysts is often hampered by limited insight into the kinetics of the reaction and the transformation of the catalyst during turnover, enforcing empirical optimization. Rational catalyst and reaction development is only possible through thorough understanding of catalyst activation and de-activation mechanisms, potential resting or dormant states, and the kinetics of the productive cycle (i.e. rate-limiting steps). We have built a setup in which a reaction vessel is coupled to a NMR flow tube via air-tight small diameter HPLC tubing. With this we can continuously circulate a reaction mixture through the spectrometer, thereby follow the reaction progresses and catalyst transformation under catalytically relevant conditions in real time.

We have characterised the hydrodynamic characteristics of the setup and measured flow effects on continuous NMR acquisition to quantify changes in  $T_1$ ,  $T_2$  and signal intensity as function of volumetric flow velocity. Application in real-time reaction and catalyst monitoring under strictly inert conditions has been demonstrated, and multiple solvent suppression and selective excitation techniques allow the detection of minor intermediates even in non-deuterated solvents.<sup>[1]</sup>

Using this setup, we have followed the asymmetric transfer-hydrogenation of acetophenone using Noyori's chiral TsDPEN-ligated (arene)Ru<sup>II</sup> complexes as catalysts in basic iso-propanol (figure 1).<sup>[2]</sup>

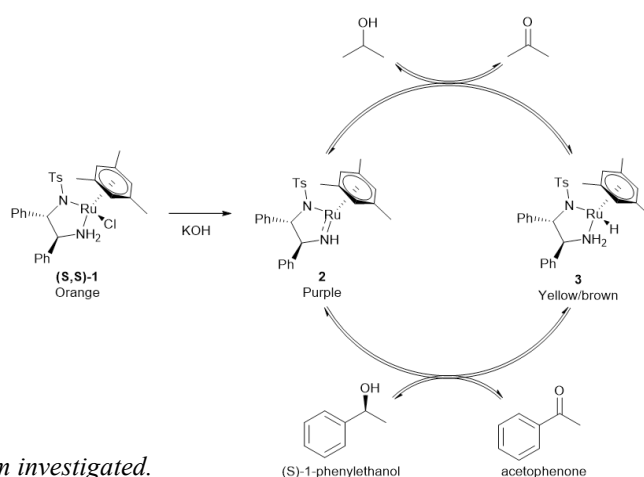


Figure 1. Catalytic system investigated.

As continuous NMR acquisition can be started on pure solvent flow, and the reaction initiated by sequential addition of reagents, the entire reaction can be followed without any lag phases. High quality kinetic data is obtained for this air-sensitive transition metal catalysed reaction (figure 2).



Importantly, both conversion and enantioselectivity of the reaction are identical to the results obtained in a sealed Schlenk flask, demonstrating that several hundred pumping cycles do not affect the chemistry in solution.

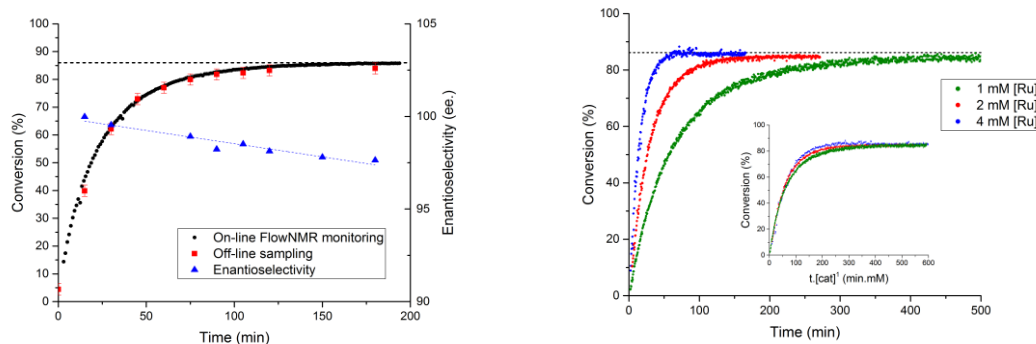


Figure 2. Reaction kinetics of the system shown in figure 1 as obtained by  $^1\text{H}$  FlowNMR.

Furthermore, using selective excitation techniques, we were able to observe metal-hydride intermediates during the reaction under the same conditions. These can be quantified over time and directly correlated to product formation kinetics (figure 3).

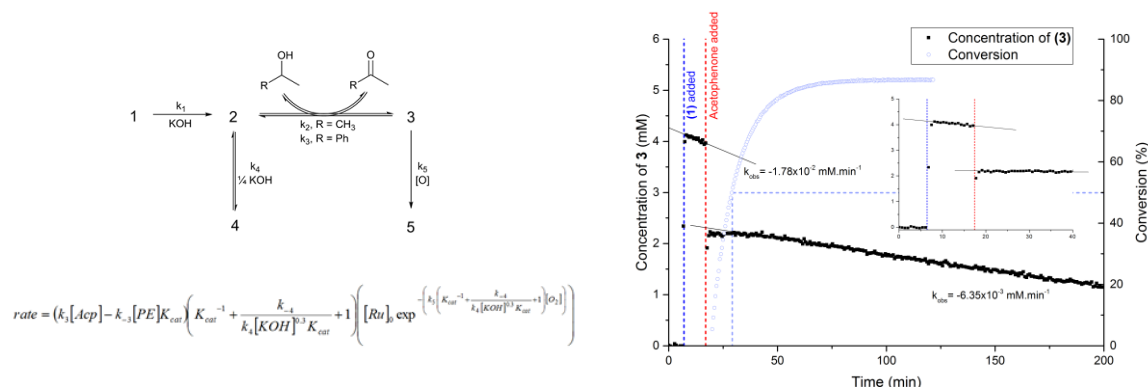


Figure 3. Correlation of Ru-H intermediates with product formation (right) leads to an expanded mechanism including two independent deactivation pathways (left).

We will present a full account of our results<sup>[3]</sup> and discuss their implications for this widely used chemistry.

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# Gold(III) hydrides: unexpected interplay of *cis*- and *trans*-influence on stability, insertion reactivity and NMR chemical shifts

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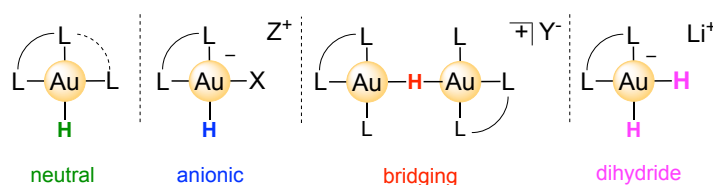
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Gold hydrides have been postulated as part of various homogeneous and heterogeneous catalytic cycles. However, isolation and characterization of these species has been long regarded as challenging, owing to the mismatch between oxidising nature of the metal and reducing character of the H<sup>-</sup> ligand. This is particularly true for square planar Au(III) species, where reductive elimination is a dominating decomposition pathway and the usage of pincer ligands is required for their stabilization. Only two examples of Au(III) hydrides have been reported so far<sup>1</sup> and they both exploit C<sup>^</sup>N<sup>^</sup>C pincer-type ligands,<sup>2</sup> where the nitrogen donor is in *trans*-position to the hydride, making the Au–H bond stronger and less reactive. In this contribution, we report the interception of three new types of Au(III) hydrides featuring a C-donor in the form of a cyclometalated aryl in *trans* position. By using biphenyl– [(C<sup>^</sup>C) or (C<sup>^</sup>C<sup>^</sup>N)] and phenylpyridine– (C<sup>^</sup>N–CH)<sup>3</sup> based ligands, we have successfully intercepted a number of Au(III) hydrides in *trans* to a carbon atom, as well as the first examples of anionic hydride, dihydride and bridging hydride. The stability of these species depends remarkably on ligand combinations. In some cases, the hydrides can only be observed by low-temperature NMR while, in other cases, thermally stable species were obtained, allowing crystallographic characterization. The <sup>1</sup>H NMR chemical shift values of the hydrides are surprisingly strongly influenced by spin-orbit contributions as a function of the ligand environment, as well as a strong *cis* effect. The investigation of the reactivity of these new hydrides towards alkynes reveals that they differ distinctly from the previously known compounds.

## Novel Au(III) hydrides *trans* to C<sup>-</sup>



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## Breaking the rules, trans-dihalide ruthenium complexes as anticancer agents

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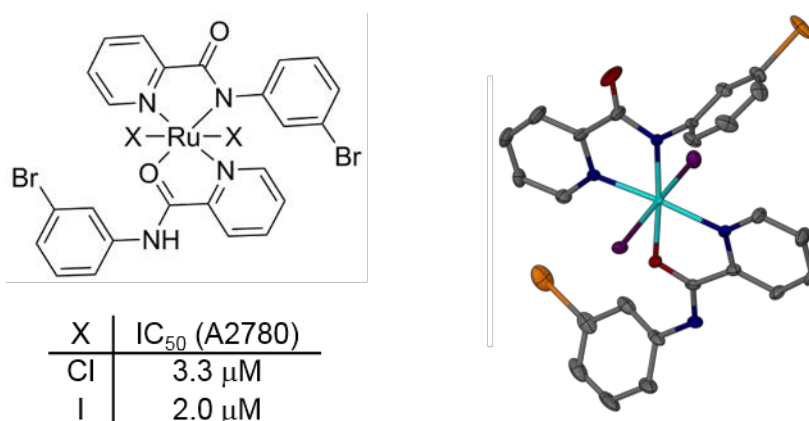
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KP-1019 and NAMI-A are the most promising ruthenium alternatives to the current platinum based drugs, exhibiting important biological properties targeting mainly cancer cells.<sup>1</sup> Recently, a novel ruthenium family of the type RuL<sub>2</sub>X<sub>2</sub> was reported where the trans-dihalide arrangement showed a great cytotoxic activity falling in the nanomolar range compared to the cis-conformation.<sup>2</sup>



**Figure 1.** Left, *trans*-dihalide backbone with the IC<sub>50</sub> of lead compounds; Right, crystal structure of diiodo bis-bromopicolinamide Ru(III)

Our work is focused on selectively synthesising and characterising a library of trans-dihalide ruthenium bis-quinaldamide complexes type RuL<sub>2</sub>X<sub>2</sub>, test their anticancer activity and determine structure activity relationships (SARs). The quinaldic core was carefully selected due to its less flexible backbone and the increase of anticancer activity.<sup>3</sup>

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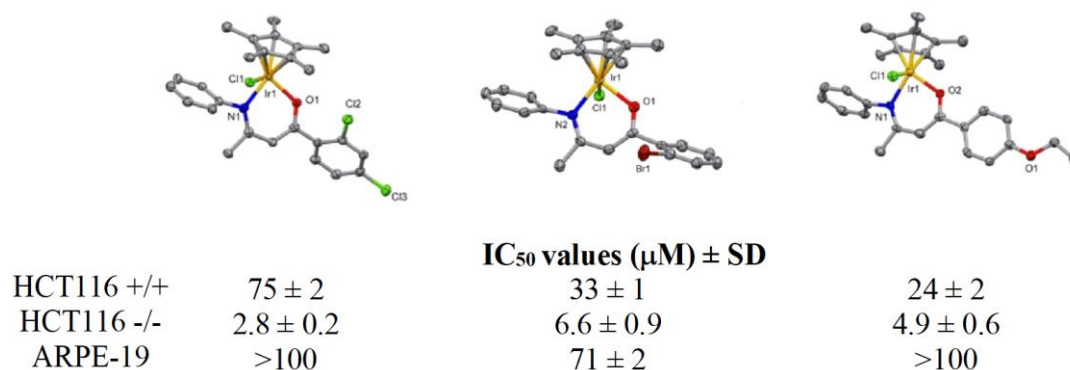
# Organometallic Iridium Complexes: Highly Cytotoxic and Selective Towards Colorectal Cancer

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Colorectal cancer (CRC) is the third most common cancer worldwide with nearly 1.4 million new cases and 694,000 deaths in 2012.[1] Many cancer types show a high occurrence of p53 mutations, and there is growing evidence that these mutant genes can lead to tumour progression.[2] It has been shown that p53 mutation occurs in approximately 40-50% of irregular CRC,[3] and has since become the most appealing target for mechanism-driven anticancer drug discovery, with some small molecules being investigated for reactivation and restoration of p53. To date, there are very few inorganic complexes being studied for their interactions with p53, however, some researchers have shown metal complexes to be active against natural CRC which have an active p53 function (HCT116 +/+, p53-wt).[4] Herein, we have synthesised a library of iridium(III) complexes (**Fig. 1**) and tested the cell viability against a range of tumour lines. We show the first iridium complexes to show preferential activity towards CRC cells with non-functional or mutated p53, suggesting the activity is via a p53-independent pathway. Our data will conclude the complexes' potential for further *in vitro* and *in vivo* assays.



**Fig. 1** IC<sub>50</sub> values against human colorectal cancers and normal AREP-19 cells

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## Activation of Cp\* Rings in Rhodium(III) Anticancer Complexes

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Cp\* ligands are usually considered to be innocent in metallodrugs. However, we observed rapid sequential deuteration of all 15 Cp\* methyl protons in Rh(III) anti-cancer complexes  $[(\eta^5\text{-Cp}^x)\text{Rh}(\text{N},\text{N}')\text{Cl}]^+$ , where  $\text{Cp}^x = \text{Cp}^*$ , phenyl or biphenyl-Me<sub>4</sub>Cp, and N,N' = bipyridyl or phenylpyridine, in aqueous media at ambient temperature. The extent of deuteration can be controlled by interactions with dienophiles and dienes. DFT calculations revealed the crucial role of  $p_\pi$  orbitals of N,N'-chelated ligands in stabilizing deprotonated Cp<sup>x</sup> ligands and suggested the accessibility of Rh(I)-fulvene intermediates. Remarkably such an intermediate was trapped by a Diels-Alder reaction with biologically important dienes in aqueous media, including cell culture medium, the first report of a Diels-Alder reaction of a metal-bound fulvene in aqueous solution. DFT calculations also provided insight into why biologically-inactive Rh(III)Cp\* en and Ir(III)Cp\* bpy complexes do not have activated Cp\* rings. Facile deuteration of Cp\* allows studies of reactions by <sup>2</sup>H NMR. These findings will stimulate new approaches to the design of biologically active organometallic complexes with novel mechanisms of action.

## **Chemical modulation of cellular redox balance for cancer treatment**

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Platinum complexes, are the most widely used anticancer drugs. However, these DNA-targeting treatments are a low selectivity approach with deleterious consequences and a high incidence of resistance. The societal need for new anti-cancer drugs is very substantial, hence, the commercial demand for new anti-cancer agents is very high. Although targeted chemotherapeutics with novel mechanisms of action (for example kinase inhibitors) have been developed more recently, these often have a much narrower clinical utility than platinum-based drugs and generally suffer from rapid onset of resistance, which means that there is still a large unmet clinical need. Hence there is a wide interest in new metal-based drugs with alternative mechanisms of action. The chemical scaffold offered by metal-based complexes has significant scope for molecular diversity and has the possibility of accessing chemical reactions beyond reach of organic molecules alone. Furthermore, these complexes could effectively be harnessed to target the redox balance in cancer cells and induce both oxidative and reductive stress, perturbing the cellular balance of reactive oxygen species. Cancer cells are primed for this intervention, because they are already redox-hyperactive and in most cases present malfunctioning mitochondria. Dysfunctional mitochondria are unable to control ROS generation efficiently. This allows metal-based complexes, to exert selective toxicity towards cancer cells over normal cells. The design of such drugs is relatively unexplored and, even more so, is their MoA at cellular level.

Noyori-type ruthenium and osmium catalysts are prime examples of metal-based complexes that can be used to perturb the redox balance in cancer cells, particularly through in-cell transfer hydrogenation reactions. Other non-catalytic piano-stool complexes based on ruthenium, osmium and iridium exert their anti-proliferative activity after the induction of superoxide bursts that lead to cell death. Combinations of organic redox modulators with these organometallic complexes can not only potentiate their anti-proliferative activity but also dramatically increase their cell selectivity. Such redox synergism provides a basis for 'smart' combination therapy. In addition to providing novel therapies for parental cancers, manipulation of the cellular levels of reactive oxygen species and, in general, cellular redox balance, may also provide a highly effective strategy for treating Pt-resistant cancers.

# Reactivity of Diiron Complexes with a Bridging Amino-Alkylidyne Ligand, and Cytotoxicity Results

Gabriele Agonigi,<sup>a</sup> Lucinda K. Batchelor,<sup>b</sup> Paul J. Dyson,<sup>b</sup> Nicola Ferri,<sup>c</sup> Fabio Marchetti,<sup>a</sup> Guido Pampaloni<sup>a</sup>

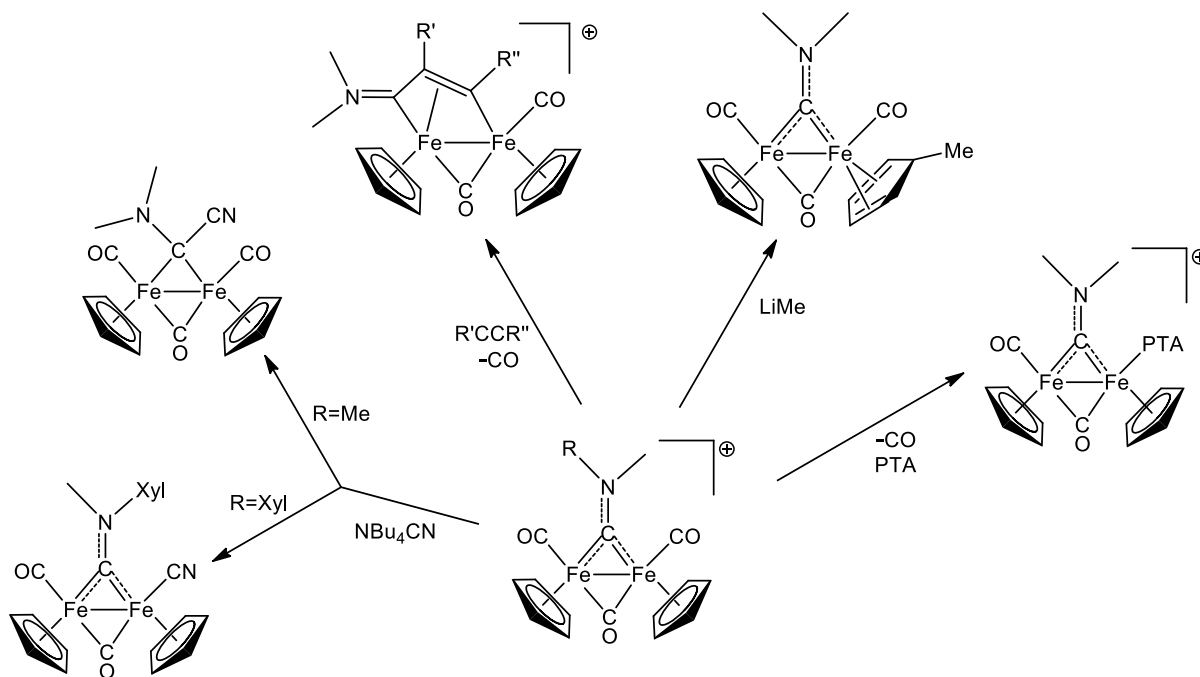
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Dinuclear iron complexes containing a bridging amino-alkylidyne ligand are available by a two-step procedure from commercial  $\text{Fe}_2\text{Cp}_2(\text{CO})_4$  and a variety of isocyanides.

The cationic complexes undergo additions by nucleophiles, the latter addressing selectively to different sites depending on the nature of the N-substituents [1]. Moreover, introduction of amphiphilic phosphines and alkyne insertion into the metal-carbyne bond, affording vinyliminium complexes [2], are viable upon removal of one carbonyl ligand. The cytotoxic behaviour of the air stable and water tolerant compounds towards different cancer cell lines will be discussed.



**Figure 1.** Reactivity of diiron amino-alkylidene compounds.

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# The synthesis and validation of a multimodal PET/fluorescence zinc sensing probes as potential imaging agents for prostate cancer

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Justin Sturge,<sup>1</sup> and **Graeme J. Stasiuk**<sup>1\*</sup>:

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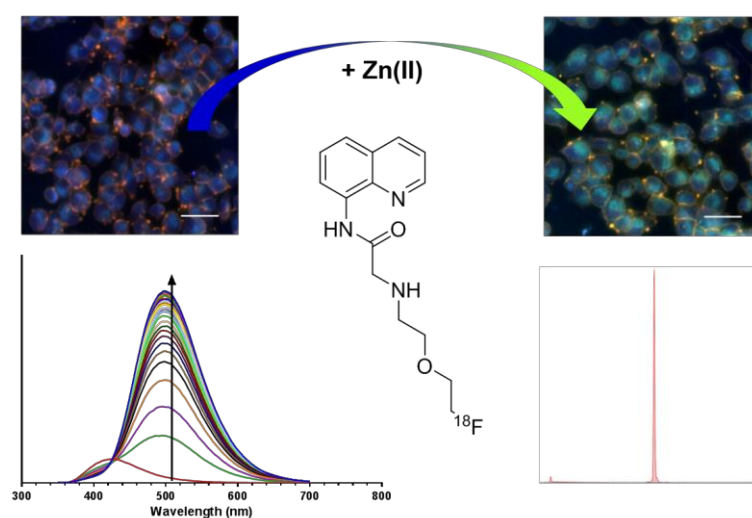
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Prostate cancer (PCa) is the 2nd most common cancer worldwide for males, and the 4th most common cancer overall, accounting for 15% of all male cancers in 2012<sup>1</sup>. PCa is asymptomatic in its early stages and advances in medical imaging are improving diagnosis, however novel simple non-invasive diagnostic tests are needed to catch the disease early. Zinc has emerged as a promising diagnostic target in PCa progression as it's accumulation in PCa cells is significantly lower compared to normal prostate<sup>2</sup>.

In this study we show **AQA-F**, a selective fluorescent probe for Zn(II). **AQA-F** exhibits a ratiometric shift in emission of up to 80 nm upon binding Zn(II). An enhancement of quantum yield from  $\Phi = 4.2\%$  to  $\Phi = 35\%$  is also observed. This probe has been shown to respond to endogenous Zn(II) levels *in vitro* in prostate and prostate cancer cell lines. The dual modal PET/fluorescence probe [<sup>18</sup>F]**AQA-F** has been synthesized with a radiochemical yield of 8.6% and a radiochemical purity of 97% in 88 minutes. **AQA-F** shows the potential for a dual modal PET/fluorescence imaging probe for Zn(II)



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## Bacterial metallothioneins that respond to Zn limitation

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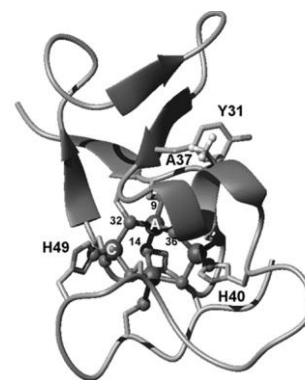
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Cyanobacteria of the genera *Synechococcus* and *Prochlorococcus* are major contributors to global CO<sub>2</sub> fixation.<sup>1</sup> Hence, understanding zinc metabolism in these organisms is critical because oceanic zinc availability may directly affect CO<sub>2</sub> fixation capacity.

Metallothioneins are small cysteine-rich proteins capable of protecting cells from heavy metal toxicity. In several well-studied cyanobacteria they are regulated by the Zn excess sensor, SmtB.<sup>2</sup> Intriguingly, it has been found that in some *Synechococcus* strains, metallothioneins (BmtAs) are regulated by the Zn deficiency sensor Zur. The Zur protein usually controls expression of zinc uptake components, such as the high affinity ZnuABC system, in response to zinc availability.<sup>3</sup> Potential Zur regulation of *bmtA* is unexpected and was investigated here.



EMSA experiments revealed that Zn-loaded Zur from *Synechococcus* sp. WH8102 binds to the operator-promoter region of *bmtA* with high affinity, confirming regulation. In *Synechococcus* sp. PCC9311 RT-qPCR showed high expression levels of three of the four *bmtA* genes under zinc-limited conditions, strongly suggesting a role other than in zinc detoxification. To study zinc-binding properties of BmtA from *Synechococcus* sp. WH8102 (SwBmtA), the protein was cloned, over-expressed in *E. coli* and characterised. ESI-MS and ICP-OES showed that SwBmtA contains 4 Zn ions per molecule. Competition experiments with metal chelators indicate that SwBmtA binds Zn with extremely high affinity. We speculate that Zur-regulated BmtAs confer an advantage at ultra-low zinc concentrations, potentially by providing a thermodynamic Zn sink in the cytosol.

*This project is supported by a Chancellor's International Scholarship, University of Warwick, UK.*

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## Misbehaving Lanthanide Binding Sites in Designed Peptide Trimers.

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The binding of lanthanides in biological systems has received a great deal of attention for both their photophysical and magnetic properties. Previous work within the group involved the preparation of lanthanide binding coiled coil trimers, however, attempts to gain structural information beyond circular dichroism have proven unsuccessful.<sup>1,2</sup> Herein we report the design, synthesis and structural characterisation of a family of lanthanide binding coiled coil trimers. The resultant x-ray diffraction results have provided a wealth of structural information regarding the binding site coordination and other external features. The peptides were studied via solution state luminescence and circular dichroism titrations revealing the presence of external binding sites. Interestingly, the metallated complexes were observed by mass spectrometry providing a useful tool to probe the oligomerisation states.

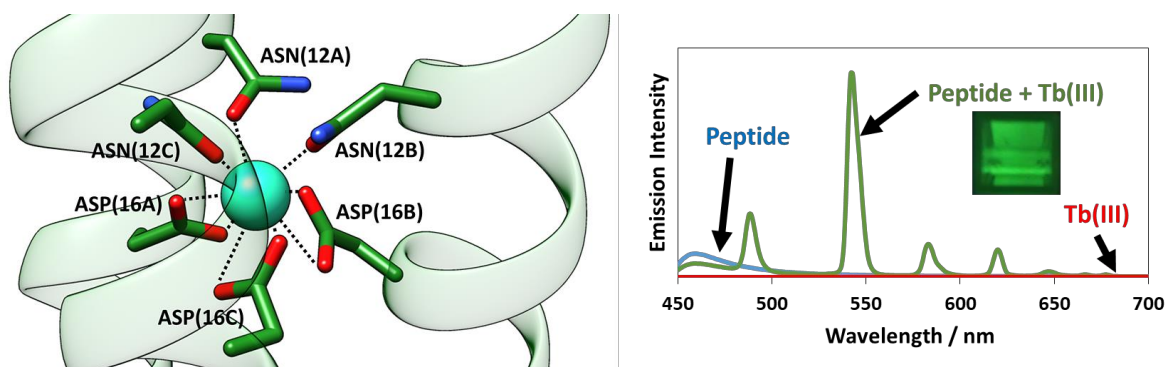


Figure 1: Right) The crystallographically determined structure of the lanthanide binding site with a resident terbium ion (oxygen is shown in red, nitrogen in blue, carbon in green and terbium in cyan with the ribbon kept transparent for clarity). Left) An emission profile of one of the designed coiled coils with a bound terbium ion,  $\lambda_{ex} = 280$  nm. Insert is a photograph of one of the peptides excited with UV light, the resultant green emission is from bound terbium.

DSTL is gratefully acknowledged for a PhD studentship and for the support of this research project through the National PhD Scheme.

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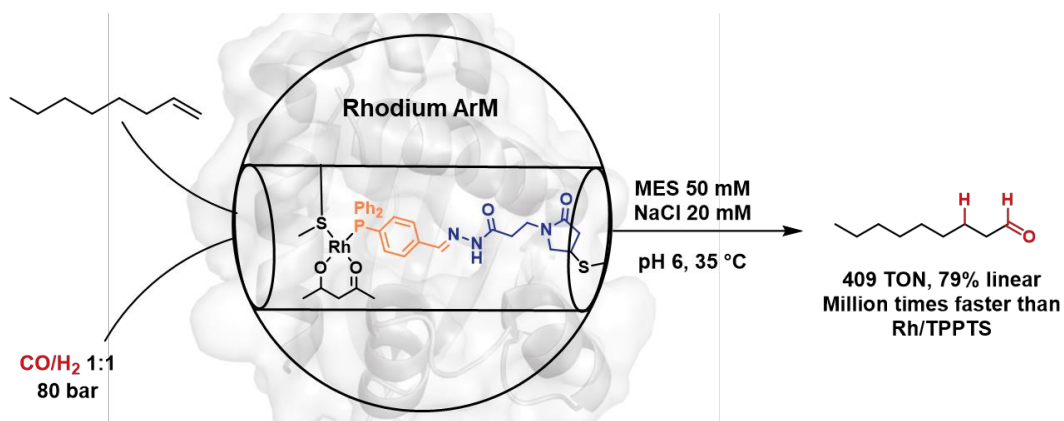
## Enzyme activity by design: an artificial rhodium hydroformylase

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The development of artificial enzymes is an emerging field driven by the prospect of highly selective and active catalytic chemical conversions for which natural enzymes are unavailable.<sup>1</sup> Nature exploits the molecular recognition properties of proteins to perform chemical transformations with high product specificity and excellent activity under benign conditions. Meanwhile, industry still relies on traditional transition metal catalysis due to a lack of enzymes for desired reactions such as CO and alkene insertion reactions. Artificial metalloenzymes (ArMs) combine synthetic metal catalysts with selective substrate binding protein scaffolds, thereby adding to the catalytic toolbox.

We have combined robust site specific phosphine bioconjugation methodology with a lipid-binding protein (SCP-2L) aiming at rational design of an artificial rhodium hydroformylase.<sup>2</sup> This novel ArM displays remarkable activities and selectivities for the production of higher linear aldehydes under benign aqueous conditions. The ArM provides enzyme-like rate enhancement when compared to the traditional Rh-TPPTS system. Extensive characterization of the rhodium environment in this ArM by MS, IR, and XAFS supports the presence of a monophosphine-rhodium center stabilized by amino acid residues within the protein scaffold potentially accounting for the high selectivities observed. Overall, our study demonstrates that specific protein binding scaffolds can be adapted to obtain enzymes that provide the reactivity of the introduced metal center combined with specifically intended product selectivity. Such approaches should inspire the development of new catalytic systems that utilize the powerful substrate binding capabilities of proteins.



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## The role of seed-specific type 4 metallothionein in *Brassica napus* seeds

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Zinc is involved in almost every conceivable metabolic process, and consequentially, the effects of zinc deficiency are severe and in plants include stunted growth, chlorosis, necrosis and reduced crop yield. Among several proteins involved in zinc handling in cells,<sup>1</sup> there are metallothioneins (MTs) that are ubiquitous low-molecular weight (<10 kDa) proteins able to bind a range of heavy metal ions via multiple cysteine residues. Depending on the number and arrangement of cysteine residues, plant MTs (pMTs) are classified into four main types. Type 4 pMTs have 17 cysteines and two conserved metal-binding histidines grouped into three Cys-rich regions separated by two short Cys-free stretches.

We have studied the *in vitro* and *in vivo* metal binding abilities of a type 4 metallothionein from one of the most frequently cultivated oil-plants, i.e. *Brassica napus* (BnMT4), using mass spectrometry, inductively coupled plasma optical emission spectrometry and UV/Vis spectroscopy. BnMT4, similarly to all type 4 pMTs studied up to date,<sup>2</sup> has strict Zn-thionein character. <sup>1</sup>H NMR spectroscopy revealed that the nature of the bound metal impacts protein folding: Zn<sub>6</sub>BnMT4 is well-folded, whereas Cd<sub>6</sub>BnMT4 is only partially folded. When overexpressed in *E. coli*, BnMT4 did not confer enhanced tolerance to either copper or cadmium; however, an increased growth rate of transformants was observed in the presence of zinc. Analysis of expression levels of *BnMT4* in *B. napus* at early stages of ontogenic development revealed elevated levels of mRNA in response to cadmium and zinc. Therefore, we suggest that BnMT4 may not only play a role in zinc homeostasis during early ontogenesis<sup>3</sup> but also may have potential to discriminate between essential Zn and toxic Cd.

This work was supported by the European Commission (“Enhancing Educational Potential of Nicolaus Copernicus University in the Disciplines of Mathematical and Natural Sciences” conducted under Sub-measure 4.1.1: Human Capital Operational Programme-Task 7 (Project No POKL.04.01.01-00-081/10)” and a Marie Skłodowska-Curie Individual Fellowship (MSCA-IF-EF-ST 701492) to AMA).

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## Unprecedented Iron-Oxygen Reactivity in a Ferritin

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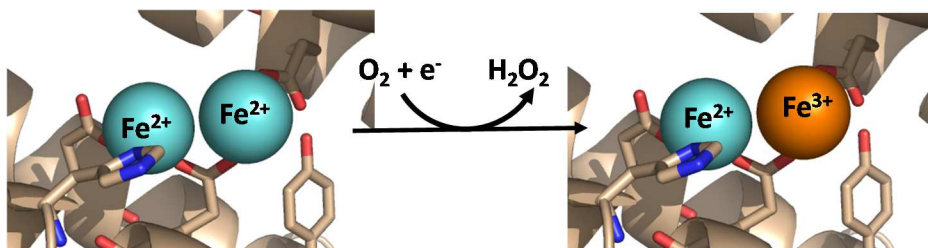
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Ferritins constitute a widely distributed superfamily of proteins found in all domains of life. They are key players in iron homeostasis since large amounts (several thousands of Fe<sup>3+</sup> ions per ferritin) of this metal can be reversibly stored within the central cavity of the protein. In addition to providing a means for storage of an essential but potentially toxic micronutrient, ferritins can also mediate against oxidative stress. Plants and bacteria often contain genes for more than one predicted ferritin, each of which may have evolved to fulfill distinct roles within the cell<sup>1</sup>.

The genome of the coastal dwelling cyanobacterium *Synechococcus* CC9311 contains three predicted ferritins. One of these sync\_1539 (*SynFtn*) is expressed in response to copper stress<sup>2</sup>. Here we present the crystal structure of *SynFtn* which reveals a di-iron catalytic centre unlike those of other prokaryotic ferritins, instead closely resembling those of their eukaryotic counterparts. Despite this, EPR and iron oxidation activity data demonstrate unique iron-oxygen chemistry producing a mixed valent Fe<sup>2+</sup>/Fe<sup>3+</sup> form on reaction with molecular oxygen. This mixed valent species is continually generated during Fe<sup>2+</sup> oxidation, demonstrating that it is a key intermediate for the entire mineralization process. The one electron oxidation of the *SynFtn* di-Fe<sup>2+</sup> centre by oxygen does not produce superoxide but peroxide is formed stoichiometrically. This implies that di-iron centres function in pairs, each delivering a single electron to a shared O<sub>2</sub> substrate. Given that these centres are separated by a minimum of 24 Å, long range electron transfer through the protein is implicit in such a mechanism and this is mediated by the transient formation of a radical on Tyr40, a strictly conserved residue which lies ~4 Å from the di-iron centre.



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## A “sweet approach” to the targeted anticancer chemotherapy: gold-based glycoconjugates

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Some gold(III)-dithiocarbamate complexes have shown promising antitumor activity, both *in vitro* and *in vivo*, together with negligible systemic and organ toxicity, although selective tumor targeting is still a major issue.<sup>1</sup>

In order to maximize the impact on cancer cells and minimize side-effects, our latest approaches focus on the conjugation of biologically-active molecules to potential metallodrugs. In particular, we aim at designing “Trojan Horse”-type complexes characterized by an improved selectivity provided by selected coordinated ligands exploiting specific receptors up-regulated in cancer cells, so as to achieve biomolecular recognition and tumor targeting.

Rapidly dividing tumor cells require higher amounts of nutrients and energy for their fast proliferation, and glucose is no exception (the so-called “Warburg effect”). Accordingly, such increased demand of glucose by cancer cells makes it very attractive to selectively target tumor sites. In particular, tailored glucose-like substrates can be conjugated to chemotherapeutics (including metal-containing anticancer agents) to attain the site-specific delivery of drugs into the affected tissues.<sup>2</sup>

Starting from the rationale behind our research work, we here report on a new generation of gold-dithiocarbamate glycoconjugates generated *via* an innovative synthetic approach,<sup>3</sup> which can combine the antitumor properties and the favorable toxicological profile of the gold-dithiocarbamate scaffold, along with an improved selectivity and cellular uptake provided by the glucose-containing ligands coordinated to the metal center, through the exploitation of the glucose-mediated cellular internalization provided by glucose transporters (GLUTs).

Financial support by NUI Galway (*College of Science Scholarship* to AP; *Millennium Fund Minor Project 2013* to LR), Irish Research Council (*Postgraduate Scholarship* to AP), and COST Action CM1105 is gratefully acknowledged.

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## **Ruthenium (II) complexes for *in vitro* and *ex vivo* sensing of carbon monoxide**

Jonathan Robson, Cristina de la Torre, Anita Toscani, Cristina Marín-Hernández, María Carmen Terencio, María José Alcaraz, Félix Sancenón, Ramón Martínez-Máñez and James Wilton-Ely

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In the body, endogenous CO acts as a gaseous signalling molecule serving many functions, including anti-inflammatory, antiapoptotic and anticoagulative roles.<sup>1</sup> The potential of CO as a therapeutic agent has received significant attention, particularly since CO-releasing molecules (CORMs) are capable of liberating controlled amounts of CO in biological systems.<sup>2</sup> One of the major obstacles limiting progress in understanding the biological role of CO and its therapeutic application is the lack of real-time methods to selectively track CO in biological systems.

Equipped with fluorophores suited for imaging in biological environments, new water-soluble ruthenium vinyl probes have been designed based on the system we have used for detection of CO in air.<sup>3</sup> In the presence of CO *in vitro*, these probes exhibit a rapid and selective fluorogenic response, the probes are selective for CO even in high reactive oxygen species (ROS) environments. Coupled with their pH stability and low toxicity, these attributes allow fluorescence imaging of range cellular environments and permit the visualisation of very low levels of CO in cells. For the first time, these two-photon fluorescent probe detected endogenous carbon monoxide *ex vivo* using mice with a subcutaneous air pouch.<sup>4</sup> The combination of selectivity, sensitivity and inexpensive, straight-forward synthesis make the system described here a very attractive and efficient probe for the facile fluorogenic detection of this gas in realistic biological environments.

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# Photoinduced Guanine Oxidation in Telomeres by Dinuclear Ruthenium (II) polypyridyl complexes.

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Metal ion complexes have received much attention in recent years as probes for physical structure properties of DNA, and have the potential to form new therapeutic agents for photodynamic therapy<sup>[1,2]</sup>. Of particular interest are those based around  $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$  and its analogues, however these do not readily enter live cells. Our work has recently focussed on related dinuclear structural analogues (**1**) which *are* spontaneously taken up by live cells, and demonstrate a high affinity for quadruplex DNA structure such as the Human Telomere Sequence<sup>[3]</sup>. Here we report our initial investigations into an analogous complex containing the 1,4,8,10-tetrapyridophenazine (TAP) ligand (**2**). The solution state photophysics, pH sensitivity, and DNA binding properties will be discussed. This compound selectively photo-oxidises guanine residues in solution and when bound to both duplex and quadruplex DNA, in a similar manner to its mononuclear counterpart<sup>[4]</sup>. This, combined with cellular uptake in MCF-7 cell lines makes it a promising candidate for photo-dynamic therapy.

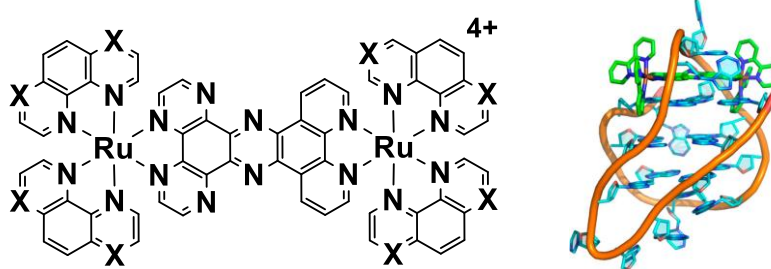


Figure 1. Left- “RuRu” complexes **1** X = C-H, **2** X = N. Right - NMR-based structure of structural analogue **1** bound to the diagonal loop end of HTS.

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## The mechanism of iron sensing by the iron-sulfur cluster regulator RirA

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Iron is essential for virtually all forms of life, but the redox properties that make it indispensable also mean that it is potentially extremely toxic. Thus, its concentration and speciation in the cell must be carefully controlled. Iron regulation in bacteria is often associated with Fur (ferric uptake regulator) found in *Escherichia coli* and many other bacteria, or the DtxR (Diphtheria toxin Repressor) of *Corynebacterium diphtheriae* and related species, which both bind Fe<sup>2+</sup> as a co-repressor. However, in the alpha-proteobacteria, which include nitrogen-fixing Rhizobia, iron regulation occurs via a distinct set of regulators, including RirA (Rhizobial iron regulator A).

RirA belongs to the widespread Rrf2 super-family of transcriptional regulators and features three conserved Cys residues that characterise the binding of an iron-sulfur cluster in other Rrf2 family regulators. Here we report biophysical studies demonstrating that RirA contains a [4Fe-4S] cluster, and that this form of the protein binds RirA-regulated DNA, consistent with its function as a repressor of expression of many genes involved in iron uptake. Under low iron conditions, [4Fe-4S] RirA undergoes a cluster conversion reaction resulting in a [2Fe-2S] form, which exhibits much lower affinity for DNA. Under prolonged low iron conditions, the [2Fe-2S] cluster degrades to apo-RirA, which does not bind DNA and can no longer function as a repressor of the cell's iron-uptake machinery. [4Fe-4S] RirA was also found to be sensitive to O<sub>2</sub>, suggesting that both iron and O<sub>2</sub> are important signals for iron metabolism. These data lead us to propose a novel regulatory model for iron homeostasis, in which RirA senses iron via the incorporation of a fragile iron-sulfur cluster that is sensitive to iron and O<sub>2</sub> concentrations.

## Dual-modal SERS/fluorescence AuNP probe for mitochondrial imaging

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### Introduction

The increased potential of mitochondria in cancerous cells makes them excellent targets for molecular imaging of cancer,<sup>1</sup> and a probe that can accumulate there will lead to a tumor-targeting agent. Recently gold nanoparticles (AuNP) have been validated as nanocarriers for imaging agents,<sup>2</sup> and the large strong fields enhancement they provide can greatly increase Raman signals of nearby molecules, resulting in Surface Enhanced Raman Scattering (SERS).<sup>3</sup> Combining both optical and SERS imaging provides key complimentary information on the local chemical environment *in vivo*.<sup>4</sup> Rhodamine derivatives have received attention as fluorescence sensors due to their excellent photo physical properties.<sup>5</sup> Herein we show the first multimodal SERS/fluorescent probe based on AuNPs and thiol rhodamine derivatives that localise within mitochondria.<sup>6</sup> AuNPs of 12 nm have been synthesised and modified with rhodamine thiols to obtain the multimodal probe. The physical properties have been characterised by fluorescence, Raman, TGA and TEM. Confocal microscopy in HEK293, A2780 and Min6 cells have been undertaken.

The normal pH dependant acidic fluorescence of the rhodamine is inversed when conjugated with the AuNP, and correlates to a *pKa* of 6.62. Raman spectroscopy of the probe, taken at different pH, further confirms the change in the molecular structure of the ligand. Confocal microscopy has shown that the probe enters all cell lines and localises in the mitochondria.

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# Lipophilic and Cationic Gallium-68 Chelates for Imaging Mitochondrial Function

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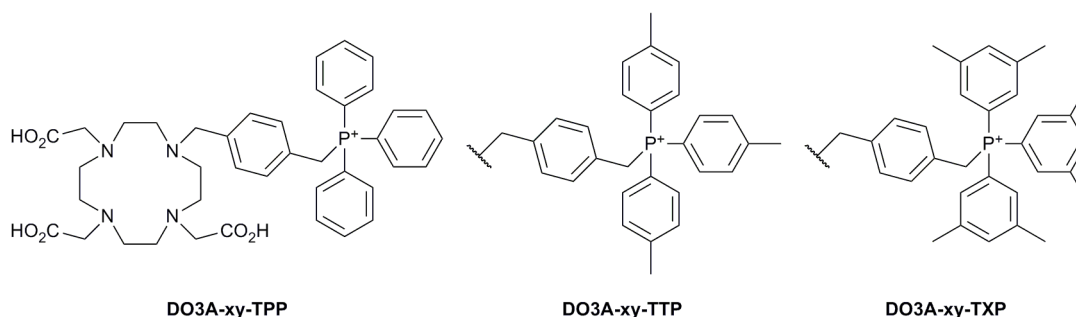
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Lipophilic cationic radiotracers such as [<sup>99m</sup>Tc]Tc-sestamibi (MIBI) are used to non-invasively report on mitochondrial function and dysfunction since their uptake and retention is dependent on the magnitude of the mitochondrial membrane potential ( $\Delta\Psi_m$ ).<sup>1</sup> The PET isotope gallium-68 affords higher resolution than equivalent SPECT methods, whilst its generator-produced nature simplifies clinical translation.<sup>2</sup>

We present a series of triarylphosphonium-functionalized DO3A chelators (DO3A-xy-TAP, see Figure 1) for gallium-68 chelation. RCY values of over 95 % are achieved in all cases, and upon altering the alkyl functionalization the compounds display differing and tunable log D values, which could be used to change the pharmacokinetics of the tracer.

To assess the selectivity of our radiotracers for  $\Delta\Psi_m$ , we are using our custom-built triple gamma-detector system to monitor tracer retention in isolated perfused rat hearts.<sup>3</sup> A two radiotracer-injection protocol was verified using MIBI, then used as an effective screen for lipophilic cations. Our first candidate PET tracer, [<sup>68</sup>Ga]Ga-DO3A-xy-TXP, did not show appreciable myocardial uptake, although we believe it shows potential for imaging tumour mitochondria.<sup>4</sup> We are currently developing tracers with more favourable lipophilicities.



**Figure 1** The DO3A-xy-TAP series of lipophilic cationic chelators for [<sup>68</sup>Ga]GaCl<sub>3</sub>

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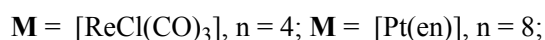
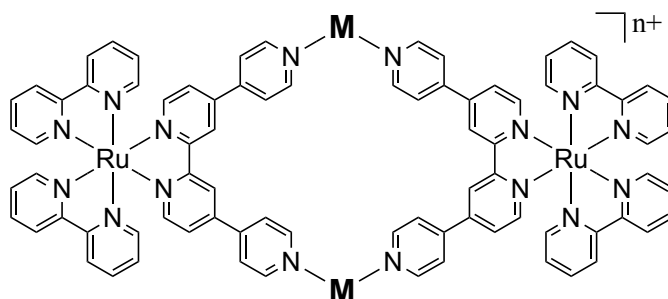
## Targeting biomolecules with self-assembled photoactive ruthenium(II)-based metallomacrocycles

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Although metal templated self-assembled architectures have been intensively studied in the last two decades, photoactive examples – particularly those based on Ru<sup>II</sup> centres - are still relatively rare.<sup>1</sup> Furthermore, reports on the biological properties of such species have only emerged in the last few years.<sup>2</sup>



The Thomas group has reported on the interaction of macrocycles such as  $\mathbf{1}^{n+}$  with bio-anions and biomolecules. *Inter alia*, this work has led to the identification of specific optical probes for ATP,<sup>3</sup> systems that interact with DNA through unique binding motifs,<sup>4,5</sup> and phototherapeutic leads.<sup>6</sup> Now, using enantiomerically pure mononuclear building blocks, the self-assembly of specific stereoisomers of these systems has been targeted and their biological properties are being explored.

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