Number	First Name	Surname	Title of contribution
P1	Isabel	Abanades	Surface Modification of Metal-Organic Frameworks (MOFs) for Drug Delivery Applications
P2	Gemma	Adams	Rhodium complexes of POP–type ligands: towards controlled amine–borane dehydropolymerisation
P3	Hope	Aitchison	Upgrading Ethanol; Mechanistic Insights
P4	Matthew	Allison	Heterobimetallic Ruthenium Complexes Containing Ferrocene as Anti-Cancer Agents
P5	Thaer Mahdi Madlool	Al-Rammahi	Kinetics and Mechanisms of Acid-Catalyzed Substitution and Substrate Binding Reactions of $[Fe_4S_4Cl_4]^{2-}$
P6	Mohammed	Altahan	A newpolyborate anion, $[B_7O_9(OH)_6]^{3-}$: Self assembly, XRD and thermal properties of s-*fac*-$[Co(dien)_2][B_7O_9(OH)_6]\cdot 9H_2O$
P7	Ahmed	Al-Yasari	Organo-Imido Polyoxometalates: High Transparency, High Activity Redox-Active NLO Chromophores
P8	Rhiann	Andrew	Synthesis of mechanically interlocked complexes of enynes
P9	Mathew	Anker	Group Two Mediated CO Homologation and Reductive Catalysis
P10	Samantha	Apps	Tripodal phosphine ligands for small molecule activation
P11	Gareth	Ashworth	Chlorinated m-Terphenyl Ligands in the Synthesis of Low-Coordinate Transition Metal Complexes
P12	Nick	Beattie	DFT studies on Rh-mediated Dehydrocoupling of Phosphine-Boranes
P13	Sophie	Benjamin	Pt Group stibine complexes: μ^3 bridging $SbMe_3$ and other unexpected coordination behaviours
P14	Callum	Benson	A Versatile Soft-Hard N/S-Ligand for Metal Coordination and Cluster Formation
P15	Hayley	Bignell	Gallium-68 radiolabelling of macrocyclic chelators on a microfluidic device for use in positron emission tomography imaging
P16	Alessandro	Bismuto	Aluminium-Catalysed Hydroboration
P17	Robin	Blagg	Frustrated small molecule reactivities
P18	Kay	Burrows	Exploiting a spin-crossover module in materials chemistry
P19	Michael	Butler	Heterobimetallic Mg---Zr and Zn---Zr Hydrides: application to alkene and diene isomerisation
P20	Kelly	Butterfield	Dicarbadodecaborane as a C2 spacer: A Boron-rich JohnPhos
P21	Alexa	Caise	Group 13 hydrides as catalysts for reduction of carbon dioxide.
P22	David G.	Calatayud	Core-shell Ceramic Nanoparticles of Silica and Transition Metals Doped with Rare-earths for Luminescence Imaging of Prostate Cancer Cells
P23	Christopher	Cameron	Time-Resolved Kinetic Studies on Porous Coordination Materials at Diamond Light Source I19 EH2
P24	Izar	Capel Berdiell	Spin Crossover Nanoparticles for Sensors and Molecular Delivery
P25	Innis	Carson	Computational Modelling Techniques for the Design of Solvent Extractants for Metals
P26	Feng	Chen	Ruthenium (II) complexes as catalysts for transfer hydrogenation of coenzyme NAD$^+$
P27	Simon	Child	Enhancing a Cobalt Bis-Iminopyridine Hydrogen Evolution Catalyst with an Axially Coordinating Proton Relay
P28	Annie	Colebatch	Rechargeable Xantphos-based Rhodium Complexes in Amine-borane Dehydropolymerisation

P29	Charlotte	Coleman	Hybrid phosphasalen/salen initiators for the ring-opening polymerisation of rac-lactide
P30	Nathan	Coles	Catalytic dehydrocoupling of amine and phosphine-boranes using low coordinate Fe(II) complexes
P31	Chris	Collins	Accelerated discovery of two new structure types in a complex inorganic phase field
P32	Juliet	Collins	Synthesis and characterisation of novel fluorescent vanadyl complexes and their evaluation as CBP inhibitors and intracellular probes
P33	David	Collison	EPSRC National EPR Spectroscopy Facility
P34	Daniel	Cook	Solvothermal Synthesis of mixed metal gallium spinels
P35	Fernando	Cortezon-Tamarit	Investigations into novel aromatic mono(thiosemicarbazonato) metal complexes and their applications in molecular imaging
P36	James	Coverdale	Generating reductive stress in cancer cells using osmium transfer hydrogenation catalysts
P37	Jasmine	Cross	Anticancer Pyridylphosphinate Complexes
P38	Massimiliano	Curcio	Coordination chemistry and redox activity of a bis(iminothienyl) compound
P39	Lucy	Currie	Photoluminescent Gold(III) Thiolates: The Importance of Supramolecular Interactions
P40	Mateusz	Cybulski	Stoichiometric and catalytic C-F bond activation by *trans*-dihydride ruthenium N-heterocyclic carbene complexes
P41	Oliver	Daubney	Coordinating Natural Chromophores to De Novo Peptide Structures Designed for Light Harvesting
P42	Caroline	Davies	Metal-Organic Structures in the Cambridge Structural Database (CSD)
P43	Benjamin	Day	Towards Radical Pnictogen and Chalcogen Bridged Lanthanide Single Molecule Magnets
P44	Nichabhat	Diteepeng	Alkaline Earth Organohydroborate Complexes for the Ring-Opening Polymerisation of *rac*-Lactide
P45	Lily	Dixon	One-Pot Synthesis of Benzo-1,2-Diphospholides.
P46	Dinh Cao Huan	Do	Amino-Functionalized Beta-Diketiminate Ligands: Synthesis, Characterization and Co-ordination Chemistry with Group 13/14 Elements
P47	Euan	Doidge	Selective Recovery of Gold from Secondary Sources: Solvent Extraction and Supramolecular Chemistry
P48	Juozas	Domarkas	Synthesis, radiolabelling and in vitro validation of 99mTc amidocyclam-triphenylphosphonium (TPP) conjugate for mitochondria targeted cardiac imaging by SPECT
P49	Mark	Driver	Glycidyl phosphines - A versatile synthon for the synthesis of chiral mixed donor ligands
P50	Alexander	Dunn	Controlled hydrothermal synthesis of Bi-doped ceria
P51	Felicia	Ejiah	Synthesis, Characterization and Antibacterial Screening of Novel Copper(II) Complexes from m-Aminobenzoic Acid Schiff Bases
P52	Jack	Emerson-King	Photochemically promoted C–H bond activation of fluoroarenes using an iridium(I) pincer complex
P53	Maialen	Espinal-Viguri	Hydroboration of unsaturated C-C bonds using an iron complex
P54	Peter	Evans	pπ-pπ interactions in diphosphatetrylenes
P55	Francois	Eya'ane Meva	Copper and silver nanoparticles for sustainable development

P56	Simon	Fellows	Solid-gas reactions and polymorphism of copper halide compounds
P57	Jonathan	Fowler	Tuneability of Azole-appended cavitands – from carbenes to cubes
P58	Iurii	Galadzhun	Liquid Crystalline Spin-Crossover Complexes
P59	Kimberley	Gallagher	Iron Catalysed Hydrophosphination: A comparative study of two highly active μ-oxo species
P60	Karen	Gamero-Vega	Tantalum hydrazide complexes supported by a trianionic ligand
P61	Jennifer	Garden	Highly Active and Selective New Heterodinuclear Polymerization Catalysts
P62	Anna	Gatti	Organometallic ruthenium and osmium thiosemicarbazone complexes
P63	Kathryn	George	Coordination Complexes of Plutonium (IV) and (VI) with Imidodiphosphinate Ligands
P64	Laura	Ghandhi	Cobalt picolinamide complexes as anti-cancer agents
P65	Carolina	Goncalves	New coordination mode of a thiosemicarbazonate ligand derived from pyrene to PdII and PtII centres
P66	Sam	Greatorex	Triptycenes as Redox-Active Components in Complexes and Frameworks
P67	Ross	Green	Alkaline Earth-Transition Metal Complexes
P68	Sarah	Griffin	Synthesis of Zirconium and Hafnium MOFs with Incorporated Functionality
P69	Richard	Grindell	Organometallics vs. coordination complexes: Contrasting approaches to SMM design
P70	Lara	Groves	Cationic, luminescent cyclometalated iridium(III) complexes based on substituted 2-phenylthiazole and 2-phenylquinoline ligands
P71	Matthew	Gyton	Late Transition Metal Catalysed C(sp^3)–C(sp^3) coupling reactions
P72	Hugh	Hamilton	Extending the Frustrated Lewis Pair Model
P73	Mikko	Hanninen	3d Transition Metal Complexes with N-heterocyclic Silylenes
P74	Louise	Hazeland	C1, C1-ligands. One-step route to optically-active methylene diphos ligands
P75	Oliver	Hemming	Reactive Metal-Carbon Bonds in Three-Coordinate Iron and Cobalt NHC Complexes.
P76	Alexandra	Hicken	Characterisation and Reactivity of σ-Complexes of Copper(I) with Zinc and Magnesium Hydrides
P77	James	Hickson	Yttrium and Scandium Complexes of 1,10-Phenanthroline-5,6-Dione
P78	Alexander	Hinz	Investigation of the 2-Arsaethynolate Anion
P79	Jordan	Holmes	A Tethered NHC-Carborane Ligand: Selective C-H Activation And Versatile Coordination
P80	Andrew	Hones	Iridium Catalysed C-H Borylation of Indazoles
P81	Thomas	Hood	Imidazolin-2-iminato Ligands: Applications in Group 14 Chemistry
P82	George	Hughes	Novel iridium(III) anticancer agents for ovarian and nasopharyngeal cancer
P83	Chris	Inman	A Novel U(III) Complex based on a Bidentate Phenoxide Ligand for Activation of CO_2
P84	Thompson	Izuagie	Non-aqueous strategy to a range of tin-substituted polyoxotungustates
P85	Vibe	Jakobsen	Resolution of Chiral Spin States
P86	Christopher	Jennings	Ruthenium based HDAC Inhibitors

P87	Alice	Johnson	An Efficient and Sustainable Synthesis of NHC Gold Complexes
P88	Claire	Jones	Lanthanide complexes of bulky hybrid ligands
P89	Graham	Jones	Synthetic analogues of the active site of the [NiFe] hydrogenases
P90	Andrew	Jupp	Synthesis and Reactivity of Phosphorus Analogues of Cyanate and Urea
P91	Farah	Kanwal	Synthesis and Characterization of Polysaccharide-coated Nickel Ferrite Nanoparticles as a Biomaterial Candidate
P92	Kristine	Kay	Kinetic control of metal ion transfer between copper trafficking proteins from *Bacillus subtilis*
P93	Demet	Kekilli	Proximal versus Distal Heme-NO binding in Cytochrome c' is determined by a balance of affinities mechanism: Insights into Selective Gas Response in Heme-Based Sensors
P94	Evan	Keyzer	Synthesis, Electrochemistry, and Electrode Interactions of $Mg(PF_6)_2$-Based Electrolytes in Mg-Ion Batteries
P95	Andrew	King	Facile, Catalytic Dehydrocoupling of Phosphines Using β-Diketiminate Iron(II) Complexes
P96	Richard	Knighton	Synthesis and characterisation of a series of low coordinate complexes $[M(2,2'\text{-biphenyl})(PR_3)_2]^+$ (M = Rh, Ir)
P97	Evgeny	Kolychev	Chelating bis(diazaboryl) ligands for the preparation of cyclic bisboryl complexes
P98	George	Kostakis	3d/4f Coordination Clusters in Catalysis
P99	Andreas	Kostopoulos	Linking antiferromagnetic rings through lanthanide ions
P100	Tobias	Kraemer	Solid-state density functional study of a rhodium(I) pentane s-complex
P101	Lilja	Kristinsdóttir	Electronic Modification of NHCs Using Boryl Substituents
P102	Samantha	Lau	Room Temperature Ruthenium-Mediated C–O Bond Activation
P103	Matthew	Leech	Towards Multi-Metallic Cyaphide Complexes
P104	Ji-Dong	Leng	Solid-state density functional study of a rhodium(I) pentane s-complex
P105	Alice	Leung	New Route to Layered Zinc Hydroxides (LZHs) using Organometallic Precursors and the Exfoliation of LZH with Oleate Ligands
P106	Marina	Lledos	New Multimodal Nanocomposites for PET and SPECT Imaging
P107	Siu Kwan	Lo	Geometry Constrained Main-Group Complexes for Small Molecules Activation
P108	Edward	Loukopoulos	A copper-benzotriazole based coordination polymer promotes an easy access to dihydropyridines
P109	Cecilia	Madzivire	Ruthenium(II) carbonyls-Potential anti-cancer agents?
P110	Robert	Mangan	Anionic N-Heterocyclic Carbenes in Transition Metal Chemistry
P111	Ross	Marshall	Stereoselective Halogenation of Integral Unsaturated C-C Bonds in Chemically and Mechanically Robust Zr and Hf MOFs
P112	Kayleigh	Marshall	Hydrofluorothermal synthesis of novel, fluoride containing transition metal phosphates and sulfates
P113	Emma	McCabe	Proper Ferroelectricity in the Dion-Jacobson Material $CsBi_2Ti_2NbO_{10}$: Experiment and Theory
P114	Alasdair	McKay	Anion Effects on the Stability of Sigma-Alkane Complexes
P115	Natthaya	Meundaeng	Complexes of cobalt(II), nickel(II) and copper(II) with 4-thiazolecarboxylic acid
P116	Alexandra	Miles-Hobbs	Is enantioselective hydrogenation catalysis possible using achiral phosphines?

P117	Krishna	Mistry	Pt(0) Monocarbonyl Complexes for Small Molecule Activation
P118	Matthew	Molloy	Facile Dehydrogenation of Amine Boranes with a Bimetallic Titanium Pentalene Sandwich Complex
P119	Mauro	Monti	Poly-Phosphono Cyclen Based Ligands for Complexation of PET Metals
P120	Tadeo	Moreno Chicano	Developing structural movies of catalysis by heme-containing enzymes: first frames.
P121	David	Moulding	Stablisation of Uranyl(V) with Bulky Alkylsilylamide Ligands
P122	Rebecca	Musgrave	Metallopolymers at the Covalent-Supramolecular Boundary Based on Nickelocene
P123	Adi	Nako	Sc catalysed hydroaminoalkylation of simple tertiary amines
P124	Erica	Neves de Faria	Control of the architecture of Na(PCO) and nitrilium salts reactions
P125	Sarah	Newton	Optimisation of a coiled coil peptide for use as a MRI contrast agent
P126	Hannah	Nicholas	Physical Properties of Linear Transition Metal Complexes
P127	Haoyu	Niu	Experimental and Theoretical Studies of Strong s-donating Ligands
P128	Samuel	Oldknow	Structurally dynamic metallocryptophane systems
P129	Nicola	Oldroyd	Highly Sterically Demanding Chelating Borylamide Ligands in Main Group Chemistry
P130	Michael	O'Neill	^{19}F Fingerprinting to Track the Binding Preferences of a Ruthenium Piano Stool Complex
P131	Hector	Oyem	Ag$_4$ Clusters in Water-in-oil emulsion synthesis
P132	Ruth	Patchett	Potassium binding calix[4]arenes
P133	Maria Teresa	Pellicer Martinez	RsrR, a new member of the Rrf2 superfamily from Streptomyces venezuelae that functions as a redox sensitive response regulator.
P134	Katy	Pellow	Catalytic conversion of methanol/ethanol to isobutanol – a highly selective route to an advanced biofuel
P135	Andreas	Phanopoulos	Flexible Binuclear β-Diketiminate Complexes of Copper(I)
P136	Jack	Pike	Ruthenium sandwich complexes for catalysis
P137	Amy	Price	Phosphinidene boranes; reactions with bases and alkynes
P138	Thomas	Price	Rapid Chelation of Gallium-68 at Neutral pH
P139	Jamie	Purkis	Synthesis and Reactivity of Stable Bimetallic Uranium (V) 'Pacman' Complexes
P140	Nasir	Rajabi	DFT study of Cooperative H2 Activation across the Ru-Zn Bond in [Ru(IPr)$_2$(CO)ZnEt]$^+$
P141	Thomas	Rees	[M(C^N^N)2] Complexes of Group 8 and 9: The Expected and the Unexpected
P142	Diego	Resendiz-Lara	Catalysis in the Service of Main Group Chemistry: Synthesis of New p-Block Materials.
P143	Jose Adan	Reyes-Sanchez	Synthesis and Reactivity of New Alkaline Earth Gallyl Complexes
P144	Alexander	Riley	Catalytic Upgrading of Bioethanol to n-Butanol
P145	Wasupol	Rungtanapirom	Activities of N-heterocyclic Carbenes at Copper
P146	Niamh	Ryall	A Schottky Barrier Device on Steel for use in Photovoltaics
P147	Emma	Sackville	Molecular Electro-Oxidation Catalysts
P148	Sophia	Sarpaki	Synthesis of new mono-substituted thiosemicarbazone ligands and of their corresponding biocompatible metal complexes
P149	Nathalie	Segaud	Radical stabilization in water by an artificial metalloprotein

P150	Anbu	Sellamuthu Kooduthurai	De novo designed lanthanide coiled coils as catalysts in phosphodiester hydrolysis reaction in aqueous medium
P151	Sachin	Shah	Fabrication of Hollow and Porous Platinum Nanotube Derived From Tomato Mosaic Virus
P152	Helen Rose	Sharpe	Exploring and modifying reactivity of m-terphenyl complexes
P153	Paul	Shaw	Reactivity of 5 Coordinate Pt(IV) Complexes.
P154	Rena	Simayi	Ortho and peri C-H activations using different metal salts
P155	Trevor	Simmons	Cobaltocenium coupled [FeFe]-hydrogenase analogues: Modelling the H-Cluster
P156	Frances	Singer	Catalytic Applications of Complexes Bearing NHC-Carborane Ligands
P157	Kundan Kumar	Singh Sagar	Catalytic Epoxidation by Bioinspired Fe(H_2O)-bTAML Complex using O_2 and NaOCl
P158	Louise	Slope	Ln(III) Binding and Discrimination Within a De Novo Designed Coiled Coil
P159	Martin	Slusarczyk	Reactions of a Titanium Borylimide
P160	Zoe	Smallwood	Homoleptic Cyano Complexes of Silicon and Tin
P161	Adam	Smith	New Gallium-68 Chelates for Mitochondrial Imaging
P162	Hualong	Song	Functionalised peptidomimetic metallohelices
P163	Ji-Inn	Song	Cellular redox modulation using an organometallic Os(II) complex
P164	Anna	Spearing-Ewyn	Exploring Cationic Rhodium "PONOP" Pincer Complexes for Amine-Borane Dehydropolymerisation
P165	Helen Victoria	Stafford	Coordination Chemistry and Photophysical Studies of f-element Imidodiphosphinate Complexes
P166	Martin	Stanford	Phospha-Amidinate Silylenes
P167	Caroline	Storey	Synthesis, structure and dynamics of NHC-based Palladium macrocycles
P168			
P169	Vanessa	Timmermann	Lanthanide and Uranium tert-Butyloxycarbonyle Appended Cyclen Derivatives
P170	Oliver	Townrow	Zn_2Y_2 Catalyst for High-Efficiency Chiral Michael Addition Reactions at Room Temperature
P171	Gemma	Trott	Mechanistic and Kinetic Investigations into Homodinuclear and Heterodinuclear Catalysts for CO2-epoxide Copolymerization
P172	Rebecca	Ullah	The Development of a ^{68}Ga labelled Plant Virus Capsid for PET Imaging
P173	Stephanie	Urwin	Reductive Elimination from Al(III): Exploring the Mechanism and the Effect of Coordinated Base
P174	Petra	Vasko	Small Molecule Activation under Ambient Conditions by Main Group Metalloid Clusters
P175	Robbin	Vernooij	Vibrational spectroscopic studies of photoactivatable diazido Pt(IV) anticancer complexes
P176	Gabriele	Wagner	Preparation, characterisation and *in-vitro* cytotoxicity of mesoporous silica nanoparticles loaded with cytotoxic Pt(II) oxadiazoline complexes
P177	Gabriele	Wagner	Removal of cytotoxic platinum compounds from aqueous media by photolysis in the presence of 2,4,6-trimercaptotriazine

P178	Jordan	Waters	Synthesis of Ditopic Carbanionic N-Heterocyclic Carbene Complexes
P179	Cath	Weetman	Lipophilic perrhenates as catalysts for REDOX reactions
P180	Fu-Sheng	Guo	TBA
P181	Jordan	Wells	Towards small molecule activation with tethered bimetallic uranium aryloxides
P182	Ellis	Wilde	Bacterial Iron Uptake: Designing Siderophore Mimics to Understand periplasmic Binding Proteins
P183	Lewis	Wilkins	Diverging reactivity of B(C6F5)3 in Lewis acid mediated organic transformations: carboboration, cyclisation and propargyl rearrangement.
P184	Martin	Wills	Asymmetric reductions using ruthenium and iron complexes
P185	Joseph	Wright	Photoresponsive carbon monoxide release: towards therapeutic applications
P186	Bowen	Xie	Synthesis and Reactivity of Zirconium and Hafnium Borylimido Compounds
P187	Steven	Yap	Modification of viral nanoparticle for use in diagnosis and treatment of cancer
P188	Francois-Joseph	Yazigi	Incorporation of new functionalities into Metal-Organic Frameworks for catalysis and metal binding
P189	Pingyu	Zhang	Multi-colour Luminescent Ir(III) Compounds for Photodynamic Therapy
P190	Ili	Zulkifly	Intramolecular frustrated phosphine/borane Lewis pairs with a dimethylxanthene backbone: synthesis and applications
P191	Colin	Evesson	The role of ligand symmetry in spin-labile mononuclear Mn(III) complexes

Surface Modification of Metal-Organic Frameworks (MOFs) for Drug Delivery Applications

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Metal-organic frameworks (MOFs) are a class of hybrid macromolecules composed of metal ions or metal clusters linked by multidentate organic ligands, forming crystalline, porous and three dimensional structures. Some of their properties, such as potential porosity, high surface area, thermal stability and structural tailorability have made them attractive for a wide variety of applications, including heterogeneous catalysis, gas storage and drug delivery.

Despite the recent increased interest in nanoparticles as carriers for drug delivery, most of them are purely organic or inorganic, each of them with their own strengths and weaknesses. Hybrid materials, such as MOFs, are promising candidates, as they can have properties from both organic and inorganic materials, and it has been reported that some nano MOFs (NMOFs) present exceptional high loadings compared to other nanocarriers.[1] In addition, their properties can be tuned by the thoughtful choice of metal and linkers, and post-synthetic modifications are accessible.[2]

In spite of the growing interest in NMOFs for drug delivery and their post-synthetic modifications, only few studies have been focused on their surface modifications.[3] Herein, we present an innovative method for the synthetic modification of NMOFs during and after synthesis, introducing functional groups on the surface during the synthetic process that subsequently we use for further post-synthetic modifications. By post-synthetically modifying the NMOFs surfaces we can tune their stability, pore opening size and chemistry and therefore, drug release kinetics.

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Rhodium complexes of POP–type ligands: towards controlled amine–borane dehydropolymerisation

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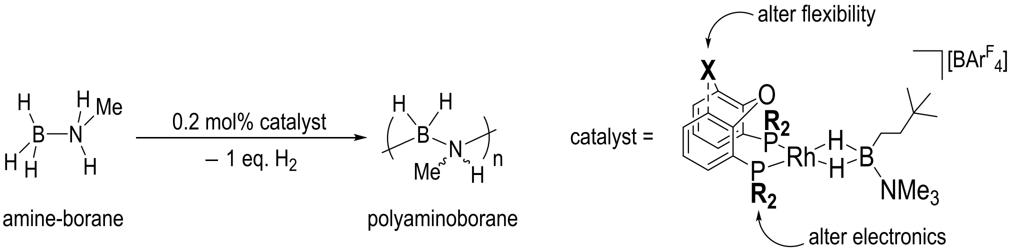
Polyaminoboranes, $[H_2BNRH]_n$, are a remarkably underdeveloped class of materials given that they are isoelectronic with technologically ubiquitous polyolefins. Their potential applications are wide–ranging, for example as precursors to BN ceramics and as hydrogen storage materials. Only recently has the fundamental understanding of the mechanism of amine–borane dehydropolymerisation started to be investigated.[1] We report the synthesis of new $\{Rh(POP)\}^+$ dehydropolymerisation catalysts with modified ligand backbones (**Scheme 1**), based upon the previously reported $\{Rh(XantPhos)\}^+$ system,[2] and examine their catalytic ability. In particular, a more detailed study of $[Rh(\kappa^2_{P,P}\text{–DPEPhos})(\eta^2\text{–}H_2(CH_2CH_2{}^tBu)B{\cdot}NMe_3)][BAr^F_4]$ (DPEPhos = *bis*-[(2-diphenylphosphino)phenyl] ether) is carried out, with a view to investigate further mechanistic detail of the dehydropolymerisation reaction. At 0.2 mol% catalyst loading in an open system, the $\{Rh(DPEPhos)\}^+$ fragment produces polymer (M_n = 33 000 g mol^{-1}, $Đ$ = 2.1) with a turnover frequency of 250 h^{-1}, and the potential to control polymer molecular weight is explored.



Scheme 1: Formation of polyaminoborane using $\{Rh(POP)\}^+$.

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Upgrading Ethanol; Mechanistic Insights

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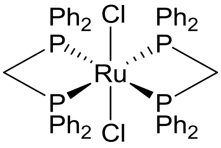
The search for renewable and sustainable sources of energy is a matter of exceptional importance and demands substantial attention and research effort. Numerous studies have shown the damaging and detrimental effects increased carbon dioxide can have on the Earth's fragile climate; a direct consequence of utilising fossil-based fuels. All alternative fuels presently being used have both distinct advantages and inadequacies, such as the current plant-based fuel bioethanol. For example bioethanol has exhibited corrosive properties within current engine infrastructure, and also has a decreased boiling point when blended into gasoline. These detrimental characteristics render bioethanol unsuitable as a replacement fuel.

Research within the Wass group has focused on the synthesis of *n*-butanol and *iso*-butanol from ethanol and ethanol/methanol blends respectively. Both butanol isomers have energy densities similar to that of gasoline (>86%), and their more alkane-like features assist in reducing the disadvantages bioethanol presents as a sustainable biofuel. The proposed feedstock is waste plant-matter, hence combustion of biobutanol results in a complete carbon cycle and does not adversely affect the environment.

Specifically novel transition metal catalysed routes are currently under investigation. The reaction is postulated to proceed *via* a well-known process known as the Guerbet reaction. We have developed ruthenium based catalysts that achieve unprecedented selectivity in the catalytic upgrading of ethanol and ethanol/methanol blends. The catalytic capability of these systems have been studied, and several important and intriguing observations highlight the need to investigate the specifics of the mechanism.



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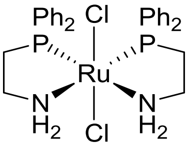

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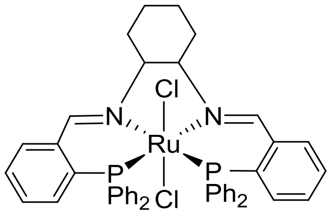

(3)

Subtle changes in the ligand sets allow for *n*-butanol, *iso*-butanol (catalysts 1 and 2) and ethyl acetate (catalyst 3) formation. Unambiguously defining the origins of the selectivity of these ruthenium systems will enable selectivity tuning. This is a mechanistic feature that will undoubtedly provide information necessary for scale-up, as well as future design of new catalysts for the transformation of alcoholic substrates.

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Heterobimetallic Ruthenium Complexes Containing Ferrocene as Anti-Cancer Agents

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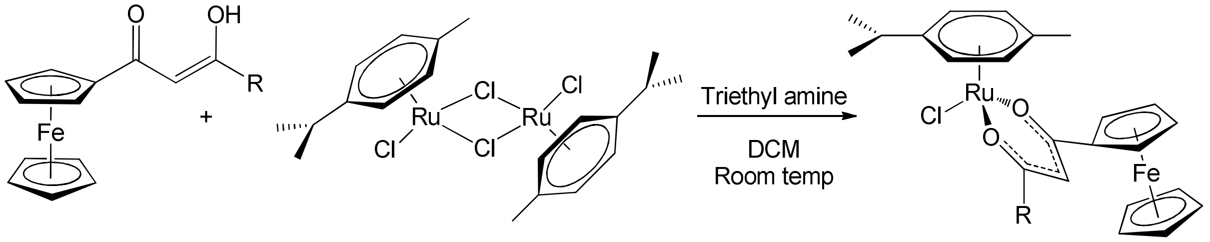
Ferrocene is becoming an increasingly popular addition to many already well established anti-cancer drugs; incorporation of a biologically active metal with a biologically active molecule often results in a collaborative effect which enhances the anti-cancer properties of both species.[1, 2] The activity of the ferrocene moiety is still not yet fully understood. One theory suggests that the ferrocene may act as a redox antenna inside the hypoxic cancer cells, this in turn aids the formation of reactive oxygen species which cleave DNA stands.[3] Alternatively the ferrocene may increase drug binding to transferrin proteins which will selectively deliver the drug to cancerous cells as they have many receptors with a high affinity towards transferrin.[4]



Scheme 1. General synthetic pathway for the formation of ruthenium(II) ferrocene complexes

This project focuses on the synthesis of novel ruthenium(II) metal complexes bound to ferrocene through *β*-diketonate ligands (**Scheme 1**), building upon the "piano stool" like ruthenium complexes with (N,N), (N,O) and (O,O) chelating ligands which have been previously studied in the McGowan group.[5] X-ray crystallographic data for the ruthenium(II) ferrocene complexes will be presented along with electrochemical interactions with a bio-membrane DOPC monolayer, demonstrating the complexes ability to disrupt the cell membrane.

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Kinetics and Mechanisms of Acid-Catalyzed Substitution and Substrate Binding Reactions of $[Fe_4S_4Cl_4]^{2-}$

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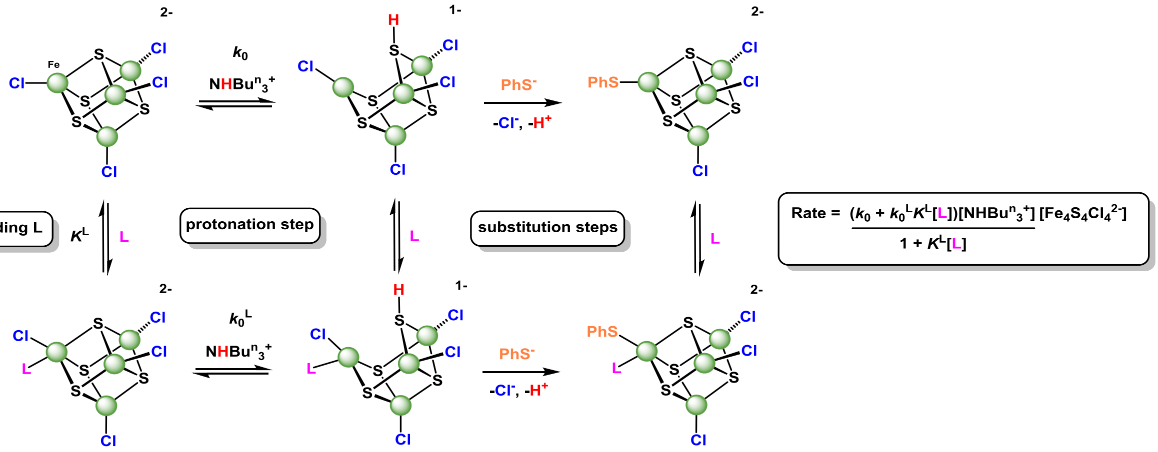
A variety of metalloenzymes contain Fe-S-based clusters as the catalytic site where substrates are transformed by sequential addition of electrons and protons. The ways in which substrates bind and are transformed by natural clusters remains unclear. In this poster, we report the kinetics of protonation and binding of substrates to a synthetic Fe-S cluster, using methodologies established earlier[1]. The observed kinetics are more consistent with recent DFT calculations which propose that protonation of μ_3-S is coupled to concomitant Fe-S bond elongation/cleavage as shown in the figure, and our results are elaborated in terms of this suggestion[2].

The kinetics of the acid-catalyzed substitution reactions of the terminal chloro-ligands in $[Fe_4S_4Cl_4]^{2-}$ by PhS^- in the presence of the acids NHR_3^+ (R = Me, Pr^n or Bu^n) have been studied. All these acids have very similar pK_as (17.6-18.4). Nevertheless, the reactions exhibit a variety of different kinetics: the reaction in the presence $NHBu^n{}_3^+$ involves rate-limiting proton transfer from acid to the cluster ($k_0 = 490 \pm 20$ dm^3 mol^{-1} s^{-1}), whilst with $NHMe_3^+$ the rate is significantly slower than predicted from consideration of the pK_a.

In further studies, a variety of small molecules and ions {L = substrate = Cl^-, Br^-, I^-, $RNHNH_2$ (R = Me or Ph), Me_2NNH_2, HCN, NCS^-, N_3^-, Bu^t NC or pyridine} have been shown to bind to $[Fe_4S_4Cl_4]^{2-}$ and this affects the rate of subsequent protonation by $NHBu^n{}_3^+$. The equilibrium constants for substrate binding (K^L) and the rates of proton transfer from $NHBu^n{}_3^+$ to $[Fe_4S_4Cl_4(L)]^{n-}$ ($k^L{}_0$) have been determined using the rate law shown in the figure.



$$\text{Rate} = \frac{(k_0 + k_0^L K^L[L])[NHBu^n{}_3^+][Fe_4S_4Cl_4^{2-}]}{1 + K^L[L]}$$

The results indicate the following general features. (i) Bound substrates increase the rate of protonation of the cluster, but the rate increase is modest ($k^L{}_0/k_0$ = 1.6 to ≥72). (ii) When K_L is small, so is $k^L{}_0/k_0$. (iii) Binding substrates which are good σ-donors or good π-acceptors lead to the largest $k^L{}_0/k_0$.

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A new polyborate anion, $[B_7O_9(OH)_6]^{3-}$: Self assembly, XRD and thermal properties of s-*fac*-$[Co(dien)_2][B_7O_9(OH)_6]\cdot 9H_2O$

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The title compound, s-*fac*-$[Co(dien)_2][B_7O_9(OH)_6]\cdot 9H_2O$ (**1**) (dien = $HN(CH_2CH_2NH_2)_2$), has been prepared as a crystalline solid in moderate yield (35 %) from the reaction of $B(OH)_3$ with $[Co(dien)_2][OH]_3$ in aqueous solution (10:1 ratio).[1] The structure contains a novel polyborate anion $[B_7O_9(OH)_6]^{3-}$ which is structurally based on the known 'ribbon' isomer of $[B_7O_9(OH)_5]^{2-}$, with an additional $[OH]^-$ group coordinated to a B atom in one of the outer boroxole rings. Compound **1** is formed by a self-assembly process in which the cation and anion mutually template themselves from equilibrium mixtures under reaction conditions. The $[B_7O_9(OH)_6]^{3-}$ anions are H-bonded to each other in layers with 'cavities' suitable for the $[Co(dien)_2]^{3+}$ complex. Three $[B_7O_9(OH)_6]^{3-}$ anions are in the secondary coordination sphere (via H-bonds) of each cation, with each anion H-bonded to three cations.

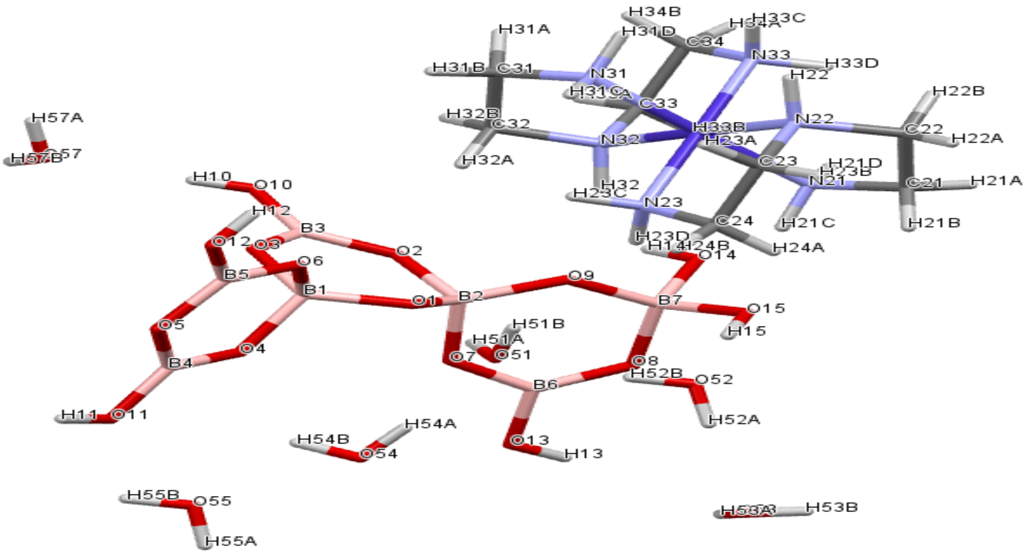

Figure **1:** The structure of s-*fac*-$[Co(dien)_2][B_7O_9(OH)_6]\cdot 9H_2O$

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Organo-Imido Polyoxometalates: High Transparency, High Activity Redox-Active NLO Chromophores

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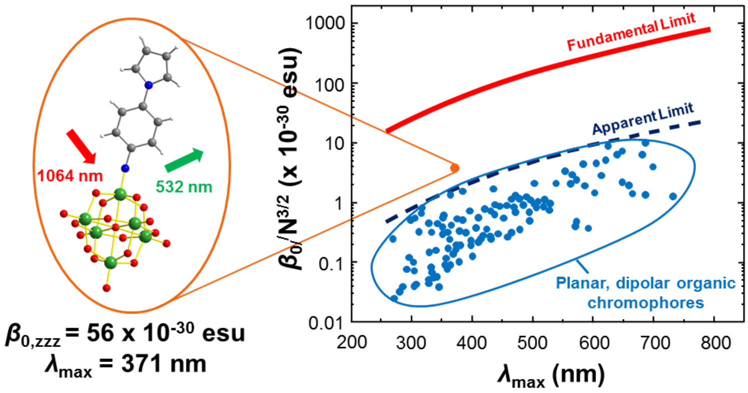
Polyoxometalates (POMs), a diverse class of molecular metal oxide clusters,[1] offer a number of highly attractive features for application in photonic materials. In particular, their ability to act as electron acceptors combining multiple (often highly stable) redox states and a high density of heavy atoms suggests an interesting basis for charge-transfer chromophores. These could find application in redox-switched non-linear optical (NLO) materials, or as sensitizer dyes.



We will present the synthesis, and NLO properties of charge-transfer chromophores based on POMs connected to conjugated organic groups through imido linkages.[2] These hybrid compounds have an unusual combination of high NLO activity, and high transparency, breaking through empirical performance limits that apply to the vast majority of purely organic materials. We are now working towards electropolymerization of these materials into redox-switchable thin films.

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Synthesis of mechanically interlocked complexes of enynes

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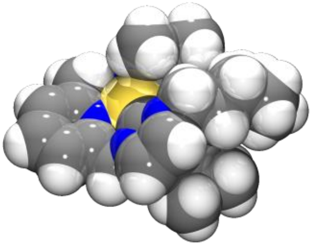
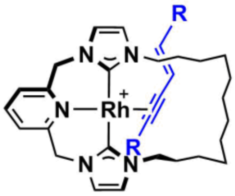
Pincer ligand architectures featuring N-heterocyclic carbene (NHC) donors are becoming increasingly prominent in organometallic chemistry and catalysis, combining the strong σ-donor characteristics of NHCs with the favourable thermal stability and reaction control possible with a mer-tridentate geometry.[1] With a view to exploiting their unique steric profile and topology in organometallic and supramolecular chemistry, we have recently become engaged in the investigation of macrocyclic variants of these ligands.[2]

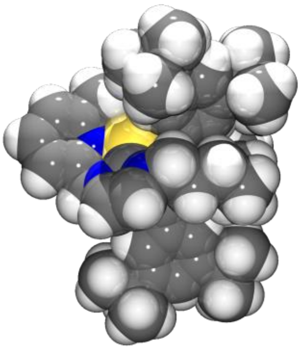
Building on the demonstration of catalytic alkyne-dimerisation using rhodium pincer complexes,[3] here we describe the reaction of terminal alkynes with an *in-situ* generated rhodium macrocycle that affords interlocked enynes **1** and **2**. As well as inhibiting dissociation of the enyne, the macrocyclic ligand renders the complex stable to air, moisture and mild oxidants (MeI, O_2). Enclosed by the ring, the enyne is not hydrogenated, even under forcing conditions.



1 R = ^{t}Bu



1 R = ^{t}Bu
2 R = 3,5-di^{t}Bu-C_6H_3



2 R = 3,5-di^{t}Bu-C_6H_3

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Group Two Mediated CO Homologation and Reductive Catalysis

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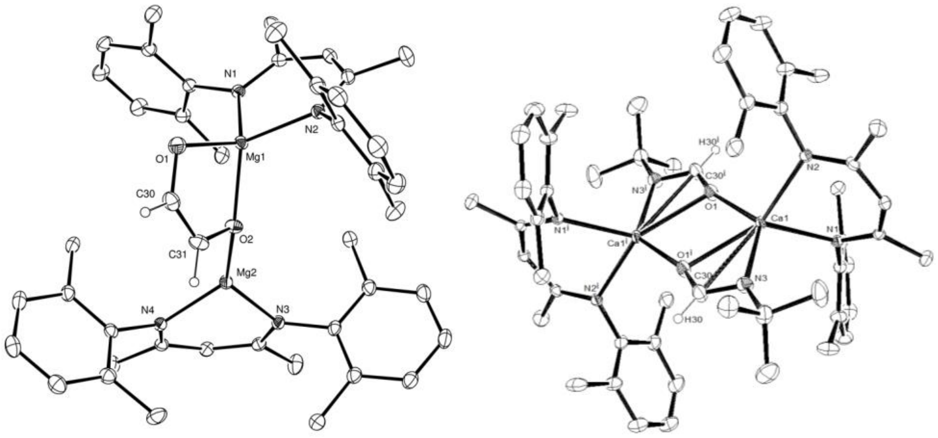
The deoxygenative conversion of carbon monoxide to hydrocarbon fuels and lower oxygenates is typically achieved through heterogeneous catalytic methods.[1] Although Fischer-Tropsch (F-T) chemistry and related processes have been successfully implemented for some eighty years to produce a Schultz-Flory distribution of hydrocarbons, only limited success has been achieved with well-defined homogeneous systems at CO pressures typically in excess of 1000 atm.[1]



Figer 1: Left, dinuclear magnesium enediolate species. Right, dinuclear calcium formimidate species.

Our own research efforts have focused on the development of a homogeneous catalytic chemistry for complexes derived from the inexpensive and environmentally benign alkaline earth elements, in particular magnesium and calcium; respectively the eighth and fifth most abundant elements in the lithosphere. In this contribution we demonstrate that CO homologation reactivity may be achieved through exposure of both the β-diketiminato magnesium[2] and calcium hydride[3] to one atmosphere of CO and that this and other alkaline earth species enable the highly selective catalytic reduction of the carbon monoxide molecule under similarly mild reaction conditions. Extension of this chemistry to Ae-E bonds (E = N, P) disclosed the high propensity for CO insertion yielding a range of formimidate complexes. Current work is focusing on extending this to a catalytic regime.

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Tripodal phosphine ligands for small molecule activation

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Tripodal phosphines have recently resurfaced as effective ligands for a range of catalytic transformations.[1] The *facially* capping geometries enforced by these ligands result in *cis* coordination sites for substrates necessary for catalytic transformations, and also impart inherent stability to a metal centre via multidentate coordination. Carbon-centred, methylene-bridged tripodal phosphine ligands (‘triphos’) have been widely investigated, but analogous frameworks with varying bridgehead atoms are less-well known. We have previously investigated the synthesis of the nitrogen-centred triphos ligand (N-triphos, **L**, fig. 1) via a stable hydroxyphosphonium intermediate (**L’**, fig. 1) that allows access to a range of phosphine substituents,[2] and the coordination chemistry to tungsten centres (**1**, fig. 1), as well as ruthenium complexes for the catalytic hydrogenation of biomass-derived levulinic acid (**2**, fig. 1).[3–5]

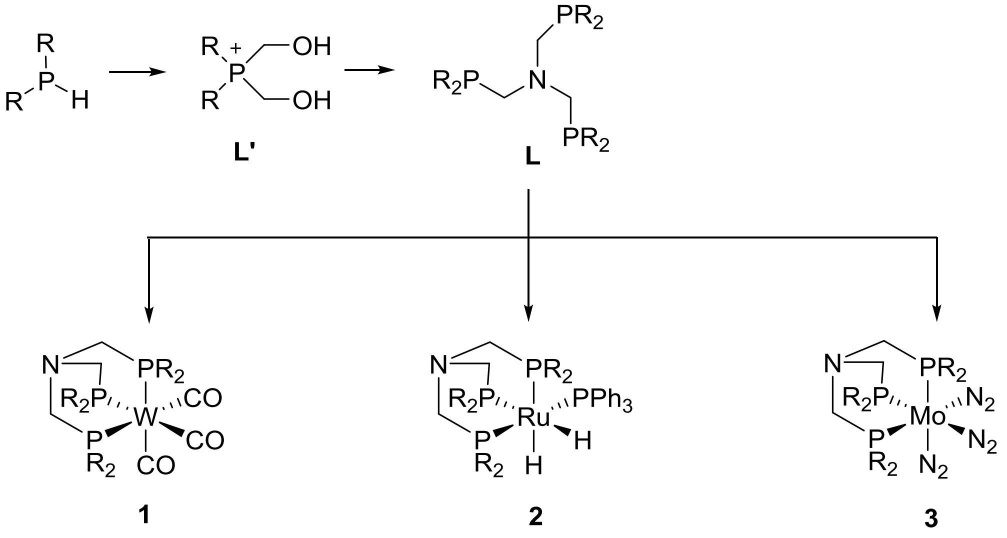

Fig. 1. *Synthesis of N-triphos ligands (**L**) and corresponding complexes formed (**1-3**).*

We also propose the novel synthesis of N-triphos transition metal dinitrogen complexes for applications into the catalytic formation of ammonia; tripodal-type ligand architectures already feature in some of the few examples of reported nitrogen fixation catalysts.[6,7] The synthesis of new N-triphos molybdenum complexes will be presented alongside initial data on the activation of coordinated dinitrogen (**3**, fig. 1).

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Chlorinated *m*-Terphenyl Ligands in the Synthesis of Low-Coordinate Transition Metal Complexes

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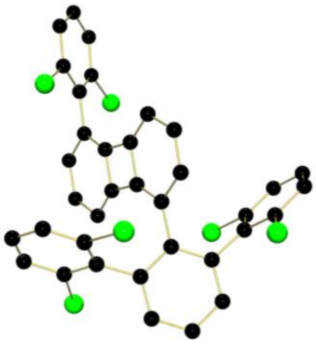
The synthesis of low coordinate transition metal complexes has advanced alongside the development of increasingly sterically demanding ligand systems.[1] Such ligands have enabled the stabilisation and investigation of novel species demonstrating previously unreported bonding modes, few more so than *m*-terphenyl ligands.[2] Within our group this has prompted an interest in how *m*-terphenyl ligand systems can be varied to control the environment around the metal centre[3] and therefore the structure, reactivity and magnetic properties of the resulting complex. Herein we report stabilisation of homoleptic, low-coordinate group 12 and transition metal (M = Mn, Fe, Co) complexes through the application of the $[2,6\text{-Dcp}_2C_6H_3]^-$ (Dcp = 2,6-dichlorophenyl) ligand. The resulting group 12 complexes $(2,6\text{-Dcp}_2C_6H_3)_2M$ (M = Zn, Cd and Hg) are strictly linear with regards to the central C-M-C bond angle. Among the transition metals only $(2,6\text{-Dcp}_2C_6H_3)_2Mn$ appears stable, where attempts to synthesise the Fe and Co analogues resulted in coupling of the ligands (**1**). It is also possible to synthesise the heteroleptic complex $(2,6\text{-Dcp}_2C_6H_3)(2,6\text{-Mes}_2C_6H_3)Mn$ (**2**), the first two-coordinate, transition metal complex featuring metal-carbon bonds to two different *m*-terphenyl ligands.



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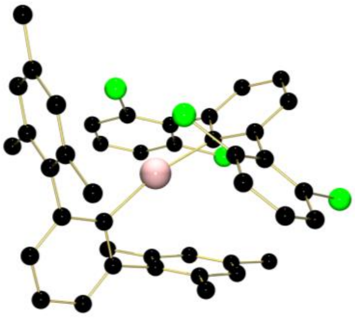

2

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DFT studies on Rh-mediated Dehydrocoupling of Phosphine-Boranes

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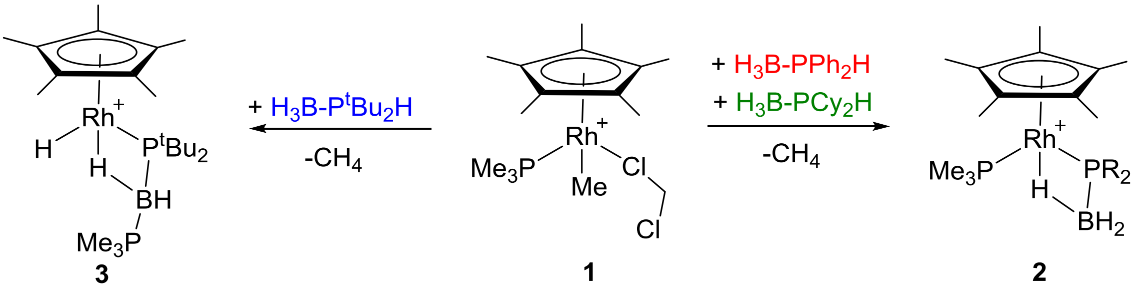
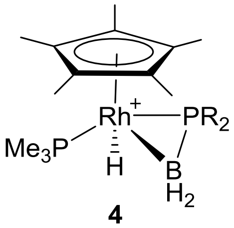
Polyphosphino-boranes and polyamino-boranes, are isoelectronic with polyolefins. However, the mechanism by which these main-group polymers are formed is considerably less well understood.[1] Experimentally, the catalytic formation of $[H_2B\text{-}PPhH]_n$ was demonstrated using $[RhCp^*Me(PMe_3)(CH_2Cl_2)][BAr^F_4]$ **1**, as a pre-catalyst.[2] However, repeating the reaction with $H_3B\text{-}PPh_2H$ formed the dimer $H_3B\text{-}PPh_2\text{-}BH_2\text{-}PPh_2H$. Stoichiometric reactions were then investigated to gain further understanding of the polymerisation mechanism. These showed that the reactions of $H_3B\text{-}PPh_2H$ and $H_3B\text{-}PCy_2H$ with **1** resulted in the formation of phosphido-borane species **2**, while with $H_3B\text{-}P^tBu_2H$, PMe_3 transfer occurred to form **3**.





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Using Density Functional Theory (DFT) we propose mechanistic pathways that allow for the formation of **2** and **3** to be discriminated. The mechanism for $H_3B\text{-}PPh_2H$ and $H_3B\text{-}P^tBu_2H$ were analogous up to the formation of an alkene-like complex with a $\{R_2PBH_2\}$ moiety, **4**. The formation of **2** is achieved through a two-step rotation of this $\{R_2PBH_2\}$ moiety. For R = Ph, Cy this results in the formation of the thermodynamically and kinetically favoured product, **2**. For, R = ^{t}Bu, **2** is also the kinetically favoured product, however, steric interactions between the ^{t}Bu groups and the Cp* ring render this process reversible. This allows for an alternate pathway involving PMe_3 transfer to form **3** which is, in this case, the thermodynamically favoured product and hence is observed in the stoichiometric reaction.

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Pt Group stibine complexes: μ_3 bridging $SbMe_3$ and other unexpected coordination behaviours

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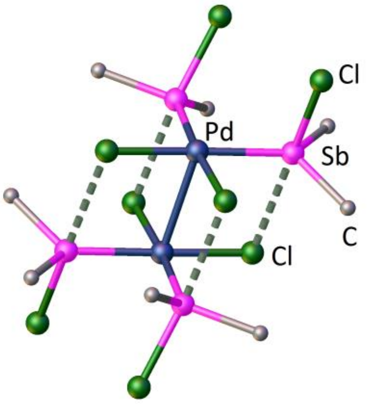
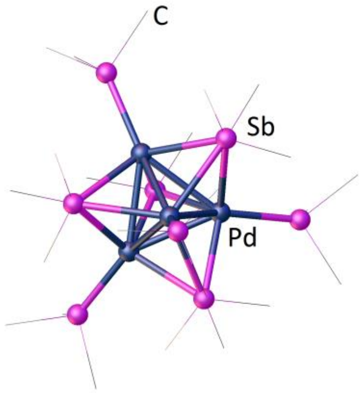
While platinum group phosphine complexes are important cross-coupling catalysts widely used in both industry and research, less is known about the coordination chemistry of stibines (SbR_3) with these metals. Recent investigation of complexes with polydentate Sb/P or Bi/P ligands has highlighted the 'non-innocent' reactivity these heavier donors can display.[1]





Our interest in the Lewis amphoteric behaviour of Sb(III) ligands[2,3] has led us to investigate the coordination chemistry of stibines and halostibines with Pd(II) and Pt(II) halides, revealing considerable structural diversity. The products include dimers with hyper-coordination of Sb to halide substituents on neighbouring metal atoms. Complexes containing reactive M-X centres both at the transition metal and at Sb have been synthesised and their reactivity investigated. A number of cluster complexes have also been isolated, including $[Pd_4(\mu_3\text{-}SbMe_3)_4(SbMe_3)_4]$ in which a $SbMe_3$ ligand is coordinated symmetrically to one face of a Pd(0) tetrahedron. This unprecedented triple bridging mode challenges the view that monodentate pnictines are only capable of terminal coordination.[4] Electronic structure and bonding have been examined using a number of computational methods, confirming the stability of the μ_3-bridged tetramer and shedding light on the bonding in these unusual complexes. Analogous μ_3-phosphine complexes are a current target.

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A Versatile Soft-Hard N/S-Ligand for Metal Coordination and Cluster Formation

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Deprotonation of the thialdiphosphazane $[S{=}PH(\mu\text{-}N^tBu)]_2$ (**1**)[1] with a range of metal bases gives the stable dianion $[[S\text{-}P(\mu\text{-}N^tBu)]_2{}^{2-}$, valence-isoelectronic with the widely-used $[[RN\text{-}P(\mu\text{-}NR)]_2{}^{2-}$ ligand.[2] When $MgBu_2$ is used, the resulting anion is isolated in good yields and crystallises as the bridged species **2** (Fig 1.). The deprotonation with BnNa (Bn = benzyl) leads to the formation of the remarkable cage $[Na_{16}([[RN\text{-}P(\mu\text{-}NR)]_2{}^{2-})_8{\cdot}NaSH{\cdot}8thf]$ (**3**) (Fig. 1).[3] The structure consists of eight phosphazane dianions and sixteen sodium cations templated around a NaSH monomer in a complex two-tiered cage with multiple Na^+ ion coordination geometries. The potential of the dianion as a ligand is demonstrated by its transfer to main group metals (Sn, Ge) to give a bridged phosphazane species structurally similar to **2**.

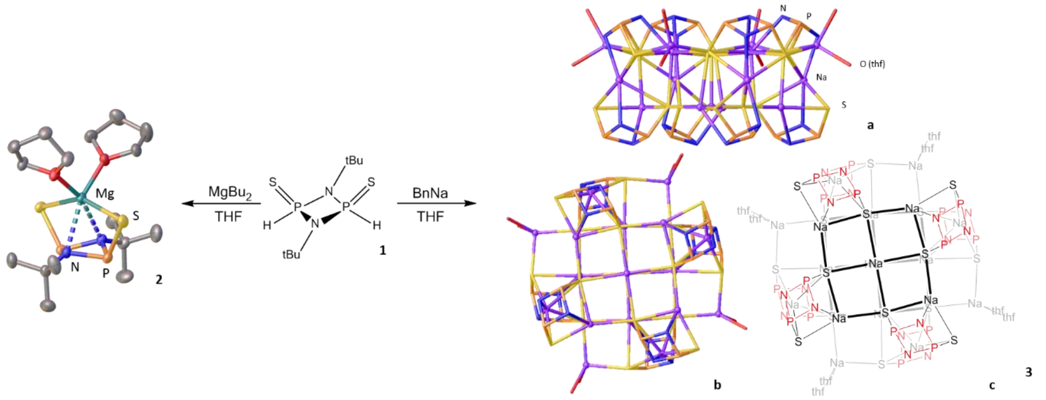

Figure 1: Synthesis and solid-state structure of the Mg-bridged species **2** and the cage **3** from the dithialphosphazane **1**. Side-on view (**a**) and bottom view (**b**) show the two-tiered nature of the cage and the schematic drawing (**c**) highlights the phosphazane units surrounding the Na-S core. H-atoms omitted for clarity, and thf molecules omitted for **3**.

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Gallium-68 radiolabelling of macrocyclic chelators on a microfluidic device for use in positron emission tomography imaging

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Positron emission tomography (PET) is a medical imaging technique which detects radioactive biomarkers in the body to locate abnormalities. Fluorine-18 ($t_{1/2}$ = 109.8 min) is the current 'gold standard' radionuclide for PET imaging,[1] although recently radiometals have become more attractive alternatives due to their range of decay characteristics and half lives but have not yet been fully exploited due to isotope availability and complex stability. Gallium-68 ($t_{1/2}$= 68 min) is quickly emerging as the main competitor for fluorine-18 due to cost-effective generator production and shorter half-life.[2]

Microreactor technology offers the potential to greatly improve radiolabelling efficiency due to greatly enhanced mass transfer.[3] Reduced shielding requirements and shorter reaction times than batch processes offer the ability to generate 'dose-on-demand' quantities of the radiotracer for patients within a clinical environment. A microfluidic reactor containing a serpentine mixing channel with staggered herringbone micromixers was fabricated and evaluated for high efficiency radiolabelling of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA),[4] the most commonly used bifunctional chelator for gallium-68 complexation in commercial radiopharmaceuticals. Reactor compatibility and radiolabelling experiments illustrate the capability of the microreactor to produce higher specific activities and radiochemical yields using milder conditions than batch processes, demonstrating its potential for translation to a wide range of radiometals and chelators in PET applications.

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Aluminium-Catalysed Hydroboration

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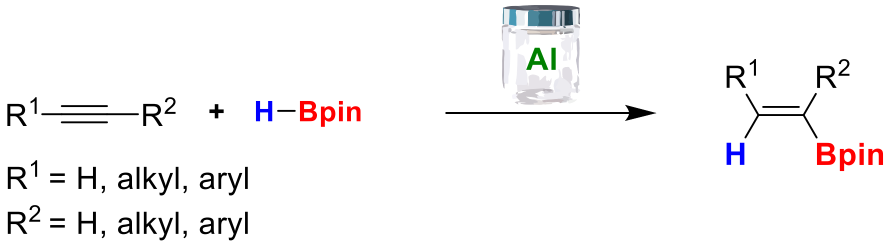

Hydrofunctionalisation, the addition of E-H (e.g. E = B, N, Si) across an unsaturated bond, is an important process relevant to both industry and academia.[1] Many catalysts for hydrofunctionalisation are based on transition metals,[2] however, recently main group systems have emerged for hydrofunctionalisation of polar, unsaturated bonds such as aldehydes and imines.[3]

Here, we report an aluminium hydride catalysed hydroboration of terminal and internal alkynes using readily available alkyl-aluminium species as precatalysts.

We have performed mechanistic studies which show that the alkyl aluminium precatalyst is activated by HBPin, generating a reactive aluminium hydride species *in-situ*. Hydroaluminiation of the alkyne by the resulting aluminium hydrides is a key step in the catalytic cycle.

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Frustrated small molecule reactivities

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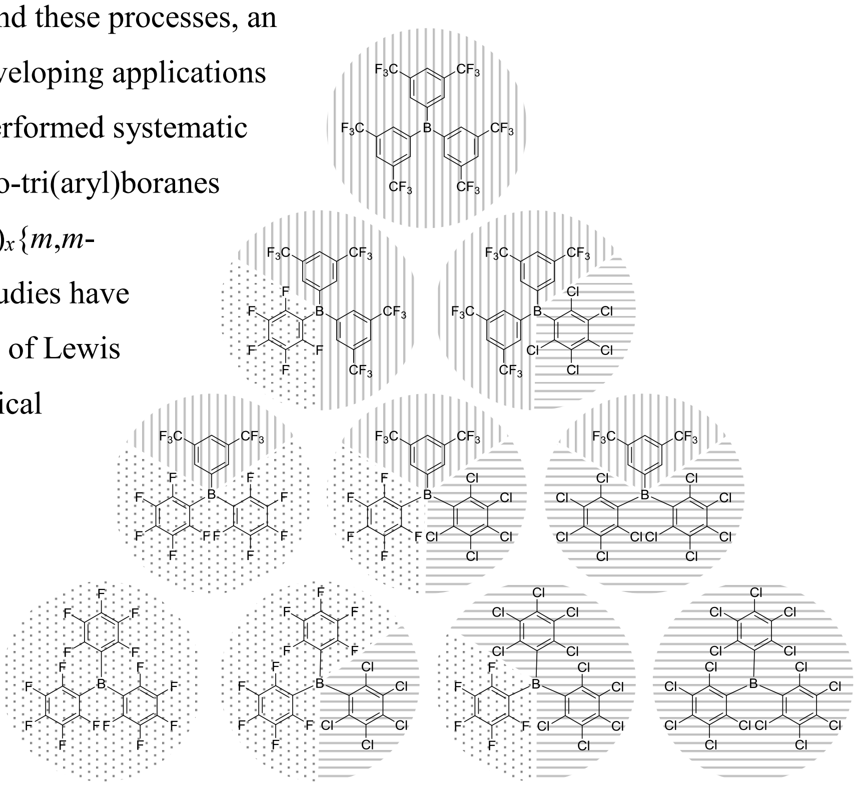
School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, U.K., r.blagg@uea.ac.uk

The cleavage of H_2 by frustrated Lewis pairs (FLPs) with an electron-deficient borane as the Lewis acid is now well established, with $B(C_6F_5)_3$ as the archetypal example.[1] Reactivities of FLPs with other small molecules such as CO_2 has also been reported.[2]

In order to further understand these processes, an essential requirement in developing applications for these systems; we've performed systematic studies on homo- and hetero-tri(aryl)boranes of the general form $B(C_6F_5)_x\{m,m\text{-}(CF_3)_2C_6H_3\}_y(C_6Cl_5)_z$.[3,4] Studies have included: the quantification of Lewis acidities using electrochemical and spectroscopic methods; probing their reactivities (together with various Lewis bases) with small molecules including H_2, H_2O and CO_2; and the electrochemical regeneration of the borane from the small molecule activation products.



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Exploiting a spin-crossover module in materials chemistry

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Transition metal complexes with a d^4-d^7 electron count can exist in a low-spin or high-spin form. Specific conditions can trigger a switch between these forms, known as spin-crossover. Iron(II) spin-crossover compounds have interesting properties, including changes in magnetic behaviour and colour during the transition.

Spin-crossover chemistry has developed significantly since its inception. It was initially considered an interesting area of coordination chemistry, however ongoing research has shown that it is of interest to multiple fields, including chemistry, physics, materials science, biochemistry and spectroscopy.[1] Research has diversified from the search for fundamental information about the behaviour of spin-crossover compounds and now extends to include different types of materials with a broad range of potential applications.[2]

Previous work in the group has developed a spin-crossover centre with optimised properties (Figure 1).[3] Using this structure as a starting point, spin-crossover polymers will be prepared. When a spin transition occurs, these polymers will act as reporter groups or as effectors to trigger a physical change in the material.

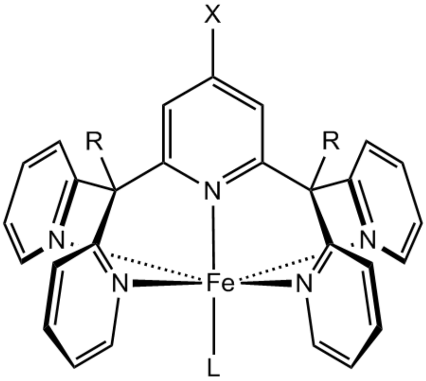

Figure 1 - The structure of the spin-crossover centre.

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Heterobimetallic Mg---Zr and Zn---Zr Hydrides: application to alkene and diene isomerisation

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The development of new heterobimetallic complexes has, in part, stemmed from the promise they hold in catalysis and synthesis. Co-location of two, or more, metals offers the opportunity not only to develop new fundamental reactivity but also fine tune selection events in known reactions.[1] Here we describe the preparation of **Mg•Zr** and **Zn•Zr**: well-defined heterobimetallic hydrides of M(II) and Zr(IV) (M = Mg, Zr).[2]

The **Mg•Zr** analogue is an active catalyst for the isomerisation of terminal alkenes to internal alkenes across one position with a strong bias for (*E*)-stereochemistry in the products. Control reactions with a series of heterobimetallic complexes under identical conditions demonstrate a pronounced heterobimetallic effect. At very low loadings, the parent Zr hydride, [Cp$_2$ZrH(μ-H)]$_2$, will also isomerise alkenes efficiently. Whilst **Mg•Zr** also isomerises cycloocta-1,5-diene to cycloocta-1,3-diene, the reaction of **Zn•Zr** with this substrate occurred with concomitant production of complex **1** (**Figure 1b**), an alkyne-bridged heterobimetallic with little precedent.[3] Calculations demonstrate that the contrathermodynamic isomerisation of the organic fragment is aptly compensated for by the large binding energy of the alkyne to the heterobimetallic. The reaction is again sensitive to the nature of the heterobimetallic and has only been observed for the zinc analogue of the series.

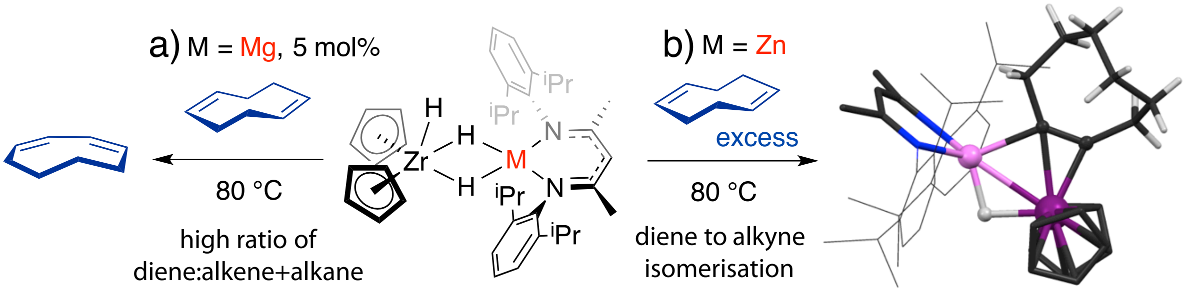

Figure 1 a) Isomerisation of terminal alkenes by **Mg•Zr** in benzene-d$_6$. b) synthesis from **Zn•Zr** and 1,5-COD and crystal structure of **1** (alkyne protons and hydride shown).

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Dicarbadodecaborane as a C_2 spacer: A Boron-rich JohnPhos

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Dicarbadodecaborane ($C_2B_{10}H_{12}$) is an electron-poor but highly thermally stable molecule which has found many uses in areas of chemistry such as supramolecular, liquid crystals, molecular imaging and ionic liquids.[1] One of the expanding areas is its use as a rigid and inert backbone supporting bidentate phosphine ligands.[2]

We have sought to employ carboranes in building scaffolds where the C_2 linker is used to link the donor atom to remote but important functionality. We drew inspiration from Buchwald-type ligands which are important in catalysis, and have been used extensively in C-N, C-C and C-O couplings.[3] The flanking ortho-phenyl is often credited as stabilising a transition metal complex through π-stacking interactions which leads to *both* steric and electronic stabilisation of the metal centre.

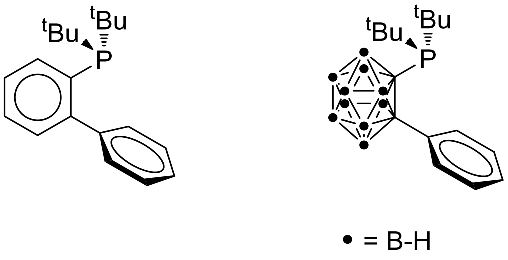

Figure 1: JohnPhos (left) and the *o*-carboranylphosphine analogue (right)

In this work we report a series of *o*-carboranylphosphines with a close structural relationship to Buchwald ligands (Figure 1) and investigate the steric and electronic properties in comparison to the celebrated biphenyl equivalents.

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Group 13 hydrides as catalysts for reduction of carbon dioxide.

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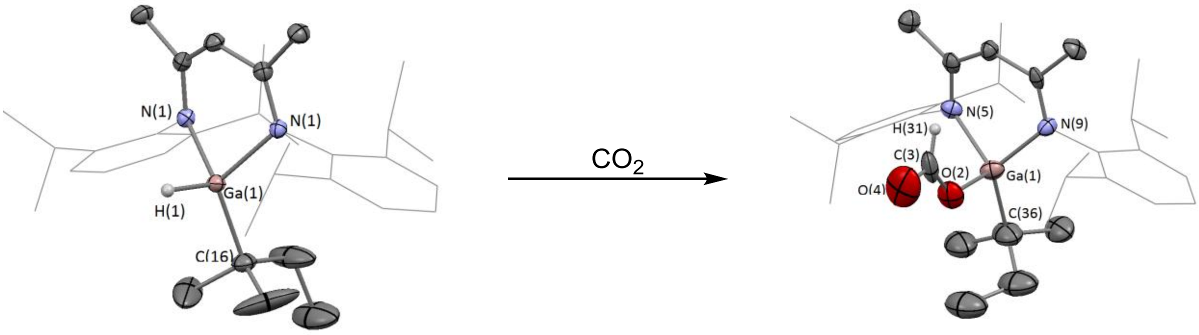
There has been much scientific focus in recent years on the catalytic reduction of CO_2. This is partly due to environmental factors, but also due to its inflammable, nontoxic and inexpensive nature as a potential C_1 chemical feedstock In particular, recent efforts have concentrated on the development of main group catalysts which are capable of effecting this transformation due to their reduced cost, toxicity and increased abundance relative to transition metals. A particularly successful method is the catalytic reduction of the C=O functionality of CO_2 by insertion into a metal hydride bond. There have been a variety of single site systems reported that are capable of accomplishing this, with one of the most efficient being a gallium hydride system, $Dipp_2NacNacGa(^tBu)H$, reported by the Aldridge group, which has attained turnover frequencies of up to 2.5 h^{-1} at 10 mol% and 60^oC.[1]

Given the observed propensity of Group 13 hydrides for such reactivity,[2] a variety of systems of the type $Dipp_2NacNacM(R)H$ ($[Dipp_2NacNac =\{N(Dipp)C(Me)\}_2CH)]$; M = Al, Ga) have been developed and their reactivity towards CO_2 probed. Through systematic investigation of both stoichiometric and catalytic reactivity, insight has been obtained into the effects that both the metal and the metal-bound R group have on (i) the insertion of CO_2 into the metal hydride bond and (ii) the metathetical regeneration of the hydride. As such, this understanding can used in the development of a single-site main group catalyst which has the potential to rival the catalytic activity of transition metal hydrides with respect to catalytic CO_2 reduction.



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Core-shell Ceramic Nanoparticles of Silica and Transition Metals Doped with Rare-earths for Luminescence Imaging of Prostate Cancer Cells

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Optical imaging for biological applications requires highly sensitive tools. Luminescence nanoparticles enable highly sensitive *in vivo* optical detection.[1,2] Here, we described a generation of fluorescent nanoparticles, based on group IV and V transition metal species doped with rare-earths elements (REEs) and silica. The luminescent core-shell nanostructures composed by rare-earth doped transition metal oxides (group IV and V) cores and encapsulated in a silica shell have been synthesized using a soft-processing approach based on hydrothermal synthesis and the Stober process. Synthetic conditions were optimised to achieve highly homogeneous core-shell structures with spherical morphology and fluorescent properties suitable for *in vitro* imaging. The nature of the cores control the luminescence response of the nanostructures. In this sense, both red and green fluorescence emissions have been obtained doping with different rare-earths. Moreover, the variation of the synthesis parameters enables to modify the size and dispersibility of the core-shell clusters. In order to evaluate the potential application of these compounds as luminescence probes for cell imaging, epi and fluorescence confocal microscopy studies were carried out in PC3 cell line. These results showed that such core-shell nanoparticles are taken-up by the cells and can be successfully used for *in vitro* bio-imaging and 3D rendering.

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Title: Time-Resolved Kinetic Studies on Porous Coordination Materials at Diamond Light Source I19 EH2

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A modified high-pressure capillary cell technique has been developed to facilitate kinetic experiments on single-crystal guest exchange in metal-organic frameworks. Iodine diffusion in the porous network materials $[(ZnI_2)_3(TPT)_2]\cdot(1)\cdot 1.67C_6H_{12}\cdot 0.75C_6H_5NO_2$ (TPT = 2,4,6-tris(4-pyridyl)triazine; 1 = triphenylene or perylene) was subsequently studied between 270 K and 300 K over a period of several hours. Crystal structure analysis suggests the potential formation of three partially occupied iodine guest positions in the triphenylene derivative, leading to the formation of two Zn-I…I-I triiodide moieties and one weakly interacting pore molecule.

Title: Spin-Crossover Nanoparticles for Sensors and Molecular Delivery

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Different metal complexes show reversible and repeatable thermal transition between low-spin and high-spin states. The high-spin state is stabilized relative to the low-spin under the influence of external perturbation. It is usually triggered by temperature, pressure or laser irradiation. The spin-crossover (SCO) event is accompanied by changes in a material's colour, magnetic moment and electrical resistance, which leads to potential applications in display devices. That makes it important to design bistable materials with predictable switching properties.[1,2]

The combination of gold nanoparticles or quantum dots with spin crossover complexes is expected to present interesting applications. Here it is planned to use iron(II) complexes as an effector to trigger quenching of nanoparticle fluorescence (**Figure 1**).[3,4] In other words, the aim is to obtain fluorescent sensing at the nanoscale. Furthermore, SCO photo-switching could be produced thanks to strong plasmon absorption of gold nanoparticles at visible region as a light-harvesting antennae feature. That combination could work in a molecular delivery-type application.[5,6]

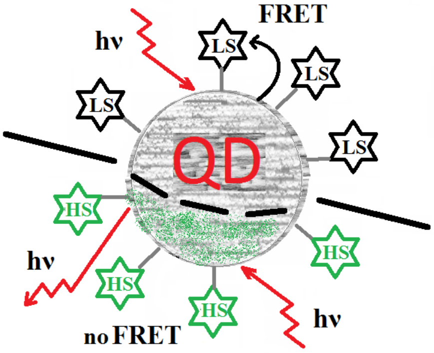

Figure 1. Quantum dot luminescence switching throughout SCO phenomena

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Computational Modelling Techniques for the Design of Solvent Extractants for Metals

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Computational techniques have proven highly valuable in the design of reagents for solvent extraction of metals,[1] both as a means of screening potential extractants before experimental work is undertaken, and as an analytical tool to probe the modes of action of established solvent extractants.

We have successfully applied geometry optimisation and molecular dynamics methods to the design of solvent extractants targeting a variety of metals in acidic media. An example is the recently-reported development of a novel class of amidoamine and amidoether extractants for platinum (Figure 1),[2] for which DFT formation energy calculations were able to reproduce and rationalise experimentally-observed trends in extractant strength, as well as the observed selectivity of these reagents for platinum chloridometalates over chloride. Classical and quantum mechanical molecular dynamics methods also show significant promise as means of investigating the mode of action of solvent extractants, particularly where the formation of supramolecular assemblies (such as reverse micelles) plays an important role in the extraction process.[3]

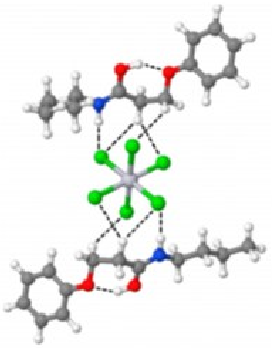

Figure 1: Assembly formed by outer-sphere complexation of $PtCl_6^{2-}$ anion by amidoether extractants, with key hydrogen-bonding interactions shown as dotted lines.[2]

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Ruthenium (II) complexes as catalysts for transfer hydrogenation of coenzyme NAD$^+$

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‡Department of Physics, University of Kaiserslautern, Erwin-Schrödinger-Str. 46, 67663
Kaiserslautern, Germany.

ABSTRACT: A series of neutral pseudo-octahedral Ru^{II} complexes of the type [(*p-cym*)Ru(N, N')Cl] where N, N' is N-(2-aminoethyl)-4-toluenesulfonamide (TsEn) (**1**)[1], N-(2-(methylamino)ethyl) 4-toluenesulfonamide (TsEnMe) (**2**), N-(2-(dimethylamino)ethyl)-4-toluenesulfonamide (TsEnMe$_2$) (**3**), N-(2-(ethylamino)ethyl)-4-toluenesulfonamide (TsEnEt) (**4**), N-(2-(benzylamino) ethyl)-4-toluenesulfonamide (TsEnBz) (**5**), N-(2-((4-fluorobenzyl)amino)ethyl)-4-toluene sulphonamide (4-F-BzTsEn) (**6**) and N-(2-((naphthalen-2-ylmethyl)amino)ethyl)-4-toluene sulphonamide (TsEnNaphth) (**7**) were synthesized and fully characterized including the X-ray crystal structure of **4**. NAD$^+$ can be reduced regioselectively to 1, 4-NADH using these complexes as catalysts and sodium formate as hydride source under relevant biological conditions. The turnover frequencies (TOFs) when the substituent of the ligand is varied increases in the order: (**1**) < (**2**) < (**4**) < (**5**), with the maximum TOF of 7.68 h^{-1}, and the yield of 1, 4-NADH increase from 77% to 95%. The effect of pH and formate concentration on the reaction rates of the complex [(*p-cym*)Ru(TsEnBz)Cl] were determined. Determination of the anti-proliferative activity of the complexes against A2780 human ovarian cancer cells gave IC$_{50}$ values from 1 to 31 μM, with the most potent complex [(*p-cym*)Ru(TsEnBz)Cl] (IC$_{50}$ = 1.0±0.1μM), which has similar activity to cisplatin. This work highlights the strong dependence of catalytic activity and selectivity on the steric hindrance by the substituents on the chelating ligand of these complexes. The sterically demanding functional groups on the terminal N in these complexes can also modulate the reaction rate as well as the selectivity, and reaches a maximum when the substituent is benzyl but decreases when the substituent becomes bulkier (4-F-BzTsEn (**6**) and TsEnNaphth (**7**)).

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Enhancing a Cobalt *Bis*-Iminopyridine Hydrogen Evolution Catalyst with an Axially Coordinating Proton Relay

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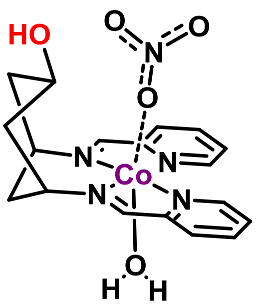
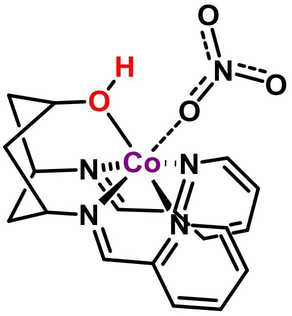
We are developing bio-inspired modular catalytic systems using *bis*-iminopyridine derivatives of 1,3,5-substituted cyclohexanes as ligands. 1st row transition metal complexes of related N_4 chelators are competent electrocatalysts for H_2 production at moderate pH,[2] but in our case, the rigid cyclohexane backbone allows us to fix the location of a pendant base[3] (proton relay) in relation to the metal, depending on the geometry of the ligand.



$Co[DDOP](NO_3)_2$ (1)



$Co[DDOPi](NO_3)_2$ (2)

Here we will focus on two cobalt complexes, where the cyclohexane based ligand enforces a hydroxyl 'relay' group proximal (*cis* geometry, **1**) or distal (*trans* geometry, **2**) to the cobalt centre. These show very different acid dependence in the hydrogen evolution reaction. In the proximal case, an X-ray crystal structure reveals that the –OH group binds to the axial coordination site of Co^{II}. At low acetic acid concentrations (in MeCN), catalysis of proton reduction by proximal complex **1** occurs at significantly higher overpotential (750 mV) than for distal complex **2** (400 mV), consistent with coordinated –OH making a more electron rich cobalt centre. At high acid concentrations the overpotential of **1** becomes comparable to that of **2**, and **1** is also significantly faster. This suggests a competition between –OH coordination and protonation that, at the right acid concentration, may both increase the basicity of the metal centre and provide a pendant proton relay.

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Rechargeable Xantphos-based Rhodium Complexes in Amine-borane Dehydropolymerisation

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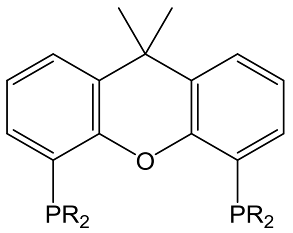
The dehydrogenation of amine-boranes ($R_3N\cdot BH_3$) for the preparation of polyaminoboranes $(R_2N\cdot BH_2)_n$ is a relatively unexplored field with vast potential considering the global polymer market is worth US$500 billion.[1] We have previously had considerable success using the $[Rh(Xantphos)]^+$ fragment (Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) to catalyse the dehydropolymerisation of $MeH_2N\cdot BH_3$.[2] Importantly, this system provides control over polymer molecular weight, by variation of the solvent and of the presence of H_2, enabling production of poly(methylaminoborane) with M_n values of 2,800 – 52,200 g mol^{-1}.

We have extended this work to study alkyl Xantphos derivatives (^{i}Pr and ^{t}Bu) to determine the effect of the ligand on the dehydropolymerisation of amine-boranes. The cationic complexes $[Rh(H)_2(\kappa^1\text{-}H_3B\cdot NMe_3)(^{iPr}Xantphos)][BAr^F_4]$ and $[Rh(H)_2(^{tBu}Xantphos)][BAr^F_4]$ have been prepared as sources of “$Rh(^{R}Xantphos)^{+}$”, and their activity in the dehydropolymerisation of $MeH_2N\cdot BH_3$ is reported. Additionally, preliminary investigations into the activity of neutral complexes $[RhH(^{R}Xantphos)]$ are presented.[3]

$$MeH_2N\cdot BH_3 \xrightarrow[-\,H_2]{\substack{[Rh]\text{ precatalyst}\\ 0.2\text{ - }1\text{ mol\%}}} \left(MeHN\cdot BH_2\right)_n$$



^{R}Xantphos

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Hybrid phosphasalen/salen initiators for the ring-opening polymerisation of *rac*-lactide

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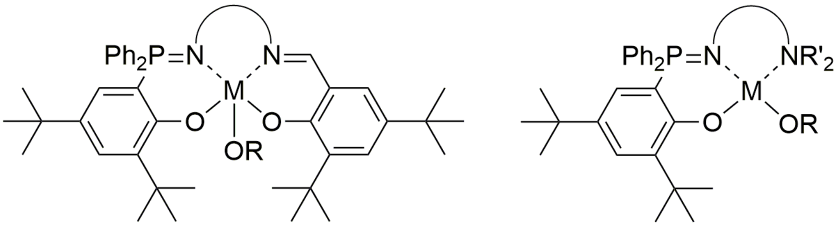
Polylactide (PLA) is a bio-derived aliphatic polyester made from lactic acid and has suitable properties as a ‘green’ replacement for polyolefins, whilst also being compostable/degradable. The ring-opening polymerisation (ROP) can be initiated by Lewis acidic metal alkoxides, which control features such as the rate, molecular weight and stereochemistry of the polymer chain. Stereoselective initiators are of particular interest as the tacticity of the resulting PLA allows tuning of chemical-physical properties such as melting temperature/degradation rate. This work applies new types of phosphasalen ligands and more industrially viable metals as initiators for *rac*-lactide ROP.



M = Y, In, Al
R = Et, *t*Bu

M = Zn, Mg
R' = Alkyl

Figure 1 General structure of the phosphasalen ligand systems.

This presentation will describe the synthesis and characterisation of novel half-phosphasalen and mixed phosphasalen/salen ligands and the coordination chemistry with Zn(II), Mg(II), Group 13 and Group 3 metals (Figure 1). Polymerisation kinetics, multi-nuclear NMR studies and structure-activity relationships have been conducted in order to allow comparisons with known phosphasalen and salen initiators. The hybrid nature of the mixed phosphasalen/salen ligands allows easier access to metal centres which have been previously hard to synthesise within the phosphasalen or salen motifs. As a result, this new ligand class offers exciting opportunities, for lactide, other cyclic lactones and carbon dioxide/epoxide co-polymerisation, investigated here for the first time.

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Catalytic dehydrocoupling of amine and phosphine-boranes using low coordinate Fe(II) complexes

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Main group polymers are of interest as functional materials, due to their more unusual properties when compared to traditional polymers, such as acting as surface modifiers.[1] Manners *et al.* have previously shown that dehydrocoupling (DHC) of amine-boranes (ABs) and phosphine-boranes (PBs) is possible with Fe or Rh catalysts.[2-4] It has also been shown that with select substrates it is possible to form rings or polymeric chains (**Fig. 1a**).[1, 4, 5]

Recent work by our group has shown that DHC between phosphines is possible using a cheap and easily synthesised low coordinate Fe(II) complex (**Fig. 1b**).[6] Due to the success of this catalyst system we have investigated its activity in the DHC of ABs and PBs.

Optimisation of the catalyst has been undertaken along with varying the structure of the AB and PB substrates. Preliminary mechanistic studies are underway and these results will also be presented.

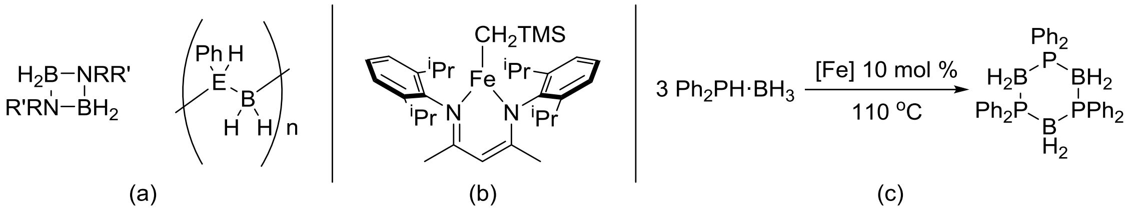

Fig. 1 a) Possible DHC products (E = N or P). **b)** The optimised catalyst for DHC. **c)** Typical PB DHC reaction using the catalyst shown in Fig. 1b (C_6D_6, 110 °C, 72 h, 100% conversion).

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Title: Accelerated discovery of two new structure types in a complex inorganic phase field

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In this work we present the use of computational “probe” structures to accelerate the exploration of the unreported Y-Sr-Ca-Ga-O phase field, with the results guiding subsequent synthesis. Probe structures are created using a Monte-Carlo implementation of the Extended Module Materials Assembly (EMMA) method, with density functional theory and force fields used to calculate energies. Once probe structures have been calculated, the convex hull (including known materials) of the phase field was then constructed and the energies of the probe structures compared to the hull.

These calculations indicate the presence of a low energy region, where the energies of probe structures were comparable to known binary and ternary oxides, indicating an area of the phase field where new compounds may be found. Synthesis was then focused around this region. Single crystal and powder crystallography reveal the existence of two new oxide materials: a 4 x 4 x 4 triclinic supercell of $A_{1-x}B_{1-y}O_{3-z}$ Perovskite and a layered $A_{2.5}B_3O_7$ Melilite material (fig 1), with both materials containing novel co-ordination environments.

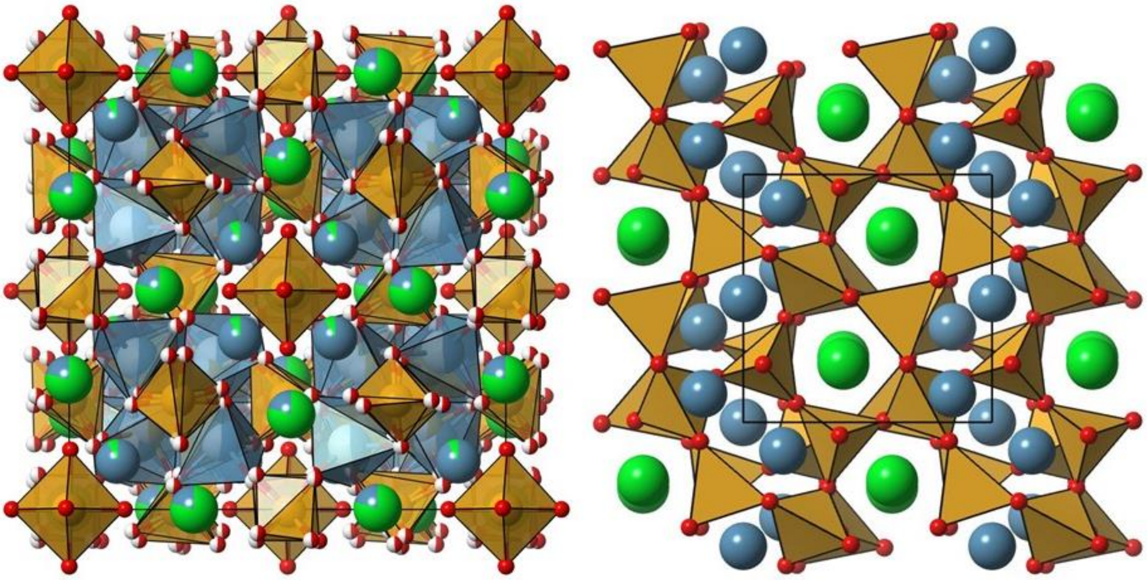

Fig1. The two new structures discovered within this work: Perovskite related (left) and Melilite related (right).

Synthesis and characterisation of novel fluorescent vanadyl complexes and their evaluation as CBP inhibitors and intracellular probes.

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Cysteine based phosphatases are a diverse family of enzymes that act to remove the phosphate group from proteins, phosphatidylinositols and other biomolecules. These enzyme act to counteract the effects of kinases and included in this family are protein tyrosine phosphatases (PTPs), inositol phosphatases and dual specificity phosphatases[1]. Due to the wide range of roles they play in the cell the CBPs are implicated in many diseases and therefore it is of interest to develop compounds to study these enzymes[2]. In recent years, a variety of inhibitors have been reported including small molecules, peptides and metal complexes[3]. One such family of compounds are the vanadium complexes. Both vanadium(IV) and vanadium(V) have been shown to inhibit a range of CBPs with and potency and selectivity that can be tuned by varying the ligand and the oxidation state of the vanadium centre[4,5]. One subset of interest is the vanadium complexes utilising picolinic acid and its derivatives as ligands. These complexes have an inhibition range against phosphatases of low nM to high µM depending on the derivative of picolinic acid used and the enzyme studied[6,7].

Based on this knowledge we have synthesised a small selection of novel fluorescent vanadyl complexes based on the picolinic acid motif as novel phosphatase inhibitors. The ligands were developed using 5-hydroxypicolininc acid as the starting point to allow for incorporation of an amine-functionalised spacer providing a handle for incorporation of fluorescent dansyl group. Due to a change in fluorescence intensity of the dansyl-labelled ligand on forming a vanadyl complex, the fluorophore could also be used to determine whether the complex remains intact in the presence of the enzyme. The fluorophore would also be to study the interaction of the vanadyl complexes with the enzymes, and to investigate cell uptake. The complexes showed good inhibition properties against the PTPs investigated in a range similar to that of free vanadyl. From the fluorescence and binding data obtained it appears that the vanadyl complexes are stable in the presence of the enzymes and under assay conditions. Preliminary data also indicates that the complexes are taken up into cells.

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Solvothermal Synthesis of Doped Mixed Metal Gallium Spinels

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The spinel oxides are a large and important family of oxides known for their interesting electronic and magnetic properties.

We present the results regarding our investigation into two solvothermal synthetic routes for doping cobalt and aluminium into γ-Ga_2O_3. The synthesis of the former involves doping cobalt directly into preformed spinel γ-Ga_2O_3 using an aminoalcohol to yield $CoGa_2O_4$. This material has a composition typical of the spinel family in that it contains M^{2+} and M^{3+}. $CoGa_2O_4$ is largely an inverse spinel.
The synthesis of the aluminium doped gallium oxide requires the use of diols and yields a mixed metal defective spinel since both metals are present as M^{3+}. As such this oxide contains cation vacancies in its structure.

These materials have been characterized by a variety of techniques including XRD, in situ thermodiffractometry, electron microscopy, Raman spectroscopy, XANES and the magnetic properties of $CoGa_2O_4$ have been measured on a SQUID. Solid state NMR of a 30% aluminium doped γ-Ga_2O_3 indicates the tetrahedral preference of the aluminium cation.

TEM shows the morphology of $CoGa_2O_4$ (Figure 1) whilst EELS mapping shows a homogenous distribution of the cobalt within the γ-Ga_2O_3 spinel. The aluminium doped gallium oxide has nanosized particles ~5-10 nm. This is in agreement with the poorly crystalline nature of the material observed by XRD and the high (BET) surface area measured for this oxide (~250 $m^2\ g^{-1}$).

A new mixed gallium aluminium oxyhydroxide with the formula $Ga_{5-x}Al_xO_7(OH)$ prepared from prolonged reaction of the γ-$Ga_{2-x}Al_xO_3$ synthesis has been properly characterised for the first time. In-situ thermodiffractometry reveals that this material is stable up to 560 °C at which point it then decomposes into a disordered ε-$Ga_{2-x}Al_xO_3$ polymorph.

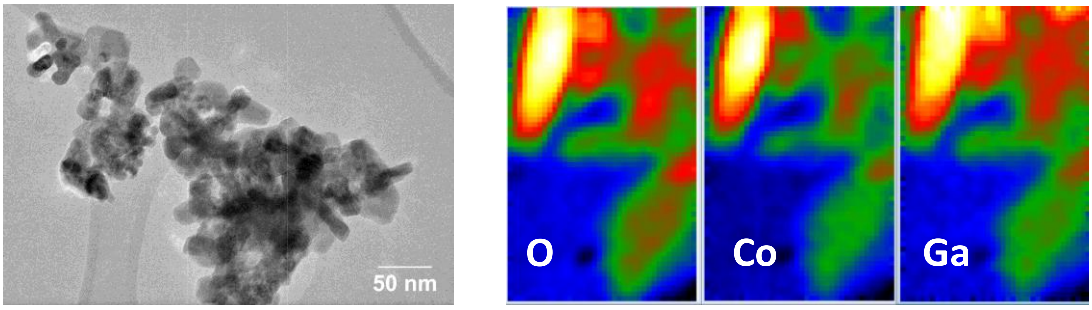

Figure 1 TEM images of *(left)* $CoGa_2O_4$ spinel and *(right)* EELS mapping of $CoGa_2O_4$

Investigations into novel aromatic mono(thiosemicarbazonato) metal complexes and their applications in molecular imaging

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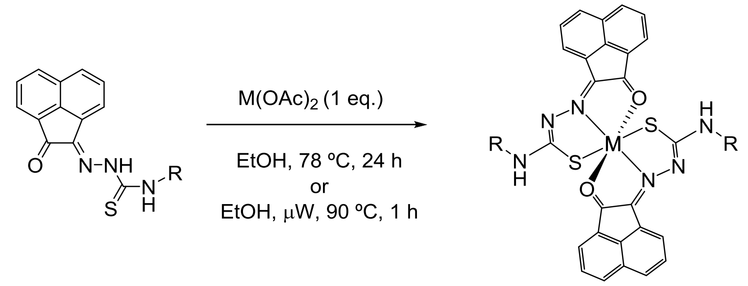
The application of bis(thiosemicarbazonato) complexes with acenaphthenequinone backbone has been a field of interest due to their inherent fluorescence, capability to accommodate different metals and possibility to be radiolabelled yielding multimodal imaging probes.[1] Some derivatives in this family have proven to be hypoxia selective *in vitro*.[2] However, the application of the ligands to the synthesis of mono(thiosemicarbazonato) metal complexes have been less explored.[3] We report on the synthesis and potential applications of new mono(thiosemicarbazone) ligands and mono(thiosemicarbazonato) complexes with several different aromatic backbones and incorporating metals of interest to molecular imaging such as Zn(II), Cu(II) or Ga(III). The synthesis of the ligands has been found to be greatly improved (in terms of time and conversion yields) by the application of microwave-assisted heating. This procedure was also attempted in the synthesis of Zn(II), Cu(II) and Ga(III) complexes. These as-prepared species were fully characterised by standard spectroscopic methods and structural investigated by X-ray diffraction crystallography. Their abilities to act as optical imaging probes were evaluated in living PC-3 cells.



The authors would like to acknowledge Dr P. Waghorn, Dr R. Arrowsmith and all the Master students of the group who contributed to the initial stages of this work since 2005. We also thank the Marie Curie ITN PROSENSE and EC ERC-Consolidator grant O2SENSE for funding.

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Title: Generating reductive stress in cancer cells using osmium transfer hydrogenation catalysts

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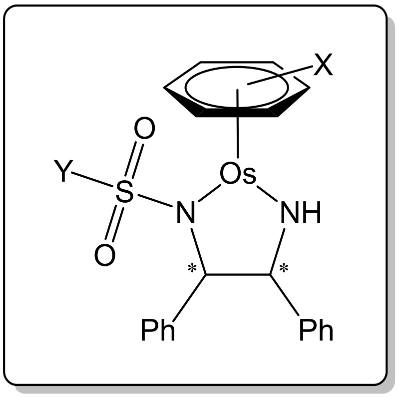
The catalytic properties of many metal complexes are well understood,[1-3] and the potential role of catalysts in medicine is a rapidly-expanding field of research. Catalytic therapies would facilitate lower dosages, with a view to circumventing side effects.[4] We have synthesised a series of active osmium diamine 16-electron catalysts, of general formula [Os(arene)(diamine)] capable of transfer hydrogenation in formic acid / triethylamine.[5]

The complexes can carry out transfer hydrogenation reactions at higher rates than existing, structurally-similar ruthenium(II) Noyori-type systems. We have investigated the anticancer activity of such complexes towards a series of human cancer cell lines and catalysis inside cells by co-administration with sodium formate as a hydride source. Importantly, human ovarian cancer cells were significantly more sensitive to the reductive environment generated by the catalysts in the presence of sodium formate, than healthy fibroblasts. The generation of reductive stress by combination therapy is a new mechanism of anticancer activity that might be useful for combatting resistance to current cancer therapies and for increasing selectivity for cancerous cells.



We thank the ERC (grant no. 247450, 324594), Science City (AWM and ERDF), WCPRS and Bruker Daltonics (Studentship for J.P.C.C.), and EPSRC for support, as well as EC COST Action CM1105 for stimulating discussions.

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Organometallic Anticancer Complexes Incorporating Phosphinate Ligands

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A myriad of pseudo octahedral complexes have been studied as anticancer agents. One example, Dyson's RAPTA-C complex[1] contains the monodentate, phosphorus-based 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane ligand. This complex has shown excellent antimetastatic effects and stimulated our interest in developing new phosphorus-containing anticancer metal complexes.

We have synthesised a series of 25 *N*,*O*-bidentate phosphorus-based ligand and their metal-arene complexes (Figure 1). The metal-phosphinate bonds are stable under aqueous conditions but metal-halide hydrolysis occurs rapidly to form the aqua adduct. NMR spectroscopy was used to measure the pK_a of bound H_2O and several trends are observed based on the nature of the metal and pyridyl substituent.

Anticancer activity was measured against the H460 human non-small cell lung carcinoma cell line, with iridium iodide complexes displaying the greatest toxicity. Binding studies with selective amino acids and nucleobases provide a potential explanation of the toxicity of these metal complexes.[2]

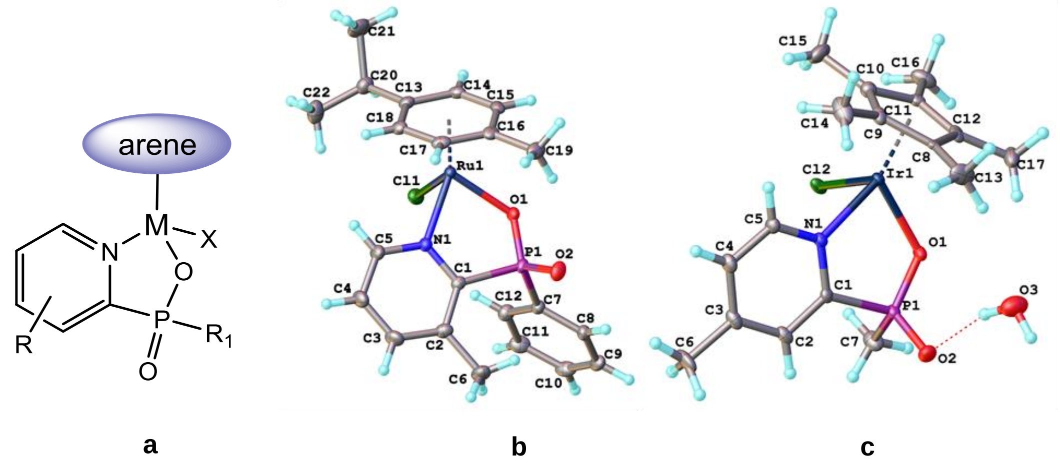

Figure 1. Generic compound structure, R = H, Me, NH_2, OCD_3 and R_1 = Me, Ph (**a**). Crystal structures of ruthenium(II) (**b**) and iridium(III) (**c**) compounds.

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Coordination chemistry and redox activity of a bis(iminothienyl) compound

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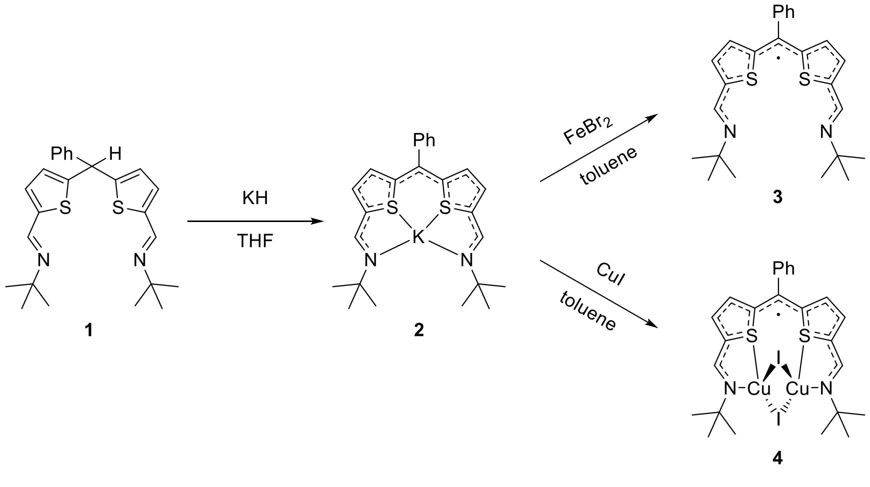
Transition-metal complexes containing sulfur ligands are essential components of redox-active metalloenzymes.[1] While transition-metal sulfide and thiolate complexes are well known, ligands built on aromatic sulfur-containing heterocycles such as thiophene and their σ-coordinated thiophene complexes are very rare.[2]

Inspired by recent results on transition-metal complexes of donor-expanded dipyrrins,[3] we are investigating the chemistry of the related dithienyl scaffold **1** (Scheme 1). In this work, we show that deprotonation of the methine bridge of **1** leads to the fully conjugated aromatic anion **2** whose thiophene moieties act as σ-donors to K thanks to their partial thiolate character. Unexpectedly, upon reaction of **2** with $FeBr_2$ simple salt-metathesis does not occur, instead forming the stable, neutral radical **3** in high yield. Alternatively, reaction between **2** and CuI forms the dicopper radical complex $Cu_2I_2(L^\bullet)$ **4**, as confirmed by crystallographic and spectroscopic data.



Scheme 1. Reactions of the bis(iminothienyl) compound **1**.

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Photoluminescent Gold(III) Thiolates: The Importance of Supramolecular Interactions

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In contrast to thiolates of gold(I), those of gold(III) are less common and are reported as weakly or non-emissive. We have found that Au(III) thiolates stabilised by C^N^C pincer ligands are highly photoluminescent, and that this luminescence is controlled by supramolecular packing, even in solution.

We have synthesised gold(III) thiolates stabilised by the cyclometallated 2,6-diphenylpyrazine ligand. This ligand gives strong photoluminescence even when the analogous pyridine C^N^C pincers do not.[1]

Surprisingly, dual photo-emission pathways are observed: some complexes emit from conventional ^{3}IL triplet states based on the pincer ligands (green), while others give red emission, which is enhanced by aggregation, Figure 1. X-ray crystal structures coupled with ^{1}H and diffusion NMR studies suggest that only certain types of π-stacking leads to the red emission. Two polymorphs with different π-stacking interactions are observed in the solid state, this results in an on/off type luminescence behaviour. It is also possible to switch between these two emission pathways in solution by controlling the conditions. The reasons for this intriguing behaviour will be discussed.

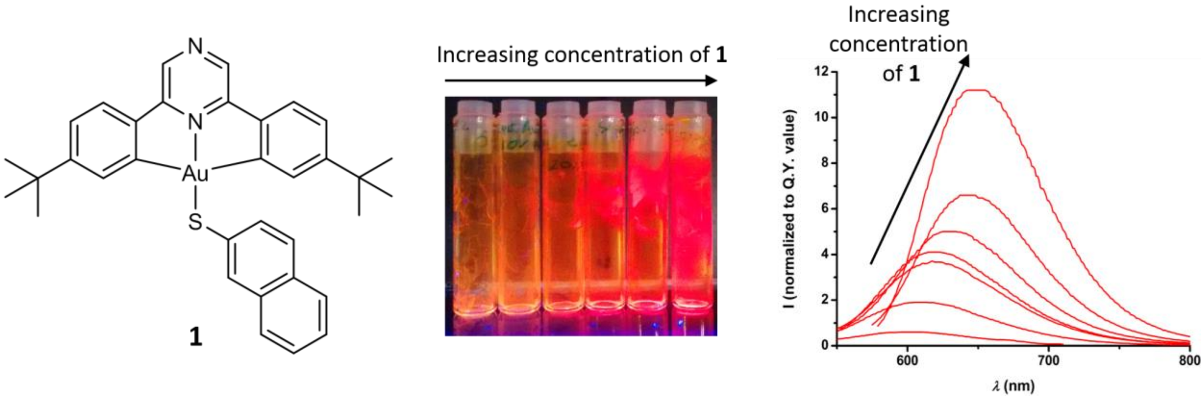

Figure 1, The aggregation enhanced emission of complex **1** in a polymer matrix.

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Stoichiometric and catalytic C-F bond activation by *trans*-dihydride ruthenium N-heterocyclic carbene complexes

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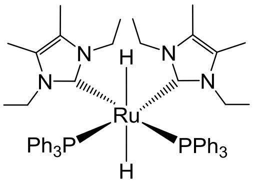
In light of our previous work on catalytic hydrodefluorination (HDF) of fluorinated aromatics using ruthenium N-heterocyclic carbene (NHC) dihydride precursors and a well understood mechanism involving nucleophilic attack by metal-bound hydride ligands investigated with DFT calculations [1], we now present our recent findings on stoichiometric and catalytic C-F activation by Ru NHC complexes containing increasingly more nucleophilic hydride ligands. The mixed carbene-phosphine species, $Ru(IEt_2Me_2)_2(PPh_3)_2H_2$ (**1**), proved to be a viable precursor for HDF, converting C_6F_6 to a mixture of tri, di and monofluorobenzenes over several days at 363 K (10 mol% catalyst) using Et_3SiH as the reductant [2]. The employment of the tetra-carbene species, $Ru(IMe_4)_4H_2$ (**2**) and $Ru(IMe_2)_4H_2$ (**3**), allowed for milder reaction conditions, affording selective formation of 1,2,4,5-tetrafluorobenzene within significantly shorter times (minutes-hours) at 298 K (5 mol% catalyst). Increasing the temperature to 363 K brought about two subsequent HDF steps yielding 1,4-difluorobenzene as the sole product of the reaction.



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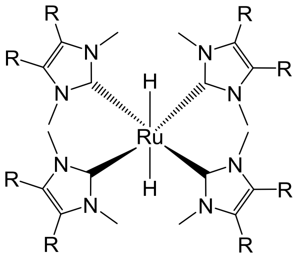
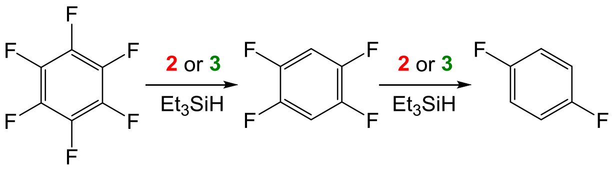


2 R = Me
3 R = H



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Coordinating Natural Chromophores to *De Novo* Peptide Structures Designed for Light Harvesting

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Natural light harvesting complexes make use of α-helical coiled coil proteins as structural building blocks. Utilising a recently designed trimer that spontaneously assembles in the presence of lanthanide ions, we are probing the behaviour of chlorophylls that interact with the external face of the superhelix.[1]

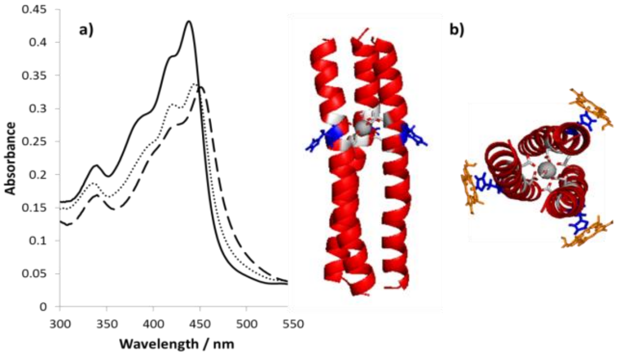

Figure 1: a) The Soret band from the absorption profile of chlorophyll a (solid line) and the influence of the addition of histidine (dotted line) and the histidine containing trimer (dashed line). b) The cartoon representation of the coiled coil trimer.

The peptide has been synthesised and each coil was decorated with a histidine residue on the external face adjacent to the lanthanide binding site ***(Fig. 1b)***, the lone pair from the imidazole has been shown to direct chlorophyll coordination via ligation to the central magnesium ion.[2] Having extracted natural pigments from spinach leaves and isolated chlorophylls we have observed that the absorption profile shifts when either histidine or peptide is added to the pigments ***(Fig. 1a)***.

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

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Metal-Organic Structures in the Cambridge Structural Database (CSD)

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Crystallographers have been responsible for some remarkable scientific feats, demonstrated by the multitude of Nobel prizes awarded and the penetration of structural studies in the fields of chemistry and biology.

The crystallographic community can also claim a remarkable accomplishment: every structure ever published is available for all. These individual structures each tell their own story, but the stories told by the collection of structures are truly fascinating.

The Cambridge Structural Database (CSD) is one of the collections of crystallographic data - it contains all the organic and metal-organic structures ever published. Thanks to the exemplary approach to data sharing by the crystallographic community, it now contains over 800,000 entries and the rate of growth continues to increase. Amazingly over 57% of these entries are metal-organic and these structures have been rising steadily since the first metal-organic structure with 3D coordinates was determined back in 1937.

As we look forward to the next fifty years of the Cambridge Structural Database, this poster will explore how the field of metal-organic crystallography has evolved and highlight trends in structural chemistry, from authorship to publication patterns, from crystallographic statistics to seminal structures. Most importantly, we will celebrate the remarkable contribution of crystallographers from the metal-organic community.

Towards Radical Pnictogen and Chalcogen Bridged Lanthanide Single Molecule Magnets

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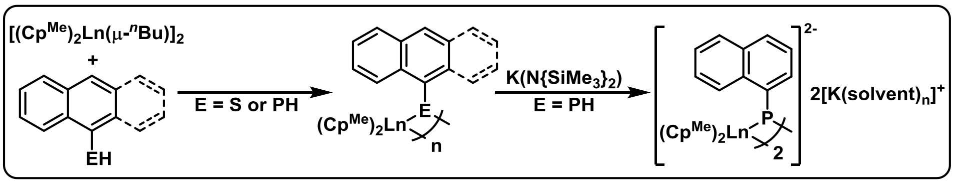
Molecules that possess an energy barrier to reversal of their magnetic moment are *single-molecule magnets (SMMs)*.[1] SMMs can display magnetic hysteresis that is purely molecular in origin, leading to unique quantum effects that create opportunities for fundamental research, and for constructing novel nano-scale devices with applications in molecular spintronics and, potentially, quantum computing.[2] The big challenge is to address the temperature regime in which SMMs function. The highest temperature at which an SMM displays hysteresis is the *blocking temperature (T*B*)* however most SMMs only display hysteresis at liquid helium temperatures.[3] Room-temperature SMMs are the ultimate goal, however systems that function at 77 K, the temperature at which nitrogen liquefies, would be transformative.

Recent work in our group demonstrated that polymetallic lanthanide complexes containing bridging heavy P-block ligands of the type $[RE]^-$ (where R = mesityl and E = P(H), As(H) or Se) show relatively impressive effective energy barriers (U_{eff} = 210 – 301 cm^{-1}) but only show butterfly-shaped hysteresis loops up to 4.2 – 5.4 K.[4]

Applying an external magnetic field can suppress QTM by lifting the degeneracy of the *mJ* doublets and moving them out of resonance.[5] An alternative way of achieving the same outcome is to use radical ligands that generate an ‘internal’ field through strong direct exchange coupling. The resulting *exchange bias* gives a chemical route to preventing QTM, leading to much higher blocking temperatures. This effect has been observed for the $[N_2]^{3-}$ radical bridged complex $[Tb_2(N\{SiMe_3\})_4(\mu\text{-}N_2)(THF)_2]^-$ which shows hysteresis up to 14K.[6]



Our current research in this area is focused on using bridging heavy P-block ligands containing redox active polyaromatic substituents (e.g. naphthyl and anthracenyl) to enable the synthesis of radical bridged analogues of our previously reported systems and examine subsequent changes in the magnetic behaviour. The work presented here describes our progress towards these aims.

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Title: Alkaline Earth Organohydroborate Complexes for the Ring-Opening Polymerisation of *rac*-Lactide

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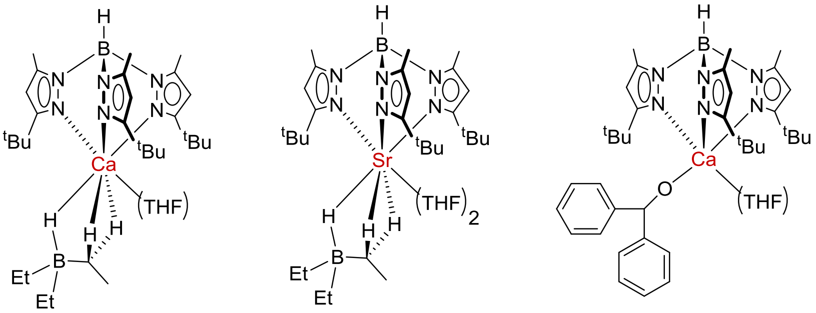
Polymers from renewable resources such as polylactide (PLA) have gained great attraction from both commercial and academic perspectives because of their environmental advantages and various applications ranging from drug delivery to packaging materials. The preparation of well-characterised metal complexes employed as ring-opening polymerisation (ROP) catalysts has been a focus in both industrial and academic research.[1] The hydride transfer and reducing potential of metal organohydroborate complexes allows them to be candidates for *rac*-LA ROP initiators. To date, no alkaline earth organohydroborate complexes have been established as ROP initiators.[2] Here we report mechanistic investigations and polymerisation studies of the ROP of *rac*-LA using alkaline earth organohydroborate complexes ($HBEt_3$) supported by 3-methyl,5-*tert*-butyl tris(pyrazolyl)hydroborate ligands ($Tp^{tBu,Me}$) (**1-2,** Figure 1)[3] and the synthesis, structure and ROP of *rac*-LA capability of a new calcium alkoxide complex, $(Tp^{tBu,Me})Ca(OCHPh_2)(THF)$ derived from the hydride transfer between $(Tp^{tBu,Me})Ca(HBEt_3)(THF)$ and benzophenone (**3,** Figure 1).



1 **2** **3**

Figure 1: New alkaline earth initiators (**1** – **3**) for the ROP of *rac*-LA.

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One-Pot Synthesis of Benzo-1,2-Diphospholides.

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The relationship between phosphorus and carbon chemistry has been realised for many years. Phosphorus relatives of classical organic ligands (like cyclopentadienide, Cp^-) in which carbon atoms have been substituted for phosphorus atoms are important classes of organometallic ligands, which are relevant to catalysis. Often, however, a limit to applying the phosphorus counterparts is the low-yielding and circuitous nature of their synthesis. A case in point is the 1,2-diphospholide ligand framework, an important analogue of the cyclopentadienyl ligand which has only been obtained from multistep syntheses.

A high-yielding and direct route to 1,2-diphospholides is reported using a simple one-pot approach. Treatment of ArPHM (M = Li, K; Ar = mesityl, *o*-tolyl, (2-methyl-4-methoxy)phenyl, (*o*-ethyl)phenyl) with $Sb(NMe_2)_3$ in the presence of a base generates the corresponding 1,2-diphospholide anion. These are some of the first 1,2-diphospholide analogues of indenyl.[1,2] Structural and NMR spectroscopic investigations suggest that this unique reaction, involves double-C H deprotonation of an ortho-CH_3 group, and rearrangement of cyclic phosphanes.

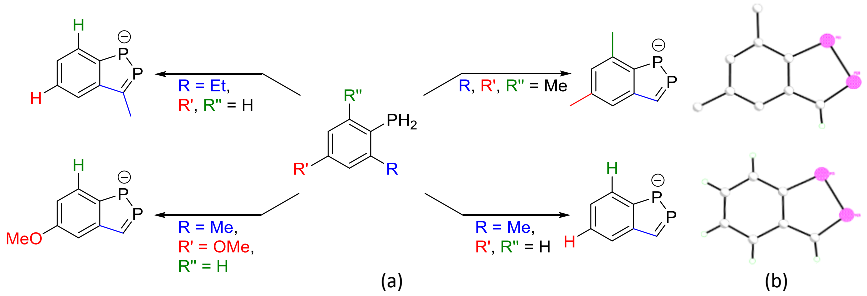

Figure 1. *(a) Scheme showing the range of 1,2-diphospholides that have been synthesised. (b) X-ray structures of the 4,6-dimethyl- and tetrahydro- benzo-1,2-diphospholides, Li(TMEDA)$_2$ counter ion omitted.*

Pre-functionalisation of the starting phosphine allows for the production of an array of these compounds, demonstrating the diversity of this synthetic method. The ability to tune the electronic and steric properties prior to formation of the 1,2-diphospholide framework can both preserve yield and minimise purification steps.

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Amino-Functionalized Beta-Diketiminate Ligands: Synthesis, Characterization and Co-ordination Chemistry with Group 13/14 Elements

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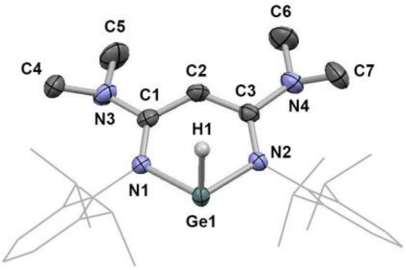
Since its appearance in 1968, the β-diketiminate ligand family (or "Nacnac", $\{N(R)C(R')\}_2CH$) has been widely employed to stabilize reactive low-valent Main Group and Transition Metal compounds for small-molecule activation[1]. These uses owe much to the sterically demanding and electron rich nature of these ligands. Generally speaking, Nacnac ligands have been employed which feature bulky (sometimes perfluorinated) alkyl/aryl R and R' groups. Although the use of alternative π-donating R' groups (such as dimethylamino-) was initially discussed nearly five decades ago[2], such systems have not been explored in any depth. With this in mind, we are exploring the chemistry of Main Group metal complexes featuring this class of Me_2N-functionalized β-diketiminate ligand ("NnacnacH"), in particular with a view to probing the role of the amino group in modulating electronic structure and metal-centred reactivity.

Spectroscopic and crystallographic evidence indicates that, while NacnacH pro-ligands typically adopt an amino-imine configuration, NnacnacH systems prefer the alternative non-conjugated diimine structure. Complexation studies reveal that the $NnacnacAlMe_2$ systems can be accessed via direct metalation of the pro-ligands with $AlMe_3$, while NnacnacEH systems (E = Ge, Sn) can be obtained in a facile manner via lithiation of the neutral pro-ligand and quenching with ECl_2, followed by chloride/hydride metathesis with a superhydride source. Structural studies (NMR spectroscopy, X-ray crystallography) confirm the more electron-rich nature of these new Nnacnac ligands compared to classic Nacnac systems.



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Selective Recovery of Gold from Secondary Sources: Solvent Extraction and Supramolecular Chemistry

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Waste electrical and electronic equipment (WEEE) such as mobile phones contain a variety of metals,[1] often in higher concentrations than is found in primary mineral deposits.[2] Efficient recovery and recycling of these metals from secondary sources would reduce the environmental impact of energy and emission intensive mining processes.[3]

The recovery of gold, the most valuable metal in mobile phones to recycle, is plagued by hazardous processing conditions, including cyanide leaching and volatile solvents.[4] We report the use of a new simple, non-toxic, recyclable solvent extractant[5] for the selective separation of gold from a mixture of metals typically found in secondary source feeds (Figure 1).

The reagent exploits supramolecular chemistry to extract gold into an organic phase, showing remarkable selectivity over other metals that are present in higher concentrations, and with marked advantages over existing commercial reagents.

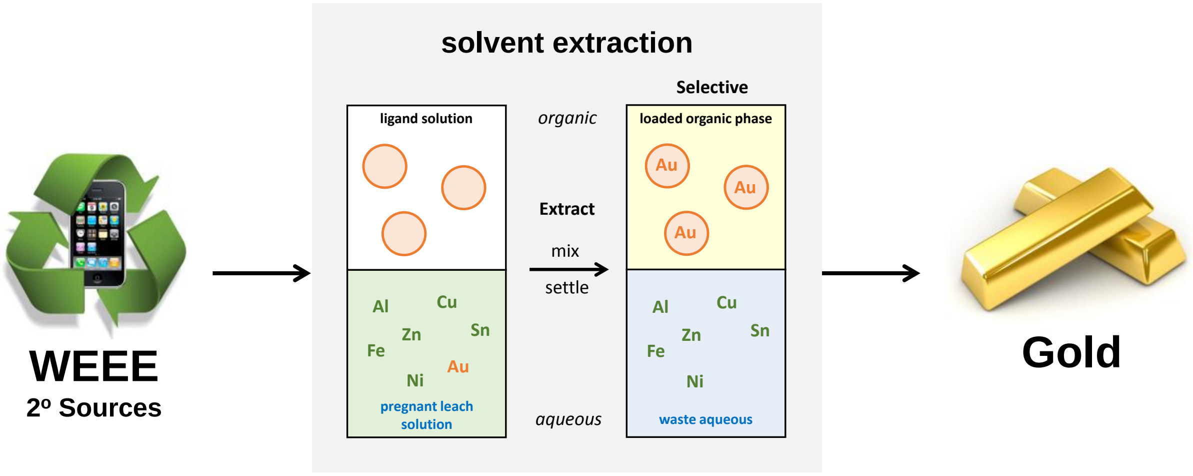

Figure 1 Recovery of gold from secondary (WEEE) sources using solvent extraction.

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Synthesis, radiolabelling and *in vitro* validation of ^{99m}Tc amidocyclam-triphenylphosphonium (TPP) conjugate for mitochondria targeted cardiac imaging by SPECT

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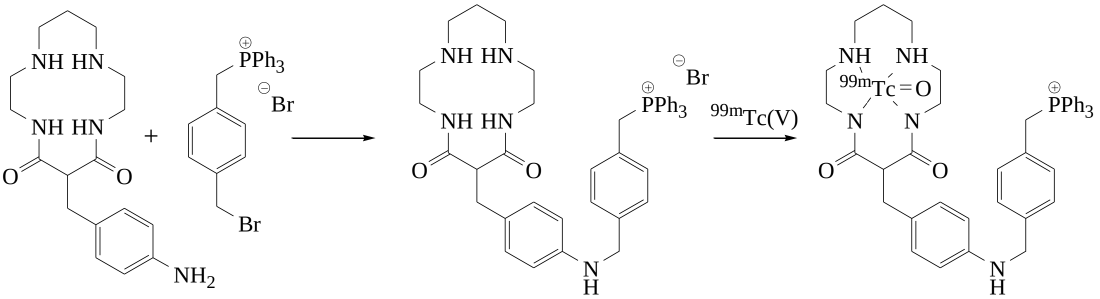
Single photon emission computed tomography (SPECT) is the most clinically available nuclear medicine imaging technique. In general it uses longer lived radioisotopes than positron emission tomography, such as iodine-123 ($t_{1/2}$ = 13 h) and 131 ($t_{1/2}$ = 13 days), indium-111 ($t_{1/2}$ = 67 h) and, most importantly, technetium-99m (^{99m}Tc, $t_{1/2}$ = 6 h), which is produced in a generator and can be easily incorporated into a tracer by a radiopharmacy technician using a standardised kit.

^{99m}Tc-MIBI and ^{99m}Tc-Tetrofosmin, the most used tracers in cardiac imaging, are perfusion agents and, therefore, are not cardiac tissue specific. Delocalised lipophilic cations, such as triphenylphosphonium (TPP), are known to cross cell membranes and concentrate in mitochondria. Thus, a TPP based radiotracer should be capable of selectively imaging viable cardiac tissue/cells rich in mitochondria.

Previously described ^{99m}Tc-Mito10-MAG39[1], containing an acyclic ^{99m}Tc chelating moiety linked to TPP via a long alkyl chain, did not show any cardiac uptake. More recently investigated derivatives[2], containing the ^{99m}Tc chelating moiety linked to TPP via a *p*-tolyl linker, have shown a moderate cell/mitochondria uptake. However, they have not been evaluated *in vivo* for cardiac uptake. Here we describe synthesis, radiolabelling and *in vitro* validation of a novel ^{99m}Tc tracer, containing a C-functionalised amidocyclam chelator linked to a TPP moiety via 4-aminobenzyl/*p*-tolyl spacers.



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Glycidyl phosphines – A versatile synthon for the synthesis of chiral mixed donor ligands

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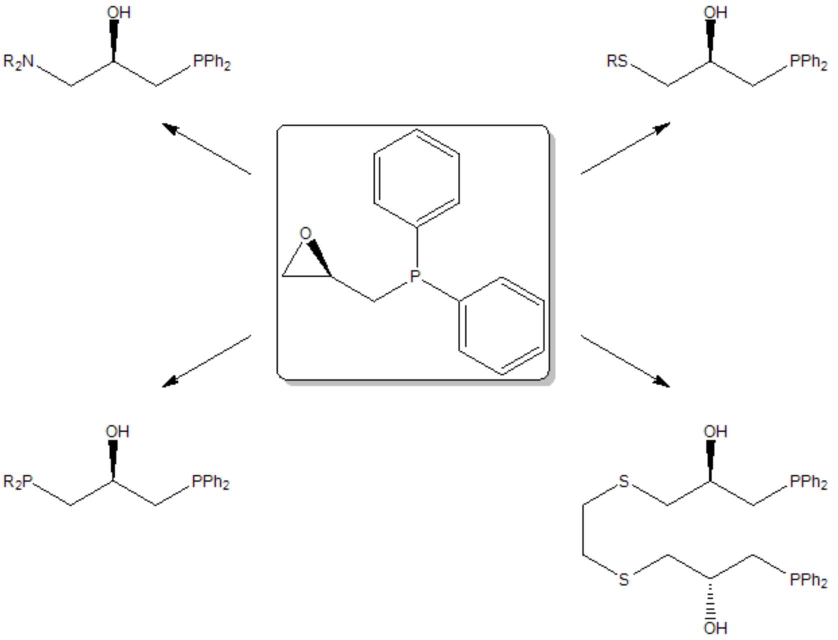
A glycidyl phosphine species has proved to be an effective synthon in the synthesis of numerous multidentate, mixed donor ligands. Reactions with appropriate nucleophiles result in the formation of NOP, SOP and POP tripodal ligands. Reactions are carried out on a multigram scale in a one-pot procedure by sequential nucleophilic attack on epichlorohydrin. This route affords easy access to a number of chiral α-phosphino alcohols. Ligands combining both hard (N, O) and soft (P, S) donors are of interest due to their recent use in homogeneous catalysis where hemilabile ligands have been shown to outperform traditional ligand sets in numerous applications.[1]



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Controlled hydrothermal synthesis of Bi-doped ceria

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Ceria-based catalysts are extensively used, principally due to their redox properties.[1] The interest is in the doping of ceria with metals of different oxidations states/atomic radii in order to alter these properties.[2] Nanocrystalline $Ce_{0.5}Bi_{0.5}O_{2-\delta}$ were successfully synthesised via hydrothermal synthesis at 240°C using four different combinations of chemical reagents: Ce^{3+}/Bi^{3+}, Ce^{4+}/Bi^{3+}, Ce^{4+}/Bi^{5+} and Ce^{3+}/Bi^{5+}. Various analytical techniques were used to determine how the alterations in precursors affect the structural and functional characteristics of the products in order to determine the underlying formation mechanisms that influence the crystal structure, particle growth and particle size. XRD analysis confirms that the materials exhibit the cubic fluorite structure ($Fm\bar{3}m$). Qualitatively the XRD pattern shows that the materials produced from Ce^{3+} have a higher crystallite size in comparison to the materials produced by Ce^{4+}. This is confirmed further by Scherrer and Williamson-Hall plot analyses which estimates the sizes of the particles to be within the 30 to 400 nm region. TEM was used to view the morphology of the materials and it can be observed that all four samples are composed of aggregated and uniform nanocrystals with crystallite sizes ranging in the few 100 nm region. Preliminary in-situ hydrothermal XANES measurement were successfully able to monitor the interchange between oxidation states of cerium ($Ce^{3+} \rightarrow Ce^{4+}$) which occurs predominately before the temperature of reaction exceeds 100°C.

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Synthesis, Characterization and Antibacterial Screening of Novel Copper (II) Complexes from *m*-Aminobenzoic Acid Schiff Bases

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Abstract

Antibacterial resistance is one of the growing problems that make treating infections difficult. Schiff bases have shown promising antibacterial activities. Schiff bases are a class of versatile ligands with variable coordination modes. The coordination of these ligands with transition metal ions has resulted in formation of complexes with interesting biological and photochemical properties. In this study, six copper (II) complexes of aminobenzoic acid Schiff bases derived from *m*-aminobenzoic acid and substituted benzaldehydes were synthesized and characterized using elemental analysis, infrared spectroscopy (IR), electronic absorption spectroscopy and magnetic susceptibility measurements. Results indicate that all metal complexes had a 1:2 metal ligand ratio with magnetic moments characteristic of octahedral and tetrahedral geometry around the metal ion. The Schiff bases and their metal complexes were screened for *in-vitro* antibacterial activities against 6 human pathogenic bacteria. The complexes exhibited higher antibacterial activity than the free ligands. The results show that the investigated metal complexes can be an alternative therapeutic option for bacterial resistance treatment.

Keyword: Aminobenzoic acid, Antibacterial, Metal complexes, Photochemical, Schiff bases.

Photochemically promoted C–H bond activation of fluoroarenes using an iridium(I) pincer complex

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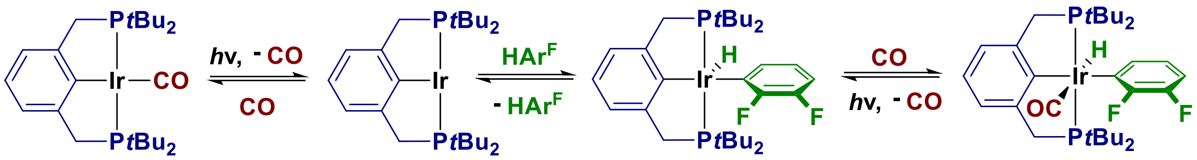
The selective oxidative addition of the C–H bonds of fluorinated arenes is an important objective in organometallic chemistry and catalysis.[1] Iridium pincer complexes are notable examples of systems capable of effecting this reaction.[2] Additionally, some of us have previously reported the reversible and regioselective C–H bond activation of fluoroarenes using a transient 14 VE iridium(I) complex bearing NHC ancillary ligands.[3]

Herein we present our work employing an iridium(I)-carbonyl complex supported with an anionic PCP pincer ligand. Photochemically induced dissociation of the carbonyl ligand leads to selective *ortho*-C–H bond activation of a range of fluoroarenes, with the resulting complexes exhibiting rotameric preference for the fluorine atoms to be *syn* to carbonyl. The energetics and mechanism have been interrogated computationally using TD-DFT, leading to the identification of key electronic transitions associated with carbonyl dissociation.



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pπ-pπ interactions in diphosphatetrylenes.

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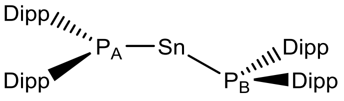
The low oxidation state chemistry of group 14 is dominated by *N*-heterocyclic carbenes while there are significantly fewer examples of divalent systems of the heavier elements. In addition, there are only a small number of low oxidation state group 14 compounds containing phosphide ligands[1] and even fewer monomeric diphosphatetrylenes[2-4] [$E(PR_2)_2$, E = C, Si, Ge, Sn, Pb] compared to the corresponding amides. This is due to the high energy barrier to inversion at the phosphorus centre, preventing efficient pπ-pπ interactions to the tetrel centre. Recently, the Izod group isolated the first germylene, $Ge(PDipp_2)_2$, stabilised by efficient pπ-pπ interactions from a planar phosphorus by exploiting the sterically demanding $[Dipp_2P]^-$ ligand [Dipp = 2,6-diisopropylphenyl].[4]



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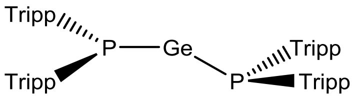
We have now used this ligand system to synthesise the analogous stannylene. $Sn(PDipp_2)_2$ (**1**) crystallises as discrete monomers with two distinct phosphorus centres, P(A) trigonal planar [sum of angles = 355°] and P(B) trigonal pyramidal [sum of angles = 311°].

To further investigate the how the ligand affects the pπ-pπ interactions, tetrylenes using Tripp as substituents were synthesised [Tripp = 2,4,6-triisopropylphenyl]. The Ge(II) compound $Ge(PTripp_2)_2$ (**2**) was found to crystallise as a methylcyclohexane solvate that had an isostructural skeleton with the previously prepared germylene $Ge(PDipp_2)_2$.

The Sn(II) compound $Sn(PTripp_2)_2$ (**3**) crystallised as distinct monomers that are not stabilised by pπ-pπ interactions as seen in the previously prepared stannylene $Sn(PDipp_2)_2$ (**1**). Both phosphorus centres are trigonal pyramidal and are not orientated to donate into the vacant tin orbital.



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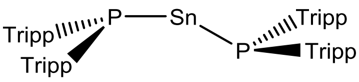

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The role of ligand symmetry in spin-labile mononuclear Mn(III) complexes

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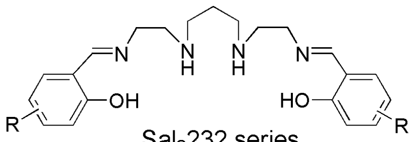
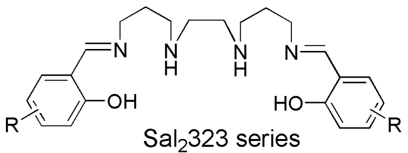
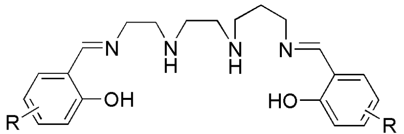
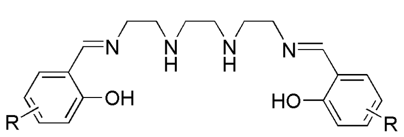
Mononuclear Mn(III) complexes are highly prized in catalysis,[1] particularly in water oxidation[2] and increasingly in molecular magnetism.[3] In our work we have concentrated on the ability of mononuclear Mn(III) complexes to exist in both high spin (HS) and low spin (LS) forms when co-ordinated by flexible hexadentate Schiff-base ligands of the Sal_2323 series,[4] and many of these also show spin crossover.[5,6]


Sal_2232 series
7C backbone


Sal_2323 series
8C backbone


Sal_2223 series
7C backbone


Sal_2222 series
6C backbone

We are now interested in breaking the symmetry in the parent ligand and investigating the effect this has on the resulting Mn(III) complexes in terms of geometric constraint, orbital populations, magnetic properties and reactivity. We present here structural, magnetic and spectroscopic data on several Mn(III) complexes with 7 carbon backbone ligands which show a range of spin states and unusual reactivity.

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Title: Copper and silver nanoparticles for sustainable development.

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Due to rapid industrialization and urbanization, our environment is undergoing great damage and a large amount of hazardous and unwanted chemicals, gases or substances are released. It is our need to learn about the secrets that are present in Nature and its products which lead to advancements in the synthesis of nanoparticles. [1]

We present in this work the cheap, environmentally friendly green synthesis of silver nanoparticle as antimicrobials mediated by Central African plants extracts from *Corchorus olitorus*, *Ipomoea batatas*, [2] *Ricinodendron heudelotii*, *Megaphrynium macrostarchyum* and *Gnetum bucholzianum*. We highlight the nanoparticles’ effectiveness in the conservation of fruit tomato and consider their potential as biocides in a wide range of products in food industry.

The synthesis of new copper nanoparticles from *Musanga cecropioides* and halide stabilization gives good activity for the biodegradation of textile organics such as methylene blue or orange red, consideration of their use in water treatment and purification will be presented. These syntheses have been optimized and monitored by ultraviolet-visible spectroscopy. X-ray diffraction analysis enables phase and crystallinity identification. Nanoparticles between 30 and 60 nm can be synthesized. We present the first screening of potential preservatives of fruit crops.

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Solid-gas reactions and polymorphism of copper halide compounds

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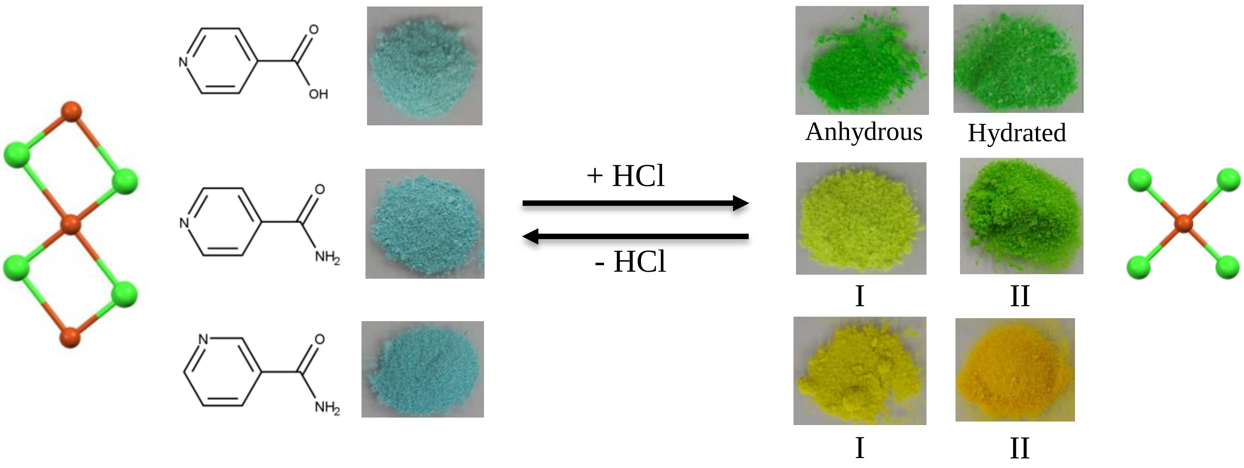
The reaction of many pyridine based ligands with copper (II) halides results in highly predictable polymeric compounds, usually blue in colour, consisting of chains of edge-sharing $CuCl_4$ rhombi decorated by the pyridyl ligand. Brammer *et al.* discovered that this type of compound reacts readily with gaseous hydrogen chloride to form the corresponding, usually yellow, cuprate ($[CuCl_4]^{2-}$), which once left exposed to the air loses HCl to return to the polymeric structure. [1] Additionally, Brammer *et al.* also discovered that in some cases prolonged exposure to the acidic conditions can lead to the formation of additional polymorphs of the cuprate salt. [2] A similar investigation is presented here with pyridine-4-carboxylic acid (INAc) and pyridine-3/4-carboxamide (NAm, INAm). All three adducts display the polymeric structure mentioned above with predictable hydrogen bonding arrangements, and all react reversibly with damp HCl gas though the cuprate salts of INAm and NAm display polymorphism.



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Tuneability of Azole-appended cavitands – from carbenes to cubes

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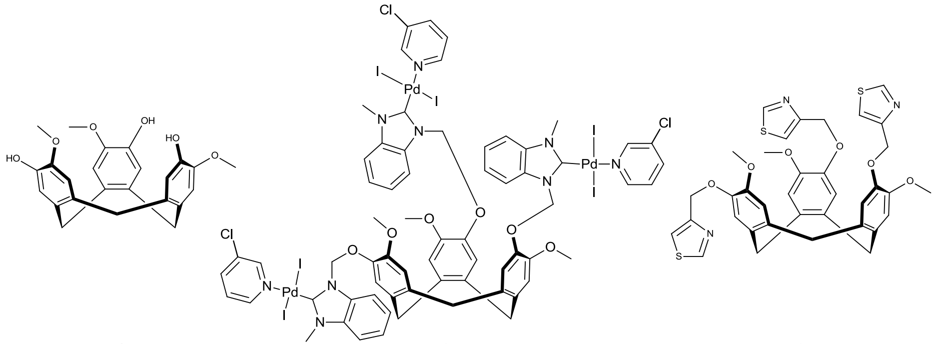
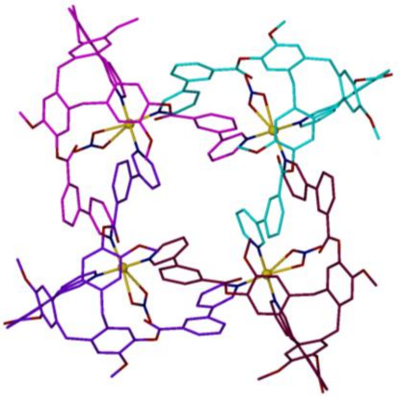
Cavitands are bowl-shaped molecules which are commonly utilised in host-guest chemistry. In our research, cyclotriguaiacylene (CTG) (**1**) based cavitands are used. The highly tuneable hydroxyl groups on the upper-rim can be functionalised with azole groups for the preparation of metallo-supramolecular assemblies with unique topologies. A previous example is $[Pd_4L_4]$ Solomon cube **4**.[1] Additionally; the azole can be further functionalised for the synthesis of metal NHC complexes.



1 **2** **3**

Flexible calix[4]arene appended NHCs have shown to be excellent ligands for Pd(II) and Ni(II) complexes in cross-coupling reactions.[2] Trimetallic complex **2** has been prepared as a potential organometallic catalyst, whilst the self-assembly of novel ligand **3** with two silver salts gave chirally resolved, isostrucutral $[Ag_{12}L_8]^{12+}$ metallo-cubes (**5**).



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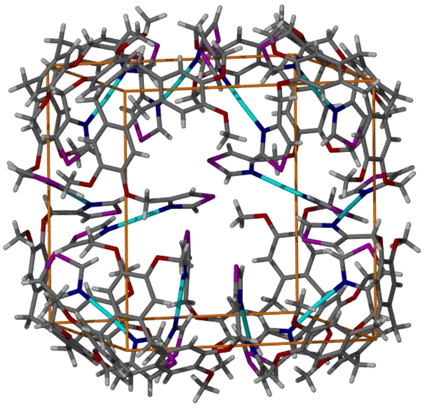

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Liquid Crystalline Spin-Crossover Complexes

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Spin-crossover complexes undergo a change in magnetic moment upon application of heat, light or some other physical stimulus. This corresponds to a rearrangement of electrons at a transition metal centre, and is often accompanied by a colour change. The spin-crossover phenomenon is well-known, and is usually studied in the solid state where crystal packing interactions between molecules can lead to cooperative (abrupt and hysteretic) switching properties. Such materials have been used in prototype display and memory devices and in nanoscience, and are also good testbeds for new theories and techniques in crystal engineering and solid state science.

Spin-crossover switches in soft materials (polymers, gels and liquid crystals) have also been prepared, but are much less well-developed. In particular, while several groups have produced mesogenic spin-crossover compounds, only a handful of these are liquid crystalline around room temperature (most known examples only work above room temperature, and require heating).[1] The goal of my work is to produce new liquid crystals that are chemically robust, and undergo spin-crossover switching at room temperature.[2] We will also seek to introduce extra functionality such as fluorescence into the compounds, to produce liquid crystals showing thermochromic emission.

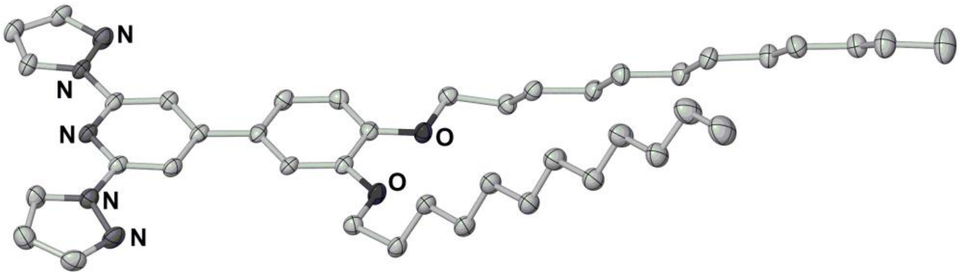

Figure A potentially mesogenic ligand produced in the Halcrow group.

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Iron Catalysed Hydrophosphination: A comparative study of two highly active μ-oxo species

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Phosphines are of key importance as ligands for transition metal catalysis. Hydrophosphination reactions are most commonly catalysed by Group 10 (Ni, Pd, Pt), Group 3 (Y) and lanthanide (La, Sm, Yb) metal salts reactions and provide access to these desirable products through a 100% atom-economic pathway.[1]

Building on work of Gaumont et. al. using iron salts for hydrophosphination, a particularly appealing approach due to the vast abundance and low toxicity of the metal, we have shown that a simple iron(salen)oxo compound is able to catalyse the hydrophosphination of diphenylphosphine with a variety of functionalised styrenes at room temperature and loading of 0.5 mol%.[2,3a,b] We will further describe the catalytically active iron(porphyrin)oxo complex which, under similar conditions, shows a greater level of reactivity with more challenging alkene substrates. Increasing to a 5 mol% loading, we have also demonstrated the hydrophosphination of phenylphosphine – a reaction mediated by only a handful of metals - can take place with relative ease.[4a,b,c]

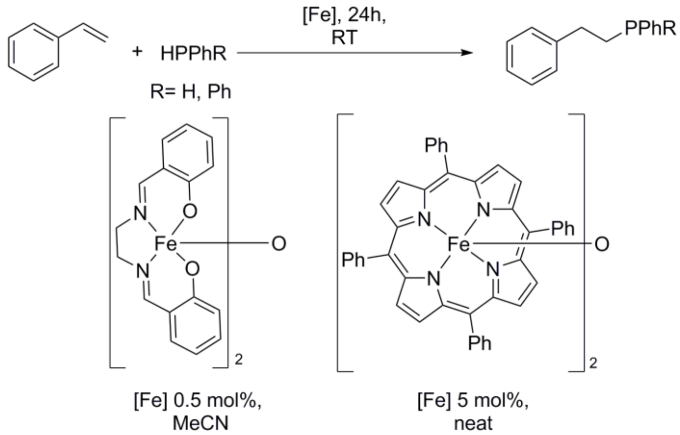

Figure 1 Hydrophosphination reactions with Fe μ-oxo species

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Tantalum hydrazide complexes supported by a trianionic ligand

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The chemistry of metal-nitrogen multiple bonds has been an ongoing area of extensive interest. The study of imido and hydrazido complexes of Group 4 and 6 metals is well established and many applications have been reported.[1] The synthesis, properties and applications of complexes featuring high valence metals supported by tridentate trianionic pincer ligands have been explored over the past decade.[2]

In this presentation we report the attempted synthesis of the first Group 5 hydrazido complex with a tridentate trianionic ligand and the investigation of its reactivity with small molecules. Synthetic routes involving 2,2´-bis(trimethylsilylamino)diphenylamine[3], 1,1,1-tris(trimethylsilylaminomethyl)ethane and 1,1,1-tris(isopropylaminomethyl)ethane[4] are reported (Fig. 1).

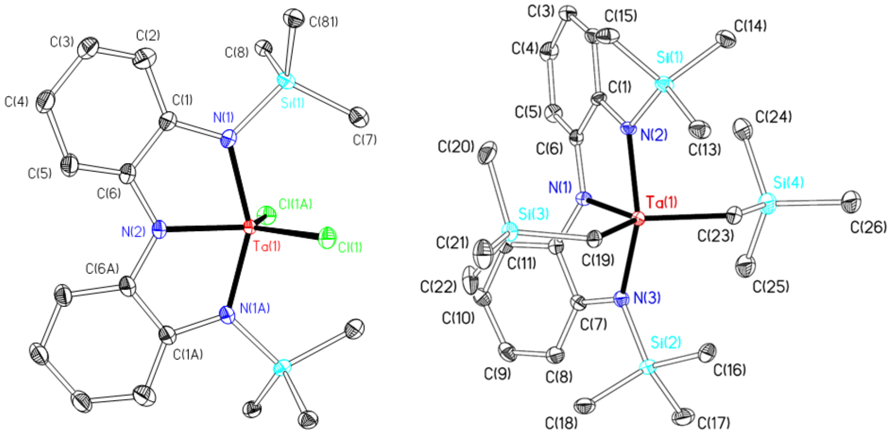

Figure 1. Tantalum complexes supported by tridentate, trianionic ligands.

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Highly Active and Selective New Heterodinuclear Polymerization Catalysts

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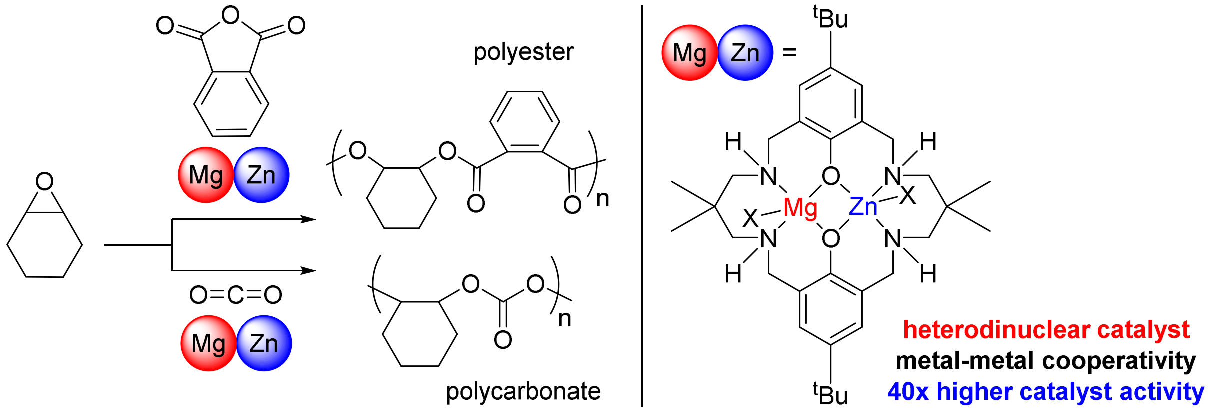
Heterometallic cooperativity is an attractive means to enhance catalyst activity and selectivity. Although homodinuclear catalysts have good precedent for the copolymerization of epoxides with CO_2 or anhydrides, pure heterodinuclear catalysts are so far unknown in this field. Detailed kinetic and mechanistic studies have suggested that a heterodinuclear catalyst could exhibit enhanced activity, by operating through a cooperative metal-metal mechanism.[1]



heterodinuclear catalyst
metal-metal cooperativity
40x higher catalyst activity

Fig. 1 Heterodinuclear catalysts for the copolymerization of epoxides with CO_2 or anhydrides

Herein, we report the first examples of heterodinuclear homogeneous catalysts known for CO_2-epoxide copolymerization (Fig.1). These catalysts show significantly improved performance metrics compared to the homodinuclear analogues, either alone or in combination.[2] The presentation will describe the syntheses and characterizations of the new heterodinuclear catalysts, with a particular focus towards magnesium and zinc containing compounds. Application of these catalysts for the efficient and well controlled copolymerization of CO_2-cyclohexene oxide will be described. Notably, such hybrid catalyst systems have shown double the activity of homodinuclear magnesium analogues, which themselves are amongst the most active catalysts for CO_2-epoxide copolymerization.

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Organometallic ruthenium and osmium thiosemicarbazone complexes

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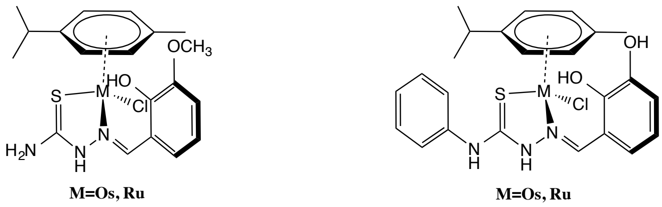
The development of more efficient anticancer drugs with better selectivity but less toxic side effects is currently an area of intense research in bioinorganic chemistry.

Half-sandwich organometallic Ru^{2+} complexes have demonstrated potential as anticancer agents.[1] The analogous Os^{2+} complexes are relatively unexplored, perhaps due to the reputation of osmium as being highly toxic and kinetically inert. Nevertheless, several half sandwich "piano stool" osmium(II) complexes have emerged as promising prodrugs in vitro with no cross-resistance to cis-platin.[2]

In general organo-ruthenium and organo-osmium half-sandwich complexes have similar structures but different rates of reaction[3]. The aim of the present study is to evaluate the chemical reactivity as well as stability in different aqueous media of two ruthenium-arene thiosemicarbazone complexes in comparison to the heavier congener Os^{2+} (Figure 1),



M=Os, Ru **M=Os, Ru**

Figure 1. Structures of Os and Ru thiosemicarbazone complexes studied here.

Two differently substituted thiosemicarbazones ligands, a class of compounds known for their pharmacological activity, that previous tests have demonstrated to be the most cytotoxic against Mia Paca-2 cancer cells, were chosen.

All compounds were fully characterized by elemental analysis, NMR, MS and single crystal X-ray crystallography. The stability of the complexes was evaluated by ^{1}H-NMR in different solvents such as methanol and acetone; also DMSO and H_2O-DMSO(10%) were employed to mimic the biological tests conditions.

Acknowledgements.

We thank Fondazione Cariparma for support. We also thank Dr. Guy Clarkson for XRD analyses.

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Coordination Complexes of Plutonium (IV) and (VI) with Imidodiphosphinate Ligands

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There is a need to address the environmental problems the nuclear age has brought about, including the identification of radiotoxic actinide ions, their oxidation state and chemical form with regards to decommissioning, separation and environmental remediation. In this regard, we have previously shown that the TPIP (tetraphenylimidophosphinate) ligand stabilises neptunium and uranium exclusively in the +VI oxidation states.[1,2] Moreover, TPIP is able to form oligomeric species of uranyl(VI) ions assembled by Lewis acid base adducts (cation-cation interactions (CCIs)) that can be fingerprinted by emission spectroscopy and evidence suggests a mixed metal cation-cation aggregate occurs in mixtures of neptunyl(VI) and uranyl(VI). The study of CCIs is extremely important in evaluating and developing new separation processes based on new and simplified versions of the PUREX process.

Here we report the coordination chemistry of TPIP and its related counterpart with peripheral *iso*-propyl groups (TIPIP) with Pu(IV) and Pu(VI). The reaction of TPIP and TIPIP with Pu(VI) and TPIP with Pu(IV) yielded single crystals, XRD studies of which showed the Pu(VI) complexes to be $[PuO_2(HTIPIP)_2(H_2O)][NO_3]_2$, a rare example of bidentate HTIPIP coordination, and $[PuO_2(TPIP)(HTPIP)(NO_3)]$, with monodentate HTPIP coordination, and the Pu(IV) complex to be $[Pu(TPIP)_3(NO_3)]$. Attempts to displace $[NO_3^-]$ using coordinating solvents or Ph_3PO to form plutonyl(VI) cation-cation aggregates were unsuccessful. The complexes have been analysed by MS, UV-vis, IR, Raman and NMR spectroscopy that gave invaluable insights into the nature of the paramagnetic complexes in solution. Mixed metal systems of uranyl(VI) or neptunyl(V) with plutonyl(VI) and uranyl(VI) with plutonium(IV) were also investigated in order to establish whether mixed metal cation-cation aggregates formed . The results obtained will be discussed in detail.

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Cobalt picolinamide complexes as potential anti-cancer agents

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Cobalt complexes have recently shown great promise as anti-cancer agents with cobalt(III) nitrogen mustard complexes[1] and Co-ASS[2] (a dicobalt hexacarbonyl aspirin derivative). Much of this interest stems from the easily accessible oxidation states. Due to the reducing nature of hypoxic cancer cells, a drug can be administered in the cobalt(III) form and potentially reduced *in vivo* to a more potent cobalt(II) analogue.[1, 3]

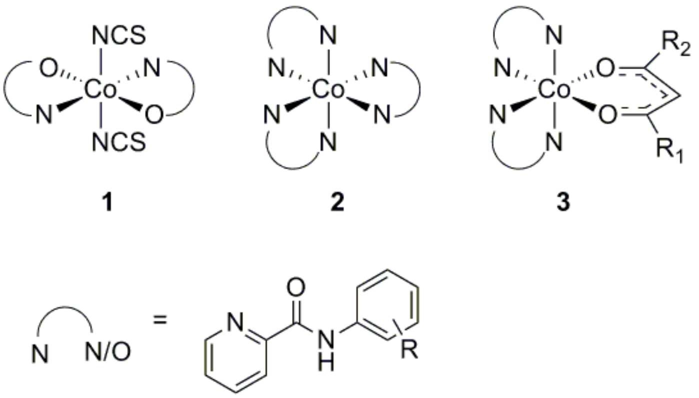

Figure 1 Cobalt picolinamide complex classes

This project is concerned with the synthesis and characterisation of a series of novel *N*,*N*- and *N*,*O*- cobalt(III) and cobalt (II) compounds (Figure 1). The project is based on previous work carried out within the McGowan group, in which a range of hypoxia sensitive ruthenium(II) arene complexes were prepared.[4] Three classes of compounds have been prepared: *bis*-picolinamide cobalt(II) complexes (**1**), *tris*-picolinamide cobalt(III) complexes (**2**) and mixed ligand cobalt(III) complexes (**3**). The data presented will include cell cytotoxicity studies against a range of cancer cell lines with comparison to a non-cancerous cell line, under both normoxic and hypoxic conditions and correlation with biomembrane interaction.

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New coordination mode of a thiosemicarbazonate ligand derived from pyrene to Pd^{II} and Pt^{II} centres

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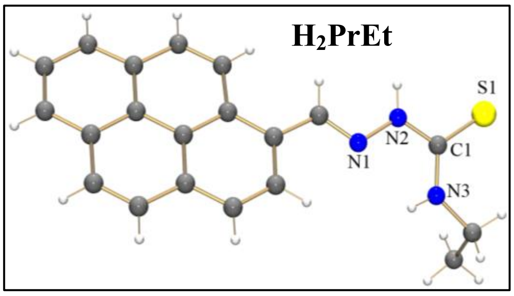
Thiosemicarbazones (TSCs), $(R^1R^2)C=N^1–N^2–C(=S)–N^3(R^3R^4)$, have been extensively studied due to their rich coordination chemistry and remarkable pharmacological properties [1]. They usually bind the metal centres through the N^1 and *S* donor atoms in bidentate chelating mode or in *S*-monodentate mode [2]. The sulphur atom can also form bridges between two metal centres. A less common situation, however, involves the coordination of the N^2 and *S* atoms [2]. In the present work, we describe the synthesis and characterization of Pt^{II} and Pd^{II} complexes with a TSC ligand derived from pyrene (a polycyclic condensed aromatic system with interesting fluorescent properties). The H_2PrEt ligand was prepared by the condensation reaction of pyrenecarboxaldehyde and ethylthiosemicarbazide in EtOH. The Pd^{II} and Pt^{II} complexes of type **I** and **II** have been prepared by reactions of the metal precursors $[MCl_2(PPh_3)_2]$ (M = Pd or Pt) in MeCN by changing the molar proportion of H_2PrEt as well as the order of addition of the chemicals. The crystallographic studies revealed the formation of analogue Pd^{II} and Pt^{II} complexes for both types. In type **I**, two TSC ligands are bound to the metal centres in different coordination modes. One ligand is coordinated in the expected monoanionic N^1,*S*-bidentate mode, while the second one binds the metal monoanionically through the nitrogen N^2 perpendicularly to the chelate ring. The remaining binding site is occupied by a phosphorus atom from the PPh_3 ligand. In type **II**, HPrEt$^-$ binds the metal ion through the N^2 in monoanionic mode *trans* to a chloride ligand, while two PPh_3 ligands occupy the remaining coordination sites. To our knowledge there is no precedent a TSC ligand coordinated preferentially through the N^2 atom instead of the sulphur or the imine nitrogen N^1 atoms. This fact can be explained by a combination of effects which includes the *trans* effect of the chlorido ligand, the bulkiness of the phosphine and, specially, of the pyrene group. More studies are underway in order to fully understand such behavior.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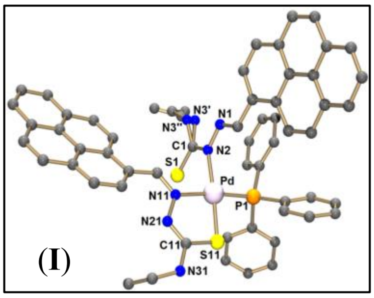
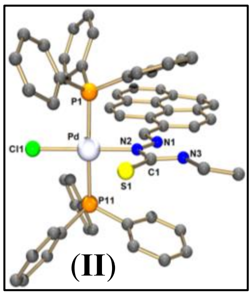


(**I**)



(**II**)

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Triptycenes as Redox-Active Components in Complexes and Frameworks

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Coordination complexes containing dioxolene ligands possess extensive ligand-based redox activity and can cycle between one of three accessible oxidation states (catechol, semiquinone, or quinone) by low-potential electron transfer or chemical oxidation.[1]

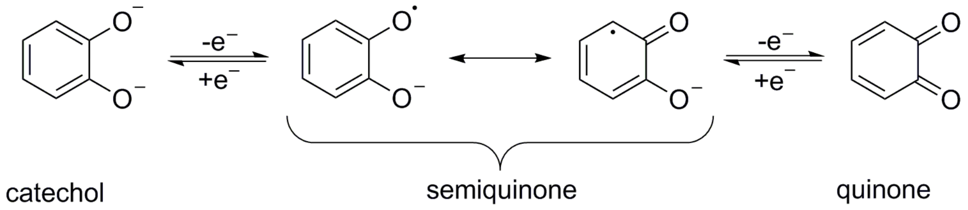

Figure 1 Redox forms of catechol.

The literature contains a wealth of mononuclear dioxolene complexes exhibiting varying degrees of redox activity.[2] However, multi- or poly-nuclear complexes of this class that exhibit valence tautomerism, mixed-valency or spin-state change are relatively rare. Previous work in the group has explored the mixed-valency of multinuclear dioxolene complexes, and stable semiquinone radicals have been characterized crystallographically.[3,4] This project is concerned with the development of functional supramolecular assemblies based on poly-dioxolene ligands. Ligands such as triptycene **1** (a triangular node) and tribenzotriquinocene **2** can act as templates for the formation of higher dimensional coordination polymers such as 2D zig-zag sheets or honeycombs. These ligands and their corresponding Pt complexes have been prepared with chelating diphosphine capping ligands and characterized spectroscopically.

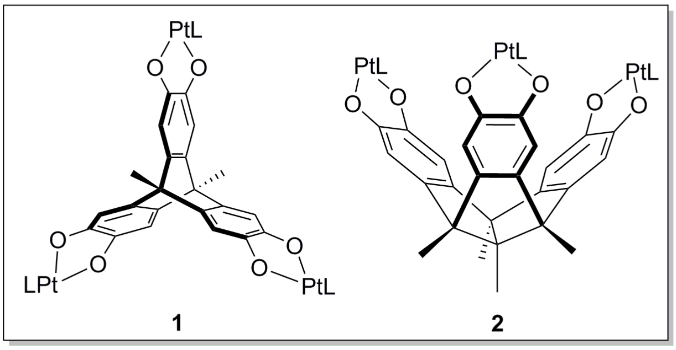

Figure 2 Trinuclear dioxolene complexes prepared.

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Alkaline Earth-Transition Metal Complexes.

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Molecular compounds containing metal-metal bonds have long been of interest in inorganic chemistry.[1] Although there are numerous examples of compounds with bonds between transition metal (TM) elements, there exist relatively few between transition metals and the alkaline earth (Ae) elements.[2]

Mountford *et al.* have recently reported several compounds containing Ae–TM bonds. The reaction of the β-diketiminate magnesium species Mg(NacNac)I(THF) with KFp (Fp = CpFe(CO)$_2$) afforded Mg(NacNac)Fp(THF) (Mg–Fe = 2.6326(4) Å).[3] This was shown to react with TolNCNTol to afford Mg(NacNac){(NTol)$_2$CFp}; the first net insertion of an unsaturated substrate into an alkaline earth-transition metal bond.

We have recently developed amidinate species of the form Mg{RC(NR')$_2$}M'(THF) (M' = CpFe(CO)$_2$, CpRu(CO)$_2$ or Co(CO)$_3$(PCy$_3$), R = Mes, R' = ^{i}Pr, Dipp or Mes), which feature fewer carbon atoms in the ligand backbone and yield a more sterically open system which may have the potential for increased reactivity with respect to the analogous system. In addition, a guanidinate species of the form [Mg{Me$_2$NC(NDipp)$_2$}Fp]$_2$ has been synthesised which features two Mg–Fe bonds (Mg–Fe = 2.5279(4) Å). These are the shortest known Mg–Fe bonds to date.

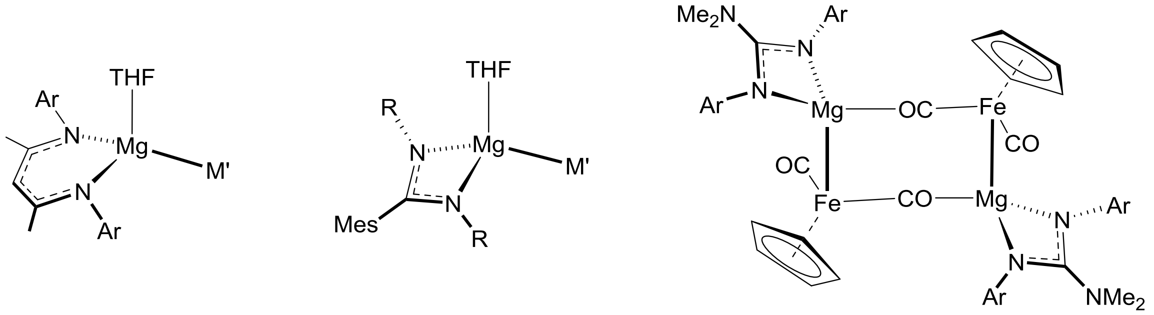

Figure 1: Mg–TM bonded complexes featuring β-diketiminate, amidinate and guanidinate ligands.

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Synthesis of Zirconium and Hafnium MOFs with Incorporated Functionality

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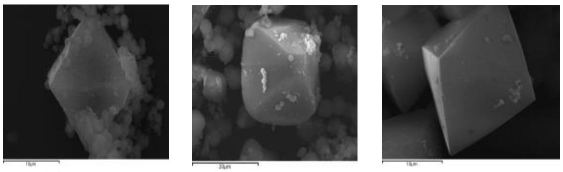
Interest in metal-organic frameworks has greatly increased in recent time due to their wide range of properties, thus allowing for potential use in a vast array of both industrial and commercial applications. The wide range of properties associated with MOFs can be attributed to their ability to incorporate organic ligands of varying size and functionality. Zirconium centred MOFs are of high interest due to their increased thermal and chemical stability compared to that previously observed in MOFs. Three ligands were designed for incorporation into MOFs, containing unsaturated C-C bonds and increasing in length across the series, resulting in MOFs expected to show a high degree of flexibility and containing reactive moieties ideal for postsynthetic modification., Three novel zirconium MOFs were synthesised as single crystals, with the crystal structures determined via single crystal XRD.[1]

Research has also begun on examining the effect of microwave synthesis of Zr MOFs compared to conventional solvothermal synthesis. Via the use of microwave assisted synthesis with amino acid modulation, synthesis time of MOFs can be greatly reduced, from hours to minutes, whilst maintaining the crystallinity of the material.



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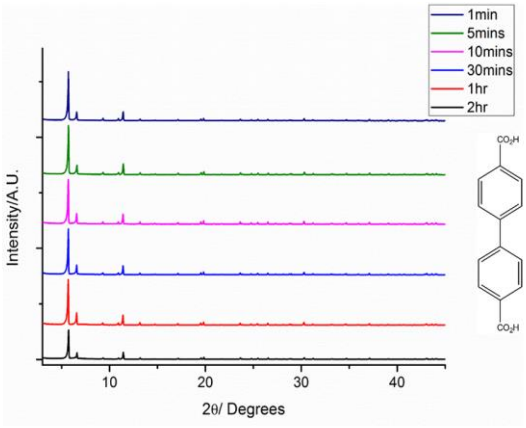

SEM images of UiO 67 with a synthesis time of 60 mins, 10 mins and 5 mins (above) and PXRD pattern showing the crystallinity (right).

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Organometallics vs. coordination complexes: Contrasting approaches to SMM design

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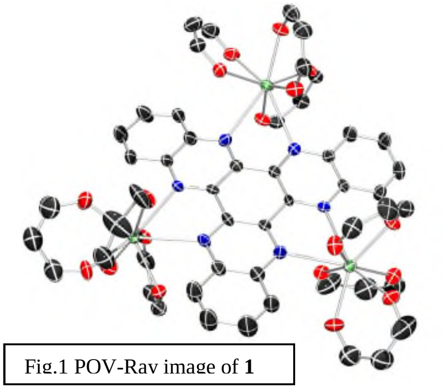

Fig.1 POV-Ray image of **1**

Utilisation of coordination chemistry can produce symmetrical systems with magnetic bistability.[1,2] Organometallic complexes with soft-atom bridging donors (P, As, Se) give energy barriers to spin inversion that increase with the size of the bridging atom.[3,4] The coordination complex, $[(Dy(thd)_3)_3HAN]$ - **1**, bridged by hexaazatrinapthalene (HAN), is synthesised by adding toluene to $Dy(thd)_3$ and HAN and stirring until consumption of the HAN is complete. **1** shows slow magnetic relaxation, up to 19 K in zero dc field. This is due in part to the coordination geometry around each Dy^{III} ion (approximately square antiprismatic), which stabilises the oblate $m_J = \pm 15/2$ ground state. The energy barrier to spin inversion is $U_{eff} \approx 22\ cm^{-1}$ which is relatively small, due to deviation from ideal D_{4d} symmetry. Despite the relatively low energy barrier to spin inversion, magnetic blocking is observed up to 2.2 K with relatively wide butterfly hysteresis loops at this temperature. This demonstrates the complex nature of lanthanide SMMs, as the radially contracted 4f orbitals make it difficult to control the symmetry around the Ln ion.

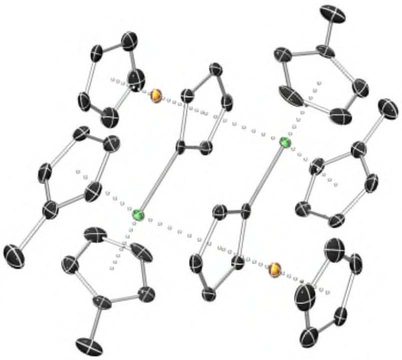

Fig. 2 POV-Ray image of **2**

Deprotonation of ferrocene with the butyl lanthanide complex $[Cp'_2Ln(n\text{-}Bu)]_2$ - **2** in toluene affords the ferrocenyl complex $[Cp'_2Ln((C_5H_4)FeCp)]_2$ - **3**. **2** is surprisingly stable, keeping for hours at room temperature, allowing for its isolation and use as a versatile, mild base. The strong sigma donating nature of the donor carbon atoms in complexes **2** and **3** increases the equatorial field around the metal and destabilises the ground state of Dy^{III}, resulting in no ac response at all in these complexes.

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Cationic, luminescent cyclometalated iridium(III) complexes based on substituted 2-phenylthiazole and 2-phenylquinoline ligands.

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The poster describes the synthesis and characterisation of a range of new cationic, luminescent iridium(III) complexes with tunable luminescence and added functionality. Firstly, a range of cationic heteroleptic complexes, [Ir(emptz)$_2$(N^N)](PF$_6$) were prepared from a cyclometalated iridium dimer precursor involving two ethyl-4-methylphenylthiazole-5-carboxylate (emptz) ligands. One X-ray crystallographic study was undertaken where the ancillary diimine (N^N) ligand was 4,7-diphenyl- 1,10-phenanthroline and revealed the anticipated structure, showing a distorted octahedral coordination geometry at Ir(III). The complexes were visibly luminescent with modestly structured emission at 540–590 nm and lifetimes (60–340 ns) consistent with a phosphorescence. TD-DFT calculations suggest that strong MLCT character contributes to the visible absorption characteristics, whilst the moderately structured emission profiles might indicate a ^{3}MLCT/^{3}IL admixture of states to the phosphorescence.

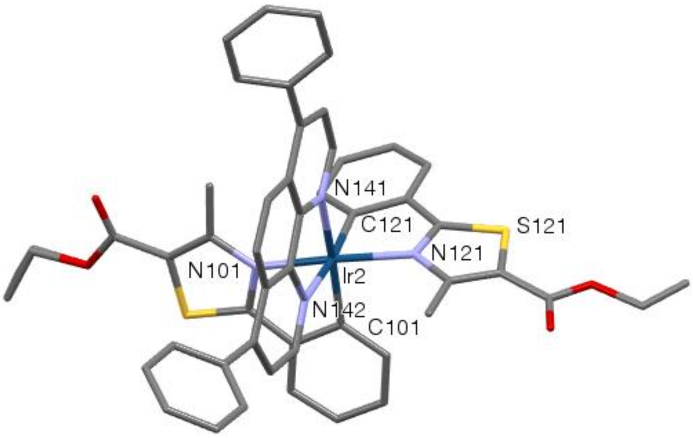

Figure 1 – Structural representation of [Ir(emptz)$_2$(dpphen)]$^+$. Just one of the crystallographically different moieties is shown with the solvent molecules. PF$_6^-$ and hydrogen atoms omitted for clarity.

Following this, a further four iridium(III) complexes were synthesised and investigated with an aim to bathochromically shift the emission wavelength and extend the functionality of the complexes. The complexes were similarly prepared from a cyclometalated iridium chloro-bridged dimer incorporating 4-substituted 2-phenylquinoline ligands. Further functionalisation was introduced to the complex by the use of an ancillary diimine-type chelate with a pendant alkyl amine group allowing attachment to nanoparticles and surfaces. All complexes were visibly luminescent with a red-shifted phosphorescence around 610 nm.

Late Transition Metal Catalysed C(sp^3)–C(sp^3) coupling reactions

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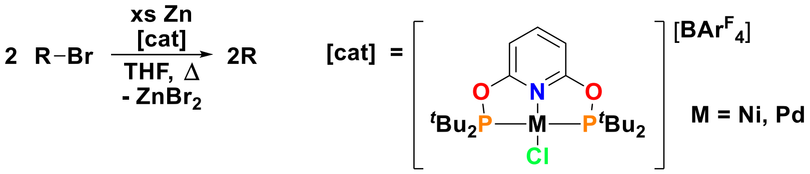
In contrast to C–C coupling reactions involving aryl substrates, alkyl substrates are challenging for conventional cross coupling systems. In short, this difference is due to a combination of less favourable C–X bond oxidative addition and detrimental β-hydride elimination reactions of the resulting metal–alkyl intermediates.[1] Early examples of this reaction involved dialkyl zinc reagents and alkyl halides with unsaturated functional groups as the cross-coupling partners.[2] Cross-coupling between alkyl halides and alkyl magnesium reagents has also been reported.[3] These aforementioned examples, however, involved poorly defined nickel catalysts. Palladium catalysed systems have also been reported involving alkyl halides and boranes as the cross-coupling partners.[4] With a view to using well-defined pre-catalysts for the homocoupling of unfunctionalised alkyl halides under mild conditions, in this report we describe our work involving nickel and palladium PNP pincer complexes in combination with zinc powder as a mild reducing agent.



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Extending the Frustrated Lewis Pair Model

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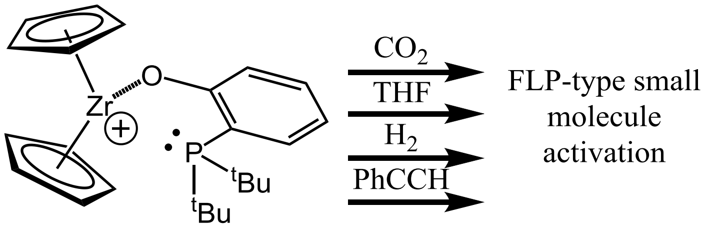

Since the seminal work by Stephan *et al.* in 2006, research into frustrated Lewis pair (FLP) chemistry has vastly increased. Significant developments have been made in utilising these main group systems for a variety of useful applications, such as hydrogen storage and small molecule activation.[1] More recently however, the frustrated Lewis pair paradigm has been extended to include transition metals, with early transition metals (Zr, Ti, Hf) employed as Lewis acids, and late transition metals (Pt, Pd) used as Lewis bases.[2, 3] Work by the Wass group has shown zirconocene/phosphine FLPs to be effective at both the catalytic dehydrogenation of amine boranes,[4] and the activation of small molecules.[5] These systems have been shown to be effective as either intra- or inter-molecular Lewis pairs, whilst also demonstrating that the "frustration" which is often inherent in these systems is not always required.[6]

In order to develop these ideas, and allow for improved reactivity with small molecules and other compounds, current work is exploring the use of other ligands in place of the previously used cyclopentadienyl ligand set. One aim is to alter the oxophilicity of the metal centre, allowing for reversible CO_2 activation, which is currently inhibited by the high M-O bond strength in these systems.

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3d Transition Metal Complexes with N-heterocyclic Silylenes

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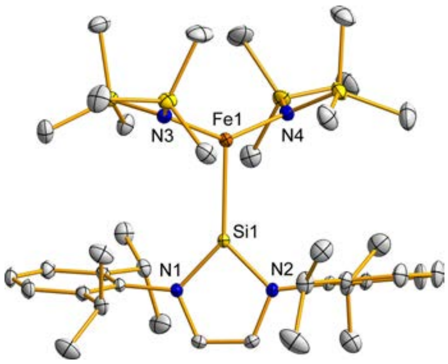

Fig. 1 Crystal structure of $Fe[N(SiMe_3)_2]_2$–**1**.

Dispersion forces have been shown to stabilize extremely low-coordinate transition metal complexes as well as main group compounds but they also appear to play a role in catalytic transformations.[1-4] We have synthesized the first example of high-valent 3d metal complex with N-heterocyclic silylene (NHSi) ligand (**1**) characterized it by variety of experimental and computational techniques. Crystal structure of $Fe[N(SiMe_3)_2]_2$–**1** displays the coordination of silylene ligand to Fe(II) cation with the longest Fe–Si bond length ever reported between Fe and any monodentate silicon donor ligand (2.496(1) Å). In solution state, coordination of silylene to iron is highly fluxional as evidenced by the variable temperature NMR study. Computational study demonstrates that $Fe[N(SiMe_3)_2]_2$–**1** is stabilized by weak interactions (dispersion effects) between *i*Pr groups of silylene and methyl groups of the silyl-amide ligands. Further insight to the bonding was obtained with energy decomposition (EDA) and ETS-NOCV analyses. Molecular orbital (MO) analysis reveals worse σ-donor capability of **1** compared to its NHC analogue. However, lowest unoccupied MO (LUMO) of **1** is π-symmetric and low in energy thus appearing to be well suitable for π-back-bonding. Hence silylene complexes with lower valent metals [M(I) or M(0)] can be expected to be have stronger Fe–Si bonds. The hypothesis was confirmed by preparation of $[Fe(CO)Cp–\mathbf{1}]_2$ in which the Fe–Si bond lengths are about 0.2-0.3 Å shorter (compared to $Fe[N(SiMe_3)_2]_2$–**1** regardless the bridging nature of the ligand.

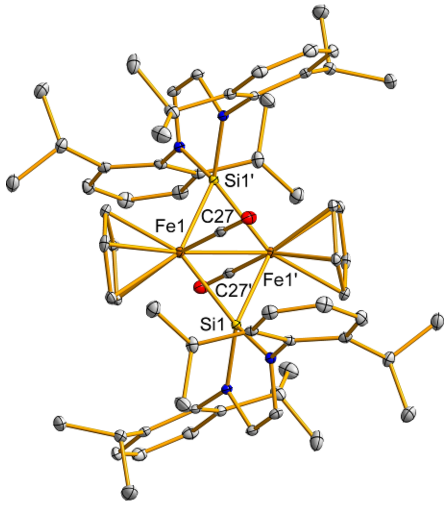

Fig. 2 Crystal structure of $[Fe(CO)Cp–\mathbf{1}]_2$

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C$_1$, C$_1$-ligands. One-step route to optically-active methylene diphos ligands

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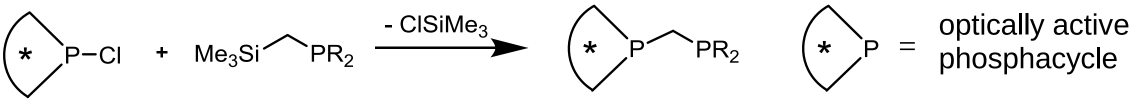
Efficient asymmetric hydrogenation using metal-phosphine catalysts is one of the success stories of modern chemistry with multiple industrial applications.[1] The field is over 40 years old but challenges still remain. For example, there are many prochiral substrates for which highly enantioselective catalysts have not been discovered. One-step automated routes to chiral monophos ligands have been a major development since 2000 and led to the application by DSM of high-throughput catalyst discovery methods.[2] Chiral diphosphines have advantages over monophos ligands for several asymmetric catalytic processes but the routes that are available for their preparation are complicated, multistep processes. We report here a simple route to chiral diphos ligands (Scheme 1) which has the potential for the application of high-throughput catalyst discovery methods.[3]



Scheme 1: General one-step route where R = Ph, ^{t}Bu, ^{i}Pr or Cy.

This presentation will focus on the exploitation of this route to synthesise a range of novel *C*$_1$-symmetric, C$_1$-backbone, diphos ligands for asymmetric hydrogenation. In addition, mechanistic insights into the P-Si exchange reaction and evidence of an unprecedented secondary phosphine ylide-type intermediate will be provided.

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Reactive Metal-Carbon Bonds in Three-Coordinate Iron and Cobalt NHC Complexes.

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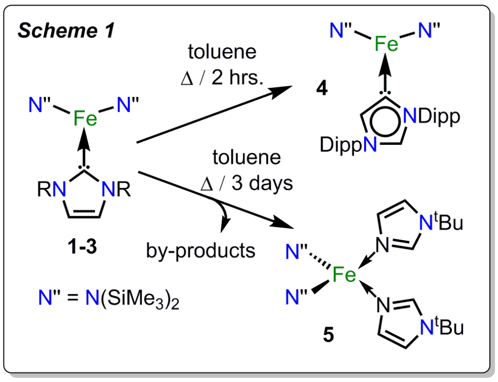
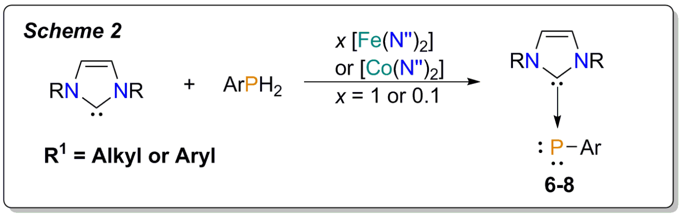
The use of NHC ligands in iron chemistry is a growing topic with applications in the stabilization of novel coordination environments and unusual oxidation states, biomimetic chemistry, and homogeneous catalysis.[1]

We recently reported the three-coordinate iron-NHC complexes [(IPr)Fe(N′′)$_2$] (**1**), [(IMes)Fe(N′′)$_2$] (**2**),[2] and [(I^{t}Bu)Fe(N′′)$_2$] (**3**) (Scheme 1), and our initial studies of the reactivity of **1-3** have produced some unexpected results. Refluxing **1** in toluene results in a normal-to-abnormal rearrangement of the NHC, giving [(*a*IPr)Fe(N′′)$_2$] (**4**) (Scheme 1). Refluxing **3** in toluene affords a C–H/C–N activation reaction, in which a ^{t}Bu substituent is eliminated from the NHC ligand as isobutene. The same outcomes were observed with the cobalt analogues of **1-3.**[3]



We have recently reported the reactivity of [(NHC)M(N’’)$_2$] (M = Fe, Co) towards primary phosphines. Reacting [(IMe$_4$)M(N’’)$_2$] with mesityl phosphine produced the phosphinidene-bridged dimers [(IMe$_4$)$_2$Co(PMes)]$_2$. In an attempt to form a terminal phosphinidene complex bulkier NHCs were utilised. Unexpectedly, these reactions yielded carbene-phosphinidene adducts (**6-8**) (Scheme 2). Remarkably, **6-8** can be formed using a stoichiometric or catalytic amount of [M(N’’)$_2$]. Overall, the observations depicted in Scheme 2 provide evidence for metal-catalyzed phosphinidene transfer.[4]



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Characterisation and Reactivity of σ-Complexes of Copper(I) with Zinc and Magnesium Hydrides

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We recently documented the synthesis of a series of σ–complexes of copper in which M–H (M = Al, Zn) and E–H (E = B) σ–bonds reversibly coordinate to a copper(I) fragment.[1,2] Herein, we report a new series of copper(I) arene complexes containing fluorinated ligands along with a phosphine stabilised copper(I) complex.[3] In solution, displacement of the arene or the phosphine with molecular magnesium and zinc hydrides has allowed the generation of new heterobimetallic complexes of copper(I), including the first examples that incorporate a Mg–H bond. In many cases, our data are consistent with tightly bound molecular hydride species with no evidence for ligand dissociation in solution. We expect these species to serve as useful starting materials to explore new reactivity.

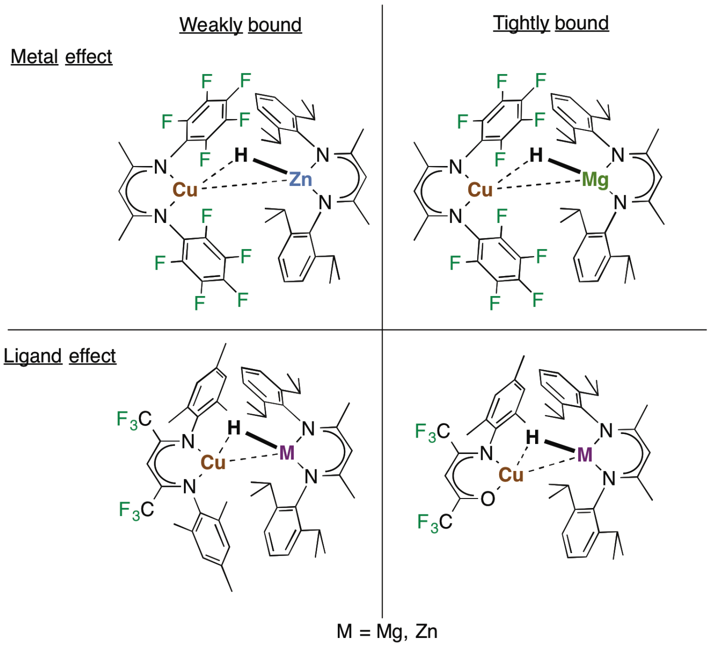

Figure 1 - The effect of changing metal and ligand on the formation of σ- and molecular hydride complexes of copper(I)

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Yttrium and Scandium Complexes of 1,10-Phenanthroline-5,6-Dione.

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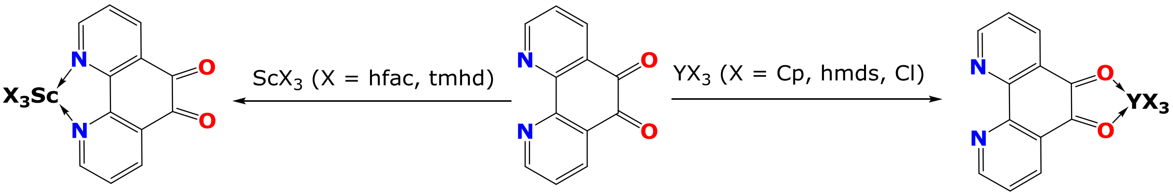
The use of organometallic building blocks for the controlled synthesis of complex molecular materials is an important area of research. The distinct properties observed in molecular materials *vs* bulk materials, represent an opportunity to develop future materials and technologies. Elements with f-electrons are particularly exciting in the scope of their applications. Our interest is in development of organolanthanide and actinide systems that allow for the engineering of cooperativity between multiple metal centres. This is a way to develop high performance systems such as multi-metallic single molecule magnets, photocatalysts or the multi-modal systems used in medical imaging. Our research has targeted ligand systems based around 1,10-Phenanthroline, in particular 1,10-Phenanthroline-5,6-Dione (PDO), for the synthesis of heterobimetallic complexes. Here we present the initial complexation strategies and the characterisation of yttrium and scandium complexes of PDO. Thereby generating a "roadmap" to follow for future work on more complex multi-component systems containing paramagnetic metal ions.



Investigation of the 2-Arsaethynolate Anion

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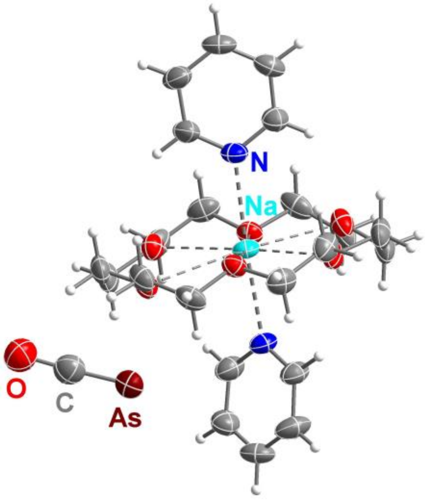
The 2-phosphaethynolate anion, PCO^-, was discovered in 1992 by Becker et al. and isolated as a lithium salt.[1] Since then, various ways to synthesize PCO^- salts have been devised, starting from either Na_3P or from K_3P_7.[2, 3] These salts are more suitable for reactivity studies due to their higher stability compared to the Li^+ salt. Consequently, the reactivity of the PCO^- anion has been extensively studied in recent years. It has been employed for the synthesis of phosphinecarboxamides and in cycloaddition reactions, as well as for the formation of metal complexes and as a phosphide source.[4]

In contrast, the chemistry of the heavier homologous species has not yet been explored. Earlier attempts by Hübler and Becker to generate the 2-arsaethynolate anion, $AsCO^-$, surprisingly yielded a Li_3As_7 complex.[5] Theoretical studies nevertheless indicated the stability of the heavier members of the homologous ECO^- series (E = As, Sb, Bi).[6] Thus, we were prompted to reinvestigate the synthesis of $AsCO^-$ salts, which are hitherto only known from matrix isolation experiments.[7] The reactivity of $AsCO^-$ was then probed with respect to metathesis and cycloaddition reactions and as an "As^-" transfer agent.



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A Tethered NHC-Carborane Ligand: Selective C-H Activation And Versatile Coordination

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The development of new catalysts and catalytic processes is essential for a sustainable and green future. Ligand design is central to these developments as they control the activity and reactivity of a metal centre. Whilst modifying current ligands may induce incremental changes in the outcome of a reaction, brand new ligand architectures can lead to more diverse pathways and processes. The fusion of two very different ligand families namely N-Heterocyclic carbenes (NHCs)[1] and carboranes[2], gives rise to a brand new ligand architecture; dicarba-dodecaboranes bearing imidazolium tethers. This ligand system exhibits unprecedented C-H activation with divergent reactivity towards cyclometalation leading to versatile coordination to a Rh^{I} centre.

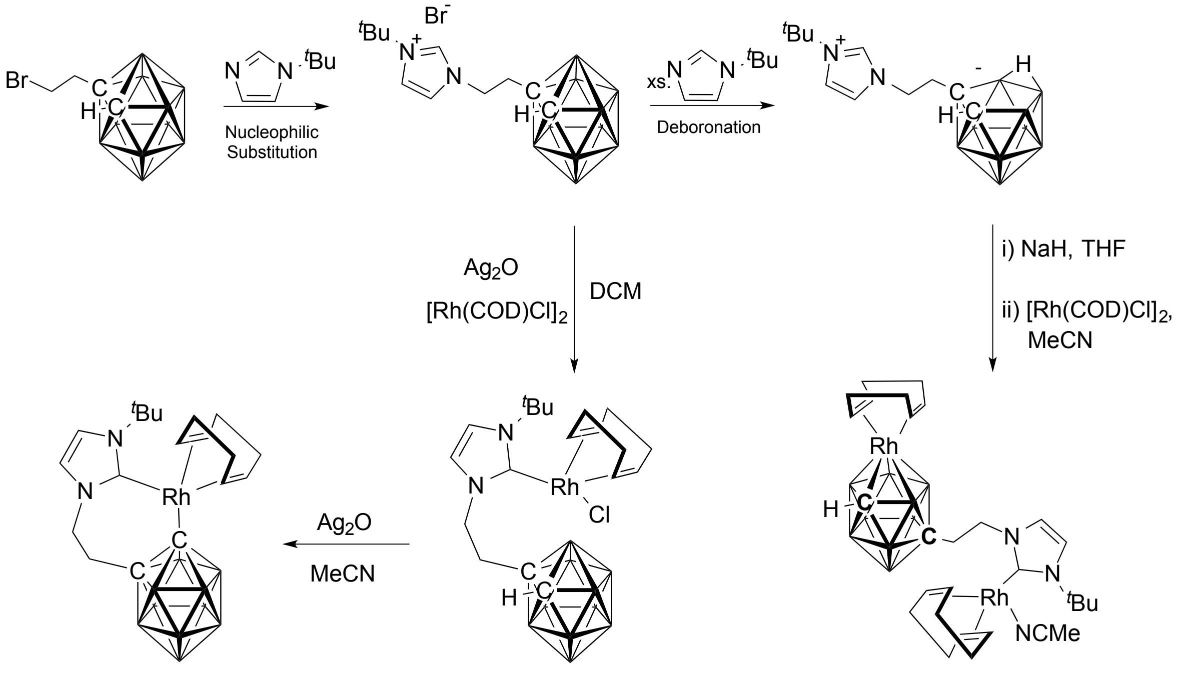

Figure 1. Synthesis of a tethered NHC-carborane ligand and its subsequent coordination to Rh^{I}

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Iridium Catalysed C-H Borylation of Indazoles

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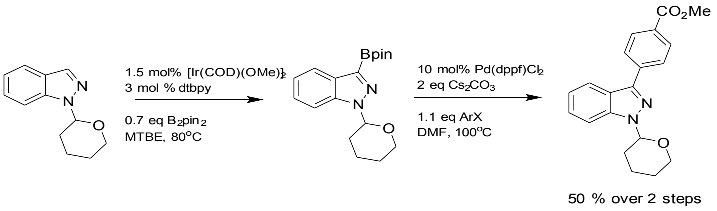
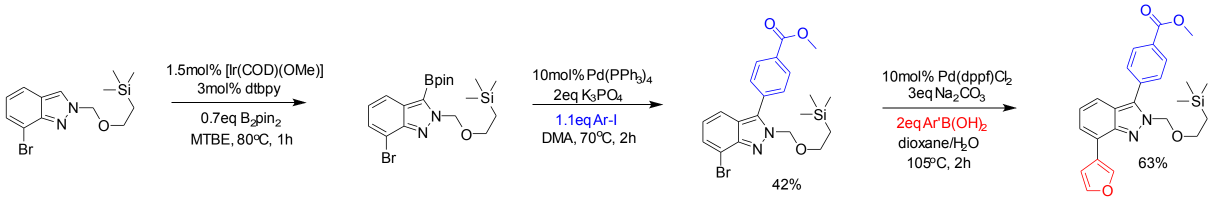
Boronic acids and their boronate esters are versatile reagents in synthesis, being used in many C-C and C-heteroatom bond forming processes as well as functional group interconversions. The borylation of heteroaromatic systems is of particular interest. Their boronate esters are often not commercially available but can be valuable intermediates in the synthesis of various pharmaceuticals and other compounds. Borylation of protected indazoles proceeds selectively on the heterocyclic ring to afford 3-boryl indazoles.

Protected indazoles can be reacted in a one-pot iridium catalysed C-H borylation and cross-coupling procedure to give 3-aryl indazoles in moderate yields.



The functional group tolerance of the borylation reaction allows the borylation to be carried out on bromoindazoles. Sequential cross coupling of the boronate ester and then the bromide allows multidirectional synthesis of substituted indazoles to be carried out.



Imidazolin-2-iminato Ligands: Applications in Group 14 Chemistry

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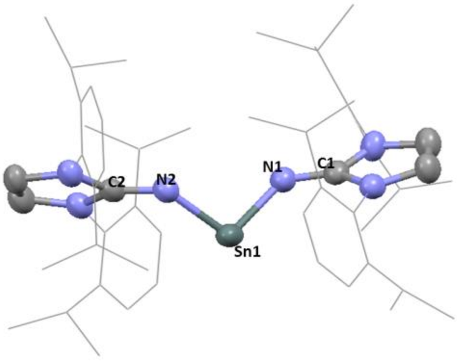
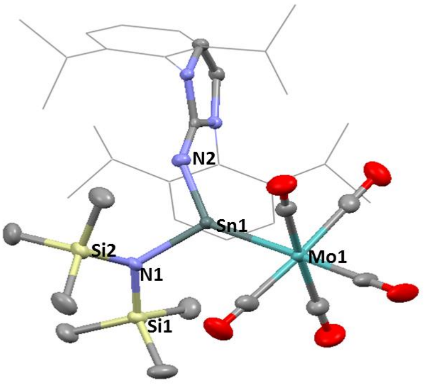
Since its appearance in 2007, the imidazolin-2-iminato ligand class has been widely employed to stabilize reactive low-valent Main Group and Transition Metal compounds for small-molecule activation[1]. The imidazolin-2-iminato ligands are typically functionalised with sterically demanding groups in order to stabilize these low-valent systems.[1,2] In 2015 these ligands were used to stabilise a germylene system, and attempts were made to isolate the corresponding silylene.[1] This led us to explore the chemistry of other Group 14 systems, namely that of tin.

Complexation studies show that iminato stannylene systems can be obtained via the reaction of two equivalents of the Dipp-functionalised proligand (IDippN)H with $Sn\{N(SiMe_3)_2\}^1{}_2$; in addition the mono-substituted stannylene can be selectively synthesized via the reaction with one equivalent (IDipp)NH. Due to the fact that the mono-substituted systems is not crystalline, a $[Mo(CO)]_5$ complex was synthesized by further reaction with $Mo(CO)_6$, and characterized by X-ray crystallography.





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Novel iridium(III) anticancer agents for ovarian and nasopharyngeal cancer

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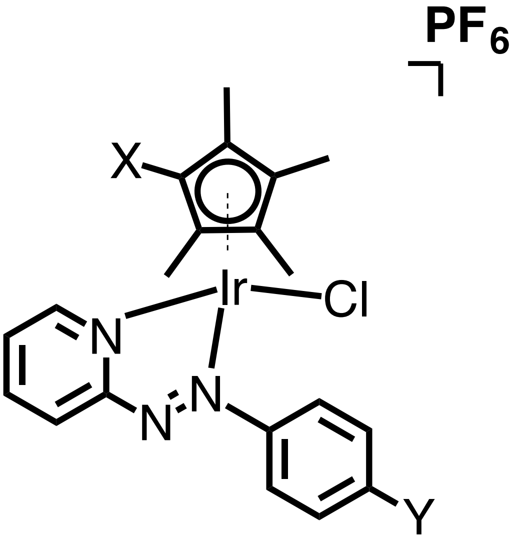
Abstract:

There were ca. 14 million new cases of cancer and 8.2 million cancer-related deaths in 2012.[1] The vast majority of chemotherapeutic regimes rely on the platinum-based drugs Cisplatin, Oxaliplatin and Carboplatin. These drugs kill cancer cells by targeting the DNA and inducing apoptosis. The drawback of this mechanism of action is that many cancer cells acquire resistance which drastically reduces the patient's likelihood of survival.[2] Organometallic iridium half-sandwich complexes offer the prospect of a different mechanism of action and activity towards Pt-resistant cancers, with many showing higher potency than cisplatin towards, e.g. A2780 ovarian carcinoma cells.[3]

We have synthesised a library of compounds with general formula $[Ir(Cp^{*/xph/xbiph})(azpyY)Cl]PF_6$ and screened their activity against ovarian (A2780) and nasopharyngeal cancer (SUNE-1, OE-19) cell lines. Complex ZL109 ($[Ir(Cp^{xph})$(N,N-dimethyl-4-(pyridin-2-yldiazenyl)aniline)$Cl]PF_6$) has been shown to target cancer cell mitochondria, thereby possessing the potential to bypass the resistance mechanisms of cisplatin-resistant cancers.[3, 4] Here we investigate the structure-activity relationships for these iridium complexes including the influence of lipophilicity and variations in substituent groups on their antiproliferative activity. Our goal is to design new iridium-based complexes that more effectively target cancer cells than current therapeutic modalities for a range of cancers.



Acknowledgments:

We thank the ERC (247450), Science City (AWM and ERDF), EPSRC (1501751) and MOAC DTC and International Partnership Fund of the University of Warwick for support, as well as EU COST Action CM1105 for stimulating discussions. Guy J. Clarkson at The University of Warwick for determining crystal structures.

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A Novel U(III) Complex based on a Bidentate Phenoxide Ligand for Activation of CO_2

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Previous work from our laboratory has shown how small molecules such as CO and CO_2 can undergo unique reductive transformations induced by mixed sandwich uranium(III) complexes incorporating cyclopentadienyl and cyclooctatetraeneyl ligands.[1] [2] The synthesis and characterisation of a novel uranium(III) complex based on a combination of a cyclopentadienyl group and a new chelating bisphenoxide ligand will be presented, along with electrochemical and CO_2 activation studies.

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Non-aqueous strategy to a range of tin-substituted polyoxotungustates

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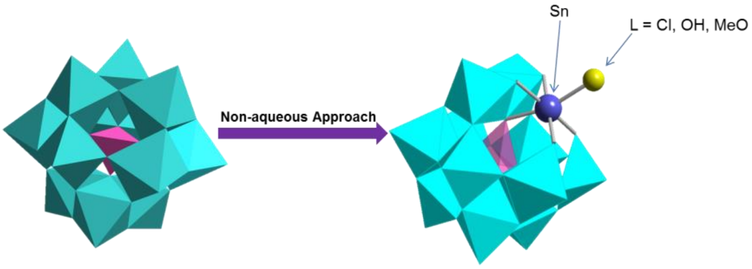
Polyoxometalates (POMs) are nano-sized molecular metal oxide clusters with wide application in catalysis, energy systems, and medicine.[1, 2, 3] They are formed mainly by early transition metals (W, Mo, V, Nb, Ta) in their highest oxidation states. Non-aqueous studies of POMs provide an opportunity to develop a better understanding of their solution properties, speciation and reactivity. This knowledge is crucial for molecular level control of their self-assembly and tuning their surface Brønsted basicity and Lewis acidity for catalytic applications.[3, 4] Herein, we present our non-aqueous strategy to a range of tin-substituted Polyoxotungstates, $(TBA)_4[(L)SnPW_{11}O_{39}]$ where L= Cl (**1**), OMe (**2**), OH (**3**) and OD (**4**) and the μ-oxo dimer, $(TBA)_8[(SnPW_{11}O_{39})_2O]$ **(5)**. **1**, **2**, **3** and **4** were accessed via ligand metathesis whereas dimerization of **3** and **4** was attempted in the preparation of **5.** Reactions were monitored by ^{31}P NMR and compounds were characterized by elemental analysis, IR and solution and solid state Multinuclear NMR (^{1}H, ^{13}C, ^{31}P, ^{119}Sn and ^{183}W).



Scheme 1: Non-aqueous synthesis of $(TBA)_4[(L)SnPW_{11}O_{39}]$ (L = Cl, OH, OD, OMe) from $Na_3[PW_{12}O_{40}]$

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Resolution of Chiral Spin States

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Many small molecule complexes with chelating ligands have Δ and λ optical forms depending on the direction of the ligand twist around the coordinated ion. Most of these crystallise in non-chiral space groups, with the pair of enantiomers related by an inversion centre. In our recent work we have studied several metal ligand combinations where spin crossover in either iron(III)[1] or manganese(III)[2] can be induced with judicious choice of chelating ligand. We now present a series of iron(III) complexes where spin crossover is accompanied by a structural phase transition which results in spin state ordering of high spin and low spin sites in a 1:1 ratio. During the ordering transition loss of the inversion centre between Δ and λ forms also results in chiral resolution of the enantiomers, a rare example of combined spin state ordering and chiral resolution.[3] We report here our structural, magnetic and spectroscopic studies on the extent and reproducibility of the phenomenon in multiple crystals.

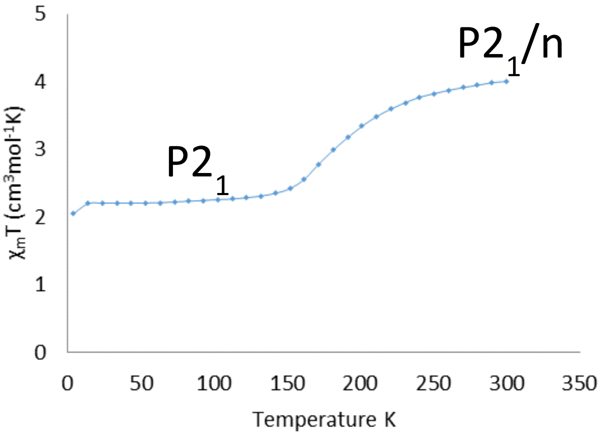

Figure 1 Plot of $X_M T$ versus T for mononuclear iron(III) complex showing spin state ordering and chiral resolution.

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Ruthenium-based Organometallic HDAC Inhibitors

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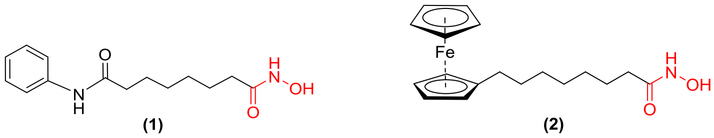
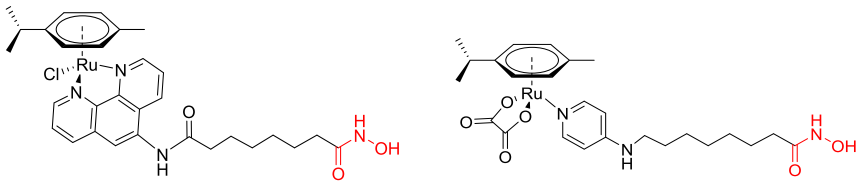
The inhibition of zinc-dependent (class I/II) histone deacetylase (HDAC) enzymes has emerged as a focal therapeutic target for the treatment of cancer, as well as other diseases.[1] Vorinostat (SAHA, **1**) has been in clinical use for the treatment of cutaneous T cell lymphoma for close to a decade,[2] and the ferrocene-based JAHA (**2**) has recently been shown to exhibit promising cytotoxic activity towards cells with certain lines of breast cancer.[3]



(1) **(2)**

Figure 1 - SAHA and JAHA, with highlighted hydroxamic acid functionality.

The inherent advantages of organometallic based therapeutics, including their modular syntheses, redox capabilities, exchangeable ligands and variable geometries have led to our interest in the exploration of ruthenium-based organometallic HDAC inhibitors. We have been investigating metal-based HDAC inhibitors with an assortment of bonding modes between the metal and alkyl-chain spacer group (fig. 2). We present the synthesis and biological results of our initial target complexes. The most active compounds report IC_{50} values in the μM range against A2780 ovarian cancer cells, highlighting the potential for these species as anticancer agents.



(3) **(4)**

Figure 2 – A selection of ruthenium complexes to be investigated as HDAC inhibitors.

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An Efficient and Sustainable Synthesis of NHC Gold Complexes

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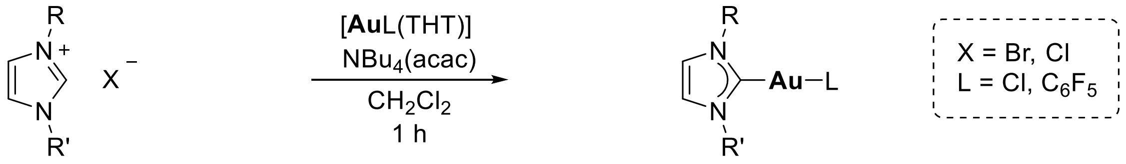
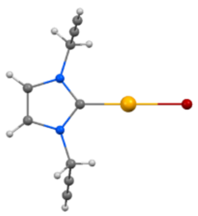
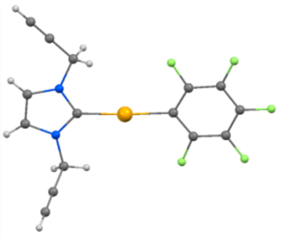
N-Heterocyclic carbenes (NHCs) are of ever-increasing importance in organometallic chemistry due to their structural versatility and excellent capacity to act as ligands to transition metals. NHC gold complexes are of particular interest due to their diverse catalytic, biological, medicinal and optical properties[1-3]. For NHC gold complexes to be fully exploited, they must be accessible, and therefore simple, economical and efficient syntheses are vital.

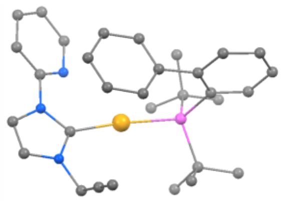
A new method for the synthesis of NHC gold complexes has been developed in which tetrabutylammonium acetylacetonate, $NBu_4(acac)$, is used to deprotonate imidazolium salts to form the NHCs. Reactions are carried out at room temperature, in air and with short reaction times and high yields. This method has been shown to work with both sterically small as well as bulky NHCs.



A series of propargyl functionalised NHC gold complexes have been prepared from their corresponding imidazolium salts using $NBu_4(acac)$. The propargyl side arms provide an additional coordination site whilst also giving the complexes a degree of water solubility. The emissive and biological properties of the complexes have been studied.







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Lanthanide complexes of bulky hybrid ligands

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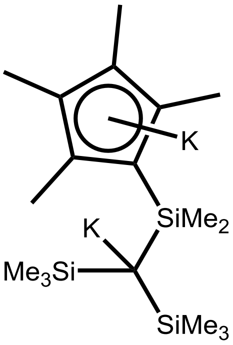
Much well known organolanthanide reduction chemistry is based on pentamethylcyclopentadienyl (Cp*) complexes[1–4], especially those of samarium. SmCp$^*_2$ reduces unsaturated substrates via the metal redox couple $2Sm^{2+} \rightarrow 2Sm^{3+} + 2e^-$, while SmCp$^*_3$ complexes act as reductants via the ligand redox couple $2[C_5Me_5]^- \rightarrow (C_5Me_5)_2 + 2e^-$. Dialkyllanthanide complexes have been previously prepared by our group[5], e.g. Yb(trisyl)$_2$ [trisyl = $(Me_3Si)_3C$]. We have designed a new ligand which is a combination of a cyclopentadienyl and an alkyl group.



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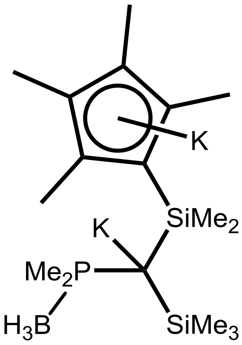

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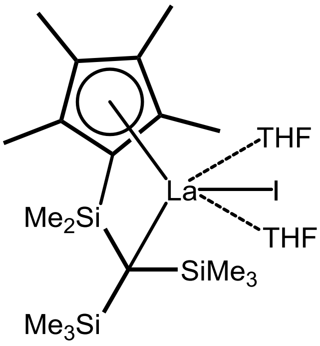
Two isoelectronic hybrid ligand systems have been synthesised; both are dianions containing a Cp or Cp^{4Me} [Cp^{4Me} = 1,2,3,4-Tetramethyl-Cp] ring but they differ in the alkyl carbanion part of the ligand. $[(Cp^{4Me}Me_2Si)(Me_3Si)_2C]K_2$ (**1**) has a'trisyl-like' $[(Me_2Si)(Me_3Si)_2C]$ group whereas $[(Cp^{4Me}Me_2Si)(Me_3Si)C\{PMe_2(BH_3)\}]K_2$ (**2**) has a phosphine-borane stabilised carbanion[6–8].

We have prepared a new trivalent lanthanum organometallic complex $[(Cp^{4Me}Me_2Si)(Me_3Si)_2C]LaI(THF)_2$ (**3**) which crystallises as monomers from toluene/THF at -18ºC. The complex has both a C-Ln σ-bond and a cyclopentadienyl ring interaction from a single hybrid ligand. Study of the chemistry of these compounds offers opportunities to uncover new organolanthanide redox chemistry.



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Synthetic analogues of the active site of the [NiFe] hydrogenases.

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The [NiFe]-hydrogenases catalyse the two-electron inter-conversion of two protons and molecular hydrogen.[1] Catalytic H_2 cleavage is associated with changes in the formal oxidation state of the Ni centre while the Fe centre remains in the Fe^{II} state during turnover. Despite the large number of diamagnetic $Ni^{II}Fe^{II}$ complexes that have been prepared as analogues of the [NiFe] hydrogenases, the syntheses of paramagnetic analogues have proven to be more challenging.[2]

We report a family of [NiFe] complexes containing a common $[Ni(N_2S_2)]$ (N_2S_2 = N,N'-diethyl-N,N'-bis-2-mercaptoethyl-1,3-propanediamine)[3] core bound to a Fe^{II} centre co-ordinated by four isocyanide ligands (Fig. 1). These complexes possess a reversible, single-electron reduction process at -1.3 to -1.4 V vs $Fc^{+/0}$, associated with the generation of a formal $Ni^{I}Fe^{II}$ centre, which is confirmed by EPR and IR spectroscopic studies. These complexes reproduce the formal $Ni^{I}Fe^{II}$ electronic structure proposed for the Ni-L state of the [NiFe] hydrogenases.[4]

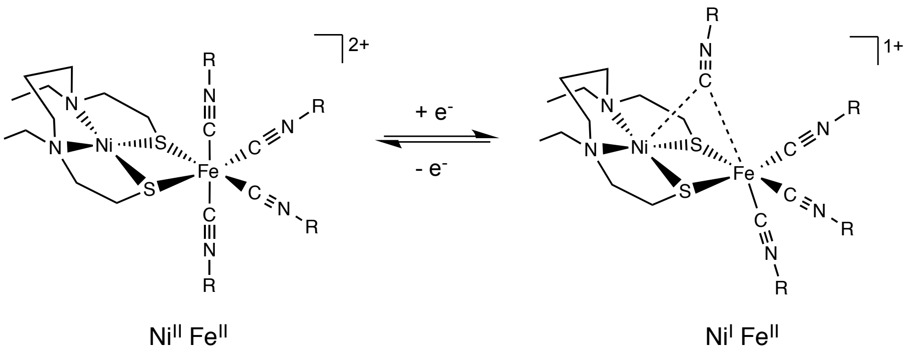

Figure 1: $[Ni(N_2S_2)Fe(CN\text{-}R)_4]$ (R = ^{t}Bu, benzyl, ^{i}Pr, cyclohexyl, n-butyl, 4-OMe-Ph) undergo a reversible reduction process.

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Synthesis and Reactivity of Phosphorus Analogues of Cyanate and Urea

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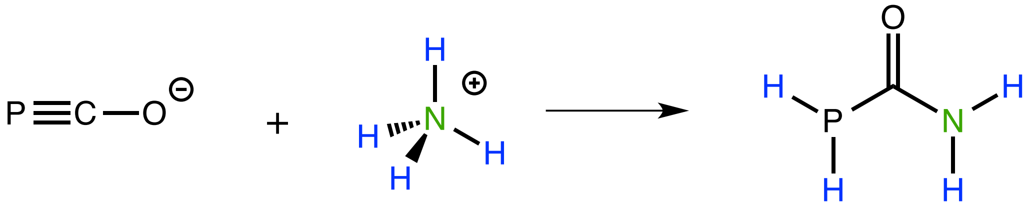
We recently reported the synthesis of the 2-phosphaethynolate anion, PCO^-, by an unprecedented activation of the group 15 Zintl cluster, P_7^{3-}.[1] This phosphorus-containing analogue of the ubiquitous cyanate anion has been the subject of a number of recent articles by our group and that of Grützmacher.[2] We have systematically explored the cycloaddition chemistry of PCO^-,[1,3] and compared its ligand properties to other isoelectronic pseudohalides in both transition metal[4] and actinide element complexes.[5]



Furthermore, by analogy with Wöhler's paradigm-shifting synthesis of urea in 1828, the reaction of PCO^- with ammonium salts yields the novel phosphinecarboxamide.[6] This inorganic analogue of urea is a rare example of an air-stable primary phosphine, and its ligand properties have been probed.[7] We have also studied its Brønsted acidity to afford a series of novel phosphides, secondary and tertiary phosphines, and phosphine oxides.[8]

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Synthesis and Characterization of Polysaccharide-coated Nickel Ferrite Nanoparticles as a Biomaterial Candidate

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Abstract:

Nickel ferrite, $NiFe_2O_4$ nanoparticles (NFNPs) have been synthesized by chemical co-precipitation method. To enhance biomaterial potential of nickel ferrite NPs, their surface was tuned with biocompatible food grade polysaccharide polymer called glucomannan. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and thermal gravimetric analysis (TGA) were used to probe the effect and nature of coating on surface of nickel ferrite NPs. The surface morphology and dispersion of native and coated NFNPs was studied by scanning electron microscope (SEM), atomic force microscopy (AFM) and dynamic light scattering (DLS) respectively. Vibrating Sample Magnetometer (VSM) studies reveals that no particular effect of coating was observed on magnetic saturation (Ms),76.22 emu/g and ferromagnetic behaviour of NFNPs. Cell culture studies are exhibiting the less cytotoxicity mode of glucomannan coated NFNPs (NFNPs-Glu) over uncoated ferrite nanocrystals when tested against Chinese hamster ovary (CHO) cell line upto 2.0 mg/ml. The non-toxic, monodisperse, magnetic and biocompatible behaviour of glucomannan modified NFNPs make them a promising candidate for biomaterial applications as a contrast agent in magnetic resonance imaging (MRI) and drug delivery.

Keywords

Nickel ferrite nanoparticles, glucomannan coating, biomaterial applications.

Kinetic control of metal ion transfer between copper trafficking proteins from *Bacillus subtilis*.

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Copper is an essential metal throughout biology. Although exploited in essential enzymes, the ability of copper to readily cycle its oxidation state makes this metal potentially toxic. In order to carefully manage cellular copper demand, highly conserved protein networks have evolved that distribute and detoxify Cu(I), such that it does not exist freely in the cytoplasm. In the model Gram-positive bacterium *Bacillus subtilis*, key components of this network include the highly conserved Atx1-like copper chaperone CopZ, and the membrane-bound exporting P_{1B}-ATPase CopA. Copper is transferred from cytoplasmic CopZ to membrane bound CopA at its two soluble cytoplasmic N-terminal metal-binding domains (MBDs), CopAab.

The extremely high stabilities of copper-chaperone complexes means that the mechanism of copper transfer does not comprise release of Cu(I) by chaperones, followed by chelation by receptor proteins. Rather, it has been demonstrated that a Cu-mediated hetero-protein complex is formed that facilitates delivery of copper from the chaperone to the ATPase MBDs[1,2]. Copper exchange within the heteroprotein complex is not dictated by any substantial thermodynamic gradient for copper transfer, but rather, it is proposed, by lowering of the kinetic barrier to Cu(I) dissociation from the chaperone. Here, we present studies of Cu(I) exchange between *B. subtilis* CopZ and CopAab. Through measurements of the rate of copper transfer in the presence and absence of protein interactions, we show that, direct interaction of the proteins facilitates extremely rapid Cu(I) transfer, enhancing the rate of dissociation from CopZ by several orders of magnitude. Electrospray mass spectrometry studies provided clear evidence of complex formation between CopZ and CopAab. The data provide direct experimental evidence that a principal function of complex formation is to dramatically lower the kinetic barrier to copper exchange.

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Proximal versus Distal Heme-NO binding in Cytochrome *c′* is determined by a balance of affinities mechanism: Insights into Selective Gas Response in Heme-Based Sensors

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Proximal vs distal heme-NO coordination is a novel strategy for selective gas response in heme-based NO-sensors. In the case of *Alcaligenes xylosoxidans* cytochrome *c′* (AXCP), formation of a transient distal 6cNO complex is followed by scission of the *trans* Fe-His bond and conversion to a proximal 5cNO product via a putative dinitrosyl species. Here we show that replacement of the AXCP distal Leu16 residue with smaller or similar sized residues (Gly, Ala, Val or Ile) traps the distal 6cNO complex, whereas Leu or Phe residues lead to a proximal 5cNO product with a transient or non-detectable distal 6cNO precursor. Crystallographic, spectroscopic, and kinetic measurements of 6cNO AXCP complexes show that increased distal steric hindrance leads to distortion of the Fe-N-O angle and flipping of the heme 7-propionate. However, it is the kinetic parameters of the distal NO ligand that determine whether 6cNO or proximal 5cNO end products are formed. Overall, our data support a "balance of affinities" mechanism in which proximal 5cNO coordination depends on relatively rapid release of the distal NO from the from the dinitrosyl precursor. This mechanism, which is applicable to other proteins that form transient dinitrosyls, represents a novel strategy for 5cNO formation that does *not* rely on an inherently weak Fe–His bond.

Synthesis, Electrochemistry, and Electrode Interactions of $Mg(PF_6)_2$-Based Electrolytes in Mg-Ion Batteries

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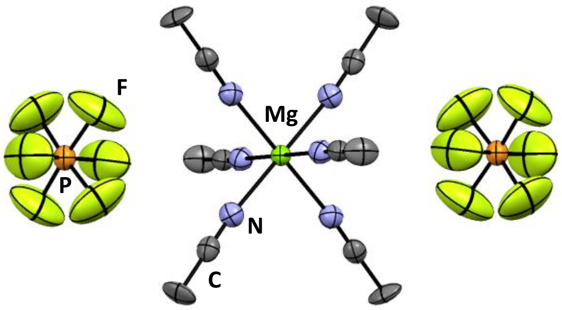
The development of the rechargeable lithium-ion battery has facilitated the production of many modern wireless devices such as mobile phones, laptop computers, and digital cameras, revolutionizing global communication. Nonetheless, Li-ion battery technology is still faced with many challenges, including the possibility of combustion and a moderate theoretical maximum capacity of 2046 $mAh \cdot cm^{-3}$. Magnesium-ion batteries have been proposed as safer and cheaper alternatives to Li-based systems with theoretical capacities of 3833 $mAh \cdot cm^{-3}$, nearly twice that of Li systems.[1] However, a major limiting factor in developing competitive Mg-ion batteries is the formation of electrolytes that are stable over a wide voltage range and compatible with Mg.[1]

Due to a balance of several properties, $LiPF_6$ in mixed carbonate solvents has become the preferred electrolyte for Li-ion systems and was first commercialized by SONY corp. in 1990.[2] These $LiPF_6$-based electrolytes have been found to be highly electrochemically stable (stable above 4.5 Volts vs Li/Li^+) and ionically conductive.[3] Despite the ubiquity of $LiPF_6$ in Li-ion systems, $Mg(PF_6)_2$ has not received the same attention as it is generally accepted that the PF_6^- anion decomposes on Mg anodes, forming passivating MgF_2 layers.[4] Here, we report the first synthesis of $Mg(PF_6)_2$ and present electrochemical and prototype battery studies using solutions of this salt along with electrode surface analysis.



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Facile, Catalytic Dehydrocoupling of Phosphines Using β-Diketiminate Iron(II) Complexes

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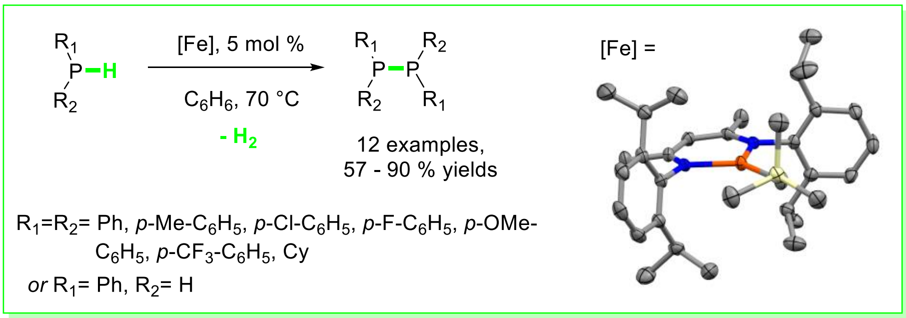
Catalytic dehydrocoupling is an attractive and a well developed methodology for the synthesis of bonds between main group elements, with H_2 being produced as the only by-product.[1] In particular the synthesis of P–P bonds *via* dehydrocoupling has previously been achieved using late transition metal catalysts.[2-5] Iron catalysis is an ever expanding field due to the high abundance and low cost of the metal. In reactions with three coordinate iron β-diketiminate complexes we have shown high catalytic dehydrocoupling activity. This has been achieved under relatively mild conditions without the need for any additives (Scheme 1).



Scheme 1 Dehydrocoupling of phosphines using a three coordinate iron β-diketiminate pre-catalyst.

To the best of our knowledge, this is the first example of catalytic dehydrocoupling of primary and secondary phosphines with an iron catalyst.[6] The synthetic catalytic methodology will be presented along with preliminary mechanistic details, which demonstrate that the reaction is most likely radical mediated.

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Synthesis and characterisation of a series of low coordinate complexes $[M(2,2'\text{-biphenyl})(PR_3)_2]^+$ (M = Rh, Ir)

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The coordination chemistry of complexes of 2,2'-biphenyl is less well explored compared to the related and ubiquitous 2,2'-bipyridine ligand.[1–5] Motivated by the possibility to exploit the unique bidentate arrangement of strong σ-donors for the isolation of reactive low coordinate complexes,[6] in this work we report the synthesis and characterisation of a series of formally 14 VE rhodium and iridium 2,2'-biphenyl complexes. These compounds are readily accessed via halide abstraction from 16 VE $[M(2,2'\text{-biphenyl})(PR_3)_2Cl]$ (M = Rh, Ir; R = Ph, Cy, ^{i}Pr, ^{i}Bu) and stabilised by formation of either solvent adducts or C-H agostic interactions depending on the phosphine substituent. The strength of the aforementioned C–H bond interactions have been probed using variable-temperature NMR and single crystal X-ray crystallography.

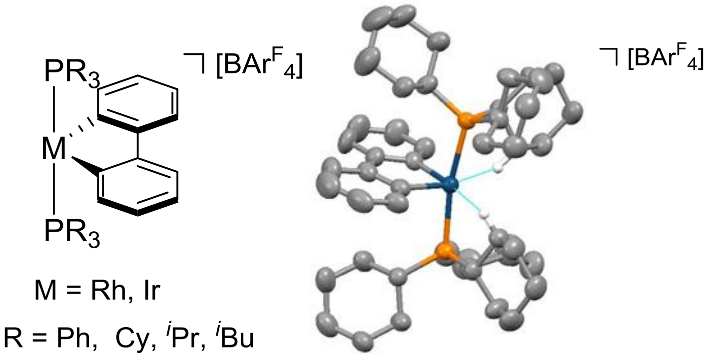

Figure: General structure of cationic 2,2'-biphenyl complexes (left) and XRD structure of $[Ir(2,2'\text{-biphenyl})(PCy_3)_2][BAr^F_4]$ (right)

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Chelating bis(diazaboryl) ligands for the preparation of cyclic bisboryl complexes.

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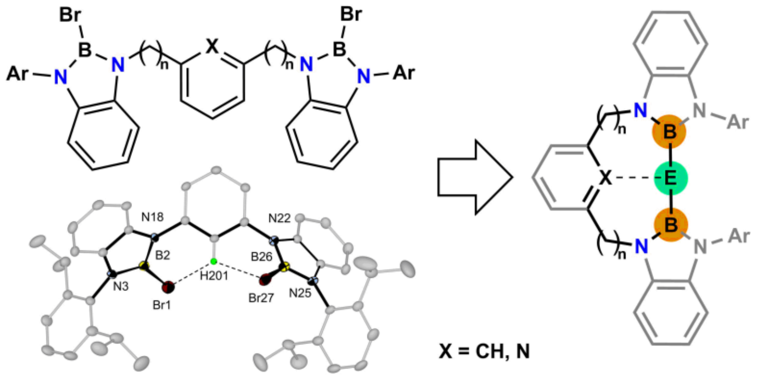
Recent reports by Yamashita and Nozaki et al. on the isolation[1] and reactivity[2] of the first stable boryllithium reagent have opened new possibilities for the application of diazaboryl fragments as strong σ-donor anionic ligands. Preliminary studies conducted in our laboratory showed that diazaboryl complexes of Main Group elements[3] are encouraging candidates as transition metal free bond activation reagents. Further investigation is currently focused on the preparation of bifunctional boryl ligands, with the aims (i) of increasing the stability of complexes by the chelate effect, and (ii) of facilitating re-reduction to lower oxidation states due to the presence of constrained ring systems with appropriately narrow bite angles.

Synthetically, key precursors for such chelate systems are bis(diazaboryl) dibromides which can be prepared by high yielding procedures starting from commercially available starting materials. In subsequent steps, a range of approaches including metathesis using alkali metal boryl complexes and oxidative insertion of low valent metal centres into B-H bonds of the analogous boryl hydrides have been examined to establish reliable synthetic routes to chelating boryl complexes.



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3d/4f Coordination Clusters in catalysis

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The coordination chemistry of 3d/4f elements offers many opportunities to connect Chemistry, Physics, Biology and Materials Science. However, the use of these materials for catalytic purposes has received less attention.[1]

Our laboratory has recently committed to study the catalytic properties of tetranuclear 3d/4f coordination clusters (CCs) possessing a rigid defect dicubane topology assembled by a Schiff base organic ligand. The combination under aerobic conditions of the organic ligand H_2L with freshly prepared $Ln(NO_3)_3$ xH_2O and $Zn(NO_3)_2{\cdot}6H_2O$ in the presence of Et_3N in EtOH afforded, in very good yields, precipitates subsequently crystallized by vapour diffusion of Et_2O in N,N'-DMF solutions, affording the isoskeletal air-stable tetranuclear defect dicubane compounds with the general formula $[Zn^{II}_2Ln^{III}_2L_4(NO_3)_2(DMF)_2]$ where Ln is Y (**1Y**), Nd (**1Nd**), Gd (**1Gd**), Dy (**1Dy**), Tb (**1Tb**) and Yb (**1Yb**). The lanthanide metal could be replaced by Y^{III} or Gd^{III} without altering the core topology, therefore ^{89}Y-NMR or EPR spectroscopy can also be used for the dissolved species characterization. In this work, we showcase the effectiveness of these 3d/4f species towards a domino[2] as well Friedel Craft alkylation,[3] Petasis-Manich[4] and multicomponent reactions.

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Linking antiferromagnetic rings through lanthanide ions

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The {Cr_7Ni} ring clusters have been proposed as qubits for quantum information processing [1]. Using bottom-up synthetic methods, our goal is to make spin based supramolecular systems with sufficient number of qubits and study their application in quantum computing [2]. Starting with assemblies where there are two components (a qubit and a linker) our aim is to understand the nature of the interaction between the different components and determine which linkers are suitable. The aim of this work is to design the molecular components that could lead to complex assemblies and in the long term into useful devices.

Herein we present some of the results obtained by functionalizing the {Cr_7Ni} rings with N-oxide ligands in order to synthesize dimers of wheels linked by lanthanide ions. Their magnetic properties have been probed using SQUID magnetometry, CW and Pulsed EPR spectroscopy.

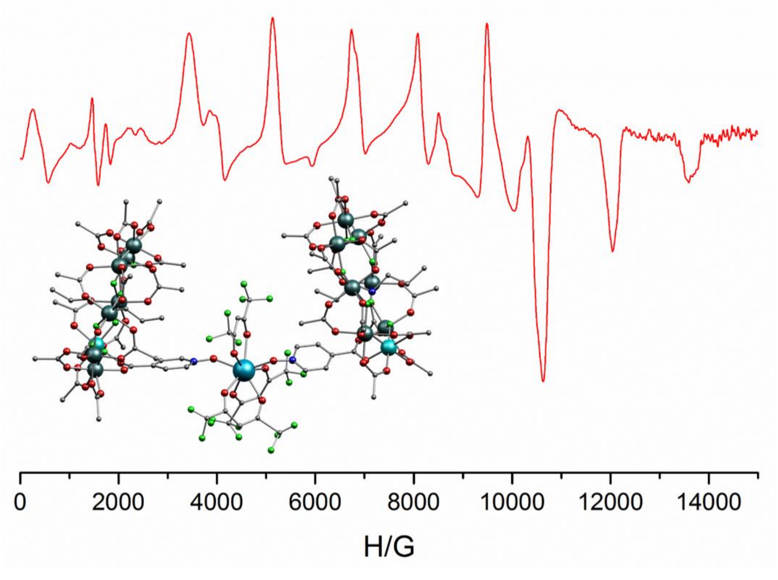

Figure. K band CW powder EPR spectrum of [{Cr_7Ni}$_2$Gd(hfac)$_3$] measured at 5 K

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Solid-state density functional study of a rhodium(I) pentane σ-complex

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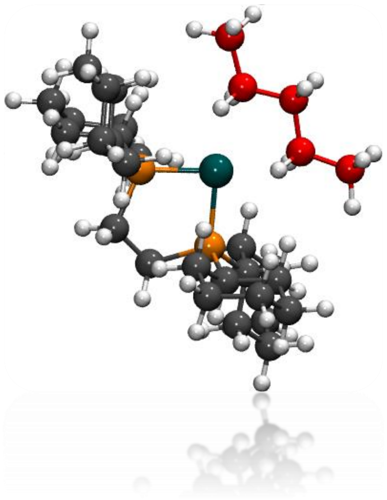
Transition metal alkane σ-complexes, in which an alkane fragment coordinates directly to the metal centre through a 3-centre-2-electron M···H–C bond, are key intermediates in catalytic C–H activation processes.[1] Detailed insight into the electronic structure of these species is fundamental for the understanding of C–H activation and functionalisation, and ultimately will guide the design of efficient catalysts to be utilised in such reactions. Recently the Weller group reported an approach for the targeted generation of alkane σ-complexes by using solid/gas single-crystal to single-crystal transformations. This synthetic route facilitated the isolation of the first two examples of such alkane σ-complexes, [Rh($R_2PCH_2CH_2PR_2$)(η^2:η^2-norbornane)][BAr$^F{}_4$] (R = Cy, ^{i}Bu, Ar^F = 3,5-(CF_3)$_2$(C_6H_4)).[2] Remarkably, the very same approach also led to the successful generation of a well-defined σ-complex of a light, linear open-chain alkane, [Rh($Cy_2PCH_2CH_2PCy_2$)(η^2:η^2-pentane)][BAr$^F{}_4$].[3]



The thermodynamic stability of the complex under ambient conditions allowed for full characterisation by single-crystal X-ray diffraction and solid-state NMR spectroscopy. Periodic density functional theory calculations were employed parallel to experiment to gain insight into the electronic structure of the metal-alkane structure and the effect of the surrounding crystal matrix. Molecular dynamics simulations in combination with solid-state NMR techniques revealed a fluxional process occurring in the solid state. The theoretical prediction of isotropic NMR chemical shifts was critical for the assignment of experimental spectra.

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Electronic Modification of NHCs Using Boryl Substituents

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Recent results suggest that the unique electronic properties of the boryl ligand class, -BX_2, can be employed to decrease the HOMO-LUMO gap of metal complexes.[1,2] While the direct formation of metal BX_2 systems of the type $L_nM(BX_2)_n$ type relies on the use of a synthetically challenging boryllithium reagent, the alternative use of boryl groups as peripheral substituents on C, N or O donor ligands is more readily accomplished and offers to provide systems with unusual steric/electronic properties.

Our work focuses on boryl substituted N-heterocyclic carbenes (NHCs). On NHCs, boryl substituents are likely to influence the σ-donor and π-acceptor properties of the carbene centre. Additionally, Dipp substituted diazaboryl substituents are likely to give super bulky NHCs. In this fashion, both the steric and the electronic properties of the NHCs can be altered merely by changing the N-substituents. Attempts to deprotonate 1,3-Dipp-1,3,2-diazaboryl disubstituted imidazolium salt have displayed the electronic properties expected.

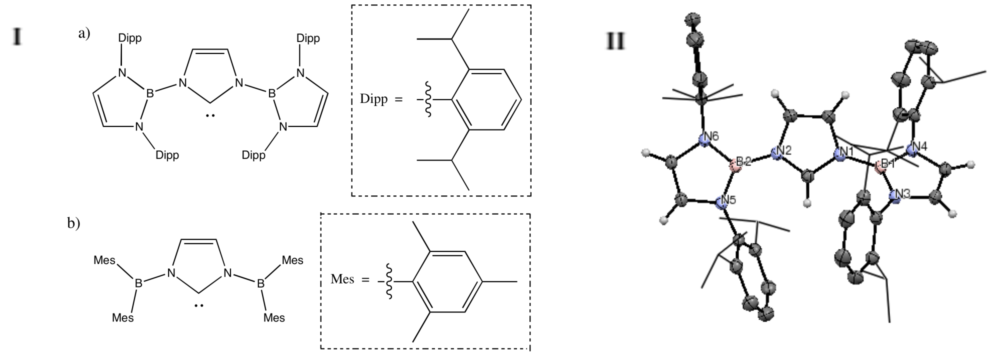

Figure 1: I a) 1,3-Dipp-1,3,2-diazaboryl disubstituted NHC **b)** Bis(dimesitylboryl) NHC **II** Crystal structure of 1,3-Dipp-1,3,2-diazaboryl disubstituted imidazolium salt.

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Room Temperature Ruthenium-Mediated C–O Bond Activation

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Contemporary interest in organometallic catalysts capable of carbon–oxygen bond cleavage stems from a broad desire to upgrade low-value bio-derived chemical feedstock to more useful molecules. While a number of phosphine supported ruthenium catalysts are now known for C–O bond cleavage little is known about the fundamental steps surrounding these reactions.[1,2] Although oxidative addition of the C–O bond to a reactive organometallic intermediate is often proposed as key step in the mechanism there are only a few well studied examples this reaction in literature.[3,4]

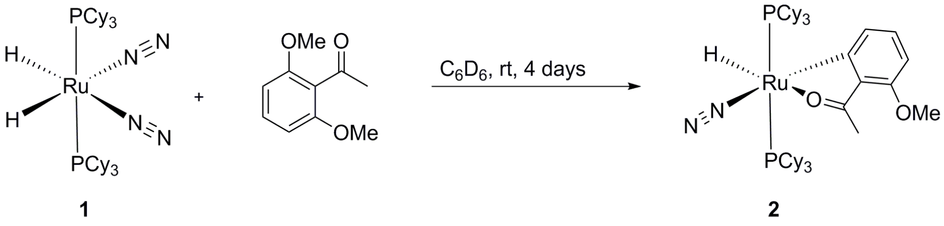

Figure 1 Ru catalyzed room temperature C–O cleavage

Here we show that, under an atmosphere of N_2, $[RuH_2(N_2)_2(PCy_3)_2]$ can be isolated,[5] and that this complex is capable of room temperature C–O bond cleavage of the sp^2C–O bond of 2,6-dimethoxyacetophenone to generate the cyclometallated intermediate **2** (Figure 1).

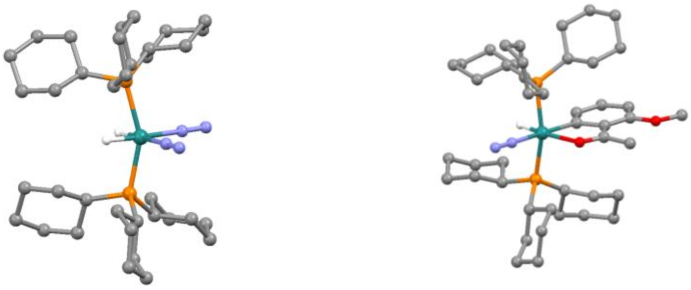

Figure 2 X-ray crystal structure of **1** and **2** respectively

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Towards Multi-Metallic Cyaphide Complexes

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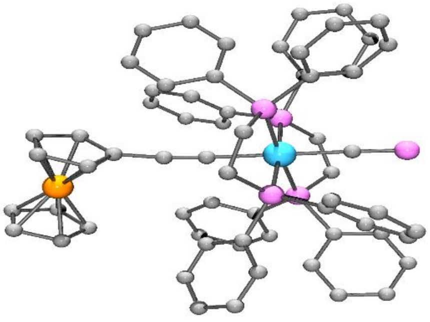
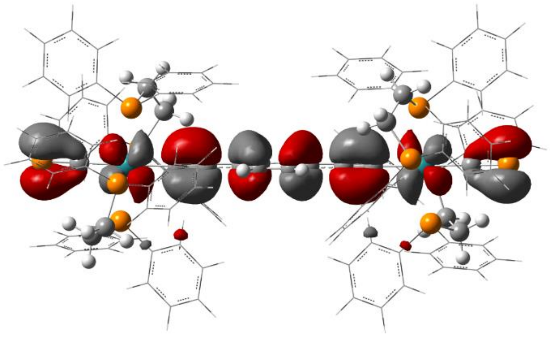
Cyaphide ($^-C\equiv P$) has long proven to be an elusive moiety, both as a discrete salt and ligated to a transition metal centre. While first alluded to in 1992 as the transient species $[PtCl_2(PEt_3)(C\equiv P)]$,[1] it was only in 2006 that an unequivocal example of a ligated cyaphide was produced in the complex *trans*-$[RuH(dppe)_2(C\equiv P)]$, formed *via* the intermediacy of the η^1-phosphaalkyne complex $[RuH(dppe)_2(P\equiv CSiPh_3)]OTf$.[2]

Recently, we have reported an enhanced synthetic methodology for the introduction of cyaphide to transition metal centres bearing alkynyl ligands in the *trans* position,[3] and have begun to investigate the electronic structures of these complexes; using a combined experimental and computational approach. Furthermore, it has been possible to furnish a variety of monometallic cyaphide complexes with relative ease and in good yields.

We have now applied this method to the synthesis of complexes featuring multiple metal centres. The synthesis and study of the first homo- and hetero-bimetallic cyaphide complexes will be discussed.[4]





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3d-5f rings constructed by chromium horseshoes as polydentate fluoride ligands

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We have shown that {Cr_6} horseshoes can act as ligands to sodium[1] and lanthanides[2] leading to novel heterometallic rings. Now we manage to extend this system to 5f block tetravalent ions, such as Th(IV) and U(IV).

The reaction between [$Th(O_2C^tBu)_4$] and Cr_6 horseshoe in refluxing toluene led to a Cr_6Th_2 ring [$(^nPr_2NH_2)_2(Cr_6Th_2F_{12}(O_2C^tBu)_{16})$] (**1**), while the reaction in THF/MeCN mixture led to a Cr_6Th ring [$Cr_6ThF_7(O_2C^tBu)_{15}(Me_2SO)$] (**2**). The H-bonds of protonated amines to terminal fluoride groups in play important role in constructing these two different 3d-5f rings.

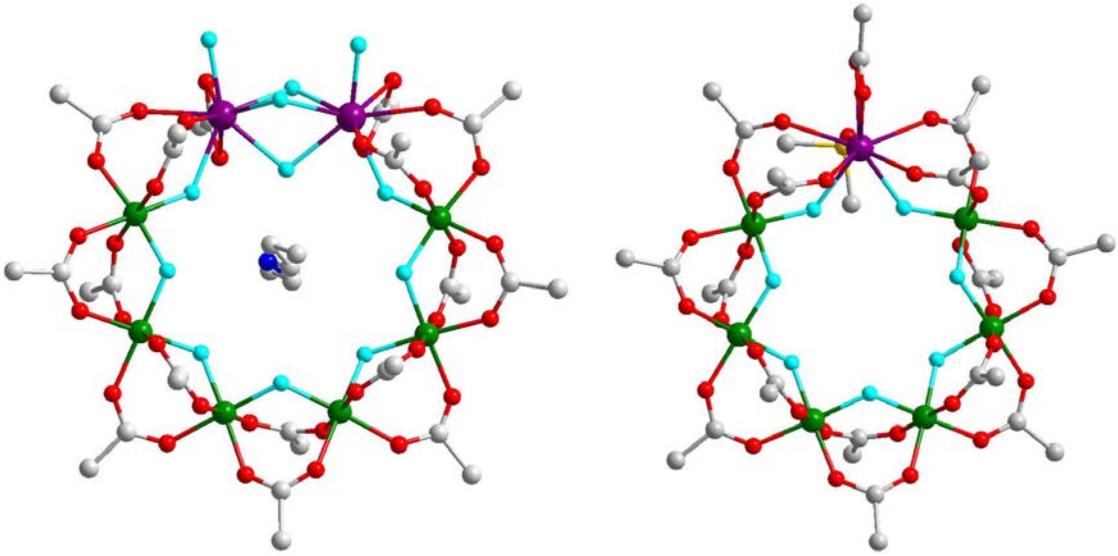

Fig.1 The structures of **1** and **2** in the crystal. Colours: Cr, green; Th, violet; O, red; F, turquoise; N, blue; S, yellow; C, gray.

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New Route to Layered Zinc Hydroxides (LZHs) using Organometallic Precursors and the Exfoliation of LZH with Oleate Ligands

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Layered zinc hydroxides (LZHs) are 2D layered compounds consisting of an inorganic unit (zinc hydroxide sheets) and an organic unit (intercalated organic anions). The general formula is $Zn_5(OH)_8(A^-)_2 \cdot nH_2O$ and typically they are synthesised through methods with harsh conditions such as high temperature, high alkalinity and long reaction time.[1,2] Typically the exfoliation of these layers is achieved through ultrasonication in polar solvents, *e.g.* formamide/1-butanol. One disadvantage to existing exfoliation systems is the degradation of LZHs to ZnO.[3,4] Herein, we present a new synthetic route for LZHs through the controlled hydrolysis of organometallic precursors (figure 1), which uses mild reaction conditions. A range of carboxylates were successfully intercalated into LZHs. LZH with oleate ligands has good solubility in an apolar organic solvent, toluene, and the exfoliation of LZH–Ole in toluene through mechanical stirring for 2 h was achieved (figure 2). Exfoliation of small nanosheets is confirmed using atomic force microscopy (AFM) and transmission electron microscopy (TEM/STEM). Degradation of LZH–Ole to ZnO was not observed after the exfoliation treatment. LZH–Ole shows potential to be a good candidate in fabrication of electronic devices and other applications, such as biomedical applications.

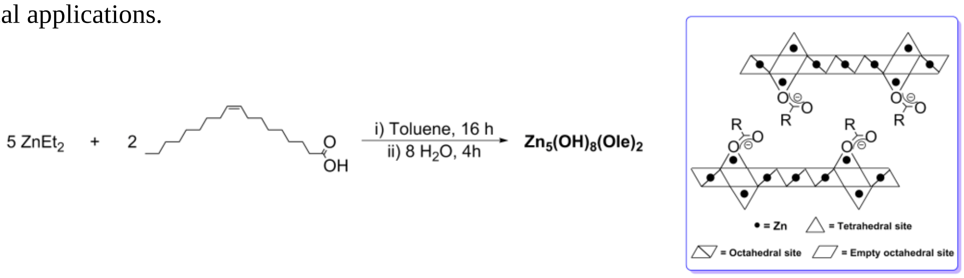

Figure 1. The synthesis of LZH–Ole through controlled hydrolysis of a mixture containing $ZnEt_2$ and oleic acid (*left*). Blue box shows the general structure of LZH (*right*).

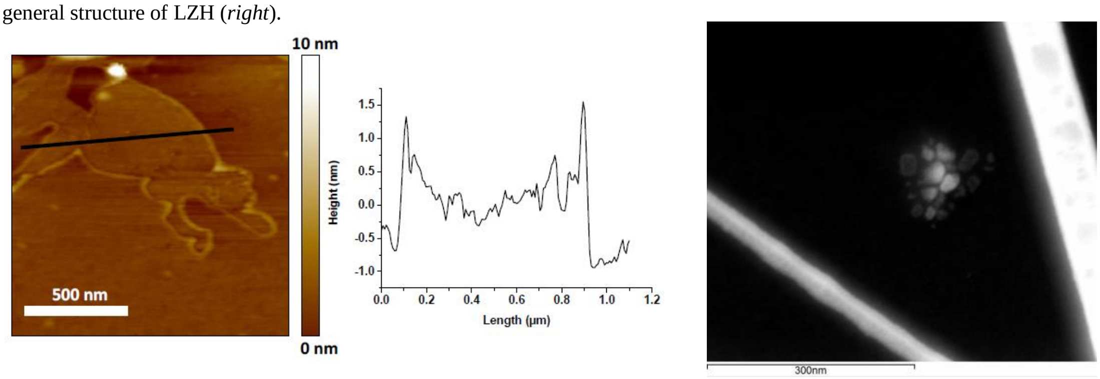

Figure 2. AFM image and height profile (*left*) of a monolayer of LZH–Ole from exfoliation of bulk material through mechanical stirring in toluene for 2 h. STEM–HAADF image (*right*) of exfoliated LZH–Ole.

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New Multimodal Nanocomposites for PET and SPECT Imaging

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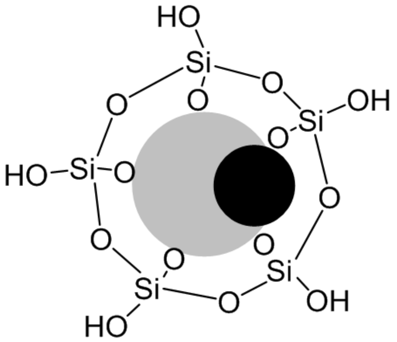
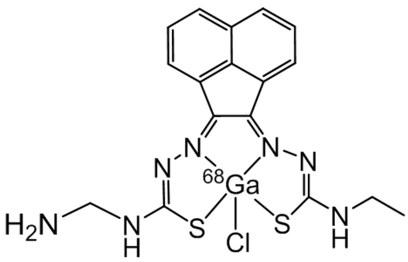
Cancer is one of the top ten causes of death in the world, and the survival rate is higher at the earlier the stage at which the tumour is diagnosed. For this reason, accurate diagnosis through medical imaging is crucial for the effective management of the disease and paves the way to personalised medicine.[1] The majority of medical imaging methods are based on the use of radioisotopes. For example, positron emission tomography (PET) uses positron emitting radioisotopes such as ^{68}Ga ($t_{1/2}$ = 67.71 min), ^{64}Cu ($t_{1/2}$ = 12.70 h), or ^{89}Zr ($t_{1/2}$ = 78.41 h). When these radioisotopes are anchored onto an adequate *in vivo* delivering vehicle in precancerous stages, they selectively concentrate around infected sites and can report on areas of rapid cell division. In this context, there is a need to develop new multifunctional composites with specific radioisotopes to radiolabel cancer cells by using PET and SPECT (single-photon emission computed tomography). In this respect, magnetic iron oxide nanoparticles are biocompatible and have great potential as contrast agents in magnetic resonance imaging.[2] The functionalisation of their surface with silica improves their stability, in addition to creating biocompatible surfaces for the immobilisation of antibodies, which allows them to be used for biomedical applications.[3] It also facilitates the attachment of organic molecules such as ligands suitable to chelate radioisotopes. Quantum dots can also be incorporated to the nanoparticles, allowing the analysis of the systems by fluorescence imaging. We have synthesised and characterised iron oxide/silica core-shell nanoparticles, and several different ligands suitable to chelate radioisotopes based on thiosemicarbazones and DFO (Deferoxamine mesylate salt) together with their complexes. Future work implies the assembly of the different components of the system and their trial in "hot" chemistry.



[^{68}Ga]Ga-BTSC



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GEOMETRY CONSTRAINED MAIN-GROUP COMPLEXES FOR SMALL MOLECULES ACTIVATION

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Precious transition metals are well known for undergoing reversible redox processes in the activation of small molecules and subsequent catalytic synthesis of many compounds. However these metals are rare and expensive, therefore creating a lot of interest in abundant main-group alternatives. In line with this, recent studies have highlighted a number of main-group systems that are able to activate challenging small molecules.[1] The Arduengo group has previously shown that by distorting a P(III) compound into a planar "T-shaped" geometry it provides an orbital arrangement akin to transition metal, which allow for the cleavage of polarised E–H bonds and preliminary evidence of catalytic activity.[2] Radosevich and his group has successfully developed catalytic hydrogenations using the Arduengo's compound.[3]

Our group is interested in tuning the steric and electronic properties of a variety of novel geometry constrained ligands of group 15 elements. Our under study includes redox active ligands as well as saturated and unsaturated ligands (see figure 1). Our investigation expands to arsenic analogous of described ligands. The +3 oxidation state of arsenic is lowered in energy which should enhance the reactivity of the reductive elimination step. We are currently investigating the reactivity of these compounds towards small molecules.

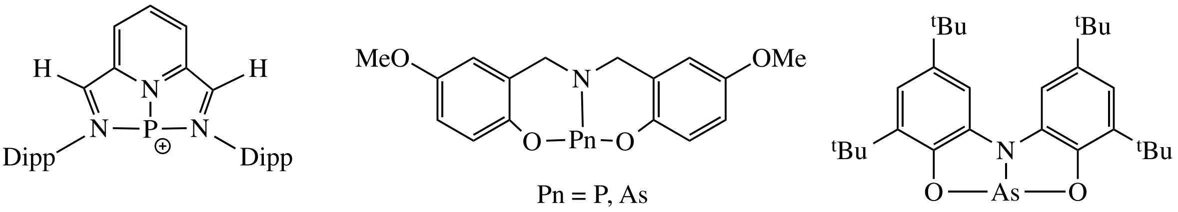

Figure 1

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A copper-benzotriazole based coordination polymer promotes an easy access to dihydropyridines

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In view of the importance of the synthesis of pyridine derivatives, the metal-catalyzed access to 1,4-dihydropyridines (1,4-DHPs) has been receiving considerable attention from numerous studies. 1,4-DHPs and their derivatives are an important class of biologically active organic compounds, notably the calcium channel blocker amlodipine. They have also been used extensively in pharmacology as antidepressants, antitumoral, antianxiety and anti-inflammatory agents. Since the first synthesis (Hantzsch reaction), numerous multicomponent reactions (MCRs) have been achieved for the synthesis of 1,4-DHPs derivatives. In recent years, a series of metal-complexes or salts and solid supports have been used for such a reaction, however expensive reagents and hazard conditions (high temperature and tedious work up) were required. Therefore, it is desirable to develop an efficient and practical method for the synthesis of 1,4-DHPs under eco-friendly conditions.

In the present work, a novel benzotriazole-based ligand was employed to afford a one-dimensional Copper (II) coordination polymer, $[Cu(L)_2(MeCN)_2]\cdot 2(ClO_4)\cdot MeCN$. This compound displays remarkable homogeneous catalytic activity towards the one-step synthesis of 5-aryl-1-(benzylideneamino) 1,4-dihydropyridines, through a new Cu-catalyzed coupling between symmetrical electron rich azines and the triple bond of alkyl propiolate. This method provides good yields, with catalyst loadings as low as 0.3% and under mild conditions. Crystal structures of the coordination polymer, as well as the 1,4-DHP have been obtained for characterization.

Ruthenium(II) carbonyl complexes-Potential anti-cancer agents?

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In the search for new anti-cancer drugs with better cytotoxic properties, ruthenium based complexes have become one of the most promising of this new generation of anti-cancer agents. Compared to platinum complexes, ruthenium complexes have been found to be less toxic to healthy cells and are also able to treat platinum resistant cell lines. NAMI-A, a Ru(III) complex, was the first to successfully finish Phase 1 clinical trials, and has been shown to exhibit low cytotoxicity with better efficacy against metastatic tumours. Despite these successes there is still need to develop novel anti-cancer drugs with better selectivity and cytotoxicity.[1,2]

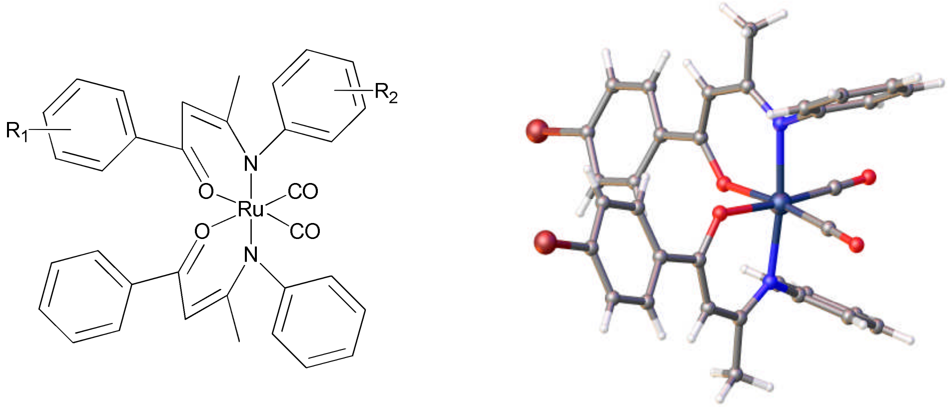

Figure 1: Ruthenium(II) carbonyl complexes

This project is concerned with the design, synthesis and characterisation of a library of novel ruthenium complexes of the type RuX_2L_2, where X = halogen or CO, and L is a functionalised bidentate acnac ligand. The acnac ligands coordinate to the ruthenium metal centre *via N,O-* coordination and in *trans* geometry, with the CO ligands in a *cis* geometry (**Figure 1**). Fully characterised complexes will be tested for their structural-activity relationships (SARs) including cytotoxicity (IC_{50}), to demonstrate the validity of our approach to design novel anti-cancer agents. Investigative studies to determine the source of the CO ligands will be carried out.

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Anionic N-Heterocyclic Carbenes in Transition Metal Chemistry

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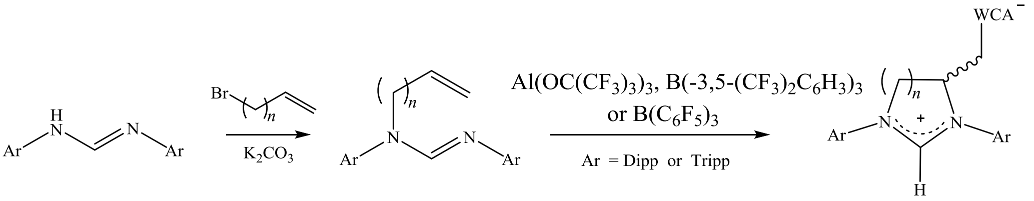
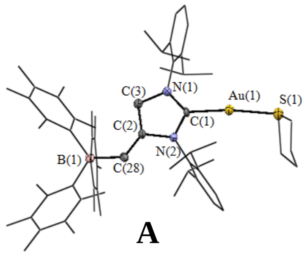
N-heterocyclic carbenes (NHCs) have been widely exploited in cationic metal species implicated in homogenous catalysis.[1] In recent years, NHC ligands have been reported incorporating pendant anionic groups, which when partnered with mono-cationic metal systems generate zwitterions with enhanced solubility in apolar solvents.[2] Systems in which the anionic group is a remote weakly co-ordinating anion (WCA) are especially attractive, due to the minimal interference by the WCA in ligation properties. However, existing methodologies are limited in terms of heterocycle ring size, WCA and N-functionality.[3]



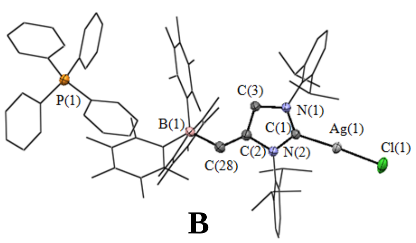
Herein, we report a general synthetic route to a library of protonated NHC pro-ligands via Lewis acid promoted exocyclic ring closure, notably with $B(C_6F_5)_3$. 5, 6 and 7-membered ring variants can be accessed for both Ar = Dipp and Tripp. C(2) deprotonation leads to the synthesis and characterisation of 5-Dipp^{BCF} complexes of silver and lithium, which are useful transfer agents to generate further complexes (e.g. with copper, and gold and rhodium). Crystallographic data (through %V_{bur} calculations)[4] and NMR data indicate the WCA component is sufficiently well isolated to have minimal impact on the steric and donor properties of the NHCs, but to bring about markedly higher solubility in hydrocarbons.[5]



A

A = (5-Dipp^{BCF})Au(THT)

B = [PPh$_4$][(5-Dipp^{BCF})AgCl]



B

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Stereoselective Halogenation of Integral Unsaturated C-C Bonds in Chemically and Mechanically Robust Zr and Hf MOFs

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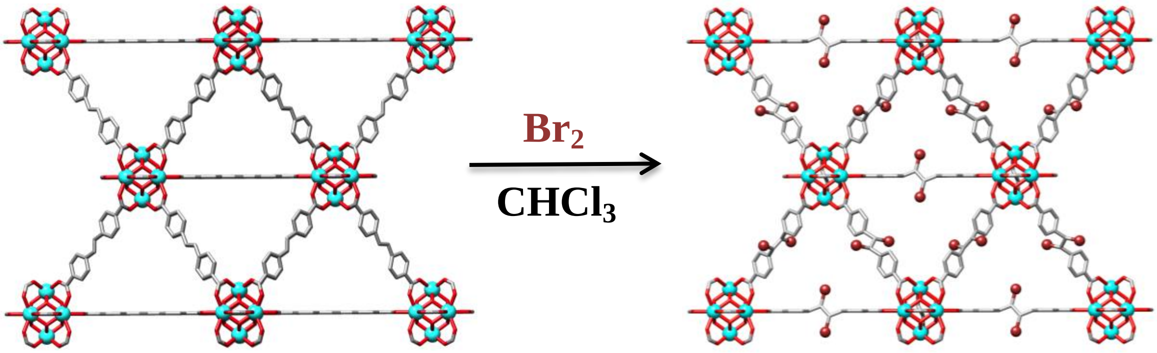
Zirconium and Hafnium MOFs, containing $M_6O_4(OH)_4$ clusters (M= Zr or Hf), as in the UiO-66 isoreticular series, have received large amounts of interest due to their high chemical and mechanical stabilities. We demonstrate the successful synthesis and characterisation of a range of extended UiO-66 type MOFs, both as bulk microcrystalline and single crystal forms, containing integral unsaturated alkene, alkyne and butadiyne units, which are susceptible to postsynthetic halogenation. The combined chemical and mechanical stabilities of the MOFs enable facile quantitative bromination of integral reactive sites to occur in a **single-crystal to single-crystal** (SCSC) manner,[1] resulting in unprecedented levels of crystallographic characterisation surrounding the stereoselectivity of the transformation and the resulting mechanical contraction,[2] which in the utmost case is 0.76 Å.[3] We also investigate the capacity of these materials for I_2 sequestration from the vapour phase with an interpenetrated Zr MOF demonstrating an I_2 storage capacity of 279 % *w/w* – comparable to benchmark materials – through a combination of both physi- and chemi-sorption.



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Hydrofluorothermal synthesis of novel, fluoride containing transition metal phosphates and sulfates

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The required step-wise increase in the performance of rechargeable Li-ion and Na-ion batteries demands fundamental advances in the properties of their component materials. This can be only be achieved through the discovery and characterisation of novel electrode and electrolyte materials which exhibit higher working cell potentials, increased specific capacities and improved recycling. Polyanionic transition metal framework materials containing Li^+ and Na^+ cations in the inter-framework space have shown promising cell potentials and capacities when employed as electrode materials.[1] The inclusion of fluoride anions into transition metal phosphate and sulfate structures is particularly favourable as it increases the cell potentials of batteries employing these material as cathodes.[2] The work to be presented will focus on the high fluoride hydrothermal ("*hydrofluorothermal*") synthesis of novel transition metal framework materials with structural features favourable for use as battery electrode or electrolyte materials. Specific materials to be described include the potential Li-ion electrolyte, $Li_2TiF_2(SO_4)_2$, whose structure, shown in Fig. 1, contains chains of interconnected $[TiF_2(SO_4)_2]^{2-}$ anions in a three-dimensional, interconnected, array of lithium ions.

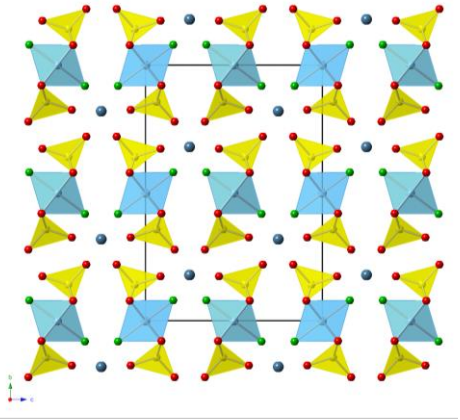

Figure 1 *Structure of $Li_2TiF_2(SO_4)_2$ shown along the a-axis. TiO_4F_2 octhedra shown in pale blue, SO_4 tetrahedra shown in yellow and Li, O and F atoms shown in dark blue, red and green respectively. The unit cell is outlined in black.*

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Proper ferroelectricity in the Dion-Jacobson material CsBi$_2$Ti$_2$NbO$_{10}$

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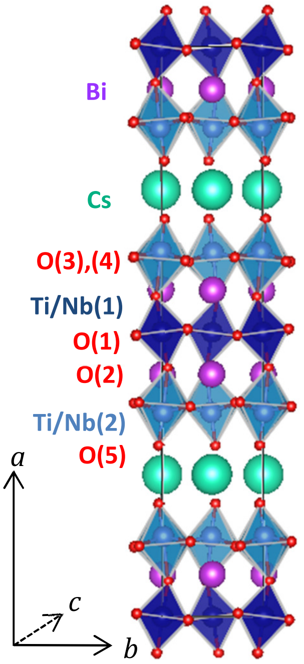
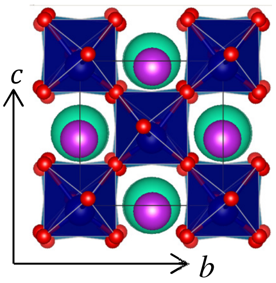
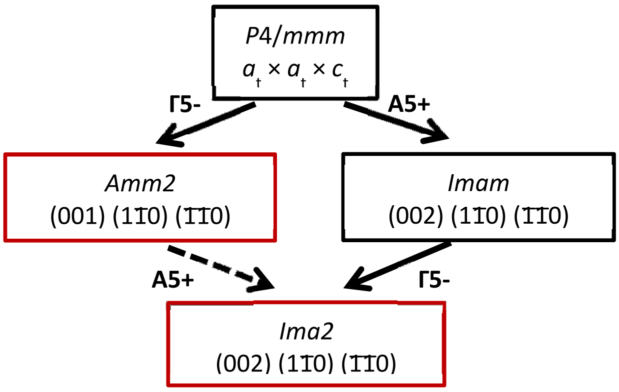
A diverse range of materials and properties are exhibited by layered perovskites. We report on the synthesis, characterization and computational investigation of a new ferroelectric - CsBi$_2$Ti$_2$NbO$_{10}$ - an n = 3 member of the Dion-Jacobson (DJ) family.[1] Structural studies using variable temperature neutron powder diffraction indicate that a combination of octahedral rotations and polar displacements result in a polar, ferroelectric structure below 545°C. Density functional theory calculations reveal that the wider perovskite blocks in CsBi$_2$Ti$_2$NbO$_{10}$ stabilise proper ferroelectricity, in contrast to the hybrid-improper ferroelectricity reported for other DJ phases.[2-3] Our results raise the possibility of a new class of proper ferroelectric materials analogous to the well-known Aurivillius phases.[4]







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Title: Anion Effects on the Stability of σ-Alkane Complexes

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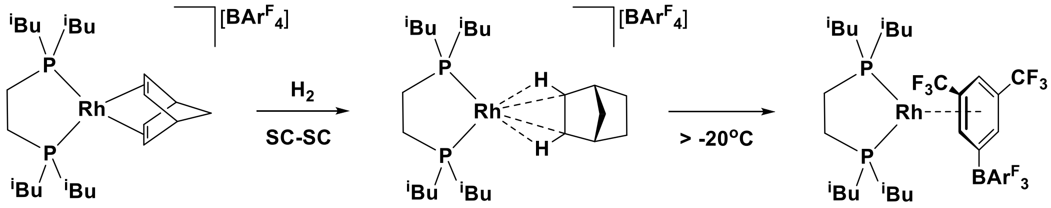
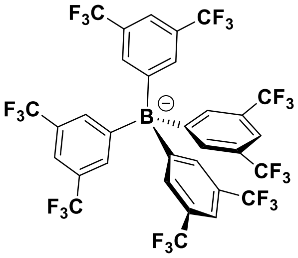
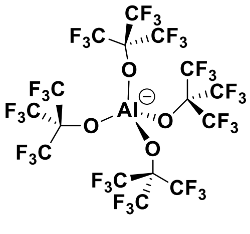
Transition metal catalysed functionalisation of alkanes to create higher value chemicals has been an intense area of research over the last 30 years. σ-Alkane complexes are considered key intermediates in C-H activation processes. The non-polarised C-H bond renders σ-alkane complexes highly labile and thus typically characterised at very low temperatures by NMR spectroscopy.[1] Weller recently reported the first example of a σ-alkane complex that is stable in the solid-state at temperatures below -20 °C.[2] This complex was synthesized by a solid/gas single-crystal to single-crystal procedure (below). This novel approach eliminates species such as solvents that may compete with the alkane for the metal coordination sites.

The alkane was rapidly displaced by the [BAr$^F{}_4$]$^-$ anion at ambient temperature in the solid-state (below) and upon dissolving in $CDCl_2F$ at -110 °C. This poster presents the use of the tetrakis(perfluoro-*tert*-butoxy)aluminate anion,[3] [Al(O^{t}Bu^F)$_4$]$^-$ (below), as an alternative weakly coordinating anion to [BAr$^F{}_4$]$^-$ and explores the impact of this anion substitution on the stability of σ-alkane complexes.





[BAr$^F{}_4$]$^-$



[Al(O^{t}Bu^F)$_4$]$^-$

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Complexes of cobalt(II), nickel(II) and copper(II) with 4-thiazolecarboxylic acid.

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Five new molecular complexes of chemical formula [M(4-tza)$_2$(H$_2$O)$_2$] (M = Co, Ni, and Cu) and a complex of [Cu(4-tza)$_2$]·2H$_2$O using 4-thiazolecarboxylic acid (4-tza) as ligand have been successfully synthesized and structurally characterized by single crystal X-ray diffraction. Two district polymorphs (α and β) are found for both [Co(4-tza)$_2$(H$_2$O)$_2$] and [Ni(4-tza)$_2$(H$_2$O)$_2$]. The effects of solvent composition and temperature on the formation of these polymorphs have been investigated and phase behaviour of the polymorphs was studied through powder X-ray diffraction. Unlike two complexes of Co and Ni, [Cu(4-tza)$_2$(H$_2$O)$_2$] complex does not display polymorphism but exhibits irreversible structural transformation from [Cu(4-tza)$_2$(H$_2$O)$_2$] to the dehydrated form, [Cu(4-tza)$_2$], upon heating.

Is enantioselective hydrogenation catalysis possible using achiral phosphines?

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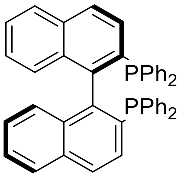
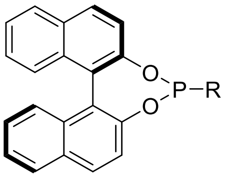
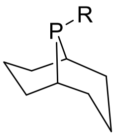
The enantioselective asymmetric hydrogenation of alkenes is an important process with industrial applications and has attracted much academic attention. Optically active phosphorus ligands are preeminent in this field. The asymmetric induction achieved with complexes of diphos ligands such as binap is associated with the rigidity of the backbone producing a highly defined chiral environment.[1] More subtly, restricted M-P rotation is postulated to be the source of the high enantioselectivites obtained with complexes of monodentate P-ligands such as Monophos.[2]



(R)-BINAP

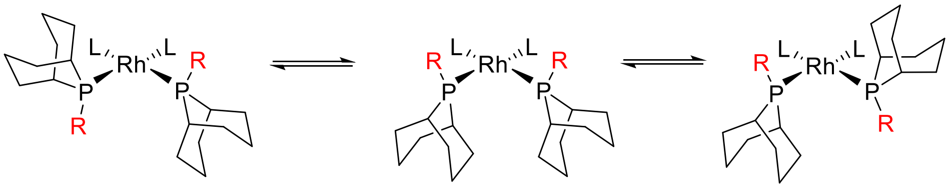


Monophos



PhobPR

It has recently been demonstrated that bicyclic PhobPR complexes display unexpected high barriers to M-P bond rotation, where M = Pd, Pt, or Ru.[3] In complexes of the type cis-[Rh(diene)PhobPR)$_2$][BF$_4$] syn and anti rotamers are anticipated. The anti form is in fact a pair of enantiomers (labelled δ/λ in the figure below) by the virtue of the C_2 symmetry.



λ
C_2 (anti)

meso
C_2 (syn)

δ
C_2 (anti)

Here, this new form of chirality is demonstrated to be present by $^{31}P\{^1H\}$ NMR spectroscopy of diastereoisomers featuring the δ/λ rotamers. Furthermore, the major rotamer has been resolved, separated and used in Rh-catalysed asymmetric hydrogenation.

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Pt(0) Monocarbonyl Complexes for Small Molecule Activation

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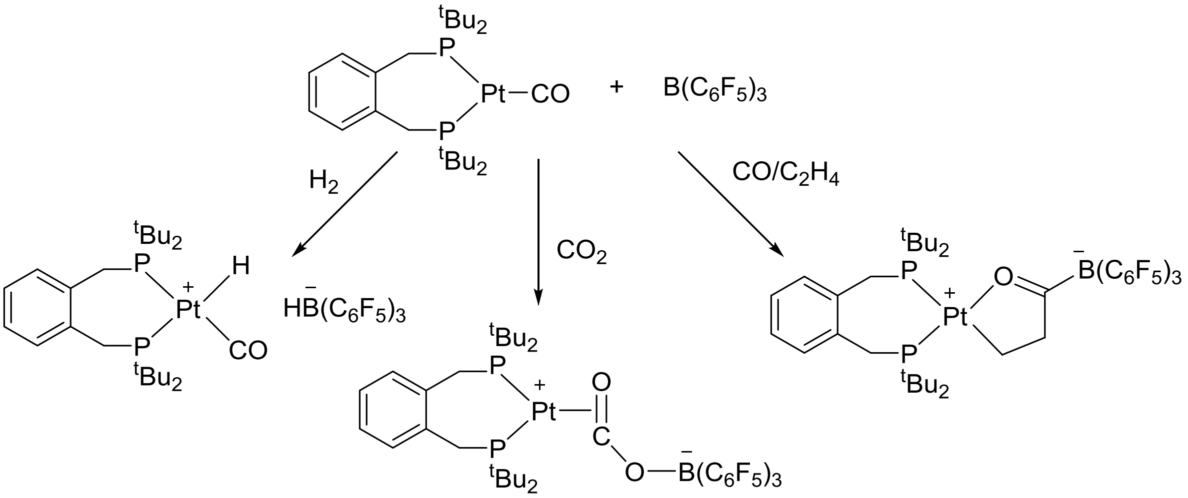
Small molecules have the potential to be sustainable building blocks in the chemical industry. However, developing new catalytic transformations of these molecules into useful compounds can be challenging. In recent years, the field of Frustrated Lewis Pair (FLP) chemistry has grown exponentially.[1] We, amongst others,[1,2] have extended this chemistry to involve early transition metal-containing FLPs which are capable of undergoing novel transformations such as cleavage of carbon-halogen bonds.[3] However, exploiting these reactions for catalysis has been inhibited by the high oxophilicity of the early transition metals. We have recently reported the use of an electron rich platinum(0) complex where the metal centre acts as the Lewis base cooperatively with tris(pentafluorophenyl)borane (BCF) as the Lewis acid.[4] The results presented here will include successful FLP activity and the unprecedented coupling of CO and ethene to form an acyl borate.[5] Both computational and experimental investigations of this system suggest the potential application to catalytic activation of small molecules.



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Facile Dehydrogenation of Amine Boranes with a Bimetallic Titanium Pentalene Sandwich Complex

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University of Sussex, Brighton BN1 9RH.

Amine boranes have been extensively studied as practical hydrogen storage materials[1-3]. The homoleptic bimetallic complex $Ti_2(Pn^{\dagger})_2$ **(Figure 1)** has been found to catalytically dehydrogenate several amine boranes in catalyst concentrations as small as 5 molar percent at room temperature. A range of characterised organic products and intermediates will be presented, in addition to novel inorganic species involved in this process that have been isolated and analysed *via* X-ray diffraction and spectroscopic methods **(Figure 2)**.

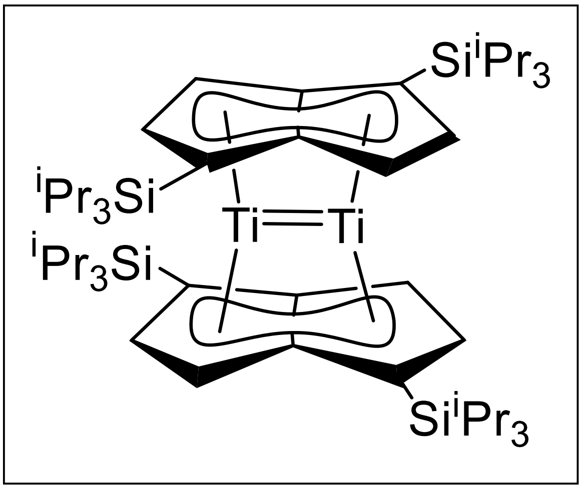

Figure 1

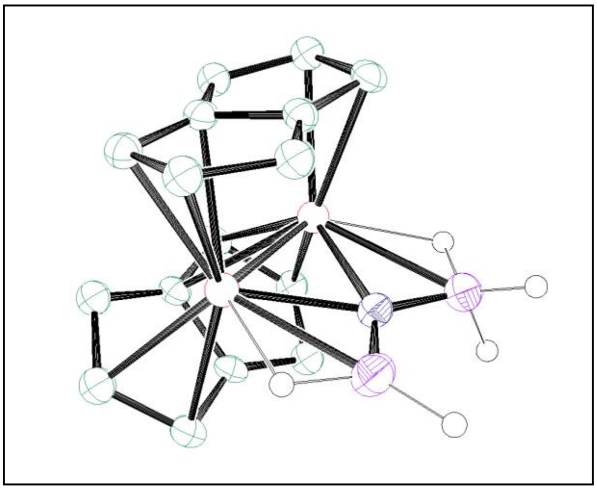

Figure 2

References:

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Poly-Phosphono Cyclen Based Ligands for Complexation of PET Metals

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Molecular imaging has became the technique of choice for the management of patients with cancer and other diseases. It is also a valuable investigative tool for the study of drug action and the development of new therapeutic approaches. A number of techniques based upon fundamentally different physical principles give rise to 3D images with diagnostic value and are now well established in clinical applications and in drug discovery research. Our interest focuses in particular upon Positron Emission Tomography (PET) and Single-Photon Emission Computed Tomography (SPECT) which may be used to give information on functional process as well as structure. In certain disease conditions, these techniques provide diagnostic support for clinicians for which other methods are not well suited and they are becoming of increasing importance in obtaining 3D images of patients *in vivo*,.[1]

The basis of PET relies upon administering a radiopharmaceutical agent that contains a positron emitting radioisotope. Non-metallic radionuclides such as ^{15}O, ^{11}C and ^{18}F are currently most widely used in PET imaging, but their short half-lives limits their application.[2]
Metallic radionuclides such as ^{64}Cu, ^{86}Y, ^{89}Zr, ^{68}Ga, present longer half-lives and deliver the opportunity to form imaging probes that better match the biological half-lives of several important classes of biological molecules such as poly-peptides or antibodies.[3]

Clearly, the successful design of a PET imaging probe (as with other applications of metal-based imaging agents), requires that the metal is bound to a suitable ligand system (or set of ligands) that will form complexes that remain robust under physiological conditions. Most studies to date rely upon ligand systems that have been shown to be effective for some metal, predominantly applied to applications in MRI, but have not been optimized for binding Y and Zr PET isotopes. One of the most widely used approaches is to apply ligands based upon the cyclen core structure; examples include DOTA, DO3a, DO2a, etc. [4]

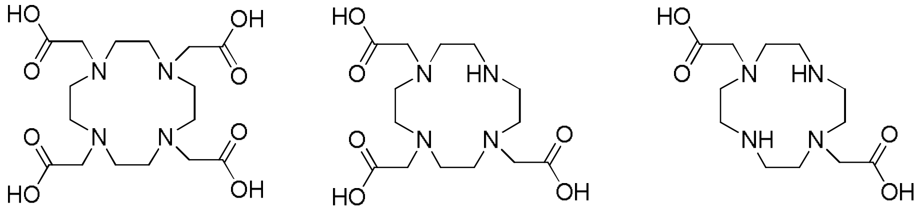

Fig 1: DOTA, DO3a and DO2a

The aim of this research is to develop macrocyclic ligands suitable for chelating Y and Zr radionuclides and to compare these ligands to the 'industry standard' chelator desferrioxamine (DFO).[5]
An example of our approach that we will discuss includes extending the functionality of this ligand system by incorporation of an alcohol group, thus enabling the attachment of biological targeting entitites.

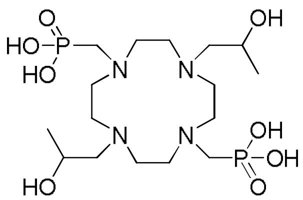

Fig 2: The ligand synthesised

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Poster title: Structural movies of enzyme catalysis in hemeproteins: first frames.

Tadeo Moreno and Mike Hough.

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Catalytic processes carried out by enzymes can be of great complexity, involving several steps and intermediates prior to arriving to the final product. X-ray crystallography just provides time-lapse moments of these dynamic processes. We aim to overcome this inherent limitation by combining the successive acquisition of diffraction datasets of protein crystals with Single Crystal Spectroscopies (SCS; e.g. UV-vis, Raman, Fluorescence), while enzymatic reactions within the crystals are driven by synchrotron radiation. Spectroscopic data will be a valuable complementary information to correctly assign structures with its oxidation and/or ligand state, and be able to relate each structure with an intermediate state. Our final aim is to build up structural movies of the catalytic processes studied. The proteins we are working with are all heme cointaining enzymes such as dehaloperoxidase (DHP) and dye-decolorising peroxidase (DyP).

So far we have been able to obtain atomic resolution structures of complexes with different ligands for DHP, and we have also characterized all of them spectroscopically with Resonance Raman spectroscopy at Swiss Light Source (SLS, Villigen). As a test for the structural movies, we have also collected successive datasets coupled with Resonance Raman for a ferric DHP crystal, observing changes in the spectra as datasets go on and the dose absorbed by the crystal increases.

For DyP we have measured X-ray crystallography data coupled with UV-vis spectroscopy at ESRF (Grenoble, France), with the final aim to characterize the different intermediates in the peroxidase cycle of the protein. We have been able to observe the reduction of the protein by the beam, and the fingerprint when ligands are bound and when DyP has been treated with hydrogen peroxide.

At this point, we have demonstrated that we can tell between different oxidation and ligand states, and that we have to tools needed to structurally characterize and assign different intermediates within a mechanism. Our next steps would be to apply this approach to protein crystals soaked or co-crystallized with the substrate and optimize the conditions at the beamline to drive reactions *in situ* and generate the different frames for our structural movies.

Stabilisation of Uranyl(V) with Bulky Alkylsilylamide Ligands

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Despite the important role of uranyl(V) in redox reactions in fuel corrosion,[1] and in biological and mineral samples,[2] this oxidation state still remains under studied compared to its +VI counterpart. This is primarily due to the highly unstable nature of the +V state. Uranyl(V) has a strong tendency to disportionationate to the more stable uranyl(VI) and uranium(IV) species.[3]

Our area of interest is attempting to stabilise uranyl(V), using bulky alkylsilylamine ligands, predominantly focusing on hexamethyldisilylamide (HMDS, Figure 1).[4] Work conducted within the group has shown that bulky alkylsilyl amide ligands are capable of stabilising uranyl in the +V oxidation state thereby discouraging disportionation. Study of this ligand with varied R groups have shown great promise in stabilising low oxidation state lanthanides and uranium.[5] The study of these ligands with uranyl will be discussed, as well as the effectiveness of bulky alkylsilyl amine ligands to inhibit the disportionation of the uranyl(V) derivatives.

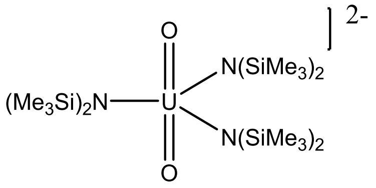

Figure 1: Uranyl(V) tris(HMDS)

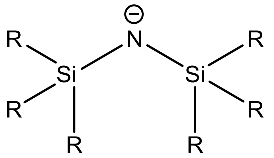

Figure 2: General structure of alkylsilylamide ligands, R = alkyl group

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Metallopolymers at the Covalent-Supramolecular Boundary Based on Nickelocene.

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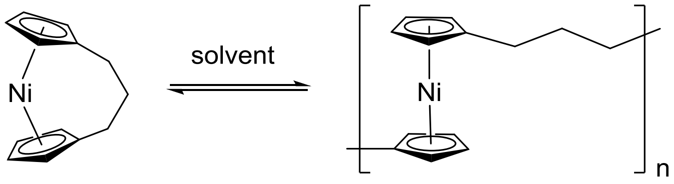
The interactions of metal ions with ligands in metal-containing polymers can involve covalent bonding, which is essentially static in nature, or labile coordination bonds, which lead to dynamic, supramolecular materials.[1] We have recently synthesised a main chain polynickelocene with a trimethylene spacer, **2**.[2] This material is either static or dynamic in behaviour depending on the polarity of solvent due to the relatively weak Ni–cyclopentadienyl ligand interactions. As a result of the small free energy of polymerisation, at low concentration or at elevated temperatures in a polar solvent, the polynickelocene **2** depolymerises via a retro-ring-opening polymerisation to the moderately strained [3]nickelocenophane monomer **1**.[3]



1 **2**

Figure 1. Reversible ring-opening polymerisation of tricarba[3]nickelocenophane.

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Scandium-Catalyzed Intermolecular Hydroaminoalkylation of Olefins with Unactivated Tertiary Amines

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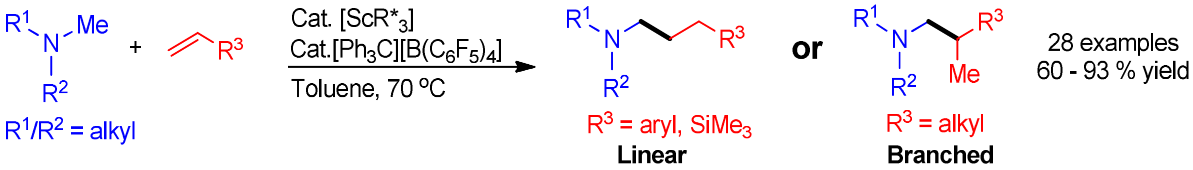
Tertiary amines are ubiquitous across the chemical sciences and there is currently great interest in selectively forming these species *via* atom efficient routes. In this regard, intermolecular catalytic hydroaminoalkylation of olefins presents an attractive, 100% atom economic method for forming new C–C bonds which complements the C–N bond forming reaction, hydroamination.[1] A number of efficient catalysts for hydroaminoalkylation of olefins have been reported, most of which are based on group IV and V metal centres and the mechanism for this processes are widely believed to occur *via* metallaziridine intermediates.[2] A substrate N–H bond must be broken for such a species to form, and this mechanistic requirement restricts the substrates to primary and secondary amines. Whilst limited examples of hydroaminoalkylation with tertiary amines have been reported for Ru, a pyridyl- directing group is essential for reactivity in these systems.[3]



We have recently shown that half sandwich mono-cationic rare-earth alkyl species act as efficient catalysts for olefin polymerization as well as for the alkylation of sp^2 and sp^3 C–H bonds of aromatic compounds such as anisoles and pyridines.[4] Here we report that the simple homoleptic trialkyl complex $[Sc(CH_2C_6H_4NMe_2\text{-o})_3]$ is a highly active catalyst for the hydroaminoalkylation of a variety of olefins with unactivated, aliphatic amines when activated with one equivalent of $[Ph_3C][B(C_6F_5)_4]$. This represents the first example of rare-earth catalysed hydroaminoalkylation as well as the first example of direct, 100% atom efficient, catalytic C–H alkylation of unactivated tertiary amines.

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Control of the architecture of Na(PCO) and nitrilium salts reactions

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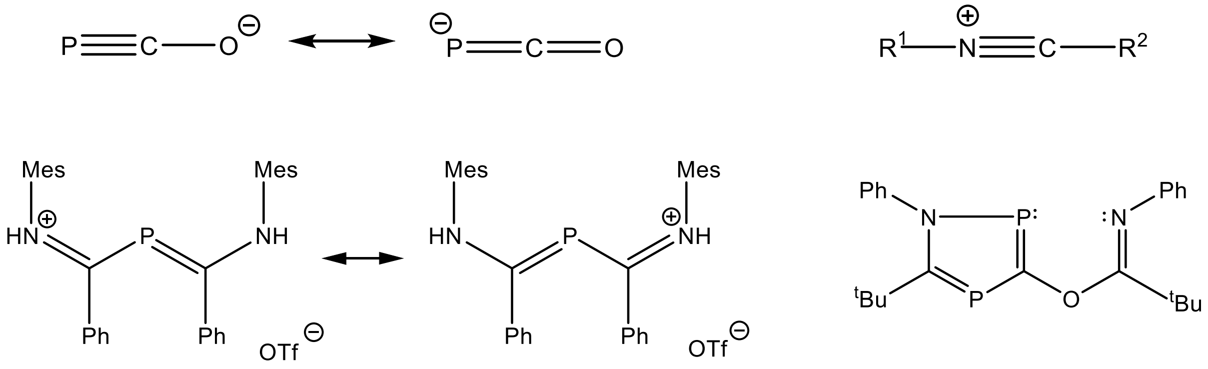
The 2-phosphaethynolate anion, PCO^-, was first described in 1992 as a lithium salt[1] and can be used as a buiding block for the formation of organophosphorus compounds.[2] This simple anion has been shown to undergo cycloaddition density with unsaturated molecules to afford phosphorus-containing heterocycles.[3,4] In order to extend the reactivity studies of PCO^-, we have collaborated with the Slootweg research group to explore the reactivity of this anion with nitrilium salts.[5]



In this study we describe how the different substituent groups on the nitrilium salts can influence the structure of the products obtained in reactions with the PCO^- anion.

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Optimisation of a coiled coil peptide for use as a MRI contrast agent

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PSIBS, School of Chemistry University of Birmingham, Edgbaston, B15 2TT, UK

Previously we reported that Gd(III) coiled coils can display promising MRI relaxivity,[1] and that introduction of the Gd(III) binding site towards the N-terminus, Gd(MB1-1)$_3$, yielded the highest relaxivity complex (r_1 = 11.7± 1.5 mM^{-1} s^{-1} and r_2 = 86.8 ± 5.4 mM^{-1} s^{-1} at 7 T).[2] We adopted this design for subsequent optimisation, specifically to evaluate if the dependence of relaxivity on molecular rotation,[3] could be exploited to further modulate the MRI efficiency of the Gd(III) complex. We investigate a series of three peptides of varying length; MB1-1S, MB1-1 (original design[2]) and MB1-1L, which feature four, five and six heptads, respectively and have differing rotational correlation times calculated to be 4.6, 6.9 and 10 ns (see Figure 1).

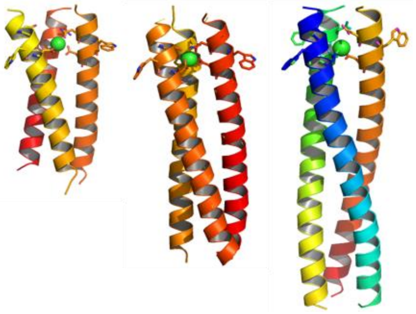

Figure 1: Designed Gd(III) complexes with MB1-1S, MB1-1 and MB1-1L consisting of 4, 5 and 6 heptads

We find that the presence of six heptads has only a small impact on folding in the apo and lanthanide bound forms (Apo: 80 ± 6 and 84 ± 2 % for MB1-1 and MB1-1L; Metallo: 83 ± 7 and 85 ± 2 % for MB1-1 and MB1-1L). The addition of a heptad theoretically improves stability by 5-9 kcal mol^{-1},[4,5] this is shown in this system, where the stability increases in the apo complex from 18.2 ± 3.5 to 21.6 ± 2.5 kcal mol^{-1} and the metallo complex from 17.8 ± 1.5 to 21.8 ± 5.6 kcal mol^{-1}. MB1-1S remains poorly folded on the addition of Gd(III) (33% folded) despite this, all three peptides have the same inner sphere water coordination, coordination chemistry and their potential as an MRI contrast agent is not altered.

Support from the University of Birmingham and the EPSRC (GDGD GAS1607), are gratefully acknowledged.

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Physical Properties of Linear Transition Metal Complexes

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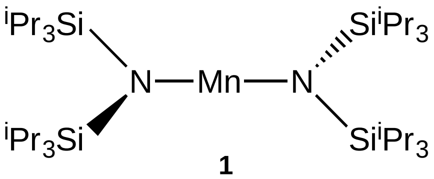
Two coordinate transition metal (TM) complexes are among the least investigated species in coordination chemistry. This is due to the difficulty in preventing monomeric species from aggregating or forming extended ionic lattices. Sterically demanding monodentate amide ligands have previously been employed to prevent oligomerisation by blocking the vacant coordination sites on the metal centre. A series of first row TM complexes in the +2 oxidation state containing $\{N(SiMe_3)_2\}^-$ (N’’) have been prepared. [1,2] These are two coordinate and monomeric in the gas phase but in the solid and liquid phase they exist as dimers, thus this ligand does not provide enough steric bulk to stabilise two-coordinate metal centres in solution chemistry.

We have recently been developing a series of near linear two coordinate first row transition metal (Co, Mn, Fe, Cu and Cr) complexes using the sterically demanding silylamide ligand, $\{N(Si^iPr_3)_2\}^-$ (N^{tt}). This ligand offers more steric bulk than N’’, which can force the target complexes to crystallize as monomers rather than dimers. [3]

Crystal structures have been obtained of a near linear two coordinate manganese(II) complex, $[Mn(N^{tt})_2]$ (**1**) and a copper(I) homologue. The crystal structure of a dimeric iron(II) complex, $[Fe(N^{tt})(\mu\text{-}Br)]_2$ (2), has also been obtained. The steric demands of the N^{tt} ligand prevented disubstitution of $FeBr_2$ in this case.



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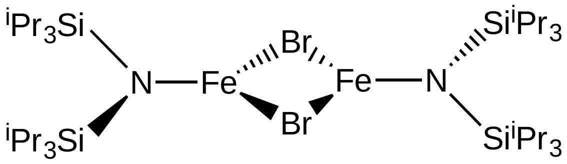

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These two coordinate complexes will be oxidised and reduced in order to synthesise a series of 2 coordinate first row TM (Cr, Mn, Fe, Co, Ni and Cu) complexes in the +1, +2 and +3 oxidation states, and their potential as SMMs will be investigated.

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Experimental and Theoretical Studis of Strong σ-donating Ligands

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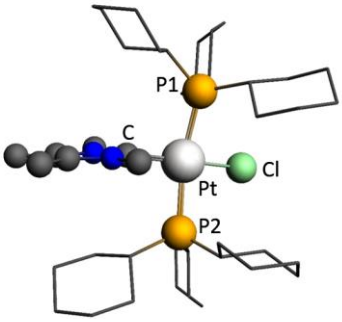
N-heterocyclic carbenes (NHCs) have been an important class of ligands since their first successful isolation and characterization in 1991,[1] as they are strong σ-donor and able to maintain strong metal-ligand bonds. As such as range of catalysts have been developed containing NHC ligands (e.g. Grubb's 2nd generation metathesis catalyst).[2] Anionic boryl ligands are isoelectronic analogues of NHCs which were first isolated and characterised in 2006[3]. They are of interest, in part due to their implication in C-H functionalization chemistry.[4] Understanding the electronic properties of NHCs and anionic boryl ligands is key to understanding their involvement in catalysis processes such as C-H activation and therefore worth investigations, with computational chemistry methods in our project.

The effects of ring size, backbone substituents, donor atom and net charge on donor properties were investigated by calculating the σ and π orbital energy of a library of carbene and boryl ligands. Calculations on the related Ni complexes have also been carried out, and the σ-donor strengths of ligands assayed via tran-influence and fragmentation calculations. In general the σ orbital energy decreases with electron withdrawing groups on backbone and with decreasing ring size. A negative charge on the ligand increase the σ energy and in general, the σ-donors strength would be expected to follow the trend: boryl anions > WCA-NHCs > NHCs. Syntheses of relevant Pt complexes have been carried out to support the quntum chemical results and so far Pt complex with 1,3,4,5-(CH_3)-1H-imidazol-2-ylidene has been isolated. The data of calculated structure is coherent with those from X-ray structure.



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Structurally dynamic metallocryptophane systems

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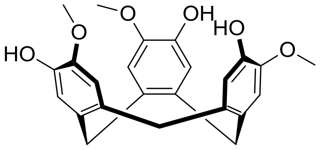
Metallocryptophanes are discrete coordination complexes formed from the self-assembly of metal precursors with bridging cavitand ligands.[1] Such systems have applications ranging from molecular recognition to nanoscale reaction vessels. Our work utilises cavitands based on the cyclotriguaiacylene framework (**1**) which can be readily functionalised with groups such as pyridyl units and self-assembles with metal cations such as Pd(II) to give the M_3L_2 metallocryptophane architecture **2**:[2]



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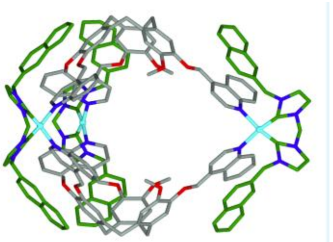

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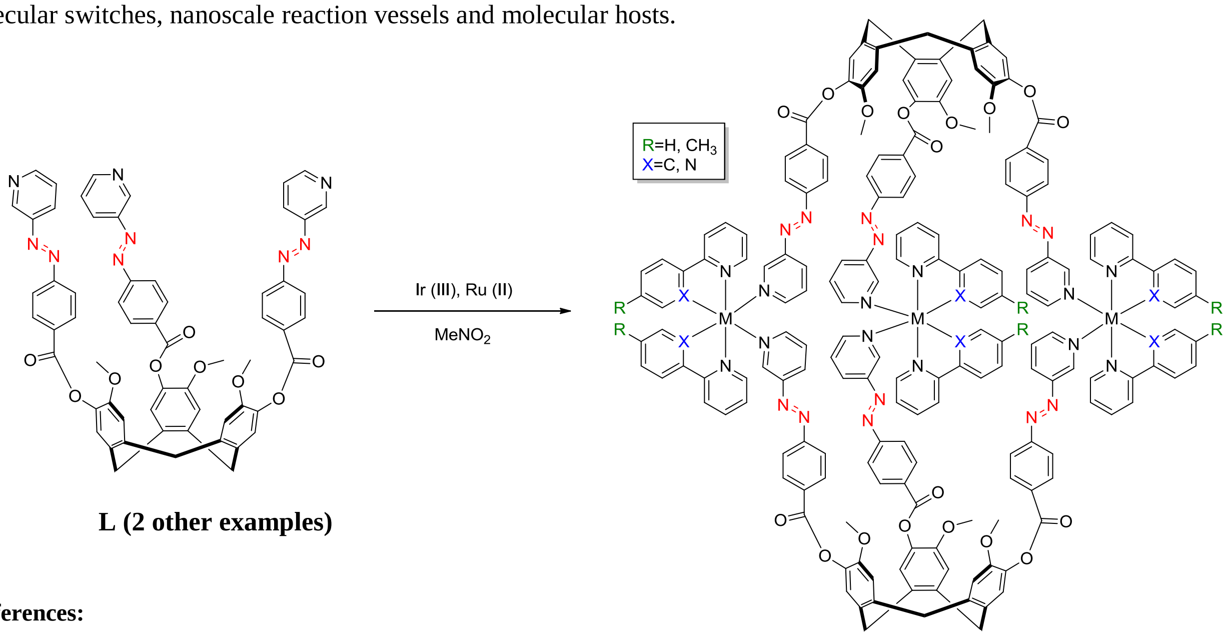
The incorporation of the azobenzene group (AZB) into the ligand design introduces dynamic behaviour into these systems; AZB units can undergo light induced isomerisations between *cis* and *trans* when irradiated at the appropriate wavelength.[3] Three novel ligands have each been shown to assemble with Ir (III) and Ru(II) in solution into M_3L_2 metallocryptophanes with tunable AZB units; these have exciting potential applications as molecular switches, nanoscale reaction vessels and molecular hosts.



L (2 other examples)

M_3L_2 Cages (5 examples)

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Highly Sterically Demanding Chelating Borylamide Ligands in Main Group Chemistry

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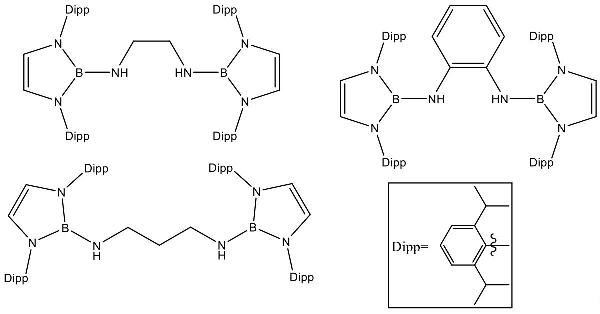
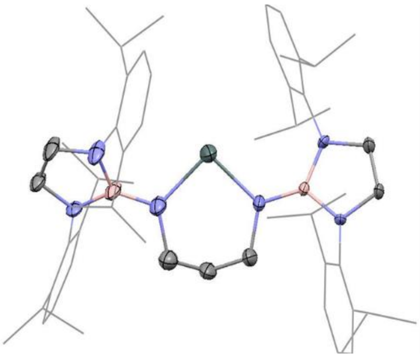
Small molecule activation is a highly topical area in Main Group chemistry reflecting economic and environmental drivers to develop alternatives to established late Transition Metal systems. Of critical importance in such chemistry is control of frontier orbital energies, and we have been using very strongly donating boryl substituents,[1] to synthesize low valent Main Group carbenoids for E-H bond activation (E = H, B, N, O, S).[2,3]

Recently, a boryl amido ligand was used to stabilise the first monomeric, acyclic diaminosilylene, a compound which activates NH_3 and O_2.[4] This class of ligand makes use of the strong σ-donating properties and steric bulk of a boryl group whilst avoiding the use of the synthetically challenging boryllithium reagent. Moreover, the potential for N-B π interactions could reduce the π-donation to the metal, resulting in a lower HOMO-LUMO gap and hence increased reactivity of the metal centre. This work focuses on using bulky, chelating borylamido ligands to stabilise divalent Group 14 complexes of the elements C-Pb, given their potential for increased stability over non-chelating ligands. Initial work has focussed on the synthesis of a library of pro-ligands (e.g. **1a-c**) and their exploitation in Ge^{II} and Sn^{II} chemistry (e.g. **II**).



Ia-c



II

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^{19}F Fingerprinting to Track the Binding Preferences of a Ruthenium Piano Stool Complex.

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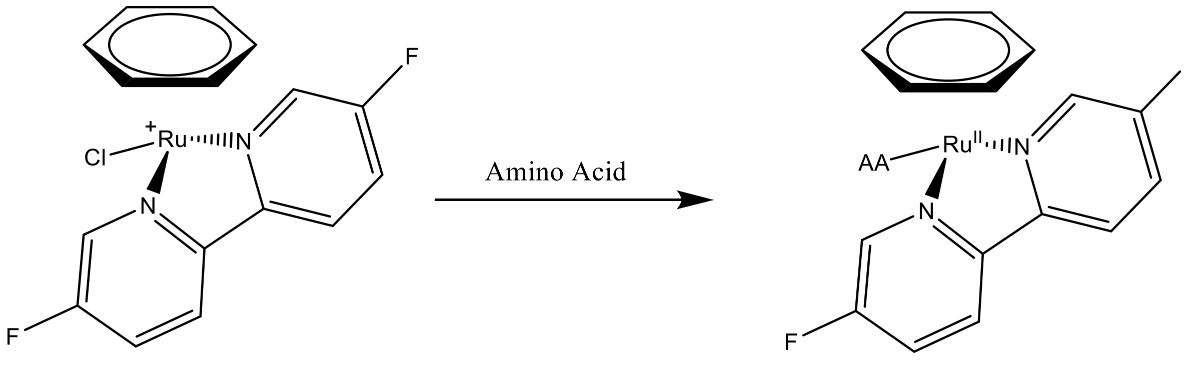
Cisplatin is an extremely useful and widely-used drug for treating certain cancers, but its **side effects** can be vicious and rapidly-mutating cancerous cells can develop a **resistance** to it.

Many groups are currently investigating **ruthenium complexes** as an **alternative platform** to cisplatin for cancer therapies. We are investigating Ru(II) arene 'piano stool' complexes.

As part of this research, we wanted to identify the **preferred binding partner** of a Ru(II) arene complex in solution.

This poster presents work carried out to **quantify** the solution-phase binding preferences of a **fluorinated Ru(II) arene** complex**.** **^{19}F NMR spectroscopy** of a solution of the complex and a mixture of amino acids shows an **absolute preference for cysteine** (thiolate) binding, but not before raising some interesting issues on **symmetry**, chemical/magnetic **equivalence**, and the tension between **kinetics** and **thermodynamics**.



Scheme: The central reaction to the work in this poster.

Ag_4 clusters by water-in-oil microemulsion synthesis

Hector Oyem

Abstract

Ag_4 nanoclusters were synthesized in water-in-oil microemulsions by mixing separate emulsions containing $AgNO_3$ and $NaBH_4$ in the aqueous phase. The reaction was carried out at room temperature with dioctyl sodium sulfosuccinate (AOT) as surfactant and isooctane as the oil phase. The use of microemulsion droplets to contain the reagents allows us to restrict the number of Ag atoms in each cluster and produce fluorescent Ag clusters without the need for multidentate ligands such as DNA.[1]

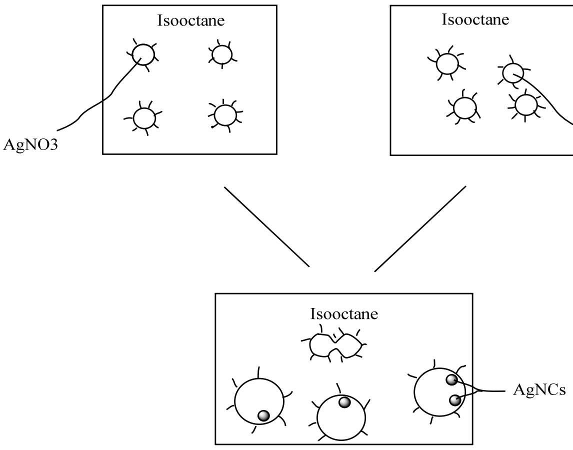


Figure 1: Synthesis scheme for AgNCs in microemulsion.

The as-synthesized AgNCs was characterized by UV-vis, and fluorescence spectroscopy, as well as dynamic light scattering (DLS), atomic force microscopy (AFM), photoluminescence microscopy, and electrospray ionization mass spectroscopy (ESI-MS).

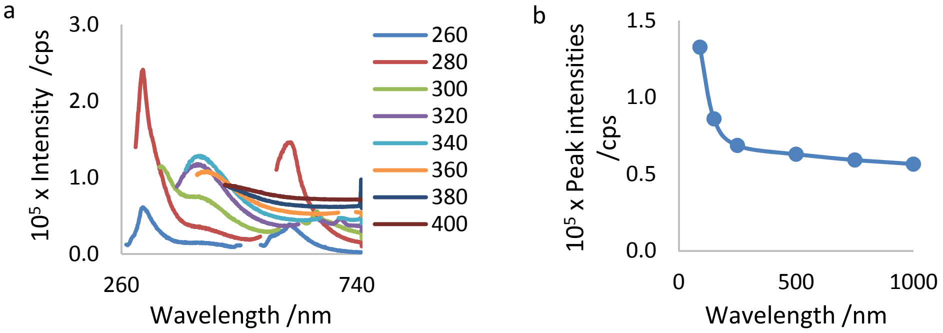


Figure 2: Emission spectrum of AgNCs (b) Emission peak intensities (at 434 nm) versus increasing AgNCs concentration.

The clusters show strong blue-fluorescence, ESI-MS provides evidence for a molecular formula of **$[Ag_4B_3O_5BH_3.2H_2O]^-$** and AFM shows particles approximately 1.7 nm in height.

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Potassium binding calix[4]arenes

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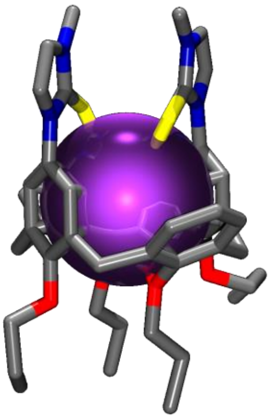
Calix[4]arenes are well established macromolecular cavitands, comprising four aryl units connected by methylene bridges and presenting a distinctive concave "chalice" topology. The ready functionalisation of these macromolecules makes them attractive molecular scaffolds and tuneable complexing agents. The central hydrophobic cavity has been exploited for use in a wide range of host-guest chemistry, including applications as sensors for metal ions and organic molecules, enzyme mimics and in supramolecular catalysis.[1] In particular, several examples of alkali metal inclusion within calix[4]arene structures have previously been reported, exploiting crown ether appendages or strong electrostatic interactions.[2] As part of our on-going investigation of the coordination chemistry of imidazolium functionalised calix[4]arenes,[3] we report our work associated with systems capable of binding potassium within the central cavity.



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RsrR, a new member of the Rrf2 superfamily from *Streptomyces venezuelae* that functions as a redox sensitive response regulator.

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Streptomyces bacteria are well adapted for life in the complex soil environment and more than a quarter of their ~9 Mbp genomes encode one and two-component signalling pathways that allow them to rapidly sense and respond to changes in their environment. They are obligate aerobes and have multiple systems for dealing with redox, oxidative and nitrosative stress.

RsrR, a previously uncharacterised protein from *S. venezuelae,* contains three C-terminal cysteine residues which are characteristic of Rrf2 proteins that ligate iron-sulfur clusters. To investigate the cofactor and DNA binding activity of RsrR, the *rsrR* gene was expressed in *E. coli* and the resulting protein purified under strictly anaerobic conditions. As isolated, RsrR was found to contain a reduced $[2Fe\text{-}2S]^{1+}$ cluster and to be dimeric, whether or not the cluster is present (in each monomer). Upon exposure to air, the cluster was rapidly oxidized to the $[2Fe\text{-}2S]^{2+}$ form, but not destroyed by O_2, in contrast to most other Fe-S containing transcriptional regulators, and consistent with the fact that *S. venezuelae* is an obligate aerobe. In fact the cluster can readily cycle between oxidized and reduced states. The $[2Fe\text{-}2S]^{2+}$ form was found to bind strongly to RsrR-controlled promoters in vitro, whereas $[2Fe\text{-}2S]^{1+}$ exhibited, at best, significantly weaker binding and the apo form did not bind DNA at all. Thus, we propose that the DNA-binding activity of RsrR is modulated by the oxidation state of its cluster, becoming activated for DNA binding through oxidation and inactivated through reduction. Exposure to O_2 is sufficient to cause oxidation, but other oxidants may be important *in vivo*. The properties of RsrR described here are reminiscent of another well-known [2Fe-2S] cluster protein containing regulator, SoxR, which belongs to the distinct MerR family.

Catalytic conversion of methanol/ethanol to *iso*butanol – a highly selective route to an advanced biofuel

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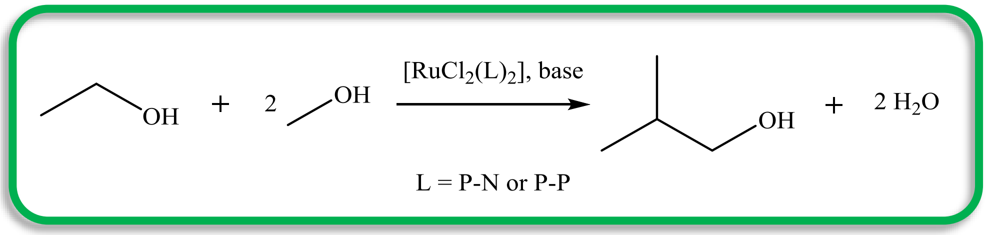
The need to find alternatives to fossil fuels is crucial from an environmental perspective and to ensure energy security and sustainability. Higher alcohols, such as butanol, are ideal "drop in" gasoline alternatives, outperforming (bio)ethanol both in terms of energy content and ease of use. Easily obtainable (bio)ethanol may be converted into the "advanced biofuel" butanol by way of the Guerbet reaction.[1] We have previously reported that (bio)ethanol may be successfully converted to *n*-butanol with good yields and high selectivity using ruthenium catalysts with P-P or P-N supporting ligands.[2-4] Although *n*-butanol is a viable gasoline alternative the branched isomer, *iso*butanol, has more advantageous properties such as a higher energy content and a more suitable octane number. Although it is not obvious how *iso*butanol could be formed from ethanol alone, the co-condensation of methanol (which may be obtained from biosustainable sources) and ethanol allows formation of the branched structure.[5-8] We now report the catalytic upgrading of methanol/ethanol mixtures to *iso*butanol via a Guerbet-type mechanism with extremely high selectivity (>99 %) and good conversion (>75 %) using ruthenium P-P and P-N complexes.[9]



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Flexible Binuclear β-Diketiminate Complexes of Copper(I)

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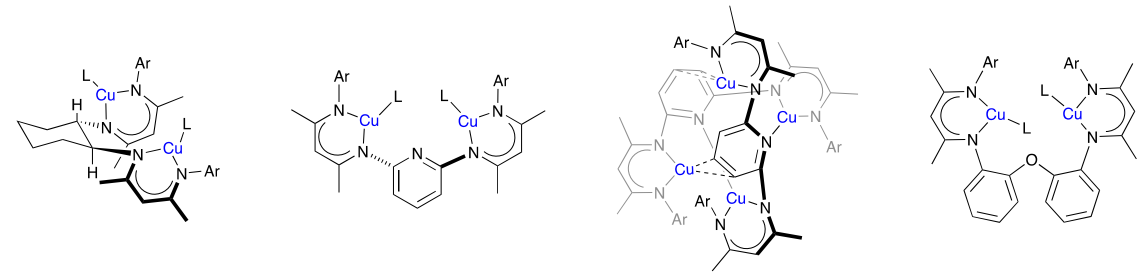
The recently crystallographically characterised methanotrophic enzyme particulate methane monooxygenase (pMMO), which is capable of methane conversion to methanol under mild conditions, was found to contain a dicopper active site.[1] The two copper ions are exceptionally close (~ 2.6 Å), making synthetic mimics challenging, and necessitating bespoke ligand design.[2] To this end, the reaction of a series of dinucleating *bis*(β-diketiminate) pro-ligands (**1-H$_2$**, **2-H$_2$**, **3-H$_2$**) with mesitylcopper in the presence and absence of mono and diphosphines afforded a new series of dicopper(I) complexes. Four new copper(I) phosphine complexes **[1-Cu$_2$(PPh$_3$)$_2$]**, **[2-Cu$_2$(PPh$_3$)$_2$]**, **[2-Cu$_2$(DPPE)]** and [**3-Cu$_2$(PPh$_3$)$_2$]** were isolated (Figure 1). While these compounds display large Cu---Cu separations of 5.4–7.9 Å in the solid state, solution data are consistent with a large degree of conformational freedom. Although acetonitrile adducts of this series could also be generated *in situ*, reaction of the 2,6-pyridyl bridged ligand (**2-H$_2$**) with mesitylcopper led to the formation of **[2-Cu$_2$]$_2$**, a dimer of dicopper(I) complexes in which the *bis*(β-diketiminate) ligand now binds four copper(I) centres through not only the expected κ^2-*N,N'*-chelation but also κ^1- and η^2-binding of the central pyridine through orthogonal Cu–N and Cu–arene interactions.



[1-Cu$_2$(PPh$_3$)$_2$] Cu---Cu = 5.44 Å

[2-Cu$_2$(PPh$_3$)$_2$] Cu---Cu = 6.33 Å
[2-Cu$_2$(DPPE)] Cu---Cu = 6.01 Å

[2-Cu$_2$] Cu---Cu = 4.97 Å
Cu---Cu' = 3.24 Å

[3-Cu$_2$(PPh$_3$)$_2$] Cu---Cu = 7.94 Å

Figure 1. Copper(I) complexes of *bis*(β-diketiminate) ligands with different spacer groups

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Catalytic Ruthenium Sandwich Complexes for Arene Substitution Reactions

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Binding arenes to transitions metals allows for interesting reactivity due to the electron withdrawing effect of the metal centre.[1] Commonly used chromium and manganese systems are limited to requiring stoichiometric amounts of metal,[2,3] whereas ruthenium holds potential for catalytic transformations through arene exchange (figure 1).[4]

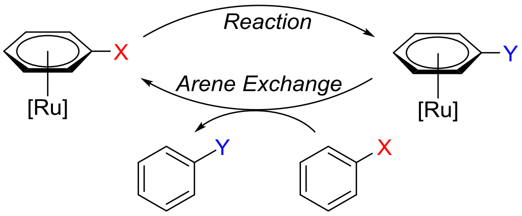
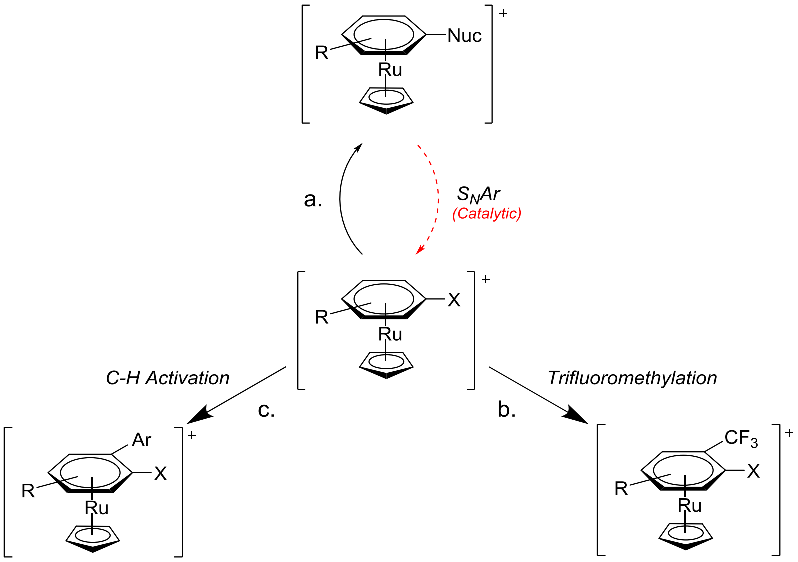


Figure 1. Catalytic reactivity via arene exchange on metal centre.

We are investigating a variety of catalytic processes based on activation by metal-arene bond formation including: S_NAr; aryl trifluoromethylation and reductive coupling via C–H activation. Here we report an optimised catalytic S_NAr reaction[4] of a variety of substrates, using microwave reactor conditions (scheme 1a). We also report a stoichiometric trifluoromethylation reaction that has potential to be catalytic in Ru (scheme 1b) and our early findings on a catalytic C-H activation reaction (scheme 1c).



Scheme 1. Potential catalytic transformations of η^6-bound arene complexes.

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Phosphinidene boranes; reactions with bases and alkynes

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The chemistry of imino boranes, which are isoelectronic to alkynes and the related heavier group 14 congeners, is relatively well established.[1] By contrast the literature for the isoelectronic phosphinidene boranes is still confined to a handful of Lewis base and acid stabilised examples, and the knowledge that thermolysis of diphosphadiboretane **1** generates the free phosphinidene borane **2** in the vapour phase.[2] We present two methods of stabilised phosphinidene borane preparation: base promoted elimination of chlorotrimethylsilane from a functionalised phosphinoborane, and thermal trapping of phosphinidene borane **2** with bases to generate **3a** and **b**. Investigations into the reactivity of phosphinidene borane **2** showed that **2** can undergo cycloaddition with phenyl acetylene and its derivatives to form cyclic products such as **4**, which has its own interesting reactivity.

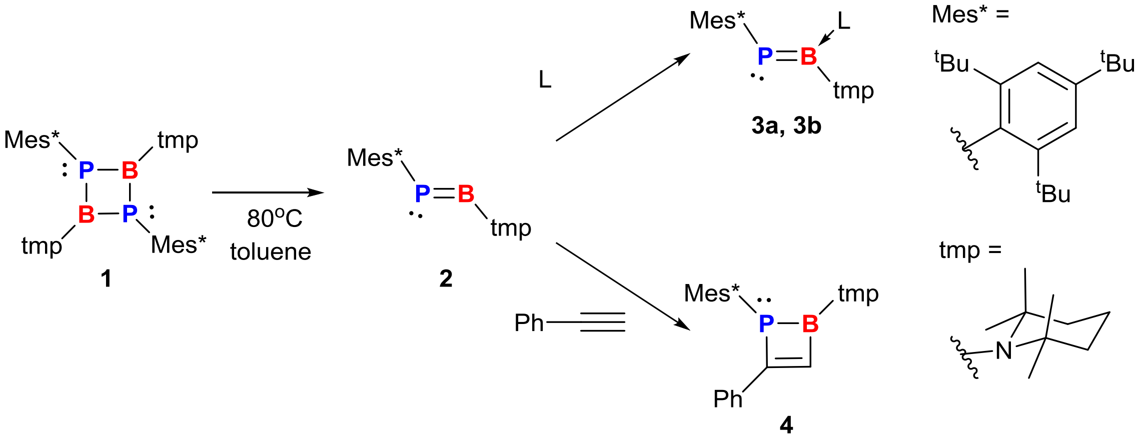

Figure 1. The thermal trapping of phosphinidene borane **2** with bases and phenyl acetylene. For **3a** and **3b**, L = dimethylaminopyridine and 1,3,4,5-tetramethylimidazol-2-ylidene respectively

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Rapid Chelation of Gallium-68 at Neutral pH

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Gallium-68 is a useful isotope for positron emission tomography (PET) imaging due to its generator-based production.[1] Whilst the 1, 4, 7, 10-tetraazacyclocodecane–N, N', N'', N'''-tetraacetic acid (DOTA) chelate is often seen as the "gold standard" for gallium-68 chelation,[2] it requires harsh conditions (pH 3.5 and 90 °C) to achieve modest yield (58% in 4 minutes).[3] 1, 4, 7-triazacyclononane-N, N', N''-triacetic acid (NOTA) is able to complex gallium-68 under milder conditions (pH 3.5, room temperature, 95% in 10 minutes),[4] but still requires acidic conditions for radiolabeling. This study demonstrates the viability of a selection of new chelates for the coordination of gallium-68 under mild conditions – physiological temperature and neutral pH.

In this study, 3 new chelates were tested for their ability to complex gallium-68 in 15 minutes at 37 °C at pH 7.4. The chelate EDTA-bisamide-His was particularly suitable for rapid gallium-68 coordination with a 72% RCY achieved by 50 µM of chelate, and a yield of 69% by 10 µM. In addition, 50 µM of EDTA-bisamide-Meth achieved a RCY of 52% under these conditions. Additional complexation of gallium-68 was seen in all cases, likely due to the formation of dimers or alternative coordination modes. The stability of the resultant complexes was assessed in a trans-metalation challenge with apo-transferrin, with 61% of the ^{68}Ga-EDTA-His complex remaining intact after 60 minutes.

While these results have not yet been optimized, they are highly promising for future development due to the mild radiolabeling conditions used – this may make potential *in vivo* application possible without the need to adjust the solution pH after radiolabeling, and will allow for a range of targeting motifs to be employed in future studies.

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Synthesis and Reactivity of Stable Bimetallic Uranium (V) ‘Pacman’ Complexes

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Uranium predominates in aqueous nuclear and mining discharges in the environment. Yet uranyl, $[U^{VI}O_2]^{2+}$, the most abundant form of uranium in water, is remarkably inert and so is difficult to selectively remediate from waste mixtures.[1]

Through a Schiff-base polypyrrolic macrocyclic ligand framework (Fig.1), we have probed the fundamental chemistry of uranyl. Using this ‘Pacman’ scaffold it is now possible to isolate complexes of highly unstable $[U^{V}O_2]^{+}$, by reductive functionalisation of strong U≡O bonds in $[U^{VI}O_2]^{2+}$.[2]

This has enabled novel, bimetallic U^V oxo-group chemistry, including the first air-stable $U^V_2O_4$ ‘Butterfly’ motif, when M = $SiMe_3$.

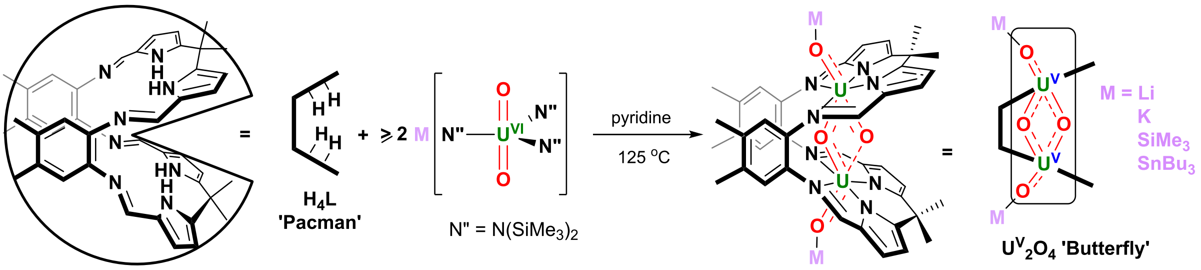

Figure 1 – The ‘Pacman’ ligand, and synthesis of the $U^V_2O_4$ ‘Butterfly’ motif

Unusually for two adjacent uranium (**V**) centres, our system does not disproportionate, with *exo*-oxo silylation rendering the motif inert to oxidation and hydrolysis, even at elevated temperatures. Here, we present our studies in expanding the range of stable ‘Butterfly’ complexes, and investigations in their reactivity.

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DFT study of Cooperative H_2 Activation across the Ru-Zn Bond in $[Ru(IPr)_2(CO)ZnEt]^+$

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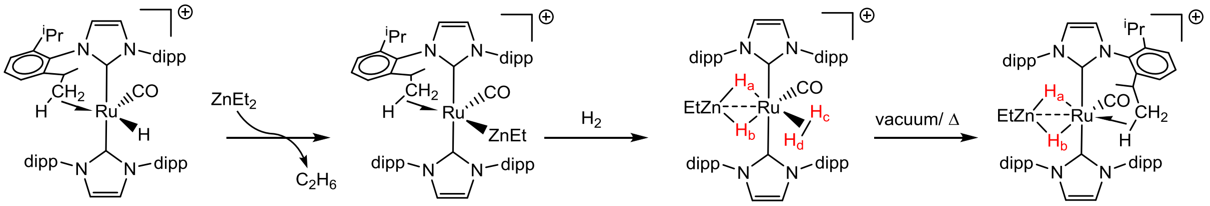
Many M–L combinations have been shown to facilitate the cooperative cleavage of H_2.[1] However, much less is known about analogous reactivity across transition metal–main group metal bonds. Recently, Whittlesey and co-workers isolated the Ru–Zn species $[Ru(IPr)_2(CO)ZnEt]^+$, **2**, from reaction of the hydride precursor, **1**, with $ZnEt_2$. Further reaction with H_2 led to the formation of **3** in which two hydrides bridge the Ru-Zn axis. **3** loses H_2 under vacuum to give **4**, while treatment of **3** with D_2 demonstrates exchange between the dihydrogen and bridging hydride positions in that species.



1 2 3 4

DFT calculations have been performed to define the mechanism of these reactions. The reaction of **1** with $ZnEt_2$ involves initial Et group transfer onto Ru followed by reductive elimination of ethane to give the Ru(0) species **2**. Adding two equivalents H_2 to **2** forms a *bis*-η^2-H_2 intermediate in which heterolytic cleavage of one H_2 ligand adds a hydride onto Zn while formally protonating the Ru centre to give Ru(II) species **3**. Loss of H_2 from **3** is computed to be endergonic and gives **4** in which the η^2-H_2 ligand is replaced by a C–H agostic interaction. The computed mechanism for H/H exchange in **3** involves a series of hydride transfer and H_2 rotation steps. Exchange of the proximal hydrogen, H_b, with the H_2 ligand is found to be more accessible than that of exchange with the distal position, H_a.

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[M(C^N^N)$_2$] Complexes of Group 8 and 9: The Expected and the Unexpected.

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Complexes which contain terdentate cyclometalated ligands of are interest for a variety of applications from photovoltaics to cancer therapies.[1,2,3] While many heteroleptic complexes containing one or two terdentate ligands are reported in the literature, to date there are very few examples of homoleptic terdentate cyclometalated complexes.[4,5]

In this work we explored the synthesis and optoelectronic properties of [M(C^N^N)$_2$] complexes based on ruthenium, osmium, rhodium and iridium (**Figure 1**).

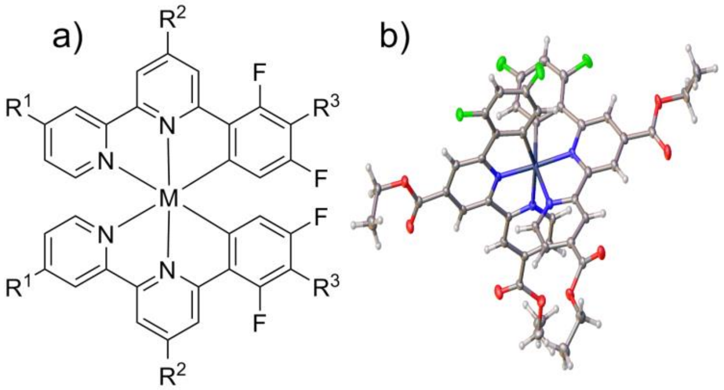

Figure 1 a) Example complex structure, where M = Ru or Os, R^1 and R^2 = CO$_2$Et or CF$_3$ and R^3 = H or CF$_3$, b) Example x-ray crystal structure.

This talk will focus on the synthetic challenges posed by these molecules and methods developed to overcome them, as well as some unexpected outcomes.

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Catalysis in the Service of Main Group Chemistry: Synthesis of New p-Block Materials.

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Catalytic dehydrocoupling chemistry is a versatile approach to the formation of p block element-element bonds, and is becoming a promising methodology for the formation of inorganic polymers under mild conditions, often with higher yields than alternative routes (e. g. condensation reactions, reductive coupling, etc.).[1]

Recently, iron-based complexes have been reported to catalyse the polymerisation of phosphine-boranes,[2] and the molecular weight of the resulting polymeric material was found to vary as a function of the catalyst loading. The synthesis and characterization of two novel phosphine-borane monomers and their respective polymers will be presented.

$$\mathrm{RPH_2{\cdot}BH_3} \xrightarrow[-\,\mathrm{H_2}]{[\mathrm{Fe}]} [\mathrm{RPH{-}BH_2}]_n$$

Scheme 1. Dehydrocoupling of arylphosphine-boranes by [Fe] catalyst.

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Synthesis and Reactivity of New Alkaline Earth Gallyl Complexes

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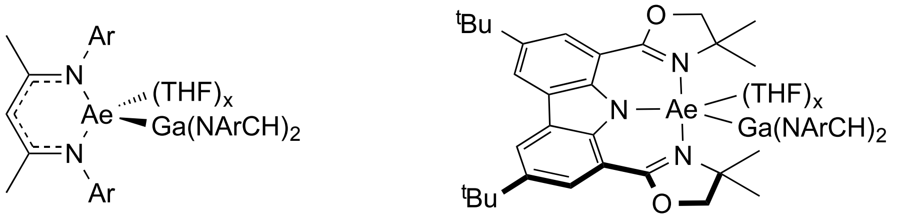
The synthesis, structure, bonding and reactivity of molecular compounds containing metal–metal bonds has undergone a renaissance during the last 10-15 years.[1] One of the remaining underdeveloped areas of this chemistry centers around the Group 2 (Alkaline Earth, Ae) elements. For example, Mg^{I}–Mg^{I} bonded dimers of the type $[(^{R}NacNac)Mg]_2$ and their analogues have been prepared and intensely studied since 2007.[2]

We recently reported the synthesis of complexes containing alkaline earth–transition metal[3] and lanthanide–gallium or –boron[4] bonds. Building on these developments, we report new complexes containing alkaline earth–gallium bonds (Fig. 1). These were synthesised by the salt-elimination reaction between $[K(Et_2O)\{Ga(NArCH)_2\}]_2$ (Ar = 2,6-$C_6H_3{}^{i}Pr_2$) and (L)AeI where L is a β-diketiminate (^{Ar}NacNac) or carbazolide ($CzOx^{Me2}$) supporting ligand. The reactions of these Ae–Ga bonded complexes with small molecules such as carbodiimides and epoxides has been studied.



Ae = Mg, Ca, Sr

Ae = Mg, Ca

Figure 1. New alkaline earth–gallium bonded complexes

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Catalytic Upgrading of Bioethanol to *n*-Butanol

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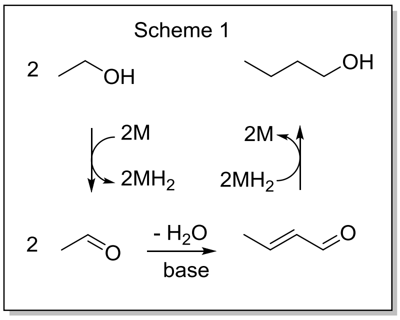
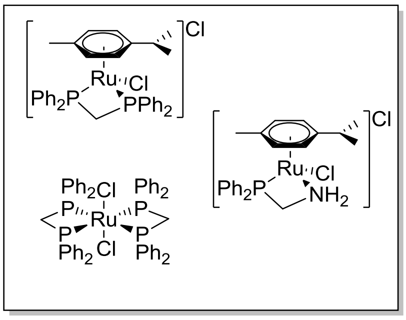
Attaining liquid transportation fuels from renewable biomass sources has become a crucial goal for future energy provision. Bioethanol, from fermentation of starch and sugar containing crops, has long been earmarked as a sustainable replacement for gasoline, however, ethanol suffers from a number of shortcomings when compared to gasoline. These include an energy density only 70% that of gasoline, a greater degree of hygroscopicity and it is highly corrosive towards engine infrastructure. Higher alcohols such as butanol have fuel properties that more closely resemble those of gasoline and can be used with little or no modification to existing systems. Unfortunately current butanol production uses the oxo process which is dependent on non-renewable petrochemical feedstocks. Butanol has historically been produced via the ABE fermentation process although poor conversion and modest selectivity remain key issues.[1] A new and sustainable pathway to butanol is the catalytic upgrading of bioethanol. The Wass group has reported a number of homogeneous ruthenium diphosphine catalysts for upgrading ethanol to butanol via Guerbet chemistry which show unparalleled selectivity to *n*-butanol with good conversion (Scheme 1).[2] This paper reports the additional development of this process and the impact of catalyst structure on guiding the selectivity of ethanol coupling towards *n*-butanol and other chemicals of commercial interest. More recent work has produced a range of catalysts with mixed donor bidentate phosphine-amine ligands. These systems, formed in situ from mixtures of the ligand and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$, show enhanced activity at higher water concentrations to the diphosphine equivalent congeners with high selectivity and good conversion.[3]





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ACTIVITIES OF N-HETEROCYCLIC CARBENES AT COPPER

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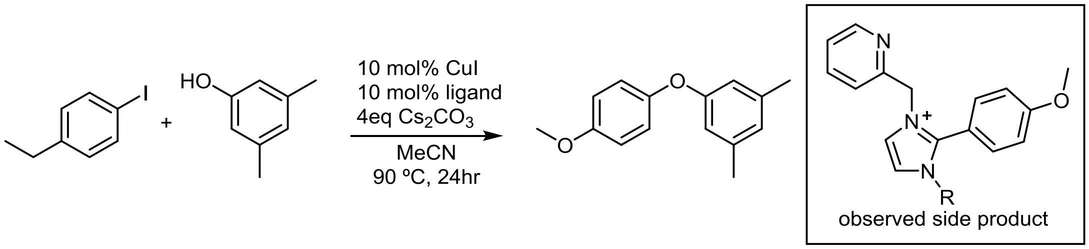
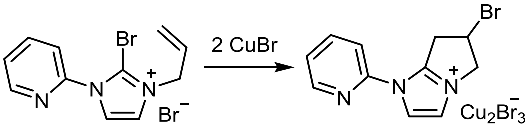
Over the last decade, *N*-heterocyclic carbenes (NHCs) have emerged as a useful class of ancillary ligand which support a wide array of transition metals throughout numerous catalytic cycles.[1] In certain cases however, 'non-innocent' behaviour of these ligands may be observed which results in additional catalyst deactivation pathways.[2]

In this presentation, a range of bidentate ligands including pyridyl/picolyl-appended NHCs coordinated at copper have been screened and evaluated as catalysts for an Ullman-type etherification reaction (Scheme 1). Following these results, it has been identified that a common ligand-fate results from reductive elimination of the NHC ligand and aryl coupling partner from the copper centre, forming a new NHC-aryl product and deactivated, non-ligated catalyst. In addition, we are using experimental and computational techniques to probe an unusual copper-mediated annulation reaction involving *N*-allyl substituted bromoimidazolium salts (Scheme 2). Similar annulation reactions of this type have been reported at Ni and Rh, with no current examples involving Cu known.[3] Finally, we are currently developing a synthetic approach toward isolation and characterisation Cu^{III}-NHCs, which are postulated as transient intermediates in a variety of Cu^{I} catalytic cycles.



Scheme 1. Ullmann-type etherification for ligand catalytic reactivity screening.



Scheme 2. Annulation reaction of an allyl-substituted bromoimidazolium salt at copper.

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Title: A Schottky Barrier Device on Steel for use in Photovoltaics.

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A diodic Schottky barrier device can be fabricated from a transition metal semiconductor and a noble metal by means of formation of a Schottky barrier between the two materials. In this work we report a Schottky barrier device formed between silver nanowires and a TiO_2 layer, on a stainless steel substrate. The fabrication method is important to the performance of the device, and the electrical characteristics depend on the temperature and time of sintering of the TiO_2 layer. The TiO_2 layer was fabricated from a titania precursor sol, followed by dip coating onto the substrate and sintering. Commercial silver nanowires were drop cast from suspension onto the TiO_2 layer and annealed. This method requires no specialist equipment.

The current-voltage characteristics of these devices are predictable and show good diodic characteristics. The electrical characteristics can be altered by the absorption of small organic molecules or inorganic dyes, often favourably. Using a $Ru(dcbpy)_2(NCS)_2$ dye (where dcbpy is (2,2’-bipyridine)-4,4’dicarboxylic acid) a small visible photoresponse for cells of amorphous TiO_2 can be seen, demonstrating a potential use in low cost photovoltaics. Cells fabricated with anatase TiO_2 show a good UV photoresponse, demonstrating external quantum efficiencies of ~10% at 300 nm, with an estimated nanowire coverage of ~13% by area by SEM. Cells sensitized with visible light absorbing nanocrystals show an improvement in the visible light response of these devices, though with low external quantum efficiencies. Further improvements are expected in the visible photoresponse of these cells.

Molecular Electro-Oxidation Catalysts

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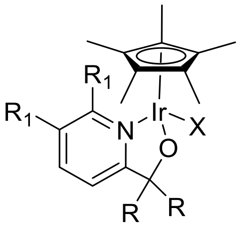
The water oxidation half reaction is of great importance for the realisation of effective solar fuels. Given the high energetic demands of this reaction, development of appropriate water oxidation catalysts is therefore key. Molecular pre-catalysts of the type [Cp*Ir(N-O)X], in which N-O is a chelating pyridine-alkoxide ligand and X a halide or hydroxide (Fig. 1), have shown high activity in catalytic water oxidation[1] and also CH-oxygenation reactions[2] with chemical oxidants such as $NaIO_4$. Previous work has established the homogeneous nature of these promising systems,[3] and true electrocatalytic O_2 evolution has been demonstrated.[4]



RR = Me, Ph, *t*-Bu, cyclohexyl, tetramethylcyclohexyl

R_1R_1 = H, benzyl

X = OH, Cl, SbF_6

Figure 1. Molecular iridium catalysts for water and CH oxidation

We have now systematically varied the privileged pyridine-alkoxide ligand in these precursors in order to exploit their molecular tunability. A series of six novel Cp*Ir complexes has been synthesised and their oxidative activation with aq. $NaIO_4$ followed by UV-vis spectroscopy, detailing significant variations in the activation based on the ligand substructure. Electrochemical interrogation yielded complementary data on their oxidative behavior and revealed key information about the solution species. CH-oxygenation kinetics of the complexes showed that both catalyst rates as well as C-H vs. O-H selectivities can be effectively steered by fine-tuning the chelating N-O ligand. Immobilisation of these molecular catalysts onto nanoITO spin-coated onto FTO glass has produced functionalised electrodes for applied electrocatalysis.

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Synthesis of new mono-substituted thiosemicarbazone ligands and of their corresponding biocompatible metal complexes

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Despite the fact that thiosemicarbazonate (TSC) based derivatives have been shown to have antitumor activity since 1960's, some extraordinary revival in their "chemistry for imaging" research has recently occurred, due to their recent role played by their multimodal imaging properties, particularly of relevance to hypoxia tracing. Some recent research has also indicated that the metal complexes appear to show some enhanced activity against tumour progression with respect to the actual free ligands, and the precise reasons for this remain under investigation.[1] Such complexes also showed promising radiolabelling through mild methods, and we demonstrated recently that the Gallium-68, Copper-64 and Indium-111 derivatives have high kinetic stability in vitro. This could be an advantage in their use as PET and SPECT imaging, whilst the Zn(II) derivatives show fluorescence emissive properties and biocompatibility, which renders these promising imaging agents for confocal fluorescence imaging in cells. [2,3]

Here we present the novel synthesis of a new class of monosubstituted thiosemicarbazone incorporating acenapthenoquinone backbones (TSCAc) along with the synthesis of corresponding bis-substituted and / or unsymmetrical metal complexes of Zn(II) and Ga(III)), which could potentially be used towards both the visualisation and selective destruction of different cancer cells types.

Acknowledgement: The authors thank the Royal Society, ERC Consolidator grant O2SENSE and FP7 MC ITN PROSENSE for funding and training opportunities.

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Radical stabilization in water by an artificial metalloprotein

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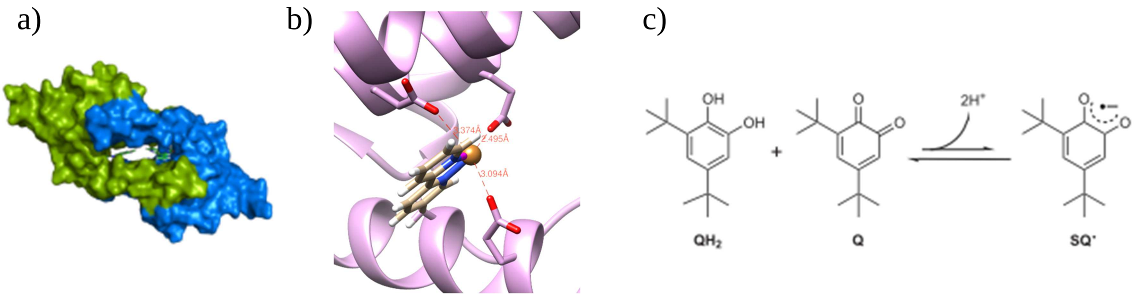
One of the major current challenges is to develop sustainable approaches to chemical synthesis. The power of chemical and biological synthesis can be merged by integrating non-natural synthetic chemistry into bio-synthetic pathways. By developing novel artificial metalloenzymes and incorporating them into cells, sustainable synthesis of molecules with novel structural features that are difficult to achieve in any other way could be achieved.[1]

A new approach to artificial metalloenzymes was reported recently by our group,[2] which comprises of a new active site in the hydrophobic pocket of the dimeric protein LmrR(figure below, a). The incorporated unnatural amino acid bipyridine alanine demonstrated in vivo binding of iron to afford an air-stable Fe(II) artificial metalloprotein (figure below, b).



Oxidase activity of this new artificial metalloprotein has been investigated, using di-*tert*-butylcatechol (QH_2) as a substrate. While no catalytic activity has been observed, interestingly, the radical semiquinone ($SQ^{\bullet}$) was stabilized in the active site (figure above, c). This work is only a second example of metalloprotein capable of stabilizing an organic radical that is normally unstable in water.[3]

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De novo designed lanthanide coiled coils as catalysts in phosphodiester hydrolysis reaction in aqueous medium

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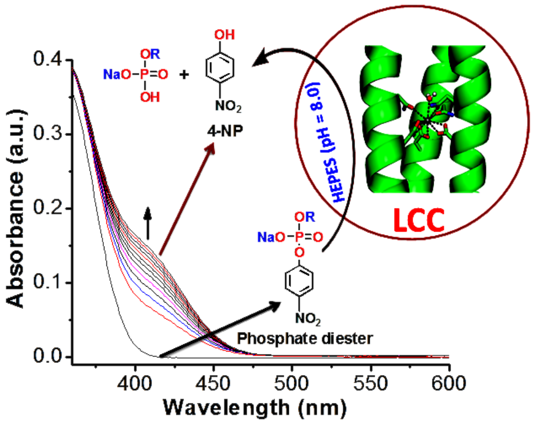
Development of new water soluble catalysts for the cleavage of phosphodiester P-O bonds, which are extremely resistant to hydrolysis, is challenging.[1] Phosphate esters are vital chemical features of both nucleic acids and several chemical toxins.[2] Among the reported catalysts,[3] Ln^{n+} based complexes are particularly active due to the hydrolysis by Lewis acid activation of substrate.[3c] For the first time we couple the catalytic features of Ln^{n+} complexes, with *de novo* designed coiled coils, which in turn offer the advantages afforded by the protein ligand in metalloenzymes. Importantly Ln^{n+} binding sites within the coiled coil can be designed in order to accommodation a varying number of inner sphere water molecules coordinated to Ln^{n+}, which is essential for hydrolysis.[4] We have tested the hydrolysis of 4-nitrophenyl phosphate and bis-(*p*-nitrophenyl) phosphate with La^{3+}, Eu^{3+}, Tb^{3+}, Ce^{3+} and Ce^{4+}, of aforesaid lanthanide coiled coils (LCCs) as catalysts in aqueous solution. The observed catalytic activity trend for both substrates is as follows $Ce^{4+} > Ce^{3+} > La^{3+} > Eu^{3+} > Tb^{3+}$.



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Title: Fabrication of Hollow and Porous Platinum Nanotube Derived From Tomato Mosaic Virus.

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Plant viral nanostructures can be exploited in the preparation of novel assemblies for applications in nanoelctronics, batteries, catalysis and therapeutics. Icosahedral biological nanostructures, such as cowpea mosaic virus (CPMV)[1] and tubular structures such as Trp-RNA attenuation protein (TRAP)[2] and tobamoviruses (TMV and ToMV),[3] can act as templates for materials such as metals and metal oxides.We are investigating the tomato mosaic virus (ToMV), which is nanotubular and non-infective to animals. Each viral particle consists 2130 identical coat proteins arranged in a hollow, helical tubular motif around a single genomic 6400 base strand of RNA. The outer and inner diameters of this nanotube are 18 nm and 4 nm, respectively, and it is 300 nm in length.

The external surface of a ToMV was mineralized via a wet chemical process to generate a uniform and dense platinum nanoparticle layer. ToMV was removed via annealing at high temperature. High-resolution 3D-TEM tomography and SEM (Figure 1) revealed that the platinum nanotubes contained a central hollow channel of diameter ~13 nm running along their lengths and showed the metallic layer to be porous with voids of various size up to 10 nm.[4]

These hollow tubular nanostructures could be useful for production of bespoke platinum catalysts and may be adaptable to different metal and metal oxides for use in catalytic and sensor applications.

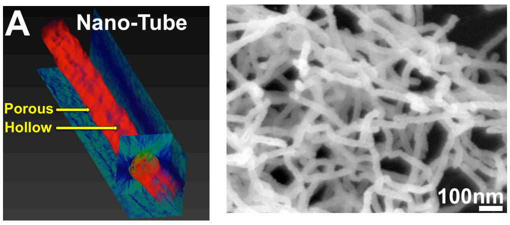

Figure 1: *3D TEM tomography and SEM of platinum nanotube.*

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Exploring and modifying reactivity of *m*-terphenyl complexes

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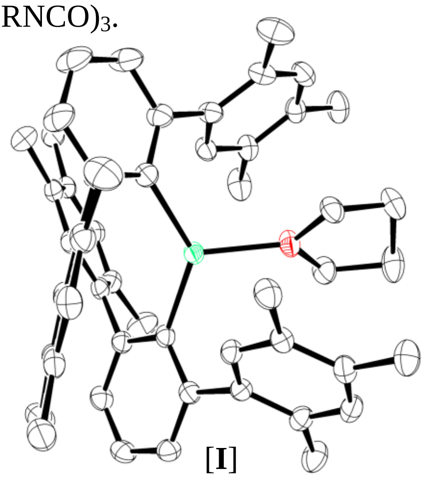
The use of sterically demanding aryl ligands allows the isolation of highly unsaturated transition complexes which often show unusual bonding modes and varied reactivity.[1] Recent success using *m*-terphenyl ligands has allowed the isolation of a series of first row two coordinate $M(2,6\text{-}Mes_2C_6H_3)_2$ (Mes = $2,4,6\text{-}Me_3C_6H_2$; M = Mn, Fe, Co)[2] and three coordinate transition metal complexes $M(2,6\text{-}Tmp_2C_6H_3)_2(THF)$ (Tmp = $2,4,5\text{-}Me_3C_6H_2$; M = Mn, Fe [**I**]). Variation of the flanking aryl on the *m*-terphenyl ligand alters the steric pocket in which the transition metal is encapsulated, enabling us to modify the reactivity of these complexes towards small molecules. Cobalt diaryls $Co(2,6\text{-}Ar_2C_6H_3)_2\cdot(OEt)_n$ undergo insertion reactions with CO to produce an encumbered ketone and an organic fluorenone with concomitant formation of $Co_2(CO)_8$ (where Ar = Mes, n = 0; Ar = 1-Naph, n = 1).[3] Current research is being aimed towards investigating the reactivity of other *m*-terphenyl complexes with carbon monoxide.

Manganese(II) and iron(II) *m*-terphenyl complexes have also been used as catalysts in hydrophosphination reactions and in the cyclotrimerisation of isocyanates forming the corresponding isocyanurates $(RNCO)_3$.



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Reactivity of 5 Coordinate Pt(IV) Complexes.

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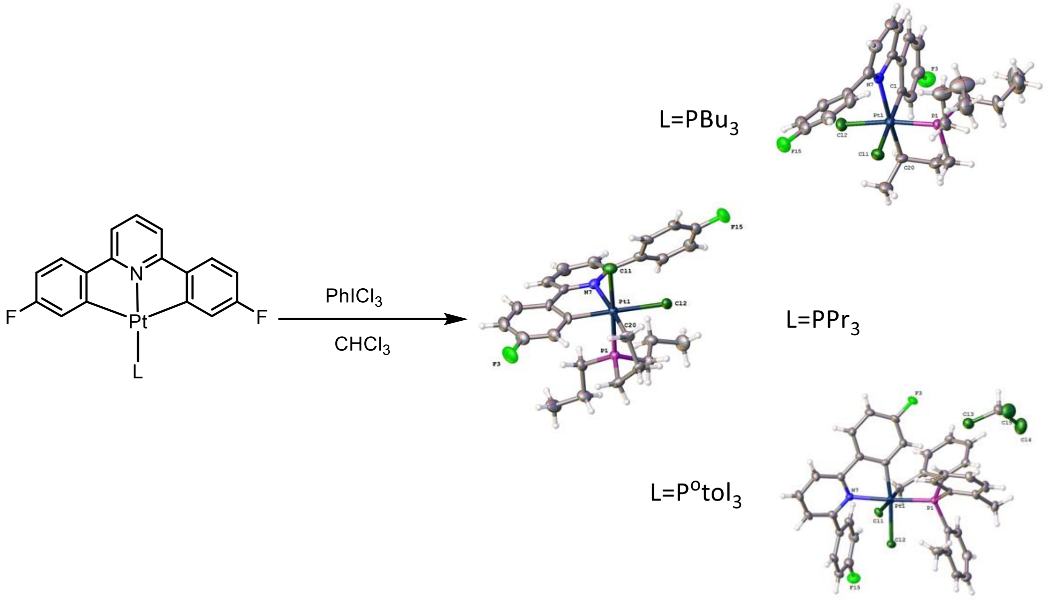
Oxidative addition and reductive elimination are fundamental transformations in chemistry. These reactions are known to go through 5-coordinate intermediates, and so the study of these intermediates are of academic interest.[1]

Oxidation of C^N^C Pt(II)PR$_3$ complexes with PhICl$_2$ (where R= PPr$_3$, PBu$_3$ and P^{o}tol$_3$), give phenyl-alkyl dicyclometallated Pt(IV) complexes along with the expected dichloro Pt(IV) complexes (scheme 1).[2] The presence of these alkyl cyclometallated complexes indicates a 5-coordinate intermediate.



Scheme 1.

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Ortho and peri C-H activations using different metal salts

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In this project, the C-H activation of four ligands with three different metal salts was investigated. Ortho and Peri activations on the aromatic ring were observed when the C-H activation was facilitated with different metal salts. The type of Nitrogen donor atoms, i.e. imine/amine/ketamine/bi-pyridine, also influences the activation process.

Cobaltocenium coupled [FeFe]-hydrogenase analogues: Modelling the H-Cluster

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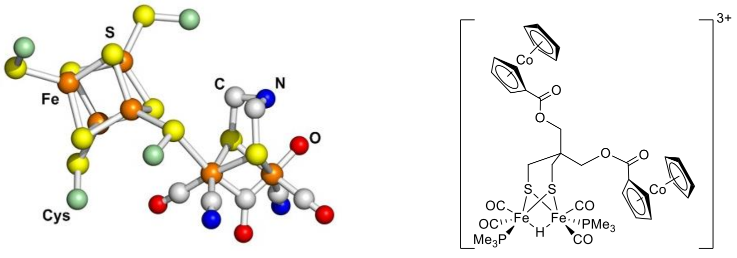
The [FeFe]-hydrogenases catalyse the reversible reduction of protons to evolve H_2.[1] A key feature of its active subsite, the H-cluster, is a cysteine bridged {4Fe4S} cluster, which functions as an electron transfer relay.

Whilst earlier work has shown that a {4Fe4S} cluster can be attached to a synthetic subsite to give an analogue of the H-cluster,[2] there are very few reports of model systems that incorporate this functionality.[3]



(a) **(b)**

Figure (a) X-ray structure of H-Cluster of the [FeFe]-hydrogenase (PDB code 3C8Y) **Figure (b)** Schematic of a cobaltocenium coupled [FeFe] active subsite analogue

Herein we report on the synthesis, electrochemical and spectroscopic analysis of H-cluster model units possessing alternative electron transfer centres, in the form of robust cobaltocenium moieties.

Reduction of these metallocene units occurs at potentials comparable to the {4Fe4S} cluster, and results in delivery of electrons to the di-iron core at potentials up to 600 mV more positive than is required for direct reduction.

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Catalytic Applications of Complexes Bearing NHC-Carborane Ligands

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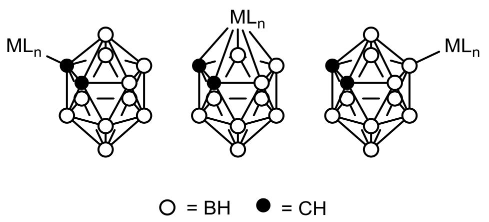
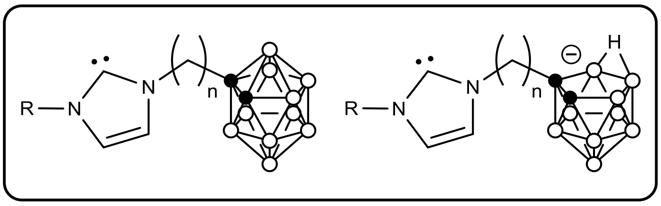
The past quarter of a century has seen a period of tremendous growth in the field of N-heterocyclic carbenes (NHCs), which can now be found in areas of chemistry as diverse as homogeneous catalysis, metallopharmaceuticals and liquid crystals. This success is largely due to NHCs being excellent 2-electron donors, combined with their highly tuneable steric and electronic properties.[1]

Icosahedral carboranes are a less well known, but nonetheless important class of ligand, with their rigidity and robustness lending themselves well to applications in catalysis, pharmaceuticals and materials.[2] Coordination to metal centres may occur through a carbon or boron atom, or through the open face of a *nido*-carborane, in a mode analogous to that of the cyclopentadienyl ligand. Facile tuning of electronic and steric properties is possible by modification of the groups on the cluster carbons.[3]





Ligand types used in this work

While much work in catalysis is focused on minor modification to known catalytic systems, large progress may be achieved by using completely new ligand classes. Recent work by Lavallo *et al.* has fused the previously unrelated areas of NHCs and carboranes for the first time; concurrent work in the Willans group has devised a totally new class of NHC-carborane tethers, which act as ligands for a range of transition metals.[4] These complexes offer a starting point for devising a range of NHC and carborane containing catalysts.

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Catalytic Epoxidation by Bioinspired Fe(H_2O)-bTAML Complex using O_2 and NaOCl.

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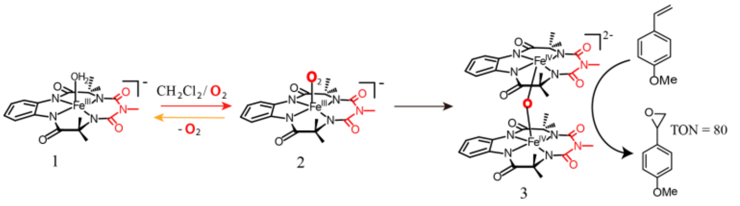
Abstract. Interaction of dioxygen molecule with iron containing metalloenzymes is an integral process for biological functions. For example, Cytochrome P450 does reductive activation of molecular oxygen and transfer the oxygen atom to various organic molecules in enzymatic reactions. These reactions consist of several steps in which superoxo, peroxo, hydroperoxo and oxo as intermediates are formed. Despite rigorous studies on chemically synthesized high valent iron-oxo complexes (iron-superoxo, iron-peroxo, iron-hydroperoxo, iron(IV)-oxo and iron(V)-oxo), there exists very few examples wherein iron-oxo complexes have been generated using molecular oxygen and among them there are no reports in which molecular dioxygen have been used as the O-atom source for catalytic epoxidation reaction without coreductant. Here, for first time we report the use of Fe(H_2O)-bTAML complex and oxygen molecule (O_2) for catalytic epoxidation reaction without any sacrificial reductant (Scheme 1). In another approach, high valent Fe^V(O) has been synthesized using NaOCl and Fe-bTAML complex at room temperature[1] for the mechanistic investigation of oxygen atom transfer (OAT) in C=C bond epoxidation. Hammett ρ value of −0.56 was obtained for the *para*-substituted styrene derivatives which indicates the electrophilic character of Fe^V(O). The use of *cis*-stilbene as a mechanistic probe leads to the formation of both *cis*- and *trans*-stilbene epoxides (73:27) suggests the formation of a radical intermediate.[2]

Scheme 1.



$$\mathrm{Fe^{IV}{-}O{-}Fe^{IV}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe^{V}(O)} + \mathrm{Fe^{III}} \qquad (3)$$

$$\mathrm{Fe^{V}(O)} + \text{Substrate} \xrightarrow{k_2} \text{Products} \qquad (4)$$

$$\text{Rate} = \frac{k_1\, k_2\, [\mathrm{Fe^{IV}{-}O{-}Fe^{IV}}][\text{Substrate}]}{k_{-1}[\mathrm{Fe^{III}}] + k_2[\text{Substrate}]} \qquad (5)$$

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Ln(III) Binding and Discrimination within a *De Novo* Designed Coiled Coil

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We present a trimeric coiled coil sequence that is designed to embed a Ln(III) binding site within its interior.[1] Translating the binding site along the coiled coil, at 1 nm intervals, generates a series of four peptide complexes, that although similar, behave differently and bind Tb(III) in different coordination environments.[2]

Using these designs we have shown, for the first time, that protein sites can now be engineered that are selective for different Ln(III) ions based on their size, thereby achieving unprecedented Ln(III) discrimination and selectivity. These findings have been used to generate a coiled coil capable of accommodating two different Ln(III) ions, selected for their size and differing chemical properties. More importantly the binding sites are designed so as to selectively bind these two different Ln(III) ions to the two distinct sites, with a high degree of control. This represents the first example of a Ln(III) selective binding site utilising a protein scaffold, and the first dual lanthanide binding coiled coil. We have also been able to control the proximity between the two Ln(III) ions (Figure 1), and are currently investigating the opportunities that might be afforded by hetero-Ln(III) complexes and if it is possible to determine if the two Ln(III) ions can communicate with each other, and whether this is distance dependent.

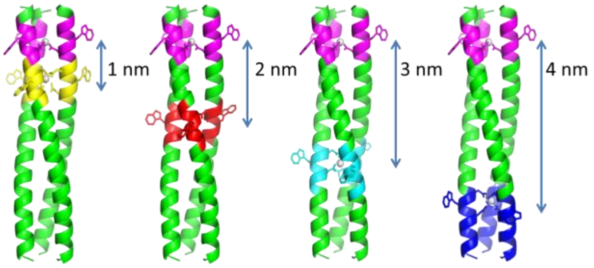

Figure 1. Pymol images of the double binding site coiled coils, showing the proximity between the two Ln(III) ions.

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Reactivity of a Titanium Borylimido Complex

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Over the past 20 years, the reactivity of Group 4 alkyl- and arylimido (L)M=NR complexes (L = ancillary ligand set, M = Group 4 metal, R = alkyl, aryl group) was explored in considerable depth.[1] More recently, the hydrazido[2] and alkoxyimido[3] analogues (L)Ti=N-NR and (L)Ti=N-OR were the focus of much interest, and were shown to exhibit a rich chemistry with both saturated and unsaturated substrates.

In contrast, examples of the less π-electron rich Group 4 borylimido complexes (L)M=N-BR_2 are extremely rare, and the reactivity of this motif is virtually unexplored.[4] Here, we wish to report the first comprehensive study of the chemistry of Group 4 borylimido complexes. Specifically, we will showcase the reactivity of titanium borylimido compound **1** with a variety of carbonyl and alkyne functionalities (for examples see Fig. 1).

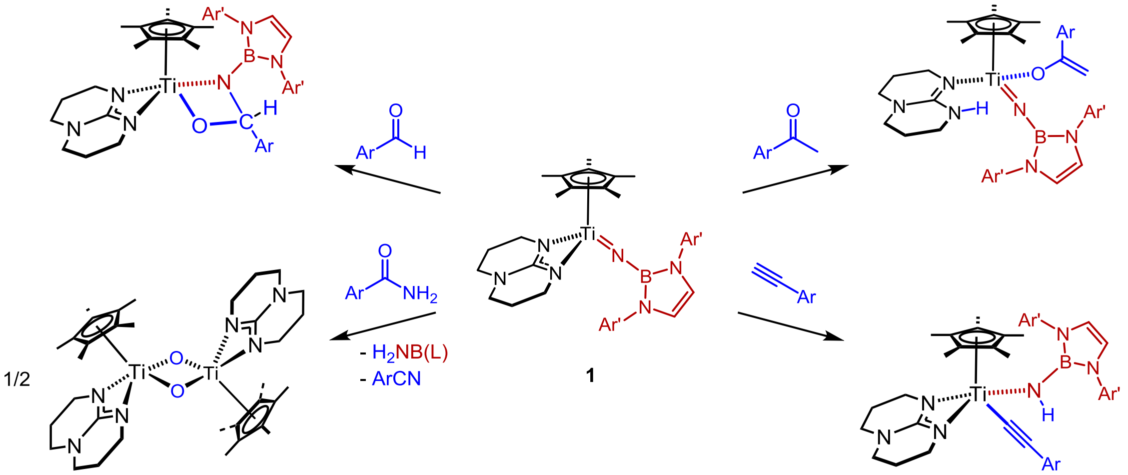

Figure 1: Reactions of Borylimido Complex **1**.

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(3) For examples, see: *Chem. Commun.* **2011**, *47*, 4926–4928; *Organometallics* **2013**, *32*, 7520–7539; *Inorg. Chem.* **2011**, *50*, 12155–12171.
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Homoleptic Cyano Complexes of Silicon and Tin

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This work concerns homoleptic hexacoordinate cyano complexes of p-block elements. To the best of our knowledge, these complexes are unknown (with the exception of $[Sn(CN)_6]^{2-}$, which was formed *in situ*) and no structural data reported.[1] $E(CN)_4$ (E = Ge, Sn) have been reported previously.[2–5] The compound $(PPN)_2[Si(CN)_6]$ (**1,** PPN = bis(triphenylphosphine)iminium cation) was synthesised by chloride-cyanide ligand exchange involving $SiCl_4$ and PPN(CN). The analogous reaction involving $GeCl_4$ and PPN(CN) forms a mixed-ligand complex (**2**). The reaction of SnF_4 and Me_3SiCN, in MeCN or pyridine, gives $Sn(CN)_4(L)_2$ (**3a,b**) (L = MeCN, **3a**; or pyridine, **3b**). Compound **3a** reacts with PPN(CN) to form $(PPN)_2[Sn(CN)_6]$ (**4**, figure 1). Compounds **1** and **4** adopt octahedral geometry and have E-C-N bond angles that deviate slightly from 180°. The compounds have been characterised by single crystal X-ray diffraction studies (**1,** space group P_{cba} ; **4,** space group $P2_1/n$), infra-red spectroscopy (**1-4**), NMR spectroscopy (**1, 2, 3b, 4**) and elemental analysis (**1, 2, 4**). All compounds were prepared under the exclusion of air. Investigations into the cyclisation reactions of the title compounds are ongoing.

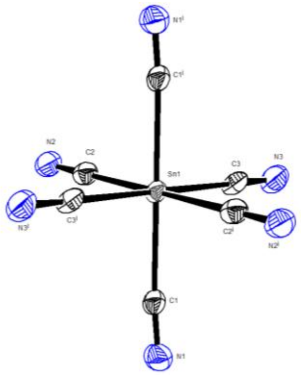

Figure 1. *ORTEP plot of the $[Sn(CN)_6]^{2-}$ anion in a crystal of $(PPN)_2[Sn(CN)_6]$. Ellipsoids are plotted at 50% probability. The symbol ^{i} indicates symmetry equivalence between crystallographically identical atoms with the same label.*

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New Gallium-68 Chelates for Mitochondrial Imaging

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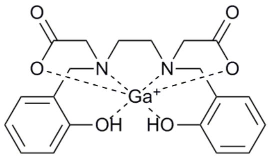
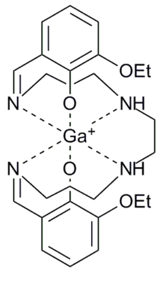
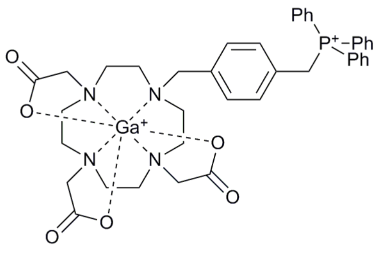
Cardiotoxicity is a fundamental limiter of chemotherapeutic dose, which is an increasing problem as cancer detection rates improve and patients then become at risk of heart failure. Non-invasive visualisation of cardiotoxicity as a means of optimising and personalising chemotherapeutic regime, and developing cardioprotectants, is therefore an attractive prospect. We have recently demonstrated proof of principle that the lipophilic cation ^{99m}Tc-sestamibi, widely used clinically to quantify myocardial perfusion by SPECT, can be repurposed to report on mitochondrial membrane potential as a read-out of cardiotoxicity. However, the approach that we envisage requires dynamic imaging, which is better suited to PET. We are therefore developing a range of lipophilic cationic Ga-68 tracers to identify cardiac mitochondrial toxicity by PET. Being generator produced, Ga-68 has significant practical advantages over F-18 and C-11 (which both require a cyclotron), with a convenient half life of 68 minutes. Our initial work has involved the synthesis and radiolabelling of the Ga-68 chelators pictured below in order to determine the best candidate for further study, including the development of a novel HBED synthesis. In order to tune lipophilicity to enable cell penetration while minimising non-selective trapping in cell membranes, aryl-functionalised triphenylphosphines DO3A-TPP have been synthesised through Grignard methodologies and appended to the DO3A chelator. The best potential candidates will be tested *in vitro* and *ex vivo* to determine their efficacy for mitochondrial imaging in our in-house preclinical models of cardiac toxicity, creating an on-going iterative loop of design-synthesis-evaluation-redesign.



[Ga HBED]$^+$



[Ga 3-Eabi]$^+$



[Ga DO3A-TPP]$^+$

Functionalised peptidomimetic metallohelices.

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Recently, we have demonstrated a unique approach to highly stereoselective asymmetric self-assembly of very stable, functionalized metallohelices which they have termed triplex. The metallohelices display high, structure-dependent toxicity to the human colon carcinoma cell-line HCT116 p53++, causing dramatic changes in the cell cycle without DNA damage. They have lower toxicity to human breast adenocarcinoma cells (MDA-MB-468) and, most remarkably, they show no significant toxicity to the bacteria methicillin-resistant *Staphylococcus aureus* and *Escherichia coli*. Here we report the successful design and synthesis of functionalised peptidomimetic metallohelices *via* click chemistry. We synthesised a series of sugar and aromatic clicked triplexes and tested their anticancer activities.

Cellular redox modulation using an organometallic Os(II) complex

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Platinum complexes are widely used anticancer drugs which exert their activity by a DNA-based mechanism of action with deleterious consequences for patients. However, their use is limited by the range of treatable malignancies and the incidence of resistance, in particular that which develops after the first round of treatment.[1] New generations of novel precious metal complexes are being developed to overcome the drawbacks of platinum therapy. Piano-stool complexes based on Ru(II), Os(II) and Ir(III) offer a highly versatile chemical scaffold for drug design which can be fine-tuned to improve anticancer activity.[2]

We are investigating the half-sandwich organometallic complex FY26, [Os(η^6-*p*-cymene)(4-(2-pyridylazo)-*N*,*N*-dimethylaniline)I]PF_6 which is highly potent *in vitro* and *in vivo*. FY26 exerts its activity by a mechanism of action which has a redox arm and involves perturbing the cellular balance of reactive oxygen species (ROS) in cancer cells, inducing changes in mitochondrial pathways.[3] This mechanism of action allows for the possibility of targeting the redox balance in cancer cells as a highly effective strategy, especially since it is a multiple site approach and offers selectivity over normal cells.[4] We are exploring the use of combination therapy with redox modulators to further increase the potency of FY26. This includes the use of ammonium tetrathiomolybdate, bromo pyruvic acid and maleimide.

Acknowledgements

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Exploring Cationic Rhodium “PONOP” Pincer Complexes for Amine-Borane Dehydropolymerisation

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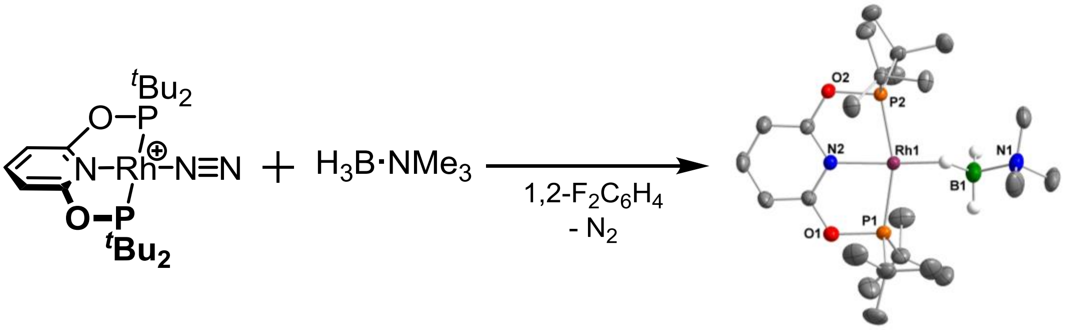
Over the last decade, the dehydrogenation of amine-boranes has been an area of significant interest due to its potential for the preparation of hydrogen storage materials, pre-cursors to boron-nitride ceramics and polyaminoboranes, $[H_3B{\cdot}NRH_2]_n$.[1] Polyaminoboranes are isoelectronic with polyolefins, which are socially and technologically ubiquitous and the chemistry of which is well understood. However, reliable syntheses of polyaminoboranes are less well developed and the precise mechanism of their formation is still unclear.

In 2008, Manners *et al.* reported an Ir-based dihydrogen “POCOP” pincer complex to be the first catalyst to dehydropolymerise $H_3B{\cdot}NMeH_2$, yielding high molecular weight polymer.[2] More recently, cationic Rh-based systems have also been employed to afford high molecular weight polyaminoboranes. In particular, the $[Rh(Xantphos)]^+$ fragment allows for control over the molecular weight of polymer produced by varying the solvent or concentration of H_2 present.[3]

This poster presents the use of a cationic Rh “PONOP” pincer complex in stoichiometric and catalytic reactions with various amine-boranes. Furthermore, initial studies towards elucidating the mechanism of this process are discussed.



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Coordination Chemistry and Photophysical Studies of *f*-element Imidodiphosphinate Complexes

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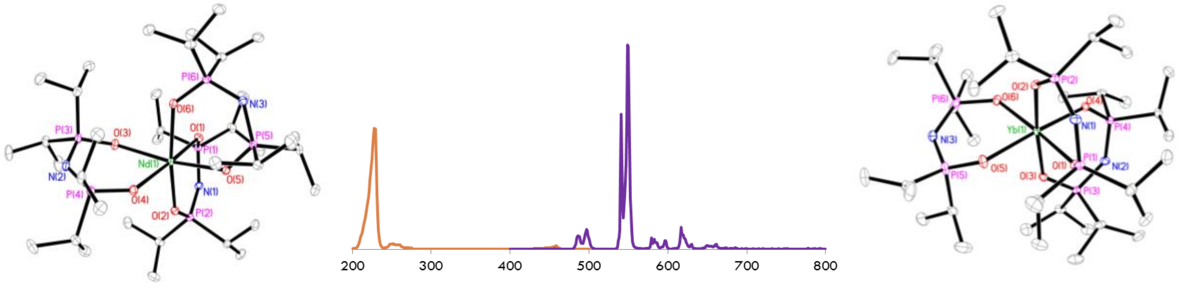
Imidodiphosphinates ($R_2P(O)NHP(O)R'_2$) are seen as complementary inorganic structures to *β*-diketonates that are already well known for forming luminescent lanthanide complexes.[1] Those with bulky substituents in particular are very attractive for use in *f*-block chemistry due to the potential to sterically protect the metal centre. This, along with the fact that there are no O-H, C-H or N-H oscillators within the binding site that can lead to quenching of the emission, means they are ideal for luminescence applications utilising the photophysical properties inherent to lanthanide(III) ions.[2,3,4]

We have recently been investigating the unique coordination chemistry and optical properties of uranyl(VI) and neptunyl(VI) tetraphenylimidodiphosphinate (TPIP) complexes that form monomeric, dimeric and trimeric moieties depending on the reaction conditions.[5,6] Interestingly, each oligomer possesses a unique and distinguishable emission profile that can be used to fingerprint such aggregated species in solution that has importance in understanding the environmental mobility of actinides.

Here we introduce two unexplored imidodiphosphinate ligands to *f*-element chemistry; tetra*iso*-propylimidodiphosphinate (TIPIP) and tetra*tert*-butylimidodiphosphinate (TBIP). Importantly, these ligands, which contain no chromophores within the ligand framework, enable us to study pure metal emission without any competing ligand emission processes that currently hamper observations of actinide luminescence. We will present the synthesis, coordination chemistry and photophysical properties of TIPIP and TBIP with lanthanide(III) ions as well as preliminary results of the reactions of the two ligands with uranium.



1

2

Figure 1. Excitation and emission spectra for the complex $Tb(TIPIP)_3$ (λ_{ex} = 248/366 nm, λ_{em} = 541/545/550 nm) and crystal structure for the analogous Nd (**1**) and Yb (**2**) complexes.

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Phospha-Amidinate Silylenes.

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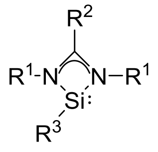
The chemistry of silylenes, heavier analogue of carbenes, is in many respects considerably more diverse than their carbon analogues. Base stabilisation of silylenes has enabled the isolation of a huge variety of compounds but their ability to undergo catalytically relevant E-H oxidative addition reactions is highly dependent on the nature of the ligands employed.[1,2] One particularly powerful class of stabilising ligands for silylenes is the amidinate ligand[3] (**1**), which is strongly donating and diminishes the ability of silylenes to activate E-H bonds. This research focuses on the development of phospha-amidinate silylenes in order to assess their potential for (reversible) oxidative addition reactivity.



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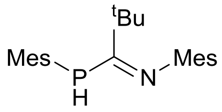

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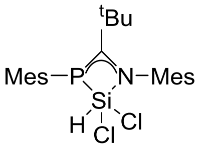

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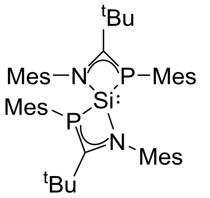

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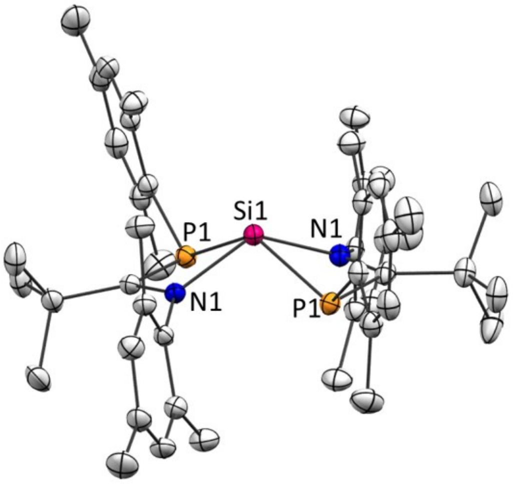

*X-ray crystal structure of **4**. Thermal ellipsoids drawn at 50% probability and hydrogen atoms omitted for clarity.*

We synthesised the novel phospha-amidinate ligand **2** and prepared the phospha-amidinate dichlorosilane **3** as a convenient intermediate in the synthesis of a series of new silylenes. For example, the phospha-amidinate ligand **2** stabilises the hypercoordinate silicon(II) compound **4**. The geometry around the silicon centre of **4** confirms the expected non-bonding lone pair at silicon and suggests N-Si dative interactions and P-Si covalent bonds. Here, we will present further details concerning the synthesis, structure and reactivity of compound **3** and related species.

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Synthesis, structure and dynamics of NHC-based Palladium macrocycles

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Combining stronger σ-donor properties and tuneable steric profiles, *N*-heterocyclic carbenes (NHCs) are increasingly used alternatives to more traditional phosphine ligands.[1] Notably, incorporation of these donors within rigid tridentate pincer architectures is becoming ever more prominent in organometallic chemistry and catalysis, providing additional thermal stability and reaction control at the bound metal centres.[2]

Our research focuses on the development and coordination chemistry of macrocyclic NHC-based pincer complexes. Herein we report the synthesis, structure and fluxional behaviour of macrocyclic palladium complexes.[3] In particular, we have systematically probed the impact ring size has on the structural properties of these complexes, both in solution and the solid state, using variable temperature NMR spectroscopy and X-ray crystallography.

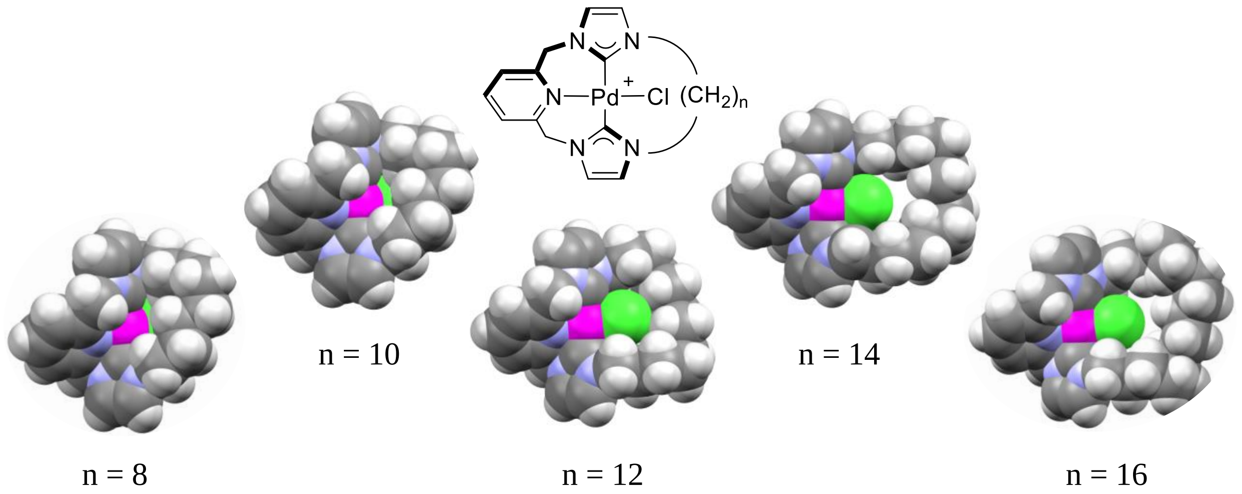

Figure 1.

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Lanthanide and Uranium *tert*-Butyloxycarbonyle Appended Cyclen Derivatives.

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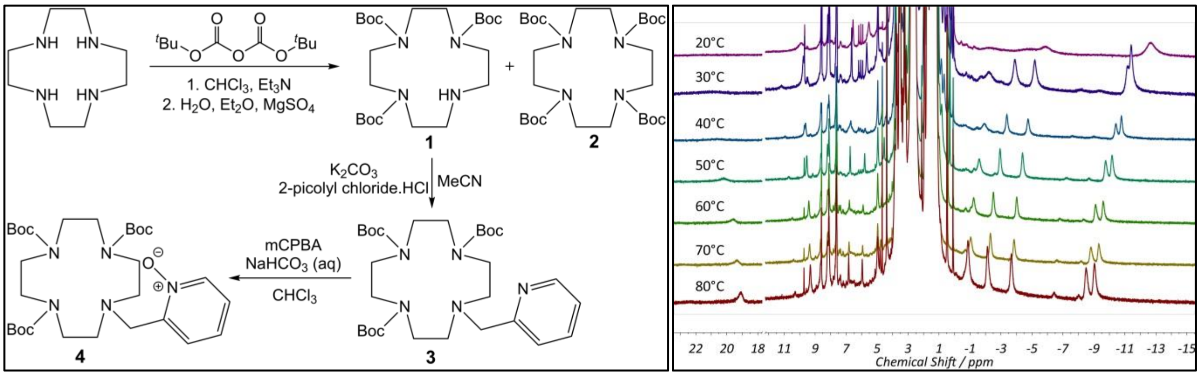

Figure 1a,b: Synthesis of the *tert*-butyloxycarbonyle appended cyclen ligands (a) and temperature dependent ^{1}H NMR spectra (400 MHz) of a mixture of Eu(OTf)$_3$ and ligand **4** in MeCN-d_3 (b).

Over the past decade, the research in actinide (especially uranium) chemistry has increased significantly. This is due to emerging topics such as the stabilisation of new or unusual oxidation states, unprecedented magnetic properties as well as unexpected reactivities.[1] The most common oxidation states for uranium are +IV and +VI, yet the +II, +III and +V oxidation states between also exist. In environmental chemistry in particular, the importance of studying oxidation states between +IV and +VI is growing with a specific focus on the bio-generation of the environmentally immobile U^{4+} ion.[2] As with many other higher oxidation state actinide ions, uranium readily forms the linear actinyl cation, with uranium in the +VI oxidation state. This uranyl ion $\{UO_2^{2+}\}$ shows a bright green LMCT emission in aqueous solution and in the solid state. However, the emission spectroscopy of other uranium (and indeed actinide) complexes has not been widely examined.[3]

Despite the fact that macrocyclic lanthanide complexes of cyclen derivatives (such as DOTA and DO3A) have been well studied, analogous complexes of the actinides remain scarce. These macrocycles are well suited as ligands for low oxidation state actinide cations, and in the lanthanide series, these ligands find widespread use as imaging agents in medicinal studies such as magnetic resonance (MRI) and optical imaging.[4]

We have recently reported the emissive properties of U(IV) encapsulated in DO3A (DO3A = [4,7,10-tris-carboxymethyl-1,4,7,10-tetraaza-cyclododec-1-yl]-acetic acid) and shown this ion is emissive from the $5f^1\,6d^1$ excited state.[5] We now present a selection of *tert*-butyloxycarbonyl protected and other cyclen derived ligands that are suitable complexing agentes for actinide ions in the +III and +IV oxidation states. The synthesis of these ligands and their lanthanide and uranium complexes will be presented along with a discussion of their ^{1}H NMR and photophysical properties.

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Zn_2Y_2 Catalyst for High-Efficiency Chiral Michael Addition Reactions at Room Temperature

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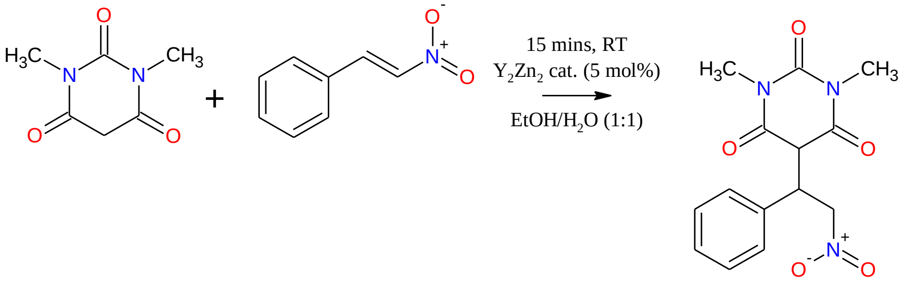
In recent years, growing attention has been paid to developing a new generation of catalysts from 3d/4f Coordination Clusters (CCs) to improve the efficiency of organic chemical reactions. [1,2], Our research group have committed to developing polynuclear 3d/4f CCs with an organic Schiff base framework to find interesting core topologies that show catalytic capabilities.[3]

In the present work, we have developed a $Zn^{II}_2Y^{III}_2$ catalyst, a tetranuclear CC with a defect dicubane topology to demonstrate its ability to perform chiral Michael additions at room temperature with high efficiency. A catalysed reaction at room temperature between 1,3-dimethylbarbaturic acid and beta-trans-nitrostyrene in 1:1 H_2O/EtOH produced the adduct in a quantitative yield.



Quantitative yield

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Mechanistic and Kinetic Investigations into Homodinuclear and Heterodinuclear Catalysts for CO_2-epoxide Copolymerization

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Using a viable catalyst, the copolymerization of CO_2 and epoxides can yield polycarbonates from captured CO_2. Homodinuclear catalysts (Fig 1. **1** and **2**) have previously shown activities and selectivities amongst the highest known for this copolymerization and are active under only 1 bar CO_2 pressure. Detailed mechanistic, kinetic and theoretical studies suggest metal-metal cooperativity, with each metal playing a different role in the catalysis.[1] Heterodinuclear analogues have now been shown to be up to 40 times more active than their homodinuclear analogues for ring-opening copolymerization of epoxides and anhydrides.[2]

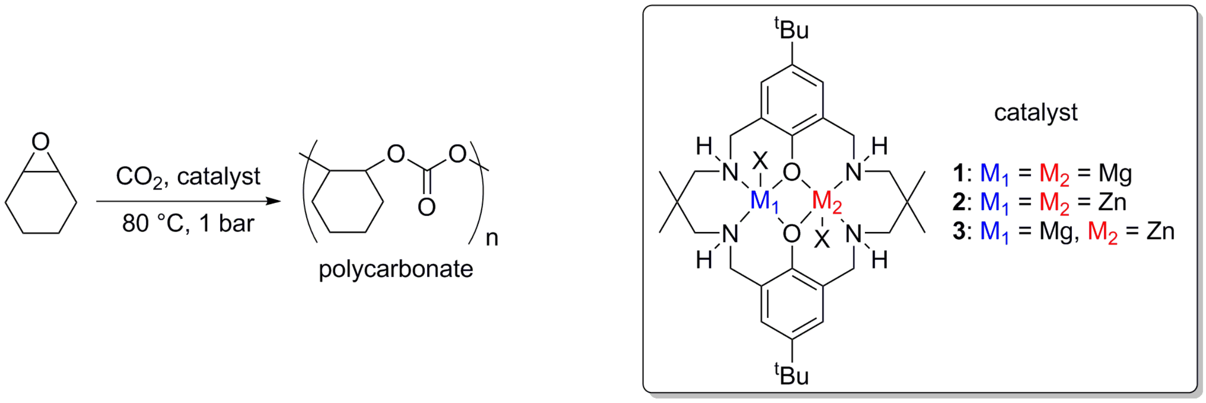

Fig 1. Homo- and heterodinuclear catalysts for CO_2-cyclohexene oxide copolymerization.

For the first time, detailed kinetic studies have been carried out on a heterodinuclear catalyst for CO_2-cyclohexene oxide copolymerization. These studies will be presented and compared to the homodinuclear catalysts to provide mechanistic insights. The effect of different co-ligands has been studied through initial rates and DFT investigations, for a range of homodinuclear catalysts. These findings provide insight into the underlying mechanisms of the catalysis, giving key information for future novel catalyst development.

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The Development of a ^{68}Ga labelled Plant Virus Capsid for PET Imaging

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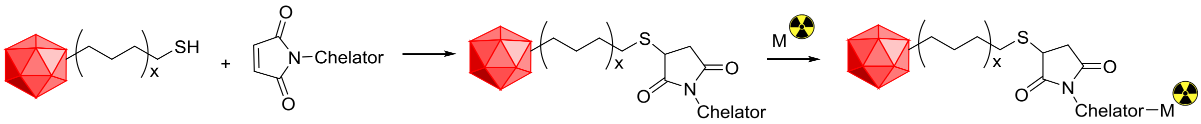
Cowpea mosaic virus (CPMV), a 28 nm icosahedral plant virus, is well characterised and has been found to withstand extremes of temperature and pH along with a variety of organic solvents.[1] The particles are monodisperse, inexpensive to isolate on a gram scale and are targeted naturally to cancer cells, through an interaction with surface expressed vimentin.[2] CPMV has also been shown to reduce established lung melanoma following inhalation of the virus like particles, making it an attractive platform for molecular imaging.[3,4]

Although CPMV has previously been exploited as an imaging agent, much of the research has been tailored towards magnetic resonance and optical imaging.[5] Positron emission tomography (PET) is a functional imaging technique dependent on the emission of a positron from a radionuclide. The aim of this research is to radiolabel CPMV nanoparticles with a positron emitting radionuclide (gallium-68, $t_{1/2} = 68$ mins). This is achieved by conjugating a chelator to the surface of CPMV and radiolabeling the modified virions with ^{68}Ga (**Scheme 1**).



Scheme 1: Conjugation and radiolabeling of CPMV with ^{68}Ga.

Radiolabelled CPMV for PET imaging could provide an effective way of imaging tumour cells and monitoring therapies, without the need for a more complex targeting moiety. It will also increase the understanding of the behaviour of CPMV *in vivo* and potentially provide evidence for understanding the mechanism of tumour targeting.

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Reductive Elimination from Al(III): Exploring the Mechanism and the Effect of Coordinated Base

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Aluminium is taught in undergraduate chemistry to exist only in the +3 oxidation state, and indeed, the reactivity of compounds in this state is ubiquitous in industry. Whilst there are a some examples of stable Al(I) compounds, they must overcome the favourable disproportionation to Al(0)/Al(III). Reductive elimination provides access to lower oxidation states in transition metal chemistry, however for aluminium this pathway is not necessarily expected. What if we could access the Al(I) state with the same ease as low valent transition metal compounds?

Here we examine the mechanism and find a possible transition state (Figure 1) of Fischer's reported reductive elimination of Cp*H from $\mathrm{Cp^*{}_2AlH}$ to give Cp*Al,[1] a stable tetrameric compound known since the early 1990s.[2] The addition of coordinating *N*-heterocyclic carbenes to the system creates a thermally stable compound, inhibiting reductive elimination. Dimethylaminopyidine was found to be able to dissociate under the reaction conditions, allowing reductive elimination to take place but at a slower rate.

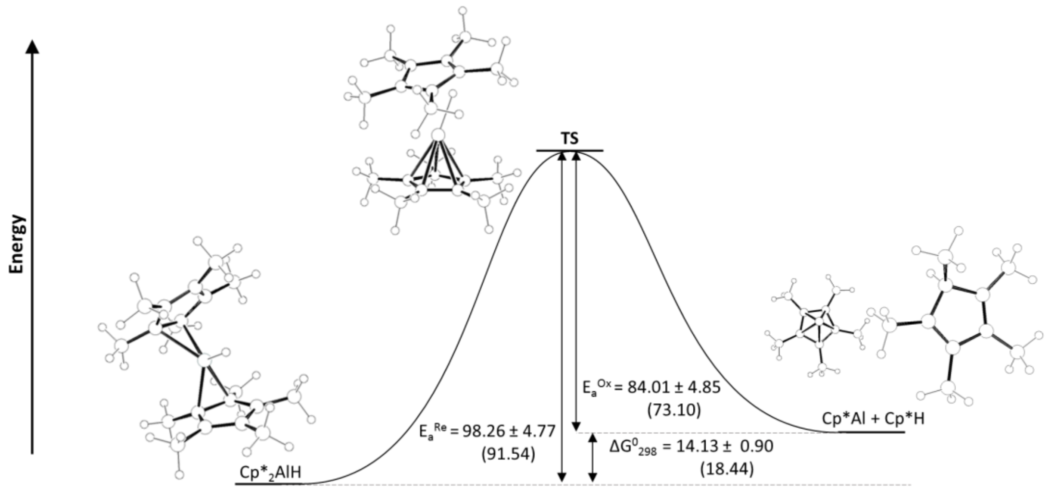

Figure 1. Potential energy diagram with energies (theoretical) stated in kJ $\mathrm{mol^{-1}}$. Calculated energies predicated at the BP86/def-TZVPP level of theory using the BP86/def2-SVP optimised geometries (shown)

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Small Molecule Activation under Ambient Conditions by Main Group Metalloid Clusters

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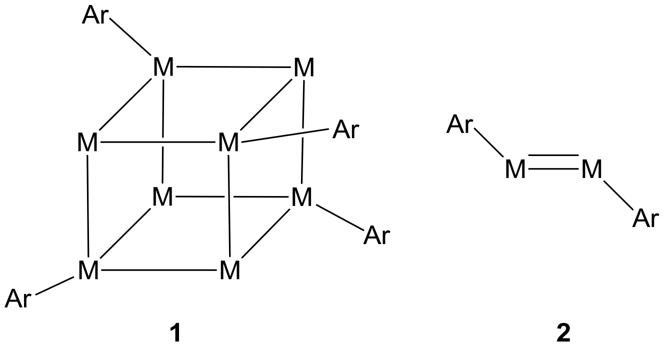
In recent years several main group 13 and 14 compounds have been utilized in small molecule activation.[1] The reactions occur due to strained geometry of the main group metals and favorable matching of the frontier orbitals. However, these reactions have been limited to mainly monomeric or dimeric main group complexes. The properties and reactivity of multinuclear main group metal clusters have been scarcely examined even though compounds of the form M_8Ar_4 (M = In or Sn; Ar = C_6H_3-2,6-Mes_2, **1**)[2,3] possess unsubstituted metal atoms which can readily react with small molecules in a similar manner to formally multiply bonded ArMMAr species (M = group 13 or 14 metal; Ar = bulky organic ligand, **2**). In this presentation, we report the reactions of the cluster compound **1** with small molecules such as H_2 and ethylene to form unprecedented main group systems. The role of reaction conditions in the preparation molecular clusters like **1** is also discussed.



M = group 13 or 14 metal; Ar = bulky terphenyl ligand

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Vibrational spectroscopic studies of photoactivatable diazido Pt(IV) anticancer complexes

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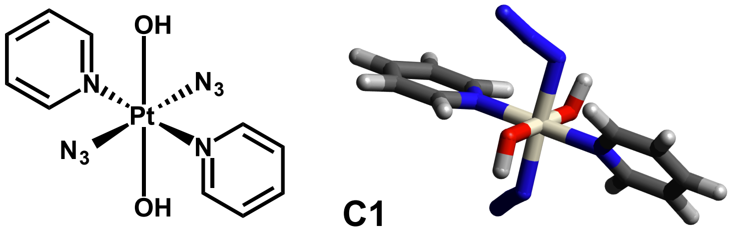
Pt(IV) diazido complex, *trans*,*trans*,*trans*-[Pt(N_3)$_2$(OH)$_2$(pyridine)$_2$] (**C1,** Figure 1), is a promising anticancer pro-drug candidate, which exhibits potent activity towards a range of cancer cells upon irradiation with UV-A and visible light.[1,2] Such photoactivated anticancer Pt(IV) pro-drugs have the potential to overcome side-effects and resistance encountered with the current clinically-approved Pt-based chemotherapeutics such as cisplatin, carboplatin and oxaliplatin. Previous studies on **C1** suggest that Pt(II), nitrene and radical photoproducts, as well as cleaved ligands, act in concert to elicit the observed multi-targeted biological activity.[2,3] In this work, we present the use of state-of-the-art vibrational spectroscopic techniques to gain insight into the mechanism of action of such photoactivated Pt(IV) compounds. More specifically, our aim is to use Infrared and Raman spectroscopy, Synchrotron Far-Infrared spectroscopy and Synchrotron Infrared Microspectroscopy to follow the changes in the Mid- and Far-IR regions due to changing metal coordination environment as well as cellular and biomolecular interactions of the Pt(IV) pro-drugs upon irradiation. These vibrational spectroscopic techniques offer excellent non-destructive and label-free methods for the analysis of biological specimens.[4] Density Functional Theory calculations have been carried out in concert to complement the spectroscopic analysis.



C1

*Figure 1. Structure of trans,trans,trans-[Pt(N_3)$_2$(OH)$_2$(pyridine)$_2$] (**C1**, left) and its lowest energy geometry optimized by Density Functional Theory calculations (right).*

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Preparation, characterisation and *in-vitro* cytotoxicity of mesoporous silica nanoparticles loaded with cytotoxic Pt(II) oxadiazoline complexes.

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Cytotoxic platinum compounds play a major role in the chemotherapy of a large number of human cancers. However, due to the severe side effects for the patient and other problems associated with their use, there is a need for the development of more efficient drugs and new methods for their selective delivery to the tumours. One way to achieve the latter could be in the use of nanoparticular carrier materials that can adsorb or chemically bind the drug. In the cell, the drug is supposed to be slowly released, either by physical desorption or by dissolution of the particle framework. Ideally, the cytotoxic properties of the platinum drug unfold only then, in the cancer cell, and over a longer period of time due to the gradual release.

Herein, we report on our first steps in this direction. The adsorption rate of a series of cytotoxic Pt(II) oxadiazoline compounds to mesoporous silica particles has been studied by NMR and UV/vis spectroscopy, and the loading capacity of the material has been determined. The untreated and Pt(II) loaded particles were characterised by C,H,N combustion analysis, BET/BJH nitrogen sorption, electron microscopy (REM and TEM) and EDX. With the latter methods we were able to demonstrate the homogenous distribution of the Pt(II) compound on and in the silica particles, and no Pt(II) bulk precipitate had formed.

The *in vitro* cytotoxicity in a human cancer cell line (HeLa) has been determined for one of the new platinum compounds adsorbed to mesoporous silica particles of different size, and compared with the corresponding compound in solution. The IC50 data are similar in all cases, suggesting that the release of the Pt(II) compound was relatively fast and possibly occurred before the particles reached the cells. Overall, the platinum drug is chemically stable on silica and retained its activity upon prolonged storage.

Removal of cytotoxic platinum compounds from aqueous media by photolysis in the presence of 2,4,6-trimercaptotriazine.

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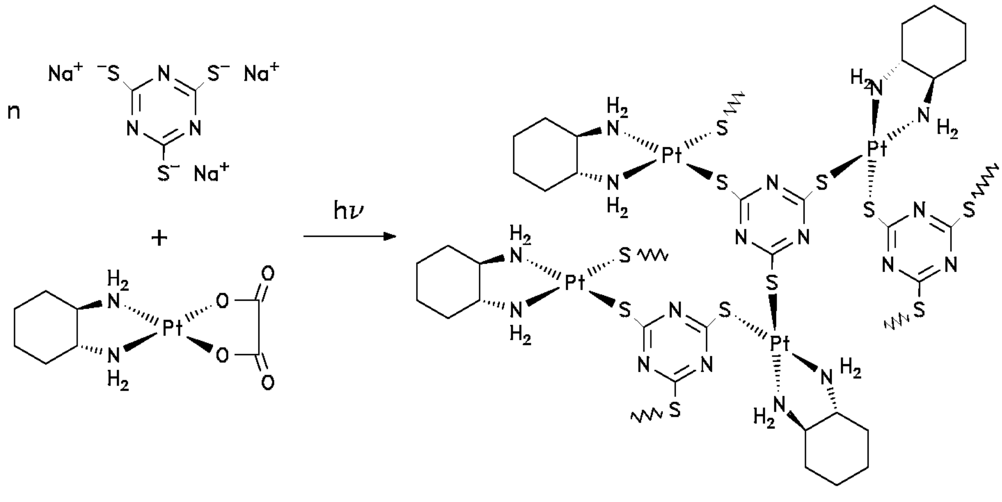
Platinum based anticancer agents such as cisplatin, carboplatin and oxaliplatin are widely used in the treatment of human cancers. The major part of these drugs is excreted through the patients urine and released into the environment, with so far unknown effects. Although the platinum emission from hospitals appears relatively minor (as compared to the PGM contamination from car catalysts,[1]), the bioavailability and bioactivity of soluble Pt(II) compounds from medicinal applications, in particular that of unmetabolised carboplatin,[2] may pose a higher risk.

Herein, we report on the use of 2,4,6-trimercaptotriazine as a scavenger reagent for the relatively selective and fast removal of a series of water soluble Pt(II) compounds, including the currently available cancer drugs. The product of the reaction of oxaliplatin with the sodium salt of 2,4,6-trimercaptotriazine has been isolated and characterised as a coordination polymer of the overall composition [(1,2-cyclohexanediamine)Pt]$_3$[2,4,6-trimercaptotriazine]$_2$ shown below.



Based on these results, a solid supported TMT material was developed that scavenges platinum compounds from aqueous solutions. This is planned to be used for the treatment of hospital waste water and urine samples of cancer patients who received platinum based chemotherapy.

Acknowledgments: The authors thank Johnson-Matthey for a loan of platinum compounds and the Universities of Chester and of Augsburg for general support of this work.

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Synthesis of Ditopic Carbanionic N-Heterocyclic Carbene Complexes

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Since the discovery of the first isolable N-heterocyclic carbene (NHC) 24 years ago,[1] these compounds have gone from chemical curiosities to ubiquitous ligands in modern organometallic chemistry. NHCs can bond to metals through the "conventional" (C2) or "abnormal" (C4) positions.[2] Recently, Robinson reported the synthesis of an NHC capable of binding through the C2 and C4 positions simultaneously.[3] Accordingly, we have recently reviewed the known chemistry of such ditopic carbanionic NHCs.[4] We have been investigating the reactivity of the lithium salt of the deprotonated IPr carbene towards $E[N(SiMe_3)_2]_2$ complexes (E = Ge, Sn, Pb). Such reactions in an equimolar ratio result in the formation of novel germylene, stannylene or plumbylene species.[5]

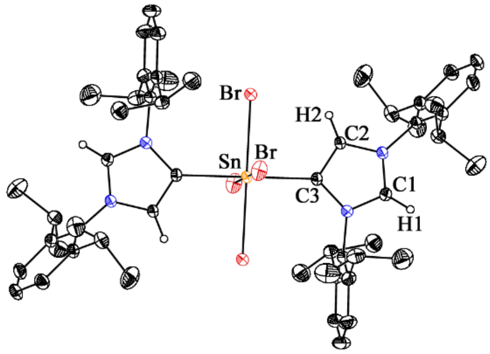

Figure 1. Crystal structure of $SnBr_4(aIPr)_2$

In a similar manner, we have gone on to react KIPr with various group 14 halides and $HgCl_2$ to afford neutral complexes bearing abnormally bonded NHCs such as $SiCl_2(aIPr:)_2$ and $Hg(aIPr:)_2$.[7] Finally, we have also been investigating alternative routes to ditopic carbanionic NHC complexes via the thermal isomerisation of normal NHC complexes. Refluxing an IPr solution with SnX_4 (X = Cl or Br) will result in the isomerisation of the NHC and crystallisation of the zwitterionic, distorted octahedral complex $SnX_4(aIPr)_2$.[7]

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Lipophilic perrhenates as catalysts for REDOX reactions

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Dynamically assembled, lipophilic perrhenate ion pairs have recently been shown to be successful catalysts for the epoxidation of alkenes by hydrogen peroxide.[1] Rhenium oxo compounds have also been exploited as catalysts for the reduction of carbonyls to alcohols by hydrosilanes,[2] therefore showing the potential of this high oxidation state, and recyclable catalyst for CO_2 reduction. In this work we have prepared the new $[N(hexyl)_4][ReO_4]$ complex and have found that it acts as a catalyst for the selective formation of methanol from CO_2 using hydrosilanes (Figure 1a).[3]

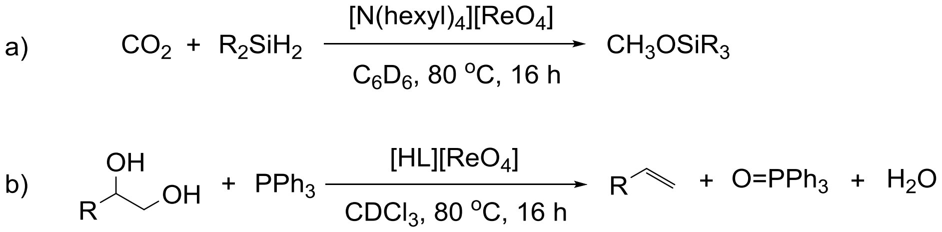

Figure 1. Perrhenate catalysis: a) Hydrosilylation of CO_2 to form a methanol equivalent. b) Deoxydehydration of glycols to alkenes

Furthermore, the development of catalytic process for biomass conversion to value-added chemicals is also of great importance. We have successfully applied the simple, lipophilic perrhenate catalyst system to the deoxydehydration (DODH) of glycols to alkenes (Figure 1b). The details of these catalytic reactions and insight from the study of their mechanisms will be discussed.

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Towards small molecule activation with tethered bimetallic uranium aryloxides

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Both increasing quantities of anthropogenic atmospheric carbon dioxide and the rapid depletion of fossil fuels mean that transforming C1 feedstocks into commercially relevant products is of great interest. A range of uranium (III) complexes can reductively couple carbon monoxide to generate ynediolate, deltate and squarate ($[C_nO_n]^{2-}$, $n = 2$, 3 and 4 respectively) ions coordinated between the two U centres.[1–3] In addition, our group has reported C-H bond functionalisation chemistry mediated by uranium (III) aryloxidesthat can form diuranium inverse-arene complexes.[4]

Using a bulky tetraphenolate ligand (H_4L) which incorporates a central arene ring, we are investigating the synthesis and reactivity of mono and bimetallic arene complexes of uranium. The synthesis of bimetallic uranium (IV) uranium-amido (1) and and-iodo (2) adducts of L will presented (Figure 1), along with preliminary redox and small molecule activation reaction studies.[5]

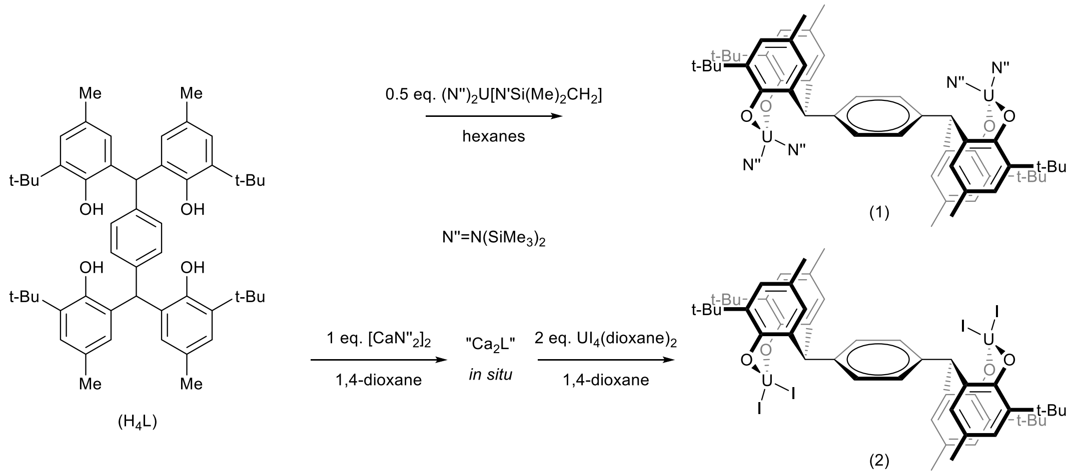

Figure 1: Synthetic routes to new diuranium complexes supported by an arene tethered tetraphenol ligand

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Bacterial Iron Uptake: Designing Siderophore Mimics to Understand Periplasmic Binding Proteins

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Iron is essential for optimal growth of almost all bacteria. For iron uptake, many bacteria utilise iron-chelating siderophores alongside a dedicated set of transport proteins.[1] *Campylobacter jejuni* does not produce siderophores but is able to take up a number of iron-bound siderophores, including enterobactin of *E. coli*. It was previously thought that siderophores must be hexadentate, however CeuE, the periplasmic ferric siderophore binding protein in *C. jejuni*, has been studied via X-ray crystallography and revealed the interactions with tetradentate siderophores, such as H_4-4-LICAM.[2]

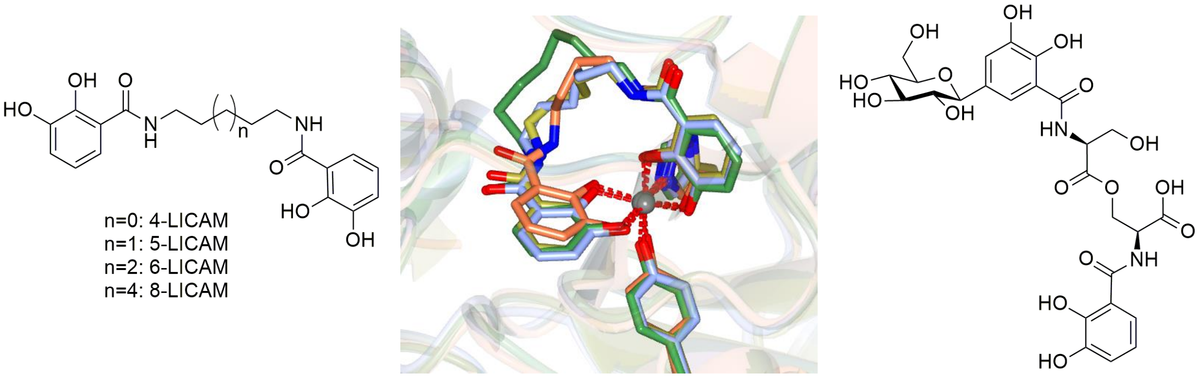

Figure 1. Left: 4-,5-,6- and 8-LICAM bound to iron in the siderophore binding pocket of CeuE, Tyr and His complete octahedral coordination. Centre: The n-LICAM siderophore mimic series. Right: Salmochelin S1, a C5 functionalised catecholate siderophore.

Using co-crystal structures, circular dichroism and intrinsic fluorescence quenching experiments, we have shown that a series of n-LICAM^{4-} (Figure 1: Left) tetradentate siderophore mimics bind to CeuE (Figure 1: Centre). Linker lengths between the iron-binding catecholamide units increased from four carbon atoms (4-LICAM^{4-}) to five, six and eight (5-, 6-, 8-LICAM^{4-}). CeuE recognizes and binds all four mimics and selects Λ-configured complexes. The binding affinity is slightly higher for the 5- compared to 4-LICAM^{4-} with dissociation constants of <10 nM and 24 ± 9 nM, respectively. For the 6- and 8-LICAM^{4-} the affinity decreases, with dissociation constants of 33 ± 8 nM and 59 ± 8 nM, due to the entropic cost of longer, more flexible linkers. The optimum linker length of five matches a number of natural siderophores. We continue to probe the ligand binding promiscuity of CeuE, with salmochelin siderophore mimics (Figure 1: Right). It is proposed that CeuE may also bind C5 functionalised catecholate siderophores: enhancing the iron scavenging ability of *C. jejuni*.

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Diverging reactivity of $B(C_6F_5)_3$ in Lewis acid mediated organic transformations: carboboration, cyclisation and propargyl rearrangement.

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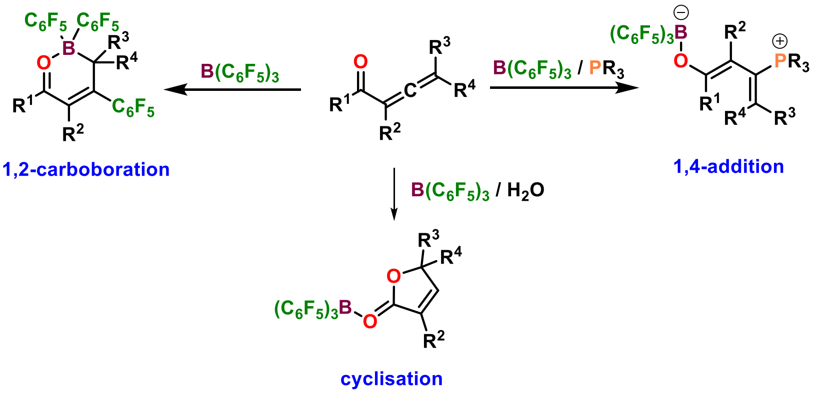
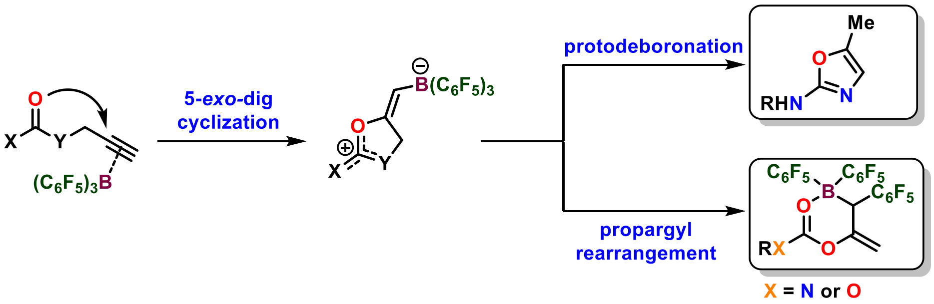
The chemistry of frustrated Lewis pairs (FLPs) has exploded since their first report in 2006.[1] FLPs have also been shown to effect 1,2-additions to both alkynes and alkenes. In the last few years, the Erker group extended the use of boron Lewis acids in various carboboration reactions utilising the strong Lewis acids $B(C_6F_5)_3$ or $RB(C_6F_5)_2$ to generate alkenylboranes from terminal and internal alkynes.[2]



The treatment of allenyl ketones or esters with (frustrated) Lewis acid-base pairs results in the nucleophilic attack of the phosphine to the β-carbon as a result of σ-activation of the ketone by the Lewis acidic boron. In the absence of an external Lewis base, σ-activation triggers a 1,2-carboboration mechanism yielding a 6-membered heterocyclic species with a chelating boron.[3] In the presence of water the formation of γ-lactone products could be observed which is reminiscent of reactivity typically observed with π-Lewis acidic transition metals.[4] Further reactivity using $B(C_6F_5)_3$ in conjunction with unsaturated carbon-carbon frameworks, namely propargyl ureas, carbamates and carbonates, result in an array of various organic products through propargyl rearrangement, cyclisation or carboboration steps.[5]



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Asymmetric reductions using ruthenium and iron complexes

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A number of Ru/TsDPEN complexes have been reported for the asymmetric reduction of ketones to alcohols and of imines to amines. We have described the synthesis and applications of complexes of general structure **1**, which contain a linking 'tether' between the arene ring and the diamine ligand components,[1] serves to improve the stability and activity of the complexes (Figure 1). The synthesis and applications to asymmetric catalysis of this series of tethered complexes to the asymmetric reduction of ketones and imines will be described.

The synthesis of a series of novel iron complexes such as **2** has been investigated (Figure 2), together with their applications to asymmetric reductions.[2] Products have been obtained with modest ees to date, however the use of an iron catalyst provides a basis for the development of environmentally compatible reagents in the future. Recent developments and innovations in this area will be described.

Figure 1 – Asymmetric reduction using tethered catalysts **1**.

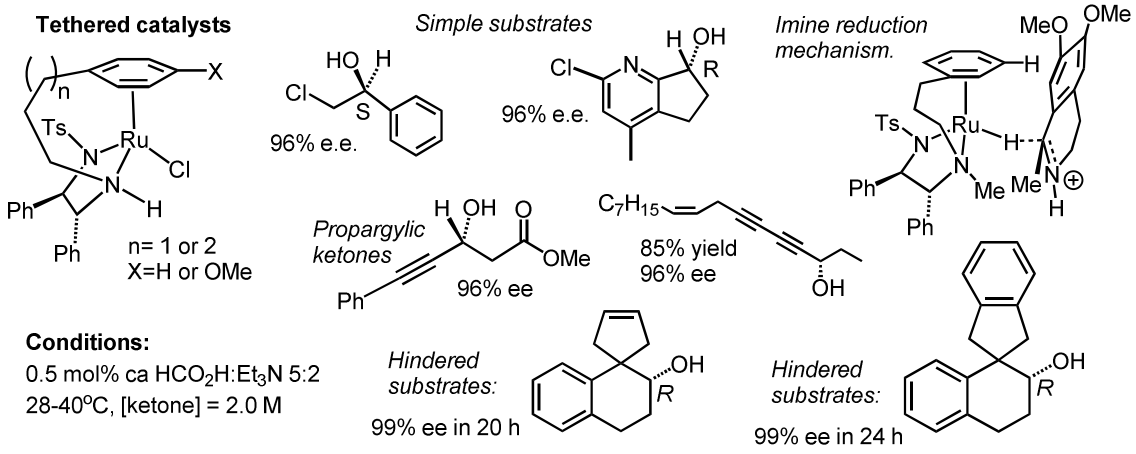
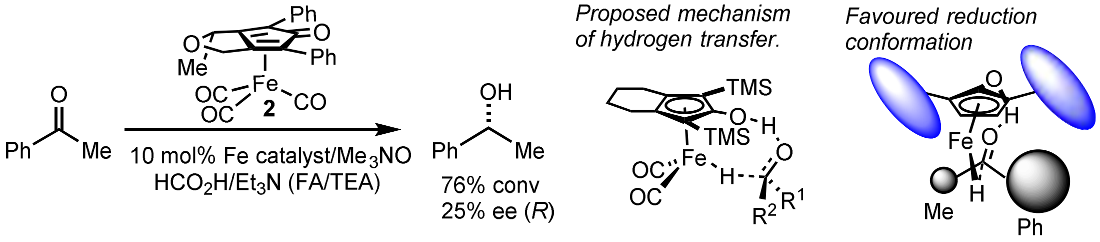


Figure 2 – Transformations using iron complexes **2**.



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Photoresponsive carbon monoxide release:
towards therapeutic applications

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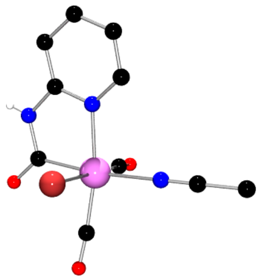
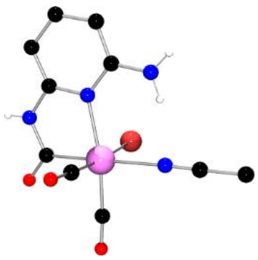
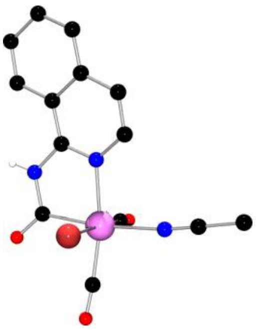
The role of carbon monoxide (CO) in mammalian physiology has a surprising bifurcated character: while its toxicity is well-known, the unforeseen beneficial nature of CO as a signalling molecule is becoming increasingly apparent.[1] Preclinical trials have shown that exogenous CO brings about a range of therapeutic effects including vasodilation[2] and inflammation suppression.[3] Difficulties associated with handling this gas has prompted researchers into developing metal carbonyl complexes (CORMs): CO delivery vehicles which only release their load when subjected by specific stimulus.

We have been exploring the triggered CO-release of a family of carbonyl complexes of iron and ruthenium. These complexes feature two discrete CO ligands, with a third latent in the carbamoyl metallocycle, and release CO when irradiated with *visible* light. Subtle changes in the ligand framework lead to a significant enhancement in light sensitivity, pointing the way from lab curios to real-world therapeutic applications. The medicinal applications of CO continue to progress rapidly and it is probable that CO-releasing molecules will play an important role in establishing CO within human medicine in the near future.







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SYNTHESIS AND REACTIVITY OF ZIRCONIUM AND HAFNIUM BORYLIMIDO COMPOUNDS

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Complexes containing transition metal-nitrogen multiple bonds have been applied in a range of important organic and inorganic transformations.[1] The synthesis and small molecule reactivity of Group 4 imido and hydrazido complexes, (L)M=NR and (L)M=NNR_2, have been extensively studied within this research group and by others.[2] Of relevance to this contribution, imidozirconocene complexes Cp_2Zr=NR(THF) have shown a wild range of reactivity with different small molecules.[3]

Only five examples of the related borylimides, (L)M=NBR_2, have been reported across all of the transition metals to date,[4] and we here report the synthesis of the first zirconium and halnium borylimido complexes using the borylamine $H_2NB(NAr'CH)_2$ (Ar' = 2,6-$C_6H_3{}^iPr_2$) (see Figure 1). The zirconium complex was found to give some unusual E-H (E = H, C) activation reactions. Furthermore, C-H activations and cycloadditions with alkynes were found to be selectively controlled kinetically and thermodynamically, which we also report here.

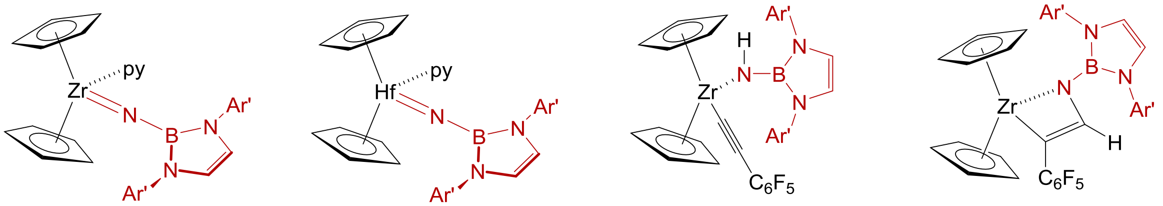

Figure 1: Examples of new zirconium and hafnium borylimido complexes, and reactivity products.

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Modification of viral nanoparticle for use in diagnosis and treatment of cancer.

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Plant-derived viral nanoparticles (VNP) and their genome free counterpart, virus-like particles (VLP), have seen a growing interest as platforms for delivering large payloads of drugs[1]. In this project, cowpea mosaic virus (CPMV) are being functionalised internally with high affinity ligands for either ^{99m}Tc (Single Photon Emission Computed Tomography (SPECT) imaging radiotracer) or ^{68}Ga (Positron Emission Tomography (PET) imaging radiotracer) and externally with photosensitisers for photodynamic therapy (PDT).

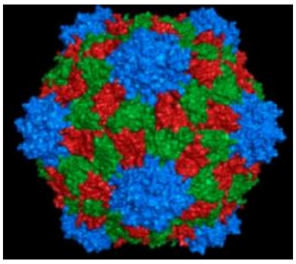

Figure 1 Crystal structure of CPMV[1]

PDT involves the administration of a photosensitising drug, which accumulates in tumorous tissues and, upon irradiation with visible or near IR light, generates reactive oxygen species, inducing a toxic response in surrounding tissues, eventually culminating in cell death. Porphyrins are the molecules of choice due to their well-established photophysical properties and relative ease of synthesis and functionalization.

While PDT is a well-established cancer treatment technique, imaging using SPECT or PET to locate and stage the tumour prior to treatment is still required. The combination of diagnostic and therapeutic modalities into a single entity is of particular interest and is a growing area of research[2], often referred to as theranostics. Not only will this approach negate the requirement for administering separate imaging agent and drug, but for PDT, which requires light activation *in situ*, the diagnostic modality of the drug will provide information on the degree of accumulation in the target tissue, allowing optimisation of treatment protocols.

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Incorporation of new functionalites into Metal-Organic Frameworks for catalysis and metal binding

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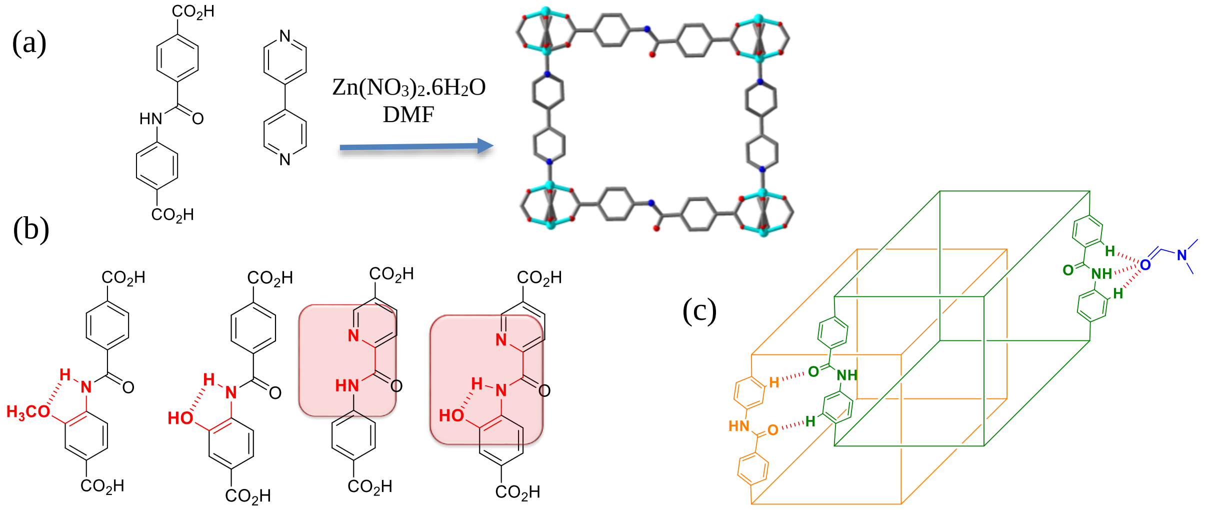
The predictable topologies of MOFs' constituent units have opened the way to rational design and the study of their structure-property relationships.[1] In keeping with that reasoning, a systematic study of incorporation of a new series of amide containing linkers and pillars in Zn MOFs (a) has been carried out to get an insight on structural, physical and chemical properties modification of new series of MOFs.[2] Potentially, catalytic properties of those new compounds can be achieved either though the presence of inter- and intramolecular hydrogen bonds or through the presence of metal ions coordinated to the linker through two novel coordination pockets (b).



The presence of stabilizing inter-molecular hydrogen bonds ensures the overall stability of the amide containing **pcu** topologies (c). Removing those interactions by engaging the amide moieties into intra-molecular H-bonds result in supressing the possibility of forming the **pcu** structures. Therefore, the incorporation of the amide linkers in the UiO-66, Zr-based framework types has been undertaken. We report the synthesis of these structures, which have been then modified post-synthetically by metalation for catalytic studies.

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Multi-colour Luminescent Ir(III) Compounds for Photodynamic Therapy

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Abstract: Photodynamic therapy (PDT) has expanded the range of medical techniques available to treat certain types of cancer, such as lung, bladder, ophthalmologic cancer, and urinary tumours. PDT treatments rely on the use of a combination of a photosensitizer (PS) and light. Ideally, a PS should be nontoxic in the absence of light, but have a high toxicity for cancer cells upon light exposure.[1] Specifically, the excited state of the PS reacts with the ground state of molecular oxygen ($^3O_2$) to generate reactive oxygen species and notably singlet oxygen ($^1O_2$). In PDT, $^1O_2$ is considered as the primary toxic species that can induce cellular organelle or vasculature damage.[2] Here we have designed and synthesized a series of iridium-dithiolate compounds with structures tunable for emission of various colours of light (green, yellow, red, **Fig.1**). Upon light irradiation, these compounds can generate singlet oxygen ($^1O_2$), which will induce a deep cellular cascade that finally leads to cell death.

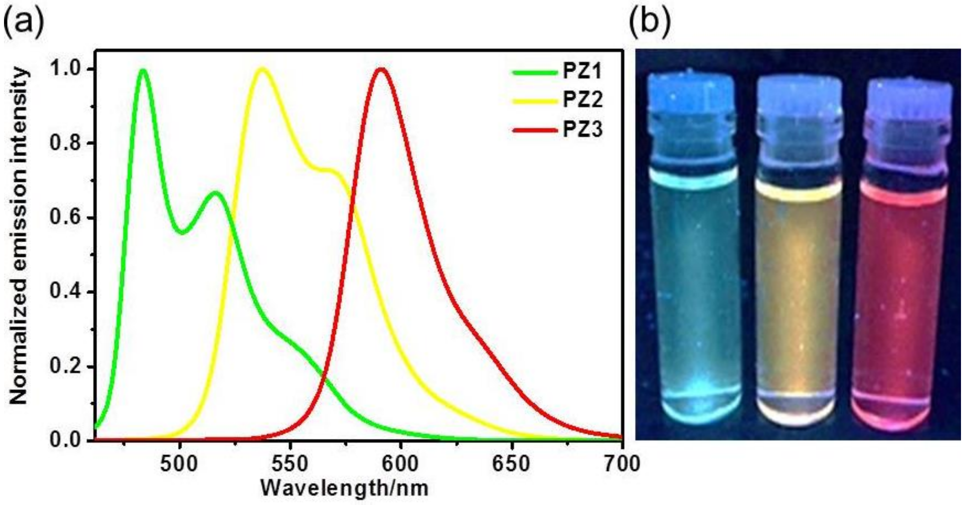

Fig.1 (a) Emission spectra of **PZ1-PZ3** (20 μM) in PBS (1% DMSO) solution; (b) Photograph of the emission.

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Intramolecular frustrated phosphine/borane Lewis pairs with a dimethylxanthene backbone: synthesis and applications

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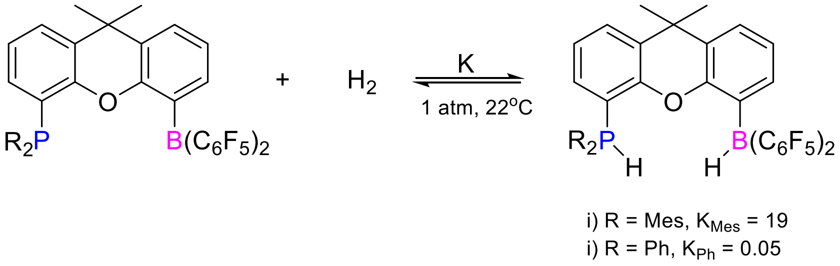
Frustrated Lewis pair (FLP) chemistry is of enormous current interest because it provides a versatile "metal free" way of carrying out bond activation, and ultimately, catalysis. The key design features of FLPs are strong Lewis acid and Lewis base components (usually a tertiary phosphine, PR_3, and a borane BR'_3) which can be separate molecular entities or be combined in one species, where the R and R' groups are too bulky to allow them to come together via coordinate bond formation ($R_3P \rightarrow BR_3$).[1]

While hundreds of FLP papers have been published since Stephen's landmark Science paper on 2006, none of these shows a system capable of existing in equilibrium with the corresponding dihydrogen activation product in solution at room temperature. By contrast, our recent work on rigid FLPs based on the dimethylxanthane backbone shows exactly this ability (See Scheme).[2] The position of equilibrium is dependent on the R group attached to the phosphorus with more of the activated H^+/ H^- system being present at equilibirium with the more strongly donating— $PMes_2$ (Mes = $C_6H_2Me_3$) group than with the PPh_2. This equilibrium is essential where it allows the FLP to capture small molecules, — such as H_2 and N_2O, catalyse catalytic B—N dehydrogenation of ammonia/amine borane and selective hydroboration of alkyne[3].



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The role of ligand symmetry in spin-labile mononuclear Mn(III) complexes

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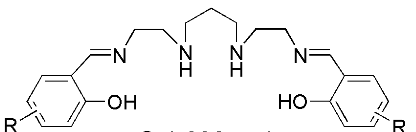
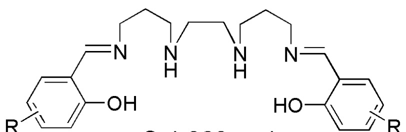
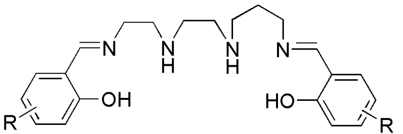
Mononuclear Mn(III) complexes are highly prized in catalysis,[1] particularly in water oxidation[2] and increasingly in molecular magnetism.[3] In our work we have concentrated on the ability of mononuclear Mn(III) complexes to exist in both high spin (HS) and low spin (LS) forms when co-ordinated by flexible hexadentate Schiff-base ligands of the Sal$_2$323 series,[4] and many of these also show spin crossover.[5,6]



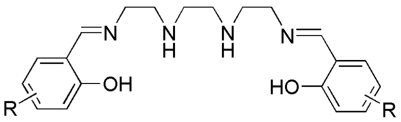
Sal$_2$232 series
7C backbone



Sal$_2$323 series
8C backbone



Sal$_2$223 series
7C backbone



Sal$_2$222 series
6C backbone

We are now interested in breaking the symmetry in the parent ligand and investigating the effect this has on the resulting Mn(III) complexes in terms of geometric constraint, orbital populations, magnetic properties and reactivity. We present here structural, magnetic and spectroscopic data on several Mn(III) complexes with 7 carbon backbone ligands which show a range of spin states and unusual reactivity.

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