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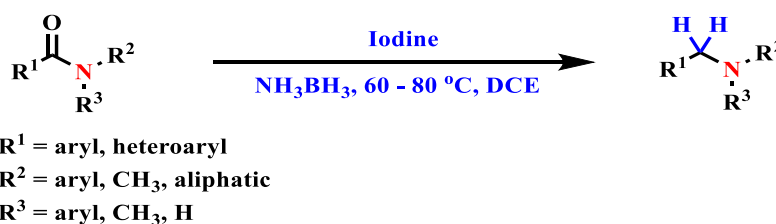
Boron-nitrogen reagents for organic transformations: *In-situ* generated μ -aminodiborane from ammonia borane and iodine for deoxygenative reduction of carboxamides

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Reduction reactions of carbonyl compounds are among the most important transformations in organic chemistry with the carboxamide group being one of the most challenging to reduce. Ammonia borane ($\text{NH}_3\cdot\text{BH}_3$, AB) has proved to be an efficient solid hydrogen source that is stable in air and moisture and easy to handle.¹ The use of AB as a reagent for carrying out various functional group transformations is well documented.² In contrast, very little has been reported on the easy synthesis and utility of μ -aminodiborane ($\mu\text{-NH}_2\text{B}_2\text{H}_5$, $\mu\text{-ADB}$) as a reagent for organic functional group transformations.³

In this presentation we report a new, simple, and cost-effective method for the reduction of amides to amines using *in-situ* generated $\mu\text{-ADB}$ from the reaction of AB and elemental iodine (I_2) (Scheme 1). This method of reduction is applicable to various secondary, tertiary and trifluoroamides with yields in the range of 67-94%. Control experiments and mechanistic studies indicate that the active reagent in case of reduction of secondary amides is $\mu\text{-ADB}$ and in the case of tertiary amides, it is polyaminoboranes.



Scheme 1: Reduction of secondary and tertiary amides to corresponding amines by using ammonia-borane and iodine

References

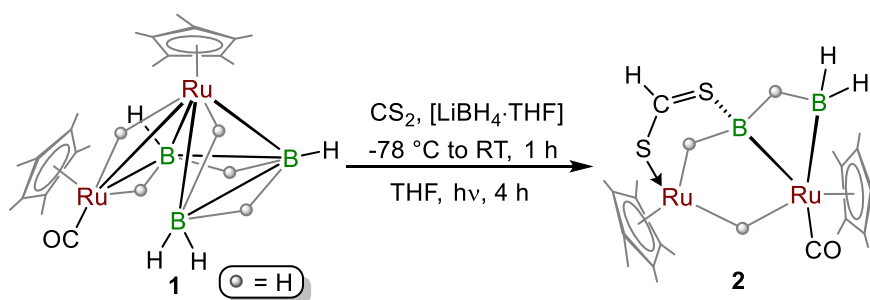
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The transition metal (TM) diborane and their derivatives are of significant interest due to their application in various fields such as catalytic borylation of unsaturated hydrocarbons, dehydrocoupling reactions and storage of dihydrogen.¹ Apart from their intriguing applications, TM-diboranes can also act as a ligand to form metal complexes that provide a close link with organometallic systems.² As a result, finding viable synthetic methods for TM-diborane species became of interest. The general synthetic route for the TM-diboranes includes the reaction of TM carbonyl or cyclopentadienyl chloride of TM precursors with mono or polyborane reagents.³ In addition, TM-diboranes also can be synthesised from preformed metallaboranes.³ With an objective to synthesize thiolate stabilized diborane species, we performed the photolytic reaction of a ruthenium triborane *arachno*-[1,2-(Cp**RuH*)(Cp**RuCO*)-B₃H₈] (**1**) with in situ generated intermediate from the reaction of CS₂ and [LiBH₄·THF]. The reaction led to the formation of metal stabilized diborane(6) [(Cp**RuCO*)(Cp**Ru*)(B₂H₄)(μ-H)(SCH=S)] (**2**) (Scheme 1) by metal-assisted hydroboration with a dithioformato ligand (CHS₂). The [B₂H₄(SCH=S)]⁻ ligand is asymmetrically coordinated in η³-co-ordination mode to diruthenium moiety [(Cp**RuCO*)(Cp**Ru*)] having a hydrido ligand. The key results of this work will be presented.



Scheme 1. Synthesis of metal stabilized diborane(6) analogue (**2**).

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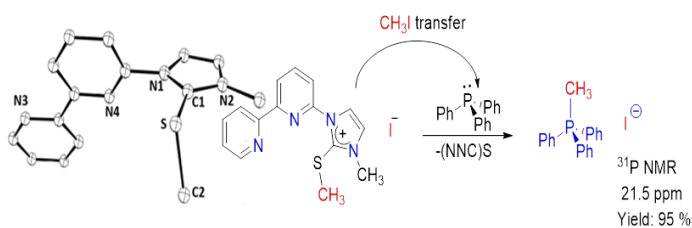
(*N,N,C*) Carbenes Supported Group-16 Cations: Synthesis, Structures, and Reactivity Towards Methyl Iodide Transfer Reactions

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Since the seminal discovery of stable N-heterocyclic carbenes (NHCs) in 1992 by Arduengo,^[1]NHCs have been explored in various fields of chemical sciences. NHCs as ligands in the stabilization of various main-group element chemistry,^[2,3] and transition metals have gained wide-spread interest due to their high sigma-donating, and weak pi-accepting abilities. NHC adducts of group 16 elements can be connected back to Ansell first observation already in 1970, as this group reported the first isolation of 1,3-dimethylimidazolin-2-thione (IMe)S^[4]. Novel hybrid ligands, especially consisting of NNC-type species may serve as novel multidentate NHC supported ligands. Such species containing pyrid-2-yl type moiety bearing nitrogen donor atoms may show new applications in coordination, and organometallic synthesis as novel ancillary ligands.

A series of bipyridyl functionalized imidazolin-2-thiones and selones of the type (NNC)E (E = S (**1**), Se (**2**)) were isolated, and subsequent reactions with MeX furnished cationic [(NNC)EMe]X (E = S (**3**), Se (**4**); X = I or OTf) derivatives. The coordinating ability of **3** and **4** were explored and isolated a series of cationic copper(I) complexes. The ⁷⁷Se NMR studies indicated a gradual down-field chemical shifts of the free (Imidazolin-2-selone) to cationic methyl derivative to its copper(I) complex, which indicated a different electronic situation around the selenium atom in all the isolated derivatives. In addition to these studies, the cationic species **3** and **4** containing iodide counter parts were also introduced as methylating reagents toward a series of nucleophiles, and isolated the corresponding salts as pure substances (see Scheme).^[5]



Scheme. Sulfenyl-methyl (SMe) cation as methyl transfer reagent.

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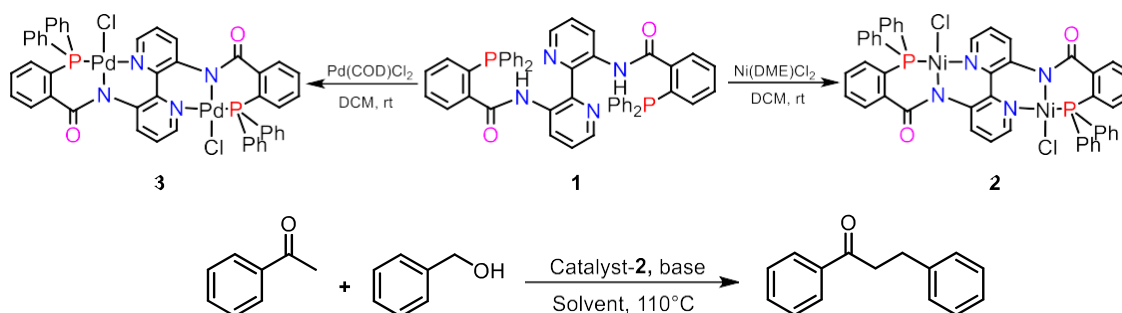
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The chemistry and catalysis of organometallics depend significantly on ligand choice.¹⁻² One can control the activity of the resulting metal complexes by methodically adjusting the ligand backbone. Due to their significance in coordination chemistry and catalysis, sterically demanding phosphines have attracted a lot of interest among the numerous classical ligands in recent years.³ Recently, we reported the synthesis of sterically challenging mono- and bis-phosphine ligands and investigated their coordination characteristics and catalytic applications.⁴⁻⁶ In continuation of that, we have synthesized bipyridine based bulky bisphosphine ligand **1** and investigated their coordination properties as well as catalytic applications. The reaction of **1** with [Ni(DME)Cl₂] in 1:2 molar ratio, afforded dipincer complex **2**, whereas the reactions of **1** with [Pd(COD)Cl₂] in 1:2 molar ratio produced dipincer complex **3**. With very little catalyst loading, Complex **2** promoted the alkylation and transfer hydrogenation processes. The synthetic details and structural aspects will be presented in poster.



Scheme 1. Synthesis of Ni^{II}, Pd^{II} complexes and catalytic studies

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P5

Mechanistic Investigations on Bismuth-Catalysed Reduction of Ketones and Phosphine Oxides

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Lewis acidic bismuth compounds have found catalytic applications in the reduction of unsaturated bonds. Hydrosilylation reaction is a class of reduction reaction where the Si-H bond is added across the unsaturated bonds and hydrosilanes are used as the hydride sources. In carbonyl hydrosilylation, two possible pathways are via Si-H activation and C=O activation. Recently, a less sterically hindered bismuth dication, [NMe₂C₆H₄Bi][B(3,5-C₆H₃Cl₂)₄]₂, was reported possessing three electrophilic sites and was employed as a catalyst for the hydrosilylation of aldehydes and ketones. The mechanism could advance through two possible routes – Si-H activation or C=O activation; it was hypothesised that it followed the C=O activation route. In this study, the weakly coordinating borate anion was replaced by [Al{OC(CF₃)₃}]₄⁻ leading to increased reaction rates and better reactivity as illustrated by the deoxygenation of some ketone substrates. The solvent effect played a significant role in the catalysis and masked the electrophilic sites on the Bi centre. Kinetic studies inferred that Si-H activation was the driving force of the carbonyl reduction reaction in the solution state. This was also supported by DFT analysis. Reduction of the stronger P=O was also explored. In this poster, we will present the key results of this study.



Figure 1. The difference in reactivity of bismuth dication by replacing anion

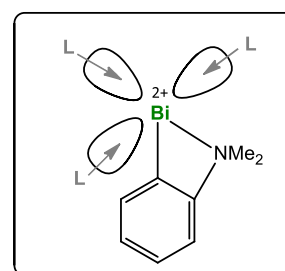


Figure 2. Qualitative representation of the electrophilic sites on the Bi centre

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P6

**2-(2-Hydroxyphenyl) Benzimidazole -Based Four Coordinate Boron
Compounds: Synthesis, Structural Characterization and Photophysical studies**

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ABSTRACT:

Design, synthesis and photo-physical studies of light emitting materials are of interest due to their applications in the field of organic light emitting diodes.¹⁻³ In view of this interest we synthesized four coordinated boron compounds from differently substituted 2-(2-hydroxyphenyl) benzimidazole (HBI) chelating ligands. These are air- and moisture-stable and are soluble in organic polar solvents. These compounds were characterized by multinuclear spectroscopic methods as well as single-crystal X-ray diffraction analysis. The photophysical properties of these ligands and boron complexes have been studied both in solution and solid state. The ligands 2-(2-hydroxyphenyl) benzimidazole display aggregation-induced emission (AIE) behaviour upon the addition of water in THF leading to a sizable enhancement of fluorescence intensity. Additionally, some of the boron complex was found to sense picric acid.

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In catalytic activation of small molecules, metal-ligand cooperation (MLC) has become an important tool.¹ Small molecules such as H₂, CO₂, boranes, or silanes can be activated by MLC across the metal-ligand bond.² Our analysis of the 1,3-*N,S*-chelated ruthenium species revealed that the combination of redox-active ligands and metal-ligand cooperativity has a significant effect on the multisite borane and silane activation.³ We have explore the hemilability of the κ^2 -*N,S*-bidentate ligand, and investigated the reactivity of [PPh₃(κ^2 -*N,S*-(NC₇H₄S₂)Ru{ κ^3 -H,S,S'-H₂B(NC₇H₄S₂)₂}), with boranes and silanes.³ The aerial oxidation of these borate complexes [PR₃{ κ^2 -*N,S*-(L)}Ru{ κ^3 -H,S,S'-BH₂(L)₂}] (R = Cy or Ph; L= NC₇H₄S₂), produced, EPR active *mer*-[PR₃{ κ^2 -*N,S*-(L)}₂Ru { κ^1 -S-(L)}], (R = Cy or Ph; L= NC₇H₄S₂) complexes. Treatment of these complexes with BH₃.THF led to the isolation of *fac*-[PR₃Ru{ κ^3 -H,S,S'-(NH₂B₂SBH₂N)(S₂C₇H₄)₂}] (R = Cy or R = Ph) that captured boranes at both sites of the κ^2 -*N,S*-chelated ruthenacycles. In contrast, when EPR active complex was treated with BH₂Mes it led to the formation of *trans*- and *cis*-bis(dihydroborate) complexes [{ κ^3 -S,H,H-(NH₂BMes)Ru(S₂C₇H₄)₂ }].³ We have further examined the capability of these flexible borate moieties and hemilabile 1,3-*N,S*-chelating mercaptobenzothiazolyl ligand that adopt different spatial arrangements at ruthenium center. The key results of these works will be discussed.

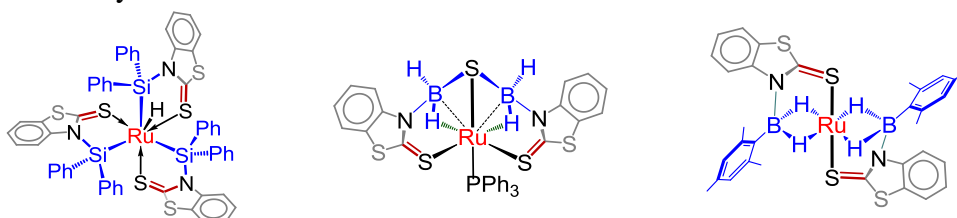


Figure 1. Activation of silanes and boranes by using Ru-N bonds.

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P8

“Four-Coordinate Germylene and Stannylene and their Reactivity
towards Se & Te”

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The “heavy ketones”, which contain a double bond between heavier group 14 and 16 elements, are attractive synthetic targets due to their reactive nature. The synthesis of heavy ketones is very much dependent upon the bulkiness of the substituents as an increase in bulk favors the stabilization of double-bonded compounds. In order to synthesize the double-bonded chalcogenides, we utilized a bulky ligand ((E)-1-(2-bromophenyl)-N-(2,6-dibenzhydryl-4-methylphenyl) ethan-1-imine) with a sterically crowded Ar* group [Ar*=2,6-(dibenzhydryl-4-methylphenyl)] on the nitrogen atom. In this work we report sterically demanding chlorogermylene, chlorostannylene, homoleptic germylene, homoleptic stannylene, germaselenone, stannaselenone, and stannatellurone. Furthermore, the reactivity of homoleptic germylene, and homoleptic stannylene with elemental selenium and tellurium afforded heavy ketones. All the complexes are well characterized by NMR spectroscopic techniques, mass spectrometry, and single crystal X-ray diffraction studies.

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P9

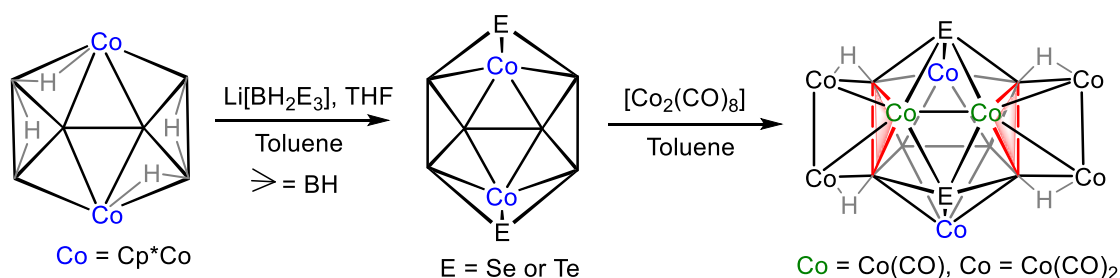
Sequential Cluster Expansion Reactions: Octaborane(12) to Icosahedron

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Metallaborane chemistry has grown in a pleasing fashion based on its structural, bonding and reaction chemistry. During the last few decades Fehlner *et al.*,¹ Kennedy *et al.*,² and us³ developed various synthetic strategies that led to the emergence of many single-cage and condensed metallaborane clusters having unique geometries. In this regard, we have isolated various mono and doubly face-fused icosahedral clusters from octaborane(12) [(Cp*Co)₂B₆H₁₀] (Cp* = η⁵-C₅Me₅) having heavier chalcogen atoms in cluster framework (Scheme 1). These higher-nuclearity clusters have been extremely useful in the investigation of unique bonding and very large size electronic structures.⁴ The key results of this work will be described.



Scheme 1. Sequential cluster expansion of octaborane(12).

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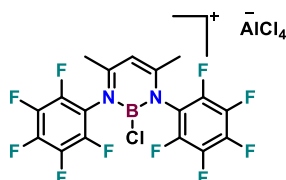
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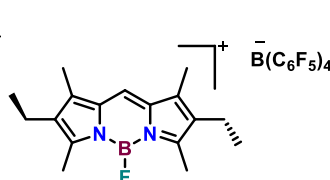
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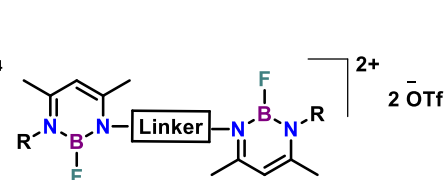
Group 13 elements quintessentially known for their Lewis acidic behaviour because of their electron deficiency. The observed bonding pattern and their tendency to undergo reactions to fulfil their valence shell is governed by electron deficiency. For example, neutral group 13 species are electrophilic in nature and their corresponding cationic species are even more electrophilic in nature because of greater electron deficiency and coordination unsaturation. The chemistry of higher group 13 (Al, Ga, In and Tl) cationic species has been reviewed,^[1] however low coordinate boron cation was not explored much till 1985.^[2] In 2008 Cowley and co-workers reported the betadiiminate (BDI) substituted borenium cation^[3] and later Piers and co-workers in same year reported Borenium cation derived by BODIPY dyes.^[4] Inspired by Cowley and Piers results, we demonstrated the synthesis of various betadiiminate ligands and their boron complexes which became the starting point for bis-borenium cation via halide abstraction. The details of the work will be discussed.



Cowley (2008)



W.E. Piers (2008)



This Work

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P11

Primary and secondary interactions in main group Lewis acids: consequence on reactivity manifested on antimony center

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Primary and secondary bonding interactions form the basis of any substrate activation in Lewis-acid mediated organic transformations since substrate activation occurs at secondary bonding site. The nature of primary bond determines the strength of the secondary interactions, often substantiated using the concept of σ -hole and characteristics of lowest unoccupied molecular orbital (LUMO). An adequately strong nucleophilic substrate attacking a secondary site can drastically change the relative reactivity at a main group Lewis center. The choice of a suitable ligand can effectively control these interactions and help design molecular systems to activate unsaturated bonds facilitating Lewis acid mediated catalysis. Investigating on the boundaries of primary and secondary interactions, neutral and cationic models of (Mesityl)₂EX (E = Sb, Bi and X = Cl, OTf) were synthesized demonstrating a reversal of Lewis acidity from bismuth to antimony. This concept was used to show the superiority of (Mesityl)₂SbOTf over (Mesityl)₂BiOTf in the catalytic reduction of phosphine oxides to phosphines. Further, two series of antimony cations, [(NMe₂CH₂C₆H₄)(Mesityl)Sb]⁺ (**A**) and [(NMe₂C₆H₄)(Mesityl)Sb]⁺ (**B**) were explored by coordinating ligands of varying nucleophilicity at the position trans to N-donor. Whereas a reversal from primary to secondary bonding was observed in case of **A**, a constrained N-coordination in **B** results in diminished borders between primary and secondary interactions. Carbonyl activation was performed as a proof of concept exhibiting greater reactivity of **B** due to substrate activation at primary bonding site.

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P12 Visible light driven oxidation of indole to trisindoline conversion catalyzed by A₃ and A₂B tin and antimony corroles

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Cytochrome P450 monooxygenase is a heme-containing enzyme abundant in animals, plants and microorganisms. It selectively oxygenates C-H bond with molecular oxygen and involves in many organic transformations in metabolism. Iron containing porphyrin was developed as a synthetic model of cytochrome P450 to understand the enzyme's mechanism and mimic its peculiar catalytic behaviour. Later, porphyrin was coordinated with different metal ions and has taken to various applications, including solar cell, therapeutic agents, sensor ORR and OER. The electronic and redox properties of this metalloporphyrins can be tuned by varying the meso substitutions. Corrole is another macrocyclic ligand under the porphyrinoid family, having a similar skeletal structure to vitamin B12 and resembles porphyrins in few properties. Corrole is particularly interested because of its tri-anionic nature and small cavity, which enables it to stabilize central metal ions with higher oxidation states. After the development of facile synthetic methods, the corrole chemistry had boosted growth for the last two decades, but P- block corroles were less discussed than transition metal corroles. P-block corroles were reported in recent years as being used in catalytic, solar cell, and PDT applications. So we synthesized [5,10,15-tris(4-cyanophenyl)corolato]antimony(III), [5,10,15-tris(4-cyanophenyl)corolato]tin(IV), [5,15-di(4-cyanophenyl)-10-(methyl-5-formyl-2-methoxybenzoate)corolato]antimony(III), [5,15-di(4-cyanophenyl)-10-(methyl-5-formyl-2-methoxybenzoate)corolato]tin(IV) complexes and confirmed its purity by various spectroscopic techniques. Due to the enriched redox potential and electronic properties, we have taken this P-block metal complexes for the photocatalytic applications. Surprisingly all the catalysts oxidized 3-methyl indole and indole selectively at C-3 position, resulting in bisindoline (2-methyl-2-(2-methyl-1*H*-indol-3-yl)indolin-3-one) and trisindoline (2,2-di(3-indolyl)-3-Indolone) products respectively in high yield, which is a medicinally valuable, naturally occurring alkaloid compounds. Transition metallo corroles and main group metallo porphyrins did not show any catalytic activity under the same reaction condition. The study has demonstrated the significance of corrole ring and central metal ion for product conversion.

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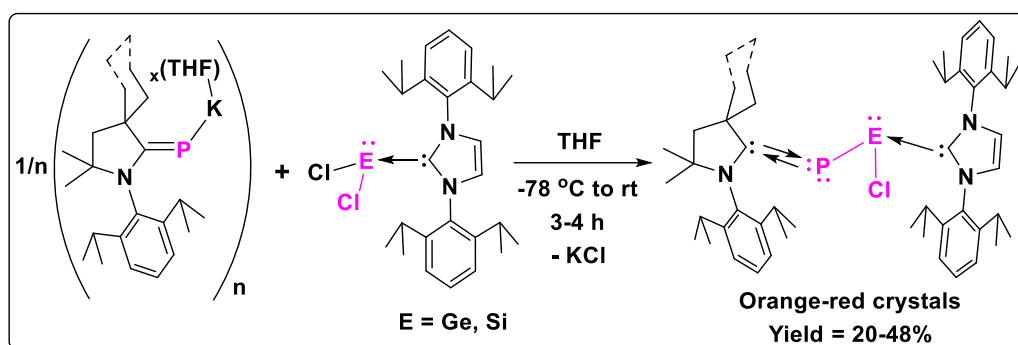
Stabilization of Elusive Chloro-Tetrylenes Using Cyclic Alkyl(Amino) Carbene (cAAC)-Anchored Monoanionic Phosphorus as the Ligand

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The theoretically predicted¹ neutral, monomeric, elusive hetero-bileptic phosphinidene-chlorotetrylenes, the heavier analogue of cyanogen halide [N≡C–Cl] have been isolated at room temperature by using hetero-bileptic donor base ligands, e.g., N-Heterocyclic carbenes (NHCs) or cyclic alkyl(amino) carbenes (cAACs), with general formulae (L)P–ECl(L') (E = Ge, Si) [(L' = NHC; L = cAAC)]. The phosphinidene-chlorogermaylenes (cAAC)P–GeCl(NHC) and phosphinidene-chlorosilylenes (cAAC)P–SiCl(NHC) were synthesized by the reaction of cAAC-supported potassium phosphinidenides [cAAC=PK(THF)_x]_n² with NHC-stabilized dichlorogermanium NHC:→GeCl₂ and NHC-stabilized dichlorosilylene NHC:→SiCl₂ in 1:1 molar ratio with 20-48% yield.³ All compounds have been thoroughly characterized by single-crystal X-ray diffraction, NMR spectroscopy and mass spectrometric analyses. DFT and EDA-NOCV analyses of the model compounds revealed that the heteroatom P has two lone pairs; one is the non-bonding pair, whereas the other is involved in the π backdonation to the C_{cAAC}–N π* orbital of cAAC.



Scheme 1: Syntheses of cAAC-supported mono-anionic phosphorus-stabilized elusive chloro-tetrylenes.

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P_n ring size dependence on NHC-induced ring contraction reactions of [CoCp^{'''}(η⁴-P₄)] and [FeCp^{*}(η⁵-P₅)]. A DFT Study.
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Cyclopolyphosphorus rings (cyclo-P_n) as ligands, isolobal to aromatic carbon rings, have intrigued chemists for the past few decades.¹⁻³ The reactivity of transition metal stabilized cyclo-P_n [TM-cyclo-P_n] through phosphorus has led to several facile transformations with retention, expansion, fragmentation, and even contraction of the ring.⁴⁻⁹ In a recent report, Sheer et al. observed carbene induced facile ring contraction of [CoCp^{'''}(η⁴-P₄)], and [Ta(CO)₂Cp^{''}(η⁴-P₄)] (Cp^{'''} = 1,2,4-tri-tert-butyl-cyclopentadienyl, Cp^{''} = 1,3-di-tert-butyl-cyclopentadienyl).^{5,6} However, a similar reaction with [FeCp^{*}(η⁵-P₅)] ends up giving an intermediate with ring retention.⁸ In order to answer these discrepancies, arising as the ring size increases, we have computed the energetics for the ring contraction with variation in ring size (Figure 1). We have employed different theoretical tools to show that the inherent ring strain in the P_n ring plays a decisive role in determining the ring contraction capability of [TM-cyclo-P_n] complex.¹⁰ We also report the mechanism of ring contraction by NHC in triple decker complexes with varying valence electron count (VEC), the role of halogens in inducing ring contraction and product distribution in double decker and triple decker complexes.^{5,11,12}

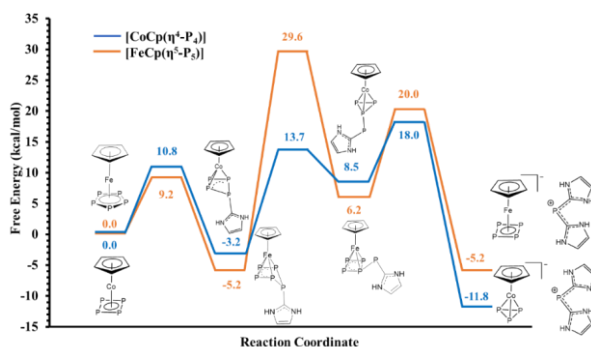


Figure 1. Free energy landscape for the carbene induced ring-contraction reaction of [CoCp(η⁴-P₄)] and [FeCp(η⁵-P₅)] computed at B3LYP/Def2SVP level of theory with the IEFPCM solvation model for THF solvent at 298 K.

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CS₂ on a New Route as a Bioregulator in H₂S and NO Signalling Processes

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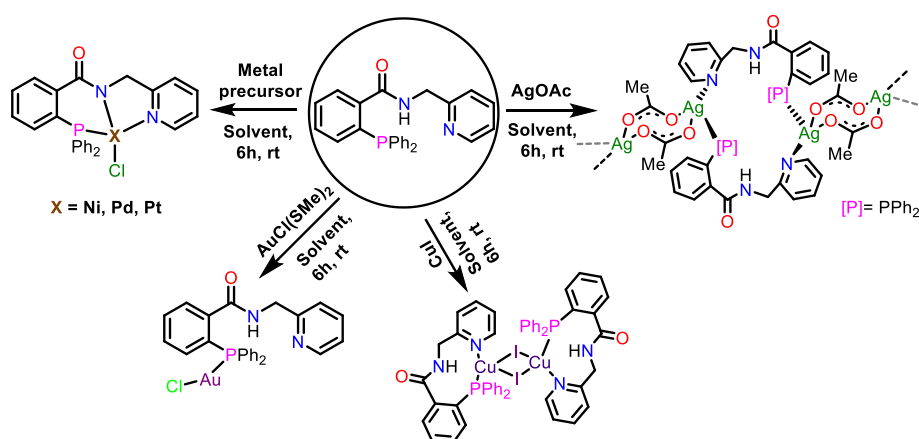
Hydrogen sulfide (H₂S) and nitric oxide (NO) jointly serve as gasotransmitters, thereby exerting pivotal roles in a wide array of physiological activities including vasorelaxation, angiogenesis and neuro-transmission.^[1] As both H₂S and NO are known as extremely toxic molecules, their generation and utilization are tightly controlled by a large set of complex chemical transformations under biologically relevant conditions. It is also noteworthy that H₂S is reducing in nature, while NO displays both oxidizing and reducing reactivity trends. As a consequence, cross-talks between H₂S and NO leads to the possible generation of a large variety of reactive sulfur, oxygen, and, nitrogen species (RSONs).^[2] For instance, thionitrite (SNO⁻) and perthionitrite (SSNO⁻) serve as reactive intermediates, which plays critical roles in H₂S and NO biochemistry. Inspired by the recent review by Ford *et al* evaluating the potential of carbon disulphide (CS₂) or CS₂ donors as bioregulators in signalling processes,^[3] this work focuses on providing molecular level insights into the activation of CS₂ and related molecules towards the generation of H₂S, NO, and other RSONs under ambient conditions.

Employing a structurally characterized phenolate bridged dinuclear zinc(II)-aqua complex {LZn^{II}(OH₂)₂(ClO₄)₂} as a hydrolase model, this work illustrates hydrolysis of CS₂ leading to the release of H₂S and CO₂.^[4] Spectroscopic analyses suggest the involvement of carbonyl sulphide (COS) and zinc(II)-thiocarbonate, thereby providing insights into the transformation of CS₂ + 2H₂O → CO₂ + 2H₂S mediated by the [Zn^{II}]-OH₂ site. Intrigued by the facile nucleophilic attack on CS₂ in the above-mentioned route towards H₂S, this work further aims to demonstrate simultaneous generation of NO and H₂S from the cross-talk between CS₂ and molecular relatives of NO.^[5] A detailed spectroscopic investigations including multinuclear NMR, UV-vis, HRMS confirms the formation of thionitrite (SNO⁻) and perthionitrite (SSNO⁻) as the transient intermediates. Further, the reactivity profile of perthionitrite (SSNO⁻), thus generated, has been investigated.

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The catalytic potential of phosphorus chemistry as well as the great structural diversity that may be attained in the design of phosphorus-based ligands, have sparked attention and development. Tertiary phosphines (PR₃) are widely used in coordination chemistry and metal mediated catalysis due to their varied donor and acceptor properties and also their ability to stabilize metals in their low valent states¹. Phosphines with hemilabile donor functionalities have generated considerable interest both as ligands and ideal candidates for catalyst generation because of unique reactivity and coordination modes²⁻³. Pincer complexes of phosphines with hemilabile donor centres have proved to be efficient catalysts for a variety of organic transformations⁴⁻⁵. Herein we describe the synthesis of a PNN type pincer capable ligand and its metal complexes.



Scheme 1: Synthesis of transition metal complexes

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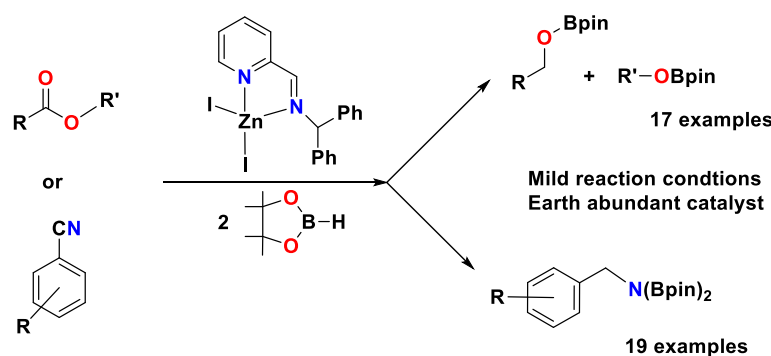
Hydroboration of Esters and Nitriles in the Presence of Bench Stable Zinc (II)
Metal Complex

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In organic chemistry, reducing esters into alcohols is an important transformation that has wide applications in the pharmaceutical industry.¹ The reduction can be performed in the presence of hydride donors such as LiAlH₄, LiBH₄ and NaBH₄. However, this methodology has a few drawbacks, such as less functional group tolerance, explosive and difficulty handling the reagents. Further, hydrogenation can also be used as an alternative methodology for the reduction of carbonyl bonds. But, it requires high pressure and specialized equipment for the conversion of the reactants.² Due to these drawbacks, researchers have extensively used boron reagents such as pinacolborane (HBpin) and catecholborane (HBcat) as an alternative methodology for the reduction of unsaturated bonds. In the last decade, various research groups extensively employed boron reagents using s-block, p-block, transition and lanthanides metals to reduce unsaturated bonds.³ However, there are few catalysts which effectively reduce esters into alcohols. Further, there is one report which employs zinc metal as an active catalyst for the reduction of esters into alcohols. Recently, Yang and workers reported ZnEt₂ as an active catalyst for the reduction of esters. Here, the use of ZnEt₂ as a catalyst for the reduction under mild reaction conditions.⁴ However, there are no reports in which zinc metal supported ligands for the reduction of esters. Recently, we have developed a titanium metal complex [{Ph₂P(BH₃)N}₂C₆H₄Ti(CH₂SiMe₃)₂] for the hydroboration of nitriles. Further, we also explored a zinc metal complex supported by imidazoline-2-imine ligand [{ImtBuNZn(CH₂CH₃)₂] for the hydroboration of nitriles. Here, we developed a bench stable zinc metal complex [κ²-(PyCH=N(CHPh₂))ZnI₂] (**3**) as an active catalyst for the hydroboration of esters and nitriles at mild reaction conditions. Electron-withdrawing and donating substituents on the phenyl ring were well tolerated to form the alkoxyboronates. The catalytic efficiency was studied by chemo selective reactions with different functional groups.

This Work:





International Conference on Main Group Synthesis and Catalysis

9-12 February 2023

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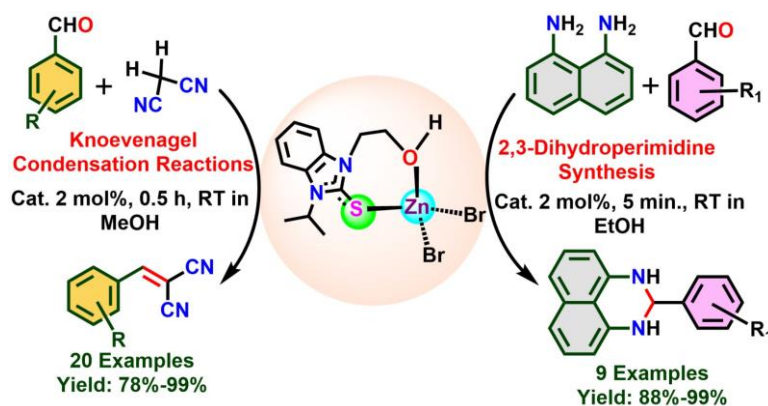
Highly Active Cyclic Zinc(II) Thione Catalyst for C-C and C-N Bond
Formation Reactions

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Abstract: The chemicals for materials and medicinal applications have been achieved by C-C double bond formation reaction such as Knoevenagel condensation. The catalysts including ionic liquid, organocatalyst and metal-based catalysts have limitations due to environmental toxicity, selectivity, sustainability, limited substrate scope, and longer reaction time. Zinc(II) based catalyst has emerged for the Knoevenagel condensation reaction. Herein, we have reported the unique seven-membered cyclic zinc(II) complex $[(L)(ZnBr_2)]$ from the reaction between 1-(2-hydroxyethyl)-3-isopropyl-benzimidazol-2-thione (L) and $ZnBr_2$. Besides, the catalytic application to isolate methylene malonitrile derivatives through the Knoevenagel condensation reaction and also used for the synthesis of 2,4-dihydroperimidine derivatives in a highly efficient manner. The present investigation features a mild and fast synthetic approach along with excellent functional group tolerance.



Germylene cation catalyzed hydrosilylation of aldehydes and ketones

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The use of main-group compounds as catalysts for organic transformations has advanced significantly. Germylenes, a class of low-valent main-group compounds, have been used as catalysts for the hydroboration and cyanosilylation of carbonyl compounds.¹ Hydrosilylation of CO₂ using germylene→borane adduct and germylene cation are also reported recently.^{2,3} However, the hydrosilylation of carbonyl compounds using a germylene catalyst is hardly known. In this regard, this poster reports the dipyrinate ligand stabilized germylene cation ([DPMGe][[(HO)B(C₆F₅)₃]] (2) (Figure 1) as a valuable catalyst for the hydrosilylation of various aldehydes and ketones. Using 1 mol% of compound 2, a variety of aldehydes and ketones were hydrosilylated with 99% conversion (Scheme 1). Further details of this work will be shown on the poster.

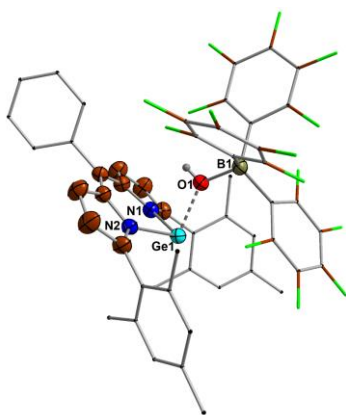
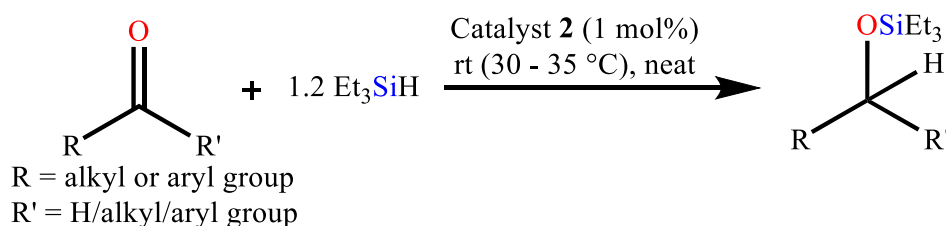


Figure 1: Molecular structure of catalyst 2.



Scheme 1: Hydrosilylation of aldehydes and ketones catalyzed by germylene cation 2.

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***N,N* vs *N,E* (E = S or Se) Coordination Behavior of Imino-Phosphanamidinate Chalcogenide Ligands towards Aluminum Alkyls. Efficient Hydroboration Catalysis of Nitriles, Alkynes, and Alkenes**

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The design of specific ligand systems always gets priority to prepare metal complexes of particular nuclearity, coordination number, geometry, and reactivity in coordination and organometallic chemistry. Ligand provides proper stereoelectronic modulation on the metal center which allows for the improvement of specific properties of that metal complex, for example, catalytic specificity and efficiency. Recently, we prepared the chalcogenide derivatives of imino-phosphanamide [NHI^RP(Ph)(E)NHDipp] [R = Dipp, E = S (**2a**), Se (**2b**); R = Mes, E = S (**2c**), Se (**2d**); R = ^tBu, E = S (**2e**), Se (**2f**)] which can act as *N,N*- or *N,E*- donor monoanionic ligand system (E = S or Se). Further we synthesized their corresponding aluminum complexes [κ^2_{NN} -{NHI^RP(Ph)(E)N-Dipp}AlMe₂] [R = Dipp, E = S (**3a**), Se (**3b**); R = Mes, E = S (**3c**), Se (**3d**)] and [κ^2_{NE} -{NHI^RP(Ph)(E)NDipp}AlMe₂] [R = ^tBu, E = S (**3e**), Se (**3f**)]. All the compounds were characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction analysis. Then the aluminum complexes **5a-5f** were tested as pre-catalysts for the hydroboration reaction of nitriles, alkynes and alkenes.

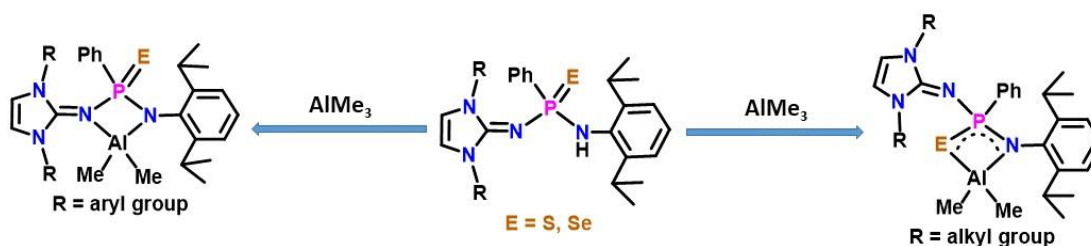


Figure 1. *N,N*- and *N,E*- coordination behavior of imino-phosphanamidinate chalcogenide ligands.

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P21

Computational Insights into the Iron-Catalyzed Magnesium-Mediated
Hydroformylation of Alkynes

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Abstract

Iron is one of the most abundant transition metals in the earth's crust. It has attracted a lot of attention due to its low toxicity, bio-compatibility, and high natural abundance. Iron-catalyzed hydroamination, hydroalkoxylation, hydrocarboxylation, hydrosilylation, hydroboration, hydrophosphination, hydromagnesiation, and carbonylation reactions have therefore been developed over the past decades. However, despite many experimental and theoretical studies^{1,2,3,4}, a complete mechanistic understanding of iron-catalyzed hydrofunctionalisation at the molecular level has not yet been achieved. In this work, through density functional theory (DFT) calculations, we have shown the most feasible path for the hydroformylation of alkynes for an experimentally studied system. We have looked at the iron salt as a precatalyst without any external donor ligand, and the calculations revealed that hydrometalation followed by β -hydride elimination was favorable over the direct migration of the β -hydrogen to carbon. Furthermore, our calculations show that the solvent plays an important role in the hydromagnesiation reaction. Furthermore, we have employed an explicit solvent model, where the attachment of one molecule of solvent to the iron center was seen to stabilise the transition states significantly.

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Unprecedented ring expansion and substitution reactions of 6-SNHC·AlH₃

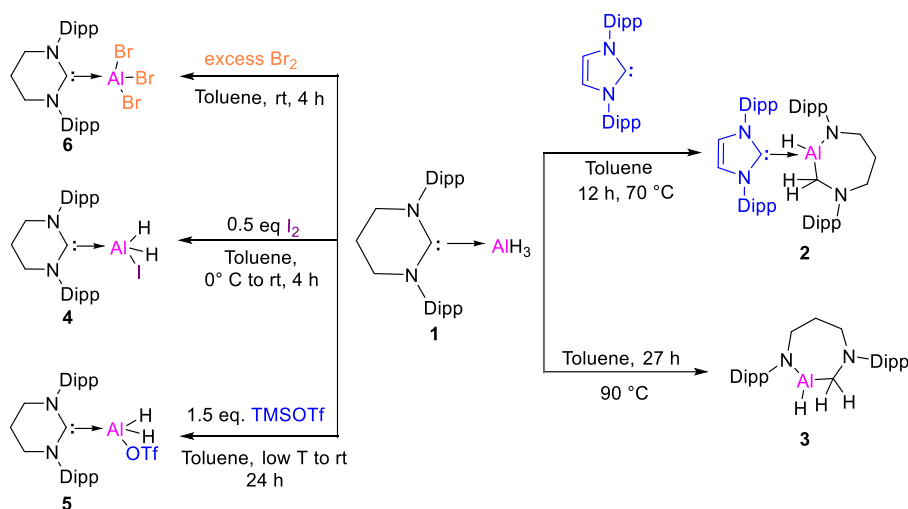
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The chemistry of ring-expanded N-heterocyclic carbenes has not been much developed^[1,2] compared to typical five-membered Arduengo type NHCs. Treatment of 6-SIPr·AlH₃ (**1**) (6-SIPr = 1,3-di(2,6-diisopropylphenyl)-tetrapyrroline-2-ylidene) with another equivalent of IPr carbene ([1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene]) at 70 °C for 12 h resulted into quite unprecedented ring expansion of six membered ring into seven membered ring keeping the five membered ring intact. This is unusual because the expansion of five-membered NHC to six-membered ring is generally more favoured. To further investigate the role of Lewis-base, we heated **1** itself and observed the ring expansion of 6-SIPr·AlH₃ to a seven membered ring **3**.

We have further studied the substitution chemistry of **1**. The mono-substitution of hydride in **1** with iodine was accomplished by treating it with 0.5 equiv. of I₂ to give **4**. The reaction of **1** with 1.5 equiv. TMSOTf in toluene for 24 h at room temperature yielded triflate substituted alane adduct **5** directly *via* silane elimination. The treatment of **1** with excess bromine water led to the formation of NHC supported aluminium tribromide adduct **6**. The resulting products are of very rare classes of functionalized aluminium compounds.



Scheme 1: Ring expanded (**2** and **3**) and substituted (**4,5** and **6**) 6-SIPr·alane adducts

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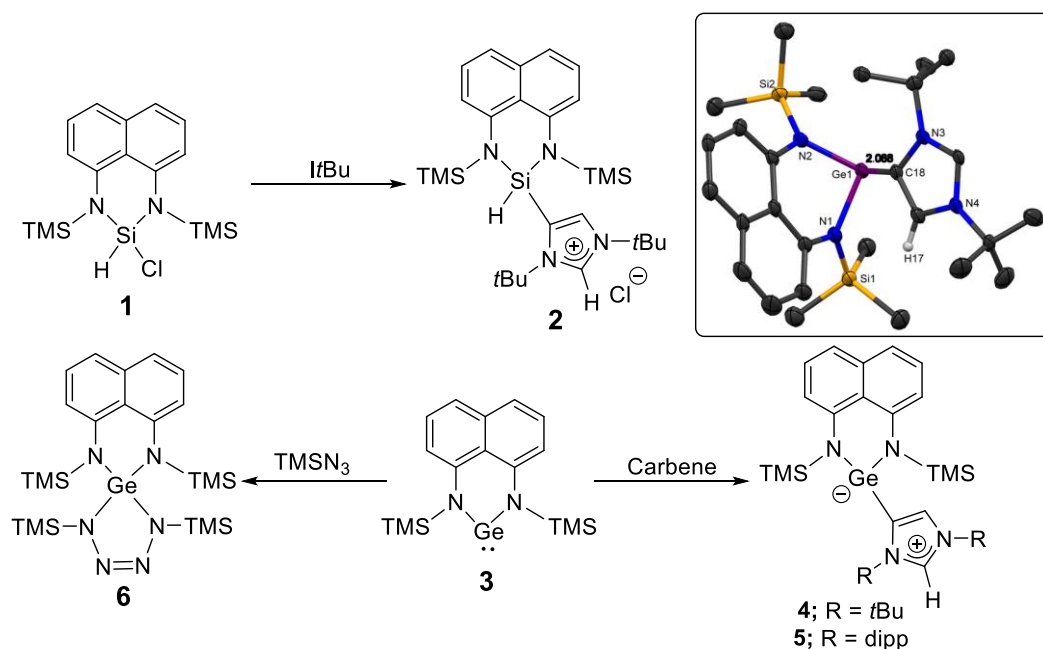
Activation of Alkenic C–H Bond of NHC by Tetrylene

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We are demonstrating the design and development of new ligand systems based on the *N,N'*-disubstituted diamino naphthalene scaffold as (a) it is a rigid chelating ligands with a bite angle comparable to those of β -diketiminates and (b) the coordinated element would be placed in a six-membered heterocyclic ring with the extended aromatic system from the naphthalene backbone. The ligand is utilized for silicon and prepare (TMS)₂DANSiHCl (**1**). We have attempted to generate silylene from **1** using *I*tBu, but the reaction resulted in the activation of the backbone C–H in the imidazole moiety and formation of a silyl functionalized imidazolium salt (**2**). Extension of the work to germanium afforded an N-heterocyclic germylene (**3**), which upon reaction with *I*tBu and *I*dipp led to the similar C–H bond activation product **4** and **5**. Subsequent reaction of **3** with TMSN₃ led to an unusual GeN₄ cycle (**6**) which is also a Ge centred spiro compound.



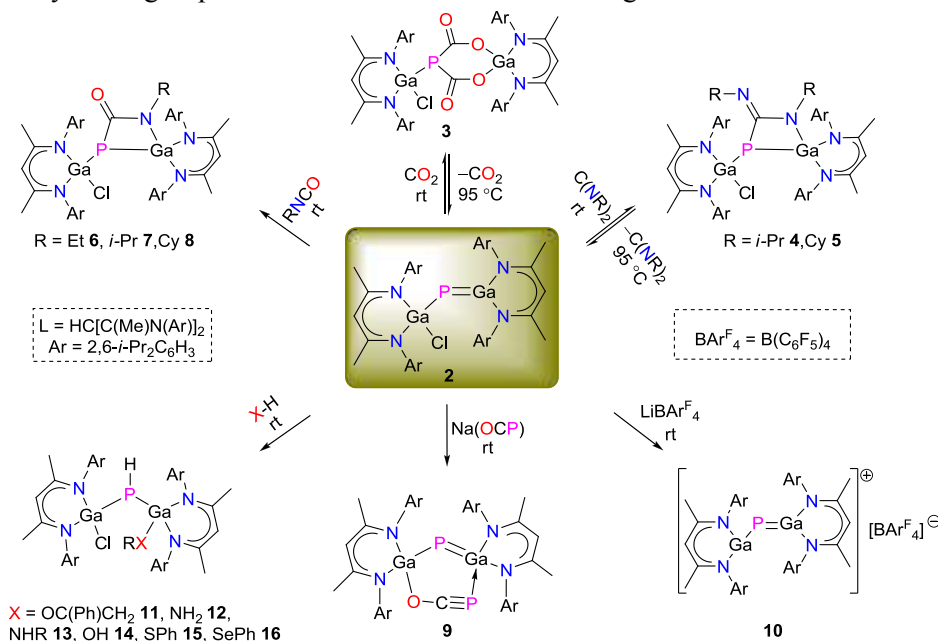
A Multi-talented Gallaphosphene and its Remarkable Reactivities

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Abstract: Gallaphosphene LGa(Cl)PGaL **2** (L = HC[C(Me)N(2,6-*i*-Pr₂C₆H₃)₂]), which is synthesized by reaction of LGa(Cl)PCO **1** with LGa, undergo reversible [2+2] and [2+2+2] cycloaddition reactions with heteroallenes (CO₂, isocyanates, carbodiimides),^{1,2} while the reactions with compounds with polar X–H bonds, i.e. ammonia, primary amines, water, phenol, thiophenol, and selenophenol, selectively with 1,2 addition at the polar Ga–P double bond.³ Remarkably, the reactions with ketones proceeded via a C(sp³)–H bond activation at the Ga–P double bond.¹ Salt metathesis reaction of **2** with [Na(OCP)(dioxane)_{2,5}] yielded LGa(OCP)PGaL, whereas chloride abstraction with LiBAR^F₄ yielded a heteronuclear analogue of the allyl cation [LGaPGaL][BAR^F₄] (BAR^F₄ = B(C₆F₅)₄), according to quantum chemical calculations.¹ Furthermore, gallaphosphene LGa(OCP)PGaL activates the N–H and O–H bonds of aniline and phenol at the Ga–P bond with an unprecedented rearrangement of the phosphoethynolate group from Ga–OCP to Ga–PCO bonding.⁴



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Highly Electrophilic Mononuclear Cationic Aluminum Alkoxide Complexes:
Synthesis, Reactivity and Catalytic Applications

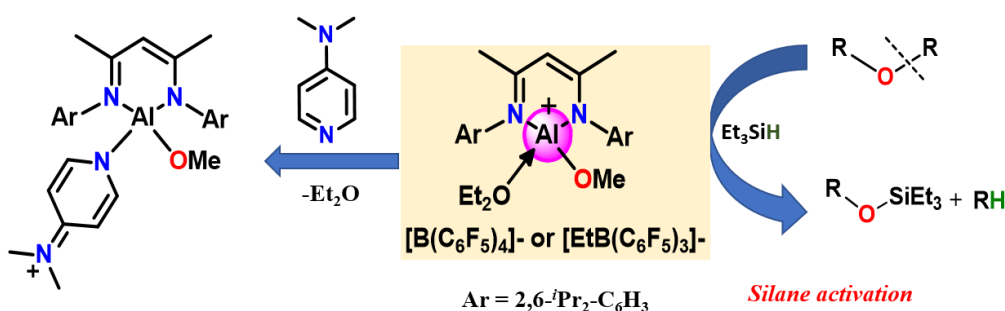
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Over the last few decades, covalent aluminum complexes have witnessed a tremendous growth, owing to their high Lewis acidity.^[1] Efforts have been made to advance their Lewis acidity *via* turning them into low coordinated cationic polar reagents, which might exhibit the reactivity far superior than their covalent analogues.^[2] Additionally, the substituents in the primary coordination sphere of aluminum can also play a significant role in modulating the Lewis acidity and subsequent reactivity.^[3] Majority of the aluminum cations are equipped with hydride or alkyl functionality supported by bidentate chelating ligands.^[4] Aluminum compounds bearing electronegative alkoxide group are expected to exhibit higher Lewis acidity as compare to their hydride and methyl analogues.

Herein, we present the synthesis of diverse β -diketiminato (**L**) stabilized novel neutral and cationic aluminum complexes bearing terminal alkoxide group; **LAiOMe(Et)** (**1**), **LAiO^tBu(Et)** (**2**), **[LAiOMe(μ -OMe)-Al(Et)**L**][EtB(C₆F₅)₃]** (**3**), **[LAiOMe(OEt₂)][EtB(C₆F₅)₃]** (**4**), and **[LAiO^tBu(OEt₂)][EtB(C₆F₅)₃]** (**5**). These electrophilic cationic species are well characterized by spectroscopic and crystallographic techniques. The assessment of Lewis acidity done by Gutmann Beckett method revealed the superior Lewis acidity of the alkoxy substituted cations in comparison to the previously reported methyl analogue. Complexes **4** and **5** are capable of activating Et₃SiH in stoichiometric reaction and are efficient in catalytic hydrosilylation of ethers, carbonyls and olefins (see Figure below).



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Molecules with extended π -conjugation have drawn considerable attention in the last two decades because of their intriguing optical and electronic properties,¹ and also their wide applications in organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs), polymer solar cells (PSCs) and organic photovoltaics (OPVs).² The incorporation of heteroatoms such as boron, nitrogen and phosphorus assists in fine tuning the optical and electronic properties of natural π -conjugated materials. Herein, we report the synthesis of 2,2'-bipyridine based bisphosphine [C₅H₃N{N(H)CH₂PPh₂}]₂ (**2**) and its bischalcogenide derivatives [C₅H₃N{N(H)CH₂P(E)Ph₂}]₂ (**3**, E = O; **4**, E = S; **5**, E = Se) which were further reacted with BF₃·Et₂O/Et₃N to form doubly B ← N fused compounds [C₅H₃N(BF₂){NCH₂P(E)Ph₂}]₂ (**6**, E = O; **7**, E = S; **8**, E = Se) in excellent yields.³ Reactivity and photophysical study of **7** were carried out with copper(I) salts.

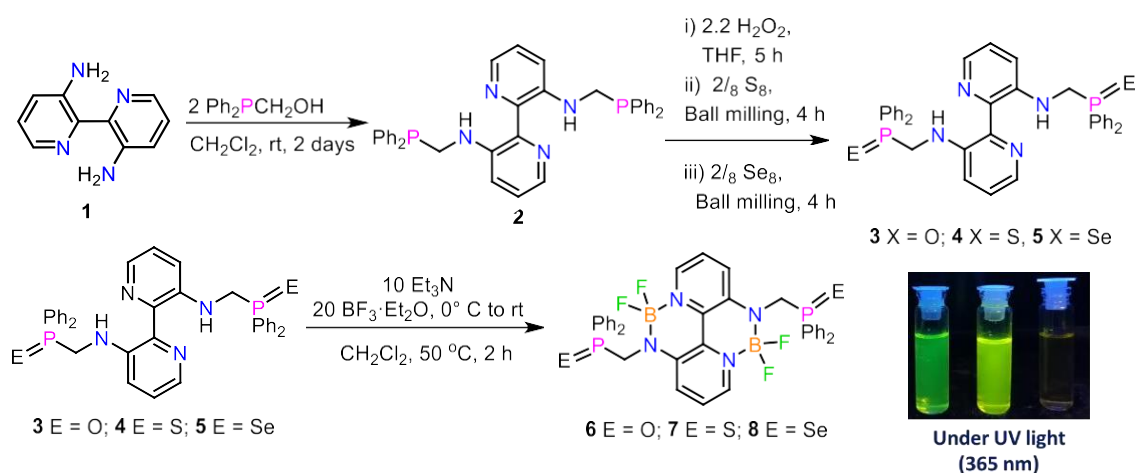


Figure 1. Photophysical studies of **6** - **8**

Scheme 1. Synthesis of bisphosphine ligand and its chalcogenide derivatives.

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P27

Boron Containing Perylenediimides: A Next Generation Agents for Boron Neutron Capture Therapy (BNCT)

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BNCT is a binary system in which boron is targeted to tumor cells specifically, bombarded with *in situ* high LET radiations and the outcomes of the therapy depends on the biochemical and biophysical differences generated between normal and proliferating cells.¹ BPA and BSH, two boron compounds emerged as the only clinically proven delivery agents for treatment of neoplastic cells.² In order to meet the basic requirements like the distribution ratio for tumor to normal cells must be higher than 3 : 1, low toxicity, the retention time of boron compounds in cancer cells must be a few hours, relatively rapid clearance of boron-containing compound from normal healthy cells etc.³ We have designed and synthesized some good biocompatible and stable nanocarriers of boron based perylenediimide derivatives for the precise, target delivery and long-term accumulation in tumor sites by EPR effect and nanometer size effect. In the boron drug development project, establishment of a pharmacokinetic monitoring system is one of the most important part along with the easiness of drug synthesis, internal stability of a drug, and cost of drug manufacture. Keeping all these key points in view, we have synthesised these compounds and *in vitro* experiments suggests their efficacy as BNCT agents.

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Synthesis, Structure, and Reactivity of an Acyclic Amino(ylide)stannylene

P28

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Phosphorus ylide-functionalized main group compounds displayed fascinating reactivities. For example, due to the unique π -electron donating ability of ylides, they can be used to synthesize electron-rich phosphines and thus be applied in homogeneous catalysis such as C-N coupling reactions.¹ Likewise, since ylide substituents are more potent donors ligand than amines and terphenyl ligands, they are suitable for stabilizing electron-deficient group 13/14 compounds.^{1,2} Recently, Our group reported the gram-scale syntheses of metallated ylides amongst the cyanido-substituted ylide which exhibited diverse structures with the different alkali metals.³ Here, we reported the isolation of ylide-substituted low-valent Sn(II) compounds. The reaction of **YCN-K** with tin precursors SnXR and (HMDS)SnCl, is afforded the formation of chloro(ylide)stannylene **[1a]** and amino(ylide)stannylene **[1b]**, respectively. Moreover, the reactivity of **1b** towards different unsaturated compounds is discussed.

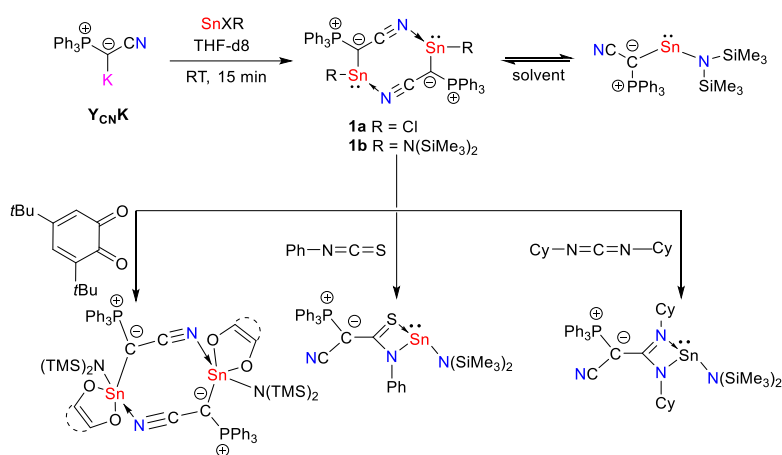


Fig: Synthesis of chloro(ylide)stannylene and amino(ylide)stannylene. Reactivity of amino(ylide)stannylene towards hydroquinone and heteroallenes.

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Synthesis of NHSi/NHGe-Supported Copper(I) Halide and Pseudohalide
Complexes and Their Application in CuAAC Reaction

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and Shabana Khan^{*a}

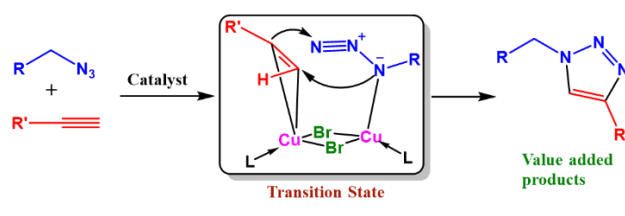
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NHSi and NHGe are the higher analogue of NHC, which containing a lone pair of electrons at Si or Ge centre. NHSi and NHGe are highly reactive in nature and air and moisture sensitive. Herein, we have synthesized a series of NHSi- and NHGe-supported copper(I) halide and pseudo halide complexes **1-6** (LSiCuX and LGeCuX; where, L = [PhC(N^tBu)₂N(TMS)₂] and X = Br, I and SCN). All the four newly synthesized complexes (**2**, **4-6**) are well characterized by NMR spectroscopy, mass spectrometry and single-crystal X-ray diffraction technique. Further, all these complexes were investigated as efficient catalysts in copper azide-alkyne cycloaddition (CuAAC) reaction. We have introduced a broad substrate scope, kinetic studies and theoretical mechanistic studies in this work.



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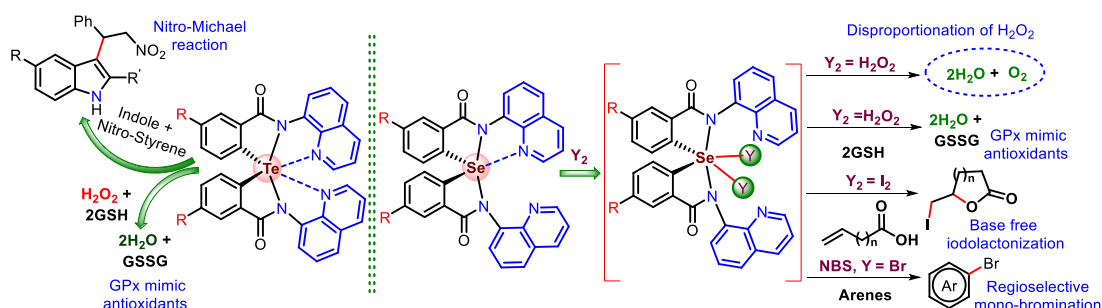
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Intramolecular Chalcogen (Se/Te)···N Bonded Spirocycles: Catalytic Small Molecule Activation and Organic Transformations

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Chalcogen bonding interactions have recently gained considerable attention in the field of biology, synthetic chemistry, structure and bonding.^{1,2} However, the study of chalcogen bonding is limited to low-valent organo-chalcogen compounds due to synthetic difficulties and stability at their high valence states. Here, firstly we have synthesized a series of new intramolecular Se/Te···N bonded tetravalent spirocyclic compounds *via* copper(I) assisted methodologies.³ The catalytic activation of H₂O₂ toward disproportionation H₂O and O₂ is achieved by intramolecular Se···N bonded spirocycles, by the virtue of reactive hexavalent-Se-intermediates and it is the first report by any organochalcogen species.^{3a} Subsequently, it activates I₂ & efficiently catalyzed the base-free iodolactonizations and catalyzed the electrophilic bromination of arenes by activating NBS. Similarly, tetravalent spirotelluranes exhibit high GPx-mimic antioxidant activity and also catalysed the nitro-Michael reactions to afford substituted 3-(2-nitro-1-phenylethyl)-1H-indoles efficiently by the virtue of high Lewis acidic nature of tellurium, attributed to the high oxidation state in the spirotelluranes and the presence of intramolecular Te···N bonds.^{3b}



Scheme 1: Catalytic activities by chalcogen (Se/Te)···N bonded spirocycles

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Bis(Silatellurone) with C-H...Te Interaction

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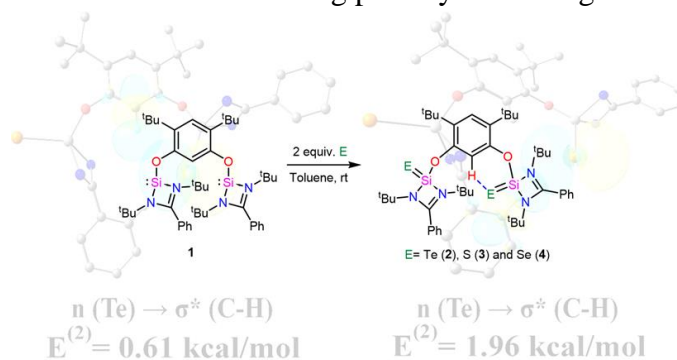
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Multidentate pincer ligands comprising of fascinating aromatic backbone are attractive multi-electron donor species. These systems can be finely tuned with various electrophilic and nucleophilic systems opening up a regime of new class of multidentated systems. This urged us to revisit the synthesis of a bissilylene based pincer ligand (SiCSi)¹ and explore multiple bond forming ability towards elemental chalcogens i.e. group 16 elements. Owing to their poor overlapping of the π orbitals between the silicon and chalcogen atoms, makes the Si=E bonds highly polar, reactive and synthetic challenge for chemists to overcome which is unlikely for its lighter congener (R₂C=E).² Herein, we attempted to synthesize SiCSi pincer based Bissilachalcogenones (O, S, Se, Te), which shows intramolecular C-H...Ch (Ch= S, Se, Te) interaction which are being validated by X-Ray diffraction, temperature-dependent ¹H-NMR in combination with natural bonding orbital (NBO) analysis.³ Our work deals with an in-depth analysis of the bonding pattern and the stability of non-covalent interactions. This gives idea of the chemical environment of proton involved in interaction, which gives the basis of fundamental understanding of C-H...Ch interaction and the role of silicon lending polarity to chalcogens.



Schematic view of SiCSi based bischalcogenone showing C-H...Ch interaction

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Rare Mesoionic Selone Bismuth(III) Trihalide Clusters: Application in Relay Catalysis

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Over the last few years, metal complexes of mesoionic carbenes (MICs) surpassed NHC metal complexes as a better catalyst in most of the organic reactions.¹ Their rapid rise in various applications over NHC comes as an inherent property of being a better σ -donor and weaker π -acceptor. From the first reported MIC metal complex by Crabtree and co-workers, the chemistry of these compounds have only grown and now they have widespread applications.² However, the mesoionic chalcogenone metal complexes have been barely studied. In continuation to this research, we report the first bismuth chalcogenone clusters [(IPaulTrzSe)₃Bi₃Cl₉] and [(IPaulTrzSe)₃Bi₃Br₉] by using triazoline chalcogenone ligand (IPaulTrzSe) (IPaulTrzSe = 1-(2-benzhydryl-4,6-dimethylphenyl)-3-methyl-4-phenyltriazolin-5-selone). Both molecules shows the stronger intermolecular hydrogen bonding interactions (C–H \cdots X, X = Cl, Br), additionally molecule [(IPaulTrzSe)₃Bi₃Cl₉] shows the C–H \cdots π interactions. Further, these mesoionic selone bismuth(III) halide clusters were used as a catalyst for the C–H functionalization through relay catalysis mechanism (Figure 1).

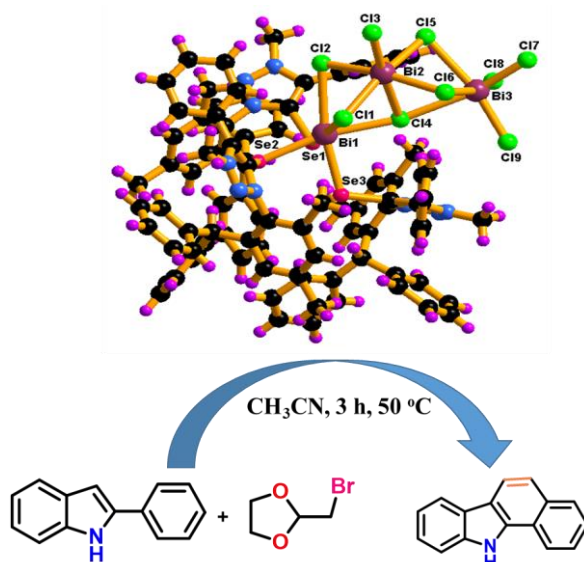


Figure 1: Synthesis of carbazole derivatives using bismuth catalysts.

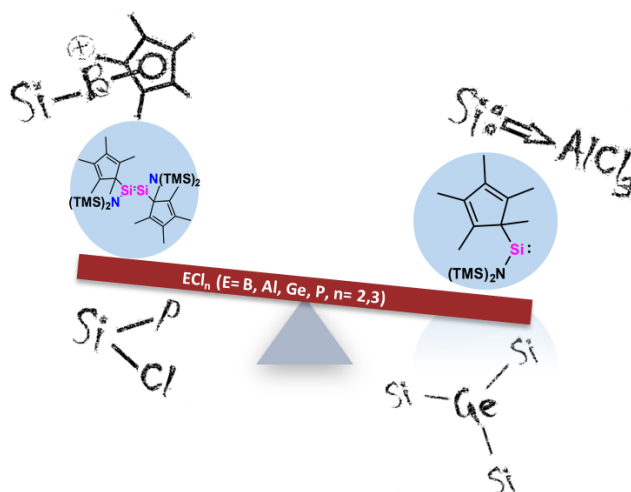
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We have demonstrated the unique reactivity of a previously reported disilene $[(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si}=\text{Si}(\eta^1\text{-Me}_5\text{C}_5)\text{N}(\text{TMS})_2]$ ^[1] (**1**) with the halides of groups 13–15, which resulted in the formation of silicon–E (E = B, Al, Ge, P) bonds. Treatment of (**1**) with Lewis acidic BCl_3 led to the formation of a cationic boron species $[\text{Cp}^*\text{BSi}(\text{Cl})_2\text{N}(\text{TMS})_2][\text{BCl}_3\text{SiCl}_3]$. In contrast, the reaction of **1** with BCy_2Cl afforded an oxidative addition product $[(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si}(\text{BCy}_2)(\text{Cl})]$ via the insertion of a Si(II) atom into the B–Cl bond. Extending the reaction with its higher congener led to classical Lewis acid-base adducts, $(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si} \rightarrow \text{AlCl}_3$ and $(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si} \rightarrow \text{AlBr}_3$, respectively. The reaction of GeCl_2 with **1** proceeded in a completely different manner and resulted in a hybrid dendrimeric compound $[\text{HGe}(\text{Si}(\text{Cl})_2\text{N}(\text{TMS})_2)_3]$, whereas, with SnCl_2 , it led to Cp^*SnCl . Lastly, the reaction of Ph_2PCl followed the same pattern like Cy_2BCl and led to the formation of an oxidative addition product $[(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si}(\text{PPh}_2)(\text{Cl})]$ with a Si–P bond.^[2]



Reactivity of disilene with different main group halides

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FLP-Catalyzed Dearomative Transformation of Indoles to Indolines via B–H Bond Activation

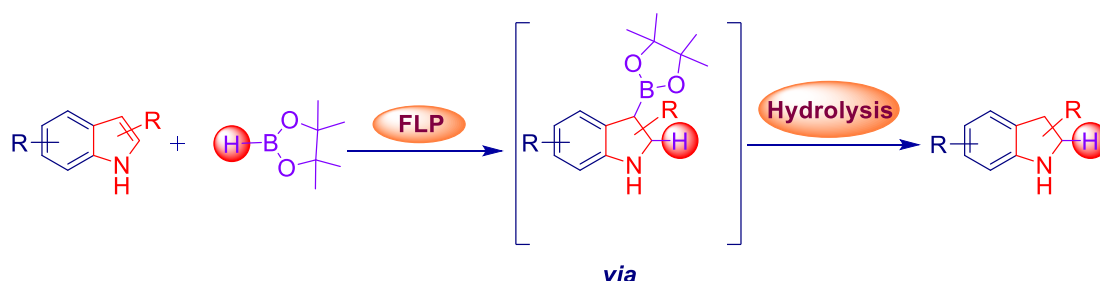
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Abstract

Hydroboration is a well-established and convenient method in reductive chemistry in which the hydroborane adds to the unsaturation site of the substrate. Over the past decades, a significant effort has been made to develop suitable catalytic methods for the hydroboration of various substrates. In this context, several transition metal and metal-free systems have exhibited promising activity.¹⁻² Herein, we present a sustainable metal-free protocol for the hydroboration of various substituted indoles with frustrated Lewis pair (FLP) system (Scheme 1).³ The FLP system can activate the B–H bond of pinacolborane followed by hydroboration of indoles.³ Further, control experiments have been carried out to understand the mechanistic process of the present protocol.



Scheme 1. Reduction of indoles to indolines

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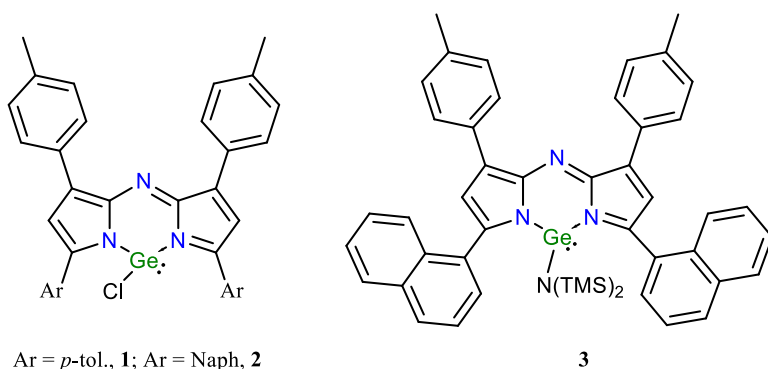
Aza-dipyrrin Stabilized Germylenes

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The use of dipyrrin ligands to isolate air and water stable germylenes was demonstrated recently.¹ Aza-dipyrrins are the nitrogen analogs of dipyrrins where nitrogen (imine type) replaces the *meso*-carbon (a CR unit; R = H, alkyl, aryl).^{2a} Aza-dipyrrins are highly conjugated ligand systems that afford compounds with rich photophysical properties,^{2a} and their use in main-group chemistry is limited.^{2b-c} Therefore, we report here the germylenes, such as aza-DPM(*p*-tol)GeCl (**1**), aza-DPM(Naph)GeCl (**2**), and aza-DPM(Naph)GeN(TMS)₂ (**3**) stabilized by aza-dipyrrin ligands. Compounds **1-3** were characterized through multinuclear NMR spectroscopy and single-crystal X-ray diffraction studies. Germylenes **1-3** are air and water stable; they show an absorption maximum at around 640 nm. Further details about the work will be presented in the poster.



Ar = *p*-tol., **1**; Ar = Naph, **2**

3

Scheme 1. Aza-dipyrrinatogermylenes **1-3**



Figure 1. Molecular structure of **1**

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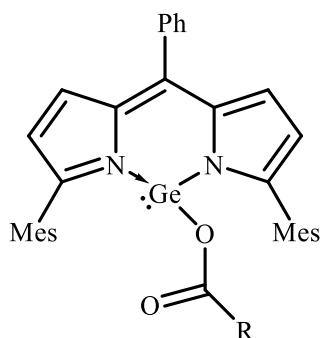
Germlyenes with Solid-State Emission

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Germlyenes that show fluorescence in the solution are known; however, germlyenes displaying solid-state fluorescence are not known until now.¹ In this regard, germlyene carboxylates **2-7** that show solid-state fluorescence are isolated and reported here. Compounds **2, 3, 4, 5, 6,** and **7** were synthesized through the reactions of dipyrromethene stabilized germlyene pyrrolide **1** with acetic acid, trifluoroacetic acid, benzoic acid, *p*-cyanobenzoic acid, *p*-nitrobenzoic acid, and acetylsalicylic acid respectively.² Photoluminescence studies on compounds **2-7** were carried out in the solution- and solid-state using a 405 nm laser source and found to be significantly red-shifted in the solid-state. Further, details will be presented in the poster.



R = CH₃ (**2**); CF₃ (**3**); C₆H₅ (**4**);
C₆H₄-CN (**5**); C₆H₄-NO₂ (**6**);
C₆H₄-OC(O)CH₃ (**7**)

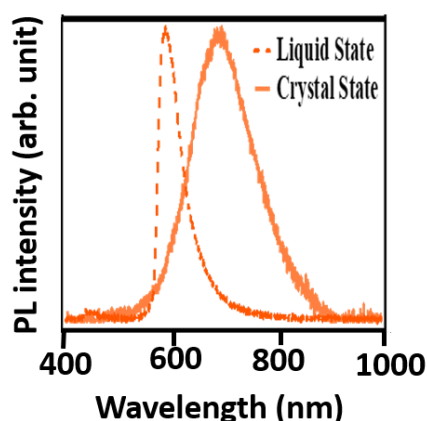


Chart 1. Structure of compound **2-7**.

Figure 1. PL spectrum of compound **3**.

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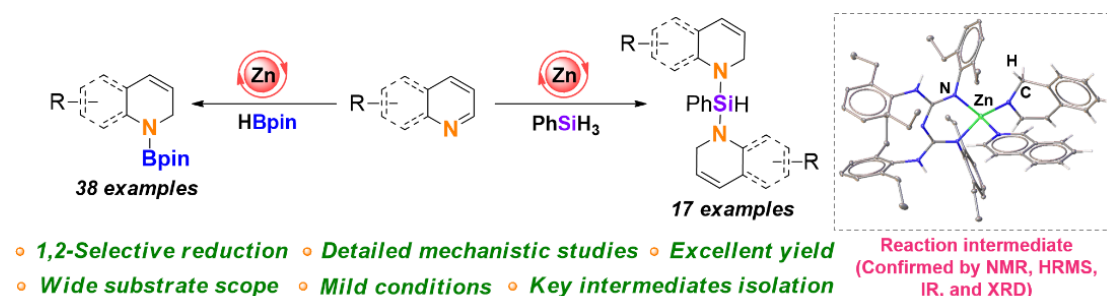
Intermediates Isolation and Mechanistic Insights into Zinc Hydride Catalyzed 1, 2-Regioselective Hydrofunctionalization of N-Heteroarenes

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An unprecedented molecular bridged zinc hydride, $[\{LZnH\}_2]$; $L = \{(ArHN)(ArN)-C=N-C=(NAr)(NHAr)$; $Ar = 2,6-Et_2-C_6H_3\}$ (**I**) catalyzed highly demanding exclusive 1,2-regioselective hydrofunctionalization of N-heteroarenes is demonstrated with excellent yields. This protocol is compatible with many pyridines and N-heteroarene derivatives, including electron-donating and withdrawing substituents. Furthermore, the intermolecular chemoselective hydroboration reaction over other reducible functionalities has been studied. The catalytic intermediates were isolated and thoroughly characterized by NMR, HRMS, IR, and X-ray single-crystal diffraction studies. The complete catalytic cycles have been proposed based on the isolation of well-defined key intermediates, stoichiometric experiments, and in situ studies. More importantly, for the first time, we revealed the mechanism for metal-catalyzed hydrosilylation of N-heteroarenes to exclusively bis-1,2-hydrosilylated products.



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Probing the Mechanism of Abnormal N-Heterocyclic Silylene Formation and its
Reactivity with CO-A DFT Study

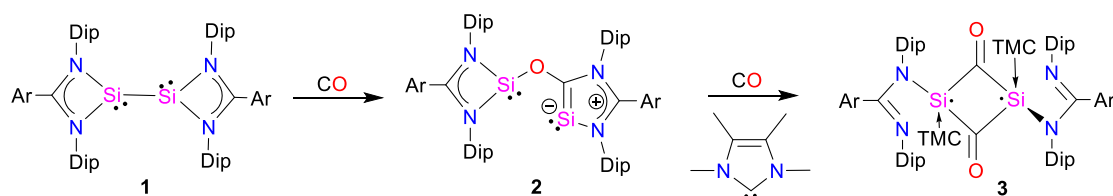
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The low oxidation state of silicon in silylenes are found to be promising candidates for activating small molecules in the recent years.¹⁻² Jones and co-workers have shown that the interaction of disilylenes (**1**) with CO results in a novel abnormal N-heterocyclic silylene (**2**).³⁻⁴ We investigated the mechanistic pathway for the CO activation using DFT methodology and performed NBO analysis to understand the electronic structure of N-heterocyclic silylene. Furthermore, the complex **2** is reactive with CO only in the presence of TMC resulting in Si(CO)₂Si four membered ring in complex **3**. The reactivity of complex **2** is also elucidated using the DFT methodology.



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Photoluminescent Amidinate Ligated Boron Compounds

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Four- coordinate organoboron compounds having a N[^]N chelating ligands attracted enormous interest due to their applications in a wide range of areas like bioimaging, sensors, OLEDs, and dyes.^[1] Meantime, reports on synthesis and reactivity studies of anionic amidinate [(Ar)C (NR'₂)]⁻ ligated four-coordinate boron compounds are scarce.^[2] In particular, the applicability of those compounds in synthesizing light emitting materials, exploring their photo-physical properties is remains unexplored. In view of that interest, we designed a novel series of amidinate [(Ar)C (NR'₂)BX₂] (Ar = aryl; R' = alkyl; X = halides) based four- coordinate boron compounds by extending π -conjugation on aryl moieties, explored their photophysical and electrochemical properties.

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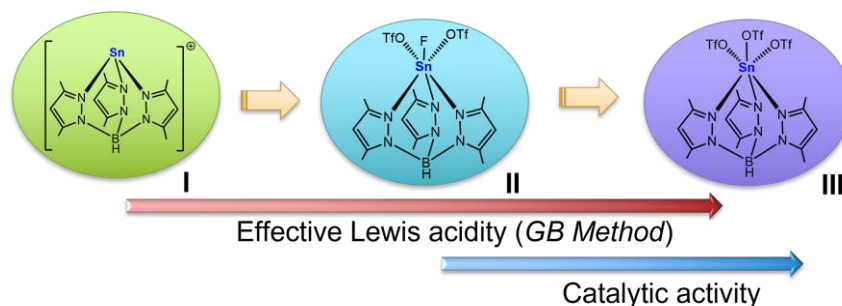
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Hydrotris(pyrazolyl)borate ligand is a popular ligand to stabilize both Lewis acidic and Lewis basic main group compounds.¹⁻² Recently, we have analyzed the low-valent group 13-15 compounds of hydrotris(3,5-dimethyl-pyrazolyl)borate ligand, $[\text{Tp}^*\text{E}]^x$, (E = group 13 element, $x = 0$; E = group 14 element, $x = 1+$; E = group 15 element, $x = 2+$) based on density functional theory.³ A periodic increment in intrinsic Lewis acidity is observed down the group due to increased E-N bond polarization towards nitrogen, resulting in lower energy secondary binding sites. This study underscores the potential of the Tp^* ligand in stabilizing the reactive low-valent p-block elements. In this context, to explore the Lewis acidic Sn complexes, Sn(II) Tp^* cations (**I**) were synthesized from Tp^*SnCl by halogen abstraction. Modified Gutmann-Beckett test shows the mild Lewis acidity of these Sn(II) cations.⁴ Oxidation of $[\text{Tp}^*\text{Sn(II)}]^+$ to $[\text{Tp}^*\text{Sn(IV)F(OTf)}_2]$, (**II**) increases the effective Lewis acidity of the complex significantly and further increment is observed for $[\text{Tp}^*\text{Sn(IV)(OTf)}_3]$, (**III**). The effect of Lewis acidity at the metal center is reflected in the catalytic deoxygenation of various phosphine oxides.⁵ The key results of this work will be presented.



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Magnetic and Redox Properties of Silylene Ligated Transition Metal Complexes

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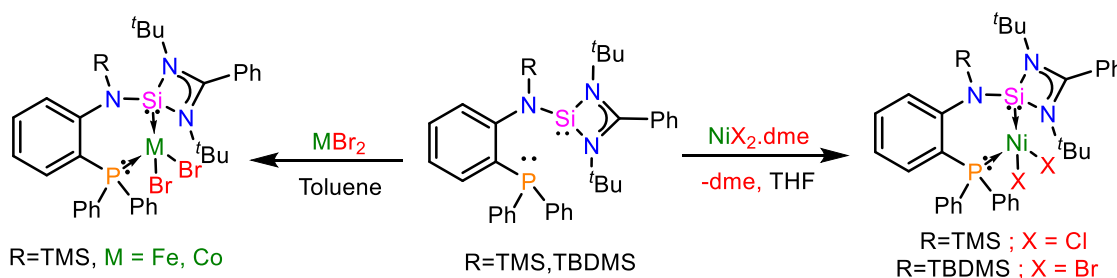
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ABSTRACT

This work highlights the preparation of two new silylene-phosphine-based hybrid ligands Si{N(R)C₆H₄(PPh₂)₂}{PhC(N^tBu)₂} (R = TMS {trimethylsilyl} (1), TBDMS {tert-butyldimethylsilyl} (2)), which possess two donor sites. Further to explore the coordination behaviour, we treated the bidentate ligand 1 with base metal halides (FeBr₂, CoBr₂, NiCl₂·dme (Nickel chloride(II) ethylene glycol dimethyl ether)) and 2 with NiBr₂·dme (Nickel bromide(II) ethylene glycol dimethyl ether) which afforded four-coordinate six-membered metal complexes, that feature coordination from both Si(II) and P(III) sites. The solid-state structures of these complexes have been validated by single-crystal X-ray diffraction studies, NMR spectroscopy, and mass spectroscopy. Subsequently, complexes are studied for their redox and magnetic properties with the help of UV-Vis spectroscopy, cyclic voltammetry, SQUID magnetometry. Complexes were found to display paramagnetic behaviour. Theoretical studies were also performed to understand the bonding scenario as well as origin of magnetism.



Schematic representation of hybrid silylene coordinated 3d-metal complexes.

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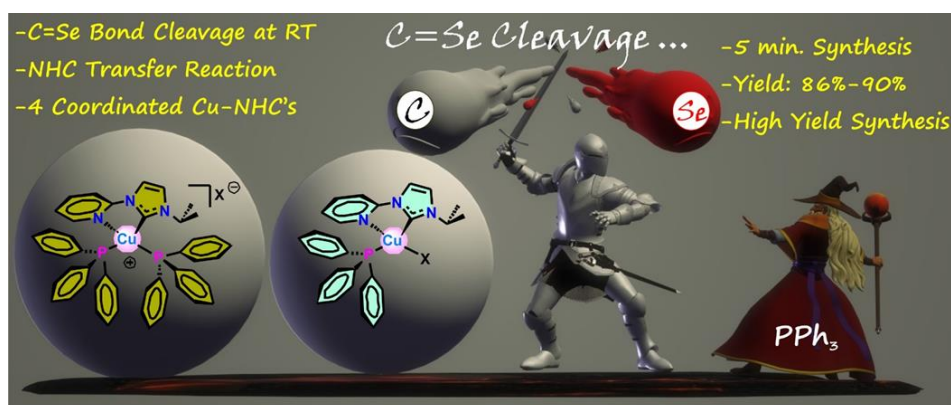
A Simple and Fast Access to Phosphine Substituted Copper(I)-Carbene
Complexes via C=Se Bond Cleavage Reaction

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ABSTRACT: Phosphine coordinated Cu(I)NHC complexes can be synthesized by various synthetic routes such as transmetallation, basic copper precursors, free carbene and copper powder. A facile route to access the copper(I)-carbene phosphine complexes were reported. In this synthetic strategy N-heterocyclic carbene gets transferred from N-heterocyclic selone through a C=Se bond cleavage reaction to form copper(I) complexes within five minutes at room temperature. The complexes [(Py[^]NHC)Cu(PPh₃)₂]X, X = BF₄, ClO₄, PF₆ and OTf; Py[^]NHC = 3-isopropyl-1-(pyridin-2-yl)-imidazol-2-ylidene, and [(Py[^]NHC)Cu(PPh₃)(X)], X = Br and I were synthesized by treating 1-isopropyl-3-(pyridin-2-yl)-imidazole-2-selone with corresponding copper(I) precursors and triphenylphosphine. These reactions were not sensitive to moisture and oxygen.



P43 Synthesis of low oxidation state zinc(I) complexes and their catalytic studies in dehydroborylation of terminal alkynes

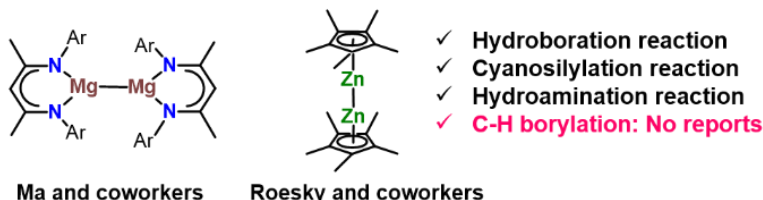
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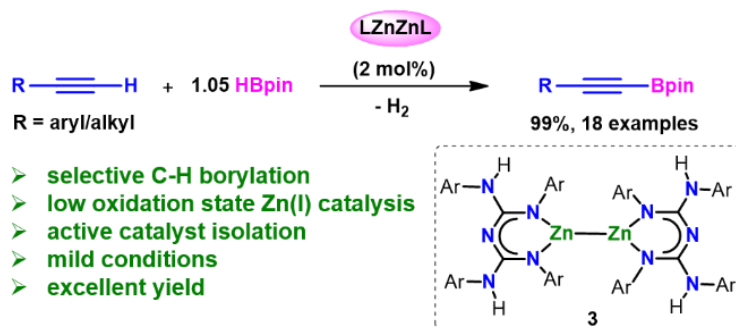
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The syntheses of low oxidation state metal-metal bonded complexes have attracted interest in several areas of chemical science due to their unique properties. A new example of structurally characterized conjugated bis guanidinate supported zinc (I) dimer, *i.e.*, LZnZnL (**3**) (L = {(ArNH)(ArN)-C=N-C=(NAr)(NHAr)}; Ar = 2,6-Et₂-C₆H₃) with a Zn-Zn bond is reported. Furthermore, heteroleptic (Cp*ZnZnL, **2**) (Cp* = 1,2,3,4,5-pentamethylcyclopentadienide) and homoleptic (LZnZnL, **3**) and zinc(I) dimers are employed as precatalysts in the dehydroborylation of a variety of terminal alkynes. Additionally, CBG zinc acetylide (LZn-C≡C-Ph-4-Me)₂, (**5**), which is validated by X-ray crystal structure investigation, is isolated as the active catalyst. A possible reaction mechanism has been proposed by a number of stoichiometric studies.

A. Mg(I) and Zn(I) dimers in main group catalysis



B. This work: Zinc - Zinc precatalyzed dehydrogenative borylation of alkynes



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P44

Hybrid Silylene Based Pd Catalyst for C-N Coupling of Sterically Hindered and Chiral Amines

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We have employed N-heterocyclic silylene (**1**) [$\text{PhC}(\text{NtBu})_2\text{SiN}(\text{PPh}_2)(2,6\text{-iPr}_2\text{-C}_6\text{H}_3)$] & (**2**) [$\text{PhC}(\text{NtBu})_2\text{SiN}(\text{PiPr}_2)(2,6\text{-iPr}_2\text{-C}_6\text{H}_3)$] with $\text{Pd}(\text{dba})_2$ as an effective catalyst in Buchwald-Hartwig amination reactions to form C-N bonds for a wide range of substrate with different electronic and steric demands of coupling partners with ~99% isolated yields. The crowning points are that **1**/ $\text{Pd}(\text{dba})_2$ is very productive for wide range of substrates including optically active amines, sterically bulky amines, unreactive primary amines, heterocyclic amines, secondary amine with aryl halides ($x = \text{Br}, \text{Cl}$). It is observed that **1**/ $\text{Pd}(\text{dba})_2$ is more efficient than traditional phosphine ligands. Additionally, to understand reaction pathway, we have performed kinetic studies by using simple substrates.

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Ligand Modulated Stability of Low Coordinated Zinc Cations and their
Catalytic Activity

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The environment friendly base metals have gained much eminence in the past few years due to their good earth abundance. Within this frame, well-defined cationic zinc complexes have been found as excellent catalysts for a wide range of organic transformations.^[1] However, to get access to these reactive cationic Zn species an appropriate ligand scaffold to impart steric and electronic protection, without significantly compromising with the reactivity, is essential.

In the present work, sterically tunable bis(phosphinimino)amide and iminophosphonamide ligand frameworks have been exploited to afford the cationic zinc complexes. It was observed that the stability of low coordinated Zn cations essentially depends on steric bulk of the ligand, counter anion and solvent. In the absence of these conditions the sterically accessible zinc(II) cation can undergo rapid exchange reaction with the counter anion to form covalent complexes. The most stable discreet cationic zinc complex, $[\text{LZn}]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ (**2**) was successfully synthesized, using bulky dipp substituted bis(phosphinimino)amide ligand supported $[\text{LZn}-\text{CH}_3]$ (**1**) precursor, *via* methyl abstraction using $\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{LH} = \{[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{P}(\text{Ph}_2)]_2\text{N}\}\text{H}$). The molecular structure of **2** was established *via* X-ray crystallography, which revealed the weak interaction of methyl protons of the anion with the cationic zinc center. The results clearly demonstrate that the choice of ligand play a crucial role in the successful synthesis of cationic zinc complexes. Moreover, with prolonged time the slow exchange reaction of **2** leading to the products $[\text{LZn}-\text{C}_6\text{F}_5]$ and $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_2$ through B-C₆F₅ bond cleavage strongly affirms the retained electrophilicity of $[\text{LZn}]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$.² The benefits of Lewis acidity of titled complex **2** is exploited for hydrosilylation and hydroboration of imines as depicted in the Figure below.

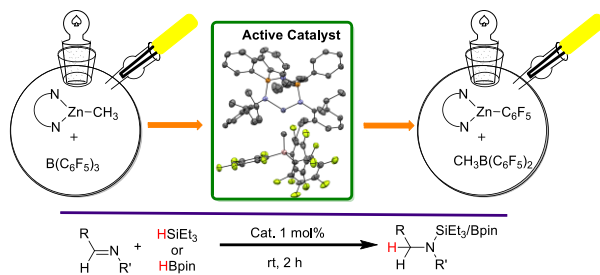


Figure. Hydrosilylation and hydroboration of imines catalyzed by cationic zinc complex.

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Coordination behavior of the Tellurium Incorporated
Mercuraazametallamacrocycle and Investigation of $d^{10}\cdots d^{10}$ Interactions between
Ag, Hg metal centers

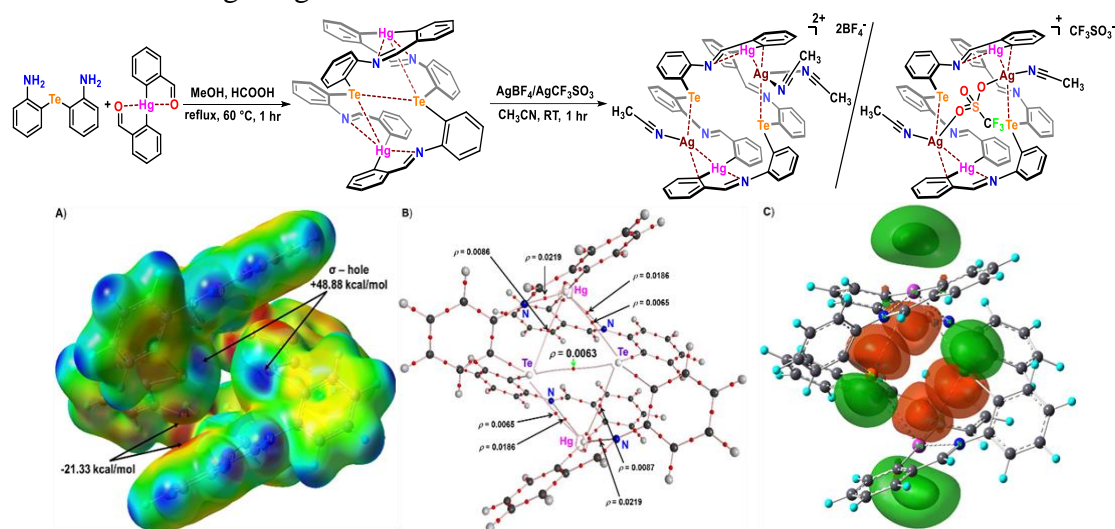
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Tellurium incorporated mercuraazametallamacrocycle has prepared via (2+2) condensation of bis(*o*-aminophenyl) telluride and *o*-formylphenyl mercury(II)bromide/bis(*o*-formylphenyl)mercury(II). The ligand mercuraazametallamacrocycle isolated as a bright yellow solid which adopted as a 28 membered ring with *Tennis Ball Seam Line* conformation. This macrocycle treated with two equivalents of silver salts (AgBF_4 , AgOTf) at room temperature and isolated greenish-yellow bimetallic complexes. These isolated metal complexes are examined by single crystal X-ray diffraction analysis and the molecular structures are displaying weak $\text{Hg}\cdots\text{Ag}$ interactions as well as a strong intermolecular $\text{Hg}\cdots\text{Hg}$ interactions. These metal \cdots metal interactions are examined via DFT calculations, Electrostatic potential map(ESP), the Atoms in Molecule (AIM) analysis and Natural Bond Orbital(NBO) analysis revealed that the intermolecular $\text{Hg}\cdots\text{Hg}$ interaction is stronger than intramolecular $\text{Hg}\cdots\text{Ag}$ interactions.



Schematic picture of Tellurium assisted Mercuraazametallamacrocycle with A) ESP, B) AIM and C) NBO pictures

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P47

Organoaluminum Cation Catalyzed Selective Hydrosilylation of Carbonyls, Alkenes, and Alkyne

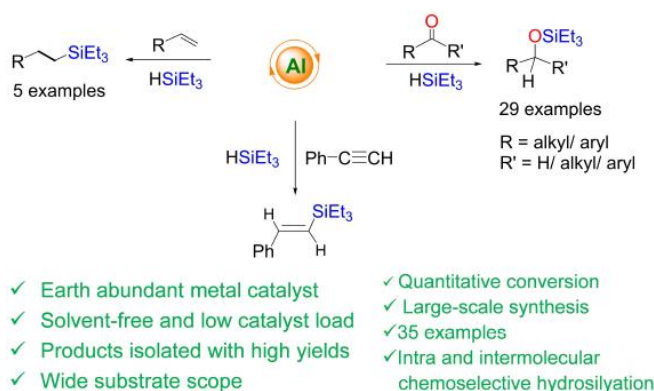
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Currently our research group is focusing on main group metal catalysed organic transformations. Main group elements are cheaper, non-toxic and are having large abundance on the earth crust when compared to transition or lanthanide elements. In recent years, the application of molecular compounds containing main group elements in catalysis is an emerging area of recent research interest. In view of this, we have synthesized well-defined various amine-imine, conjugated bis-guanidine, N-heterocyclic carbene and “NHC-CDI” adducts or zwitterionic supported main group metal complexes and utilized as (pre)-catalysts for various organic transformations such as dehydrocoupling of silanes with amines, hydroboration of carbonyl compounds, guanylation reaction etc. Moreover, we have synthesized well-defined bulky conjugated bis-guanidine supported aluminum alkyl and alkyl cation complexes as per literature procedure.

Herein we present the synthesis and characterization of N-donor supported organoaluminum methyl and its cationic complexes. In addition, molecular aluminum methyl cation catalyzed organic transformations such as reduction of carbonyls, alkenes and phenylacetylene will be presented via hydrosilylation method.



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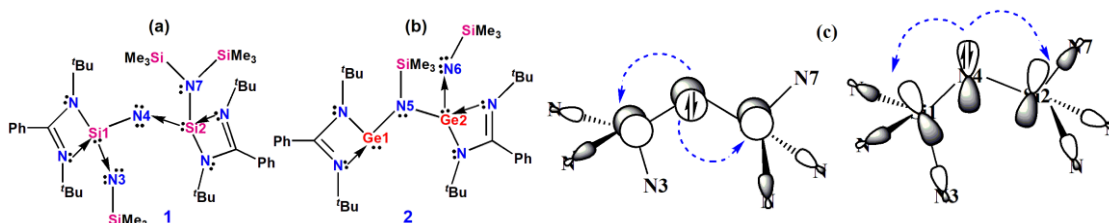
Pseudo-Bonds Formed by Hyperconjugative Interactions in Stabilizing
Monovalent Nitrogen Compounds

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As per the IUPAC, hyperconjugation is defined as “In the formalism that separates bonds into σ and π types, hyperconjugation is the interaction of σ -bonds (e.g., C–H, C–C, etc.) with a π -network.” It has been described as a mild sort of conjugation.^[1] However, hyperconjugation plays a pivotal role in deciding the structure, stability, and reactivity of molecules. Here, we report the bonding and reactivity of two monovalent dicoordinated nitrogen compounds viz., $L(\text{Me}_3\text{Si})\text{NSi}-\text{N}\leftarrow\text{SiN}(\text{SiMe}_3)_2L$ (**1**) and $L\text{Ge}-\text{N}(\text{SiMe}_3)-\text{GeN}(\text{SiMe}_3)L$ (**2**) [$L = \text{PhC}-(\text{N}^t\text{Bu})_2$] by quantum mechanical calculations at M06/def2-TZVPP//BP86-D3(BJ)/def2-TZVPP level of theory.^[2, 3] The bonding analysis indicates that compounds **1** and **2** contain monovalent, dicoordinated nitrogen atoms having two active lone pair orbitals with σ and π local symmetry. These lone pairs are stabilized by hyperconjugative donation to Si–N_{amidinate}/Ge–N_{amidinate} σ^* - orbitals (34.9 - 49.0 kcal/mol in **1** and 57.1 kcal/mol in **2**) imparting pseudo-multiple bond character to the N3–Si1–N4–Si2 skeleton in **1** (Scheme 1-c) and Ge2–N6 bond in **2** respectively. Accordingly, the N3–Si1–N4–Si2 skeleton in compound **1** can be considered as pseudo-silaazatriene and the Ge2–N6–SiMe₃ fragment in **2** can be considered as a pseudo-germylimine. The high first and second proton affinity values of the monovalent, dicoordinated nitrogen atoms show their tetrylone-like reactivity.



Scheme 1. Schematic representation of (a) silaazatriene **1** (b) germylimine **2** (c) representative hyperconjugative interaction which stabilizes the monovalent, dicoordinated nitrogen atom in **1**.

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P49

Aluminum Borohydrides: Synthesis, Structure and Catalytic Reduction of Carbon Dioxide

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In recent years, significant progress has been made in the development of catalysts and reductants for the fixation of carbon dioxide to valuable C1 feedstock. Various transition and main group metal complexes are known to catalyze the reduction of carbon dioxide using silicon hydrides as reductants. Aluminum catalysts have been extensively explored due to their high abundance and low toxicity compared to transition metal catalysts. Various aluminum hydrides have also been implemented to catalyze carbon dioxide. Owing to their high reactivity, aluminum hydrides in the presence of borane result in the formation of aluminum borohydride complexes. The most prevailing feature of aluminum borohydride is the formation of Al-H-B bonds like $3c-2e$.¹⁻³ In this work, we present the reaction of aluminum hydride, $\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{AlH}_2$ (**1**)⁴ with different boranes to synthesize aluminum borohydride complexes. Depending on the Lewis acidity of the borane, these aluminum borohydrides display the dissociation of the borane at room temperature, leaving free aluminum hydride in the solution. Borane dissociation displays differences in its reactivity towards CO_2 . These observations have prompted us to explore the aluminum borohydrides using various boranes and demonstrate their catalytic activity in the reduction of carbon dioxide using silanes as reductants.

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A greener approach towards the synthesis of N-heterocyclic thiones and selones using the mechanochemical technique

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Abstract: This work describes the synthesis of N-heterocyclic thiones and selones of a variety of imidazolium salts involving an eco-friendly and solventless ball-milling technique.¹⁻⁴ The products have been isolated in almost quantitative yield, involving a minimum quantity of solvents, only for the isolation of products, for column chromatography, and in some cases for purification purposes. Both mono- and bisimidazolium salts afforded N-heterocyclic thiones and selones. The methodology is found to be superior in terms of reaction time, yield and energy efficiency as compared to conventional solution-state reactions. The synthetic details and structural aspects will be presented in poster.

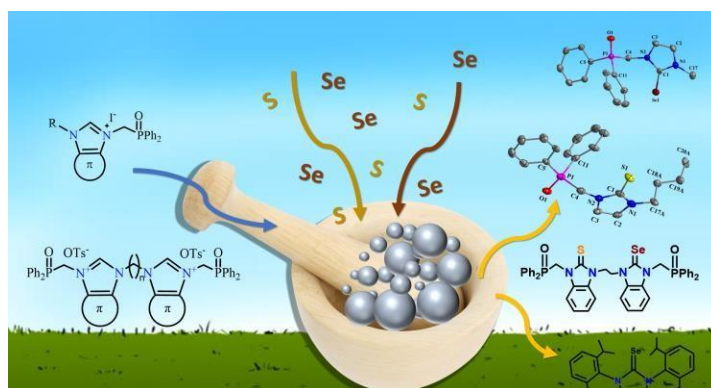


Figure 1. Synthesis of N-heterocyclic thiones and selones of a variety of imidazolium salts via Ball Milling technique.

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Computational Insights into the “Crowning” of Noble Gas Trioxides

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Quantum chemical calculations were carried out to investigate the nature of bonding between electron-rich crown ethers (9-Crown-3, 12-Crown-4, 15-Crown-5, 18-Crown-6 and 21-Crown-7) and the noble gas trioxides (“NgO₃”). The basis set superposition error (BSSE) corrected interaction energies for these adducts range from -15.4 kcal/mol to -41.2 kcal/mol, which is relatively high for non-covalent interactions. The formation of these adducts was observed to be more favorable with the increase in the ring size of the crown ethers and less favorable while going from XeO₃ to ArO₃. These unconventional interactions, which arise due to the presence of the σ -hole at the location of the lone pair of NgO₃ (**Fig.1**), also termed as “aerogen bonding”, were further analyzed by various computational tools such as the mapping of the electrostatic potential (ESP), Wiberg bond indices (WBIs), Bader’s theory of atoms-in-molecules (AIM), natural bond orbital (NBO) analysis, non-covalent interaction (NCI) plots and the energy decomposition analysis (EDA). The comprehensive analysis done reveals that the hydrogen bonding interactions, which increase with the increase in the size of the crown ethers, play a significant role in stabilizing these adducts.

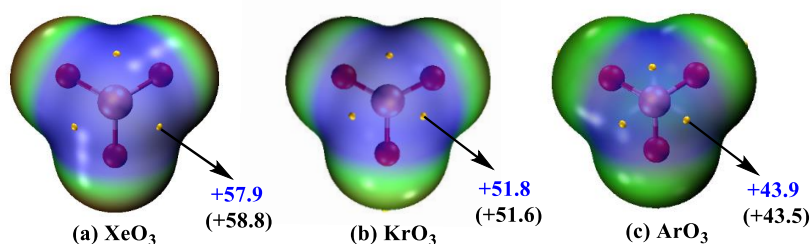


Fig. 1: The molecular electrostatic potentials (MEPs) of the NgO₃ with their respective maxima ($V_{s,max}$ in kcal/mol) around their σ -holes. The values shown in blue and the bracketed values in black represent the $V_{s,max}$ computed at the APFD/def2-TZVPD and MP2/aug-CC-pVQZ levels of theory, respectively.

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P52

Coordination and Hydroboration of Ru(II)-Borate Complexes: Dihydridoborate vs. Bis(dihydridoborate)

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Owing to the presence of unique bonding modes and their inclination to undergo hydroboration, C-H functionalization and dehydrogenation reactions, the transition metal (TM) σ -borane/borate complexes are very appealing for various organic reactions as well as catalytic reactions. The growth of this chemistry was aided primarily by the introduction of Trofimenko's scorpionate ligands and in this regard, the heterocyclic borate ligands bearing both hard (N) and soft (S) donor atoms were observed to be quite dynamic.[1] In the course of our recent studies for the isolation of diverse borate complexes and E-H bond activations (E = C, B or Si),[2] we have investigated the reactivity of $[\text{Cp}^*\text{RuCl}_2]_2$, $[\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}]$, $[\text{Cp}^*\text{Mo}(\text{CO})_3\text{Me}]$, $[(\text{COD})\text{MCl}]_2$ (M = Rh or Ir) and $[(p\text{-cymene})\text{RuCl}_2]_2$ with different types of borate ligands that showed diverse reactivity patterns and produced unusual σ -borate[3] complexes. The results from these investigations exhibit the role of both ligands and the metal precursors in coordination as well as hydroboration reactions with alkynes.

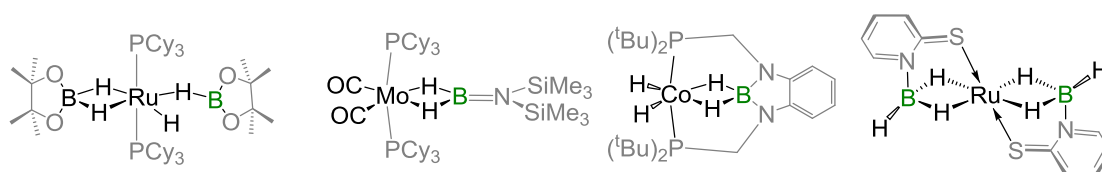


Figure: Examples of σ -borane/borate complexes of transition metals

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P53

**Cationic Magnesium and Calcium Hydrides:
Catalysts or Pre-Catalysts?**

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MgH₂ and CaH₂ find applications as reducing agents in organic chemistry. [1] They have generated significant interest as hydrogen storage materials. To understand elementary chemical reactions involved with MgH₂ and CaH₂, chemists ventured into the isolation of the molecular hydrides. [2] Today, we find a handful of examples of molecular hydrides of alkaline earth metals showing relevance in the stoichiometric and catalytic reduction of unsaturated molecules. [3] Our studies on cationic alkyl, amides, and alkoxy derivatives [4] have opened the possibilities in accessing reactive hydride compounds. While there are no straightforward routes to obtain cationic hydrides, we have identified the challenges and developed new ways. [5,6] Investigations on the elementary reactions involving these newly synthesized hydrides have provided vital proof for understanding their roles as catalysts and pre-catalysts in the hydroelementation of unsaturated organic molecules. [6]

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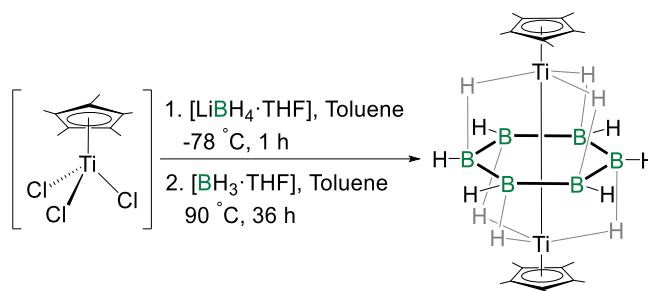
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Hexagonal Planar [B₆H₆] within a [B₆H₁₂] Borate complex

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Rules for boron and other group 13 elements are only evolving. Polyhedral boranes, not flat structures, dominate borane chemistry.¹ The obvious benzene-graphene equivalent, B₆H₆ to borophenes and borophites, does not exist. We synthesized the first flat B₆H₆ unit, stabilized as a part of [(Cp*Ti)₂(μ-η⁶:η⁶-B₆H₆)(μ-H)₆].² The synthetic inspiration came from several sources: (a) Fehner's synthesis of [(Cp*Re)₂(μ-η⁶:η⁶-B₆H₄Cl₂)] with a near flat [B₆H₄Cl₂]₂;³ (b) Our explorations on metallaborane clusters using similar strategy; (c) Our study of the dependence of the planarity of the middle ring in a triple decker complex on the size of the ring and the valence electron count of the complex.⁴ Treatment of [Cp*TiCl₃] with three equivalents of [LiBH₄·THF] at -78 °C followed by thermolysis in the presence of excess [BH₃·THF] led to the complex. The implications of the first planar B₆H₆ ring stabilized by transition metal fragments to metallaborane chemistry are immense, but these go beyond. The nature of the six bridging hydrogens that give support to the hexagonal B₆ ring suggests possibilities in stabilizing hexagonal borophenes as stand-alone species with bridging hydrogens—an area of current research. The key results of this work will be discussed.



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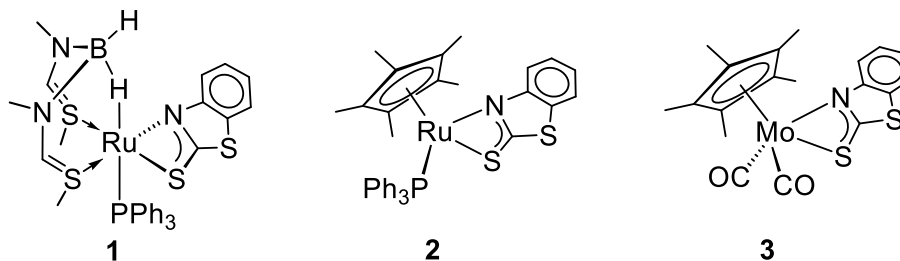
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In small molecule activation, metal-ligand cooperation (MLC) has become an important tool.¹ Small molecules such as H₂, CO₂, boranes, or silanes can be activated by MLC across the metal-ligand bond.² The transition metal complexes with M-S (M = Ru and Fe) or redox non-innocent ligands in combination with MLC can activate boranes and other small molecules.³ Recently, we have demonstrated 1,3-N,S-chelated ruthenium borate complex, [κ^2 -N,S-(NC₇H₄S₂)}(PPh₃)Ru{ κ^3 -H,S,S'-H₂B(NC₇H₄S₂)₂}] (**1**), comprising polar Ru-N bonds, which is inclined to C-H, B-H and Si-H bond activation.⁴ The aerial oxidation of this borate complex generate redox-active κ^2 - N,S-chelated ruthenium species that participate in multisite borane activation to form bis(dihydroborate) ruthenium complexes.⁵ Further, the borate site of this κ^2 - N,S-chelated ruthenium complexes were replaced by the Cp* moiety to generate [Cp*RuPPh₃{ κ^2 -N,S-(NC₇H₄S₂)}] (**2**). The role of complex **2** in B-H bond activation have been studied.^[6] Further, we have analysed the reactivity of Cp* based κ^2 - N,S-chelated molybdenum complex [Cp*Mo(CO)₂{ κ^2 -N,S-(NC₇H₄S₂)}] (**3**) towards boranes.^[6] The key results of this work will be discussed.



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P56

NO Generation from Nitrite at a Tripodal Zinc(II) Site: Ambiphilic Reactivity of Nitrite and Role of Thiol Persulfidation

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Persulfidation of thiol plays a pivotal role in the biochemistry related to H₂S signaling and thus supports multifaceted bioactivities such as neurotransmission, vasorelaxation, and anti-inflammation.¹ Notably, persulfide of a thiol (RSSH) is more nucleophilic as compared to its thiol counterpart (RSH), thereby exhibiting several unique reactivity patterns, including important antioxidant properties under biologically relevant conditions.² While there are several routes available for thiol persulfidation,¹ cysteinyl tRNA synthetase (CARS) mediates persulfidation of cysteine (Cys) in the presence of sulfane sulfur.³ Our recent work illustrates that a tripodal [Zn^{II}] complex [(Bn₃Tren)Zn^{II}-OH₂](ClO₄)₂ is capable of facilitating interaction between thiol and sulfane sulfur species (*e.g.* S₈ and organic polysulfides) leading to thiol persulfidation.⁴ Accordingly, we hypothesize that the persulfides, thus generated, may serve as suitable reductants for reducing nitrite (NO₂⁻) to nitric oxide (NO) at a redox-neutral metal site, namely zinc(II). While nucleophilic reactivity of free nitrite anion with sulfane sulfur species has been previously demonstrated to yield perthionitrite anion (SSNO⁻),⁵ this work experimentally outlines that the nitrite anion bound to zinc(II) site in [(Bn₃Tren)Zn^{II}-ONO](ClO₄) acts as non-nucleophilic.⁶ The nitrite moiety in [(Bn₃Tren)Zn^{II}-ONO](ClO₄) undergoes a nucleophilic attack by thiol (RSH) to yield NO in ~6% through S-nitrosothiol (RSNO). Intriguingly, reactions of the zinc(II)-nitrite complex and thiol in the presence of sulfane sulfur (*e.g.* S₈ and R-S_n-R) enhance NO yield ten-fold. Detailed mechanistic investigations utilizing UV-vis, ESI-MS, persulfide trapping experiments suggest the intermediacy of persulfide anions (RSS⁻). Thus, this work hints that sulfane sulfur species are not only important in H₂S biochemistry but also may play critical roles in promoting NO signaling activities.

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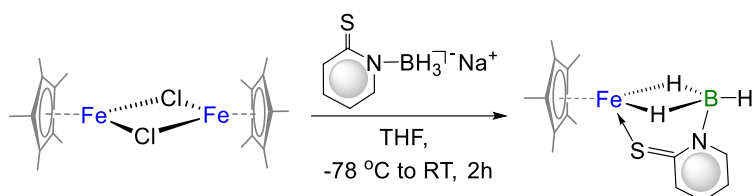
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Recent years have witnessed significant growth in the field of transition metal (TM) boron chemistry. The TM σ -borane/borate complexes are appealing due to the presence of unique bonding modes and their inclination to undergo hydroboration, C-H functionalization and dehydrogenation reactions.¹ These complexes are classified as: i) σ -borane complexes comprising tri-coordinated boron, and ii) Lewis base stabilized borane or borate complex comprising tetracoordinated boron.² The base-stabilized borane/borate complexes are typically synthesized from the chelation of a metal by a scorpionate type borane/borate ligand. A broad range of scorpionate ligands that play a key role in the stabilization of these TM σ -borate complexes have been reported over the years and in this regard, the heterocyclic borate ligands bearing both hard (N) and soft (S) donor atoms were observed to be quite dynamic.³ In the course of our recent studies for the isolation of diverse transition-metal borate complexes, we investigated the reactivity of $[\text{Cp}^*\text{FeCl}_2]_2$ with small heterocyclic borate ligand, $[\text{Na}[(\text{H}_3\text{B})\text{mp}]]$ ($\text{mp} = 2$ -mercatopyridine).³ The reaction led to the isolation of iron dihydridoborate complex, $[\text{Cp}^*\text{Fe}(\mu\text{-H})_2\text{BH}(\text{mp})]$ (**1**), wherein the Cp^*Fe is confined by tridentate $[\text{H}_3\text{B}(\text{mp})]$ (Scheme 1). In addition, the role of both ligand and the metal precursor in hydroboration reactions has been explored. The key results of this work will be discussed.



Scheme 1 Synthesis of iron dihydridoborate complex (**1**).

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A Zwitterionic Disilanylium from an Unsymmetric Disilene

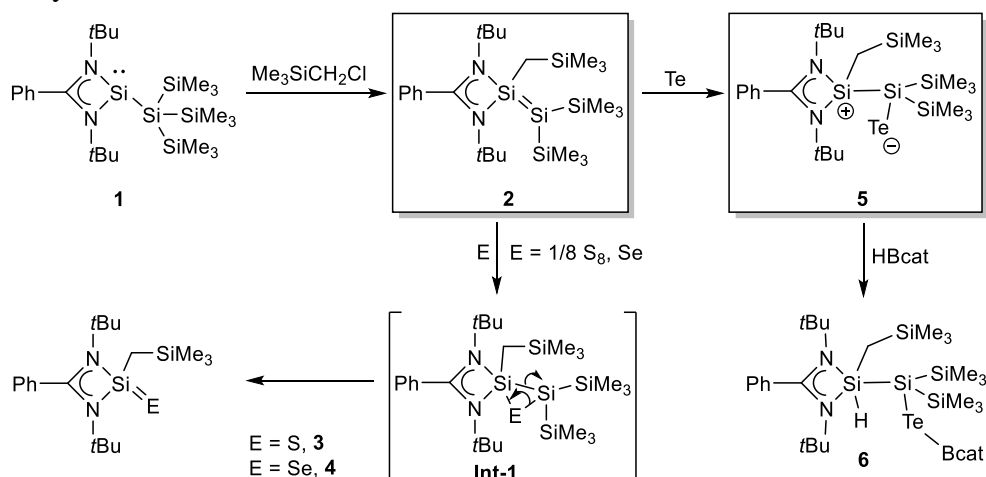
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The reaction of benz-amidinato hypersilylsilylene [PhC(N*t*Bu)₂SiSi-(SiMe₃)₃], (**1**) with Me₃SiCH₂Cl led to the formation of a new unsymmetrical sp²-sp³ disilene, **2** where both the Si atoms have different substitution as well as coordination numbers. Subsequently, we have treated **2** with sulphur and selenium, which gave rise to **3** and **4** featuring with a Si=S and Si=Se bond, respectively. Tellurium reacted in a different way with **2** and furnished a unique zwitter ionic compound, **5** rather than a silicon tellurium double bond. The unique compound, **5** where central Si atom is bearing a positive charge and the negative charge is located on the Te atom keeping the Si-Si bond intact during the reaction can be called as disilanylium telluride. The heavier element tellurium is reluctant to form a three membered ring due to its bigger size compared to sulphur and selenium. **5** showed a cooperative B-H bond activation when treated with HBcat to access the activated product, **6** which is very rare in main group chemistry.



Scheme 1. Synthesis of disilene **2**, reactions with chalcogens to yield compounds **3**, **4** and **5**. Cooperative bond activation to get **6**.

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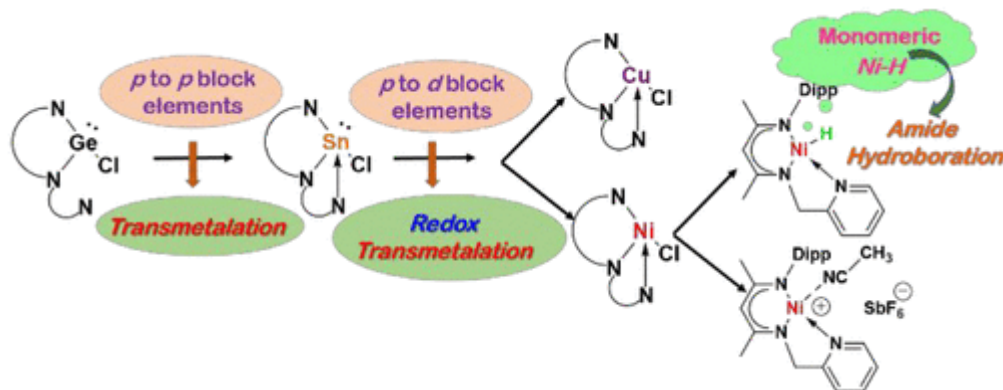
Tridentate NacNac Stabilized Tin and Nickel Complexes: Access to a Monomeric Nickel Hydride and Its Catalytic Application

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The transmetalation reaction of picolyl-supported tridentate nacnac germylene monochloride [2,6-*i*Pr₂-C₆H₃NC-(Me)CHC(Me)NH(CH₂py)]GeCl (1) (py = pyridine) with SnCl₂ results in an analogous stannylene chloride (2). The three -coordinated stannylene cation [{2,6-*i*Pr₂-C₆H₃NC(Me)CHC-(Me)NH(CH₂py)}Sn]⁺ with SnCl₃⁻ as a counteranion (3) has been generated through the abstraction of chloride ligand from 2 using an additional equivalent of SnCl₂. Instead of forming a donor-acceptor complex, 2 undergoes a facile redox trans-metalation reaction with Ni(COD)₂ (COD = cyclooctadiene) and CuCl to afford analogous nickel and copper complexes [2,6-*i*Pr₂-C₆H₃NC(Me)CHC(Me)NH(CH₂py)]MCl [M = Ni (4) and Cu (5)]. The reactions of 4 with potassium tri-sec-butylborohydride (commonly known as K-selectride) and AgSbF₆ provide access to monomeric Ni(II) hydride, [2,6-*i*Pr₂-C₆H₃NC(Me)CHC(Me)NH(CH₂py)]NiH (6) and a Ni(II) cation, [{2,6-*i*Pr₂-C₆H₃NC(Me)CHC(Me)NH(CH₂py)}Ni][SbF₆] (7), respectively. 6 was found to be an effective catalyst for the hydroboration of amides.



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Reductive Homologation of CO by Activated Magnesium(I) Reductants:
Reactivity of Lewis base Adducts vs $[\text{Mo}(\text{CO})_6]$

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Carbon monoxide is a cheap and abundant industrial feedstock. In combination with H_2 (i.e. in synthesis gas: CO/H_2) it is utilized as a versatile C_1 building block in, for example, the Fischer-Tropsch (F-T) process.¹ In order to model the fundamental steps of the F-T process, recent interest has lain with the reductive homologation of CO (possessing one of the strongest bonds known, $\text{BDE} = 257 \text{ kcal/mol}$)² with low-valent organometallic compounds, yielding cyclic and acyclic oxocarbon anions, e.g. ethynediolate $[\text{C}_2\text{O}_2]^{2-}$ and cyclic aromatics $[\text{C}_n\text{O}_n]^{2-}$ ($n = 3-6$), under mild conditions. In this context, the first molecular Mg(I) complexes were synthesised in 2007, and have been shown to be versatile reducing agents,³ but they do not couple CO under normal conditions. However, reactions of magnesium(I) complexes with 1 equivalent of an NHC (N-heterocyclic carbene) or DMAP (4-dimethylaminopyridine) yield unsymmetrical magnesium(I)-adduct complexes, $[(\text{L})(\text{D})\text{Mg}-\text{Mg}(\text{L})]$ ($\text{L} = \beta$ -diketiminate), which have markedly increased Mg–Mg bond distances, relative to uncoordinated magnesium(I) compounds, and are much more reactive than those systems. Interestingly, subtle changes to the bulk of 1:1 adducts of DMAP with magnesium(I) complexes leads to steric control over the products arising from their reductive oligomerisations of carbon monoxide. Deltate complexes $[\{(\text{L})(\text{D})\text{Mg}\}(\mu\text{-C}_3\text{O}_3)\{\text{Mg}(\text{L})\}]_2$ are obtained with bulkier adduct complexes, whereas ethynediolate complexes ($[\{(\text{L})\text{Mg}\}(\mu\text{-OC}(\text{H})=\text{C}(\text{DMAP-H})\text{O})\{\text{Mg}(\text{L})\}]_2$) result from the smaller adducts^{4,5}. In addition, Reactions of two magnesium(I) compounds with CO in the presence of catalytic $[\text{Mo}(\text{CO})_6]$ lead to the reductive hexamerization of CO, and formation of magnesium benzenehexolate complexes, $[\{(\text{L})\text{Mg}\}_6(\text{C}_6\text{O}_6)]$.⁶

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