Towards P-block Catalysts: Making Chemical Bonds on a Budget

by

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Abstract

The work in this thesis describes advancements made towards developing main group catalysts and designing new ligands. *N*-Heterocyclic imine (NHI) ligands were used to support novel boron, silicon and germanium complexes. The new boron compounds demonstrated the ability to dehydrogenate amine-boranes and instigate their dehydrocoupling. In one case, the catalytic dehydrogenation of amine-boranes was observed. Although the synthesized silicon and germanium compounds were structurally similar, they exhibited very different reactivity under reducing conditions. The former underwent a highly unusual ligand rearrangement, while the latter formed the desired two-coordinate acyclic germylene. In addition, new olefin-based ligands featuring mixed element donors were designed and their coordination chemistry with Lewis acids BH_3 and AuCl revealed different binding sites. These findings led to the isolation of a bimetallic complex that employed both donors at the same time. Finally, the preliminary photoluminescent properties of copper and gold complexes supported by the new N-heterocyclic olefin-phosphine (NHOP) ligands will be discussed.

Preface:

Portions of the work discussed in the thesis were completed in collaboration with other researchers within the Rivard Group in the Department of Chemistry at the University of Alberta. All X-ray crystallographic studies described in this thesis were performed by Dr. R. McDonald or Dr. M. J. Ferguson, including the mounting of crystals, set-up and operation of the diffractometer, refinement of the structures and preparation of the crystallographic data report. Elemental analyses were performed by the Analytical Instrumental Laboratory at the University of Alberta. N. Dabral and M. Miskolzie helped to obtain the ^{2}H and ^{29}Si NMR spectra.

In Chapter 2, the preparation and characterization of IPr=N-BPh_2 were completed with the assistance of N. R. Paisley. Dr. C. Hering-Junghans assisted with the theoretical calculations.

In Chapter 3, the theoretical calculations were completed by Dr. C. Merten, under the supervision of Prof. Y. Xu.

In Chapter 4, the optimization of the new ligand syntheses as well as their BH_3 complexes were prepared in collaboration with N. R. Paisley.

In Chapter 5, the theoretical calculations were performed by M. S. Oakley, under the supervision of Prof. M. Klobukowski. Dr. O. Shynkaruk assisted with the photoluminescence measurements.

According to the policy within our research group, each chapter of this thesis is essentially self-contained and prepared in the form of a paper that is

intended for publication in peer-reviewed journals. A portion of this thesis has been published previously elsewhere, and these publications are listed below:

Chapter 2: M. W. Lui, N. R. Paisley, R. McDonald, M. J. Ferguson, E. Rivard. Metal-free Dehydrocoupling of Amine-boranes by Tuneable *N*-Heterocyclic Imine-supported Boranes. *Chem. Eur. J.* **2016**, *22*, 2134 – 2145.

Chapter 3: M. W. Lui, C. Merten, R. McDonald, M. J. Ferguson, Y. Xu, E. Rivard. Contrasting Reactivities of Silicon and Germanium Complexes supported by *N*-Heterocyclic Guanidine Ligands. *Inorg. Chem.* **2015**, *54*, 2040 – 2049.

Chapter 4: N. R. Paisley[†], M. W. Lui[†], McDonald, R.; Ferguson, M. J.; Rivard, E. Structurally versatile phosphine and amine donors constructed from *N*-heterocyclic olefin units. *Dalton Trans.* **2016**, *45*, 9860 – 9870. ([†] = equal contribution).

Publications, not highlighted in this thesis, are as follows:

G. He, O. Shynkaruk, M. W. Lui, E. Rivard. Small Inorganic Rings in the 21st century: From Fleeting Intermediates to Novel Isolable Entities. *Chem. Rev.* **2014**, *114*, 7815 – 7888.

P. A. Lummis, M. R. Momeni, M. W. Lui, R. McDonald, M. J. Ferguson, A. Brown, E. Rivard. Accessing Zinc Monohydride Cations via Coordinative Interactions. *Angew. Chem., Int. Ed.* **2014**, 53, 9347 – 9351.

Dedicated to my family

"You are here to learn the subtle science and exact art of potion-making.
As there is little foolish wand-waving here,
many of you will hardly believe this is magic."
– Severus Snape

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Lastly thanks, but NO THANKS: Microsoft Word error reports, Chemdraw quit unexpectedly, Chemistry West Shutdown, Avogadro quit unexpectedly, long distance, Chester stealing my food, plop plop, melted NMR caps, UV lamp setup, holes in the gloves, holes in the glovebox gloves caused by HOTf, finding oil baths with more water than oil, no more clean NMR tubes, broken mercury thermometers, no more clean stir bars, and the diffractometer is down.

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List of Symbols, Nomenclature or Abbreviations

Å	Ångstrom
Ar	Aryl
br	Broad
°C	Degrees Celsius
C_6D_6	Deuterated benzene
ca.	Circa; approximately
CAAC	Cyclic(alkyl)(amino)carbene
$CDCl_3$	Deuterated chloroform
COD	1,5-Cyclooctadiene
Cp*	Tetramethylcyclopentadienyl ligand (η^5-C_5Me_5)
d	Doublet
dd	Doublet of doublets
DFT	Density functional theory
Dipp	Diisopropylphenyl
DTBP	2,6-di-tertbutylpyridine
equiv.	Equivalent
Et_2O	Diethyl ether
eV	Electron volt
FTIR	Fourier transform infrared spectroscopy
g	Gram
HOMO	Highest occupied molecular orbital
Hz	Hertz

IMes	1,3-Bis(2,4,6-trimethylphenyl)imidazole-2-ylidine
^{i}Pr	Isopropyl
IPr	1,3-Bis(2,6-diisopropylphenyl)imidazole-2-ylidine
K	Kelvin
Kcal	Kilocalorie
LUMO	Lowest unoccupied molecular orbital
Me	Methyl
Mes	Mesityl
mg	Milligram
MHz	Megahertz
min	Minute
mL	Millilitre
mmol	Millimole
mole	Mole
Mp	Melting point
NBO	Natural bond order
NHC	*N*-Heterocyclic carbene
NHI	*N*-Heterocyclic imine
NHO	*N*-Heterocyclic olefin
NHON	*N*-Heterocyclic olefin amine
NHOP	*N*-Heterocyclic olefin phosphine
$^{n}J_{AB}$	n-bond AB coupling constant
NMR	Nuclear magnetic resonance
ORTEP	Oakridge Thermal Ellipsoid Plot

OTf	Trifluoromethansulfonate, triflate
Ph	Phenyl
PL	Photoluminescence
ppm	Parts per million
t	Triplet
THF	Tetrahydrofuran
TOF	Turnover frequency
TON	Turnover number
vide infra	See below
vs.	Versus
WBI	Wiberg Bond Index
XPhos	2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl
δ	Partial charge or chemical shift in ppm
λ_{ex}	Excitation wavelength
λ_{emis}	Emission wavelength
η	Eta, the number of atoms that a ligand coordinates
π	Pi
σ	Sigma

Chapter 1: Introduction

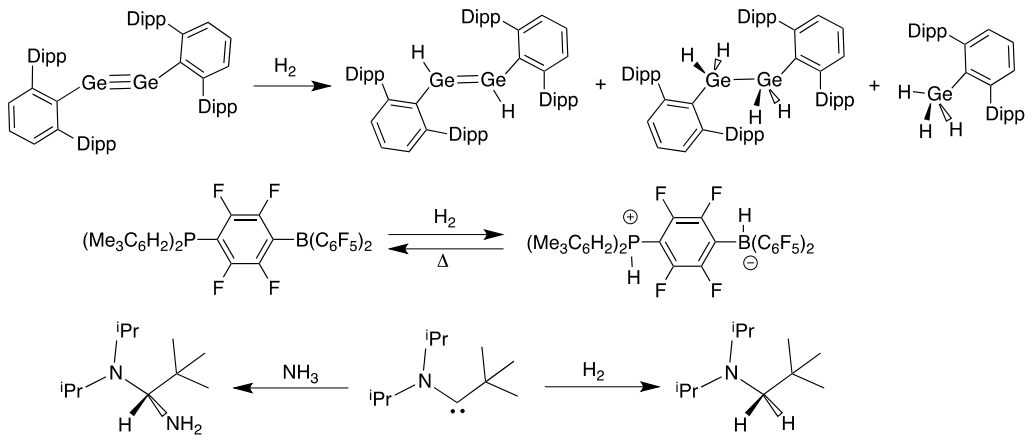
1.1 The Significance of Catalysis

The ability to control bond formation is an important technology that supports the global economy. Many of the commercial products we rely upon are prepared via catalytic bond forming reactions, for example, hydrogenation, C-C/C-N cross-coupling, and hydrosilylation. Specifically, metal-based catalysts are used to construct polymers, synthesize pharmaceuticals and detoxify emissions from motor vehicles. Although these catalysts are effective, they often contain expensive transition metals, such as Pt, Pd, Ir, and Ru. In addition, these heavy-metal containing compounds have environmental concerns associated with their waste disposal, and pose potential health threats if found in consumer goods. To address these problems, novel main group compounds are emerging in the literature as efficient catalysts.[1]

1.2 Moving Towards Main Group Catalysis

In the past decade, there has been growing excitement over compounds containing p-block elements that exhibit similar reactivity to transition metal complexes, particularly in the activation of small molecules (e.g. H_2, NH_3, CO_2, ethylene).[1a] There is currently a significant effort in inorganic chemistry that is moving away from purely exploratory synthesis towards applying these reactive main group compounds as reagents to effect desirable chemical

transformations. The addition of H_2 to a metal center is a simple reaction, yet it is analogous to a key step in many transition metal-mediated catalytic cycles, such as olefin and alkyne hydrogenation. In 2005, Power and coworkers demonstrated the first example of main group element reactivity with dihydrogen at ambient temperature using the germanium heavy-alkyne analogue $Ar^{Dipp}GeGeAr^{Dipp}$ (Ar^{Dipp} = 2,6-$Dipp_2C_6H_3$; Dipp = 2,6-$^iPr_2C_6H_3$) (Scheme 1) that afforded mono- and di-hydrogenated products.[2] A year later, the group of Stephan demonstrated the Frustrated Lewis Pairs (FLP) concept whereby sterically-demanding Lewis bases and acids (in this case, a phosphine and a borane) do not form adducts, but can react cooperatively with small molecules like H_2.[3] This was also the first report of the reversible addition of H_2 to a main group species. Soon after, Bertrand and coworkers showed that stable acyclic carbenes could not only split the H-H bond in dihydrogen, but also insert into an N-H bond in ammonia NH_3; this form of oxidative addition is not readily accomplished with transition metal centers.[4] (Scheme 1.1). These discoveries promptly led other chemists to now routinely check whether their new inorganic compounds could activate H_2 or related small molecules.

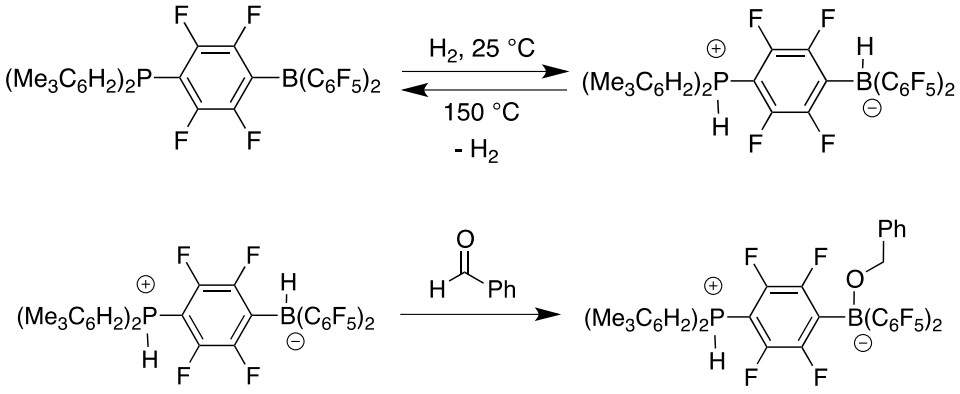


Scheme 1.1. First examples of a low-valent main group species: (top) reacting with H_2 under ambient conditions.[2] (middle) reversible H_2 addition.[3] (bottom) reaction of a carbene with H_2 and NH_3.[4]

A recurring theme in main group element complexes that can perform small molecule activation is the presence of unsaturation; in other words, these species have available coordination sites and frontier orbitals with a relatively small energy gap, such that they are readily available to accept or donate electron density from small molecules.[1a] An approach to preparing stable unsaturated compounds involves developing new ligands that are both good donors and sterically demanding, since strong bonds to the featured element in addition to large flanking substituents will prevent the compound from reacting with itself. This thesis will focus on applying the concepts of Frustrated Lewis Pairs and heavier carbene analogues to uncover main group element reactivity towards small molecules, as well as some concentration on new ligand design.

1.3 Frustrated Lewis Pairs (FLPs)

Frustrated Lewis Pairs (FLPs) are compounds or mixtures containing sterically congested Lewis basic and acidic sites that do not form classical adducts; thus, their unquenched Lewis basicity and acidity can be employed to carry out unusual reactions.[5] In the presence of dihydrogen, the intramolecular bulky phosphine/borane pair $Mes_2P(C_6F_4)B(C_6F_5)_2$ (Mes = 2,4,6-$Me_3C_6H_2$) was effective in the heterolytic cleavage of H_2, resulting in the zwitterionic salt containing a protic phosphonium moiety in addition to a borohydride fragment (Scheme 1.2).[3] Upon heating to 150 °C, Stephan and coworkers observed the elimination of H_2 and the regeneration of the initial intramolecular phosphine/borane FLP. To demonstrate an application for the hydrogen addition product, the zwitterion salt $Mes_2P(H)(C_6F_4)B(H)(C_6F_5)_2$ was treated with benzaldehyde to yield a B-H carbonyl insertion product.[6]



Scheme 1.2. Heterolytic cleavage of H_2 by $Mes_2P(C_6F_4)B(C_6F_5)_2$ and subsequent reaction with benzaldehyde.

Shortly after, $B(C_6F_5)_3$ and P^tBu_3[7] were shown to not only evade classical Lewis acid/base adduct formation, but also split dihydrogen

heterolytically; thus, demonstrating that FLP behaviour is not exclusive to the arylene-spaced phosphine-borane $Mes_2P(C_6F_4)B(C_6F_5)_2$. These discoveries paved the way for the investigation of different inter- and intramolecular combinations of bulky Lewis bases and acids to see if heterolytic H_2 activation was a general process. Active FLPs that have been reported include carbon/boron, nitrogen/boron and even phosphine/Group 4 transition metal complexes (Chart 1.1). [7-10]

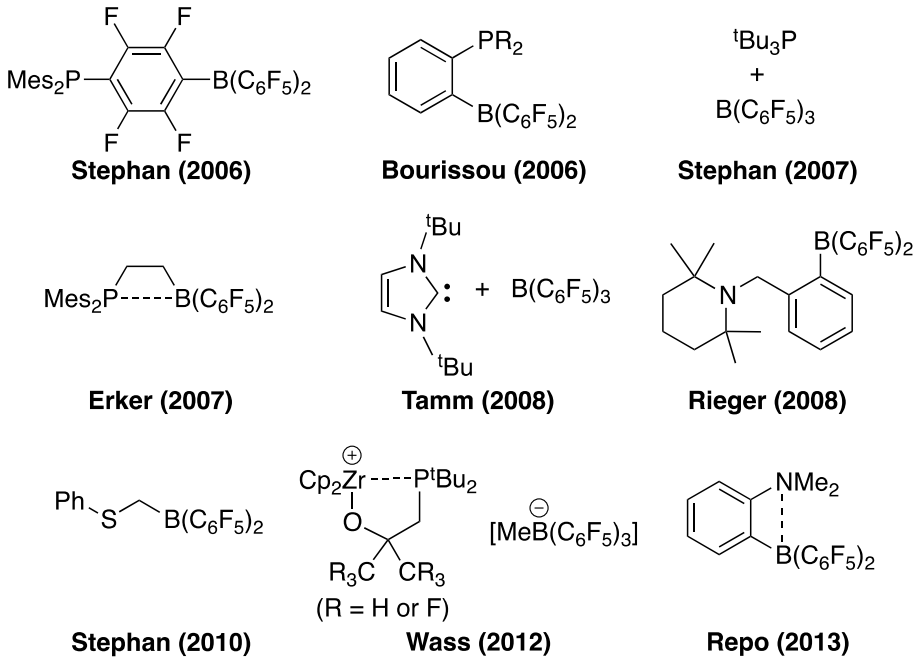
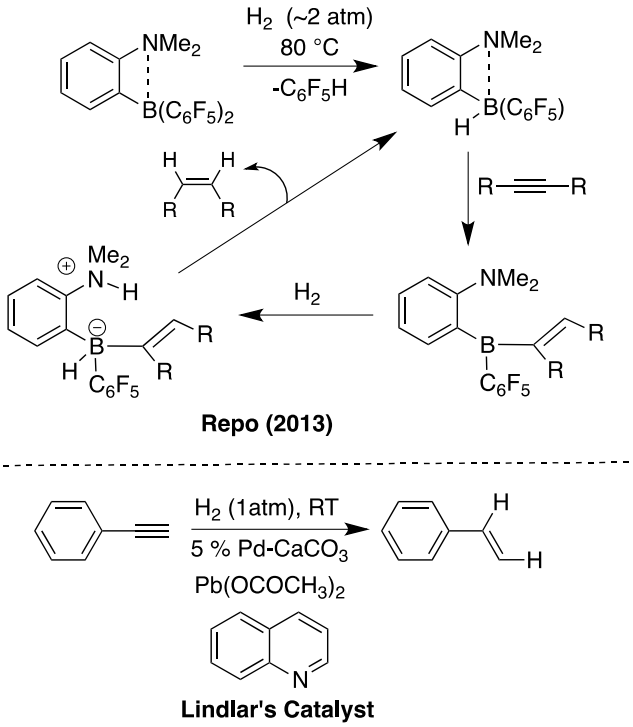


Chart 1.1. Select examples of Frustrated Lewis Pairs.

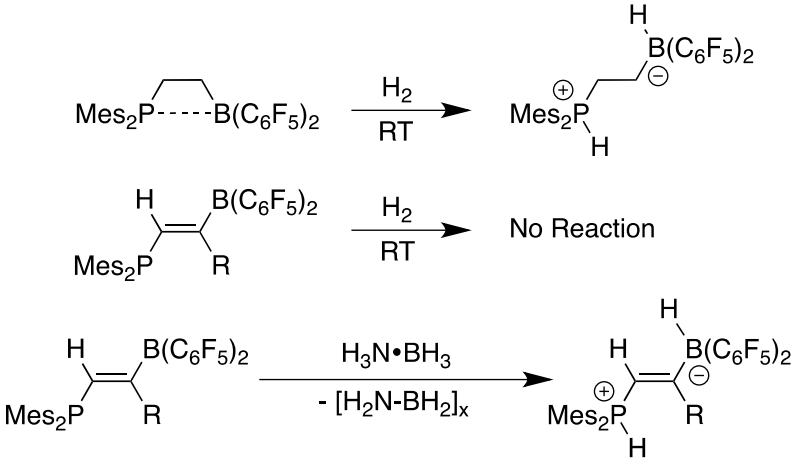
The potential for FLPs to behave as hydrogenation catalysts for unsaturated substrates was then investigated. The phosphonium borohydride salts $R_2P(H)(C_6F_4)B(H)(C_6F_5)_2$ (R = Mes or ^{t}Bu) were combined stoichiometrically with activated imines to afford the amine adducts $(R_2P)(C_6F_4)B(C_6F_5)_2$-$(NHR'CH_2R'')$ (R = Mes or ^{t}Bu; R′= ^{t}Bu; R′′ = Ph)

proving that dual proton/hydride transfer onto activated unsaturated substrates could occur.[6] Substoichiometric amounts of the hydrogenated salts $R_2P(H)(C_6F_4)B(H)(C_6F_5)_2$ (R = Mes or ^tBu) were then combined with imine substrates in 1-5 atm of H_2 at elevated temperatures (80 – 140 °C) to demonstrate the metal-free catalytic reduction of imines to amines.[6] The substrate scope for FLP-catalyzed hydrogenation was then extended to enamines,[11] silyl enol ethers,[12] alkenes,[13] and alkynes.[9e] Remarkably, Repo and coworkers have discovered that an amine-tethered borane FLP can catalytically and selectively hydrogenate internal alkynes to give cis-alkenes, making it a suitable substitute for Lindlar's alkyne reduction catalyst, which requires the use of a toxic lead reagent.



Scheme 1.3. Alkyne hydrogenation that is selective for *cis*-alkenes by (top) Frustrated Lewis Pair (bottom) Lindlar's Catalyst.

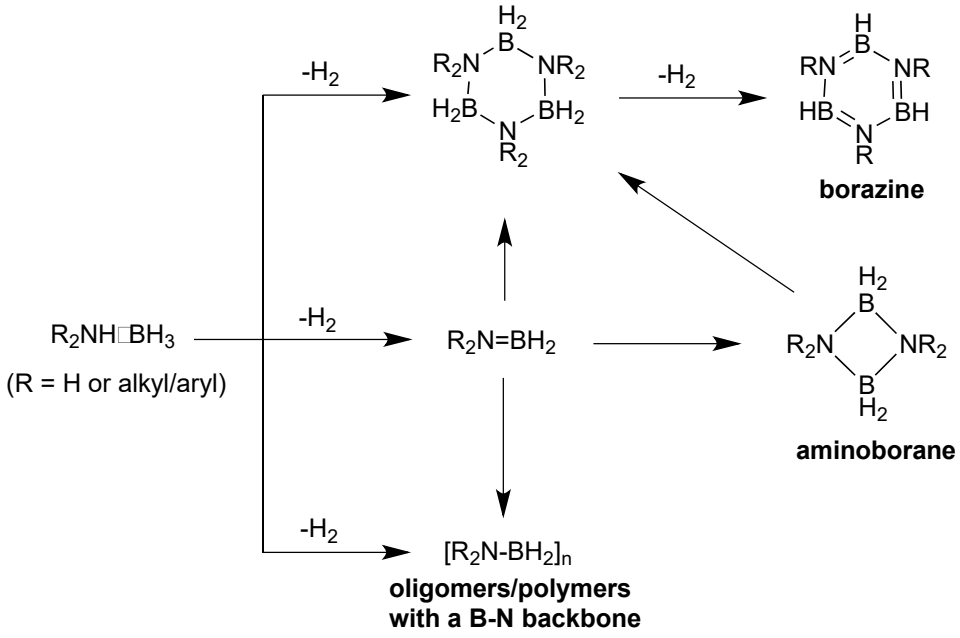
One of the most active FLP systems for catalytic metal-free hydrogenation of activated organic substrates was reported by Erker and coworkers.[9b, 11] $Mes_2PCH_2CH_2B(C_6F_5)_2$ is a intramolecular P/B system, where the phosphine and borane are tethered by a flexible ethylene linker. Despite the formation of a Lewis base-acid interaction, the heterolytic cleavage of hydrogen was rapid; only 15 minutes at room temperature for the full conversion of $Mes_2PCH_2CH_2B(C_6F_5)_2$ to the phosphonium borohydride salt $Mes_2P(H)CH_2CH_2B(H)(C_6F_5)_2$. However, the analogous alkene-linked P/B systems, $Mes_2PCH{=}CRB(C_6F_5)_2$ (R = Me or Ph), were inert to H_2. It was briefly described in two reviews[5b, 5c] that $Mes_2PCH{=}CRB(C_6F_5)_2$ (R = Me or Ph) could also accept the equivalent of H_2 from ammonia borane, $H_3N{\bullet}BH_3$, via transfer hydrogenation.



Scheme 1.4. Erker group's ethylene-linked P/B FLP reacts with H_2, but their alkene-linked P/B system is inert to H_2; however, the alkene-linked FLP reacted with amine-boranes.

1.4 Advancements in the Dehydrocoupling of Amine-boranes

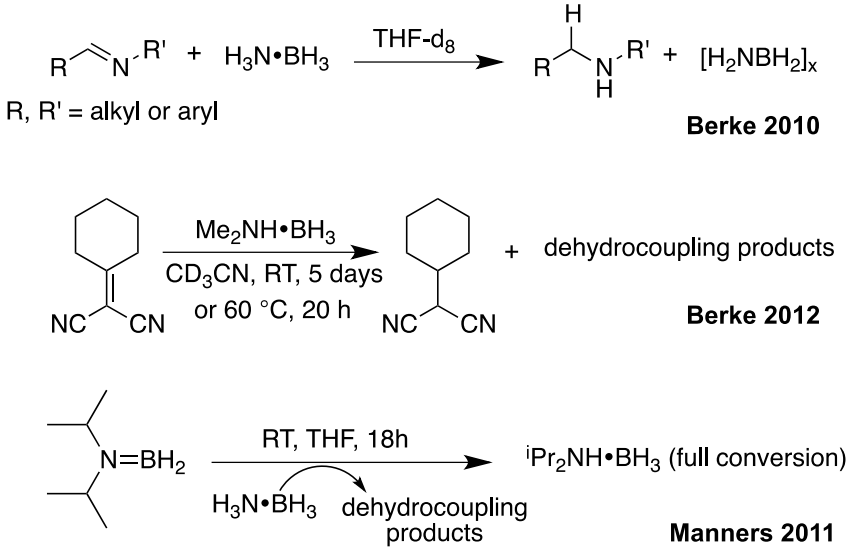
Amine-borane adducts have been heavily investigated for their potential as safer-to-handle chemical sources of dihydrogen and as prospective precursors to inorganic polymers and boron nitride ceramics.[14] The dehydrogenation or dehydrocoupling of amine-boranes is the process of releasing H_2 and subsequent coupling of two or more aminoborane species, which can oligomerize (to give products in Scheme 1.5) or react with more amine-boranes. Products from dehydrogenation include aminoboranes $[R_2NBH_2]_x$, borazines $[RNBH]_3$, oligomers and polymers with a B-N backbone (Scheme 1.5). Dehydrocoupling is an attractive synthetic practice as it allows new bonds to be formed in an atom-economical way with only H_2 as a byproduct. Although amine-boranes will decompose to oligomeric or polymeric species at high temperatures (over 100 °C), several transition metal catalysts have been discovered to facilitate this process under milder conditions. [15-17] Main group element-based catalysts suitable for the dehydrogenation of amine-boranes have been slower to develop.



Scheme 1.5. Possible reaction pathways for amine-borane dehydrogenation.

In 2010, the bulky $P^tBu_3/B(C_6F_5)_3$ FLP system demonstrated stoichiometric reactivity with $Me_2NH•BH_3$ and $H_3N•BH_3$, affording dehydrocoupled products, such as $[R_2NBH_2]_x$ (R = Me or H), and the phosphonium borohydride salt $[HP^tBu_3][HB(C_6F_5)_3]$.[18] In the same year, Berke and coworkers discovered that an equivalent of H_2 from amine-boranes can be stoichiometrically abstracted by organic species, such as polarized imines, via transfer hydrogenation to give amines as well as dehydrocoupling products $[H_2NBH_2]_x$ (Scheme 1.6).[19] They discovered that imines, in particular the aromatic Schiff base derivatives, were the most effective in dehydrogenating $H_3N•BH_3$ at 60 °C with reaction times varying from 0.5 h to several days. Amine-boranes with alkyl substituents on the nitrogen atom had slower reactivity than ones with aromatic substituents. The mechanism was

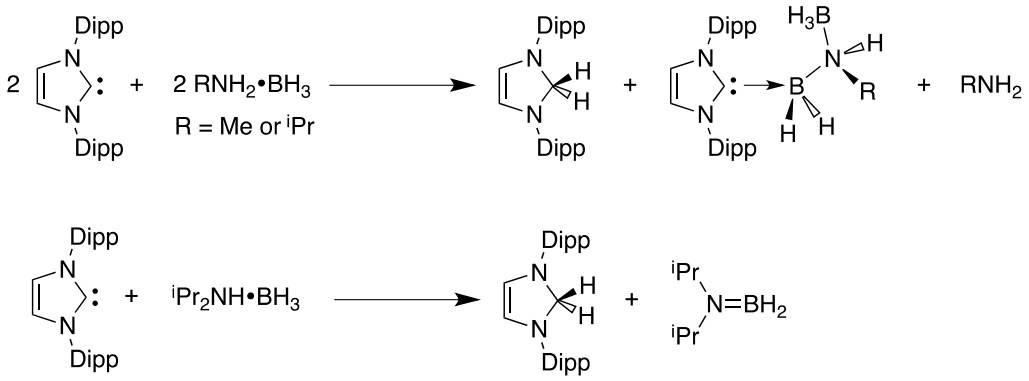
computed to occur in a concerted reaction pathway with a 6-membered transition state containing B-H···C and N-H···N bridging interactions.



Scheme 1.6. Select examples of stoichiometric transfer dehydrogenation involving amine-boranes.

Shortly after, Berke and coworkers discovered that polarized olefins were also appropriate unsaturated substrates to accept hydrogen from various amine-borane adducts.[20] In general, olefins with geminal electron-withdrawing groups and H, alkyl or aromatic substituents on the other side can undergo transfer hydrogenation by amine-boranes at room temperature or upon heating to 60 °C (Scheme 1.6). Mechanistic studies showed that unlike the concerted pathway for H^+/H^- addition postulated for polarized imines, these activated alkenes underwent transfer hydrogenation in a stepwise process: first came a rapid hydroboration step where the hydride from the borane is transferred to the olefin, followed by the transfer of the protic hydrogen on nitrogen.[20]

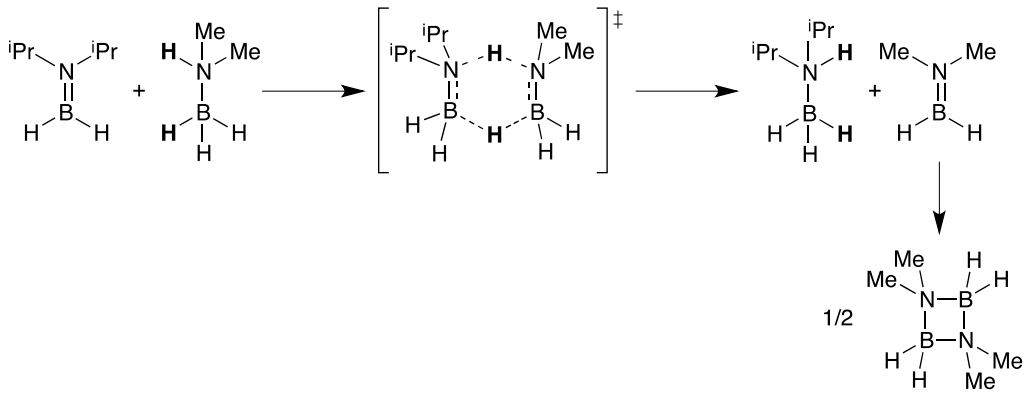
The Rivard Group has reported that the *N*-heterocyclic carbene, IPr (IPr = [(HCNDipp)$_2$C:]), could act as a stoichiometric amine-borane dehydrogenation agent.[21] In the case of secondary amine-boranes, dehydrocoupling products as well as the dihydroaminal IPrH$_2$ were obtained; whereas, when primary amine-boranes were used, carbene adducts in the form IPr•BH$_2$-NH(R)BH$_3$ (R = Me or ^{i}Pr) adducts were isolated (Scheme 1.7).



Scheme 1.7. Using an NHC as a stoichiometric amine-borane dehydrogenation agent.

Another form of metal-free stoichiometric hydrogen transfer was discovered by Manners and coworkers where aminoborane ^{i}Pr$_2$N=BH$_2$ was found to accept H^+/H^- from different amine-boranes at room temperature on the timescales of 18 h or more (Scheme 1.8).[22] Mechanistic studies revealed that this type of amine-borane dehydrogenation was closer to that of activated imines[19] than the polarized olefins[20] reported by Burke and coworkers, due to similar atom electronegativity in the heteroatomic double bonds. Amine-boranes transferred hydrogen to ^{i}Pr$_2$N=BH$_2$ in a bimolecular concerted process involving a six-membered transition state (Scheme 1.8).[23] These findings were important because they suggested that B-N compounds could instigate the

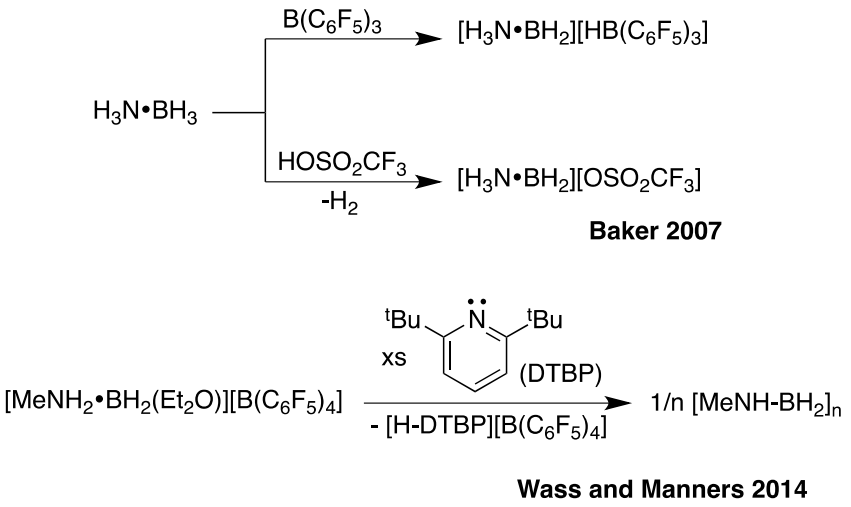
dehydrocoupling of amine-boranes and that their potential applications in metal-free catalysis or in the regeneration of amine-borane hydrogen storage materials should be further explored.



Scheme 1.8. Proposed mechanism for the hydrogen transfer of $Me_2NH{\bullet}BH_3$ to $^{i}Pr_2N{=}BH_2$.

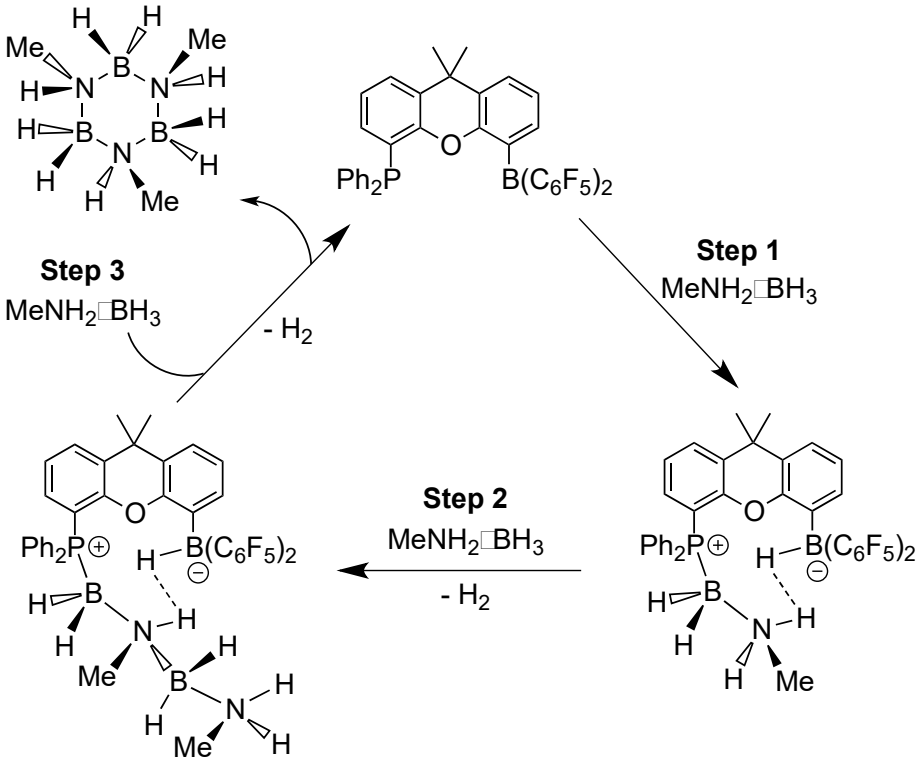
In addition to the stoichiometric dehydrogenations mentioned above, main group species have emerged with abilities to dehydrogenate amine-boranes catalytically. In 2007, Baker and coworkers demonstrated the sub-stoichiometric use of the Lewis acid, $B(C_6F_5)_3$, and the Brønsted acid, $HOSO_2CF_3$, to initiate the dehydrocoupling of $H_3N{\bullet}BH_3$ at 60 °C, with the proposed formation of amine-boronium cations as intermediates (Scheme 1.9).[24] Later, Wass, Manners and coworkers showed that the deprotonation of amine-boronium cations can lead to dehydrocoupling products.[25] Alternatively, the Lewis base 1,8-$(Me_2N)_2C_{10}H_6$ (proton sponge) was reported to promote dehydrocoupling of amine-boranes.[26] Besides boron-based systems, other suitable group 13 compounds, including various Al(III) and Ga(III) amide precatalysts developed by Wright and coworkers, have been

shown to catalytically dehydrocouple amine-boranes.[27] Specifically, the isolable dimeric Al(III) hydride species $[H_2Al(\mu\text{-}N^iPr_2)]_2$ exhibited a modest turnover frequency (TOF) of 2.5 h^{-1} in the presence of $^iPr_2NH{\bullet}BH_3$.[27b] Meanwhile, the related catalytically active Ga(III) hydride species, generated *in situ* from the precatalyst $Ga[N(SiMe_3)_2]_3$ and amine-boranes, was found to be unstable over time; this resulted in catalyst deactivation and the formation of Ga metal.



Scheme 1.9. Preparation of amine-boronium cation intermediates and the formation of polyaminoboranes in the presence of excess base.

Very recently Aldridge and coworkers demonstrated the catalytic dehydrogenation (TOF *ca*. 4 h^{-1}) of amine-boranes promoted by a dimethylxanthene-derived Frustrated Lewis Pair (Scheme 1.10). In addition, they were able to isolate intermediates from the stepwise stoichiometric reactions with $MeNH_2{\bullet}BH_3$ leading up to the formation of cyclic aminoborane chains.[28]



Scheme 1.10. Frustrated Lewis Pair system by Aldridge and coworkers and the stepwise addition product of $MeNH_2 \bullet BH_3$ was isolated and characterized.

Notable s-block species capable of catalytically dehydrocoupling amine-boranes include magnesium and calcium complexes involving alkyl, amide or sterically demanding β-diketiminate ligands. Harder and coworkers have shown that (Dipp-nacnac)$MgN(SiMe_3)_2$ (Dipp-nacnac = $CH\{(CMe)(2,6\text{-}^{i}Pr_2C_6H_3N)\}_2$) is capable of catalytically converting $DippNH_2 \bullet BH_3$ into $HB(NHDipp)_2$.[29] Building on these results, the Hill group demonstrated that $Mg[CH(SiMe_3)_2]_2(THF)_2$, (Dipp-nacnac)$Mg(^{n}Bu)$, $Ca[CH(SiMe_3)_2]_2(THF)_2$, and (Dipp-nacnac)$Ca[N(SiMe_3)_2]$ were effective in dehydrogenating $Me_2NH \bullet BH_3$ with heating (60 °C) and longer reaction times (48 – 72 h).[30] It was reported that the calcium complexes were less reactive towards

dehydrocoupling $Me_2NH•BH_3$ than the magnesium-based systems, and this was rationalized by the role of cation size and charge density on the efficacy of insertion into polarized M-N bonds (M = Mg, Ca).[31]

Although main group systems for facilitating the catalytic dehydrocoupling of amine-boranes has been slower to develop compared to the transition metals, there exists several examples that highlight the plausible use of s- and p-block complexes for these applications. Nevertheless, there remains room to discover more efficient ways to access polyaminoboranes and boron nitride ceramics via main group chemistry.

1.5 Carbenes and their Heavier Group 14 Analogues

1.5.1 Carbenes and a Brief History

A year after the discovery of Frustrated Lewis Pairs by Stephan and coworkers, the Bertrand group reported the activation of H_2 and NH_3 by an alkyl(amino)carbene (Scheme 1.1).[4] In general, a carbene is a divalent species (R_2C:) with six electrons in its valence shell which can adopt either a singlet or a triplet configuration. Today, the use of carbenes is ubiquitous in the chemical literature;[32] however, their prominence has only spread in the past 25 years due to synthetic advances. Although their existence has been suspected by chemists for a long time,[33] the first metal-carbene complex was only isolated and characterized by Fischer in 1964.[34] The metal-bound singlet carbene within the isolable complex $(OC)_5W=C(OMe)Ph$ featured a π-donating heteroatom substituent on the carbene carbon. From a molecular orbital

perspective, the singlet carbene lone pair donates into an empty d-orbital on the W center while electron density from an occupied metal orbital back-donates into the vacant p-orbital of the carbene (Figure 1.1).

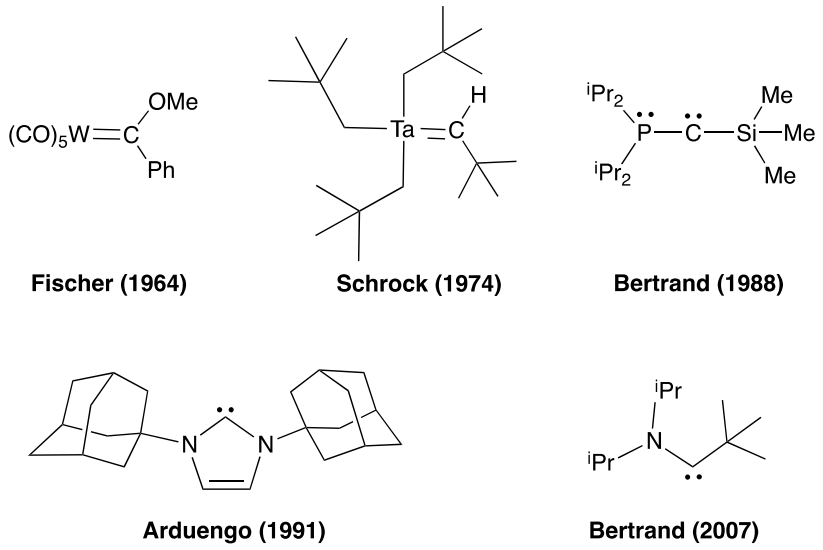


Chart 1.2. Selected examples of isolated carbenes and carbene complexes.

In the mid 1970's, Schrock carbene or alkylidene complexes were discovered. These species contain formally triplet carbenes as ligands (Figure 1.1) with a partial negative charge found on the carbene carbon atom due to low electronegativity of the metals (Mo, W or Ta).[35] At this time, the obstacle to isolating a free carbene without coordination to a metal center was the undesired dimerization of carbenes (R_2C:) to yield alkenes. The solution to this problem was to select ligands with the right balance of electronic effects and steric protection. The isolation of the first free, stable carbene [($^iPr_2N)_2PC(SiMe_3)$] was achieved by the Bertrand group in 1988.[36] Unfortunately, the synthetic approach used was difficult and this carbene was a poor ligand, thus limiting its widespread use. The seminal work by Arudengo

and coworkers in 1991 introduced the concept of *N*-heterocyclic carbenes (NHCs) to the chemical community.[37] The initial Arduengo carbene featured a five membered heterocycle where the carbene carbon was flanked by two nitrogen atoms each containing a bulky adamantyl group for steric protection. Another preventative action against dimerization was the adjacent placement of the nitrogen atoms, whose lone pairs that could donate into the singlet carbene carbon's vacant p-orbital. As a result, NHCs are good σ-donors and relatively poor π-acceptors. The formation of strong NHC-metal bonds in combination with the ease of synthesis and tunability of Arduengo carbenes has facilitated their general use as ligands in metal-mediated cross-coupling reactions.[38, 39]

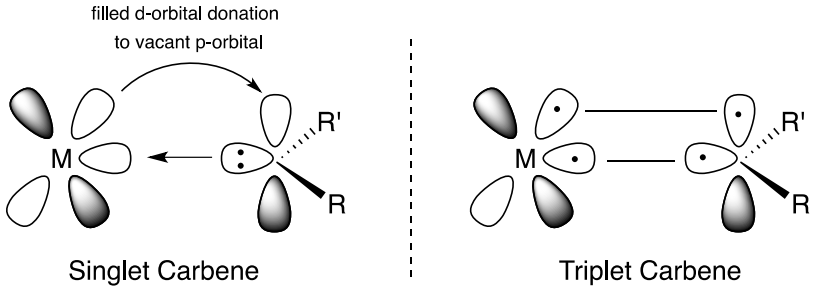


Figure 1.1. A comparison of the molecular orbitals involved in a singlet carbene and a triplet carbene complex.

In 2007, Bertrand and coworkers reported a new class of carbenes.[4] These alkyl(amino)carbenes feature only one nitrogen atom adjacent to the carbene center, with the other site occupied by a carbon-based substituent. Consequently, the vacant p-orbital at the singlet carbene center in an alkyl(amino)carbene is now more available for accepting incoming π-electron density and the carbene lone pair is slightly more donating due to the existence of the neighboring electron-donating alkyl moiety. Both the cyclic and the

acyclic forms of alkyl(amino)carbenes are capable of activating dihydrogen and ammonia. While diaminocarbenes, such as NHCs, tend to be inert to these small molecules, the more nucleophilic and more electrophilic alkyl(amino)carbenes apparently have the right balance of Lewis acidity and basicity to activate H_2 and NH_3 (Scheme 1.1). Unlike the heterolytic cleavage of H_2 by FLP systems, the reactivity of alkyl(amino)carbenes with dihydrogen was described as a formal oxidative addition process, reminiscent of the cleavage of H_2 by transition metal complexes.[40]

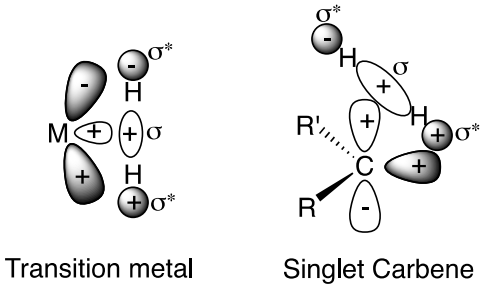


Figure 1.2. Comparison of the formal oxidative addition step between transition metal complexes and singlet carbenes.

1.5 Heavy Group 14 Carbene Analogues

With the sustained interest in developing new stable carbenes, heavier Group 14 analogues (silylene R_2Si:, germylene R_2Ge:, stannylene R_2Sn:, and plumbylene R_2Pb:) have also been examined more actively. Collectively, these Group 14 molecules are known as metallylenes or tetrelylenes. Carbenes can be found in both the singlet (in Fischer complexes, NHCs, alkyl(amino)carbenes) and triplet (in Schrock carbene complexes) ground states, but as you go down the group, metallylenes are almost exclusively in the singlet ground state.[41] A

singlet ground state consists of a lone pair with high s-character (which increases down Group 14) and a vacant p-orbital, which is the major cause of instability for these species; consequently, novel reactivity can be observed.[42,43] By seeking out heavier Group 14 carbene analogues and studying them, it is believed that their structural relation carbenes could be important in uncovering new main group catalysts featuring p-block elements that are typically more abundant and less expensive than many transition metals.[41b]

The heavier Group 14 element carbene analogues have an oxidation state of E(+2) and as you go down the group (as the principal quantum number *n* increases), the stability of these heavier analogues increases; in fact, dichloroplumbylene ($PbCl_2$) and dichlorostannylene ($SnCl_2$) are stable species that are commercially available. The dichlorogermylene is stable as an adduct and is sold in the form of a dioxane complex $GeCl_2$•dioxane. On the other hand, dihalosilylenes are notorious for being highly reactive.[41a] Ligands must be judiciously selected in order to stabilize a dihalosilicon(II) source.[44-46]

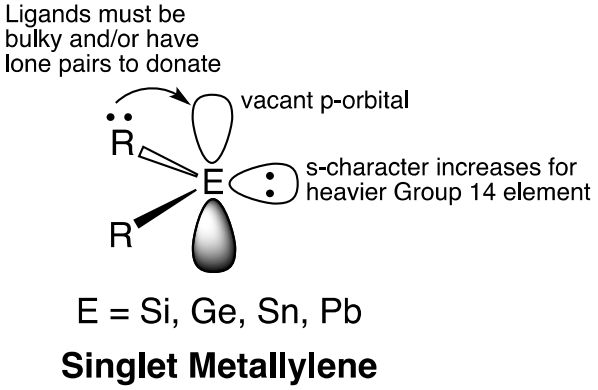


Figure 1.3. Stabilization of metallylenes.

Stabilization of the vacant p-orbital site via bulky protecting groups or the use of adjacent heteroatoms have been shown to be successful methods to attain monomeric metallylenes. For this dissertation, there will be a focus on silylenes and germylenes; the work in this thesis was also motivated by previous work done by the Rivard Group involving the isolation of donor-acceptor stabilized EH_2 species (E = Si, Ge and/or Sn). [47, 48]

1.5.1 Silylenes

Silylenes are more reactive than germylenes, thus for many decades, the silicon analogues of carbenes were only reported as transient species in the gas phase, in solution or in frozen matrixes.[49-51] The first isolable monomeric divalent silicon(II) species Cp^*_2Si: ($Cp^* = C_5Me_5$) was reported by Jutzi and coworkers, which cleverly relied upon pentamethylcyclopentadienyl ligands for both their steric bulk and ability to coordinate through multiple atoms in order to stabilize the silylene (Chart 1.3).[52] In 1994, West and coworkers were able to synthesize the *N*-heterocyclic silylene [$(HCN^tBu)_2Si$:];[53] this work led to the discovery for several more cyclic silylene derivatives afterwards.[54] A notable strategy for silylene stabilization involved Lewis-base donation into the reactive, vacant p-orbital on silicon. [55, 56] The Rivard group was able to trap H_2Si: through donor-acceptor stabilization, wherein an NHC is donating into the Si(II) vacant p-orbital and providing steric protection, while the lone pair on Si(II) is coordinated to a Lewis acid, BH_3.[48b]

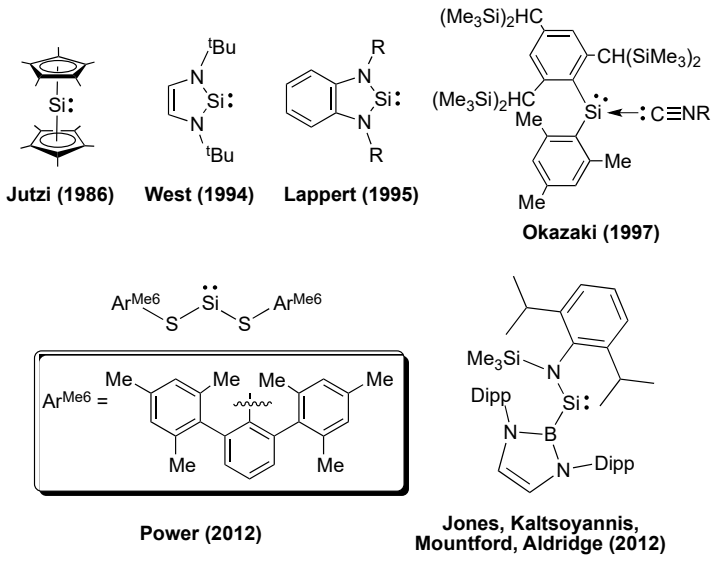
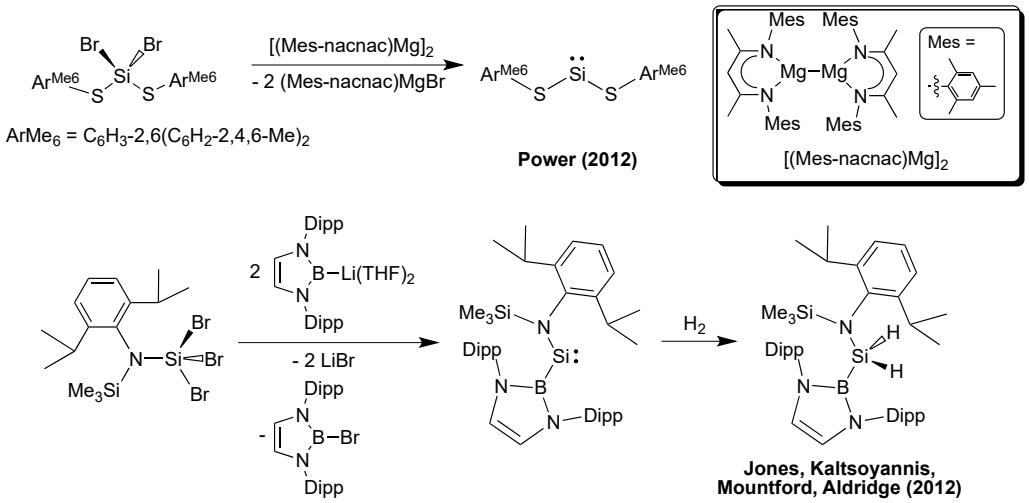


Chart 1.3. Selected examples of silylenes stable at room temperature.

Until 2012, a free stable two-coordinate acyclic silylene had not been discovered. Two different teams independently developed routes to isolate such species and their results were published simultaneously in the *Journal of American Chemical Society*. It was a rare opportunity for a side-by-side comparison of the different approaches and results obtained by leading researchers in the field. The Power group utilized very bulky and electron-releasing terphenylthiolate ligands that offered the required steric protection as well as heteroatom lone-pair donation to the vacant p-orbital of the silylene for π-stabilization.[42c] They first prepared the dibromodithiolated precursor, $Br_2Si(SAr^{Me6})_2$ (Ar^{Me6} = C_6H_3-2,6(C_6H_2-2,4,6-Me)$_2$) and then reduced this species with Jones' Mg(I) complex $[(Mes\text{-}nacnac)Mg]_2$ to obtain the silylene $(Ar^{Me6})_2Si$:. Meanwhile, the collaboration involving the groups of Jones, Aldridge, Kaltsoyannis and Mountford sandwiched a Si(II) center between a bulky π-donating amido ligand and a nucleophilic boryl ligand to prepare their

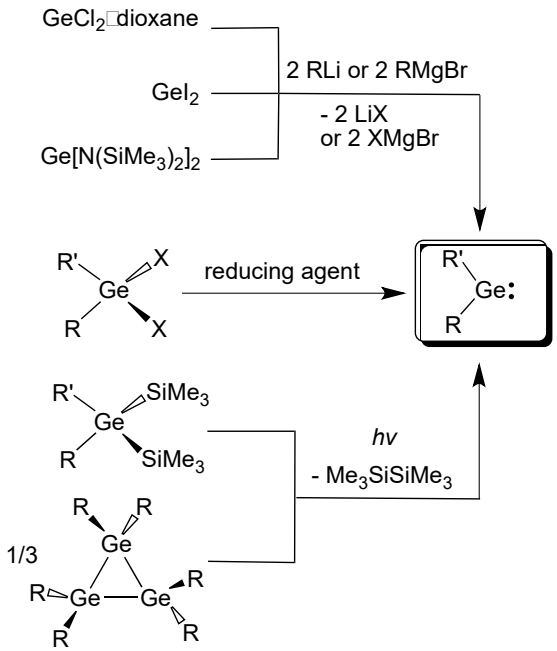
room-temperature isolable silylene (Dipp)N(SiMe$_3$)Si[B(HCNDipp)$_2$] (Scheme 1.11).[43a] Since there were no convenient sources of divalent Si(II), this group also went through a Si(IV) precursor and used Yamashita's boryl salt Li[(HCNDipp)$_2$B] as both a ligand source and a reductant. Remarkably, this amido(boryl)silylene was shown through computations to have a small singlet-triplet gap of 103.9 kJ/mol, which suggested that it was suitable for small molecule activation under mild conditions. Indeed, this amido(boryl)silylene was capable of reacting with dihydrogen and also intramolecular alkyl C-H bonds. In contrast, the thiolate-supported silylene Si(Ar^{Me6})$_2$ was reported to have a much higher singlet-triplet gap of 4.3 eV (*ca.* 415 kJ/mol) and was consequently inert to hydrogen gas. It was postulated that its stability, and thus unreactivity towards H_2, were due to a combination of a high electronegativity of adjacent sulfur atoms in the thiolate ligands, S-Si π-interactions and geometric constraints (narrow S-Si-S angle of 94.41(2)°).[57]



Scheme 1.11. Comparison of two synthetic routes to access monomeric acyclic silylenes.

1.5.2 Germylenes

Two-coordinate monomeric germylenes have been obtained with relative ease compared to silylenes due to the commercial availability or the straightforward preparations of divalent Ge(II) sources. In addition, the lone pair in germylenes (R_2Ge:) have more s-character than silylenes, improving their stability. $GeCl_2$•dioxane, GeI_2 and $Ge[N(SiMe_3)_2]_2$ can be reacted with RLi or RMgBr (R = bulky substituent) to generate stable monomeric diorganogermylenes (R_2Ge:) with simultaneous elimination of a salt. Other methods of preparing room-temperature stable, acyclic, monomeric germylenes include photolysis of cyclotrigermanes or bis(trimethylsilyl)germanes, and the reduction of the dihalodisubstituted Ge(IV) precursors, R_2GeCl_2 (Scheme 1.12).[43b, 58-60]



Scheme 1.12. General synthetic routes to access monomeric, two-coordinate germylenes.

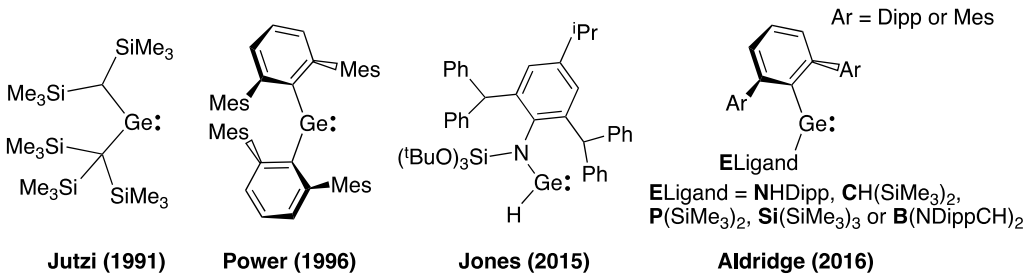
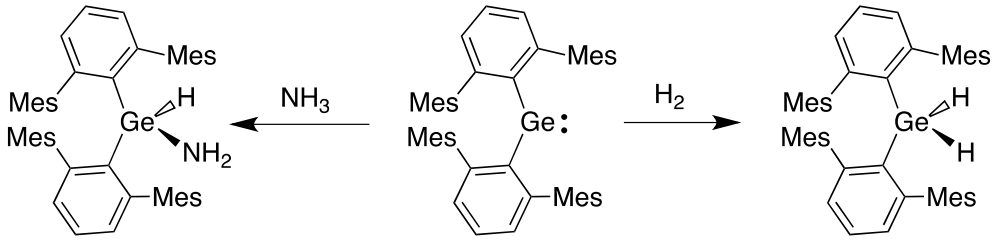


Chart 1.4. Notable monomeric two-coordinate acyclic germylenes.

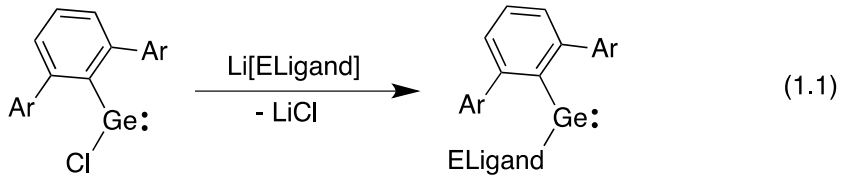
Exploration into the reactivity of monomeric germylenes, particularly in the context of E-H bond activation, was initially led by Power and coworkers (Scheme 1.13). In 2009, they reported the reaction of terphenyl-protected germanium(II) centers with H_2 and NH_3 to give Ge(IV) products.[42b] Since then, a wide variety of small molecules in the form of HR (R = CN, N_3, F, SO_3CF_3, PH_2, NHNRR′) have been shown to react with germylenes in a formal oxidative addition process. [42a,b, 61]



Scheme 1.13. Terphenyl-protected germylene, :Ge(Ar^{Me6})$_2$, and its reaction with H_2 and NH_3.

In 2016, Aldridge and coworkers created a small library of monomeric germylenes (Equation 1.1) and executed a systematic study of how E-H bond activation is affected by the steric bulk and electronic properties of the ligand. [43b] They discovered that the HOMO-LUMO gaps for the germylene

complexes, and thus their reactivities, were correlated to the angle between the two ligands on the Ge(II) center, <R-Ge-R′, as well as the π-donating abilities of the atoms directly coordinated to germanium. Wider angles resulted in smaller HOMO-LUMO gaps and higher reactivity. The presence of π-donors led to a larger HOMO-LUMO energy difference; on the contrary, a smaller HOMO-LUMO gap was observed when more electropositive substituents were directly attached to germanium. Despite the E-H activation observed by the germylenes with electropositive σ-donors, none of the resulting Ge(IV) products suggested the possibility of reductive elimination; the oxidative addition products appeared to be thermodynamically stable.



(1.1)

Ar = Mes or Dipp

ELigand = NHDipp, $CH(SiMe_3)_2$, $P(SiMe_3)_2$, $Si(SiMe_3)_3$, $B(DippNCH)_2$

It is clear that the steric and electronic properties of ligands play an important role in determining the reactivity of carbenes and their heavier Group 14 analogues towards the activation of small molecules. In order for silylenes and germylenes to be incorporated into catalytic cycles, there exists an opportunity for the development of new ligands that can facilitate oxidation state changes on the main group element during its formal oxidative addition and reductive elimination steps.

1.6 Ligand Design

The performance of a catalyst is governed by the steric and electronic environments around the metal center. Thus, creating new ligands that give chemists control of the metal coordination sphere is essential. By studying how ligands influence the reactivity of transition metal complexes, metal-mediated catalysis was discovered and the syntheses of new molecules and materials became more accessible.[62] Advances in ligand design have also led to the isolation of reaction intermediates and the elucidation of reaction mechanisms, which have led to a better understanding of existing biological and industrial processes as well as encouraged the discovery of improved synthetic routes.[62]

In general, a ligand behaves like a Lewis base that has electron density to donate to a Lewis acidic metal center. There are two types of ligands: reactive and ancillary. Reactive ligands are species coordinated to the metal center than undergo chemical change, such as redox processes or an irreversible chemical transformation. A few examples include, halide, hydride, alkyl and aryl substituents. Ancillary ligands contribute by influencing the activity occurring at the metal center, but they themselves do not undergo any irreversible chemical transformations; for example, bulky phosphines, *N*-heterocyclic and (alkyl)(amino)carbenes. However, there are reports of ancillary ligands undergoing undesirable reactivity, resulting in complex decomposition or catalysis deactivation.[62] Other ligands, such as CO, can behave as a reactive or auxiliary ligand, depending on the reaction conditions. The development of new auxiliary ligands will be the major focus of this section as it is relevant to this thesis.

Although many exotic ligands have been prepared and shown to be effective in supporting catalysis, only robust donors that have straightforward synthetic routes and high structural tuneability gain widespread use. Variations of bulky phosphine donors, by Buchwald[63] and coworkers, have dominated metal-mediated cross-coupling reactions, followed closely by the use of *N*-heterocyclic carbenes.[39, 64] Buchwald's biaryl phosphines and NHCs are effective due to their steric protection around the metal center and their strong σ-donation to low-oxidation state metal centers; both these features prevent metal deactivation. Buchwald's ligand also works well because of secondary ligand(aryl)···M interactions.

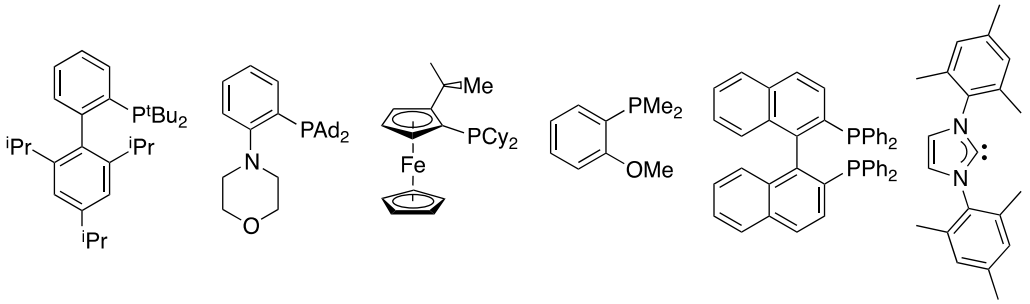


Chart 1.5. Representative bulky ligands used in metal-mediated catalysis.

Ligands in catalysis need to be able to help stabilize a low-oxidation state at a metal center, as well as facilitate transformations, such as oxidative addition, reductive elimination or transmetallation (transfer of ligands from one metal to another), so that they occur smoothly at the metal center. A growing topic of interest involves ligands featuring both hard and soft donor sites within the same framework.[65, 66] Their coordination chemistry and catalytic reactivity

suggest that mixed element donor systems may be suitable for assisting in oxidation state changes around the metal.[67]

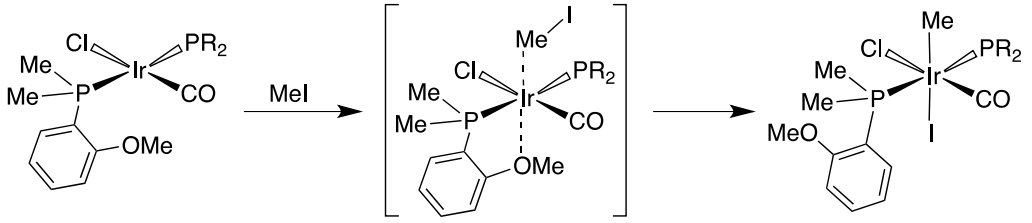


Figure 1.5. Mixed element donor ligands can facilitate oxidation changes occurring at the metal center.[67]

The use of main group elements as active sites for catalysis is a relatively new concept, as this field has been traditionally dominated by the use of transition metal complexes. By studying the ideal ligand traits for transition metal-based catalysts, we can apply these findings to synthesize novel low-coordinate main group species capable of reacting with small molecules. Already, NHCs have been shown to be effective in the stabilization of rare low-valent main group compounds.[48b, 68, 69] Using NHCs as a guide, related analogues featuring an exocyclic olefin donors (*N*-heterocyclic olefins, NHOs)[48a, 68a, 70] or exocyclic imines (*N*-heterocyclic imines, NHIs)[71] are emerging in the literature as ligands for both transition metal complexes and low-valent main group compounds (Chart 1.6). NHOs and NHIs feature the similar structural tuneabilty and initial synthetic routes as the NHCs, but they differ in electron donating ability. The NHOs have considerable electron density at the exocyclic carbon, which allows it to behave as a neutral two-electron donor; whereas, the NHIs can donate both σ and π electron density,

making it very strongly electron releasing and suitable for stabilizing electron deficient metal centers.

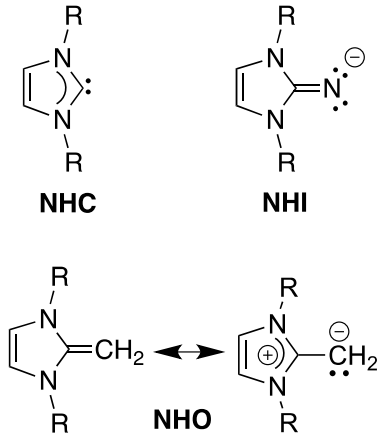


Chart 1.6. *N*-heterocyclic carbene (NHC) and its related *N*-heterocyclic olefin (NHO) and *N*-heterocyclic imine (NHI) ligands.

Despite recent advances in ligand design, there exists room for the development of new ligands that serve to extend the limits of existing catalytic reactivity. With our knowledge of ideal ligand characteristics, our group was motivated to investigate the use of *N*-heterocyclic imines to stabilize rare low-coordinate main group (boron, silcon, and germanium) compounds, in addition to developing new classes of mixed element donor systems for catalysis.

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Chapter 2: Metal-free Dehydrogenation of Amine-boranes by Tunable *N*-Heterocyclic Iminoboranes

2.1 Introduction

In the past decade, there has been growing interest in main group element compounds that can facilitate chemical transformations once reserved for d- or f-block complexes.[1] Specifically, the use of non-metal reagents to activate small molecules, such as H_2 or CO, is a notable achievement.[2] A related area of intense study is the use of Frustrated Lewis Pairs (FLPs) in main group element catalysis.[3] The Stephan group was the first to show reversible H_2 activation under mild conditions with a phosphine/borane combination.[3] Shortly after, Erker and coworkers demonstrated that the tethered phosphineborane FLP, $Mes_2PCH_2B(C_6F_5)_2$, could act as a metal-free catalyst for the hydrogenation of imines or enamines under mild conditions.[4]

Of particular relevance to this Chapter, bulky phosphine-borane FLPs, such as $P^tBu_3/B(C_6F_5)_3$, have been shown to abstract an equivalent of dihydrogen from amine-boranes ($R_2NH{\bullet}BH_3$) to afford dehydrocoupled products $[R_2NBH_2]_x$ and phosphonium borohydride salts (*e.g.* $[HP^tBu_3]HB(C_6F_5)_3$).[5] The metal-free dehydrogenation of amine-boranes has also been reported by Manners and coworkers, where they observed that the monomeric aminoborane $^iPr_2N{=}BH_2$ can behave as a hydrogen acceptor; thus, allowing stoichiometric hydrogen transfer to occur from amine-borane adducts under ambient conditions.[6] Moreover our group has shown that *N*-heterocyclic

carbenes (NHCs) are able to effectively remove H^+/H^- equivalents from amine-boranes.[7] In addition, very promising examples of both Lewis acid ($B(C_6F_5)_3$)[8a] and Lewis base (Proton sponge; 1,8-$(Me_2N)_2C_{10}H_6$)[8b] promoted dehydrocoupling of amine-boranes have been developed by the groups of Baker and Sneddon, respectively.

Amine-boranes (*e.g.* $H_3N{\bullet}BH_3$) have been well-studied as easier to handle chemical sources of hydrogen with gravimetric H_2 storage densities up to 19.6 wt. %.[9, 10] Amine-boranes undergo dehydrocoupling in the bulk state at high temperatures (> 100 °C) or in the presence of a catalyst under milder conditions.[11] Loss of an equivalent of H_2 leads to formally unsaturated aminoboranes that can sometimes undergo polymerization to afford polyaminoboranes $[RNH\text{-}BH_2]_n$, which are isoelectronic analogues of polyolefins.[12] Soluble polyaminoboranes are of interest as precursors for bulk or nanodimensional boron nitride, and even for amorphous boron-rich materials in boron neutron capture therapy.[13] Although there have been many examples of effective metal dehydrocoupling catalysts,[14] main group element-based catalysts are now emerging as potential low-cost alternatives.[15]

Inspired by the Rivard group's use of the *N*-heterocyclic olefin, $IPr{=}CH_2$, (IPr = $[(HCNDipp)_2C]$; Dipp = 2,6-$^iPr_2C_6H_3$) (Chart 2.1) to stabilize main group hydrides,[16] we are now exploring the more nucleophilic imido donor $[IPr{=}N]^-$,[17-22] as a supporting ligand in main group element chemistry. Herein the synthesis and characterization of new *N*-heterocyclic iminoboranes $IPr{=}N\text{-}BR_2$ (R = Cl and/or Ph) is reported, and the ability of these species to abstract an equivalent of H_2 from various amine-boranes under mild conditions

is demonstrated; in one instance metal-free catalytic dehydrocoupling was noted.

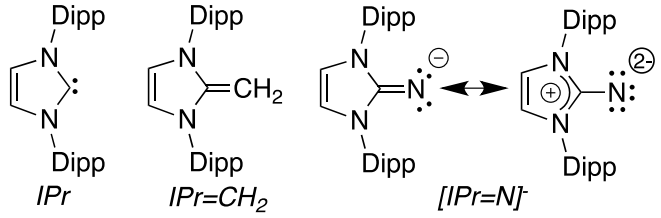
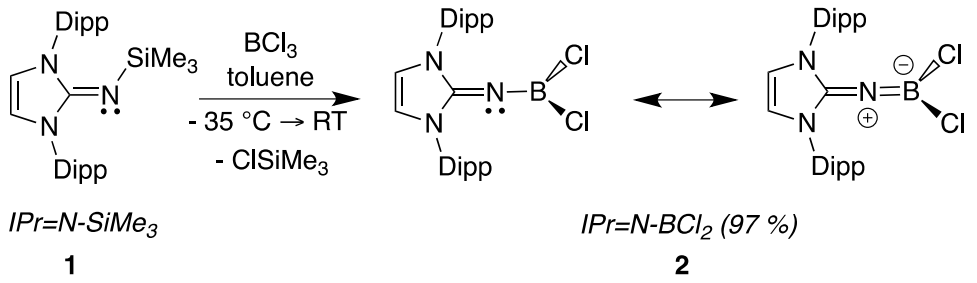


Chart 2.1. Representative *N*-heterocyclic ligands: IPr, IPr=CH_2, $[IPr=N]^-$, with key canonical forms presented for $[IPr=N]^-$.

2.2 Results and Discussion

2.2.1 Synthesis and characterization of *N*-heterocyclic iminoboranes

The synthetic strategy for accessing *N*-heterocyclic imine-coordinated boranes with changeable groups began with the preparation of IPr=N-BCl_2 (**2**). This was achieved by slowly adding a toluene solution of the known silylated imine IPr=$NSiMe_3$ (**1**)[17] to a solution of BCl_3 in heptane/toluene at -35 °C, followed by warming to room temperature (Scheme 2.1). This method afforded **2** as an extremely air- and moisture-sensitive off-white solid with yields as high as 97 %. The ^{11}B NMR resonance of compound **2** lies at 23.0 ppm, which supports the presence of a three-coordinate boron environment.



IPr=N-SiMe3

1

IPr=N-BCl2 (97 %)

2

Scheme 2.1. Synthesis of IPr=N-BCl_2 (**2**) with the isolated yield in parentheses.

The structure of IPr=N-BCl_2 (**2**) was determined by single-crystal X-ray diffraction and the refined structure is presented as Figure 2.1. The B-N bond length in **2** is 1.302(6) Å, which is significantly shorter than the tri-coordinate boron–nitrogen bond of 1.4355±0.0021 Å in borazine,[23] suggesting some π – interaction between a nitrogen lone pair and an adjacent p-orbital on boron in **2**. The geometry of the N-C-B unit in **2** is reminiscent of organic allenes ($R_2C=C=CR_2$) with a crystallographically imposed 180.0° B-N(2)-C(1) angle and a short N(2)-C(1) bond length of 1.273(5) Å, suggesting the presence of multiple bond character. Moreover the C-N and B-N π -manifolds lie in mutually orthogonal arrangements as one sees within allenes, as evidenced by computational studies (*vide infra*). Compound **2** has comparable internal imino N-C and B-N bond lengths as in the iminoborane $Ph_2C=N-BMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$) (1.31±0.02 and 1.40±0.03 Å, respectively).[24]

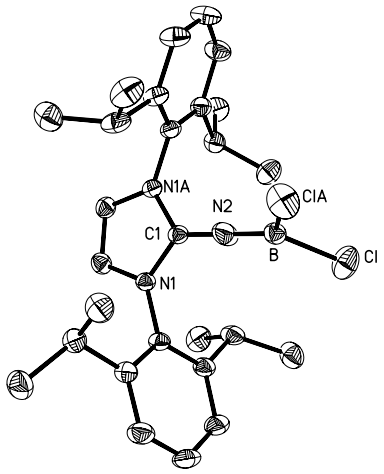


Figure 2.1. Molecular structure of **2** with thermal ellipsoids at a 30 % probability level. A two-fold rotational axis lies through the B-N(2)-C(1) unit in **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): B-Cl 1.791(3), B-N(2) 1.302(6), N(2)-C(1) 1.273(5); B-N(2)-C(1) 180.0 (lies on two-fold axis), Cl-B-Cl(1A) 111.5(2), Cl-B-N(2) 124.26(12).

The HOMO for **2** was computed using Density Functional Theory (DFT) at the B3LYP/6-31+G(d,p) level and shows major N-C and C-C π contributions located on the cyclic imidazole unit (Figure 2.2). The LUMO shows C-C antibonding interactions on the flanking Dipp groups, which is often noted for main group compounds supported by *N*-heterocyclic imino donors.[19] Second order perturbation analysis revealed that there is a π-interaction between the central nitrogen lone pair and the p-orbital on boron. The Wiberg bond order also suggests some B-N multiple bond character (1.23) is present in **2**, while the adjacent C-N double bond within the *N*-heterocyclic imine unit [N(2)-C(1)] has a computed bond order of 1.43. Despite the lack of steric bulk

on the boron atom, IPr=N-BCl_2 (**2**) does not dimerize in the solid state, likely due to the encumbered nature of the $[IPr=N]^-$ ligand.

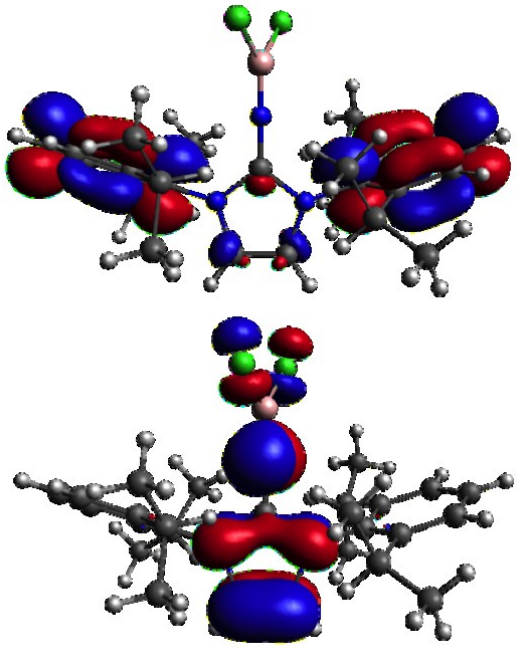
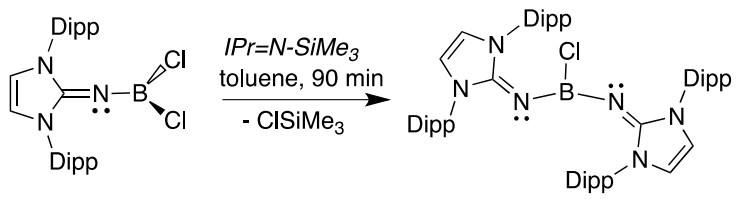


Figure 2.2. Computed HOMO (bottom) and LUMO (top) of IPr=N-BCl_2 (**2**).

Occasionally during the synthesis of IPr=N-BCl_2 (**2**), 5 – 20 mol. % of the disubstituted chloroborane $(IPr=N)_2BCl$ (**3**) may form, but this compound can be easily extracted away with hexanes as IPr=N-BCl_2 has poor solubility in this non-polar solvent. Compound **3** was characterized by multinuclear NMR spectroscopy, elemental analysis as well as single crystal X-ray crystallography (Figure 2.3). Compound **3** can also be synthesized independently by combining one equivalent of IPr=$NSiMe_3$ (**1**) with IPr=N-BCl_2 (**2**) in toluene at room temperature for 90 minutes (Equation 2.1). Perhaps the most salient structural feature of **3** is the presence of non-linear C-N-B angles [133.77(14) and 136.26(14)°] consistent with loss of allenic bonding (in relation to **2**).



IPr=N-BCl$_2$ **2**

(IPr=N)$_2$BCl (82 %) **3**

(2.1)

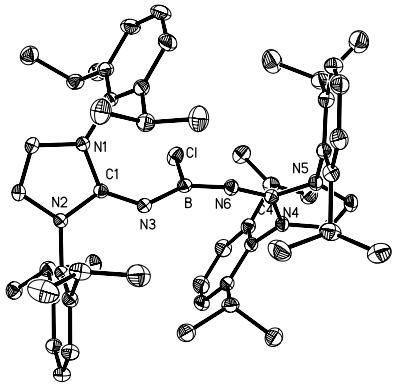
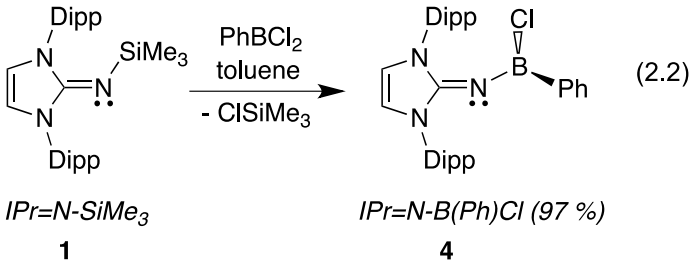


Figure 2.3. Molecular structure of **3** with thermal ellipsoids at a 30 % probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): B-Cl 1.8455(18), B-N 1.399(2), N(3)-C(1) 1.280(2), N(6)-C(4) 1.2825(19); B-N(3)-C(1) 133.77(14), B-N(6)-C(4) 136.26(14), Cl-B-N(3) 116.76(12), Cl-B-N(6) 117.87(12), N(3)-B-N(6) 125.37(15).

Given the potential for IPr=N-BCl$_2$ (**2**) to act as an intramolecular Frustrated Lewis Pair (*vide infra*),[4] we decided to exchange the chlorine atoms attached to boron by phenyl substituents to see how this would influence reactivity. When IPr=N-BCl$_2$ (**2**) was combined with 1 equiv. of PhLi at -35 °C in toluene, the monosubstituted borane IPr=N-B(Ph)Cl (**4**) was obtained; however this product was contaminated with disubstituted IPr=N-BPh$_2$ (**5**) and starting material IPr=N-BCl$_2$ (**2**), which were hard to separate from **4** due to their similar solubilities. IPr=N-B(Ph)Cl (**4**) was later prepared as a pure

material in a 98 % yield by adding pre-cooled (-35 °C) toluene solutions of IPr=N-$SiMe_3$ (**1**) to one equiv. of $PhBCl_2$, followed by stirring at room temperature for 90 minutes (Equation 2.2). Pale yellow crystals of **4** of suitable quality for X-ray crystallography were obtained from fluorobenzene at -35 °C, and the refined structure is shown in Figure 2.4. Although the plane created by the B, Cl, and Ph substituents in **4** lies in a perpendicular fashion relative to the central imidazole ring of the IPr unit (as with the BCl_2 group in **2**), compound **4** does not have allenic type bonding. Instead of observing a linear B-N-C bond angle in **4**, the B-N(2)-C(1) angle is appreciably bent [131.7(2)°] with a B-N bond length of 1.350(3) Å that is elongated in comparison to the respective B-N distance in **2** [1.302(6) Å]. This data suggests that a slightly weaker B-N π interaction is present in **4** (Table 2.1). According to NBO analysis, compound **4** has multiple bonding character between the boron and nitrogen atoms despite the bent B-N-C geometry, as reflected by a Wiberg bond order of 1.24; as with many B-N π bonds, this weak π-interaction is polarized towards the nitrogen (82 %). The computed HOMO of **4** is similar to that of IPr=N-BCl_2 (**2**), and features contributions from the *N*-heterocyclic ring (π-bonding), the chlorine and the central nitrogen atoms (Figure 2.5); the LUMO has C-C antibonding character from the Dipp groups.



(2.2)

IPr=N-SiMe$_3$

1

IPr=N-B(Ph)Cl (97 %)

4

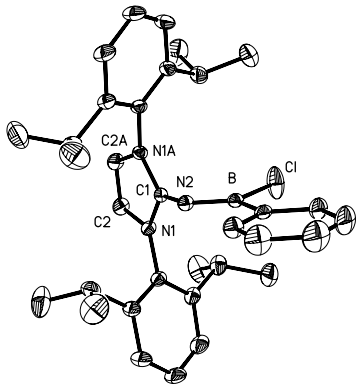


Figure 2.4. Molecular structure of IPr=N-B(Ph)Cl (**4**) with thermal ellipsoids at a 30 % probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): B-Cl 1.830(3), B-N(2) 1.350(3), N(2)-C(1) 1.307(3); B-N(2)-C(1) 131.7(2), Cl-B-N(2) 118.80(18).

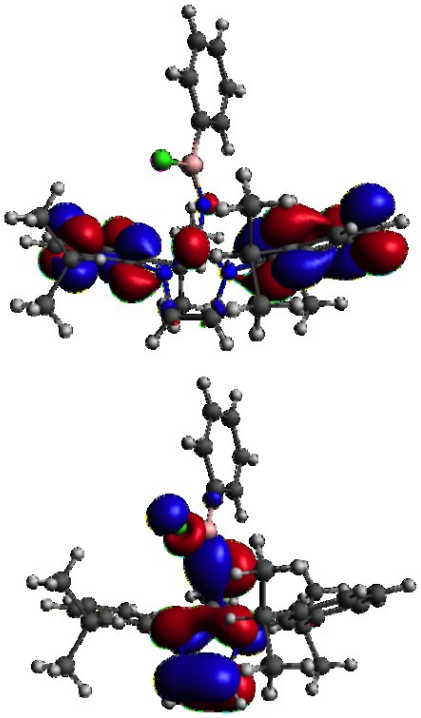
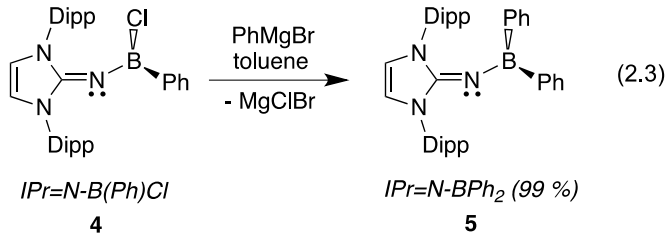


Figure 2.5. Computed HOMO (bottom) and LUMO (top) of IPr=N-B(Ph)Cl (**4**).

The last structural member of the *N*-heterocyclic iminoborane series to be discussed in this paper, IPr=N-BPh_2 (**5**), was prepared in pure form by combining IPr=N-BPhCl (**4**) with one equiv. of PhMgBr (Equation 2.3). Notably, reacting IPr=N-BCl_2 (**2**) with 2 equiv. of PhLi (1.8 M in dibutyl ether) or combining IPr=N-BPhCl (**4**) with one equiv. of PhLi did not give clean conversions to the desired product. Compound **5** was structurally authenticated by X-ray crystallography and the refined structure is shown in Figure 2.6. IPr=N-BPh_2 (**5**) contains a bent core geometry with a B-N-C angle [150.5(4)°] that is in between the values found for IPr=N-BCl_2 (**2**) [180.0°] and IPr=N-BPhCl (**4**) [131.7(2)°]. However, the B-N length in **5** [1.394(5) Å] is longer than the corresponding B-N distance in IPr=N-BPhCl (**4**) [1.350(3) Å]. One

possible explanation for the wider B-N-C angle in IPr=N-BPh_2 (**5**) relative to **4** is the alleviation of intramolecular repulsion between the phenyl groups in the terminal -BPh_2 unit and the proximal Dipp groups.



(2.3)

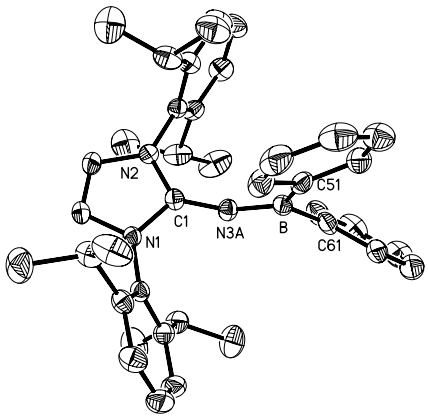


Figure 2.6. Molecular structure of IPr=N-BPh_2 (**5**) with thermal ellipsoids at a 30 % probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): B-N(3A) 1.394(5), N(3A)-C(1) 1.295(4), B-C(51) 1.588(5), B-C(61) 1.568(5); B-N(3)-C(1) 150.5(4).

Table 2.1. Selected Bond Distances and Angles for Compounds **2** to **5**.

Compound	C=N (Å)	N-B (Å)	C-N-B (°)
IPr=N-BCl_2 (**2**)	1.273(5)	1.302(6)	180.0
$(IPr=N)_2BCl$ (**3**)	1.280(2), 1.2825(19)	1.399(2)[a]	133.77(14), 136.26(14)
IPr=N(Ph)Cl (**4**)	1.307(3)	1.350(3)	131.7(2)
IPr=N-BPh_2 (**5**)	1.295(4)	1.394(5)	150.5(4)

[a] Both N-B bond distances in $(IPr=N)_2BCl$ (**3**) were 1.399(2) Å.

The computed HOMO of IPr=N-BPh_2 (**5**) is similar to that of IPr=N-BCl_2 (**2**) and IPr=N-B(Ph)Cl (**4**) with contributions from the *N*-heterocyclic ring, imine nitrogen atom and B-C(phenyl) σ-bonding (Figure 2.7). The LUMO features pronounced quinoidal character within the two boron bound Ph substituents leading to some B-C π-overlap. The Wiberg bond order also suggests that there is B-N multiple bond character (1.18) in **5**, while the adjacent C-N double bond within the *N*-heterocyclic imine unit (corresponding to [N(3)-C(1)] in Figure 2.6) has a computed bond order of 1.50.

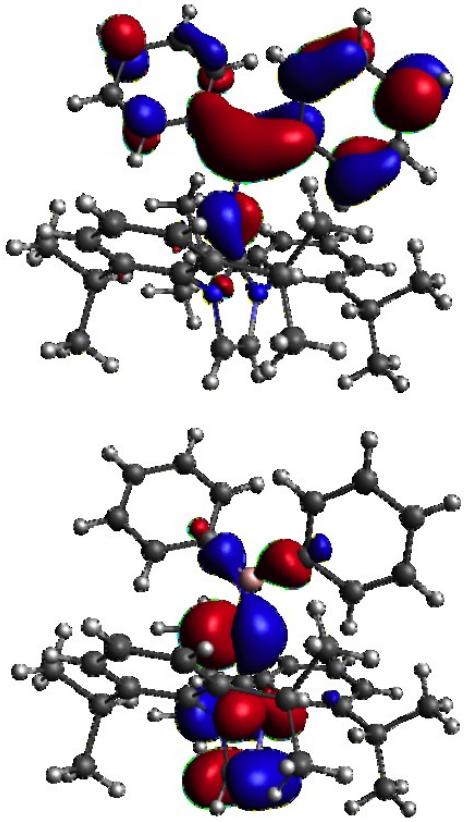
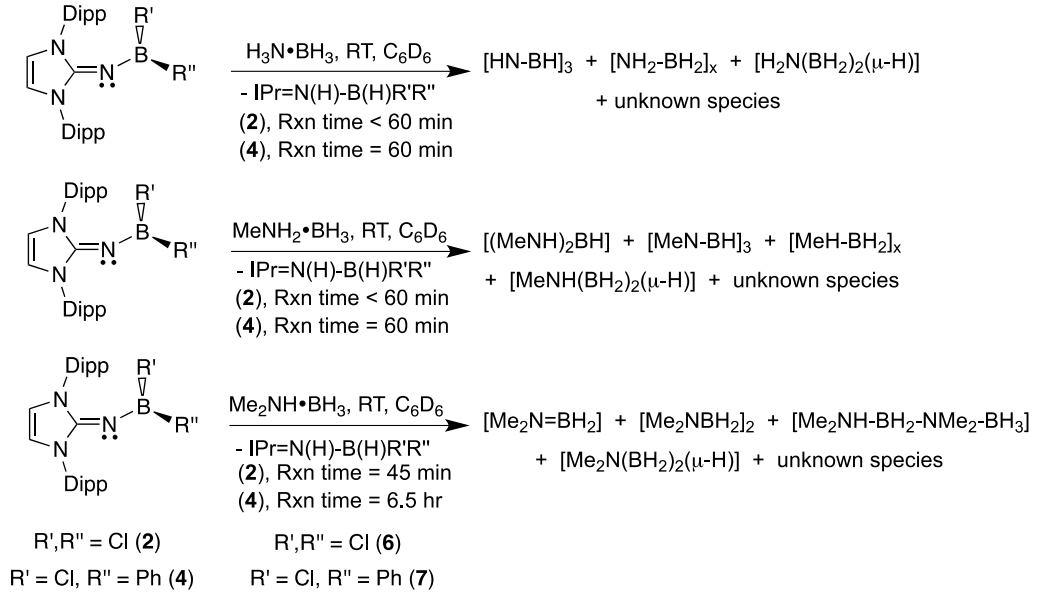


Figure 2.7. Computed HOMO (bottom) and LUMO (top) of IPr=N-BPh_2 (**5**).

2.2.2 Stoichiometric reactivity of *N*-heterocyclic iminoboranes with amine-boranes

One of the quintessential reactions of a Frustrated Lewis Pair is its ability to split dihydrogen into formal protic and hydridic units.[3] Thus far we see no evidence of a reaction between molecular H_2 and the *N*-heterocyclic iminoboranes **2**, **4** and **5** at room temperature or upon heating to 70 °C in benzene solvent. Fortunately these hindered B-N species are able to abstract H^+/H^- from $H_3N{\bullet}BH_3$, $MeNH_2{\bullet}BH_3$, $Me_2NH{\bullet}BH_3$, and/or $^iPr_2NH{\bullet}BH_3$ to afford dehydrogenated B-N compounds[11c] and the corresponding zwitterionic addition products IPr=N(H)-B(H)R_2 (R = Cl and/or Ph). Specifically when IPr=N-BCl_2 (**2**) was combined with one molar equivalent of $Me_2NH{\bullet}BH_3$ in C_6D_6 at room temperature, the formation of a colorless precipitate occurs after a few minutes, with complete consumption of **2** after 45 minutes (according to NMR spectroscopy). The precipitate formed was isolated and identified as the H^+/H^- addition product IPr=N(H)-B(H)Cl_2 (**6**) on the basis of NMR spectroscopy and elemental analysis. The ^{11}B NMR spectrum of the reaction mixture showed the presence of known dehydrocoupling products, such as $[Me_2N\text{-}BH_2]_2$, $Me_2NH\text{-}BH_2\text{-}NMe_2\text{-}BH_3$ and $Me_2N(BH_2)_2(\mu\text{-}H)$, while no signal corresponding to the starting amine-borane $Me_2NH{\bullet}BH_3$ was present. Although $H_3N{\bullet}BH_3$ and $MeNH_2{\bullet}BH_3$ have poor solubilities in non-polar solvents such as C_6D_6, the high solubility of compound **2** in benzene-d_6 still allows for transfer dehydrogenation to proceed to completion within one hour (Scheme 2.2). In these cases, precipitation of IPr=N(H)-B(H)Cl_2 (**6**) likely drives the H^+/H^- transfer from the amine-boranes. Despite multiple attempts, crystals of **6** that

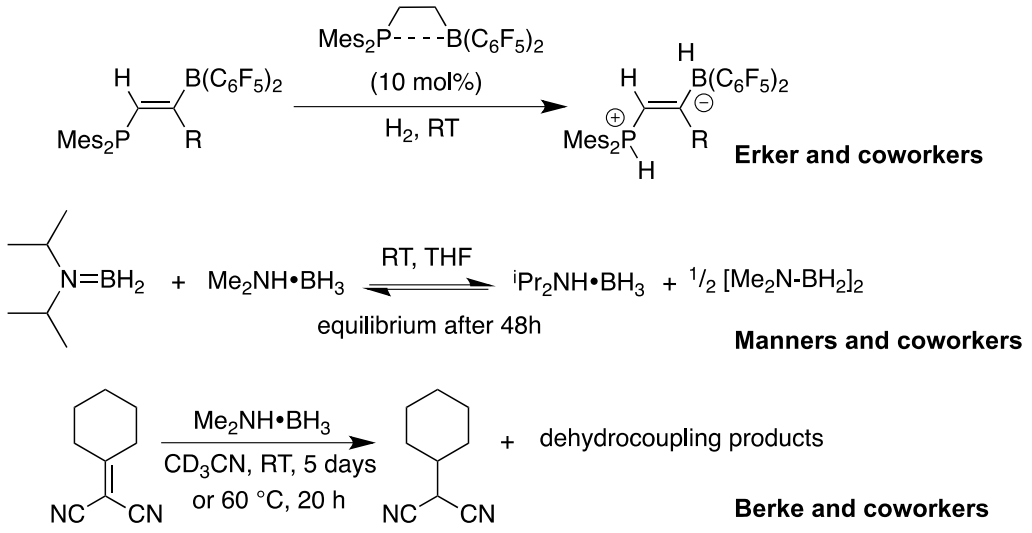
were suitable for X-ray crystallography could not be obtained. The electron-withdrawing chlorine atoms make the adjacent boron quite Lewis acidic, and accordingly, IPr=N-BCl_2 (**2**) is extremely air- and moisture-sensitive. Furthermore, THF shows spectroscopic signs of Lewis acid-mediated ring-opening in the presence of **2**.



Scheme 2.2. Stoichiometric reactions of the IPr=N-BCl_2 (**2**) and IPr=N-B(Ph)Cl (**4**) with various amine-boranes.

The dehydrocoupling ability of IPr=N-BCl_2 (**2**) towards amine-boranes is one of the most rapid metal-free examples at the moment. As mentioned in the introduction, bulky phosphine-borane pairs, $^tBu_3P/B(C_6F_5)_3$,[5] have also been shown to initiate the noticeable dehydrocoupling of $Me_2NH•BH_3$ within 30 minutes, but 24 hours was required to achieve a *ca.* 97 % conversion to $[Me_2N\text{-}BH_2]_2$. Additionally, $^tBu_3P/B(C_6F_5)_3$ reacted with $H_3N•BH_3$ at room temperature, but only 85 % conversion to $[^tBu_3PH][HB(C_6F_5)_3]$ occurred after an undescribed amount of time. Erker and coworkers reported that the tethered

FLPs $Mes_2PCH=CHRB(C_6F_5)_2$ (R = Me or Ph) were inert towards dihydrogen even up to pressures of 60 bar, yet they were able to accept H^+/H^- (transfer dehydrogenation) from a hydrogenated FLP system (i.e. $Mes_2P(H)CH_2CH_2RB(H)(C_6F_5)_2$) (Scheme 2.3).[4] It was also briefly mentioned in two reviews[3b, 3c] that $Mes_2PCH=CHRB(C_6F_5)_2$ (R = Me or Ph) could also accept dihydrogen from ammonia-borane $H_3N•BH_3$ and then transfer H^+/H^- to imines, leading to the reduction and formation of amines under mild conditions.[25] A related example of metal-free hydrogen transfer, in terms of structural resemblance to **2**, would be the use of $^iPr_2N=BH_2$ by Manners and coworkers to dehydrogenate less hindered 1° and 2° amine-boranes.[6a] When $H_3N•BH_3$ and $MeNH_2•BH_3$ were each combined with $^iPr_2N=BH_2$ at room temperature, the slow dehydrogenation (> 90 % conversion after *ca.* 20 hrs.) of these amine-borane adducts and formation of $^iPr_2NH•BH_3$ was noted. The reactivity of $^iPr_2N=BH_2$ with $Me_2NH•BH_3$ was also investigated and an equilibrium was observed between $^iPr_2N=BH_2$, $Me_2NH•BH_3$, $^iPr_2NH•BH_3$, and $Me_2N=BH_2$ (Scheme 2.3).[6a] Berke and coworkers also demonstrated that polarized olefins could act as hydrogen acceptors in the presence of various amine-boranes (Scheme 2.3).[26a] Although the solvent-free reaction of 2-cyclohexylidenemalonitrile with ammonia-borane $H_3N•BH_3$ is rapid (at room temperature: <10 minutes in THF-d_8; 1 hour in CD_3CN; 20 hours in C_6D_6), substantially longer reaction times of up to 5 days were noted with alkyl-substituted amine-boranes.



Scheme 2.3. Selected examples of metal-free transfer dehydrogenation.

With IPr=N(H)-B(H)Cl_2 (**6**) in hand, we tried to effect hydrogen release through different avenues, a key step required for catalysis. To begin, compound **6** was heated in refluxing C_6D_6, however no dehydrogenation was found. The only change noted was an increase in solubility in C_6D_6 at elevated temperatures. IPr=N(H)-B(H)Cl_2 (**6**) also did not transfer dihydrogen (as H^+/H^-) to stoichiometric amounts of cyclohexene, the activated imine, PhCH=N^{t}Bu, or to an enamine, *N*-(1-styryl)piperidine, at room temperature or under refluxing C_6D_6. Even in the presence of the known dehydrogenation catalyst $[RhCl(COD)]_2$ (5 mol%; COD = 1,5-cyclooctadiene), compound **6** remained unchanged after stirring for two days in toluene at room temperature or in refluxing C_6D_6. The related hindered bis(imino)chloroborane (IPr=N)$_2$BCl (**3**) was unreactive towards $Me_2NH•BH_3$ at room temperature or in refluxing C_6D_6. The boron atom lies in a deep steric pocket between the two $[IPr=N]^-$ ligands that likely hinders its reactivity with amine-boranes.

The *B*-phenylated iminoborane IPr=N-B(Ph)Cl (**4**) reacted rapidly with $H_3N{\bullet}BH_3$ and $MeNH_2{\bullet}BH_3$, with no sign of starting materials by *in situ* ^{11}B NMR spectroscopy after 60 min in C_6D_6. The reaction with the bulkier amine-borane $Me_2NH{\bullet}BH_3$ required a longer reaction time of 6.5 hrs in order to see the full consumption of compound **4** (Scheme 2.2). Unlike IPr=N(H)-B(H)Cl_2 (**6**), the addition product IPr=N(H)-B(H)PhCl (**7**) is highly soluble in C_6D_6 and gives a broad ^{11}B NMR resonance at -2.5 ppm ($^1J_{BH}$ coupling could not be resolved). The increased steric bulk about the boron center in **4** and the fact that compound **7** does not precipitate out of solution (while IPr=N(H)-B(H)Cl_2 (**6**) does), leads to a slightly slower reaction of **4** with amine-boranes relative to **2**. Despite multiple attempts, crystals of **7** were only suitable to show atom connectivity via X-ray crystallography; however, multinuclear NMR and elemental analysis each support its formation. Heating compound **7** in a sealed J-Young NMR tube in C_6D_6 at 70 °C for 3.5 days led to full dehydrogenation back to IPr=N-B(Ph)Cl (**4**) (Equation 2.4); in addition to resonances belonging to **4**, a singlet was detected at 4.47 ppm in solution, which was assigned to the release of molecular H_2.[28] Since IPr=N-B(Ph)Cl (**4**) does not react with dihydrogen, it has the potential to be a dehydrocoupling catalyst for amine-boranes *(vide infra*). At room temperature and with warming to 55 °C in C_6D_6, IPr=N(H)-B(H)PhCl (**7**) does not transfer a chemical equivalent of dihydrogen to cyclohexene, PhC=N^{t}Bu or the enamine, *N*-(1-styryl)piperidine.

2.2.3 Metal-free dehydrocoupling catalysis instigated by an *N*-heterocyclic iminoborane

In order to verify if IPr=N-B(Ph)Cl (**4**) could act as a dehydrogenation catalyst, the reaction between $MeNH_2•BH_3$ and substoichiometric quantities of **4** was examined. Since IPr=N-B(Ph)Cl (**4**) is stable in dry THF, and Manners and coworkers had shown that the polymer $[MeNH\text{-}BH_2]_n$ was soluble in THF,[14b] we decided to explore the possible catalytic polymerization of $MeNH_2•BH_3$ by **4** in tetrahydrofuran. Importantly the blank reaction, heating $MeNH_2•BH_3$ in refluxing THF under N_2 gas, did not lead to any thermal decomposition. To test catalytic activity, compound **4** was combined with a large excess of $MeNH_2•BH_3$ (50 equiv.) in 1.6 M THF at *ca.* 70 °C for 17 hrs in a Schlenk flask that was open to a nitrogen line. Analysis by *in situ* ^{11}B NMR spectroscopy indicated the presence of $[MeN\text{-}BH]_3$ (δ = 32.8 ppm; 18 %), trace IPr=N(H)-B(H)PhCl (**7**) along with unknown dehydrogenation products (δ = -2.4 ppm; 11 %), a broad triplet at -4.7 ppm (60 %) with $^1J_{BH}$ = 111 Hz that is tentatively assigned to $[MeNH\text{-}BH_2]_3$ and its higher oligomers, and unreacted $MeNH_2•BH_3$ (δ = -18.2 ppm; 11 %). Poly(*N*-methylaminoborane) $[MeNH\text{-}BH_2]_n$ has been reported to give a broad ^{11}B NMR resonance at -6.5 ppm in $CDCl_3$ with no discernable B-H coupling in the proton-coupled $^{11}B\{^1H\}$ NMR spectrum.[12,14b] This chemical shift is similar to that of the 6-membered $[MeNH\text{-}BH_2]_3$ ring (triplet at δ = -5.4 ppm in acetone-d_6, $^1J_{BH}$ = 107 Hz;[29] δ = -5.9 ppm in THF-d_8[7a]). A broad triplet resonance was found at -4.7 ppm which featured a spectral tail that extends upfield to *ca.* -6.2 ppm, the possible

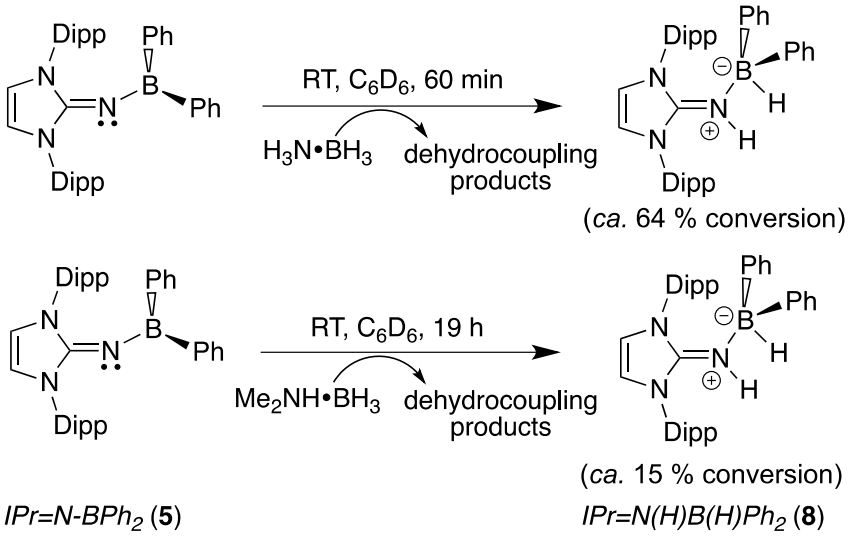
formation of $[MeNH\text{-}BH_2]_x$ oligomers was investigated. When the crude product was precipitated into cold (-35 °C) hexanes and the resulting product was analyzed by ESI-MS, oligomeric aminoboranes of up to 17 $[MeNH\text{-}BH_2]$ repeat units were found (Figure 2.8).[30] As a result of the low molecular weights present, we were unable to detect any polymeric species using our gel permeation chromatograph (samples run with solely THF as a solvent or with THF in the presence of 0.1 % $^nBu_4NBr$). This result is important as it suggests that under suitable conditions, metal-free catalysts could be used to prepare oligomeric aminoboranes.

When one calculates the activity of compound **4** towards the dehydrocoupling of $MeNH_2{\bullet}BH_3$, a modest turnover number (TON) of *ca.* 43 and a turnover frequency (TOF) of 2.5 h^{-1} are obtained. These values are still much lower than those reported using transition metal complexes. For example Brookhart's catalyst, $(POCOP)IrH_2$, where POCOP = [η^3-1,3-$(^tBu_2PO)_2C_6H_3$] was reported by Heinekey, Goldberg and coworkers to completely dehydrogenate $H_3N{\bullet}BH_3$ at a 0.5 mol % catalyst loading within 14 min at room temperature.[27] However the activity of **4** as a dehydrocoupling catalyst for amine-boranes is comparable to other main group catalysts. Wright and coworkers have shown that 5 mol. % of $Al(NMe_2)_3$ catalytically dehydrocouples $Me_2NH{\bullet}BH_3$ with complete consumption (50 turnovers) at 50 °C in toluene after 48 hrs.[15a,b] IPr=N-B(Ph)Cl (**4**) (10 mol %) can also catalytically dehydrogenate $Me_2NH{\bullet}BH_3$ at 50 °C in C_6D_6 with full H_2 loss from $Me_2NH{\bullet}BH_3$ after 16 hrs.

When Wright's $Al(N^iPr_2)_3$ catalyst (2 mol %) was combined with $^iPr_2NH•BH_3$, they observed a TON of *ca.* 25 and TOF of *ca.* 2.5 h^{-1}. The related aluminium hydride catalyst $[H_2Al(\mu\text{-}N^iPr_2)]_2$ (0.5 mol %) promotes H_2 loss from $^iPr_2NH•BH_3$ with up to 50 % conversion to $^iPr_2N=BH_2$ after 4 days at room temperature (TON = 90, TOF = 1 h^{-1}). Our system is not very effective at performing transfer dehydrogenation with the bulky substrate $^iPr_2NH•BH_3$. Even the most reactive member of our imine-borane series IPr=N-BCl_2 (**2**) could not convert $^iPr_2NH•BH_3$ completely to $^iPr_2N=BH_2$ (1:1 ratio of reagents) after 6 hrs at room temperature in C_6D_6. Only *ca.* 20 % conversion of $^iPr_2NH•BH_3$ to $^iPr_2N=BH_2$ was observed *in situ* by ^{11}B NMR spectroscopy, along with the presence of unreacted IPr=N-BCl_2 (**2**) in solution and newly formed IPr=N(H)-B(H)Cl_2 (**6**) in the precipitate.

IPr=N-BPh_2 (**5**) also reacts with amine-borane adducts, albeit more slowly than its halogenated analogues **2** and **4**. IPr=N-BPh_2 (**5**) underwent transfer dehydrogenation with $Me_2NH•BH_3$ leaving *ca.* 40 % of unreacted $Me_2NH•BH_3$ as well as IPr=N-BPh_2 (**5**) remaining after stirring in C_6D_6 at room temperature after 12 hrs; from this mixture, the addition product IPr=N(H)B(H)Ph_2 (**8**) could be observed in a 15 % spectroscopic yield. The reaction between the least hindered amine-borane $H_3N•BH_3$ and **5** was effective, with full consumption of ammonia-borane to various dehydrogenated products noted after 60 min; in this process compound **5** was partially converted to the H^+/H^- addition product IPr=N(H)B(H)Ph_2 (**8**) (Scheme 2.4) (64 % by ^1H NMR), along with the formation of two new unidentified IPr-

containing products. The nature of the dehydrogenated products (from $H_3N{\bullet}BH_3$) is unclear at this time as their ^{11}B NMR shifts do not correspond to known B-N species in the literature. One possibility is that compound **5** is undergoing additional complexation with newly formally unsaturated B-N by-products; further exploration of this reaction is ongoing.



Scheme 2.4. Reactions of the IPr=N-BPh_2 (**5**) with $H_3N{\bullet}BH_3$ and $Me_2NH{\bullet}BH_3$; in addition to generating **8**, unknown carbene-containing products were also formed.

Mechanistic studies of hydrogen transfer from amine-boranes to Berke's polarized olefin[26a] and imines,[26b] as well as to the aminoborane $^{i}Pr_2N{=}BH_2$[6a] have been reported. In the case of the polarized olefin $(H_2C)_5C{=}C(CN)_2$, a step-wise mechanism was postulated where fast hydride addition was followed by slower proton transfer.[26a] In contrast, the H^+/H^- transfer to imines (RCH=N-Ph; R = electron withdrawing group) was proposed to occur via a concerted 6-membered transition state on the basis of DFT calculations.[26b] Manners showed that the transfer of H^+/H^- from $Me_2NH{\bullet}BH_3$ to $^{i}Pr_2N{=}BH_2$ also

occurred in a bimolecular process with a 6-membered transition state, and measured kinetic isotope effects supported the initial B-to-B transfer of the hydride from $Me_2NH•BH_3$ to $^iPr_2N=BH_2$, followed by the N-to-N transfer of a proton.[6b] To better understand the mechanism of dehydrogenation by *N*-heterocyclic iminoboranes, IPr=N-BCl_2 (**2**) and IPr=N-B(Ph)Cl (**4**) were combined independently with $Me_2NH•BD_3$ and were able to isolate the addition products IPr=N(H)-B(D)Cl_2 (**6d**) and IPr=N(H)-B(D)PhCl (**7d**), respectively. This suggests that our system resembles Manners' transfer dehydrogenation chemistry using $^iPr_2N=BH_2$, which involves the B-to-B transfer of a hydride, and the N-to-N transfer of a proton (from the amine-borane to compounds **2** and **4** in our case). Diagnostic doublet patterns for the N-H groups are present in the ^{1}H NMR spectra of compounds **6** and **7** (IPr=N(H)-BCl(H)R; R = Cl and Ph) due to coupling to a neighbouring B-H hydrogen atom. In the deuterated species **6d** and **7d**, the N-H residues are singlets, as expected. The B-H stretch at 2556 cm^{-1} in the IR spectrum of IPr=N(H)-B(H)Cl_2 (**6**) is replaced by a B-D vibration at 1911 cm^{-1} in IPr=N(H)-B(D)Cl_2 (**6d**). Similarly, IPr=N(H)-B(H)PhCl (**7**) has an observable B-H stretch at 2468 cm^{-1}, while the B-D stretch for IPr=N(H)-B(D)PhCl (**7d**) is centered at a shifted position of 1828 cm^{-1}.

To see if *N*-heterocyclic iminoboranes could induce transfer dehydrogenation with other reagents, compounds **2** and **4** were treated with stoichiometric amounts of 9,10-dihydroanthracene, a demonstrated chemical source of hydrogen;[31] however no reaction was observed at room temperature or upon heating to 70 °C in C_6D_6.

2.3 Conclusions

By linking a nucleophilic *N*-heterocyclic imine unit with an electron-deficient borane, a new class of structurally tunable intramolecular Frustrated Lewis Pair has been developed that has the ability to rapidly dehydrogenate various amine-boranes under ambient conditions. With carbenes being ubiquitous in the literature, there exists a broad range of NHCs that can be used as precursors for the *N*-heterocyclic imine moiety.[17, 19] To our knowledge, the newly reported IPr=N-BR_2 (R = Cl and/or Ph) species represent one of the most effective non-metal amine-borane dehydrogenation agents to date. It was shown that IPr=N-B(Ph)Cl (**4**) can be regenerated from the H^+/H^- addition product IPr=N(H)B(H)PhCl (**7**) with gentle heating. In addition, **4** is a competent catalyst for the dehydrocoupling of $MeNH_2•BH_3$ to yield $[MeN\text{-}BH]_3$ along with oligomeric aminoboranes $[MeNH\text{-}BH_2]_x$ ($x \leq 17$). This work should facilitate the future usage of *N*-heterocyclic iminoboranes as metal-free catalysts for the dehydrocoupling of amine-boranes and related species (*e.g.* silanes).

2.4 Experimental Section

2.4.1 General

All reactions were performed in an inert atmosphere glove box (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[32] manufactured by Innovative Technologies, Inc., degassed and stored under an atmosphere of nitrogen prior to use. BCl_3 (1.0 M

solution in heptanes), dichlorophenylborane, phenylmagnesium bromide (3.0 M solution in diethyl ether), borane-ammonia complex ($H_3N{\bullet}BH_3$), borane-dimethylamine ($Me_2NH{\bullet}BH_3$), borane-tetrahydrofuran (1.0 M solution in THF), were each purchased from Aldrich and used as received. Fluorobenzene was also purchased from Aldrich, dried over calcium hydride overnight and then distilled under nitrogen prior to use. IPr=N-$SiMe_3$[33] (IPr = [(HCNDipp)$_2$C:]; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$), $MeNH_2{\bullet}BH_3$,[34] *N*-(1-styryl)piperidine,[35] PhC=N^{t}Bu,[36] $Me_2NH{\bullet}BD_3$,[37] and ^{i}Pr$_2$NH•BH_3[34] were prepared following literature procedures. ^{1}H and ^{13}C{^{1}H} spectra were recorded on a Varian VNMRS-500 MHz or Varian Inova-400 MHz spectrometer and referenced externally to $SiMe_4$; ^{11}B NMR spectra were referenced to $F_3B{\bullet}OEt_2$; ^{2}H{^{1}H} NMR spectra were referenced to $Si(CD_3)_4$. Infrared spectra were recorded on a Nicolet IR100 FTIR spectrometer as thin films between NaCl plates. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

2.4.2 X-ray Crystallography

Crystals for single-crystal X-ray diffraction studies were removed from a vial in a glove box and immediately coated with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fiber, and quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer.[38] All data were collected using a Bruker APEX II CCD

detector/D8 diffractometer using Mo Kα or Cu Kα radiation, with the crystals cooled to -100 °C. The data were corrected for absorption through Gaussian integration from the indexing of the crystal faces. Crystal structures were solved using intrinsic phasing SHELXT[39] (compounds **2**, **4** and **5**) or direct methods (**3**) and refined using full-matrix least-squares on F^2. The assignment of hydrogen atoms positions were based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20 % greater than those of their parent atoms.

Special Refinement Conditions: *Compound **4***. The crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program *CELL_NOW* (Bruker AXS Inc., Madison, WI, 2004). The second twin component can be related to the first component by 180º rotation about the [1 0 0] axis in both real space and reciprocal space. Integrated intensities for the reflections from the two components were written into a *SHELXL-2014* HKLF 5 reflection file with the data integration program *SAINT* (version 8.34A), using all reflection data (exactly overlapped, partially overlapped and non-overlapped). The refined value of the twin fraction (*SHELXL-2014* BASF parameter)[39] was 0.3188(17).

2.4.3 Computational Studies.

All computations were carried out using the Gaussian09 program package.[40] The hybrid DFT functional B3LYP[41] and a 6-31+G(d,p) basis set[42] were used for all calculations. The molecular orbitals and NBO analysis

outputs for **2**, **4** and **5** were obtained by single point calculations at the B3LYP/6-31+G(d,p) level with the initial geometries derived from crystallographic data. It should be emphasized that the computations were carried out for single, isolated, gas phase molecules.

2.4.4 Synthetic Procedures

Synthesis of IPr=N-BCl_2 (2). A cooled (-35 °C) solution of IPr=N-$SiMe_3$ (0.104 g, 0.218 mmol) in 8 mL of toluene was added dropwise to a -35 °C solution of BCl_3 (239.4 μL, 0.24 mmol, 1.0 M solution in heptanes) diluted with 6 mL of toluene, and the resulting mixture was stirred vigorously. After warming to room temperature, the orange colored reaction mixture was stirred for another hour. The reaction mixture was then filtered and removal of the volatiles from the filtrate afforded **2** as an off-white powder (0.1020 g, 97 %). Occasionally 5 – 20 % of disubstituted $(IPr=N)_2BCl$ (**3**) may form, but this can compound be easily removed by extraction with hexanes (in which compound **2** is insoluble). Crystals suitable for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of **2** in a 1:1 ratio of toluene/hexanes mixture. ^{1}H NMR (500 MHz, C_6D_6): δ 1.09 (d, $^3J_{HH}$ = 6.5 Hz, 12H, $CH(CH_3)_2$), 1.41 (d, $^3J_{HH}$ = 7.0 Hz, 12H, $CH(CH_3)_2$), 2.99 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, $CH(CH_3)_2$), 6.00 (s, 2H, N-C*H*-), 7.06 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar-*H*), 7.16 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 23.5 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 115.9 (-N-*C*H-), 124.4 (Ar-*C*),

130.5 (Ar-C), 131.9 (Ar-*C*), 146.2 (Ar-*C*), 147.2 (N-*C*-N). ^{11}B NMR (159 MHz, C_6D_6): δ 23.0. Mp (°C): *ca.* 145 - 148 (decomp., turns brown). Anal. Calcd. for $C_{27}H_{36}N_3BCl_2$: C, 66.96; H, 7.49; N, 8.68. Found: C, 66.32; H 7.59; N, 8.35.

Synthesis of (IPr=N)$_2$BCl (3). A solution of IPr=N-SiMe$_3$ (0.390 g, 0.819 mmol) in 8 mL of toluene was added dropwise to a solution of IPr=N-BCl_2 (**2**) (0.397 g, 0.819 mmol) in 8 mL of toluene, and the resulting mixture was stirred for 90 minutes at room temperature, giving a yellow-orange colored reaction mixture. After filtration, removal of the volatiles from the filtrate gave **3** as an off-white powder (0.390 g, 84 %). Crystals suitable for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of **3** in toluene. ^{1}H NMR (500 MHz, C_6D_6): δ 1.11 (d, $^3J_{HH}$ = 6.5 Hz, 24H, CH(C*H*$_3$)$_2$), 1.13 (d, $^3J_{HH}$ = 6.5 Hz, 24H, CH(C*H*$_3$)$_2$), 3.05 (septet, $^3J_{HH}$ = 7.0 Hz, 8H, C*H*(CH$_3$)$_2$), 5.96 (s, 4H, N-C*H*-), 7.08 (d, $^3J_{HH}$ = 7.5 Hz, 8H, Ar-*H*), 7.25 (t, $^3J_{HH}$ = 7.5 Hz, 4H, Ar-*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 23.6 (CH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 114.7 (-N-*C*H-), 123.9 (Ar-*C*), 129.1 (Ar-C), 134.3 (Ar-*C*), 144.4 (Ar-*C*), 147.7 (N-*C*-N). ^{11}B NMR (159 MHz, C_6D_6): δ -6.7. Mp (°C): *ca.* 135 (decomp., turns brown). Anal. Calcd. for $C_{54}H_{72}N_6BCl$: C, 76.17; H, 8.52; N, 9.87. Found: C, 75.67; H 8.50; N, 9.61.

Synthesis of IPr=N-B(Ph)Cl (4). A cold (-35 °C) solution of IPr=N-SiMe$_3$ (0.318 g, 0.668 mmol) in 8 mL of toluene was added dropwise to a solution of $PhBCl_2$ (86.7 μL, 0.668 mmol) in 2 mL of toluene at -35 °C. The

resulting mixture was warmed to room temperature and stirred for another 90 min to give a pale yellow reaction mixture. After filtration, removal of the volatiles from the filtrate afforded **4** as a pale yellow powder (0.344 g, 98 %). Crystals suitable for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of **4** in fluorobenzene. ^{1}H NMR (500 MHz, C_6D_6): δ 1.13 (d, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.41 (d, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 3.24 (septet, $^{3}J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 6.12 (s, 2H, N-C*H*-), 7.01 (d, $^{3}J_{HH}$ = 7.0 Hz, 4H, Ar-*H*), 7.07-7.10 (overlapping multiplets, 5H, Ar-*H* and Ph), 8.03 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H, Ph). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 23.4 (CH(*C*H$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 116.0 (-N-*C*H-), 124.2 (Ar-*C*), 125.0 (Ar-C), 127.2 (Ar-C), 129.9 (Ar-*C*), 130.2 (Ar-*C*), 132.7 (Ar-*C*), 135.4 (Ar-*C*), 147.3 (Ar-*C*), 148.9 (N-*C*-N). ^{11}B NMR (159 MHz, C_6D_6): δ 29.7. Mp (°C): *ca.* 133 (melts), *ca.* 173 (decomp., turns brown). Anal. Calcd. for $C_{33}H_{41}N_3BCl$: C, 75.36; H, 7.86; N, 7.99. Found: C, 74.43; H 7.75; N, 7.66.

Synthesis of IPr=N-BPh$_2$ (5). A cold (-35 °C) solution of PhMgBr (3.0 M in diethyl ether, 132.4 µL, 0.397 mmol) was added dropwise to a cold solution (-35 °C) of IPr=N-B(Ph)Cl (**4**) (198.9 mg, 0.378 mmol) in 12 mL of toluene. The resulting mixture was warmed to room temperature and stirred for another 2 hrs. to give a pale yellow reaction mixture. After filtration, removal of the volatiles from the filtrate afforded **5** as a colorless solid (213.5 mg, 99 %). Crystals suitable for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of **5** in toluene. ^{1}H NMR (500 MHz, C_6D_6): δ 1.10 (d,

$^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.14 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 3.29 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 6.07 (s, 2H, N(C*H*)$_2$N), 7.04 (d, $^3J_{HH}$ = 7.5 Hz, 4H, Ar*H*), 7.14 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 7.19 – 7.18 (m, 6H, Ar*H*), 7.46 – 7.44 (m, 4H, Ar*H*). ^{13}C{^{1}H} (126 MHz, C_6D_6): δ 22.6 (CH(*C*H$_3$)$_2$), 25.6 (CH(*C*H$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 115.1 (-N-*C*H-), 124.2 (Ar-*C*), 127.2 (Ar-*C*), 129.7 (Ar-*C*), 133.7 (Ar-*C*), 134.7 (Ar-*C*), 147.9 (Ar-*C*). ^{11}B NMR (159 MHz, C_6D_6): δ 37.5. Mp (°C): 174. Anal. Calcd. for $C_{39}H_{46}BN_3$: C, 82.51; H, 8.17; N, 7.40. Found: C, 78.27; H, 7.88; N, 7.03.

Reaction of IPr=N-BCl$_2$ (2) with Me$_2$NH•BH$_3$. A solution of IPr=N-BCl$_2$ (**2**) (0.156 g, 0.32 mmol) in 3 mL of C_6D_6 was added to a solution of Me$_2$NH•BH$_3$ (0.019 g, 0.32 mmol) in 1 mL of C_6D_6 at room temperature; there is a formation of precipitate within two minutes. After the resulting mixture was stirred for 45 minutes, a small aliquot (*ca.* 0.2 mL) was removed and diluted with 0.8 mL of $CDCl_3$ for ^{11}B NMR analysis. ^{11}B NMR (159 MHz, $CDCl_3$): δ 5.4 ([Me$_2$NBH$_2$]$_2$, t, $^1J_{BH}$ = 113 Hz, 57 %), -2.1 (IPr=N(H)-B(H)Cl$_2$, br s, 4 %), -2.9 ([Me$_2$NH-*B*H$_2$-NMe$_2$-BH$_3$], t, $^1J_{BH}$ = 117 Hz, 8 %), -12.8 ([Me$_2$NH-BH$_2$-NMe$_2$-*B*H$_3$], q, $^1J_{BH}$ = 97 Hz, 29 %), -17.4 (Me$_2$N(BH$_2$)$_2$(μ-H), td, $^1J_{BH}$ = 129 Hz, $^1J_{BH}$ = 32 Hz, 2 %). The mother liquor was filtered and the volatiles were removed from the resulting precipitate to give IPr=N(H)-B(H)Cl$_2$ (**6**) as a white solid. Recrystallization of **6** was achieved by cooling (-35 °C) a saturated solution of this compound in CH$_2$Cl$_2$/hexanes (1:2 ratio); Yield = 0.119 g, 76 %.

Data for IPr=N(H)-B(H)Cl$_2$ (6). ^{1}H{^{11}B} NMR (500 MHz, $CDCl_3$): δ 1.22 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.36 (d, $^3J_{HH}$ = 6.5 Hz, 12H, CH(C*H*$_3$)$_2$), 2.74 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 3.12 (br s, 1H, B-*H*), 4.68 (d, $^3J_{HH}$ = 8.0 Hz, 1H, N-*H*), 6.62 (s, 2H, N-C*H*-), 7.34 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar-*H*), 7.54 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 23.1 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 117.6 (-N-*C*H-), 125.0 (Ar-*C*), 129.9 (Ar-C), 131.7 (Ar-*C*), 146.6 (Ar-*C*), 146.8 (N-*C*-N). ^{11}B NMR (159 MHz, C_6D_6): δ -1.2 (br s). Mp (°C): *ca.* 210 (decomposes). Anal. Calcd. for $C_{27}H_{38}N_3BCl_2$: C, 66.68; H, 7.88; N, 8.64. Found: C, 66.11; H 7.89; N, 8.53. IR (cm^{-1}): 3355 (m, ν_{N-H}), 2556 (m, ν_{B-H}).

Reaction of IPr=N-BCl$_2$ (2) with MeNH$_2$•BH$_3$. A solution of IPr=N-BCl_2 (**2**) (0.121 g, 0.206 mmol) in 2 mL of C_6D_6 was added to a solution of MeNH$_2$•BH$_3$ (0.0114 g, 0.322 mmol) in 1 mL of C_6D_6 at room temperature; a white precipitate formed within two minutes. After the resulting mixture was stirred for one hour, two small aliquots (*ca.* 0.2 mL) were removed; one was diluted with 0.8 mL of C_6D_6, and the other with 0.8 mL of $CDCl_3$ for ^{11}B NMR analysis. ^{11}B NMR (159 MHz, C_6D_6): δ 34.1 ([MeN-BH]$_3$, d, $^1J_{BH}$ = 156 Hz, 5 %), 2.1 (unknown species, br s, 12 %), -5.7 ([MeNH-BH$_2$]$_x$, t, $^1J_{BH}$ = 115 Hz, 39 %), -16.9 (unknown species, t, $^1J_{BH}$ = 98 Hz, 5 %), -22.0 (MeNH(BH$_2$)$_2$(μ-H), t, $^1J_{BH}$ = 128 Hz, 39 %). ^{11}B NMR (159 MHz, $CDCl_3$): δ 33.5 ([MeN-

$BH]_3$, d, $^1J_{BH}$ = 148 Hz, 43 %), 1.5 (unknown species, s, 6 %), -1.6 (IPr=N(H)-$B(H)Cl_2$, br s, 37 %), -22.3 ($MeNH(BH_2)_2$(μ -H), t, $^1J_{BH}$ = 159 Hz, 14 %).

Reaction of IPr=N-BCl_2 (2) with H_3N•BH_3. A solution of IPr=N-BCl_2 (**2**) (0.119 g, 0.246 mmol) in 2 mL of C_6D_6 was added to a solution of H_3N•BH_3 (0.008 g, 0.2 mmol) in 1 mL of C_6D_6 at room temperature; there is a formation of a precipitate within two minutes. After the resulting mixture was stirred for one hour, two small aliquots (*ca.* 0.2 mL) were removed; one was diluted with 0.8 mL of C_6D_6, and the other with 0.8 mL of $CDCl_3$ for ^{11}B NMR analysis. ^{11}B NMR (128 MHz, C_6D_6): δ 30.6 ($[HN-BH]_3$, d, $^1J_{BH}$ = 141 Hz, 12 %), -2.4 ($[H_2N-BH_2]_x$, br, s, 83 %), -8.5 ($H_2N(BH_2)_2$(μ-H), t, $^1J_{BH}$ = 118 Hz, 5 %). ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.2 ($[HN-BH]_3$, d, $^1J_{BH}$ = 141 Hz, 8 %), -2.4 (IPr=N(H)-$B(H)Cl_2$ overlapping with $[H_2N-BH_2]_x$ products, br, 73 %), -8.7 ($H_2N(BH_2)_2$(μ-H), t, $^1J_{BH}$ = 111 Hz, 19 %).

Reaction of IPr=N-BCl_2 (2) with ^{i}Pr_2NH•BH_3. A solution of IPr=N-BCl_2 (**2**) (0.082 g, 0.17 mmol) in 2 mL of C_6D_6 was added to a solution of ^{i}Pr_2NH•BH_3 (0.020 g, 0.17 mmol) in 1 mL of C_6D_6 at room temperature to give a clear, yellow solution. A small amount of white precipitate was formed after 1.5 hours. After the resulting mixture was stirred for 6 hours, a small aliquot (*ca.* 0.2 mL) was removed and diluted with 0.8 mL of $CDCl_3$ for ^{11}B NMR analysis. ^{11}B NMR (159 MHz, $CDCl_3$): δ 35.3 (^{i}Pr_2N=BH_2, t, $^1J_{BH}$ = 118 Hz, 11 %), 22.6 (IPr=N-BCl_2, br s, 26 %), 4.4 (unknown decomposition product of IPr=N-BCl_2, s, 11 %), -1.3 (IPr=N(H)-$B(H)Cl_2$, br s, 10 %), -21.5 (^{i}Pr_2NH•BH_3, q, $^1J_{BH}$ = 100 Hz, 42 %). The mother liquor was filtered and the

volatiles were removed from the resulting precipitate to give IPr=N(H)-B(H)Cl_2 (**6**) as a white solid. Recrystallization of **6** was achieved by cooling (-35 °C) a saturated solution of this compound in CH_2Cl_2/hexanes (1:2 ratio); Yield = 0.022 g, 27 %.

Reaction of IPr=N-BPhCl (4) with $Me_2NH•BH_3$. A solution of IPr=N-BPhCl (**4**) (0.108 g, 0.205 mmol) in 3 mL of C_6D_6 was added to a solution of $Me_2NH•BH_3$ (0.0123 g, 0.209 mmol) in 1 mL of C_6D_6 at room temperature. After the resulting mixture was stirred for 6.5 hrs, a small aliquot (*ca.* 0.2 mL) of the resulting solution was removed and diluted in C_6D_6 for ^{11}B NMR analysis. The volatiles were removed from the reaction mixture and IPr=N(H)-B(H)PhCl (**7**) was recrystallized from a saturated solution of toluene and hexanes (1:3 ratio) at - 35 °C; Yield = 0.074 g, 69 %. NMR data for the reaction mixture: ^{11}B NMR (159 MHz, C_6D_6): δ 39.6 ([$Me_2N=BH_2$], t, $^1J_{BH}$ = 126 Hz, 6 %), 5.4 ([$Me_2NBH_2]_2$, t, $^1J_{BH}$ = 112 Hz, 7 %), -2.9 (IPr=N(H)-B(H)PhCl overlapping with [Me_2NH-*B*H_2-NMe_2-BH_3], t, $^1J_{BH}$ = 120 Hz, 59 %), -9.6 (unknown species, d, $^1J_{BH}$ = 128 Hz, 9 %), -13.1 ([Me_2NH-BH_2-NMe_2-*B*H_3], q, $^1J_{BH}$ = 99 Hz, 3 %), -17.6 ($Me_2N(BH_2)_2$(μ-H), t, $^1J_{BH}$ = 123 Hz, 16 %).

Data for IPr=N(H)-B(H)PhCl (7): $^1H\{^{11}B\}$ NMR (400 MHz, C_6D_6): δ 1.01 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.04 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.30 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.40 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 2.86 (septet, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 2.99 (septet, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 3.68 (br s, 1H, B-*H*), 4.77 (d, $^3J_{HH}$ = 8.5 Hz, 1H, N-*H*), 5.85 (s, 2H, N-C*H*-), 6.97 – 7.07 (m, 3H, Ph), 7.11 (d, $^3J_{HH}$ = 7.5 Hz, 4H, Ar-

H), 7.18 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ar-*H*), 7.61 (dd, $^{3}J_{HH}$ = 6.5 and 7.5 Hz, 2H, Ph). $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6): δ 23.0 ($CH(CH_3)_2$), 23.3 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 25.0 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 117.2 (-N-*C*H-), 124.8 (Ar-*C*), 124.9 (Ar-*C*), 125.5 (Ar-*C*), 127.2 (Ar-C), 130.9 (Ar-*C*), 131.4 (Ar-*C*), 132.4 (Ar-*C*), 146.9 (Ar-*C*), 147.1 (Ar-*C*), 149.5 (N-*C*-N). ^{11}B NMR (159 MHz, C_6D_6): δ -2.5. Mp (°C): *ca.* 180. Anal. Calcd. for $C_{33}H_{43}N_3BCl$: C, 75.07; H, 8.21; N, 7.97. Found: C, 75.66; H, 8.11; N, 7.29. IR (cm^{-1}): 3353 (m, ν_{N-H}), 2468 (m, ν_{B-H}).

Reaction of IPr=N-BPhCl (4) with $MeNH_2$•BH_3. A solution of IPr=N-$BPhCl_2$ (**4**) (0.098 g, 0.19 mmol) in 2 mL of C_6D_6 was added to a suspension of $MeNH_2$•BH_3 (0.0082 g, 0.18 mmol) in 1 mL of C_6D_6 at room temperature. After the resulting mixture was stirred for 60 min, a small aliquot (*ca.* 0.2 mL) were removed and diluted with 0.8 mL of C_6D_6 for ^{11}B NMR analysis. The volatiles were removed from the reaction mixture and pure IPr=N(H)-B(H)PhCl (**7**) was obtained by cooling a saturated solution of dichloromethane and hexanes (1:2 ratio) to -35 °C; Yield = 0.031 g, 32 %. NMR data of the reaction mixture: ^{11}B NMR (159 MHz, C_6D_6): δ 39.6 ($(MeNH)_2BH$, d, $^{1}J_{BH}$ = 137 Hz, 4 %), 33.4 ($[MeN-BH]_3$, d, $^{1}J_{BH}$ = 144 Hz, 3 %), -2.9 ($[MeNH-BH_2]_x$ overlapping with IPr=N(H)-B(H)PhCl, br s, 62 %), -13.4 (unknown species, d, $^{1}J_{BH}$ = 126 Hz, 29 %), -21.4 ($MeNH(BH_2)_2(\mu\text{-}H)$, t, $^{1}J_{BH}$ = 107 Hz, 2 %).

Reaction of IPr=N-BPhCl (4) with H_3N•BH_3. A solution of IPr=N-BPhCl (**4**) (0.095 g, 0.18 mmol) in 2 mL of C_6D_6 was added to a suspension of

$H_3N{\bullet}BH_3$ (0.006 g, 0.2 mmol) in 1 mL of C_6D_6 at room temperature. After the resulting mixture was stirred for one hour, a small aliquot (*ca.* 0.2 mL) was removed and diluted with 0.8 mL of C_6D_6 for ^{11}B NMR analysis. The volatiles were removed from the reaction mixture and IPr=N(H)-B(H)PhCl (**7**) was obtained by cooling a saturated solution of toluene and hexanes (1:2 ratio) to -35 °C; Yield = 0.052 g, 55 %. NMR data for the reaction mixture: ^{11}B NMR (128 MHz, C_6D_6): δ 30.4 ([HN-BH]$_3$, d, $^1J_{BH}$ = 141 Hz, 27 %), -2.8 ([H_2N-BH_2]$_x$ overlapping with IPr=N(H)-B(H)PhCl, br s, 70 %), -18.5 (unknown species, d, $^1J_{BH}$ = 28 Hz, 2 %), -25.9 ($H_2N(BH_2)_2$(μ-H), t, $^1J_{BH}$ = 131 Hz, 1 %).

Reaction of IPr=N-BPh$_2$ (5) with Me$_2$NH•BH$_3$. A solution of IPr=N-BPh_2 (**5**) (0.043 g, 0.075 mmol) in 2.0 mL of C_6D_6 was added $Me_2NH{\bullet}BH_3$ (0.004 g, 0.08 mmol) at room temperature. After the resulting solution was stirred for 12 hours, a small aliquot (*ca.* 0.2 mL) was removed and diluted in C_6D_6 for ^{11}B NMR analysis. NMR data for the reaction mixture: ^{11}B NMR (159 MHz, C_6D_6): δ 39.8 ([Me_2N-BH_2], d, $^1J_{BH}$ = 118 Hz, 4 %), 5.4 ([Me_2N-BH_2]$_2$, t, $^1J_{BH}$ = 112 Hz, 4 %), -4.3 ([Me_2NH-*B*H_2-NMe_2-BH_3], t, $^1J_{BH}$ = 95 Hz, 53 %), -5.9 (unknown species, s, 3 %), -9.6 (unknown species, d, $^1J_{BH}$ = 128 Hz, 3 %), -13.1 ([Me_2NH-BH_2-NMe_2-*B*H_3], q, overlapping with unreacted $Me_2NH{\bullet}BH_3$, 21 %), -17.3 ($Me_2N(BH_2)_2$(μ-H), t, $^1J_{BH}$ = 123 Hz, 12 %). Despite collecting many scans (> 130), the broad signal of IPr=N-BPh_2 (**5**) at 37 ppm could not be detected by ^{11}B NMR; however, I see evidence of **5** (*ca.* 40 % unreacted) and IPr=N(H)-B(H)Ph_2 (**8**) (15 %) in the ^1H NMR spectrum after 12 hrs.

Reaction of IPr=N-BPh$_2$ (5) with H$_3$N•BH$_3$. A solution of IPr=N-BPh$_2$ (**5**) (0.063 g, 0.11 mmol) in 2 mL of C_6D_6 was added to H$_3$N•BH$_3$ (0.003 g, 0.1 mmol) at room temperature. After the resulting mixture was stirred for 1 hour, a small aliquot (*ca*. 0.2 mL) was removed and diluted with 0.8 mL of C_6D_6 for ^{11}B NMR analysis. The volatiles were removed from the reaction mixture and IPr=N(H)-B(H)Ph$_2$ (**8**) was recrystallized twice from cooling (-35 °C) a saturated solution of toluene and hexanes (1:2 ratio); Yield = 0.008 g; 12 %. NMR spectrum of the reaction mixture: ^{11}B NMR (128 MHz, C_6D_6): δ 41.8 (unknown species, br s, 6 %), -7.2 (IPr=N(H)-B(H)Ph$_2$, br s, 70 %), -12.0 (unknown species, br s, 4 %), -20.5 (unknown species, br s, 20 %).

Data for IPr=N(H)-B(H)Ph$_2$ (8). ^{1}H{^{11}B} NMR (400 MHz, C_6D_6): δ 1.01 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.12 (d, $^3J_{HH}$ = 6.5 Hz, 12H, CH(C*H*$_3$)$_2$), 2.88 (septet, $^3J_{HH}$ = 6.5 Hz, 4H, C*H*(CH$_3$)$_2$), 3.32 (br s, 1H, B-*H*), 4.79 (d, $^3J_{HH}$ = 7.5 Hz, 1H, N-*H*), 5.81 (s, 2H, N-C*H*-), 7.00 (d, $^3J_{HH}$ = 7.0 Hz, 4H, Ar-*H*), 7.08 (t, $^3J_{HH}$ = 7.0 Hz, 2H, Ar-*H*), 7.19 (m, 6H, Ph), 7.30 (d, $^3J_{HH}$ = 7.5 Hz, 4H, Ph). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 22.4 (CH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 29.3 (*C*H(CH$_3$)$_2$), 116.7 (-N-*C*H-), 124.1 (Ar-*C*), 124.6 (Ar-*C*), 125.5 (Ar-*C*), 127.1 (Ar-C), 131.0 (Ar-*C*), 133.3 (Ar-*C*), 133.7 (Ar-*C*), 147.1 (Ar-*C*), 147.2 (Ar-*C*), 149.7 (N-*C*-N). ^{11}B NMR (159 MHz, C_6D_6): δ -7.4. Mp (°C): *ca.* 186. Anal. Calcd. for $C_{39}H_{48}N_3B$: C, 82.23; H, 8.49; N, 7.38. Found: C, 78.67; H, 8.20; N, 7.78. IR (cm^{-1}): 3350 (m, ν_{N-H}), 2373 (m, ν_{B-H}).

Synthesis of IPr=N(H)B(D)Cl$_2$ (6d). A solution of IPr=N-BCl$_2$ (**2**) (0.089 g, 0.18 mmol) in 3 mL of C_6D_6 was added to Me$_2$NH•BD$_3$ (0.011 g, 0.18 mmol) at room temperature; there is a formation of a precipitate within two minutes. After the resulting mixture was stirred for 60 min, a small aliquot (*ca.* 0.2 mL) was removed and diluted with 0.8 mL of $CDCl_3$ for ^{11}B NMR analysis; all of the IPr=N-BCl$_2$ had been converted into IPr=N(H)B(D)Cl$_2$ (**6d**). The reaction mixture was filtered and the volatiles were removed from the reaction precipitate and IPr=N(H)-B(D)Cl$_2$ (**6d**) was recrystallized from a saturated solution of CH_2Cl_2 and hexanes (1:3 ratio) at - 35 °C; Yield = 0.080 g, 89 %. Data for **6b**: ^{1}H NMR (500 MHz, $CDCl_3$): same as **6** but N-H resonance is a singlet at δ 4.68. ^{2}H{^{1}H} NMR (61.39 MHz, $CHCl_3$): δ 3.21. IR (cm^{-1}): 3356 (m, $\nu_{N\text{-}H}$), 1911 (m, $\nu_{B\text{-}D}$).

Synthesis of IPr=N(H)B(D)PhCl (7d). A solution of IPr=N-BPhCl (**4**) (0.091 g, 0.17 mmol) in 3 mL of C_6D_6 was added to Me$_2$NH•BD$_3$ (0.010 g, 0.17 mmol) at room temperature. After the resulting mixture was stirred for 7 hours, a small aliquot (*ca.* 0.2 mL) was removed and diluted with 0.8 mL of $CDCl_3$ for ^{11}B NMR analysis; all of the IPr=N-BPhCl was converted into IPr=N(H)B(D)Cl$_2$ (**7d**). The volatiles were removed from the reaction mixture and IPr=N(H)-B(D)PhCl (**7d**) was obtained by cooling a saturated solution of toluene and hexanes (1:2 ratio) to -35 °C; Yield = 0.038 g, 41 %. Data for **7b**: ^{1}H NMR (500 MHz, $CDCl_3$): same as **7** but N-H resonance is now a singlet at

δ 4.77. $^{2}H\{^{1}H\}$ NMR (61.39 MHz, $CHCl_3$): δ 3.65. IR (cm^{-1}): 3354 (m, ν_{N-H}), 1828 (m, ν_{B-D}).

Representative catalytic dehydrocoupling of $MeNH_2•BH_3$. A solution of IPr=N-BPhCl (**4**) (0.091 g, 0.093 mmol) in 2 mL of THF was added to $MeNH_2•BH_3$ (0.211 g, 4.70 mmol) in 1 mL of THF at room temperature. The Schlenk flask was attached to a nitrogen line and heated with an oil bath at 70 °C for 17 hours. The reaction mixture was allowed to cool to room temperature, the volatiles were removed, and the remaining colorless semi-solid was analyzed by ^{1}H and ^{11}B NMR in $CDCl_3$. The residue was then dissolved in 1.5 mL of THF and precipitated into 15 mL of hexanes at -35 °C. The mother liquor was decanted from the resulting precipitate and dried to give a white powder that was analyzed by ESI-MS and GPC.

2.5 X-ray Crystallographic Data

Table 2.2: Crystallographic Data for Compounds **2** - **5**.

Compound	(**2**)	(**3**)	(**4**)	(**5**)
formula	$C_{27}H_{36}BCl_2N_3$	$C_{54}H_{72}BClN_6$	$C_{33}H_{41}BClN_3$	$C_{39}H_{46}BN_3$
formula weight	484.30	851.43	525.95	567.60
cryst. dimens. (mm)	0.28 x 0.21 x 0.16	0.35 x 0.11 x 0.04	0.27 x 0.19 x 0.05	0.19 x 0.14 x 0.12
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*C*2/*c*	$P2_1/c$	*Pnma*	*C*2/*c*
a (Å)	17.1012 (4)	21.5933 (4)	17.6917 (6)	17.2297 (7)
b (Å)	9.1402 (2)	12.0430 (2)	17.4096 (6)	19.9930 (8)
c (Å)	17.2832 (4)	20.0683 (4)	10.0002 (3)	19.9782 (8)
β (deg)	91.1067 (15)	104.0691 (10)		92.208 (3)

V (Å^3)	2701.01 (11)	5062.18 (16)	3080.12 (18)	6876.8 (5)
Z	4	4	4	8
ρ_{calcd} (g cm^{-3})	1.191	1.117	1.134	1.096
μ (mm^{-1})	2.294	0.966	1.272	0.477
temperature (°C)	–100	–100	–100	–100
$2\theta_{max}$ (deg)	144.53	145.41	144.52	148.07
total data	8769	34379	14373	67301
unique data (R_{int})	2634 (0.0242)	9994 (0.0326)	3139 (0.0600)	6989 (0.1046)
obs [I > 2σ(I)]	2284	8662	2415	4984
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$] [a]	0.0644	0.0464	0.0496	0.0653
wR_2 [all data]	0.1814	0.1330	0.1518	0.1890
max / min Δr (e Å^{-3})	0.610/–0.383	0.212/ –0.284	0.232/–0.467	0.260/–0.185

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(Fo^4)]^{1/2}$.

2.6 Relevant Spectrum

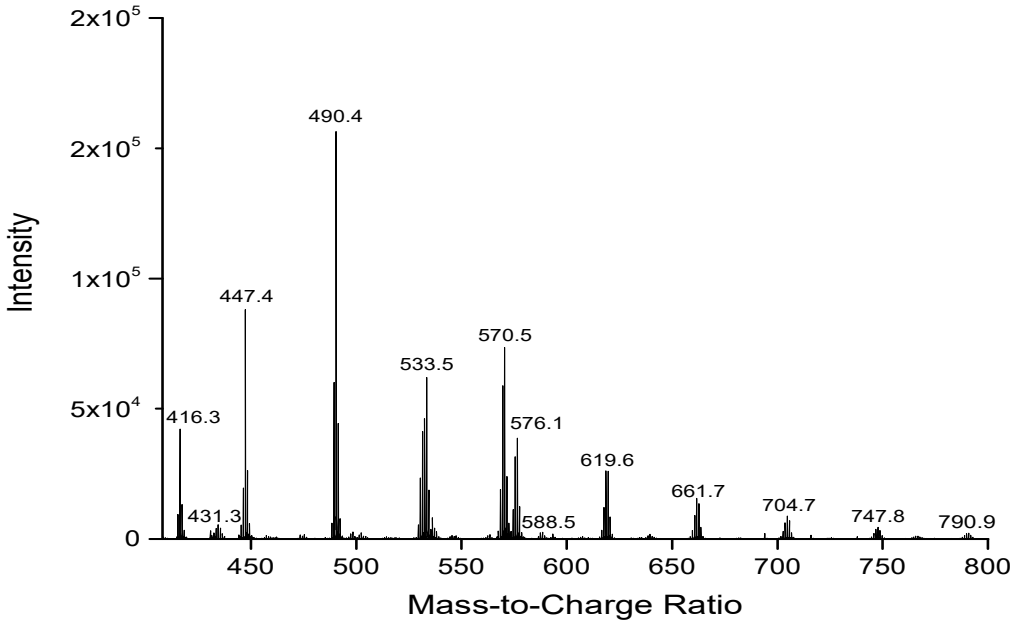


Figure 2.8. Mass Spectrum of $[MeNH\text{-}BH_2]_x$ from the reaction of IPr=N-B(Ph)Cl (**4**) and 50 equiv. of $MeNH_2 \bullet BH_3$. The peak at 570.5 m/z represents an unknown mass fragment.

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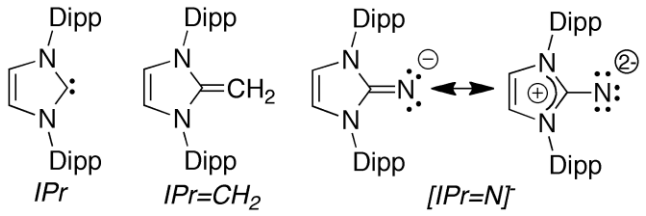
Chapter 3: Contrasting Reactivities of Silicon and Germanium Complexes Supported by *N*-Heterocyclic Imine Ligands

3.1 Introduction

The placement of sterically hindered aryl groups about an imidazole ring forms the structural basis of many widely used ligands, such as *N*-heterocyclic carbenes and their olefinic and imine counterparts. In this regard, the recently developed anionic iminato ligand $[IPr{=}N]^-$ (Scheme 3.1) is strongly electron donating with considerable proximal bulk, drawing parallels with ubiquitous Cp^- and phosphoraniminato R_3PN^- analogues.[1] Tamm and coworkers have used $[IPr{=}N]^-$ to prepare active metal catalysts for olefin polymerization[2] and alkyne metathesis,[3] while various low coordinate main group element species,[4] including the first stable monomeric phosphazene (L_2PN),[5] have been obtained using related *N*-heterocyclic imine donors. In general, the peripheral aryl substituents in the aforementioned ligands are considered to be inert, however in this Chapter it is demonstrated that N-C(Aryl) bond cleavage can transpire at room temperature under reducing conditions commonly employed for accessing low oxidation state inorganic species. [6, 7]



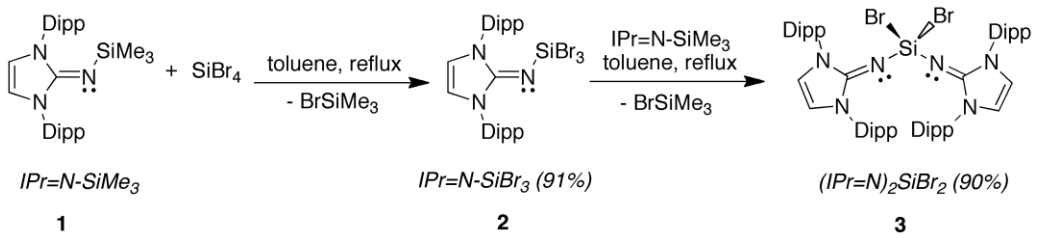
Scheme 3.1. Representative ligands featuring flanking ring-bound *N*-aryl substituents: IPr, IPr=CH_2 and $[IPr=N]^-$ with salient canonical forms presented (IPr = $[(HCNDipp)_2C:]$; Dipp = 2,6-$^i Pr_2C_6H_3$]).

Motivated by our group's earlier work involving the isolation of low oxidation state Group 14 species, including the syntheses of inorganic methylene EH_2 and ethylene H_2EEH_2 complexes (E = Si, Ge and/or Sn), [8] the use of the sterically encumbered $[IPr=N]^-$ ligand to gain access to the possibly monomeric silylenes and germylenes $:E(N=IPr)_2$ (E = Si and Ge) was explored. In line with prior work, [9] these species could possibly activate small molecules (*e.g.* H_2, NH_3 or CO) and contribute to the advancement of the burgeoning concept of main group element catalysis.[9f] As will be seen, a monomeric germylene was successfully obtained, however a rare process was unconvered in the case of silicon whereby ligand activation via reproducible *N*-C(aryl) bond scission occurred.

3.2 Results and Discussion

The planned route to the silylene $:Si(N=IPr)_2$ began with the synthesis of the dibromosilane $(IPr=N)_2SiBr_2$ (**3**) (Scheme 3.2). In order to install *N*-heterocyclic imine functionality at silicon, two equivalents of the known silylated imine $IPr=NSiMe_3$ (**1**)[1a] were combined with $SiBr_4$ in refluxing

toluene; in place of obtaining pure $(IPr{=}N)_2SiBr_2$ (**3**), the resulting product mixture was contaminated with the mono-substituted analogue $IPr{=}N\text{-}SiBr_3$ (**2**), which proved difficult to separate from **3** by fractional crystallization. Therefore a step-wise approach to **3** was conducted wherein $IPr{=}N\text{-}SiBr_3$ (**2**) was first prepared from an equimolar ratio of $IPr{=}N\text{-}SiMe_3$ (**1**) and $SiBr_4$ (Figure 3.1); treatment of **2** with added $IPr{=}NSiMe_3$ (**1**) then afforded $(IPr{=}N)_2SiBr_2$ (**3**) as an orange solid in a 90 % yield.



Scheme 3.2. Synthesis of the dibromosilane **3** with isolated yields in parentheses.

Both $IPr{=}N\text{-}SiBr_3$ (**2**) and $(IPr{=}N)_2SiBr_2$ (**3**) were obtained as pale yellow crystalline solids and structurally authenticated by X-ray crystallography; their structures are presented as Figures 3.1 and 3.2, respectively.[11] The presence of two electron releasing $IPr{=}N^-$ units in $(IPr{=}N)_2SiBr_2$ (**3**) leads to substantial elongation of the Si-N bonds [average value of 1.642(2) Å] by ca. 0.07 Å relative to the corresponding Si-N distance in the mono-imine $(IPr{=}N)SiBr_3$ (**2**). In addition, the Si-Br bonds in **3** lie within a deep steric pocket formed by the flanking hindered IPr=N residues (Figure 3.2). Notably, the ^{29}Si NMR spectrum of $(IPr{=}N)_2SiBr_2$ (**3**)[11] shows coupling between Si and proximal ^{14}N nuclei (I = 1) to yield a pentet resonance at -21.9

ppm, and the associated $^{1}J_{Si\text{-}14N}$ value (7.4 Hz) lies within the range typically found for Si-N single bonds (6.4 to 8.1 Hz).[12]

With $(IPr{=}N)_2SiBr_2$ (**3**) in hand, various reductive routes towards the target silylene $:Si(N{=}IPr)_2$ were explored. To our initial surprise, $(IPr{=}N)_2SiBr_2$ (**3**) did not react with either (Figure 3.2). sodium or potassium metal, nor with Jones' Mg(I) reducing agent $[(^{Mes}nacnac)Mg]_2$ ($^{Mes}nacnac = [HC(MeCNMes)_2]^-$; Mes = 2,4,6-$Me_3C_6H_2$)[13] at room temperature in either toluene, THF or Et_2O. In addition, compound **3** remained unchanged in the presence of excess Na in refluxing toluene (three days) and the Si-Br residues in **3** did not react with either an excess of $Li[AlH_4]$ or two equiv. of MeLi in THF. Thus it appears that the two flanking IPr=N units in **3** collectively serve to create a significant steric shield which limits access to the Si center by nucleophiles. Moreover computational studies on **3** reveal that the electron releasing nature of the $IPr{=}N^-$ ligands raise the Si-Br σ^* orbitals to a high energy LUMO+8 state (*ca.* 5.7 eV above the HOMO) making nucleophilic attack more difficult.

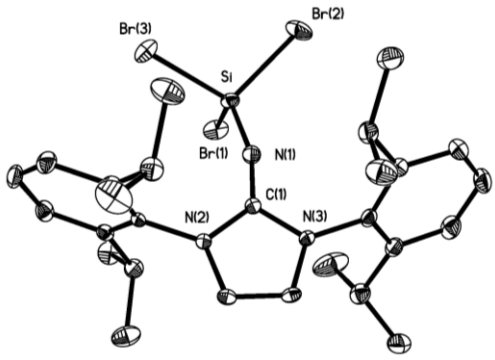


Figure 3.1. Molecular structure of **2** with thermal ellipsoids at the 30 % probability level. Hydrogen atoms and toluene solvate have been omitted for clarity. Selected bond lengths (Å) and angles (°): Si-Br 2.2123(9) to 2.2232(9), Si-N(1) 1.583(2), N(1)-C(1) 1.290(3); Br-Si-Br 104.81(4) to 105.45(4), Br-Si-N 111.16(10) to 116.52(10), Si-N(1)-C(1) 163.0(2).[11]

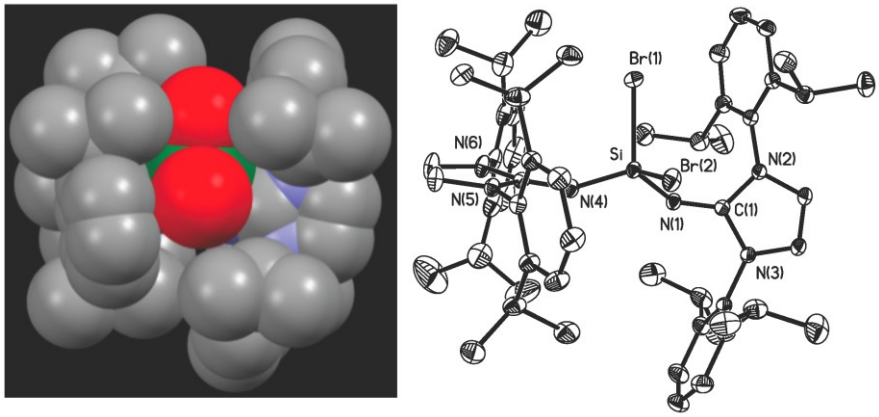
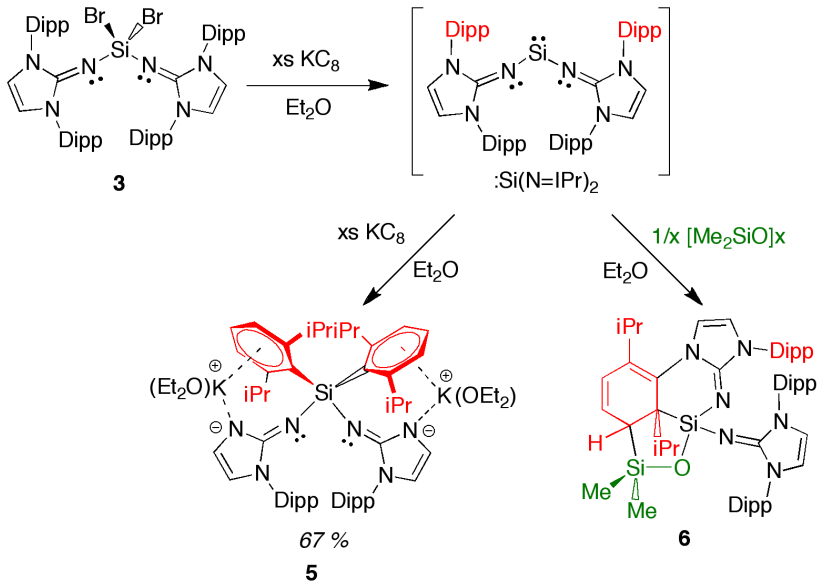


Figure 3.2. Space-filling model (C = grey, N = blue, Si = green, Br = red), and molecular structure of $(IPr{=}N)_2SiBr_2$ **3** with thermal ellipsoids at the 30 % probability level; all hydrogen atoms and fluorobenzene solvate have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Si-Br(1) 2.2635(5), Si-Br(2) 2.2664(5), Si-N(1) 1.6462(14), Si-N(2) 1.6377(14), N(1)-C(1) 1.281(2), N(4)-C(4) 1.276(2); Br(1)-Si-Br(2) 100.490(18), Si-N(1)-C(1) 139.97(12), Si-N(4)-C(4) 146.61(12), N(1)-Si-N(4) 112.72(7).

When compound **3** was combined with 2 equiv. of sodium naphthalenide ($Na[C_{10}H_8]$), analysis of the resulting product mixture by ^1H NMR spectroscopy after 2 days revealed the presence of unreacted **3** (85 %) and a new product with a complicated series of Dipp resonances, suggesting that activation of the $[IPr{=}N]^-$ ligands had occurred. When 4 equiv. of $Na[C_{10}H_8]$ in THF was added to **3**, the activation product (**4**; of likely analogous structure as the dipotassium salt **5** depicted in Scheme 3.3) was produced in *ca.* 90 % spectroscopic yield, however X-ray quality crystals could not be obtained. By repeating the reduction of **3** with excess KC_8 (8 equiv.) a product with similar NMR spectral features as the above mentioned ligand activation product could be isolated and identified as the dipotassium salt (**5**); furthermore, this product was characterized by X-ray crystallography (Figure 3.3). Attempts to trap the putative silylene $:Si(N{=}IPr)_2$ during the reduction of **3** in the presence of exogenous Lewis bases (*e.g.* IPr or ^{t}BuCN) were unsuccessful; IPr appears to be too bulky of a nucleophile to coordinate to the vacant p orbital that would be expected to be present if the silylene $[:Si(N{=}IPr)_2]$ was generated, while ^{t}BuCN reacted preferentially with the KC_8 in the reaction mixture. In addition, we attempted to prepare $[:Si(N{=}IPr)_2]$ via combining $IPr{=}N\text{-}SiMe_3$ and $IPr{\bullet}SiCl_2$[14] in a 2:1 ratio in toluene at room temperature or reflux, however inseparable product mixtures were obtained in both cases.



Scheme 3.3. Synthesis of the ligand activated product **5** and the siloxane co-product **6** via the reduction of **3** with KC_8.

Compound **5** can be obtained as a bright yellow solid from $(IPr{=}N)_2SiBr_2$ (**3**)/KC_8 mixtures in isolated yields as high as 67 % after crystallization. We have been able to prepare two distinct adducts of **5**[11] by crystallizing this dipotassium salt from either Et_2O or toluene. Figure 3.3 contains the refined structure of **5•(Et$_2$O)$_2$** and indicates that one Dipp group within each IPr=N unit is cleaved from the imidazoline ring and transferred to the central Si atom. This process leads to the formation of two anionic ring-positioned nitrogen atoms; the accompanying K^+ ions are held in close proximity to the cleaved imino-imidazoline arrays via short N---K^+ contacts [*ca.* 2.70-2.77 Å] along with discernable K^+---aryl interactions involving both activated and unactivated Dipp groups [*ca.* 3.00-3.20 Å]. Related alkali metal-aryl interactions are commonly observed in terphenyl ligand-supported main group element species and could provide added stabilization to **5**.[16] The Si-N

bonds in **5•(Et$_2$O)$_2$** are significantly lengthened [1.7158(12) Å] with respect to the related bond lengths in **3** [1.631(5) Å avg.] and this effect could be partially due to a reduction in N(p)→Si-E(σ*) hyperconjugative interactions (E = element) in the dianion **5•(Et$_2$O)$_2$**. The exocyclic C(1)-N(1) and C(1A)-N(1A) distances within the Dipp-cleaved imidazoline-imine units in **5•(Et$_2$O)$_2$** [1.3269(14) Å] are slightly longer than in **3** [1.279(3) Å *avg.*].

The cleavage of *N*-bound alkyl substituents within an *N*-heterocyclic carbene (NHC) ligand has been reported for both early and late transition metal complexes.[17] However there are only two other very recent and relevant examples of Dipp-group cleavage/migration from an *N*-heterocyclic ligand. The first transpired under reducing conditions where a Dipp-group migrated from a cyclic alkyl(amino)carbene ligand to a proximal silicon atom.[7a] The second example involved the thermally-induced migration of a Dipp group within an [SIPr=N]$^-$ ligand ([SIPr=N]$^-$ = [(H$_2$CNDipp)$_2$C=N$^-$]) to a phosphorus center within the phosphazene complex [SIPr=N]$_2$PN.[7b] Accordingly the unusual ligand activation process leading to the formation of **5** was investigated by computational methods at the B3LYP/6-31G(2d,p) level of theory.

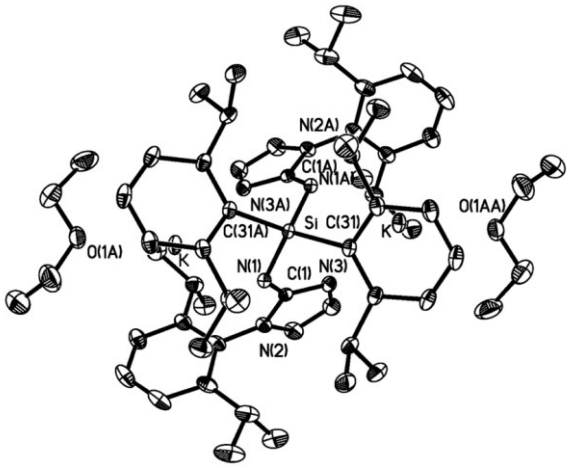


Figure 3.3. Molecular structure of **5•(Et$_2$O)**$_2$ with thermal ellipsoids at the 30 % probability level; all hydrogen atoms have been omitted for clarity. The molecule is situated on a crystallographic twofold rotational axis upon which the Si atom is located. Selected bond lengths [Å] and angles [°]: Si-N(1) 1.7158(12), N(1)-C(1) 1.3269(19), C(1)-N(2) 1.4093(19), C(1)-N(3) 1.3543(19), K---N(1) 2.7013(12), K---N(3A) 2.7686(15); N(1)-Si-N(1A) 115.31(8), C(31)-Si-C(31A) 113.55(9), Si-N(1)-C(1) 119.49(10).[11]

To begin, the structure of the possible silylene intermediate :Si(N=IPr)$_2$ that could be formed en route to **5** was computed.[11] The HOMO for this species contains C-N π-bonding contributions from the exocyclic imino groups within the IPr=N ligands along with pronounced non-bonding (lone pair) electron density at silicon: 74 % s-character according to NBO analysis. The LUMO in :Si(N=IPr)$_2$ (Figure 3.4) has C-C anti-bonding character on the Dipp groups, along with p-orbital contribution localized on Si. The singlet state for :Si(N=IPr)$_2$ was computed to be 44.5 kcal/mol lower in energy than the corresponding triplet state. For comparison, a singlet-triplet gap of *ca.* 98 kcal/mol was computed for :Si(SAr^{Mes})$_2$ (Ar^{Mes} = 2,6-Mes$_2$C$_6$H$_3$),[9b] while the

more reactive amido(boryl) silylene {Dipp(Me$_3$Si)N}Si{B(NDippCH)$_2$}, which spontaneously activates H_2, has a smaller computationally-derived $\Delta E_{S\text{-}T}$ of *ca.* 25 kcal/mol.[9a]

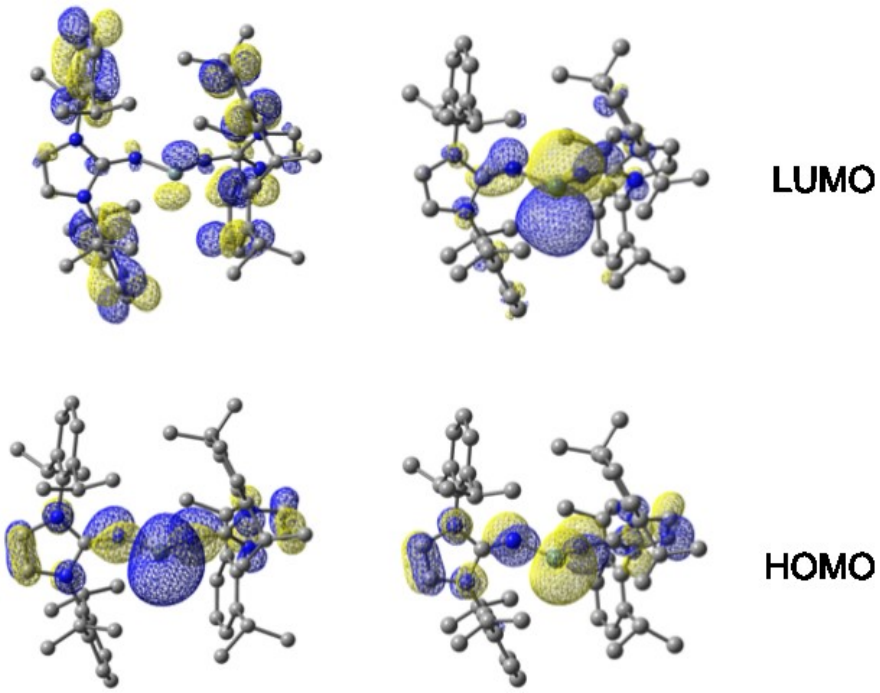
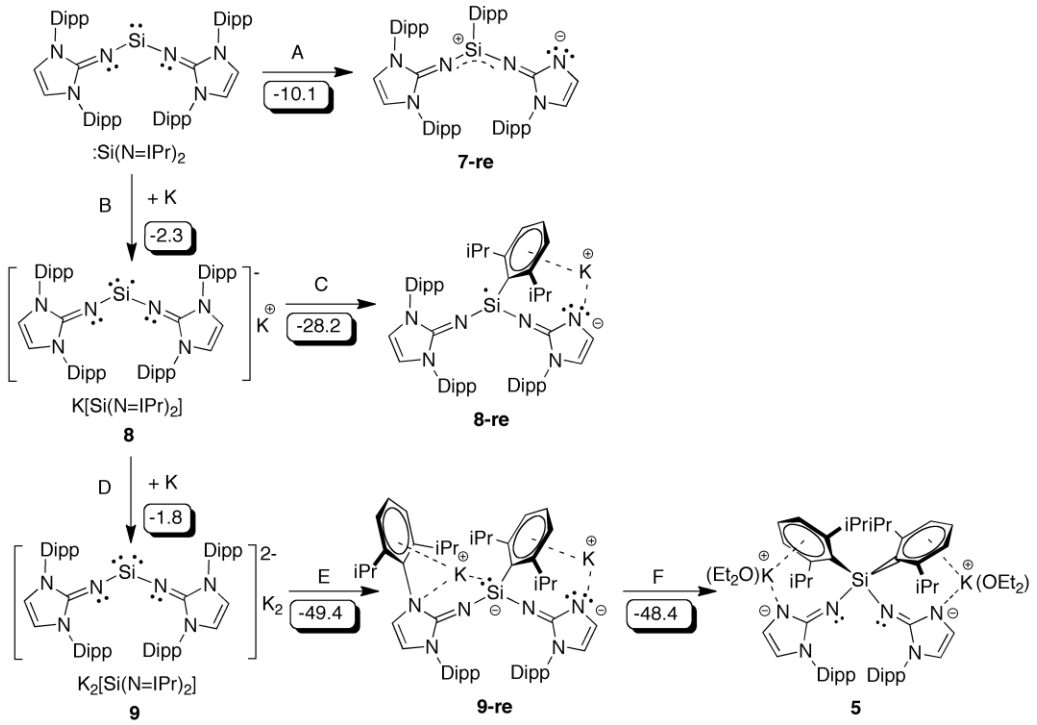


Figure 3.4. Computed HOMO (bottom) and LUMO (top) for :Si(IPr=N)$_2$ (left) and :Ge(IPr=N)$_2$ (right).

Various pathways to the Dipp-cleavage product **5** starting from :Si(N=IPr)$_2$ were examined by density functional theory (DFT) (Scheme 3.4) in the gas phase with the inclusion of an Et$_2$O polarized continuum model (PCM).[11] It was found that the direct rearrangement of :Si(N=IPr)$_2$ into the zwitterionic species, **7-re** was exoergic (ΔG = -10.1 kcal/mol; Scheme 3.4). However the computed activation barrier for the direct Dipp group migration from N to Si was prohibitively high (ca. 45 kcal/mol), suggesting that further reduction was required prior to rearrangement. Unfortunately significant

difficulties were encountered when attempting to locate transition states and measure the activation barriers associated with the migration of a Dipp group within the reduced species K[Si(N=IPr)$_2$] and K$_2$[Si(N=IPr)$_2$ (**8** and **9**; Scheme 3.4). In each case no plausible reaction coordinate could be found, suggesting that potassium ion dissociation and/or migration might be required for Dipp transfer to occur.[18] On the basis of energetics, it is evident that Dipp group migration becomes increasingly thermodynamically favorable as the silicon complexes become reduced (Scheme 3.4). For example, the isomerization of K$_2$[Si(N=IPr)$_2$] **9** to the Dipp activated product **9-re** has a ΔG value of -43.5 kcal/mol, thus further reduction of :Si(N=IPr)$_2$ is likely required for Dipp group activation.[7] A similar aryl group cleavage/migration process was recently reported by Roesky and coworkers. In line with our computational results, they noted that the stable Si(0) complex, formally (Cy-CAACSi=Si(CyCAAC) (Cy-CAAC = [:CN(Dipp)CMe$_2$CH$_2$C(CH$_2$)$_5$]) reacts with potassium metal to yield a product wherein N-C(Dipp) bond scission and migration of the Dipp group to a Si center occurs; again this transformation appears to be triggered by reduction.[7a]



Scheme 3.4. Computed [B3LYP/6-31G(2d,p)][11] pathways (**A-F**) for the possible synthesis of **5** from :Si(N=IPr)$_2$ with free energies associated for each process with an Et_2O solvation model listed in kcal/mol.

In addition to obtaining **5** from the reaction mixture, a few crystals of the "Me_2SiO" addition product **6** (Scheme 3.2) were isolated, which represents the formal activation of silicone grease by a transiently produced silylene :Si(N=IPr)$_2$. [11, 15] Attempts to obtain **6** in a reproducible manner by conducting the reduction of **3** with excess KC_8 in the presence of added silicon grease or the cyclic species $[Me_2SiO]_3$ and $[Me_2SiO]_4$ were unsuccessful. Instead, preferential reactivity of the poly- and cyclosiloxanes with KC_8 transpired to give products that were consistent with the formation of anionic oligosiloxanes (*e.g.* $K_2[O\text{-}(SiMe_2)_x\text{-}O]$).[15d] The formal addition of a "Me_2SiO" unit to [:Si(N=IPr)$_2$] led to dearomatization of one Dipp aryl ring, as evidenced by

bond elongation of C(12) - C(13) to 1.526(2) Å, which is characteristic of a C-C single bond. The energy penalty associated with loss of aromaticity may be offset by the formation a strong Si-O single bond with Si(1).

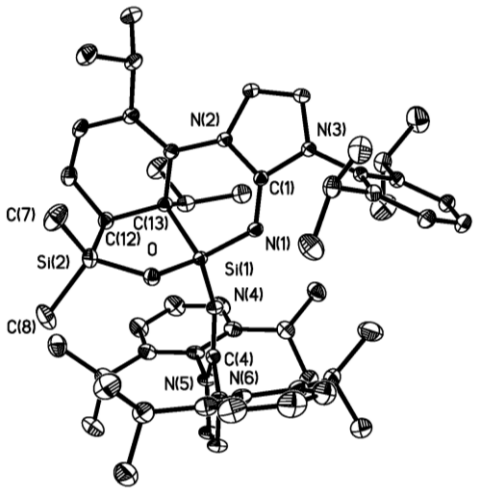


Figure 3.5. Molecular structure of **6** with thermal ellipsoids at the 30 % probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)-O 1.6567(12), Si(2)-O 1.6409(13), Si-N(1) 1.7015(13), Si(1)-N(4) 1.6639(13), Si(1)-C(13) 1.9311(15) Si(2)-C(12) 1.9072(18); O-Si(1)-N(1) 113.37(6), O-Si(1)-N(4) 110.03(6), O-Si(1)-C(13) 101.06(7), N(1)-Si-N(4) 114.28(7), N(1)-Si(1)-C(13) 107.60(6), Si(1)-O-Si(2) 116.00(7).

In general, the synthesis of low oxidation state Ge species is more facile than its lighter congener Si.[21] In order to gain insight into the above reduction chemistry involving $(IPr{=}N)_2SiBr_2$ (**3**), we treated the structurally related dihalogermane $(IPr{=}N)_2GeCl_2$ (**11**) with 2.5 equiv. of $Na[C_{10}H_8]$. Instead of observing ligand activation, the target germylene $:Ge(N{=}IPr)_2$ (**12**) was isolated as a highly air- and moisture- sensitive yellow crystalline solid in a 40 % yield (Scheme 3.5; Figure 3.9). The lower isolated yield occurs as a result of the

recrystallization of the product in order to separate out the naphthalene and minor amounts of unreacted starting material, since these compounds have similar solubilities in common organic solvents. Attempts to directly prepare **12** via the condensation reaction between two equiv. of IPr=$NSiMe_3$ (**1**) and $GeCl_2$•dioxane in refluxing toluene yielded mostly starting material (**1**) and 15 % of $(IPr{=}N)_2GeCl_2$ (**11**), suggesting that some disproportionation occurred during the course of the reaction. Efforts to access **12** with the known salt Li[N=IPr][10] (**13**) was also unsuccessful, with similar disproportionation being observed. Compound **13** was not previously characterized by X-ray crystallography, and its solid state structure, which features a dimeric form is described in Figure 3.6.

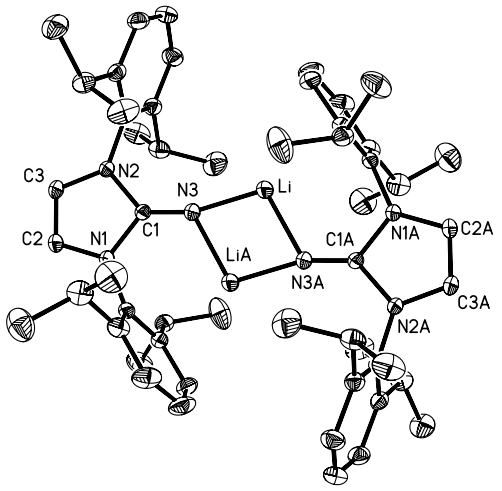
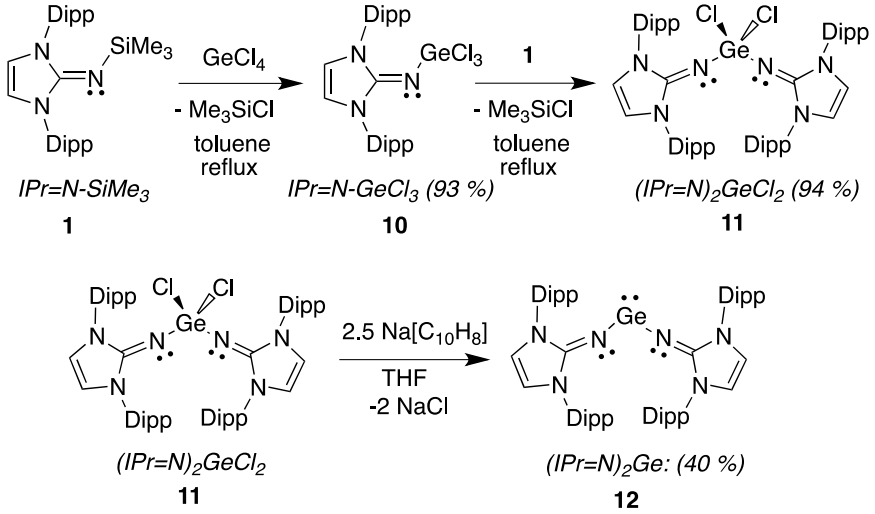


Figure 3.6. Molecular structure of $[Li(N{=}IPr)]_2$ (**13**) with thermal ellipsoids at the 30 % probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Li-N(3) 1.853(2), Li(A)-N(3) 1.984(2), Li-Li(A) 2.385(4), N(3)-C(1) 1.2425(14); N(3)-Li-N(3A) 76.74(9), C(1)-N(3)-Li 162.74(10), C(1)-N(3)-Li(A) 120.45(9).

The germylene :Ge(N=IPr)$_2$ (**12**) is stable for at least one week in arene solvents (at 25 °C), and also survives under refluxing C_6D_6 for a few hours; however heating **12** in the solid state to 55 °C leads to its decomposition into free IPr=NH (as determined by ^{1}H, and ^{13}C{^{1}H} NMR spectroscopy) and unidentified insoluble products. Compound **12** was also characterized by single X-ray crystallography (Figure 3.9). The Ge-N bonds in **12** are 1.819(15) Å (*avg.*), which represents an increase of *ca.* 0.06 Å and 0.009 Å relative to the corresponding distances in (IPr=N)$_2$GeCl$_2$ (**11**) and (IPr=N)GeCl$_3$ (**10**), respectively. Moreover, the N-Ge-N angle also decreased from 106.33(7)° in **11** to 99.48(10)° in **12**, indicating an increase in p-character within the N-Ge bonds in **12**. When **12** was combined with an excess (2-4 equiv.) of the reducing agents KC$_8$ or Na[C$_{10}$H$_8$], a complicated product mixture was identified by ^{1}H NMR spectroscopy with no sign of the characteristic signal patterns one would expect if a Ge congener of **5** was obtained.



Scheme 3.5. Synthesis of the germylene **12** with isolated yields in parentheses.

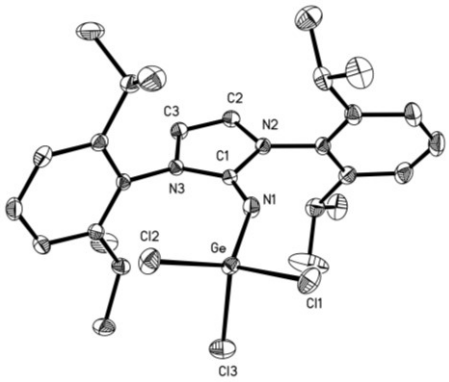


Figure 3.7. Molecular structure of **10** with thermal ellipsoids at the 30 % probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ge-Cl(1) 2.1354(4), Ge-N(1) 1.7310(11), N(1)-C(1) 1.2972(17); Cl(1)-Ge-Cl(2) 103.361(16), Cl(1)-Ge-N(1) 105.53(4), Ge-N(1)-C(1) 139.43(10).

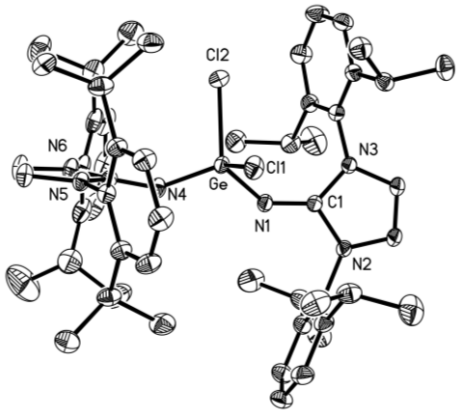


Figure 3.8. Molecular structure of **11** with thermal ellipsoids at the 30 % probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ge-Cl(1) 2.1862(5), Ge-N(1) 1.7582(14), N(1)-C(1) 1.288(2); Cl(1)-Ge-Cl(2) 99.47(2), Cl(1)-Ge-N(1) 105.36(5), Ge-N(1)-C(1) 133.48(12).

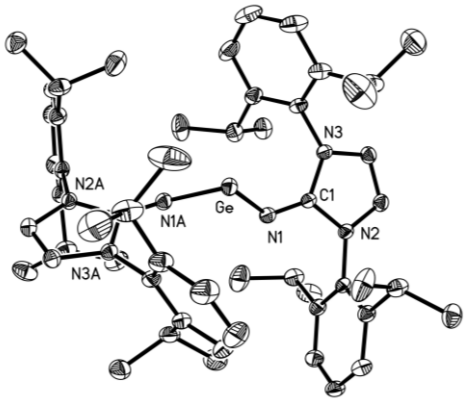


Figure 3.9. Molecular structure of $(IPr{=}N)_2Ge$: (**12**) with thermal ellipsoids at the 30 % probability level. All hydrogen atoms and 4.5 % occupancy of co-crystallized **11** have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge-N(1) 1.8194(15), N(1)-C(1) 1.273(2); N(1)-Ge-N(1A) 99.48(10), Ge-N(1)-C(1) 131.21(13).

The germylene [$:Ge(N{=}IPr)_2$] (**12**) was also examined by DFT calculations. As shown in Figure 3.4, both the HOMOs of $:Si(N{=}IPr)_2$ and $:Ge(N{=}IPr)_2$ (**12**) show similar orbital contributions, with significant electron density positioned on the Si and Ge atoms in the form of a lone pair; as expected, NBO analysis revealed a slight increase in s-character within the lone pair at Ge in **12** (83 %) in relation to $:Si(N{=}IPr)_2$ (74 %). On the other hand, the LUMOs of these two species are noticeably different in the amount of orbital participation from the N-bound Dipp substituents. For the LUMO of the silylene $:Si(N{=}IPr)_2$, there is significant orbital participation from the ligand aryl groups, while the IPr=N ligand contributes minimally to the LUMO for $:Ge(N{=}IPr)_2$ (**12**). The reduction of the germylene to give first the mono radical anion $K[Ge(N{=}IPr)_2]$ and then the dianion $K_2[Ge(N{=}IPr)_2]$ were computed to be less favorable (ΔG = -2.7 and -7.3 kcal/mol, respectively) in relation to the

silicon congener, :Si(N=IPr)$_2$. Thus, it appears that the lack of suitable low-lying ligand-based orbitals (*e.g.* LUMO) in :Ge(N=IPr)$_2$ renders ligand activation less feasible than with :Si(N=IPr)$_2$.

Interestingly, we noted a similar singlet-triplet gap for :Ge(N=IPr)$_2$ (**12**) (45.8 kcal/mol) as in :Si(N=IPr)$_2$ (44.5 kcal/mol). These values suggest that the germylene could react with H_2.[9a, b] Accordingly, :Ge(N=IPr)$_2$ (**12**) reacts rapidly with molecular hydrogen in Et_2O,[9] however the only soluble product obtained was IPr=NH, suggesting that the initially expected product, H_2Ge(N=IPr)$_2$, is unstable.[19] There is also an insoluble solid formed in this reaction, which is presumed to be elemental germanium. The analogous reaction of **12** with D_2 resulted in the formation of IPr=ND. In line with our experimental observations, our computations show that the addition of H_2 to :Ge(N=IPr)$_2$ to form H_2Ge(N=IPr)$_2$ has a favorable ΔG value of -9.3 kcal/mol in the gas phase. With the goal of directly obtaining the possible intermediate H_2Ge(N=IPr)$_2$, the reaction of (IPr=N)$_2$GeCl$_2$ (**11**) with various hydride sources was explored. When (IPr=N)$_2$GeCl$_2$ and potassium hydride (2 equiv.) were combined at room temperature in THF for four days, we obtained 40 % IPr=NH and 60 % of unreacted starting material **11** according to ^{1}H NMR spectroscopy. Compound **11** also reacted with 2 equiv. of K[HB^{s}Bu$_3$] to give a compound with ^{1}H NMR resonances that are slightly shifted compared to that of IPr=NH (by *ca.* 0.01 to 0.03 ppm). This may be due to a weak interaction of IPr=NH with the Lewis acidic byproduct tri-s-butyl borane, ^{s}Bu$_3$B; a broad signal at 84.8 ppm was also noted in the ^{11}B NMR spectrum of the crude mixture, as expected for a three-coordinate borane.[20] IR spectroscopy yielded a weak

signal at 3329 cm^{-1}, which is characteristic of an N-H stretch and there was no evidence of the expected Ge-H vibrations around 1900 cm^{-1} (which would be present if $H_2Ge(N{=}IPr)_2$ had formed). Separation of the IPr=NH from $^{s}Bu_3B$ was not possible by fractional crystallization due to their similar solubilities in organic solvents, however $^{s}Bu_3B$ can be removed by passing a toluene solution of the product mixture through a short plug of silica gel (under nitrogen) leaving pure HN=IPr.[1a] Therefore it appears that the target germane $H_2Ge(N{=}IPr)_2$ is unstable under the synthetic conditions employed and readily decomposes to yield Ge metal and the imine HN=IPr.

3.3 Conclusions

A monomeric germylene supported by two sterically encumbered $[IPr{=}N]^-$ ligands was successfully isolated and spontaneous reactivity with hydrogen gas was noted. Attempts to prepare the corresponding silylene $:Si(N{=}IPr)_2$ led to the reductive cleavage of *N*-bound aryl (Dipp) substituents with transfer to a proximal Si center. Computations show that this rearrangement process becomes more favorable as reduction to Si(I) and Si(0) states occurs, thus one should be aware of such ligand activation processes when *N*-heterocyclic frameworks are utilized to support low oxidation state inorganic chemistry.

3.4 Experimental Section

3.4.1 General.

All reactions were performed in an inert atmosphere glove box (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[22] manufactured by Innovative Technologies, Inc., degassed (freeze-pump-thaw method) and stored under an atmosphere of nitrogen prior to use. $SiBr_4$, sodium cubes, potassium cubes, naphthalene, potassium hydride, $K[HB^sBu_3]$ (1.0 M in THF), and $Li[AlH_4]$ were purchased from Aldrich, while $GeCl_4$ was purchased from Strem; all of these reagents were used as received. Fluorobenzene was purchased from Aldrich, dried over calcium hydride overnight and then distilled under nitrogen. The hydrogen gas (99.995 %, pre-purified) was purchased from Praxair and used as received. The deuterium gas (99.7 %, CP grade) was purchased from Matheson and dried by passage through a column packed with activated aluminum prior to use. IPr=N-$SiMe_3$[23] (IPr = $[(HCNDipp)_2C:]$; Dipp = 2,6-$^iPr_2C_6H_3$]), KC_8[24] and $[Li(IPr{=}N)]_2$[10] were prepared following literature procedures. ^1H, $^{13}C\{^1H\}$, ^{29}Si NMR spectra were recorded on a Varian VNMRS-500 spectrometer and referenced externally to $SiMe_4$; ^{11}B NMR was referenced to $F_3B{\bullet}OEt_2$. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded on a Nicolet IR100 FTIR spectrometer as Nujol mulls between NaCl plates. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

3.4.2 X-ray Crystallography.

Crystals for X-ray diffraction studies were removed from a vial (in a glove box) and immediately coated with thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fiber, and quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer. [25] All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα or Cu Kα radiation, with the crystals cooled to -100 °C. The data were corrected for absorption through Gaussian integration from the indexing of the crystal faces. Crystal structures were solved using either direct methods[26] (SHELXS-97; compounds **2** and **5•(Et$_2$O)$_2$**), intrinsic phasing (SHELXT; compounds **3**, **5•(tol)$_2$**, **10** , **11** and **12**), [26] and direct methods/dual space (SHELXD; compound **6** and [Li(N=IPr)]$_2$[10] and refined using SHELXS-97. [27] The assignment of hydrogen atoms positions were based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20 % greater than those of their parent atoms.

Special Refinement Conditions. *Compound **2***: A rigid-bond restraint was used on the inversion-disordered solvent toluene molecule.

*Compound **5•(Et$_2$O)$_2$***: The O–C and C–C distances within the minor orientation of the disordered diethyl ether were restrained to be the same by use of the *SHELXL* SADI instruction.

*Compound **5•(tol)$_2$***: The disordered toluene molecule was constrained to be an idealized hexagon with C–C distances of 1.39 Å and distance between the methyl and ortho carbon atoms was restrained to be 2.50(1) Å. The sum of the

occupancies of the three disordered toluene orientations was restrained to be 1.0000(1).

*Compound **12***: This crystal contained 95.5% of **12** and a contaminant 4.5% of unreacted precursor **11**.

3.4.3 Computational Methods.

All calculations were carried out using the Gaussian 09 Rev. C.01 software package.[28] Input structures were taken from the crystal structures when possible. The geometries were optimized at the B3LYP/6-31G(2d,p) level of theory in the gas phase with tight convergence criteria and an ultrafine integration grid. Potential reaction intermediates (*e.g.* **8**, **9** etc...; Scheme 4.4) were subsequently generated based on related structures, and their geometries were optimized at the same level of theory. All optimized structures were then confirmed to be local energy minima on the potential energy surface by frequency analysis. The energy differences ΔE_{gas} and ΔG_{gas} (at standard conditions 1 atm, 298 K) refer to the zero-point energy corrected electronic energy and the Gibbs free energy in the gas phase. In order to account for the polar solvent environment, the relative energy differences ΔE_{PCM} were calculated based on single-point energy calculations at the B3LYP/6-31G(2d,p) level of theory which employed the integral equation formalism version of the polarizable continuum model (IEFPCM) for diethyl ether.[29]

3.4.4. Synthetic Procedures

Synthesis of IPr=N-SiBr$_3$ (2). A solution of IPr=N-SiMe$_3$ (0.755 g, 1.59 mmol) in 10 mL of toluene was added to SiBr$_4$ (197.9 μL, 1.587 mmol) dissolved in 2 mL of toluene, and the resulting mixture was stirred and heated to reflux at 120 °C overnight to give a slightly cloudy, orange mixture. This reaction can also be done in a sealed, partially evacuated Teflon-capped, thick-walled glass Schlenk flask with heating to 120 °C. The precipitate was allowed to settle and the mother liquor was isolated after filtration. Removal of the volatiles from the mother liquor afforded **2** as a yellow powder (0.974 g, 92 %). Crystals suitable for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of **2** in toluene. ^{1}H NMR (500 MHz, C_6D_6): δ 1.10 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.42 (d, $^3J_{HH}$ = 6.5 Hz, 12H, CH(C*H*$_3$)$_2$), 2.91 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 5.92 (s, 2H, N-C*H*-), 7.10 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar-*H*), 7.47 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 23.5 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 115.7 (-N-*C*H-), 124.4 (Ar-*C*), 130.5 (Ar-C), 132.7 (Ar-*C*), 142.8 (Ar-*C*), 147.1 (N-*C*-N). ^{29}Si NMR (80 MHz, C_6D_6): δ -121.4. Mp (°C): *ca.* 125 °C (decomp., turns brown). Anal. Calcd. for $C_{27}H_{36}N_3Br_3Si$: C, 48.37; H, 5.41; N, 6.27. Found: C, 49.57; H 5.52; N, 5.98.

Synthesis of (IPr=N)$_2$SiBr$_2$ (3). A solution of IPr=N-SiMe$_3$ (0.433 g, 0.910 mmol) in 10 mL of toluene was added to a solution of IPr=N-SiBr$_3$ (0.610 g, 0.910 mmol) in 8 mL of toluene and the resulting mixture was stirred and heated to reflux overnight at 120 °C to give a slightly cloudy, orange

mixture. This reaction can also be done in a thick-walled sealed, partially evacuated Teflon-capped, glass Schlenk flask with heating to 120 °C. The precipitate was allowed to settle and the mother liquor was isolated after filtration. Removal of the volatiles from the mother liquor afforded **3** as a pale yellow powder (0.814 g, 90 %). Crystals suitable for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of **3** in fluorobenzene. ^{1}H NMR (500 MHz, C_6D_6): δ 1.11 (d, $^{3}J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 1.27 (d, $^{3}J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 3.06 (septet, $^{3}J_{HH}$ = 7.0 Hz, 8H, CH(CH$_3$)$_2$), 5.90 (s, 4H, N-CH-), 7.10 (d, $^{3}J_{HH}$ = 7.5 Hz, 8H, Ar-H), 7.22 (t, $^{3}J_{HH}$ = 8.0 Hz, 4H, Ar-H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 23.9 (CH(CH$_3$)$_2$), 25.2 (CH(CH$_3$)$_2$), 28.9 (CH(CH$_3$)$_2$), 115.4 (-N-CH-), 124.1 (Ar-C), 129.5 (Ar-C), 134.5 (Ar-C), 143.8 (Ar-C), 147.6 (N-C-N). ^{29}Si NMR (80 MHz, C_6D_6): δ -21.9 (pentet, $^{1}J_{NSi}$ = 7.4 Hz). Mp (°C): *ca.* 150 °C (decomp., turns brown). Anal. Calcd. for $C_{54}H_{72}N_6Br_2Si$: C, 65.31; H, 7.31; N, 8.46. Found: C, 65.06; H, 7.36; N, 8.49.

Synthesis of Compound 5. In a Schlenk flask, a solution of (IPr=N)$_2$SiBr$_2$ (0.416 g, 0.419 mmol) in 40 mL diethyl ether was added to excess KC_8 (0.431 g, 3.19 mmol). The resulting mixture was stirred at room temperature for three days. The precipitate was allowed to settle and the mother liquor was filtered through a glass fiber tipped cannula. Removal of the volatiles from the filtrate afforded a crude orange powder (0.175 g). Purification was accomplished by washing the crude product with hexanes (3 x 4 mL). The resulting solid was dried under vacuum to give **5** as a yellow solid

(0.161 g, 42 %). Crystals of **5** of suitable quality for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of **5** in Et_2O/hexanes (**5•(Et$_2$O)$_2$**) or toluene (**5•(tol)$_2$**). In one preparation, a few crystals of **6** were obtained from a cooled Et_2O/hexanes solution containing the crude product mixture. Experimental data for **5:** ^{1}H NMR (500 MHz, C_6D_6): δ 0.56 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.01 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.44 (two overlapping doublets, $^3J_{HH}$ = 6.5 Hz, 12H, CH(C*H*$_3$)$_2$), 3.27 (septet, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 3.72 (septet, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 4.11 (septet, $^3J_{HH}$ = 6.5 Hz, 2H, C*H*(CH$_3$)$_2$), 5.21 (septet, $^3J_{HH}$ = 6.5 Hz, 2H, C*H*(CH$_3$)$_2$), 6.34 (d, $^3J_{HH}$ = 2.0 Hz, 2H, N-C*H*-), 6.49 (d, $^3J_{HH}$ = 1.5 Hz, 2H, N-C*H*-), 6.90 (two overlapping doublets, $^3J_{HH}$ = 8.0, 2H, Ar-*H*), 7.06 (m, 4H, Ar-*H*), 7.19 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ar-*H*), 7.29 (two overlapping doublets, $^3J_{HH}$ = 8.0, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 23.4 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 26.4 (CH(*C*H$_3$)$_2$), 26.7 (CH(*C*H$_3$)$_2$), 27.0 (CH(*C*H$_3$)$_2$), 27.6 (CH(*C*H$_3$)$_2$), 28.0 (*C*H(CH$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 29.3 (*C*H(CH$_3$)$_2$), 32.7 (*C*H(CH$_3$)$_2$), 114.2 (Ar-N-*C*H-), 122.7 (Ar-*C*), 123.8 (Ar-*C*), 123.9 (Ar-*C*), 124.0 (Ar-*C*), 125.0 (Ar-*C*), 139.5 (Ar-C), 144.6 (Ar-*C*), 145.4 (Ar-*C*), 146.3 (Ar-*C*), 149.3 (Ar-*C*), 156.2 (N-*C*-N), 156.8 (N-*C*-N), 160.4 (K-N-*C*H-). ^{29}Si NMR (80 MHz, C_6D_6): δ -38.4 (s). Mp (°C): 70 °C (crystals melts) 150-155 °C (decomp., turns light brown). Anal. Calcd. for $C_{54}H_{72}N_6K_2Si$: C, 71.16; H, 7.96; N, 9.22. Found: C, 71.26; H 8.16; N, 7.34.

Despite repeated attempts, combustion analyses gave consistently low values for nitrogen content (lower by *ca.* 2 %). See Figures 3.10-3.12 in the Section 3.6.

Synthesis of IPr=N-GeCl$_3$ (10). A solution of IPr=N-SiMe$_3$ (0.606 g, 1.27 mmol) in 10 mL of toluene was added to GeCl$_4$ (145.2 μL, 1.27 mmol) dissolved in 2 mL of toluene, and the resulting mixture was stirred and heated to reflux at 120 °C overnight to give a slightly cloudy, yellow mixture. This reaction can also be done in a sealed, partially evacuated Teflon-capped, thick-walled glass Schlenk flask with heating to 120 °C. The precipitate was allowed to settle and the mother liquor was isolated after filtration. Removal of the volatiles from the mother liquor afforded **10** as an off-white powder (0.686 g, 93 %). Crystals suitable for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of **10** in toluene. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 1.10 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.40 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.96 (septet, $^3J_{HH}$ = 6.5 Hz, 4H, C*H*(CH$_3$)$_2$), 5.91 (s, 2H, N-C*H*-), 7.09 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar-*H*), 7.18 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ 23.4 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 115.9 (-N-*C*H-), 124.6 (Ar-*C*), 130.7 (Ar-C), 132.7 (Ar-*C*), 147.3 (N-*C*-N), 149.0 (Ar-*C*). Mp (°C): *ca.* 85 °C (decomp., turns brown). Anal. Calcd. for C$_{27}$H$_{36}$N$_3$Cl$_3$Ge: C, 55.76; H, 6.24; N, 7.22. Found: C, 55.36; H 6.41; N, 6.90.

Synthesis of (IPr=N)$_2$GeCl$_2$ (11). A solution of IPr=N-SiMe$_3$ (0.563 g, 1.18 mmol) in 10 mL of toluene was added to a solution of IPr=N-GeCl$_3$ (0.686 g, 1.18 mmol) in 8 mL of toluene, and the resulting mixture was stirred and

heated to reflux at 120 °C for 4 days to give a slightly yellow reaction mixture. This reaction can also be done in a thick-walled sealed, partially evacuated Teflon-capped, glass Schlenk flask with heating to 120 °C. The precipitate was allowed to settle and the mother liquor was isolated after filtration. Removal of the volatiles from the mother liquor afforded **12** as a pale yellow powder (1.052 g, 94 %). Crystals suitable for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of **11** in fluorobenzene. ^{1}H NMR (500 MHz, C_6D_6): δ 1.12 (d, $^{3}J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 1.25 (d, $^{3}J_{HH}$ = 6.5 Hz, 24H, CH(CH_3)$_2$), 3.05 (septet, $^{3}J_{HH}$ = 7.0 Hz, 8H, CH(CH$_3$)$_2$), 5.89 (s, 4H, N-CH-), 7.09 (d, $^{3}J_{HH}$ = 7.5 Hz, 8H, Ar-H), 7.22 (t, $^{3}J_{HH}$ = 7.5 Hz, 4H, Ar-H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 23.7 (CH(*C*H$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 115.2 (-N-*C*H-), 124.1 (Ar-*C*), 129.5 (Ar-C), 134.4 (Ar-*C*), 147.66 (N-*C*-N), 147.68 (Ar-*C*). Mp (°C): *ca.* 150 °C (decomp., turns brown). Anal. Calcd. for $C_{54}H_{72}N_6Cl_2Si$: C, 68.36; H, 7.65; N, 8.86. Found: C, 67.79; H, 7.38; N, 8.70.

Synthesis of (IPr=N)$_2$Ge: (12). A solution of dark green $NaC_{10}H_8$ (prepared from 0.0124 g of Na and 0.0681 g of $C_{10}H_8$; 0.532 mmol) in 8 mL of THF was added to a solution of (IPr=N)$_2$GeCl$_2$ (0.203 g, 0.214 mmol) in 4 mL of THF, and the resulting mixture was stirred at room temperature for 24 hours to give a dark orange mixture. Removal of the volatiles gave a brown crude solid which was washed with hexanes (3 x 4 mL) and **12** was obtained as a pale yellow crystals from a recrystallization of the remaining solid from hexanes at -35 °C (0.075 g, 40 %). Crystals suitable for X-ray crystallography were

obtained by cooling (-35 °C) a saturated solution of **12** in hexanes. ^{1}H NMR (500 MHz, C_6D_6): δ 1.15 (d, $^{3}J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 1.18 (d, $^{3}J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 3.07 (septet, $^{3}J_{HH}$ = 7.0 Hz, 8H, CH(CH$_3$)$_2$), 5.93 (s, 4H, N-CH-), 7.09 (d, $^{3}J_{HH}$ = 7.5 Hz, 8H, Ar-H), 7.25 (t, $^{3}J_{HH}$ = 7.5 Hz, 4H, Ar-H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 23.6 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 113.8 (-N-*C*H-), 123.8 (Ar-*C*), 129.0 (Ar-C), 134.6 (Ar-*C*), 148.5 (N-*C*), 148.5 (N-*C*-N). Mp (°C): *ca.* 55 °C (decomp., turns brown). Anal. Calcd. for $C_{54}H_{72}N_6Ge$: C, 73.88; H, 8.27; N, 9.57. Found: C, 72.47; H, 8.22; N, 9.30.

Synthesis of [Li(N=IPr)]$_2$: This compound was prepared according to a published procedure by Tamm and coworkers.[10] Spectroscopic data were identical to those previously reported for this compound. Crystals of **[Li(N=IPr)]$_2$** of suitable quality for X-ray crystallography were obtained by cooling (-35 °C) a saturated solution of this compound in hexanes.

Reaction of (IPr=N)$_2$Ge: (12) with H$_2$: To a solution of **12** (0.0190g, 0.0216 mmol) in 2 mL of Et_2O, was added H_2 (0.52 mL, 0.0216 mmol) using a gas tight syringe, and the clear yellow solution was stirred for 2 hours to give a colorless solution over a precipitate. Filtration of the mixture followed by the removal of the volatiles afforded a white powder (0.0105 g, 60 %) which was identified as the previously known imine IPr=NH[1a] by NMR spectroscopy.

Reaction of (IPr=N)$_2$Ge: (12) with D$_2$: To a solution of **12** (0.0157g, 0.0179 mmol) in 2 mL of Et_2O was added D_2 (0.43 mL, 0.0179 mmol) using a syringe, and the clear yellow solution was stirred for 2 hours to give a colorless

solution over a precipitate. Filtration of the mixture followed by the removal of the volatiles afforded a white powder (0.0081 g, 56 %) with spectroscopic data consistent with the formation of DN=IPr (*i.e.* similar ^{1}H NMR data as HN=IPr[1a] but with an absence of the N-H signal).

Reaction of KH with 11: To a mixture of **11** (0.0232 g, 0.0245 mmol) and KH (0.0023g, 0.0573 mmol) was added 3 mL of Et_2O and the resulting mixture was stirred at room temperature for 4 days. Analysis of the products by ^{1}H NMR spectroscopy revealed the presence of 60 % unreacted $(IPr{=}N)_2GeCl_2$ **11** and 40 % IPr=NH.

Reaction of K[HB^{s}Bu$_3$] with 11: A solution of $(IPr{=}N)_2GeCl_2$ **11** (0.0812 g, 0.0856 mmol) in 3 mL of toluene was added to a solution of K[HB^{s}Bu$_3$] (171.2 μL, 0.171 mmol) in 2 mL of toluene, and the clear, pale yellow solution was stirred overnight. Filtration of the resulting orange mixture (containing B^{s}Bu$_3$ according to ^{11}B NMR spectroscopy; δ = 84.8 ppm), followed by the removal of the volatiles afforded a viscous dark yellow oil. This product mixture was redissolved in 2 mL of toluene and filtered through a short (1 cm) plug of silica gel to yield HN=IPr as a colorless solid.[1a]

3.5 X-ray Crystallographic Data

Table 3.1. Crystallographic Data for Compounds **2**, **3•C_6H_5F**, and **5•$(Et_2O)_2$**.

	2•1/2 C_7H_8	**3•C_6H_5F**	**5•$(Et_2O)_2$**
formula	$C_{30.50}H_{40}Br_3N_3Si$	$C_{60}H_{77}Br_2FN_6Si$	$C_{62}H_{92}K_2N_6O_2Si$
formula fw	716.47	1089.18	1059.70
cryst. dim. (mm)	0.31 x 0.27 x 0.08	0.38 x 0.36 x 0.35	0.48 x 0.09 x 0.06
cryst. syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	*Pccn*
a (Å)	9.3324 (7)	19.1921 (12)	15.5900 (2)
b (Å)	9.5737 (7)	12.6413 (8)	17.6069 (3)
c (Å)	19.7142 (14)	25.6094 (16)	22.2395 (3)
α (deg)	91.4794 (10)	90	90
β (deg)	96.1262 (10)	110.5957 (7)	90
γ (deg)	111.4156 (9)	90	90
V (Å^3)	1626.4 (2)	5816.1 (6)	6104.56 (15)
Z	2	4	4
ρ_{calcd} (g cm^{-3})	1.463	1.244	1.153
μ (mm^{-1})	3.781	1.459	1.904
T (K)	173(1)	173(1)	173(1)
$2\theta_{max}$ (deg)	53.54	54.99	140.49
total data	13645	88187	38659
unique data (R_{int})	6903 (0.0362)	13315 (0.0251)	5820 (0.0623)
obs [I > 2σ(I)]	4870	11139	5207
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$][a]	0.0379	0.0326	0.0475
wR_2 [all data][a]	0.0837	0.0940	0.1384
max / min $\Delta\rho$ (e Å^{-3})	0.691/–0.487	0.429/–0.525	0.387/–0.251

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(Fo^4)]^{1/2}$

Table 3.2. Crystallographic Data for Compounds **5•(toluene)$_2$**, **6**, and **10•1/2 C$_7$H$_8$**.

	5•(toluene)$_2$	**6**	**10•1/2 C$_7$H$_8$**
formula	$C_{68}H_{88}K_2N_6Si$	$C_{56}H_{78}N_6OSi_2$	$C_{30.50}H_{40}Cl_3GeN_3$
formula fw	1095.73	907.42	627.59
cryst. dim. (mm)	0.37 x 0.19 x 0.13	0.30 x 0.10 x 0.09	0.34 x 0.25 x 0.13
cryst. syst.	orthorhombic	monoclinic	triclinic
space group	*Pccn*	$P2_1/n$	$P\bar{1}$
a (Å)	15.7413 (5)	12.1444 (2)	9.3618 (3)
b (Å)	16.9705 (5)	21.8298 (3)	9.4782 (3)
c (Å)	23.1230 (7)	20.3141 (3)	19.3727 (7)
α (deg)	90	90	89.2845 (4)
β (deg)	90	94.4491 (7)	84.2790 (4)
γ (deg)	90	90	69.4191 (4)
V (Å^3)	6177.0 (3)	5369.24 (14)	1600.80 (9)
Z	4	4	2
ρcalcd (g cm^{-3})	1.178	1.123	1.302
μ (mm^{-1})	0.218	0.921	1.230
T (K)	173(1)	173(1)	173(1)
$2\theta_{max}$ (deg)	54.98	143.08	55.74
total data	52442	36037	14548
unique data (R_{int})	7081 (0.0409)	10277 (0.0639)	7497 (0.0099)
obs [I > 2σ(I)]	5463	8416	6953
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$][a]	0.0446	0.0434	0.0247
wR_2 [all data][a]	0.1274	0.1238	0.0676
max / min Δρ (e Å^{-3})	0.372/–0.398	1.023/–0.874	0.363/–0.259

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(Fo^4)]^{1/2}$

Table 3.3. Crystallographic Data for Compounds **11•C_6H_5F**, **12**, and **[Li(N=IPr)]$_2$**.

	11•C_6H_5F	**12**	**[Li(N=IPr)]$_2$.**
formula	$C_{60}H_{77}Cl_2FGeN_6$	$C_{54}H_{72}Cl_{0.09}GeN_6$	$C_{54}H_{72}Li_2N_6$
formula fw	1044.76	880.95	819.06
cryst. dim. (mm)	0.33 x 0.25 x 0.15	0.36 x 0.17 x 0.03	0.41 x 0.21 x 0.10
cryst. syst.	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$Pbcn$	$P2_1/n$
a (Å)	19.1837 (3)	11.8062 (3)	10.9982 (2)
b (Å)	12.5630 (2)	19.8956 (5)	18.7313 (2)
c (Å)	25.6436 (4)	21.8851 (5)	12.0421 (2)
α (deg)	90	90	90
β (deg)	110.8290 (5)	90	94.2202 (6)
γ (deg)	90	90	90
V (Å^3)	5776.33 (16)	5140.6 (2)	2474.07 (7)
Z	4	4	2
ρcalcd (g cm^{-3})	1.201	1.138	1.099
μ (mm^{-1})	1.915	1.143	0.481
T (K)	173(1)	173(1)	173(1)
$2\theta_{max}$ (deg)	145.96	136.82	140.32
total data	39308	31779	16759
unique data (R_{int})	11507 (0.0173)	4722 (0.0468)	4695 (0.0219)
obs [$I > 2\sigma(I)$]	10800	3862	4252
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$][a]	0.0373	0.0355	0.0402
wR_2 [all data][a]	0.1056	0.0996	0.1103
max / min $\Delta\rho$ (e Å^{-3})	0.610/–0.734	0.513/–0.429	0.237/–0.229

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(Fo^4)]^{1/2}$

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Chapter 4: Structurally Versatile Phosphine and Amine Donors Constructed from *N*-Heterocyclic Olefin Units

4.1 Introduction

Sterically encumbered phosphines and *N*-heterocyclic carbenes (NHCs) are effective ligands for supporting a variety of catalytic bond-forming processes,[1] and can stabilize highly reactive molecular entities via strong coordinative interactions.[2] Common traits between these two ligand classes are the presence of a strongly σ-donating atom, ease of synthesis, and a high level of structural tuneability. A related ligand group that is attracting increasing attention of late are *N*-heterocyclic olefins (NHOs),[3] which contain considerable nucleophilic character due to the highly polarized nature of the exocyclic C=C double bond, allowing these species to be strong neutral 2-electron donors (Chart 4.1; left). Accordingly, NHOs are now being used to intercept reactive inorganic species,[4,5] as organocatalysts for various polymerization strategies,[6] and as a component of pincer-type ligands.[7]

In this Chapter, efficient routes to phosphine and amine donors that contain an NHO moiety $[IPr{=}CH]^-$ directly linked to P- and N-donor sites are discussed. As shown in Chart 4.2, there is a possibility of coordination through either the NHO (via carbon-ligation) or the terminal P/N atoms. This study was motivated in part by the prior work of Beller who demonstrated that imidazolium-alkylphosphines (Chart 4.1; right) when combined with Pd(II) sources and base, afford active catalysts (*in situ*) for the hydroxylation of

arylhalides, and for both C-N (Buchwald-Hartwig) and C-C (Sonogashira) coupling reactions.[8] Despite the possible formation of neutral NHO-linked phosphines (NHOPs; Chart 4.2; E = P) during Beller's catalytic processes, such ligands were not isolated, nor were any well-defined metal complexes with these ligands reported. As a result, I decided to explore this ligand class in more detail and consequently uncovered divergent coordination behavior towards AuCl, depending if hard amine or soft phosphine groups are appended to an NHO unit.

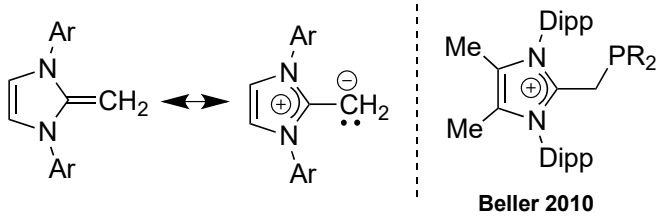


Chart 4.1. (Left) Canonical forms for a generic *N*-heterocyclic olefin (NHO); (Right) Beller's imidazolium phosphines.

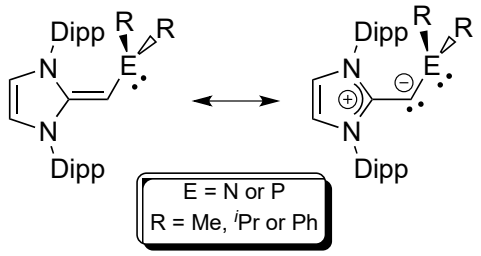
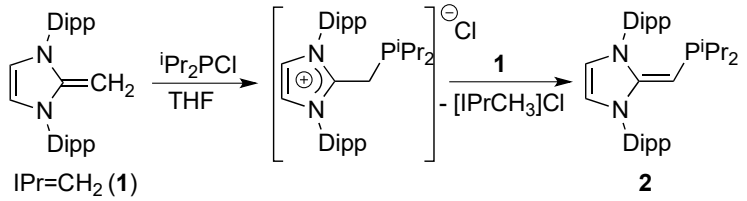


Chart 4.2. *N*-Heterocyclic olefin-phosphines (NHOP) or -amines (NHON) discussed in this paper; Dipp = 2,6-$^{i}Pr_2C_6H_3$.

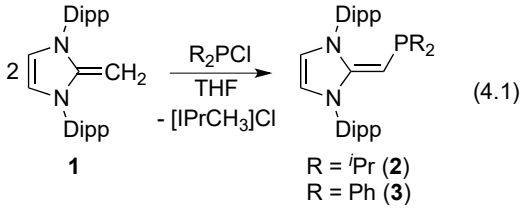
4.2 Results and Discussion

4.2.1 Synthesis of *N*-heterocyclic olefin phosphines (NHOPs)

This study began with exploring the synthesis of the diisopropylphosphine-capped *N*-heterocyclic olefin (IPr=CH)P^{i}Pr$_2$ **2** (IPr = [(HCNDipp)$_2$C]; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$). In line with prior work from our group,[9] the readily available NHO, IPr=CH$_2$ **1**,[3d] was combined with ClP^{i}Pr$_2$ in a 1:1 ratio in THF (Scheme 4.1) with the intention of first isolating the imidazolium salt [IPr-CH$_2$-P^{i}Pr$_2$]Cl, which would be isostructural to Beller's pre-ligands shown in Chart 4.1. While there was spectroscopic evidence for the formation of the desired imidazolium salt, the starting material IPr=CH$_2$ **1** was sufficiently basic to deprotonate [IPr-CH$_2$-P^{i}Pr$_2$]Cl to give **2** and the known by-product [IPrCH$_3$]Cl.[9] Fortunately **2** and [IPrCH$_3$]Cl have quite different solubilities, allowing for their easy separation. By altering the ratio between IPr=CH$_2$ **1** and ClP^{i}Pr$_2$ to 2:1 (Equation 4.1) and conducting the reaction in THF at room temperature for 20 hrs, pure (IPr=CH)P^{i}Pr$_2$ **2** was isolated in a 81 % yield after extracting **2** from the product mixture (containing [IPrCH$_3$]Cl) with hexanes. Following a similar procedure, the phenyl-substituted NHOP (IPr=CH)PPh$_2$ **3** was prepared in an isolated yield of 83 %. The new NHOPs **2** and **3** were each characterized by NMR spectroscopy, elemental analysis and X-ray crystallography (colorless crystals grown from hexanes at -30 °C; Figures 4.1 and 4.2).



Scheme 4.1. In the reaction of IPr=CH_2 (**1**) and $^{i}Pr_2PCl$ in a 1:1 ratio, the formation of the imidazolium-alkylphosphine salt [IPr-CH_2-$P^{i}Pr_2$]Cl was observed, as well as the desired neutral NHO-appended phosphine.



(4.1)

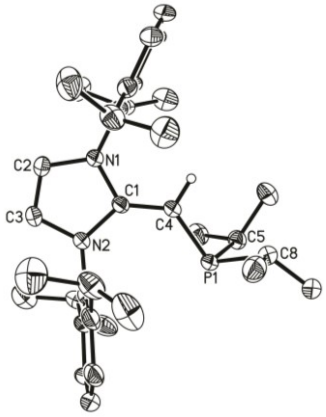


Figure 4.1. Molecular structure of **2** with thermal ellipsoids at the 30 % probability level. Only one of four crystallographically-independent molecules in the unit cell is presented. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P-C(4) 1.780(3) - 1.788(3), P-C(5) 1.835(4) - 1.883(3), P-C(8) 1.859(4) - 1.896(4), C(1)-C(4) 1.364(4) - 1.366(4); P-C(4)-C(1) 126.9(2) - 129.8(2), N(1)-C(1)-N(2) 104.0(2), C(4)-P-C(5) 101.03(14) - 105.72(18), C(4)-P-C(8) 99.71(15) - 104.29(17), C(5)-P-C(8) 99.12(14) - 101.57(17).

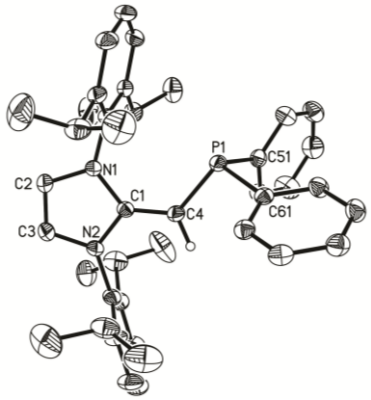
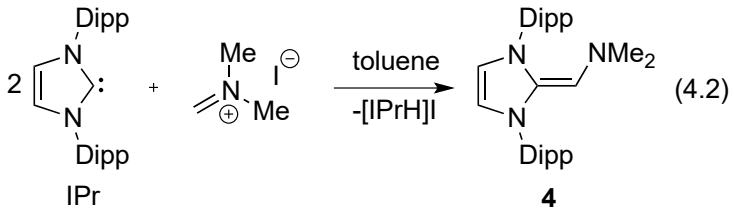


Figure 4.2. Molecular structure of **3** with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) with values corresponding to a second molecule in the asymmetric unit in square brackets: P(1)-C(4) 1.7762(15) [1.782(2)], P(1)-C(51) 1.8411(16) [1.839(2)], P(1)-C(61) 1.8406(15) [1.8448(18)], C(1)-C(4) 1.365(2) [1.377(2)]; C(4)-P(1)-C(51) 104.37(7) [104.50(9)], C(4)-P(1)-C(61) 99.75(6) [99.70(8)], P(1)-C(4)-C(1) 126.25(11) [126.16(16)], N(1)-C(2)-N(2) 104.08(12) [104.29(12)].

4.2.2 Synthesis of *N*-heterocyclic olefin amine (IPr=CH)NMe_2 4

In addition to preparing NHOPs, I wanted to see if a harder amine donor could be incorporated onto an NHO scaffold. The target dimethylamino-substituted NHO, (IPr=CH)NMe_2 **4**, was prepared by combining two equivalents of the commercially available carbene IPr with one equivalent of Eschenmoser's salt [H_2C=NMe_2]I[12] in toluene (Equation 4.2). In this process, the first equivalent of IPr is believed to undergo a nucleophilic attack on the iminium moiety to form [IPr-CH_2-NMe_2]I which is then subsequently deprotonated by a second equivalent of IPr to yield (IPr=CH)NMe_2 **4** and the imidazolium by-product [IPrH]I (which can be recycled for the preparation of

IPr) (Equation 4.2). In a similar fashion as the syntheses of **2** and **3**, the salt by-product [IPrH]I is much less soluble than the target ligand **4**, thus separation could be achieved by filtering the reaction mixture. One drawback with this synthesis is that the crude samples of **4** occasionally contain *ca.* 5-10 % of unreacted IPr (as determined by ^{1}H NMR), which is difficult to separate from (IPr=CH)NMe_2 **4** due to their similar solubilities in common organic solvents. However, a successful way to remove the IPr contaminant involves adding a small amount of BPh_3 to form the known adduct IPr•BPh_3,[13] which is much less soluble in hexanes than **4**.



(4.2)

The structure of (IPr=CH)NMe_2 **4** was authenticated by X-ray crystallography (Figure 4.3) and this study revealed an exocyclic C(1)-C(4) bond length of 1.3463(14) Å which is slightly shorter than the corresponding distances in the NHOPs **2** and **3**, suggesting the retention of substantial C-C π-bonding in this unit. The C(1)-C(4)-N(1) angle was also consistent with sp^2-hybridization at C(4) [122.98(9)°], while the nitrogen atom of the –NMe_2 group is significantly pyramidalized [Σ°(N) = 333.35(17)°] consistent with a lack of substantial N(3)-C(4) π-bonding.

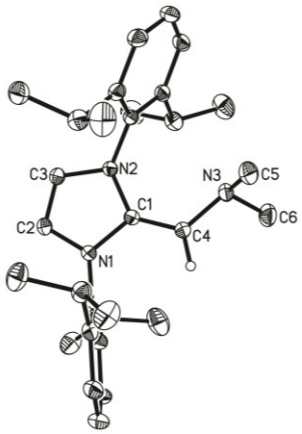


Figure 4.3. Molecular structure of **4** with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)-C(1) 1.4024(12), N(2)-C(1) 1.4009(12), C(1)-C(4) 1.3463(14), C(4)-N(3) 1.4299(13), N(3)-C(5) 1.4563(16), N(3)-C(6) 1.4570(16); N(1)-C(1)-N(2) 104.44(8), N(1)-C(1)-C(4) 125.71(9), C(1)-C(4)-N(3) 122.98(9), C(4)-N(3)-C(6) 110.19(10).

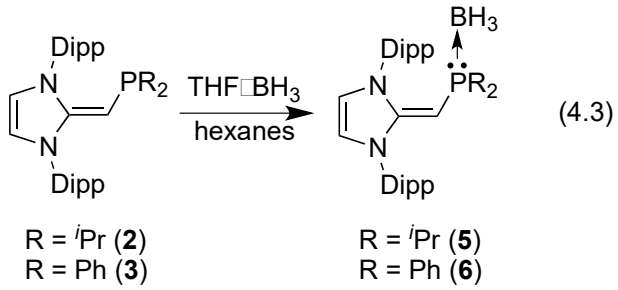
4.2.3 Coordination of the NHOPs 2 and 3 to BH_3 and AuCl

With the new NHOPs in hand, their reactivity was tested in the presence of the Lewis acid source THF•BH_3. When either (IPr=CH)P^{i}Pr$_2$ **2** or (IPr=CH)PPh_2 **3** was combined with THF•BH_3 in hexanes (Equation 4.3), the reaction mixture changed from yellow to colorless after 90 min. at room temperature. After the volatiles were removed, the respective phosphine-borane adducts (IPr=CH)^{i}Pr$_2$P•BH_3 **5** and (IPr=CH)Ph_2P•BH_3 **6** were isolated as colorless crystals in 52 and 56 % yields after recrystallization from cold (-30 °C) hexanes or toluene (slow evaporation), respectively. As expected, coordination of a BH_3 unit was evident by NMR spectroscopy, which showed broad ^{11}B NMR resonances at -42.0 and -35.8 ppm for **5** and **6**, respectively,

consistent with the presence of four-coordinate boron environments. In addition, considerable downfield shifts in the ^{31}P resonances were noted within the NHOPs upon BH_3 coordination: from -17.4 ppm in **2** to 21.9 ppm in (IPr=CH)^{i}Pr$_2$P•BH$_3$ **5**; from -31.4 ppm in **3** to 7.3 ppm in (IPr=CH)Ph$_2$P•BH$_3$ **6**. Such a substantial change in ^{31}P NMR chemical shift indicated the likely presence of BH_3 units bound to the phosphorus centers; this postulate was confirmed by performing single-crystal X-ray crystallography (**5**: Figure 4.4; **6**: Figure 4.5).

As show in Figure 4.4, (IPr=CH)^{i}Pr$_2$P•BH$_3$ **5** contains a P-bound borane residue with a P-B bond length of 1.9166(18) Å; for comparison, the dialkyphosphine-borane adduct ^{t}Bu$_2$PH•BH$_3$ has a P-B bond length of 1.936(2) Å.[14] In the case of (IPr=CH)^{i}Pr$_2$P•BH$_3$ **5**, the P(1)-C(4) length [1.7504(14) Å] is contracted in comparison to the corresponding distance in the free phosphine (IPr=CH)P^{i}Pr$_2$ **2** [1.780(3) to 1.788(2) Å]. The exocyclic C(1)-C(4) double bond within the NHO unit in **5** [1.3749(18) Å] is essentially the same length within experimental error as the exocyclic C=C bond distances in the phosphine **2** [1.364(4) to 1.366(4) Å]. The main structural change noted upon coordination of BH_3 is a widening of the P-C(4)-C(1) from 126.9(2) in the free ligand **2** to 138.02(11)° in adduct **5**. Similarly, the P-C(4)-C(1) angle in the phenyl analogue (IPr=CH)Ph$_2$P•BH$_3$ (**6**) [138.31(9)°] (Figure 4.5) is wider than in the free phosphine (IPr=CH)PPh$_2$ (**3**) [126.0(2)° *avg.*]. In both compounds **5** and **6**, the BH_3 unit is oriented in an *anti*-fashion with respect to the exocyclic olefinic C-H group, placing the BH_3 group in close proximity to one of the flanking

Dipp aryl groups of the NHO ligand; such a coordination mode could enhance aryl---metal interactions within NHOP-metal complexes.[1d]



R = ^{i}Pr (**2**)
R = Ph (**3**)

R = ^{i}Pr (**5**)
R = Ph (**6**)

(4.3)

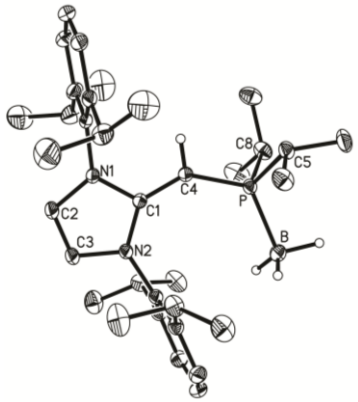


Figure 4.4. Molecular structure of **5** with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P-B 1.9166(18), P-C(4) 1.7504(14), C(1)-C(4) 1.3749(18), P-C(5) 1.8486(14), P-C(8) 1.8495(16); C(4)-P-B 124.56(7), P-C(4)-C(1) 138.02(11), C(4)-P-C(5) 102.07(7), C(4)-P-C(8) 106.76(7), B-P-C(5) 110.56(8), B-P-C(8) 107.50(8).

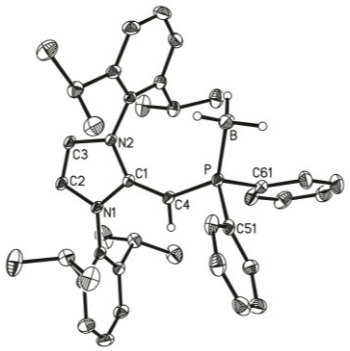


Figure 4.5. Molecular structure of **6** with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (°): P-B 1.9242(18), P-C(4) 1.7479(11), C(1)-C(4) 1.3811(15), P-C(51) 1.8292(12), P-C(61) 1.8300(13); C(4)-P-B 125.76(6), P-C(4)-C(1) 138.31(9), C(4)-P-C(51) 101.10(5), C(4)-P-C(61) 107.67(6), B-P-C(51) 109.21(7), B-P-C(61) 108.15(7).

After demonstrating the successful coordination of the small Lewis acid BH_3 to the NHOPs **2** and **3**, the interaction of these donors with transition metals was explored. The complexes with the noble metals Pd and Pt were targeted as these elements in conjunction with bulky phosphines[15] and NHCs[16] are often used in metal-mediated cross-coupling reactions. Despite the presence of a potentially strongly coordinating terminal -P^iPr_2 unit in (IPr=CH)P^iPr_2 **2**, no discernable reaction was noted when excess **2** (2-3 equiv.) was combined with either $Pd(PPh_3)_4$ or $Pt(PPh_3)_4$ in hot C_6D_6 (50 °C) for 4 days (monitored by ^{31}P NMR spectroscopy). A similar lack of reactivity was found with the two coordinate Pt(0) complex $Pt(P^tBu_3)_2$. Attempts to form a bis NHOP-$PdCl_2$ pre-catalyst[16a] by treating $PdCl_2(NCPh)_2$ with two equiv. of **2** in toluene, led to an immediate color change of the reaction mixture from yellow

to dark red, however ^{31}P NMR analysis revealed the formation of six spectroscopically distinct products from which a single clean product could not be isolated.

Reports of using $[PdCl(cinnamyl)]_2$ (cinnamyl = η^3-$H_2CCHCH(Ph)$) as a palladium source to generate active L•Pd(cinnamyl) pre-catalysts (L = ligand)[18] in cross-coupling reactions motivated the reaction of $[PdCl(cinnamyl)]_2$ with (IPr=CH)P^{i}Pr$_2$ **2**. When **2** was mixed with $[PdCl(cinnamyl)]_2$ in toluene several new species were found by ^{31}P NMR spectroscopy. In one case, layering of the crude reaction mixture with hexanes, followed by cooling to -30 °C gave a small batch of yellow crystals (2-3 mg) that were identified by X-ray crystallography as the target Pd(II) complex (IPr=CH)P^{i}Pr$_2$•PdCl(cinnamyl) **7** (Figure 4.6).

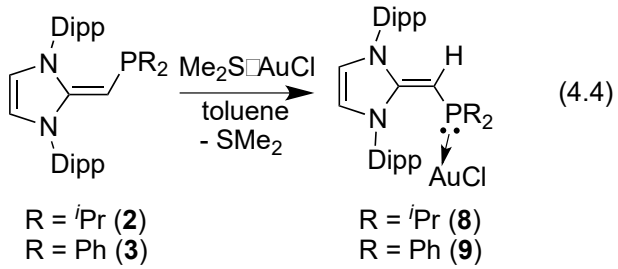
Upon closer inspection of the structure of **7** (Figure 4.6), it is clear that the –P^{i}Pr$_2$ unit is free to rotate with respect to the bulky IPr=CH- group. In the BH_3 adduct **5**, the isopropropyl groups are rotated away from the IPr unit, while in (IPr=CH)P^{i}Pr$_2$•PdCl(cinnamyl) **7** the phosphorus bound ^{i}Pr substituents are positioned toward one Dipp group, enabling the more hindered PdCl(cinnamyl) array to occupy a more open side of the NHOP ligand coordination sphere. Therefore despite the bulk of (IPr=CH)P^{i}Pr$_2$, there exists sufficient torsional flexibility to allow different coordination pockets to be formed (a useful property for catalysis when various intermediates need to be stabilized). The Pd-cinnamyl bonding interactions in **7** range from 2.113(6) Å to 2.261(5) Å with the longest Pd-C bond to C(53) positioned *trans* to the phosphine donor. In

the NHC complex IPr•PdCl(cinnamyl), the related *trans*-positioned Pd-C bond length (with respect to the IPr donor) is 2.201(17) Å,[19] indicating that the ligand (IPr=CH)P^{i}Pr$_2$ exerts a similar degree of *trans*-influence as IPr.

Figure 4.6. Molecular structure of (IPr=CH)P^{i}Pr$_2$•PdCl(cinnamyl) **7** with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd-P 2.3086(12), Pd-Cl 2.3582(12), Pd-C(51) 2.113(6), Pd-C(52) 2.143(5), Pd-C(53) 2.261(5), P-C(4) 1.765(4), C(1)-C(4) 1.386(6), P-C(5) 1.847(5), P-C(8) 1.863(5); P-Pd-Cl 102.23(4), C(4)-P-Pd 103.85(15), P-C(4)-C(1) 136.1(3), C(4)-P-C(5) 105.8(2), C(4)-P-C(8) 110.7(2), Pd-P-C(5) 117.51(16), Pd-P-C(8) 113.69(18), C(51)-C(52)-C(53) 120.4(6).

Given the difficulties faced in introducing an NHOP as a ligand to Pd and Pt centers, the coordination of this ligand class to gold(I) centers was explored. Added motivation for this work stems from the rapidly growing use of Au(I) complexes in catalysis (*e.g.* in the hydroamination of alkynes).[20] A toluene solution of (IPr=CH)P^{i}Pr$_2$ **2** was added to a molar equivalent of Me$_2$S•AuCl, and after stirring at room temperature for 2 hrs, (IPr=CH)^{i}Pr$_2$P•AuCl **8** was obtained as a pale yellow solid in an 85 % yield after filtration of the reaction mixture and removal of the volatiles (Equation

4.4); the resulting product was analytically pure as judged by satisfactory C, H and N analyses. Compound **8** was characterized by X-ray crystallography and the refined molecular structure is shown in Figure 4.7. The metrical parameters within the IPr=CH- unit in **8** are similar to the BH_3 adduct (IPr=CH)$^{i}Pr_2P$•BH_3 **5**, with comparable P-C(4) and exocyclic C(1)-C(4) bond lengths [1.7742(19) and 1.376(3) Å, respectively]. Interestingly, the -P^{i}Pr$_2$ unit in **8** is rotated in such a fashion as to place the hindered isopropyl groups away from the Dipp groups within the IPr=CH- unit; as a result the Au(I) center lies over the π-face of a Dipp substituent (Au---C(ipso) distance = 3.507 Å), and accordingly the P-Au-Cl angle [171.40(2)°] is distorted from the expected linear geometry. For comparison, shorter arene-Au(I) interactions have been noted within a series of Buchwald biarylphosphine-Au(I) complexes L•Au(NCMe)$^{+}$ (3.04-3.19 Å) prepared by the Buchwald group.[21] The corresponding diphenylphosphine-capped NHO complex (IPr=CH)PPh_2•AuCl **9** was prepared in a similar straightforward manner as **8** (98 % yield) and exhibited the same overall geometry as in **8** (Figure 4.8) with a slightly narrower P-Au-Cl angle of 168.72(4)°.



(4.4)

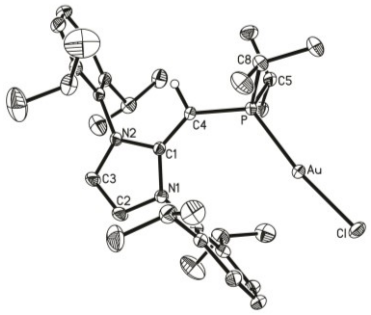


Figure 4.7. Molecular structure of **8** with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au-P 2.2348(5), Au-Cl 2.2991(5), P-C(4) 1.7442(19), C(1)-C(4) 1.376(3), P-C(5) 1.848(2), P-C(8) 1.845(2); P-Au-Cl 171.40(2), C(4)-P-Au 122.82(7), P-C(4)-C(1) 136.20(15), C(4)-P-C(5) 105.69(10), C(4)-P-C(8) 104.31(10), Au-P-C(5) 106.89(7), Au-P-C(8) 110.83(7).

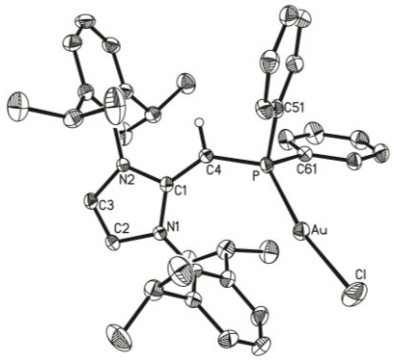
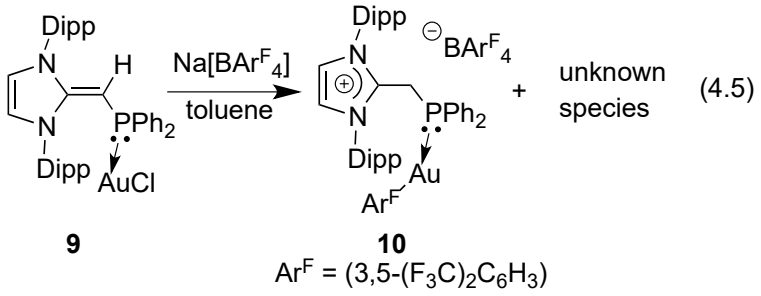


Figure 4.8. Molecular structure of **9** with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au-P 2.2334(8), Au-Cl 2.2914(10), P-C(4) 1.741(3), C(1)-C(4) 1.381(4), P-C(51) 1.831(3), P-C(61) 1.826(3); P- Au-Cl 168.72(4), C(4)-P-Au 128.48(11), P-C(4)-C(1) 136.9(3), C(4)-P-C(51) 99.84(15), C(4)-P-C(61) 109.43(15), Au-P-C(51) 106.45(11), Au-P-C(61) 106.46(11).

In an attempt to prepare a more reactive Au(I) complex for future catalytic trials,[20d] the NHO-Au complex (IPr=CH)Ph_2P•AuCl **9** was treated with Na[BAr^F_4] ([BAr^F_4]$^-$ = B(3,5-(F_3C)$_2C_6H_3$)$_4$) in toluene. This reaction afforded a gummy orange precipitate from which a product of [BAr^F_4]$^-$ anion activation, [IPr-CH_2-PPh_2•Au(3,5-(F_3C)$_2C_6H_3$)]BAr^F_4 **10**, could be isolated and structurally characterized (Equation 4.5; Figure 4.9). While the mechanism of this process is under investigation, protonation of the exocyclic olefin within the NHO unit occurred to yield an imidazolium-alkyl phosphine ligand,[8] along with the removal of one Ar^F unit from the generally unreactive weakly coordinating [BAr^F_4]$^-$ anion. One possible source of the proton would be C-H activation of the backbone olefin within the IPr unit.[22] The generation of a highly electron deficient Au(I) center during the reaction process could facilitate the abstraction of Ar^F from the [BAr^F_4]$^-$ anion; although rare, related processes have been noted with both phosphine and NHC-bound Au(I) centers.[23] The structure of **10** is shown in Figure 4.9 and, as expected, a nearly linear coordination geometry exists at the Au(I) center [P-Au-C(71) angle = 174.82(11)°]. The coordinative Au-P interaction in **10** [2.2798(8) Å] is only marginally elongated in relation to the Au-P distance in (IPr=CH)^iPr_2P•AuCl **8** [2.2348(5) Å], while the adjacent P-C(4) bond length in **10** is longer by *ca.* 0.12 Å when compared to the P-C(4) distance in **8** as a result of a hybridization change at carbon from sp^2 in **8** to sp^3 in **10**. No reaction was observed when (IPr=CH)Ph_2P•AuCl **9** was treated with Na[SbF_6].



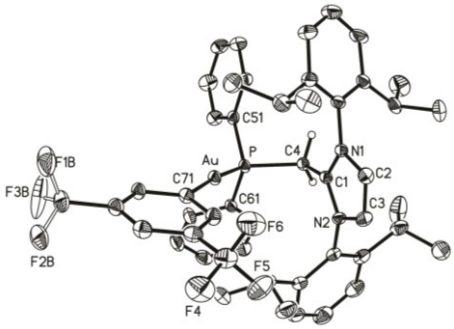
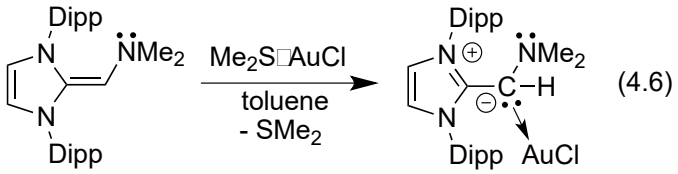


Figure 4.9. Molecular structure of **10** with thermal ellipsoids at the 30 % probability level. The hydrogen atoms attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms and the B(3,5-$(F_3C)_2C_6H_3)_4^-$ anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au-P 2.2798(8), Au-C(71) 2.070(23), P-C(4) 1.864(4), C(1)-C(4) 1.487(4); P-Au-C(71) 174.82(11), C(4)-P-Au 112.43(11), C(1)-C(4)-P 116.5(2).

To further evaluate the donation abilities of the new phosphines, the preparation of NHOP•$Rh(CO)_2Cl$ complexes was attempted with the hope of obtaining informative *ν*(CO) IR data.[3d] When the NHOPs **2** and **3** were each combined with 0.5 equiv. of $[RhCl(CO)_2]_2$, three different Rh-P containing products were found in the form of $^{31}P\{^1H\}$ doublet resonances due to coupling to Rh (I = ½) . Despite multiple attempts, I could not separate the products due to their similar solubilities in common organic solvents, and as such further investigations were not pursued.

4.2.3 Divergent coordination chemistry of (IPr=CH)NMe_2

As presented above, the NHOPs **2** and **3** exclusively bind to Lewis acidic units through the terminal phosphine residues. However in the corresponding amine-capped NHOs (such as **4**) featuring hard N-donor sites, there exists a chance that olefin coordination could transpire with soft Lewis acids (Chart 4.1). Somewhat to our surprise, (IPr=CH)NMe_2 **4** did not yield clean reactivity with THF•BH_3, and multiple products were found by ^{11}B NMR spectroscopy. In contrast, an isolable 1:1 complex (IPr=CH)NMe_2•AuCl **11** formed in 89 % yield as a yellow solid when **4** was combined with Me_2S•AuCl in toluene (Equation 4.6). The most drastic change in the NMR spectra of the (IPr=CH)NMe_2 unit was the upfield shift of the olefinic *C*HNMe_2 carbon from 89.0 ppm in free (IPr=CH)NMe_2 **4** to a position of 58.4 ppm in **11**; this latter spectroscopic signature suggested possible olefin coordination to gold in **11**. Crystals of **11** were obtained for X-ray crystallographic analysis and despite the lower quality of the data, (IPr=CH)NMe_2 coordination through a C-Au linkage was confirmed with a distance of 2.044(15) Å; moreover a nearly linear geometry was present at gold [C(3)-Au-Cl angle = 177.6(4)°; [Figure 4.10]. Therefore one can see direct evidence for the two possible binding modes of NHO-supported amines and phosphines in this study (Chart 4.2).



4 **11** (4.6)

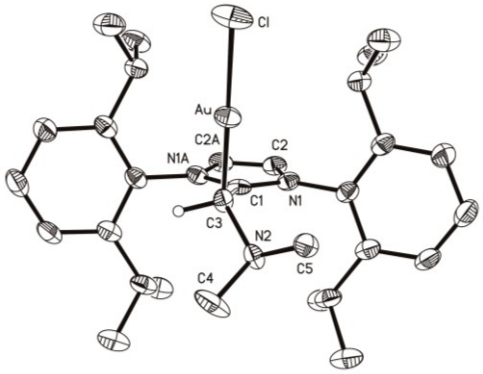


Figure 4.10. Molecular structure of **11** with thermal ellipsoids at the 30 % probability level. The hydrogen atoms attached to C(3) is shown with an arbitrarily small thermal parameter; all other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au-C(3) 2.044(15), Au-Cl 2.300(4), N(2)-C(3) 1.444(10), C(1)-C(3) 1.513(6); C(3)-Au-Cl 177.6(4), N(2)-C(3)-Au 121.7(15), C(1)-C(3)-N(2) 110.9(16).

4.3 Conclusions

Efficient syntheses of neutral *N*-heterocyclic olefin-appended phosphines and amine donors are reported, including preliminary coordination behavior with the Lewis acids BH_3 and AuCl. Interestingly, modulation of the donor properties enables either NHO-based coordination (via an olefinic carbon atom) or standard phosphine binding modes to be adopted. As a result, the Rivard group is now exploring these coordinatively versatile ligands within the context of late metal-mediated catalysis.

4.4 Experimental

4.4.1 General

All reactions were performed in either an inert atmosphere glove box (Innovative Technology, Inc.) or using Schlenk techniques. Solvents were dried using a Grubbs-type solvent purification system manufactured by Innovative Technologies, Inc. and stored under an atmosphere of nitrogen prior to use.[24] Chlorodiisopropylphosphine, chlorodiphenylphosphine, N,N-dimethyliminium iodide ($[Me_2N{=}CH_2]I$), borane tetrahydrofuran complex, dimethylsulfide gold(I) chloride, $Na[SbF_6]$, and $[PdCl(cinnamyl)]_2$ were used as received from Sigma Aldrich; $Na[B(3,5\text{-}(F_3C)_2C_6H_3)_4]$ was obtained from Sigma Aldrich and dried under vacuum at 100 °C for 12 hrs. prior to use. IPr=CH_2 **1**[3d] and IPr[25] were prepared according to literature procedures. ^{1}H, $^{1}H\{^{31}P\}$, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, ^{11}B, and $^{11}B\{^{1}H\}$ NMR spectra were recorded on a Varian VNMRS-400 or Varian VNMRS-500 spectrometer and referenced externally to $SiMe_4$, 85 % H_3PO_4, or $F_3B{\bullet}OEt_2$. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

4.4.2 X-ray Crystallography

Crystals for X-ray diffraction studies were removed from a vial and immediately coated with thin a layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fiber, and quickly placed in a low

temperature stream of nitrogen on the X-ray diffractometer. All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα or Cu Kα radiation, with the crystals cooled to -80 °C and -100 °C. The data was corrected for absorption through Gaussian integration from the indexing of the crystal faces. Crystal structures were solved using intrinsic phasing SHELXT[26] (**2**, **4**, **5**, **6**, **9** and **11**), direct methods (**3**), or Patterson/structure expansion (**7** and **8**)[27] and refined using full-matrix least-squares on F^2. The assignment of hydrogen atoms positions were based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20 % greater than those of their parent atoms.

Special refinement conditions:

(IPr=CH)P^{i}Pr$_2$•BH$_3$ 5: Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent hexane carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in *PLATON*.[28] A total solvent-accessible void volume of 1145 $Å^3$ with a total electron count of 212 (consistent with 4.24 molecules of solvent hexane, or ~0.25 molecules per formula unit of **5**) was found in the unit cell.

(IPr=CH)P^{i}Pr$_2$•PdCl(cinnamyl) 7: The crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program *CELL_NOW* (Bruker AXS, Inc., Madison, WI, 2004). The second twin component can be related to the first component by a 7.4° rotation about the [0.2 1 -0.35] axis in real space and about the [0.1 1 -0.4] axis in reciprocal space. Integrated intensities for the reflections from the two

components were written into a *SHELXL-2014*[26] HKLF 5 reflection file with the data integration program *SAINT* (version 8.34A), using all reflection data (exactly overlapped, partially overlapped and non-overlapped). The refined value of the twin fraction (*SHELXL-2014* BASF parameter) was 0.3198(17).

(IPr=CH)PPh$_2$•AuCl 9: Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent toluene or hexane carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in *PLATON*.[28] A total solvent-accessible void volume of 517 Å^3 with a total electron count of 110 (consistent with 2 molecules of solvent toluene, or 0.5 molecules per formula unit of the Au complex) was found in the unit cell.

(IPr=CH)NMe$_2$•AuCl 11: The crystal used for data collection was the 'best' of a bad lot. The unit cell was indexed using the program CELL_NOW, and the major component fit ~60 % of the thresholded reflections. There were at least an additional six components, and attempts to integrate a multicomponent dataset were not particularly successful. The noisy difference map can most likely be attributed to the fact that there are a number of additional partially overlapping components contributing to the measured intensities (this is also apparent in the list of most disagreeable reflections in the SHELXL-2014 output with Iobs larger than Icalc for the top 50 reflections). Attempts to refine the structure in $P2_1$ instead to $P2_1/m$ gave massive correlations of the ADPs and a more poorly-behaved structure.

4.4.3 Synthetic Procedures

Synthesis of (IPr=CH)P^{i}Pr$_2$ (2). ^{i}Pr$_2$PCl (100 μL, 0.77 mmol) was added dropwise to IPr=CH$_2$ **1** (0.508 g, 1.26 mmol) in 8 mL of THF. The resulting mixture was stirred for 20 hrs to give an orange suspension. The mixture was then filtered and the volatiles were removed from the filtrate to afford an orange solid that was extracted with 4 mL of hexanes and filtered again. Removal of the volatiles from the filtrate gave **2** as a light brown solid (0.267 g, 81 %). Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution of **2** in hexanes. ^{1}H NMR (400 MHz, C_6D_6): δ 7.26 – 7.11 (m, 6H, Ar*H*), 5.88 (dd, $^3J_{HH}$ = 2.4 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, NC*H*CHN), 5.85 (dd, $^3J_{HH}$ = 2.4 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, NC*H*CHN), 3.28 (overlapping septets, 4H, ArC*H*(CH$_3$)$_2$), 2.66 (d, $^2J_{HP}$ = 5.6 Hz, 1H, C*H*P^{i}Pr$_2$), 1.45 (d, $^3J_{HH}$ = 7.2 Hz, 6H, ArCH(C*H*$_3$)$_2$), 1.33 (d, $^3J_{HH}$ = 7.2 Hz, 6H, ArCH(C*H*$_3$)$_2$), 1.25 (broad septet,$^3J_{HH}$ = 7.2 Hz, 2H, PC*H*(CH$_3$)$_2$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH(C*H*$_3$)$_2$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH(C*H*$_3$)$_2$), 0.96 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 11.6 Hz, 6H, PCH(CH$_3$)C*H*$_3$), 0.90 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 12.8 Hz, 6H, PCH(CH$_3$)C*H*$_3$). ^{13}C{^{1}H} (126 MHz, C_6D_6): δ 154.5 (Ar-*C*), 154.3 (Ar-*C*), 148.7 (Ar-*C*), 148.1 (Ar-*C*), 134.6 (N*C*N), 129.7 (Ar-*C*), 129.4 (Ar-*C*), 124.6 (Ar-*C*), 123.9 (Ar-*C*), 117.8 (H*C*CH), 115.0 (HC*C*H), 51.4 (d, $^1J_{CP}$ = 114.7 Hz, H*C*P^{i}Pr$_2$), 29.1 (Ar*C*H(CH$_3$)$_2$), 28.7 (Ar*C*H(CH$_3$)$_2$), 26.5 (d, $^2J_{PC}$ = 11.1 Hz, PCH(*C*H$_3$)$_2$), 25.9 (Ar-CH(*C*H$_3$)$_2$), 24.9 (ArCH(*C*H$_3$)$_2$), 23.4 (ArCH(*C*H$_3$)$_2$), 22.6 (Ar-CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ -17.4. Mp (°C): 132-135. Anal. Calcd. for $C_{34}H_{51}N_2P$: C, 78.72; H, 9.91; N, 5.40. Found: C, 77.76; H 9.85; N, 5.21.

Synthesis of (IPr=CH)PPh$_2$ (3). Ph_2PCl (41.2 μL, 0.16 mmol) was added dropwise to a solution of IPr=CH_2 **1** (0.150 g, 0.37 mmol) in 3 mL of THF. The resulting mixture was stirred overnight to give an orange suspension. The precipitate was allowed to settle and the mother liquor was isolated after filtration. The volatiles were removed from the mother liquor to afford (IPr=CH)PPh_2 **3** as a brown solid (0.078 g, 83 %). Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution in hexanes. ^{1}H NMR (400 MHz, C_6D_6): δ 7.35 – 6.92 (m, 16H, Ar*H* and Ph*H*), 5.92 (s, 2H, N(C*H*)$_2$N), 3.34 (d, $^3J_{HP}$ = 5.6 Hz, 1H, C*H*PPh_2), 3.26 (overlapping septets, 4H, ArC*H*$(CH_3)_2$), 1.33 (d, $^3J_{HH}$ = 7.2 Hz, 6H, ArCH(C*H*$_3)_2$), 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 6H, ArCH(C*H*$_3)_2$), 1.18 (d, $^3J_{HH}$ = 7.0 Hz, 6H, ArCH(C*H*$_3)_2$), 1.12 (d, $^3J_{HH}$ = 7.2 Hz, 6H, ArCH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 154.0 (d, $^1J_{CP}$ = 35 Hz, Ph-*C*), 148.5 (Ar-*C*), 147.9 (Ar-*C*), 146.2 (d, $^2J_{CP}$ = 13 Hz, Ph-*C*), 136.6 (Ar-*C*), 134.2 (Ar-*C*), 132.3 (d, $^2J_{cp}$ = 20 Hz, Ph-*C*), 130.0 (Ar-*C*), 129.7 (Ar-*C*), 127.7 (Ar-*C*), 126.8 (Ar-*C*), 124.5 (d, $^1J_{CP}$ = 41 Hz, Ph-*C*), 117.1 (HC*C*H), 115.5 (H*C*CH), 52.7 (H*C*PPh_2), 29.1 (*C*H$(CH_3)_2$), 28.8 (*C*H$(CH_3)_2$), 25.1 (CH(*C*H$_3)_2$), 24.7 (CH(*C*H$_3)_2$), 23.4 (CH(*C*H$_3)_2$), 22.5 (CH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ -31.4. Mp (°C): 172-176. Anal. Calcd. for $C_{40}H_{47}N_2P$: C, 81.87; H, 8.07; N, 4.77. Found: C, 81.34; H 8.33; N, 5.05.

Synthesis of IPr=CHNMe$_2$ (4). A solution of IPr (0.481 g, 1.24 mmol) in 3 mL of toluene was added to finely ground [H_2C=N$(CH_3)_2$]I (0.115 g, 0.62 mmol). The resulting mixture was stirred overnight to give a cloudy yellow reaction mixture. The mother liquor was isolated after filtration. The volatiles

were then removed from the mother liquor to afford a yellow solid that was extracted with 2 mL of hexanes and filtered. Removal of the volatiles from the filtrate afforded **4** as a yellow solid (227 mg, 82 %, product also contains 7 % of unreacted IPr). Further purification can be performed by adding BPh_3 (ca. 2 mg) to **4** (0.050 g) in minimal amount of benzene (ca. 0.5 mL). The solution was stirred for 15 mins. and 2 mL of hexanes was added to yield a white precipitate. The mother liquor was isolated after filtration and the volatiles were removed from the filtrate to afford **4** (0.040 g) containing <1 % of unreacted IPr. Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution in hexanes. ^{1}H NMR (500 MHz, C_6D_6): δ 7.23 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 7.14 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 5.86 (dd, $^3J_{HH}$ = 2.5 Hz, $^5J_{HH}$ = 1.0 Hz, 1H, (*H*CCH)), 5.77 (d, $^3J_{HH}$ = 2.0 Hz, 1H, (HCC*H*)), 3.51 (septet, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*$(CH_3)_2$), 3.47 (s, 1H, C*H*N$(CH_3)_2$), 3.36 (septet, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*$(CH_3)_2$), 1.97 (s, 6H, N(C*H*$_3)_2$), 1.41 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3)_2$), 1.38 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3)_2$), 1.27 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3)_2$), 1.22 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 149.0 (Ar-*C*), 148.1 (Ar-*C*), 145.0 (Ar-*C*), 138.1 (N*C*N), 129.1 (Ar-*C*), 128.3 (Ar-*C*), 124.6 (Ar-*C*), 123.1 (Ar-*C*), 117.4 (H*C*CH), 114.4 (HC*C*H), 89.0 (H*C*N$(CH_3)_2$), 49.8 (*C*H$(CH_3)_2$), 28.7 (N(*C*H$_3)_2$), 28.6 (N(*C*H$_3)_2$), 25.6 (CH(*C*H$_3)_2$), 24.4 (CH(*C*H$_3)_2$), 23.8 (CH(*C*H$_3)_2$), 22.9 (CH(*C*H$_3)_2$). Mp (°C): 89-94. Anal. Calcd. for $C_{30}H_{43}N_3$: C, 80.85; H, 9.72; N, 9.43. Found: C, 79.04; H 9.43; N, 8.52. Despite repeated attempts, analyses were consistently low in the carbon content.

Preparation of (IPr=CH)P^{i}Pr$_2$•BH$_3$ (5). 106 μL of THF•BH$_3$ (1.0 M solution in THF, 0.11 mmol) was added dropwise to a solution of IPr=CHP^{i}Pr$_2$ **2** (50 mg, 0.096 mmol) in 2 mL of hexanes. The reaction mixture was stirred for 1.5 hrs and then filtered. The volatiles were removed from the filtrate and the resulting solid was dissolved in approximately 0.5 mL of hexanes and cooled (-30 °C) to afford (IPr=CH)P^{i}Pr$_2$•BH$_3$ as a white microcrystalline solid (27 mg, 52 %). Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution in hexanes. ^{1}H NMR (500 MHz, C_6D_6): δ 7.24 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 7.17 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 5.87 (s, 2H, N(C*H*)$_2$N), 3.16 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, ArC*H*(CH$_3$)$_2$), 2.09 (d, $^2J_{HP}$ = 10.0 Hz, 1H, C*H*P^{i}Pr$_2$), 1.44 (d, $^3J_{HH}$ = 6.5 Hz, 12H, C*H*(CH$_3$)$_2$), 1.44 (broad septet, 2H, P(C*H*(CH$_3$)$_2$)$_2$), 1.14 (d, $^3J_{HH}$ = 6.5 Hz, 12H, ArCH(C*H*$_3$)$_2$), 1.06 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 14.5 Hz, 6H, PCH(C*H*$_3$)$_2$), 0.93 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 13.5 Hz, 6H, PCH(C*H*$_3$)$_2$), 0.25 (broad d, $^2J_{HP}$ = 15.0 Hz, 3H, B*H*$_3$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 154.3 (d, $^2J_{CP}$ = 11.6 Hz, N*C*N), 147.9 (Ar-*C*), 130.2 (Ar-*C*), 128.4 (Ar-*C*), 128.2 (Ar-*C*), 128.0 (Ar-*C*), 124.8 (N(*C*H)$_2$N), 40.2 (d, $^1J_{CP}$ = 73.8 Hz, H*C*P^{i}Pr$_2$), 28.8 (Ar*C*H(CH$_3$)$_2$), 26.7 (d, $^2J_{CP}$ = 39.5 Hz, P(CH(*C*H$_3$)$_2$)$_2$), 25.3 (ArCH(*C*H$_3$)$_2$), 22.9 (ArCH(*C*H$_3$)$_2$), 17.2 (d, $^1J_{CP}$ = 58.9 Hz, P(*C*H(CH$_3$)$_2$)$_2$). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ -42.0. ^{31}P{^{1}H} NMR (201 MHz, C_6D_6): δ 21.9. Mp (°C): 154-156. Anal. Calcd. for $C_{34}H_{54}BN_2P$: C, 76.67; H, 10.22; N, 5.26. Found: C, 75.94; H 10.10; N, 5.42.

Preparation of (IPr=CH)PPh$_2$•BH$_3$ (6). 93.8 μL of THF•BH$_3$ (1.0 M solution in THF, 0.094 mmol) was added dropwise to a solution of IPr=CHPPh$_2$ **3** (50.0 mg, 0.085 mmol) in 2 mL of hexanes. The reaction mixture was stirred

for 90 mins. The solvent volume was then reduced *in vacuo* until the mixture just turned cloudy and then cooled (-30 °C) to afford **6** as an off-white microcrystalline solid (29 mg, 56 %). Crystals suitable for X-ray crystallography were obtained by slow evaporation of a saturated solution of (IPr=CH)PPh_2•BH_3 **6** in toluene at room temperature. ^{1}H NMR (500 MHz, C_6D_6): δ 7.70 (m, 4H, Ph*H*), 7.72 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 7.12 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 6.98 – 6.95 (m, 6H, Ph*H*), 5.93 (s, 2H, N(C*H*)$_2$N), 3.15 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*(CH_3)$_2$), 2.83 (d, $^2J_{HP}$ = 9.5 Hz, 1H, C*H*PPh_2), 1.24 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.12 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 0.98 (broad d, $^2J_{HP}$ = 16.0 Hz, 3H, B*H*$_3$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 153.2 (d, $^2J_{CP}$ = 15.6 Hz, N*C*N), 147.7 (Ar-*C*), 137.7 (d, $^1J_{CP}$ = 58.7 Hz, Ph-*C*), 132.0 (d, J_{CP} = 9.3 Hz, Ph-*C*), 130.4 (Ar*C*), 129.1 (d, J_{CP} = 2.0 Hz, Ph-*C*), 128.3 (Ar-*C*), 128.0 (d, J_{CP} = 9.5 Hz, Ph-*C*), 125.0 (N(*C*H)$_2$N), 117.6 (Ar-*C*), 44.2 (d, $^1J_{CP}$ = 84.8 Hz, H*C*PPh_2), 29.0 (*C*H(CH_3)$_2$), 25.2 (CH(*C*H_3)$_2$), 22.8 (CH(*C*H_3)$_2$). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ -35.8. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 7.3. Mp (°C): 164-170. Anal. Calcd. for $C_{40}H_{50}BN_2P$: C, 79.99; H, 8.39; N, 4.66. Found: C, 79.36; H 8.38; N, 4.68.

Reaction of IPr=CHNMe$_2$ with THF•BH$_3$. 63.8 μL of THF•BH_3 (1.0 M solution in THF, 0.058 mmol) was added dropwise to a solution of IPr=$CHNMe_2$ **4** (26 mg, 0.058 mmol) in 1 mL of hexanes. Once THF•BH_3 was added the yellow solution became colorless. The reaction was stirred for approximately 2 hours and then the volatiles were removed. ^{11}B NMR analysis showed that there was no THF•BH_3 remaining, however 5 new unidentifiable products were formed; attempts to obtain pure products were not successful.

Reaction of (IPr=CH)P^{i}Pr$_2$ with [PdCl(cinnamyl)]$_2$. [PdCl(cinnamyl)]$_2$ (0.024 g, 0.046 mmol) was combined with (IPr=CH)P^{i}Pr$_2$ **2** (0.048 g, 0.093) in 2 mL of toluene. The reaction mixture rapidly became yellow in color. The solution was left to stir overnight to yield a red solution and the volatiles were removed. ^{1}H and ^{31}P NMR spectroscopy showed a mixture of several products. On one occasion, yellow crystals (2-3 mg) suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution of the reaction mixture in toluene/hexanes. Data for (IPr=CH)P^{i}Pr$_2$•PdCl(cinnamyl) **7**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.55 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.22 – 7.00 (m, 8H, Ph*H* and Ar*H*), 5.90 (s, 2H, N(C*H*)$_2$N), 5.41 (ddd, $^2J_{HH}$ = 13.2 Hz, $^2J_{HH}$ = 9.2 Hz, $^2J_{HH}$ = 9.2 Hz, 1H, CH$_2$C*H*CHPh), 4.98 (m, 3H, C*H*$_2$CHC*H*Ph), 4.01 (broad d, $^3J_{HH}$ = 11.2 Hz, 3H, PCH(C*H*$_3$)$_2$), 3.49 (broad d, $^3J_{HH}$ = 6.8 Hz, 3H, PCH(C*H*$_3$)$_2$), 3.23 (broad septet, 4H, ArC*H*(CH$_3$)$_2$), 2.79 (broad s, (IPr=C*H*)P^{i}Pr$_2$), 2.44 (broad d, $^3J_{HH}$ = 12.0 Hz, 3H, PCH(C*H*$_3$)$_2$), 1.88 (broad s, 3H, PCH(C*H*$_3$)$_2$), 1.38 (broad, m, 12H, ArCH(C*H*$_3$)$_2$), 1.14 (broad m, 1H, PC*H*(CH$_3$)$_2$), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 12H, ArCH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 34.0. There was not enough sample to record a meaningful ^{13}C{^{1}H} NMR spectrum.

Synthesis of (IPr=CH)P^{i}Pr$_2$•AuCl (8). A solution of (IPr=CH)P^{i}Pr$_2$ **2** (99 mg, 0.19 mmol) in 5 mL of toluene was added dropwise to solid Me$_2$S•AuCl (56 mg, 0.19 mmol) to give a yellow solution. This reaction mixture was stirred at room temperature for 2 hours and a small amount of metallic precipitate was observed. The mixture was then filtered and the volatiles were then removed from the filtrate to afford (IPr=CH)P^{i}Pr$_2$•AuCl **8** as

a pale yellow solid (121 mg, 85 %). Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution in a 1:1 mixture of toluene/hexanes. ^{1}H NMR (500 MHz, C_6D_6): δ 7.49 (t, $^{3}J_{HH}$ = 7.0 Hz, 2H, Ar*H*), 7.23 (d, $^{3}J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 5.78 (s, 2H, N(C*H*)$_2$N), 3.01 (septet, $^{3}J_{HH}$ = 7.0 Hz, 4H, ArC*H*(CH$_3$)$_2$), 2.22 (d, $^{2}J_{HP}$ = 6.0 Hz, 1H, C*H*P^{i}Pr$_2$), 1.38 (d, $^{3}J_{HH}$ = 7.0 Hz, 12H, ArC*H*(CH$_3$)$_2$), 1.28 (septet, $^{3}J_{HH}$ = 8.0 Hz, 2H, P(C*H*(CH$_3$)$_2$)$_2$), 1.07 (d, $^{3}J_{HH}$ = 7.0 Hz, 12H, ArCH(C*H*$_3$)$_2$), 0.87 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HP}$ = 18.0 Hz, 6H, PCH(C*H*$_3$)$_2$), 0.80 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HP}$ = 16.0 Hz, 6H, PCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 153.7 (d, $^{2}J_{CP}$ = 10.3 Hz, N*C*N), 147.0 (Ar-*C*), 134.3 (Ar-*C*), 131.2 (Ar-*C*), 129.3 (Ar-*C*), 125.4 (Ar-*C*), 117.5 (N(*C*H)$_2$N), 40.7 (d, $^{1}J_{CP}$ = 81.3 Hz, H*C*P^{i}Pr$_2$), 29.3 (d, $^{2}J_{CP}$ = 41.6 Hz, P(CH(*C*H$_3$)$_2$)$_2$), 28.8 (Ar*C*H(CH$_3$)$_2$), 25.0 (ArCH(*C*H$_3$)$_2$), 23.2 (ArCH(*C*H$_3$)$_2$), 19.1 (d, $^{1}J_{CP}$ = 3.8 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 18.3 (ArCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (201 MHz, C_6D_6): δ 28.7. Mp (°C): 90 (decomp., turned black). Anal. Calcd. for $C_{34}H_{51}AuClN_2P$: C, 54.36; H, 6.84; N, 3.73. Found: C, 54.82; H 6.86; N, 3.61.

Synthesis of (IPr=CH)PPh$_2$•AuCl (9). A solution of (IPr=CH)PPh$_2$ **3** (78 mg, 0.13 mmol) in 5 mL of toluene was slowly added to solid Me$_2$S•AuCl (40 mg, 0.14 mmol) to give a yellow solution. This reaction mixture was stirred at room temperature for 90 minutes and a small amount of metallic precipitate was observed. The mixture was filtered and the volatiles were then removed from the filtrate to afford (IPr=CH)PPh$_2$•AuCl **9** as a pale yellow solid (108 mg, 98 %). Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution in a 2:1 mixture of toluene/hexanes. ^{1}H NMR (400 MHz, C_6D_6): δ 7.50 – 7.47 (m, 4H, Ph*H*), 7.41 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.18

(d, $^{3}J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 6.86 – 6.87 (m, 6H, Ph*H*), 5.83 (s, 2H, N(C*H*)$_2$N), 3.00 (septet, $^{3}J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 2.80 (d, $^{2}J_{HP}$ = 6.4 Hz, 1H, C*H*PPh$_2$), 1.20 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.08 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ 152.3 (d, $^{2}J_{CP}$ = 13.6 Hz, N*C*N), 146.9 (Ar-*C*), 139.1 (d, $^{1}J_{CP}$ = 63.9 Hz, Ph-*C*), 137.8 (Ar-*C*), 133.7 (Ar-*C*), 132.6 (d, $^{2}J_{CP}$ = 14.1 Hz, Ph-*C*), 131.4 (N(*C*H)$_2$N), 129.7 (d, J_{CP} = 2.3 Hz, Ph-*C*), 117.5 (Ar-*C*), 44.6 (d, $^{1}J_{CP}$ = 92.6 Hz, H*C*PPh$_2$), 29.0 (*C*H(CH$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ 8.1. Mp (°C): 122 (decomp., turned black). Anal. Calcd. for C$_{40}$H$_{47}$AuN$_2$P: C, 58.65; H, 5.78; N, 3.42. Found: C, 58.83; H 5.89; N, 3.13.

Reaction of IPr=CHPPh$_2$•AuCl and Na[BAr$^{F}_4$]: Isolation of [IPr-CH$_2$-PPh$_2$•Au(3,5-(F$_3$C)$_2$C$_6$H$_3$)]BAr$^{F}_4$ (10). (IPr=CH)PPh$_2$•AuCl **9** (17 mg, 0.020 mmol) and Na[BAr$^{F}_4$] (18 mg, 0.020 mmol) were combined in 2 mL of toluene and stirred at room temperature overnight. A pale orange solution formed along with a gummy orange precipitate. The mother liquor was decanted away and the precipitate was exposed to prolonged vacuum to yield an orange solid. This solid was then extracted with CH_2Cl_2 (2 x 1 mL) and the combined extracts were filtered. The filtrate was then layered with 2 mL of hexanes before cooling to -30 °C, leading to colorless crystals of **10** (19 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (broad d, $^{3}J_{HH}$ = 5.5 Hz, 2H, Ar^{F}-*H*), 7.69 (broad m, 8H, Ar*H* in BAr$^{F}_4$), 7.66 (s, 2H, N(C*H*)$_2$N), 7.64 (broad s, 1H, Ar^{F}-*H*), 7.52 (m, 6H, Ph-*H*), 7.40 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 7.29 (d, $^{3}J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 7.23-7.25 (m, 4H, Ph-*H*), 6.94-6.98 (m, 4H, Ar*H* in BAr$^{F}_4$), 3.82 (d, $^{2}J_{HP}$ = 10.4 Hz, 2H, C*H*$_2$PPh$_2$), 2.82 (broad septet, 4H, C*H*(CH$_3$)$_2$), 1.18 (d,

$^{3}J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.13 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, (CH(CH_3)$_2$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -6.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -62.3 [$BAr^{F}_{4}^{-}$], -62.6 [Au-Ar^{F}]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 34.4. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 161.7 (q, $^{1}J_{BC}$ = 49.6 Hz, Ar-*C* in $BAr^{F}_{4}^{-}$), 146.7 (Ar-*C*), 144.9 (Ar-*C*), 137.9 (Ar-*C* in Au-Ar^{F}), 134.8 (Ar-*C* in $BAr^{F}_{4}^{-}$), 133.7 (Ar-*C*), 132.8 (Ar-*C*), 131.9 (d, $^{2}J_{CP}$ = 14.0 Hz, Ar-*C*, 129.9 (d, $^{2}J_{CP}$ = 19.5 Hz, Ar-*C* or Ar^{F}), 128.8 (q, $^{1}J_{BC}$ = 49.6 Hz in $BAr^{F}_{4}^{-}$), 126.2 (Ar-*C*), 125.6 (d, $^{2}J_{CP}$ = 12.7 Hz, Ar-*C*), 123.5 (Ar-*C*), 121.3 (N(*C*H)$_2$N), 119.9 (Ar-*C*), 117.5 (Ar-*C* in $BAr^{F}_{4}^{-}$), 30.0 (*C*H(CH$_3$)$_2$), 26.9 (H*C*PPh$_2$), 26.1 (CH(*C*H$_3$)$_2$), 22.7 (CH(*C*H$_3$)$_2$). The CF_3 groups in the Au-Ar^{F} unit could not be located in the ^{13}C{^{1}H} NMR spectrum. Mp (°C): 97 (decomp.; turned brown) Anal. Calcd. for $C_{80}H_{63}AuBF_{30}N_2P$: C, 51.63; H, 3.41; N, 1.51. Found: C, 51.31; H, 3.62; N, 1.52.

Synthesis of (IPr=CH)NMe$_2$•AuCl (11). A solution of IPr=CHNMe$_2$ **4** (98 mg, 0.22 mmol) in 5 mL of toluene was added dropwise to solid Me$_2$S•AuCl (65 mg, 0.22 mmol) to give a dark yellow reaction mixture. This reaction mixture was stirred at room temperature for 90 minutes and a metallic precipitate was observed. The reaction mixture was then filtered and the volatiles were then removed from the filtrate to afford (IPr=CH)NMe$_2$•AuCl as a pale yellow solid (133 mg, 89 %). Crystals of **11** were obtained by cooling a 2:1 toluene/hexanes solution overnight to -30 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.13 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H, Ar*H*), 7.01-7.04 (m, 4H, Ar*H*), 6.10 (s, 2H, N(C*H*)$_2$N), 4.02 (s, 1H, C*H*NMe$_2$), 3.04 (septet, $^{3}J_{HH}$ = 6.4 Hz, 4H, C*H*(CH$_3$)$_2$), 1.79 (broad s, 6 H, N(CH_3)$_2$), 1.47 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 1.47 (d,

$^{3}J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 0.95 (d, $^{3}J_{HH}$ = 7.2 Hz, 6H, CH(CH_3)$_2$), 0.95 (d, $^{3}J_{HH}$ = 7.2 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 161.0 (N*C*N), 147.5 (Ar-*C*), 145.3 (Ar-*C*), 132.2 (Ar-*C*), 131.2 (Ar-*C*), 124.7 (Ar-*C*), 124.5 (Ar-*C*), 120.8 (H*CC*H), 58.4 (H*C*N(CH$_3$)$_2$) 29.8 (CH(*C*H$_3$)$_2$), 29.4 (CH(*C*H$_3$)$_2$), 26.0 (CH(*C*H$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 23.2 (N(*C*H$_3$)$_2$), 23.1 (N(*C*H$_3$)$_2$). Mp (°C): 123 (decomp., turned dark brown) Anal. Calcd. $C_{30}H_{43}AuN_3$: C, 53.14; H, 6.39; N, 6.20. Found: C, 52.68; H, 6.33; N, 6.00

4.5. X-ray Crystallographic Data

Table 4.1. Crystallographic Data for Compounds **2**-**5**.

Compound	**2**	**3**	**4**	**5**•0.5C_6H_{14}
formula	$C_{34}H_{51}N_2P$	$C_{40}H_{47}N_2P$	$C_{30}H_{43}N_3$	$C_{35.50}H_{57.50}BN_2P$
formula weight	518.73	586.76	445.67	554.11
cryst. dimens. (mm)	0.34 × 0.17 × 0.17	0.21 × 0.18 × 0.07	0.20 × 0.15 × 0.08	0.49 × 0.08 × 0.06
crystal system	monoclinic	monoclinic	monoclinic	trigonal
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	*R-3*
a (Å)	21.3382 (6)	10.7803 (2)	9.3774 (2)	42.1750 (6)
b (Å)	18.3587 (5)	16.7651 (3)	20.2169 (4)	
c (Å)	17.2832 (4)	39.0845 (6)	20.2169 (4)	10.4933 (2)
β (deg)	33.3817 (9)	95.7606 (9)	100.0916 (11)	
V (Å^3)	13053.4 (6)	7028.2 (2)	2799.90 (10)	16164.1 (6)
Z	16	8	4	18
*ρ*calcd (g cm^{-3})	1.056	1.109	1. 057	1.025
μ (mm^{-1})	0.897	0.894	0.463	0.835
temperature (°C)	–100	–100	–100	–100
$2\theta_{max}$ (deg)	146.35	146.98	148.31	148.11
total data	75117	48771	108108	38050
unique data (R_{int})	25575 (0.0449)	13861 (0.0370)	5659 (0.0433)	7292 (0.0561)
obs [I > 2σ(I)]	17632	11433	5104	6290
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$] [a]	0.0698	0.0461	0.0417	0.0497
wR_2 [all data]	0.2012	0.1292	0.1151	0.1428
max / min Δ*r* (e Å^{-3})	0.954/–0.511	0. 444/–0.299	0.238/–0.256	0.552/–0.453

[a] $R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$; $wR_2 = [\Sigma\, w(F_o^2 - F_c^2)^2 / \Sigma\, w(F_o^4)]^{1/2}$.

Table 4.2. Crystallographic Data for Compounds **6**-**8**.

Compound	**6**	**7**	**8**
formula	$C_{40}H_{50}BN_2P$	$C_{50}H_{68}ClN_2PPd$	$C_{34}H_{51}AuClN_2P$
formula weight	600.60	869.88	751.15
cryst. dimens. (mm)	0.24 × 0.20 × 0.12	0.14 x 0.13 x 0.10	0.32 x 0.18 x□0.16
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\text{-}1$	$P2_1/n$
a (Å)	10.7033 (2)	10.3535 (3)	10.4781 (4)
b (Å)	18.7813 (3)	12.5649 (4)	16.3684 (6)
c (Å)	17.9853 (3)	18.9321 (6)	20.9256 (7)
α (deg)		72.828 (2)	
β (deg)	92.3243 (8)	100.0916 (11)	101.6635 (4)
γ (deg)		89.231 (2)	
V (Å^3)	3612.46 (11)	2304.58 (13)	3514.8 (2)
Z	4	2	4
ρcalcd (g cm^{-3})	1.104	1.254	1.419
μ (mm^{-1})	0. 874	4.357	4.330
temperature (°C)	–100	–100	–80
$2\theta_{max}$ (deg)	145.02	147.88	56.66
total data	24968	87008	32818
unique data (R_{int})	7118 (0.0257)	8901 (0.1174)	8717 (0.0238)
obs [I > 2σ(I)]	6558	7672	7584
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$] [a]	0.0371	0.0566	0.0200
wR_2 [all data]	0.1037	0.1547	0.0532
max / min Δr (e Å^{-3})	0.311/–0.366	1.436/–1.103	1.076/–0.505

[a] $R_1 = \Sigma \big| \big| F_o \big| - \big| F_c \big| \big| / \Sigma \big| F_o \big|$; $wR_2 = [\Sigma\, w(F_o^2 - F_c^2)^2 / \Sigma\, w(F_o^4)]^{1/2}$.

Table 4.3. Crystallographic Data for Compounds **9**-**11**.

Compound	**9**•0.5C_7H_8	**10**	**11**
formula	$C_{43.50}H_{51}AuClN_2P$	$C_{80}H_{63}AuBF_{30}N_2P$	$C_{30}H_{43}AuClN_3$
formula weight	865.25	1861.07	678.09
cryst. dimens. (mm)	0.19 x 0.18 x 0.06	0.48 x 0.13 x 0.01	0.11 x 0.10 x 0.05
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	*P21/m*
a (Å)	9.7488 (6)	14.0570 (4)	8.9505 (3)
b (Å)	20.0872 (13)	25.1328 (6)	18.1602 (7)
c (Å)	20.8717 (14)	22.7564 (7)	9.8838 (3)
β (deg)		102.1003 (18)	110.4098 (17)
V (Å^3)	98.4585 (10)	7861.0 (4)	1505.69 (9)
Z		4	2
ρcalcd (g cm^{-3})	4042.8 (5)	1.573	1.496
μ (mm^{-1})	4	4.750	10.14
temperature (°C)	1.422	–100	–100
$2\theta_{max}$ (deg)	3.776	148.42	146.18
total data	–80	55754	10578
unique data (R_{int})	55.22	12419 (0.0808)	3026 (0.0306)
obs [I > 2σ(I)]	36511	7672	2927
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$] [a]	9373 (0.0430)	0.0420	0.0606
wR_2 [all data]	7578	0.1156	0.1230
max / min Δr (e Å^{-3})	0.0316	1. 078/–2.636	2.060/–4.228
	0.0855		
	1.671/–1.292		

[a] $R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$; $wR_2 = [\Sigma\, w(F_o^2 - F_c^2)^2 / \Sigma\, w(F_o^4)]^{1/2}$.

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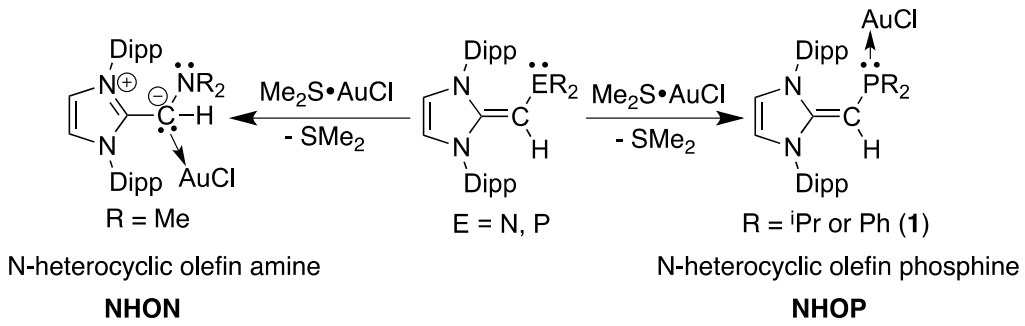
Chapter 5: Engaging the Dual Donor Sites of an *N*-Heterocyclic Olefin Phosphine Ligand

5.1 Introduction

Mixed element donor systems in catalysis are emerging in the literature, suggesting that ligands with both a hard and soft donor site can assist in stabilizing the various changes metal oxidation states that occur in catalytic cycles (e.g. after oxidative addition and reductive elimination).[1] The most commonly used ligands in catalysis are bulky phosphines,[1c, 2] *N*-heterocyclic carbenes (NHCs),[3] with the related *N*-heterocyclic olefins (NHOs)[4] becoming more ubiquitous in the literature. Despite the difficulties in developing an ideal ligand for catalysis and for the synthetic community, the investigation of new ligand donation motifs and their associated coordination chemistry is required to stimulate future research. By using known studies of phosphines, NHCs and, NHOs as a guide, a straightforward synthetic route to access neutral ligands was reported (See also Chapter 4) where an NHO moiety $[IPr{=}CH]^-$ can be directly linked to P- or N-donor sites (*N*-heterocyclic olefin phosphine/amine, NHOP or NHON).[5] When the NHOP and the NHON ligands were separately reacted with $Me_2S{\bullet}AuCl$ (Scheme 5.1), the NHOPs exclusively bound to the gold atom through the terminal phosphine moieties; whereas, the NHON coordinated to gold(I) via the olefinic site. This can be rationalized by the harder N-donor site being less compatible with soft Lewis acids in comparison to the softer olefinic donor site.



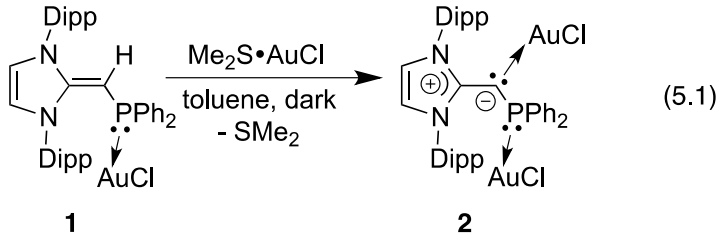
Scheme 5.1. Contrasting the coordination of gold(I) chloride with NHON and NHOP ligands.

This Chapter reports the synthesis and characterization of (IPr=CH)PPh_2•2AuCl, a new homobimetallic complex where the olefin and phosphine donor sites are both coordinated to independent gold(I) chloride moieties. In addition, attempts to isolate an heterobimetallic species involving copper (I) and gold(I) will also be discussed. Along the way it was discovered that the neutral ligand (IPr=CH)PPh_2 and its copper (I) iodide and gold (I) iodide complexes were emissive in the solid state, but not the chloride analogues. These preliminary studies demonstrate the different prospective avenues that the gold/copper halide-NHOP complexes can be further investigated.

5.2 Results and Discussions

This study began with exploring the synthesis of a dinuclear gold species supported by one diphenylphosphine-capped *N*-heterocyclic olefin, (IPr=CH)PPh_2 (IPr = [(HCNDipp)$_2$C]; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$). When a toluene solution of (IPr=CH)PPh_2•AuCl **1** was added to a cooled toluene solution of

Me_2S•AuCl in the dark, the bis adduct (IPr-CH)PPh_2•□AuCl **2** was obtained as a white solid (84 % yield) (Equation 5.1) with poor solubility in common organic solvents; it has partial solubility in toluene or fluorobenzene.



1 **2** (5.1)

Colorless crystals of **2** suitable for X-ray crystallography were grown from cooling a saturated solution (CH_2Cl_2 and hexanes in a 1:1 ratio) at -30 °C. (IPr-CH)PPh_2•□AuCl is unstable in CH_2Cl_2 at room temperature, and decomposes to [(IPr-CH_2)PPh_2•AuCl][$AuCl_2$] overnight. When (IPr=CH)PPh_2 was combined with 2 equiv. of Me_2S•AuCl at room temperature and stirred for 60 min in the dark, the reaction resulted in the formation of an insoluble metallic precipitate and a soluble mixture of unreacted (IPr=CH)PPh_2, (IPr=CH)PPh_2•AuCl and (IPr-CH)PPh_2•□AuCl, where the bimetallic complex can be separated from the product mixture by fractional recrystallization in toluene (37 % isolated yield). (IPr=CH)PPh_2 and **1** have similar solubilities in organic solvents, thus their separation was difficult. The stepwise coordination to two gold (I) chloride units, going through the isolation of **1**, is a cleaner and higher yielding synthetic route to access (IPr-CH)PPh_2•□AuCl **2**.

Upon coordination to the second gold(I) center, there is a noticeable elongation of the P-C(olefin) bond in **2** to 1.836(9) and 1.832(11) Å (two independent molecules in the crystalline lattice) compared to 1.741(3) Å in (IPr=CH)PPh_2•AuCl (**1**). In addition, the C(NHC)-C(olefin) bond lengths of

1.466(9) and 1.486(10) Å in (IPr-CH)PPh_2•□AuCl (**2**) are also larger than 1.381(4) Å in **1**, suggesting a decrease in double-bond character within the exocyclic olefin unit in **2**. These findings are consistent with reduced electron delocalisation over the NHOP ligand as a consequence of electron donation to AuCl. In the previously reported **1**, it was observed that the Au(I) center was positioned near the π-face of a Dipp-substituent with an Au···C(ipso) distance of 3.507 Å in addition to a non-linear P-Au-Cl angle of 168.72(4)°. In the bimetallic species **2**, both the P-Au-Cl [173.9(6) and 177.2(10)°] and the C(olefin)-Au-Cl [173.4(4) and 175.9(5)°] angles are closer to the expected linear geometry; furthermore, the Au(I) center on the phosphine no longer appears to be interacting with the Dipp substituent, with a significantly longer Au···C(ipso) distance of 4.719 Å. From the crystallographic data, there is no discernable aurophillic interaction in **2** as the distance between the two Au(I) centers is 5.304 Å; moreover the gold atoms are oriented in a *trans* fashion across the P-C(olefin)bond with a dihedral angle of 177.7(9)° [175.4(12)° for orientation B].

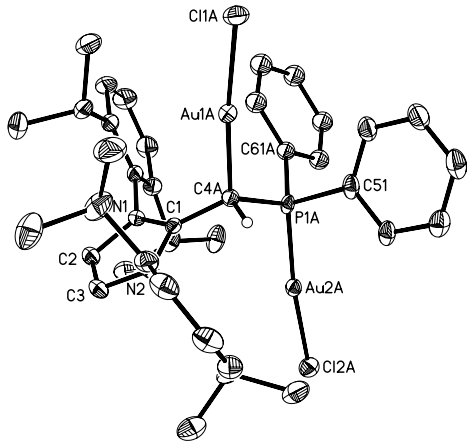


Figure 5.1. Molecular structure of **2** with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Orientation A has an occupancy factor or 0.55 and orientation B has an orientation of 0.45, only orientation A is shown here. Selected bond lengths (Å) and angles (°) of orientation A and [orientation B]: Au(1A)-C(4A) 2.066(13) [2.048(17)], Au(1A)-Cl(1A) 2.300(5) [2.286(7)], Au(2A)-Cl(2A) 2.066(13), [2.289(14)], P(1A)-Au(2A) 2.235(8) [2.230(9)], P(1A)-C(4A) 1.836(9) [1.832(11)], C(1)-C(4A) 1.466(9) [1.486(10)]; C(4A)-Au(1A)-Cl(1A) 173.4(4), [175.9(5)], P(1A)-Au(2A)-Cl(2A) 173.9(6) [177.2(10)], Au(2A)-P(1A)-C(4A) 114.4(7) [118.2(10)].

According to the Cambridge Structural Database, there are only two other monomeric species authenticated by X-ray crystallography that feature coordination of two gold (I) centers by a phosphine and by an adjacent carbon atom (Figure 5.2). These were both reported by Jones and coworkers in the mid-1980's, where they explored the multidentate behaviour of the bis(diphenylphosphino)methanide ligands.[6] They discovered that deprotonation of the carbon atom resulted in excess electron density on the

methanide, which was utilized as a donor ligand. The bis(diphenylphosphino)methanide species have a formal negative charge on the carbon carbon, but in our case, the nucelophilic character of the olefinic carbon is due to the highly polarized exocyclic double bond, allowing it to be a neutral 2-electron donor.

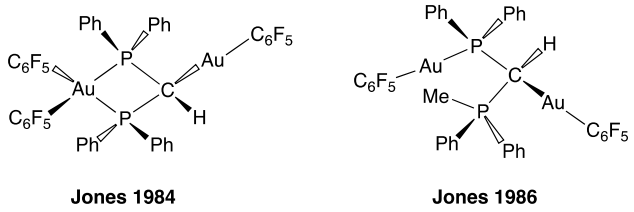


Figure 5.2. Multidentate behaviour of bis(diphenylphosphino)methanide ligands with gold chloride.

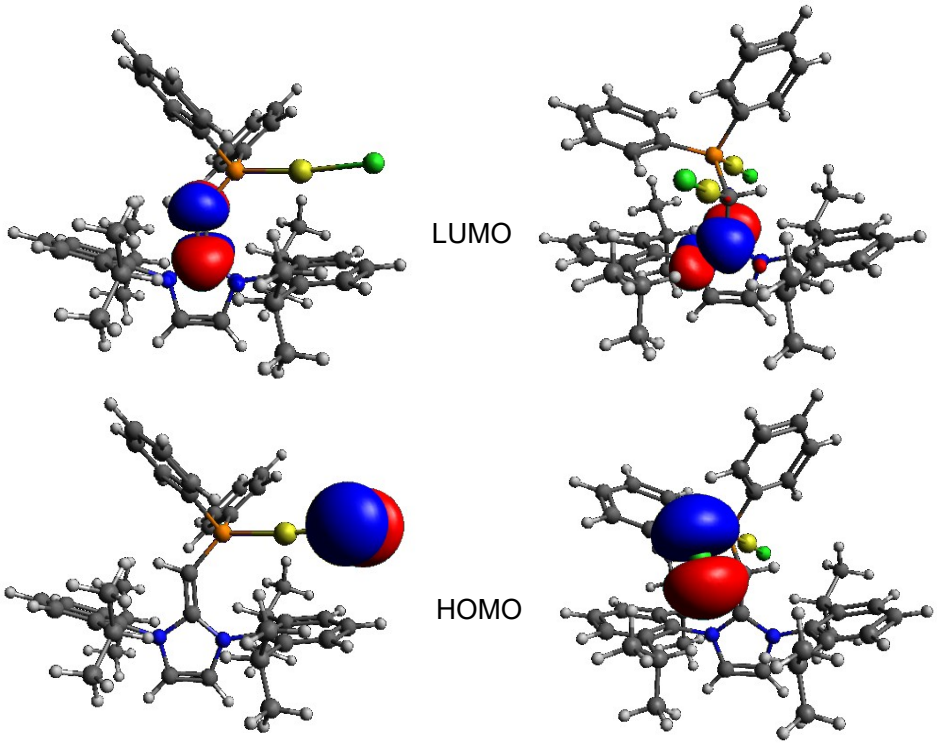


Figure 5.3. Computed HOMO and LUMO for (IPr=CH)PPh_2•AuCl **1** (left) and (IPr-CH)PPh_2•□AuCl **2** (right).

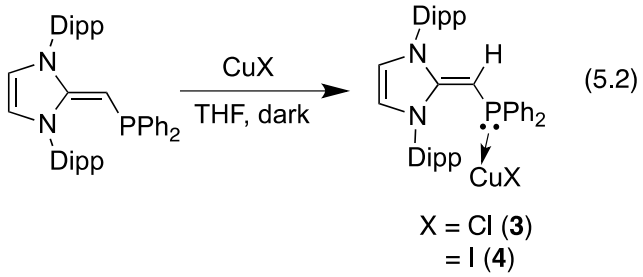
The computed frontier orbitals for the Au(I) NHOP complexes **1** and **2** (Figure 5.3) were obtained via density functional theory (DFT) at the B3LYP/(6-31G(d,p) level for the lighter atoms and LANL2DZ for gold (to account for relativistic effects). Both the HOMOs for **1** and **2** show contributions from the chloride atoms, but in **2**, it is chloride closest to the olefinic donor, as opposed to the chloride near the phosphine donor in **1**. The lone pair contributions for the chloride near the phosphine donor in **2** are situated at HOMO-3 and HOMO-4. The LUMO of (IPr=CH)PPh_2•AuCl shows major C-C π* contributions of the exocyclic olefin; whereas in **2** the LUMO shows N-C antibonding interactions located on the cyclic imidazole unit and a small contribution on the olefinic carbon. The HOMO-LUMO gap of the mono- and digold complexes **1** and **2** were 6.35 and 4.44 eV, respectively. The Wiberg bond order for the exocyclic C-C unit in **2** (1.12) suggests a decrease in multiple bond character upon complexation of AuCl; for comparison, the Wiberg bond order for the uncomplexed C=C unit in **1** is 1.45.

Cationic gold (I) species have been shown to be effective in catalytic studies, such as for hydroamination or oxidative cyclization.[7, 8] Accordingly, compound **2** was treated with Na[SbF_6] (1 equiv. or 2 equiv.), but no reactivity was observed. When Ag[SbF_6] (1 equiv.) was combined with **2**, the formation of a black precipitate was noted immediately and four different phosphorus containing products were found. When Ag[SbF_6] (2 equiv.) was added to **2**, six different species containing phosphorous were found, as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy, with no products overlapping with the products in the reaction with 1 equiv. of Ag[SbF_6]. Compounds with Au-F bonds have been

reported to have signals from -236 to -249 ppm in the $^{19}F\{^{1}H\}$ NMR,[8d, e] but no signals this downfield were observed. With the recent advances in σ,π-digold acetylide complexes,[7] I was intrigued to see if incorporating an acetylene into **2** would induce an interaction between the two gold (I) centers. Trimethylsilylacetylene was treated with **2**, with the intention that the acetylene would first coordinate to the more reactive olefin donor-Au site with a concomitant elimination of $ClSiMe_3$; however, no reaction was observed. **2** was then reacted with the lithiated trimethylsilylalkyne, with the hope that the trimethylsilyl group could later be useful, but the product could not be identified by ^{1}H NMR spectroscopy. **2** also did not react with bis(trimethylsilyl)acetylene at room temperature overnight.

Copper (I) complexes are also becoming increasingly popular in the literature due to their ability as inexpensive, efficient catalysts.[9] I was inspired to synthesize a heterobimetallic species supported by $(IPr{=}CH)PPh_2$, featuring one copper (I) center and one gold (I) center. Added motivation for this work is the emerging prominence of tandem catalysis, where multiple active metal sites and reagents are combined in 'one-pot' (or within a single molecule) to instigate cooperative substrate activation.[10] It would also be of interest to the synthetic community if our mixed Au/Cu bimetallic species could selectively perform separate catalytic reactions, such as hydroamination at the Au(I) center and the azide-alkyne cycloaddition on the Cu(I) center. It was expected that the harder phosphine would coordinate to harder Lewis acidic copper(I) center, and that the softer and more polarizable olefinic donor would coordinate to the softer gold(I) center, in line with previous observations.

The requisite (IPr=CH)PPh_2•CuX complexes, where X = Cl (**3**) or I (**4**), were prepared in a straightforward manner by combining the neutral (IPr=CH)PPh_2 with stoichiometric amounts of CuCl or CuI in THF, followed by stirring in the dark at room temperature for 90 minutes (Equation 5.2). Both (IPr=CH)PPh_2•CuCl **3** and (IPr=CH)PPh_2•CuI **4** were isolated as crystalline white solids (in 96 and 66 % yields, respectively) and characterized by NMR spectroscopy, X-ray crystallography and elemental analysis. These Cu(I) complexes exhibited the same overall geometry (Figures 5.4 and 5.5) including significant deviation from the expected linear geometry within the P-Cu-X residues. (IPr=CH)PPh_2•CuI (**4**) had a significantly narrower <P-Cu-I angle of 144.52(2)° compared to the related P-Cu-Cl angle of 156.724(19)° in (IPr=CH)PPh_2•CuCl (**3**). The interactions between the Cu(I) and the flanking Dipp group are quite pronounced; the Dipp···Cu distances were as low as 3.103 Å for the **3** and 2.706 Å for **4**. For comparison, arene-Cu(I) complexes featuring bis[2-(2-pyridyl)ethyl]amine tridentate ligands that have been structurally characterized with η^2 coordination have distances from 2.172(9) – 2.655(9) Å.[11, 12]



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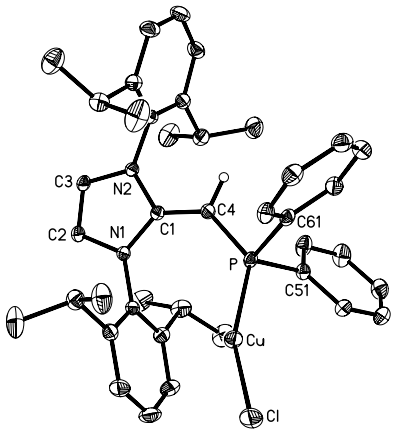


Figure 5.4. Molecular structure of (IPr=CH)PPh_2•CuCl (**3**) with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (°): P-Cu 2.1715(4), Cu-Cl 2.1203(4), P-C(4) 1.7525(14), C(1)-C(4) 1.3755(18), P-C(51) 1.8316(14), P-C(61) 1.8333(15); P-Cu-Cl 156.724(19), Cu-P-C4 131.09(5), P-C(4)-C(1) 133.74(11), C(4)-P-C(51) 108.14(7), C(4)-P-C(61) 99.87(6), Cu-P-C(51) 106.52(5), Cu-P-C(61) 105.86(5).

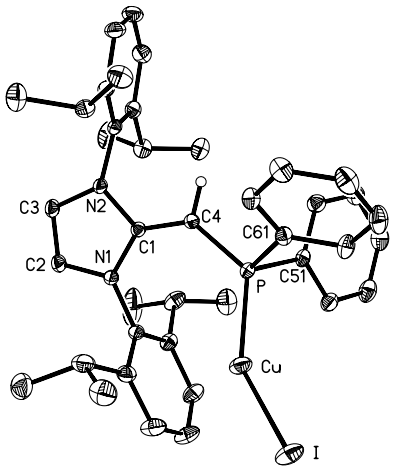


Figure 5.5. Molecular structure of (IPr=CH)PPh_2•CuI (**4**) with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (°): P-Cu 2.2025(5), Cu-I 2.4394(3), P-C(4) 1.7596(18), C(1)-C(4) 1.375(3), P-C(51) 1.8355(19), P-C(61) 1.8356(19); P-Cu-I 144.52(2), Cu-P-C(4) 128.41(6), P-C(4)-C(1) 132.02(14), C(4)-P-C(51) 106.50(9), C(4)-P-C(61) 102.30(8), Cu-P-C(51) 110.86(6), Cu-P-C(61) 106.50(9).

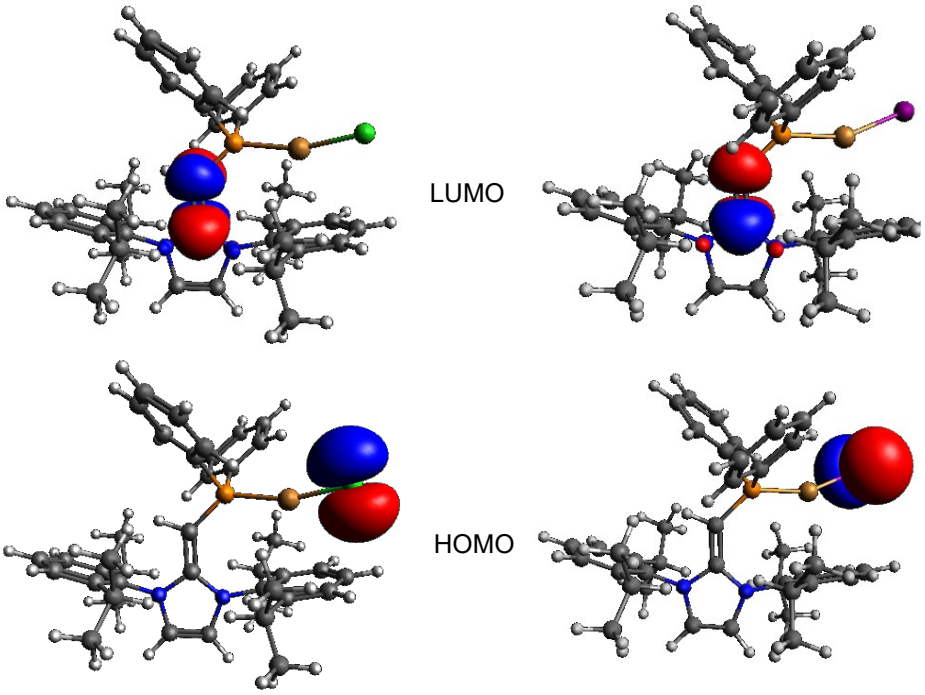
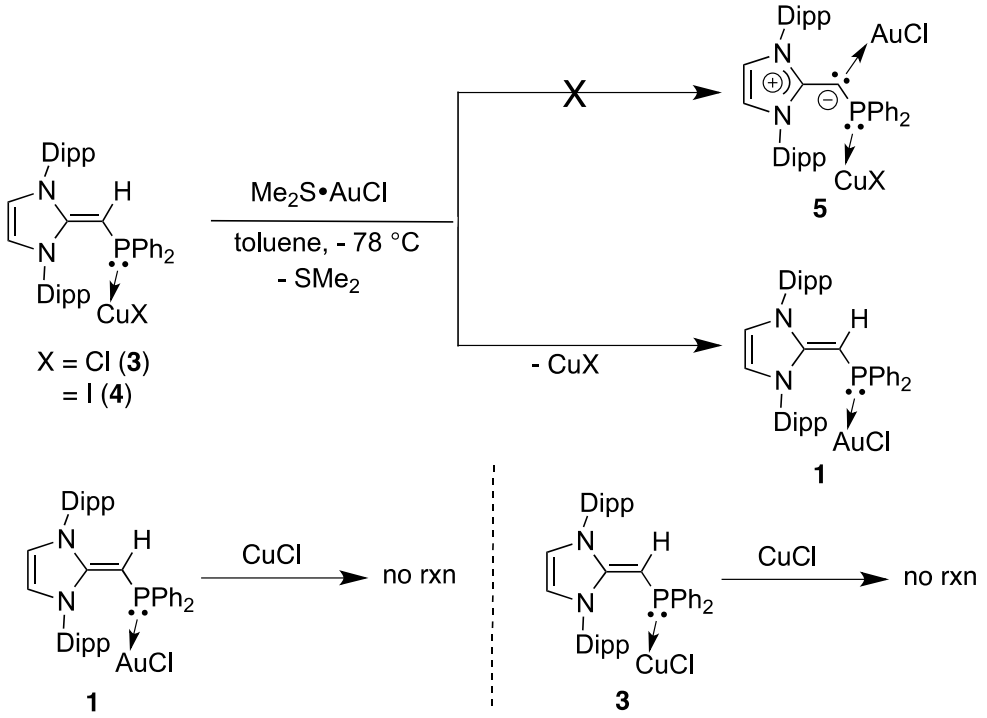


Figure 5.6. Computed HOMO and LUMO for (IPr=CH)PPh_2•CuCl **3** (left) and (IPr=CH)PPh_2•CuI **4** (right).

The HOMO and LUMO of both NHOP copper complexes **3** and **4** (Figure 5.6) were similar according to computational studies. The HOMO a lone pair featured contributions on the halide atom, while both LUMO exhibited C=C π* interactions on the exocyclic olefin of the ligand. Compound **3** has a HOMO-LUMO gap of 6.30 ev and **4** has a smaller HOMO-LUMO gap of 5.44 eV.

Starting from the newly synthesized Cu(I) complexes **3** and **4**, the synthesis of mixed heterobimetallic species were attempted by reacting them independently with Me_2S•AuCl to encourage coordination at the exposed olefinic donor site (Scheme 5.2). Somewhat surprisingly, the clean conversion to (IPr=CH)PPh_2•AuCl (**1**) was consistently observed. Even when the reaction

was performed at -78 °C and worked up after 15 minutes, the quantitative displacement of the CuX (X = Cl or I units) on the phosphine with AuCl transpired. As a control experiment and to confirm the initial rationalization that a copper (I) center would be a hard-soft mismatch with the olefinic donor, (IPr=CH)PPh_2•AuCl **1** was combined with stoichiometric amounts of CuCl, but no reaction was observed (Scheme 5.2). In addition, (IPr=CH)PPh_2•CuCl **3** was treated with second equiv. of CuCl, but no reaction occurred either.



Scheme 5.2. Attempted reactions to prepare new bimetallic species supported by the $NHOPPh_2$ ligand.

Gold and copper hydride complexes are considered intermediates in many homogeneous Au and Cu-catalyzed reactions, such as hydrosilylation and hydroborylation.[13] Group 11 hydrides, in general, are difficult to isolate, thus many catalytic systems generate the gold or copper hydride *in situ*. The first

stabilized form of copper hydride is the hexameric $[(Ph_3P)CuH]_6$, which was prepared by Osborn and coworkers[14] and later described as an efficient reducing agent for carbonyl compounds by Stryker and coworkers.[15] More recently, Sadighi et al. demonstrated that NHCs could support a monomeric gold hydride IPr•AuH as well as a dimeric copper hydride $[IPr•CuH]_2$ and demonstrated their reactivity with alkynes.[16] Motivated by these important studies, I wanted to determine if the NHO-linked phosphine ligand was sufficiently electron donating and sterically demanding to support a gold or copper hydride. When $(IPr{=}CH)PPh_2$•AuCl **1** was treated with KH, $K[HB^sBu_3]$, or Et_3SiH at -30 °C, an insoluble metallic precipitate formed immediately and only free $(IPr{=}CH)PPh_2$ was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Similar results were observed when $(IPr{=}CH)PPh_2$•CuCl **3** was combined with $K[HB^sBu_3]$, or Et_3SiH at -30 °C, where again $(IPr{=}CH)PPh_2$ was the only soluble product isolated. It was evident that $(IPr{=}CH)PPh_2$ was not a suitable scaffold to support a stable gold or copper hydride. Inspired by previous group work involving zinc hydrides,[20] attempts to apply the transiently-generated Group 11 hydride to catalyze the hydrosilylation of benzophenone was attempted. Unfortunately, the catalystic hydrosilylation of benzophenone with $MePhSiH_2$ was not observed at room temperature with $(IPr{=}CH)PPh_2$•MCl (M = Au or Cu) at 4 mol %.

Since highly photoluminescent copper(I) complexes are being intensely investigated with potential applications in organic light-emiting diodes (OLEDs),[17] the potential for the NHOP•CuX compounds **3** and **4** to show photoluminescence was tested by irradiation from a handheld UV-lamp.

Surprisingly, (IPr=CH)PPh_2•CuCl **3** exhibited no visible luminescence in solution or solid state, whereas, (IPr=CH)PPh_2•CuI **4** exhibited a bright yellow emission in the solid state but is only very weakly emissive in solution (THF). The solution fluorescence spectrum of (IPr=CH)PPh_2•CuI exhibited two emission peaks, a weak one at λ_{emis} = 386 nm and a prominent peak at λ_{emis} = 518 nm (Figure 5.7). The peak at λ_{emis} = 386 nm overlaps with a Raman band from the solvent; however, by changing the excitation wavelength, the Raman band shifted accordingly and the two emission peaks persisted.

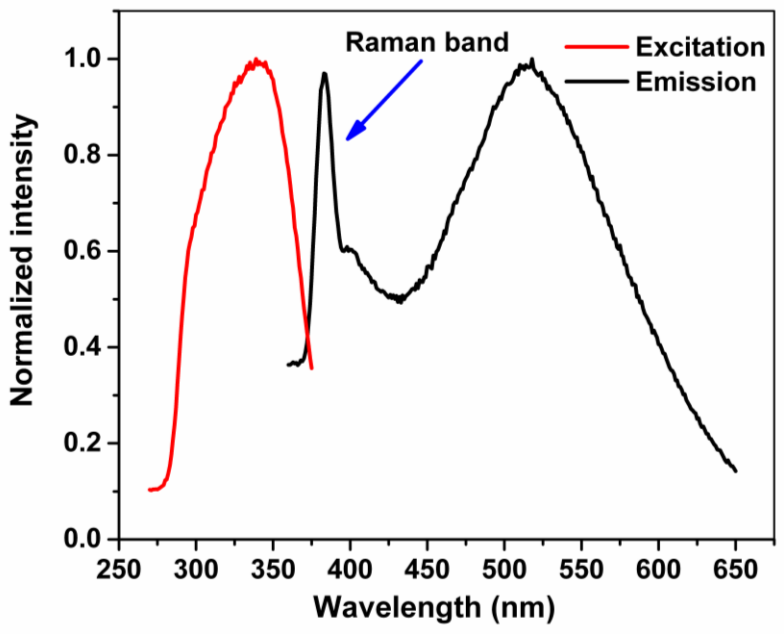


Figure 5.7. Normalized photoluminescence (PL) excitation and emission spectra of (IPr=CH)PPh_2•CuI **4** with λ_{ex} = 343 nm in THF.

The above luminescence in **4** prompted further investigation into the luminescence properties of the neutral ligand (IPr=CH)PPh_2 and its gold(I) complexes. Interestingly, (IPr=CH)PPh_2 appeared to be emissive in the solid state (green) and weakly emissive in solution (THF) with blue-green

photoluminescence (λ_{emis} = 487 nm) (Figure 5.8). However, (IPr=CH)PPh_2•AuCl (**1**) and (IPr=CH)PPh_2•□AuCl (**2**) were both non-emissive in the solid state and in solution.

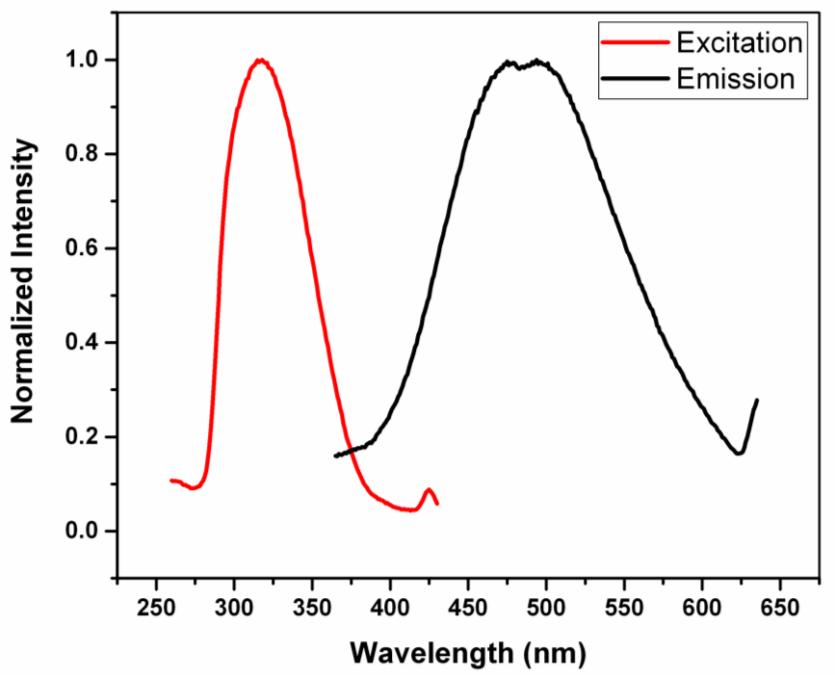
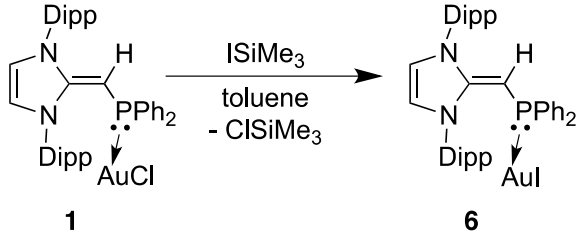


Figure 5.8. Normalized PL excitation and emission spectra of (IPr=CH)PPh_2 with λ_{ex} = 317 nm in THF.

The observation that the ligand (IPr=CH)PPh_2 and its copper (I) iodide complex (**4**) were emissive, but not other Group 11 chloride NHOP complexes led to studies to answer whether the iodide played a role in the luminescence in **4**. By reacting (IPr=CH)PPh_2•AuCl with 1 equiv. of $ISiMe_3$ in toluene, the desired product (IPr=CH)PPh_2•AuI (**6**) (Equation 5.3) was isolated as an off-white crystalline solid in a 39 % yield, characterized by NMR spectroscopy, X-ray crystallography and elemental analysis. The overall geometry of **6** resembled that of its chloro congener (IPr=CH)PPh_2•AuCl (**1**), except that (IPr=CH)PPh_2•AuI **6** had a slightly longer P-C(olefin) bond of 2.2635(9) Å (cf.

2.2334(8) Å in **1**) (Figure 5.9); likewise the DFT-calculated HOMO and LUMO for **6** were similar to those of its chloride analogue **1** (Figure 5.10). However, **6** was blue emissive in the solid state and very weakly blue emissive in solution (λ_{emis} = 463 nm in THF) (Figure 5.11), unlike its non-emissive chloro derivative **1**.



1 **6** (5.3)

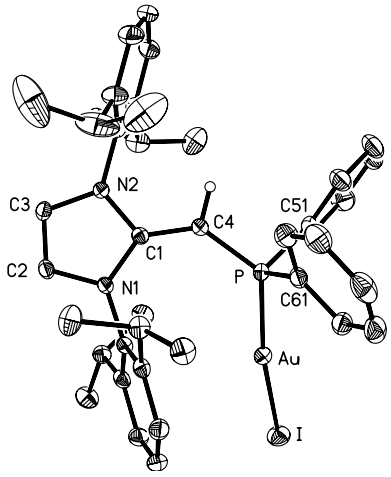


Figure 5.9. Molecular structure of (IPr=CH)PPh_2•AuI **6** with thermal ellipsoids at the 30 % probability level. The hydrogen atom attached to C(4) is shown with an arbitrarily small thermal parameter; all other hydrogens have been omitted for clarity. Selected bond lengths (Å) and angles (°): P-Au 2.2635(9), Au-I 2.5680(3), P-C(4) 1.742(4), C(1)-C(4) 1.381(5), P-C(51) 1.836(4), P-C(61) 1.827(4); P-Au-I 169.47(3), Au-P-C(4) 124.69(13), P-C(4)-C(1) 135.4(3), C(4)-P-C(51) 100.23(17), C(4)-P-C(61) 109.01(19), Au-P-C(51) 105.08(14), Au-P-C(61) 111.68(13).

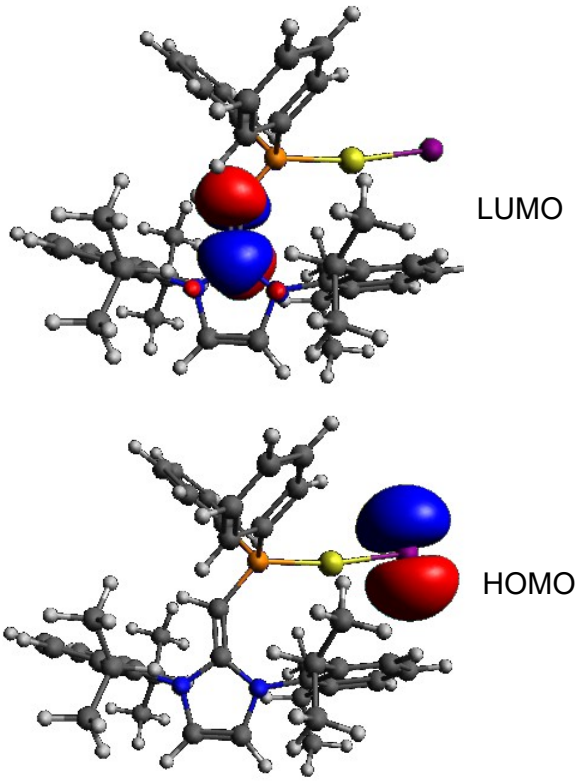


Figure 5.10. Computed HOMO and LUMO for (IPr=CH)PPh_2•AuI **6**.

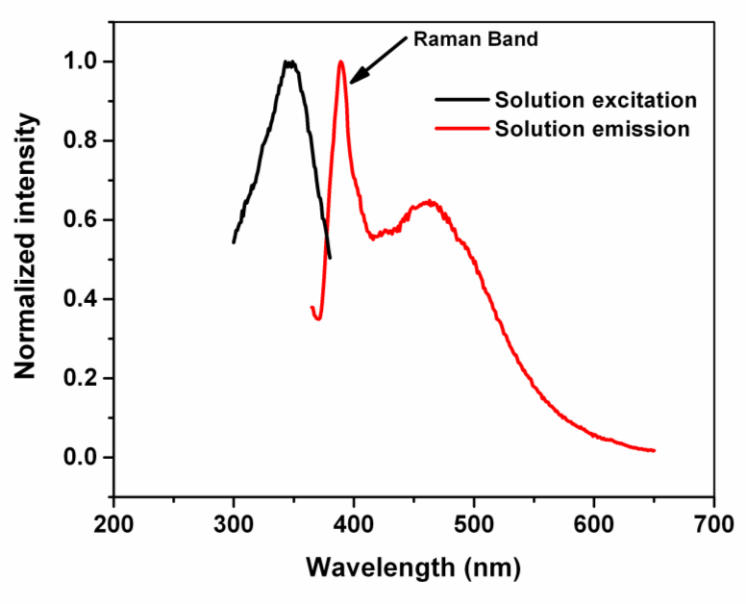


Figure 5.11. Normalized PL excitation and emission spectra of (IPr=CH)PPh_2•AuI **6** with λ_{ex} = 348 nm in THF.

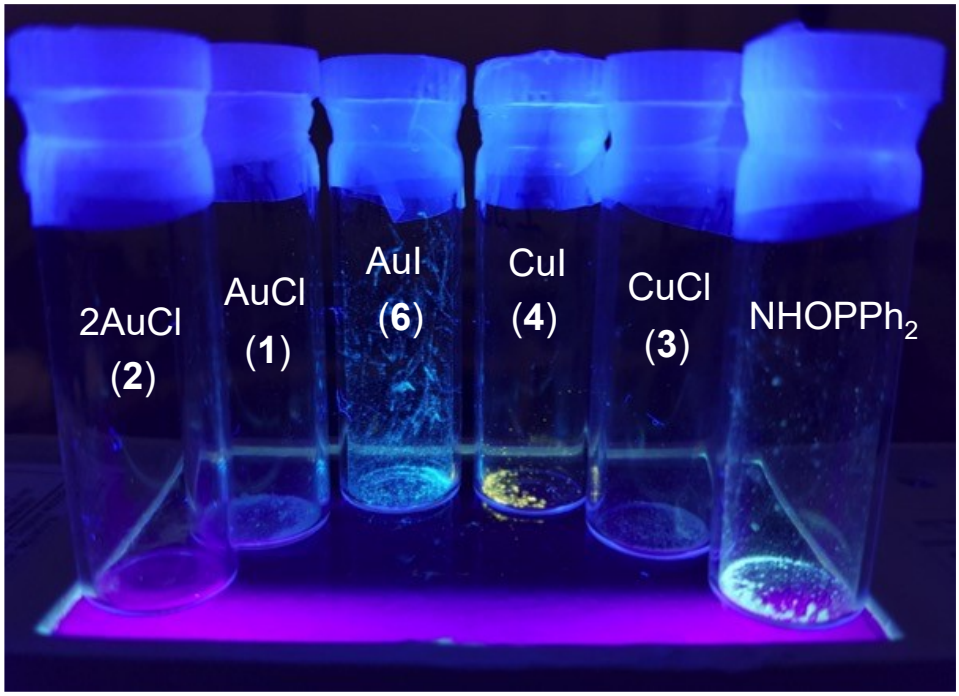


Figure 5.12. Compounds **1**-**4**, **6** and (IPr=CH)PPh_2 in the solid state under UV light in an N_2 atmosphere.

5.3 Conclusions

The preparation and characterization of a new digold (I) chloride complex (IPr=CH)PPh_2•□AuCl **2** is reported, demonstrating that the two donor sites of the (IPr=CH)PPh_2 ligand can be accessed at the same time. Attempts to prepare a mixed bimetallic complex featuring copper (I) and gold (I) centers with this mixed donor system were unsuccessful. The copper (I) and gold (I) iodide complexes **4** and **6** were discovered to be emissive in the solid state and preliminary luminescence data was reported. Our group is currently exploring these luminescence properties with more experimental data as well as TD-DFT methods in collaboration with the Klobukowski group to better understand the nature of the emission.

5.4 Experimental

5.4.1 General

All reactions were performed in either an inert atmosphere glove box (Innovative Technology, Inc.) or using Schlenk techniques. Solvents were dried using a Grubbs-type solvent purification system manufactured by Innovative Technologies, Inc. and stored under an atmosphere of nitrogen prior to use.[18] Chlorodiphenylphosphine, dimethylsulfide gold(I) chloride, copper (I) chloride, copper (I) iodide, trimethylsilyliodide were used as received from Sigma Aldrich. IPr=CH_2,[4a] IPr,[19] and (IPr=CH)PPh_2[5] were prepared according to literature procecures. ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Varian VNMRS-400 or Varian VNMRS-500 spectrometer and referenced externally to $SiMe_4$, 85 % H_3PO_4, or $F_3B{\bullet}OEt_2$. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected. The luminescence measurements were conducted on a Photon Technoogy International (PTI) MP1 fluorescence system.

5.4.2 X-ray Crystallography

Crystals for X-ray diffraction studies were removed from a vial and immediately coated with thin a layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fiber, and quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer. All data were

collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα or Cu Kα radiation, with the crystals cooled to -100 °C. The data was corrected for absorption through Gaussian integration from the indexing of the crystal faces. Crystal structures were solved using intrinsic phasing SHELXT[21] (compound **4** and **5**), or Patterson/structure expansion[22] (compounds **2** and **3**) and refined using full-matrix least-squares on F^2. The assignment of hydrogen atoms positions were based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20% greater than those of their parent atoms.

Special refinement conditions:

(IPr-CH)PPh$_2$•2AuCl. The following pairs of distances were constrained to be equal (within 0.03 Å) during refinement: d(Au2A–P1A) = d(Au2B–P1B); d(P1A–C4A) = d(P1B–C4B); d(C1–C4A) = d(C1–C4B). The ring carbons of the disordered phenyl groups C61A–C62A–C63A–C64A–C65A–C66A and C61B–C62B–C63B–C64B–C65B–C66B were refined as idealized regular hexagons, with C–C distances of 1.390 Å and C–C–C bond angles of 120.0°.

5.4.3 DFT Computations

All DFT computations were carried out using the Gaussian 09 software package (Rev. C. 01)[23] with the hybrid density functional B3LYP[24-26] in combination with the LANL2DZ basis set for gold, copper and iodide and 6-31(d,p) for all other atoms. Input geometries were generated from the xyz atomic coordinates determined in the solid-state X-ray crystal structures of the molecules being

studied and fully optimized in the gas phase without symmetry constraints. The obtained optimized geometries were confirmed to be a local energy minimum structure by performing a vibrational frequency analysis.

5.4.4 Synthetic Procedures

Synthesis of (IPr-CH)PPh_2•2AuCl (2). In the dark, a cooled (-30 °C) solution of (IPr=CH)PPh_2•AuCl (193 mg, 0.236 mmol) in 5 mL of toluene was slowly added to a cooled (-30 °C) solution of Me_2S•AuCl (69 mg, 0.24 mmol) in 2 mL of toluene to give a pale yellow solution. This reaction mixture was stirred for 15 minutes leading to the formation of a small amount of precipitate. The precipitate was allowed to settle, and the supernatant was filtered before the volatiles were removed from the filtrate to afford (IPr-CH)PPh_2•2AuCl as a white solid. The reaction precipitate was extracted with fluorobenzene (3 x 2 mL), filtered, followed by the removal of volatiles to yield a second crop of (IPr-CH)PPh_2•2AuCl as a white solid. The toluene and fluorobenzene fractions were combined (208 mg, 84 %). This compound decomposes over time at room temperature; it was stored in the freezer (-30 °C) when not being used. Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution of CH_2Cl_2 and hexanes (1:1 ratio). Note: exposure to CH_2Cl_2, even at cold temperatures will result in the decomposition to [(IPr=CH_2)PPh_2•AuCl][$AuCl_2$]. If recrystallization of (IPr=CH)PPh_2•2AuCl is desired, use toluene or fluorobenzene as a solvent is preferable. ^{1}H NMR (400 MHz, BrC_6D_5, -10 °C): δ 7.89 (dd, $^3J_{HP}$ = 14.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, Ph*H*),

7.62 (dd, $^{3}J_{HP}$ = 14.0 Hz, $^{3}J_{HH}$ = 8.0 Hz, 2H, Ph*H*), 7.19 – 7.04 (br m, 4H, Ar*H*), 7.00 – 6.68 (m, 9H, Ar*H*, Ph*H*, N(C*H*)$_2$N), 6.46 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, N(C*H*)$_2$N), 3.97 (septet, $^{3}J_{HH}$ = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 3.73 (septet, $^{3}J_{HH}$ = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 3.60 (d, $^{2}J_{HP}$ = 12.8 Hz, 1H, C*H*PPh$_2$), 3.59 (septet,$^{3}J_{HH}$ = 8.4 Hz, 1H, C*H*(CH$_3$)$_2$), 2.55 (septet, $^{3}J_{HH}$ = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 1.87 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.86 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.80 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.22 (br, 6H, CH(C*H*$_3$)$_2$), 0.92 (br, 9H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ 154.5 (d, $^{2}J_{CP}$ = 2.5 Hz, N*C*N), 145.4 (br, Ar-*C*), 137.3 (Ar-*C*), 133.9 (Ar-*C*), 133.6 (d, $^{1}J_{CP}$ = 14.2 Hz, Ph-*C*), 133.3 (Ar-*C*), 133.1 (d, $^{1}J_{CP}$ = 14.7 Hz, Ph-*C*), 132.5 (br, Ph-*C*), 132.1 (br, Ph-*C*), 131.6 (br, Ph-*C*), 130.3 (d, $^{2}J_{CP}$ = 2.4 Hz, Ph-*C*), 128.6 (d, $^{2}J_{CP}$ = 51.0 Hz, Ph-*C*), 128.2 (Ar-*C*), 127.9 (d, $^{2}J_{CP}$ = 12.0 Hz, Ph-*C*), 125.7 (br, N(*C*H)$_2$N), 124.6 (br, Ar-*C*), 124.2 (br, Ar-*C*), 121.5 (br, Ar-*C*), 115.1 (d, $^{2}J_{CP}$ = 20.7 Hz H*C*PPh$_2$), 34.6 (*C*H(CH$_3$)$_2$), 29.9 (br, *C*H(CH$_3$)$_2$), 29.6 (br, *C*H(CH$_3$)$_2$), 29.1 (br, *C*H(CH$_3$)$_2$), 26.9 (br, CH(*C*H$_3$)$_2$), 26.1 (br, CH(*C*H$_3$)$_2$), 25.7 (br, CH(*C*H$_3$)$_2$), 25.5 (br, CH(*C*H$_3$)$_2$), 25.3 (br, CH(*C*H$_3$)$_2$), 25.2 (br, CH(*C*H$_3$)$_2$), 23.3 (br, CH(*C*H$_3$)$_2$), 22.7 (CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, BrC$_6$D$_5$): δ 37.7. Anal. Calcd. for C$_{40}$H$_{47}$Au$_2$Cl$_2$N$_2$P: C, 45.68; H, 4.50; N, 2.66. Found: C, 44.31; H, 4.92; N, 1.96.

NMR Data for byproduct [(IPr-CH$_2$)PPh$_2$•AuCl][AuCl$_2$]. This byproduct was the only compound isolated (*ca.* 0.007 g) after (IPr-CH)PPh$_2$•2AuCl (*ca.* 0.006 g) was left in CH$_2$Cl$_2$ after 2 days at -30 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.81 (s, 2H, N(C*H*)$_2$N), 7.38 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.42 – 7.39 (m, 2H, Ph*H*), 7.33 (d, $^{3}J_{HH}$ = 10.5 Hz, 4H, Ar*H*), 7.34 – 7.29 (m, 4H, Ph*H*)

7.27 – 7.23 (m, 4H, Ph*H*), 4.11 (d, $^{2}J_{HP}$ = 12.5 Hz, 2H, CH_2PPh$_2$), 2.81 (septet, $^{3}J_{HH}$ = 6.5 Hz, 4H, C*H*(CH$_3$)$_2$), 1.47 (d, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.23 (d, $^{3}J_{HH}$ = 6.5 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 162.9 (Ar-*C*), 145.4 (Ar-*C*), 133.6 (Ar-*C*), 133.0 (br, Ph-*C*), 132.6 (d, $^{2}J_{CP}$ = 14.6 Hz, Ph-*C*), 129.9 (d, $^{2}J_{CP}$ = 12.6 Hz, N*C*N), 129.1 (N(*C*H)$_2$N), 126.2 (Ar-*C*), 126.0 (Ar-*C*), 117.3 (Ar-*C*), 30.2 (*C*H(CH$_3$)$_2$), 26.8 (H*C*PPh$_2$), 26.7 CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 20.5.

Synthesis of (IPr=CH)PPh$_2$•CuCl (3). A solution of (IPr=CH)PPh$_2$ (297 mg, 0.51 mmol) in 2 mL of THF was slowly added to a 1 mL THF solution of CuCl (51 mg, 0.51 mmol) in the dark to give a pale orange solution. This reaction mixture was stirred in the dark at room temperature for 90 minutes before filtration and removal of the volatiles from the filtrate to afford (IPr=CH)PPh$_2$•CuCl as an off-white solid (335 mg, 96 %). Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution in toluene. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.53 – 7.48 (m, 4H, Ph*H*), 7.21 (br s, 4H, Ar*H*), 6.88 – 6.85 (m, 8H, Ph*H* and Ar*H*), 5.79 (s, 2H, N(C*H*)$_2$N), 3.01 (septet, $^{3}J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 2.79 (d, $^{2}J_{HP}$ = 9.0 Hz, 1H, C*H*PPh$_2$), 1.18 (d, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.07 (d, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ 152.3 (d, $^{2}J_{CP}$ = 18.1 Hz, N*C*N), 146.9 (Ar-*C*), 139.3 (d, $^{1}J_{CP}$ = 45.8 Hz, Ph-*C*), 133.7 (Ar-*C*), 132.2 (d, $^{2}J_{CP}$ = 15.3 Hz, Ph-*C*), 131.7 (Ph-*C*), 129.1 (N(*C*H)$_2$N), 128.5 (d, $^{2}J_{CP}$ = 10.3 Hz, Ph-*C*), 125.8 (Ar-*C*), 116.9 (Ar-*C*), 44.5 (d, $^{1}J_{CP}$ = 71.5 Hz, H*C*PPh$_2$), 28.9 (*C*H(CH$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ -18.5. Anal.

Calcd. for $C_{40}H_{47}CuClN_2P$: C, 70.05; H, 6.91; N, 4.08. Found: C, 69.82; H 7.09; N, 4.05.

Synthesis of (IPr=CH)PPh$_2$•CuI (4). A solution of (IPr=CH)PPh$_2$ (42 mg, 0.080 mmol) in 2 mL of THF was slowly added to a 0.5 mL THF solution of CuI (16 mg, 0.84 mmol) in the dark to give a pale orange solution. This reaction mixture was stirred at room temperature for 100 minutes before filtration and removal of the volatiles from the filtrate to afford (IPr=CH)PPh$_2$•CuCl as a pale yellow solid (25 mg, 40 %). Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution in toluene. ^{1}H NMR (400 MHz, C_6D_6): δ 7.63 – 7.58 (m, 4H, Ph*H*), 7.11 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*), 7.06 – 6.99 (m, 3H, Ar*H*), 6.91 – 6.85 (m, 6H, Ph*H*), 5.79 (s, 2H, N(C*H*)$_2$N), 2.99 (septet, $^3J_{HH}$ = 7.2 Hz, 4H, C*H*(CH$_3$)$_2$), 2.83 (d, $^2J_{HP}$ = 8.8 Hz, 1H, C*H*PPh$_2$), 1.16 (d, $^3J_{HH}$ = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$), 1.04 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 152.2 (d, $^2J_{CP}$ = 18.6 Hz, N*C*N), 139.4 (d, $^1J_{CP}$ = 42.6 Hz, Ph-*C*), 137.8 (Ar-*C*), 132.3 (d, $^2J_{CP}$ = 15.2 Hz, Ph-*C*), 129.0 (N(*C*H)$_2$N), 128.5 (d, $^3J_{CP}$ = 3.3 Hz, Ph-*C*), 116.7 (Ar-*C*), 44.4 (d, $^1J_{CP}$ = 66.2 Hz, H*C*PPh$_2$), 29.0 (*C*H(CH$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ -22.5. Mp (°C): 122 (decomp., turned black). Anal. Calcd. for $C_{40}H_{47}CuIN_2P$: C, 61.61; H, 6.10; N, 3.60. Found: C, 61.21; H 6.11; N, 3.55.

Alternate synthesis of **(IPr=CH)PPh$_2$•CuI.** Me$_3$Si-I (10 mg, 0.050) was added to a solution of (IPr=CH)PPh$_2$•CuCl (34 mg, 0.050 mmol) in 2 mL of toluene to give a pale yellow solution. This reaction mixture was stirred at room temperature for 90 minutes. The mixture was filtered and the volatiles were

removed from the filtrate to afford (IPr=CH)PPh_2•CuI as a white solid (26 mg, 66 %).

Synthesis of (IPr=CH)PPh_2•AuI (6). Me_3Si-I (8 mg, 0.04 mmol) was added to a solution of (IPr=CH)PPh_2•AuCl (32 mg, 0.039 mmol) in 2 mL of toluene to give a very pale yellow solution. This reaction mixture was stirred at room temperature for 80 minutes. The mixture was filtered and the volatiles were then removed from the filtrate to afford (IPr=CH)PPh_2•AuI as an off-white solid (14 mg, 39 %). Crystals suitable for X-ray crystallography were obtained by cooling (-30 °C) a saturated solution of toluene layered with hexanes. ^{1}H NMR (400 MHz, C_6D_6): δ 7.56 – 7.50 (m, 4H, Ph*H*), 7.38 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.16 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 6.86 – 6.84 (m, 6H, Ph*H*), 5.80 (s, 2H, N(C*H*)$_2$N), 2.99 (septet, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 2.79 (d, $^2J_{HP}$ = 6.8 Hz, 1H, C*H*PPh_2), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 152.1 (d, $^2J_{CP}$ = 14.2 Hz, N*C*N), 146.8 (Ar-*C*), 139.4 (d, $^1J_{CP}$ = 60.0 Hz, Ph-*C*), 133.7 (Ar-*C*), 132.4 (d, $^2J_{CP}$ = 14.5 Hz, Ph-*C*), 131.6 (N(*C*H)$_2$N), 129.6 (d, $^2J_{CP}$ = 2.4 Hz, Ph-*C*), 128.4 (d, $^2J_{CP}$ = 11.3 Hz, Ph-*C*), 125.9 (Ar-*C*), 117.6 (Ar-*C*), 44.7 (d, $^1J_{CP}$ = 86.9 Hz, H*C*PPh_2), 29.0 (*C*H(CH_3)$_2$), 24.6 (CH(*C*H_3)$_2$), 23.1 (CH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 15.7. Anal. Calcd. for $C_{40}H_{47}AuIN_2P$: C, 52.76; H, 5.20; N, 3.08. Found: C, 52.08; H 5.41; N, 2.80.

5.5 X-ray Crystallographic Data

Table 5.2: Crystallographic Data for Compounds **2**, **3**, **4**, and **6**.

Compound	**2**•CH_2Cl_2	**3**•0.5C_7H_8	**4**	**6**•0.5C_6H_{14}
formula	$C_{41}H_{49}Au_2Cl_4N_2P$	$C_{43.5}H_{51}ClCuN_2P$	$C_{47}H_{55}CuIN_2P$	$C_{43}H_{54}AuIN_2P$
formula weight	1136.52	731.82	869.34	953.72
cryst. dimens. (mm)	0.46 × 0.06 × 0.05	0.42 × 0.09 × 0.09	0.17 x 0.14 x 0.05	0.12 × 0.08 × 0.05
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	*Ia*	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	18.6168 (5)	9.82456 (15)	10.1058 (2)	10.3405 (4)
b (Å)	13.3772 (3)	20.1043 (3)	13.4540 (3)	18.0429 (7)
c (Å)	19.0712 (5)	20.4797 (3)	16.1604 (3)	21.9333 (8)
α (deg)			79.2065 (8)	
β (deg)	115.6488 (11)	99.4697 (7)	79.8317 (10)	97.4577 (19)
γ (deg)			80.8758 (9)	
V (Å^3)	4281.51 (19)	3989.94 (10)	2106.48 (7)	4057.5 (3)
Z	4	4	2	4
ρ_{calcd} (g cm^{-3})	1.763	1.218	1.371	1.561
μ (mm^{-1})	15.57	1.993	7.088	13.38
temperature (°C)	–100	–100	–100	–100
$2\theta_{max}$ (deg)	148.03	148.18	148.08	140.51
total data	14947	28198	15212	27037
unique data (R_{int})	8539 (0.0233)	7929 (0.0222)	8243 (0.0146)	7725 (0.0215)
obs [I > 2σ(I)]	8201	7415	7894	7414
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$] [a]	0.0262	0.0330	0.0282	0.0293
wR_2 [all data]	0.0677	0.0921	0.0728	0.0638
max / min Δ*r* (e Å^{-3})	1.316/ –1.035	0.581/ –0.622	0.715/–0.970	0.983/–0.612

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(Fo^4)]^{1/2}$.

5.6 References

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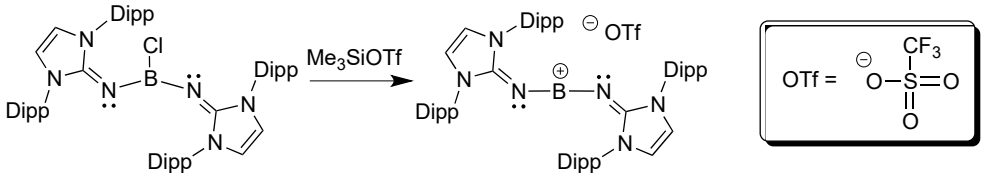
Chapter 6: Summary and Future Work

Chapter 2 described the preparation and characterization of a series of new *N*-heterocyclic iminoboranes that had the ability to abstract H^+/H^- from amine-boranes and instigate their dehydrocoupling. Mild heating of IPr=N(H)-B(Ph)Cl released H_2 and regenerated the starting iminoborane IPr=N-B(Ph)Cl, which made it suitable to be used as a metal-free catalyst. The strong electron donating ability of the *N*-heterocyclic imine (NHI) ligand was demonstrated, especially in the compound $(IPr{=}N)BCl_2$, where its solid state structure and DFT computed data suggested considerable π-interaction between the central nitrogen lone pair to the p orbital of the boron atom. Future work in this project could involve investigating the underexplored species $(IPr{=}N)_2BCl$ that was formed as a side product in the synthesis of $(IPr{=}N)BCl_2$. It did not react with amine-boranes, but I believe that the NHI ligands are bulky and strong enough donors to support a two-coordinate boron cation of the form $[(IPr{=}N)_2B]X$ (X = weakly-coordinating anion), which was be obtained by treating $(IPr{=}N)_2BCl$ with a halide abstracting agent, such Me_3SiOTf (OTf = O_3SCF_3) (Scheme 6.1).



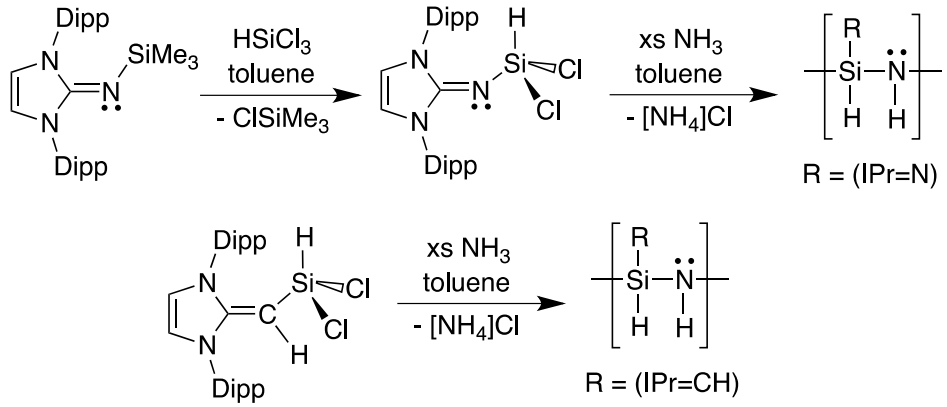
Scheme 6.1. Proposed synthetic route to a NHI-supported borinium cation $[(IPr{=}N)_2B]OTf$.

Two-coordinate borinium cations are typically unstable species at room temperature;[1] sterically encumbering and/or strong electron donating groups

are required for boriniums to survive, which is also the case in Scheme 6.1. Boranes with three substituents are generally viewed as Lewis acids and their ability to accept electron density has driven boron chemistry thus far. Two coordinate boron cations are in theory more electron-deficient than boranes and could serve as a tool for Lewis-acid promoted reactions, such as FLP-type chemistry or cationic initiation for polymerization. Another route this work could take is seeing if polyphosphinoboranes can be generated from the dehydrogenation of phosphine-boranes by *N*-heterocyclic iminoboranes. Polyphosphinoboranes are of interest for their physical properties, such as flame-retardent behaviour. A few transition metal complexes have been reported to catalytically dehydrogenate $PhPH_2 \bullet BH_3$ to give high molecular weight polyphenylphosphinoboranes,[2] which are soluble in aromatic solvents as well as air- and moisture-stable in the solid state.

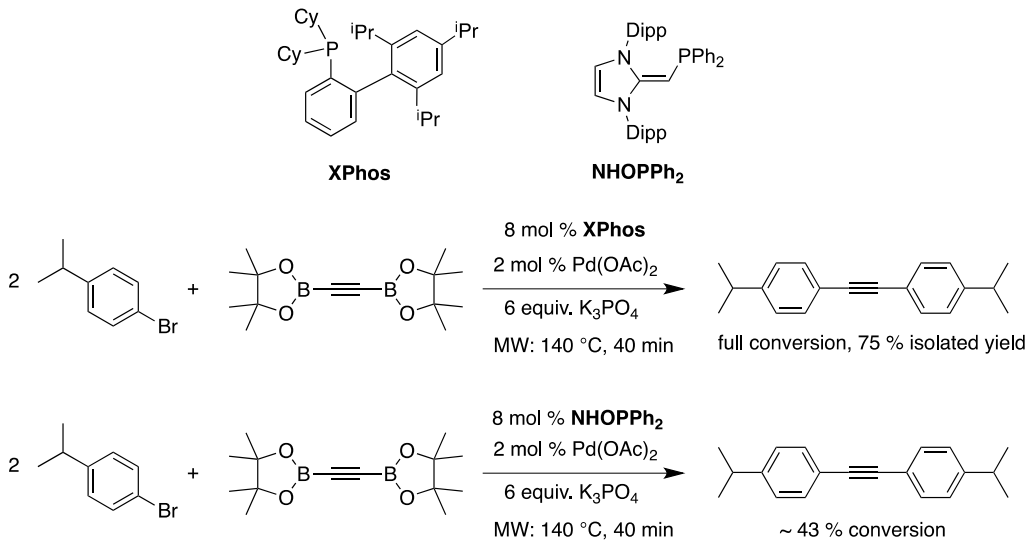
Chapter 3 focused on attempts to prepare heavy carbene analogues featuring the strongly electron releasing NHI ligands. In the case of the silylene, an unusual ligand rearrangement was observed under reducing conditions; whereas, the germylene $(IPr{=}N)_2Ge$: was successfully prepared and exhibited reactivity with H_2, but resulted in the formation of IPr=NH and a precipitate presumed to be germanium metal. An obvious extension of this work would be to explore the reactivity of the germylene with other small molecules, such as CO_2, with hopes of converting it into a more useful product. NHCs have been shown to capture CO_2 directly to form the NHC-CO_2 adduct.[3] Under basic conditions, NHCs were reported to facilitate the reaction of CO_2 with aldehydes to generate carboxylic acids.[3] It would be very interesting if analogous

chemistry could be observed with $(IPr{=}N)_2Ge$:. A potential direction that can be taken with the silicon chemistry is generating soluble polysilazanes (Scheme 6.2), a prospective precursor for ceramics.[4] This inorganic polymer has a backbone consisting of alternating silicon and nitrogen atoms $[R_2Si\text{-}NR]_n$. Since the Si-H bond is stronger than the Ge-H bond, there is a possibility that structures of the form $(IPr{=}N)Si(H)R_2$ (R = halide) may not decompose to give IPr=NH and a silicon-based by-product. In addition, Si(IV) species will be utilized instead of the less stable Si(II) compounds. In Chapter 2, the precursor $IPr{=}N\text{-}SiBr_3$ was prepared by reacting $IPr{=}N\text{-}SiMe_3$ with $SiBr_4$ with a loss of $BrSiMe_3$. Likely, $IPr{=}N\text{-}Si(H)Cl_2$ can be generated in a similar manner. Oligomeric or polymeric chains of $[(IPr{=}N)SiH\text{-}NH]_n$ can then be accessed by reaction with excess NH_3. Ideally, the byproduct $[NH_4]Cl$ would precipitate out and drive the polymerization. The *N*-heterocyclic olefinic derivative $(IPr{=}CH)Si(H)Cl_2$ was recently reported by Ghadwal and coworkers;[5] this would be a suitable monomer to react with excess ammonia as well.



Scheme 6.2. Proposed route to access polysilazanes featuring NHI or NHO substituents on the silicon atom.

Chapter 4 described the design and preparation of new mixed element donor systems based on *N*-heterocyclic olefins and the preliminary coordination of these ligands with Lewis acids were reported. Future work in this area can be further exploring these versatile donors in late transition metal-mediated reactions. Beller and coworkers have demonstrated that the *in situ* generation of NHOP ligands, featuring alkyl substituents on the phosphine, in the presence of a Pd(II) source was effective in the hydroxylation of arylhalides, Sonogashira (C-C) and Buchwald-Hartwig (C-N) coupling reactions.[6] In the Rivard group, the Suzuki cross-coupling reaction between organoboronic acids and halides is often used to prepare starting materials and polymers. The group recently reported the use of the commercially available XPhos[7] ligand under optimized conditions to prepare a bis(cumene)alkyne precursor.[8] Preliminary tests showed that (IPr=CH)PPh_2 was also effective in facilitating the same reaction (Scheme 6.3), albeit under unoptimized reaction conditions. The fact that that the neutral (IPr=CH)PR_2 (R = alkyl or aryl) can be prepared on the multigram scale by undergraduate students independently provides our research team a cost-effective alternative to purchasing XPhos.



Scheme 6.3. Demonstrating the use of $NHOPPh_2$ in Suzuki coupling for a precursor required in the Rivard Group.

Chapter 5 focused on engaging both the phosphine and the olefinic donors to form a digold (I) complex $(IPrCH)PPh_2 \bullet \square AuCl$. Attempts to prepare a bimetallic system featuring a copper and a gold center were unsuccessful. It was also discovered that some of the Group 11 complexes containing $(IPr{=}CH)PPh_2$ as a ligand, were emissive in the solid state, and the initial findings on their luminescent properties were presented. Future work here requires further characterization involving solid state fluorescence measurements and looking for any correlation between the TD-DFT calculated data with the experimental results. The data obtained from the measurements would describe whether these materials would be practical in LEDs. If the data looks promising, perhaps the luminescent NHOP complexes can be incorporated into devices (potential ATUMS collaborative project) and further explored on their utility in LEDs. With the successful isolation of these gold(I)

complexes, it would also be worth testing whether these species can facilitate the catalytic hydroamination of alkynes.[9]

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