Step-Growth Polymerization of Secondary Phosphines with Polyimines: A Modular Route to Functional Poly(α-aminophosphorus-chalcogenide)s

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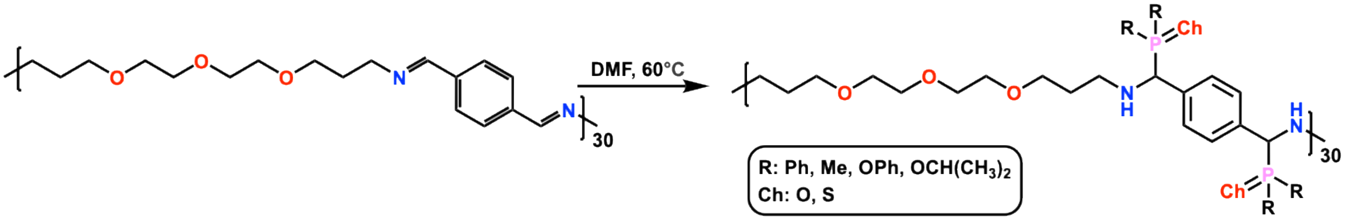
Primary phosphines in the presence of an oxidant (e.g., O_2, S_8) directly react with imines to create α-aminophosphine chalcogenide addition products. We have expanded this approach using secondary phosphines (R_2PH) and PEG-based diimines (n=3).[1,2] This represents a modular synthesis and prepares soluble, low-dispersity poly α-aminophine chalcogenides. By changing the phosphorus side groups (R), polymer properties can be modified. This approach gives a range of poly(α-aminophosphorus-chalcogenide)s with customizable heteroatom content. We aim to explore their utility for binding metal-ions.



Scheme 1 Step-growth synthesis of poly(α-aminophosphorus-chalcogenide)s from PEG-derived polyimines with tunable P(V)=Ch units and R-groups to control metal binding and solubility.

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Synthesis and Reactivity of an Operationally Unsaturated Ru Complex

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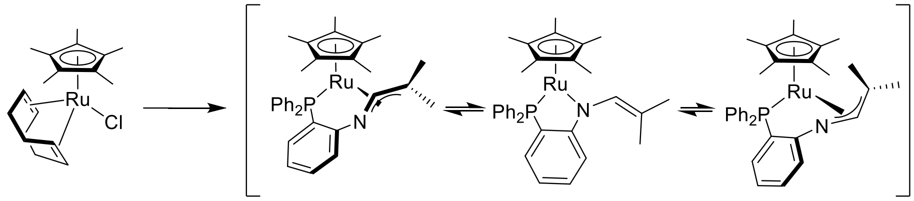
In the field of homogeneous catalysis, developing molecules that balance both stability and reactivity is a constant target. One promising strategy to achieve this equilibrium involves designing complexes with lower coordination numbers—i.e., less than 18 e^-—stabilized by the steric and electronic contributions of the ligands. These complexes, referred to as "operationally unsaturated," are distinguished by their open coordination sites, which enable substrate binding and can promote catalytic activity toward small molecules.[1, 2] Recently, the Blacquiere group demonstrated that changes in the hapticity of a phosphine 1-azaallyl ligand (P^AzA) can stabilize low-coordinate complexes and favor Lewis base coordination under mild conditions,[3] which raises the potential utility of [Ru(Cp*)(P^AzA)] for small molecule activation. The synthetic route to [Ru(Cp*)(P^AzA)] involved ligand substitution with [Ru(Cp*)(PPh_3)$_2$], but purification to remove PPh_3 proved challenging. Therefore, a new synthetic route is being developed to overcome the limitations observed. The benefits of the new synthetic route and the spectroscopic characterization will be discussed, as well as the preliminary reactivity of [Ru(Cp*)(P^AzA)] with CO.



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Synthesis and Reactivity of [(η^5-$C_5H_4PR_2$)Fe(η^5-$C_5H_4AlR'_2$)] Compounds

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The synthesis and isolation of bis(cyclopentadienyl)iron, “ferrocene”, proved to be revolutionary for organometallic chemistry,[1] and its derivatives have been invaluable in the fields of catalysis and small molecule activation.[2] While earlier studies have explored group 13 Lewis acids with ferrocenyl substituents, more recent work has looked at using ferrocene as the backbone to synthesize ambiphilic compounds (i.e., those with both Lewis basic and Lewis acidic groups) such as 1,1'-substituted [(η^5-$C_5H_4PR_2$)Fe(η^5-$C_5H_4BR'_2$)].[3,4] However, the aluminum analogues of these species have not been reported.

Herein, we describe the synthesis, structural characterization and reactivity of the first examples of [(η^5-$C_5H_4PR_2$)Fe(η^5-$C_5H_4AlR'_2$)] (R = ^{i}Pr, Ph; R' = Me, Ph, C_6F_5) compounds. The reaction of [(η^5-$C_5H_4PR_2$)Fe(η^5-$C_5H_4AlMe_2$)] (R = ^{i}Pr (**1a**), Ph (**1b**)) with isocyanates, isothiocyanates, and CO_2 resulted in insertion of a C=N or C=O bond of the substrate into the backbone aluminum–carbon bond to yield dimeric structures containing an 8-membered $(ECNAl)_2$ or $(OCOAl)_2$ ring (E = O or S). By contrast, the reaction of phenylisothiocyanate with [(η^5-$C_5H_4P^iPr_2$)Fe(η^5-$C_5H_4AlPh_2$)], featuring bulkier and more electron-withdrawing substituents on the Lewis acid, led to typical Frustrated Lewis Pair (FLP) coordination. Additionally, the reaction of **1a** with $[(COD)Ir(\mu\text{-}Cl)]_2$ (COD = 1,5-cyclooctadiene) resulted in the elimination of dimethylaluminum chloride and the formation of [κ^2-*P,C*-{(η^5-$C_5H_4PR_2$)Fe(η^5-C_5H_4)}Ir(COD)], whereas the reaction of **1a** with $[Pt(Nor)_3]$ (Nor = norbornene) afforded [κ^2-*P,Al*-{(η^5-$C_5H_4PR_2$)Fe(η^5-$C_5H_4AlMe_2$)}$Pt(Nor)_2$].

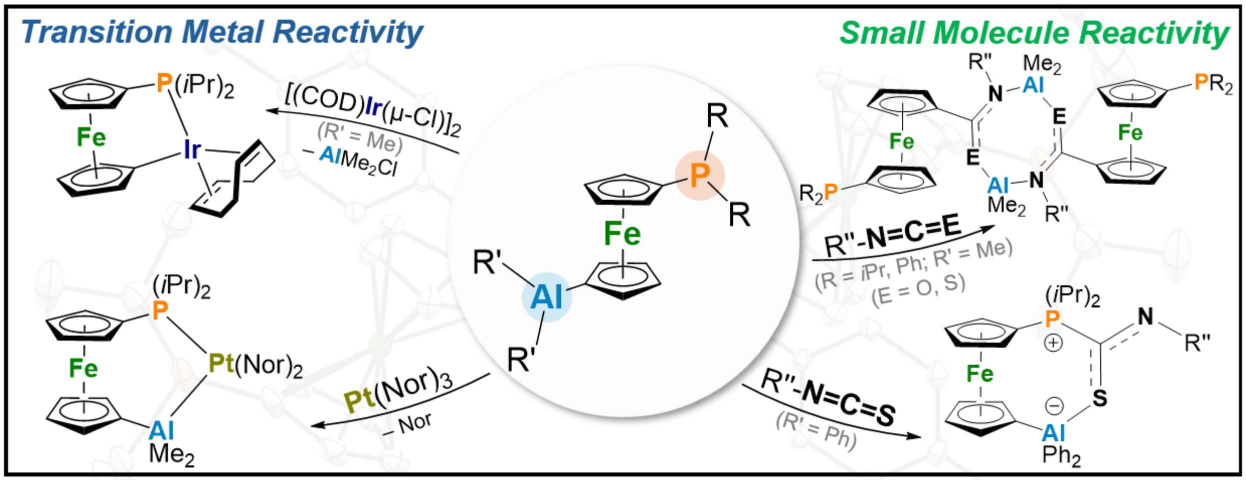

Figure 1. Reactivity of [(η^5-$C_5H_4PR_2$)Fe(η^5-$C_5H_4AlR'_2$)] complexes.

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Exploration of Intermolecular Hydrofunctionalization by a Cooperative Ruthenium Catalyst with Z Selectivity

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Within the field of synthetic organic chemistry there presently exists a demand for new methodologies to hydrofunctionalize alkynes without the use of an exogenous base and using minimal alcohol, particularly aromatic alcohols.[1] Hydrofunctionalization reactions utilizing metal catalysts are of interest due to their near complete atom economy. Hydrofunctionalizing catalysts that proceed via a M-vinylidene intermediate pathway are of particular interest due to the controlled selectivity for *anti*-Markovnikov products. The Blacquiere group has previously developed several [Ru(Cp)($P^{R}_{2}N^{R'}_{2}$)(MeCN)][PF_6] (Cp = cyclopentadienyl, $P^{R}_{2}N^{R'}_{2}$ = 1,5-diaza-3,7-diphosphacyclooctane) complexes which have been shown to successfully hydrofunctionalize a variety of alkynes to selectively facilitate the *intra*molecular formation of *anti*-Markovnikov products.[2] Herein, the [Ru(Cp)($P^{R}_{2}N^{R'}_{2}$)(MeCN)][PF_6] catalysts will be utilized to facilitate the selective formation of a variety of *anti*-Markovnikov products via the *inter*molecular hydrofunctionalization of alkynes. This poster will focus on the hydroalkoxylation of alkynes and the observed selectivity for the *Z* isomer (Figure 1). Additionally, the features of the catalyst that control this selectivity, and the kinetics of the mechanism will be discussed.

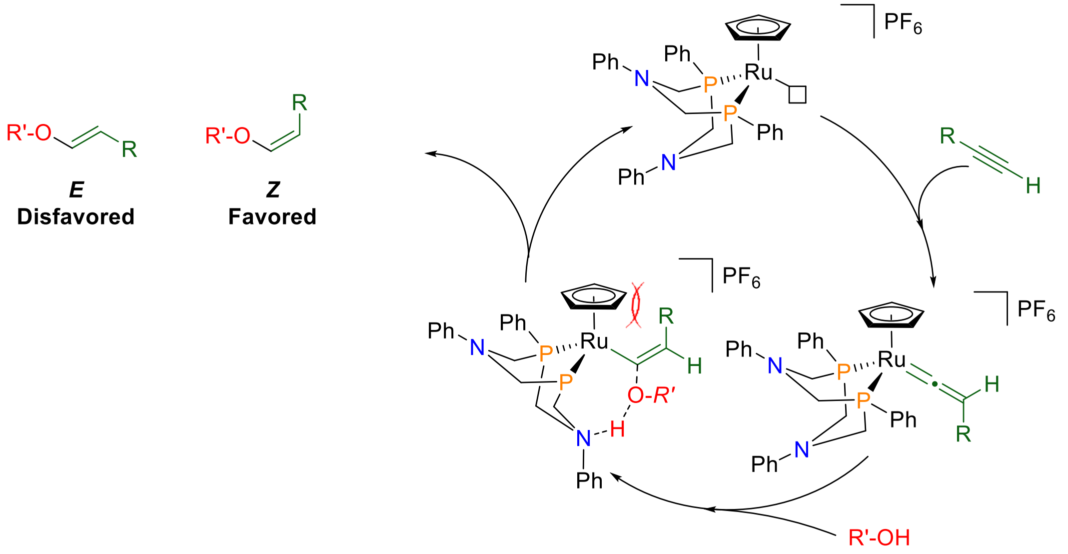

Figure 1. Mechanistic pathway rationalizing *Z*-selective isomer formation via a Ru-$P^{Ph}_{2}N^{Ph}_{2}$ catalyst

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Polymerizations Using Transition Metal Complexes of Monoanionic Bidentate Guanidine-Ethenolate, Phenolate, and Benzene Sulfonate Ligands

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We describe the design of novel guanidine-containing ligand systems for lactide and olefin polymerization using transition metal catalysts. Leveraging facile modification of ligands' substituents in order modulate the steric and electronic properties of corresponding complexes provides control over the physical properties of the resultant polymer. Polylactide, exemplifying the principles of green chemistry, provides a biodegradable alternative for many one time use polymers.[1] We utilize the aforementioned ligands in zinc-based catalysts as non-toxic alternatives to the tin-based industrial standard.[2] In addition, we utilize these ligands to investigate the synthesis of functionalized polyolefins through copolymerization with polar olefins using late transition metal catalysts.

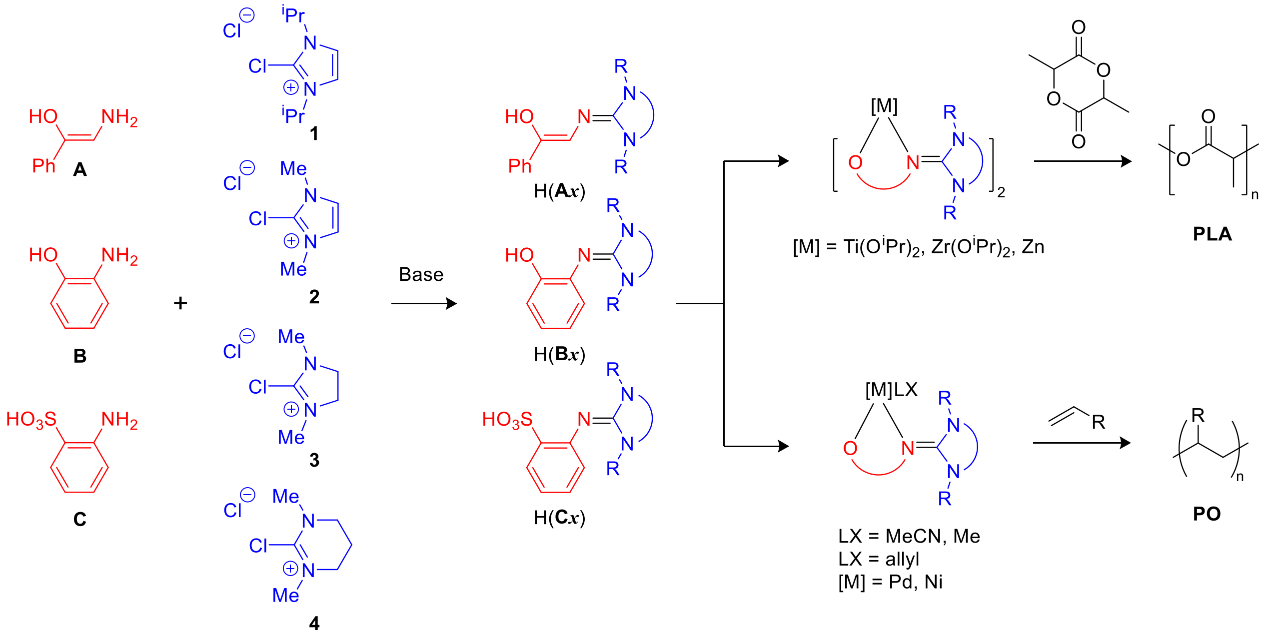

Figure 1. Preparation of guanidine-ethenolate, phenolate, and benzene sulfonate ligands for use in lactide and olefin polymerization.

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Unusual Phosphorus-Nitrogen (PN) Heterocycles

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Phosphorus-nitrogen (PN) heterocycles are an exciting, relatively new analogue of the well-explored boron-nitrogen (BN) heterocycle. Like their BN counterparts, PN heterocycles have found potential utility in material sciences for solar cells and for medicinal applications in fluorescence imaging.[1,2] The Gilroy group is interested, and has succeeded in, coordinating various N, N ligands to phosphorus species, to make and explore the reactivity of novel PN heterocycles. Most notably, the use phosphadiazonium cations revealed PN heterocycles with interesting reactivity.[3,4] Phosphadiazonium cations are stable sources of PN triple bonds, and their reactivity with different species is vastly unknown, especially when trapped in a scaffold, as in PN heterocycles. This work showcases the reactivity of different phosphorus species, including chloro(imino)phosphines and different phosphadiazonium cations, in the presence of Schiff base ligands. The unusual results prompted further investigation into reactions with imines, with promising preliminary data.

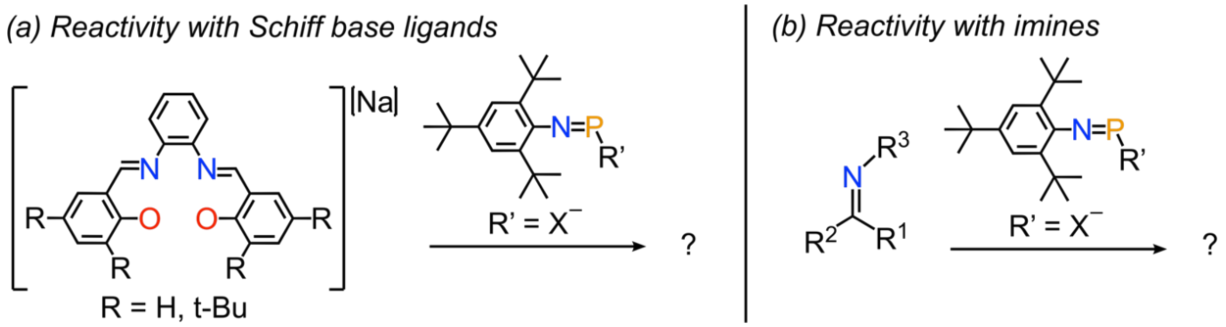

Figure 1. (a) Reactivity of Schiff base ligands with different phosphorus species. (b) Reactivity of imines with different phosphorus species.

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Balancing Catalyst Stability Against Reactivity in Olefin Metathesis: Examining the Impact of Remote Steric Bulk on Initiation Rates

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Ruthenium-catalyzed olefin metathesis is now a cornerstone transformation in organic synthesis, with the Hoveyda complex **HII (**fig. 1) being the dominant catalyst in current use. Critical to the performance of this important catalyst class is the capacity to limit decomposition, which generates ruthenium species that promote unwanted side reactions. Bimolecular coupling (BMC) represents a leading decomposition manifold. [1,2] This study examines the impact on catalyst initiation of a recently-developed solution to BMC: that is, the design of new catalysts in which the N-heterocyclic carbene (NHC) ligand is functionalized to inhibit the mutual approach of two [Ru]=CHR centres. With the intention of inhibiting BMC while retaining high metathesis activity, we incorporate remote steric bulk on the N-aryl functionality (e.g., **HII-Tr**). Here we examine the impact on initiation kinetics, and inferences for the balance between catalyst stability and initiation efficiency.

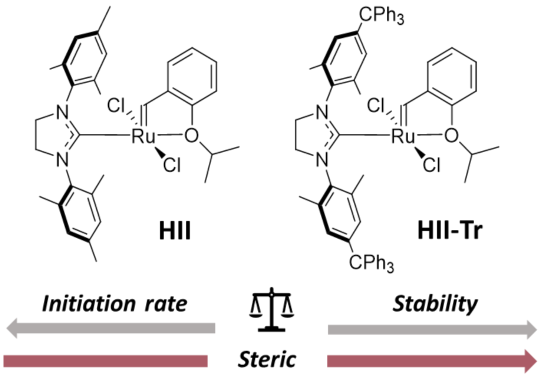

Figure 1. Olefin metathesis catalysts

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The Influence of Surface Hydroxylation Media on the Luminescence and Electronic Structure of Cr^{3+}-Doped Zinc Gallate Nanoparticles

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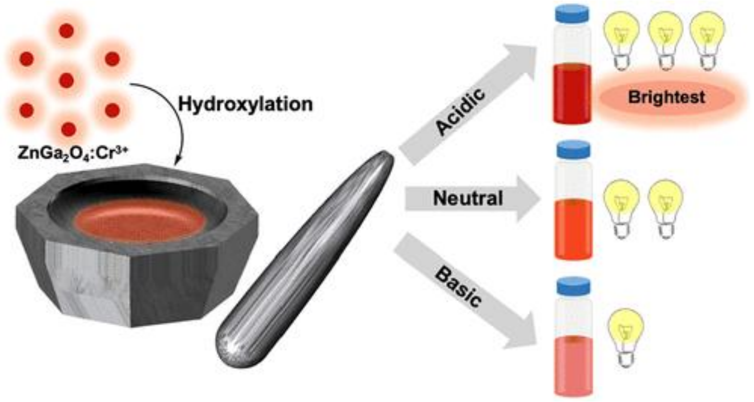
Cr^{3+}-doped zinc gallate ($ZnGa_2O_4$:Cr^{3+}, CZGO) are promising near-infrared (NIR) persistent luminescent (PersL) nanomaterials for biomedical imaging due to their distinctive optical properties. Surface hydroxylation is a common approach to improve colloidal stability, which is crucial for achieving stable dispersions in aqueous media. Although previous studies suggested that both acidic and basic treatments can hydroxylate CZGO surfaces, it is unclear why such drastically chemically different environments both achieve hydroxylation and whether the particles show comparable luminescent and long-term colloidal stability. In this work, CZGO nanoparticles were treated under acidic, neutral, and basic conditions and were evaluated on their morphology, dispersibility, and luminescence. A stable colloidal dispersion was achieved in all treatments, but acid-treated samples exhibited the strongest and longest-lasting luminescence. These findings illustrate how different hydroxylation conditions influence both the surface chemistry and optical performance of the nanomaterial, providing insights for the optimization of PersL nanoparticles for biomedical use.



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Metal–Organic Frameworks: a Gateway for Functional Solid-State Materials using Surface Organometallic Chemistry Approach.

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Surface organometallic chemistry (SOMC) is a rigorous strategy to incorporate molecules into functional solid-state materials, achieved by grafting molecular precursors onto a supporting material to generate well-defined surface species.[1,2] SOMC was originally rooted in grafting transition metal complexes onto pre-treated oxidic materials for controlled heterogenization of homogeneous catalysts.[3] To expand the applicability of SOMC in molecular-to-material transformations, we have identified more suitable supports, namely the metal oxide-like secondary building units (SBUs) of metal–organic frameworks (MOFs).[4] MOF SBUs possess surface hydroxyl groups that function as isolated and uniformly dispersed grafting sites within the porous, crystalline material. Although the translation of SOMC principles from traditional oxide supports to MOFs is in its initial stages, early studies have shown that the coordination environment around surface hydroxyl groups and the crystallinity of MOFs have allowed for greater precision in grafting.[5–7]

To date, the grafting of lanthanide complexes remains absent in MOF SOMC studies, despite their diverse properties (i.e. luminescence, magnetism) and applications (i.e. optoelectronics, therapeutics, information storage, sensors).[8–10] Bis(trimethylsilyl)amide complexes are a suitable candidate for studying lanthanide grafting on MOF SBUs as they are considered canonical molecular precursors in SOMC. This work summarizes our ongoing efforts toward grafting lanthanide(III) bis(trimethylsilyl)amide complexes onto NU-1000, a robust mesoporous MOF, and to ultimately develop a better understanding of MOFs as SOMC supports.

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N-heterocyclic Isocyanide Ligands with Extreme Electronic Properties

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The design of new classes of ligands has the potential to enable unprecedented catalytic applications or to unlock the commercial applicability of existing catalytic processes. Isocyanides (R-NC) are well established in organic chemistry and in the field of coordination chemistry, they are often described as analogues of carbon monoxide, albeit with uniquely remote and tunable steric properties. Indeed, isocyanides have notably been utilized to stabilize low-valent, reactive transition metal complexes, acting as σ donors and π acceptors. [1,2]

From an electronic perspective, however, isocyanides are found to be stronger electron donors than CO, but weaker acceptors. Compared to other donor ligands, isocyanides are considerably weaker than arylphosphines (already weak donors), which may explain their lability from metal centers, and thus their limited use in catalysis. In addition, the impact of substitution on the electronic properties of isocyanides is generally weak.[3]

We have designed and synthesized new classes of isocyanides in which the resonance from a N-heterocyclic group can affect their electronic properties. These ligands retain the unique steric properties of isocyanides, while displaying extreme electronic properties. The synthesis of these ligands, as well as quantitative measurements of their electronic properties will be discussed.

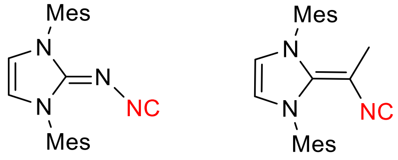

Figure 1. Our design of N-heterocyclic Isocyanides

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Cooperative Reactivity of a Ni-Al Heterometallic Complex with Alkynes

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N-Heterocyclic compounds such as pyridine and DMAP are valuable structural motifs in pharmaceuticals, materials, and catalysis, yet their selective functionalization remains a long-standing challenge. A promising strategy to address this problem involves the use of heterometallic complexes.[1] Among these, Ni-Al systems stand out: the strong Lewis acidity of aluminum allows it to coordinate to the Lewis-basic nitrogen, positioning nickel for efficient C(sp^2)–H activation selectively at the pyridine 2-position. Previous work from our laboratory has demonstrated the synthesis of such a Ni-Al heterometallic and its use in N-heterocycle C-H bond activation. In this work, we show this Ni-Al complex exhibits cooperative reactivity, exhibiting a pronounced ability to bind alkynes and reduce them into alkenes at close proximity to the N-heterocycle via hydroalumination. This behavior represents a key mechanistic step toward realizing the full catalytic functionalization of N-heterocycles through heterocycle alkynylation.

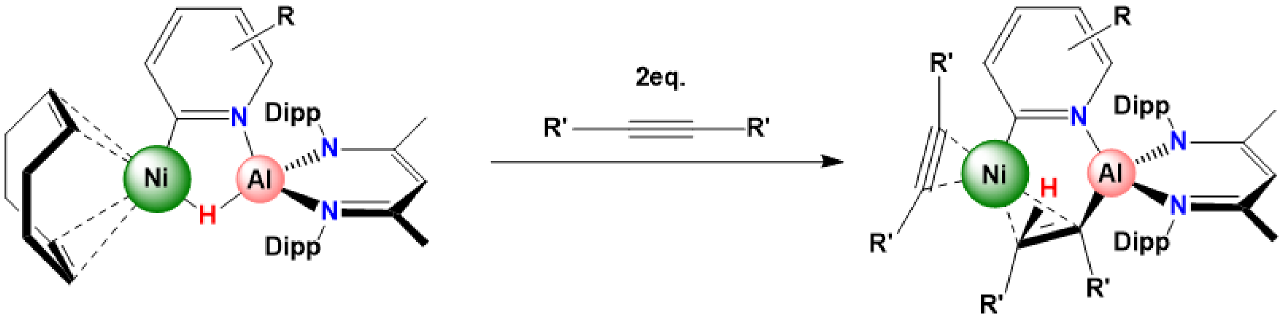

Figure 1. The chemical structure of the Ni-Al heterometallic complex of interest and its subsequent reaction with an alkyne. Dipp = Diisopropylphenyl.

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Synthesis of Novel 3-bpp Derivatives and Study of Fe(II) Spin Crossover Complexes as Potential Thermosensitive LipoCEST Agents for Magnetic Resonance Imaging

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Spin crossover complexes (SCO’s) are coordination compounds that can switch between low-spin (LS) and high-spin (HS) electronic configurations, due to changes in the external environment such as light, pressure or temperature. The subsequent change in spin state can be followed in solution by Evan’s method ^{1}H NMR, and UV-Vis spectroscopy, and in the solid state by variable temperature X-ray crystallography and SQUID magnetometry. Magnetic Resonance Imaging (MRI) contrast agents (CAs) contain paramagnetic ions, which change the local magnetic field strength of a tissue and interact with surrounding protons of water molecules, shortening the relaxation rate of water protons which in turn enhances the MRI image. These CAs often contain Gd(III) ions, which over time have been proven to accumulate in the brain. Due to this, a new class of MRI CAs called chemical exchange saturation transfer (CEST) agents have been developed by selectively reducing the magnetization of the water signal and with minimal effects on its longitudinal relaxation rate. PARACEST CAs are paramagnetic complexes which possess exchangeable protons, close to the vicinity of the metal ion in slow exchange with bulk water protons. Fe(II) complexes that exhibit a thermally induced spin crossover represent ideal temperature-responsive PARACEST agents since they can have spin ground states that change significantly with temperature. One family of SCO complexes that show such behavior in solution within the biological window are $[Fe(3\text{-bpp})_2(BF_4)_2]$, where 3-bpp = 2,6-bis(pyrazol-3-yl)pyridine.[1-4] The preparation of a new 3-bpp ligand with an electron donating methoxy group on the para position of the pyridyl ring will be presented together with its Fe(II) complex.[5] Preliminary studies to encapsulate this family of Fe(II) complexes into a suitable liposome to make the Fe(II) PARACEST agents more bioavailable will also be discussed.[6]

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Photoswitchable Ligands on Silver Nanoclusters for Stable, Tunable Organic Photovoltaics

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Molecular-level control over optoelectronic properties is essential for next-generation organic photovoltaics (OPVs), yet few materials combine reversible optical switching with structural precision and operational stability. Metal nanoclusters are promising candidates in this regard. Achieving reversible switching, stability of the nanoclusters core and suitable electronic properties has been a challenge. Here, we report a carbonate templated Ag_{20} nanocluster surface-functionalized with azobenzene derivatives that function as a single-component photoswitch with enhanced stability compared to a non-functionalized core. The precise atomic structure of the functionalized cluster was determined with single-crystal X-ray diffraction (SCXRD). UV-Vis spectroscopy monitored photoswitch shows the trans-cis isomerization of the ligand shell is near-quantitative through multiple cycles. This tailored ligand shell also confers photostability, significantly reducing the rate of oxidation of the silver core. The ability to optically modulate the cluster's electronic properties alongside increased workability & stability highlights its potential as a molecular switch for photovoltaic activity in OPVs. Current work focuses on exploring the solid-state properties and integrating C_{60}/C_{70} fullerenes to realize a single-component switch-acceptor hybrid material. We established a design strategy for precise tuning of the nanocluster surface while modifying optoelectronic properties and enhancing stability[1,2].

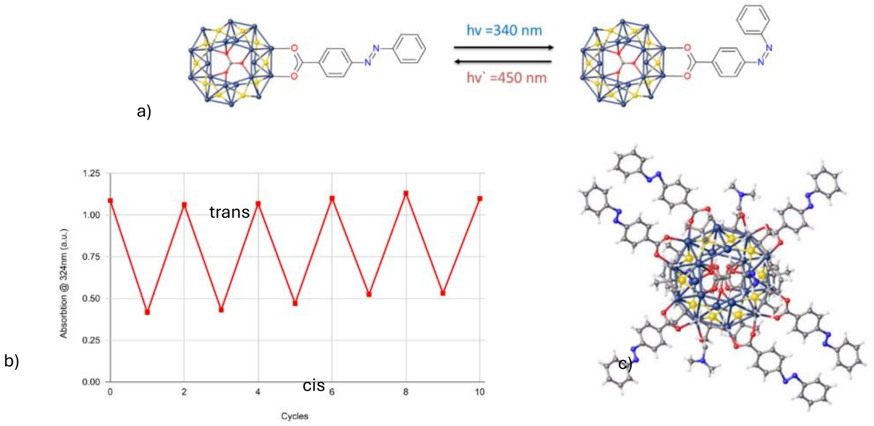

Figure 1. a) Illustration of cis-trans isomerization of surface bound azobenzene[1] b) UV-vis monitored photo switch tracking the change in absorbance at 324nm. Cycling from E-trans to Z-cis by irradiation at 350 nm for 30 mins, and Z-cis-E-trans by irradiation at 254 nm for 30 mins. c) Crystal structure of Ag_{20}6-azoNC [1]

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Composition Control in Molecular Cluster-Aggregates: A Toolbox for Optical Output Tunability via Energy Transfer Pathways

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Composition control is an effective strategy for obtaining high-performing lanthanide (Ln) materials with tunable luminescence properties. The characteristic discrete, ladder-like energy levels of Ln^{III} make them ideal for building systems with precise control over energy transfer (ET) and back energy transfer (BET) processes. This approach is particularly well-established for hierarchically structured nanoparticles doped with different Ln^{III} ions; however, due to the small number of metal centers in a single unit, this strategy is not often explored in molecular systems.[1,2] In this work, we present a series of molecular cluster-aggregates (MCAs) with an icosanuclear core, $\{Ln_2Eu_2Tb_{16}\}$ (Ln = Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, and Yb), in which composition control was explored, akin to nanoparticles, by taking advantage of its large metal core to modulate the optical output.[3] More precisely, we aimed to comprehend the potential effects of a third Ln^{III} doping ion on the $Tb^{III} \rightarrow Eu^{III}$ ET and the ratiometric optical thermometry performance based on the Tb^{III}/Eu^{III} pair. Based on experimental data and well-known intrinsic features, such as spin−orbit coupling (SOC) strength and Ln^{III} 4*f* energy levels' structure, we discuss the possible luminescent processes present in each MCA and provide insight into qualitative trends that can be rationally correlated throughout the series (Figure 1). These findings not only deepen our understanding of the complex interplay between composition, SOC, and energy-level positions in Ln-based MCAs but also pave the way for the rational design of next-generation luminescent materials.

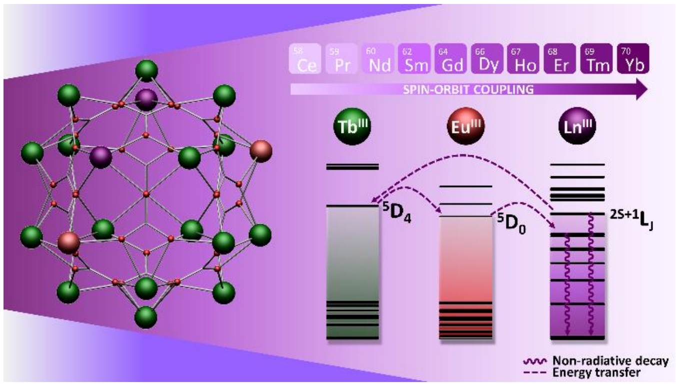

Figure 1. Icosanuclear metal core structure, SOC trend, and general scheme with possible energy transfer pathways of $\{Ln_2Eu_2Tb_{16}\}$ systems.

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Antimony(III)-nitrogen Heterocyclic Compounds

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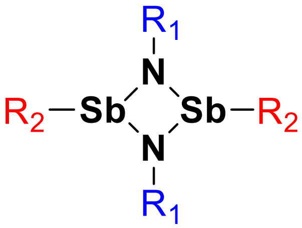
Pnictogen-nitrogen materials have garnered a lot of interest as they have applications in small molecule activation catalysis,[1] flame retardant,[2] and semiconductors.[3] Although this area of chemistry is relatively rich for phosphorus, there has been limited investigation into the heavier pnictogen (As, Sb, Bi) analogues of heterocycles with equally interesting characteristics and properties. We are exploring novel antimony(III)–nitrogen heterocycles and thermally characterizing them. Derivatives of the main Sb_2N_2 core will also be examined for their influence on ring strain, reactivity and chemoselectivity. The work aims to further advance understanding of pnictogen–nitrogen chemistry and provide insight into the design of new pnictogen-based functional materials.



R_1= H, Alkyl, Aryl

R_2= Alkyl, Aryl, NR_x

Figure 1. General molecular structure of Sb-N 4 membered heterocycles.

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Tetradentate NP_3 Ligands and their First-row Metal Complexes

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Phosphorus has had prevalent use in ligand design through their soft donor characteristics and polarizability, however the concomitant use of phosphines to synthesize many phosphorus-based ligands poses a disadvantage in terms of safety and accessibility. A safer, air-and-water-stable alternative has been demonstrated by the Morris group through the phosphonium dimer – a dimer of two protonated phosphine aldehydes that under basic conditions, releases the aldehydes *in situ*. These dimers are easily modified by changing the R groups on the phosphorus and have previously shown applications in various ligand designs and template syntheses. A useful application is the simpler and safer synthesis of tetradentate NP_3 ligands,[1] previously synthesized through mustard-like reagents. New advances in this direct synthetic method will be reported, alongside the resulting first-row transition metal complexes and their properties.

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Understanding the Structural Variability in Fe-Substituted Nickel Hydroxide Electrocatalysts

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Iron incorporation into $Ni(OH)_2$ has been widely recognized as an effective strategy to enhance electrical conductivity and oxygen evolution activity by modifying the electronic configuration and inducing lattice distortion[1)]. Recent studies have shown that Fe doping generates non-traditional Fe(III) coordination environments within the $Ni(OH)_2$ framework, which play a key role in activating surface redox sites[1-3)]. The uniformity in electrochemical behavior of $Fe_xNi_{1-x}(OH)_2$ despite measurable changes in structure is remarkable. This consistency is observed through samples prepared using many synthesis methods and with varied compositions, but the change in measured structure has led to conflicting reaction mechanisms being reported. We used Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to demonstrate how Fe(III) is incorporated into $Ni(OH)_2$ prepared by alkaline precipitation. Building upon previous research that revealed new crystal site locations for Fe(III) in $Ni(OH)_2$ lattices, this work extends the investigation to examine how Fe incorporation into Ni(OH)2 lattices changes with variation in alkali cations and pH used for synthesis[3, 4)]. Samples prepared under different pH and with various alkali sources (LiOH, NaOH, KOH) exhibit distinct Fe-induced structural distortions in the $Ni(OH)_2$ lattice, seen as shifts in frequency of vibrational modes and location of Bragg peaks in XRD patterns. The degree of lattice contraction and extent of stacking disorder varies when the synthesis is performed with specific anions and pH ranges. This study shows that the synthesis environment, especially the pH and the type of alkali used, controls how Fe is incorporated into the $Ni(OH)_2$ structure. By adjusting the synthesis conditions, it is possible to control the Fe coordination and the lattice structure, which will enable more detailed structure-property analyses to be performed.

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Biaryl Pd(II) Phosphine 1-Azaallyl Complexes for Insertion and Isomerization

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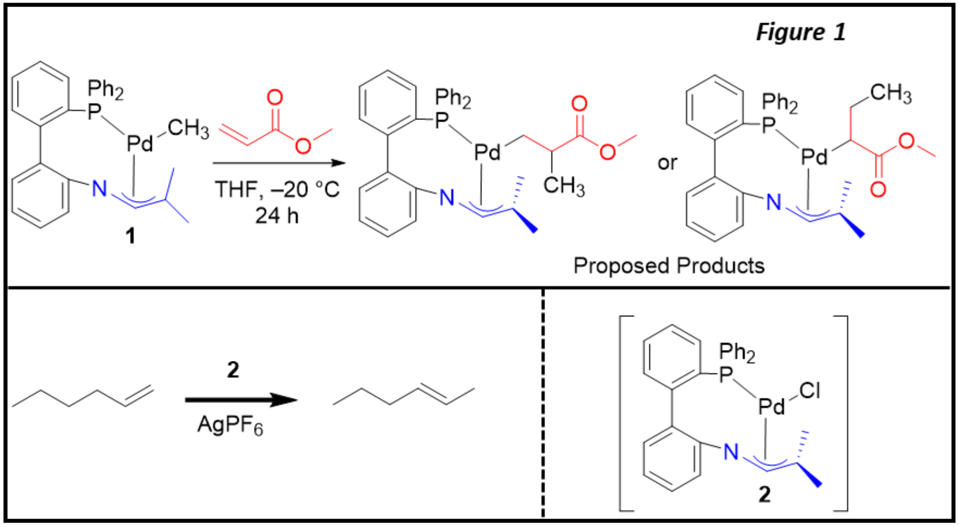
Structurally responsive ligands (SRLs) are a growing class of ligands that can undergo changes in coordination mode to facilitate binding of incoming substrates and to stabilise low-coordinate intermediates.[1] An example of an SRL is the azaallyl ligand, which can exhibit an η^3-NCC coordination mode when bound to a late transition metal. Previously, our group has synthesized the first phosphine 1-azaallyl (P^AzA) ligand, supported by a monoaryl backbone, which displayed a dynamic change between κ^2-P,N and κ^1-P;η^3-NCC coordination modes when bound to a Ru(Cp*) centre.[2] Recently, a P^AzA derivative with a biaryl backbone has been synthesized, with the biaryl backbone chosen to provide a wide enough bite angle to facilitate η^3-NCC coordination from the azaallyl arm to a square planar Pd metal centre. The ligand was successfully coordinated to Pd and a complex displaying the desired η^3-NCC coordination mode was successfully isolated (**1**), confirmed through spectroscopic analysis. Currently, work is being done to investigate the ability of **1** to facilitate insertion chemistry through the Pd-CH_3 bond with various polar alkenes. The azaallyl arm should sterically hinder cyclization of a polar group after successful insertion (such as a nitrile) to the metal centre, limiting catalyst deactivation. The addition of methyl acrylate to **1** has shown to form two major products in solution, possibly both the 2,1- and 1,2- insertion products (Figure 1, top). Lastly, efforts are currently ongoing for the optimized synthesis of a PdCl(P^AzA) derivative (**2**), since preliminary studies with this complex demonstrate it is catalytically active for the isomerization of alkenes (Figure 1, bottom).[3]

Figure 1



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Optimizing the Purification of Carbon Quantum Dots through a Multiplex Analysis of Common Techniques

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Carbon dots (CDs) are a distinct class of carbon-based nanomaterials, notable for their tunable photoluminescence, with applications in bioimaging, catalysis and optoelectronics. They can be synthesized from a wide range of carbon-rich precursors, though their size and molecular-like properties make them challenging to purify thoroughly. Poor characterization and sample heterogeneity within existing literature represents a significant complication for researchers attempting to reproduce or interpret data from other groups. Existing literature reviews compare purification techniques applied to entirely different synthesis protocols, and few studies compare the impact of different purification methods on the same sample. This project provides a quantitative comparison between popular methods of carbon dot purification, identifying the relative effectiveness of a 'multiplex' of protocol combinations. By 'multiplex', we mean a matrixed set of workflows in which multiple purification techniques are applied alone and in defined sequences to aliquots of the same parent CD batch, enabling direct, like-for-like comparisons.

The model samples consist of blue-emitting carbon dots created via the hydrothermal synthesis of citric acid and urea, two precursors frequently used to prepare CDs. Trends in sample homogeneity, optical properties, stability and electrical properties are compared before and after combinations of centrifugation, filtration, dialysis, size exclusion chromatography (SEC), and high-performance liquid chromatography (HPLC). Preliminary results have identified time after synthesis and quantum yield of emission (Φ) to have significant and underreported negative relationship, the presence of multiple fluorescent populations even after centrifugation and dialysis (the current benchmark), and repeatable population separation for SEC. Importantly, this study reports which analytical tests can reliably track purification, providing researchers with all the tools needed to optimize their own processes. The project's resulting 'multiplex' data will describe the trends in sample properties, creating standardized recommendations to inform future research design and contextualizing past results.

A Computational Prediction of a Synthesis Route to Adamant-triyl Titanium

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Adamantane ($C_{10}H_{16}$) is a building block of diamond, and adamantyl complexes have shown remarkable utility as an anti-viral agent against influenza virus.[1] Sigma-bond metathesis reaction is used with the presence of a transition metal center to make these compounds better precursors in inorganic and organometallic synthesis. This study aims to synthesize adamant-triyl-Titanium species from an available commercial agent, $TiCl_4$, computationally via kinetic and thermodynamic parameters. We hypothesize that the ligand substitution occurs stepwise from $TiCl_4$ to $Ti(2\text{-}Ad)_4$, then forming a diyl intermediate and finally a triyl-spicies.

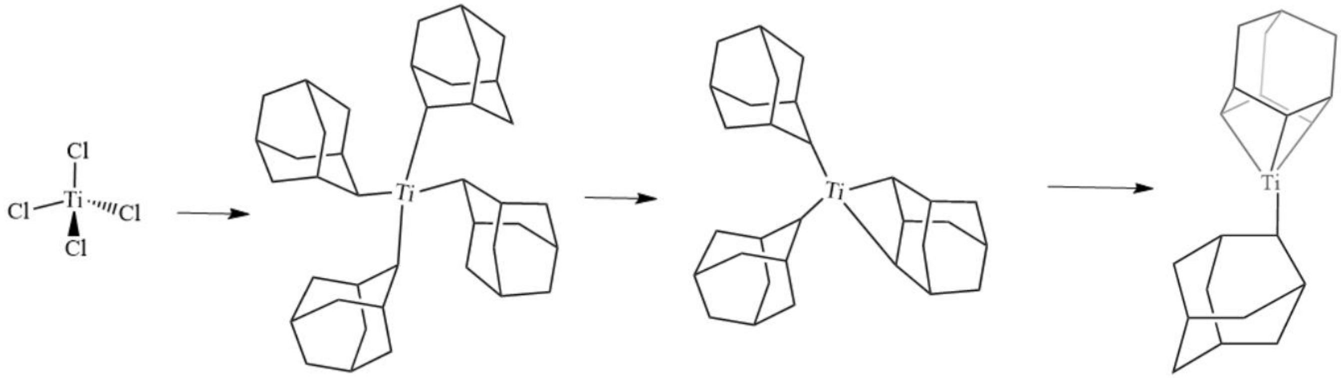

Figure 1: The first synthetic scheme of an adamant-triyl-titanium species with major intermediates.

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Unveiling the Coordination Environments of Divalent Metal Centers in Boron Imidazolate Frameworks by Solid-State NMR and DFT Calculations

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Boron imidazolate frameworks (BIFs) represent one of the most promising classes of metal-organic frameworks (MOFs) that structurally mimic zeolites. In BIFs, it replaced the oxygen atoms in the inorganic zeolite structure with the imidazole ligand, and the tetrahedral nodes are composed of boron (B^{3+}) and metal ions, forming $AlPO_4$-like topologies [1]. Since one nitrogen of each imidazolate coordinates to B^{3+}, the charge balance in conventional BIFs typically requires monovalent metal cations (e.g., Li^+, Cu^+), leading to neutral $M^IB(im)_4$ frameworks. By introducing additional terminal or carboxylate ligands to compensate for the charge of $M^{II}B(im)_4^+$ frameworks, divalent metal ions (e.g., Zn^{2+}, Cd^{2+}, Co^{2+}) can be successfully incorporated into BIF frameworks. Such substitutions significantly broaden the structural and functional diversity of BIFs, enhancing their potential in photocatalysis, electrocatalysis, and gas adsorption [2,3]. However, the introduction of divalent centers and auxiliary ligands increases the structural complexity and asymmetry, making it challenging to elucidate the precise local environments of the metal centers. In this research, ^1H, ^7Li, ^{11}B, ^{13}C, ^{67}Zn, ^{111}Cd solid-state NMR spectroscopy in combination with density functional theory (DFT) calculations were employed to unravel the local coordination environments of divalent metal centers in a series of BIFs. This integrated experimental-computational approach provides molecular-level insight into the structure-property relationships of BIFs, thereby advancing our understanding of their coordination chemistry and guiding the design of new BIF materials with tailored functionalities.

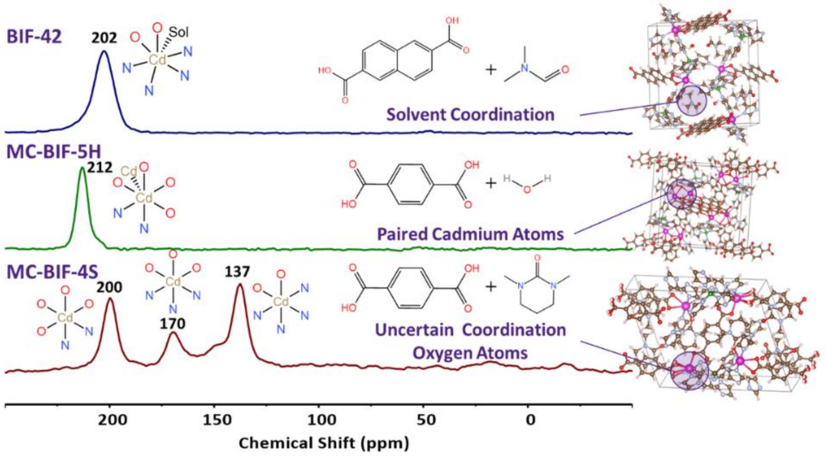

Figure 1. ^1H - ^{111}Cd CP/MAS NMR spectroscopy and the structural models for DFT calculations.

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Rapid Synthesis of Doped and Filled $CoSb_3$ Skutterudites for Thermoelectric Applications

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Thermoelectric materials can convert waste heat into electricity. Among them, the skutterudite materials based on $CoSb_3$ have attracted significant interest due to their tunable structure and properties. Many studies show that Yb-filled skutterudites ($Yb_xCo_4Sb_{12}$) contain Yb_2O_3 impurities because of high vapor pressure of Yb and its subsequent reaction with silica tube, and potentially long synthesis process. In this study we are trying to optimize synthesis of the $Yb_xCo_{4-y}Ni_ySb_{12}$ skutterudites. Phases with the nominal compositions Co_4SB_{12}, $Co_{3.95}Ni_{0.05}Sb_{12}$ and $Yb_{0.3}Co_{3.95}Ni_{0.05}Sb_{12}$ are melted at 1100°C, quenched in room temperature water and then annealed for 12 hrs at 650°C. The samples were ground using the ball mill and consolidated through spark plasma sintering. This strategy decreased the oxide impurities and yielded samples suitable for transport properties measurement. The samples are characterized by X-Ray diffraction, scanning electron microscope. The Seebeck coefficient and electrical conductivity are measured from 300 K to 773 K. The $Yb_xCo_{4-y}Ni_ySb_{12}$ samples show an n-type behavior as the majority charge carriers are electrons whereas the pristine $CoSb_3$ sample exhibits a p-type behavior because of holes are dominant carriers.

The filling fraction limit (FFL) or solubility of fillers in n-type skutterudites is lower when compared to the p-type skutterudites.

Key Words:

Thermoelectric, Quench and Anneal, Spark plasma Sintering, Yb filling, Oxide Phase.

Figure 1. McMaster University.

Nitrogen Radical Cations as Potent Electrophilic Catalysts

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The chemistry of acids and bases is the foundation of many chemical processes, from biological functions to chemical transformations. In recent years, the concept of Lewis acidity has been expanded into catalysis, however, the ability of a Lewis acid to achieve catalysis is highly dependent on the strength of the interaction with the base, which is directly related to the catalyst's electrophilicity. Tuning Lewis acid strength and understanding its impact on catalytic reactivity has become a major research focus over the past two decades, particularly following the emergence of frustrated Lewis pairs (FLPs) as metal-free alternatives for bond activation and catalysis.[1]

The electrophilicity of organic radicals has been quantified in a recent computational study, where nitrogen radical cations have been shown to possess highly electrophilic character.[2] Previous work in the Slanina and Caputo groups has shown that compounds possessing a nitrogen radical cation can be highly active towards several catalytic transformations.[3,4] This work describes the catalytic reactivity of triarylamminium radical cations towards classically Lewis acid mediated transformations. Catalysts were selected to explore both steric and electronic effects, through introducing propeller, helical and planar geometries, as well as variously substituted triarylamines. A series of control experiments were performed to rule out previously reported single-electron transfer (SET) reactivity and computational assessments of electrophilicity were completed to scale electrophilicity with previously reported radical cations. A myriad of reactions were shown to be catalyzed by triarylamminium radical cations, highlighting their utility as organic catalysts and opening the door to thinking about Lewis acid catalysis in a new way.

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Synthesis of Oligo Alkynes Stabilized by Boron Difluoride Adducts of Pyridyl Hydrazone Ligands

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Boron difluoride dyes are an exciting focus of current research due to their unique redox, optoelectronic, and photoluminescent properties arising from molecular π-conjugation. Found in applications ranging from materials science to biomedical research and drug discovery, new advances in this class of molecule are essential for the development of next-generation electronics and the advancement of therapeutic approaches. Combining oligoynes, *sp*-hybridized carbon atoms containing alternating single and triple bonds, with boron difluoride adducts can result in compounds with unique redox and optical properties that cannot be achieved by the individual components. In this presentation, we will describe an approach for the design of boron difluoride complexes of pyridyl nitrogen donor ligands (BF_2) as end-caps for symmetric $BF_2–[C\equiv C]_n–BF_2$ and asymmetric $BF_2–[C\equiv C]_n–Si(Me)_3$ (Figure 1). We hypothesize that the BF_2 end-caps assist in stabilizing the oligoynes while also providing redox and optical properties to these molecules including aggregation induced emission. This research provides valuable insights into the design and development of redox-active fluorescent dyes and their future potential applications in materials science.

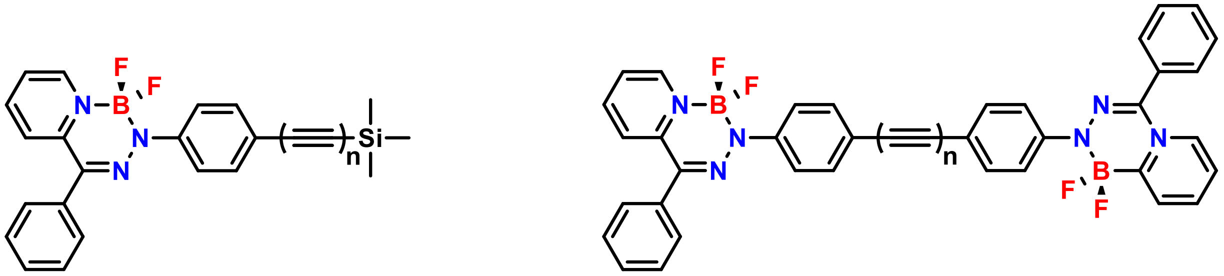

Figure 1. Example of compounds using BF_2 end-caps to stabilize oligo alkynes.

The Incorporation of Trigonal Planar Phosphonium Cations into Conjugated Molecules

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Highly conjugated molecules play a significant role in material science as they often have unique photophysical, electronic and structural properties. While there is extensive interest in all-carbon conjugated scaffolds, it has been found that incorporating main-group elements into these systems can open the door to unprecedented properties.[1] Phosphorus in particular, has been of interest due to its ability to accommodate multiple oxidation states, impacting distinct reactivity and optoelectronic properties.[1]

Building on our group's recent discovery of a novel pathway to incorporate low-valent P(V), trigonal planar phosphonium cations into a conjugated [3]cumulene framework, this project investigates if the synthetic approach can be extended to other conjugated motifs, particularly quinoidal aromatic structures.[2] This presentation will detail our progress and the synthesis, characterization and molecular properties will be reported.

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Boosting the Persistent Luminescence of Cr^{3+}-Doped Zinc Gallate Nanoparticles

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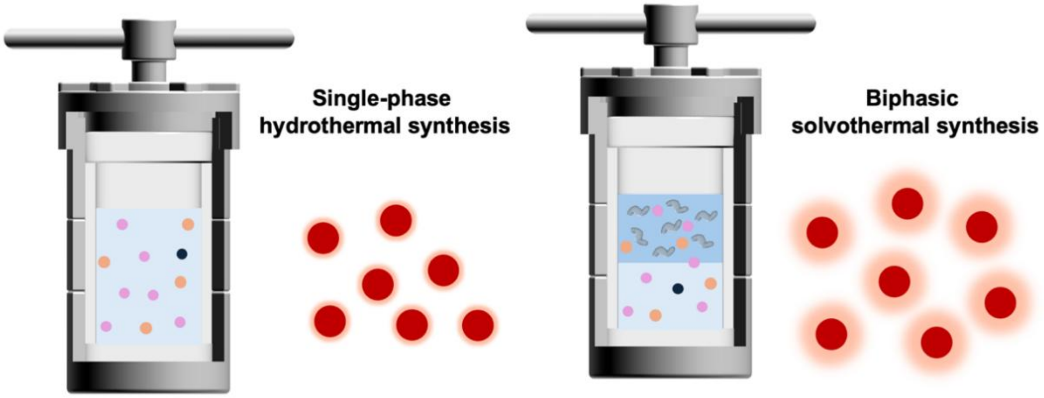
Persistent luminescence (PersL) is a unique optical phenomenon in inorganic phosphors where prolonged luminescence can be observed upon the removal of its excitation source.[1] Near-infrared PersL can be achieved when a Cr^{3+} dopant is used as the emission center, with Cr^{3+}-doped zinc gallate (CZGO) being one of the most studied inorganic luminophores.[2] The biphasic solvothermal synthesis is a promising method to synthesize ultrasmall CZGO nanoparticles,[3] but the optical properties using the existing protocol remain insufficient. In this study, the luminescence of CZGO nanoparticles was improved by optimizing the precursor ratios and solvothermal synthesis temperature. A post-annealing calcination further enhances the luminescence intensity and PersL by up to 10-fold compared to CZGO synthesized utilizing a hydrothermal approach, with the particle size being smaller. It is surprising to observe CZGO of smaller size exhibit stronger and longer PersL. Therefore, detailed spectroscopy studies were performed to investigate mechanism behind the enhanced luminescence. An X-ray photoelectron spectroscopy (XPS) fitting was developed to analyze the defects present in the synthesized CZGO nanoparticles, and the correlation between the luminescence and the electronic structure was successfully established.



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Oxidative Addition Utilizing a Lewis-Acidic Secondary Coordination Sphere

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Cross-coupling reactions are employed to form strong carbon-carbon bonds that are present in the structures of pharmaceuticals, for example. The first step in cross-coupling involves oxidative addition, which is often rate determining in nickel catalysis. Development of new methods to increase the rate of oxidative addition can give access to an improved/superior catalyst system. (1) Herein, we present an investigation into the effect of incorporation of a Lewis-acidic secondary coordination sphere (SCS) onto a diphosphine ligand scaffold. Accordingly, nickel complexes, (Ni^0(diphosphine)COD) (COD= 1,5-Cyclooctadiene) were reacted with aryl-halide substrates. The rate of oxidative addition was determined with respect to the identity of internal Lewis-acid. Overall, Lewis-acid incorporation was found to have a positive effect on reactivity by luring and shuttling Lewis-basic substrates to the nickel-center. These complexes were characterized by nuclear magnetic resonance spectroscopy (NMR), X-Ray crystallography, and using computational chemistry including density functional theory (DFT) calculations.

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

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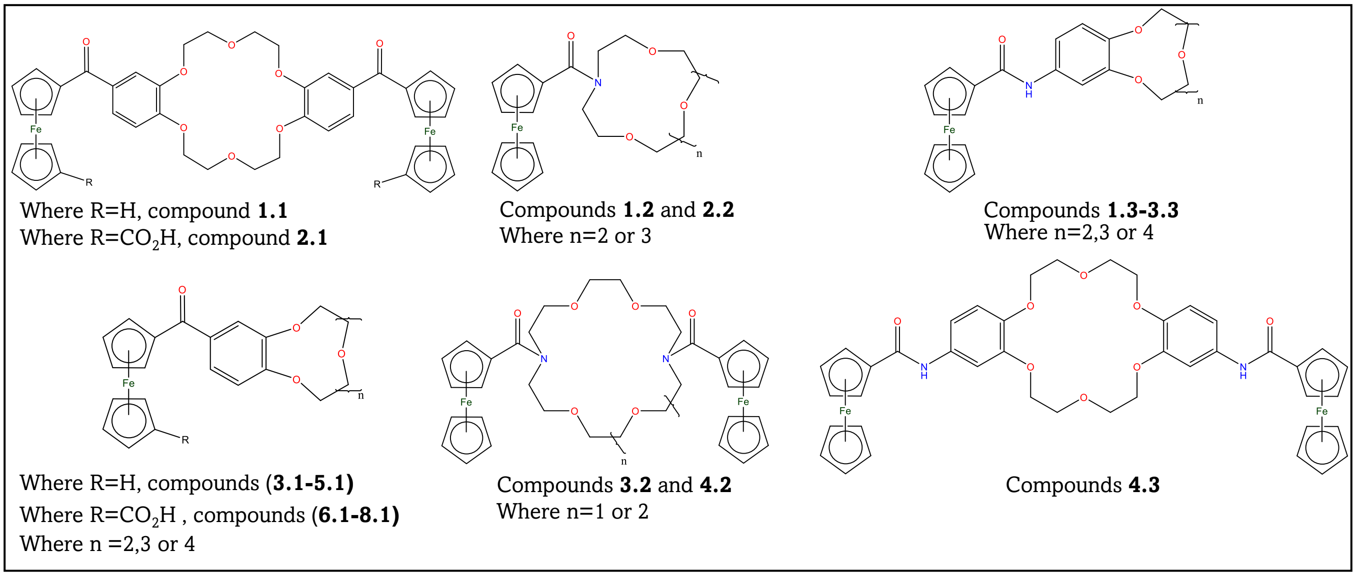
Previous research within the Pilkington group has involved the use of crown ether macrocycles for the preparation of 4f SMMs due to the compatibility of oxophilic Ln(III) ions with the oxygen donors of traditional crowns. Furthermore, the versatility of crown ethers permits facile modification of the 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.[1,2] 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.



Where R=H, compound **1.1**
Where R=CO_2H, compound **2.1**

Compounds **1.2** and **2.2**
Where n=2 or 3

Compounds **1.3-3.3**
Where n=2,3 or 4

Where R=H, compounds (**3.1-5.1)**
Where R=CO_2H , compounds (**6.1-8.1)**
Where n =2,3 or 4

Compounds **3.2** and **4.2**
Where n=1 or 2

Compounds **4.3**

Figure 1: Ferrocenoyl appended crown ether macrocycles

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Ditopic Carbenes for Metal-Organic Interfaces

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Ditopic N-heterocyclic carbenes (dNHCs) offer a modular framework for studying metal–ligand bonding and cooperative reactivity at extended surfaces. We describe the vapor-phase deposition of dNHCs onto coinage and early transition metals, where both coordination and surface attachment can be tuned through backbone and N-substituent variation. Self-limiting adsorption behavior is quantified by in-situ quartz crystal microbalance (QCM) and spectroscopic ellipsometry, while X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and atomic force microscopy (AFM) reveal distinct binding motifs and surface organization. The resulting dNHC monolayers display high thermal and chemical stability, consistent with strong σ-donation and restricted surface mobility. Ongoing work establishes how the donor strength and geometry of ditopic carbenes influence surface coverage, metal selectivity, and post-coordination chemistry. These findings expand the scope of carbene coordination beyond discrete complexes, bridging molecular and surface organometallic chemistry through well-defined carbene-metal interfaces.

Re-examining the X-ray Absorption Edge Dependence on Oxidation State by Analyzing Jahn-Teller Distortions

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X-ray absorption spectroscopy (XAS) has become a common technique for the analysis of element's oxidation state and local symmetry in molecules and materials. Conventional analyses utilize the correlation between the element's absorption edge energy and changes in its average oxidation state, while local symmetry is analyzed by the pre-edge shift and intensity. However, it is known that local symmetry and ligand identity also contribute significantly to absorption edge shape and energy. No analysis technique yet exists to unambiguously determine the relative contribution of oxidation state, average local symmetry, and ligand identity on absorption edge locations. We attempt to analyze and differentiate the independent contributions of oxidation state and symmetry using a series of spinel oxides, which can incorporate ions of several valences for the analysis of oxidation state changes. Additionally, spinel can exhibit a variety of defects including site disorder and unit cell distortions, providing a probe for geometric changes. A manganese oxidation state change from Mn(III) to Mn(IV) is examined using a $LiMn_{2-y}X_yO_4$ series, where X is Ti(IV) or Cr(III), while the local symmetry is monitored as the concentration of the Jahn-Teller distorted Mn(III) ion changes. This presentation will examine the local symmetry effects that may inhibit precise oxidation state determinations across a series of structural crystal structures.

High-Pressure Study on Structures and CO_2 Adsorption Performance of MOF UTSA-74

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Over the past decades, metal-organic frameworks (MOFs) have been regarded as one of the most promising materials in adsorption and storage of greenhouse gases, especially CO_2. Among these, UTSA-74 is particularly attractive owing to its binuclear Zn clusters provide two accessible open metal sites (OMSs) per metal center [1], enabling stronger host-guest interactions compared to conventional MOF structures and enhancing both adsorption capacity and selectivity. While its performance under ambient conditions has been extensively characterized, the high-pressure structural responses and adsorption behavior of UTSA-74 remain largely unexplored. In this study, we systematically investigated the structural stability and CO_2 adsorption performance of UTSA-74 under compression using *in situ* high-pressure Fourier transform infrared (FTIR) spectroscopy. The framework displayed progressive structural distortion under compression, followed by the onset of partial amorphization at elevated pressures. Most of these structural changes were largely reversible upon decompression. The presence of residual solvent molecules was found to stabilize the pore structure and mitigate framework collapse in the as-synthesized sample relative to the activated form. When loaded with CO_2, UTSA-74 revealed multiple adsorption environments, including the pore-confined CO_2, and OMS-bound CO_2. Notably, the OMS-bound CO_2 species exhibited pronounced blue-shifts upon compression, indicating stronger host-guest interactions at higher pressure. This study provides a preliminary understanding of the high-pressure responses of UTSA-74, establishing the correlations of structural changes with adsorption performance. These findings are essential for guiding further high-pressure investigations, and provide new insights into the adsorption mechanism related to the OMSs.

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A Novel Diamondoid Co-Crystal

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Advances in quantum information science are increasingly reliant on developments in the design of suitable qubits. Diamondoid co-crystals, inspired by the lattice of diamond, are an appealing bottom-up approach to scalable and chemically diverse qubit structures, in particular if persistent radicals can be created in a crystal containing carbon-halogen bonds Toward this goal, we report the synthesis and characterization of a novel diamondoid co-crystal, $(AdBr_4)_1(HMTA)_1(PTA)_1$, achieved by the co-crystallization of *1,3,5,7*-tetrabromoadamantane ($AdBr_4$), hexamethylenetetramine (HMTA), and *1,3,5*-triaza-*7*-phosphaadamantane (PTA) in chloroform *via* slow evaporation.

Powder X-ray diffraction (PXRD) confirms the formation of a new crystalline phase. The structure was solved by single-crystal X-ray crystallography. It is broadly consistent with a half-Heusler diamondoid lattice,[1] with PTA successfully substituting one HMTA molecule per formula unit. However, this structure is novel in that it is a polar crystal and in the hexagonal system. The classic half-Heusler structures described by Reddy/Craig/Desiraju were cubic. This result highlights the structural flexibility and chemical design potential of the $AdBr_4$–HMTA framework for future materials engineering. Ongoing work includes probing radical formation and spin-state characterization *via* electron paramagnetic resonance spectroscopy.

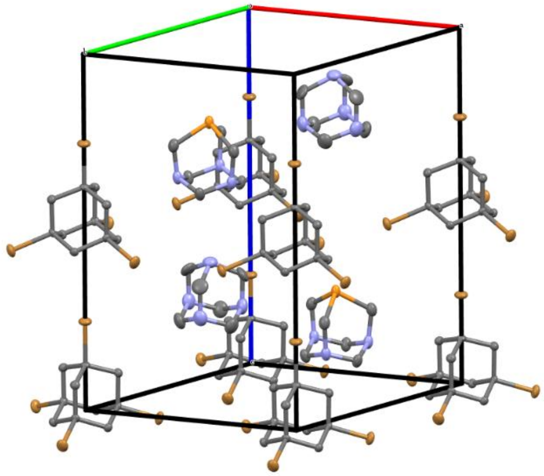

Figure 1. Crystal structure of polar, hexagonal $(AdBr_4)$(HMTA)(PTA). Space group: $P6_3mc$.

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Synthesis and Characterization of Group 13 Complexes of Tetradentate Formazanate Ligands

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Formazans (R^1–NH–N=CR^3–N=N–R^5) are a historical class of compounds that are comprised of nitrogen-rich backbones which result in their characteristic intense colour and redox chemistry.[1] These properties lead to their applications as dyes, especially for cell-viability assays in chemical biology.[1,2] Furthermore, simply through structural variation of the substituents on the backbone, the properties of the compounds can be modified. This project explores the synthesis of group 13 complexes with $N_2O_2^{3-}$ formazanate ligands, which contains *o*-hydroxyphenyl substituents at the R^1 and R^5 position of the nitrogen-rich backbone. Previously, the attempted synthesis of a boron formazanate complex using this ligand led to the unexpected formation five unique complexes due to the strain of the heterocycle.[3] Then, aluminum formazanate complexes supported by phosphine oxide donors were synthesized. The absorption and emission properties of the family of aluminum formazanate complexes were measured, and the electrochemiluminescence properties of one of the derivatives was explored. Our current efforts are focused on the incorporation of gallium to generate unique heterocycles. The findings of these studies suggest applications of these complexes as functional materials.

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Preventing Phase Segregation to Maximize Exsolution Potential

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Over the past decade, exsolution has emerged as a prominent method for forming stabilized nanoparticles within perovskite supports.[1] However, stabilizing dopants that readily undergo reduction such as Pt in perovskite lattices is challenging due to premature metallic segregation and reduction preventing uniform incorporation of the dopant into the lattice.[2-4] Herein, we present an expedient molten salt synthesis as an effective route to incorporate Pt in the 4+ oxidation state at the B site of a $CaTiO_3$ perovskite, producing a homogeneously doped lattice. By working in a molten state, ion distribution not only remains uniform but, provides an oxidative environment that prevents premature reduction of Pt and maintains the desired oxidation state. Upon subsequent heating under reducing conditions, Pt ions migrate to the surface, forming well-dispersed metallic nanoparticles that remain partially embedded in the perovskite lattice in a process known as exsolution. This work highlights the versatility of molten salt synthesis in reproducibly synthesizing homogenously doped perovskites for exsolution, further extending to the realms of catalysis and higher-order industrial applications.

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Making Iron Complexes Uncomfortable: The Effects of Cp substituents on Reactivity

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Cyclopentadienyl (Cp) ligands have been an essential scaffold in organometallic chemistry, offering rich reactivity pathways through the multitude of possible substituents present on the ring system. In the Drover lab, the Cp* (1,2,3,4,5 -pentamethylcyclopentadienyl) has been utilized extensively, namely for the development of the first ever room temperature stable iron diphosphine 'tucked-in' compound. This tucked-in compound offers a nucleophilic carbon allowing for extreme reactivity, and a broad range of products, often involving environmentally relevant small molecules such as CO_2, therefore being relevant targets for green chemistry. Herein we describe the generation of multiple Cp based iron diphosphine compounds, targeting the generation of nucleophilic carbons, and followed up chemistry for the modification of small molecules, including CO_2, carbonyl bearing compounds, and N_2. This work also explores the generation of the first ever generated PCP η^3 bound diphosphine iron compound and it's strained, very reactive [4, 3] membered ring system.

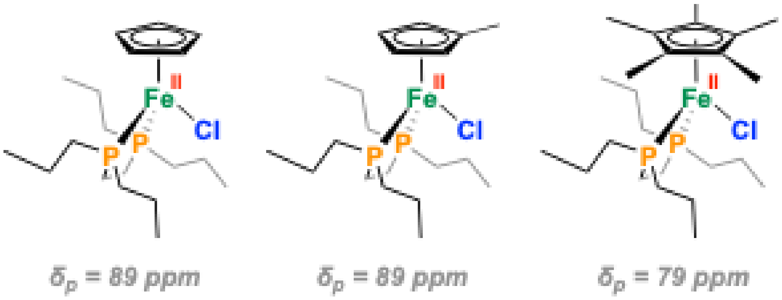

Figure 1. Preliminary iron compounds for synthesis of strained iron compounds

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Facilitating the Conversion of Aluminum-Silicide to Intermetallic Phases

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Most hot stamping lines use roller hearth furnaces to austenitize the steel blanks prior to the combined forming/quenching stage [1 2]. To avoid oxidation and decarburization of the steel during the hot stamping process, the steel is normally coated with a layer of aluminum-silicide. [3] Throughout the austenitization step, the steel|Al-Si interface undergoes a series of reactions as the iron from the steel diffuses into the Al-Si layer, leading to an Fe-Al-Si intermetallic layer that provides some corrosion protection [5 6]. Unfortunately, the Al-Si layer melts at ca. 600°C, and can contaminate the furnace rollers, leading to costly replacement and operational downtime[4].

In this work, we show how depositing an iron-rich layer on top of the Al-Si layer can facilitate iron diffusion into the Al-Si coating, accelerating the coating transformation compared to the standard Al-Si coating. [7] This facilitation of intermetallic phase formation decreases the time that the coating spends in the liquid state, which will decrease liquid transfer of the Al-Si layer to the furnace components.

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Post-Functionalization of Metal–N-Heterocyclic Carbene Complexes via Backbone Reactivity

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N-Heterocyclic carbenes (NHCs) are privileged ligands in organometallic chemistry, known for their strong σ-donor ability and tunable electronic properties. Though most studies focus on modifying the N-substituents to influence metal-carbene bonding, few have explored the reactivity originating from the heterocycles backbone itself. Here, we present NHC ligands bearing polar unsaturated substituents such as aldehydes and imines that enable post-functionalization of preformed metal-NHC complexes through simple condensation or addition reactions. These transformations proceed under mild conditions, expanding structural diversity without altering the primary metal-carbene bond. Spectroscopic and crystallographic analyses reveal that such backbone derivatization can modulate the coordination environment, conjugation, and overall electronic profile of the metal center. This approach introduces a new dimension to NHC ligand design chemically adaptable frameworks that can bare and allow for late-stage modification of metal complexes for catalysis and molecular materials.

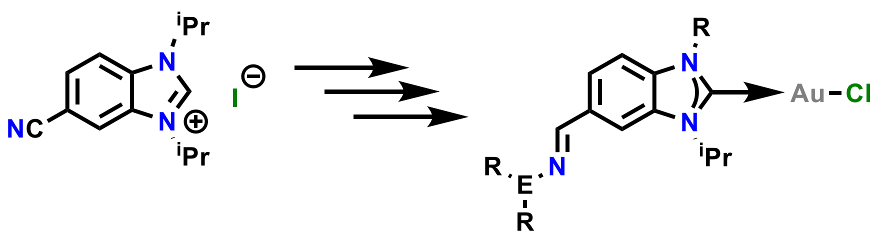
Coordination and Hydroelementation

Figure 2: *Hydroelementation of a N-Heterocyclic carbene metal-complex.*

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A Powerful Carbanion from the Smallest Nano-Diamond: The Synthesis of bis-2-Adamantyl Magnesium

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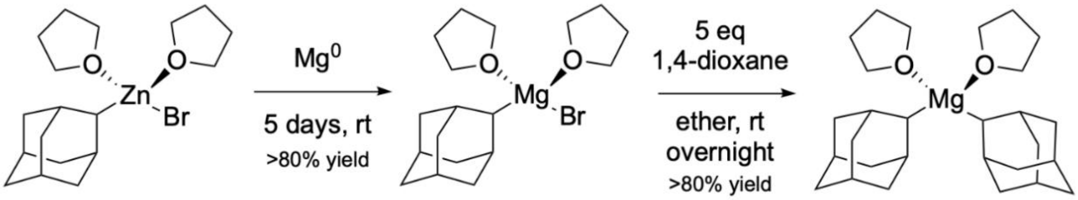

Figure 1. Synthesis of bis-2-adamantyl magnesium from 2-adamantyl zinc bromide

Adamantane, the smallest nano-diamond, offers structural rigidity and lipophilicity, making its derivatives valuable for pharmaceuticals and materials. However, accessing 2-adamantyl carbanions is challenging due to poor reproducibility and side reactions in traditional Grignard syntheses. This work develops scalable, high-yield syntheses of 2-adamantylmagnesium bromide ((2-Ad)MgBr) and bis-2-adamantylmagnesium ($(2\text{-Ad})_2Mg$), enabling their use as potent carbanion equivalents.

Starting from 2-adamantylzinc bromide ((2-Ad)ZnBr), we optimized magnesium reductive transmetallation to yield (2-Ad)MgBr in >80% yield, isolable as a solid or solution in THF or diethyl ether. This improves prior methods[1] by minimizing impurities and enhancing scalability through controlled conditions and streamlined work-up. Using ether-solvated (2-Ad)MgBr, we overcame solubility issues in the Schlenk equilibrium, achieving $(2\text{-Ad})_2Mg$ in >80% yield via the dioxane precipitation method. This process requires only simple filtration, avoiding complex lithium-based reductions (e.g., Li biphenylide)[2]. The product, obtained as an ether solution or air-sensitive solid, exhibits room-temperature stability for months, unlike unstable 2-adamantyllithium[3]. Characterization by NMR spectroscopy and two different titration methods confirm yield and purity.

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An Investigation into the Structure of $[Ru(Ind)(P^{Cy}{}_2N^{Ph}{}_2)]^+$ Pre-catalysts

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Heterocycles are a relevant class of molecules in the pharmaceutical, agricultural, and natural products industries.[1] This makes them valuable structural motifs and highlights the importance and need for an efficient and economic pathway to these molecules.[1] Previously, the properties of the family of pre-catalysts $[Ru(Cp/Cp^*)(P^R{}_2N^{R'}{}_2)MeCN][PF_6]$, as well as their ability to perform catalytic cycloisomerizations to produce heterocycles was investigated.[2],[3] It has also been previously demonstrated by Basolo and colleagues that in certain associative substitutions, indenyl complexes perform 3.8×10^8 times more rapidly than their Cp complex counterpart.[4] It is on this basis that the use of an indenyl group as the ancillary ligand will be investigated as opposed to further investigation into the Cp or Cp* (Cp = cyclopentadienyl, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) analogues. The aim of this research is to broaden the scope of the information related to this family of catalysts. This will be done through the optimization of the preparation of $RuCl(Ind)(P^{Cy}{}_2N^{Ph}{}_2)$, as well as its thermal stability after undergoing halide abstraction. The subsequent synthesis of $[Ru(Ind)(P^{Cy}{}_2N^{Ph}{}_2)(MeCN)][PF_6]$ and its effectiveness in the catalytic transformations mentioned above will also be investigated. Results suggest the successful optimization of $RuCl(Ind)(P^{Cy}{}_2N^{Ph}{}_2)$, as well as comparable thermal stability information to the previously conducted experiments with Cp/Cp* analogues.[2]

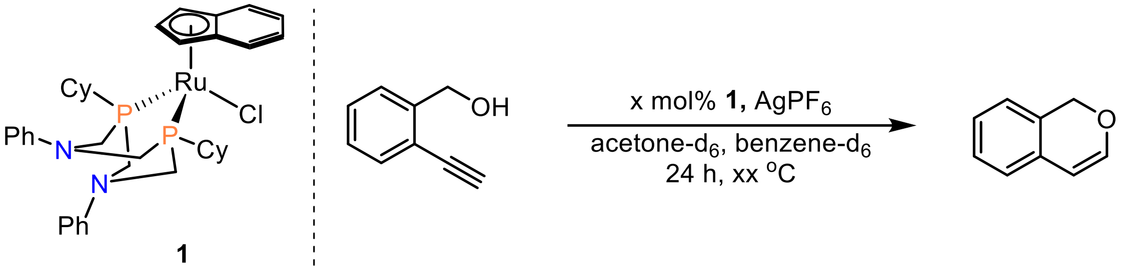

Figure 1. The investigated pre-catalyst $[Ru(Ind)(P^{Cy}{}_2N^{Ph}{}_2)Cl]$ **1**, and catalytic reaction scheme.

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Incorporating Dithienophosphole into Quinoidal Structures toward Biradical Species

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The development of low-bandgap π-conjugated small molecules is critical for next-generation optoelectronic and energy-storage devices. Their near-infrared absorption, high conductivity, and strong electron affinity make them attractive for applications in transistors, photodetectors, batteries, and particularly as non-fullerene acceptors (NFAs) in organic solar cells (OSCs).[1] Quinoidal structures are of special interest since their drive toward aromaticity imparts biradical character, narrows the bandgap, and introduces unique electronic and magnetic properties.[2] Incorporation of heteroatoms further enhances these systems; notably, phosphorus-based motifs such as the phosphole ring lower the LUMO via σ*-π* hyperconjugation, strengthen electron-accepting ability.[3,4]

In this work, we report a dithienophosphole-based quinoidal compound with extended π-delocalization. UV-Vis spectroscopy revealed strong visible absorption, while cyclic voltammetry showed reversible reduction processes, underscoring its stability and pronounced electron affinity. These results highlight dithienophosphole-based quinoids as promising redox-active and electron-transport materials.

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