



**IDW**

53<sup>rd</sup> Inorganic  
Discussion  
Weekend  
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# Book of Abstracts

53rd Annual Inorganic Discussion Weekend

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## Post-Synthetic Modification of 4-(2'-benzimidazolyl)-1,2,3,5-dithiadiazolyl in the Pursuit of Molecule-Based Materials

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In recent decades, research in the design of molecule-based materials with technologically relevant properties has gained much attention. Molecule-based materials provide the opportunity for the incorporation of attractive functionalities such as solubility, volatility, and conductivity via careful selection of structural features. In the pursuit of such materials, our group specializes in the design of 1,2,3,5-dithiadiazolyl (DTDA) radicals for use as paramagnetic ligands. Coordination of DTDA radical ligands to metal ions can result in strong exchange coupling between metal- and ligand-based moments, increasing the net magnetic moment and providing a pathway for coupling between coordination centers. DTDA radicals are known to demonstrate desirable properties such as magnetic bistability, [1] and magnetic ordering. [2] Tunability of materials properties can be achieved by careful incorporation of various functional groups. Our most recent advances have included the post-synthetic modification to one of our DTDA radical ligands, 4-(2'-benzimidazolyl)-1,2,3,5-dithiadiazolyl (HbimDTDA).

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## Nickel-Catalyzed Arylation of Cyclic Alkyl Sulfones: Access to Functionalized Chiral Sulfones and Sulfonamides

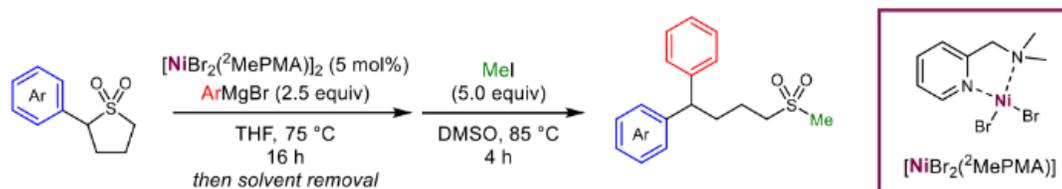
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In recent years our group has demonstrated the versatility of sulfones as both directing groups and electrophiles in metal-catalyzed cross-coupling reactions.<sup>1-4</sup> However, in all cases, these reactions proceed via loss of the sulfonyl group to afford the cross-coupled product. Yet, sulfones and sulfonamides are valuable moieties in organic molecules.<sup>5-9</sup> In order to retain the sulfonyl group, we sought to develop a new cross-coupling method. Herein we report that a simple Ni<sup>II</sup> precatalyst  $[\text{NiBr}_2(^2\text{MePMA})]_2$  is capable of affecting the cross-coupling reaction between cyclic sulfones and aryl Grignard reagents  $[\text{Csp}^3\text{-Csp}^2]$ , without the need of further additives (<sup>2</sup>MePMA = N,N-dimethyl-1-(pyridin-2-yl)methanamine) (Scheme 1). Highlighting the ability to functionalize the resulting sulfinate intermediate, with a wide range of electrophiles. In turn yielding, for the first time, difunctionalized sulfones and sulfonamides, in a one-pot synthetic manner. Detailed mechanistic analyses and reaction monitoring experiments, have allowed us to propose a catalytic cycle. With further determinations supporting that this process allows access to functionalized chiral derivatives.



Scheme 1. Ring opening cross-coupling reaction of  $\alpha$ -substituted cyclic sulfones and aryl Grignard reagents, catalyzed by  $[\text{NiBr}_2(^2\text{MePMA})]_2$ .

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O3

## Synthesis of Redox-Active Phenalenol Substituted Ligands and Coordination in Rare Spin-Crossover Conducting Complexes

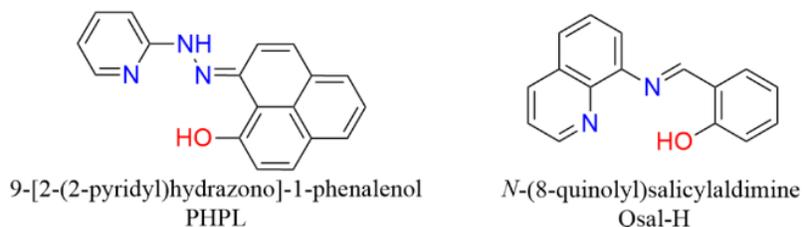
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Molecular switches are species capable of reversibly switching between two or more different states through environment stimuli.<sup>1</sup> The application of molecular switches can vary from photochromatic systems to our interested area of paramagnetic switches (spin-crossover complexes). Our research interest is in developing novel multifunctional materials that incorporate the spin-crossover (SCO) phenomena accompanied with conductive properties.

Our methodology in producing these complexes is through the usage of aryl-azo ligands. The redox nature of these ligands may produce open-shell radical states in which conductive properties arise.<sup>2</sup> In 2019, Lemaire et al. reported a novel phenalenol-substituted ligand “phpl”.<sup>3</sup> The reported Fe(phpl)<sub>2</sub> complex featured semi-conductive properties, however, no SCO transition due to the strong-ligand field. Furthermore, we’ve designed heteroleptic complexes using “qsal”, a known weak-field ligand that has produced SCO properties.<sup>4,5</sup> Herein, I will present on the findings of novel heteroleptic SCO conductive complexes featuring phpl and qsal.



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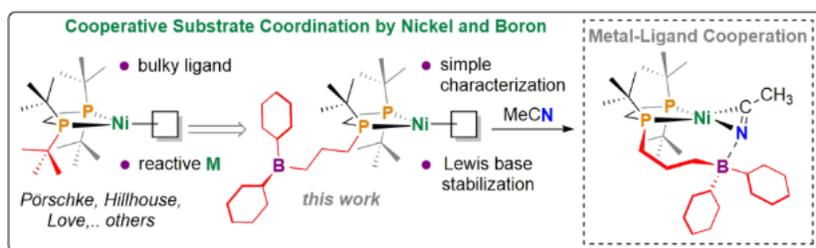
## Small molecule activation at Ni(0) – Stabilization effects achieved by a boron-based secondary coordination sphere

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Redox active ligands, and more recently, secondary coordination sphere (SCS) effects have been used to guide the reactivity of base metal systems. Of relevance, catalysts comprised of nickel (Ni) have become increasingly popular, capable of performing a multitude of transformations ranging from cross-coupling to CO<sub>2</sub> reduction. Recent research within the Drover group has highlighted the benefits of including Lewis acidic borane moieties in the SCS to tune metal Lewis acidity, alter redox potential, and participate in the stabilization of reactive intermediates.<sup>1–3</sup> In an effort to expand the “diphosphine ligand toolbox” the Drover group has reported two symmetrical diphosphine Ni(0) species featuring four and two boranes.<sup>2,4</sup> Herein we will discuss the synthesis and application of a monoboranyl diphosphinoethane Ni(0) analogue for the activation of small molecules, taking advantage of the stabilizing effects of the single peripheral borane moiety.



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O5

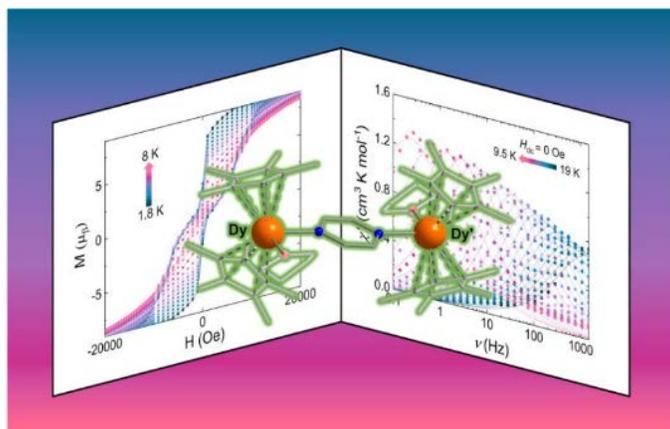
## Slow magnetic relaxation and strong magnetic coupling in lanthanide radical bridged metallocenes

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Promoting magnetic interactions in lanthanide-based single-molecule magnets (SMM) is an ongoing challenge in the field of molecular magnetism. To overcome the lack of strong magnetic communication between Ln(III) ions, which stems from the core-like electron density of 4f orbitals, employment of paramagnetic bridging ligands as a direct exchange pathway is a promising avenue.<sup>[1,2]</sup> With the aim to synthesize such strongly coupled complexes, we sought to utilize for the first time in lanthanide metallocene complexes, pyrazine (pyz) as a bridging ligand. Due to its redox active six-member ring, incorporation of the radical pyz<sup>•-</sup> in lanthanide metallocenes afforded [(Cp\*<sub>2</sub>Ln)<sub>2</sub>(pyz<sup>•-</sup>)(THF)<sub>2</sub>][BPh<sub>4</sub>] (Cp\* = pentamethylcyclopentadienyl; THF= tetrahydrofuran; Ln = Gd; (**1**), Dy; (**2**)). Strong magnetic exchange coupling was observed in **1** where  $J_{\text{Gd-Gd}} = 0.049 \text{ cm}^{-1}$  and  $J_{\text{Gd-rad}} = -15.98 \text{ cm}^{-1}$ , which to this day is the highest exchange coupling in Gd complexes mediated by an organic monoanionic radical. This in combination with the high performing [Cp\*<sub>2</sub>Dy]<sup>+</sup> units of Dy in **2** led to zero-field SMM behaviour with an energy barrier of  $U_{\text{eff}} = 111 \text{ cm}^{-1}$  and a coercive field of 2000 Oe.



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## Breaking Bonds and Breaking Rules: Multiple Redox States of Pentanuclear Nickel Hydride Clusters

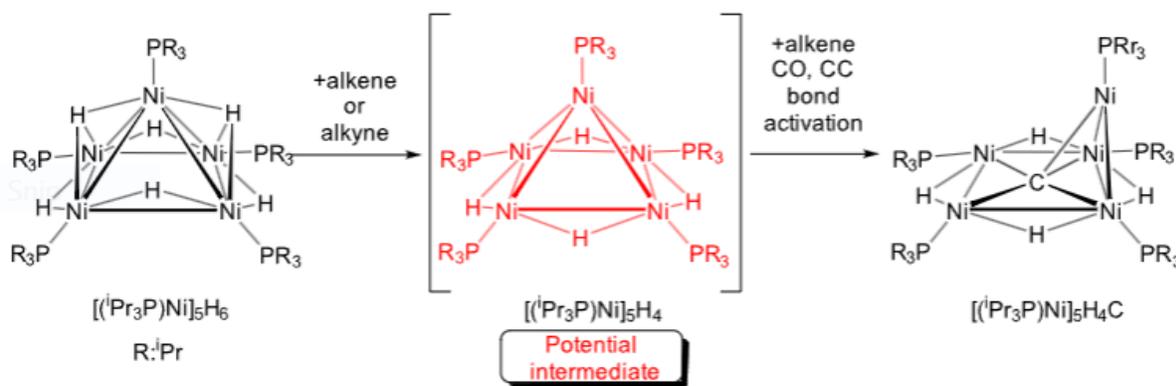
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The activation of chemically inert bonds such as CH, CC, and CO bonds by first-row transition metal complexes has advanced rapidly in the past decades. Besides mononuclear complexes, first-row transition metal clusters have demonstrated the ability to activate traditionally inert bonds through metal-metal cooperativity. Our group has previously synthesized a pentanuclear nickel hydride cluster  $[(iPr_3P)Ni]_5H_6$  (**1**)<sup>1</sup> and several unprecedented bond transformations have been reported, such as room temperature H/D exchange with benzene<sup>2</sup>, carbon atom abstraction from ethylene at cryogenic temperatures<sup>3</sup>, and the reaction of  $H_2C=CHO^tBu$  via multiple inert bond activations to give  $[(iPr_3P)Ni]_4H_4(C-CH_3)NiO^tBu$ ,  $[(iPr_3P)Ni]_4H_4(C-CH_2O^tBu)NiO^tBu$ , and  $[(iPr_3P)Ni]_5H_4C$ .<sup>4</sup> Despite this astonishing reactivity, the  $[(iPr_3P)Ni]_5H_6$  cluster is remarkable stable to many functional groups and small molecules, such as  $H_2O$ .

We have previously reported that the addition of  $H_2$  to **1** give a complex assigned by NMR spectroscopy as  $[(iPr_3P)Ni]_5H_8$ .<sup>1</sup> The activation of substrates by **1** seems likely to proceed by the initial formation of the tetrahydride  $[(iPr_3P)Ni]_5H_4$  (**2**) by alkene hydrogenation. This presentation describes attempts to synthesize and characterize the  $[(iPr_3P)Ni]_5H_4$  cluster, with the end goal of understanding the factors that governs its remarkable reactivity for inert bond activation under ambient conditions.



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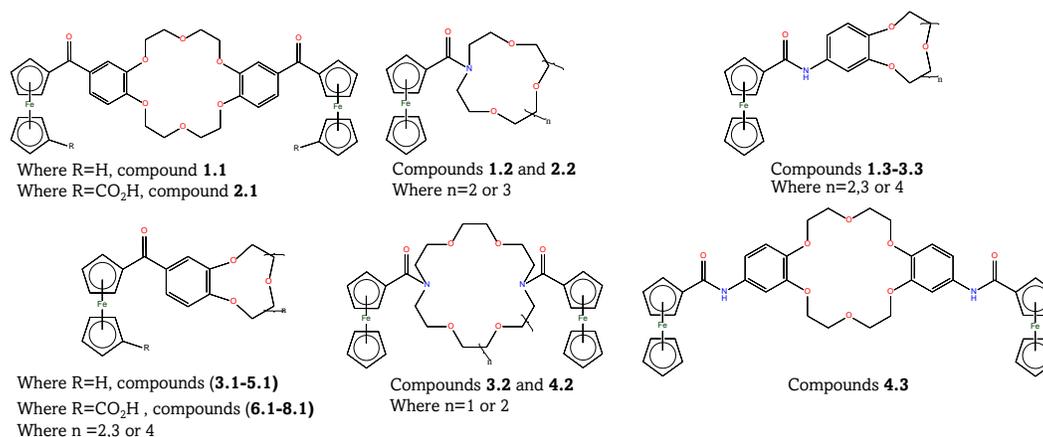
## Development of Redox Active Crown Ether Macrocycles - Towards Switchable Single Molecule Magnets

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Previous research within the Pilkington group has involved the use of crown ether macrocycles for the preparation of  $4f$  SMMs due to the compatibility of oxophilic Ln(III) ions with the oxygen donors of traditional crowns. Furthermore, the versatility of crown ethers permits facile modification of the macrocyclic cavity by varying the type and number of the donor atoms, as well as synthetically altering the organic framework, to tune the crystal field around the Ln(III) ions. Exploiting crown ether macrocycles as suitable ligands for  $4f$  ions, several families of Ln(III)-based single molecule magnets (SMMs) comprising of 15C5, benzo15C5 and dibenzo15C5 macrocycles have been structurally and magnetically characterized in recent years.<sup>1,2</sup> To advance these studies further, the objectives of this project are to append a redox switchable moiety onto the organic framework of multiple families of crown ether macrocycles in order to chemically address their magnetic properties. Following this strategy, the synthesis and characterization of six different families of ferrocene appended crown ether macrocycles; benzo-crown, aza-crown, and aza-benzo crown ethers will be presented.



**Figure 1:** Ferrocenoyl appended crown ether macrocycles

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O8

### Highly Active Iron-NHC Complexes for Catalytic Hydrosilylation

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1. Developing catalytic systems based on iron offers a greener alternative to expensive and toxic noble metals. N-Heterocyclic carbenes (NHCs) have been applied as ancillary ligands due to their unique donating properties to stabilize metal complexes. Our group has used chelating NHC ligands with a bifunctional scaffold to enhance the stability of the iron complexes and potentially activate substrates by a synergic cooperation between the metal center and the ligand. The hydrosilylation of carbonyl groups into alcohols is a powerful transformation in the laboratory and industry. Despite the recent advances in this field, the development of catalytic systems that can activate inexpensive silanes like polymethylhydrosiloxane (PMHS) under mild conditions and low catalyst loadings is still a challenge. To get some insights into the reaction mechanism and increase the stability of the catalyst, a series of analogous iron complexes with the formulation  $\text{FeL}_2$  (L = bifunctional chelating-NHC) was synthesized and their application towards the hydrosilylation of ketones is presented.

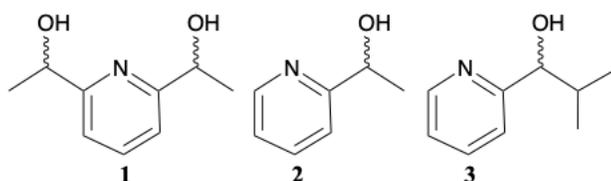
**Pyridyl Alkoxide-Based Ligands in 3d/4f-Metal Cluster Chemistry: Syntheses and Magneto-Structural Studies of New Families of Cu(II)/Ln(III) Clusters**

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Single molecule magnets (SMMs) are discrete coordination complexes typically comprised of transition metal and/or lanthanide ions that can be magnetized in the presence of an applied magnetic field and below their blocking temperatures, remain magnetized when that field is subsequently removed<sup>1</sup>. There is currently intense worldwide interest in SMMs given their potential applications for high-density information storage, magnetic qubits and spintronic devices<sup>2</sup>. The cluster chemistry of three pyridyl alkoxide ligands bhpH<sub>2</sub> (**1**), mpmH (**2**) and dmpmH (**3**) together with auxiliary carboxylate ligands has been explored for the preparation of heterometallic 3d/4f clusters. This strategy has afforded several new complexes with [Cu<sub>2</sub>Ln<sub>2</sub>], [Cu<sub>6</sub>Ln<sub>5</sub>], and [Cu<sub>4</sub>Ln<sub>2</sub>] cores, (where Ln(III) = Gd, Tb and Dy). The syntheses, structural and magnetic properties of these clusters will be presented, highlighting how by carefully fine tuning their molecular structures it is possible to suppress quantum tunnelling mechanisms and switch on their SMM properties.



**Figure 1:** Molecular structures of bhpH<sub>2</sub> (**1**), mpmH (**2**) and dmpmH (**3**).

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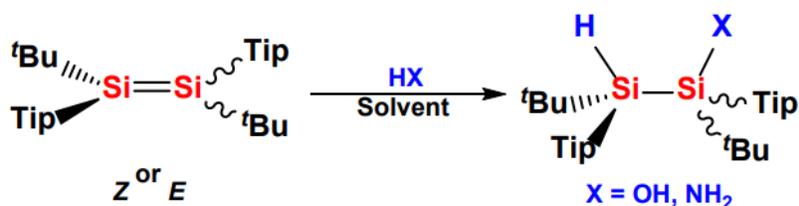
O10

### Insight Into the Stereochemistry and Mechanism of $\sigma$ -Addition in Disilenes

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The functionalization of ammonia and organoamines is an important reaction in pharmaceutical. Disilenes have been shown to readily functionalize ammonia.<sup>[1,2]</sup> This work includes the stereochemistry of the addition of ammonia and water to the *E* or *Z* stereoisomers of 1,2-di-*tert*-butyl-1,2-bis(2,4,6-triisopropylphenyl)disilene. Computational studies of the mechanism behind the addition of ammonia to the disilene. Kinetic studies on the reaction of tetramesityldisilene with isopropyl amine (i PrNH<sub>2</sub>) to find the reactant order of amine or disilene using VTNA, and KIE studies to determine the rate determining step. The implication of the experimental work outcomes on the mechanism of the reactions will be presented.



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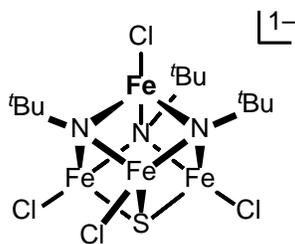
O11

### Synthesis and reactivity of a 3:1 site-differentiated iron-imide-sulfide cubane cluster

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The chemistry of site-differentiated multimetal clusters is a subject of continuing interest, particularly with respect to the controlled reactivity of biologically-relevant, weak-field iron-sulfur clusters.<sup>1-3</sup> Here we report on  $[\text{Fe}_4(\mu_3\text{-N}^t\text{Bu})_3(\mu_3\text{-S})\text{Cl}_4]^{1-}$ , a 3:1 site-differentiated iron-imide-sulfide cubane cluster with a  $C_{3v}$ -symmetric cluster core.<sup>4,5</sup> The unique iron center is coordinated within a sterically hindered pocket, which allows for selective substitution of the terminal ligands at the less hindered subsites, further differentiating the cluster coordination environment. We present initial reactivity studies of the resulting species, including terminal ligand substitution at the unique iron center and cluster redox transformations, as well as related chemistry and characterization.



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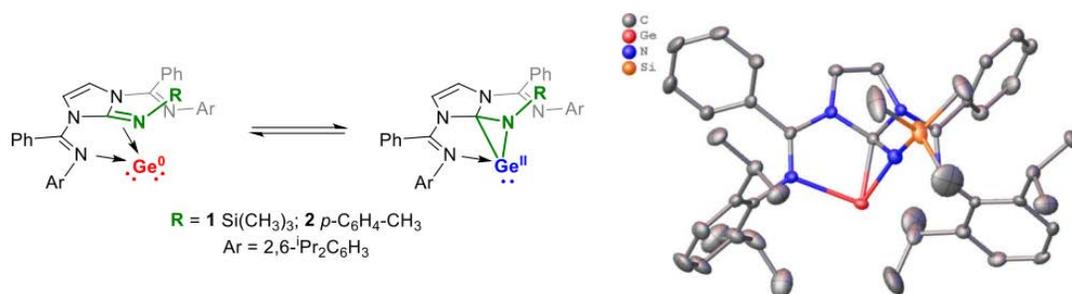
### Novel Ge(0) compounds supported by diimino-guanidine and their reactivity

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Low-valent main group compounds attract much interest of the scientific community.<sup>[1]</sup> In particular, the chemistry of recently discovered tetrylones, where the central group 14 element in the zero-oxidation state, is on surge. Tetrylones provide high reactivity through their two lone pairs.<sup>[2]</sup>

In this presentation, the synthesis, characterization, and reactivity studies of novel low-valent germanium complexes **1** and **2**, supported by a neutral diimino-guanidine ligand, will be reported. Their electronic structure is best described by the gerymlone/germylene forms shown in Scheme 1. Most of the previously reported tetrylones are stabilized by carbene or carbenoid ligands,<sup>[3]</sup> so that complexes **1** and **2** are the first of their kind. New bond activation patterns were realized by changing the ligand and the details will be presented.



**Scheme 1.** Gerymlone/germylene forms of **1** and **2** (left); Molecular structure of **1** (right)

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O13

### Further Investigation of the Synthesis and Properties of Iron-Imide Clusters

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Research in our laboratory has led to the synthesis of imide and imide-sulfide cubane-like clusters with general formula  $[\text{Fe}_4(\text{N}^t\text{Bu})_n\text{S}_{4-n}\text{Cl}_4]^z$  ( $n = 1-4$ ).<sup>1,2</sup> This series connects at  $n = 0$  to the previously known, well studied all-sulfide cluster.<sup>3</sup> The other terminal member, the  $n = 4$  all-imide cluster, has been only briefly reported by ourselves and the laboratory of Fenske.<sup>4</sup> The synthesis of  $[\text{Fe}_4(\text{N}^t\text{Bu})_4\text{Cl}_4]^-$  involves the simple reaction of  $\text{FeCl}_3$  and two equivalents of  $\text{LiNH}^t\text{Bu}$  yet  $[\text{Fe}_4(\text{N}^t\text{Bu})_4\text{Cl}_4]^-$  yields are very sensitive to reaction conditions. A ubiquitous by-product in the synthesis of iron-imide clusters is  $\text{FeCl}_2(\text{NH}_2^t\text{Bu})_2$ , which contains amine ligands that show chemical exchange under  $^1\text{H}$  NMR spectroscopic conditions (300 MHz,  $\text{CD}_3\text{CN}$ , 25 °C).  $[\text{Fe}_4(\text{N}^t\text{Bu})_4\text{Cl}_4]^-$  can be oxidized and reduced to  $\text{Fe}_4(\text{N}^t\text{Bu})_4\text{Cl}_4$  and  $[\text{Fe}_4(\text{N}^t\text{Bu})_4\text{Cl}_4]^{2-}$ , respectively. We report here the study of reaction conditions that lead to the formation of the all-imide cluster, the solution ligand exchange behaviour of  $\text{FeCl}_2(\text{NH}_2^t\text{Bu})_2$  and the structural and physical characterization of the redox series  $[\text{Fe}_4(\text{N}^t\text{Bu})_4\text{Cl}_4]^{0,1-,2-}$ .

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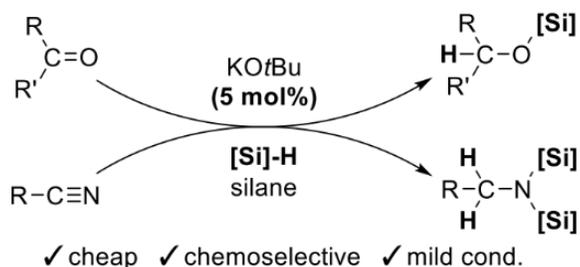
## Transition metal free, base-catalyzed hydrosilylation of unsaturated carbon heteroatom bonds

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The hydrosilylation of unsaturated C-O and C-N bonds yields valuable reagents and intermediates for organic synthesis. Traditionally, these reactions have been carried out by transition metal catalysts which are generally expensive and toxic, or stoichiometric reagents which produce a significant amount of waste. As such, transition metal-free catalytic alternatives have steadily gained popularity as a more sustainable alternative.<sup>[1]</sup> Herein we present the use of cheap and readily available potassium tert-butoxide (KOtBu) as a powerful catalyst for the hydrosilylation of carbonyls and nitriles under mild conditions.<sup>[2]</sup> Variation of silane substituents was found to play a key role in the chemoselectivity of these reductions.<sup>[2]</sup> For example, judicious choice of silane (EtO)<sub>2</sub>MeSiH allowed for the conversion of tertiary amides to aldehydes, a highly chemoselective process previously believed to be the domain of late transition metals.<sup>[3]</sup> Further application for this simple yet effective system is being explored, pushing the limits of scope and selectivity.



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O15

### Thermal characterization and Area Selective Deposition of NHCs

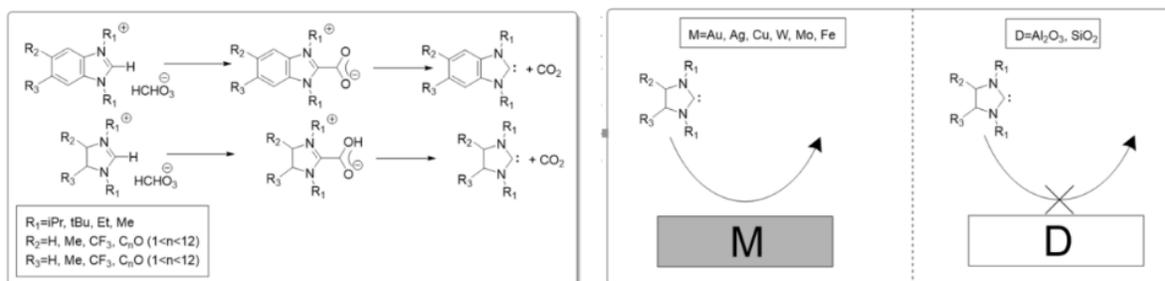
Eden Goodwin\*, Justin Lomax, Mark Aloisio, Cathleen M. Crudden, Paul J. Ragogna, and Seán T. Barry

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In nanomanufacturing, small-molecule inhibitors (SMIs) play a crucial role in preventing film growth on selected areas of the substrate during atomic layer deposition (ALD) of thin films. In this work we explore N-heterocyclic carbenes (NHCs) as area-selective SMIs. The electronic and steric tunability of NHCs enables their flexibility when using them to selectively protect metal surfaces, due to their preferential binding to metal surfaces over dielectric surfaces.

This presentation will detail thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies of a family of carbenes to be used as SMIs, highlighting the loss of water and CO<sub>2</sub> from imidazolium bicarbonates to produce volatile carbenes. These will then be exposed to plasma cleaned non-patterned (metal) and patterned (metal and dielectric) substrates using a Picosun R200 plasma-enhanced ALD tool. Films are characterized using ex-situ time of flight mass spectrometry (TOF-SIMS) and X-ray Photoelectron Spectroscopy (XPS). Finally, a series of quantitative surface saturation studies on a home-built tube furnace reactor using an in-situ quartz crystal microbalance (QCM) will be discussed.



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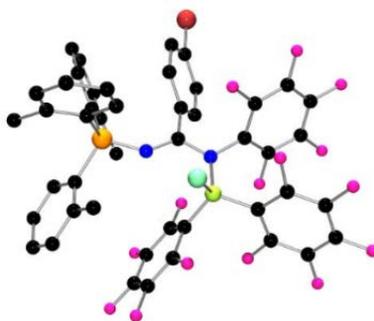
## Reactions of Frustrated Lewis Pairs with Diazirines and Diaziridines

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Since 2006, the chemistry of Frustrated Lewis Pairs (FLPs), has advanced greatly in small molecule activations stoichiometrically and catalytically functionalisation.<sup>1</sup> As such, the notion of FLP mediated dinitrogen activation is a primary focus within the group. To that, the activation and functionalization of dinitrogen which comprises remarkably strong N≡N triple bond, remains one of the most difficult challenge in main group chemistry. Inspired by nature N<sub>2</sub> fixation, many approaches were developed and those especially low valent transition metal complexes were able to bind N<sub>2</sub>. A significant breakthrough, low valence elements Fe, Mo and W were able to activate N<sub>2</sub> in conjunction with strong main group Lewis acid tris(pentafluorophenyl)borane, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>2</sup> In establishing similar chemistry, our group reported that the reaction of diphenyldiazomethane with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was found to be formed very similar transient species which were identified structurally at lower temperature.<sup>3</sup> Upon warming up at ambient temperature leading to dinitrogen elimination and that gives carbene species. Thus, it can be considered a similar system where N<sub>2</sub> can be trapped by a Lewis acid and a Lewis base and that's what an important model how FLP can cleavage N<sub>2</sub>. Here, I will talk about the reactions of chloro-diazirines or trifluoromethyl-diazirines, analogous species to dinitrogen, with FLPs where N=N double bond cleavage observed instead of N<sub>2</sub> elimination.<sup>4,5</sup> Further, FLP reactivity on diaziridines will be highlighted briefly.<sup>5</sup>



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O17

### Ligand Controlled Gold (I) Chalcogenide Complexes

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Chalcogenides ( $E^{2-}$ ) can form high-connectivity, three-dimensional networks with  $d^{10}$  group 11 metals with a  $M_2E$  core ( $M = Cu, Ag, Au, E = S, Se$ ). Although similar, differences in structure exist between  $Cu(I)$ ,  $Ag(I)$  and  $Au(I)$  due to variation in coordination modes and their abilities to aggregate through metallophilic interactions. These clusters are stabilized with surface ligands that offer the opportunity to direct structure and can also influence the luminescent properties often displayed by such clusters. The ligand, 4 – 6 *bis*(diphenylphosphino)dibenzofuran, has been previously used to stabilize group 11 metal chalcogen complexes and these clusters have demonstrated high photoluminescence quantum yields. In these studies,  $E(SiMe_3)_2$  ( $E = S, Se$ ) was added to the gold coordination complex  $[(AuOAc)_2(\alpha\text{-dbfdp})]$  to yield  $[(Au_2(\alpha\text{-S})(\alpha\text{-dbfdp}))]$  and  $[(Au_2(\alpha\text{-Se})(\alpha\text{-dbfdp}))]$  selectively and in good yields via the formation and elimination of  $AcOSiMe_3$ . The dimeric gold-chalcogenide complexes were found to be emissive in both solution and in the solid state. The structures and photophysical properties of  $[Au_2(\alpha\text{-E})(\alpha\text{-dbfdp})]$  will be presented.

O18

## Reactivities of Cyclonickellated Complexes with Hydroxylamines: Formation of $\kappa^O$ -Hydroxylamine and $\kappa^N$ -Imine Adducts and a $\kappa^O, \kappa^N$ -Aminoxide Derivative

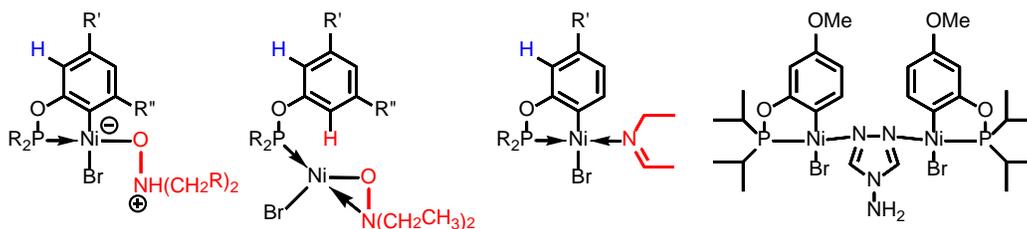
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The recent developments in Ni-catalyzed  $sp^2$  and  $sp^3$  C-H functionalization methodologies have led to practical routes to many compounds of commercial interest. While practical Ni-based protocols for C-H functionalization are becoming more and more common, there remain many unknowns about the intimate mechanism(s) of the different steps involved in these processes. For example, we know little about how the C-H nickellation step proceeds, and whether or not high-valent intermediates are involved in the subsequent C-C or C-heteroatom bond forming functionalization reactions.

Our group has been investigating various aspects of this general area of research, and we have reported our findings on the mechanism and regioselectivity of C-H nickellation with aryl phosphinites as model substrates. This presentation will focus on what we have learnt with regards to the reactivities of cyclonickellated complexes generated via C-H nickellation. More specifically, we will describe how the reaction of Ni-aryl intermediates with hydroxy amines leads to aminoxide derivatives and imine adducts and what, if any, role these species might play in C-N bond formation chemistry.



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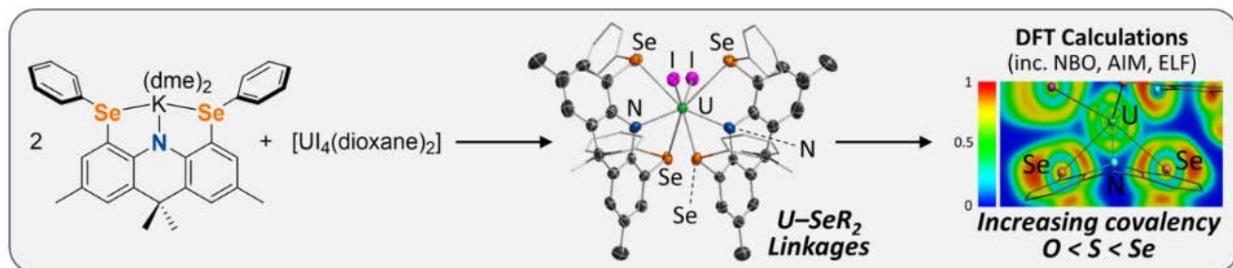
## Thio- and Selenoether Complexes of Uranium(IV): A Synthetic, Structural and Computational Study of Uranium-Chalcogenoether Bonding

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The study of actinide–soft-donor ligand interactions is an area of interest due to their ability to contribute to the fundamental understanding of *f*-element–ligand bonding, and potential relevance to the advancement of nuclear waste reprocessing strategies.<sup>1,2</sup> While a handful of uranium-thioether complexes have been structurally characterized<sup>3</sup>, there are no definitive reports of U–SeR<sub>2</sub> or U–TeR<sub>2</sub> complexes. This work will present the syntheses and characterization of rigid SNS- and SeNSE-donor pincer proligands (H[AS<sub>2</sub><sup>Ph2</sup>] and H[ASe<sub>2</sub><sup>Ph2</sup>], respectively), their alkali metal complexes, and use of these salts to prepare the U(IV) complexes [(AS<sub>2</sub><sup>Ph2</sup>)<sub>2</sub>UI<sub>2</sub>] and [(ASe<sub>2</sub><sup>Ph2</sup>)<sub>2</sub>UI<sub>2</sub>] (which feature U–S and U–Se bonds, respectively). Interactions with the flanking ER<sub>2</sub> (E = S or Se) donors is promoted by the highly rigid ligand framework, and the central amido donor which “anchors” the metal into the binding pocket. The Se-containing uranium complex, [(ASe<sub>2</sub><sup>Ph2</sup>)<sub>2</sub>UI<sub>2</sub>], features the first examples of uranium selenoether interactions. All compounds were characterized by NMR spectroscopy, UV-Vis/NIR spectroscopy and X-ray crystallography. DFT calculations were also employed to gain insight into the nature of the U–ER<sub>2</sub> bonds.



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O20

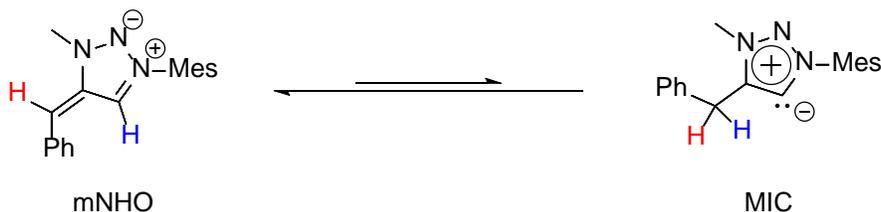
## Highly Active Iron-NHC Complexes for Catalytic Hydrosilylation

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*N*-heterocyclic olefins (NHOs) can be described as a hybrid of the charge-separated ylid form and its charge-combined olefin form. Derived from their parent *N*-heterocyclic carbenes (NHCs), NHOs show strong electron donor properties and have recently emerged as organocatalysts, polymer initiators, and as ligands in transition metal and main group chemistry. On the other hand, the reactivity of mesoionic NHOs (mNHOs), which are derived from their parent mesoionic carbenes (MICs), have been under-explored. Reported mNHOs have a substituent on the *pro*-carbenic position to prevent competing deprotonation. Herein we report a series of C5-unsubstituted mNHOs, where the installment of an electron withdrawing group on the exocyclic carbon prevents the competing deprotonation, while the *pro*-carbenic position is still available for further reactivity. Reactivities towards various Lewis Acids as well as its novel reactivity towards organic azides will be presented herein.



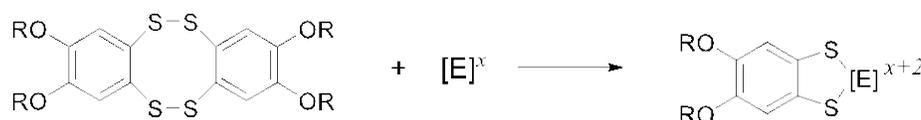
O21

### A comparative study of the oxidative addition chemistry of tetrathiocins to *p*- and *d*- block elements

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Metal dithiolene complexes exhibit intense colors, multiple oxidation states, reversible redox reactions and the ability to take on different geometric conformations, making them ideal in a variety of materials applications.<sup>1</sup> It has been shown that alkoxy-functionalized bis(benzo)-1,2,5,6-tetrathiocins are able to undergo oxidative addition to low valent group 10 metal complexes (Ni, Pd, Pt),<sup>2</sup> to afford alkoxy-functionalized benzenedithiolate complexes. This presentation describes recent studies of the oxidative addition chemistry of tetrathiocins with the group 9 complex,<sup>3</sup> CpCo(CO)<sub>2</sub>, as well as low oxidation state *p*-block complexes.



E = *p*-block or *d*-block element

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## H<sub>2</sub> Activation by titanium 'POCOP' pincer complexes

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Pincer complexes have been widely applied with late transition metals and have shown to catalyse important chemical transformations, such as reversible CO<sub>2</sub> hydrogenation and C-H bond activation of arenes.<sup>1,2</sup> Despite the vast amount of research on pincer complexes, studies with early transition metals (group 4-6), especially containing 'PCP' type pincer ligands, is underdeveloped. A small number of groups have observed exciting reactivity of early transition metal pincer complexes, including methane activation and N<sub>2</sub> activation.<sup>3,4</sup>

This work introduces the synthesis of 'PCP' type titanium pincer complexes, which have been derivatised with a range of alkyl and aryl substituents. These derivatised titanium alkyl complexes have shown the capability to activate dihydrogen at ambient conditions. Forming a rare titanium chlorohydride and titanium dihydride, which have been characterised using single crystal X-ray diffraction studies and EPR spectroscopy. This opens the door for more investigations of early transition metal 'PCP' complexes for small molecule activation.

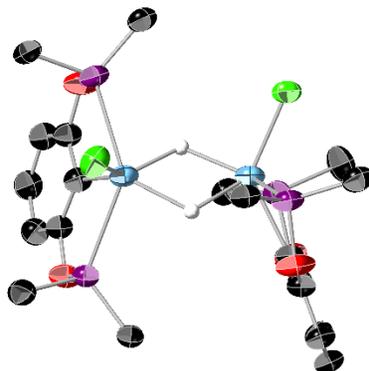


Figure 1: ORTEP plot of  $\{({}^t\text{BuPOCOP})\text{TiHCl}\}_2$ . Thermal ellipsoids at 50% probability, hydrogens (except bridging hydrides) and *tert*-butyl methyl groups omitted for clarity. Key: blue (titanium), red (oxygen), purple (phosphorus), green (chlorine), black (carbon), white (hydrogen).

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## [XeF<sub>5</sub>]<sup>+</sup> and [Xe<sub>2</sub>F<sub>11</sub>]<sup>+</sup> Salts of High-oxidation State Group 6 Oxyfluoro-anions

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Recent advances in high-oxidation-state Cr(V) oxide fluoride chemistry have exploited the fluorobasicity of XeF<sub>6</sub> and high oxidative resistance of the [XeF<sub>5</sub>]<sup>+</sup> and [Xe<sub>2</sub>F<sub>11</sub>]<sup>+</sup> cations to prepare the first examples of Cr(V) oxyfluoro-anions to be characterized by SCXRD; [XeF<sub>5</sub>]<sub>2</sub>[Cr<sub>2</sub>O<sub>2</sub>F<sub>8</sub>]·2HF and [XeF<sub>5</sub>]<sub>2</sub>[Cr<sub>2</sub>O<sub>2</sub>F<sub>8</sub>]·2XeOF<sub>4</sub>, by the reaction of XeF<sub>6</sub> with CrOF<sub>4</sub> in anhydrous HF (aHF) and CFCl<sub>3</sub>/HF mixtures.<sup>1</sup> The Cr(V) anions result from reduction of Cr(VI) to Cr(V) by elimination of F<sub>2</sub>. Now, XeF<sub>6</sub> has been shown to react with the weak fluoride-ion acceptor CrO<sub>2</sub>F<sub>2</sub> in aHF solvent and in melts at RT to yield the Cr(VI) oxyfluoro-anion salts [XeF<sub>5</sub>]<sub>2</sub>[Cr<sub>2</sub>O<sub>4</sub>F<sub>6</sub>], [XeF<sub>5</sub>]<sub>2</sub>[Cr<sub>2</sub>O<sub>4</sub>F<sub>6</sub>]·4HF (Figure 1a), [XeF<sub>5</sub>]<sub>2</sub>[Cr<sub>2</sub>O<sub>4</sub>F<sub>6</sub>]·2XeOF<sub>4</sub>, and [XeF<sub>5</sub>][Xe<sub>2</sub>F<sub>11</sub>][CrO<sub>2</sub>F<sub>4</sub>] which were characterized by low-temperature (LT) single-crystal X-ray diffraction (SCXRD) and Raman spectroscopy. These salts provide the first structural characterizations of the Cr(VI) oxyfluoro-anions [Cr<sub>2</sub>O<sub>4</sub>F<sub>6</sub>]<sup>2-</sup> and [CrO<sub>2</sub>F<sub>4</sub>]<sup>2-</sup>. In a related study, XeF<sub>6</sub> was shown to react with the heavier Group 6 MOF<sub>4</sub> (M = Mo, W) analogues in aHF solvent at RT to form [Xe<sub>2</sub>F<sub>11</sub>][MOF<sub>5</sub>] and [XeF<sub>5</sub>][M<sub>2</sub>O<sub>2</sub>F<sub>9</sub>].<sup>2</sup> In contrast, the LT reaction of CrOF<sub>4</sub> with XeF<sub>6</sub> in aHF was shown by SCXRD to yield the co-crystal, [XeF<sub>5</sub>]<sub>2</sub>[HF<sub>2</sub>]<sub>2</sub>·2CrOF<sub>4</sub>. This study showed that CrOF<sub>4</sub> is a significantly weaker F<sup>-</sup> acceptor than either MoOF<sub>4</sub> or WOF<sub>4</sub> and is incapable of abstracting F<sup>-</sup> from [(HF)<sub>x</sub>F]<sup>-</sup>. Consequently, [Xe<sub>2</sub>F<sub>11</sub>][CrOF<sub>5</sub>] was synthesized in the absence of HF in CF<sub>2</sub>ClCF<sub>2</sub>Cl solvent and the salt was characterized by LT SCXRD and Raman spectroscopy. The crystal structure of [Xe<sub>2</sub>F<sub>11</sub>][CrOF<sub>5</sub>] (Figure 1b) provides the first detailed structural characterization of [CrOF<sub>5</sub>]<sup>-</sup>.

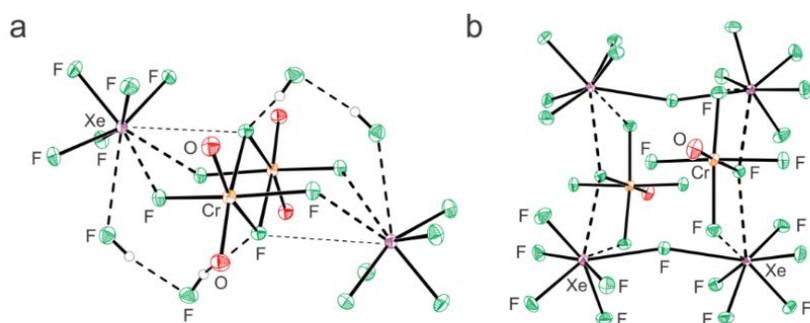


Figure 1. The X-ray crystal structures of (a) [XeF<sub>5</sub>]<sub>2</sub>[Cr<sub>2</sub>O<sub>4</sub>F<sub>6</sub>]·4HF and (b) [Xe<sub>2</sub>F<sub>11</sub>][CrOF<sub>5</sub>].

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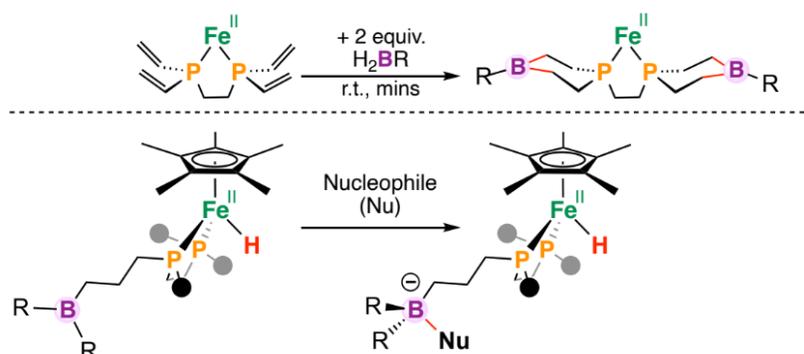
O24

## [Cp\*Fe(diphosphine)]<sup>+</sup> Complexes: Installation of a Lewis-acidic Secondary Coordination Sphere

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Diphosphines play a central role as supporting ligands in transition metal chemistry. As a theme in this area, our team has become interested in preparing diphosphines having Lewis-acidic secondary coordination spheres (SCSs) for applications in sustainable transition metal reactivity.<sup>1,2</sup> Recently, we reported the synthesis and use of a tetra-vinyl-diphosphine ligand ((1,2-bis-divinylphosphino)ethane) and its ability to act as a precursor to *bis*(1-bora-4-phosphorinane) heterocycles *via* sequential hydroboration of a [Cp\*Fe(diphosphine)]<sup>+</sup> (Cp\* = C<sub>5</sub>Me<sub>5</sub><sup>-</sup>) scaffold using mesitylborane.<sup>3</sup> To expand on this work, we are now investigating the effect of adding charge into the SCS of related Fe-complexes. Differential reactivity between an allyl (tetraallylphosphinoethane) *vs.* all-alkyl ((1,2-bis-di-*n*-propylphosphino)ethane) ligand framework is explored with an eye towards the synthesis of Fe(II) hydrides and the influence of a charged SCS on the hydride transfer propensity of the [Fe-H] moiety.<sup>4</sup>



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O25

## The CO<sub>2</sub> Adsorption Performance of MIL-53(Al) under High-Temperature and High-Pressure Conditions

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As a class of novel hybrid porous materials, metal organic frameworks (MOFs) exhibit reversible CO<sub>2</sub> adsorption capability. The external pressure and temperature can stimulate the structural changes of MOFs, which may enhance the CO<sub>2</sub> adsorption performance.<sup>1</sup> MIL-53 is a typical class of flexible MOFs with “breathing effect”, which refers to the reversible phase transition between large-pore (lp) and narrow-pore (np) phases.<sup>2</sup> In this work, the CO<sub>2</sub> adsorption performance of MIL-53(Al) were investigated under high pressure and high temperature with diamond anvil cell (DAC) and in-situ FTIR spectroscopy. With the increasing of the temperature to the melting point of CO<sub>2</sub>, CO<sub>2</sub> was gradually adsorbed into the channel of MIL-53(Al) at 0.73 GPa, accompanied by transitions between lp and np phases. The CO<sub>2</sub> adsorption capacity of the MIL-53(Al) was enhanced with the compression from 0.20 to 1.24 GPa. Besides, the appearance and the shifts of two new bands at 1230–1720 cm<sup>-1</sup> indicate the changes of the host-guest interaction manner. These findings demonstrate the potential of MOFs for capturing carbon and alleviating global warming in a larger pressure-temperature range.

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## Investigations of Chelated Azole Containing Boron Complexes

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Prior to 2003, boron-containing compounds (BCC's) were mostly overlooked when considering functionality for drug design. Since the FDA approval of Bortezomib (Velcade - a peptidemimic anticancer drug) and subsequently Tavaborole (Kerydin- an anti-fungal benzoxaborole) the field of medicinal Boron based complexes as drugs and therapeutics has blossomed as BCC's have seen increased use and research interest in pharmaceuticals. Having a particularly high affinity for oxygen, boron-oxygen chelated complexes and boronic acid esters have been increasingly popular in recent BCC's. We are interested in the development and characterisation of N,O- and N,C- chelates of BCC's and their potential as biologically active species. We intend to take advantage of the known biological activity of which oxazolines, oxazoles and thiazoles display and use them in tandem with those of the boron center to hopefully increase biological efficacies. Advancements towards the synthesis of various ligands scaffolds as well as their exciting implications in biological environments will be discussed.

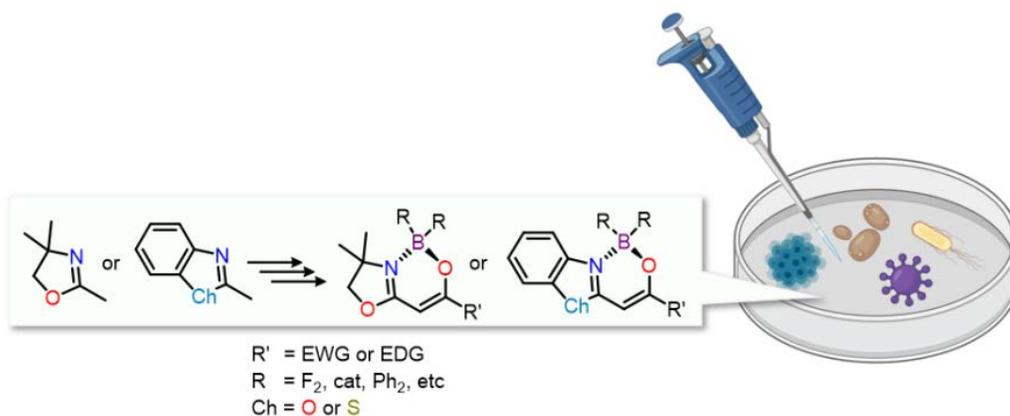


Figure 1: General scheme for the synthesis of N,O- and N,C- chelated BCC's

## Addressing Slow Relaxation of Magnetization Phenomena in Ln(III)-Based MOFs

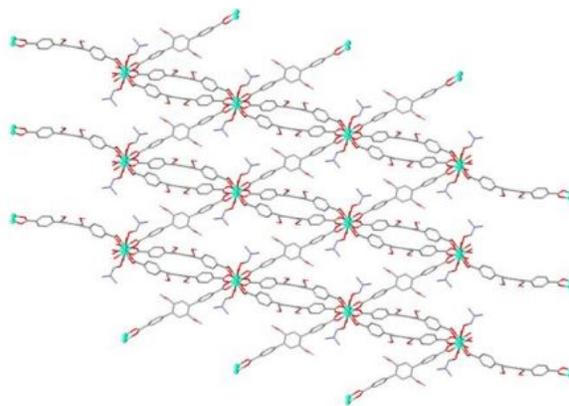
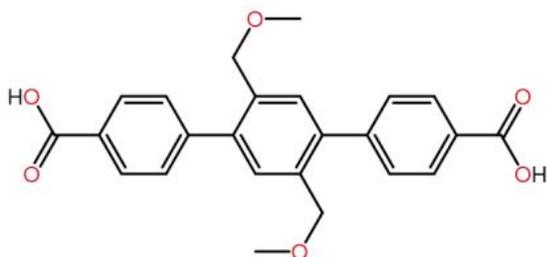
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One of the major themes of research in the Pilkington group is the study of slow relaxation of magnetization phenomena in 0-D coordination complexes, more commonly known as single molecule magnets (SMMs).<sup>1</sup> The large spin ground states and intrinsic magnetic anisotropy of select Ln(III) ions has made them widely exploited in this field, where the focus is to employ suitable ligands to tune their crystal fields to suppress quantum tunnelling and raising the blocking temperature for practical applications. An alternative class of coordination compounds well-studied for practical applications are 3-D, porous metal-organic frameworks (MOFs). In this field, Ln(III)-MOFs are studied for sensor applications since their photoluminescence properties are sensitive to the structure and concentration of chemical species in the pores of the MOFs. Given that select Ln(III) ions in these MOFs are often well-separated by connecting linkers, they are essentially “magnetically” isolated, and thus behave as single ion systems. We report herein the study of a family of Ln(III) MOFs  $[\text{Ln}_2\text{L}_3(\text{H}_2\text{O})_3(\text{DMF})](\text{H}_2\text{O})1.5(\text{DMF})0.5$  (**1**) (Ln = Gd, Tb, and Dy and L = 2',5'-bis(methoxymethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate), isostructural with the Eu-MOF reported by Yu Li *et. al.*<sup>2</sup> Changes in their dynamic magnetic properties associated with guest-host manipulation will be discussed.



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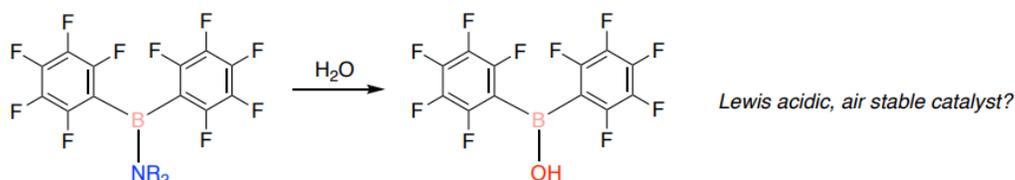
O28

## Towards a Bench-top Stable Lewis Acid Catalyst: Aminoboranes to Borinic Acids

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The use of bis(pentafluorophenyl)aminoboranes have been recently explored as catalysts in hydrosilylation and dehydrocoupling of stannanes, where bulky amino groups adjacent to the boron centre provide stability through lone pair donation without generation of a formal B-N double bond.<sup>1</sup> Catalytic transformations have been observed in donating solvents, suggesting the potential of these aminoboranes to be used as bench-top stable Lewis acid catalysts. However, further investigations on the stability of aminoboranes in ambient atmosphere show susceptibility to hydrolysis, yielding bis(pentafluorophenyl)borinic acid and protonated amines as the decomposition products (Figure 1). Bis(pentafluorophenyl)borinic acid shows similar catalytic activity as the parent aminoboranes and has previously been used as pre-catalyst to in-situ generated Piers' borane,<sup>2</sup> but has not been explored for catalytic applications under aerobic conditions. The synthesis, catalytic activity, and stability of Lewis acidic bis(pentafluorophenyl)boranes with bulky amino or hydroxy substituents will be presented in hopes of developing a class of bench-top stable Lewis acid catalysts.



**Figure 1:** The decomposition of bis(pentafluorophenyl)aminoboranes into bis(pentafluorophenyl)borinic acid.

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O29

### Therapeutic Coordination Polymer Glasses as Controlled-Drug Release Materials

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Driven by the increasing demand for rapid advancements in biomedicine, billions of dollars are spent annually on developing new technologies that offer safer and more effective clinical treatments. Drug-releasing implants offer potential alternative routes for drug administration, and recently, have been routinely used for various types of clinical therapies, including hormone replacement and chemotherapy. New classes of hybrid nanomaterials, namely, coordination polymers (CPs) have emerged as promising new platforms for drug release systems. However, many CPs only exist in their crystalline state, which limits their processability and their practical use for in-vivo applications. Herein, we report the rare event of melting of crystalline CuII -based therapeutic coordination polymers (TCPs) which result in amorphous glass formation upon cooling. The melting behaviour of our materials was characterized with DSC, TGA, and VT-PXRD. Structures and properties of the crystalline and the glass forms of our TCPs were investigated. We also report single-crystal-to-single crystal transformation from the monoatomic to diatomic Cu-TCPs upon heating, prior to melting.

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O30

### Exploring synthetic routes to cumulated methylene phosphonium analogues

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The nitrogen-based iminium cation is among the most thoroughly studied functional groups in organic chemistry. By comparison their phosphorus analogues, known as methylene phosphonium cations  $[\text{R}_2\text{P}=\text{CR}_2]^+$ , remain sparsely investigated in literature, with few reported examples to date. In this contribution, we disclose our recent attempts to prepare cumulated methylene phosphonium cations of the form  $[\text{R}_2\text{P}=\text{C}=\text{C}=\text{CR}_2]^+$ . One strategy we have explored attempts to access the target cations *via* Lewis acid mediated methoxide abstraction of alkynyl phosphine with the general formula  $(\text{R}_2\text{P}-\text{C}\equiv\text{C}-\text{C}(\text{OCH}_3)\text{R}_2)$ . Unexpectedly, we found a combination of an alkynyl phosphine and an equivalent amount of the Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$  to result in the formation of geminally substituted phosphonium borato-allene zwitterions. Experimental and computational evidence presented in this study indicate that the mechanism for this transformation likely involves an intermediate species which is a three-coordinate phosphorus electrophile akin to a methylene phosphonium cation.

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O31

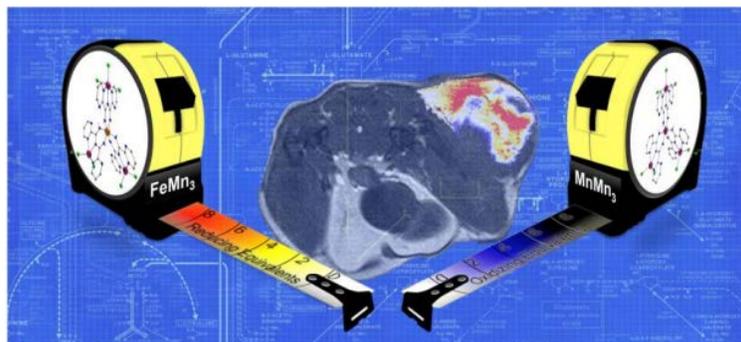
## Transition Metal Heteropolynuclear Complexes as Magnetic Resonance Imaging Redox Rulers

Alexandros A. Kitos, Raúl Castañeda, Zachary J. Comeau, Niki Mavragani, Nick D. Calvert, Alexia Kirby, Francisco Martinez-Santesteban, Peter J. Pallister, Benoit H. Lessard, Timothy J. Scholl, Muralee Murugesu,\* Adam J. Shuhendler,\* Jaclyn L. Brusso\*

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Transition metal molecular clusters hold great promise as MRI probes due to their potential to overcome nephrogenic systemic fibrosis associated with the use of gadolinium-based contrast agents in patients on dialysis or with severely impaired kidney function.<sup>1</sup> While polynuclear systems are scarce, they offer several advantages (tunability in size, shape and total spin state) since the collection of metal ions can act as a single entity. However, a key challenge that limits their application as MRI contrast agents remains, namely the molecular engineering of contrast agents that oppose dissociation/speciation in biological media. To resolve this, we employed our *N*-2-pyrimidylimidoyl-2-pyrimidylamidine chelate was employed to selectively bind 3d metal ions to form highly stable mixed metal clusters.<sup>2</sup> Through spectroscopic, electrochemical and magnetic analysis along with *in vitro* and *in vivo* studies, the data presented herein support the application of iron and manganese homo- and heterometallic triskelion-shaped complexes as MRI contrast agents capable of mapping tumor redox status through a simple  $T_{1w}/T_{2w}$  ratiometric approach.



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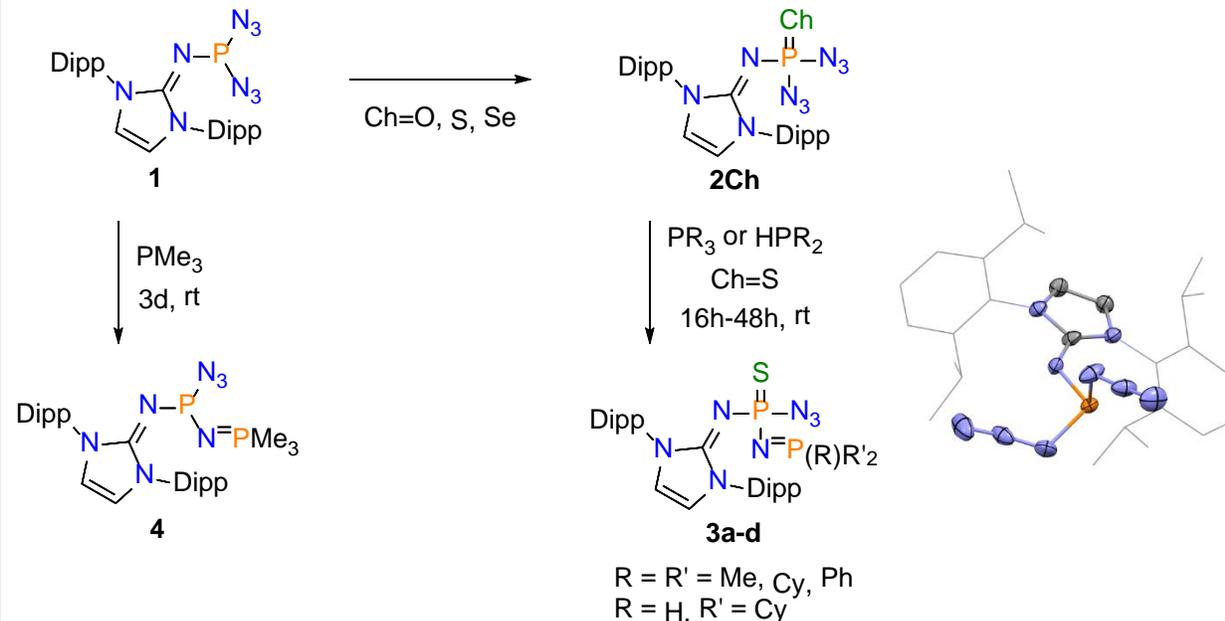
## Exploring reactivity of N-heterocyclic imine-supported bis(azido)phosphine compounds

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A series of bis(azido)phosphine chalcogenides were prepared through oxidation of the parent (IPrN)P(N<sub>3</sub>)<sub>2</sub> (**1**) [IPrN= N,N'-(2,6-diisopropylphenyl)imidazolin-2-iminato] with elemental oxygen, sulfur, and selenium. Solid state structures were obtained for the P(III) (**1**) and P(V)-sulfide (**2S**) and selenide (**2Se**) derivatives. The additions of Lewis-basic phosphines (PMe<sub>3</sub>, PCy<sub>3</sub>, PPh<sub>3</sub>, and HPCy<sub>2</sub>) to solutions of (IPrN)P(S)(N<sub>3</sub>)<sub>2</sub> (**2S**) were found to undergo mono-Staudinger reactivity producing chiral (azido)(phosphinimino)phosphine sulfides (**3a-d**) [(IPrN)P(S)(N<sub>3</sub>)(N=PR<sub>3</sub>)], even when performed with excess phosphine. Analogous reactions of (IPrN)P(N<sub>3</sub>)<sub>2</sub> (**1**) with PMe<sub>3</sub> to generate **4** were observed to progress slower than the sulfide derivative. Density Functional Theory (DFT) calculations provided insight to the selectivity of this reaction, as the frontier molecular orbitals of the model mono(azido)phosphine are predicted to possess energetically inaccessible N-N-N π\* orbital at the LUMO+4 level. Further analysis reveals an isolobal relationship between compound **4** and a bis(imidazolidin-2-iminato)phosphinoazide used by Dielmann *et al.* (2012) as a precursor to isolate phosphinonitrenes.



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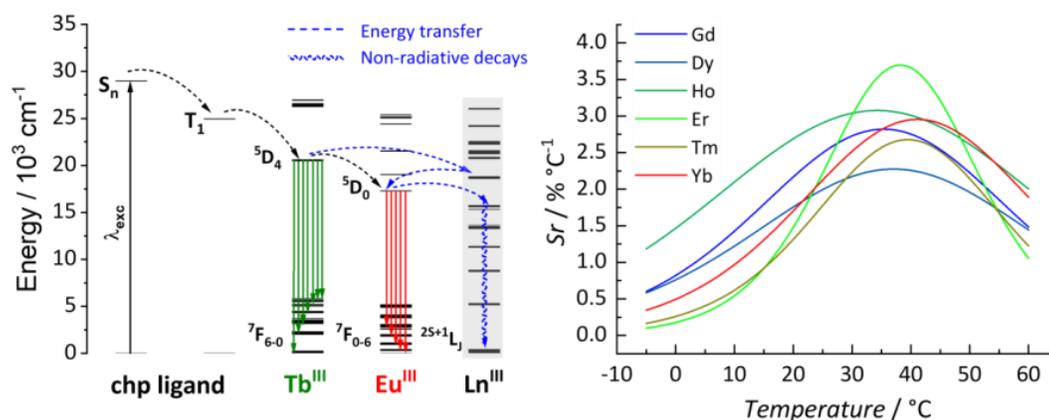
## Tuning the luminescence in molecular cluster-aggregates through composition control: impacts in energy transfer and thermometry

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Composition control is crucial for developing lanthanide(Ln)-based luminescent materials with tunable optical properties.<sup>[1]</sup> Owing to their close ionic radius and similarity in chemical characteristics, doping/dilution of Ln<sup>III</sup> ions in a lanthanide matrix is well established. Among these matrices, molecular systems offer excellent synthetic composition control, crystallinity, and uniformity. With that said, small molecules are limited by the number of metal centers which prevents attaining high performances in their luminescent properties. On the other hand, rigid molecular cluster-aggregates (MCAs) offer a distinct advantage due to their high nuclearity and composition control within the molecular unity, with reduced non-radiative processes and enhanced emission.<sup>[2]</sup> In this work, we demonstrate that by carefully fine-tuning the composition in a series of trimetallic MCAs ( $[\text{Ln}_2\text{Eu}_2\text{Tb}_{16}(\text{cph})_{30}(\text{CO}_3)_{12}(\text{NO}_3)_6(\text{H}_2\text{O})_6] \cdot \text{H}_2\text{O}$  (Ln = Gd, Dy, Ho, Er, Tm, Yb)); it is possible to tap into the energy transfer process to elucidate the intrinsic luminescent properties. Temperature dependent optical data provide an insight into the energy transfer process between the lanthanide ions with remarkable relative thermal sensitivity (Sr).



**Figure 1.** a) General energy level diagram for  $\{\text{Ln}_2\text{Eu}_2\text{Tb}_{16}\}$  MCAs with possible pathways for energy transfer, radiative and non-radiative decays, and b) their relative thermal sensibility.

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O34

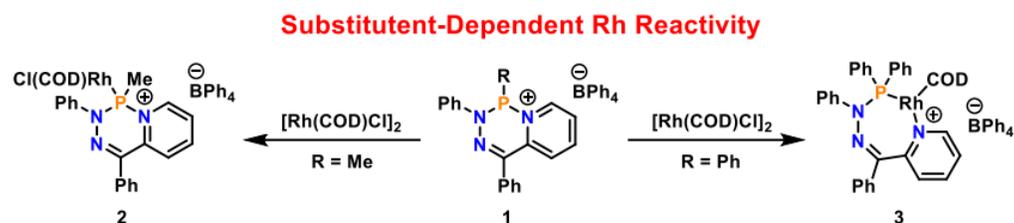
## Synthesis, Characterization, and Divergent Coordination Chemistry of Phosphenium Heterocycles

Alexander E. R. Watson, Michael J. Grant, Paul D. Boyle, Paul J. Ragona\*, and Joe B. Gilroy\*

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Chelating *N*-donor ligands are often used for stabilizing low valent atoms, such as phosphenium cations, due to their  $\pi$ -donor ability.<sup>1</sup> These ligands are also prominently used in  $\pi$ -conjugated materials, such as boron difluoride dipyromethenes (BODIPYs) and related compounds.<sup>2</sup> Despite limited presence reported in the literature, the coordination of heavier main group elements, like phosphorus, in place of boron has resulted in desirable properties ranging from water solubility to donor-acceptor characteristics.<sup>3,4</sup> A 2-pyridylhydrazonide ligand was used to stabilize a phosphenium cation (**1**). The optical and electronic properties of these cations were studied in detail with tandem experimental and computational techniques. The treatment of these cations with  $[\text{Rh}(\text{COD})\text{Cl}]_2$  resulted in divergent modes of reactivity that depended on the substitution at phosphorus (**2** and **3**). Recent results in this area will be discussed.



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O35

## Energy Transfer in Core@Shell Electrospun Nanofibres for Light Harvesting Applications

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Electrospinning is a cost-effective and efficient method of producing polymeric nanofibres and corresponding films. These nanofibres can have a monoaxial structure or a coaxial structure where there is a distinct core and shell (core@shell).<sup>1</sup> Owing to their hierarchical structure, materials can be embedded in coaxial nanofibres to allow for multi-functional properties of these films.<sup>2,3</sup>

Applications such as photovoltaic devices, lasers, sensors, OLEDs, etc., rely on light-harvesting components like dye molecules, metal nanoparticles, or quantum dots for their function. Therefore, incorporating these into coaxial nanofibres comes with benefits owing to their spatially confined distribution (in either the core or shell), constraint at specific distances from each another, with complementary tunability in fibre diameter. In this work, we demonstrate the feasibility and benefits of the incorporation of light-harvesting molecules in both the core and shell of nanofibers using two common organic dyes. For this proof-of-concept study we focused on energy transfer from the core to the shell of a nanofibre via FRET between BODIPY and rhodamine.

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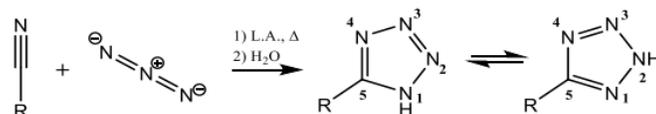
## Transition Metal Catalyzed Azide-Nitrile Cycloaddition Reactions: Mechanistic Insight into the roles of Transition Metal ions in the Formation of Tetrazoles

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The metal-catalyzed (3 + 2) cycloaddition or ‘click’ chemistry of azides with nitriles is a powerful synthetic methodology for connecting two building blocks and has been applied in many fields of research including organic chemistry,<sup>1</sup> inorganic chemistry,<sup>2</sup> and medicinal chemistry.<sup>3</sup> Zn<sup>2+</sup> ions are often the ‘go-to’ ion of choice for these reactions, however recent studies indicate that more inert metals such as Ni<sup>2+</sup> can also promote cycloaddition reactions at ambient temperature. Herein computational DFT studies (B3LYP-D3/LACV3P\*++) of the preferred metal coordination number (4,5,6) and tetrazolate coordination mode (N1 vs. N2) for Zn<sup>2+</sup> and Ni<sup>2+</sup> ions are reported. Subsequently, the thermodynamically preferred geometries for [M(H<sub>2</sub>O)<sub>n</sub>(mtz)]<sup>+</sup> (*n* = 3, 4, 5; mtz<sup>-</sup> = MeC<sub>4</sub>N<sub>5</sub>) ions were identified and compared with the literature in the Cambridge Structural Database for Zn<sup>2+</sup> and Ni<sup>2+</sup> tetrazolate complexes. DFT studies of the conversion between N1 and N2 bound coordination modes were also undertaken, and the energetically favored reaction pathways were determined



**Scheme 1.** (3 + 2) cycloaddition between an azide ion (N<sub>3</sub><sup>-</sup>) and an organic nitrile (R-CN).<sup>4</sup>

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O37

### The development of Au-titania photoanode composites toward semiflexible dyesensitized solar cells

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The conversion of windows into photovoltaic devices would be a remarkable accomplishment considering modern urban landscapes. With this in mind, a flexible dye-sensitized solar cell (DSSC) is preferred. At the core of the DSSC is the dye-sensitized photoanode. Herein we examine different nanoparticle composites within the semiconductor anode formulation and its effect on device performance. The mesoporous titania particles (TiO<sub>2</sub>) filled with Au-nanoparticles (TiO<sub>2</sub>@AuNPs) were synthesized using precipitation strategies followed by thermal treatment. The materials were then fully characterized through SEM, XRD, and DRS before and after thermal treatment. A paste prepared from the synthesized semiconductors was applied onto the substrate using the doctor blading technique. The use of high thermal treatment for glass substrates (HTT), low-temperature thermal treatment (LTT), and LTT combined with 2 hours of UV curing (LTT-UV) was explored. The anodes were loaded using a metal-free dye. For the cell construction, rigid glass substrates and polymeric substrates were contrasted. Flexible and semiflexible DSSCs were obtained with efficiencies from 0.03% to 2.4%, with a substantial performance difference seen using different thermal treatments.

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- (2) Al-Faouri T, Buguis FL, Soldouz SA, Sarycheva O v, Hussein BA, Mahmood R, et al. Exploring structure-property relationships in a bio-inspired family of bipodal and electronically-coupled bistrisphenylamine dyes for dye-sensitized solar cell applications. *Molecules* **2020**;25.

O38

**Potential-Dependent Selectivity for the Conversion of CO<sub>2</sub> to CO by a Cobalt Porphyrin-Peptide Electrocatalyst in Water**

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The light-driven reduction of CO<sub>2</sub> is a promising route to producing renewable fuels. Enzymes, known for catalyzing multi-electron, multi-proton reactions with high selectivity, make attractive systems to emulate when developing reactions requiring controlled electron and proton delivery. Herein, we describe the activity of a metalloporphyrin biocatalyst, cobalt microperoxidase-11 (CoMP11-Ac), a cobalt porphyrin attached to an eleven amino acid peptide chain. CoMP11-Ac exhibits turnover numbers as high as 32,000 for CO. Remarkably, it was shown that the selectivity for CO versus H<sub>2</sub> formation increases when lowering the applied potential, which occurs without loss of activity. We propose that the dependence of selectivity on the applied potential is due to a change in the catalytic mechanism. At lower potentials a concerted mechanism is proposed to take place avoiding formation of a Co(I) species that can be readily protonated and lead to H<sub>2</sub> formation. CoMP11-Ac is reported as an active and selective CO<sub>2</sub>-to-CO reduction catalyst in purely aqueous conditions and the impact of that catalyst structure, buffer, and applied potential had on its CO<sub>2</sub> reduction activity and selectivity were investigated.

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### Tuning the emission color of OLED devices doped with an N<sup>^C^N</sup>-Pt(II) complex

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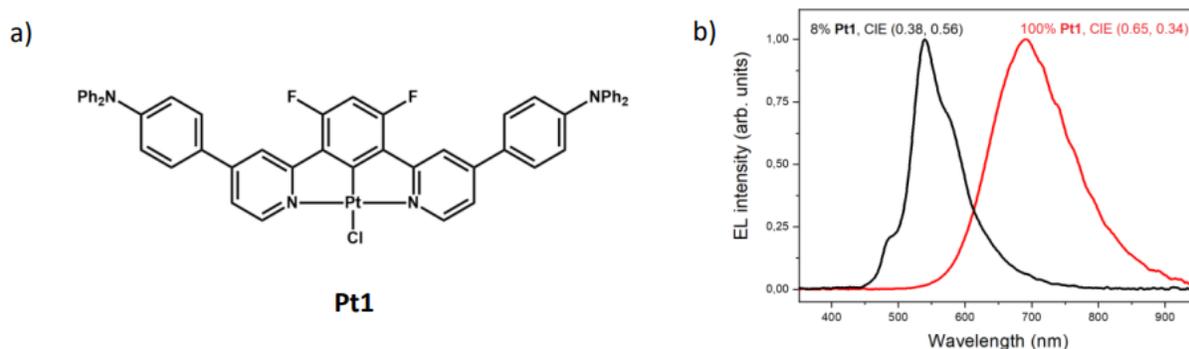
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<sup>d</sup> Istituto di Scienze e Tecnologie Chimiche (SCITEC-CNR), I-20133 Milan, Italy

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N<sup>^C^N</sup>-Pt(II) complexes can be very important for different applications related to their luminescence, since the high spin-orbit coupling of the heavy metal atom allows for an efficient triplet population, while the rigid coordination environment provided by the terdentate 1,3-di(2-pyridyl)benzene reduces non-radiative decays of the excited states. Among this class of compounds, remarkable photophysical properties (such as Quantum Yields up to 90%) are achieved by the family of complexes here discussed<sup>[1]</sup>, presenting a 4-NPh<sub>2</sub>-phenyl group on the pyridines and different substituents (difluoro, mesityl, 4-NPh<sub>2</sub>-phenyl) on the central benzene ring. Complex **Pt1** (**Figure 1a**) has been tested as dopant for the preparation of OLEDs, resulting in devices whose emitted color can be tuned by varying the concentration of the compound in the emissive layer, obtaining a shift of the emission from green to red (**Figure 1b**). In the future, further modifications of the N<sup>^C^N</sup> scaffold (by introducing other moieties on the aromatic rings or replacing the chloride ancillary ligand) could lead to an extension of the color range and to better-performing devices



**Figure 1.** a) Structure of complex **Pt1**; b) Emission spectra of the OLEDs doped with **Pt1**.

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O40

### Electrochemical Formation C-S Bonds from CO<sub>2</sub> and Small Molecule Sulfur Species

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Electrosynthesis can enable the use of CO<sub>2</sub> as a building block to generate organic compounds under mild conditions, powered by renewable electricity. Compared with the traditional carbon-based products CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), compounds with heteroatoms (N or S) can meet additional societal needs within agriculture, biology, pharmaceutical or chemical industry<sup>1-3</sup>. To this end, we combine CO<sub>2</sub>RR with sulfite co-electrolysis to synthesize molecules containing C-S bonds (hydroxymethanesulfonate, sulfoacetate and methanesulfonate). Cu<sub>2</sub>O nanoparticles are used as a model catalyst that attain ~10% selectivity in total for C-S products. Operando Raman spectroscopy and DFT calculations reveal that \*CHOH is the key intermediate, and the rate-determining step is the coupling of \*CHOH and SO<sub>3</sub><sup>2-</sup> reactants on the Cu surface. Our results provide a new avenue for CO<sub>2</sub> fixation and organic compound synthesis via green electrochemical methods.

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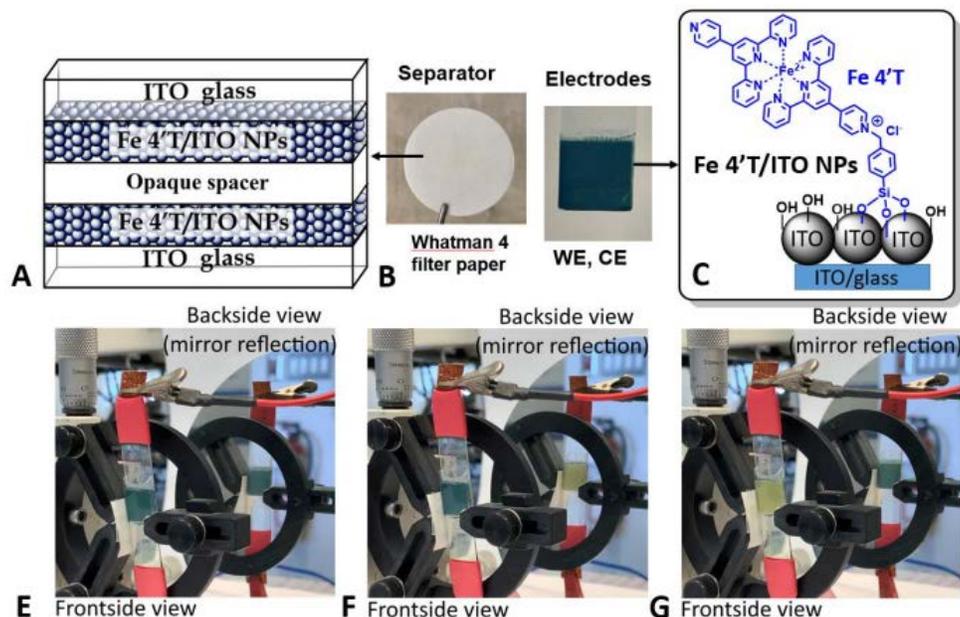
## The Architectural Development of Double-Sided Ultra-stable Metal-Organic Electrochromic Devices

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In recent years, we have seen a dramatic growth of interest in the development of effective energy-efficient electrochromic devices (ECDs). Previously, we have shown that the architecture of the device, specifically the material of the counter electrode has an impact on the functionality and longterm performance of the system. <sup>1</sup> Here we presented the methodology to create an effective doublesided electrochromic device with superior performance and unprecedented durability. The device was created from two identical Fe<sup>4+</sup>T/ITO nanoparticle electrodes that were dipped in a 5% Nafion™ dispersion and dried down. The architecture of the device contains two Nafion™ coated electrochromic electrodes separated by a white separating membrane covered with Li<sup>+</sup> gel electrolyte. Electrochemical Impedance Spectroscopy and Cyclic Voltammograms were used to monitor the performance of the device over time. The device was able to continue cycling for 70,000 cycles (100 days) and after the electrodes had been switched, was able to continue cycling for 12,000 additional cycles.



**Figure 1:** A schematic representation of the double-side solid-state electrochromic device

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O42

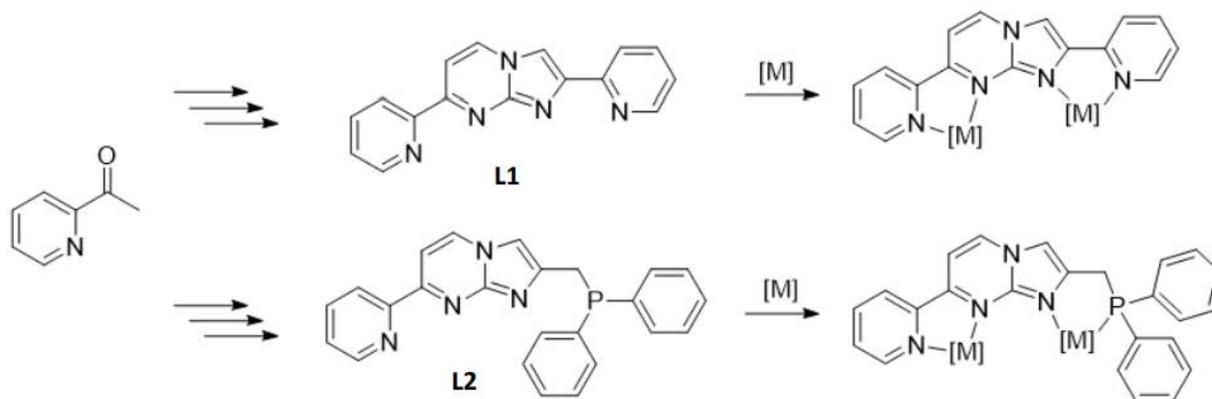
## Imidazopyrimidine-based Tetradentate Binucleating Ligand for Bimetallic Catalysis

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Bimetallic catalysis, broadly stated, is simply catalysis utilizing two metals, particularly transition metals. Of particular interest to our group is the investigation of homogeneous, bimetallic catalysts that are synthesized from chelation of metals to specially designed heterocyclic ligands. In this space of bimetallic catalysis, tetradentate, nitrogen-based heterocycles dominate, particularly derivatives of 1,8-naphthyridine.<sup>1</sup> Currently two major downsides to the development and widespread use of bimetallic catalysis exist: 1) the difficulty of synthesizing functionalized 1,8-naphthyridine ligands and 2) the inherent symmetry of the ligands. The latter is notable as the selective binding of two different metals is not possible currently with the reported ligands, meaning most bimetallic complexes studied thus far have largely focused on homonuclear bimetallic complexes. Our work proposes the development of two new ligands, L1 and L2. Both require less steps and use more convenient starting materials than current bimetallic ligands, as well as have heteronuclear bimetallic potential. The synthesis of L1 has been achieved with multiple bimetallic complexes synthesized. Synthesis of L2 is underway.



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P1

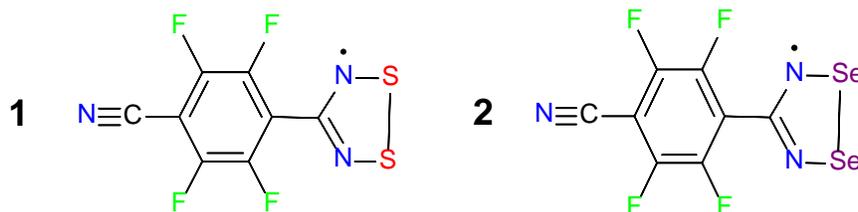
**Towards Molecular Alloys: Computational and Experimental Studies on *p*-NCC<sub>6</sub>F<sub>4</sub>CNEEN (E = S/Se)**

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The  $\beta$ -phase of the dithiadiazolyl (DTDA) radical,  $\beta$ -*p*-NCC<sub>6</sub>F<sub>4</sub>CNSSN (**1** $\beta$ ) is known to exhibit long range magnetic order below 36 K at ambient pressure.<sup>1</sup> In contrast, the corresponding diselenadiazolyl (DSDA) radical *p*-NCC<sub>6</sub>F<sub>4</sub>CNSESeN (**2**) has been reported to form a dimer, (**2**)<sub>2</sub>, in which spin-pairing occurs quenching the paramagnetism.<sup>2</sup> The present study describes theoretical studies on **2** which reveal it exhibits a similar shape, size and charge distribution to **1**, suggesting it may be possible to incorporate **2** into the host lattice of **1** $\beta$ . In addition, incorporation of **2** into **1** $\beta$  is computed to enhance magnetic communication between DTDA and DSDA radicals in relation to pure **1** $\beta$  which should favour an enhancement in the magnetic ordering temperature. Approaches to experimentally incorporate **2** into the framework of **1** $\beta$  at dopant levels < 10% are explored through cocrystallization from solution and cosublimation *in vacuo*.



**Figure: *p*-NCC<sub>6</sub>F<sub>4</sub>CNSSN (left) and *p*-NCC<sub>6</sub>F<sub>4</sub>CNSESeN (right)**

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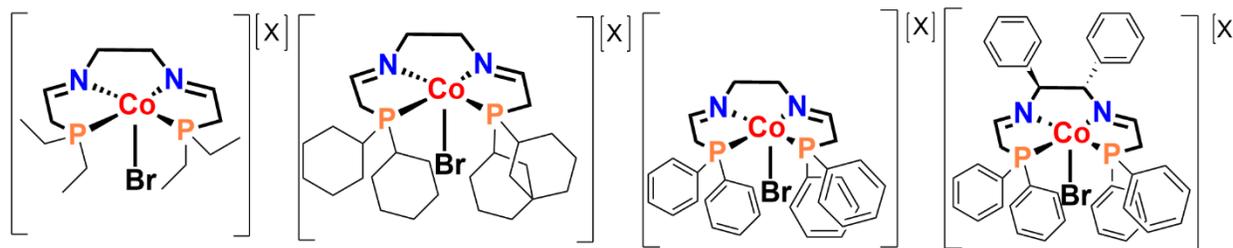
P2

## Novel Cobalt PNNP Complexes Towards Abundant Metal Catalysis

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The precious metals comprising today's industry-staple catalysts are toxic, expensive, and unsustainable.<sup>1-3</sup> Recently, 3d metals have become of interest in catalysis as a cheaper, greener alternative to precious metals.<sup>1,4</sup> However, these metals are paramagnetic, which brings both unique reactivity and unique challenges to 3d metal catalysis.<sup>1</sup> We first present our group's system for predicting thermodynamic properties of diamagnetic transition metal hydrides without experimental or computational measurements.<sup>5</sup> Next, we present a series of new cobalt PNNP complexes that have been synthesized in order to investigate this method's application to paramagnetic hydrides. A convenient template synthesis method allows these PNNP ligands to be easily customized with substituents and chiral backbones. Some interesting polymeric crystal structures have resulted from this method. Further studies will be conducted on their corresponding hydrides. We hope to gather insight on rational 3d abundant metal catalyst design.



\*Anions represented by "X"

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P3

### **Machine Learning Approaches for Spectroscopic Identification of Microplastics**

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Microplastics (fragments of plastic >5mm) are ubiquitous in the environment and have been detected almost everywhere, from the tops of the highest mountains to the deepest ocean. In the environment, these plastics undergo chemical, physical and biological changes which can lead to problems with their identification. Current identification methods can be inaccurate, long-winded or take extensive preparation of the environmental sample. In this work, a method for rapid identification of environmental microplastics is outlined. A spectroscopic database containing high resolution spectra of different plastics (>320 spectra) has been created and is being used to train machine learning classification models. Models based on k-nearest neighbor, random forest, and multi-layer perceptron algorithms yield classification models with accuracies of 95-99%. Parameters to optimize precision and accuracy of the models are being tested, including wavenumber range, spectroscopic resolution and density of data points selected. Increasing the speed and accuracy of microplastics identification introduces the possibility of using a flow-cell real-time monitoring of environmental microplastics.

P4

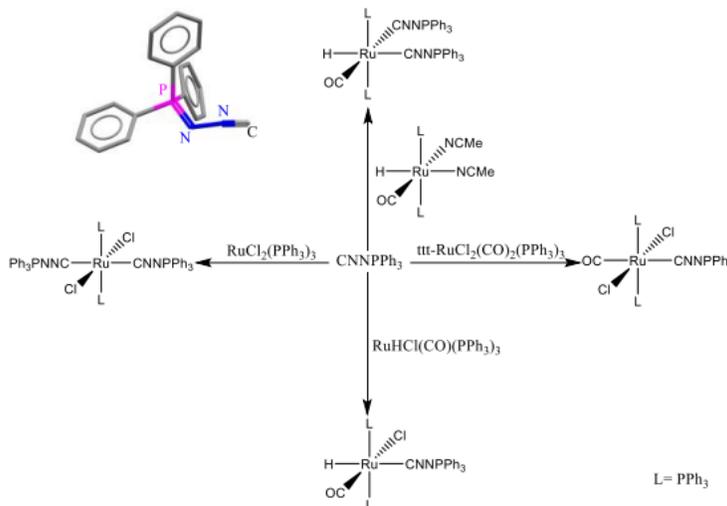
## Post-Synthetic Modification of 4-(2'-benzimidazolyl)-1,2,3,5-dithiadiazolyl in the Pursuit of Molecule-Based Materials

Philip Jacques Karageorghis, and David Scott Bohle\*

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Functional isocyanide ligands offer an excellent avenue of approach to novel transition metal chemistry due to the depth of our understanding the characteristics of isocyanide ligands while yielding secondary, post-ligation reactivity.<sup>1</sup> The reactions of N-(isocyanoimino)triphenylphosphorane (CNNPPh<sub>3</sub>) with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, ttt-RuCl<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> and OsCl(Ph)(CO)(PPh<sub>3</sub>)<sub>2</sub> yielded products structurally analogous to those obtained via reactions with nonfunctionalized isocyanides, while having some unexpected properties. Previously reported aza-Wittig type reactivity of the N=P bond has also been demonstrated for the first time in ruthenium complexes.<sup>2,3</sup>



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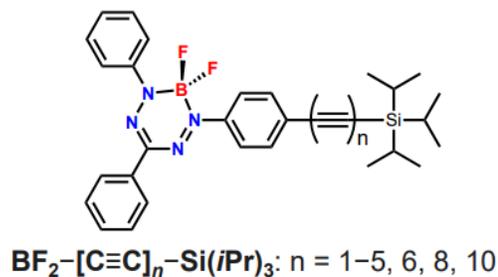
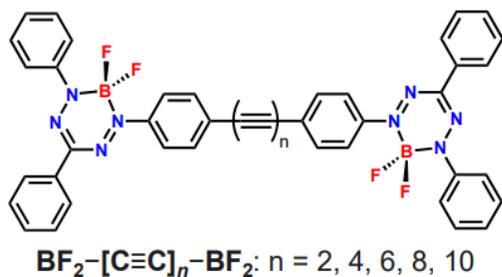
P5

## Blending the Optical and Redox Properties of Oligoynes and Boron Difluoride Formazanates

Erin L. Cotterill, Jasveer S. Dhindsa, Francis L. Buguis, Michael Anghel, Paul D. Boyle, and Joe B. Gilroy\*

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Oligoynes and polyynes consist of alternating single and triple bonds that form 1-dimensional chains of conjugated *sp*-hybridized carbon atoms.<sup>1</sup> The stability of these chains decreases rapidly with increasing chain length beyond only a few repeating units.<sup>1</sup> Bulky end-cap groups have been employed to allow for the characterization and isolation of oligoynes, while not contributing significantly to their physical properties.<sup>1</sup> In this study, boron difluoride formazanate dyes (**BF**<sub>2</sub>) of chelating *N*-donor ligands are utilized as end-caps as they have unique redox properties<sup>2</sup> and desirable applications in organic photovoltaic cells<sup>3</sup> and fluorescence cell-imaging tools.<sup>4</sup> Symmetric (**BF**<sub>2</sub>-[C≡C]<sub>*n*</sub>-**BF**<sub>2</sub>) and asymmetric (**BF**<sub>2</sub>-[C≡C]<sub>*n*</sub>-**Si**(*i*Pr)<sub>3</sub>) families of oligoynes containing up to 10 alkyne units were synthesized.<sup>5</sup> These stable oligoynes possess a blend of optical and redox properties that cannot be achieved by either oligoynes or **BF**<sub>2</sub> formazanates individually (*e.g.*, panchromatic absorption, multiple and tunable reversible redox waves). This research provides insight into the tunable optoelectronic properties of oligoynes using functional end-caps for potential development in organic electronics.



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P6

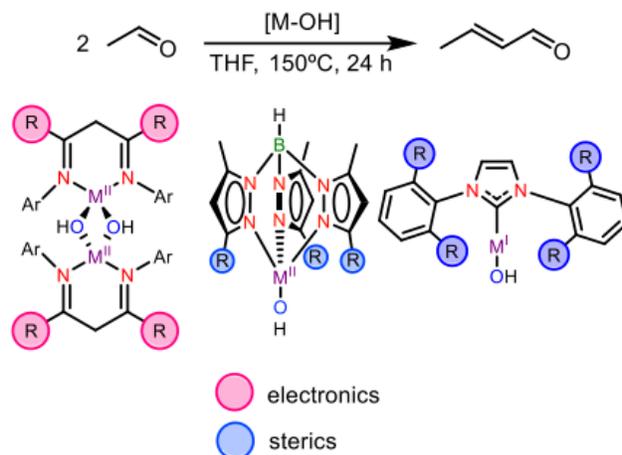
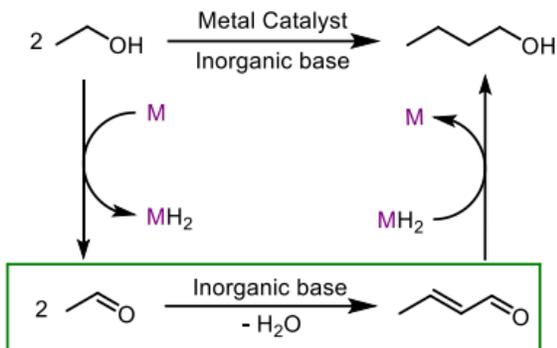
## Catalytic Activation of O-H Bonds for the Upgrading of Ethanol to Butanol

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\*jones@chem.rochester.edu

The conversion of ethanol to butanol is industrially relevant, since gasoline is usually doped with bioethanol, obtained from the fermentation of corn. However, there are certain drawbacks of using ethanol as a biofuel, mainly because of its miscibility with water. That leads to separation problems and possible motor corrosion. Because of these issues, researchers have turned to higher chained alcohols, specifically 1-butanol for gasoline doping, since it is not miscible with water and has a higher energy density than ethanol, comparable to gasoline. In particular, the Guerbet reaction describes the upgrading of ethanol using a metal catalyst and an inorganic base. While much research has been done to improve this process, the lack of selectivity and the full understanding of the mechanism for this transformation arise as the two main problems for this reaction. Wanting to mediate these problems, our group is focused on developing a system for the aldol condensation of acetaldehyde to crotonaldehyde by using sterically-hindered organometallic bases to promote overall selectivity. 1,3-diketimines, N-heterocycle carbenes (NHCs), and trispyrazolylborate (KTp) ligands are being investigated as potential bases.



P7

**“The Easter Egg Project”: Macrocyclic Inclusion Complex of Qubits**

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Quantum computation (QC) promises to revolutionize our technological capabilities. However, society is a long way from the ubiquitous use of quantum devices, mainly due to the lack of appropriate materials that can meet the required design principles. Recent advances focus primarily on determining the suitability of different classes of qubit candidates to address the two largest problems faced in QC: decoherence and scalability. Molecular spin-based qubits are promising candidates for QC research because of their synthetic tunability and addressability via microwave frequencies. While decoherence caused by nuclear spin has been effectively reduced through design principles, other sources of decoherence affects the use of spin-based qubits in QC.

Herein, we demonstrate progress toward the design and synthesis of novel macrocyclic inclusion complexes of molecular spin-based qubits. We discuss how the formation of inclusion complexes may limit decoherence caused by weak intermolecular interactions, such as magnetic dipolar interactions and vibrational interactions in the crystal lattice.

P8

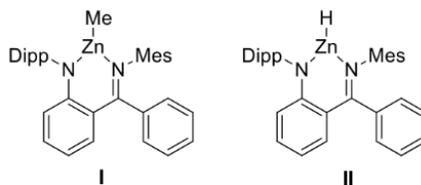
### Zinc – catalyzed reduction of N - heterocycles

Dinmukhamed Shakhman, Georgii I. Nikonov\*

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Catalytic reduction of N-heteroaromatics under mild conditions is a desired transformation for both pharmaceutical and agrochemical industries<sup>1,2</sup>.

Novel bidentate amine-imine, and amido-imine ligands have been synthesized. The former species was reacted with  $ZnMe_2$  to generate a zinc methyl complex **I**. The compound was fully characterized by  $^1H$  NMR and X-ray spectroscopy. The zinc methyl complex demonstrated a rather limited catalytic activity in hydroboration and hydrosilylation of N-heterocycles. Consequently, a new zinc hydride complex **II** was synthesized using the amido-imine ligand as a precursor. A series of nitrogen heteroaromatics were successfully hydroborated using catalytic amounts of the zinc hydride species. Deuterium – labeling experiments, and kinetic studies allowed to get insights into the reaction mechanism. It was proposed that the hydride transfer proceeds via a six – membered transition state orchestrated by the Lewis acidic zinc – hydride complex.



Dipp = 2,6-diisopropylphenyl  
Mes = mesityl

P9

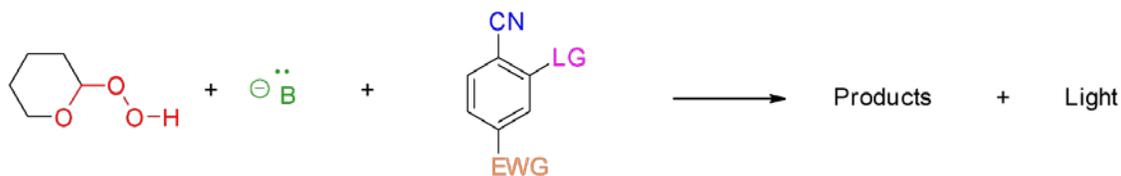
### Discovery and Investigation of a Novel Chemiluminescent Reaction

Lana K. Hiscock, Joshua LeDrew, Louise N. Dawe, and Kenneth E. Maly\*

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Chemiluminescence is a phenomenon wherein light is produced during a chemical reaction, *i.e.*, one of the reaction products is light. Through work in our lab we have discovered, rather serendipitously, a novel chemiluminescent reaction involving the action of basic alkyl ether hydroperoxides on 1-cyano-2-fluoro-substituted arenes bearing an electron withdrawing substituent. These reactions emit intense chemiluminescence, the wavelength of which is dependent on the structure of the arene substrate. Interestingly, the chemiluminescence has been shown to be highly selective towards alkyl ether hydroperoxides, with other peroxy species showing no activity. This presentation will discuss the relevant arene substrate scope, attempts at utilising the reaction as a peroxide sensor, and advances towards understanding the reaction mechanism.



P10

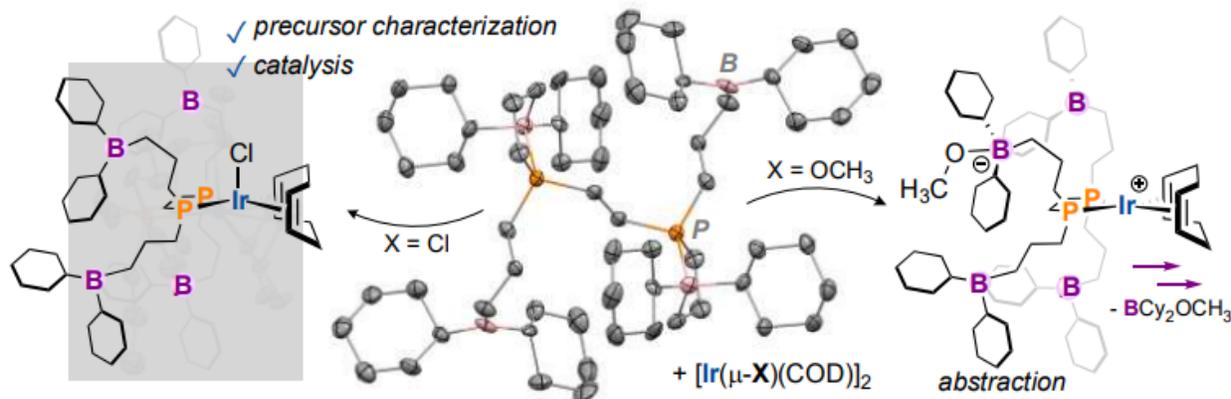
## Iridium Diphosphine Complexes Featuring Pendant Lewis Acids: Efforts Toward Selective Heteroarene Borylation

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Site selectivity in heteroarene borylation represents one means to access C-C bonds, of relevance to fine chemical synthesis. Our group is interested in the design of diphosphine ligands having a Lewis acidic secondary coordination sphere (SCS) *e.g.*, 1,2-bis[di(3-dicyclohexylboraneyl)propylphosphino]ethane ( $P_2B^{Cy}_4$ ), which has been shown to interact with Lewis basic substrates.<sup>1,2</sup> Literature precedent has shown iridium to be efficient in heteroarene borylation – we wondered if iridium compounds having a Lewis acidic secondary coordination sphere would promote selectivity in C-H borylation (i.e., activation of one C-H heteroarene bond preferentially).<sup>3</sup> With an eye towards achieving such reactivity, a number of iridium diphosphine complexes were prepared, characterized and tested in the borylation of 2-methylpyridine. These results (and other) studies using the aforementioned  $P_2B^{Cy}_4$  ligand, including some cross-coupling reactivity between nickel and gold complexes will be shared.<sup>4</sup>

### Exploring secondary-sphere boron effects for heteroarene borylation



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P11

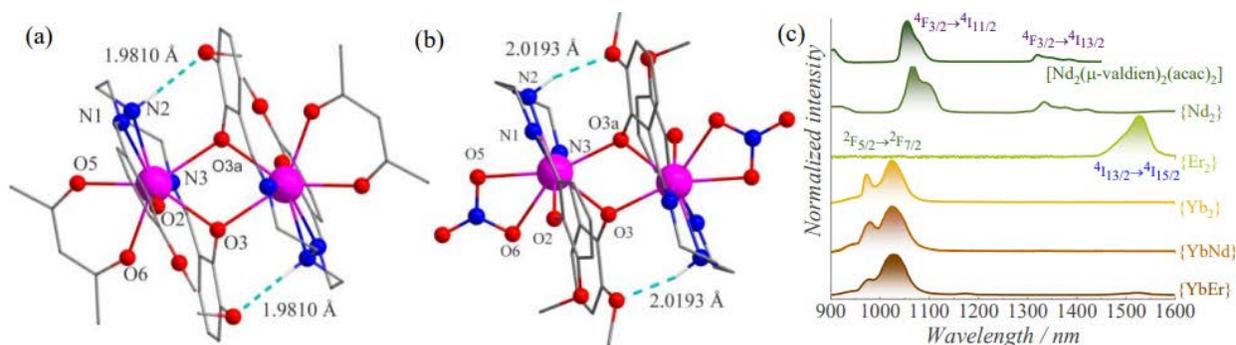
## Near-infrared luminescence of bimetallic Ln<sup>III</sup> complexes bridged by a Schiff base ligand

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Near-infrared (NIR) emission of lanthanide complexes (Ln<sup>III</sup>) have been investigated for integrated optics,<sup>1</sup> NIR fluorescence imaging,<sup>2</sup> and luminescent thermometry,<sup>3</sup> yet, coordinated water molecules usually found in such systems systematically quench the luminescence. Herein, NIR-emitting luminescent bimetallic complexes based on [Nd<sub>2</sub>(μ-valdien)<sub>2</sub>(acac)<sub>2</sub>] or [Ln<sub>2</sub>(μ-valdien)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] - Ln<sub>2</sub> = {Yb<sub>2</sub>}, {Nd<sub>2</sub>}, {Er<sub>2</sub>}, {YbNd}, {YbEr}, acac- = acetylacetonate, valdien<sup>2-</sup> = (N1,N3-bis(3- methoxysalicylidene)diethylenetriamine) - and lacking coordinated water molecules are presented, Figure 1(a) and (b). Upon 250 – 550 nm excitation, Figure 1(c), all homobimetallic complexes display intense NIR emission characteristic of intraconfigurational [4f<sup>n</sup>] Ln<sup>III</sup> transitions while for the {YbEr} composition, both Ln<sup>III</sup> emissions were noticed, and for the {YbNd} system, only the Yb<sup>III</sup> emission was detected due to Nd<sup>III</sup> -to-Yb<sup>III</sup> energy transfe



**Figure 1.** Molecular structure of (a) [Nd<sub>2</sub>(μ-valdien)<sub>2</sub>(acac)<sub>2</sub>] and (b) [Er<sub>2</sub>(μ-valdien)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]. C = light grey, O = red, N = blue, Ln = pink (hydrogen atoms have been omitted for the sake of clarity); dotted blue lines represent the intramolecular H-bonds. (c) Solid-state (298 K) emission spectra ( $\lambda_{exc} = 395$  nm) of complexes.

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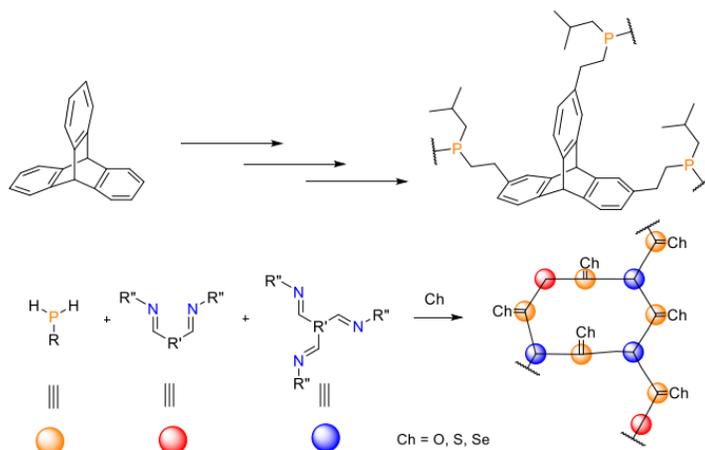
P12

## Design and Synthesis of Tunable 2D and 3D Heteroatom-Rich Polymer Networks for Heavy Metal Sequestration

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The efficient removal of heavy metals from wastewater is a central issue for the sustainability of life, due toxic heavy metal accumulation in soils, plants, and animals must be prevented. This is especially relevant for the nuclear waste industry where radioactive contaminants containing for example, beryllium, iron, cobalt, strontium, and uranium ions are produced and need to be disposed of or contained. This study aims to construct new heteroatom-rich polymer networks with tunable porosity and large surface areas to maximize metal sequestration. Triptycene is a promising candidate because this molecule offers intrinsic internal free volume along with the potential of 3 points of growth that ensures the generation of a 3D polymer network. The installation of heteroatom-rich species on the polymer backbone can be accomplished through a two or three component polymer synthesis of primary phosphine with a triptycene bearing three olefin substituents or primary phosphine chalcogenides and di or tri-imines to build poly- $\alpha$ -amino phosphine chalcogenide. With these techniques in tandem, our method aims to build 2D or 3D heteroatom-rich polymers networks that will act as membranes for heavy atom sequestration in wastewater.



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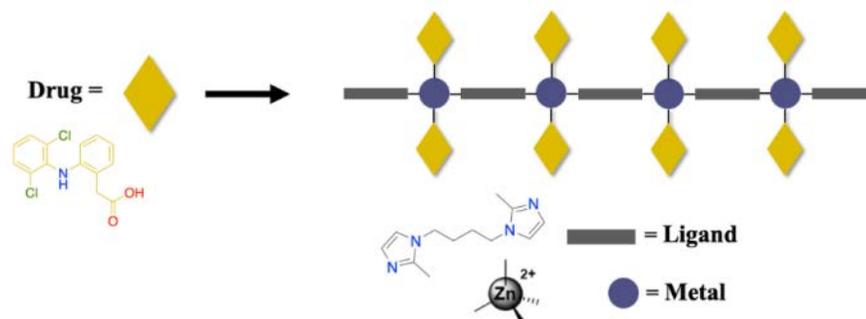
P13

## Therapeutic Coordination Polymers for Controlled Drug Release

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The development of new pharmaceuticals for medical treatments is a growing field of research. However, effective drug-release materials can improve the therapeutic effect of already available drugs by controlling how fast these drugs are released. Current materials being explored struggle to achieve good control over drug release kinetics<sup>1</sup>. My research focuses on non-steroidal anti-inflammatory drugs (NSAIDs) that are conventionally associated with an increased risk of serious gastrointestinal events<sup>2</sup>. Being able to directly target the anti-inflammatory effect of fast-dissolving NSAIDs via medical implants and sustain their release would greatly reduce the risk of adverse side effects in patients while delivering pain relief. This presentation is focused on extended-release systems based on Therapeutic Coordination Polymers (TCPs), which slowly release drugs over an extended period. Incorporation of NSAIDs directly into TCPs allows the drug release rate to be dependent on the degradation and allows the rate of release to be controlled. The single crystal structures and degradation properties of these newly synthesized TCPs in simulated body fluid will be explored.



**Figure 1.** TCP framework for extended-release systems.

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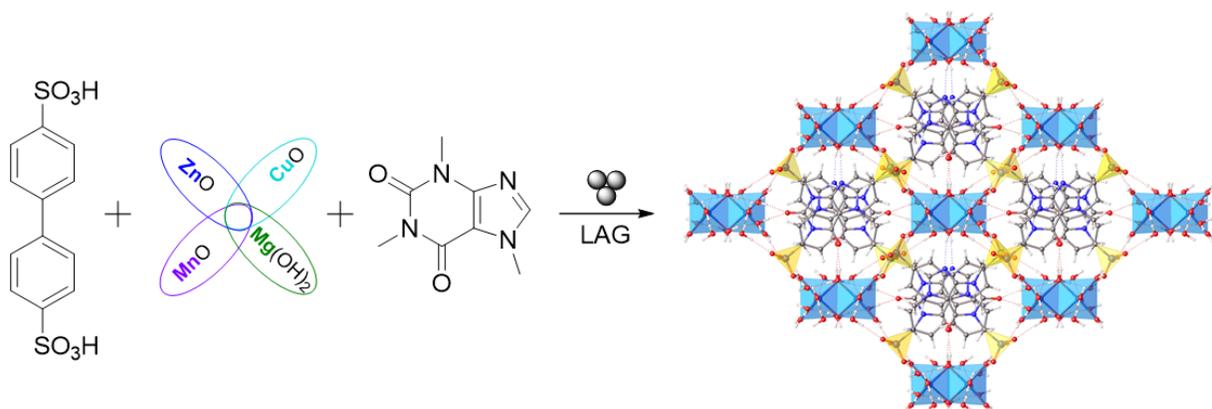
P14

## Isomorphism in the ionic co-crystals of caffeine based on the metal sulfonates

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The term “isomorphism” was originally introduced by German chemist Eilhard Mitscherlich and was used to describe the crystals of the same shape but different chemical composition.<sup>1</sup> Later, Goldschmidt demonstrated that isomorphous crystals retain their lattice symmetry while alike atoms/ions can be substituted in certain ratios, forming so-called solid solutions. Given the ability to form alternative distributions of atoms/ions in the lattice, solid solutions exhibit strong correlations between their composition and physical properties. Application of the principles of isomorphism towards the design of pharmaceutical co-crystals opens the door to fine tuning of their physiochemical properties (e.g. solubility, intrinsic dissolution rates, and bioavailability). In this work, we report new families of isomorphous ionic co-crystals of caffeine with hydrated  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  cations and 4,4'-diphenylsulfonate anions.  $\text{Mg}^{2+}$  and  $\text{Mn}^{2+}$  phases crystallize in space group  $Cc$  and exhibit a wide isomorphous capacity, while  $\text{Zn}^{2+}$  phase ( $P2_1/n$ ) demonstrates a modest mixing coefficient with  $\text{Mg}^{2+}$  and  $\text{Mn}^{2+}$ . Furthermore Jahn-Teller distortion of hydrated  $\text{Cu}^{2+}$  ions leads to a unique structure of lower symmetry ( $P-1$ ).



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P15

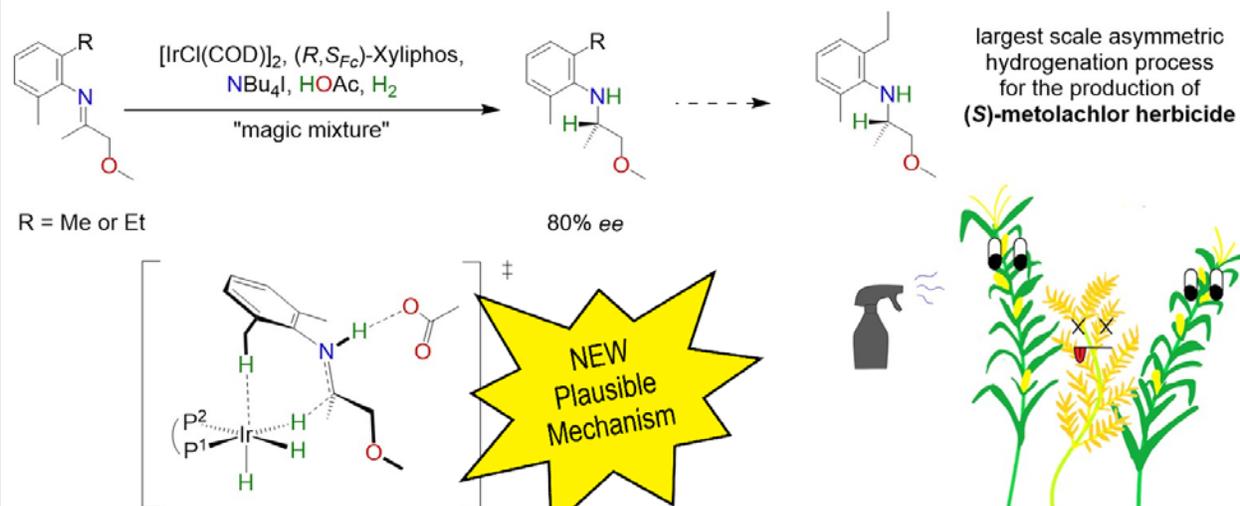
## An Outer-Sphere Mechanism for the Iridium-Catalyzed Asymmetric Hydrogenation of the *N*-Aryl Imine in the (*S*)-Metolachlor Process

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The hydrogenation of *N*-(2-ethyl-6-methylphenyl)-1-methoxypropan-2-imine is the largest scale asymmetric catalytic process for the industrial production of (*S*)-metolachlor herbicide. The challenging reduction across the sterically crowded carbon-nitrogen double bond was achieved by Ciba-Geigy (Syngenta) using an iridium-Josiphos catalyst in the presence of iodide, acetic acid, and hydrogen gas.<sup>1</sup> Despite the success of this “magic mixture”, the catalytic system is not well-defined. We recently reported a proton-first outer-sphere mechanism based on density functional theory that is consistent with the experimentally observed activity and selectivity of the industrial process.<sup>2</sup> The study found catalytically active intermediates involving five-coordinate iridium-hydride complexes, and transition states featuring acetate-assisted dihydrogen splitting and hydride transfer directed by an intermolecular C-H $\cdots$ Ir interaction.



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P16

**Electrochemical methane production driven by self-assembled hydrophobic complexes at the gas-liquid-solid interface**

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Greenhouse gas emissions, such as CO<sub>2</sub> emissions, are a global issue that needs a solution to be discovered so global warming and climate change can stop damaging the environment. Here we investigate the use of molecular catalysts, such as transition metal polypyridine complexes, coupled to gas diffusion electrodes (GDE) with the potential for high efficiencies and product selectivity. Particularly, the synthesis of a hydrophobic terpyridine ligand by introducing perfluorinated alkyl chains was done which was then complexed to a transition metal such as cobalt. Due to the hydrophobic nature of this catalyst, it can be easily integrated onto the GDEs hydrophobic layer as well as promote activity towards CO<sub>2</sub> by suppressing competing reactions like hydrogen evolution (HER). Additionally, with the aid of *in-situ* techniques further insight into the reaction mechanism and pathways for CO<sub>2</sub> reduction was observed through the use of Raman and FTIR spectroscopy.

P17

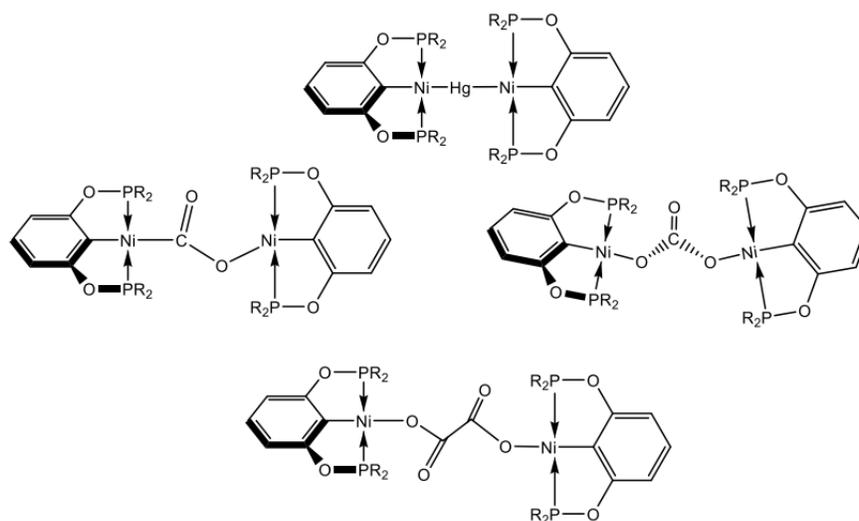
## A Trinuclear Complex Featuring A Central Ni-Hg-Ni Core: What Do We Know About Ni-Hg-Ni Interactions & How Does the Ni-Hg Bond Influence the Reactivities of Nickel ?

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Compounds possessing direct bonding interactions between mercury and transition metals are of interest due to the intriguing and ambiguous nature of their bonding interactions, as well as their reactivities. We have prepared such a compound that features a trinuclear Ni-Hg-Ni core stabilized by two pincer-type POCOP ligands. This presentation will: describe the synthesis and structure of this complex; offer some ideas on the character of Ni-Hg interactions; discuss how these might be affecting the reactivities of the nickel centres with various reagents. The reactivity observed with CO<sub>2</sub> is of particular interest not only because of the practical importance of CO<sub>2</sub> activation chemistry, but also because the rare products and intermediates that our reactivity studies have afforded can enrich our understanding of organonickel chemistry.



P18

### **Monitoring Guaiacol Nitration by UV-Vis Spectroscopy**

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Guaiacol (2-methoxyphenol, GUA) is a biomass burning pollutant that forms nitroguaiacol (NG) derivatives (4NG, 5NG, 6NG, DNG) in the atmosphere and re-distributes into the environment. NGs contribute to brown carbons that alter the climate and are hazardous for human health and aquatic systems<sup>1</sup>. The mechanism of GUA nitration and its monitoring is of fundamental as well as environmental significance. The nitration of GUA in aqueous solution was optimized. The reaction was performed in the absence and presence of Fe(III) metal ions. The nitration reaction was monitored by using UV-Vis spectroscopy, and 4NG was determined to be a major nitration product.

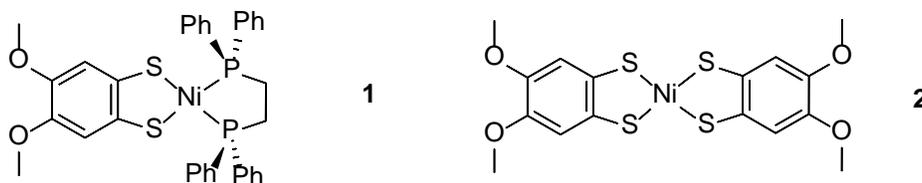
P19

**Phosphine-effects on the Oxidative Addition Chemistry of bis(4,5-dimethoxybenzo)-1, 2, 5,6-tetrathiocin with Ni(COD)<sub>2</sub>**

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The outcome of oxidative addition of bis(4, 5-dimethoxybenzo)-1,2,5,6-tetrathiocin, (dmobdt)<sub>2</sub>, to zero-valent Ni(COD)<sub>2</sub> under microwave conditions is sensitive to the nature of phosphine co-ligands present. Previously, reaction of Ni(COD)<sub>2</sub> with the chelating phosphine dppe was shown to afford the square planar Ni(II) complex Ni(dmobdt)(dppe) (**1**, Figure 1).<sup>1</sup> The current study explores the role of phosphines in modifying the outcome of the reaction chemistry. In some cases, the formal Ni(IV) complex, Ni(dmobdt)<sub>2</sub> (**2**), could be isolated. The crystal structure and electronic structure of **2** is described.



**Figure 1** Molecular structure of Ni(dmobdt)(dppe) (left) and Ni(dmobdt)<sub>2</sub> (right)

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P20

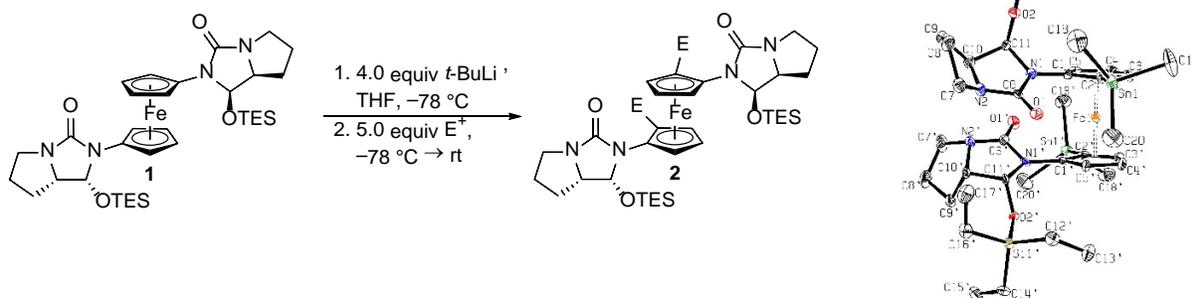
## Stereoselective Synthesis of 1,1',2,2'-Tetrasubstituted Ferrocenes by Double Lithiation of a 1,1'-Disubstituted Ferrocenyl Pyrroloimidazolone

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A 1,1'-disubstituted ferrocene bearing two pyrroloimidazolone auxiliaries<sup>1</sup> (**1**) undergoes stereoselective double lithiation to give  $C_2$ -symmetric 1,1',2,2'-tetrasubstituted products (**2**) in high diastereomeric ratio (>95:5 dr) upon electrophile quench.<sup>2</sup> The work represents an advancement on previous syntheses of planar chiral 1,2-disubstituted ferrocenes<sup>3,4</sup> and  $\eta^6$ -arene chromium tricarbonyl complexes<sup>5</sup> using epimeric pyrroloimidazolones.



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P21

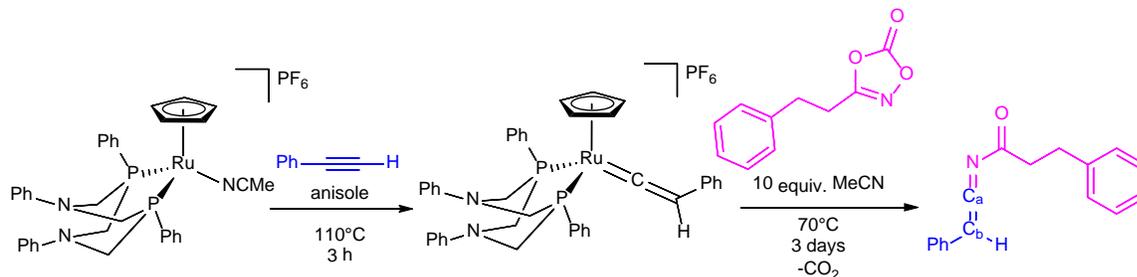
## Toward the Generation of *N*-Acyl Ketenimines from Dioxazolones

Megan A. Hoffer, Noah R. Durrell, Johanna M. Blacquiere\*

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Ketenimines are an important class of reactive species, and over the past two decades, several synthetic approaches have been developed toward their synthesis.<sup>1</sup> Ketenimines contain two cumulated reactive functionalities (N=C and C=C) which are versatile synthetic moieties for the assembly of many nitrogen-containing compounds.<sup>2</sup> Amide functionalities are common features in a variety of organic molecules.<sup>3,4</sup> However, few reliable methods to access stable and isolable *N*-acyl ketenimines exist, which could be a valuable precursor to access a wide range of amide moieties. This work explores a novel ruthenium-metal complex mediated route towards the synthesis of a variety of *N*-acyl ketenimines with different acyl functionalities through the combination of dioxazolones with phenyl acetylene. The moderately electron poor ruthenium complex, [Ru(Cp)(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(MeCN)]PF<sub>6</sub>, allows for generation of a vinylidene on reaction with phenyl acetylene. This intermediate reacts with a dioxazolone to afford a new organic product that is tentatively assigned as an *N*-acylketenimine based on <sup>1</sup>H NMR spectroscopy. Vinylidene reactivity and organic product characterization will be the focus of this poster.



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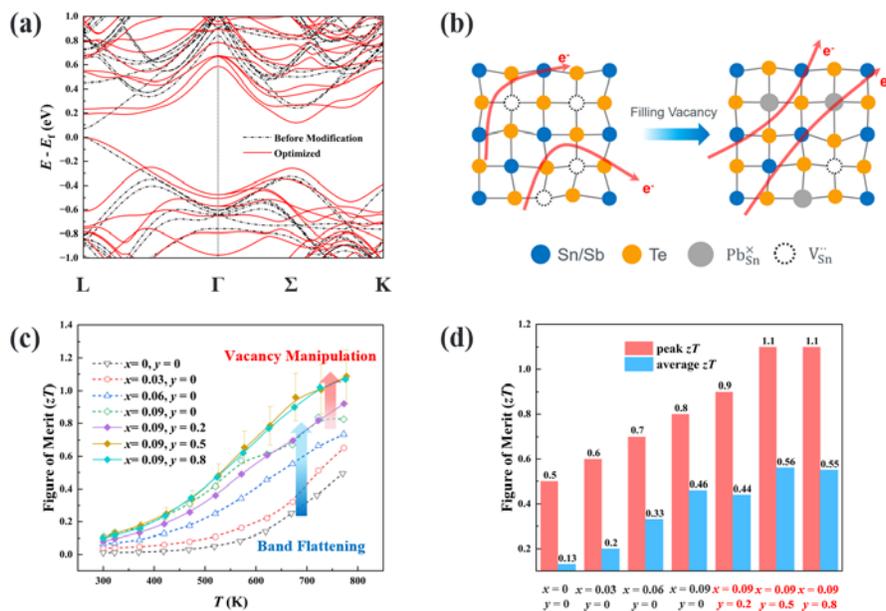
## Band and vacancy engineering in SnTe to improve its thermoelectric performance

Zan Yang, Evan Smith, Yu-Chih Tseng, Kamil Ciesielski, Sergei Novikov, Eric Toberer, Yuyang Huang and Yuriy Mozharivskiy\*

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With the ever-increasing demand for energy in human society, the resulting environmental problems are escalating globally. Thermoelectric materials can harvest and convert waste heat energy produced from various human activities into useful electricity, and thus they have received extensive attention in recent years. SnTe is a promising analog of PbTe and has the potential to replace the toxic PbTe-based thermoelectric materials. However, its performance is limited by the large energy separation between the light hole L band and lower heavy hole  $\Sigma$  band. Despite the efforts being made to induce band convergence, the improvements are limited. In this work, the band flattening was firstly induced through  $\text{Sb}_2\text{Te}_3$  alloying (**Figure 1** (a)), which increased the density of states effective mass of the L band by 300%. The carrier mobility and lattice thermal conductivity were subsequently optimized through vacancy defect manipulation via Pb compensation (**Figure 1** (b)). Eventually, a peak  $zT$  of 1.1 at 778K and an average  $zT$  of 0.56 from 300K to 778K was achieved in  $(\text{Sn}_{0.98}\text{Ge}_{0.05}\text{Te})_{0.91}(\text{Sb}_2\text{Pb}_{0.5}\text{Te}_3)_{0.09}$ , which is one of the best SnTe-based thermoelectric systems.



**Figure 1.** (a)  $\text{Sb}_2\text{Te}_3$  alloying induces band flattening. (b) Optimizing the carrier mobility via Pb compensation. (c) Temperature-dependent  $zT$  values, and (d) peak and average  $zT$  of  $(\text{Sn}_{0.98}\text{Ge}_{0.05}\text{Te})_{1-x}(\text{Sb}_2\text{Pb}_y\text{Te}_3)_x$

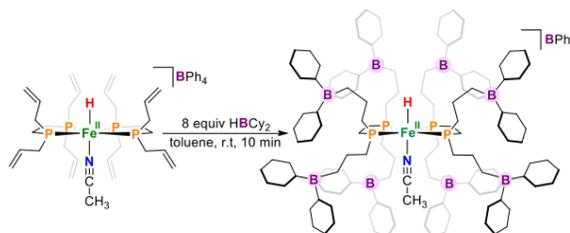
P23

## Hydride Transfer from an Octaboranyl Fe(II)—H Complex

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Metal hydrides are important intermediates in the catalytic reduction of protons and CO<sub>2</sub> as well as in the oxidation of H<sub>2</sub>.<sup>1</sup> The transfer of hydrides to organic salts is a fundamental step that is found throughout science.<sup>2</sup> Our research team has done extensive research in adding a Lewis acid into the secondary coordination sphere (SCS) of diphosphine complexes having abundant and sustainable transition metals.<sup>3–6</sup> The Lewis acidity in the SCS has been introduced into these systems by hydroboration of the allyl backbone of the phosphine ligand.<sup>3–9</sup> To examine the effect of SCS incorporation, the reactivity of [Fe(tape)<sub>2</sub>(H)(MeCN)]BPh<sub>4</sub> (tape = tetraallylphosphinoethane) is examined with known hydride acceptors (pyridinium analogues); the reactivity of this system is juxtaposed against its hydroborated analogue [Fe(P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)<sub>2</sub>(H)(MeCN)]BPh<sub>4</sub> (P<sub>2</sub>B<sup>Cy</sup><sub>4</sub> = 1,2-bis[di(3-dicyclohexylboraneyl)propylphosphino]ethane).



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P24

**Coordination Chemistry Using Strategic Design of Ligands for Switchable Properties**

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Coordination-driven self-assemblies are multifunctional molecular systems that provide an efficient method for the miniaturization of functional devices with diverse applications. Herein, the synthesis of three novel ligands is reported. These were designed using a strategy that incorporates the presence of both cationic and anionic coordination sites, and a third site for further functionalization. This design strategy has been used because there is still a knowledge gap for controlling the directionality of weak molecular forces in the presence of stronger competing forces. The structural characterization of these ligands, as well as select coordination complexes with first row transition metal cations will be discussed. Initial progress towards BODIPY analogues will also be presented.

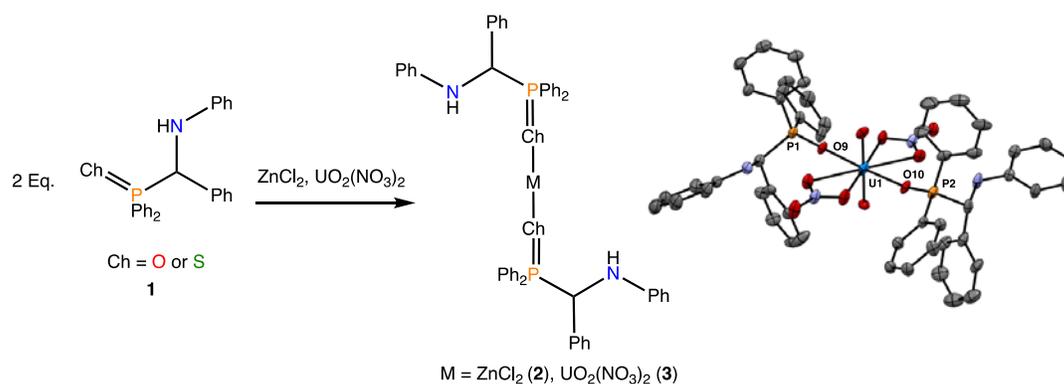
## Heavy Metal Sequestration Using an $\alpha$ -Amino Phosphine Chalcogenide Ligand

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Canada is the sixth largest producer of nuclear power in the world with six operating nuclear power plants throughout Ontario and New Brunswick.<sup>[1]</sup> Approximately 59,770 tons of heavy metal waste have been generated by reactor sites in Canada as of June 2021.<sup>[1]</sup> This work investigates the use of an  $\alpha$ -amino phosphine chalcogenide scaffold (**1**), to aid in our understanding of how to effectively remediate effluents contaminated with heavy metals such as uranium, zinc, palladium, and rhodium.<sup>[2-5]</sup> The easily prepared phosphine oxide and sulfide ligands in conjunction with the amine functional groups within the molecule offer the benefit of chelating both hard and soft metals.<sup>[2-5]</sup> These complementary Lewis basic elements make a potentially useful combination for metal sequestration.<sup>[2-5]</sup> The synthesis and characterization of the zinc (**2**), uranyl (**3**), and gold coordination complexes are explored using multinuclear NMR spectroscopy, IR spectroscopy, mass spectrometry, and X-ray crystallography. Future work aims to coordinate other relevant heavy metals such as nickel, cobalt, cadmium, and mercury. These complexes will serve as excellent models, enabling a more fulsome understanding of a macromolecular material featuring this class of ligand.



**Figure 1.** Synthesis of the  $\alpha$ -amino phosphine oxide coordination complex and X-ray crystal structure of the uranium  $\alpha$ -amino phosphine oxide complex.

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P26

**Synthesis, crystal structure, thermal and Hirshfeld surface of halogenated tin(IV) anions and pyridinium cations**

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Hybrid organic-inorganic materials combine the complementary properties of each constituent by controlling the composition and microstructure of these materials. The hybrid materials are inorganic-organic systems in which one of the constituents has a size in the nanometer range (from 0.1 to 100 nanometers). These materials have applications that cover many kinds of fields such as magnetic, optic (nonlinear optics) electroluminescence and ionic properties. Hybrid compounds based on tin and organic matrix have been the subject of several publications in recent years,. They show their importance in several fields (optical properties, thermal behavior and semiconductivity). The following salts of molecular ions were studied: Compounds (I, II and III), the formula of which are (I)  $(C_{10}H_{10}N_2)^{+2}[SnF_2Cl_4]^{2-} \cdot H_2O$ , (II)  $(C_{10}H_{10}N_2)^{2+}[SnCl_6]^{2-}$  and (III)  $(C_{15}H_{12}N_3Cl)^{2+} [SnCl_6]^{2-}$ . (I) crystallizes in the space group Pna2<sub>1</sub> (N° 33), (II) in C2/c (N° 15) and (III) in P2<sub>1</sub>/n (N° 14). The nature of the intermolecular interactions in each structure has been analysed in terms of the Hirshfeld surfaces of the cations and the anions. The thermal behavior of each compounds is reported.

P27

**Synthesis, crystal structure, thermal and Hirshfeld surface of bis(2-aminopyridinium) hexachloridostannate(IV)**

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‘Zero-dimensional’ hybrid perovskites are characterized by a structure formed of isolated inorganic anions made of octahedra or “bioctahedra” and an organic cation. They combine the properties of the organic and inorganic compounds, i.e. the flexibility of the organic part, and the thermal stability and the rigidity of the inorganic part, in a single material. By way of cooperative effects, a “synergy” is created. For example, in these hybrid materials, the organic part can have non-linear optical properties. Most of the physical properties come from the inorganic part, such as the electronic transport properties, the optical photoluminescence properties, or even magnetic properties. The synthesis and structure of the title molecular salt, bis(2-aminopyridinium) hexachloridostannate(IV),  $(C_5H_7N_2)_2[SnCl_6]$  are presented. The cation is protonated at the pyridine N atom. The N—H...Cl hydrogen bonds link the components into a three-dimensional network built up from the stacking of alternate cationic and anionic layers. The intermolecular interactions were analysed in terms of the Hirshfeld surfaces of both ions and. The thermal behaviour and the Raman spectrum are shown.

P28

### Computational study of Pd-catalyzed halogenation of 2-adamantanamine

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Selective Pd-catalyzed C-H bond activation to introduce halogen functional groups in the adamantane backbone is an interesting research topic, as halogenated adamantanes can serve as synthetic building blocks for various molecular diamondoids with diverse applications. In this poster, we will present our computational work on the selective Pd-catalyzed halogenation at the  $\gamma$ -position of 2- adamantanamine. The research plan for a computational study investigating the effects of different factors in the proposed catalytic cycle will be outlined. Our work will focus on comparing the Gibbs free energy profile to understand the role of the varied (i) halogenating agents, (ii) solvents, (iii) transient directing groups, and (iv) previously proposed addition of silver salt. In addition, we will also show how the modeled reactions of the catalytic cycle can be used to conduct a benchmarking study of selected density functional theory-based methods to generate recommendations for future work involving Pd-catalyzed C-H bond activation. It will be discussed how the insights gained from the computational work will inform our experimental work.

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P29

**Pt nanoparticles coated 2D Mg-N-C material derived from PtMg-HMT MOF for oxygen reduction reaction**

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Compared to transition metals, main-group metal-based materials lack the suitable electron orbitals required to interact with intermediates in catalysis and thus show poor catalytic activity. However, they can function as cofactors to expand their applications. In this work, we synthesized Pt nanoparticles coated on 2D layered Mg-nitrogen-carbon material (PtMg-N-C) derived from the annealing of PtMgMOF. X-ray absorption spectroscopy (XAS) reveals the Pt atoms are first anchored on Mg sites and *in situ* grow into Pt nanoparticles (NPs) supported by graphene oxide-like carbon matrix. Pt NPs, in turn, distort the original Mg local structure and coordinate the electronic structure between them. In addition, the distortion degree of Mg sites and the size of Pt NPs change with different annealing temperatures. The enhanced activity for oxygen reduction reaction is discussed and PtMg-N-C at 900 °C of annealing temperature with optimized electronic properties exhibits the highest half-wave potential. XAS is demonstrated to be a powerful tool to study the local geometric and electronic structures of materials for catalysis.

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P30

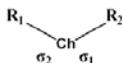
## Enhancing Se···O Chalcogen Bonding by halogenation of iso-selenazole N-oxides

Phillip L. MacDougall, Peter C. Ho, and Ignacio Vargas-Baca\*

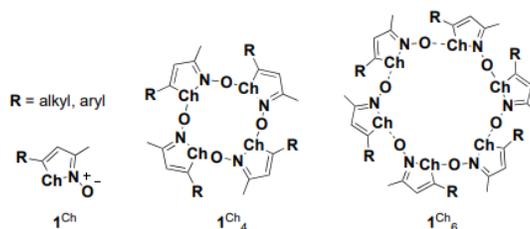
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Formally defined in 2019, Chalcogen Bonding (ChB), is a supramolecular interaction in which atoms of group-16 elements act as electrophilic sites.<sup>1</sup> The electron lone pairs of one atom (e.g., O, N) can interact with these electrophilic sites (Se/Te) and create an interaction that can be comparable in strength and reversibility to hydrogen bonding (Figure 1)<sup>2</sup>. This reversible interaction facilitates the construction of supramolecular assemblies. One of the most promising<sup>3</sup> examples of the application of these interactions is provided by iso-tellurazole N-oxides (**1<sup>Te</sup>**), which spontaneously assemble annular aggregates (**1<sup>Te</sup><sub>4</sub>**, **1<sup>Te</sup><sub>6</sub>**) that are persistent in solution and behave as actual macrocyclic molecules capable of bonding metal ions and host small molecules.<sup>4-7</sup> Se-centered ChBs are much weaker, known **1<sup>Se</sup>** derivatives form macrocycles in solution only at low temperature.<sup>7</sup> This project intends to establish strategies to strengthen the Se ChBs to build supramolecular structures at room temperature. This has been attempted by modifications of the molecular structure: introducing electron-withdrawing halogen substituents in the heterocycle, and oxidizing the chalcogen atom.



**Figure 1:** Sigma holes on a chalcogen atom (Ch = S, Se, Te) covalently bonded to two substituent groups (R1, R2).



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P31

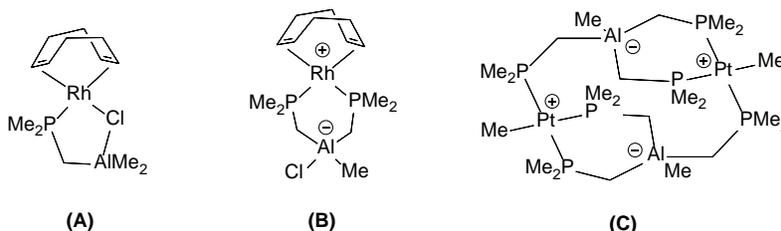
## Coordination Chemistry and Structural Rearrangements of the $\text{Me}_2\text{PCH}_2\text{AlMe}_2$ Ambiphilic Ligand<sup>1</sup>

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Transition metal complexes featuring ambiphilic ligands (that is ligands featuring one or more Lewis basic donor as well as a Lewis acidic acceptor) have been of great interest in recent years due to the ability of these ligands to influence the chemistry of the complex through various means, including modulation of the electron density at the metal centre and interaction with co-ligands. However, the majority of ambiphilic ligand transition metal complexes feature borane-based ligands, and alane-containing ligand complexes remain far rarer.<sup>2</sup> This work explores novel coordination chemistry and structural rearrangements of the  $\text{Me}_2\text{PCH}_2\text{AlMe}_2$  ( $^{\text{Me}}\text{PAI}^{\text{Me}}$ ) ligand (previously reported by Karsch<sup>3</sup>). Reactions of the  $^{\text{Me}}\text{PAI}^{\text{Me}}$  with rhodium (I), iridium (I), gold (I) and platinum (II) precursors were explored, and five distinct outcomes were found: 1) complexation of an intact  $^{\text{Me}}\text{PAI}^{\text{Me}}$  ligand (**A**), 2) *in situ* generation of a metal-coordinated bis(phosphino)aluminate ligand,  $\{\text{R}_2\text{Al}(\text{CH}_2\text{PMe}_2)_2\}^-$  (**B**), 3) formation of a dimethylphosphinomethyl ( $\text{Me}_2\text{PCH}_2^-$ ) complex, 4) chloride-methyl exchange to afford  $(\text{Me}_2\text{PCH}_2\text{AlClMe})_2$ , and 5) *in situ* generation of a metal-coordinated tris(phosphino)aluminate ligand,  $\{\text{MeAl}(\text{CH}_2\text{PMe}_2)_3\}^-$  (**C**).



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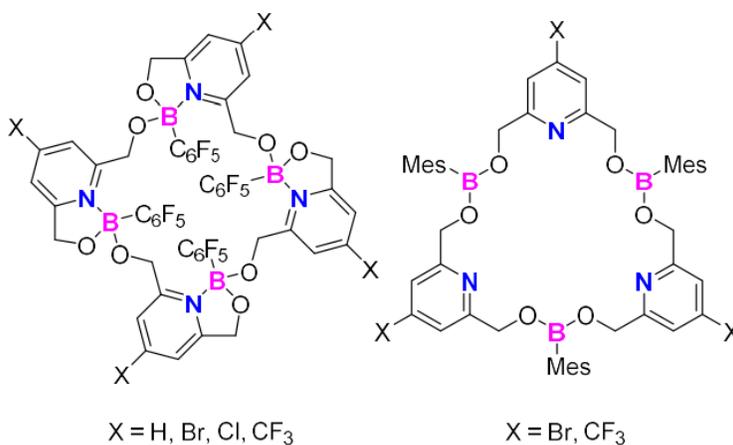
P32

## Towards macrocyclic frustrated Lewis pairs

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Frustrated Lewis pair (FLP) chemistry involving one- or two-electron donors/acceptors are well known.<sup>1-3</sup> However, examples of multi-FLP reactivity involving more than two electrons are rare.<sup>4,5</sup> In a multi-FLP system, such as a macrocycle containing multiple frustrated Lewis pairs, the catalyst will possess enhanced reactivities and efficiencies due to cooperative interactions. In this work, macrocycles with and without B–N bonds were prepared from the reaction of dihydridoboranes with 2,6-pyridinedimethanol derivatives and their subsequent reactivity with  $B(C_6F_5)_3$  and small molecules were explored.<sup>6</sup> These observations provide insights for the future design of macrocyclic FLPs for multi-electron reactions.



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P33

### **Determining Best Methods for Modeling Solvation State Organotin Complexes**

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Organotin complexes have the potential to be developed into stable long lasting polymers through the added stability provided by “hypercoordinate” bonds with ligands containing electron donating groups (N, O, P, S).<sup>[1]</sup> Computational modeling of organotin monomers can be used to help elucidate the bonding interaction as well as its behavior in solution. To determine the best functionals, basis sets and solvation models, the computational and experimental  $^{119}\text{Sn}$  NMR characterization data will be compared.<sup>[2]</sup>

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P34

### **Tin(II) Barium Fluorides and Chloride Fluorides Rich in Tin**

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Aqueous reactions between  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SnF}_2$  result in precipitation at all molar ratios of the two reactants. In an earlier work, a study of the materials formed between  $\text{SnF}_2$  and  $\text{MF}_2$  ( $\text{M} = \text{Pb}$  or alkaline earth metal fluorides) was carried out in our laboratory and resulted in a wealth of new materials. In the current work, the reaction of  $\text{SnF}_2$  with  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in aqueous solution was investigated, and the study was focused on the results obtained at low molar ratio ( $<0.5$ ) of barium chloride in the reaction mixture. For the lowest barium ratios,  $\text{BaSn}_2\text{F}_6$  was obtained. This compound had been prepared earlier by precipitation from aqueous solutions of barium nitrate and stannous fluoride. At higher barium chloride molar ratios, still lower than 0.5, a hitherto new compound,  $\text{BaSn}_2\text{Cl}_2\text{F}_4$  was obtained. Both compounds precipitate in the form of a fine powder. Neither could be recrystallized to form single crystals and both decompose on heating. The presentation will show the detailed study of the two compounds, using X-ray powder diffraction and  $^{119}\text{Sn}$  Mössbauer spectroscopy, the latter for identifying the mode of tin bonding.

P35

### Covalent and Ionic Tin(II) Barium Chloride Fluorides

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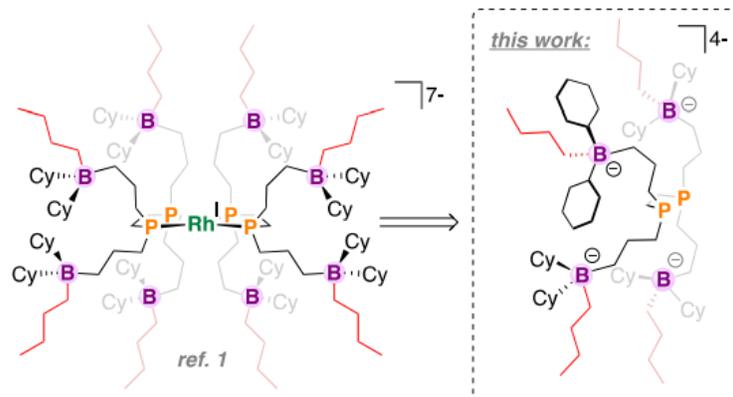
The reaction of aqueous reactions between  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SnF}_2$  result in precipitation at all molar ratios of the two reactants. In earlier works carried out in our laboratories, covalent stannous fluoride and ionic  $\text{MF}_2$  ( $M = \text{Sr}, \text{Ba}$  or  $\text{Pb}$ ) produced  $\text{MSnF}_4$  and the  $\text{Pb}_{1-x}\text{Sn}_x\text{F}_2$  high performance fluoride ion conductors. In the current work, the reaction of  $\text{SnF}_2$  with  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in aqueous solution at high molar ratio ( $X > 0.5$ ) of barium chloride in the reaction mixture was carried out. From ca.  $X = 0.5$  to  $0.85$ , the new compound  $\text{Ba}_3\text{Sn}_3\text{Cl}_4\text{F}_8 \cdot 2\text{H}_2\text{O}$  was obtained. For  $X > 0.87$ , the  $\text{Ba}_{0.85}\text{Sn}_{0.15}\text{Cl}_{1.11}\text{F}_{0.89}$  phase with the  $\text{BaClF}$  structure was formed. The latter phase is a solid solution,  $\text{Ba}_{1-x}\text{Sn}_x\text{Cl}_{1+y}\text{F}_{1-y}$ , ( $0 < x < 0.15$ ,  $-0.15 < y < 0.25$ ), hence non-stoichiometric in both metals and halogens. Both compounds precipitate in the form of a fine powder. Neither could be recrystallized to form single crystals and both decompose on heating. The presentation will show the detailed study of the two compounds, using X-ray powder diffraction and  $^{119}\text{Sn}$  Mössbauer spectroscopy for identifying the mode of tin bonding: covalent in  $\text{BaSn}_2\text{Cl}_2\text{F}_4$  and in  $\text{Ba}_3\text{Sn}_3\text{Cl}_4\text{F}_8 \cdot 2\text{H}_2\text{O}$ , and ionic in  $\text{Ba}_{0.85}\text{Sn}_{0.15}\text{Cl}_{1.11}\text{F}_{0.89}$ .

## Introducing Tetranionic Diphosphine Ligands with Borate End-Groups

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Diphosphine ligands have been used previously by the Drover group due to their versatility. They have been coordinated to multiple metals<sup>1,2,3</sup> and their reactivity in hydride transfer<sup>1</sup>, transmetalation<sup>3</sup>, oxidative addition<sup>4</sup>, and more, has been studied. Opposing charges are a simple, but effective, means to cause attraction between two molecules. In the realm of reactivity, electrostatic forces influence the likelihood of two atoms orienting themselves correctly, and closely enough to react.<sup>5</sup> The secondary coordination sphere (SCS) allows for the stabilization of small molecules and can participate in noncovalent interactions.<sup>6</sup> Hence, the addition of charged borate groups into the SCS might provide insight into the reactivity of charged diphosphine ligands. The objective of this work is to explore whether the charged ligand-metal complex will increase the rate of reaction or improve overall reactivity with charged substrates. This work expands the ligand design toolbox, by using unsaturated diphosphine ligand starting materials to construct novel charged ligand scaffolds.



**Figure 1.** Charged diphosphine ligands pertinent to this study.

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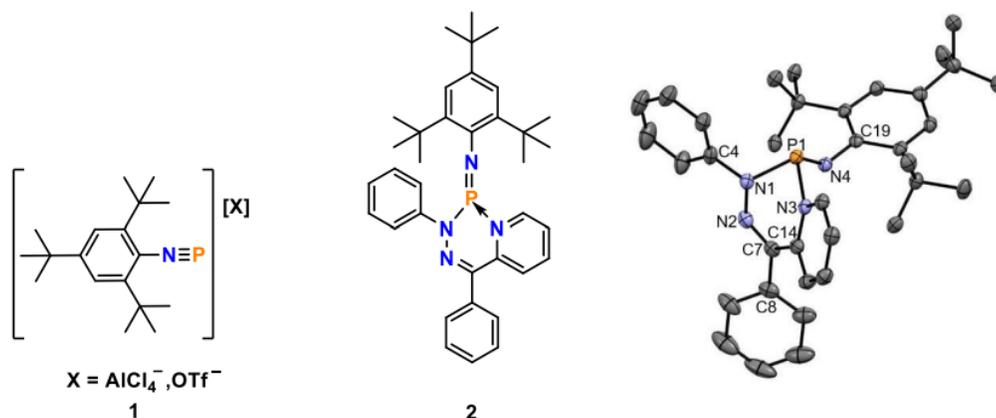
P37

## Application of Phosphadiazonium Cations in Nitrogen-based Heterocycle Chemistry

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Phosphorus mononitride was the first phosphorus containing compound detected in the interstellar medium of space in 1987. 1,2 Synthetic routes to this compound under mild conditions have remained elusive due to the inherent instability of the molecule. 3 Phosphadiazonium cations (1) capture the essence of phosphorus mononitride, as these compounds contain a  $P\equiv N$  moiety stabilized by a bulky aryl group. However, since being synthesized in the late 1980s by Niecke et al. their chemistry has remained a relatively niche field. 4,5 Burford et al. reacted phosphadiazonium cations with nitrogen-centred Lewis bases to create a wide variety of interesting adducts ( $[LPNMe_3^+][OTf^-]$ ). 6 Recent work in the Gilroy lab has focused on applying phosphadiazonium cations in heterocycle-based materials chemistry. Special emphasis has been placed on designing compatible reaction conditions for this sensitive moiety. Reacting these compounds with chelating hydrazone ligands provides an interesting avenue for growth in this niche sector of materials chemistry. Recent results towards novel heterocycles (e.g., 2) will be presented.



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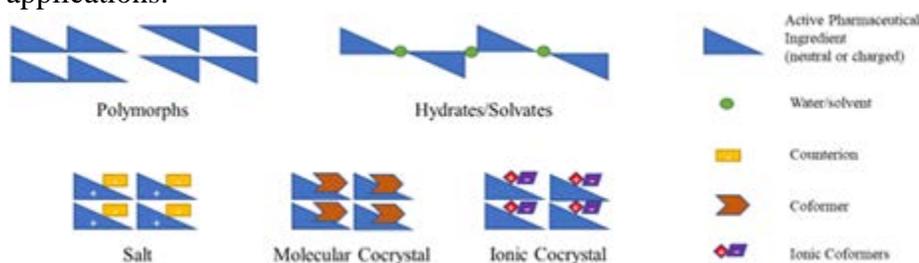
## Zinc(II) Amino Acid Complexes as Pharmaceutical Co-formers

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The development and discovery of new medicines is burdened by high costs and time-consuming research which must overcome unfavourable physiochemical properties, poor bioavailability, and narrow therapeutic windows<sup>1</sup>. Pharmaceutical drugs are often formulated into solid-state formulations, such as amorphous powders or crystalline drug polymorphs that struggle with the aforementioned properties. Recently, pharmaceutical co-crystals have been investigated to screen for and adapt new formulations of drugs that are already on the market with the aim of improving physiochemical characteristics of the active pharmaceutical ingredient (API). Co-crystals are a single crystalline phase which contains at least two principal components: i) the API and ii) a co-former which is another molecule (excluding solvates/hydrates or alternative salts). Pharmaceutical co-crystals can be used to improve the physiochemical and pharmacokinetic properties of the API by altering fundamental properties such as solubility/bioavailability, leading to desired drug release rates.

Herein, we explore the use of Zn(II) metal complexes of non-toxic amino acids as co-formers in the construction of pharmaceutical co-crystals. Our crystal engineering approach utilizes metal complexes capable of forming strong non-covalent interactions with specific drug functional groups, such as the well-known urea-carboxylate ‘synthon’. The formation of these materials is being explored by traditional crystallization methods as well as via neat and/or liquid-assisted mechanochemical approaches. The aim of our investigation is to investigate the impact metal complexes as co-formers can have on altering the release rate of APIs for rapid or controlled drug release applications.



**Fig. 1** Different forms an active pharmaceutical ingredient can crystallize in.

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P39

### **Iron-NHC Complexes for Hydrosilylation**

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Developing catalysts centered around metals that are sustainable both economically and environmentally is an important area of research. In recent years alongside the rise of green chemistry, catalysts using precious transition metals, though efficient, are understood as environmentally unfriendly. Iron has been experimented with as the center of a series of new catalysts for hydrosilylation to address this issue. As a highly abundant metal, iron seemed to be a good choice, in which its multiple oxidation states could also be taken advantage of. In our group, iron complexes of picolyl-NHCs have been used as active catalysts for hydrosilylation. This bidentate ligand can be tuned easily at the N-pendant arm on the NHC or the N-donor, thus systematic modifications at these locations can be made in the ligand structure to see different reactivities. In this work, three new heterocyclic-NHC ligands were made, and their corresponding iron (II) complexes have been developed and tested for catalytic activity in hydrosilylation. The crystal structures of the complexes were obtained, and preliminary catalytic studies will be presented

P40

## Computational study of heteroatom-vacancy centers in diamondoids: A new set of molecules with robust triplet ground states

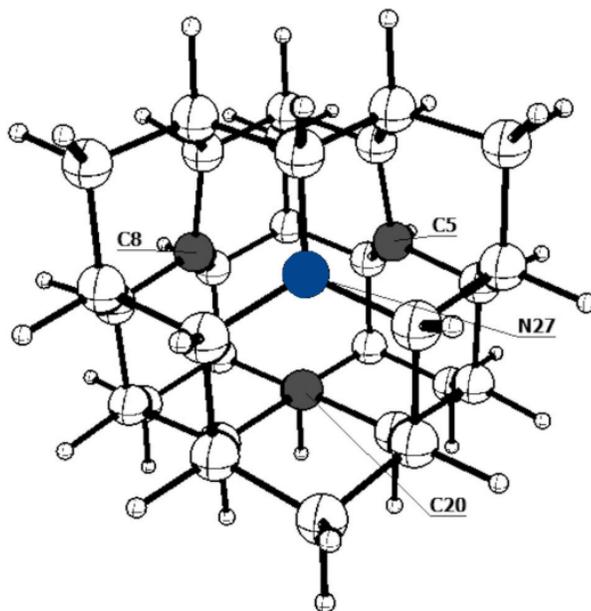
Colette Macarios<sup>1</sup>, Viki Kumar Prasad<sup>1,2</sup>, and Ulrich Fekl<sup>1,\*</sup>

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Small molecules possessing an inverted singlet-triplet energy gap are fundamentally intriguing and in high demand for applications such as quantum sensing and quantum computing. However, small molecular systems with this property that also do not possess  $\pi$ -bonds have not been studied much. In this poster, I will present the computational work undertaken to calculate the singlet-triplet energy gap performed on systems lacking  $\pi$ -bonds that draw inspiration from NV<sup>-</sup> (anionic nitrogen-vacancy) centers found in a diamond crystal lattice. Note that such NV<sup>-</sup> centers are known to possess a robust triplet ground state. I will discuss how we have investigated the possibility of heteroatom substituted diamondoids that are essentially nanoscale carbon-based building blocks with hydrogen termination as small molecule mimetics for NV<sup>-</sup> centers. My poster will show our main research findings related to the extent of inversion of the singlet-triplet energy gap observed via heteroatom functionalization in diamondoid systems.



P41

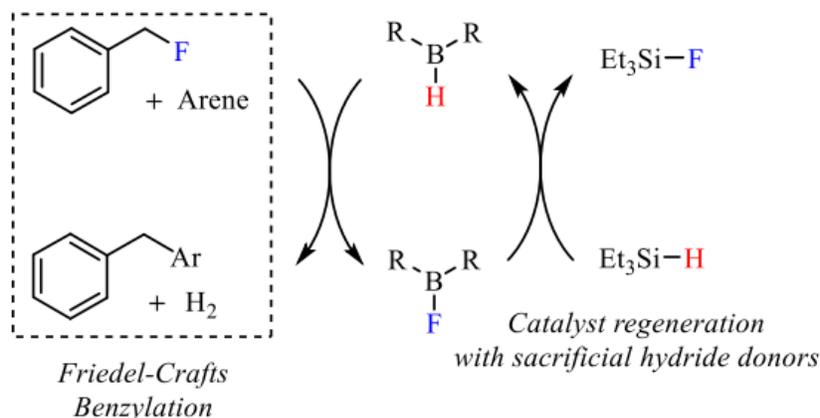
### Probing B-X to B-H conversions and applications in Friedel-Crafts catalysis

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The activation and transformation of carbon-fluorine bonds has been a continuing challenge with applications in synthesis as well as degradation of environmental pollutants.<sup>[1,2]</sup> Our group recently reported the reactivity of hydridoboranes ( $R_2BH$ ) towards C-F bonds, resulting Friedel-Crafts (FC) benzylation among other reactivity modes.<sup>[3-4]</sup> Following these stoichiometric results, we explored the reduction of haloboranes to hydridoboranes as an approach to the synthesis of  $R_2BH$  species as well as applications in catalytic FC benzylation.<sup>[5-6]</sup> Herein, we use a catalytic amount of  $[Ph_3C][B(C_6F_5)_4]$  to convert B-X to B-H bonds in the presence of silane. This was applied to several haloboranes with 9-X 9-borabicyclo[3.3.1]nonane (B-X-9-BBN, X = F, Br) and  $PhBCl_2$  requiring no initiator. The former conversion was exploited to effect catalytic FC benzylation of arenes with benzyl fluorides using a catalytic amount of B-H-9-BBN in the presence of silane. This FC catalysis was probed with a range of arenes and several benzyl fluoride derivatives. The protocol is simple, cheap and a convenient route to 1,1-diarylmethanes in good to excellent yields under mild conditions.



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## Syntheses and Structural Characterizations of Cationic Br(V) Coordination Complexes with XeF<sub>2</sub>

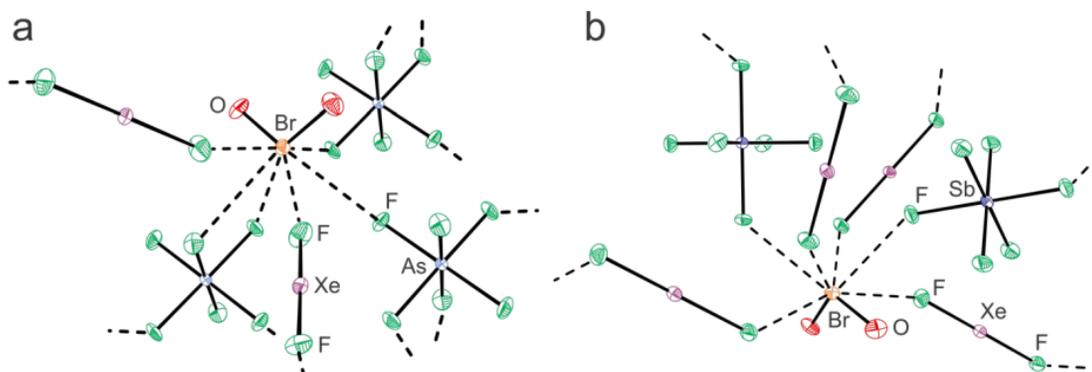
Griffin J. LaChapelle, Mark R. Bortolus, H el ene P.A. Mercier, Gary J. Schrobilgen\*

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Examples of cationic X(V) (X = halogen) coordination complexes are limited to [F<sub>2</sub>OBr(FNgF)<sub>2</sub>][AsF<sub>6</sub>] (Ng = Kr,<sup>1</sup> Xe<sup>2</sup>), [F<sub>2</sub>OBr(FXeF)][AsF<sub>6</sub>],<sup>2</sup> [O<sub>2</sub>Br(BrO<sub>2</sub>F)<sub>2</sub>][AsF<sub>6</sub>],<sup>3</sup> and [O<sub>2</sub>Cl(FXeF)<sub>2</sub>][AsF<sub>6</sub>].<sup>4</sup> Because the Lewis acid strength of [BrO<sub>2</sub>]<sup>+</sup> is only marginally less than those of [ClO<sub>2</sub>]<sup>+</sup> and [BrOF<sub>2</sub>]<sup>+</sup>, the syntheses of [O<sub>2</sub>Br(FXeF)<sub>n</sub>][PnF<sub>6</sub>] (n = 1, 2; Pn = As, Sb) were explored under reaction conditions similar to those used for [O<sub>2</sub>Cl(FXeF)<sub>2</sub>][AsF<sub>6</sub>].<sup>4</sup>

Reactions of [BrO<sub>2</sub>][PnF<sub>6</sub>] with XeF<sub>2</sub> in anhydrous HF yielded [O<sub>2</sub>Br(FXeF)<sub>n</sub>][AsF<sub>6</sub>] (n = 1, 2) and [O<sub>2</sub>Br(FXeF)<sub>2</sub>][SbF<sub>6</sub>], which were characterized by low-temperature (LT) Raman spectroscopy and LT single-crystal X-ray diffraction, provide the first examples of coordination complexes between a noble-gas difluoride and [BrO<sub>2</sub>]<sup>+</sup>. The fluorine atoms of XeF<sub>2</sub> interact with regions of high electrostatic potential on the bromine atom of [BrO<sub>2</sub>]<sup>+</sup> to form highly directional σ-hole bonds that avoid the Br(V) valence electron lone pair.



**Figure 1.** The X-ray crystal structures of (a) [O<sub>2</sub>Br(FXeF)][AsF<sub>6</sub>] showing one of two Br(V) coordination environments and (b) [O<sub>2</sub>Br(FXeF)<sub>2</sub>][SbF<sub>6</sub>]. Thermal ellipsoids are drawn at the 50% probability level.

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P43

**A Computational Study and Synthesis of Fe (II) Polymorphism for Complexes That Allow in Cross Over Mild Conditions**

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Spin cross-over (SCO) materials can change physical properties such as color, magnetic behaviour, and structural alignment by switching between high spin and low spin in response to external stimuli like temperature or electromagnetic fields. These materials offer potential applications as solid-state memory storage, molecular sensors, thin films and electroluminescent devices.<sup>1</sup> Extant computational models have poor correlation to experimental measurements, partially from not considering details of the solid phase lattice packing and orientation that may cause one polymorph to display SCO behavior, but another of the same material to be inactive.<sup>2</sup> QM analysis was performed using Gaussian to calculate the  $\Delta E_{HS/LS}$  energy gap to identify target SCO systems for synthesis. QM/MM analysis by ONIOM was employed to evaluate the solid-state of the complexes, quantifying additive weak forces in the crystal packing associated with SCO behaviour. In this presentation, we will present our efforts towards improving modelling and efforts in the synthesis of some novel SCO materials

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P44

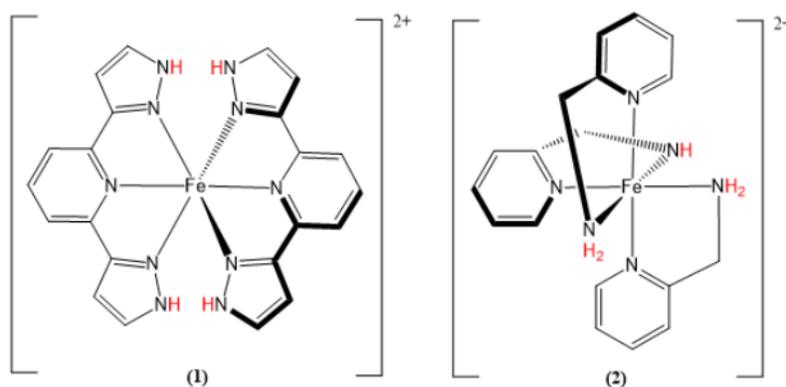
## Study of Fe(II) Spin Crossover Complexes as a Potential Temperature Probes for Magnetic Resonance Imaging (MRI)

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Spin-crossover (SCO) Fe<sup>II</sup> complexes with exchangeable NH or OH protons have demonstrated great potential as paramagnetic chemical exchange saturation transfer (PARACEST) contrast agents for magnetic resonance imaging (MRI).<sup>[1]</sup> The SCO transition between a low- (LS) and a high-spin (HS) state is a promising way of attaining bistability at the molecular level, that is intensively pursued for a broad range of potential applications.<sup>[2]</sup> In this respect, the spin-state switching which occurs due to application of external forces such as temperature, pressure and light affects the structural and physical properties of these compounds, rendering them suitable candidates for thermal sensors, switches, as well as for medical diagnostic applications. The chemistry and physics of SCO materials are typically studied in the solid-state. Studies of such systems in solution are much less common, but important for biological applications. Our goal is to develop and study Fe<sup>II</sup> complexes possessing gradual SCO transitions in aqueous media within the biological window. The syntheses and studies of two SCO Fe<sup>II</sup> complexes, (1) and (2) will be presented as potential spin switchable compounds for applications in MRI thermometry.



**Figure 1:** Molecular structures of [Fe(3-bpp)<sub>2</sub>]<sup>2+</sup> (1) and [Fe(2-pic)<sub>3</sub>]<sup>2+</sup> (2).

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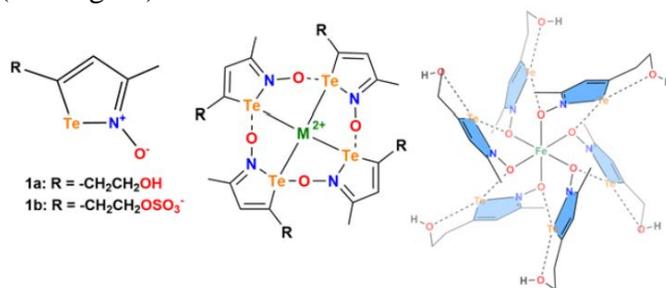
## Water-Soluble iso-Tellurazole N-oxides for Macrocyclic Complexation of Metal Ions

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The phenomenon of chalcogen bonding (ChB) has led a rapidly expanding field of supramolecular chemistry. As bonding models for this interaction are now well-established, the focus has turned into applications and the development of new supramolecular building blocks<sup>1-3</sup>. Many molecules are capable of undergoing ChB in the solid state but iso-tellurazole *N*-oxides (**1**) are unique in the fact that they spontaneously assemble annular aggregates that exist in solution<sup>4-6</sup>. These macrocycles are able to host small molecules, and coordinate to d-block metal ions<sup>4,7,8</sup>. Iso-tellurazole *N*-oxides and their complexes are fairly non-polar molecules, which constrains the development of their chemistry. We have developed iso-tellurazoles functionalized with polar groups that make them soluble in water. This strategy has permitted expanding the coordination chemistry of iso-tellurazole oxides to late light transition metal ions such as Fe(II) and Ni(II). These investigations have already led to an unusual macrocyclic hexameric ligand structure in which all the chalcogen bonds are *trans* to the Te-C bond not opposite to the Te-N bond observed in all other structures (See Figure).



Iso-tellurazole *N*-oxides and their macrocyclic tetramers/hexamers as ligands for metal ions.

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## Fluorinated amino-alkoxides as potential precursors for low-temperature thermal atomic layer deposition of copper metal

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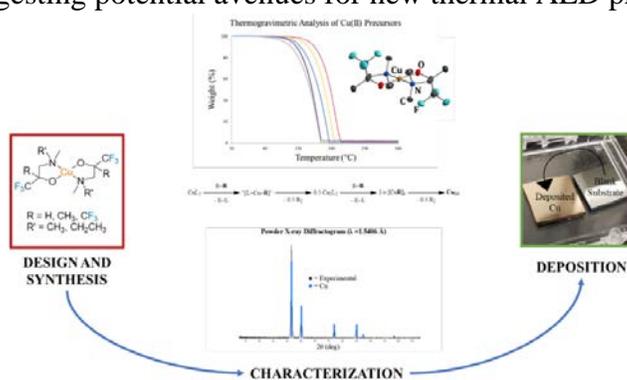
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Atomic layer deposition (ALD) is a vapour-phase technique for the deposition of (ultra-) thin films which are more uniform and conformal than those accessible via other methods. ALD relies on surface-based reactions between a precursor and a coreactant – in thermal ALD these are stable species, whereas in plasma-enhanced ALD (PEALD) one of these molecules is an unstable plasma-generated radical. The precursor and coreactant are delivered sequentially, separated by inert gas purge steps, and surface-based reactivity ensures that film growth by ALD is self-limiting, providing exceptional control over film thickness with nanometer precision.

While copper (Cu) is the primary interconnect material in integrated circuits, there are less than 15 unique methods for Cu thermal ALD, none of which afford ultra-thin films that fully combine good uniformity, conformality, conductivity, and purity.<sup>1</sup> In particular, required deposition temperatures of 100 – 500 °C often result in Cu agglomeration, ultimately leading to discontinuous films.<sup>2</sup>

We present the synthesis and characterization of Cu(II) precursors bearing fluorinated amino-alkoxide ligands, and assess their viability for low-temperature ALD of copper metal. Ligand design and synthesis is described, and the influence of ligand fluorination on the thermal properties (volatility, thermal stability, melting point) of these precursors is discussed. Solution-state studies indicate that reactivity with various coreactants – leading to metal deposition – is readily accessible, suggesting potential avenues for new thermal ALD processes.



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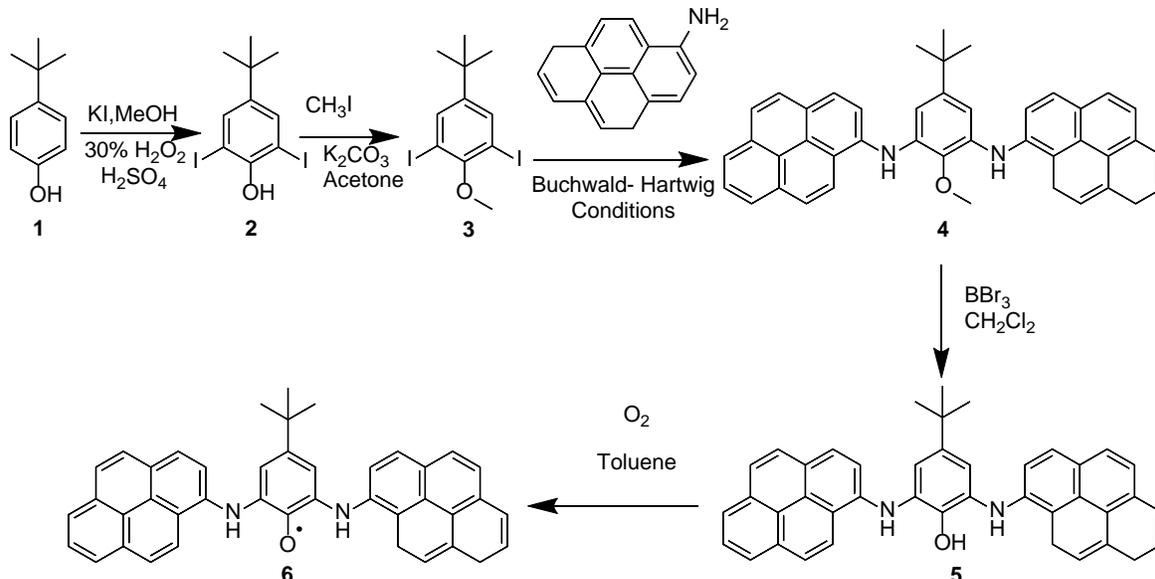
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## Synthesis and properties of a novel pi-extended phenoxyl radical

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In 2018 we reported the synthesis and structural properties of a pi-extended stable phenoxyl radical 2,6-bis-(8-quinolyl-amino)-4-*tert*-butyl-phenoxyl (BAQP) radical that was shown to undergo reversible pi-dimerization in solution.[1] In this presentation, we will report on the synthesis and properties of a pi-extended phenoxyl radical system bearing 1-aminopyrene substituents. This compound was synthesized in five steps starting from commercially available 4-*tert*-butyl phenol as shown in scheme 1. 5-(*tert*-butyl)-2-oxy-1,3-bis(1-pyrenylamino) benzene radical was obtained as green crystals suitable for x-ray crystallography. EPR spectroscopy confirmed the presence of the paramagnetic species. The UV-Vis-NIR spectrum of the radical reveals peaks at 1150 nm and 650 nm that correspond to the phenoxyl radical monomer, and pi-dimer form, respectively. X-ray data shows that in solid state, the radical exists as dimer. The DFT calculations shows that dispersion interactions between the flanking rings are responsible for the stability of the pi-dimer. Solution state dimerization is currently explored through various spectroscopy methods. The emission properties of this radical are currently being explored.



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P48

## Synthetic Efforts Towards 2-Cyanobenzoselenazole, a Precursor to a Novel 1,2,3,5-Dithiadiazolyl Radical Ligand

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To continue the advancement of technologies, molecule-based materials must be developed that execute desirable functionalities, specifically magnetic properties. Single-molecule magnets are promising candidates for the design of molecule-based materials in advanced technologies due to the ability to probe magnetic properties while also considering solubility, volatility, and conductivity via structural modifications. Previous work done by the Preuss group was focused on the development of the single molecule magnet, 4-(benzothiazol-2'-yl)-1,2,3,5-dithiadiazolyl bis(1,1,1,5,5,5-hexafluoroacetato) iron(II) ((betaDTDA)Fe(II)(hfac)<sub>2</sub>), implementing the first 1,2,3,5-dithiadiazolyl (DTDA) radical ligand with a sulfur atom outside the DTDA moiety<sup>[1]</sup>. By altering the sulfur atom in the benzothiazole ring to other chalogens, specifically to a selenium atom, the ability for the complex to act as a single-molecule magnet will be positively impacted. To synthesize the selenium analogue, 4-(benzoselenazol-2-yl)-1,2,3,5-dithiadiazolyl, the novel precursor, 2-cyanobenzoselenazole must first be produced. From the nitrile derivative, the DTDA radical ligand will be synthesized through routine synthetic techniques. Pathways towards the development of 2-cyanobenzoselenazole will be presented in the ambition to produce the radical ligand, 4-(benzoselenazol-2-yl)-1,2,3,5-dithiadiazolyl.

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P49

### Copper (II) and Iron (III)-catalyzed nitration of tyrosine

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Post translational modifications like nitration are commonly observed in disease states, leading to changes in protein structure and loss of protein activity. Tyrosine nitration involves a one-step oxidation of tyrosine to form tyrosyl radical, which then produces nitrotyrosine through a diffusion-controlled reaction with nitrogen dioxide ( $\cdot\text{NO}_2$ )<sup>1,2</sup>. The nitration reaction is mediated by reactive nitrogen species such as peroxynitrite anion ( $\text{ONOO}^-$ ) and nitrogen dioxide ( $\cdot\text{NO}_2$ )<sup>1,2</sup>. Biologically abundant and redox active Cu(II) and Fe(III) ions have the ability to catalyze nitration reactions through peroxynitrite ( $\text{ONOO}^-$ ) formation<sup>3</sup>. In this work nitration reaction was monitored *in vitro* in order to synthesize nTyr in the presence of sodium nitrite and hydrogen peroxide, and compare Cu(II) versus Fe(III) catalysis. The nitration reaction was carried out in the presence of various Cu(II) and Fe(III) salts in order to investigate the role of counter anion on the reaction yield and monitored using UV-vis absorbance. The Fe(III) perchlorate catalyzed nitration of Tyr produced the greatest yield of  $81\% \pm 3\%$  while the Cu(II) perchlorate catalyzed reaction produce a yield of  $20\% \pm 8\%$ .

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P51

**Deprotonation viability and radical anion stability: Exploring 4-[2'-(5,6-difluorobenzimidazolyl)]-1,2,3,5-dithiadiazolyl as a bridging ligand**

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Molecule-based materials provide a bottom-up approach to material design that offers access to desirable properties (e.g., magnetism, conductivity, luminescence) through crystal engineering. Our group strives to probe the fundamental properties of such materials and has done extensive work on the design of 1,2,3,5-dithiadiazolyl (DTDA) radicals for use as paramagnetic ligands. Bridging paramagnetic ligands present the opportunity for coupling between two metal ion coordination centers. A potential candidate ligand is 4-(2'-benzimidazolyl)-1,2,3,5-dithiadiazolyl (HbimDTDA) which demonstrates magnetic bistability<sup>[1]</sup> and is the focus of post-synthetic modification efforts within our group. A difluorinated analogue 4-[2'-(5,6-difluorobenzimidazolyl)]-1,2,3,5-dithiadiazolyl (F<sub>2</sub>HbimDTDA) is being explored for the tunability of material properties and for a potential increase in the stability of the desired radical anion. Current work pursuing the study of 4-[2'-(5,6-difluorobenzimidazolyl)]-1,2,3,5-dithiadiazolyl (F<sub>2</sub>HbimDTDA) will be presented.

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P52

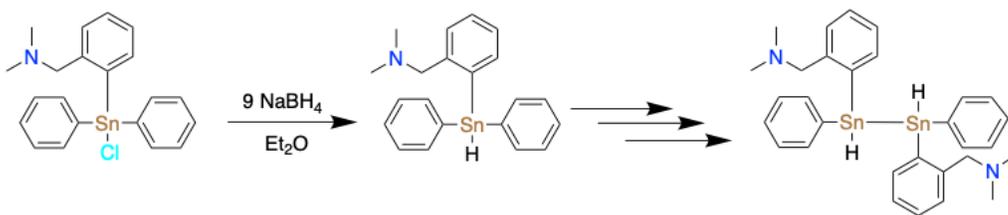
## Post-Synthetic Modification of 4-(2'-benzimidazolyl)-1,2,3,5-dithiadiazolyl in the Pursuit of Molecule-Based Materials

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The aim of my research is to synthesize and characterize novel hypercoordinate stannanes and polystannanes containing the [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]- chelating ligand. The first part of my research focused on the synthesis of organotin(IV) compound [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]-SnPh<sub>3</sub> prepared from the reaction of organolithium [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]-SnLi and Ph<sub>3</sub>SnCl. The organotin(IV) chloride, [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]-SnPh<sub>2</sub>Cl was prepared via chlorination of the triphenyl derivative. Currently, my research focuses on the synthesis of the corresponding organotin hydride [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]-SnPh<sub>2</sub>H via LiAlH<sub>4</sub>, and organotin dimer Bis-{[2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]-SnPh<sub>2</sub>} via a reaction with the hydride and Wilkinson's catalyst. The next steps of my research include the synthesis of diorganotin dichloride, Bis-{[2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]-SnPhCl}, diorganotin dibromide Bis-{[2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]-SnPhBr}, and the corresponding diorganotin dihydride Bis-{[2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]-SnPhH}. Further analysis will be completed via computational analysis using DFT level of theory with pbe1pbe method supplemented with Grimes D3 empirical dispersion and Becke-Johnson Damping (GD3BJ) as well as the LANL08d and 6-31+G (d,p) basis sets.



**Figure 1.** General scheme for the synthesis of the hypercoordinate diorganotin dihydride

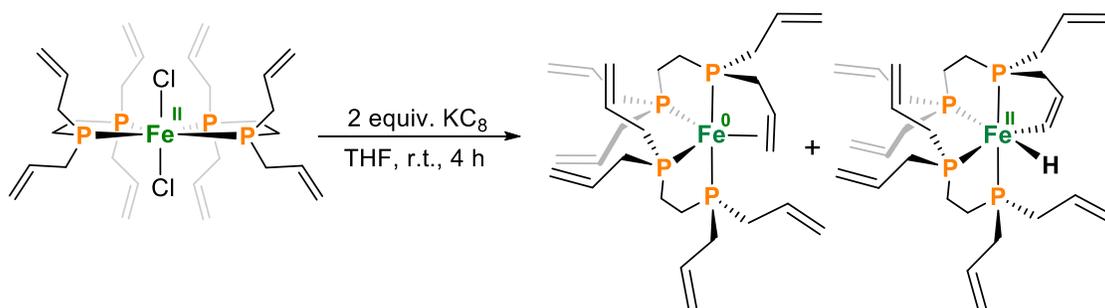
P53

## CO<sub>2</sub> Activation at Fe(0): Unraveling Secondary Coordination Sphere Effects

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In developing homogenous catalysts capable of activating and subsequently reducing CO<sub>2</sub>, coordination or interaction with a metal center is imperative.<sup>1</sup> This work aims to cooperatively activate CO<sub>2</sub> by unraveling the effects associated with installation of a Lewis acidic secondary coordination sphere (SCS).<sup>2,3</sup> This investigation follows in the footsteps of recent works highlighting the effects of intermolecular Lewis acidic stabilization of Fe-bound CO<sub>2</sub>,<sup>4</sup> and those showcasing the highly reactive nature of Fe(0) *bis*(diphosphine) compounds towards CO<sub>2</sub> activation and functionalization.<sup>5,6</sup> In order to actualize our goal of an Fe(0) species decorated with a boron-rich SCS, there are necessary precursors which require synthesis and investigation. Herein, we showcase the synthesis and characterization of an Fe(0) *bis*(tape) (tape = tetrakisallyldiphosphinoethane)<sup>7</sup> and associated metallacyclic Fe(II)—H species, whose properties counter those of similarly reported compounds;<sup>8</sup> these compounds show reactivity toward CO<sub>2</sub> and allow for the late-stage incorporation of a boron-rich SCS.



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P54

### Synthesis of Substituted Carbonate Templated Ag<sub>20</sub>-Nanoclusters for Postsynthetic Photochemical Reactions

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The field of nanocluster research continues to provide new structures of differing stoichiometries and properties. New cluster frameworks can be targeted by altering the synthetic conditions used or the stabilizing surface ligand structure. Much less focus has been on modifying cluster surfaces post-synthesis while maintaining the cluster core. Our recent efforts have been directed at preparing metal nanoclusters with reactive surface substrates to serve as templates, whose reactivity is used to alter their function post-synthesis while maintaining the core structure. Recently we targeted two atomically precise Ag<sub>20</sub> nanoclusters (NCs) platforms with 8 and 6 surface moieties based on the robust synthesis of [CO<sub>3</sub>@Ag<sub>20</sub>(*StBu*)<sub>10</sub>((NO<sub>3</sub>)<sub>8</sub>(DMF)<sub>4</sub>] [1] and subsequent substitution of nitrate moieties with functional benzoate derivatives [2]. This work expands on our recent discovery of azide modified Ag<sub>20</sub>-NCs that are capable of post-synthesis strainpromoted azide alkyne cycloaddition reactions. In this work we introduce 1) photoreactive aryl-azo-groups and 2) aryldiazirine moieties. The aryl azo-group Ag<sub>20</sub>-NC allows for a study of the photostability of these Ag-NC and to study photo switching. The aryldiazirine Ag<sub>20</sub>-NC provides a photochemical route to reactive carbenes that can be used to access cluster-surface chemistry for further modifications.

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P55

**Promotion of strong magnetic coupling in tetrazine radical-bridged Ln<sub>4</sub> metallocene complexes with a large coercive field**

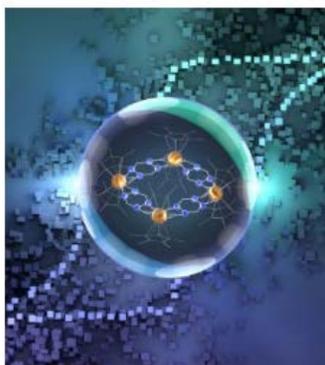
Niki Mavragani,<sup>a</sup> Dylan Errulat,<sup>a</sup> Diogo A. Gálico,<sup>a</sup> Alexandros A. Kitos,<sup>a</sup> Akseli Mansikkamäki<sup>\*b</sup> and Muralee Murugesu<sup>\*a</sup>

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Over the last years, the field of molecular magnetism has grown in fame with single-molecule magnets (SMMs) being one of the most active areas. The incorporation of paramagnetic ligands that can bridge lanthanide metallocenes has proven to be a fruitful avenue towards the isolation of strong magnetically coupled systems with enhanced SMM properties.<sup>[1]</sup> However, the ever-growing need for an organic ligand that can lead to strongly coupled polynuclear radical-bridged Ln complexes still remains. With this in mind we focused our attention on the relatively unexplored 1,2,4,5-tetrazine (tz).<sup>[2]</sup> By utilizing the high-performing {Cp\*<sub>2</sub>Ln}<sup>+</sup> (where Cp\* = pentamethylcyclopentadienyl; Ln = Dy or Gd) as building units while connecting them with tz<sup>•</sup> radical ligands, the formation of two unprecedented tetranuclear complexes [(Cp\*<sub>2</sub>Ln)<sub>4</sub>(tz<sup>•</sup>)<sub>4</sub>]·3(C<sub>6</sub>H<sub>6</sub>), **Dy<sub>4</sub>** and **Gd<sub>4</sub>**, was achieved. Through computational studies, the strong exchange coupling between the GdIII ions and the tetrazinyl ring was probed revealing  $J_{\text{Gd-tz1}} = -24 \text{ cm}^{-1}$  and  $J_{\text{Gd-tz2}} = -15 \text{ cm}^{-1}$ . Owing to this, the molecular species act as a true “giant-spin” system and promote the slow relaxation of the magnetization entirely through a thermally activated process for the **Dy<sub>4</sub>** analogue. Notably, hysteresis measurements reveal a sizeable coercive field of ~ 3 T, which makes this SMM one of the highest performing magnets in terms of magnetic hardness.



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P56

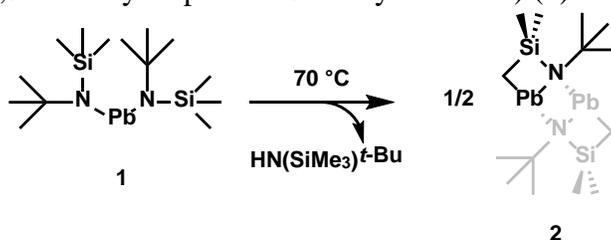
## Decomposition of a Lead(II) Silylamide to a Cyclic Alkyl Amido Plumbylene

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During our efforts to find new, volatile Pb(II) precursors for vapour deposition methods, we discovered that the acyclic diamido plumbylene lead(II) bis(*N*-*tert*-butyltrimethylsilylamide) (**1**) undergoes facile thermal decomposition into the heteroleptic cyclic (alkyl)(amido) plumbylene bis(*N*-*tert*-butyl-2-aza-3,3-dimethyl-1-plumba-3-silacyclobutane) (**2**).



Scheme 1. Thermolysis of **1** to the caaPb.

Our interest in plumbynes like **2** are as transmetalation agents for the heterocyclic ligand. We hypothesized that salt-metathesis between **2** and metal chlorides would produce similar cyclic (alkyl)(amido) metallocycles, a hypothesis that was supported by computational chemistry. There are early examples of titanium, zirconium, and hafnium complexes with a similar heterocyclic system ( $\text{CH}_2\text{Si}(\text{Me}_2)\text{NSiMe}_3$ ), and the heterocyclic  $\text{Cp}_2\text{TiCH}_2\text{Si}(\text{Me}_2)\text{NSiMe}_3$  was used as a titanium-ceramic precursor for chemical vapour deposition (CVD). However, the synthesis of these systems is unreliable.<sup>1,2</sup> As such, we further present initial reactivity studies using **2** as a transmetalation reagent to more easily access a cyclic alkyl amido system.

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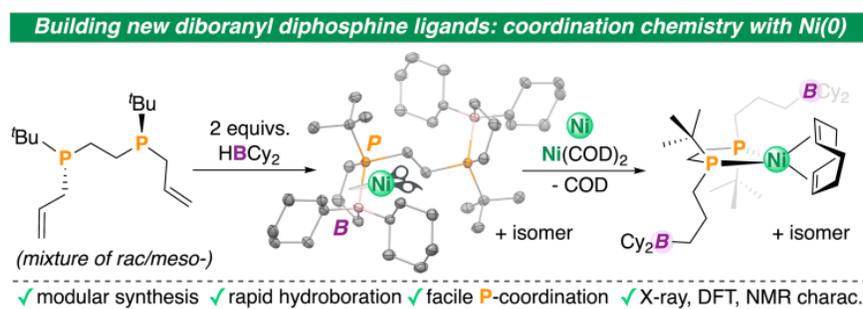
P57

## Racemic and Meso Diastereomers of a P-Chirogenic Diboranyldiphosphinoethane

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Diphosphine ligands have great promise as a supporting ligand scaffold due to an ability to not only modify their primary coordination sphere, but also their secondary coordination sphere (SCS). These changes result in significant differences in chemical reactivity for coordinated transition elements. This study focuses on the modification of a previously reported scaffold (+/-)-*rac/meso*-(*t*-Bu)CIP-CH<sub>2</sub>CH<sub>2</sub>-PCl(*t*-Bu) to create a new family of diphosphine ligands. Upon reacting this precursor with allyl magnesium chloride and subsequent hydroboration using HBCy<sub>2</sub> (Cy = cyclohexyl), a diboranyldiphosphinoethane ligand scaffold was generated, the first example in this ligand family to boast two electrophilic boranes in its SCS. This new scaffold, along with its allyl counterpart, have been appended to Ni(0) using [Ni(COD)<sub>2</sub>] (COD = 1,5-cyclooctadiene) in an attempt to determine clean methods for installation. As a result of having two stereogenic phosphorus centers, characterization required use of NMR spectroscopy, X-ray crystallography, and density functional theory (DFT) calculations.



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P58

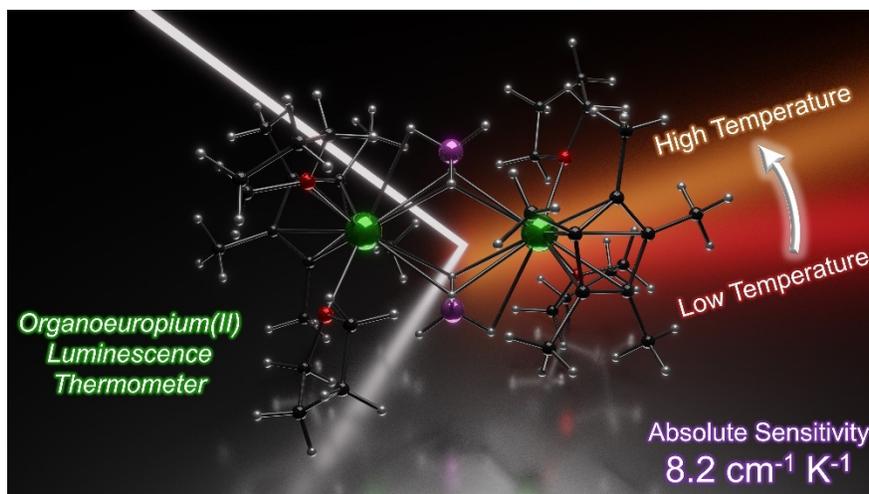
## Toward Opto-Structural Correlation to Investigate Luminescence Thermometry in an Organometallic Eu(II) Complex

Roberto M. Diaz-Rodriguez, Diogo A. Gálico, Daniel Chartrand, Elizaveta A. Suturina, and Muralee Murugesu\*

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Lanthanide-based luminescent materials have unique properties and are well-studied for many potential applications. In particular, the characteristic  $5d \rightarrow 4f$  emission of divalent lanthanide ions such as  $\text{Eu}^{\text{II}}$  allows for tunability of the emissive properties via modulation of the coordination environment. We report the synthesis and photoluminescence investigation of pentamethylcyclopentadienyleuropium(II) tetrahydroborate bis(tetrahydrofuran) dimer, the first example of an organometallic, discrete molecular  $\text{Eu}^{\text{II}}$  band-shift luminescence thermometer. The complex exhibits an absolute sensitivity of  $8.2 \text{ cm}^{-1} \text{ K}^{-1}$  at 320 K, the highest thus far observed for a lanthanide-based band-shift thermometer. Opto-structural correlation via variable-temperature single-crystal X-ray diffraction and fluorescence spectroscopy allows rationalization of the remarkable thermometric luminescence of this complex and reveals the significant potential of molecular  $\text{Eu}^{\text{II}}$  compounds in luminescence thermometry.



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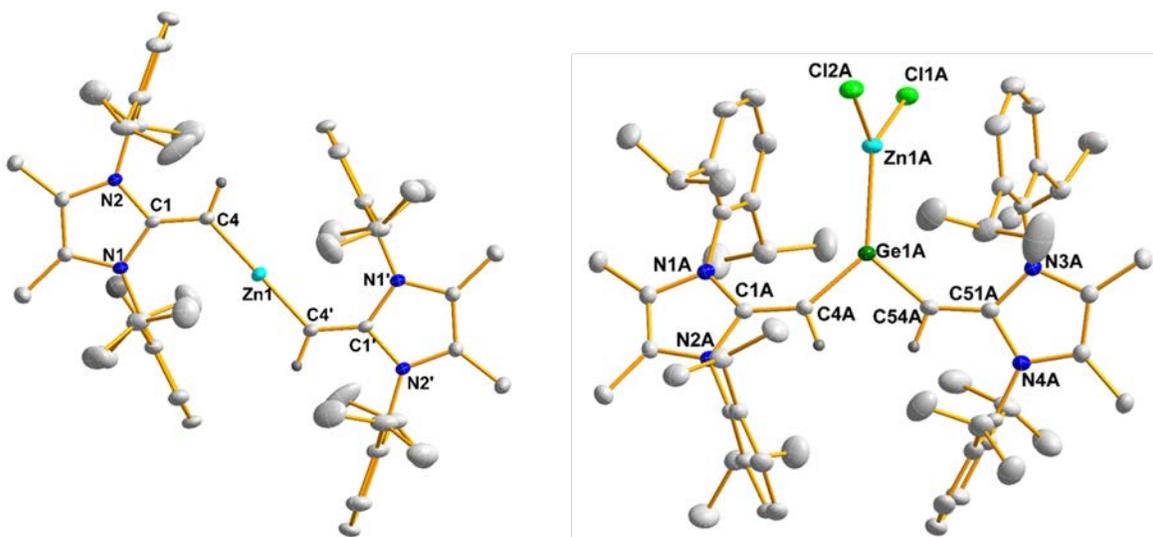
P59

## Anionic *N*-Heterocyclic Olefins (aNHOs) as Ligands for Main Group Elements and Early Transition Metals

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*N*-heterocyclic olefins (NHOs) are a class of ligand that feature a terminal exocyclic alkylidene unit appended onto an *N*-heterocyclic carbene framework. Notably, NHOs have been used as organocatalysts, as organic superbases, and as ligands in transition metal-catalyzed reactions, such as in Buchwald-Hartwig cross-coupling.<sup>1,2</sup> Recently our group found a method to access a lithiated NHO, wherein the anionic *N*-heterocyclic olefin (aNHO) unit can be used as a strongly electron-donating ligand. In this presentation, the formation of late metal and main group complexes bearing an aNHO ligand will be described, and outline the use of either salt metathesis or transmetallation to obtain the resulting low-coordinate and highly reactive aNHO complexes.<sup>2</sup> Group IV metal complexes bearing aNHO ligands are also described.<sup>3</sup>



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P60

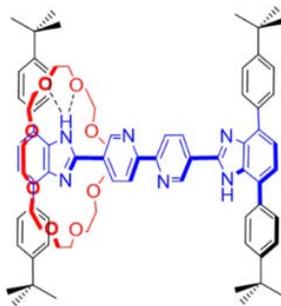
## The Dynamics of a Translationally Active Ligand Changes the Coordination Environment of Transition Metal Complexes

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The coordination sphere of a transition metal ion is typically altered by exchanging the coordinating ligands. An elegant way to ligand exchange is to exploit dynamics of a mechanically interlocked molecule (MIM). For example, we have recently reported that the rotational motion of the wheel of a [2]rotaxane can be used to "dial-up" different donor-sets of an interlocked macrocycle for coordination to a metal ion. <sup>1</sup> Herein, we describe how the ligand exchange of a transition metal complex can be achieved by using the large amplitude translational motion of a wheel of a [2]rotaxane molecular shuttle. We report on the synthesis and dynamic shuttling of a new [2]rotaxane molecular shuttle that contains both a 2,2'-bipyridine chelate as a part of a rigid, H-shaped axle and a 24- membered crown ether containing eight oxygen ethers as the wheel (Fig. 1). Initial complexation with platinum dichloride yields an unsymmetrical co-conformation of the rotaxane in which the crown ether is hydrogen bonded to a benzimidazole recognition site. This was followed by the exchange of a chloride ion with an O-donor of the crown ether which requires translational motion of the crown ether along the axle. We also show that ligand exchange in a zinc-complex of the [2]rotaxane in a coordinating solvent (DMF) can be accomplished by a molecular shuttling mechanism involving translation via coordination of the wheel to the zinc center. This concept of using the translation of wheel in a rotaxane as a translationally active ligand for ligand exchange could be an effective way to manipulate properties of a bipyridine-based metal ion complex within the realm of coordination chemistry.



**Figure 1.** A [2]rotaxane molecular shuttle with 2,2'-bipyridine as a part of the axle and a 24-crown-8 macrocycle as the wheel

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P61

**A Trivalent 4f Complex with Only Two *bis*-Silylamide Ligands Displaying Slow Relaxation of the Magnetization**

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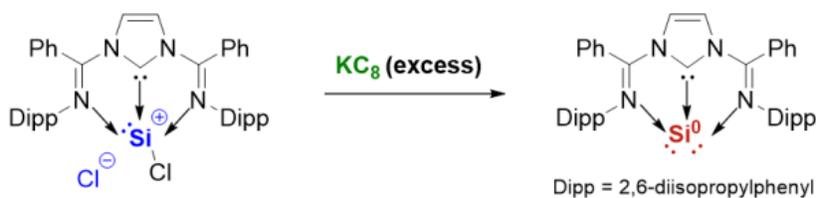
Lanthanide-based single-molecule magnets (SMMs) with low coordination numbers have been synthetically elusive targets, the most performant SMMs have historically relied on *pseudo*-axial ligands delocalized across several coordinated atoms to elicit slow relaxation of the magnetization. We report the *bis*-silylamido complex [Yb(N(SiMePh<sub>2</sub>)<sub>2</sub>)<sub>2</sub>][Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>] as the first 4f complex with only two N-donors to exhibit slow relaxation of the magnetization. The combination of the bulky ligands and weakly coordinating anion provides the ideal steric environment to stabilize the *pseudo*-trigonal geometry necessary to elicit strong ground state magnetic anisotropy in the Yb center. Resolution of the  $m_J$  states by luminescence spectroscopy is supported by *ab initio* calculations, revealing a large ground-state splitting. Successful application of this strategy to lanthanide ions with large angular momentum projections is key to achieving large spin reversal barriers for next-generation SMMs.

### Novel Si(0) On A Diimino N-Heterocyclic Carbene Ligand

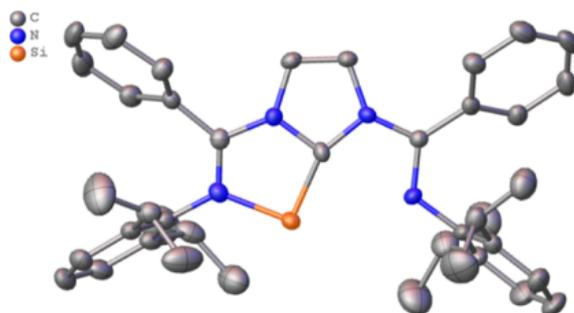
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Herein we report the synthesis and properties of a novel low-valent silylone based on a diimino-NHC ligand. Complexes of group 14 elements in an oxidation state of zero are called tetrylones, thus the silicon analogue is coined silylone. Silylones feature two high-energy lone pairs on the central silicon atom which imparts unique reactivity<sup>1</sup>. It has been previously demonstrated that low-valent main group compounds can activate small molecules including robust compounds such as nitrogen, ammonia, hydrogen, carbon dioxide and others to a similar effect as transition metals<sup>2-3</sup>. Complex 1 was prepared by the reduction of the dichlorosilylene precursor and characterized by single crystal X-ray diffraction and NMR spectroscopy (Scheme 1).



**Scheme 1.** Synthesis of the diimino-carbene stabilized silylone **1** (top); Molecular structure of **1** (bottom). Thermal ellipsoids are plotted at 50% probability level. Hydrogen atoms are omitted for clarity.



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P63

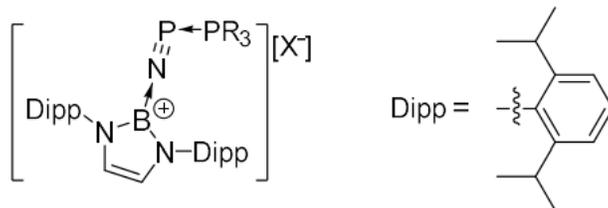
## Using Geometric Constraint to Stabilize Unusual Boron Cations

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Although di-coordinate borocations, termed borinium cations, were first isolated over 40 years ago, studies on their reactivity have only been disclosed within the last decade. In our previous work on borinium cations, we found that the range of ligand systems suitable to target reactivity at boron is quite limited. Many ligands either offer insufficient electronic and steric stabilization, leading to uncontrolled reactivity, or they are too protecting, hindering access the boron centre.<sup>1-3</sup> A 1,4- diazabutadiene derived ligand was chosen for its narrow bite angle while maintaining a high degree of steric protection and electron donation. Thus, achieving linearity about the N-B-N fragment is difficult, effectively raising the Lewis acidity of the analogous borinium cation and greatly disfavoring decoordination of a third ligand from boron. This presentation focuses on our recent efforts in trapping a phosphorus mononitride unit between a formal borinium cation and a phosphine.



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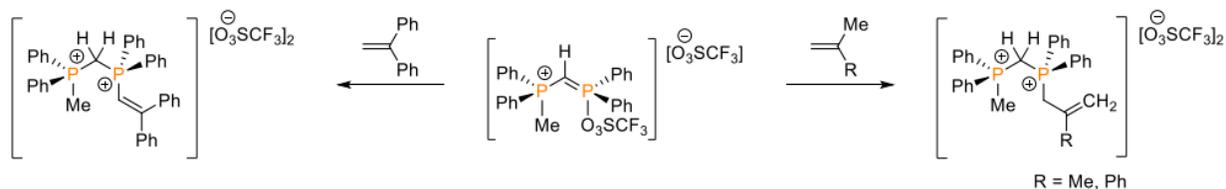
P64

## Reactions of a Lewis Acidic Methylene Phosphonium Adduct with Olefins

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The chemistry of methylene phosphonium cations presents an intriguing area of study since its initial isolation in 1989.<sup>1</sup> Subsequently, methylene phosphonium species featuring various substituents have been reported in the literature.<sup>2-4</sup> However, the balance between compound stability and reactivity remains a challenging concept as reactive methylene phosphonium cations are often unstable under ambient conditions while the stable derivatives are limited in reaction scope. In this work, we report a new synthetic avenue to a methylene phosphonium cationic adduct, and its reaction with olefins to afford vinylic or allylic bisphosphonium dications.<sup>5</sup>



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P65

### Reactivity of Mn (I) complexes bearing picolyl-NHC ligands

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The use of manganese in catalysis is particularly attractive due to its high abundance and biocompatibility.<sup>[1]</sup> N-Heterocyclic carbenes (NHCs) are useful ligands in organometallic chemistry and catalysis due to their high electron donation capacity, steric tuneability and relatively ease of preparation.<sup>[2]</sup> Nonetheless it was not until the last decade that the studies of Mn-NHC complexes demonstrated their sterling potential in catalytic transformations.<sup>[3]</sup> Herein, we present the syntheses of Mn(I) complexes bearing picolyl-NHC ligands and their reactivity towards H<sub>2</sub> and CO<sub>2</sub>.

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P66

**Catalytic Synthesis of Heterocycles using Novel Ruthenium Piano-stool Complexes**

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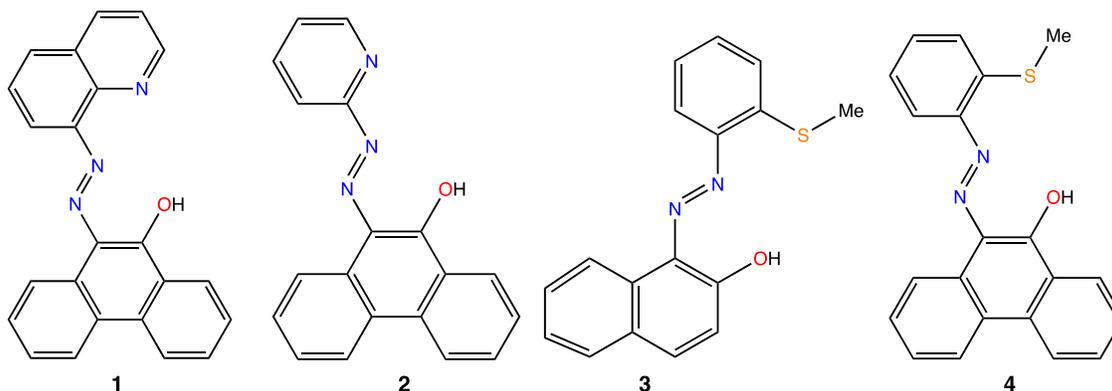
A series of new piano-stool ruthenium complexes of bifunctional *N,C*-chelating ligands were prepared and their reactivity towards alkynes evaluated. These complexes were found to be catalytically active for the *endo*-selective intramolecular hydrofunctionalization of nucleophile tethered alkyne substrates to produce 5-, 6- and 7- membered heterocycles in excellent yields under exceptionally mild conditions. The observed *endo*-specificity and the isolation of Ru-vinylidene species support their involvement in the catalytic cycle.

## The Syntheses and Coordination Chemistry of Sulfur-Bearing Aryl-Azo Ligands

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The Lemaire group is interested in the synthesis of molecule-based multifunctional materials that exhibit both spin-crossover and conducting properties. These materials are of special interest because it should be possible to tune their conductivity by switching the metal ion between high and low spin states. In recent years, aryl-azo ligands have been explored for the discovery of multifunctional complexes using the redox active ligands such as QAPL and PAPL, (**1**) and (**2**) respectively (Figure 1)<sup>1-3</sup>. In this work, the N-heterocyclic moiety in (**1**) and (**2**) is replaced with a softer thioether substituent to afford the two hemilabile Ligands (**3**) and (**4**), ultimately targeting the discovery of new spin-crossover complexes. We report herein the syntheses, characterization, and preliminary coordination chemistry of the sulfur-bearing aryl-azo ligands, MSAN (2-(methylthio)phenylazonaphtholate), (**3**), and novel MSAP (2-(methylthio)phenyl-9-phenanthrol), (**4**) (Figure 1)<sup>4</sup>.



**Figure 1.** Molecular structures of QAPL (10-(8-quinoylazo)-9-phenanthrol), (**1**); PAPL (1-(2-pyridylazo)-2-phenanthrol), (**2**); MSAN (2-(methylthio)phenylazonaphtholate), (**3**); and MSAP (2-(methylthio)phenyl-9-phenanthrol), (**4**)

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P68

**Synthesis of a Novel Mesoionic N-Heterocyclic Olefin and its Reactivity**

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We developed a novel mesoionic *N*-heterocyclic olefin (mNHO) from the deprotonation of a 1-mesityl-3-methyl-4-(pyridin-2-ylmethyl)-1H-1,2,3-triazol-3-ium salt. This mNHO is left unprotected at the *pro*-carbenic (C5) position, allowing for its tautomerization to its mesoionic carbene (MIC) form and further deprotonation. Herein we present the deprotonation of the mNHO and the subsequent coordination to BMe<sub>2</sub> (Mes= mesityl).

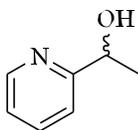
## Exploring the Coordination Chemistry of Two Pyridyl Alkoxide Ligands with Ni(II) in 3d Cluster Chemistry

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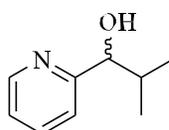
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Single-Molecule Magnets (SMMs) are coordination complexes of paramagnetic metal ions that display slow relaxation of magnetization below their blocking temperature that are currently intensively researched due to their potential applications as memory storage devices. The introduction of chirality into this family of molecules creates opportunities for new properties such as magnetochiral dichroism (MChD), as well as applications in the field of multiferroics. The Pilkington group has recently initiated a program of research aimed at developing small, potentially chiral pyridyl alkoxide ligands for the discovery of metal clusters with unprecedented structural motifs and novel magnetic and/or electronic properties.<sup>1,2</sup> The synthesis, structures and magnetic studies of a new diverse family of Ni(II) clusters prepared from  $\alpha$ -methyl-2-pyridine-methanol (mpmH) (**1**) and its closely related counterpart, dimethyl-2-pyridine-methanol (dmpmH) (**2**) will be reported.



mpmH (1)



dmpmH (2)

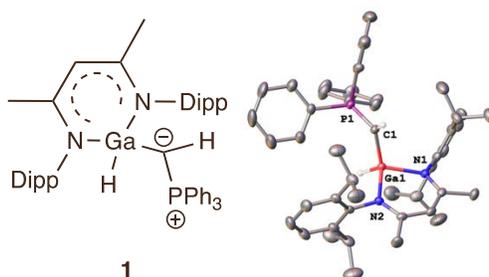
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## Synthesis and reactivity of $\alpha$ -metallated phosphorus ylide

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$\alpha$ -metallated ylides, alternatively called yldiides, represent a class of zwitterionic compounds featuring a negatively charged central carbon atom with an electron pair adjacent to a metal and a phosphonium group. Even though ylides were discovered more than 100 years ago, there is a limited number of reports on isolated and structurally characterized  $\alpha$ -metallated ylides<sup>1</sup>. Such compounds are of interest due to their increased nucleophilicity and the potential use in bond activation<sup>2</sup>. Synthesis and X-ray diffraction analysis of a new metallated ylide **1** is reported as well as its reactions with small molecules.



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P71

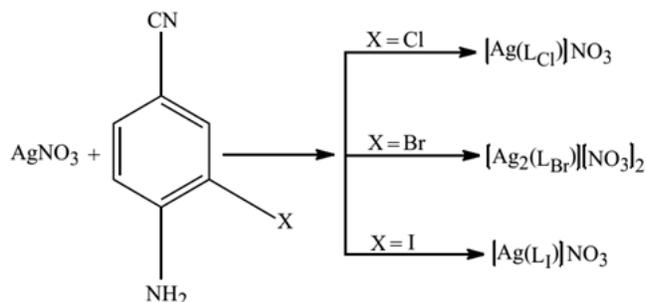
## Synthesis and Structural Characterization of Three Nano-Structured Ag(I) Coordination Polymers: Syntheses, Characterization and Structural Studies

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We report herein the crystal structure analysis of Ag(I) coordination polymers based on 4-amino-3-halobenzonitrile ligands. Three coordination polymers of general formula  $[\text{Ag}(\text{L}_x)]\text{NO}_3$ , where  $\text{X}=\text{Cl}$ (**1**), **I**(**3**) and  $[\text{Ag}_2(\text{L}_x)][\text{NO}_3]_2$ , where  $\text{X}=\text{Br}$ (**2**), were synthesized and characterized. The effect of changing the single halogen atom of 4-amino-3-halobenzonitrile on the crystal packing of a series of Ag(I) coordination polymers was studied. Our results revealed that N-H $\cdots$ O hydrogen bonds play important role in the crystal packing. Nanoparticles of these coordination polymers were also synthesized by ultrasonic irradiation of (**1**), (**2**) and (**3**), and characterized using different analytical techniques.



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## Low-Valent 3d Metal Complexes of Redox-Active Bis(imino)carbazolide Ligands in Dinitrogen Activation

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Ligand-based redox activity has emerged as a valuable strategy in small molecule activation and catalysis.<sup>1,2</sup> The development of ligand scaffolds capable of electron storage and release is central to continued progress in this field. The synthesis of sterically-demanding redox-active bis(imino)carbazolide ligands and their coordination towards various 3d transition metals is presented. The reactivity of the resulting complexes towards dinitrogen functionalization will also be discussed.

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