MONASH University

# Studies of N-heterocyclic Carbene (NHC) Complexes of the Main Group Elements

*By*

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# *Declaration*

This work presented in this thesis was carried out between January 2010 and March 2018 under the supervision of Professor Cameron Jones and Dr. Andreas Stasch. This thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Anastas Sidiropoulos

[redacted]

School of Chemistry, Monash University

Date: 08 March 2018

*Dedicated to the memory of my grandfather*

***Bill Dimstis***

*who sadly passed away during the progress of this work*

## *Acknowledgements*

Firstly, I'd like to thank Cameron and Andreas for giving me the opportunity to undertake a PhD candidature with them. They have imparted a wealth of knowledge and experience to me which I consider invaluable and I will no doubt use for the rest of my days. I'd like to add an additional thanks to Cameron for all his recent efforts in correcting my thesis and getting me over the line. You're a busy guy so it means a lot that you take time out of your days to help me close this out. I'm forever in your debt.

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To my wonderful family, thanks for your support, encouragement and patience over the years. You guys mean the world to me and I could not have done this without you.

Finally, to my darling wife, Niki, although you'd never admit it, you are truly a remarkable human being. You've been my biggest inspiration throughout this. Not only that I *couldn't* do this without you, but I *wouldn't*. I can't help but love, respect and admire just how amazing you are. Your only fault is that you have terrible taste in men – not that I'm complaining.

## *Abbreviations*

| | |
|---|---|
| 2c-2$e^{-}$ | Two-centre two-electron. |
| Å | Ångström, 1 x $10^{-10}$ m. |
| Ar | A general aryl substituent. |
| Ar* | $2,6(Ph_2CH)_2$-4-$^{i}$Pr-$C_6H_2$. |
| br | Broad. |
| butiso | $[\{(Dipp)N\}_2C\{4\text{-}^{t}BuC_6H_4\}]^{-}$. |
| *ca.* | *circa.* |
| cAAC | cyclic alkyl amino carbene. |
| cal | Calorie (1 kcal = 4.184 J). |
| CDP | carbodiphosphorane. |
| $cm^{-1}$ | Wavenumber, unit of frequency (υ/c). |
| Cp | cyclopentadienyl, $C_5H_5$. |
| Cp* | pentamethyl cyclopentadienyl, $C_5Me_5$. |
| Cy | Cyclohexyl. |
| d | Doublet. |
| DAB | $[\{(Dipp)NC(Me)\}_2]^{2-}$. |
| DCM | Dichloromethane. |
| decomp. | Decomposition. |
| $\delta$ | Chemical shift in NMR spectroscopy (ppm). |
| DFT | Density Functional Theory. |
| Dipp | 2,6-diisopropylphenyl. |
| $^{Dipp}$nacnac | $[\{(Dipp)NC(CH_3)\}_2CH]^{-}$. |
| DMAP | 4-dimethylaminopyridine. |
| DME | 1,2-dimethoxyethane. |
| ° | Degrees. |
| °C | Degrees celcius. |
| $\Delta$ | Change between final and initial |
| E | An element. |
| EPR | Electron paramagnetic resonance. |
| $e^{-}$ | Electron. |

| | |
|---|---|
| Et | Ethyl. |
| $\eta^n$ | Designates coordination to the metal centre in a “side-on” fashion through n atoms. |
| HOMO | Highest Occupied Molecular Orbital. |
| Hz | Hertz, $s^{-1}$. |
| *i* | *ipso*-substituent |
| IMes | $:C\{N(Mes)CH\}_2$. |
| IPr | $:C\{N(Dipp)CH\}_2$. |
| $^6$IPr | $:C\{N(Dipp)CH_2\}_2CH_2$. |
| $^i$Pr | isopropyl. |
| IPr$^i$Me | $:\{N(^iPr)C(Me)\}_2$. |
| IPr* | $:C\{N(Ar^*)CH\}_2$. |
| IR | Infra Red. |
| J | Joule. |
| $^nJ_{E,E'}$ | Coupling constant between nuclei E and E' separated by *n* bonds (Hz). |
| K | Kelvin. |
| $\kappa$ | Designates a chelate ring that includes one or more dative bonds. |
| λ | Wavelength. |
| L | A ligand. |
| LUMO | Lowest Unoccupied Molecular Orbital. |
| M | A general metal or molar (mol $L^{-1}$) |
| $M^+$ | A molecular or metal ion. |
| m | Multiplet (NMR); Medium (IR). |
| *m* | *meta*-substituent. |
| MALDI | Matrix-Assisted Laser Desorption/Ionization. |
| Me | Methyl. |
| Mes | 2,4,6-trimethylphenyl. |
| $^{Mes}$nacnac | $[\{(Mes)NC(CH_3)\}_2CH]^-$. |
| MG | Main group. |
| mol | Mole. |

| | |
|---|---|
| M.p. | Melting Point. |
| MS | Mass Spectrometry. |
| *m/z* | mass/charge ratio |
| $\mu$ | Designates a bridging atom, or subunit, in a molecular structure. |
| nacnac | A general $\beta$-diketiminate ligand. |
| NBO | Natural Bond Order. |
| $^{n}$Bu | Primary butyl. |
| NHC | N-heterocyclic carbene. |
| NHSi | N-heterocyclic silylene. |
| NMR | Nuclear Magnetic Resonance. |
| *o* | *ortho*-substituent. |
| *p* | *para*-substituent. |
| Ph | Phenyl. |
| ppm | Parts per million. |
| q | Quartet. |
| R | General organic substituent. |
| s | Singlet (NMR); Strong (IR). |
| $^{s}$Bu | Secondary butyl. |
| sept | Septet. |
| t | Triplet. |
| $^{t}$Bu | Tertiary butyl. |
| THF | Tetrahydrofuran |
| TM | Transition metal(s). |
| TMC | Tetramethyl carbene, $:C\{N(Me)C(Me)\}_{2}$. |
| TMS | Trimethylsilyl or tetramethylsilane. |
| Tipp | 2,4,6-triisopropylphenyl. |
| UV | Ultra Violet. |
| v | Very. |
| w | Weak. |
| $\tilde{v}$ | Wavenumber. |
| X | A halide. |

## *Abstract*

Chapter 1 gives a general introduction into low oxidation state (LOS) main group (MG) chemistry, It discusses past notions such as the "double bond rule" and the inert pair effect and how recent and ongoing research has given new understanding to these classical concepts as well as giving new understanding into the bonding modes of compounds containing heavier main group elements. It also discusses the types of ligands involved in the synthesis of LOS MG compounds, in particular, N-heterocyclic carbenes (NHCs) and the synthetic routes used to develop compounds containing these ligands.

Chapter 2 details the procedures involved in the formation of NHC-group 2 and group 12 element adducts, as well as the reduction of these adducts using various reducing agents, including a novel β-diketiminato-magnesium(I) compound. It also discusses the use of NHC analogues, such as carbodiphosphoranes (CDPs) and N-heterocyclic silylenes (NHSis), as alternatives to NHCs in this field. Finally, the use of an N-donor ligand, diazabutadiene (DAB) is introduced and its unexpected, intra-molecular cyclization yielding a novel organic product is described.

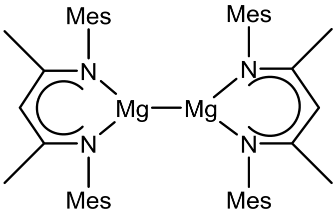
Chapter 3 communicates much of the same as chapter 2 regarding the formation of neutral donor adducts, however, describes the findings of the group 13 elements instead of group 2 and group 12 elements. Worth mentioning is the novel NHC-capped, dioxane-bridged, $Ga_4Cl_8$ centered compound, $IPr{\cdot}GaCl_2GaCl_2$-μ-dioxane-$Cl_2GaCl_2Ga{\cdot}IPr$, (IPr = :C{N(Dipp)CH}$_2$. Dipp = 2,6-diisopropylphenyl) and its dioxane-removed, "little brother" $(IPr{\cdot}GaI_2)_2$, the latter of which possesses great potential as a synthon for lower oxidation state chemistry.

Chapter 4 extends on the synthesis, isolation and further chemistry of NHC and NHC analogue adducts, with a focus on the group 14 elements. A significant amount of research is based on previous work done in the Jones group from 2009, involving the synthesis of the NHC capped, digermanium(0) fragment $(IPr{\cdot}Ge)_2$. Extending on from this, the analogous tin(0) dimer $(IPr{\cdot}Sn)_2$ was synthesized and is discussed within. N-donor amidinato-silicon and germanium complexes are also mentioned, as well as the thermal isomerization of an amidinato-silicon(I) dimer, which resulted in an asymmetric, mixed-valent silicon hydride.

Finally, chapter 5 focuses on 6-membered NHCs, in particular, $^6$IPr $(:C\{N(Dipp)CH_2\}_2CH_2)$, its coordination to group-15 element chlorides and the reduction of these NHC coordinated products. In one example, a dicationic $P_4$ centered compound is isolated $[(^6IPr)_2(\mu\text{-}P_4)][Cl]_2$ via a $KC_8$ reduction of the neutral adduct, $^6IPr{\cdot}PCl_3$.

## *Summary of Compounds*

### *Neutral donor ligands and the magnesium(I) dimer {($^{Mes}$nacnac)Mg}$_2$, ($^{Mes}$nacnac = {[(Mes)NC(Me)]$_2$CH}$^-$)*



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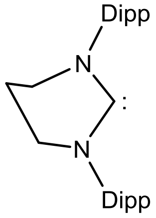

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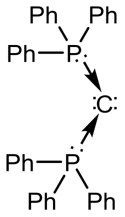

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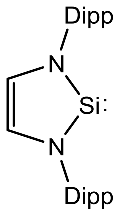

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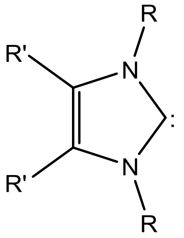
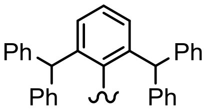
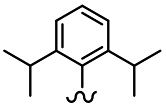
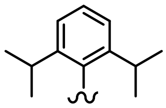
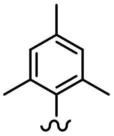
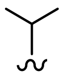
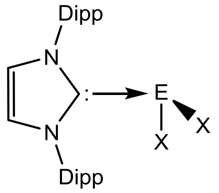
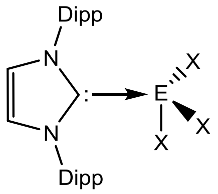


| R |  |  |  |  |  | Me |
|---|---|---|---|---|---|---|
| R' | H | Me | H | H | Me | Me |
| NHC | IPr* | $^{Me}$IPr | IPr | IMes | IPr$^{i}$Me | TMC |
|  | **1.3** | **1.4** | **1.5** | **1.6** | **1.7** | **1.8** |

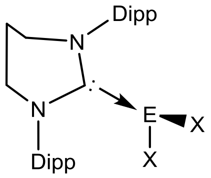
## *NHC adducts of group 2, 12-15 element fragments and amidinato-group 14 complexes*



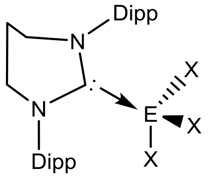
E = Zn, X = Br; **2.20**
E = Cd, X = I; **2.21**
E = Hg, X = I; **1.47**
E = Si, X = Cl; **4.4**
E = Ge, X = Cl; **1.26**
E = Sn, X = Cl; **4.30**
E = Pb, X = Br; **4.33**



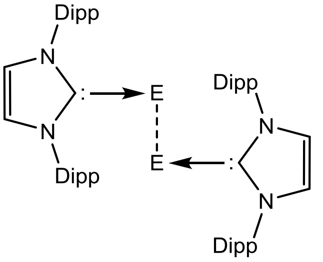
E = B, X = Br; **1.48**
E = Al, X = H; **1.57**
E = P, X = Cl; **1.88**
E = As, X = Cl; **1.90**
E = Ga, X = I; **3.24**



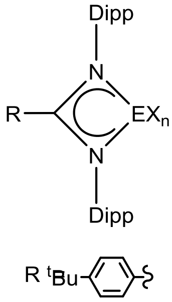
E = Zn, X = Br; **2.25**
E = Ge, X = Cl; **4.25**



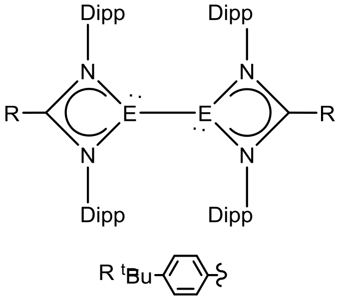
E = B, X = Br; **3.18**
E = Al, X = Cl; **3.19**
E = P, X = Cl; **5.6**
E = As, X = Cl; **5.7**
E = Sb, X = Cl; **5.8**



E = B; **1.52**
E = Si; **2.69**
E = Ge; **1.28**
E = Sn; **4.31**
E = P; **1.89**
E = As; **4.91**



E = Si, n = 3; **4.18**
E = Ge, n = 1; **4.19**
E = Sn, n = 1; **4.20**



E = Si; **4.21**
E = Ge; **4.22**
E = Sn; **4.23**

## *Contents*

# 1 General Introduction

## 1.1 Low Oxidation State Main Group Chemistry

The relative difficulty in isolating low oxidation state (LOS) main-group (MG) compounds (under standard laboratory conditions) is largely due to their low thermodynamic stability and low electron saturation of their metal coordination spheres, leaving them susceptible to coordination by unwanted electron rich species. This inhibited the synthesis and isolation of these compounds until the late 1970s/early 1980s.[1] Prior to that, MG elements (within compounds) almost exclusively existed in oxidation states equivalent to the amount of valence electrons they possessed (eg. $Mg^{II}$, $Al^{III}$, $Si^{IV}$ etc.). In order to obtain these elements in lower oxidation states, the use of high kinetic energy barriers are required to “stabilize” these meta-stable states. In the past, the use of sterically demanding ligands has often been required to provide this kinetic stability.

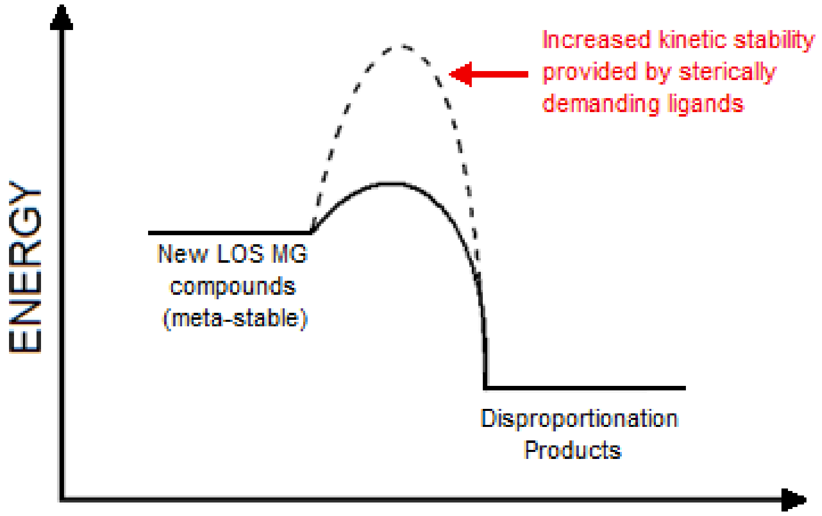


**Figure 1.1:** Kinetic stabilization of LOS MG compounds

Heavier main group elements (specifically p-block elements) behave significantly different to their lighter congeners. A large factor contributing to this is a phenomenon known as the inert pair effect. Effectively, the valence s-orbital electrons are rendered inert (relatively) as it is energetically favourable for them to remain in the lowest energy s-orbital, rather than be promoted or hybridized to higher orbitals.[2] In accordance with the inert pair effect, heavier main group elements tend to resist the formation of multiple bonds. In the case of group 14, carbon's multiple bond chemistry is extensively more documented than that of its heavier congeners.

Another notion which existed up until the late 1970s/early 1980s - that elements in period 3 or higher could not form multiple bonds - known as the double bond rule, was rendered obsolete in 1981, with the first stable compound to contain a Si=C double bond cited in the literature.[1] From this, the field of LOS main-group chemistry began. Commonalities between early reportings show the use of spatially large ligands, evident from the first article to be published on the subject. Brook *et al*. were able to synthesize $(Me_3Si)_2Si{=}C(OSiMe_3)C_{10}H_{15}$ utilizing bulky silyl ligands. An integral part of this success was attributed to the bulky silyl groups which stabilized the highly reactive Si=C core. This concept of utilizing sterically bulky ligands to stabilize highly reactive metal cores has been one of the key features implemented in forming LOS transition- and main-group element complexes to date.

## *1.2 Ligands Utilized in Low Oxidation State Chemistry*

### *1.2.1 Anionic Chelating N-Donor Ligands*

N-donor ligands commonly associated with LOS metal complexes include amidinates, guanidinates, diazabutadienediides (DABs) and β-diketiminates (nacnacs). Generally, these ligands bind to metal centers in a bidentate fashion, depending on their backbone

C- and N- substituents. Their substituents can be altered in order to control the steric and electronic properties of the ligands (figure 1.2).

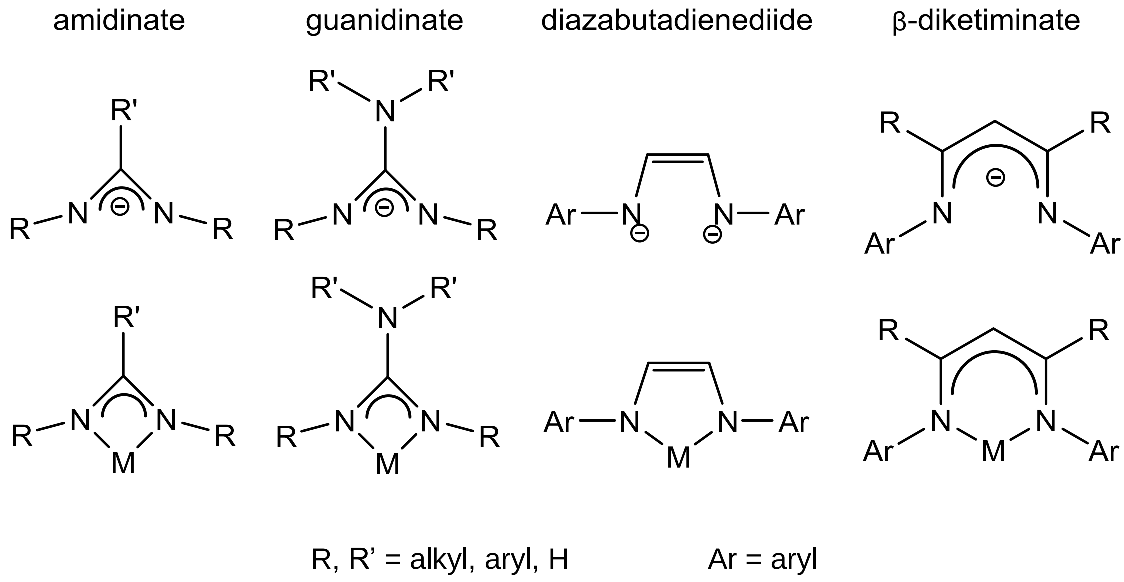
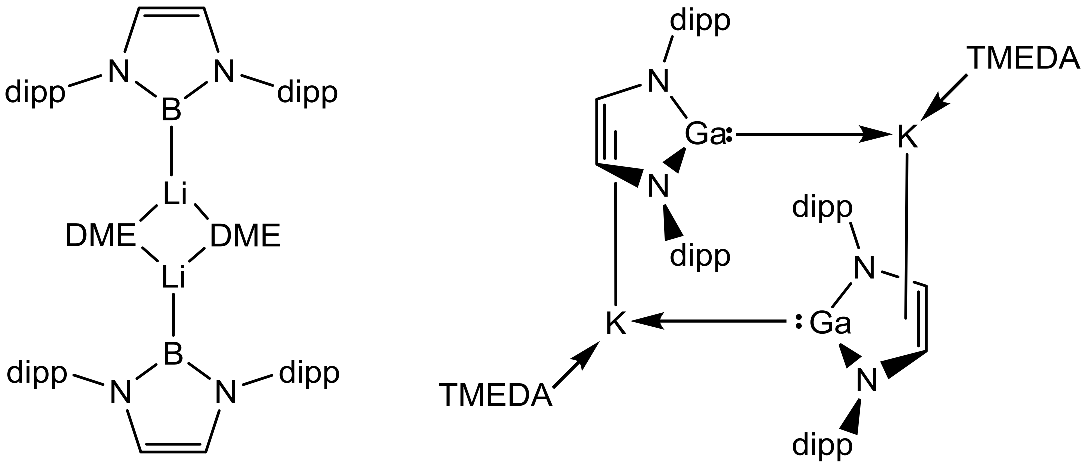


**Figure 1.2:** Amidinates, guanidinates, diazabutadienediides (DABs), β-diketiminates (nacnacs) and how they bind to metal centers in a N,N'-chelating fashion

Amidinates and guanidinates are mono-anionic and chelate to metal centers typically forming four-membered metallacycles. The versatility of these ligands has been known for several decades with the first guanidinate transition metal complex reported by Lappert and co-workers in 1970[3]. In the last couple of decades, the use of these compounds has significantly increased, with many LOS transition-metal (TM) and MG complexes being synthesized.

Diazabutadienediides are di-anionic and chelate to metal centers forming five-membered metallacycles. Some notable examples of DAB main group compounds include the recent work done by Segawa *et. al.*[4] and Baker *et al.*[5], in which the synthesis of the thermally stable B$^{I}$ compound **1.1** and Ga$^{I}$ compound **1.2** were reported (scheme 1.1).



DME = dimethoxyethane TMEDA = tetramethylethylenediamine

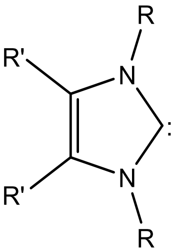
**Scheme 1.1:** Low Oxidation State diazabutadienediide group 13 complexes, boron(I) complex **1.1** and gallium(I) complex **1.2**

β-diketiminates, commonly referred to as ‘nacnacs’ or [{ArNC(R)}$_2$CH] (R = alkyl, H; Ar = aryl) are mono-anionic ligands which can chelate to metal centers forming six-membered heterocyclic rings. Two independent reports of the first metal nacnac complexes by McGeachin[6] and Parks and Holm[7] in 1968 describe the syntheses of Co$^{II}$, Ni$^{II}$ and Cu$^{II}$ complexes. Since then, significant progress has been made in the area of nacnac-main-group chemistry, with a particular focus on the Mg$^{I}$ dimers synthesized by the Jones and Stasch group[8] which will be discussed in further detail in later sub-chapters.

### *1.2.2 Carbenes*

Carbenes have become an established class of ligands in the field of main group and transition metal chemistry. Arguably one of the most popular types of carbenes reported in recent literature (past 30 years) are the nitrogen-heterocyclic carbenes (NHCs) (figure

1.3). Soon after the synthesis and isolation of the first NHC by Arduengo in 1991,[9] it did not take long for researchers to utilize these compounds as ligands in MG and TM chemistry.[10] Aside from their physical and chemical properties, their cheap and straightforward syntheses, as well as their relative ease of handling, make them ideal for chemists in a wide range of areas.



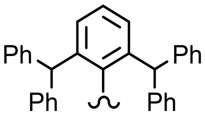
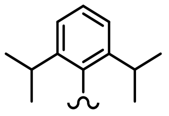
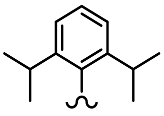
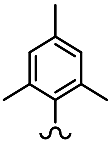
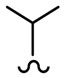
| | **1.3** | **1.4** | **1.5** | **1.6** | **1.7** | **1.8** |
|---|---|---|---|---|---|---|
| R |  |  |  |  |  | Me |
| R' | H | Me | H | H | Me | Me |
| NHC | IPr* | $^{Me}$IPr | IPr | IMes | IPriMe | TMC |

**Figure 1.3:** General structure of NHCs with some examples, showing varying levels of steric protection

Carbenes are neutral compounds, containing an electron deficient carbon atom with two non-bonding valence electrons, which can be placed in either the sp$^2$ or p orbital. Thus, carbenes can be categorized as singlet state or triplet state species, depicted in figure 1.4.

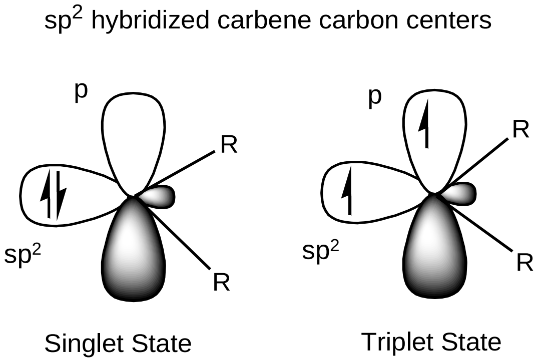


**Figure 1.4:** Singlet state vs. triplet state carbene

The nitrogen atoms adjacent to the carbene carbon center in NHCs (see figure 1.4) donate electron density into the p-orbital of the central carbon atom, stabilizing the singlet state, as well as increasing the nucleophilicity of the carbene. NHCs are strong sigma donors, which provide electronic stability to LOS main group fragments, usually, with minimal π-back-bonding. The steric bulk of NHCs can also be altered in order to provide additional kinetic stability if desired.

NHCs are the primary ligand class in this thesis and will be focused on in this introduction. However, there are a number of other related ligand classes which are also utilized and will be discussed later where appropriate.

### *1.3 Group 2 and Group 12 Chemistry*

Due to their similar chemical properties, group 2 and group 12 elements will be discussed simultaneously.

#### *1.3.1 Group 2 Chemistry*

The Group 2 elements are beryllium (Be), magnesium (Mg), calcium (Ca), Strontium (Sr), barium (Ba) and radium (Ra). The most important factors which determine the chemical properties of the group 2 elements are their atomic and ionic radii.

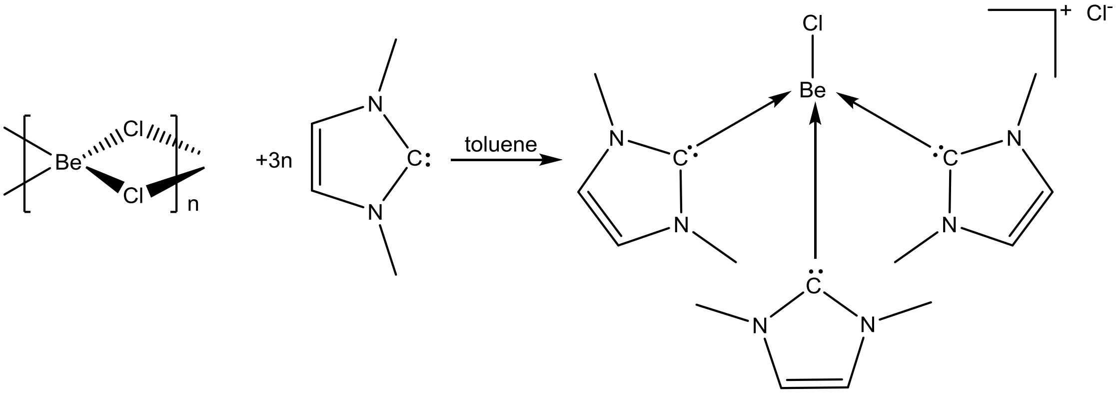
| **Element** | **Be** | **Mg** | **Ca** | **Sr** | **Ba** | **Ra** |
|---|---|---|---|---|---|---|
| **Atomic Number** | 4 | 12 | 20 | 38 | 56 | 88 |
| **Electronic Configuration** | [He]2s$^2$ | [Ne]3s$^2$ | [Ar]4s$^2$ | [Kr]5s$^2$ | [Xe]6s$^2$ | [Rn]7s$^2$ |
| **Melting Point (°C)** | 1280 | 650 | 850 | 768 | 714 | 700 |
| **Atomic Radius (pm)** | 112 | 160 | 197 | 215 | 217 | 220 |
| **Ionic Radius** | 31 | 65 | 99 | 113 | 135 | 140 |
| **Ionisation Energy (kJ/mol)** | | | | | | |
| **1st** | 899.4 | 737.7 | 589.8 | 549.5 | 502.9 | 509.3 |
| **2nd** | 1757.1 | 1450.7 | 1145.4 | 1064.2 | 965.2 | 979.0 |

**Figure 1.5:** Physical and chemical properties of the group two elements[11]

In compounds, they predominantly form ionic interactions with their ligands with the exception of beryllium which prefers a covalent interaction due to its significantly smaller size. Often referred to as the alkaline earth metals, they are harder, denser and less reactive than the elements of group 1 yet still more reactive than most other metals due to their low reduction potentials. Because of their unique reactivity and their roles in biological functions - in particular magnesium and calcium – group 2 elements are often a focus of attention throughout scientific literature.

#### *1.3.1.1 Beryllium*

The smallest of the group, possessing the most covalent character in its compounds, beryllium has a lot of potential in areas such as hydrogen storage as well as unique reduction chemistry. However, due to its toxicity, it is often overlooked and thus, little is known about its chemistry in comparison to the other group 2 elements. In 1995 Herrmann and co-workers reported the ionic beryllium-carbene complex $[L_3BeCl]^+Cl^-$ **1.9** (L = 1,3-dimethylimidazolin-2-ylidene)[12]. Using a very small NHC, they were able to disrupt the polymeric structure of beryllium chloride and form the ionic complex **1.9** (scheme 1.2).

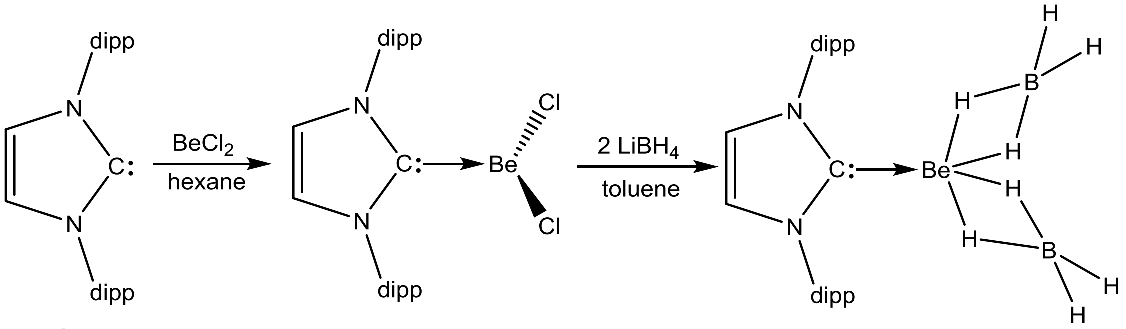


**1.9**

**Scheme 1.2:** Synthesis of the ionic NHC-beryllium complex **1.9**

Future work involving **1.9** forming LOS compounds would be difficult due to the lack of steric hindrance provided by the small NHCs, as well as the ionic natured, long Be-C bonds (1.815 Å mean). A neutral version of this compound would be preferential as a precursor to any further chemistry.

It wasn't until 2012 that Robinson and co-workers synthesized the neutral adduct IPr·$BeCl_2$ **1.10**, analogous to that of the previous reaction, utilizing a bulkier NHC, yet similar reaction conditions (scheme 1.3).[13]

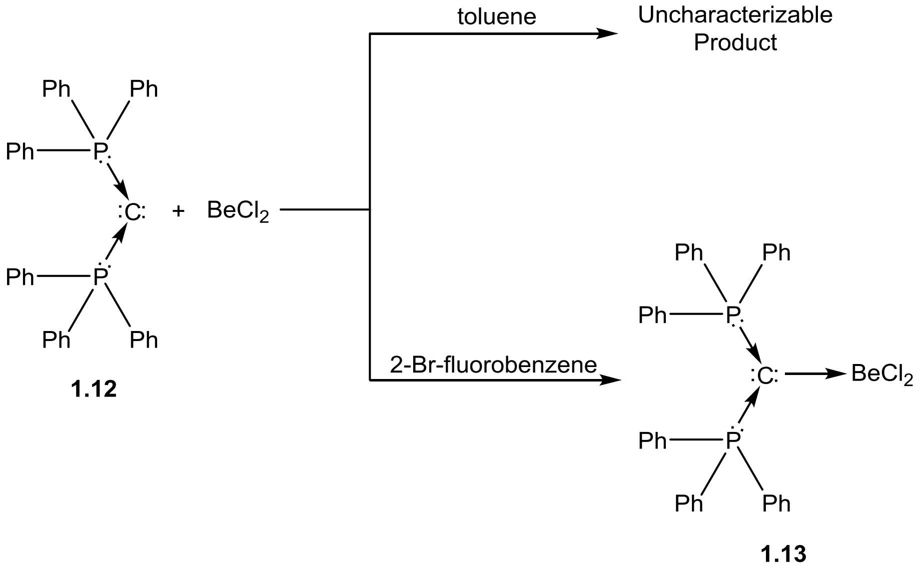


**1.5** **1.10** **1.11**

**Scheme 1.3:** Synthesis of neutral IPr·$BeCl_2$ **1.10** and the carbene-stabilized beryllium borohydride IPr·$Be(BH_4)_2$ **1.11**

In this example, the NHC incorporates much bulkier aryl groups as the N-substituents instead of methyl groups. **1.10** has a Be-C bond length of 1.773(5) Å, shorter than that of **1.9** (1.815 Å), indicating higher covalent character. In addition to the 1:1 neutral adduct **1.10**, the authors also reported its further reactivity with lithium borohydride to give a carbene-stabilized, beryllium borohydride IPr·Be($BH_4$)$_2$ **1.11**. Since its first reporting in 1940,[14] chemists have yet to conclusively determine the solid-state structure of monomeric beryllium borohydride. This compound is of particular interest since it is has the highest hydrogen storage capacity (20.8 wt%) of all metal borohydrides. The use of NHCs has shed some light on this matter via the stabilization of a Be($BH_4$)$_2$ monomer. Work in this field is currently being investigated further.

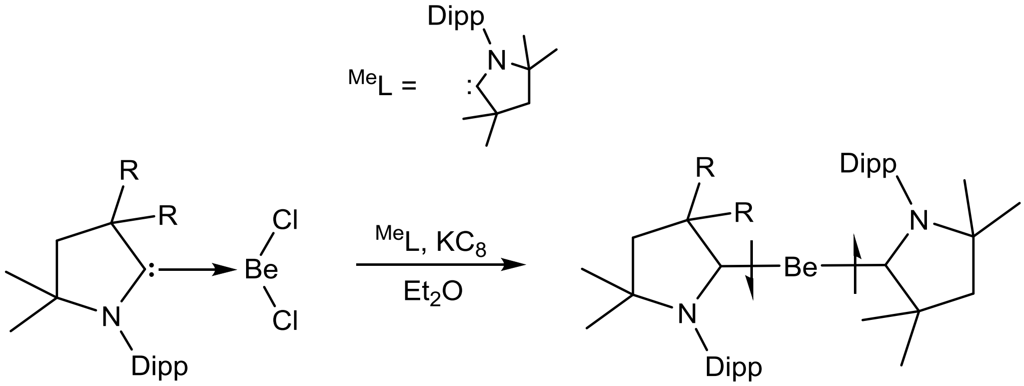
One year prior to Robinson and co-workers' report, Petz *et. al.* demonstrated that a long forgotten class of compounds, carbodiphosphoranes (CDPs) of the general formula $C(PR_3)_2$ (R = alkyl, aryl), could also be used as neutral ligands in organometallic chemistry, specifically, that of beryllium.[15] In a similar fashion to previously mentioned methods, hexaphenylcarbodiphosphorane, $C(PPh_3)_2$ was treated with solid $BeCl_2$ to give the neutral adduct complex ($\{Ph_3P\}_2C$)·$BeCl_2$ **1.13** (scheme 1.4).



**Scheme 1.4:** Synthesis of a neutral carbodiphosphorane adduct ($\{Ph_3P\}_2C$)·$BeCl_2$ **1.13**

The neutral adduct, **1.13**, has a Be-C bond length of 1.742(9) Å, once again shorter than that of **1.9** indicating the covalent nature of the bond. Although CDP ligands have the potential to form two dative bonds with two separate Lewis acidic lone pairs, only one beryllium center is coordinated in this example, which was expected from theoretical studies. Also mentioned in the article was the use of the polar aprotic solvent 2-Br-fluorobenzene and its comparison to traditional solvents such as toluene, diethyl ether or THF, which helped prevent the formation of the unwanted cationic product $(HC\{PPh_3\}_2)^+$.

A 2013 review involving theoretical studies of LOS beryllium chemistry[16] show that it is possible to form $Be^I$ and $Be^0$ compounds utilizing NHCs as well as bulky nacnac ligands. These predictions were realized last year, with Braunschweig and co-workers reporting the synthesis and isolation of cyclo-alkyl-amino-carbene (cAAC) beryllium(0) complexes[17] **1.16** and **1.17** shown in scheme 1.5 below.



R = Me; **1.14**
R, R = $(CH_2)_5$; **1.15**

R = Me; **1.16**
R, R = $(CH_2)_5$; **1.17**

**Scheme 1.5:** Synthesis of the cAAC-stabilized, beryllium(0) compounds **1.16** and **1.17**, the first neutral compounds to contain a zero-valent s-block metal, beryllium

Attempts to reduce **1.14** and **1.15** in the absence of $^{Me}$L yielded intractable mixtures, of which, no isolable product could be obtained. The need for the free, neutral-ligand, $^{Me}$L, to be present during the reduction process proved critical in the formation of the beryllium(0) complexes **1.16** and **1.17** – a concept which may prove useful for future reductions involving compounds containing MG elements.

Another key point to highlight is the theoretical studies conducted on **1.16** and **1.17**. These studies suggest strong covalent character between the cAAC ligands and the beryllium centers. They also determined the π back-bonding from the beryllium centers to the cAAC ligands (-148.6 kcal mol$^{-1}$), to be approximately double that of the σ donation in the reverse direction (-71.6 kcal mol$^{-1}$). The latter is thought to contribute to the relatively low reactivity of **1.16**, demonstrated through its low reactivity with hydrides and bulky alcohols.

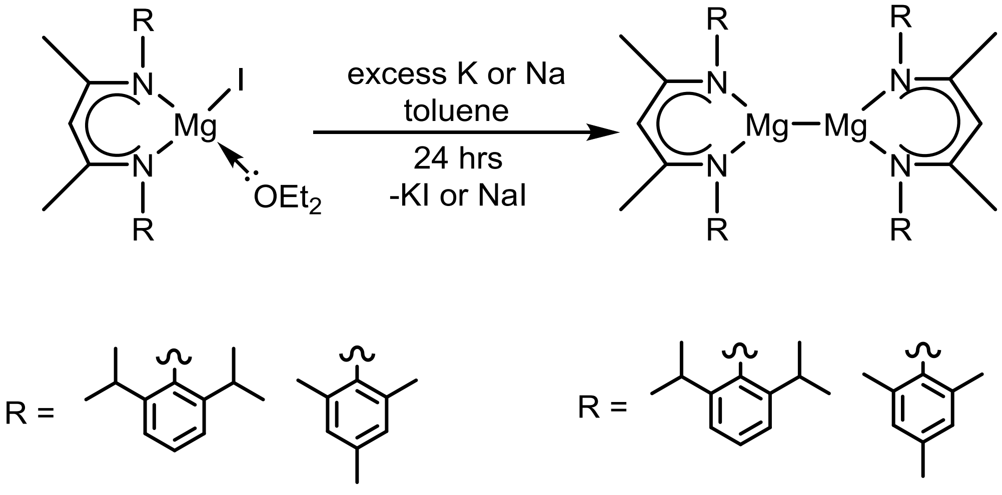
#### *1.3.1.2 Magnesium*

The 2007 discovery of the magnesium(I) dimers {(priso)Mg}$_2$ (priso = [(Dipp)NC(N$^i$Pr$_2$)N(Dipp)]$^-$, Dipp = 2,6-$^i$Pr$_2$C$_6$H$_3$) **1.18** and {($^{Dipp}$nacnac)Mg}$_2$ ($^{Dipp}$nacnac = {[(Dipp)NC(Me)]$_2$CH}$^-$, Dipp = 2,6-$^i$Pr$_2$C$_6$H$_3$) **1.19**[8] by Jones and Stasch demonstrates the stabilizing abilities of the previously mentioned guanidinate and β-diketiminate ligands. The hydrocarbon-soluble compounds, contain a singly bonded [Mg-Mg]$^{2+}$ core and can be seen as 2-center, 2-electron [2c2e] reductants. Both dimers feature long Mg-Mg single bonds (2.8457(8) Å and 2.8508(12) Å, respectively) and are stable under standard laboratory conditions (decomp. >300 °C and 170 °C respectively). Since 2007, there have been a number of follow up articles containing magnesium(I) dimers with varying nacnac and amido backbone groups including {($^{Mes}$nacnac)Mg}$_2$, ($^{Mes}$nacnac = {[(Mes)NC(Me)]$_2$CH}$^-$, Mes = mesityl) **1.20** and {($^{tBu}$nacnac)Mg}$_2$ ($^{tBu}$nacnac =

$\{[(\mathrm{Dipp})\mathrm{NC}(^t\mathrm{Bu})]_2\mathrm{CH}\}^-$, Dipp = diisopropylphenyl) **1.21**.[18]

Another recent addition to the $\mathrm{Mg_2}^{2+}$ family includes the diiminophosphinato magnesium(I) dimer **1.22**, [(LMg)$_2$] (L = $\mathrm{Ph_2P(NDipp)_2}$, Dipp = 2,6-$^i\mathrm{Pr_2C_6H_3}$).[18] The previously reported nacnacMg$^\mathrm{I}$ dimers were accessed via group-one metal reductions, however, **1.22** was formed using a (nacnac)Mg$^\mathrm{I}$ dimer as the reducing agent, extending the versatility and scope of this class of compounds.

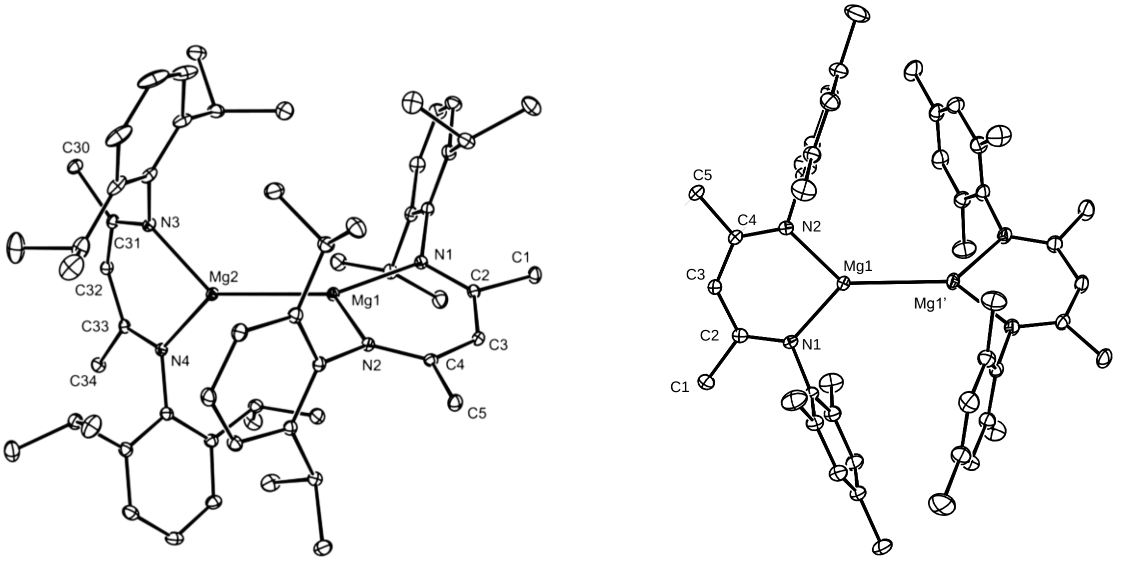
The synthesis of the (nacnac)Mg$^\mathrm{I}$ dimers involves the use of [{$^\mathrm{Ar}$nacnac}MgI·(OEt$_2$)] precursors (Ar = Dipp; **1.23**, Ar = Mes; **1.24**) being reduced over sodium or potassium mirrors, yielding the magnesium(I) dimers **1.19** and **1.20** shown in scheme 1.6.



**1.23** **1.24** **1.19** **1.20**

**Scheme 1.6:** Synthesis of [{$^\mathrm{Dipp}$nacnac}Mg$^\mathrm{I}$]$_2$ **1.19** and [{$^\mathrm{Mes}$nacnac}Mg$^\mathrm{I}$]$_2$ **1.20**

Using X-ray crystallography, the Mg-Mg bond lengths of [{$^\mathrm{Dipp}$nacnac}Mg$^\mathrm{I}$]$_2$ **1.19** and [{$^\mathrm{Mes}$nacnac}Mg$^\mathrm{I}$]$_2$ **1.20** were found to be 2.8457(8) and 2.808(1) Å respectively, showing a small, yet significant difference, due to ligand steric bulk differences.

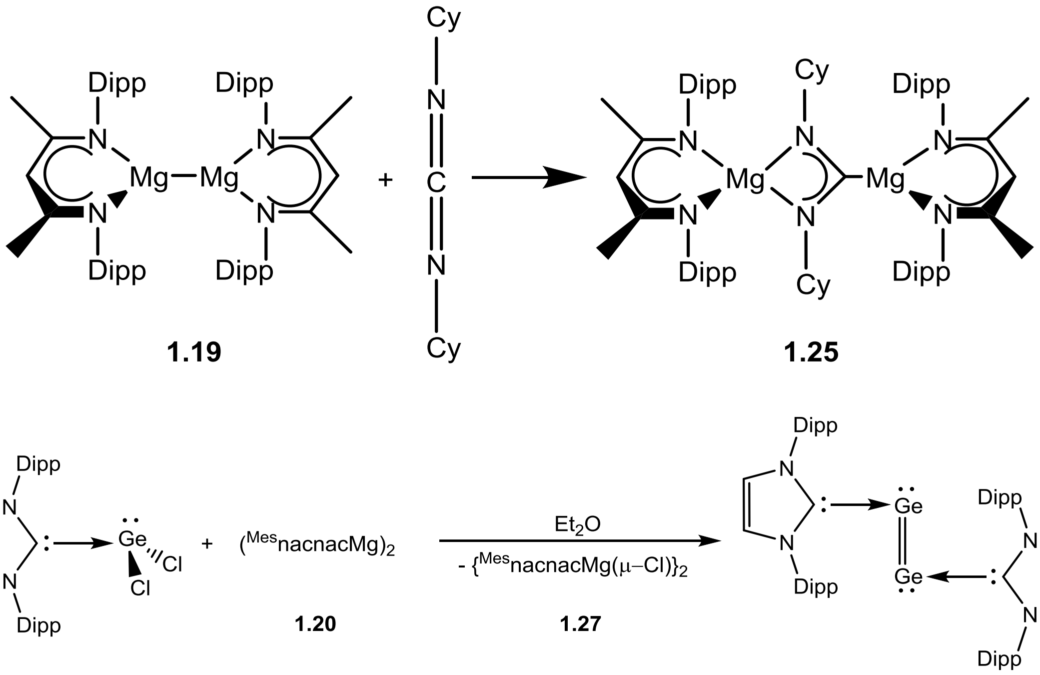


**1.19**

**1.20**

**Figure 1.6:** X-ray crystal structures of $[\{^{Dipp}nacnac\}Mg^{I}]_2$ **1.19** and $[\{^{Mes}nacnac\}Mg^{I}]_2$ **1.20**

Theoretical studies are consistent with the single bonded $[Mg\text{-}Mg]^{2+}$ core in **1.19** and **1.20** being largely covalent, with predominantly ionic interactions between the magnesium core and the anionic ligands. Furthermore, $Mg^{I}$ compounds have been shown to be useful reducing agents in organic and inorganic syntheses, as shown in scheme 1.7 below.[8, 18, 20]



**1.19** **1.25**

**1.26** **1.20** **1.27** **1.28**

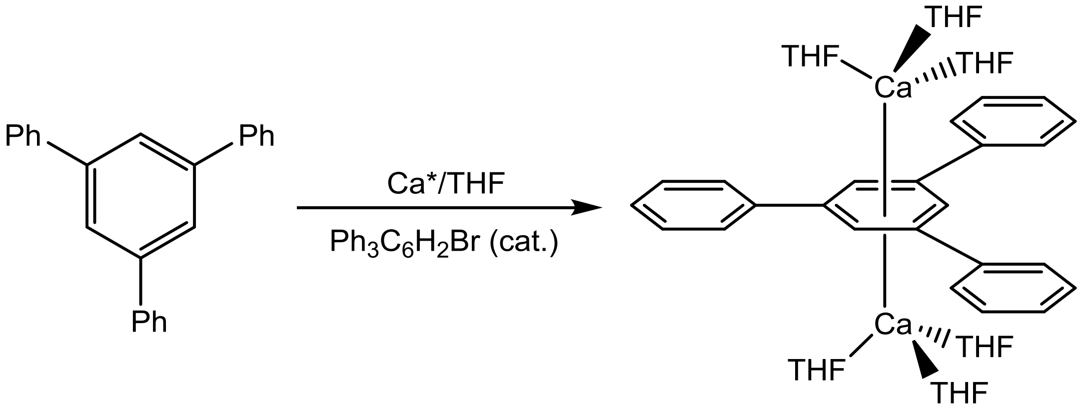
**Scheme 1.7:** Reductive insertion of DCC across the Mg-Mg bond (above) and reductive elimination of NHC-germanium(II) chloride to a germanium(0) dimer **1.28** (below)

Furthermore, in 2009, Wu *et. al.* synthesized the α-diimine stabilized magnesium(I) dimer $[K(THF)_3]_2[LMg\text{-}MgL]\cdot 2THF$ (L = $[(2,6\text{-}^{i}Pr_2C_6H_3)NC\text{-}(Me)]_2^{2-}$), **1.29**.[21] The magnesium(I) dimer, **1.29** also possesses a long Mg-Mg bond length (2.9370Å), even longer than that of the previously mentioned nacnac coordinated magnesium(I) dimers **1.19** and **1.20**, but shorter than that of their respective Lewis-base (dioxane and pyridine) coordinated equivalents **1.30** and **1.31** (3.056 Å and 3.196 Å).[8b]

Of most relevance to my work, magnesium(I) dimers have been shown to be selective reducing agents in inorganic synthesis. For example, compound **1.20** was used to reduce the NHC coordinated germanium(II) chloride **1.26** to the germanium(0) dimer **1.28** (scheme 1.7 above), which will be discussed in detail in a later subchapter.

### *1.3.1.3 Calcium*

To date, there has only been one report of LOS heavier group 2 elements stable under standard laboratory conditions.[22] In 2009 Krieck *et al.* synthesized the calcium(I) inverse-sandwich complex [(THF)$_3$Ca{μ-(C$_6$H$_5$)$_3$C$_6$H$_3$}Ca(THF)$_3$] **1.32** shown in scheme 1.8 below.



**1.32**

**Scheme 1.8:** Synthesis of the inverse sandwich organocalcium(I) complex **1.32**

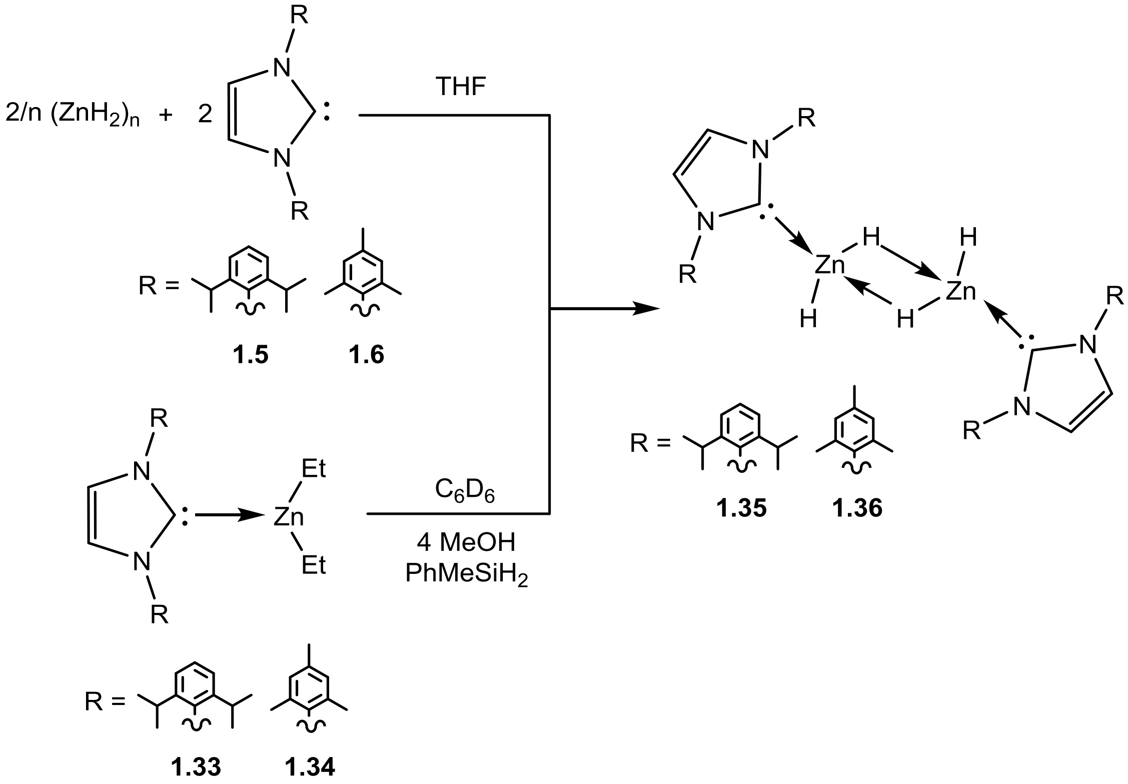
The objective was to synthesize heavier Grignard reagents of the form Aryl-Ca-X via insertion of activated calcium into the Aryl-X bond of halogenated arenes. Instead, what was isolated was the highly air and moisture sensitive **1.32** which exhibits a doubly reduced, bridging arene center capped by two calcium(I)·3THF groups. **1.32** exhibits relatively short Ca-Ca and Ca-(Ar$_{center}$) interactions of 4.279(3) Å and 2.14 Å respectively whilst the C-C bond lengths of the inner arene ring are elongated from 1.387 Å to 1.464 Å, due to the 2-electron reduction of the central ring. Although **1.32** is considered a strong reductant, the delocalization of the negative charge within the arene ring leads to low basicity. Currently there are several groups developing synthetic strategies to overcome the difficulties in obtaining compounds with LOS heavier group 2 elements.

### 1.3.2 *Group 12 Chemistry*

Due to their full d-shells, group 12 metals have characteristics resembling those of main group elements, particularly group 2 elements such as Be, Mg and Ca.

#### 1.3.2.1 *Zinc*

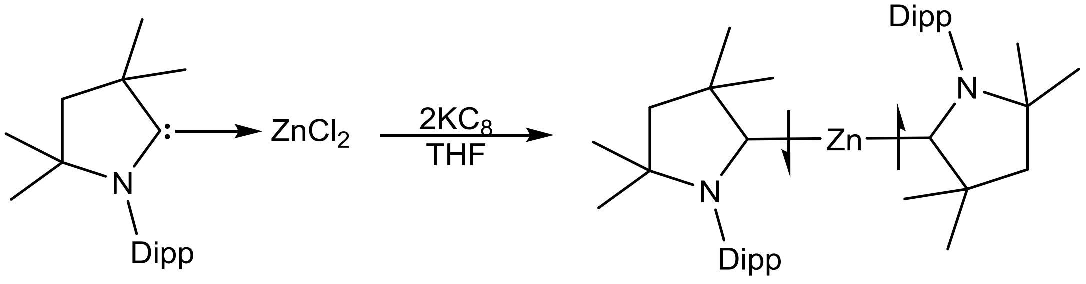
Carbenes have had a growing impact on group 12 chemistry in recent years, however, to this date, there are no reported cases of LOS NHC-coordinated-group 12 compounds. None-the-less, one notable report however, involves the synthesis of stabilized $ZnH_2$ dimers **1.35** and **1.36**, capped by two NHC ligands[23] (scheme 1.9).



**Scheme 1.9:** Synthesis of $ZnH_2$ dimers **1.35** and **1.36**, stabilized by NHCs

Under standard conditions, $ZnH_2$ is polymeric, unstable and will disproportionate to elemental zinc and hydrogen gas. This report highlights the stabilizing effects of the NHCs with **1.35** and **1.36** being stable for months at -35 °C in the solid state and having decomposition temperatures above 170 °C.

A related class of carbenes, cyclo-alkyl-amino-carbenes (cAACs), can also be used to stabilise highly reactive metal centers. Roesky and co-workers were able to isolate a cAAC-stabilized zinc monomer **1.38** shown in scheme 1.10 below.[24]

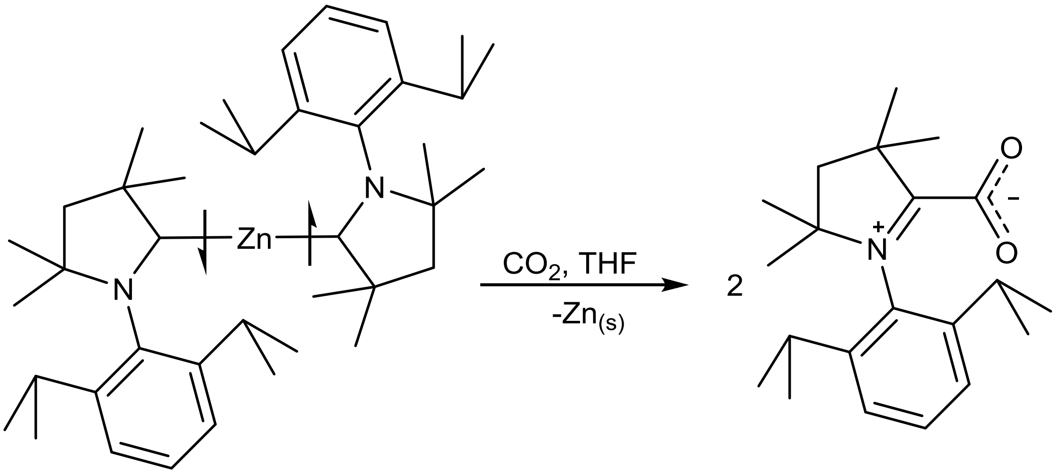


**1.37**

**1.38**

**Scheme 1.10:** Synthesis of the biradicaloid cAAC-zinc complex **1.38**

The product **1.38**, is biradicaloid and highly reactive, even reacting rapidly with $CO_2$ at temperatures as low as -30 °C, a result unheard of (particularly without a catalyst) for compounds of the type $R_2Zn$.



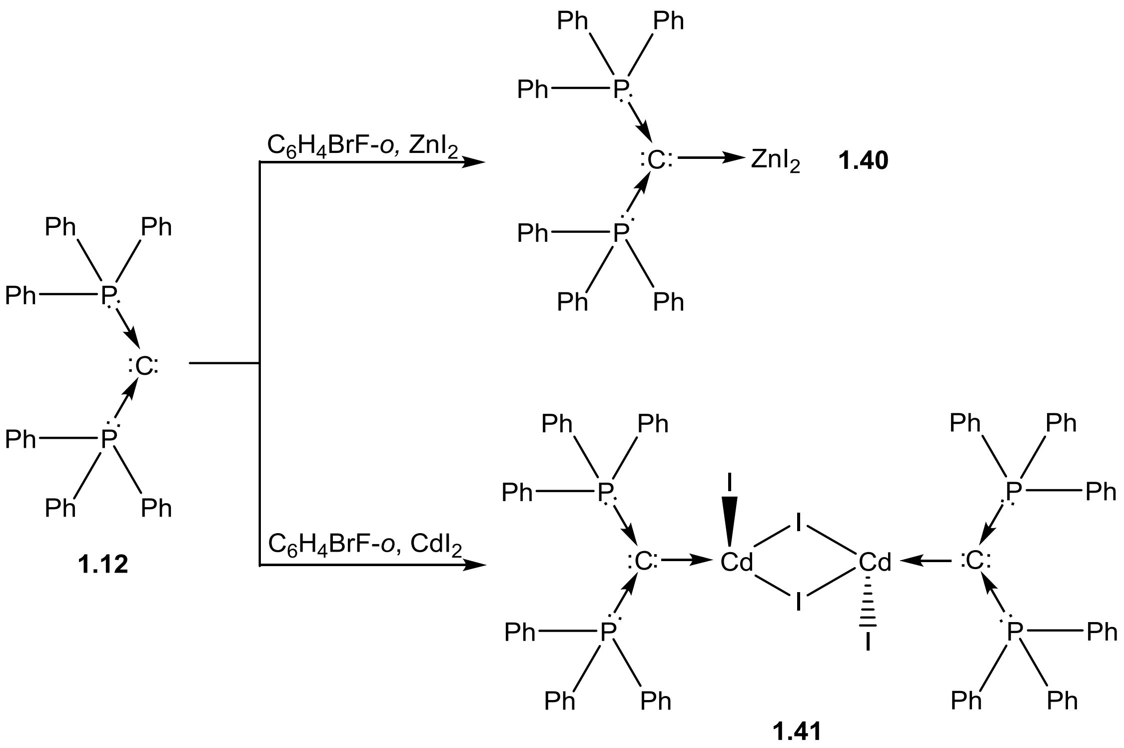
**1.38** **1.39**

**Scheme 1.11:** Unprecedented $CO_2$ activity with an $R_2Zn$ compound, **1.38**

In comparison, free cAAC reacts with $CO_2$ slowly at 25 °C, whilst the non-biradicaloid analogue, $(cAACH)_2Zn$ **1.38’** (carbene carbon is hydrogenated), does not react with $CO_2$ even at 50 °C. These results demonstrate the enhanced reactivity of the biradicaloid **1.38** towards $CO_2$ activation.

### *1.3.2.2 Cadmium*

In 2011 Petz and Neumüller reported the synthesis of CDP adducts of zinc(II) and cadmium(II) iodide, shown in scheme 1.12 below.[25] In the case of zinc, the 1:1 addition monomer is observed, however, cadmium forms the iodine bridged dimer.

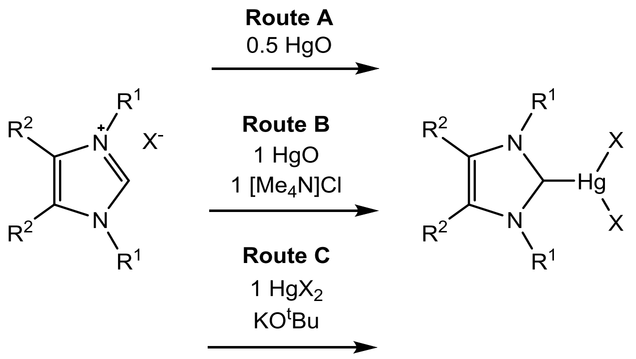


**Scheme 1.12:** Synthesis of CDP stabilized zinc(II) and cadmium(II) iodides, **1.40** and **1.41** respectively

The group also report the salt compounds (HC{$PPh_3$}$_2$)[$MI_3$(THF)] (M = Zn; **1.42**, M = Cd; **1.43**) - the result of using THF as a solvent. This effect of solvent-proton-abstraction is commonly found when using MG Lewis-acids[26] in THF. To overcome this effect, toluene was used as a less polar, aprotic solvent, however, the salt, (HC{$PPh_3$}$_2$)$_2$[$ZnI_4$] was the only isolable product. Finally, the slightly more polar, yet still aprotic solvent, 2-bromofluorobenzene was used, which afforded the addition products **1.40** and **1.41** (scheme 1.12 above). These results emphasise the sensitivity of these ligands to the solvent as significantly different products are isolated when solvents are varied. Attempts to reduce **1.40** or **1.41** were not mentioned, leaving a potentially promising area of chemistry to explore.

### *1.3.2.3 Mercury*

Mercury was the first ever metal to be coordinated to an NHC, reported in 1968 by Wanzlick and Schönerr.[27] However, in the 40 years that followed, research on the field NHC-mercury compounds was (relatively) scarcely reported.[28] It wasn't until 2011, when Pelz and Mohr reported an easy and efficient way of synthesizing NHCHg$X_2$ adducts,[29] that the field had a resurgence. In a one-pot-synthesis, an imidazolium salt reacts with $Ag_2O$, yielding a silver-NHC precursor, which then undergoes a transmetallation reaction with various mercury(II) reagents to give the corresponding mercury-NHC complexes shown in scheme 1.12 below.



$R^1$ = 2,6-$^i Pr_2C_6H_3$; $R^2$ = H; X = Cl (**1.44**)
$R^1$ = 2,4,6-$Me_3C_6H_2$; $R^2$ = H; X = Cl (**1.45**)
$R^1$ = Me; $R^2$ = Cl; X = I (**1.46**)
$R^1$ = 2,6-$^i Pr_2C_6H_3$; $R^2$ = H; X = I (**1.47**)

**Scheme 1.13:** Synthesis of NHC-mercury(II) halide adducts **1.44 – 1.47**

Multiple synthetic pathways were presented of which, all produced the desired mercury NHC complexes in moderate yields. **1.44** and **1.45** are monomeric in the solid state while **1.46** is dimeric; **1.47** did not form single crystals suitable for diffractometry. Up until this point, there had only been two other examples of $LHg^{II}X_2$ (L ≠ NHC) compounds in the literature.[30, 31]

## *1.4 Group 13 Chemistry*

The group 13 elements consist of boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). Known as the earth metals, their physical and chemical properties follow an unusual pattern going down the group. The electronegativity of *s* and *p*-block elements is expected to fall upon descending the group. However, this is not always the case with gallium having a higher electronegativity than aluminium. This anomaly, known as the alternation effect, is attributed to the poorly shielding *d*-electrons resulting in an increased effective nuclear charge. This effect is most pronounced in period four.

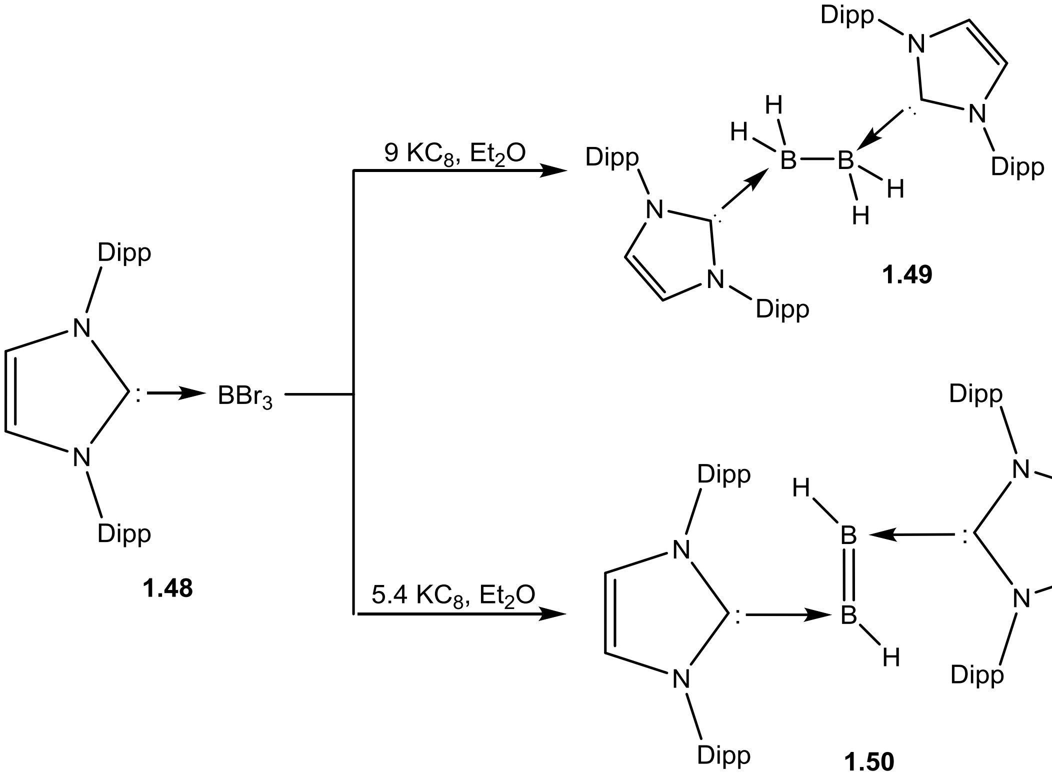
| **Element** | **B** | **Al** | **Ga** | **In** | **Tl** |
|---|---|---|---|---|---|
| **Atomic Number** | 5 | 13 | 31 | 49 | 81 |
| **Electronic Configuration** | [He]2s$^2$2p$^1$ | [Ne]3s$^2$3p$^1$ | [Ar]3d$^{10}$4s$^2$4p$^1$ | [Kr]4d$^{10}$5s$^2$5p$^1$ | [Xe]5d$^{10}$6s$^2$6p$^1$ |
| **Melting Point (°C)** | 2300 | 660.1 | 29.8 | 156.2 | 302.4 |
| **Atomic Radius (pm)** | (80-90) | 143 | 135 | 167 | 170 |
| **Ionic Radius (pm) r($M^{3+}$)** | 20 | 50 | 62 | 81 | 95 |
| **Ionisation Energy (kJ/mol)** | | | | | |
| **1$^{st}$** | 799 | 577 | 577 | 556 | 590 |
| **2$^{nd}$** | 2427 | 1817 | 1979 | 1821 | 1971 |
| **3$^{rd}$** | 3660 | 2745 | 2963 | 2704 | 2878 |
| **Electronegativity ($\chi$) (Pauling)** | 2.04 | 1.61 | 1.81 | 1.78 | 2.04 |
| **Electronegativity ($\chi$) (Allred-Rochow)** | 2.01 | 1.47 | 1.82 | 1.49 | 1.44 |

**Figure 1.7:** Physical and chemical properties of group 13 elements[11]

The physical and chemical properties of the group 13 elements prove them to be useful in modern day applications with boron being used in borosilicate glass as well as borax, a common household multi-purpose compound. Aluminium is utilized for its relatively low density, recyclability and its resistance to corrosion and is implemented in cans, foil, construction and in aircraft alloys.

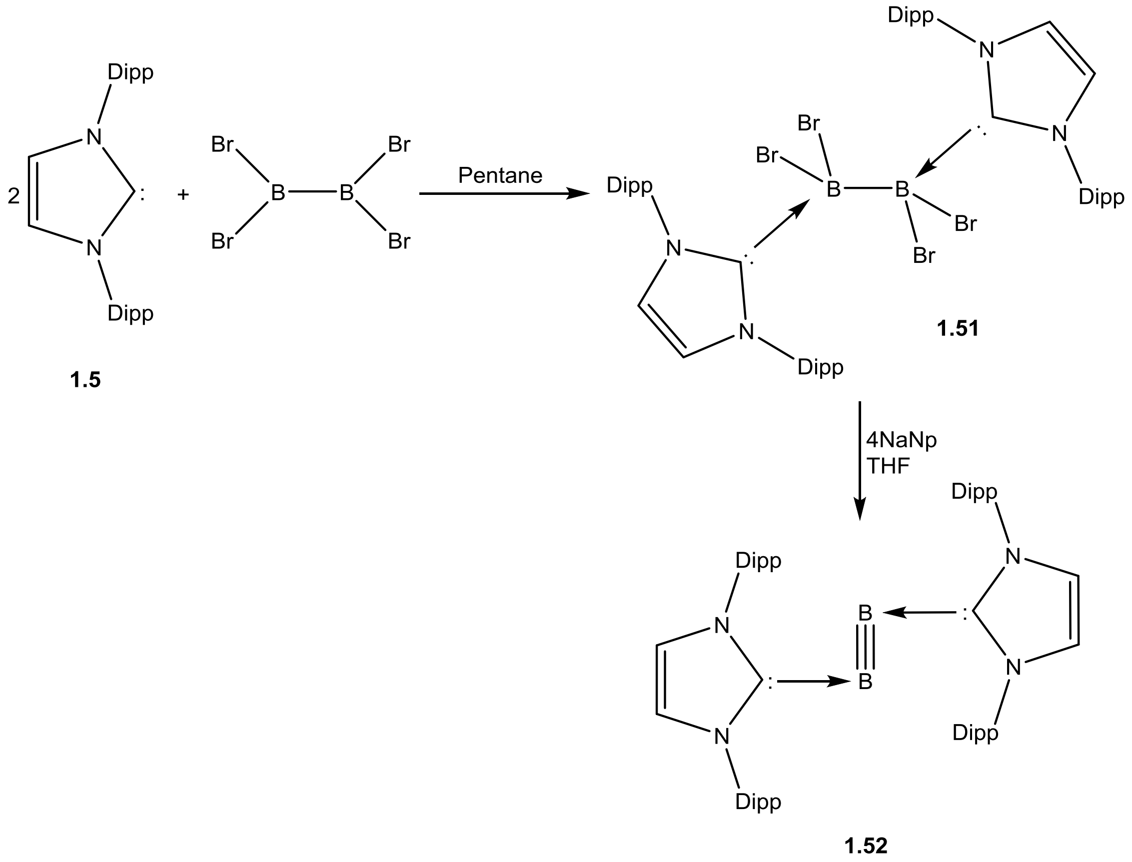
### *1.4.1 Boron*

Although the scope of boron chemistry is well documented[32], boron-boron double bonds only make up a small fraction of the field. With the use of NHCs, Robinson and co-workers were able to isolate the boron-boron dimers; the diborane $\{(\mathrm{IPr})\cdot\mathrm{BH_2}\}_2$ **1.49** and the diborene $\{(\mathrm{IPr})\cdot\mathrm{BH}\}_2$ **1.50**.[33]



**Scheme 1.14:** Synthesis of donor stabilized LOS boron dimers **1.49** and **1.50**, the latter containing a $B^{I}=B^{I}$ double bond.

The boron-boron distance of **1.50** (1.561(18) Å) is significantly shorter than that of **1.49** (1.828(4) Å), indicative of an increase in bond order. Since then, the equivalent boron(0) dimer has been reported[34] with a similar, yet slightly shorter boron-boron distance (1.546(6) Å) than that of **1.50**.



**1.5**

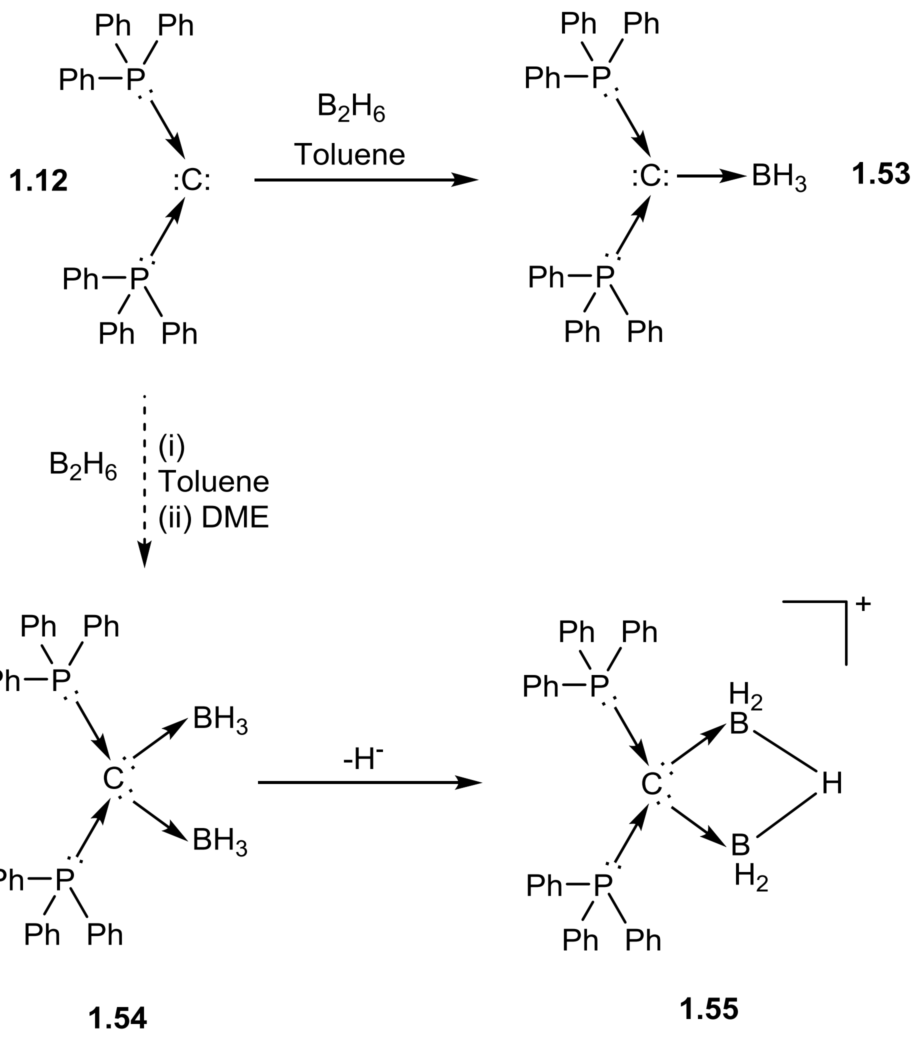
**1.51**

**1.52**

**Scheme 1.15**: Synthesis of the boron(0) dimer **1.52** from a boron(II) dimer **1.51**

The further chemistry of the boron(0) dimer, **1.52** demonstrates its versatility as a reagent in reductive-insertion reactions of heavier elemental-chalcogens and chalcogen compounds (including $CO_2$)[35], as well as the unprecedented encapsulation of alkali metal cations solely ($Li^+$, $Na^+$) through cation-π exchange alone.[36] One of the reports in particular focuses on the varying Lewis-acidity of the carbenes used, and the role it plays in the activation of small molecules. Understanding this concept allows a more targeted approach when using carbenes to synthesize LOS MG compounds for future research.

In 2009 Petz *et al.* reported the synthesis of a number of CDP boron complexes, **1.53 – 1.55**,[37] shown in scheme 1.16 below.

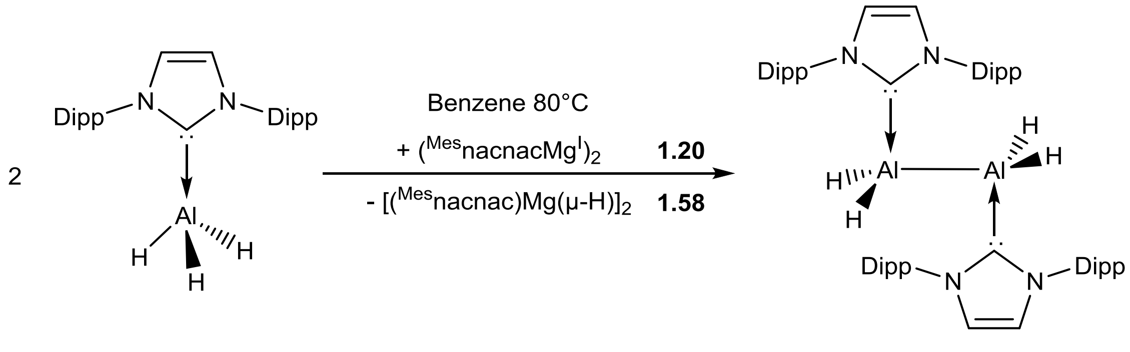


**Scheme 1.16:** Synthesis of several CDP-boron compounds including **1.55**, the first example where the CDP **1.12**, is coordinated to bridged MG Lewis acids

It was suggested that **1.55** is formed via a hydride abstraction from the bis-adduct $[(H_3B)_2\{C(PPh_3)_2\}]$ **1.54**. Compound **1.55** is the first example in which **1.12** coordinates to bridged MG Lewis-acids.

### *1.4.2 Aluminium*

Aluminium was the first MG element to be coordinated to an NHC; IMes·$AlH_3$ **1.56** was synthesized in 1992. However, it wasn't until recently that any LOS NHC-aluminium adducts were reported. The reduction of IPr·$AlH_3$ **1.57** via the magnesium(I) dimer **1.20**, affords the aluminium(II) compound **1.59** shown in scheme 1.17 below.[38]



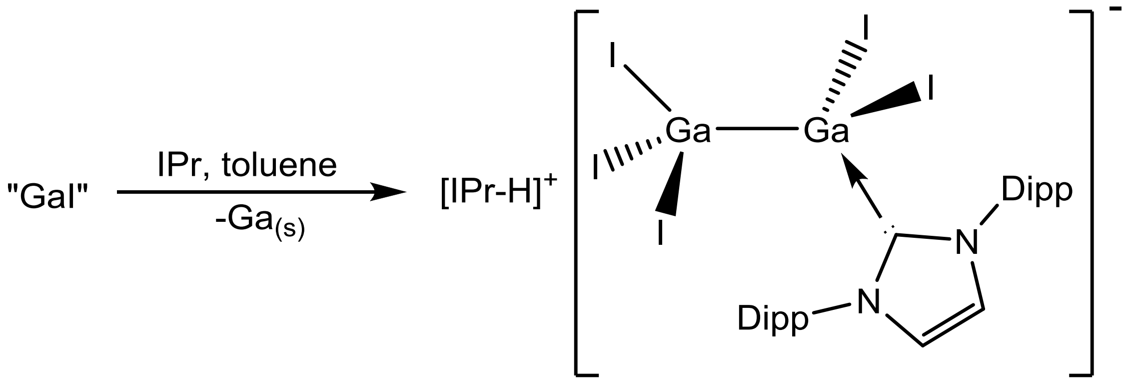
**1.57** **1.59**

**Scheme 1.17**: Synthesis of the first NHC stabilized aluminium(II) hydride {IPr·$AlH_2$}$_2$ **1.59**, using the magnesium(I) dimer **1.20** as a reducing agent

Aldridge and co-workers observed the effect that different NHCs had on aluminium(III) (and gallium(III)) hydrides.[39] 6-membered, and unsaturated 5-membered NHCs were compared. Their results showed that compounds containing 5-membered NHCs had increased thermal stability as well as shorter E-$C_{carbene}$ (E = Al, Ga) bond lengths when compared to their 6-membered counterparts.

### *1.4.3 Gallium*

The first ever NHC coordinated, LOS gallium adduct [IPr·($Ga_2I_5$)][IPr-H] **1.60**, was synthesized by the Jones group in 2003.[40] The salt **1.60**, contains an NHC coordinated Ga(II) center within the anionic Ga-Ga fragment.

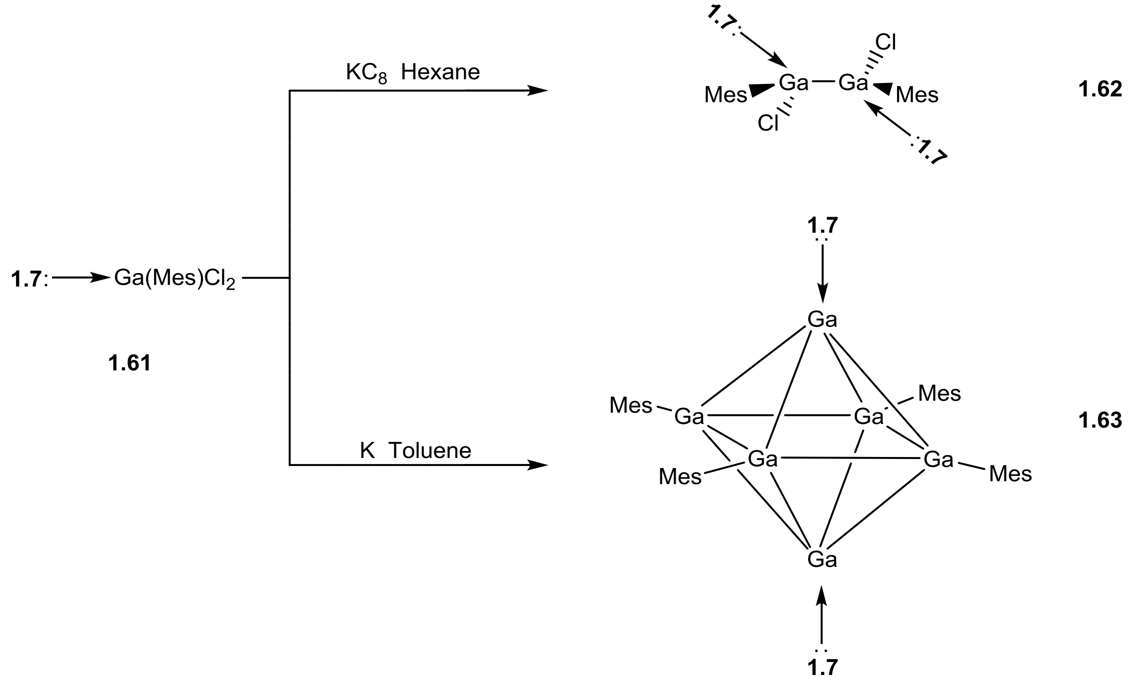


**1.60**

**Scheme 1.18:** Synthesis of the first ever NHC coordinated, LOS gallium adduct [IPr·(Ga$_2$I$_5$)][IPr-H] **1.60**

Both gallium centers have a distorted tetrahedral geometry with a Ga-Ga bond length of 2.4739(12) Å. It is suggested that only one of the gallium centers is coordinated by the NHC due to its large steric nature, hindering any efforts of subsequent coordination.

An article in 2009 by Robinson and co-workers reports the synthesis of two LOS gallium compounds stabilized by bulky aryl and NHC groups (scheme 1.19).[41] The gallium(III) adduct **1.61**, is synthesized quantitatively by adding the NHC, iPr$^i$Me **1.7**, to Ga(Mes)Cl$_2$ in a 1:1 ratio. This is then reduced using either KC$_8$ or K in a 3:1 or 2:1 ratio respectively to give **1.62** and **1.63**.

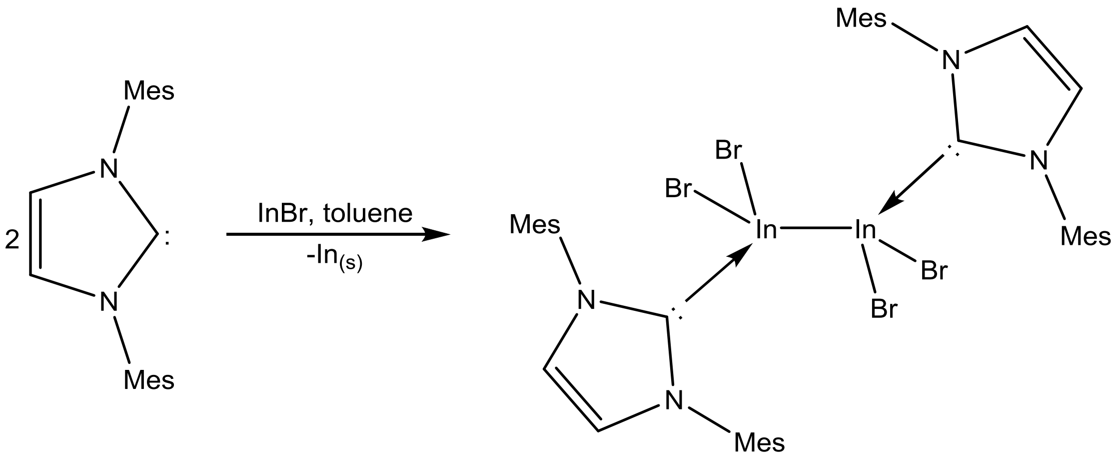


**Scheme 1.19:** Synthesis of the NHC stabilized gallium(II) dimer **1.62** and a neutral $Ga_6$ octahedron **1.63**

The $Ga_6$ cluster, **1.63** is a carbene stabilized, neutral gallium octahedron housing a 14-electron *closo*-$Ga_6$ core similar to the previously known $[Ga_6\{Si(CMe_3)_3\}_4(CH_2C_6H_5)_2]^{2-}$ anion.[42] This example shows the versatile role NHCs have in the formation of small metal clusters, as well as the contrasting results arising from the use of different reducing agents.

### *1.4.4 Indium*

The field of NHC coordinated, LOS indium chemistry is – relative to its lighter congeners – scarce in the literature. However, in 2002, Jones and co-workers synthesized the NHC-indium(II) adduct $\{(IMes)\cdot InBr_2\}_2$ **1.64** (scheme 1.20 below), the first ever compound to have an NHC coordinated to a low oxidation state MG element.[43]



**1.6** **1.64**

**Scheme 1.20:** Synthesis of the NHC-indium(II) dimer {(IMes)·InBr$_2$}$_2$ **1.64**, the first ever compound to have an NHC coordinated to a LOS MG element

The indium(II) dimer **1.64**, contains a neutral [Br$_2$In-InBr$_2$] core, stabilized by the bulky NHC, IMes **1.6**, at either end. Each indium center is in the formal oxidation state of +2 and has a distorted tetrahedral geometry. The In-In bond length of **1.64** (2.7436(7) Å) matches closely to that of the indium(II)-phosphine analogue {($^i$Pr$_3$P)·InI$_2$}$_2$ **1.65** (2.745 Å).[44]

### *1.5 Group 14 Chemistry*

The group 14 elements consist of carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). The valence electron configuration of these elements, $ns^2np^2$ is indicative of their tendency to prefer the +4 oxidation state. This is often the case in the lighter elements but is less prominent descending down the group with the most common oxidation state of lead being +2.

| **Element** | **C** | **Si** | **Ge** | **Sn** | **Pb** |
|---|---|---|---|---|---|
| **Atomic Number** | 6 | 14 | 32 | 50 | 82 |
| **Electronic Configuration** | $[He]2s^22p^2$ | $[Ne]3s^23p^2$ | $[Ar]3d^{10}4s^24p^2$ | $[Kr]4d^{10}5s^25p^2$ | $[Xe]5d^{10}6s^26p^2$ |
| **Melting Point (°C)** | 3730* | 1410 | 937 | 232 | 327 |
| **Atomic Radius (pm)** | 77 | 117 | 122 | 162 | 175 |
| **Ionic Radius (pm)**<br>**$r(M^{2+})$**<br>**$r(M^{4+})$** | <br>-<br>- | <br>-<br>- | <br>93<br>53 | <br>112<br>71 | <br>120<br>84 |
| **1st Ionisation Energy (kJ/mol)** | 1090 | 786 | 762 | 707 | 716 |
| **Electronegativity (χ) (Pauling)** | 2.55 | 1.90 | 2.01 | 1.96 | 2.33 |
| **Electronegativity (χ) (Allred-Rochow)** | 2.50 | 1.74 | 2.02 | 1.72 | 1.55 |

* graphite sublimes

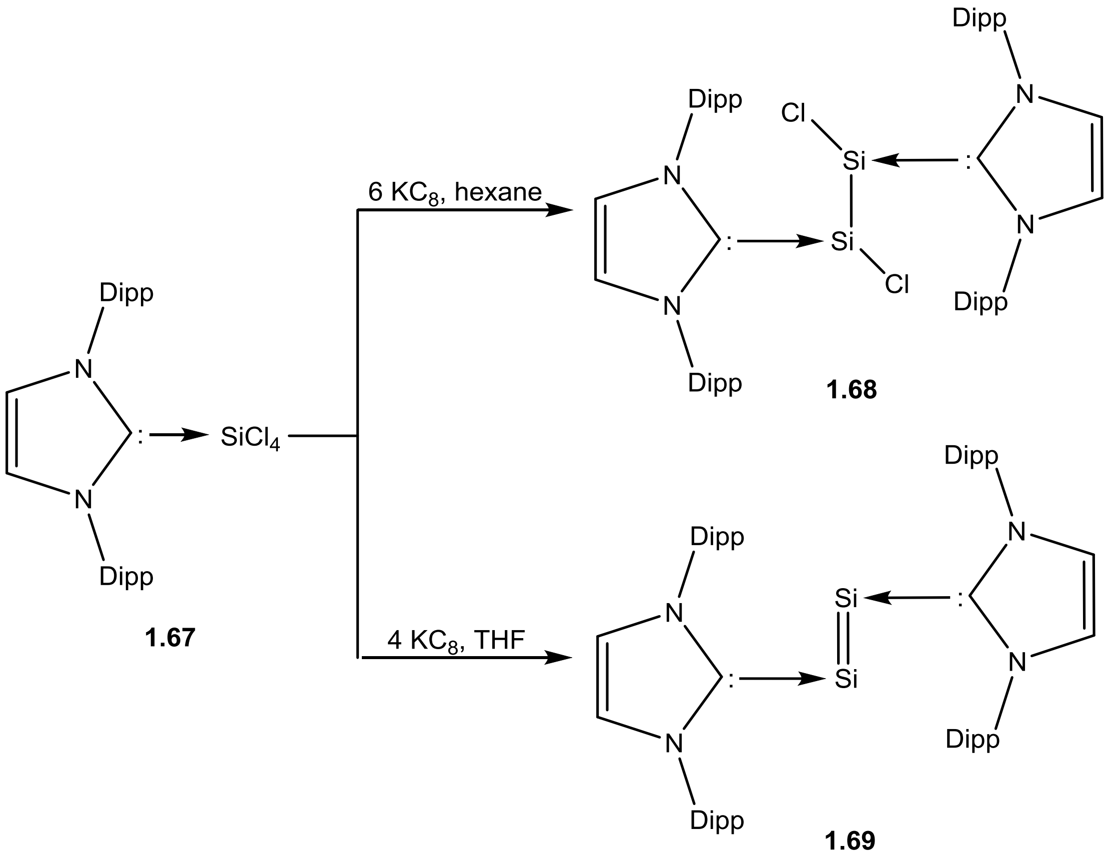
**Figure 1.8:** Physical and chemical properties of group 14 elements[11]

### *1.5.1 Silicon*

In accordance with the inert pair effect, heavier main group elements resist the formation of multiple bonds. In the case of group 14, ethane ($H_3C$-$CH_3$), ethene ($H_2C$=$CH_2$) and ethyne (HC≡CH) have been well known and well understood by the chemical community for quite some time. Yet this is not the case for heavier group 14 analogues [($R_3E$-$ER_3$), ($R_2E$=$ER_2$) and (RE≡ER) E = Si, Ge, Sn, Pb; R = bulky group]. In 1981, the first silicon analogue of ethene, ($Mes_2Si$=$SiMes_2$) **1.65** was synthesized by West *et al.*[45] However, it wasn't until 2004 that the first silicon analogue of ethyne, RSi≡SiR (R = $Si(^iPr)[CH(SiMe_3)_2]_2$) **1.66** was reported by Sekiguchi *et al.*[46]

NHCs have had a significant impact on the field of silicon chemistry. They have been involved in the formation of Si=O bonds,[47] the first ever room temperature stable dihalidosilylene,[48] and a silicon analogue of an ethene fragment,[49] the latter showing selective hydrosilylation with small organic molecules.

Another significant report emerged in 2008 when the Robinson group reduced NHC silicon adducts to form the first ever NHC coordinated silicon(I) {IPr·SiCl}$_2$ **1.68** and silicon(0) {IPr·Si}$_2$ **1.69** dimers,[50] described in scheme 1.21 below.



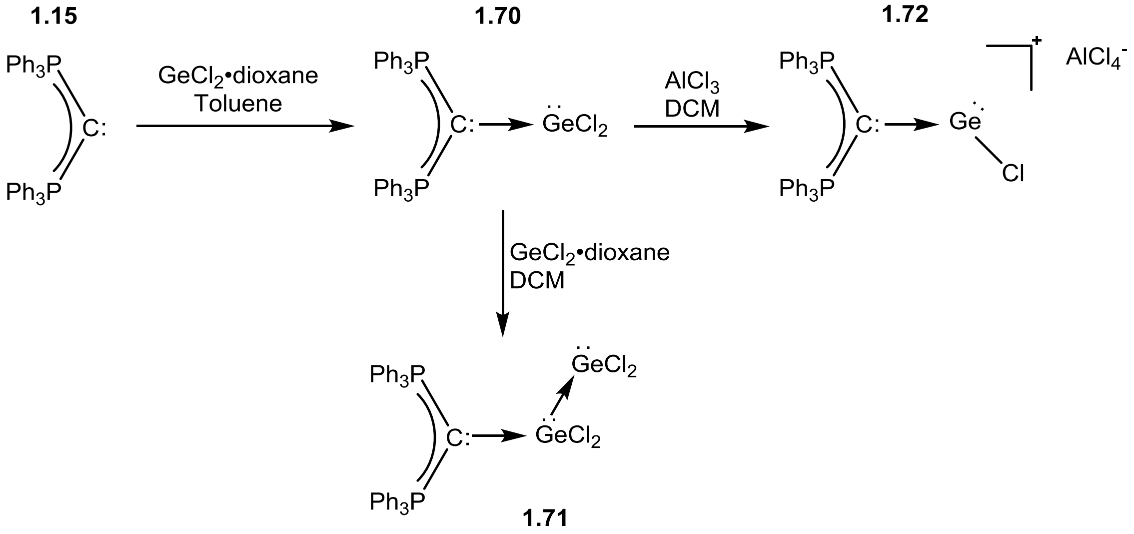
**Scheme 1.21:** Reduction of NHC silicon(IV) adduct **1.67** using KC$_8$ to form silicon(I) **1.68** and silicon(0) **1.69** dimers

Further chemistry involving hydroboration of **1.69** show the silylene to have greater Lewis-basicity than that of small phosphines and ammonia.[51]

### *1.5.2 Germanium*

In 2013 Alcarazo and co-workers reported a series of novel CDP germanium and tin compounds in an attempt to make a germanium(II)-derived monocationic compound.[52]

The use of the CDP ligand **1.15**, was employed as it was suggested to have the desired electronic properties to stabilize a monocationic germanium(II) fragment.

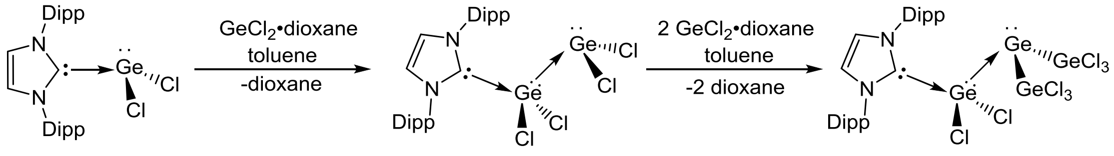


**Scheme 1.22:** Synthesis of the CDP-germanium(II) adduct **1.70** and its further reactivity

When an extra equivalent of $GeCl_2$·dioxane is added to **1.70**, it coordinates to the germanium lone pair rather than the 2nd lone pair on the carbone affording the $^{6Ph}$CDP·$GeCl_2$·$GeCl_2$ adduct **1.71**. Prior to this example there had been no documented cases of unsupported $Ge^{II} \rightarrow Ge^{II}$ dative interactions. It was suggested that the high nucleophilicity of the CDP ligand renders the central germanium atom basic enough to coordinate to a second $GeCl_2$ fragment. When treated with elemental sulfur, the germanium(II) centers of **1.71** are oxidized to germanium(IV), forming Ge=S double bonds.

$AlCl_3$ was added to **1.70** in order to abstract a chloride ligand and form the ionic complex **1.72**, furnishing the desired $[GeCl]^+$ core. This behaviour is unusual for this class of ligand, which prefers to act as a 4-electron donor, donating each electron pair to a different electrophile, rather than donating both pairs to one electrophile.[53, 54]

In 2013 Rivard and co-workers reported a series of germanium oligomers stabilized through the use of the bulky NHC ligand, IPr **1.5**.[55]



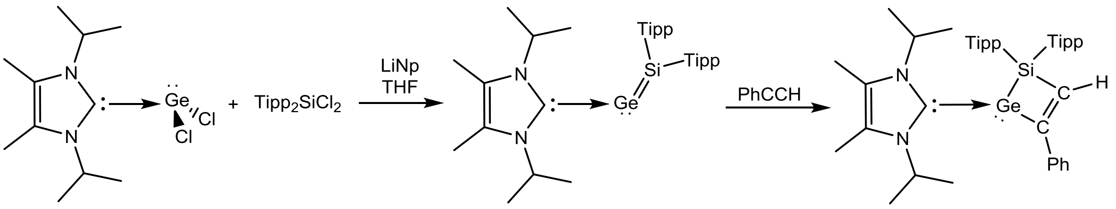
**1.26** **1.73** **1.74**

**Scheme 1.23:** Synthesis of NHC stabilized oligomers **1.73** and **1.74**

The nucleophilic NHC increases the Lewis basicity of the central germanium atom, allowing its lone pair to coordinate to the terminal germanium chloride moiety, acting as a Lewis acid. **1.73** is stable up to 130 °C in the solid state and when treated with 2,3-dimethyl-1,3-butadiene, the terminal $GeCl_2$ group cleanly undergoes cycloaddition to give the cycloadduct $Cl_2Ge(CH_2CMe)_2$ **1.75**, as well as the initial IPr·$GeCl_2$ **1.26** starting material.

Efforts to extend the oligomerization of **1.73** proved successful, with the isolation of the branched, $Ge_4$ complex, IPr·$GeCl_2Ge(GeCl_3)_2$ **1.74**. Furthermore, treating **1.74** with one equivalent of IPr, **1.5** regenerates two equivalents of **1.73**. The $Ge_4$ oligomer **1.74**, is a unique example of an NHC capped, dichlorogermylene oligomer that has been synthesized using a bottom-up, step-wise methodology which exhibits a thermodynamically favourable branched structure, also seen by its hydrocarbon analogue.

At a similar time Scheschkewitz and co-workers were working on NHC stabilized group 14 compounds containing E=E' (E, E' = Si or Ge) multiple bonds.[56]



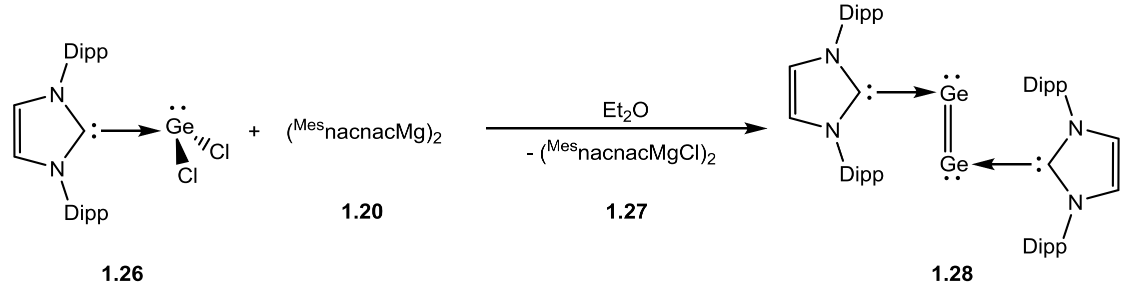
**1.76** **1.77** **1.78**

Tipp = 2,4,6-$^i$Pr$_3$C$_6$H$_2$

**Scheme 1.24:** Synthesis of the ethene analogue, silagermenylidene, **1.77** and its [2+2] cycloaddition, forming a four-membered heterocyclic ring, **1.78**

The sum of angles around the silicon atom in **1.77** is 359.8° exhibiting an almost perfectly planar geometry, indicating that almost all valence electron density is involved in bonding with minimal lone pair electron density. When treated with phenyl acetylene, the Si=Ge double bond in **1.77** undergoes a [2+2] cycloaddition, forming the four-membered heterocyclic ring in **1.78**. The cycloaddition reaction exclusively forms the regioisomer (shown in scheme 1.24) in high yield with no C-H activated products. Using the small NHC, IPr$^i$Me **1.7**, as a stabilizing Lewis-base, compound **1.77** is the first example of a fully characterized heavier vinylidene analogue which has the potential to be used as a novel synthon in LOS group 14 chemistry as well as small molecule activation, e.g. compound **1.78**.

In 2009 the Jones group successfully isolated an NHC adduct of germanium(0), containing a Ge=Ge core [IPr·Ge]$_2$ **1.28**.[20]



**Scheme 1.25:** An NHC germanium(II) adduct **1.26** reduced to a germanium(0) dimer (IPr·Ge)$_2$ **1.28** using the magnesium(I) dimer **1.20** (also seen in part of scheme 1.7)

As seen from scheme 1.25, the product **1.28**, can be thought of as a soluble allotrope of elemental germanium, which could not be isolated using classical reducing agents such as K metal or $KC_8$. Due to the relatively low yields and poor separation of unwanted bi-products, further chemistry of **1.28** proved to be systematically challenging and inconclusive.

In 2013, Lyhs *et al.* synthesized and characterized the first ever homoleptic germanium(II) azide, IPr·Ge$(N_3)_2$ **1.79**.[57]. Neutral p-block element azides are inherently difficult to synthesize and isolate due to their heat and shock sensitivity.[58] However, through the use of bulky NHCs as strong σ-donors, the first stable, neutral, p-block element azide, IPr·Ge$(N_3)_2$ **1.79**, was isolated, giving potential into this new field of research.

## *1.6 Group 15 Chemistry*

The group 15 elements consist of nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). Known as the pnictogens, their importance in organic and inorganic processes have been documented for hundreds and even thousands of years.

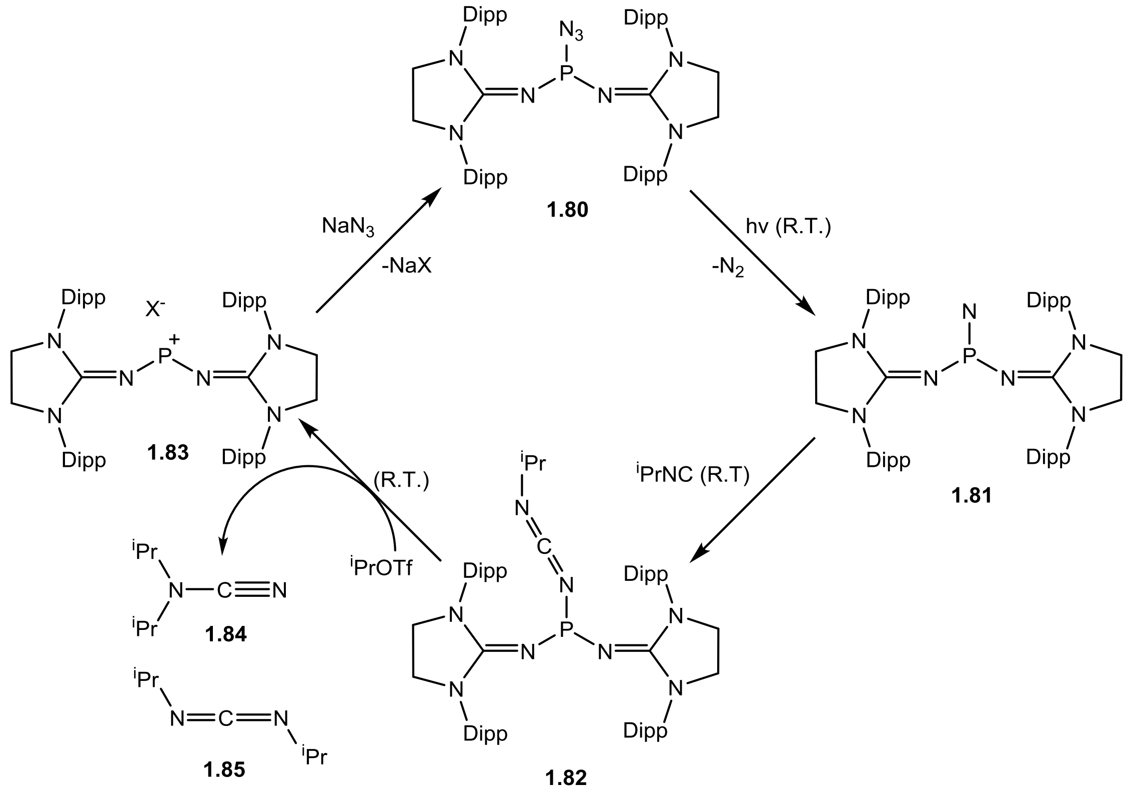
| **Element** | **N** | **P** | **As** | **Sb** | **Bi** |
|---|---|---|---|---|---|
| **Atomic Number** | 7 | 15 | 33 | 51 | 83 |
| **Electronic Configuration** | [He]$2s^2 2p^3$ | [Ne]$3s^2 3p^3$ | [Ar]$3d^{10} 4s^2 4p^3$ | [Kr]$4d^{10} 5s^2 5p^3$ | [Xe]$5d^{10} 6s^2 6p^3$ |
| **Melting Point (°C)** | -210 | 44*, $590^{\#}$ | $613^{\wedge}$ | 630 | 271 |
| **Atomic Radius (pm)** | 74 | 110 | 121 | 141 | 170 |
| **Ionic Radius (pm) r($M^{3+}$)** | 20 | 50 | 62 | 81 | 95 |
| **1st Ionisation Energy (kJ/mol)** | 1400 | 1060 | 966 | 833 | 774 |
| **Electronegativity (χ) (Pauling)** | 3.04 | 2.19 | 2.18 | 2.05 | 2.02 |
| **Electronegativity (χ) (Allred-Rochow)** | 3.07 | 2.06 | 2.20 | 1.82 | 1.67 |

* white, # red, ^ sublimes

**Figure 1.9**: Physical and chemical properties of group 15 elements[11]

### *1.6.1 Phosphorus*

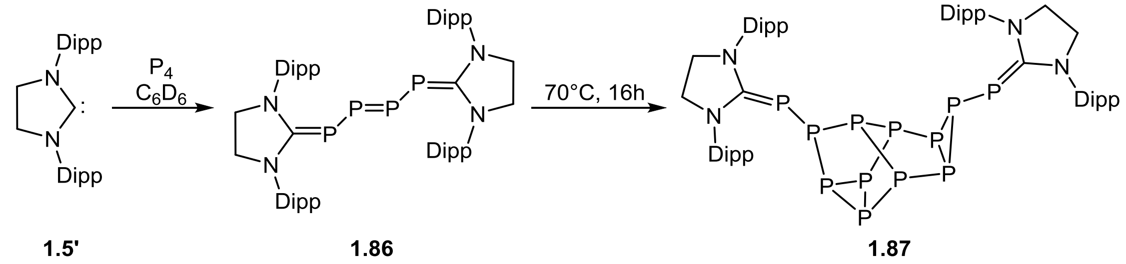
Via UV (254 nm) irradiation of a phosphoazide **1.80**, Bertrand and co-workers reported the synthesis of the first phosphinonitrene compound[59] **1.81** in 2012 (see scheme 1.26).



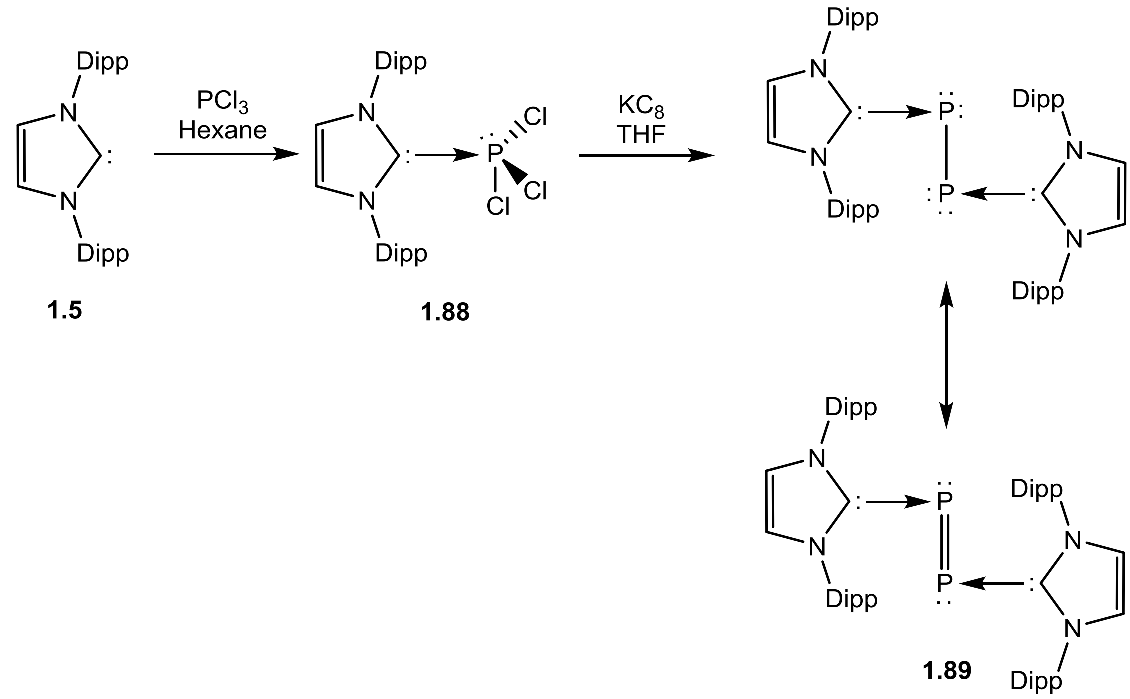
**Scheme 1.26:** Catalytic cycle of a phosphinonitrene **1.80**, yielding a cyanamide **1.84** and a carbodiimide **1.85**

The phosphinonitrene **1.81** then undergoes a catalytic cycle resulting in the formation of the cyanamide **1.84** and carbodiimide **1.85**. These synthetic cycles have been proven difficult to achieve for previously reported metalonitrenes, particularly the removal of the carbodiimide once it is bound to the phosphorus atom – a challenge not found in this example.

Three phosphorus compounds communicated independently in two papers[60, 61] by the Bertrand and Robinson groups, highlight unique features of NHC-phosphorus chemistry.



**Scheme 1.27:** Synthesis of donor stabilized $P_4$ **1.86** and $P_{12}$ **1.87** compounds containing phosphorus atoms in the formal zero oxidation state

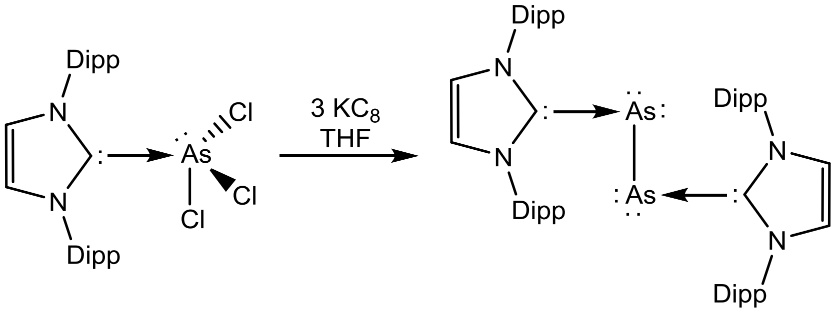


**Scheme 1.28:** Synthesis of donor stabilized phosphorus dimer **1.89** with each phosphorus atom in the formal zero oxidation state

In particular, the nature of phosphorus to act as a Lewis acid as opposed to a Lewis base, as well as giving insight into the nature of elemental $P_2$ and understanding the significant differences to its multiply bonded congener, $N_2$.

### 1.6.2 *Arsenic*

Using a similar methodology to that of **1.89**, Robinson and co-workers were able to isolate its arsenic analogue (IPr·As)$_2$ **1.91**.[62]



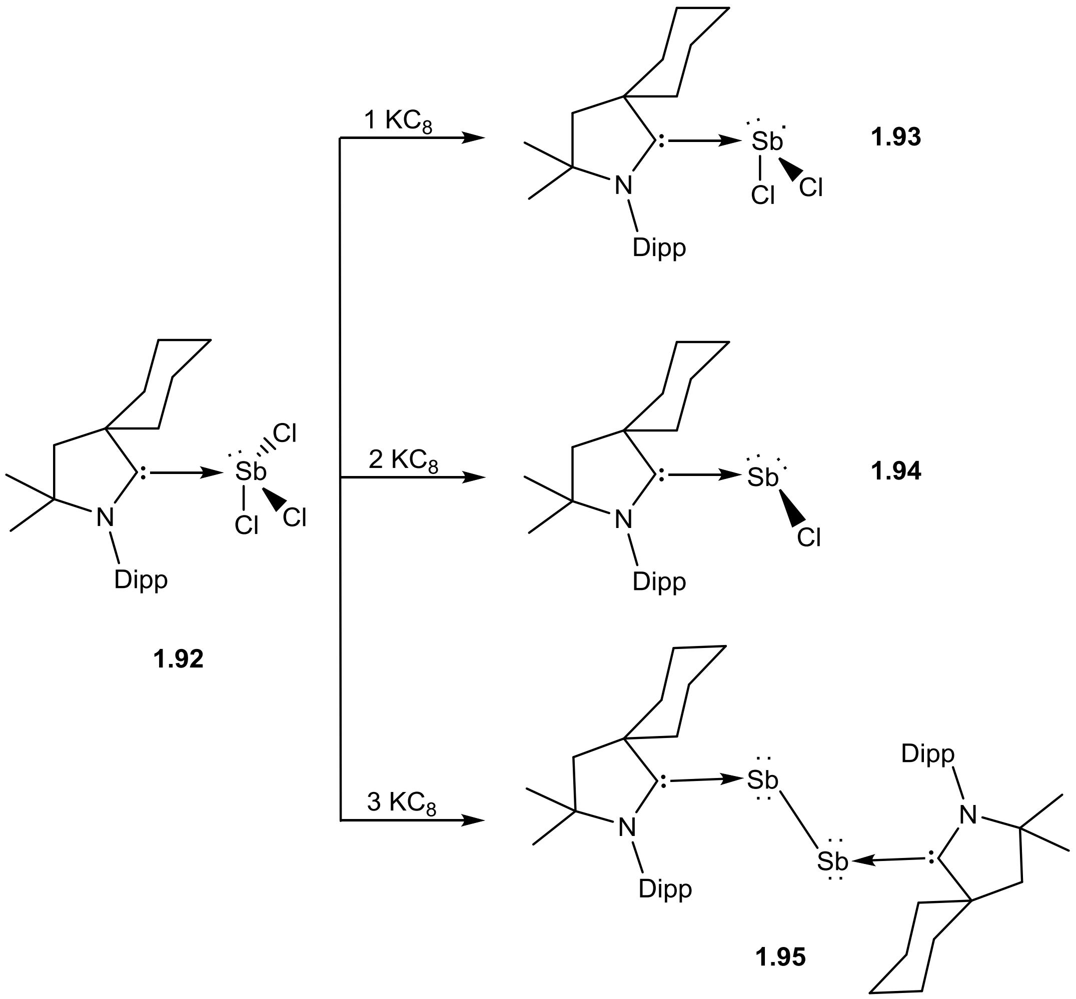
**1.90** **1.91**

**Scheme 1.29:** Synthesis of the NHC stabilized arsenic(0) dimer (IPr·As)$_2$ **1.91**

X-ray crystallographic studies show **1.91** to have an As-As bond length of 2.442(1) Å, slightly longer than the P-P bond length of 2.2052(10) Å found in **1.89**. Computational studies were carried out on **1.91** which show partial pπ back bonding from the arsenic metal centers into the empty p-orbital of the NHC carbene carbon atom, a feature also possessed by the phosphorus analogue, **1.89**.

### 1.6.3 *Antimony*

The most recent member of the group 15 elements to be isolated in the formal zero oxidation state – as part of a neutral, carbene-stabilized adduct – is antimony. The cAAC-stabilized antimony(III) adduct cAAC·SbCl$_3$ **1.92** was stoichiometrically reduced with KC$_8$ to yield the corresponding one-, two-, and three-electron-reduced products cAAC·SbCl$_2$ **1.93**, cAAC·SbCl, **1.94** and (cAAC·Sb)$_2$ **1.95**, shown in scheme 1.30 below.



1.92

1.93

1.94

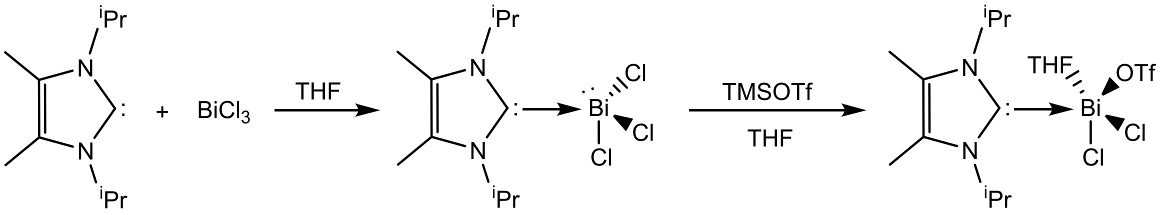
1.95

**Scheme 1.30:** One-, two-, and three-electron reduction of the cAAC-antimony(III) adduct **1.92**, yielding the respective antimony(II), antimony(I), and antimony(0) adducts **1.93**, **1.94**, and **1.95**

The antimony(II) adduct **1.93** is paramagnetic and the first ever neutral antimony-centered radical characterized in solution. The antimony(0) adduct is diamagnetic and exhibits partial π back-bonding from the Sb lone pair orbitals to the carbene-carbon empty p-orbitals, although to a lesser degree than its lighter group 15 analogous adducts $(IPr{\cdot}P)_2$ **1.89** and $(IPr{\cdot}As)_2$ **1.91**. This back-bonding, along with their relatively small HOMO-LUMO gap, is proving to be a useful attribute in stabilizing LOS MG compounds, especially those in the formal zero oxidation state.

### *1.6.4 Bismuth*

It should also be mentioned that the first ever NHC-bismuth compound was only reported in 2014[62] – the last of the non-radioactive p-block elements (noble gasses excluded) to be coordinated by an NHC.



**1.7** **1.96** **1.97**

**Scheme 1.25:** An NHC coordinated bismuth adduct **1.96** and its reactivity towards the halide abstractor, TMSOTf, yielding **1.97**

The bismuth(III) chloride **1.96**, was treated with several reducing agents, however, no LOS product was obtained. Theoretical studies on **1.96** suggest that the bismuth(0) compound, NHC→Bi-Bi←NHC, is thermodynamically unfavourable, a common problem of heavier LOS MG elements.

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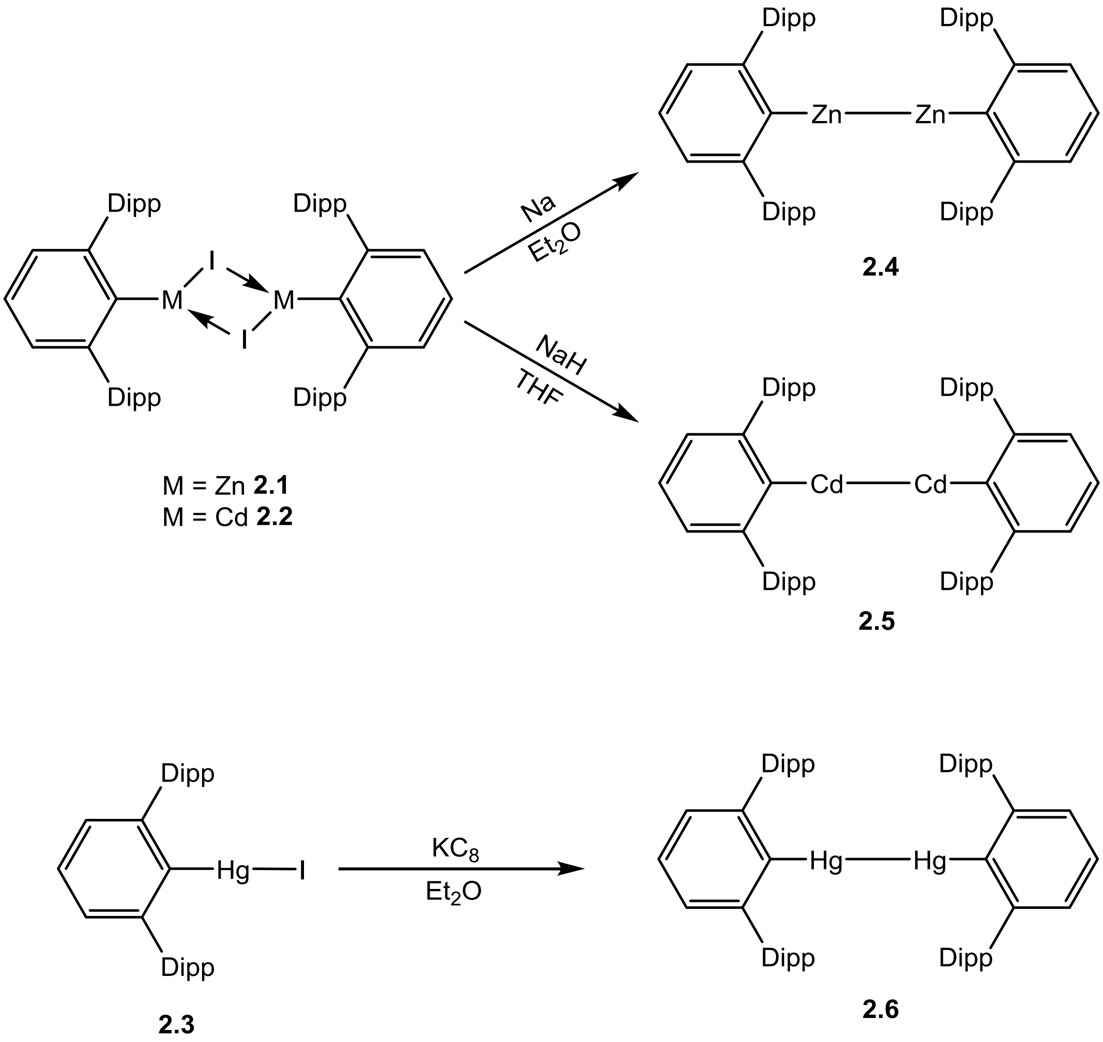
# 2 Low Oxidation State Group 2 and 12 Complexes

## 2.1 A Further Introduction to Low Oxidation State Group 2 and Group 12 Complexes

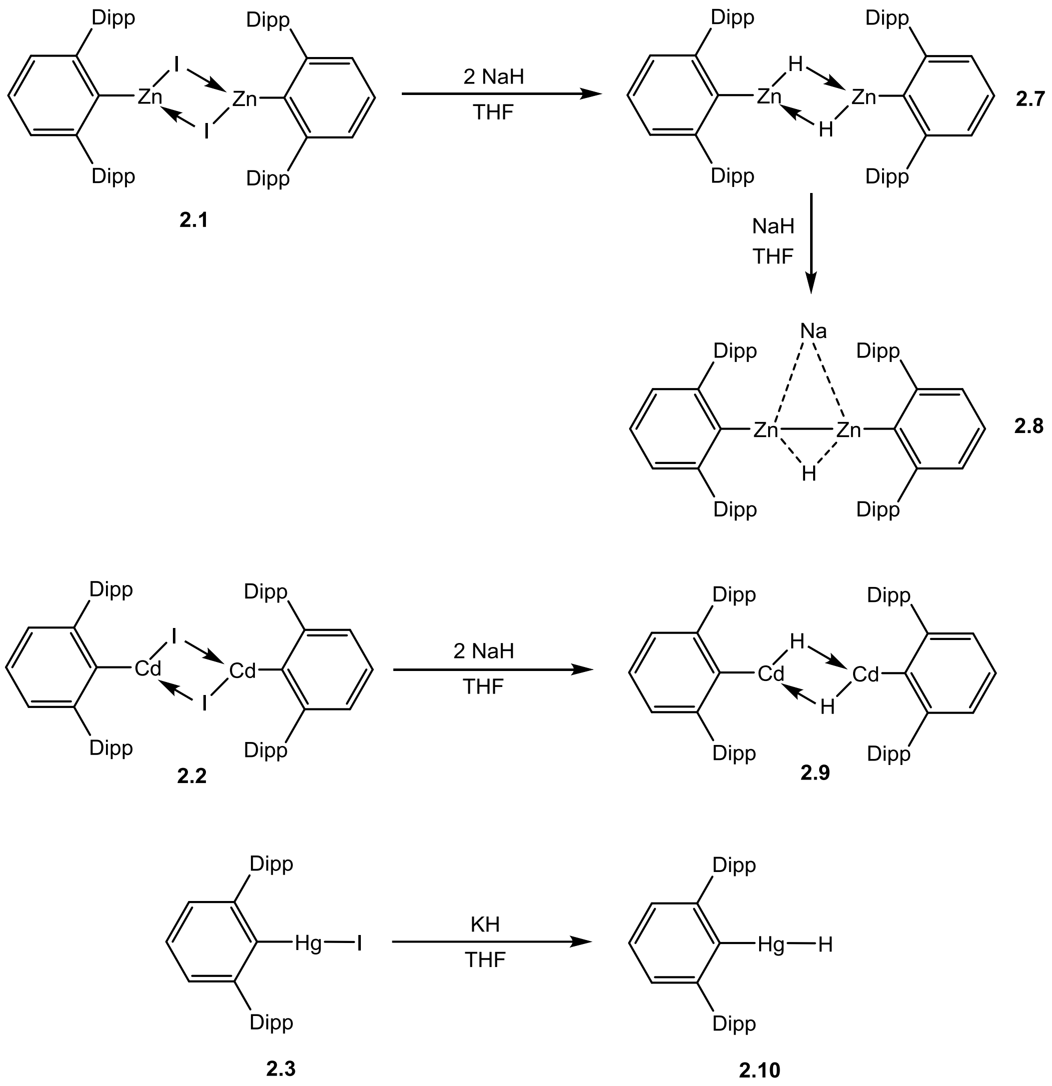
Focusing on the use of highly bulky ter-phenyl ligands, Power and co-workers reported the synthesis of group 12 metal dimers ArMMAr (Ar = terphenyl ligand, M = Zn, Cd, Hg).[1] The compounds are isostructural and possess a linear ArMMAr core with two coordinate metal centers (scheme 2.1).



**Scheme 2.1:** Synthesis of ter-phenyl LOS group 12 metal dimers **2.4 – 2.6**

The M-M bond distances do not increase down the group but rather follow an atypical pattern (Zn-Zn 2.3591(9) Å, Cd-Cd 2.6257(5) Å and Hg-Hg 2.5738(3) Å), in agreement with DFT calculations which found the strength of the Hg-Hg bond to be greater than that of the Cd-Cd analogue. All ArMMAr (M = Zn, Cd, Hg) dimers were synthesized via alkali metal reductions of the respective ArMI precursors with both zinc and cadmium iodides being dimeric in the solid state and the mercury iodide being monomeric as determined by single crystal X-ray crystallography.

In the same publication, the synthesis of the corresponding ArMH (M = Zn, Cd, Hg) hydride compounds were also reported via the hydrogenation of the ArMI precursors (scheme 2.2).

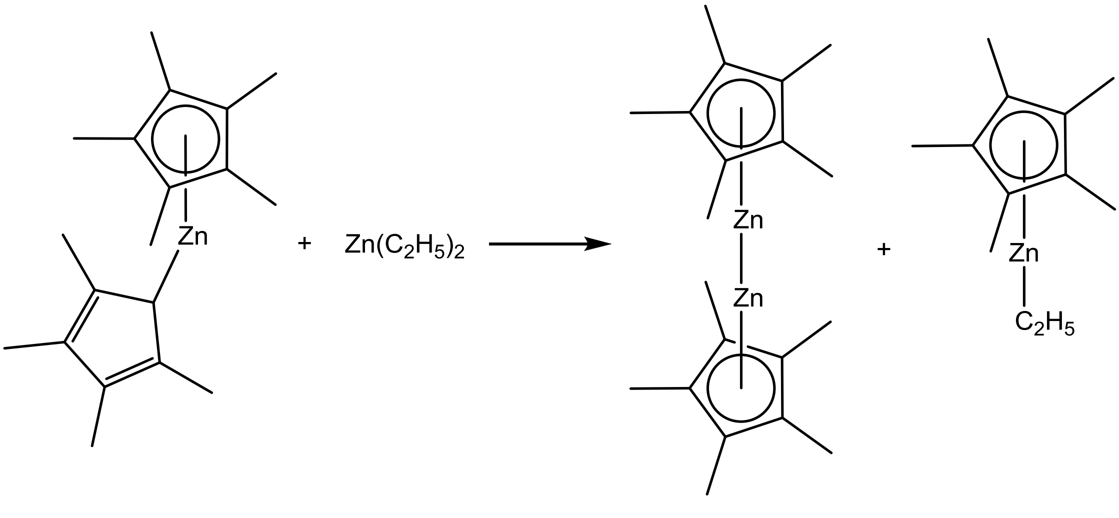


**Scheme 2.2:** Synthesis of ter-phenyl group 12 metal hydride compounds **2.7 – 2.10**

Similar to the halide precursors, the zinc and cadmium hydrides are dimeric in the solid state whereas the mercury hydride is monomeric. Further reduction of the zinc hydride dimer, **2.7** with NaH gives the Na-H bridged compound **2.8**, shown in scheme 2.2 above, which contains a σ-antiaromatic [Zn-H-Zn]$^-$ core. The cadmium hydride compound **2.9** slowly reverts to the LOS dimer **2.8** in solution with the elimination of hydrogen and is suggested as a possible transition state in the formation of the LOS cadmium dimer **2.8** from the halide.

One of the biggest breakthroughs in LOS group 12 chemistry was reported in 2004 with

Carmona and co-workers reporting the first thermally stable zinc(I) compound, $Zn_2(\eta^5-C_5Me_5)_2$, **2.12**.[2] Up until this point there had been some evidence shown for compounds containing a $[Zn-Zn]^{2+}$ unit however none were crystallographically characterized.[3,4]

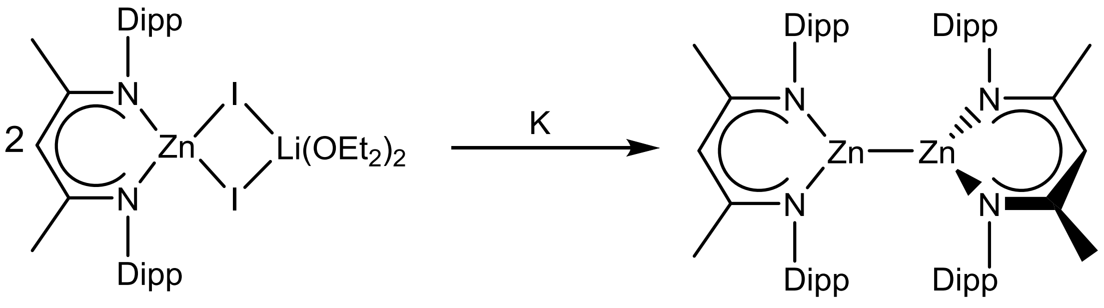


**2.11** **2.12** **2.13**

**Scheme 2.3:** Synthesis of the first crystallographically characterized zinc(I) compound, $[Zn_2(\eta^5-C_5Me_5)_2]$, **2.12**

Compound **2.12** is air and moisture sensitive in both the solution and solid state as well as spontaneously combusting in air at room temperature. Compound **2.12** can be considered as a $[Zn-Zn]^{2+}$ centered dimer, capped by planar, anionic Cp* ligands (Cp* = $C_5Me_5^-$) at both Zn centers. Even though the field of Hg-Hg homonuclear bonds had been well developed, up until this point, there was a limited understanding on the nature of the lighter congeners containing Zn-Zn bonds.

Carmona also realized that similar zinc(I) compounds could be synthesized without the use of Zn-C bonds. This notion was verified by Robinson and co-workers in 2005, who reported the zinc(I) compound RZn-ZnR (R = {$^{Dipp}$nacnac}) **2.15**[5] (scheme 2.4).

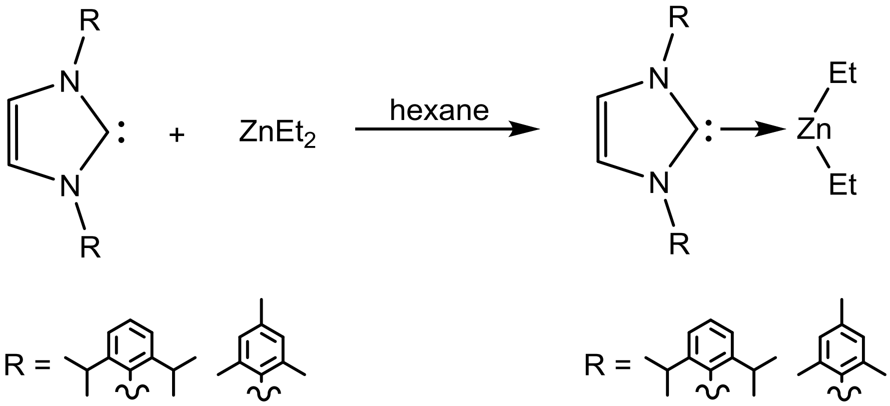


**2.14** **2.15**

**Scheme 2.4:** Synthesis of the zinc(I) compound RZn-ZnR (R = {$^{\mathrm{Dipp}}$nacnac}) **2.15**

Similar to the zinc-terphenyl compound **2.4** (scheme 2.1), the nacnac dimer **2.15** also contains a $[\mathrm{Zn{-}Zn}]^{2+}$ core, with a slightly shorter Zn-Zn bond length (2.3586(7) Å) than that of **2.4** (2.3591(9) Å). The nacnac planes are almost orthogonal, with a N-Zn-Zn-N torsion angle of 86.6 °, alleviating steric congestion of the bulky aryl substituents, as well as providing maximum steric protection of the $[\mathrm{Zn{-}Zn}]^{2+}$ core, a feature common of nacnac dimers.

One of the first metals to be coordinated to an NHC was zinc,[7] reported only a year after the first isolable NHC,[6] shown in scheme 2.5 below.

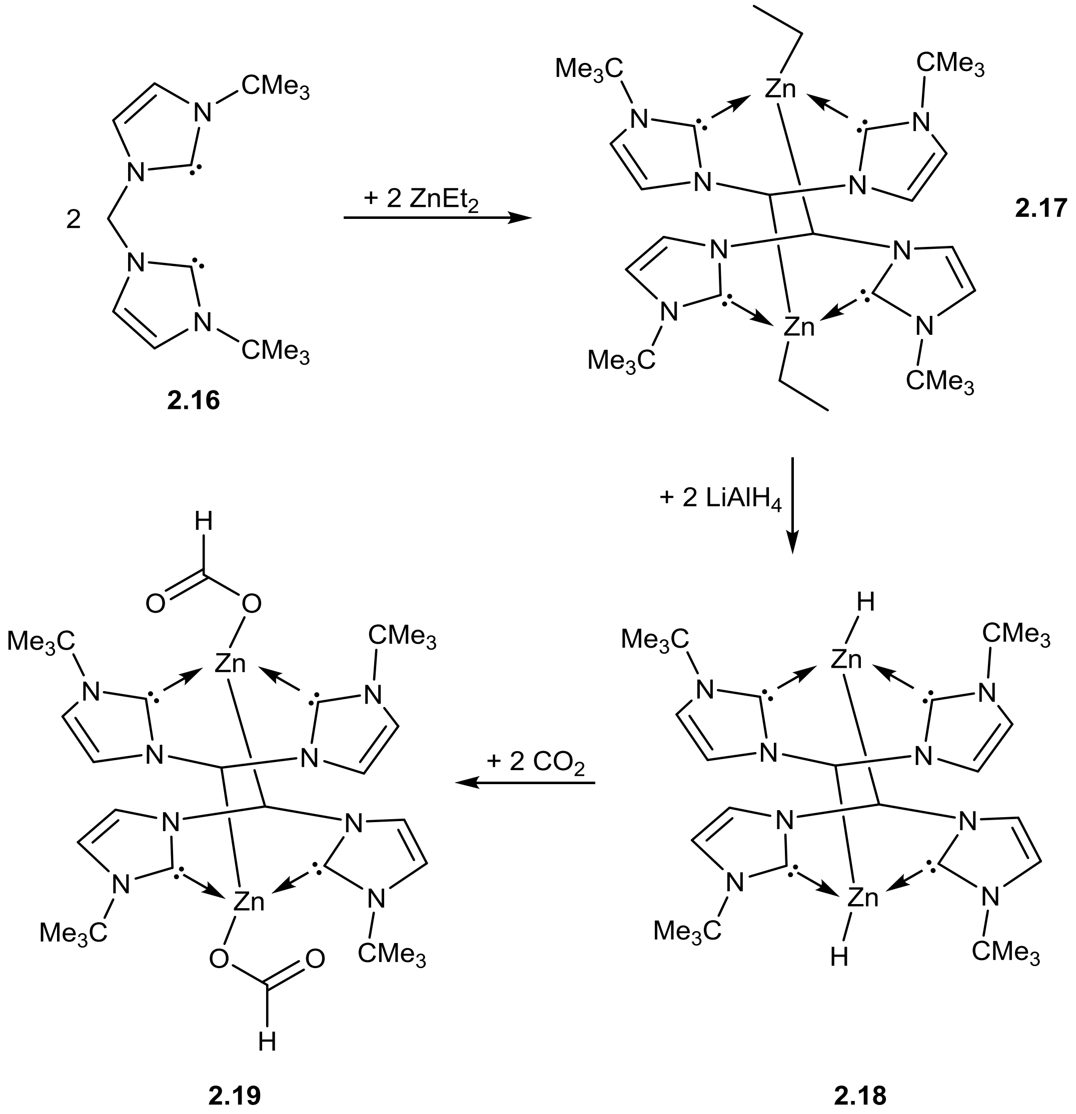


**1.5** **1.6** **1.33** **1.34**

**Scheme 2.5:** Synthesis of NHC zinc alkyl adducts **1.33** and **1.34**

This method of Lewis base/acid coordination is still used as one of the most common methods of forming NHC-metal adducts to date.

In the same year, Okuda also reported another NHC zinc hydride complex[8] using the bis-NHC ligand, bis(*N,N'*-di-*tert*-butyl-imidazol-2-ylidene) **2.16**. The reaction of diethyl zinc with **2.16** cleanly gives **2.17** via the deprotonation of the sp$^3$ C-H bond along the backbone of the ligand whilst eliminating ethane. Deprotonation of this type of ligand by a metal center is not uncommon, however, ordinarily a mixture of products is obtained rather than a single compound (scheme 2.6).



**Scheme 2.6:** Synthesis of a bis(NHC) zinc hydride, **2.18** and further reactivity using CO$_2$

Reacting **2.17** with $H_2$ gas gives no reaction even after heating to 60 °C for 2 days. However, when **2.17** is treated with $LiAlH_4$ under mild conditions, the zinc hydride complex **2.18** is obtained in a moderate yield. Compound **2.18** was treated with small organic molecules in order to investigate the viability of its further chemistry. When treated with $CO_2$, insertion of a $CO_2$ molecule between each of the Zn-H bonds is observed giving the formato complex **2.19**. Compound **2.19** is of significance since zinc formates have been shown to be important intermediates in the Cu/ZnO-catalyzed synthesis of methanol[9]. Significant research has been done on NHC-zinc-hydride compounds in recent years and due to their unique and interesting chemistry with small organic molecules, continue to be a prominent area of research.

## *2.2 Research Outline*

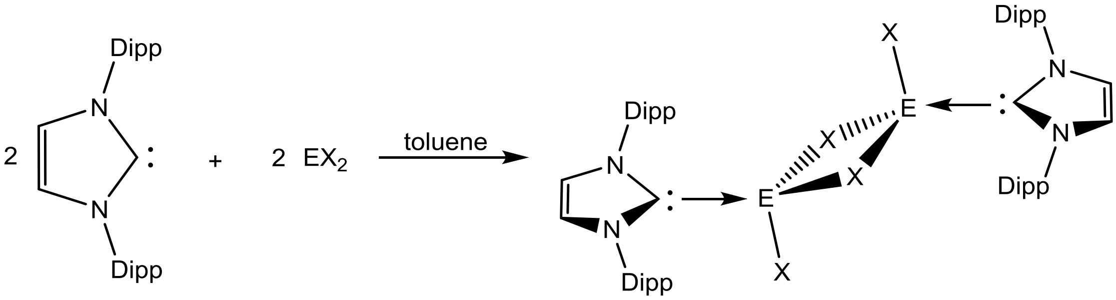
NHC adducts of MG and TM elements have had a significant impact in recent literature largely due to their unprecedented chemical structures and unique chemical properties. Extending on from this trend, NHC adducts of group 2 and group 12 element halides, were synthesized and subsequently reduced in attempts to form their corresponding LOS compounds. NHCs included 5-membered unsaturated and 6-membered saturated analogues. In addition to NHCs, nitrogen heterocyclic silylenes (NHSi), carbodiphosphoranes (CDP) and N-donor, diazabutadiene (DAB) ligands were also used in attempts to form LOS complexes with group 2 and group 12 elements.

## *2.3 Results and Discussion*

### *2.3.1 NHC Adducts of Group 2 and Group 12 Elements*

NHC adducts of element fragments (eg. element hydrides, halides, alkyl, etc.) are predominantly synthesized via two pathways. The first involves the direct coordination of the free NHC to the desired element fragment. The second method involves the reaction of silver(I) oxide, $Ag_2O$, with the HCl salt of the NHC, yielding the silver NHC adduct of the form NHC·AgCl which can then undergo a transmetallation reaction with a specific element fragment to give the desired adduct. The former route was employed for the synthesis of all adducts throughout my research, that is, the NHC was generated and isolated as a crystalline solid and then directly coordinated to element fragments.

This methodology proved successful in the synthesis and isolation of two new NHC adducts of zinc and cadmium $(IPr{\cdot}ZnBr_2)_2$, **2.20**, and $(IPr{\cdot}CdI_2)_2$, **2.21**, respectively, by adding the desired element halide to a toluene solution of IPr in a 1:1 ratio (scheme 2.7).[10] Compounds **2.20** and **2.21** were crystallographically characterized in the triclinic space group P-1 and monoclinic space group P2(1)/c respectively, and are isostructural to each other in the solid state.



**1.5**

E = Zn, X = Br **2.20**
E = Cd, X = I **2.21**

**Scheme 2.7**: Synthesis of IPr-zinc and cadmium halide adducts **2.20** and **2.21**

Compounds **2.20** and **2.21** are dimeric in the solid state even though “soft” bromide and iodide ligands were used. All metal centers are four coordinate and have a distorted tetrahedral geometry with each metal center coordinated by two bridging halides, one terminal halide and an NHC ligand. The E-C (E = Zn, 2.039(3) Å, **2.20**; E = Cd, 2.249(5) Å, **2.21**) bond lengths fall within the expected range for these types of compounds.

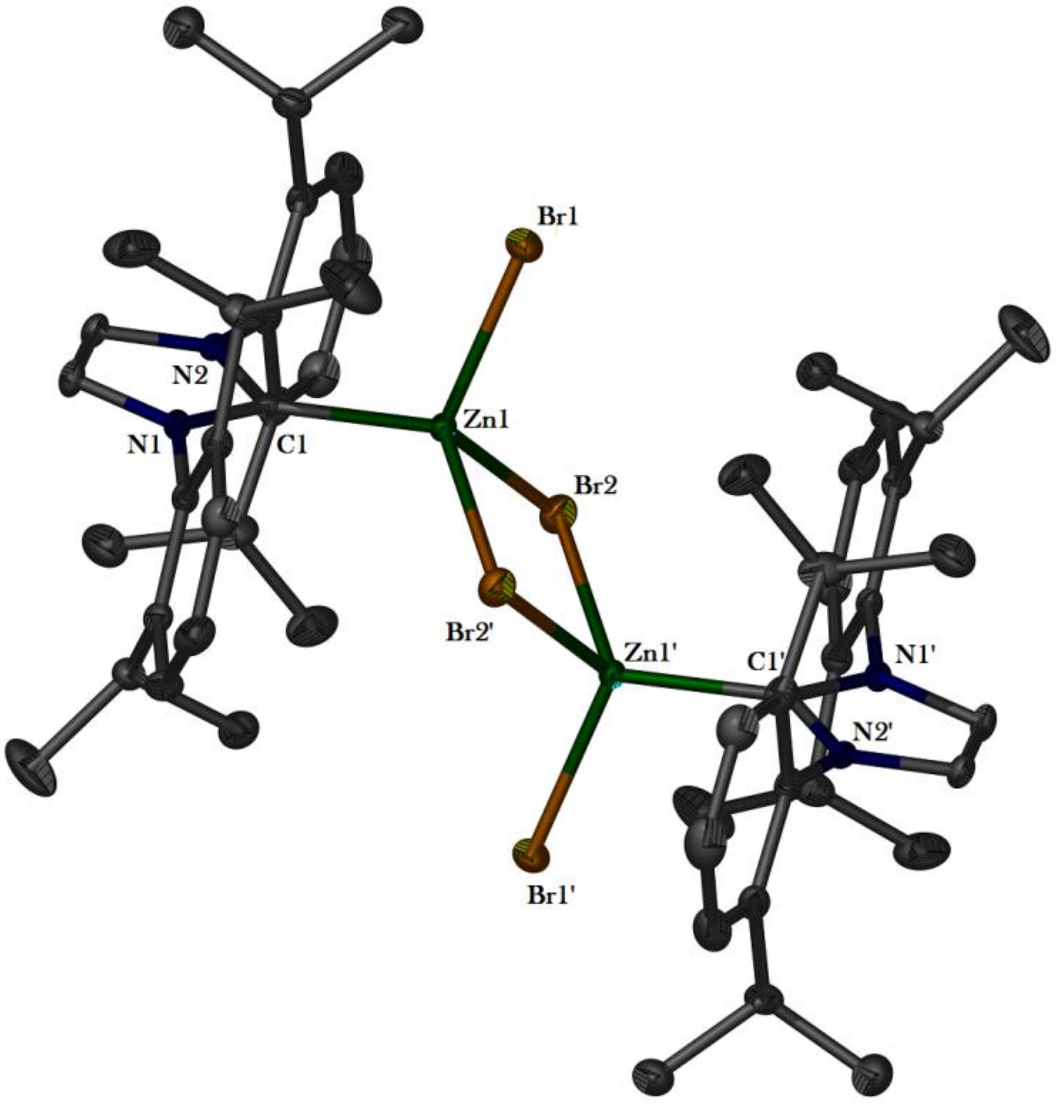


**Figure 2.1:** Molecular structure of (IPr·ZnBr$_2$)$_2$ **2.20** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): Zn1-C1 2.039(3), Zn1-Br1 2.3642(8), Zn1'-Br2 2.4658(12), Zn1-Br2 2.4866(9),Zn1'-Br2-Zn1 86.44(3), C1-Zn1-Br1 108.88(9)

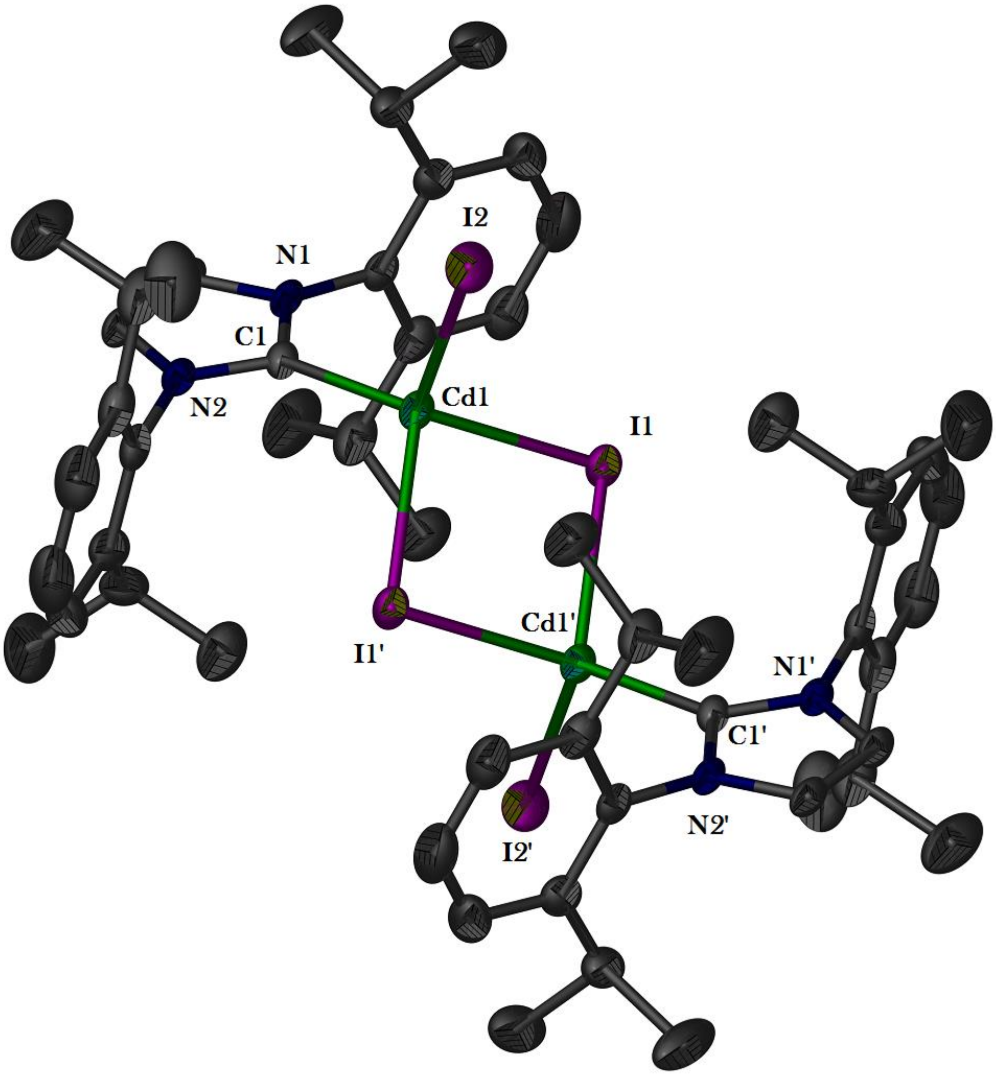


**Figure 2.2:** Molecular structure of (IPr·CdI$_2$)$_2$ **2.21** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): Cd1-C1 2.249(5), Cd1-I1 2.8518(9), Cd1-I2 2.7339(7), Cd1-I1‘ 2.8565(12), Cd1’-I1-Cd1 84.35(3), C1-Cd1-I2 113.82(13)

The $^1$H and $^{13}$C NMR spectra of **2.20** and **2.21** are similar to that of the free carbene as well as each other. No N*C*N resonances were observed in the $^{13}$C NMR spectrum for either compound. Molecular ion peaks for **2.20** and **2.21** were not seen in the mass spectra, however, in both cases the observed data matched the theoretical isotope profile for the [IPr·ZnBr]$^+$ and [IPr·CdI]$^+$ fragments (the monomeric form of each compound, minus one halide ligand).

Compounds **2.20** and **2.21** were synthesized as precursors which would then be reduced, so that each metal center would potentially be in the formal zero oxidation state. This was attempted using a number of different reducing agents including alkali metals and various nacnac magnesium(I) dimers, as well as varying solvents and temperature conditions. No characterizable products were obtained from any of these reductions; the predominant outcome being the precipitation of elemental zinc or cadmium, as well as liberated free IPr, as confirmed via $^1$H NMR spectroscopy. Worthy of note, was one reaction involving the reduction of **2.20** with the magnesium(I) dimer {($^{Mes}$nacnac)Mg}$_2$, ($^{Mes}$nacnac = {[(Mes)NC(Me)]$_2$CH}$^-$, Mes = mesityl) **1.20** in diethyl ether at -80 °C. This resulted in the instantaneous formation of a vibrant orange solution. This solution was left stirring for up to an hour at -50 °C and then stored at -80 °C for several days, over which time a red/orange crystalline product was formed. Attempts were made to crystallographically characterize this material (amongst other characterization methods), however due to its extreme thermal instability, as well as being highly soluble in silicone oil (even at low temperatures), a definitive characterization was not obtained. 1-azidoadamantane was added to the mixture in an attempt to help stabilize any unknown, low-coordinate zinc compounds as derivatives, however only the previously reported ($^{Mes}$nacnacMgN$_3$ dimer **2.22**)[11] was observed.

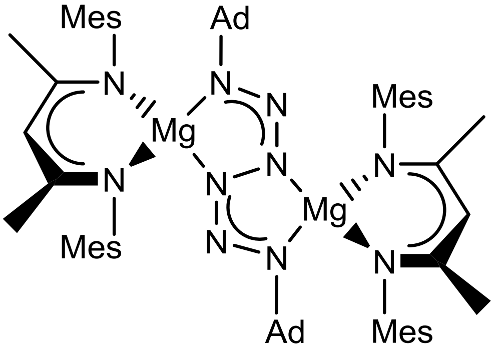


**Figure 2.3:** Visual representation of azide coupled magnesium(II) product **2.22**, isolated from attempted zinc reductions

In one case, the reduction of **2.20** with the magnesium(I) dimer **1.20**, gave an instantaneous loss of colour at -80 °C, normally a vibrant orange colour. Colourless crystals were obtained from solution and analyzed via single crystal X-ray diffractometry. The structure was found to be the $CO_2$ insertion product, **2.23**, shown below in figure 2.4.

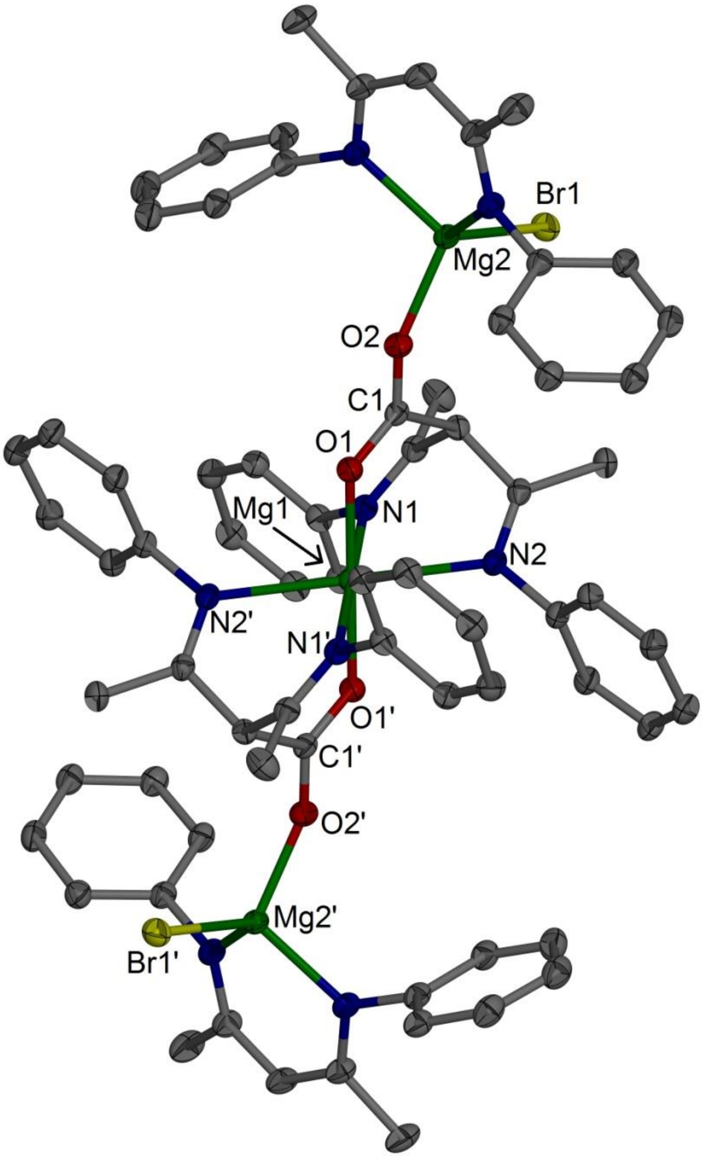
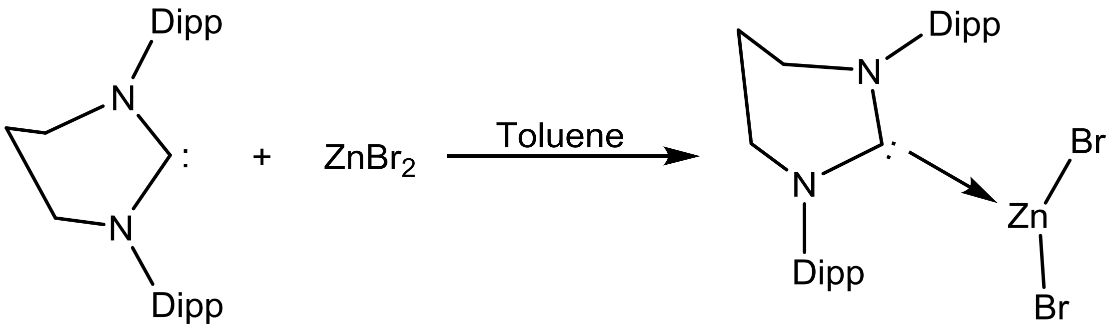


**Figure 2.4:** $CO_2$ insertion product **2.23**, obtained from magnesium(I) reduction of **2.20** (H atoms and aryl $CH_3$ groups omitted for clarity) selected bond lengths (Å) and angles (°): Mg1-O1 1.9894(12), Mg1-N1 2.3014(15), Mg1-N2 2.3813(16), Mg2-O2 1.9527(14), Mg2-$N_{avg}$ 2.0342, Mg2-Br1 2.4839(10), C-$O_{avg}$ 1.2531, O1-Mg1-O1' 180.001(1), N1-Mg1-N1' 180.001(1), N1-Mg1-N2 83.83(6), O-C-$O_{avg}$ 118.02

Compound **2.23**, contains a distorted octahedral magnesium center, with two distorted tetrahedral magnesium extensions bridged by $CO_2$ linkages. The central magnesium atom is chelated by two $^{Mes}$nacnac ligands, each of which bind through a $\kappa^3$ arrangement. The $\kappa^3$ formation stems from the backbone C-C coordinated $CO_2$ fragment. The source of $CO_2$ is presumed to be from dry ice, used to keep the reaction environment at a low temperature. Although novel in demonstrating $CO_2$ addition to the nacnac backbone, the main objective of synthesizing LOS magnesium, zinc or cadmium compounds was not achieved, therefore, attention shifted towards the formation of NHC-zinc hydride complexes (at the time, none had been reported in the literature).

In general, the methodology used to obtain NHC-zinc hydrides was to first synthesize the halogenated dimer $(IPr\cdot ZnBr_2)_2$ **2.20**, then, exchange the halogen ligands with hydrides via selective hydrogenating reagents. In one such experiment, excess $CaH_2$ was added to a toluene/THF solution of **2.20** and left stirring overnight at ambient temperature. Upon workup, the $^1H$ NMR spectrum of the resultant mixture showed only starting material present in solution. The same result was obtained after the reaction was repeated under reflux conditions. Using alternative hydride sources, such as $LiAlH_4$, $KBH_4$ or $K[BEt_3]H$, yielded the transmetallation products $IPr\cdot AlH_3$, $IPr\cdot BH_3$ and $IPr\cdot BEt_3$ respectively. When $(^{Dipp}nacnacMgH)_2$ was used as a potential hydride source for the reaction with **2.20**, an intractable mixture was formed, with the only identifiable products (by $^1H$ NMR spectroscopy) being IPr **1.5** and the previously reported $(^{Dipp}nacnacMgBr)_2$ dimer. The final attempt to form an NHC stabilized zinc hydride complex involved the use of $PhSiH_3$ being added to a benzene solution of $IPr\cdot ZnEt_2$, **1.33**. The reaction was left stirring at room temperature overnight, at which point, an aliquot of the resultant mixture was taken and analysed using $^1H$ NMR spectroscopy. The $^1H$ NMR spectrum indicated no reaction had occurred. When heated to 50 °C, multiple silane products were observed, indicated in both the $^1H$ and $^{29}Si$ NMR spectra of the mixture, which could not be separated using conventional laboratory techniques. At this point, attempts to synthesize and isolate NHC adducts of zinc hydrides ceased until 2013, when Okuda and co-workers reported the previously mentioned (NHC·ZnH$_2$)$_2$ dimers, (NHC = IPr) **1.35** and (NHC = IMes) **1.36**. Using this method to isolate usable amounts of **1.35**, subsequent reductions using the magnesium(I) dimer, **1.20** were carried out. Ether solutions of **1.35** and **1.20** were combined at -80 °C (1:1 mol ratio) and left to warm to room temperature, during which time, colourless gas evolution was observed, attributed to the formation of $H_2$. Although a red/orange colour was seen in solution at low temperatures, upon reaching room temperature, only a colourless solution was observed, with elemental zinc precipitation and free IPr as the major products. The $^1$H NMR spectrum suggests the formation of a new IPr compound in trace amounts, however, upon workup free IPr is the only product obtained as a crystalline solid. Attention turned to other five-membered NHCs in attempts to improve crystallization. Other five membered NHCs such as IPr* **1.3**, $^{Me}$IPr, **1.4** and IPr$^i$Me, **1.7** were used, however, these NHCs often yielded a higher number of products in lower yields compared to analogous IPr based reactions. Thus, a change from five-membered to six-membered NHCs was implemented. Six-membered NHCs are considered to be stronger nucleophiles, have larger cone angles and have a less strained, saturated backbone compared to their five-membered counterparts. For these reasons, six-membered NHCs were also utilized throughout my research, in particular, the ligand $^6$IPr, **2.24** (scheme 2.8).

The syntheses of six-membered NHC-group 12 metal adducts were carried out in a similar fashion to their five-membered analogues. $^6$IPr and $ZnBr_2$ were combined in a 1:1 molar ratio and stirred in toluene to yield the first example of a six-membered NHC adduct of zinc, $^6$IPr·$ZnBr_2$ **2.25** in good yield (scheme 2.8).



**2.24**

**2.25**

**Scheme 2.8:** Synthesis of the NHC-zinc(II) bromide adduct $^6$IPr·ZnBr$_2$, **2.25**

Compound **2.25** was crystallographically characterized and found to be a 1:1 monomeric adduct in the solid state (figure 2.5) below. Comparatively, the five-membered NHC IPr, **1.5** with the same ZnBr$_2$ fragment, gives the bridged, dimeric compound **2.20** (mentioned previously in scheme 2.7) in the solid state. This is believed to be caused by the increased steric bulk the six-membered NHC provides to the metal center, as well as the different electronic properties of the six-membered NHC.

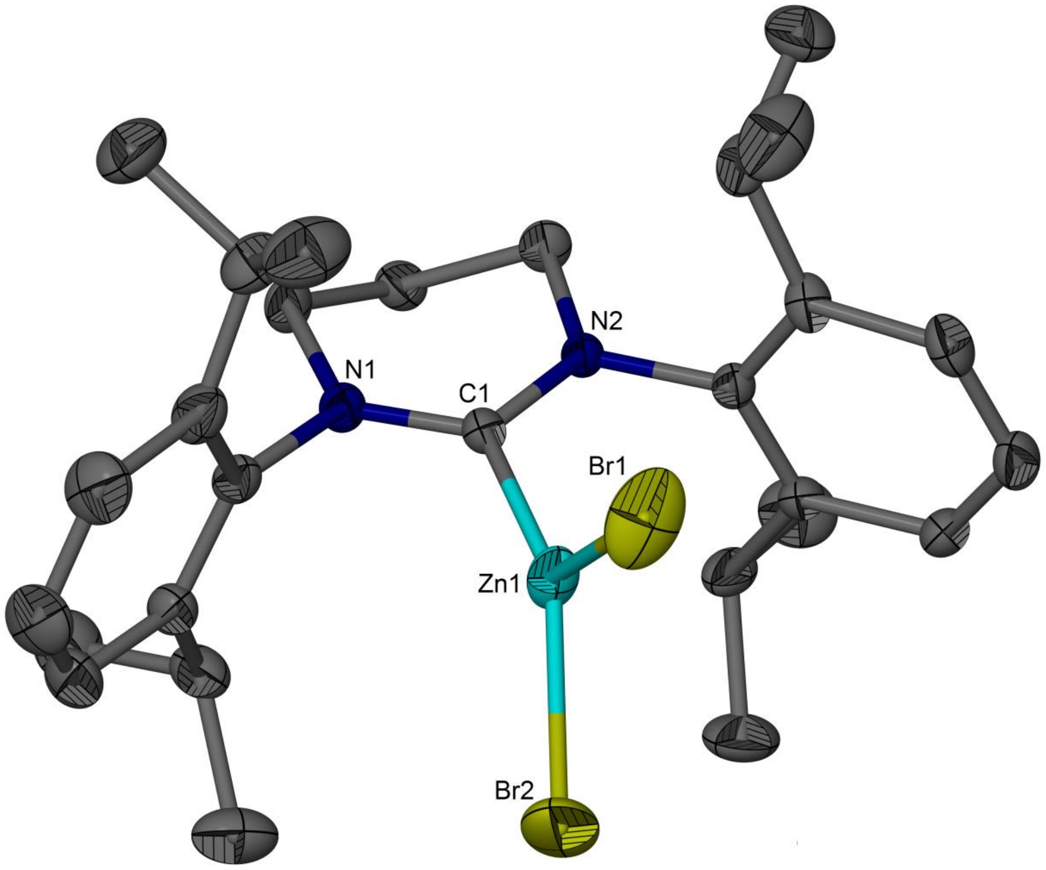


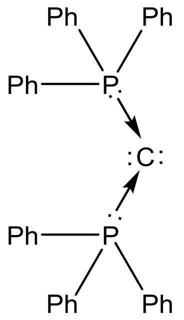
**Figure 2.5:** Molecular structure of $^{6}$IPr·$ZnBr_2$ **2.25** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): Zn1-C1 2.011(3), Zn1-Br1 2.3286(9), Zn1-Br2 2.3150(9), C1-Zn1-Br1 124.44(9), C1-Zn1-Br2 126.07(10), Br1-Zn1-Br2 109.48(4)

The Zn-C bond length (2.011(3) Å) of **2.25** is slightly shorter than that of the previously mentioned IPr analogue **2.20** (2.039(3) Å), presumably due to the dimeric nature of **2.20**. The zinc center occupies a distorted trigonal planar geometry whilst both Zn-Br bonds are virtually orthogonal to the mean NCN plane. The aryl groups on the nitrogen substituents provide shielding for the exposed sites on the zinc center, whilst the flexible isopropyl groups assist in the crystallization of the compound. From the $^{1}$H NMR spectrum it can be observed that the two (originally overlapping) doublets, corresponding to the $C(CH_3)_2$, protons now have a separation of 0.24 ppm, a common phenomenon upon coordination of this ligand to a metal halide. A feature not common however, is the signal corresponding to the backbone $CH_2CH_2CH_2$ protons, which has shifted significantly down field to δ 4.50 ppm (originally at δ 2.85 ppm). It is also worthy to note that attempts to synthesize $^6$IPr·CdI$_2$ (using $^6$IPr and CdI$_2$ as reactants) consistently gave starting materials, or decomposition products when heated.

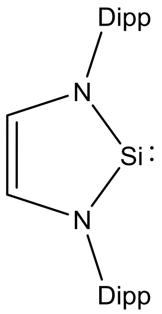
The lower solubility of the six-membered carbene (compared to IPr) required the use of DCM to be able to isolate large amounts of **2.25**. After successfully isolating a usable amount of **2.25**, attempts to reduce this compound were carried out using ($^{Mes}$nacnacMg$^I$)$_2$ dimer **2.20** under a variety of conditions. Ether solutions of **2.20** and **2.25** were combined at -80 °C and left to warm to room temperature. During this warming stage the yellow colour of **2.20** was noticeably reduced in solution and the formation of a white solid was observed with no metal precipitate. The $^1$H NMR spectrum shows complete consumption of **2.25** and no free $^6$IPr in solution, however upon workup, isolation of a pure, crystalline NHC-adduct proved inaccessible with oxidized nacnacMg compounds being the major isolable products.

### *2.3.2 Alternative Neutral Ligands: Carbodiphosphorane and Nitrogen Heterocyclic Silylene Adducts of Group 2 and 12 Elements*

Although five and six-membered NHCs had resulted in several adducts, the lack of reduced products prompted the use of other neutral donor ligands to stabilize group 2 and 12 elements. These included carbodiphosphoranes (CDPs) and nitrogen-heterocyclic silylenes (NHSis), specifically the CDP **1.12** and the NHSi **2.26** (seen in figure 2.6 below), which will be discussed herein.



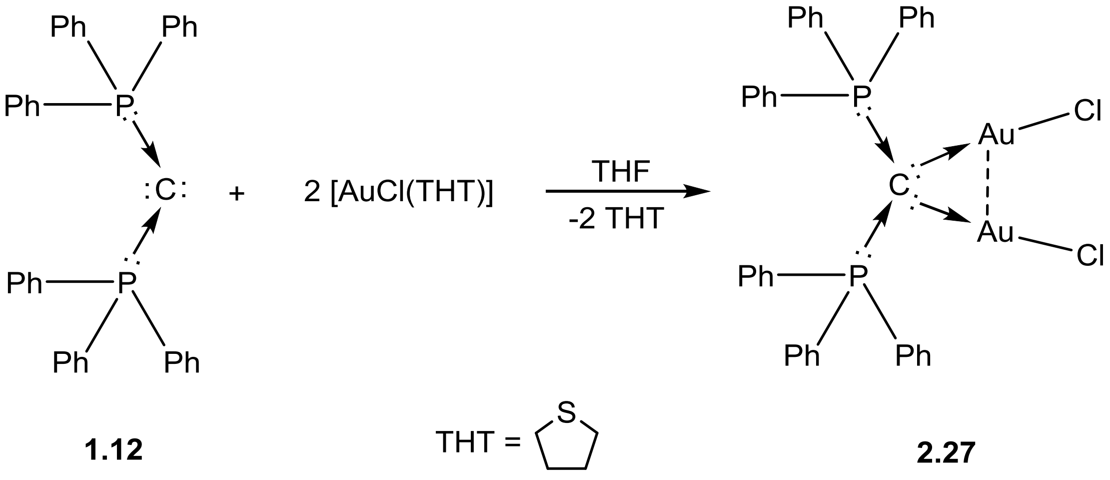
**1.12**



**2.26**

**Figure 2.6:** Neutral ligands CDP **1.12** and silylene **2.26**

Aside from steric features, the electronic characteristics of the CDP ligand also play a critical role in the type of adduct formed. A major difference between CDPs and other neutral donor ligands, is the extra lone pair on the central carbon atom. Due to the two lone pairs, CDPs have the potential to coordinate to two different metal centers such as the example reported by Schmidbaur *et al*. in 1976[12] and later, a crystallized example by Vicente *et al*. in 2002.[13] In the latter example, the DCP ligand coordinates to two AuCl fragments using both its lone pairs on the central carbone carbon atom (scheme 2.9).

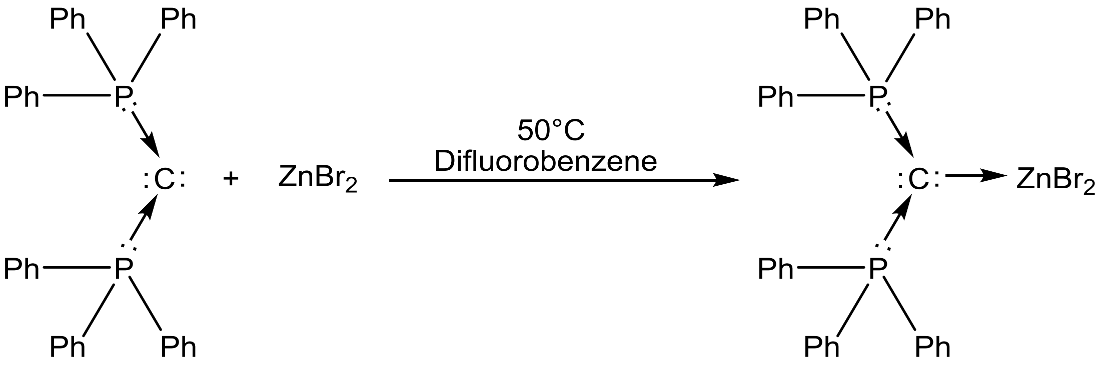


**Scheme 2.9**: Synthesis of the carbodiphosphorane-gold adduct $[(AuCl)_2\{\mu\text{-}^{6Ph}CDP\}]$

**2.27**

However, to date, compounds of this type are still uncommon, with the 1:1 adduct being the dominant form found in the literature.

Compound **1.12** is largely insoluble in hydrocarbon solvents at room temperature as well as exhibiting the “solvent proton abstraction” problem whereby the ligand is protonated by the solvent giving the undesired conjugate acid. Difluorobenzene ($F_2Bz$) was used as it remedies both of these problems significantly. Compound **1.12** and $ZnBr_2$ were combined in a schlenk to which difluorobenzene was added and sonicated for four hours at 50 °C, during which time the yellow colour of **1.12** dissipates from solution with the formation of a white precipitate (scheme 2.10).



**1.12** **2.28**

**Scheme 2.10:** Synthesis of the carbodiphosphorane-zinc adduct ${}^{6Ph}$CDP·$ZnBr_2$ **2.28**

${}^{31}P\{{}^{1}H\}$ NMR data shows the formation of a new compound attributed to a resonance at δ 16.5 ppm, whilst the resonance of the free ligand (δ -5.5 ppm) has completely disappeared. The solid was recrystallized from warm benzene to give single crystals of ${}^{6Ph}$CDP·$ZnBr_2$ **2.28** in moderate yields (figure 2.7).

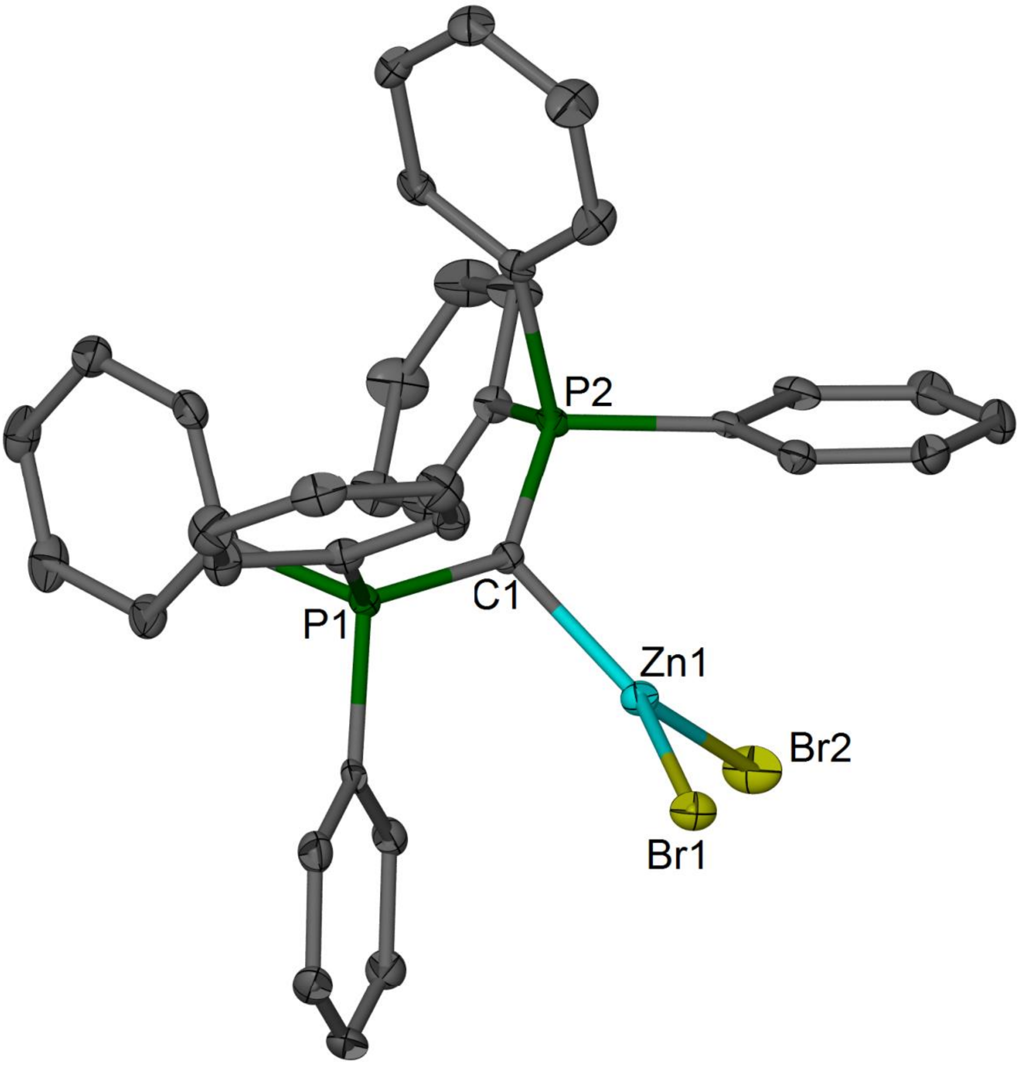


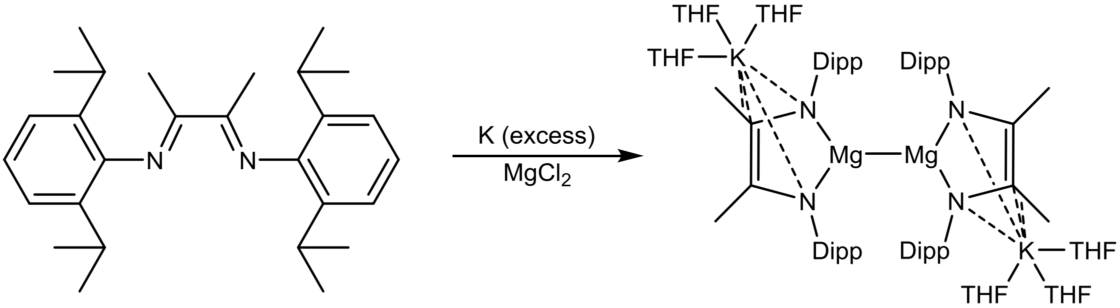
**Figure 2.7:** Molecular structure of $^{6Ph}$CDP·ZnBr$_2$ **2.28** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-Zn1 1.992(3), Zn1-Br1 2.3532(5), Zn1-Br2 2.3359(5), C1-P1 1.691(3), C1-P2 1.689(3), Br2-Zn1-Br1 113.684(19), C1-Zn1-Br$_{avg}$ 123.16, P1-C1-P2 130.48(18)

From the crystal structure (figure 2.5), it can be seen that the Zn-C bond length (1.992(3) Å) is slightly shorter than that observed in both the IPr and $^6$IPr zinc bromide adducts (**2.20** 2.039(3) Å; **2.25** 2.011(3) Å). Compound **2.28** is monomeric in the solid state, similar to that of **2.25**, presumably due to the steric nature of the six phenyl substituents, preventing dimerization. One equivalent of **2.28** was reduced with one equivalent of the magnesium(I) dimer, **1.20** which resulted in a pale yellow solution (both **1.20** and free $^{6Ph}$CDP **1.12** are both yellow). The $^{31}$P{$^{1}$H} NMR spectrum showed the re-emergence of the free ligand **1.12** with a signal at δ -5.5 ppm as well as four new resonances. Two resonances at δ 21.4 and δ 22.6 ppm are comparable to those of other neutral adducts of CDP-element halide fragments and/or ionic complexes[14] whereas the two resonances at δ -19.1 and δ -20.4 ppm are unprecedented in regards to adduct formation with this ligand. Attempts to separate/crystallize any LOS CDP-Zn compounds predominantly yielded salt products consisting of the $[Ph_3PC(H)PPh_3]^+$ fragment, or solid material that was unsuitable for single crystal diffractometry.

Finally, research using the silicon analogue of IPr, $^{Si}$IPr, **2.26** was undertaken as an alternative method of forming neutral adducts of MG elements. When using **2.26** to form adducts with MG element-halides, it was found that the ligand often acts as a reducing agent, accepting the halide groups and oxidizing the central silicon atom from $Si^{II}$ to $Si^{IV}$. This was commonly observed throughout my research and various strategies were employed to overcome this problem. One such strategy was to use NHC-coordinated element halide adducts as suitable candidates for a neutral-donor-ligand exchange reaction. In the case of zinc, $(IPr{\cdot}ZnBr_2)_2$ **2.20** was reacted with two equivalents of $^{Si}$IPr **2.26** and monitored by $^{1}$H NMR spectroscopy. Even when heated to 80 °C, both unreacted starting materials remained as the only visible products, by $^{1}$H NMR spectroscopy, demonstrating the preference for NHC coordination rather than NHSi coordination. No crystallographically suitable NHSi adducts of group 2 or 12 elements were isolated.

### 2.3.3 Diazabutadiene Complexes of Group 2 Elements

The electronic and steric properties of diazabutadienes make them excellent ligands for MG and TM fragments. Often binding in a bidentate fashion, they have been shown to be useful in stabilizing a number of elements in low oxidation states. In particular, the previously mentioned example, reported by Wu and co-workers, $[K(THF)_3]_2[LMg\text{-}MgL]\cdot 2THF$ (L = $[(2,6\text{-}^iPr_2C_6H_3)NC\text{-}(Me)]_2^{2-}$) [15] **2.30**.

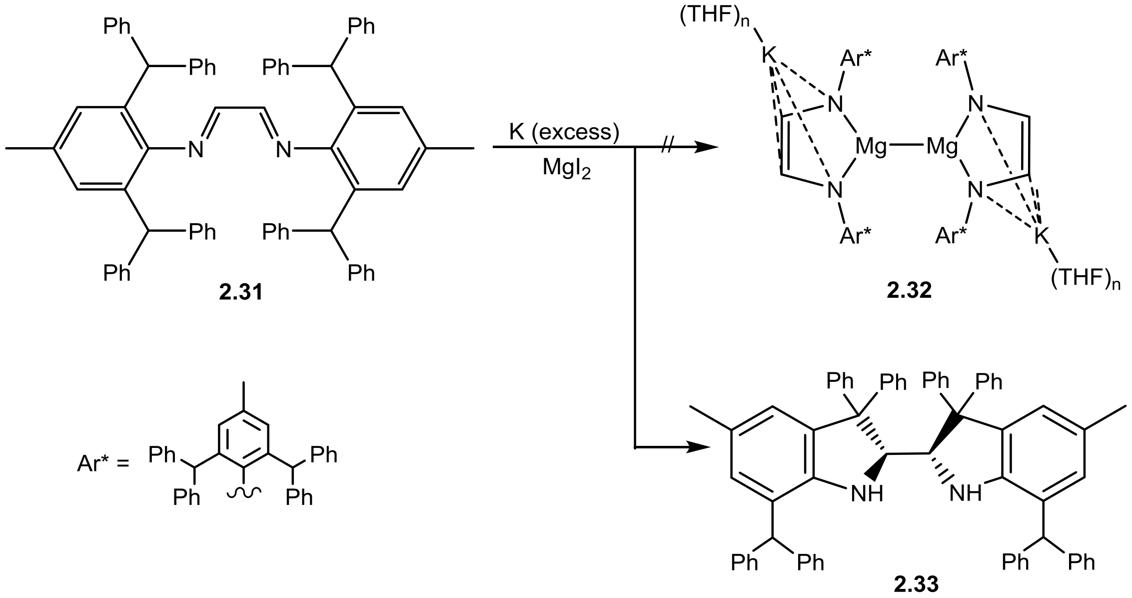


**2.29**

**2.30**

**Scheme 2.11:** Synthesis of the magnesium(I) dimer $[K(THF)_3]_2[LMg\text{-}MgL]\cdot 2THF$ **2.30**

In this example, each magnesium atom is in the formal oxidation state of +1 attributed by the counter-electrons provided by the potassium atoms coordinated to the face of each DAB ligand. The DAB ligand is doubly reduced in a mixture of $MgCl_2$ and excess potassium with the final product containing a $[Mg\text{-}Mg]^{2+}$ core. Using this methodology, a reaction was devised so that an even bulkier DAB ligand, Ar*DAB **2.31** (scheme 2.12), could be used to potentially stabilize and isolate a monomeric $Mg^I$ species. A mixture of Ar*DAB **2.31** and finely powdered $MgI_2\cdot(OEt_2)_2$ was wired onto a potassium mirror and stirred for 48 hours, during which time an intense red solution developed (it should be mentioned that the reduced ligand alone also gives rise to a red colour). The solution was filtered and concentrated in attempts to form a crystalline product of the coloured compound. However, any coloured precipitate took an amorphous form and the only crystalline compound isolated from the reaction mixture was the coupled, colourless organic compound shown in scheme 2.12 below.



**Scheme 2.12:** Attempted synthesis of the magnesium(I) dimer $[K(THF)_n]_2[Ar^*DABMg-MgAr^*DAB]$ **2.32** and the isolated product **2.33**

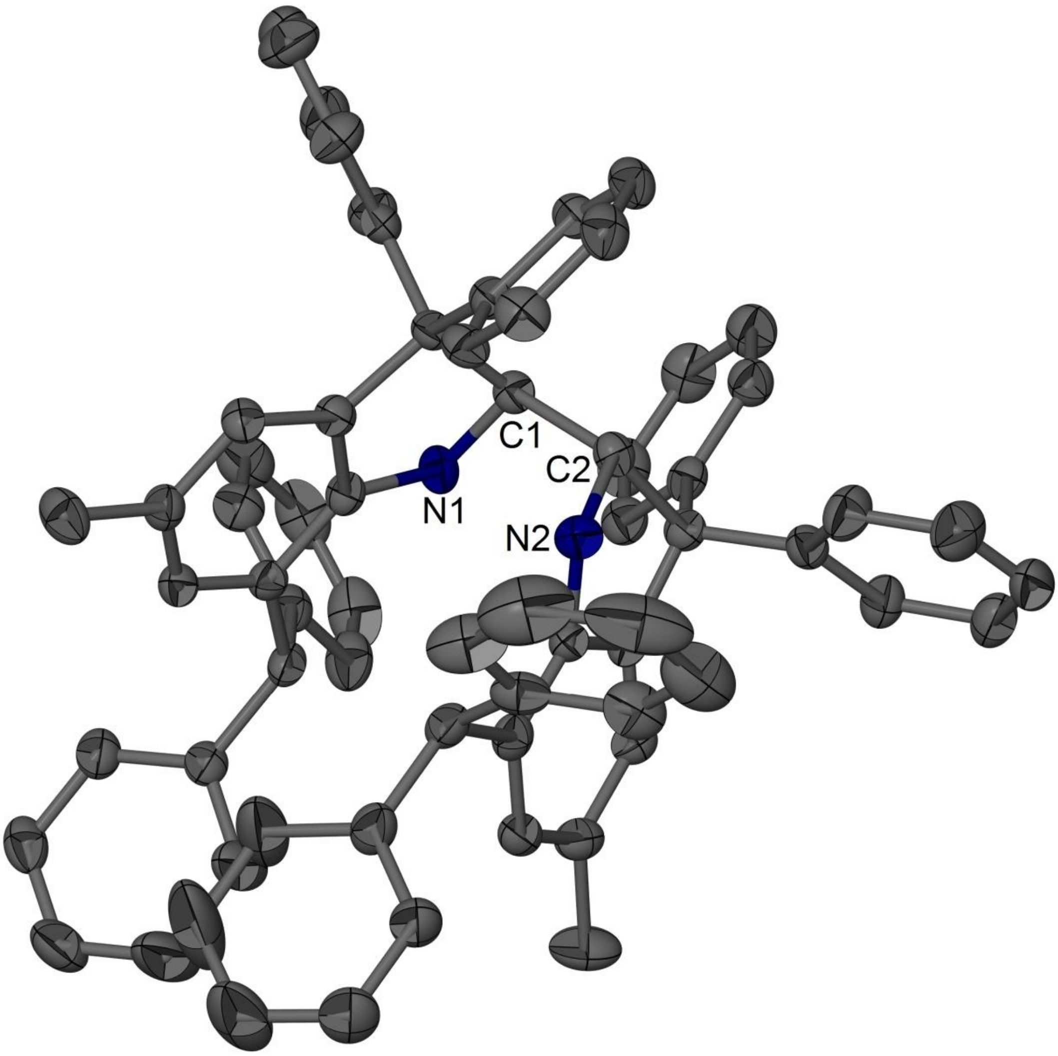


**Figure 2.8:** Molecular structure of Ar*DiByCycle **2.33** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-C2 1.543(5), C1-N1 1.457(4), C2-N2 1.459(4), N1-C1-C2 112.3(3), N2-C2-C1 112.0(3)

Compound **2.33** has a relatively long, central C-C bond (1.543(5) Å) bridging two bi-cyclic ring systems. The bi-cycles are formed via an intramolecular process in which the doubly reduced DAB backbone undergoes C-C coupling with the α-carbon atoms in the ortho positions of the flanking aryl groups. Although the intended LOS magnesium product was not obtained, the organic compound **2.33** demonstrates the reactivity of the α-carbon atoms on the flanking aryls groups, each having three adjacent phenyl rings in which to delocalize charge, if the acidic C-H bond were to be cleaved. A small “pocket” can be seen in the crystal structure (described in figure 2.8), in which a metal center has potential to coordinate within, with phenyl rings in place to provide kinetic stability and prevent oxidation/outside attack etc. However, in the solid state, the lone pair orbitals of the nitrogen atoms point in opposing directions. In solution, the central C-C bond length has the potential to rotate in order to remedy this, however, it would result in further steric congestion of overlapping aryl rings, leading to a higher energy, and therefore less stable product.

## *2.4 Experimental*

**General:** All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. THF, toluene, hexane and benzene were distilled over molten potassium metal, while diethyl ether and pentane were distilled over Na/K alloy (25:75). $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded on either BrukerDPX300, Bruker AvanceIII 400 or Varian Inova 500 spectrometers and were referenced to the residual $^{1}H$ or $^{13}C$ resonances of the deuterated solvent used. Mass spectra were recorded on an Agilent Technologies 5975D inert MSD with a solid‑state probe or obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Perkin Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates or recorded as solid samples using an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. Reproducible microanalyses could not be obtained for all compounds due to their oxygen and/or moisture sensitivity. Microanalyses were carried out by the Science Centre, London Metropolitan University.

**Preparation of ($IPr\cdot ZnBr_2$)$_2$ (2.20):** Toluene (50 ml) was added to a mixture of IPr (0.489 g, 1.26 mmol) and crystalline $ZnBr_2$ (0.285 g, 1.27 mmol) and the resultant suspension was stirred overnight at 20 °C, during which time **2.20** deposited as a colourless crystalline solid. The solid was isolated by filtration and the mother liquor concentrated in vacuo to ca. 10 ml. After placing at -30 °C overnight an additional crop of **2.20** was obtained. Yield: 0.480 g (62 %). M.p.: 311 – 316 °C. $^1$H NMR (400 MHz, 298 K, $C_6D_6$): δ 0.96 (d, 12H, CH(C*H*$_3$)$_2$), 1.55 (d, 12H, CH(C*H*$_3$)$_2$), 2.87 (sept, 4H, C*H*(CH$_3$)$_2$), 6.44 (s, 2H, C*H*), 7.11 (m, 4H, Ar-C*H*), 7.20 (m, 2H, Ar-C*H*) ppm; $^{13}$C{$^1$H} NMR (75 MHz, 298 K, $C_6D_6$): δ 26.4 (*C*H$_3$), 26.9 (*C*H$_3$), 29.0 (*C*(CH$_3$)$_2$), 121.3 (*imC*H), 126.6 (*m*-Ar-*C*), 126.8 (*p*-Ar-*C*), 141.2 (*ipso*-Ar-*C*), 148.7 (*o*-Ar-*C*) ppm; MS/ESI *m/z* (%): 533.1 (M$^{++}$Ligand-H), correct isotope pattern, 100); IR υ/cm$^{-1}$ (Nujol): 1651w, 1589w, 1574w, 1409m, 1342m, 1250m, 1097s, 1069m, 1018m, 799s, 754m.

**Preparation of ($IPr\cdot CdI_2$)$_2$ (2.21):** Toluene (30 ml) was added to a mixture of IPr (0.295 g, 0.76 mmol) and finely powdered $CdI_2$ (0.279 g, 0.76 mmol) and the resultant suspension was stirred overnight at 20 °C, during which time **2.21** deposited as a colourless crystalline solid. The solid was isolated by filtration and the mother liquor concentrated in vacuo to ca. 20 ml. After placing at -30 °C overnight an additional crop of **2.21** was obtained. Yield: 0.230 g (40 %). M.p.: 240 – 247 °C. (400 MHz, 298 K, $C_6D_6$): δ 0.92 (d, 12H, CH(C*H*$_3$)$_2$), 1.60 (d, 12H, CH(C*H*$_3$)$_2$), 2.78 (sept, 4H, CH(C*H*$_3$)$_2$), 6.43 (s, 2H, C*H*), 7.07 (m, 4H, Ar-C*H*), 7.20 (m, 2H, Ar-C*H*) ppm; $^{13}$C{$^1$H} NMR (121.5 MHz, 298K, $C_6D_6$): δ 16.5 ($_3$), 28.9 (*C*H$_3$), 29.8 (*C*(CH$_3$)$_2$), 124.9 (*imC*H), 127.6 (*m*-Ar-*C*), 128.8 (*p*-Ar-*C*), 143.3 (*ipso*-Ar-*C*), 147.7 (*o*-Ar-*C*) ppm; MS/ESI m/z (%): 629.1 (M$^{++}$Ligand), correct isotope pattern, 100); IR (Nujol): 1621w, 1589w, 1569w, 1405m, 1374m, 1254m, 1102s, 1059m, 1017m, 802s, 759m.

**Preparation of $^{6}$IPr·ZnBr$_2$ (2.25):** Toluene (20 ml) was added to a mixture of $^{6}$IPr (0.152 g, 0.38 mmol) and crystalline $ZnBr_2$ (0.085 g, 0.38 mmol) and the resultant suspension was stirred overnight at 20 °C. The resultant mixture was filtered and concentrated in vacuo to ca. 10 ml. After placing at -30 °C overnight, deposition of **2.25** was obtained as a colourless solid. Yield: 0.112 g (59%). M.p. : 244 – 247 °C. $^{1}$H NMR (400 MHz, 298 K, $C_6D_6$): δ 1.03 (d, 12H, CH(C*H*$_3$)$_2$), 1.27 (d, 12H, CH(C*H*$_3$)$_2$), 2.72 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 3.19 (sept, 4H, C*H*(CH$_3$)$_2$), 4.50 (t, (br.), 4H, NC*H*$_2$CH$_2$), 6.90 (d, 4H, *m*-Ar-*H*), 7.09 (t, 2H, *p*-Ar-*H*) ppm.

**Preparation of $^{6Ph}$CDP·ZnBr$_2$ (2.28):** Difluorobenzene (10 ml) was added to a mixture of $^{6Ph}$CDP (0.598 g, 0.932 mmol) and crystalline $ZnBr_2$ (0.209 g, 0.932 mmol) and the resultant suspension was sonicated for 30 minutes, then stirred overnight at 20 °C. The resultant colourless mixture was concentrated in vacuo to remove all volatiles. Residuals were redissolved in chloroform (5 mL) and stored at -30 °C overnight, from which, deposition of **2.28** was obtained as a colourless crystalline solid. Yield: 0.534 g (71%). M.p. : 180 – 184 °C. $^{1}$H NMR (400 MHz, 298 K, $C_6D_6$): δ 6.95 (m (br.), 15H, Ar-*H*), 7.81 (m (br.), 15H, Ar-*H*), $^{31}$P{$^{1}$H} (121.5 MHz, 298K, $C_6D_6$): δ 16.5 (C*P*Ph$_3$) ppm.

**Preparation of Ar*DiByCycle (2.33)** Toluene (45 ml) and tetrahydrofuran (5 ml) were added to a mixture of Ar*DAB (1.019 g, 1.15 mmol) and finely powdered $MgI_2{\cdot}(OEt_2)_2$ (0.490 g, 1.15 mmol) and the resultant suspension was stirred at room temperature for one hour. The mixture was then transferred *via* cannula wire onto a K mirror and stirred for 48 hours and filtered. The solvent was removed *in vacuo* and the remaining solid was extracted into hexane:diethyl ether (10 ml : 5 ml). After placing at -30 ºC overnight, colourless crystals of **2.33** were obtained. Yield: 0.164 g (16%). M.p.: 238 - 240 ºC; $^{1}$H NMR (300 MHz, 298 K, $C_6D_6$): *δ* 2.16 (s, 6H, Ar-CC*H*$_3$), 2.77 (s, 2H, C$_2$N*H*), 4.16 (s, 1H, C*H*(NH)(CPh$_2$)), 4.17 (s, 1H, C*H*(NH)(CPh$_2$)), 4.77 (s, 2H, C*H*(Ph$_3$)), 6.38 (s, 2H, *m*-Ar-C*H*), 6.72 (s, 2H, *m*-Ar-C*H*), 6.84-6.88 (m, 8H, Ar-C*H*), 6.84-6.88 (m, 8H, Ar-C*H*), 7.05-7.28 (m, 32H, Ar-C*H*) ppm; $^{13}$C{$^1$H} NMR (75 MHz, 298 K, C$_6$D$_6$): *δ* 21.7 (Ar-CCH$_3$), 52.5 (*C*H(Ph$_3$)), 62.3 (*C*(C)Ph$_3$)), 67.8 (*C*H(N)(C)), 123.8 (*p*-Ar-*C*), 125.0 (*o*-Ar-*C*), 126.4 ((backbone) *o*-Ar-*C*), 126.6 (*m*-Ar-*C*), 126.8 ((backbone) *m*-Ar-*C*), 127.3 (*p*-Ph-*C*), 127.5 ((backbone) *p*-Ph-*C*), 127.9 (*o*-Ph-*C*), 128.1 ((backbone) *o*-Ph-*C*), 129.0 ((backbone) *m*-Ph-*C*), 133.1 ((backbone) *m*-Ph-*C*), 143.1 (*ipso*-Ar-*C*), 146.9 (*ipso*-Ph-*C*), 147.1 ((backbone) *ipso*-Ph-*C*) ppm; MS/ESI *m/z* (%): 901.1 (M$^+$, correct isotope pattern, 100); acc. mass (ESI): found 901.4519; C$_{68}$H$_{56}$N$_2$ requires 901.4522; IR (Nujol): (cm$^{-1}$): 3420w, 1600w, 1446s, 1366s, 1261w, 1230m, 1077w, 1031w, 756m

## *2.5 References*

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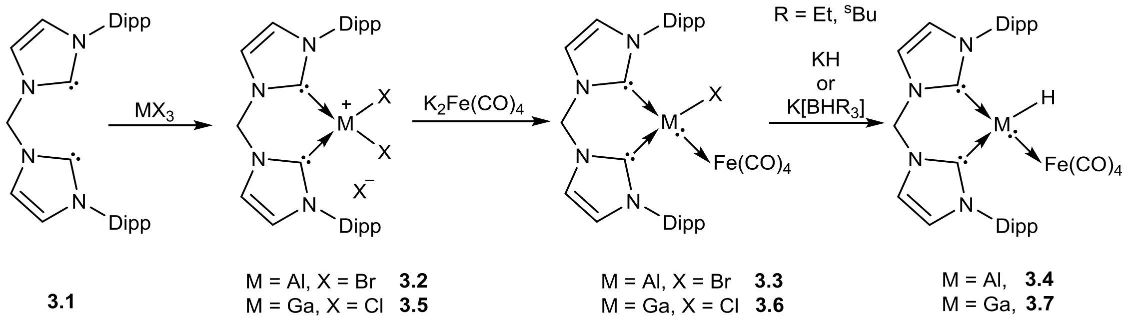
# 3 Low Oxidation State Group 13 Complexes

## 3.1 A Further Introduction to NHC and NHC-Analogues of Group 13 Complexes

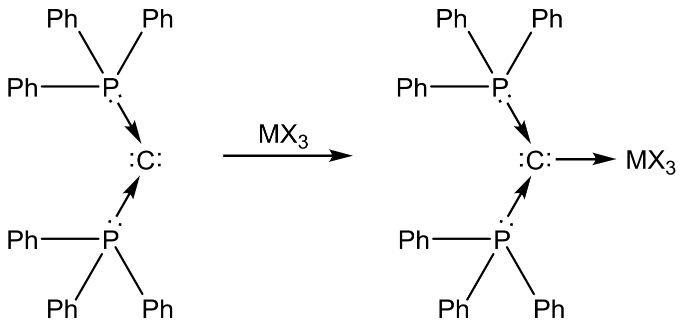
The chemistry of LOS group 13 metal hydrides is relatively underdeveloped when compared to that of their group 14 neighbours.[1] Using a bisNHC, bis(N-Dipp-imidazole-2-ylidene)methylene **3.1**, Driess and co-workers were able to synthesize aluminium(I) and gallium(I) hydrides **3.4** and **3.7** shown in scheme 3.1 below.[2]



**Scheme 3.1:** Synthesis of NHC coordinated aluminium(I) and gallium(I) hydrides **3.4** and **3.7**

The aluminium(I) and gallium(I) centers in **3.4** and **3.7** are stabilized by acting as both Lewis acids with respect to the ligand, **3.1**, as well as a Lewis bases towards the $Fe(CO)_4$. Unfortunately, the aluminium(I) hydride only exists as a transient before reacting with the solvent (THF or THP), eliminating hydrogen gas. Worthy of note, when $K[BHR_3]$ (R = Et, $^{s}Bu$) was used as the hydride source instead of KH, the THF-ring opened product (**3.1**)$Al(O^{n}Bu)[Fe(CO)_4]$ **3.8**, was observed in modest yields. These types of ring-opening mechanisms are of significance since they have been observed for transition metal-hydrido complexes[3] and FLPs.[4]

The CDP ligand $C(PPh_3)_2$ ($^{6Ph}$CDP) **1.12** has also been used as a neutral donor ligand for aluminium halide and indium alkyl complexes **3.9** and **3.10** shown in scheme 3.2 below.[5]



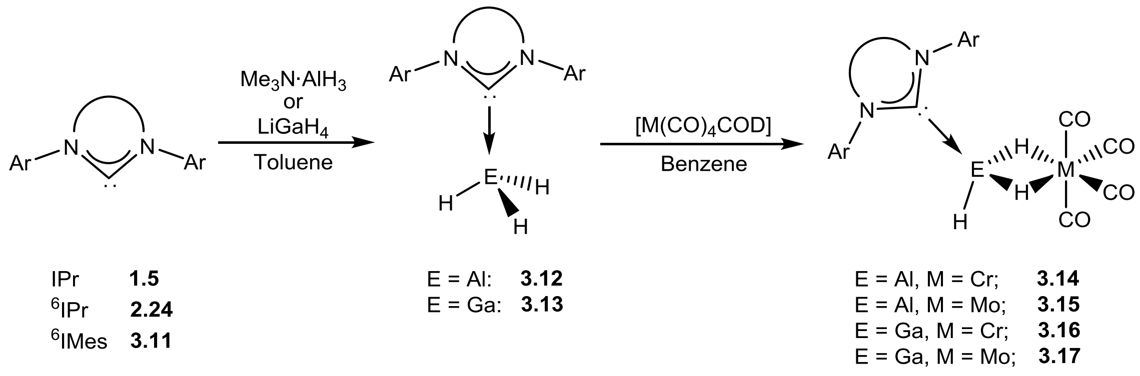
**1.12**

M = Al, X = Br **3.9**
M = In, X = Me **3.10**

**Scheme 3.2:** Synthesis of CDP coordinated aluminium and indium complexes **3.9** and **3.10** respectively

These adducts are ideal precursors for further investigation into the reductive capabilities of magnesium(I) dimers, specifically, **3.9**, as the bromide substituents are excellent leaving groups and form highly stable magnesium(II) compounds. Although the formation of adducts **3.9** and **3.10** is relatively simple, the central carbon atom is still susceptible to further reactivity with solvents, often yielding the protonated cation $[HC(PPh_3)_2]^+$ and corresponding anions eg $[MX_n]^-$. To this day, this continues to be a challenge when investigating the potential chemistry of these types of compounds.

Extending on the work done by Aldridge and co-workers mentioned in chapter one, the reactivity of aluminium(III) and gallium(III) hydrides towards 14- and 16-electron transition-metal fragments was also investigated (scheme 3.3).[6]



**Scheme 3.3:** Synthesis of NHC-coordinated aluminium(III) and gallium(III) hydrides **3.12** and **3.13**, and their coordination to TM carbonyls via M-H σ-bond formation

These results demonstrate the electronic effects NHCs have on metal hydride fragments as the adducts NHC·$EH_3$ (NHC = $^6$IPr, $^6$IMes; E = Al **3.12**; Ga **3.13**) coordinate via $\kappa^2$ binding, an unprecedented feature in the case of gallium. This type of binding was not observed when the NHC ligand was replaced with the N-donor ligand, $[(N(Dipp)C(CH_3))_2CH]^-$ “$^{Dipp}$nacnac.” Although $\kappa^2$ binding is still observed for both aluminium and gallium hydrides, $\kappa^1$ binding is preferred for the nacnac complexes, especially in the case of gallium, attributed to the relatively weak Ga-H bond strength and relative increased preference for gallium to exist in the +1 oxidation state (when compared to aluminium).

## *3.2 Research Outline*

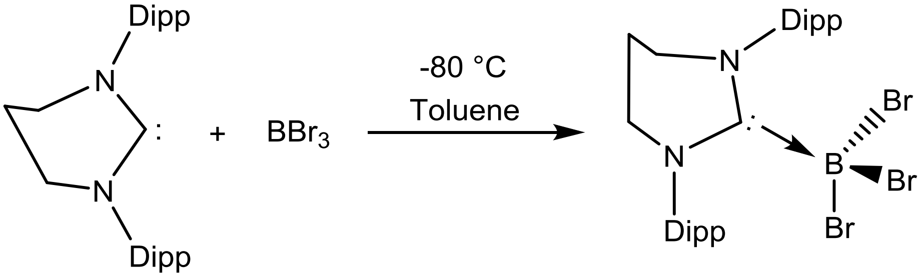
NHC adducts of MG and TM elements have had a significant impact in recent literature largely due to their unusual chemical structures and unique chemical properties.

Extending on from this trend, NHC adducts of group 13 element halides, were synthesized and subsequently reduced in attempts to form corresponding LOS compounds. NHCs included 5-membered unsaturated and 6-membered saturated analogues. In addition to NHCs, carbodiphosphoranes (CDP) ligands were used in attempts to form LOS complexes with group 13 elements.

## *3.3 Results and Discussion*

### *3.3.1 Synthesis of NHC Adducts of Group 13 Elements*

Toluene solutions of $^6$IPr and $BBr_3$ were cooled to -80 °C and combined via cannula. Immediately upon addition, a yellow solution was formed which slowly precipitated a colourless solid as it is warmed to room temperature. Upon workup, the solid was redissolved at 60 °C and left to slow cool to produce colourless crystals of $^6$IPr·$BBr_3$ **3.18** in high yield.



**2.24**

**3.18**

**Scheme 3.4:** Synthesis of the NHC coordinated boron(III) adduct $^6$IPr·$BBr_3$, **3.18**

The $^1$H NMR spectrum shows a large separation between the two $CH_3$ isopropyl resonances (0.47 ppm) which is to be expected as half the methyl groups are directed towards the $BBr_3$ fragment and the other half are directed towards the back of the NHC ring, in the solid state. No $C_{NCN}$ resonance was observed in the $^{13}C$ NMR spectrum, presumably due to the quadrupolar nature of boron. The $^{11}B\{^1H\}$ NMR spectrum shows a sharp, single resonance at δ 14.4 ppm, downfield to that of the 5-memebered NHC analogue, IPr·$BBr_3$ **1.48** (δ -16.46 ppm),[7] however, still within the range of four-coordinate, neutral boron adducts. Finally, no B-H signals were observed in the IR spectrum, indicating the absence of hydride abstraction or similar processes throughout the experiment. Single crystals of **3.18** were obtained from toluene and analysed using X-Ray diffractometry.

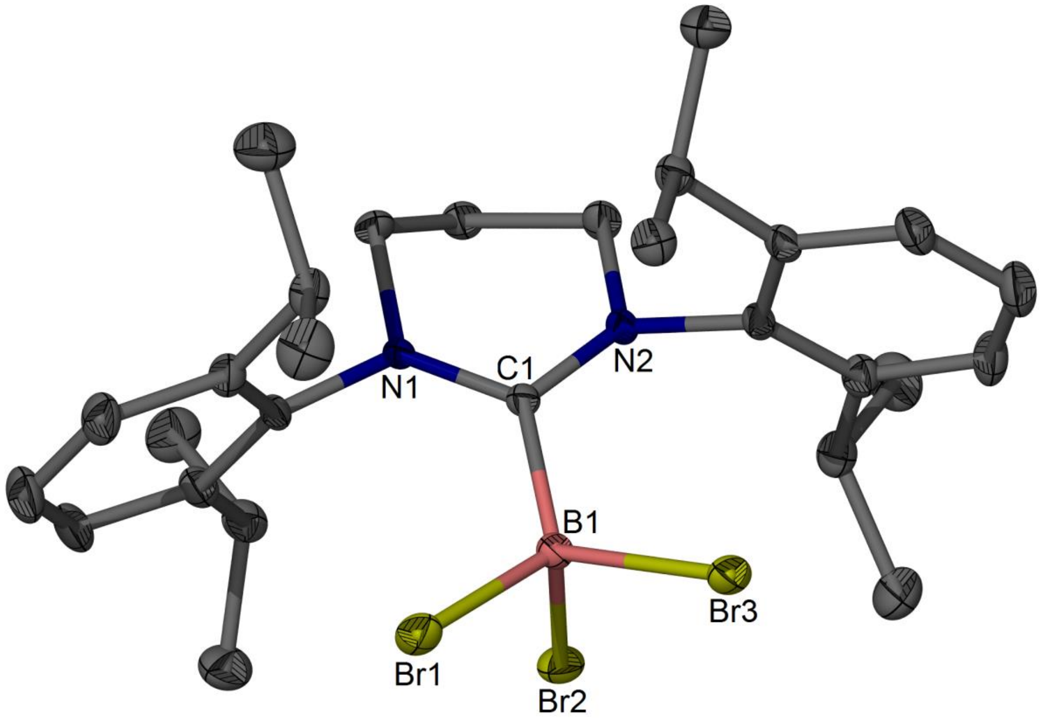


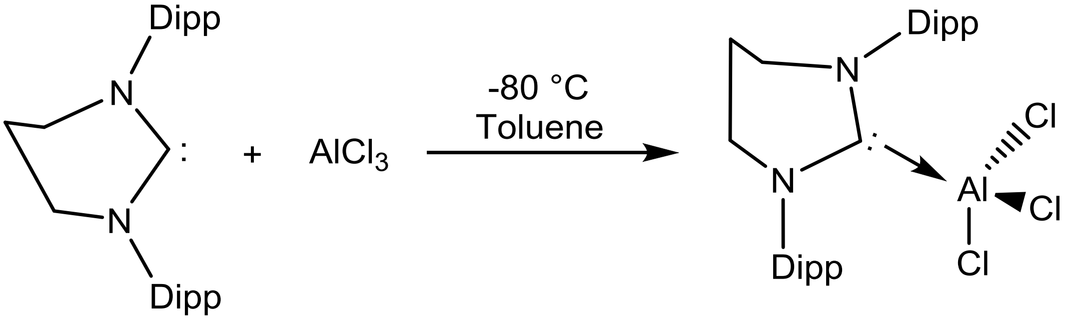
**Figure 3.1**: Molecular structure of $^6$IPr·$BBr_3$ **3.18** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-B1 1.663(4), B1-$Br_{avg}$ 2.0283, N1-C1-N2 116.4(2), C1-B1-Br1 116.59(18), C1-B1-Br2 103.23(17), C1-B1-Br3 117.57(18)

As with most other $^6$IPr adduct compounds, the NHC central ring adopts a “puckered” geometry. The boron center takes on a distorted tetrahedral geometry with inequivalent

C1-B1-Br angles. The C1-B1-Br1 and C1-B1-Br3 angles (116.59 and 117.57 ° respectively) are similar, however the C1-B1-Br2 unit (103.23 °) is *ca.* 14° narrower than the others. This may be due to the C1-B1-Br2 angle being almost orthogonal to the NHC ring, minimizing steric interactions, whereas the other bromine ligands are angled towards the aromatic ring substituents, providing sufficient kinetic stability for the boron center. It should also be mentioned that the B1-C1 bond in **3.18** (1.663(4) Å) agrees well with those of similar systems mentioned in chapter 1 (IPr·$BBr_3$ **1.48** (1.623(7))[7] and $^{6Ph}$CDP·$BH_3$ (1.603(3)) **1.53**.[8]

The first attempt to reduce **3.18** was through the use of the magnesium(I) dimer {($^{Mes}$nacnac)Mg}$_2$, ($^{Mes}$nacnac = {[(Mes)NC(Me)]$_2$CH}$^-$, Mes = mesityl) **1.20**. The reaction was initially performed in deuterated benzene in an NMR tube and gives a green solution immediately upon addition of **1.20**. After 10 minutes the $^1$H NMR spectrum shows the major product to be unreacted **3.18**. Left at room temperature for two hours, the green colour dissipates to colourless, however the $^1$H NMR spectrum remains unchanged with unreacted starting materials the only observable products. After heating at 80 °C for 72 hours, a pale orange solution formed, with the formation of a colourless precipitate. The $^1$H NMR spectrum of the mixture shows resonances representative of starting material as well as free $^6$IPr, amongst a myriad of other minor products. Heating to higher temperatures or longer reaction times produced resonances indicative of multiple products which proved to be intractable. A similar result was obtained when the reaction was repeated at low temperature, or with the use of $KC_8$ instead of **1.20**.

In a similar fashion to the formation of $^6$IPr·$BBr_3$ **3.18**, toluene solutions of $^6$IPr and $AlCl_3$ were cooled to -80 °C and combined via cannula. After a few minutes of stirring a white precipitate was observed which continued to form when stirred at room temperature.



**2.24** **3.19**

**Scheme 3.5:** Synthesis of the NHC coordinated aluminium(III) adduct $^6$IPr·AlCl$_3$, **3.19**

Hexane was added to triturate the solution and the white precipitate was analyzed via $^1$H NMR spectroscopy which showed the solid to be a composition of two compounds in a 4 : 1 ratio with no free $^6$IPr remaining. The resonances of the major product indicate it is the desired $^6$IPr·AlCl$_3$ adduct **3.19** with the minor product suggested to be an imidazolium-like salt product. Separating both products proved difficult even through the use of fractional crystallization, with which, a maximum purity of 80% was obtained.

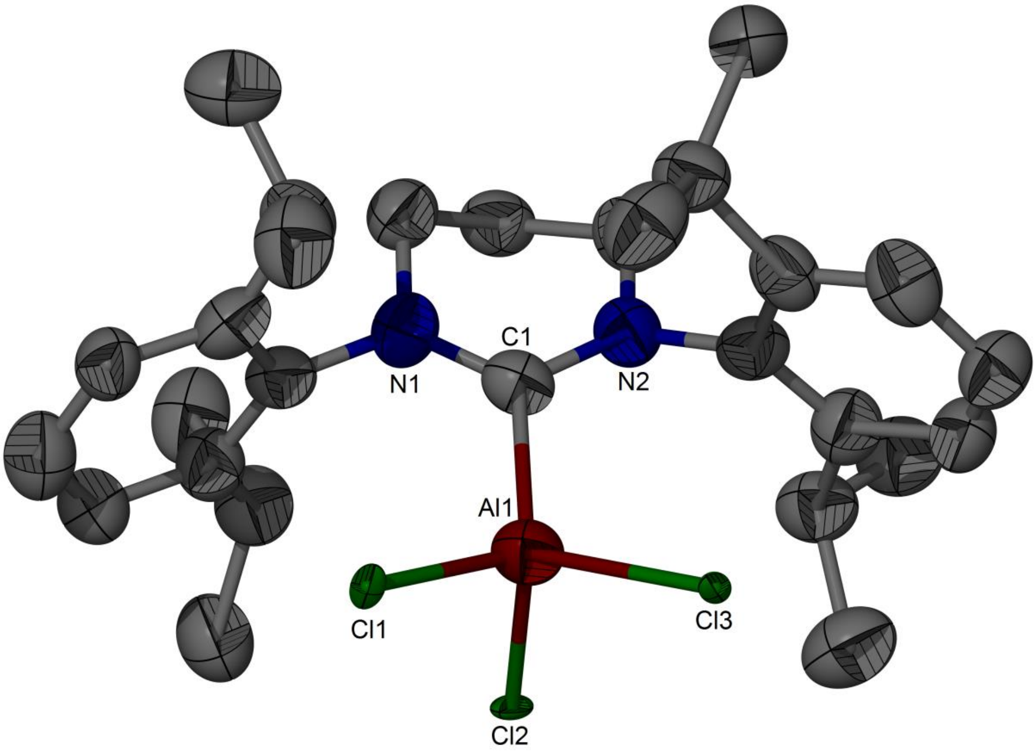
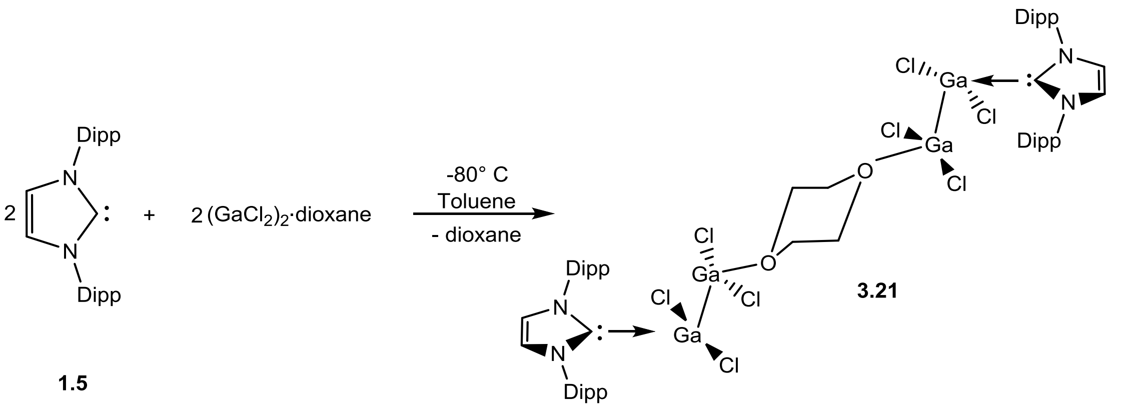


**Figure 3.2**: Molecular structure of $^{6}$IPr·AlCl$_3$ **3.19** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-Al1 2.081(9), Al-Cl$_{avg}$ 2.295, N1-C1-N2 118.1(8), C1-Al1-Cl1 117.3(3), C1-Al1-Cl2 116.8(3), C1-Al1-Cl3 101.7(2)

The crystal structure of **3.19** is isostructural to that of **3.18**, in that it also has one C1-Al1-Cl angle considerably smaller (by 15°) than the other two. The aluminium center adopts a distorted tetrahedral geometry with a slightly longer C1-Al1 bond length (2.081(9) Å) than the 5-membered NHC analogue, IPr·AlCl$_3$, **3.20** (2.017(4) Å), as well as the 5-membered NHC aluminium-hydride analogues **1.56** (2.034(3)[9] and **1.57** 2.0556(13).[10]

Reduction of the impure mixture (optimized to 80% purity **3.19** : 20% salt) was undertaken using the magnesium(I) dimer **1.20** or KC$_8$. The initial reduction was performed in an NMR tube at room temperature using one equivalent of **1.20** per **3.19** (one magnesium per three chloride ligands). However, this proved to be unreactive with large amounts of starting materials remaining in solution, as observed through $^1$H NMR spectroscopy. More **1.20** (one magnesium per chloride) was added to the reaction mixture which resulted in lowering the amount of starting materials present, as well as the formation of two new products and free $^6$IPr. Again, separating/crystallizing any LOS aluminium products proved unsuccessful due to the multiple product formation and the oxidized nacnac magnesium(II) dimer, $\{^{Mes}$nacnacMg(μ-Cl)$\}_2$ **1.27**, preferentially crystalizing out of solution over other products. The reduction of **3.19** with $KC_8$ proved to be a more efficient process, with only one major product (other than starting material) observed in the $^1$H NMR spectrum. However, when additional $KC_8$ was added to the reaction mixture, results similar to that from the magnesium(I) reduction were observed with the generation of free $^6$IPr in high yields and elemental aluminium precipitating from solution. There is one resonance pattern common to both $KC_8$ and magnesium(I) reduction mixtures, suggesting the formation of a LOS NHC-aluminium adduct. However, isolating and crystallizing this product proved unsuccessful.

At -80 °C, a toluene solution of IPr was added to a slurry of $(GaCl_2)_2$·dioxane and left to stir to room temperature overnight. The solution was filtered and concentrated to just past saturation, followed by the addition of pentane, then left at -30 °C overnight.



**Scheme 3.6:** Synthesis of the dioxane bridged IPr·GaCl$_2$GaCl$_2$-μ-dioxane-Cl$_2$GaCl$_2$Ga·IPr product **3.21**

The dioxane bridged product **3.21** was isolated as a colourless crystalline solid from a toluene/pentane mixture and analysed using single crystal diffractometry.

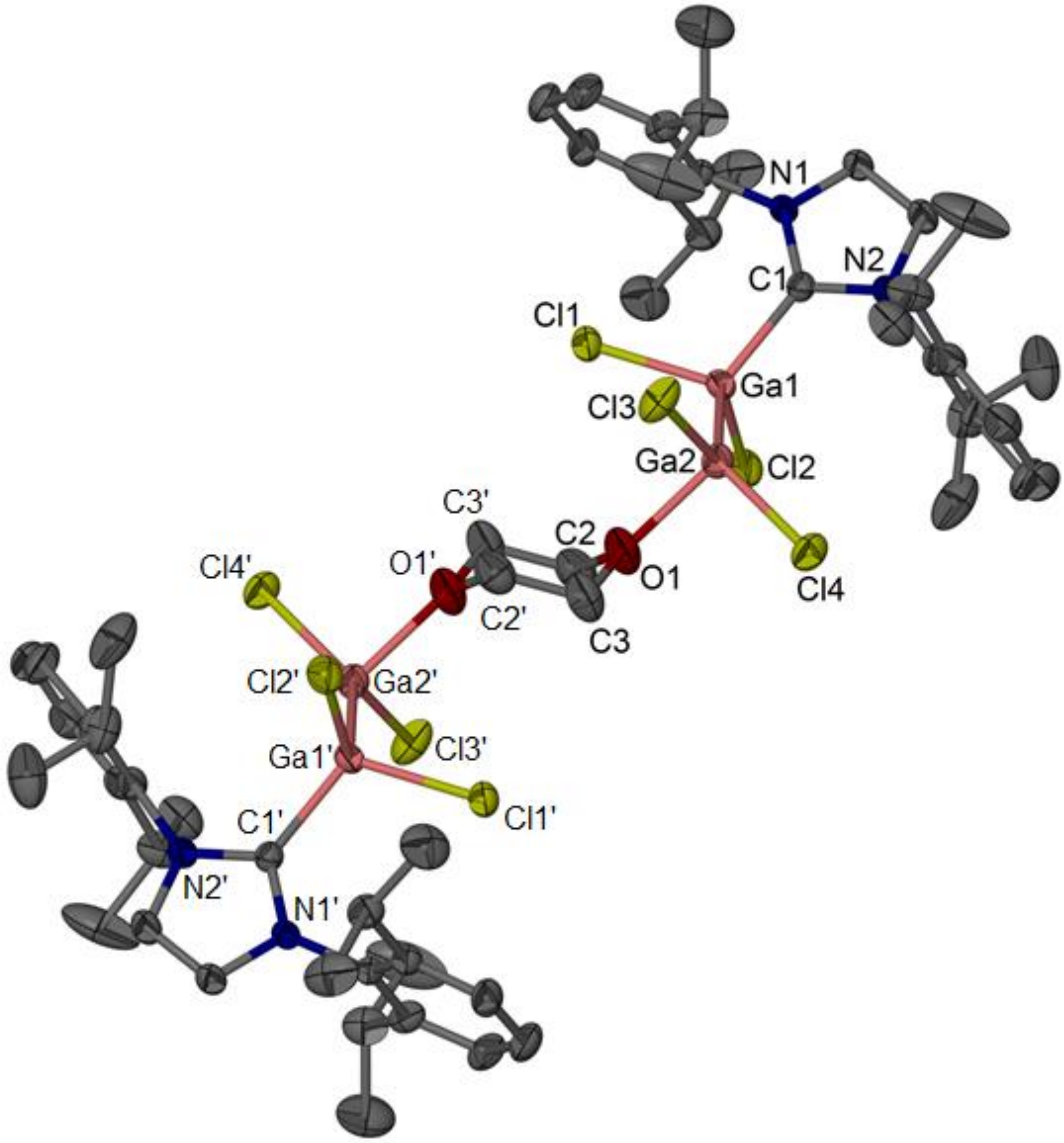
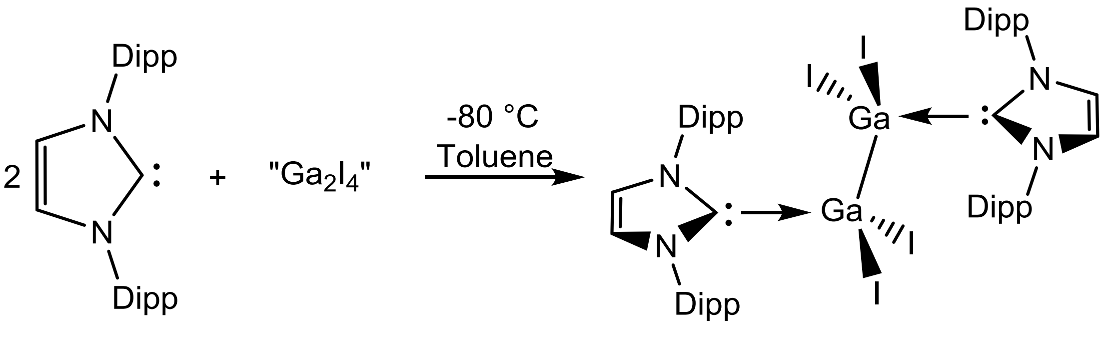


**Figure 3.4:** Molecular structure of **3.21** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-Ga1 1.992(3), Ga1-Ga2 2.4287(9), Ga1-$Cl_{avg}$ 2.2154, Ga2-$Cl_{avg}$ 2.1963, Ga2-O1 2.077(5), C1-Ga1-Ga2 123.25(13), Ga1-Ga2-O1 103.25(13)

The dioxane bridged dimer, **3.21** crystallized in the monoclinic space group P2(1)/c with a unit cell comprised of half a molecule. The Ga-Ga bond length (Ga1-Ga2 2.4287(9) Å) is marginally lengthened from the one observed in the IPr-free, diox·$Ga_2Cl_4$·diox (2.406(1) Å)[11] most likely due to the steric bulk provided by the NHC. The Ga-O distance has also lengthened from 2.027 Å to 2.077(5) Å, possibly due to the Cl ligands being further aligned towards the dioxane ring. The Newman projection of the IPr ligands show an almost eclipsed conformation with each other. This is also observed for the $Ga_2Cl_4$ units, however, the overall conformation of the molecule is twisted. Furthermore, the C-O bond lengths in the dioxane ring remain relatively unchanged, suggesting the Ga-O interactions to be high in donor-accepter character as opposed to ionic character.

Reductions of **3.21** proved difficult as it was speculated the dioxane ring sterically curtailed the reductive process, as well as difficulties in isolating **3.21** in a high purity. Finally, addition of excess IPr to **3.21** in order to displace the dioxane ring with a stronger donor proved unsuccessful with only starting material remaining even at elevated temperatures.

Continuing with gallium(II) chemistry, A toluene mixture of "$Ga_2I_4$" was prepared using a 1:2 mol ratio of Ga:I in an ultrasonic bath. In the 1950s, it was established that uncoordinated gallium(II) halides have the stoichiometry $[Ga]^+[GaX_4]^-$.[12] This can be assumed for the gallium(II) mixture prepared in the sonic bath. In a similar methodology to that of the IMes analogue, $(IMes\cdot GaCl_2)_2$ **3.22**,[13] a -80 °C solution of IPr was added to the gallium(II) mixture at -80 °C, at which point a yellow coloured solution begins to form.



**Scheme 3.7:** Synthesis of the NHC capped dimer $(IPr{\cdot}GaI_2)_2$ **3.23**

Upon warming to room temperature the solution transitions to orange, then red, then brown with the formation of a dark precipitate. After 24 hours, workup revealed the dark solid to be comprised of gallium metal and $IPr{\cdot}GaI_3$ **3.24** (via $^1H$ NMR spectroscopy). A $^1H$ NMR spectrum of the remaining red/brown solution showed a 70 : 20 : 10 ratio of $(IPr{\cdot}GaI_2)_2$ **3.23** : $IPr{\cdot}GaI_3$ **3.24** : IPr **1.5**. Fractional crystallization resulted in colourless crystals of the desired $(IPr{\cdot}GaI_2)_2$ **3.23** being isolated in moderate yield.

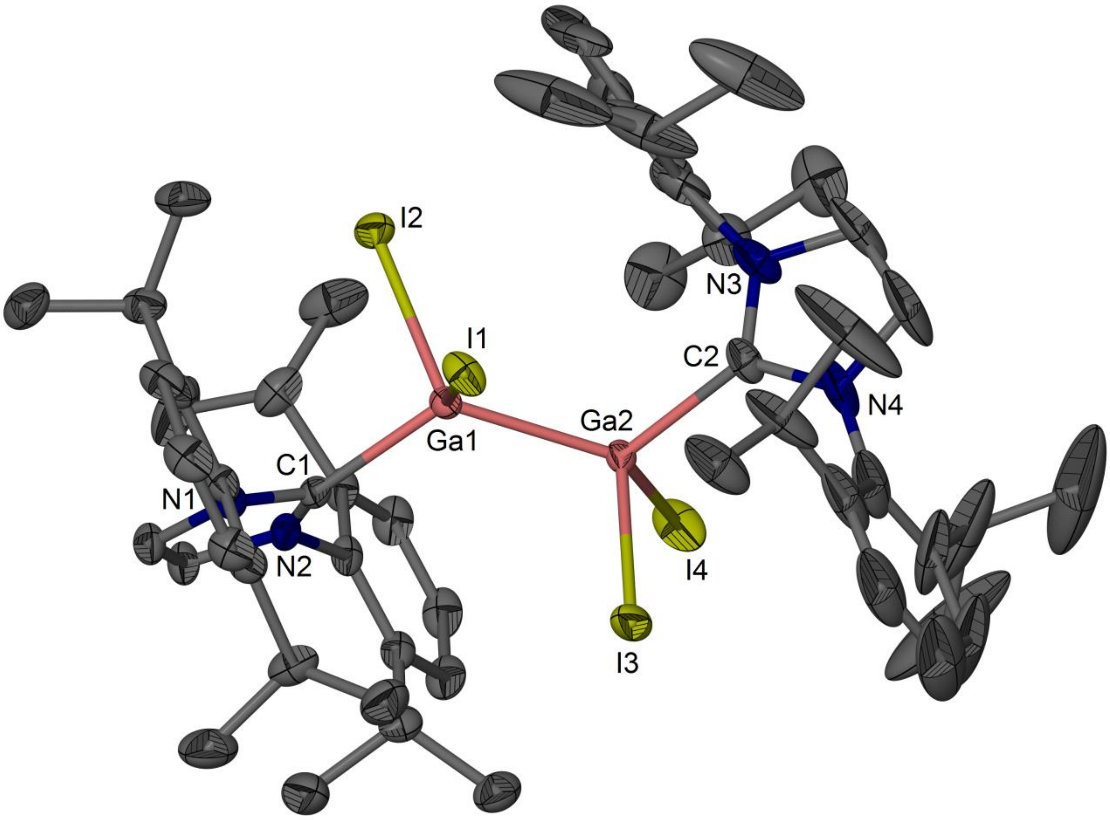


**Figure 3.5**: Molecular structure of (IPr·GaI$_2$)$_2$ **3.23** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-Ga1 2.082(4), Ga1-Ga2 2.4279(7) , Ga-I$_{avg}$ 2.5999, C1-Ga1-Ga2 124.96(10)

The most noticeable difference between the $^1$H NMR spectra of (IPr·GaI$_2$)$_2$ **3.23** and IPr·GaI$_3$ **3.24**, is the resonance belonging to the C-*H* isopropyl septet. This signal is significantly downfield (δ 3.15 ppm) in the gallium(II) example **3.23**, as opposed to the gallium(III) compound **3.24** (δ 2.76 ppm). This may be due to their close proximity with surrounding iodide ligands (shortest H$_{isopropyl}$-I 3.016 Å). No C$_{NCN}$ resonance was observed in the $^{13}$C NMR spectrum.

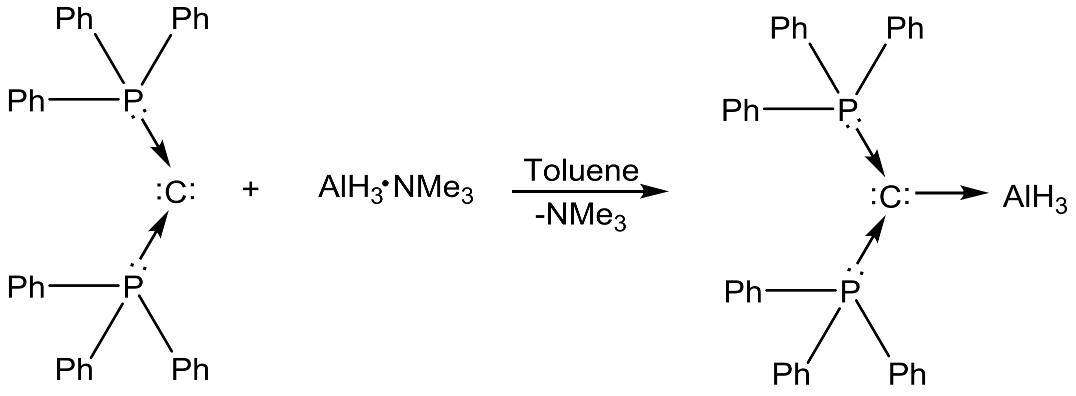
The Ga-Ga bond length of **3.23** (Ga1-Ga2 2.4279(7) Å) is almost identical to that of **3.21** (Ga1-Ga2 2.4287(9) Å) despite the use of a larger halide ligand in **3.23** and a bridging dioxane unit in **3.21**. However, the C-Ga bond length has notably increased from **3.21** (1.992(3) Å) to **3.23** (2.082(4) Å), presumably caused by the steric repulsion between the IPr and iodide ligands. Another contrast between **3.21** and **3.23** is their Newman projections; **3.21** has an almost perfectly eclipsed conformation whereas **3.23** has an almost perfectly staggered conformation.

Pure **3.23** was treated with excess iodine as a proof of principle to oxidize the gallium(II) iodide **3.23** to the gallium(III) iodide **3.24**. Upon addition of iodine, a thick red sludge develops and a colourless precipitate is formed. The $^1$H NMR spectrum indicates all gallium(II) iodide **3.23** has been converted to the gallium(III) iodide **3.24**, as well as another minor bi-product.

One of the key aspects in the successful formation of the boron(0) dimer $(\mathrm{IPr{\cdot}B})_2$ **1.52**[14] is believed to be the pre-formed B-B bond in the precursor $(\mathrm{IPr{\cdot}BBr_2})_2$ **1.51**, before reduction takes place. This idea was utilized when attempting to form the analogous $(\mathrm{IPr{\cdot}Ga})_2$ **3.25**. The first attempt at reducing **3.23** involved the magnesium(I) dimer **1.20**. Initial results indicate the major product to be IPr **1.5** (by $^1$H NMR spectroscopy) as well as gallium metal, even at low temperatures. After fractional crystallization, IPr **1.5** was removed and the minor products remain as a brown/red sludge. After various attempts to crystallize these coloured compounds, only amorphous compounds were obtained. Similar results were obtained when using KNp or $KC_8$, with free IPr **1.5** and elemental gallium the only two isolable products.

### 3.3.2 Alternative Neutral Ligands: Carbodiphosphorane and Nitrogen Heterocyclic Silylene Adducts of Group 13 Elements

Toluene solutions of $^{6Ph}$CDP **1.12** and $AlH_3{\cdot}NMe_3$ were combined and stirred at room temperature resulting in a red solution. The reaction was left stirring for two hours over which time the solution gradually became orange, then colourless, with the formation of a colourless precipitate.



**1.12**

**3.26**

**Scheme 3.8:** Synthesis of the carbodiphosphorane adduct, $^{6Ph}$CDP·$AlH_3$ **3.26**

The solid was analysed via $^{31}P\{^1H\}$ NMR spectroscopy which revealed two resonances at 15.9 and 17.7 ppm. Both resonances are upfield compared to that of compounds containing the CDP cation (*ca.* 21 ppm), suggesting the products formed are neutral adduct species. Absorptions in the IR spectrum at 1634, 1681 and 1712 cm$^{-1}$ correspond to the Al-H stretches. These bands are shifted significantly to lower wavenumber when compared to 5-membered NHC analogues IMes·$AlH_3$ **1.56** (1743 cm$^{-1}$)[9] and IPr·$AlH_3$ **1.57** (1729 cm$^{-1}$),[10] highlighting the significant impact the carbene donor has on the metal center. Colourless crystals of **3.26** were obtained from a toluene/hexane mixture and analysed via x-ray diffractometry.

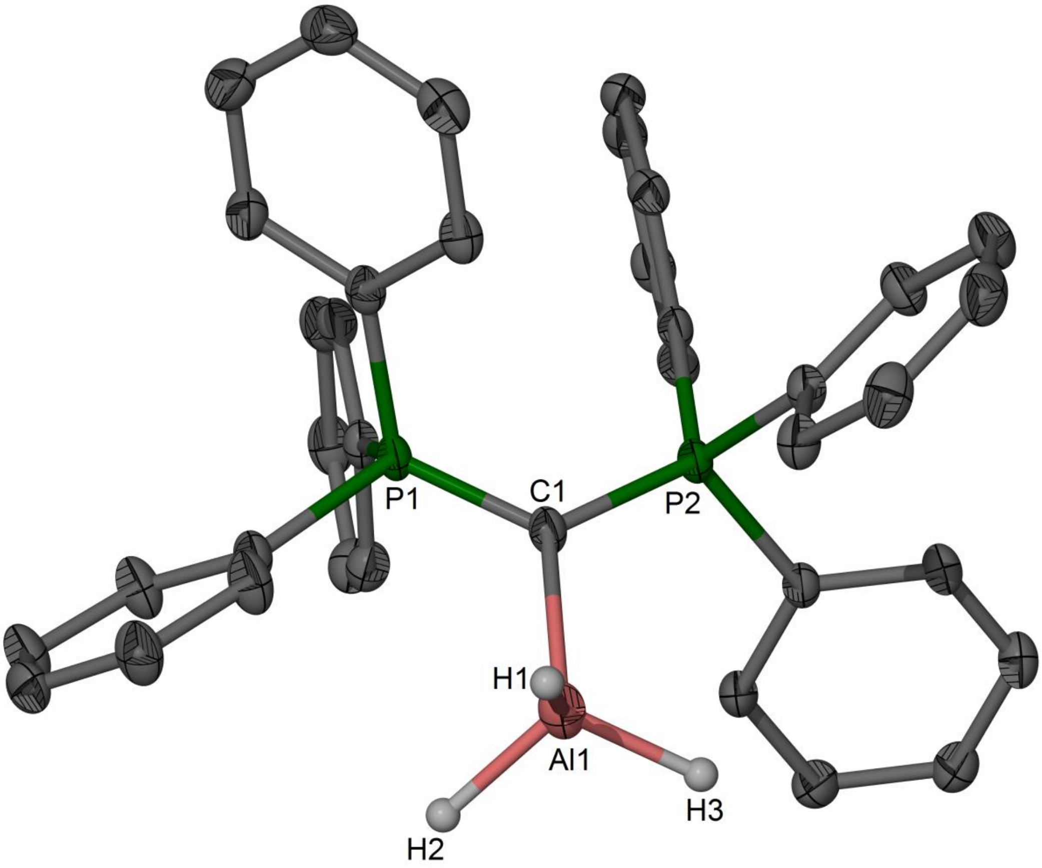


**Figure 3.3:** Molecular structure of $^{6Ph}$CDP·AlH$_3$ **3.26** (Aromatic H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-Al1 2.039(2), Al1-H$_{avg}$ 1.547, P1-C1-P2 111.83(10), C1-Al1-H1 109.5(12), C1-Al1-H2 113.1(7), C1-Al1-H3 108.8(14)

To date, compound **3.26** is the first example of a carbodiphosphorane adduct of aluminium hydride. The aluminium center adopts a distorted tetrahedral geometry with nearly equivalent C-Al-H bond angles (108.8(14), 109.5(12), 113.1(7) °). The C1-Al1 bond length (2.039 Å) compares well with those of 5-membered NHC analogues **1.56** (2.034(3)[9] and **1.57** 2.0556(13).[10] The comparison of bond angles also shows a small but significant difference between the NHC and CDP adducts. The sum of the H-Al-H angles for **3.18** (331.4 °) is significantly larger than that of **1.57** [10] (Σ angles = 316.7 °) potentially due to differences in the steric arrangement between the $^{6Ph}$CDP ligand **1.12** and the $AlH_3$ core. This is noted in the crystal structure of **3.26** (Figure 3.3) with each $PPh_3$ group contributing a face-on and side-on phenyl ring, directed towards the $AlH_3$ core.

### *3.4 Experimental*

**General:** All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. THF, toluene, hexane and benzene were distilled over molten potassium metal, while diethyl ether and pentane were distilled over Na/K alloy (25:75). $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded on either BrukerDPX300, Bruker AvanceIII 400 or Varian Inova 500 spectrometers and were referenced to the residual $^{1}H$ or $^{13}C$ resonances of the deuterated solvent used. Mass spectra were recorded on an Agilent Technologies 5975D inert MSD with a solid‑state probe or obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Perkin Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates or recorded as solid samples using an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. Reproducible microanalyses could not be obtained for all compounds due to their oxygen and/or moisture sensitivity. Microanalyses were carried out by the Science Centre, London Metropolitan University.

**Preparation of $^{6}$IPr·$BBr_3$ (3.18):** Toluene solutions of $^{6}$IPr (0.400 g, 0.99 mmol, 35 mL) and $BBr_3$ (0.248 g, 0.99 mmol, 15 mL) were cooled to -80 °C and combined via cannula

($BBr_3$ added to $^6$IPr). The resultant pale yellow suspension was stirred overnight at 20 °C then filtered. Residues were discarded and the filtrate was concentrated *in vacuo* to *ca.* 15 mL. After placing at -30 °C overnight, colourless crystals of **3.18** were obtained. Yield: 0.278 g (43 %). M.p.: 224 – 225 °C. $^1$H NMR (400 MHz, 298 K, $C_6D_6$): $\delta$ 1.11 (d, 12H, CH(C*H*$_3$)$_2$), 1.58 (d, 12H, CH(C*H*$_3$)$_2$), 1.61 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 3.20 (t, 4H, NC*H*$_2$CH$_2$), 3.40 (sept, 4H, C*H*(CH$_3$)$_2$), 7.03 (d, 4H, *m*-Ar-*H*), 7.13 (t, 2H, *p*-Ar-*H*) ppm; $^{13}$C{$^1$H} NMR (75 MHz, 298 K, $C_6D_6$): $\delta$ 20.7 (CH$_2$*C*H$_2$CH$_2$), 25.2 (CH(*C*H$_3$)$_2$), 26.6 (CH(*C*H$_3$)$_2$), 30.0 (*C*H(CH$_3$)$_2$), 56.6 (NC*H*$_2$CH$_2$), 125.9 (*p*-Ar), 130.2 (*m*-Ar), 143.9 (*o*-Ar), 145.5 (*i*-Ar) ppm; $^{11}$B NMR (128 MHz, 298 K, $C_6D_6$): $\delta$ -14.4 ppm; IR υ/cm$^{-1}$ (Nujol): 1460s, 1381m, 1297s, 1258w, 1211m, 1103w, 1038m, 1004w, 933w, 846w, 799s, 756s, 728w, 663s.

**Preparation of $^6$IPr·AlCl$_3$ (3.19):** Toluene solutions of $^6$IPr (0.380 g, 0.94 mmol, 20 mL) and $AlCl_3$ (0.125 g, 0.94 mmol, 20 mL) were cooled to -80 °C and combined via cannula ($AlCl_3$ added to $^6$IPr). The resultant suspension was stirred overnight at 20 °C then triturated with hexane (20 mL) and filtered. The residues were dried *in vacuo* yielding the desired product **3.19**. The filtrate was concentrated *in vacuo* to *ca.* 5 mL and placed at -30 °C overnight to yield colourless crystals of **3.19**. Yield: 0.162 g (32 %). M.p.: 208 – 211 °C. $^1$H NMR (400 MHz, 298 K, $C_6D_6$): $\delta$ 0.96 (d, 12H, CH(C*H*$_3$)$_2$), 1.59 (d, 12H, CH(C*H*$_3$)$_2$), 1.62 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 3.08 (t, 4H, NC*H*$_2$CH$_2$), 3.31 (sept, 4H, C*H*(CH$_3$)$_2$), 7.09 (d, 4H, *m*-Ar-*H*), 7.22 (t, 2H, *p*-Ar-*H*) ppm; $^{13}$C{$^1$H} NMR (75 MHz, 298 K, $C_6D_6$): $\delta$ 19.8 (CH$_2$*C*H$_2$CH$_2$), 25.3 (CH(*C*H$_3$)$_2$), 27.1 (CH(*C*H$_3$)$_2$), 29.6 (*C*H(CH$_3$)$_2$), 52.9 (NC*H*$_2$CH$_2$), 126.4 (*p*-Ar), 129.9 (*m*-Ar), 131.4 (*o*-Ar), 146.7 (*i*-Ar) ppm.

**Preparation of IPr·Ga(Cl)$_2$Ga(Cl)$_2$-(μ-dioxane)-Ga(Cl)$_2$Ga(Cl)$_2$·IPr (3.21):** Toluene suspensions of IPr (0.100 g, 0.26 mmol, 15 mL) and Ga(Cl)$_2$Ga(Cl)$_2$-μ-dioxane-Ga(Cl)$_2$Ga(Cl)$_2$ (0.87 g, 0.13 mmol, 20 mL) were cooled to -80 °C and combined via cannula (IPr added to $Ga(Cl)_2Ga(Cl)_2$-μ-dioxane-$Ga(Cl)_2Ga(Cl)_2$). The resultant suspension was stirred overnight at 20 °C then filtered. The filtrate was concentrated *in vacuo* to *ca.* 5 mL, to which, 1 mL of pentane was added and placed at -30 °C overnight to yield a trace amount of the desired product, **3.21**. Compound **3.21** was isolated in trace yields from impure mixtures, from which, no conclusive spectral data could be obtained.

**Preparation of (IPr·$GaI_2$)$_2$ (3.23):** Toluene solutions of IPr (2.00 g, 5.15 mmol, 50 mL) and $Ga_2I_4$ (1.80 g, 2.78 mmol, 50 mL) were cooled to -80 °C and combined via cannula (IPr added to $Ga_2I_4$). An immediate yellow coloured solution was formed which gradually phases through orange, to red, to brown, with a dark/brown precipitate formed as temperature was warmed to ambient. The resultant suspension was filtered and the filtrate concentrated in vacuo to ca. 50 mL, from which, crystallization of IPr **1.5**, (IPr·$GaI_2$)$_2$ **3.23** and IPr·$GaI_3$ **3.24** was observed. This process was repeated (three times) until **3.23** was the only product of crystallization. Yield: 1.84 g (48 %). M.p.: 186 – 191 °C. $^{1}$H NMR (300 MHz, 298 K, $C_6D_6$): $\delta$ 0.89 (d, 12H, $CH(C\mathit{H}_3)_2$), 1.64 (d, 12H, $CH(C\mathit{H}_3)_2$), 3.15 (sept, 4H, $CH(C\mathit{H}_3)_2$), 6.28 (s, 2H, *im*C*H*), 7.18 (m, 4H, Ar-C*H*), 7.32 (m, 2H, Ar-C*H*) ppm; $^{13}$C{$^{1}$H} NMR (75 MHz, 298K, $C_6D_6$): δ 25.5 ($_3$), 26.9 ($\mathit{C}H_3$), 29.5 ($\mathit{C}(CH_3)_2$), 126.0 (*imC*H), 126.9 (*m*-Ar-*C*), 132.1 (*p*-Ar-*C*), 136.7 (*i*-Ar-*C*), 147.0 (*o*-Ar-*C*), 159.9 (N*C*N) ppm; IR u/cm$^{-1}$ (Nujol): 1639w, 1558w, 1411m, 1364s, 1327s, 1259s, 1209m, 1181m, 948w, 800s, 777s, 764m, 756s, 702w.

**Preparation of $^{6Ph}$CDP·$AlH_3$ (3.26):** To a -80 °C toluene (30 mL) solution of $^{6Ph}$CDP (0.301 g, 0.56 mmol), $AlH_3$·$NMe_3$ in hexane (0.050 g, 0.56 mmol, 0.683 mL) was added drop-wise over one minute. The resultant mixture was filtered and concentrated *in vacuo* to *ca.* 3 mL and the filtrate was placed at -30 °C overnight to yield colourless crystals of the desired product, **3.26**. The residues were dried and washed with benzene (10 mL at 60 °C) to yield the desired product, **3.26**. Yield: 0.147 g (26%). M.p.: 214 – 218 °C. $^1$H NMR (400 MHz, 298 K, $C_6D_6$): *δ* 4.51 (s (br), 3H, Al*H*$_3$, 6.92 (m, 12H, *o*-Ar-C*H*), 6.93 (m, 12H, *m*-Ar-C*H*), 7.78 (t, 6H, *p*-Ar-*H*) ppm; $^{13}$C{$^1$H} NMR (75 MHz, 298 K, $C_6D_6$): δ 128.0 (*m*-Ar-*C*H), 131.5 (*o*-Ar-*C*H), 134.6 (*p*-Ar-*C*H) ppm; $^{31}$P NMR (121 MHz, 298 K, $C_6D_6$) ppm: δ 17.7 (s, Ph$_3$*P*) ppm; IR υ/cm$^{-1}$ (Nujol): 1712m (Al-H), 1681m (Al-H), 1634w (Al-H), 1437s, 1377s, 1260s, 1099s, 1077s, 1024s, 858w, 797s, 767s, 739s, 715m, 692m.

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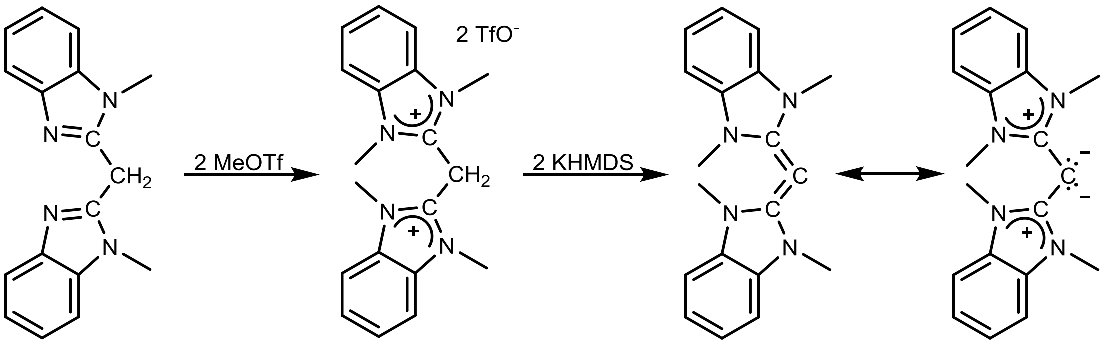
# *4 Low Oxidation State Group 14 Complexes*

## *4.1 A Further Introduction to Low Oxidation State Group 14 Complexes*

In 2007 Frenking and co-workers conducted theoretical studies on a class of compounds called carbodicarbenes (CDCs) and showed them to be experimentally accessible.[1] This concept was realized the following year, with Frenking and co-workers reporting the synthesis of the CDP **4.3** shown in scheme 4.1 below.[2]

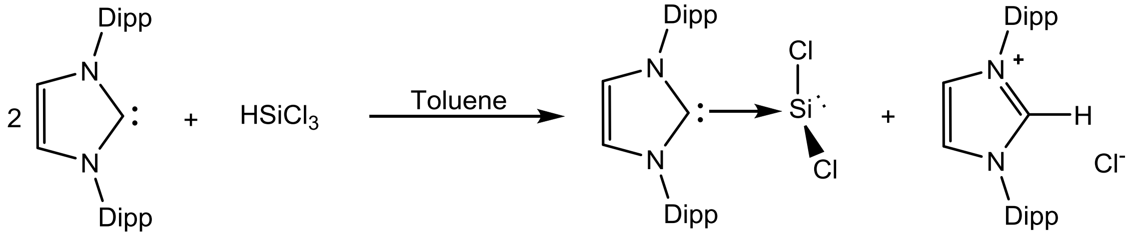


**4.1** **4.2** **4.3** **4.3'**

**Scheme 4.1:** Synthesis of the carbodicarbene, **4.3** and its resonance form **4.3’**

CDCs such as **4.3** have potential to be useful ligands in MG and TM compounds, similar to that of nitrogen heterocyclic carbenes (NHCs) and carbodiphosphoranes (CDPs).

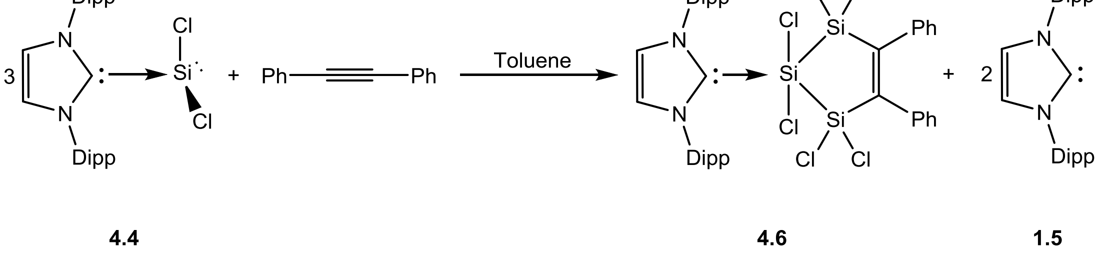
In 2009 Roesky and co-workers reported the first room temperature stable dihalidosilylene via the use of NHCs as ligands.[3] Prior to this, attempts to form $SiCl_2$ species via the reductive elimination of $HSiCl_3$ using various HCl abstractors[4] and trapping agents[5] yielded minimal success, with only one room temperature stable monochlorosilylene reported and characterized by X-ray diffraction.[6] Using a similar methodology, the group were able to successfully synthesize a Lewis base stabilized dichlorosilylene utilizing NHCs as both a ligand and an HCl abstractor.



**1.5** **4.4** **4.5**

**Scheme 4.2:** Synthesis of the NHC coordinated dichlorosilylene IPr·$SiCl_2$, **4.4**

Compound **4.4** was treated with diphenylacetylene to form the trisilacyclopentene compound **4.6** shown in scheme 4.3 below.

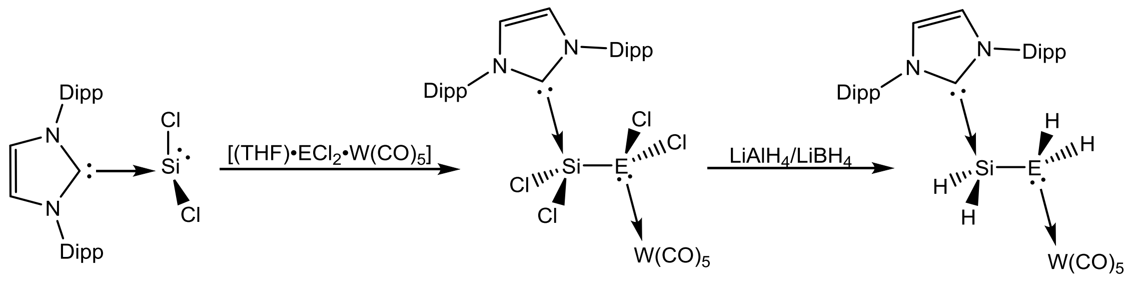


**4.4** **4.6** **1.5**

**Scheme 4.3:** Addition of diphenylacetylene to IPr·$SiCl_2$ **4.4**, resulting in the addition product **4.6**

The addition product **4.6** is of interest as it shows the lability of the C-Si donor bond between the NHC and the $SiCl_2$ fragment. Two $SiCl_2$ fragments are labile enough to detach from the NHC and form part of the trisilacyclopentene ring in compound **4.6**, eliminating two equivalents of free IPr **1.5** which can then go on to be recycled to produce more **4.4**.

Utilizing the dihalidosilylene **4.4**, Rivard and co-workers were able to synthesize two molecules that closely resemble heavier parent analogues of ethylene.[7] The compounds house a $H_2SiEH_2$ (E = Ge **4.9**, Sn **4.10**) core stabilized via a push-pull system, with **4.4** as the Lewis base and $W(CO)_5$ as the Lewis acid, shown in scheme 4.4 below.



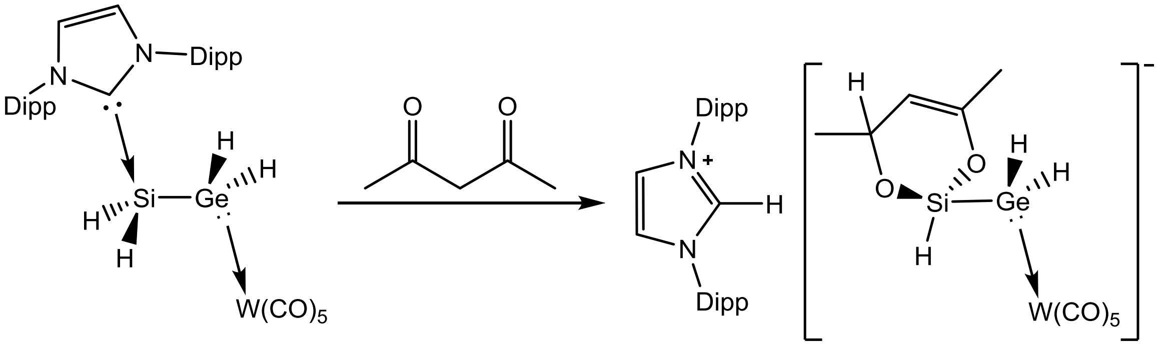
**4.4**

E = Ge **4.7**
E = Sn **4.8**

E = Ge **4.9**
E = Sn **4.10**

**Scheme 4.4:** Stabilization of $EH_2$ fragments (E = Ge **4.9**, Sn **4.10**), utilizing **4.4** as a Lewis Base and $W(CO)_5$ as a Lewis acid

Compound **4.10** decomposes at temperatures as low as -30 °C in solution. However, **4.9** showed considerably high thermal stability being able to withstand refluxing toluene for extended periods of time, therefore the focus of further chemistry was performed on the germanium species rather than the tin compound.

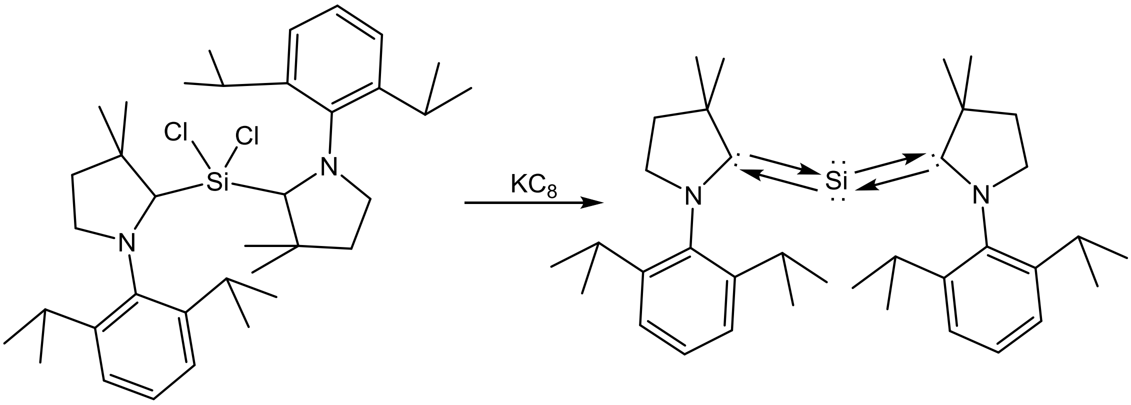


**4.9** **4.11**

**Scheme 4.5:** Hydrosilylation of acetyl acetone using **4.9**, resulting in the cyclic salt complex, **4.11**

Selective hydrosilylation takes place when the Si-Ge ethylene analogue, **4.9** is treated with acetyl acetone, yielding the salt complex **4.11** (shown in scheme 4.5 above). These heavier parent ethylene analogues open new pathways into further understanding the surface chemistry of silicon and germanium as well as Si/Ge hybrid nanomaterials.

In 2013 Roesky and co-workers reported the first compound to contain a single silicon atom coordinated by two cyclo-amino-alkyl-carbenes (cAACs) **4.13** shown in scheme 4.6 below.[8]

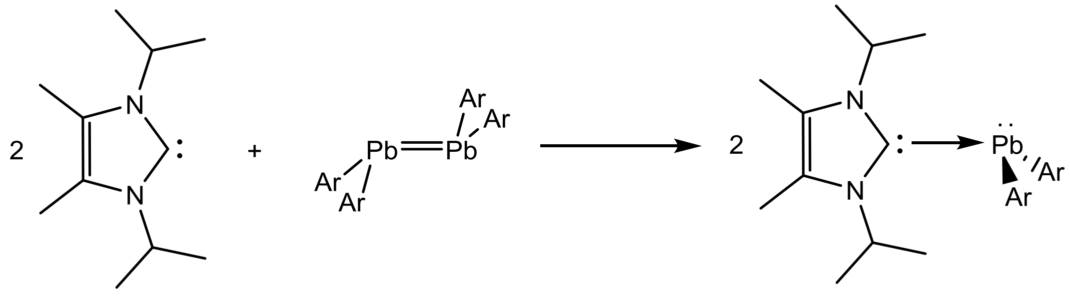


**4.12** **4.13**

**Scheme 4.6:** Synthesis of the cAAC stabilized silicon(0) fragment **4.13**

Computational investigations including MO studies, NBO analysis and proton affinities suggest that **4.13** is a singlet ground state silylone and the first silicon atom in the formal oxidation state of zero, coordinated by only two carbene molecules. It should also be noted that a similar analogue of a germylone fragment stabilized only by two carbene carbon atoms was also reported in the same year by Driess and co-workers.[9]

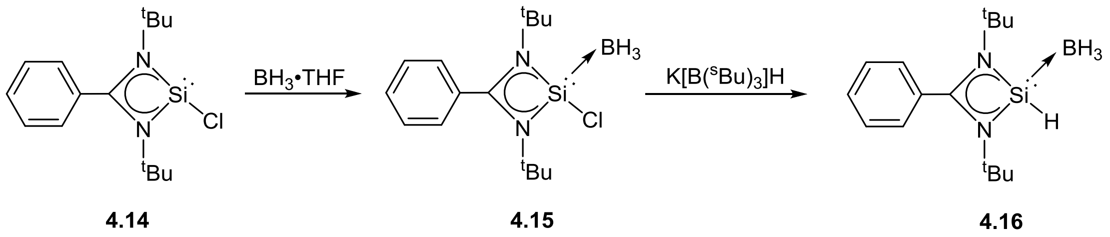
Although there has been a large increase in the number of NHC main group metal adducts reported in the literature,[10] only a small fraction of these include the use of heavier main group elements, specifically period six elements. In 1999 Stabenow and co-workers reported the NHC-lead(II) adduct IPr$^i$Me·PbAr$_2$ (Ar = Tipp = 2,4,6-triisopropylphenyl) **4.15** seen in scheme 4.7 below.[11]



**1.7** **4.14** **4.15**

**Scheme 4.7:** Coordination of IPr$^i$Me **1.7**, to the lead(II) plumbylene **4.14** forming the NHC-lead(II) adduct **4.15**

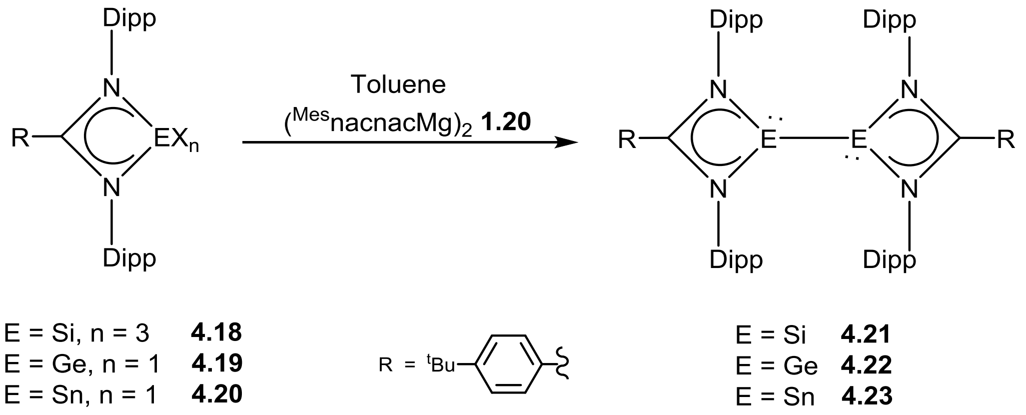
In 2011 Roesky and co-workers reported the first silicon(II) monohydride, **4.16** using the small chelating amidinato ligand PhC(N$^t$Bu)$_2$.[12]



**Scheme 4.8:** Synthesis of the first amidinato silicon(II) monohydride **4.16**

Previous attempts to substitute the chloride with a hydride proved unsuccessful[13] until the use of $BH_3$. Unlike $SiH_2$ which oligomerizes under standard laboratory conditions, **4.16** is stable in solution and does not show any signs of oligomerization or decomposition even at elevated temperatures. Compound **4.16** is a key step into further understanding the chemistry of the parent divalent $SiH_2$, which still remains elusive to this date under standard laboratory conditions.

In the same year, Jones and co-workers reported a series of amidinato silicon(I), germanium(I) and tin(I) dimers.[14] The amidinato ligand Butiso$^-$, ($[(DippN)_2C(C_6H_4\text{-}4\text{-}^tBu)]^-$ **4.17** was chosen for its steric bulk and its crystallizing properties.



**Scheme 4.9:** Synthesis of amidinato E$^I$ dimers, **4.21 – 4.23**, using the nacnac magnesium(I) dimer, **1.20** as a selective reducing agent

Previous work done by Roesky and co-workers on similar amidinato silicon(I) and germanium(I) dimers had already shown these compounds to activate small molecules.[15] The syntheses of these novel amidinate group-14 element(I) dimers, as well as the novel reducing abilities of the nacnac magnesium(I) dimers, have already shown their applicable uses in other areas of chemistry[16] and further development of both these classes of compounds continues to develop to this day.

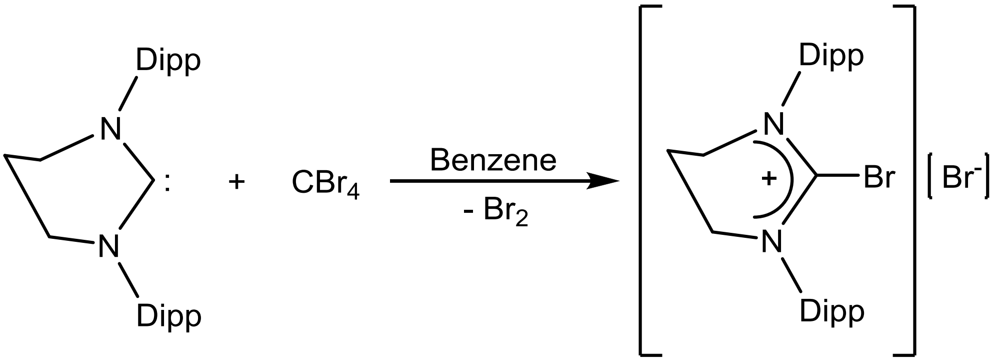
## *4.2 Research Outline*

NHC adducts of MG and TM elements have had a significant impact in recent literature largely due to their unprecedented chemical structures and unique chemical properties. Extending on from this trend, NHC adducts of group 14 element halides, were synthesized and subsequently reduced in attempts to form their corresponding LOS compounds. NHCs included 5-membered unsaturated and 6-membered saturated species. In addition to NHCs, nitrogen heterocyclic silylene (NHSi), carbodiphosphorane (CDP) and N-donor, diazabutadiene (DAB) and amidinate ligands were also used in attempts to form LOS complexes with group 14 elements.

## *4.3 Results and Discussion*

### *4.3.1 Synthesis of NHC Adducts of Group 14 Elements and Their Reductions*

The lightest element of the group, carbon, was used in an attempt to generate compounds with the element in low oxidation states and low coordination numbers. The 6-membered NHC ${}^{6}$IPr, **2.24** was treated with carbon tetrabromide, $CBr_4$ in an attempt to form a neutral adduct (eg ${}^{6}$IPr·$CBr_2$), however, the salt complex **4.24** was isolated instead.



**2.24** **4.24**

**Scheme 4.10:** Addition of ${}^{6}$IPr, **2.24** to $CBr_4$ yielding the salt product, **4.24**

When both compounds are combined in benzene at room temperature, a highly insoluble, black precipitate is generated instantly, while the solution remains colourless. Similar results are obtained when repeated at low temperatures. ${}^{1}$H NMR spectroscopic analysis of the reaction mixture shows no trace of the free ligand **2.24**. Attempts to crystalize any products from the toluene mixture proved to be challenging without the use of chlorinated solvents. Crystals of the compound shown below (see figure 4.1) were isolated from a slow-cool benzene/DCM mixture in high yield.

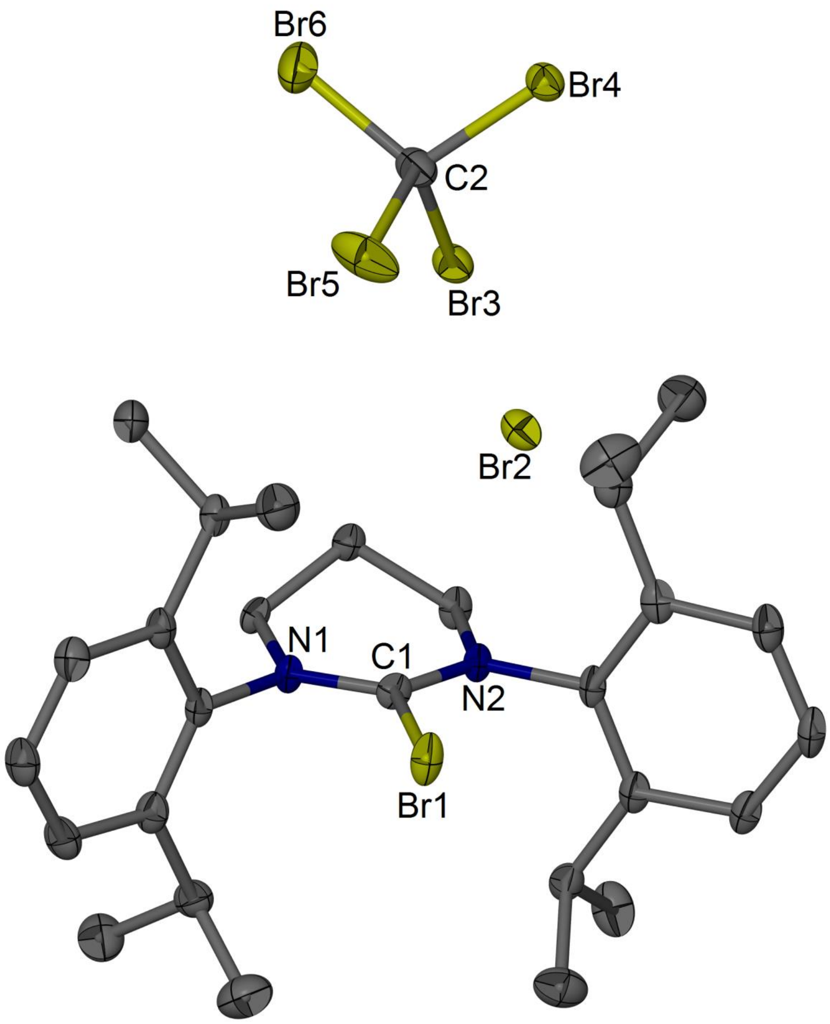


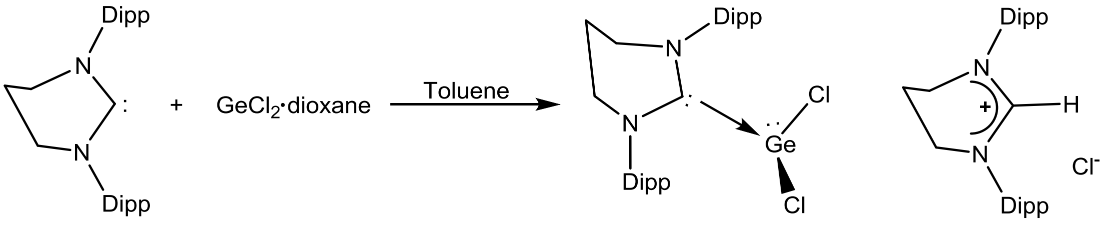
**Figure 4.1:** Molecular structure of $[^6IPrBr]^+[Br]^-$ **4.24** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-Br1 1.877(4), C2-$Br_{Avg}$ 1.943, Br1-Br2 7.700, N1-C1-N2 125.1(4)

This compound resembles the salt product of the free ligand, $^6$IPr, with the exception of having a dibromine fragment split across the ligand's carbene carbon atom. The asymmetric unit also contains a $CBr_4$ molecule. The reaction was repeated at -80 °C in toluene. Upon addition, the mixture turns a fluorescent yellow colour, which becomes dull within minutes. Slowly warming the mixture to room temperature, the yellow solution fades to colourless and the black precipitate, $[IPrBr]^+[Br]^-$, **4.24**, begins to form at *ca.* -40

°C. Although novel, this product could not be used to form suitable ligand-element fragments, therefore further investigations using this avenue were terminated.

Similar reactions with $^6$IPr **2.24** were carried out on heavier group 14 element halides (silicon, germanium, tin and lead) however, only limited success was found with germanium and silicon, while tin and lead showed no reactivity. In the case of silicon, initial reactions with $SiCl_4$ and $SiBr_4$ showed no reactivity/coordination even at elevated temperatures. Adopting a similar methodology to that of the analogous 5 membered NHC adduct by Roesky and co-workers,[3] $HSiCl_3$ was added to **2.24** in an attempt to form the divalent $^6$IPr·$SiCl_2$ via HCl elimination. No reaction occurs at room temperature even after 72 hours. Heating the reaction mixture results in a number of products including the formation of poorly soluble salts of the carbene, indicated via $^1$H NMR spectroscopy.

Coordination of the ligand to a germanium fragment however, proved successful. The reaction of $^6$IPr and $GeCl_2$·dioxane predominantly yielded a mixture of $^6$IPr·$GeCl_2$ **4.25** and $^6$IPr·HCl **4.26**, both of which were isolated from a slow cooled toluene solution as a colourless crystalline solid.



**2.37** **4.25** **4.26**

**Scheme 4.11:** Synthesis of the $^6$IPr-germanium(II) adduct, **4.25** and the HCl salt [$^6$IPr-H]$^+$[Cl]$^-$, **4.26**

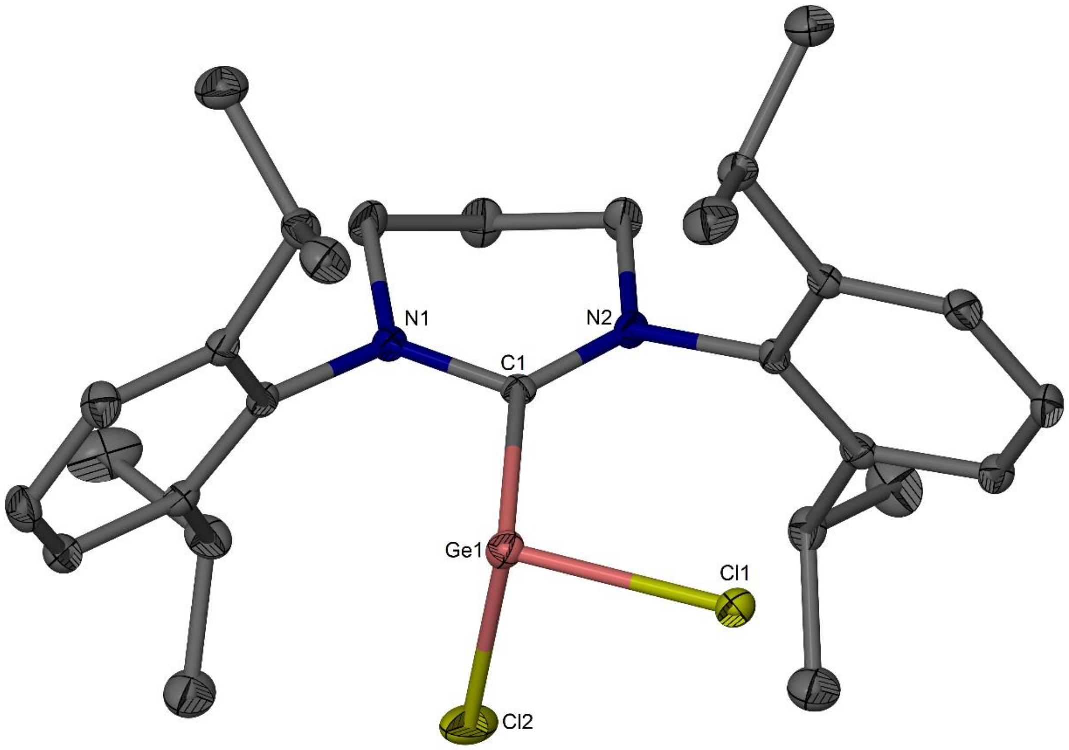


**Figure 4.2:** Molecular structure of $^{6}$IPr·GeCl$_2$ **4.25** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-Ge1 2.1894(16), Ge1-Cl1 2.2807(5), Ge1-Cl2 2.2773(4), N1-C1-N2 118.36(15), Cl1-Ge1-Cl2 94.595(17)

Separating these two products proved difficult as they had similar solubilities in most common solvents and solvent systems (max purity ratio $^{6}$IPr·GeCl$_2$ : $^{6}$IPr·HCl - 80% : 20%). In the case of the five-membered NHC, the HCl salt of the carbene is much less soluble and can be separated out using an appropriate solvent system[17] In this case however, the overall decreased solubility provided by the $^{6}$IPr ligand, led to both compounds to have similar solubilities.

X-ray data show **4.25** to be monomeric in the solid state with one $^{6}$IPr ligand coordinated to one germanium(II) center. The C-Ge bond length in **4.25** (2.2807(5) Å) is significantly longer than that of the C-Ge bond length in the 5-membered analogue IPr·GeCl$_2$, **1.26**

(2.110(4) Å) owing to the increased steric bulk provided by the $^{6}$IPr ligand over the IPr ligand. The sum of angles around the germanium center (289.6°) and its pyramidalized geometry gives evidence for the presence of a stereo-chemically active lone pair.

The $^{1}$H NMR spectrum of the crystallized product shows no remaining $^{6}$IPr ligand, however, resonances for both $^{6}$IPr·GeCl$_2$ **4.25** and $^{6}$IPr·HCl **4.26** integrating in a 4:1 ratio are evident. For the neutral adduct **4.25**, complete separation of the (originally overlapping) isopropyl doublets is observed ($\Delta\delta$ = 0.42 ppm) with a significant downfield shift ($\delta$ 0.25 ppm) of the triplet resonance attributed to the backbone NC$H_2$ protons. The significant separation of the isopropyl doublets was also reported in the five membered analogue **1.26** ($\Delta\delta$ = 0.41 ppm), indicative of the different C-H environments above and below the “plane” of the NHC ring. The carbene carbon resonance was detected in the $^{13}$C{$^{1}$H} NMR spectrum at $\delta$ 197.1 ppm, *i.e.* 48.6 ppm upfield of the free carbene $^{6}$IPr, **2.24**, and 21.8 ppm downfield to that observed in the 5-membered analogue, **1.26**.

Reductions of the 4:1 mixture of $^{6}$IPr·GeCl$_2$ : $^{6}$IPr·HCl were carried out using the magnesium(I) dimer **1.20**. A 1 : 1 ratio of germanium : magnesium(I) centers was used, with a germanium(0) product as the target compound. At -80 °C toluene was added to both solids in a Schlenk flask under an inert atmosphere and the mixture stirred. As the reaction was warmed to room temperature, a dark red/brown colour was observed at -30 °C, which increased in intensity up until room temperature. The colour was attributed to a highly insoluble precipitate, while the solution was virtually colourless. An aliquot of the mixture was taken and analysed using $^{1}$H NMR spectroscopy. The absence of $^{6}$IPr·GeCl$_2$ **4.25** resonances in the spectrum, in addition to the elemental germanium deposited during the reaction, highlight the reductive ability of the magnesium(I) dimer **1.20**. However, only two sets of NHC resonances were observed, one of which was accredited to free $^6$IPr **2.24**. The other set of NHC resonances resemble that of an ionic product, potentially $^6$IPr·HCl **4.26**. Varying reaction and crystallization processes consistently resulted in the formation of these products. The red/brown solid proved to be too insoluble in common hydrocarbon solvents to grow crystals of suitable quality for X-ray data. Ultimately, the synthesis of LOS germanium compounds using the $^6$IPr ligand proved unsuccessful, however, the synthesis of the 1 : 1 coordination adduct, $^6$IPr·GeCl$_2$, **4.25** was successful and may potentially yield more favourable outcomes in the future. As mentioned previously, silicon, tin and lead adducts using $^6$IPr could not be synthesized or isolated.

The next section of research continues on the theme of NHC-group 14 adducts (specifically, five membered NHCs and germanium) and follows on from the successful results achieved in the Jones group with the novel germanium(0) compound **1.28**.[17] Different ligand systems were investigated in attempts to improve yield and stability of LOS germanium compounds, as well as any potential further chemistry these compounds had to offer.

A major issue with salt formation was consistently observed in the coordination of the NHC to the group 14 element halide fragment. For example, the reaction involving a 1 : 1 ratio of IPr and germanium(II) chloride would often give salt products such as $[\text{IPrH}]^+[\text{GeCl}_3]^-$ **4.27** instead of the desired IPr·GeCl$_2$ adduct **1.26**. This product was observed even when the reaction was performed in aprotic, non-polar solvents such as hexane and pentane, solvents which are traditionally used to minimize solvent-proton abstraction processes. It was hypothesized that the formation of these ionic products was caused from the relatively labile backbone imidazole protons unintentionally being involved in the reaction, essentially being a proton source for any acid-product formation.

In order to resolve this reoccurring issue, the NHC, dubbed "$^{Me}$IPr" **1.4** was employed, as the backbone imidazole protons are replaced with methyl groups, effectively removing any acidic protons that could interfere with the reaction process.

The previous success with NHC germanium compounds[17] made germanium an ideal first candidate for this research. One equivalent of $^{Me}$IPr **1.4** was treated with one equivalent of $GeCl_2$·dioxane in toluene at room temperature. The resultant mixture was filtered and the residual solid was analyzed by $^1$H NMR spectroscopy which strongly suggested the formation of the desired $^{Me}$IPr·$GeCl_2$ compound **4.28**. The separation of the isopropyl doublets is substantially larger after coordination of the $GeCl_2$ unit ($\Delta\delta$ = 0.49 ppm) as opposed to the free carbene ($\Delta\delta$ = 0.12 ppm), a common indicator of successful coordination. The isopropyl septet is also shifted significantly upfield after coordination of the $GeCl_2$ unit (from δ 2.91 ppm in the free carbene to δ 2.73 ppm in the adduct). Similar shifts are also observed between the $^1$H NMR spectra of IPr, **1.5**, and IPr·$GeCl_2$, **1.26**.[17]

Crystals of the proposed $^{Me}$IPr·$GeCl_2$ **4.28**, suitable for X-ray diffraction were not obtained, however, low quality crystals were isolated and used for further synthesis. $^{Me}$IPr·$GeCl_2$ **4.28** was combined with the magnesium(I) dimer **1.20** in diethyl ether in a similar fashion to the analogous IPr·$GeCl_2$ experiment reported in 2009.[17] The reaction was initially performed at room temperature which gave an instantaneous red solution. After 10 minutes of stirring, an aliquot was taken from the mixture and analyzed via $^1$H NMR spectroscopy. The spectrum revealed resonance patterns indicative of two major $^{Me}$IPr **1.4** compounds. No resonances corresponding to the starting material, $^{Me}$IPr·$GeCl_2$ **4.28** were observed. One set was determined to be for the free NHC, $^{Me}$IPr, **1.4**, whilst the other was from an unknown species. Closer analysis of these resonances indicated the possible formation of a germanium(0) species. The resonance pattern of the proposed germanium(0) species closely resembles that of the free carbene. All chemical shifts have significantly shifted towards that of the free carbene when going from $^{Me}$IPrGe·Cl$_2$ **4.28** to ($^{Me}$IPr·Ge)$_2$ **4.29** (see table 4.3 below).

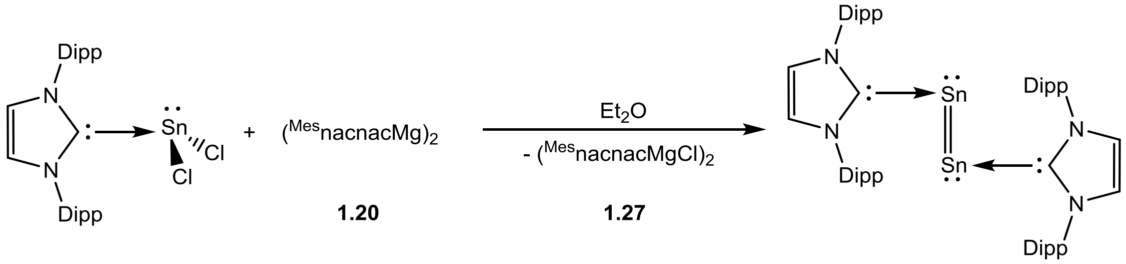
| Compound | Doublet Resonance (A) (ppm) | Doublet Resonance (B) (ppm) | Singlet Resonance (ppm) | Septet Resonance (ppm) |
|---|---|---|---|---|
| $^{Me}$IPr **1.4** | 1.20 | 1.32 | 1.67 | 2.91 |
| $^{Me}$IPr·GeCl$_2$ **4.28** | 0.98 | 1.47 | 1.43 | 2.73 |
| ($^{Me}$IPr·Ge)$_2$ **4.29** | 1.11 | 1.27 | 1.64 | 3.02 |

**Figure 4.3:** Comparison of $^1$H NMR spectroscopic resonances for compounds **1.4**, **4.28** and **4.29**

This phenomenon is to be expected, as the carbene itself is a neutral donor that has a lesser effect on the electronic and magnetic state of the metal center as opposed to anionic ligands. This pattern of proton environments is also observed in the $^1$H NMR spectra of the analogous (non-methylated) IPr system.[17]

The added methyl groups along the backbone of the NHC make any ligated product less soluble than their non-methylated counterparts (in aprotic, non-polar solvents). The isolation and extraction of the germanium(0) species (IPr·Ge)$_2$ **1.28** from the reduction of IPr·GeCl$_2$ **1.26**, was feasible due to the differences in the solubilities of products. However, this is not the case with the methylated analogue **4.28**. Both the oxidized magnesium(II) species, **1.27**, and the germanium(0) product, **4.29** have similar solubilities, making separation challenging via conventional laboratory techniques. Although it is highly likely a new germanium(0) species was synthesized, the objective to re-create a germanium(0) compound similar to **1.28** in yields that could prove practical for further research was not achieved. Changing the NHC or reductant could prove more successful in future research.

This was however achieved for the tin analogue using the ligand IPr, **1.5**. The NHC-tin halide, IPr·SnCl$_2$ **4.30** was treated with the magnesium(I) dimer **1.20** in diethyl ether at -80 °C, resulting in the formation of tin(0) dimer (IPr·Sn)$_2$, **4.31**.[18]



**4.30** **4.31**

**Scheme 4.12:** Synthesis of the NHC coordinated tin(0) dimer, **4.31** via magnesium(I) reduction of the tin(II) precursor, **4.30**

Initially, the solution takes on a red colour and becomes green at 0 °C. At room temperature, the green solution fades to colourless as **4.31** decomposes to free IPr **1.5**, and elemental tin. The instability of **4.31** is also highlighted in the solid state, as it slowly decomposes, even at room temperature. Red crystals of **4.31** were isolated from the reaction mixture and an NMR spectroscopic analysis was conducted in deuterated toluene at -30 °C. It is worth mentioning that the decomposition of **4.31** to free IPr **1.5** and elemental tin is observed even under these conditions. The $^{1}$H NMR spectrum of **4.31** is consistent with that of its proposed structure and follows the trend of its lighter congeners.[17,19] The carbene resonance at δ 210.3 ppm is further downfield than those of previously reported germanium and silicon analogues (Ge: δ 203.3 ppm, Si: δ 196.3 ppm), indicating the C-element (element = Si, Ge, Sn) interaction lessens progressing down the group.

Red crystals of **4.31** were isolated from the reaction mixture in diethyl ether and analyzed via X-ray diffractometry (figure 4.4).

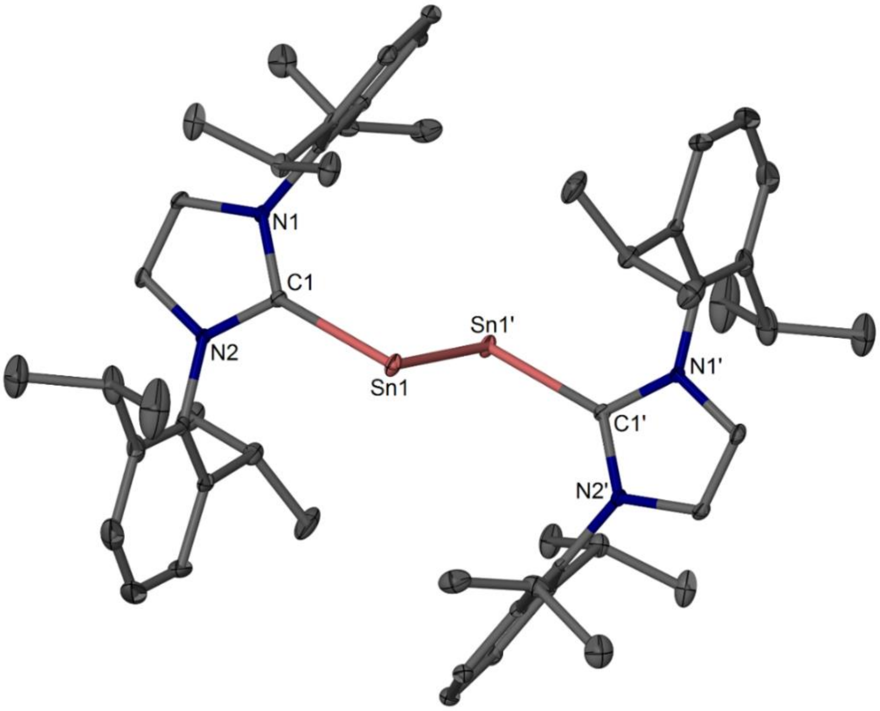


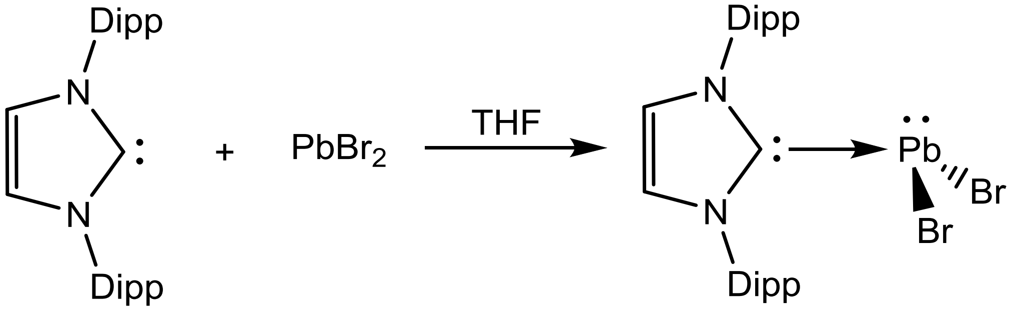
**Figure 4.4:** Molecular structure of **4.31** (hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Sn1–C1 2.280(3), Sn1–Sn1’ 2.7225(5), N1–C1 1.362(4), N2–C3 1.386(4), C2–C3 1.329(5), C1–Sn1–Sn1’ 91.82(8), N1–C1–N2 103.1(3)

The “trans-bent” structure of **4.31** is clearly evident with a C-Sn-Sn bond angle of 91.82 °, consistent with the trend of its silicon and germanium analogues.[17,19] The Sn-Sn separation (2.7225(5) Å) is within the range of previously reported for three-coordinate, doubly bonded distannenes (2.668 - 2.851 Å),[20] as well as multiply bonded distannynes (2.646 - 2.736 Å).[21]

Computational analysis on the simplified NHC-tin dimer [(NHC)Sn=Sn(NHC)] (NHC = :C{N(Me)C(H)}$_2$) **4.32** suggested the metallic core to be a singlet state, doubly-bonded :Sn=Sn: fragment. The bond dissociation energy of the C-Sn interaction in **4.32** was calculated to be 31 kcal mol$^{-1}$, significantly lower than that of the germanium analogue (37.8 kcal mol$^{-1}$). The major contribution of the C-Sn interaction is attributed to the plus (46.3%) and minus (45.5%) combinations of the carbon lone-pair orbitals. The occupied out-of-plane π MO of the $Sn_2$ fragment into the empty p(π) orbitals of the carbene carbon atoms only represent 6.6% of the interaction, indicating little Sn-C π-backbonding.

Although a major breakthrough in the field of LOS tin chemistry, the combination of low-yields, high levels of impurities and the thermal instability of the tin(0) dimer **4.31** made further chemistry impractical to investigate. None-the-less, the dimer can be thought of as an allotrope of elemental tin and helps shed light on the bonding and properties of this element.

In order to complete the series of group 14 [IPr·E=E·IPr] compounds (E = C, Si, Ge, Sn, Pb), lead(II) bromide was treated with IPr, **1.5** in THF to give IPr·$PbBr_2$ **4.33** in high yields (92% isolated). Worthy of note, the lead(II) chloride showed no reactivity when treated with IPr **1.5**, hence the use of the bromide equivalent.



**1.5** **4.33**

**Scheme 4.13:** Synthesis of the NHC-coordinated lead(II) adduct IPr·$PbBr_2$, **4.33**

Colourless crystals of **4.33** were isolated from toluene and analyzed by X-ray diffractometry. The data reveals a monomeric complex with one IPr ligand coordinated to one $PbBr_2$ fragment.

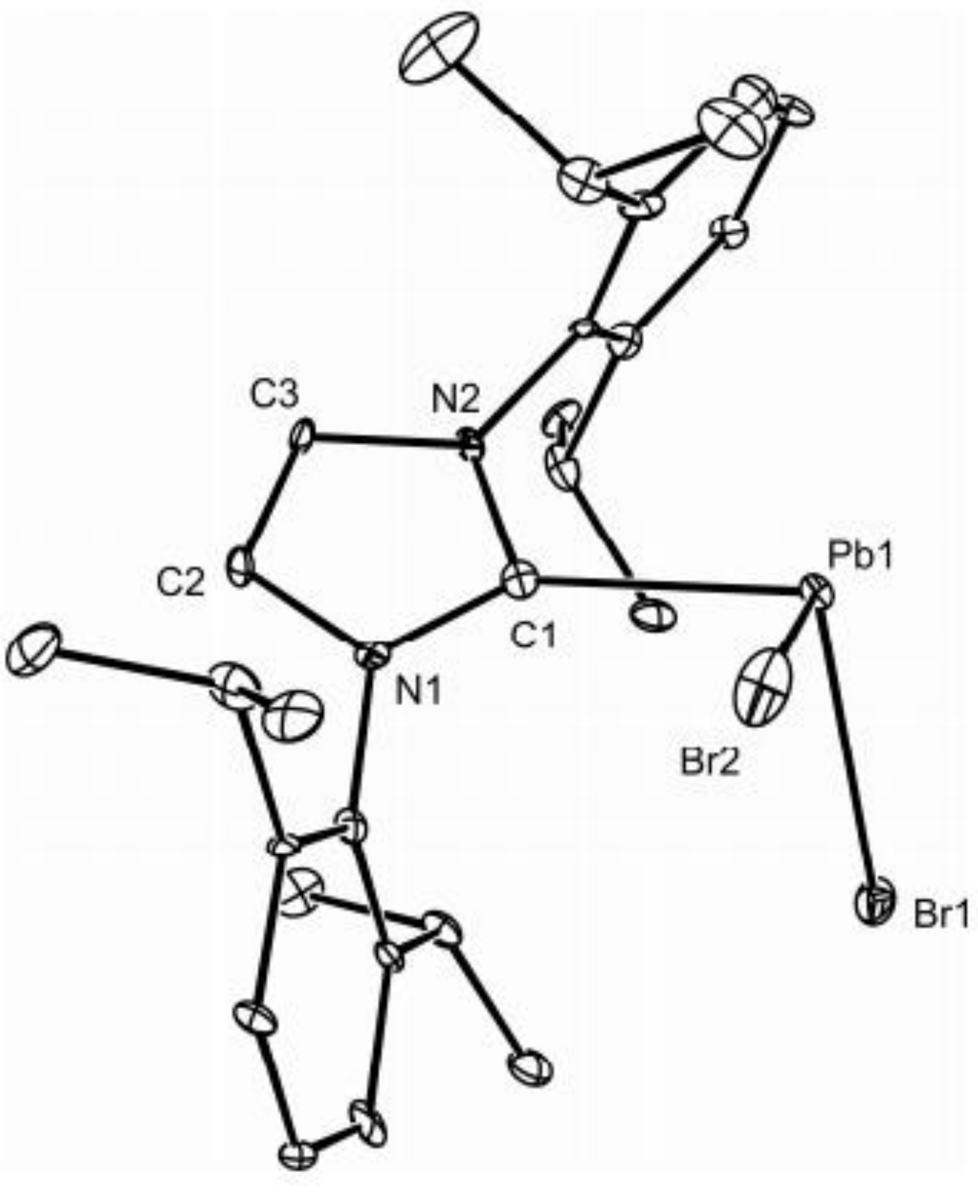


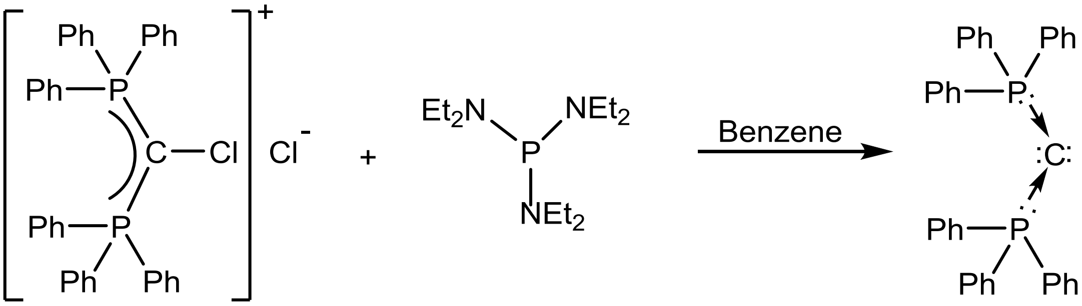
**Figure 4.5:** Molecular structure of IPr·$PbBr_2$ **4.33**, (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-Pb1 2.43(2), Pb1-Br1 2.710(2), Pb1-Br2 2.711(3), N1-C1-N2 116.6(16), Br1-Pb1-Br2 93.23(8), C-Pb1-$Br_{avg}$ 94.4

Prior to the synthesis of **4.33**, only one NHC-lead adduct had been reported in the literature,[11] IPr$^i$Me·PbTipp$_2$ (Tipp = 2,4,6-triisopropylphenyl) **4.15**, which utilized the much smaller carbene (:C(N($^i$Pr)CH)$_2$), and Tipp ligands instead of halides.

Both **4.33** and **4.15** have similar geometries around the Pb center, in that they have distorted pyramidal Pb centers. This has been observed in many NHC-ER$_2$ systems (E = Si, Ge, Sn, Pb; R = aryl, halide) and is largely attributed to the stereochemically active lone pair at the element center. In the case of the analogous germanium and silicon adducts (as well as that of **4.15**) the E-C bond (E = Ge, Sn. Pb) bond was in line with the plane of the carbene ring. However, in the example of **4.33**, the Pb-C bond is protruding on a slight angle out of the NHC plane (figure 4.4). The Pb-C$_{carbene}$ bond length in **4.33** (2.43(2)Å) is notably shorter than that of **4.15** (2.540(5)Å), possibly indicative of more C=Pb double bond character rather than a C:→Pb interaction in the former. However, the N*C*N carbene resonance of **4.33** (δ 218.9 ppm) is only slightly upfield to that of the free carbene (δ 220.6 ppm) in the $^{13}$C NMR spectrum, suggesting a weak interaction between the lead center and the carbene carbon. The N*C*N resonances in the $^{13}$C{$^1$H} NMR spectra of IPr·EX$_2$ (E = Si, Ge, Sn, Pb; X = Cl, Br) compounds are observed further downfield as molecular weight of the group 14 element increases. Attempts were made to reduce **4.33** to yield a lead(0) complex, similar to those of its lighter congeners (Si, Ge, Sn).[17,18,19] Even at low temperatures (-80 °C), the NHC proved too labile to remain coordinated to the lead center, with the visible formation of elemental lead and the almost exclusive presence of free carbene indicated by $^1$H NMR spectroscopy. The possibility of introducing “softer” neutral donor ligands could prove more suitable for lead as it is shown that Pb-C interactions are relatively weak due to poor orbital overlap.

### *4.3.2 Alternative Neutral Ligands: Carbodiphosphorane and Nitrogen Heterocyclic Silylene Adducts of Group 14 Elements*

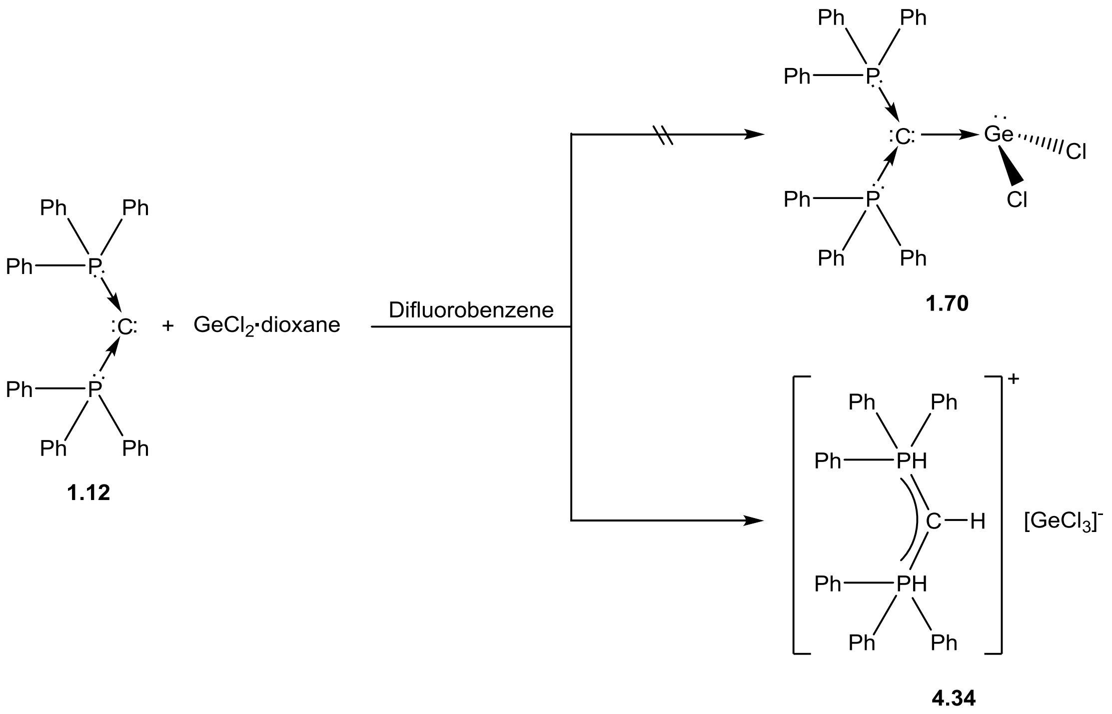
Another neutral ligand that was employed throughout my research was the carbodiphosphorane (CDP) ligand $^{6Ph}$CDP **1.12**, its synthesis is shown below in scheme 4.2.2.



**1.12**

**Scheme 4.14:** Synthesis of the neutral carbodiphosphorane ligand $^{6Ph}$CDP, **1.12**

The CDP **1.12** was introduced as an alternative to NHCs, with the intention of providing a different steric and electronic environment for coordinated metal and element fragments. Both solids, $^{6Ph}$CDP **1.12**, and germanium(II) chloride·dioxane were combined in a Schlenk flask and left to stir in difluorobenzene overnight. Difluorobenzene was used instead of less polar solvents (benzene, toluene etc.) with the intention of aiding the inherent insolubility of the CDP **1.12**.



**Scheme 4.15:** Attempted synthesis of the carbodiphosphorane-germanium adduct **1.70** and the isolated salt product **4.34**

As the reaction progressed, a highly insoluble white precipitate was formed. Single crystals were obtained from the filtered reaction mixture and analyzed via X-ray diffractometry to be the salt compound $[^{6Ph}\text{DCP-H}]^+[\text{GeCl}_3]^-$ **4.34** shown below (figure 4.6).

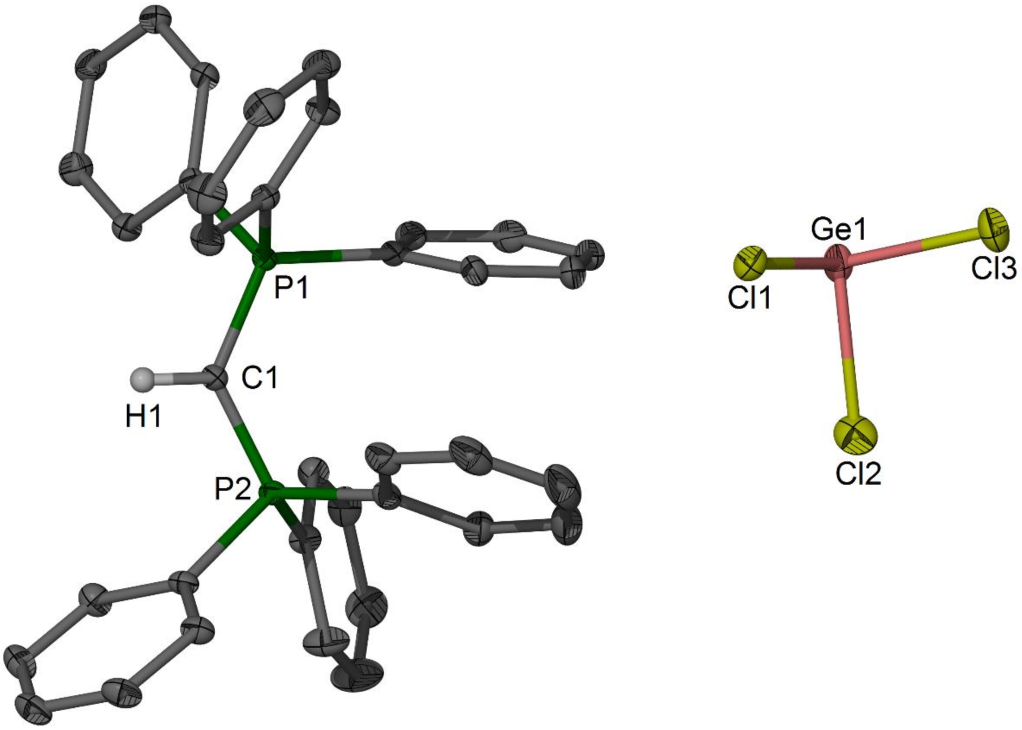


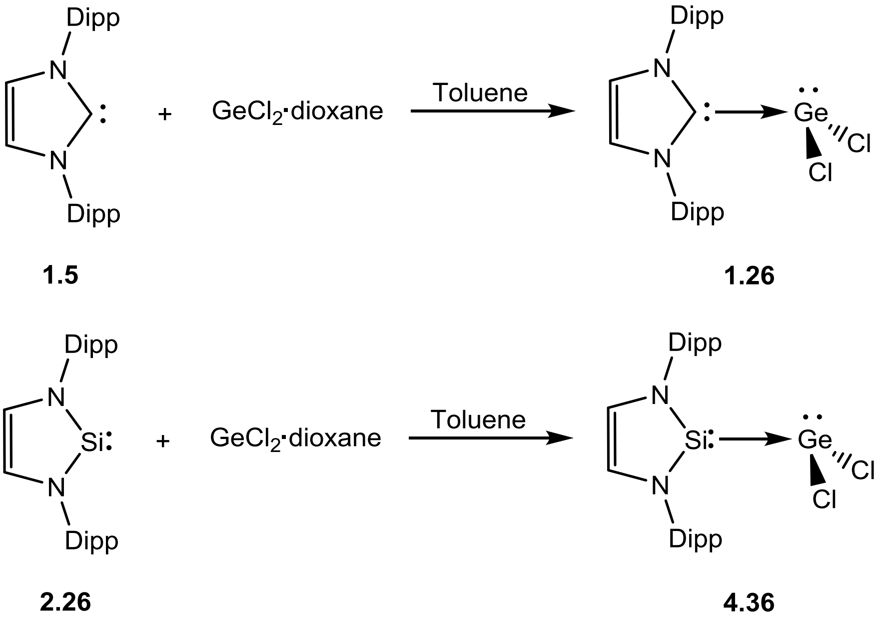
**Figure 4.6:** Molecular structure of $[^{6Ph}CDP\text{-}H]^+[GeCl_3]^-$ **4.34**, (aromatic H atoms omitted for clarity) selected bond lengths (Å) and angles (°): Ge1-$Cl_{avg}$ 2.2902, C1-P1 1.7069(17), C1-P2 1.7075(18), P1-C1-P2 130.35(11)

Unlike the neutral CDP adducts of zinc(II) and aluminium(III) halides, (mentioned in chapters 2 and 3), crystals obtained from the CDP **1.12** and germanium(II) chloride are the salt product $[^{6Ph}DCP\text{-}H]^+[GeCl_3]^-$ **4.34**. The cationic fragment of this salt is observed frequently throughout these types of coordination reactions. It's signal in the $^{31}P\{^1H\}$ NMR spectrum is very similar to that of the neutral CDP ligand **1.12** in neutral adducts ($\Delta\delta$ = *ca.* 1-2 ppm) rendering $^{31}P\{^1H\}$ NMR spectroscopy ineffective in definitively discerning between ionic products and neutral adducts. It is also worth mentioning that the doubly-protonated cationic fragment $[^{6Ph}CDP\text{-}(H)_2]^{2+}$ also has a similar chemical shift in its $^{31}P\{^1H\}$ NMR spectrum and has been known to form from these types of reactions.[22,23]

This reaction was repeated and conditions varied several times using other polar, aprotic solvents, all of which yielded the same singlet (δ 18.1 ppm) in the $^{31}P\{^{1}H\}$ NMR spectrum. It was assumed that the major product of these experiments was the salt product **4.34** described earlier. Hence, further investigations into CDP adducts of germanium(II) chloride were terminated.

It should be noted that soon after ceasing this research, Alcarazo and co-workers reported the successful synthesis of the intended target product, $^{6Ph}CDP{\cdot}GeCl_2$ **1.70**, as well as other related compounds including the tin analogue $^{6Ph}CDP{\cdot}SnCl_2$ **4.35**.[24] The group reported a methodology consistent with that of my research with the exception of toluene being used instead of difluorobenzene as the solvent. Similarly, they report a white precipitate forming quantitatively in the reaction mixture, which they found to be the target material, $^{6Ph}CDP{\cdot}GeCl_2$ **1.70**, via X-ray diffractometry.

Another neutral class of ligands utilized throughout my research were the silicon analogues of NHCs; N-heterocyclic silylenes (NHSi)s (also mentioned in chapter 2). Owing to the success of the NHC adduct, $IPr{\cdot}GeCl_2$,**1.26** reported in 2009,[18] the NHSi **2.26** was used in attempts to synthesize its silylene analogue $NHSi{\cdot}GeCl_2$, **4.36** (scheme 4.16).



**Scheme 4.16**: Comparison of the literature reported NHC-germanium adduct IPr·$GeCl_2$, **1.26** and the proposed synthesis of its NHSi analogue NHSi·$GeCl_2$, **4.36**

A mixture of $GeCl_2$·dioxane and **2.26** in toluene at -80 °C was warmed to room temperature overnight whilst stirring. An aliquot of the reaction mixture revealed no reaction had taken place via $^1H$ NMR spectroscopy. Upon heating, a slow consumption of starting materials, as well as a broad series of resonances were observed in the $^1H$ NMR spectrum, the major product of which was determined to be the silicon(IV) precursor of **2.26**; $^{Dipp}DABSiCl_2$ ($^{Dipp}DAB$ = $\{(2,6\text{-}^iPr_2C_6H_3)NC(H)\}_2$) **4.37**. This phenomenon of reverting back to the silicon(IV) precursor was observed in a number of reactions involving **2.26** and element-chloride fragments including $SiCl_4$, IPr·$SiCl_4$ **1.67**, and IPr·$GeCl_2$, **1.26**.

An asymmetric chloro-silane, **4.38** was isolated from one of the reactions and crystallographically characterized using X-ray diffractometry (figure 4.7). The reaction involved free NHSi, **2.26** and IPr·$GeCl_2$ **1.26** in THF at elevated temperatures. The oxidation of the silicon(II) center to the silicon(IV) via chloride sources was expected however, the newly formed Si-H bonds at the silicon center are presumed to be the result of solvent-hydrogen abstraction.

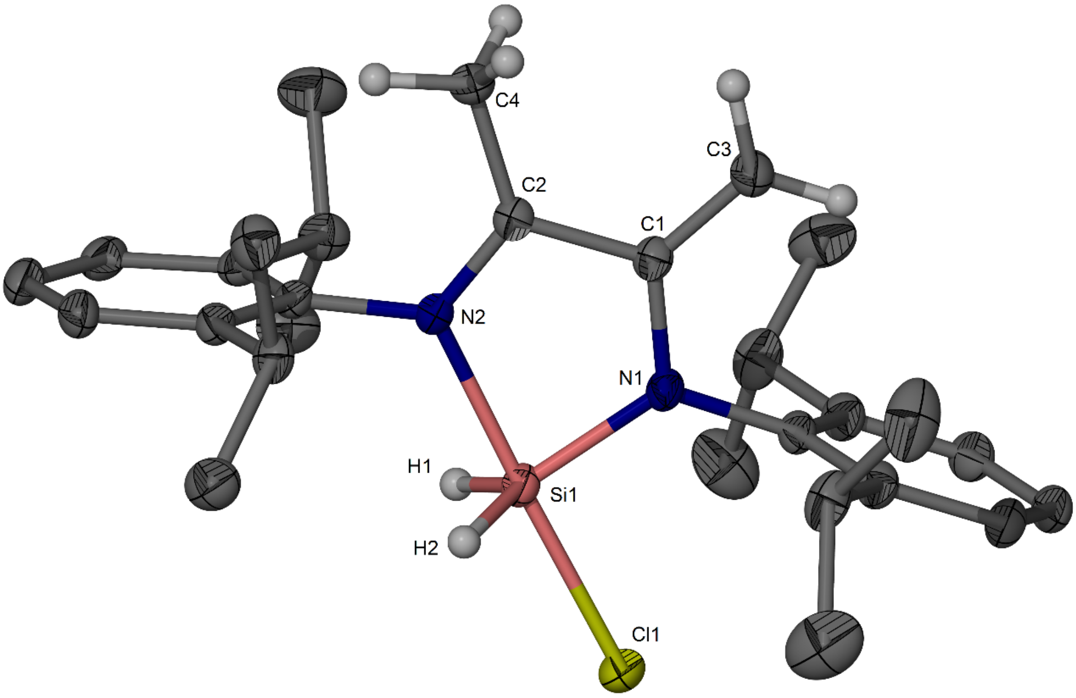
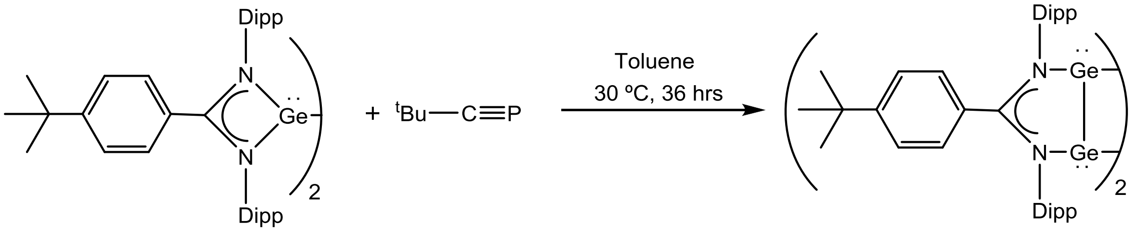


**Figure 4.7:** Molecular structure of **4.38**, (aromatic H atoms omitted for clarity) selected bond lengths (Å) and angles (°): N1-Si1 1.7672(13), N2-Si1 1.9945(14), C1-N1 1.3987(19), C2-N2 1.2892(19), C1-C2 1.475(2), C1-C3 1.344(2), C2-C4 1.483(2), N1-Si1-N2 81.93(6), C2-C1-C3 121.77(14), C1-C2-C4 123.15(13)

The silicon atom is centred in an asymmetric heterocycle. In the solid state, the two N-Si bonds are significantly different in length (1.7672(13) vs. 1.9945(14) Å) as well as having varied C-N (1.2892(19) vs. 1.3987(19) Å) and C-$C_{backbone}$ (1.344(2) Å vs. 1.475(2) Å) bond lengths due to the shortened C=N and C=C double bonds. Attempts to use **2.26** as a neutral donor ligand in the formation of main group element fragments proved unsuccessful. The most common of these outcomes was the oxidative addition of halide (chloride) ions to the central silicon atom of the NHSi, generating its silicon(IV) precursor, **4.37**, as well as a mixture of reduced element fragments (germanium, silicon etc.) which could not be separated from the reaction mixture.

### *4.3.3 Low Oxidation State Amidinato-Group 14 Chemistry*

Another experiment of interest was carried out by former fellow group members Simon Bonyhady and Sam Lim Choong. The reaction involves [(butiso)Ge]$_2$ (butiso = (DippNH)(DippN)C($C_6H_4$*p*-$^t$Bu),[25] **4.39** and $^t$BuC≡P, which unexpectedly produce the $Ge_4$ compound **4.40** with each Ge center in the formal oxidation state of +0.5 (scheme 4.17).

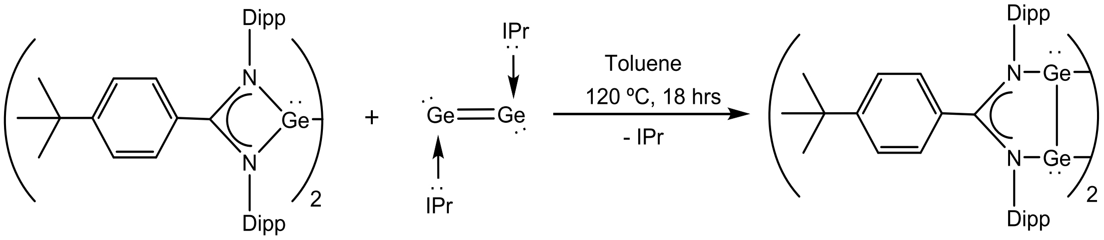


**4.39**

**4.40**

**Scheme 4.17:** Synthesis of the amidinato-$Ge_4$ compound **4.40**, with each germanium atom in the approximate formal oxidation state of +0.5

Extending on this work, a series of experiments were designed in an attempt to synthesize **4.40** in a more targeted approach and consequently improve the yield. One such experiment was designed to test the feasibility of the germanium(0) dimer[17] (IPr·Ge)$_2$, **1.28** as a soluble source of elemental germanium (scheme 4.18).

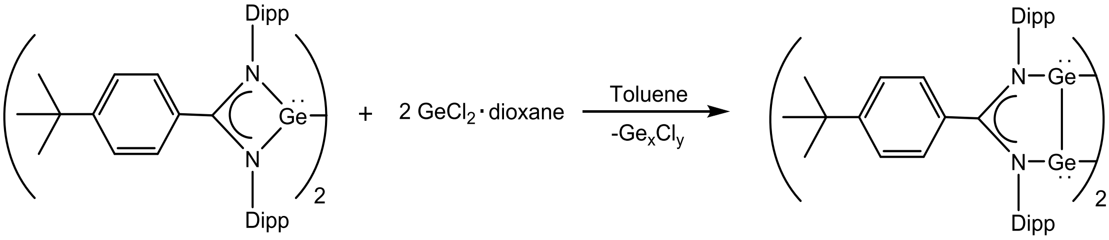


**4.39** **1.28** **4.40**

**Scheme 4.18:** Proposed synthesis of amidinate-$Ge_4$ compound **4.40** using $(IPr{\cdot}Ge)_2$ **1.28** as a soluble source of elemental germanium

Due to the difficulty of obtaining pure **1.28** in high yields, the reaction was carried out on an NMR scale in deuterated benzene. Unfortunately, even after heating the mixture to 120 °C, no reaction takes place. At this point, $(IPr{\cdot}Ge)_2$, **1.28** decomposes to free IPr **1.5** and elemental germanium as determined by $^1H$ NMR spectroscopy.

A similar experiment was carried out with germanium(II) chloride·dioxane, replacing the germanium(0) compound **1.28** with the intent of forming compound **4.40** as shown in scheme 4.19 below.

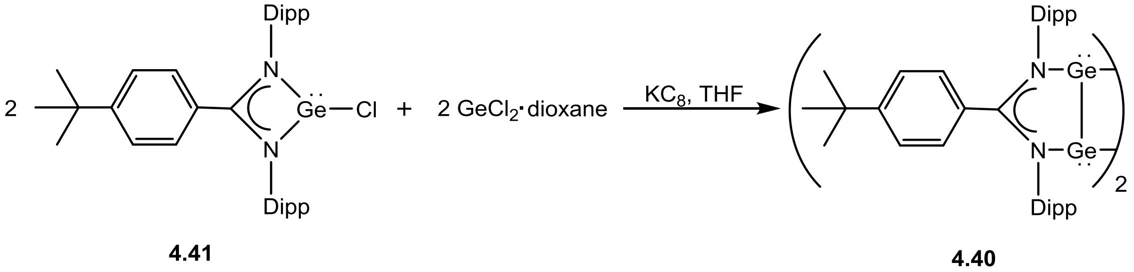


**4.39** **4.40**

**Scheme 4.19:** Proposed synthesis of the amidinate-$Ge_4$ compound **4.40** using germanium(II) chloride·dioxane as a source of germanium

Upon combination of starting materials, the change from a red solution to a murky orange suspension was observed, eventually leading to the almost-complete loss of colour from solution. The solvent was removed *in vacuo* and a small sample of the residual solid was used for $^1$H NMR spectroscopic analysis. The spectrum showed an almost quantitative conversion of the germanium(I) dimer **4.39** to its germanium(II) precursor (butiso)GeCl **4.41**. The immediate colour change indicates a high reactivity between **4.40** and $GeCl_2$.dioxane at room temperature. Therefore, repeating the synthesis at lower temperatures is worth investigating in order to try and isolate any intermediates that may form.

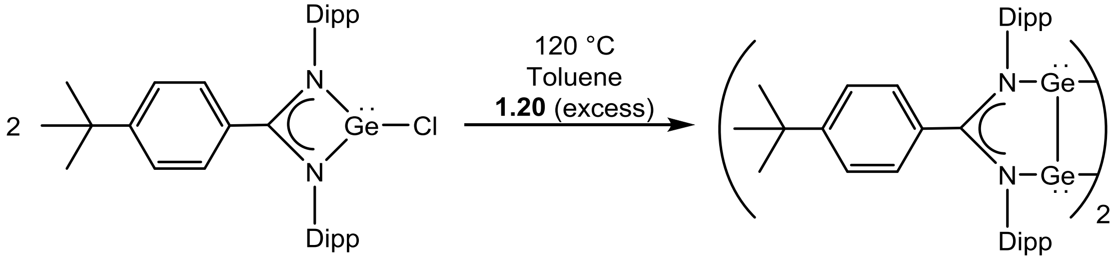
Another attempt to synthesize **4.40** in higher yields involved the addition of a $KC_8$ suspension to a solution containing (butiso)GeCl **4.41** and $GeCl_2$.dioxane at low temperature, shown in scheme 4.20 below.



**Scheme 4.20:** Proposed synthesis of amidinato-$Ge_4$ compound **4.40** via the $KC_8$ reduction of (butiso)GeCl **4.41** in the presence of $GeCl_2$·dioxane

After the suspension was allowed to warm to room temperature, a faint red colour was observed which was later shown to be the germanium(I) dimer **4.39** as the minor product in the $^1$H NMR spectrum of the mixture, the major product being the free ligand, butisoH, **4.42,** suggesting that $KC_8$ may be too harsh a reducing agent to isolate **4.40**, instead, reducing the germanium centers to their elemental form.

With this in mind, attempts to synthesise **4.40** using the previously mentioned magnesium(I) dimer **1.20** as a less harsh alternative to classical reducing agents. A slight excess of [{$^{Mes}$nacnac}Mg$^{I}$]$_2$ **1.20** was added to a solution of (butiso)GeCl **4.41** in order to try and 'over-reduce' the germanium atoms beyond the +1 oxidation state of **4.39**, forming the Ge$_4$ compound **4.40** as shown in scheme 4.21 below.



**4.41**

**4.40**

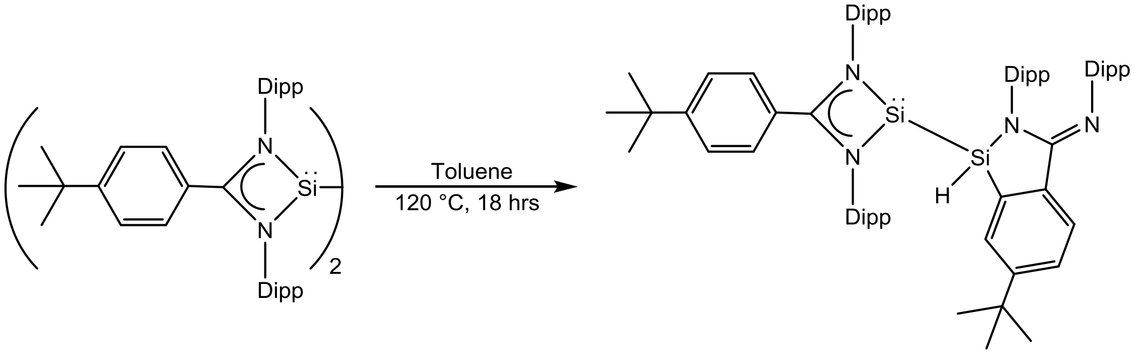
**Scheme 4.21:** Attempted synthesis of amidinato-Ge$_4$ compound **4.40** by 'over-reducing' the germanium(II) compound (butiso)GeCl **4.41** with an excess of [{$^{Mes}$nacnac}Mg$^{I}$]$_2$ **1.20**

After stirring for several days at room temperature an aliquot of the solution was taken and analyzed by $^1$H NMR spectroscopy. The spectrum revealed the minute formation of a new product which was thought to be the desired Ge$_4$ compound **4.40**. Fractional crystallization eventually yielded trace amounts of amber coloured crystals, which when analyzed via X-ray diffractometry, corresponded to **4.40**. However due to the minute yield and irreproducibility of this product, no NMR data were collected on a pure sample of **4.40**. It is also worth mentioning that the same experiment was carried out using the [(butiso)Ge]$_2$ dimer **4.39** with an excess of [{$^{Mes}$nacnac}Mg$^{I}$]$_2$ **1.20** which achieved similar results. Even with multiple, targeted approaches, the low yield, purity and reproducibility of the novel compound **4.40** lead to the termination of this research.

### 4.3.4 *Low Oxidation State Amidinato-Silicon Complexes and the Formation of an Amidinate Silicon-Hydride Complex*

After observing the large success in the use of amidinate and guanidinate ligands in the last few decades,[14,25,26] steps were taken to incorporate these compounds in novel low oxidation state silicon and germanium species. Extending the work done on the amidinate silicon(I) and germanium(I) compounds reported by the Jones group[14] in 2011 was the focus of this research.

Attempts to hydrogenate the silicon(I) amidinate complex $(ButisoSi)_2$ **4.43** (Butiso = $(DippNH)(DippN)-C(C_6H_4{}^tBu-4)$; Dipp = $C_6H_3{}^iPr_2-2,6$) with silicon hydrides ($PhSiH_3$, $Et_3SiH$) were carried out at elevated temperatures. The initially blue coloured solution gradually changes to yellow over several days at reflux. The colour change was initially thought to be the effect of the silicon hydrides. However, the result was simply caused by the addition of heat to the system, resulting in the isomerization of **4.43** yielding the mixed valent silicon hydride complex $(ButisoSi)_2$* **4.44** shown in scheme 4.22 below.



**4.43** **4.44**

**Scheme 4.22:** Isomerization of silicon(I) complex **4.43** yielding a mixed valent silicon hydride complex, **4.44**

It is worth mentioning that the experiment was repeated using only **4.43** and heat (absence of silicon hydrides), yielding the same result. The asymmetric silicon hydride, dubbed $(ButisoSi)_2$* **4.44**, is the isomerized product of heating the $(ButisoSi)_2$ precursor to reflux for extended periods of time. One half of the dimer is kept intact, while the other silicon center has undergone C-H insertion with the ortho C-H bond from the aromatic ligand backbone. Heating this complex to higher temperatures or longer periods of time did not lead to further isomerization.

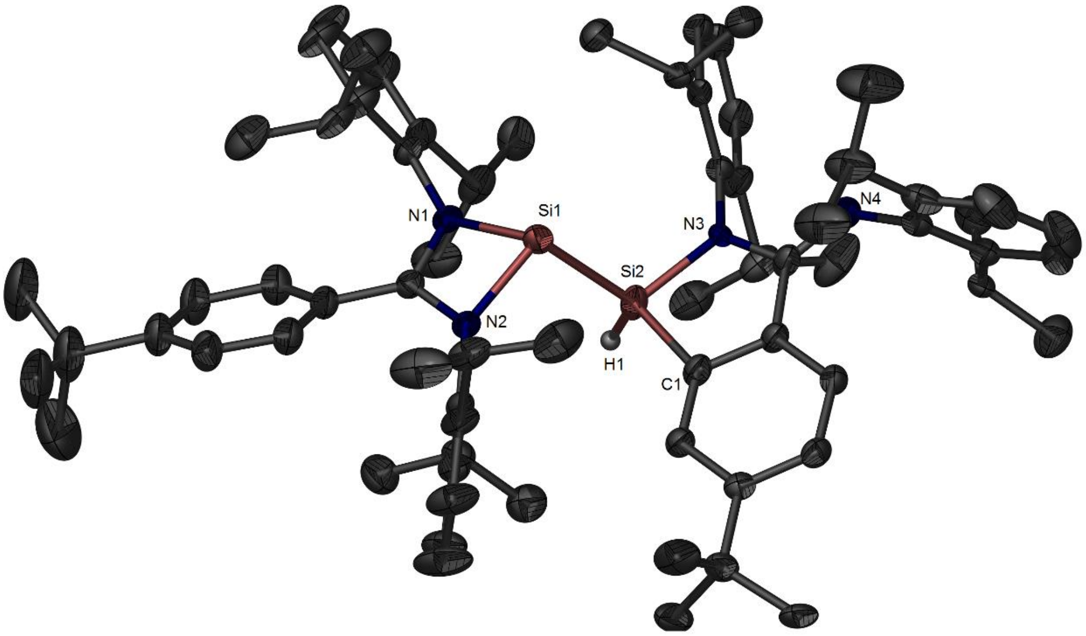


**Figure 4.8:** Molecular structure of a mixed valent silicon hydride compound **4.44** (H atoms omitted for clarity, except Si-H) selected bond lengths (Å) and angles (°): Si1-Si2 2.3938(8), Si2-H1 1.426(18), Si1-N1 1.8659(15), Si2-N3 1.847(3), Si2-C1 1.8752(17), Si1-Si2-H1 121.2(8)

The NMR spectra of **4.44** are complicated due to the asymmetric nature of the compound and the broadening of multiplets caused by silicon-hydride coupling. However, it is clear from the $^1$H NMR spectrum that no remaining **4.43** is present and the formation of any free ligand (ButisoH) is also absent. In general, the symmetric patterns that were apparent in the $^1$H NMR spectrum of **4.43** are absent in that of **4.44**, with most resonance types now appearing twice due to the asymmetric nature of **4.44**. It is also worth mentioning that the same experiment was conducted using the ButisoGe and ButisoSn analogues which only gave decomposition products such as elemental germanium, tin and free ButisoH.

## *4.4 Experimental*

**Preparation of [$^6$IPrBr]$^+$[Br]$^-$ (4.24):** Toluene solutions of $^6$IPr (0.398 g, 0.98 mmol, 20 mL) and $CBr_4$ (0.328 g, 0.98 mmol, 20 mL) were cooled to -80 °C and combined via cannula ($CBr_4$ added to $^6$IPr), resulting in a fluorescent yellow mixture. The resultant suspension was stirred overnight at 20 °C over which time, **4.24** precipitates from solution as a black solid. The mixture was then filtered, with residues dried *in vacuo,* and filtrate placed at -30 °C overnight to yield a crystalline crop of **4.24**. Yield: 0.490g (83 %); Compound **4.24** is highly insoluble in common laboratory solvents, making it difficult to obtain conclusive spectroscopic data.

**Preparation of $^6$IPr·$GeCl_2$ (4.25):** Toluene (50 mL) was added to a Schlenk flask containing a mixture of $^6$IPr (0.500 g, 1.24 mmol) and $GeCl_2$·dioxane (0.287 g, 1.24 mmol) at room temperature and left to stir overnight. The resultant suspension was filtered and concentrated to *ca.* 20 mL and placed at -30 °C overnight to yield **4.25** as a crystalline solid. Yield: 0.385 g (57 %); M.p.: 174 – 176 °C; $^1$H NMR (400 MHz, 298 K, $C_6D_6$): $\delta$ 1.11 (d, 12H, $CH(CH_3)_2$), 1.53 (d, 12H, $CH(CH_3)_2$), 1.67 (m, 2H, $CH_2CH_2CH_2$), 3.10 (t, 4H, $NCH_2CH_2$), 3.29 (sept, 4H, $CH(CH_3)_2$), 7.12 (d, 4H, *m*-Ar-*H*), 7.28 (t, 2H, *p*-Ar-*H*) ppm;

$^{13}C\{^1H\}$ NMR (75 MHz, 298 K, $C_6D_6$): $\delta$ 20.1 ($CH_2CH_2CH_2$), 24.0 ($CH(CH_3)_2$), 27.6 ($CH(CH_3)_2$), 29.7 ($CH(CH_3)_2$), 52.6 ($NCH_2CH_2$), 124.8 (*p*-Ar), 126.6 (*m*-Ar), 129.9 (*o*-Ar), 131.8 (*i*-Ar) ppm.

**Preparation of $^{Me}$IPr·GeCl$_2$ (4.28).** Toluene (50 ml) was added to a mixture of $^{Me}$IPr (0.305 g, 1.22 mmol) and crystalline $GeCl_2$·dioxane (0.283 g, 1.22 mmol) and the resultant suspension was stirred overnight at 20 °C, during which time **4.28** deposited as a colorless crystalline solid. The solid was isolated by filtration and the mother liquor concentrated *in vacuo* to *ca.* 20 ml. After placing at -30 °C overnight an additional crop of **4.28** was obtained. Yield: 0.220 g (36%). $^1H$ NMR (400 MHz, 298 K, $C_6D_6$): $\delta$ 0.98 (d, 12H, $CH(CH_3)_2$), 1.42 (s, 6H, $^{im}CCH_3$), 1.47 (d, 12H, $CH(CH_3)_2$), 2.73 (sept, 4H, $CH(CH_3)_2$), 7.11 (d, 4H, Ar-C*H*), 7.25 (t, 2H, Ar-C*H*); $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $C_6D_6$): $\delta$ 24.9 ($CH_3$), 25.1 ($^{im}CCH_3$), 29.6 ($C(CH_3)_2$), 125.4 (*m*-Ar-*C*), 129.1 ($^{im}CH$), 131.7 (*p*-Ar-*C*), 132.0 (*o*-Ar-*C*), 146.8 (*ipso*-Ar-*C*), 173.5 ($N_2C$).

**Preparation of (IPr·Sn)$_2$ (4.31).** Diethylether (10 ml, -80 °C) was added to a mixture of IPr·SnCl$_2$ **4.30** (0.120 g, 0.21 mmol) and [($^{Mes}$nacnac)Mg]$_2$ **1.20** (0.150 g, 0.21 mmol) at -80 °C. Upon dissolution of the reactants, the solution immediately took on a deep red/brown color with high amounts of metal precipitating from solution. After stirring the reaction mixture for 30 min, the suspension was left to warm to room temperature, giving the solution a green colour. The suspension was concentrated *in vacuo* to *ca.* 4 mL, filtered and the filtrate stored at -30 °C to yield red crystals of **4.31**. Yield: trace. M.p.: 40 – 60 °C, melts then decomp. giving a black solid at *ca.* 95 °C; $^1H$ NMR (400 MHz, 298 K, $C_7D_8$): $\delta$ 1.09 (d, 24H, $CH(CH_3)_2$), 1.28 (d, 24H, $CH(CH_3)_2$), 3.01 (sept, 8H, $CH(CH_3)_2$), 6.67 (s, 4H, C*H*), 7.01 (m, 8H, *m*-C*H*), 7.21 (m, 4H, *p*-C*H*); $^{13}C\{^1H\}$ NMR (100.6 MHz, 298K, $C_6D_6$): δ 23.6 (*C*$H_3$), 25.9 (*C*$H_3$), 29.2 (*C*($CH_3$)$_2$), 124.1 ($^{im}$*C*H), 125.6 (*m*-Ar-*C*), 127.5 (*p*-Ar-*C*), 138.9 (*i*-Ar-*C*), 145.9 (*o*-Ar-*C*), 210.3 ($N_2$*C*).

**Preparation of IPr·PbBr$_2$ (4.33):** Tetrahydrofuran (60 mL) was added to a mixture of IPr (0.500 g, 1.29 mmol) and $PbBr_2$ powder (0.472 g, 1.29 mmol) in a 250 mL Schlenk Flask and the resultant suspension was stirred overnight at 20 °C, during which time **4.33** deposited as a colorless crystalline solid. All volatiles were removed *in vacuo* and the residues extracted into toluene (2 x 30mL) and filtered. The solvent volume was decreased to *ca.* 30 mL and the Schlenk flask placed in a -30 °C freezer overnight during which time colourless **4.33** crystallized from solution. Yield: 0.895 g (92 %). M.p.: 230 – 235 °C, darkening of the solid occurs between 205 – 220 °C; $^1$H NMR (300 MHz, 298 K, $C_6D_6$): *δ* 1.06 (d, 12H, CH(C*H*$_3$)$_2$), 1.36 (d, 12H, CH(C*H*$_3$)$_2$), 2.86 (sept, 4H, C*H*($CH_3$)$_2$), 6.56 (s, 2H, C*H*), 7.13 (m, 4H, Ar-C*H*), 7.26 (m, 2H, Ar-C*H*). $^{13}$C{$^1$H} NMR (100 MHz, 298K, $C_6D_6$): δ 24.7 (*C*$H_3$), 25.4 (*C*$H_3$), 29.5 (*C*($CH_3$)$_2$), 124.2 ($^{im}$*C*H), 124.8 (*m*-Ar-*C*), 130.8 (*p*-Ar-*C*), 136.8 (*i*-Ar-*C*), 146.7 (*o*-Ar-*C*), 218.9 ($N_2$*C*). MS/ESI *m/z* (%): 389.1 (Ligand-H$^+$), correct isotope pattern, 100); IR (Nujol): 1604m, 1588m, 1553w, 1388s, 1366s, 1325s, 1284m, 1255m, 1231s, 1210s, 1180m, 1118m, 1092m, 1074m, 1062, 945m, 934m, 924m, 808s, 802s, 757s, 697s, 687w.

**Preparation of [$^{6Ph}$CDP-H]$^+$[GeCl$_3$]$^-$ (4.34)** Difluorobenzene (0 °C, 10 mL) was added to a mixture of $^{6Ph}$CDP (0.500 g, 0.932 mmol) and $GeCl_2$·dioxane (0.216 g, 0.932 mmol) in a 100 mL Schlenk Flask and the resultant suspension was warmed to room temperature and stirred overnight at 20 °C, during which time **4.34** deposited as an amorphous white solid. The suspension was filtered and the solvent volume was decreased to ca. 2 mL and the Schlenk flask placed in a 0 °C fridge overnight, during which time colourless **4.34** crystallized from solution. Yield: 0.410 g (61 %). M.p.: 184 – 189 °C, $^1$H NMR (400 MHz, 298 K, $C_6D_6$): *δ* 6.92 (m, 12H, *o*-Ar-C*H*), 6.95 (m, 12H, *m*-Ar-C*H*), 7.87 (t, 6H, *p*-Ar-*H*) ppm; $^{31}$P NMR (121 MHz, 298 K, $C_6D_6$) ppm: δ 18.9 (s, $Ph_3$*P*) ppm; IR u/cm$^{-1}$ (Nujol): 1452s, 1376s, 1255s, 1099s, 1079s, 1051s, 872w, 785s, 768s, 732s, 726m, 690m.

**Preparation of (ButisoSi)$_2$* (4.44):** Benzene (20 mL) was added to (ButisoSi)$_2$ **4.43** (0.094 g, 0.090 mmol in a 100 mL Young Schlenk Flask and the resultant suspension was stirred for four days at reflux, during which time the solution gradually changes from blue to yellow. The solvent volume was decreased to *ca.* 2 mL and transferred to a layering tube via cannula. Pentane (20 mL) was layered on top of the solution and placed at 0 °C overnight, during which time, yellow crystals of **4.44** deposited from solution. Yield: 0.032 g (34 %). M.p.: 231 – 236 °C (decomp.); $^1$H NMR (400 MHz, 298 K, $C_6D_6$): *δ* 0.96 (s, 6H,C(C*H*$_3$)$_3$), 0.98 (s, 6H,C(C*H*$_3$)$_3$), 1.00 (s, 6H,C(C*H*$_3$)$_3$), 1.00 – 1.40 (series of overlapping d, br, 48H, CH(CH$_3$)$_2$), 3.34 (sept, br, 2H, C*H*(CH$_3$)$_2$), 3.58 (sept, br, 2H, C*H*(CH$_3$)$_2$), 3.62 (sept, br, 2H, C*H*(CH$_3$)$_2$), 3.72 (sept, br, 2H, C*H*(CH$_3$)$_2$), 6.39 (s, br, 1H, Si-*H*), 6.76 – 7.37 (m, 19H, Ar-H).

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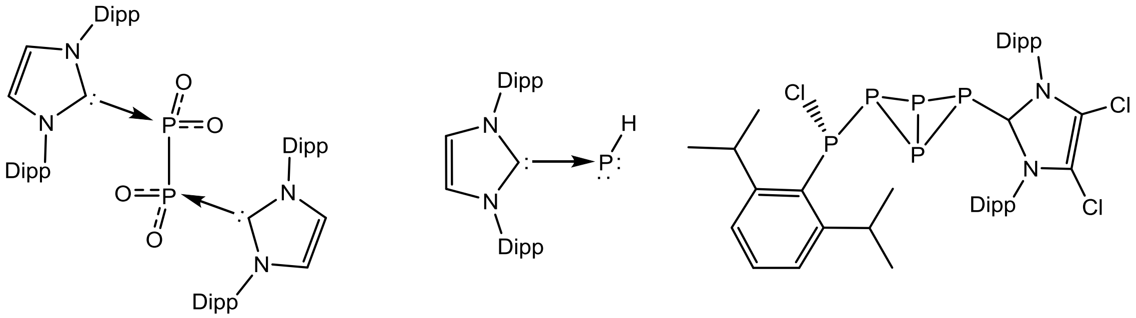
# *5 Low Oxidation State Group 15 Compounds*

## *5.1 A Further Introduction into NHC- and NHC Analogue-Adducts of Group 15 Complexes*

Since the report of the NHC-coordinated phosphorus(0) dimer $(IPr{\cdot}P)_2$ **1.89** (mentioned in chapter 1),[1] several communications regarding similar NHC-phosphorus systems, including $[IPr{\cdot}P(O)_2]_2$ **5.1**,[2] the monomeric, NHC-stabilized, parent phosphinidine, IPr·PH **5.2**[3] and the $P_5$ centered compound **5.3**[4] (figure 5.1) have appeared.

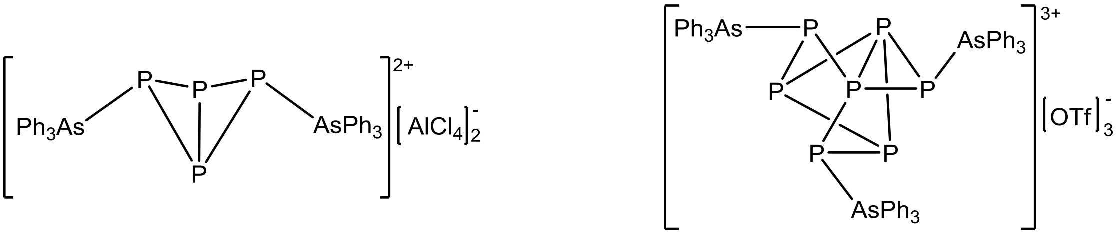


**5.1** **5.2** **5.3**

**Figure 5.1:** NHC adducts of various phosphorus containing compounds **5.1 – 5.3**

Compound **5.1** highlights the reactivity of its precursor, $(IPr{\cdot}P)_2$ **1.89** which cleaves molecular oxygen, and thus sheds light on the nature of the heavier analogue of $N_2O_4$, $P_2O_4$, which previously, had only been studied in the gas phase or in matrix isolation experiments.[5] Of particular interest to my research, **5.3** bears a close resemblance to that of an NHC capped $P_4$ compound which will be discussed later in this chapter.

NHC adducts of the remaining group 15 elements are scarcely reported throughout the literature,[6-14] however, other neutral donor adducts of group 15 elements are documented, including the cyclo-amino-alkyl carbene (cAAC)-coordinated antimony compounds cAAC·SbCl$_n$ (n = 1, 2, 3; **1.92 – 1.94**) and (cAAC·Sb)$_2$ **1.95** (mentioned in chapter 1) and the Ph$_3$As-coordinated P$_4$ **5.4** and P$_7$ **5.5** centered compounds depicted in figure 5.2 below.[15]



**5.4** **5.5**

**Figure 5.2:** Ph$_3$As-coordinated P$_4$ and P$_7$ compounds **5.4** and **5.5**

Compound **5.4** is of particular interest as it is the Ph$_3$As analogue of an NHC coordinated P$_4$ compound developed herein. In these types of compounds, the role of the "neutral donor" ligand as well as the choice of counter-ion play a significant role in the stability of the product formed.

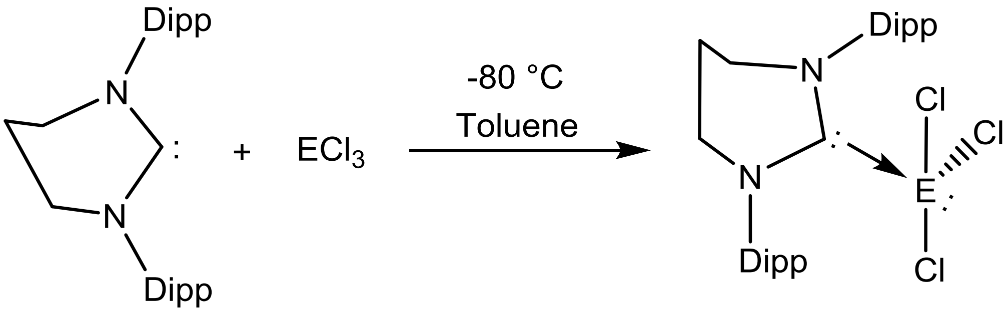
## *5.2 Research Outline*

NHC adducts of MG and TM elements have had a significant impact in recent literature largely due to their unprecedented chemical structures and unique chemical properties. Extending on from this trend, (6-membered) NHC adducts of group 15 element halides, were synthesized and subsequently reduced using a variety of reducing agents including the magnesium(I) dimer {($^{Mes}$nacnac)Mg}$_2$, ($^{Mes}$nacnac = {[(Mes)NC(Me)]$_2$CH}$^-$, Mes = mesityl) **1.20** in attempts to form their corresponding LOS compounds, and to investigate the further chemistry of these products.

## ***5.3 Results and Discussion***

### ***5.3.1 Synthesis of NHC Adducts of Group 15 Elements (Phosphorus, Arsenic, Antimony and Bismuth) and Their Reductions***

Using a similar methodology to that for group 12, 13 and 14 elements, 5- and 6-membered NHCs were used to form coordination adducts of group 15 elements. Together with a former group member (Brooke Osborne), $^6$IPr, **2.24** was reacted with ECl$_3$ (E = P, As, Sb,) and BiBr$_3$ in 1:1 ratios at -78 °C to give moderate yields of the corresponding $^6$IPr·ECl$_3$ adducts **5.6 – 5.8**.[6]



E = P; **5.6**
As; **5.7**
Sb; **5.8**

**2.24**

**Scheme 5.1:** Synthesis of the $^6$IPr-group 15 element halide adducts **5.6 – 5.8**

The $^6$IPr·BiBr$_3$ adduct is absent from scheme 5.1, as even at low temperatures, the reaction results in an intractable mixture from which, no readily identifiable products could be isolated. It should also be mentioned that when the reaction between **2.24** and PCl$_3$ is performed at room temperature, the $^{31}$P{$^1$H} NMR spectrum of the reaction mixture reveals resonance patterns of several unidentified products, as well as two identifiable products; $^6$IPr·PCl$_3$ **5.6** ($\delta$ = -10.9 ppm) and $P_2Cl_4$ ($\delta$ = 156.1 ppm). The presence of $P_2Cl_4$ is likely due to $^6$IPr acting as a reducing agent towards PCl$_3$, an effect also observed with 5-membered NHCs.[16,17]

Compounds **5.6** – **5.8** were analyzed by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy which showed them to exhibit resonance patterns indicative of symmetric compounds in solution at room temperature. The N*C*N carbene resonance was only observed in the $^{13}$C{$^1$H} NMR spectrum of **5.7** ($\delta$ = 180.8 ppm). The absence of the N*C*N carbene resonance of compounds **5.6** and **5.8** is a feature common to NHC adducts of main group element halides.[18,19] In contrast, **5.7** could not be isolated as a crystalline solid. However, **5.6** and **5.8** were analyzed via single crystal X-ray diffractometry, yielding the structures shown in figures 5.4 and 5.5 below.

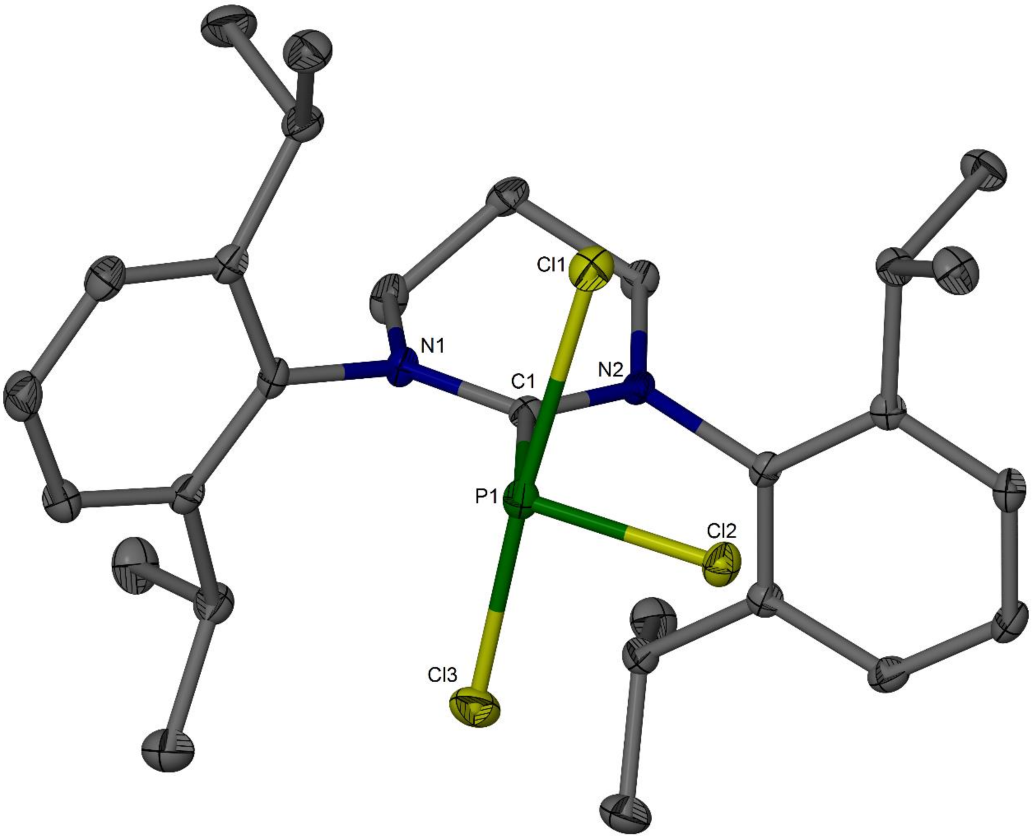


**Figure 5.4**: Molecular structure of $^6$IPr·PCl$_3$ **5.6** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): P1-C1 1.9234(14), P1-Cl1 2.2209(7), P1-Cl2 2.0642(8), P1-Cl3 2.4406(7), C1-N1 1.3409(17), C1-N2 1.3336(18), C1-P1-Cl2 106.68(5), C1-P1-Cl1 92.71(5), Cl2-P1-Cl1 89.48(2), C1-P1-Cl3 83.78(5), Cl2-P1-Cl3 87.26(2), Cl1-P1-Cl3 174.31(2), N2-C1-N1 119.60(12)

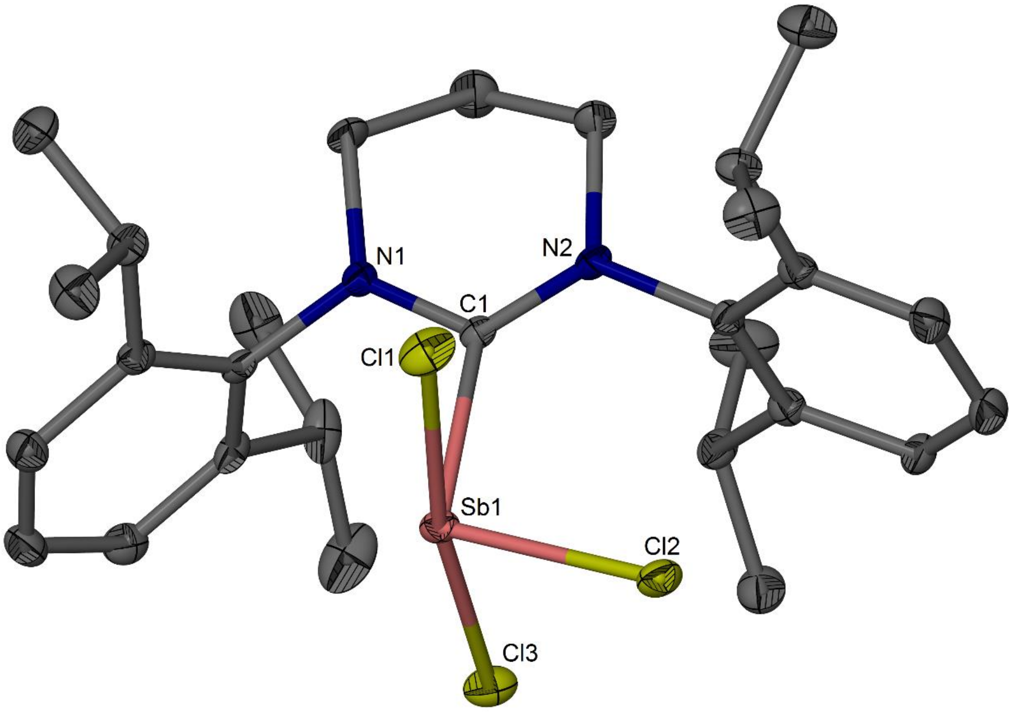
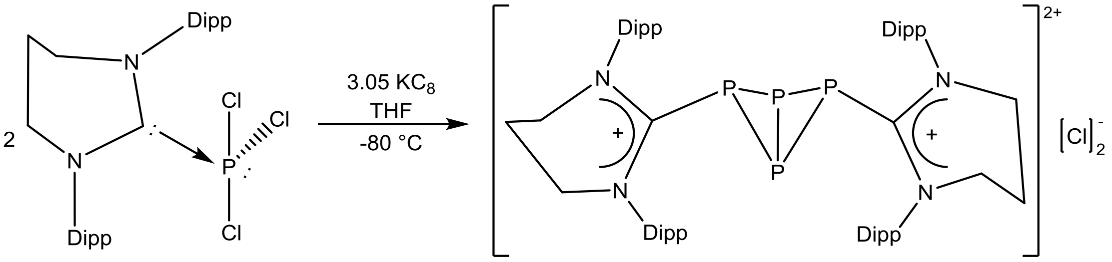


**Figure 5.5**: Molecular structure of $^{6}$IPr·SbCl$_3$ **5.8** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): C1-Sb1 2.288(2), Sb1-Cl2 2.3692(6), Sb1-Cl1 2.5260(7), Sb1-Cl3 2.5760(7), N1-C1 1.334(3), C1-N2 1.331(3), C1-Sb1-Cl2 102.61(6), C1-Sb1-Cl1 94.75(6), Cl2-Sb1-Cl1 87.59(2), C1-Sb1-Cl3 81.40(6), Cl2-Sb1-Cl3 85.35(2), Cl1-Sb1-Cl3 171.01(2), N2-C1-N1 120.3(2)

The crystal structures of **5.6** and **5.8** are virtually isostructural with the group 15 element centers in distorted see-saw geometries. Cl1 and Cl3 occupy the axial positions while C1, Cl2 and a stereochemically active lone pair occupy the equatorial positions – a common feature of carbene coordinated group 15 trichlorides. The C1-E1-Cl2 bond angle of **5.8** (102.61(6) °) is smaller than that of **5.6** (106.68(5) °), indicative of the higher s-character lone pair of **5.8**. The sterically demanding character of the $^{6}$IPr ligand is evident in the C-E bond lengths of **5.6** (1.9234(14) Å) and **5.8** (2.288(2) Å), on average, slightly longer than those of other respective carbene-ECl$_3$ compounds.[8a,13,14,20,21] In the case of **5.8**, the axial Sb-Cl$_{avg}$ bond lengths (2.551 Å) are significantly longer than the equatorial Sb1-Cl2 bond length (2.0642(8) Å). However, this is not the case in **5.6** which has one axial P-C bond (P1-Cl1, 1.9231 Å) and one equatorial P-C bond (P1-Cl2, 2.0642(8) Å) similar in length, whereas the other axial P-C bond (P1-Cl3, 2.4406(7) Å) is *ca.* 0.4 Å longer than the other P-Cl bonds. This type of arrangement can be thought of as a contact ion pair, also observed in the previously reported [IPr·PCl$_2$][OTf], **5.9**.[11] This pattern is also observed in the five-membered analogue, IPr·PCl$_3$ **1.88**.[7]

Attempts were made to reduce the group 15 adducts **5.6** – **5.8** using various reducing agents including alkalai metals sodium, potassium, KC$_8$ as well as the magnesium(I) dimer {($^{Mes}$nacnac)Mg}$_2$, ($^{Mes}$nacnac = {[(Mes)NC(Me)]$_2$CH}$^-$, Mes = mesityl) **1.20**. Almost all of these reactions gave intractable mixtures, however, the reduction of **5.6** with KC$_8$ resulted in the formation of an ionic P$_4$ complex **5.11** as a green crystalline solid, shown in scheme 5.2 and figure 5.6 below.



**5.6** **5.11**

**Scheme 5.2:** KC$_8$ reduction of **5.6** resulting in the ionic P$_4$ compound, [($^6$IPr)$_2$(μ-P$_4$)][Cl]$_2$ **5.11**

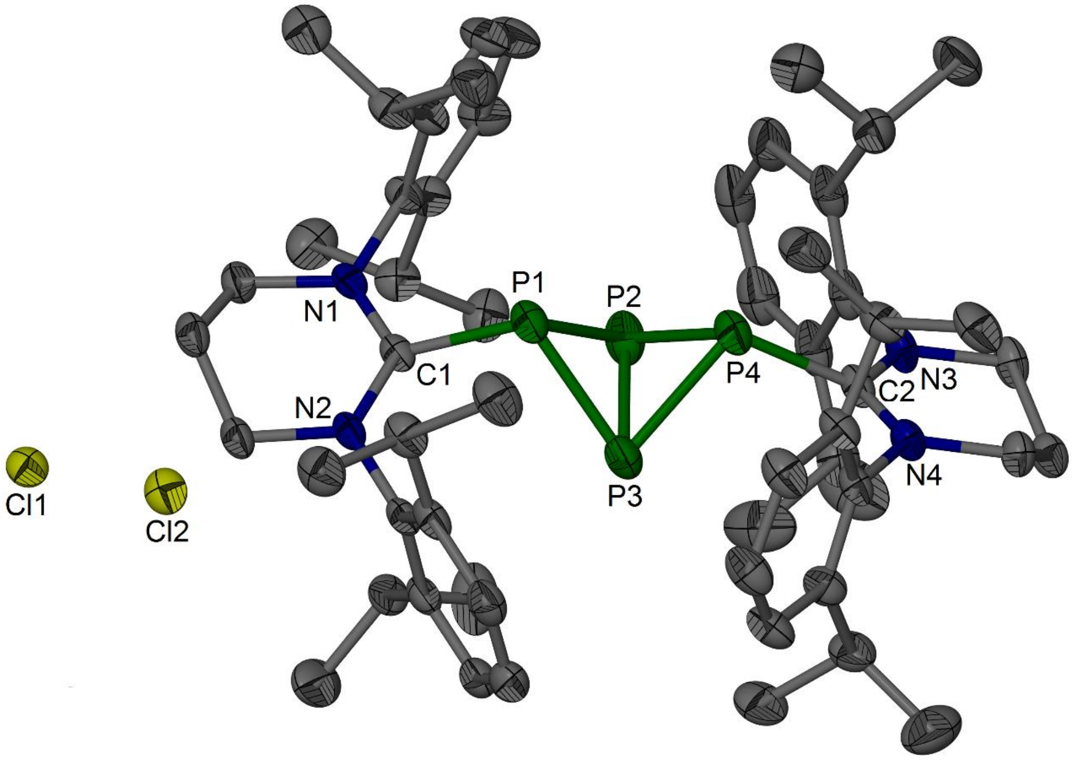


**Figure 5.6**: Molecular structure of [($^6$IPr)$_2$(μ-$P_4$)][Cl]$_2$ **5.11** (H atoms omitted for clarity) selected bond lengths (Å) and angles (°): P1-C1 1.895(3), P4-C2 1.892(3), P1-P3 2.1952(14), P1-P2 2.2077(13), P2-P4 2.2050(15), P2-P3 2.2063(16), P3-P4 2.2056(13), N1-C1 1.326(4), C1-N2 1.330(4), N3-C2 1.322(4), N4-C2 1.328(4), C1-P1-P3 108.85(11), C1-P1-P2 106.13(11), C2-P4-P2 108.22(11), C2-P4-P3 105.29(10), P3-P1-P2 60.14(5), P2-P4-P3 60.03(5), P4-P2-P1 75.84(5), P1-P3-P4 76.09(5).

It should be mentioned that the $P_4$ compound **5.11** could also be synthesized using $^6$IPr and $PCl_3$ in a 1:2 ratio, albeit in lower yields. In this case, the carbene reduces the $PCl_3$, a methodology previously reported for carbenes and phosphorus halides,[16,17] also producing the oxidation product [$^6$IPr-Cl][Cl]. The $^{31}P\{^1H\}$ NMR spectrum of **5.11** exhibits a relatively simple $A_2X_2$ system ($\delta_A$ = -325.4 ppm, $\delta_X$ = -167.0 ppm, $^1J_{AX}$ = 184 Hz) similar to that of the previously reported [($Ph_3As$)$_2$(μ-$P_4$)][$AlCl_4$]$_2$ **5.4** ($\delta_A$ = -325.9 ppm, $\delta_X$ = -

175.9 ppm, $^1J_{AX}$ = 160 Hz)[15a] suggesting **5.11** to be an ion-separate salt. In contrast, the *endo*-, *exo*-substituted $P_5$ compound **5.3** (mentioned above) exhibits a more complex ACEMX spin system due to the extra phosphorus atom and the asymmetric substitution of the central $P_4$ tetrahedron. The central $P_4$ tetrahedron however, exhibits similar, yet upfield-shifted chemical shifts in the $^{31}P\{^1H\}$ NMR spectrum ($\delta_A$ = –271.7 ppm, $\delta_C$ = –260.4 ppm, $\delta_E$ = –138.8 ppm, $\delta_M$ = –89.8 ppm, $^1J_{PP(external)}$ = (212.0 - 216.1 Hz)).[4] Figure 5.6 shows the solid state structure of **5.11** to have a central $P_4$ core, consisting of two, essentially equilateral triangles, joined in a butterfly arrangement. The $P_4$ core is capped by two $^6$IPr ligands in an *exo*-, *exo*-fashion, with two, distant chloride counter-ions. All P-P bond lengths (2.204 Å mean) are equivalent within error and both C-P distances (1.894 Å mean) are consistent with previously reported single bonds of similar systems.[22] The bond lengths and bond angles of the $P_4$ core in **5.11** are remarkably close to that of white phosphorus, however, more electronic and computational studies need to be undertaken to determine the electron density pattern of the $P_4$ core and the cation as a whole.

## *5.4 Experimental*

**Preparation of $^6$IPr·PCl$_3$ (5.6):** To a solution of $PCl_3$ (0.137 g, 0.087 mL, 1.00 mmol) in toluene (30 mL) at -78 °C was added to a solution of $^6$IPr **2.24** (0.405 g, 1.00 mmol) in toluene (15 mL). The mixture was warmed to ambient temperature, stirred for 30 minutes, then volatiles were removed *in vacuo*. The residue was extracted into benzene (40 mL), the extract concentrated *in vacuo* to 15 mL, then placed at 5 °C overnight to yield colourless crystals of **5.6** (0.46 g, 84 %). M.p: 145 – 147 °C (decomp.); $^1$H NMR (400 MHz, 298 K, $C_6D_6$): $\delta$ = 1.11 (d, 12H, CH(C$H_3$)$_2$), 1.57 (d, 12H, CH(C$H_3$)$_2$), 1.87 (m, 2H, CH$_2$C$H_2$CH$_2$), 3.60 (t, 4H, NC$H_2$CH$_2$), 3.85 (sept, 4H, C$H$(CH$_3$)$_2$), 7.07 (d, 4H, *m*-Ar-*H*), 7.14 (t, 2H, *p*-Ar-*H*); $^{13}C\{^1H\}$ NMR (75 MHz, 298 K, $C_6D_6$): $\delta$ = 20.8 (CH$_2$$C$H$_2$CH$_2$),

24.7 (CH(*C*H$_3$)$_2$), 27.6 (CH(*C*H$_3$)$_2$), 30.0 (*C*H(CH$_3$)$_2$), 55.7 (N*C*H$_2$), 125.9 (Ar-*C*), 131.6 (Ar-*C*), 137.4 (Ar-*C*), 148.2 (Ar-*C*), N*C*N signal not observed; $^{31}$P{$^1$H} NMR (121 MHz, 298 K, C$_6$D$_6$): δ = -10.9; MS/EI *m/z* (%): 542.2 (M$^+$, 1), 439.3 ($^6$IPr-Cl$^+$, 20), 405.3 ($^6$IPr-H$^+$, 100); IR (ATR) *v*/cm$^{-1}$: 1652m, 1551w, 1317m, 1256w, 1100w, 1057w, 812m, 756m, 723m, 684m; anal. calcd. for C$_{28}$H$_{40}$N$_2$PCl$_3$: C, 62.05%; H, 7.44%; N, 5.17%; found: C, 61.90%; H, 7.33%; N, 5.07%.

**Preparation of $^6$IPr·AsCl$_3$ (5.7):** To a solution of AsCl$_3$ (0.181 g, 0.084 mL, 1.00 mmol) in toluene (20 mL) at -78 °C was added to a solution of $^6$IPr **2.24** (0.40 g, 0.99 mmol) in toluene (15 mL). The mixture was warmed to ambient temperature, stirred for 30 minutes, before volatiles were removed *in vacuo*. The residue was extracted into benzene (30 mL), the extract concentrated *in vacuo* to 10 mL, then placed at 5 °C overnight to yield colourless crystals of **5.7** (0.23 g, 39 %). M.p: 148 – 150 °C (decomp.); $^1$H NMR (400 MHz, 298 K, C$_6$D$_6$): *δ* = 1.17 (d, 12H, CH(C*H*$_3$)$_2$), 1.74 (d, 12H, CH(C*H*$_3$)$_2$), 1.86 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 3.44 (t, 4H, NC*H*$_2$CH$_2$), 3.84 (sept, 4H, C*H*(CH$_3$)$_2$), 7.18 (d, 4H, *m*-Ar-*H*), 7.24 (t, 2H, *p*-Ar-*H*); $^{13}$C{$^1$H} NMR (75 MHz, 298 K, C$_6$D$_6$): *δ* = 20.4 (CH$_2$*C*H$_2$CH$_2$), 24.8 (CH(*C*H$_3$)$_2$), 27.7 (CH(*C*H$_3$)$_2$), 30.1 (*C*H(CH$_3$)$_2$), 55.2 (N*C*H$_2$), 125.9 (Ar-*C*), 131.9 (Ar-*C*), 136.8 (Ar-*C*), 148.3 (Ar-*C*), 180.8 (N*C*N); MS/EI *m/z* (%): 586.3 (M$^+$, 1), 439.3 ($^6$IPr-Cl$^+$, 10), 405.3 ($^6$IPr-H$^+$, 100); IR (ATR) *v*/cm$^{-1}$: 1654m, 1551w, 1324m, 1257w, 1098w, 1057w, 800m, 754m, 721m.

**Preparation of $^6$IPr·SbCl$_3$ (5.8):** To a solution of SbCl$_3$ (0.230 g, 1.01 mmol) in toluene (25 mL) at -78 °C was added to a solution of $^6$IPr **2.24** (0.41 g, 1.00 mmol) in toluene (10 mL). The mixture was warmed to ambient temperature, stirred for 20 minutes, before volatiles were removed *in vacuo*. The residue was extracted into benzene (30 mL), the extract concentrated *in vacuo* to 10 mL, then placed at 5 °C overnight to yield colourless crystals of **5.8** (0.38 g, 61 %). M.p: 160 – 163 °C (decomp.); $^1$H NMR (400 MHz, 298 K, $C_6D_6$): $\delta$ = 1.24 (d, 12H, CH(C*H*$_3$)$_2$), 1.51 (d, 12H, CH(C*H*$_3$)$_2$), 2.49 (br, 2H, CH$_2$C*H*$_2$CH$_2$), 3.55 (br, 4H, NC*H*$_2$CH$_2$), 3.85 (br, 4H, C*H*(CH$_3$)$_2$), 7.29 (d, 4H, *m*-Ar-*H*), 7.41 (t, 2H, *p*-Ar-*H*); $^{13}$C{$^1$H} NMR (75 MHz, 298 K, $C_6D_6$): $\delta$ = 19.7 (CH$_2$*C*H$_2$CH$_2$), 24.2 (CH(*C*H$_3$)$_2$), 25.4 (CH(*C*H$_3$)$_2$), 29.8 (*C*H(CH$_3$)$_2$), 49.5 (N*C*H$_2$), 125.8 (Ar-*C*), 131.9 (Ar-*C*), 137.2 (Ar-*C*), 146.0 (Ar-*C*), N*C*N signal not observed; MS/EI *m/z* (%): 632.1 (M$^+$, 1), 404.3 ($^6$IPr$^+$, 100); IR (ATR) *v*/cm$^{-1}$: 1655m, 1383m, 1256w, 1109m, 1057w, 800s, 755m, 711m; anal. calcd. for $C_{28}H_{40}N_2SbCl_3$: C, 53.15%; H, 6.37%; N, 4.43%; found: C, 52.94%; H, 6.35%; N, 4.35%.

**Preparation of [($^6$IPr)$_2$(μ-P$_4$)]Cl$_2$ (5.11):** A solution of $^6$IPr·PCl$_3$ **5.6** (0.10 g, 0.18 mmol) in THF (20 mL) was added to a slurry of KC$_8$ (0.075 g, 0.55 mmol) in THF (20 mL) at -80 °C. The mixture was warmed to room temperature and stirred for 4 hours. Volatiles were then removed *in vacuo*, and the residue was extracted into a hexane/benzene mixture (15/2 mL). The extract was filtered and the filtrate placed at 5 °C overnight to yield lime-green crystals of **5.11**. (0.04 g, 81 % based on P). M.p: 155 – 157 °C (decomp.); $^1$H NMR (400 MHz, 298 K, $CD_2Cl_2$): $\delta$ = 1.25 (d, 24H, CH(C*H*$_3$)$_2$), 1.38 (d, 24H, CH(C*H*$_3$)$_2$), 2.71 (br, 4H, CH$_2$C*H*$_2$CH$_2$), 3.00 (sept, 8H, C*H*(CH$_3$)$_2$), 4.13 (br, 8H, NC*H*$_2$CH$_2$), 7.33 (d, 8H, *m*-Ar-*H*), 7.41 (t, 4H, *p*-Ar-*H*); $^{13}$C{$^1$H} NMR (75 MHz, 298 K, $CD_2Cl_2$): $\delta$ = 19.1 (CH$_2$*C*H$_2$CH$_2$), 23.8 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 48.2 (N*C*H$_2$), 124.4 (Ar-*C*), 130.4 (Ar-*C*), 135.1 (Ar-*C*), 144.1 (Ar-*C*), N*C*N signal not observed; $^{31}$P{$^1$H} NMR (121 MHz, 298 K, $CD_2Cl_2$): δ = -167.0 (t, $^1J_{PP}$ = 184 Hz), -325.4 (t, $^1J_{PP}$ = 184 Hz); MS/EI *m/z* (%): 405.3 ($^6$IPr-H$^+$, 100); IR (ATR) *v*/cm$^{-1}$: 1652m, 1542w, 1320m, 1277m, 1101m, 1003w, 806m, 757m, 723m.

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[22] As determined from a survey of the Cambridge Crystallographic Database, July, 2016

# *6 Appendix*

## *6.1 Publications in Support of this Thesis*

C. Jones, **A. Sidiropoulos**, N. Holzmann, G. Frenking, A. Stasch, *Chem. Commun*., **2012**, *48*, 9855, An N-heterocyclic carbene adduct of diatomic tin, :Sn=Sn:

M. Ma, **A. Sidiropoulos**, L. Ralte, A. Stasch, C. Jones, Metal-only Lewis pairs featuring unsupported Pt→M (M = Zn or Cd) dative bonds, *Chem. Commun*., **2013**, *49*, 48

**A. Sidiropoulos**, B. Osborne, A. N. Simonov, D. Dange, A. M. Bond, A. Stasch, C. Jones, *Dalton Trans*., **2014**, *43*, 14858, Expanded ring N-heterocyclic carbene adducts of group 15 element trichlorides: Synthesis and reduction studies