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Scottish Dalton Meeting 2024 Draft Program

Time	Person	Talk Titles	Affiliation	Chair
10:00	Tea/coffee and Welcome			
10:30	Dr Erli Lu	New Horizons in Group-1 Metal Chemistry in Solution and Solid-state	Plenary (Newcastle)	Dr Cath Weetman
11:20	Dr Joy Farnaby	Synthetic routes to radical-bridged lanthanide heterobimetallic complexes	Glasgow	
11:45	Dr Stephanie Urwin	Tuneable Phosphaamidinate Ligands: Alkyl-Magnesium Complexes Responsive to Increased Ligand Bulk	Edinburgh	
12:10	Lunch & Posters			
1:10	Dr Gavin Craig	Synthesis and scrambling of porous metal-organic polyhedra	Strathclyde	Dr Nicola Bell
1:35	Dr Humphrey Yiu	Magnetic Nanoparticles for Enzyme immobilisation	Heriot-Watt	
2:00	Dr Amy Hall	Turning Crystals Blue: A Dose of Salts	Durham	
2:25	Tea Break & Posters			
3:10	Dr Venkataraman Thangadurai	Solid State Li and Na Batteries: Materials, Challanges, and Opportunities	Calgary (St Andrews)	Dr Ruairidh McIntosh
3.35	Dr Josh Makepeace	Chemical and electrochemical energy storage using lithium imide	Plenary (Birmingham) RSC Prize Winner	
4:25	Prize & Medal Presentations			
4:45	Close			

Poster	Abstract Title	Presenter	Institution
1	Using computer vision to quantitatively assess a range of structurally carbon monoxide surrogates	Kristin Donnachie	University of Strathclyde
2	A low cost and easily synthesized Bi-TiO ₂ solar photocatalyst and its journey from laboratory to field trials	Ayushi Arora	University of Edinburgh
3	Synthesis, characterisation, and energetic performance of a new copper compound based on 3,4,5-trinitro-1H-pyrazole	Ashfaq Afsar	University of Edinburgh
4	Phosphabora-[3]Dendralenes: Synthesis and Reactivity of Unsaturated P/B Compounds	Vesela Zarkina	University of Edinburgh
5	Reduction of NHC-Stabilised Aluminium(III) Complexes	Fáinché Murphy	University of Strathclyde
6	On 1,1-dithiolates	Odysseas Keramidas	University Of Glasgow
7	Exploration of the Energetic Landscape of Ga-Terephthalate Metal-Organic Frameworks	Matthew Liddle	University of Glasgow
8	Using experimental actinide chemistry to solve technical challenges in spent fuel and nuclear material management within the Nuclear Decommissioning Authority	Eilidh MacCormick	University of Glasgow
9	Unconventional ruthenium-phosphinine complexes in H-atom catalysis	Stephen Mansell	Heriot-Watt University
10	Rediscovering the unsubstituted tris(pyrazolyl)borate ligand on lanthanides: synthetic versatility, small-molecule activation, and catalysis	Tajrian Chowdhury	University of Glasgow
11	NacNac-Zn-pyridonate mediated ϵ -caprolactone ROP	Jack Hughes	University of Edinburgh

12	DFT Investigation Into The Mechanism of Transition Metal-Free Catalytic C–H Zincation and C–H Aluminatation	Justyna Losiewicz	University of Edinburgh
13	Investigating the Luminescent Properties of Radical Bridged Heterobimetallic Lanthanide Complexes	Anna Bailey	University of Glasgow
14	Rare earth fluorenyl-tethered NHC complexes for biopolymer synthesis	Joseph Walker	Heriot Watt University
15	Synthesis and Reactivity of Dilithium Arylimides	Richard Drummond Turnbull	University of Glasgow
16	Secondary-Selective Nucleophilic Substitution of Alcohols Enabled By Carbodiimides and Boranes	Dominic Willcox	University of Edinburgh
17	Isolable Rubidium and Caesium Derivatives of Common Organic Carbonyl Compounds	Jennifer Lynch	University of Strathclyde
18	Self-assembled supramolecular capsules for lanthanide and actinide Separations	Joseph O'Connell-Danes	University of Edinburgh
19	Rationalising Selective Gold Recovery through Solid State Computational Modelling	Susanna Vance	University of Edinburgh
20	Probing uranyl reduction chemistry with a tripodal pyrrole-imine ligand	Tom Obey	University of Edinburgh
21	The barocaloric and structural properties of choline-based plastic crystals	Joshua Levinsky	University of Edinburgh
22	Heavy Alkali Metal Diphenylphosphide Complexes for the Hydrophosphination of Alkenes	Michelle Crabbe	University of Strathclyde
23	Alkali metal hydride surrogates in transfer hydrogenation catalysis	Peter MacDonald	University of Strathclyde

Using Computer Vision to Quantitatively Assess a Range of Structurally Carbon Monoxide Surrogates

Kristin Donnachie, Marc Reid*

University of Strathclyde

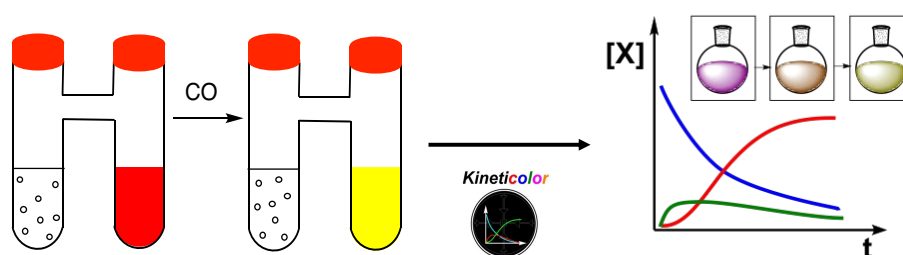
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Carbon Monoxide (CO) is critical for synthesising many compounds and is widely used in chemical industries. However, its known toxicity and flammability have reduced the use of CO cylinders in small-scale industry and academic labs. This challenge has led to the use of CO surrogates, molecules for safer and more controlled release of CO gas. A wide variety of CO surrogates have been identified, ranging from organic compounds to transition metal complexes. The current gap in literature is the quantitative analysis of the CO release rates each surrogate. Such comparison of CO surrogates is a challenge in large part due to the structural diversity and range of conditions employed for CO release

Herein, we report the use of computer vision-enabled kinetic analysis of CO surrogate capabilities via tracking of CO uptake in chemosensor technologies. To do this, we employ Kineticolor, a software developed by the Reid Group Research empowers chemists to analyse a video recording of a reaction bulk to obtain information about rates of colour change, shape, and mixing parameters.¹⁻⁴



The ability to rank each not only structurally diverse CO surrogates, but of which the release of CO is triggered in different ways, will allow for chemists to make an informed decision on which surrogate is best suited to their specific need or reaction. This could help in reducing time and materials needed to optimise a range of reaction conditions.

Key References

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A LOW COST AND EASILY SYNTHESISED Bi-TiO₂ SOLAR PHOTOCATALYST AND ITS JOURNEY FROM LABORATORY TO FIELD TRIALS

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One of the biggest global challenges is sustainable water treatment and solar photocatalysis has the potential to treat drinking water in a sustainable and cost-effective manner. In this study a low cost, easy to make semiconductor Bi-TiO₂ composite was synthesised via a reverse micelle sol-gel route and was tested for its ability to be activated under visible and near-UV light. A recycled glass substrate was used as the photocatalyst's support. The photocatalyst was characterised for its composition, morphology, optical properties and was coated on recycled-glass chips for testing. Degradation of 4-Chlorophenol and removal of *Escherichia coli* (*E. coli*) were tested in the laboratory using 410 nm wavelength light-emitting diode (LED). Subsequently, testing was conducted in rural India for photocatalytic reduction of microbial contaminants (total coliform and *E. coli*) in real world conditions. In the field, two water sources were selected in rural West Bengal in India. One was 'well water' used for drinking, with initial count of 4800 CFU/100 mL for total coliforms, and the other was 'pond water', used for washing and bathing, with initial count of 92000 CFU/100 mL for total coliforms and 3000 CFU/mL for *E. coli*. These water samples were filled into commercial PET bottles along with the catalyst coated chips and were exposed to sunlight. It was observed that the photocatalyst was able to reduce the total coliform count in water by up to 99% and *E. coli* by up to 99.9% in just 2 hrs. The developed catalyst has also shown excellent results in reusability tests where it was tested for 5 consecutive tests followed by 5 more tests post regeneration (by heating for 1 hr at 500°C). This study demonstrates the ability of solar photocatalysis to be used in real world drinking water treatment and will promote future advancements in this field.

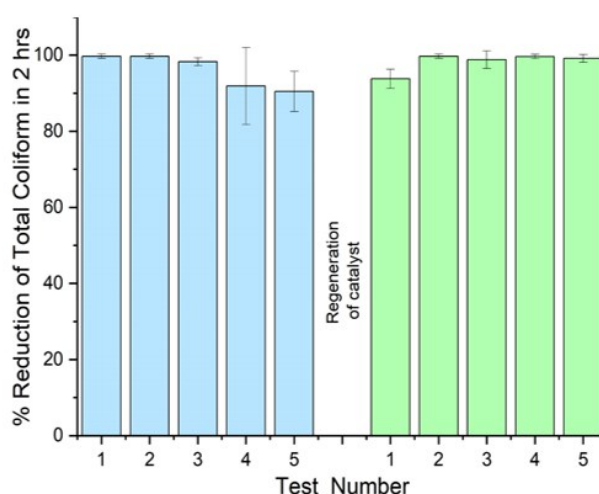


Image: Left: Test set up, Right: Plot showing reusability efficiency of developed catalyst with borewell water for reduction of total coliforms in 2 hrs. It was tested for 5 consecutive tests followed by 5 more tests after regeneration of catalyst.

Synthesis, characterisation, and energetic performance of a new copper compound based on 3,4,5-trinitro-1H-pyrazole

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Energetic materials (explosives, propellants, and pyrotechnics) play important roles in both military and civilian applications. Their sensitivities to initiation by impact, shock, friction, and spark are crucial not only for their performance, but also for safety in manufacture, processing, storage, transport, and operational use. Of increasing concern is the release of harmful compounds into the environment such as carbonaceous particulates (soot and smoke), chlorine-containing compounds (perchlorates and hydrogen chloride), and heavy metals such as lead. The design of both initiators and pyrotechnics that are more environmentally benign ("green") relies on the use of nitrogen- or oxygen-rich materials that act as efficient oxidizing agents to reduce formation of particulates, together with less toxic metals such as copper. Herein, we report the synthesis, characterisation and energetic performance of a new copper compound based on the trinitropyrazolate (TNP) ligand – ammonium copper (tetrakis) trinitropyrazolate $[\text{NH}_4]_2[\text{Cu}(\text{TNP})_4]$, which displays remarkable thermal stability, combined with a high energy output. It is therefore a promising candidate to replace particular lead-based initiators, as well as being of interest as a pyrotechnic. As part of a more comprehensive study of this material, we explored its behaviour under a range of physical conditions in order to be confident that it is sufficiently safe for wider use. This is particularly important as such materials may be subjected to a range of conditions (e.g. mechanical shock, impact, temperature) during manufacture, processing, long-term storage, and operation.

Keyword: initiators; pyrotechnics; 3,4,5-trinitro-1H-pyrazole; ammonium copper (tetrakis) trinitropyrazolate $[\text{NH}_4]_2[\text{Cu}(\text{TNP})_4]$

Phosphabora-[3]Dendralenes: Synthesis and Reactivity of Unsaturated P/B Compounds

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The incorporation of heteroatoms within π -conjugated systems and materials has proven to be an effective way of tuning their optical and electronic properties. The intrinsic electronic differences of heteroatoms compared to carbon allow the modulation of HOMO/LUMO and therefore band-gap levels.¹ Substituting C/C fragments with isosteric B/N ones has been widely explored in unsaturated oligomers, polymers and aromatic species.² Polycyclic B/N compounds have proven to be ideal precursors for precision-doped materials for optoelectronic applications.³ However, the same cannot be said about P/B containing systems due to the lack of transferable synthetic methods from B/N chemistry.⁴

[*n*]Dendralenes are acyclic, branched oligo-alkenes that serve as precursors to polycyclic systems due to their ability to undergo multiple diene-transmissive Diels-Alder reactions. During these transformations, a new diene is generated after every Diels-Alder reaction, allowing unparalleled structural complexity generation. Their potential has been widely explored in natural product synthesis, however no main group isosters of [*n*]dendralenes have been reported to this date.⁵

I will present the synthesis of phosphabora-[3]dendralene through ring opening of 1,2-phosphaboretetes.⁶ I will discuss the structures and electronic properties of phosphabora-[3]dendralenes, demonstrating how P/B incorporation alters them compared to the parent hydrocarbon system. Additionally, I will discuss the use of phosphabora-[3]dendralenes as a precursor to unsaturated polycyclic P/B doped systems.

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Reduction of NHC-Stabilised Aluminium(III) Complexes

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Recent years have seen the successful synthesis and isolation of novel main-group compounds, many of which being shown to adopt unusual electronic configurations and activate strong chemical bonds.¹⁻³ N-heterocyclic carbenes (NHCs) have been pivotal in the stabilisation of low-oxidation state main group species owing to their strong σ -donating and π -accepting nature.⁴ The key role of NHCs in the stabilisation of reactive species has been particularly exemplified in the isolation of group 13 complexes such as multiply bonded species with the first example of a boron-boron triple bond⁵ and a neutral aluminium-aluminium double bond being reported.⁶

Despite these advances NHC group 13 complexes, particularly those involving aluminium, are the least well studied to date. In this work we report synthetic strategies to access a variety of NHC stabilised mixed halides and hydrides⁷ and an examination of their reduction chemistry.

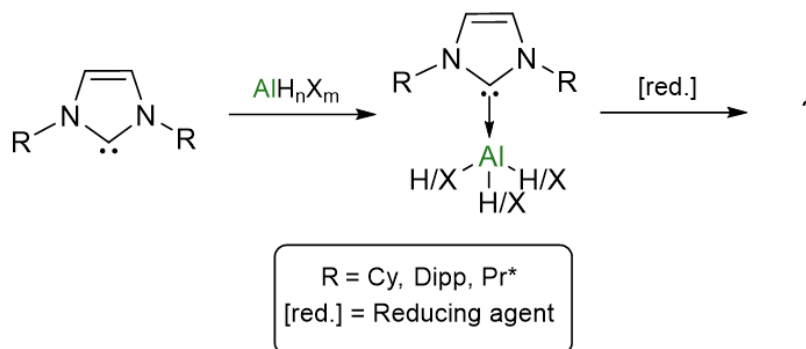


Figure 1. General route employed to produce NHC stabilised aluminium(III) hydride/halide complexes followed by reduction.

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On 1,1-dithiolates

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Keywords: 1,1-dithiolates, 1,2-dithiolates

Abstract Theme - Materials for diverse applications

From early research stages, the “innocent” nature of the 1,1-dithiolates as coordinating agents was observed.^[1] This ignited curiosity in the chemical community, as the isomeric 1,2-dithiolate ligands which were synthesized a few years earlier were proven to be “non-innocent”,^[2] (Figure 1). The little structural changes between the two isomer ligands have a dramatic effect on the electronic properties of the coordinated complexes. For instance, the 1,1-dithiolates were able to stabilize high formal oxidation states of various metallic centers, whereas the 1,2-dithiolates could not. Even though 1,1-dithiolates find plenty of uses in many fields of chemistry, only a few derivatives have been explored thoroughly.^[1,3-5]

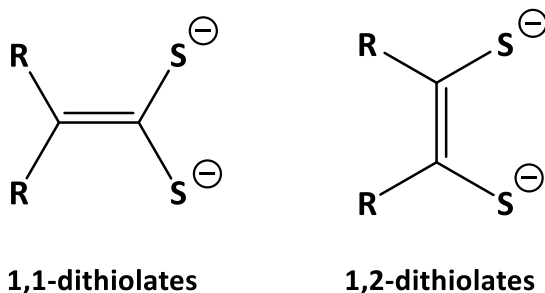


Figure 1. Chemical structure of 1,1-dithiolate and 1,2-dithiolate ligands

In this project some newly synthesized 1,1-dithiolate ligands have been synthesized, bearing electron-donating and electron-withdrawing groups on their backbone. Their properties as coordinating ligands were studied with their nickel and copper complexes. Routine spectroscopic experiments of these complexes confirmed a square planar geometry with the two 1,1-dithiolate ligands located on the xy plane.

The comparison of their electronic and bonding parameters in their metal complexes was conducted through CV, UV-vis, and EPR spectroscopy. The spectroscopic data were correlated with the Hammett parameters for each complex, and ultimately it was proven that the electronic properties of a bis homoleptic 1,1-dithiolate complex can be manipulated by changing the chemical groups of the backbone, of the 1,1-dithiolate ligand.

References

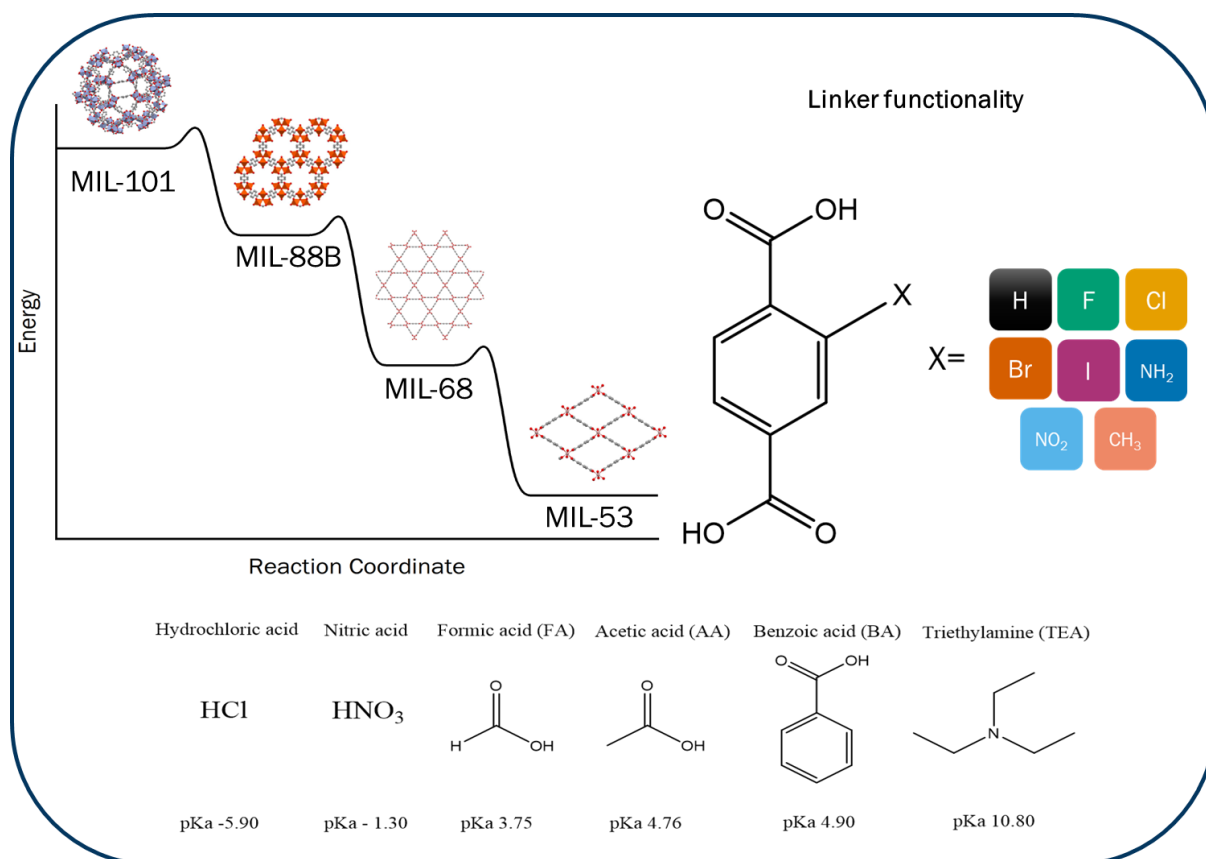
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Exploration of the Energetic Landscape of Ga-Terephthalate Metal-Organic Frameworks

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University of Glasgow

Extensive research into trivalent terephthalate based MOFs has led to the discovery of a wide range of highly stable structural isomers, of which their properties have been studied in depth. Despite this, the energetic landscape of the terephthalate MOF system has remained largely unexplored resulting in a poor understanding of the self-assembly process of this crystal array, which is especially true for the p-block metal MOFs. Herein, through the use of pH and co-ordination modulation, a greater understanding of the terephthalate energetic landscape has been developed. Using the significantly understudied p-block metal, Gallium, in combination with a range of functionalised terephthalate linkers, we have successfully isolated, fully characterised and fine-tuned reliable synthesis routes to create a library of 12 novel Gallium terephthalate MOFs, allowing us to shed light on the energetic relationship between the structural isomers.



Using experimental actinide chemistry to solve technical challenges in spent fuel and nuclear material management within the Nuclear Decommissioning Authority

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During the reprocessing of nuclear fuel, uranium and plutonium are separated from waste fission products.¹ Special nuclear material is stored in the form of PuO₂ and MOX (95% U, 5% Pu) powders in sealed packages. The interim storage of these actinide oxides (AnO₂) presents technical challenges. These include adventitious reactions of AnO₂ with atmospheric and other gases, for example radiolysis of water generates H₂.² The chemical composition and the properties of the AnO₂ have also been observed to change during storage. In this work, reactivity studies of MOX surrogates with reactive gas mixtures, aims to establish structure-property relationships to better understand the chemistry happening during interim storage. This data will contribute to the retreatment and future storage and disposition options for the UK's special nuclear material. This poster will discuss the building and testing of a catalytic microreactor, *Figure 1*, which is used to perform reactivity studies. Reactivity studies of UO₂ nanoparticles with H₂, water and other atmospheric gases will give insight into the absorbed species and the surface chemistry.³ The microreactor has been used for the decomposition of U(VI) complexes and U₃O₈ to UO₂, Raman and PXRD will be used to characterise these complexes and decomposition products.⁴ Future advanced characterisation techniques such as X-ray absorption spectroscopy (XAS) will be used. Sample preparation for XAS studies is important as the type of sample used influences how much the X-rays can pass through the sample. These studies will give insight into the U oxidation state and coordination geometry pre and post reaction with atmospheric gases.

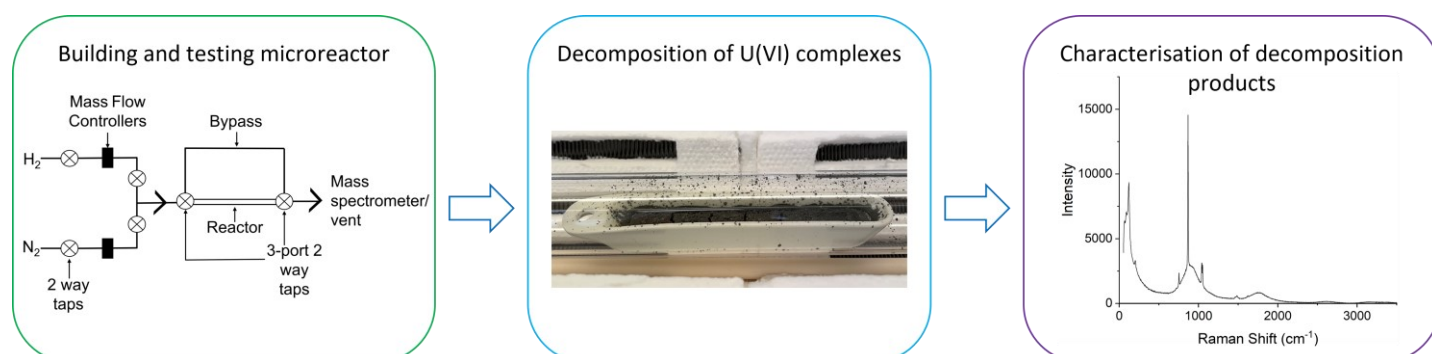


Figure 1: Workflow procedure from building and testing microreactor, the decomposition of U(VI) complexes, and characterisation of decomposition products

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Unconventional Ruthenium-Phosphinine Complexes in H-atom Catalysis

Peter A. Cleaves, Robert J. Newland, Elizabeth C. Trodden and Stephen M. Mansell

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H-atom catalysis involves moving hydrogen atoms between molecules and often utilises ruthenium-based catalysts. Examples of H-atom processes include:

1. Transfer hydrogenation, which holds great potential in chemical synthesis because it replaces hazardous reducing agents, such as hydrogen gas or metal hydrides, with more convenient chemical sources of hydrogen.¹ 2. Hydrogen-borrowing processes, which involve the oxidation of a saturated substrate by transfer of an equivalent of dihydrogen to a metal centre, thereby facilitating new reactivity, before the borrowed hydrogen is then returned.² 3. Acceptorless dehydrogenation, where two H atoms are lost as hydrogen gas.³ We have developed unconventional catalysts for these processes based on phosphinine ligands,^{3,4} the phosphorus analogue of pyridine,⁵ and describe the first transition-metal-hydride/phosphinine complexes (Fig. 1) which are important species in H-atom catalysis.^{3,6}

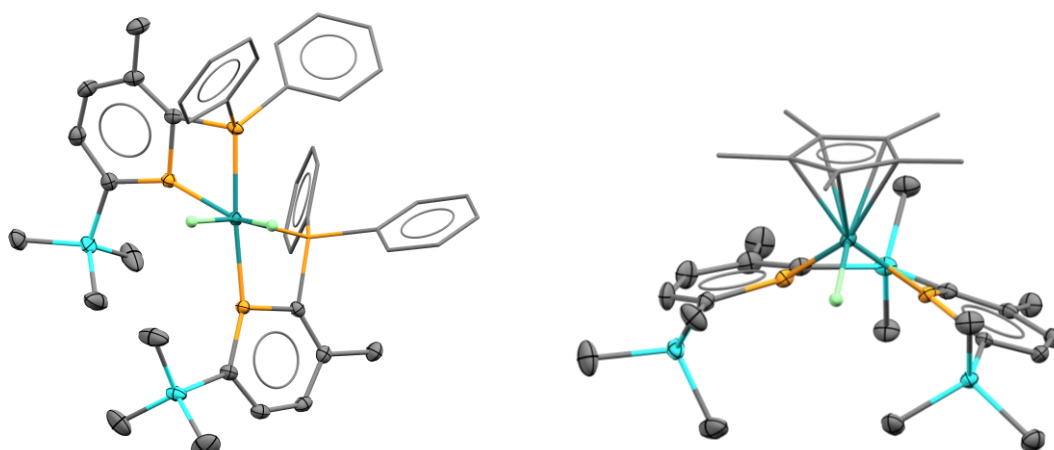


Fig. 1. Ruthenium hydride complexes featuring phosphinine ligands.

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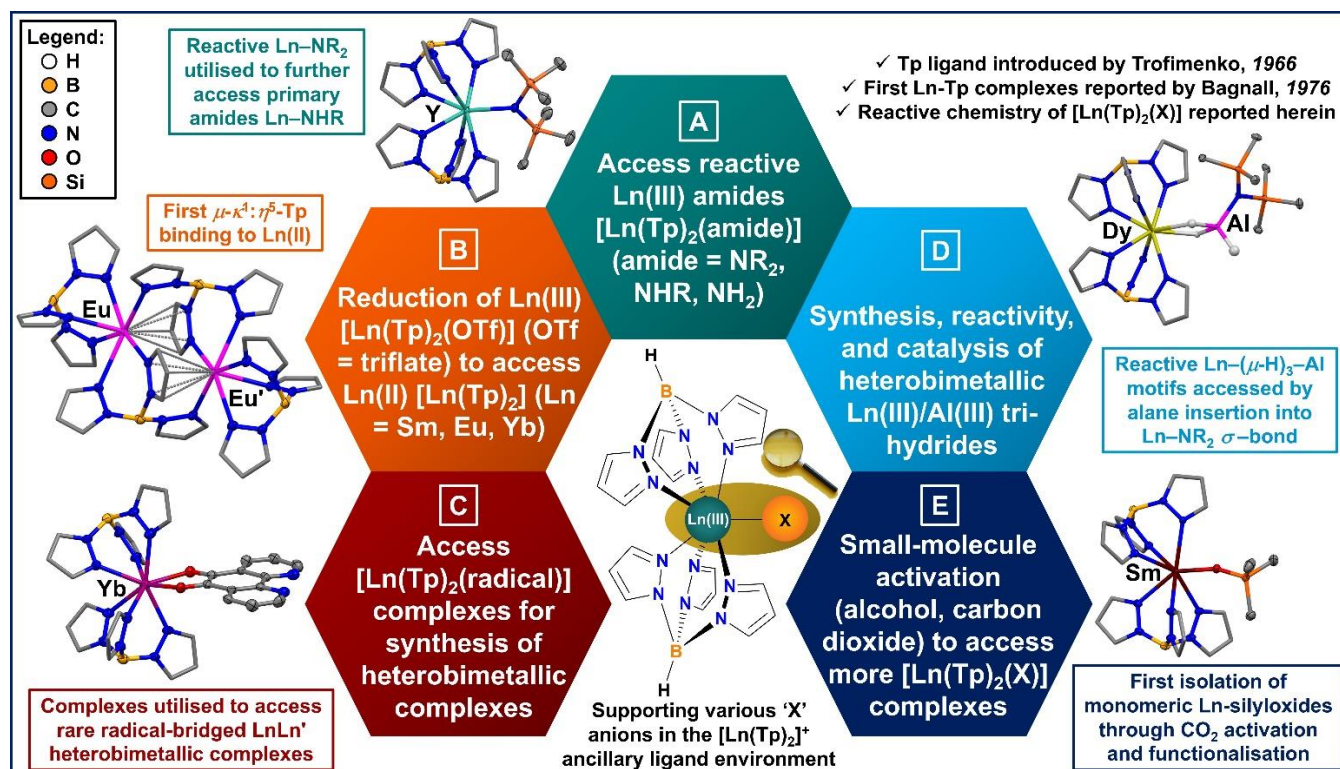
Rediscovering the unsubstituted tris(pyrazolyl)borate ligand on lanthanides: synthetic versatility, small-molecule activation, and catalysis

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Lanthanide (Ln) complexes have remarkable physical (optical,^{1a} magnetic)^{1b} and chemical (catalysis,^{1c} small-molecule activation)^{1d} properties. Heteroleptic Ln(III) [Ln(Tp^R)₂(X)] complexes (Tp^R = tris(pyrazolyl)borate derivatives, X = monoanion)² are promising reactive synthetic targets, albeit challenging to synthesise for X = bulky amides or aryloxides.³ This synthetic challenge can be addressed by utilising the small unsubstituted hydrotris(1-pyrazolyl)borate (Tp) ligand to access reactive [Ln(Tp)₂(X)] complexes.⁴ This poster communicates our work in the synthesis of [Ln(Tp)₂(X)] complexes and the Ln(II) [Ln(Tp)₂] complexes, which were previously known to be unstable in solution.³ Synthesis of the Ln(III) precursors [Ln(Tp)₂(OTf)] (OTf = triflate) allowed convenient entry into the non-aqueous chemistry of [Ln(Tp)₂(X)].^{4a,c,d} Various avenues of research in the non-aqueous chemistry of [Ln(Tp)₂(X)] was unleashed as a consequence (see Figure below) such as: (A) synthesis of Ln(III) amides [Ln(Tp)₂(amide)];^{4a,c,d} (B) reduction chemistry to access Ln(II) [Ln(Tp)₂] (Ln = Sm, Eu, Yb) complexes;^{4b,e} (C) synthesis of radical-bound Ln(III) synthons for the synthesis of rare radical-bridged LnLn' heterobimetallic complexes;^{4f} (D) synthesis of reactive and catalytic Ln(III)/Al(III) heterobimetallic trihydride complexes;^{4d} (E) small-molecule, such as CO₂ activation, by [Ln(Tp)₂(amides)].^{4a,e}



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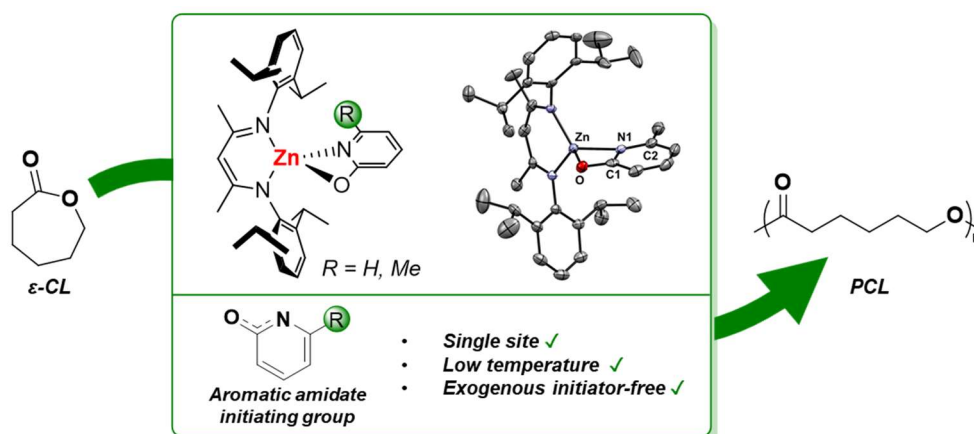
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NacNac-Zn-pyridonate mediated ϵ -caprolactone ROP

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Zinc complexes, including those of β -diketiminate (NacNac) ligands, have been extensively studied as catalysts in the synthesis of bio-based and degradable polymer materials.^{1–3} Carboxylate derivatives have shown poor activity for lactone ring-opening polymerisation (ROP) in the absence of an exogenous initiator, exhibiting poor control over polymerisation especially when compared to their alkoxide counter-parts.⁴ Subsequent mechanistic studies have revealed the importance of the solution-state aggregation of these complexes in both ROP and ring-opening copolymerisation to synthesise bio-based polymer materials.⁵ Here, we report two new NacNac-zinc complexes bearing an amidate (2-pyridonate (**1**, R = H) or 6-methyl-2-pyridonate (**2**, R = Me)) co-ligand, which were tested for the ROP of ϵ -caprolactone (ϵ -CL) to form polycaprolactone (PCL) at room temperature. To the best of our knowledge this is the first reported instance of a pyridonate-initiated ROP, and the first example of amidate initiated ROP.



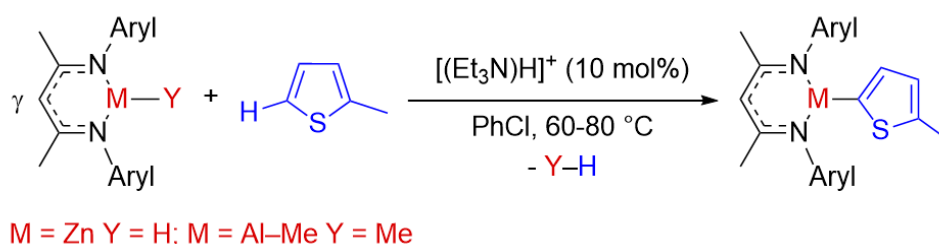
DFT calculations and ^1H DOSY NMR studies suggest that while different solid-state structures are observed for **1** and **2**, ROP likely proceeds via a single-site monometallic mechanism in solution. High molecular weight PCL was synthesised in the absence of a co-initiator, with moderate to low dispersities. Major signals in the MALDI-ToF spectra were assigned to cyclic PCL species, which are proposed to form through intramolecular transesterification reactions facilitated by loss of the pyridonate unit. Pyridonate end-groups were also observed using both complexes, which contrasts with previous reports for analogous carboxylate complexes and suggests that the pyridonate units are more efficient initiators. A small increase in the pyridonate steric bulk (**Me** vs **H**) resulted in improved catalytic activity, facilitating complete conversion of 100 equiv. monomer within 1 h at 60 °C.

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DFT Investigation Into The Mechanism of Transition Metal-Free Catalytic C–H Zincation and C–H Alumination

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Direct C–H functionalisation offers an atom-economic route to install a variety of synthetically useful functional groups, which can be transformed to increase molecular complexity. While protocols for catalytic (hetero)arene C–H borylation have been extensively developed,¹ catalytic C–H zincation and alumination remain far less explored. Zinc- and aluminium-based organometallics exhibit higher nucleophilicity than organo-boranes/-silanes, hence they are also highly desirable synthetic intermediates. Current synthetic methodologies, however, require the use of stoichiometric amounts of complex Brønsted super-bases^{2,3} or precious metal catalysts.^{4,5}



Here, novel catalytic (in ammonium cation $[(\text{Et}_3\text{N})\text{H}]^+$) C–H zincation and C–H aluminations are investigated computationally, with 2-methylthiophene used as a model substrate. DFT calculations showed that coupling of the endergonic C–H metalation step with a sufficiently exergonic dehydrocoupling step between the acidic ammonium salt and a Zn–H or Al–Me containing reagent is key to the experimentally observed reactivity. Furthermore, we identified two divergent dehydrocoupling mechanisms dependent on the metal valency and steric encumbrance around the metal centre. An unexpected mechanism involving protonation of the C_γ-position on the NacNac (NacNac = $\{(\text{Ar})\text{N}(\text{CH}_3)\text{C}\}_2\text{CH}$) ligand backbone emerged for the zinc system and is supported by experimental results such as deuterium incorporation into the C_γ-position.

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Investigating the Luminescent Properties of Radical Bridged Heterobimetallic Lanthanide Complexes.

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Abstract:

Lanthanide (Ln) complexes have unique and characteristic light emission with narrow spectral widths and long excited state lifetimes, which gives them a range of important applications.¹ Heterobimetallic Ln complexes allow us to use the light emitting properties of two or more Ln metal centres giving wavelength tunability with potential applications in biological imaging,² molecular upconversion³ and Ln-to-Ln energy transfer.⁴ This research presents the photoluminescent (PL) properties of two novel radical bridged heterobimetallic complexes $[(Tp)_2Ln(O,O'-N,N'-pd)Ln'(hfac)_3]$ (**3-LnLn'** = **3-YbEu** or **3-DyYb**) (Figure 1 (a)).^{5,6}

UV/Vis and PL spectra of these complexes (Figure 1 (b)) have demonstrated that Ln emission of these complexes is excitation wavelength dependent due to the metal centres being in different ligand environments. These spectra have also revealed potential energy transfer pathways (Figure 1 (c)) occurring within the molecule that lead to light emission. The group is currently investigating the possible light emitting applications of these novel complexes.

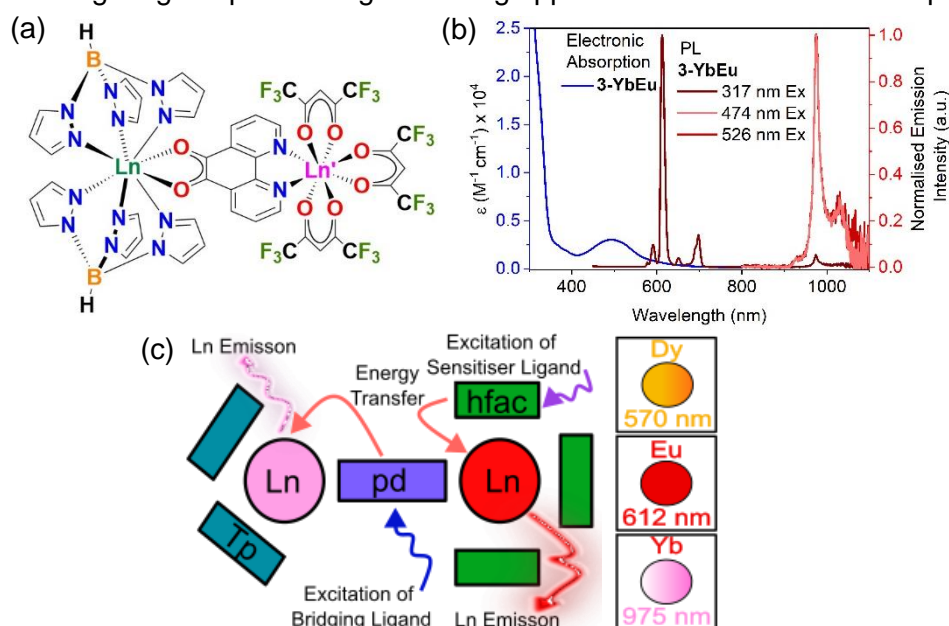


Figure 1: (a) Structure of the radical bridged heterobimetallic Ln complex $[(Tp)_2Ln(O,O'-N,N'-pd)Ln'(hfac)_3]$ (b) absorbance and PL spectra of **3-YbEu** and (c) graphic of potential energy transfer pathways occurring in heterobimetallic Ln complexes

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Rare earth fluorenyl-tethered NHC complexes for biopolymer synthesis

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Industrial synthesis of the bio-derivable/degradable polymer polylactic acid *via* ring-opening polymerisation (ROP) requires use of inorganic initiators. Currently, $\text{Sn}(\text{Oct})_2$ is widely used but has poor control over polymer properties e.g. tacticity and polydispersity. Elevated reaction temperature of ca. $\geq 140^\circ\text{C}$ and limited natural reserves of tin are also evident sustainability concerns.¹ To alleviate these issues, development of new catalysts featuring various metals for ring-opening polymerisation has been intensely researched.^{2,3} Interest in rare earth complexes for ROP has risen as the base metals are relatively abundant in the crust; they are also oxophilic, exhibit high Lewis acidity and consequently display extremely high reaction rates in ROP of cyclic esters.³

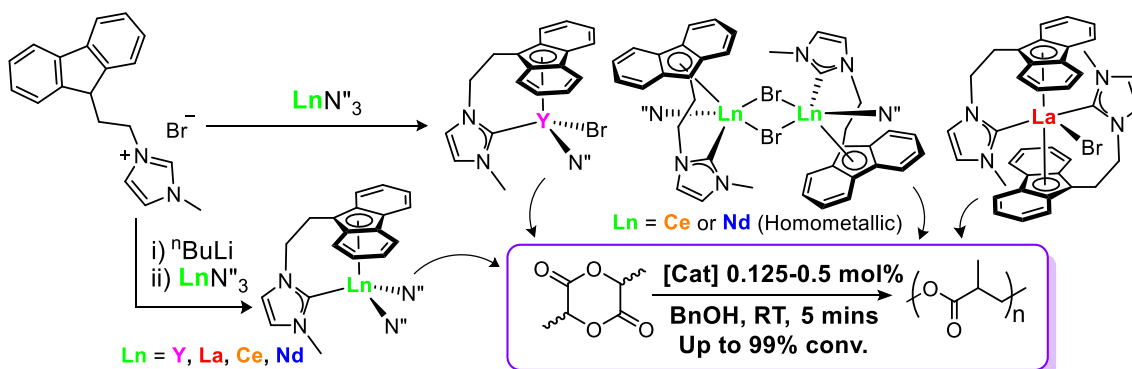


Figure 1. Synthetic pathway and catalytic conditions

We are interested in fluorenyl-tethered ligands which allow for the synthesis of heteroleptic lanthanide complexes - which is otherwise difficult due to redistribution effects. The use of a strongly electron donating NHC moiety, low steric hindrance of its methyl sidearm and the potential for ring slippage *via* fluorenyl should produce highly active catalysts. Subsequently, synthesis of a range of Y, La, Ce and Nd complexes has been achieved. All displaying high activity in ROP of lactide at room temperature, with full conversion observed in some cases in ≤ 5 minutes.⁵

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Synthesis and Reactivity of Dilithium Arylimides

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Whereas amides (MNR_2) are commonly and straightforwardly prepared derivatives of the s-block elements, their dimetalated imide analogues (M_2NR) remain an exceedingly rare motif in the published literature,¹ despite being common motifs in other parts of the periodic table. That a wide array of these useful synthons have not been forthcoming is unsurprising: accessing strongly basic s-block imides generally require stabilizing electron withdrawing groups and bespoke synthetic conditions to mitigate their aggressive reactivity.²

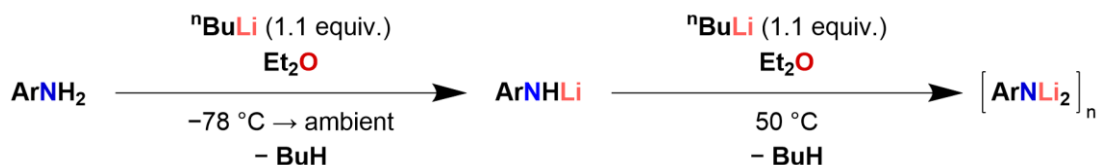


Figure 1: Generalised synthetic routes to dilithiated arylamines

We present a general route to a set of dilithiated arylimides with a range of electronic properties, including electron donating groups, which may be prepared from commercially-available organolithium reagents. Our work, supported by novel, automated approaches to traditional inorganic synthesis, also provides insights into how to stabilize these highly sensitive species.

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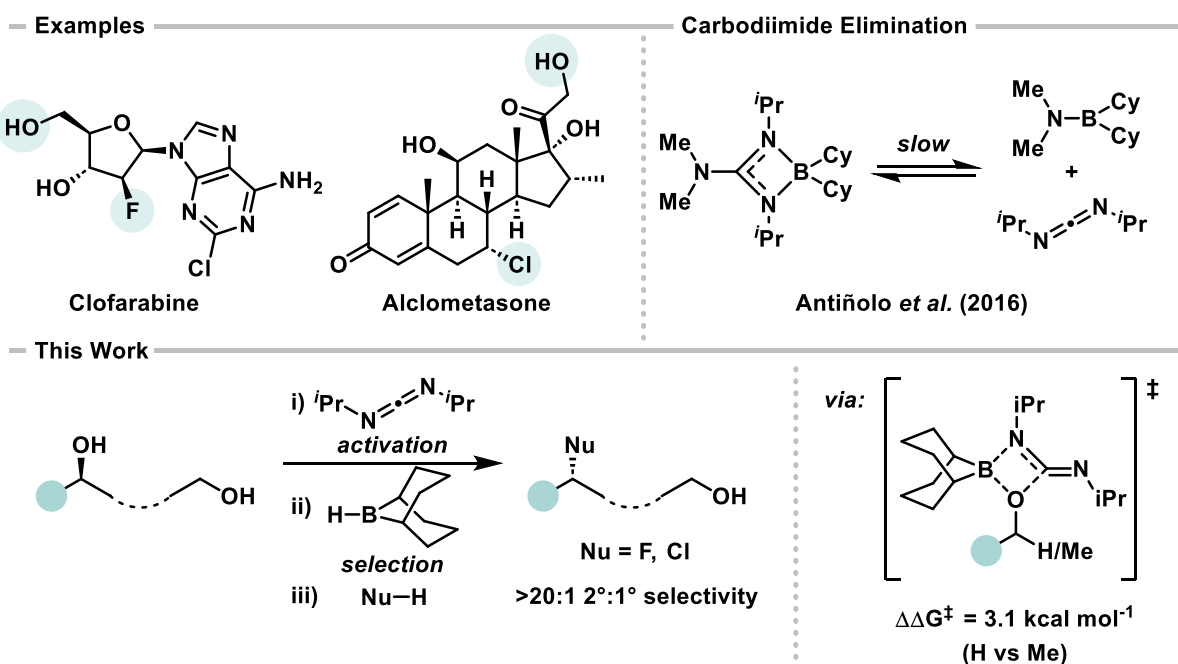
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Secondary-Selective Nucleophilic Substitution of Alcohols Enabled By Carbodiimides and Boranes

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Nucleophilic substitution is a fundamental reaction in all of synthetic chemistry, yet approaches to improving selectivity can involve complex protecting group strategies.¹ Alcohols are an abundant and inexpensive chemical feedstock, and can be activated towards nucleophilic substitution in a variety of ways. The utility of direct substitution from an alcohol is seen in a multitude of approaches, such as the Mitsunobu, Appel, and deoxyfluorination reactions, yet selectivity between primary and secondary alcohols can be difficult to control in these systems.² Dialkylboryl guanidines were reported to undergo slow elimination of carbodiimides, but reactivity for analogous iso-ureas is yet to be explored.³ Here is reported the general and selective nucleophilic substitution of secondary alcohols enabled by a novel method of activation using carbodiimides and the organoborane 9-borabicyclo(3.3.1)nonane (H-9-B-BBN). This system presents unprecedented selectivity for the reaction between *in situ* formed iso-ureas and H-9-B-BBN, and has been rationalised by steric repulsion in a 4-membered transition state, as investigated by density functional theory and reaction monitoring.



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Isolable Rubidium and Caesium Derivatives of Common Organic Carbonyl Compounds

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Light alkali metal (Li, Na, K) amides have a long history of synthetic utility, but heavier (Rb, Cs) congeners have barely been studied.¹ This study reveals remarkable structurally complex outcomes of reacting AM(HMDS) (AM = Rb, Cs; HMDS = hexamethyldisilazide) with benzaldehyde and acetophenone. Though complicated, reactions give a diversity of eye-catching isolated products, an enolate with a hexagonal prismatic network, two dienolates with distinct extended ladder motifs,² and two β -imino-alkoxides comprising zig-zag chains of metal–oxygen bonds in infinite cages.³

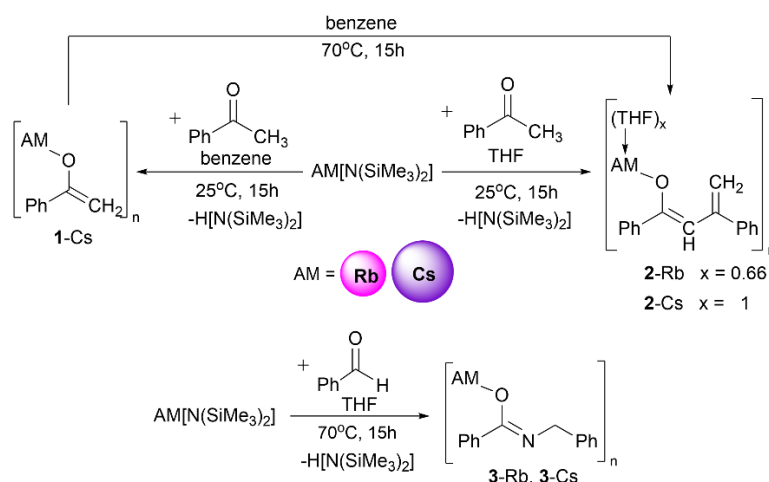


Figure 1 Reactions of RbHMDS and CsHMDS with acetophenone and benzaldehyde in this work.

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Self-assembled Supramolecular Capsules for Lanthanide and Actinide Separations

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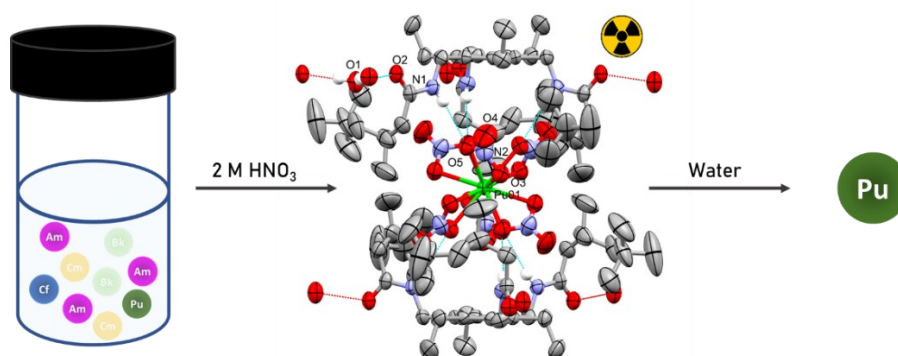
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Keywords: molecular capsules, sustainability, separations

The development of improved separations for the f-elements is a critically important challenge for a range of societally important technologies. The lanthanides are crucial for renewable energy generation and storage, electric vehicles, and electronic displays. However, access to these metals, in large part due to difficulties in their separation, is limited.¹ Improving actinide separations is key to reducing barriers to medical and industrial actinide isotope production and to address the challenges associated with the reprocessing of spent nuclear fuel. Supramolecular separation methods that target anionic metal compounds are some of the most selective found for transition metals. The exploitation of highly controllable non-covalent interactions to form supramolecular assemblies provides unparalleled specificity for anion-recognition. Despite these advantages, few examples of supramolecular anion separations for f-elements exist and there are no examples for the actinide elements.² This presentation focuses on the development of a new method for f-element separations using a pre-organised triamidoarene platform which uniquely encapsulates and selectively precipitates f-elements as their hexanitratometalates. The capsules exhibit both intra and intermolecular hydrogen bonds that promote precipitation and dictate selectivity. This discovery provides a new self-assembly route to metal separations that exploit shape complementarity, resulting in separation factors that exceed state-of-the-art existing extractants and achieve unprecedented light/heavy RE separation.³ Finally, we demonstrate the application of this system to the selective precipitation of the actinides (Th-Cf) and present the first trans-uranium crystal structures of actinide hydrogen-bonded assemblies, highlighting the structural changes in the capsule between Pu(IV) and Am(III).⁴



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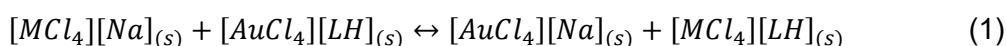
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Rationalising Selective Gold Recovery through Solid State Computational Modelling

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Waste electronics and electrical equipment (e-waste) has become the fastest growing hazardous solid waste stream in the world, with approximately only one fifth being recycled.¹ Achieving its sustainable management is therefore crucial to moving towards a circular economy, and given the high content of base and precious metals in e-waste (often exceeding those in natural mineral ores), recycling is of great economic benefit.² Many thermo- and bio-chemical processes designed to recover metals from their ores have been adapted for metal recovery from e-waste, with hydro-, bio- and pyro-metallurgical processes the most common.³ Recyclable precipitation processes have become increasingly popular as they provide significant advantages over solvent extraction and single-use precipitation methods.⁴ We have employed a simple tertiary diamide in the targeted precipitation of gold and other metals from acidic leach solutions from a variety of sources,⁵ with excellent selectivity for gold easily achieved through tuning experimental conditions (see Figure 1). However, the factors that dictate the selectivity for gold over other metals still remain elusive. Therefore we have undertaken an extensive computational study to investigate if thermodynamics play a significant role in selectivity. To achieve this, a bespoke computational approach was developed, which facilitated the calculation of exchange energies for species in the solid state (Equation 1).



In addition, ligand strain was also quantified using this method and key intermolecular interactions were studied using Hirshfeld surfaces, quantum theory of atoms in molecules (QTAIM) and non-covalent interaction (NCI) plots, which rationalised the thermodynamic results.

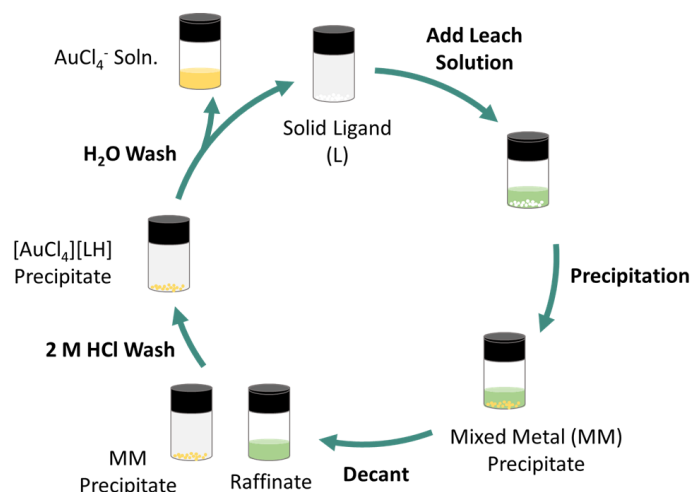


Figure 1 – Overall schematic of precipitation process

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Probing Uranyl Reduction Chemistry with a Tripodal Pyrrole-Imine Ligand

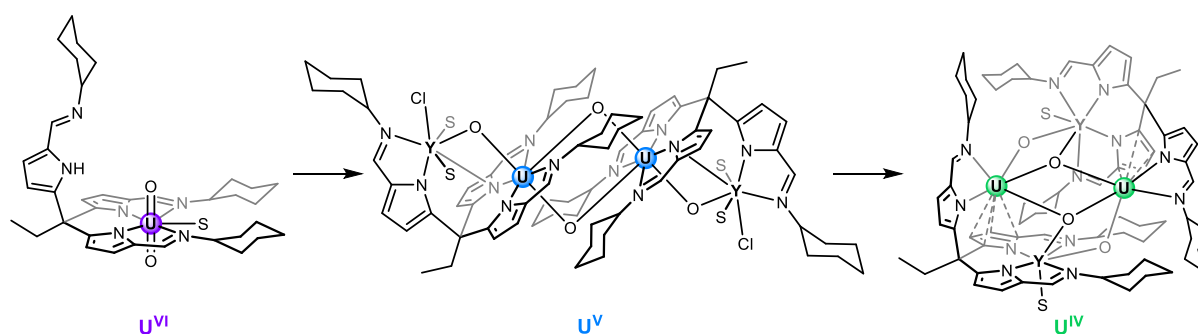
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As the least radioactive and most readily available actinyl ion ($[\text{AnO}_2]^{n+}$) the uranyl dication $[\text{UO}_2]^{2+}$ is by far the most studied. It is the most thermodynamically stable form of uranium found in the environment and is a soluble and problematic environmental contaminant from nuclear waste. It exhibits U-O bonds that are particularly strong making the uranyl oxo groups chemically inert and difficult to functionalise.

The single-electron reduction of $[\text{U}^{\text{VI}}\text{O}_2]^{2+}$ to the monocation $[\text{U}^{\text{V}}\text{O}_2]^+$ is achieved by microbes under anaerobic conditions, but is unstable in aqueous conditions and disproportionates to U(VI) and U(IV) species.^{1, 2} This disproportionation process is thought to proceed through interaction of the oxo groups on adjacent uranyls, with this cation-cation interaction (CCI) allowing electron transfer between the metals. These CCIs are also seen in heavier actinyls, that are components of nuclear waste, and have the potential to disrupt separation processes such as PUREX.³

Here we present a flexible tripodal pyrrole-imine ligand that facilitates the controlled and sequential single-electron reduction of the uranyl dication from the U(VI) oxidation state to U(V), and further to U(IV). This ligand architecture allows us to probe both metathesis reactions of the U(V) CCI complex to form new hetero-tetrametallic uranyl(V) complexes that are stable to disproportionation, and also the mechanism of uranyl reduction, a process that is important in understanding its environmental remediation.



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The barocaloric and structural properties of choline-based plastic crystals

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The currently ubiquitous vapor-compression method of refrigeration has a significant downside, namely its reliance on volatile refrigerants with large global warming potentials. In order to overcome this challenge, alternative solid-state refrigerants which exhibit similarly large entropy and temperature changes by the application of external stimuli have to be identified. A promising approach to this problem is found in the utilization of the hydrostatic pressure-induced entropy and temperature change, the so-called barocaloric effect, which accompanies structural phase transitions. This approach avoids the need for volatile refrigerants with large global warming potentials and promises a higher thermodynamic efficiency [1].

Thus far only the class of molecular plastic crystals, compounds which exhibit solid phases characterized by large degrees of orientational disorder and plastic-like mechanical properties, have been shown to exhibit colossal barocaloric effects on par with commercial hydrofluorocarbon refrigerants [2]. The exceptionally large barocaloric response found in plastic crystals originates from structural phase transitions from an ordered state to an orientationally disordered state, characterised by a large isothermal entropy change, ΔS , and large barocaloric coefficient, dT/dP . Plastic phases can also be obtained in ionic systems built from weakly interacting highly symmetric globular ions.

In this work, we study the effect of halide substitution on the structural phase transitions and barocaloric properties of choline-based ionic plastic crystals, specifically $[\text{choline}]_2\text{CoX}_4$ and $[\text{choline}]_2\text{ZnX}_4$, where $X = \text{Cl}, \text{Br}$ and I . By employing pressure- and temperature-dependent single crystal/powder diffraction and differential scanning calorimetry experiments in addition to *ab initio* molecular dynamics (MD) simulations, this structure-property relationship is studied in detail. The MD simulations reveal the important role hydrogen bonding competition plays in the observed crystallographic disorder and the observed large barocaloric response. Demonstrating the ability to tune the transition temperature over a 50 K range and ΔS (107 and 80 J kg⁻¹ K⁻¹ K for $[\text{choline}]_2\text{ZnCl}_4$ and $[\text{choline}]_2\text{ZnI}_4$ respectively) via chemical exchange, the results of this work can be used to inform the design of future solid-state refrigerants.

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Heavy Alkali Metal Diphenylphosphide Complexes for the Hydrophosphination of Alkenes

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Abstract:

Catalytic hydrophosphination is of significance when synthesising phosphorus-containing compounds.¹ With sustainability a driving force, the desirability for catalysts to switch from transition metals to the more-abundant and less toxic main group elements is increasing.² Due to its escalating use in energy technology attention is also turning from lithium to the heavier alkali metals. Previous work in our group showed sodium diphenylphosphide donor complexes as more efficient hydrophosphination catalysts under ambient conditions than the lithium congener.³ As catalytic activity has increased whilst descending the group in other applications,⁴ we sought to investigate this further in our system with the heavier alkali metals rubidium and caesium.

Here we showcase a series of rubidium and caesium diphenylphosphide complexes coordinated by the Lewis base 18-crown-6. Several different compounds have been isolated from the same complex mixture, where the number of molar equivalents of 18-crown-6 chelating the metal cations has changed. With these, a preliminary investigation into the hydrophosphination of alkenes using HPPH_2 has been undertaken, yielding promising results.

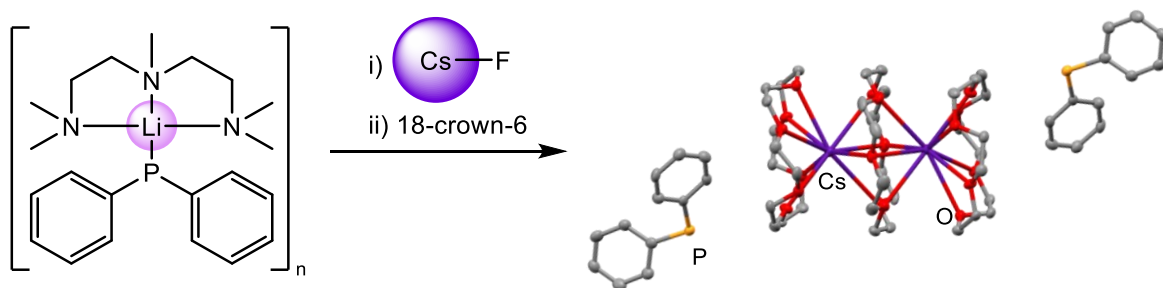


Figure 1 Synthesis of the caesium diphenylphosphide complex $[\text{Cs}_2(18\text{-crown-6})_3(\text{PPh}_2)_2]$.

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ALKALI METAL HYDRIDE SURROGATES IN TRANSFER HYDROGENATION CATALYSIS

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Molecular main group metal hydrides can be regarded as flag bearers of a drive towards sustainability that aims to increase the use of earth abundant metals in important stoichiometric and catalytic transformations to ease demand for precious transition metals which dominate this chemistry.¹ Since poor solubility and over reactivity limits the use of alkali metal hydrides in this quest, our group have synthesised lithium, sodium and potassium compounds of 2-*tert*-butyl-dihydropyridine (*t*BuDHP).² Though devoid of hydride ions, these surrogate hydrides have C-H bonds in the pyridine ring that can release hydride ions in both stoichiometric and catalytic applications.³

Encouraged by these initial results, and the fact that reactivity can increase on descending group 1, we sought to prepare the heavier alkali metal congeners [Rb(*t*BuDHP)] and [Cs(*t*BuDHP)] and compare the full AM-*t*BuDHP series in transfer hydrogenation catalysis of imines using 1,4-cyclohexadiene as the hydrogen source. Since bimetallic cooperativity is well established in alkali metal chemistry we also prepared co-complexes of AM-*t*BuDHP with organoaluminium compounds. Experimental results have been supported by DFT calculations.

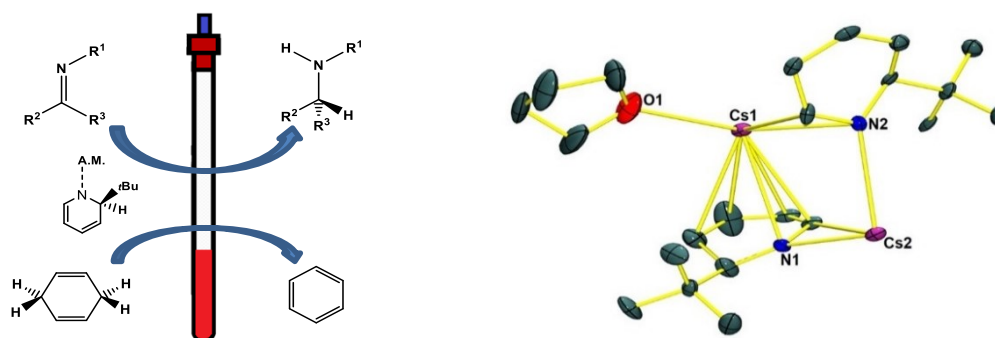


Figure 1. Imine transfer hydrogenation with Cs(*t*BuDHP) structure shown to the right.

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