GROUP 2 ORGANOMETALLIC CHEMISTRY:
AN EXCURSION INTO THE CHEMISTRY OF HIGHLY REACTIVE ORGANOBERYLLIUM COMPLEXES

by

ROBERT JERARD GILLIARD, JR.

(Under the direction of Gregory H. Robinson)

ABSTRACT

The syntheses and molecular structures of N-heterocyclic carbene-stabilized derivatives of $BeCl_2$ ([L^1:$BeCl_2$] (**1**); L^1: = :C{N(2, 6-$^iPr_2C_6H_3$)CH}$_2$), [L^1:$BeCl_2$·THF] (**2**), ([L^2:$BeCl_2$·THF] (**3**); L^2: = :C{N(2, 4, 6-$Me_3C_6H_2$)CH}$_2$, [L^1:$BeCl_2$]$_2$·dioxane (**4**)) and $Be(BH_4)_2$ ([L^1:$Be(BH_4)_2$] (**5**)), are described herein. The reaction of lithium borohydride with **1** afforded carbene-stabilized beryllium borohydride, (**5**). Notably, compound **5** is the first structurally characterized compound containing the highly reactive $Be(BH_4)_2$ monomer.

Structural analysis of **5** reveals a five-coordinate beryllium atom with distorted square pyramidal geometry. To probe the reactivity of **5**, it was combined with a well-known reducing agent, disodium tetracarbonylferrate [$Na_2Fe(CO)_4$·dioxane]. The addition of one equivalent of $Na_2Fe(CO)_4$·dioxane to a toluene solution of **5** yielded a dually reduced compound containing a BH_2 unit, (**6**). The BH_2 fragment is stabilized by an N-heterocyclic carbene ligand and a reduced N-heterocyclic carbene moiety. The isolation of **6** represents the first example of the “dual reduction" of both the C=C carbene backbone (hydroboration) and the C2 carbene center (hydrogenation) of an N-heterocyclic carbene ligand.

In comparison to carbene-complexed beryllium chlorides, the chemistry of electron-rich silicon compounds with beryllium chloride is also presented. The reaction of carbene-stabilized disilicon, L^1:Si=Si:L^1 [L^1: = :C{N(2, 6-^{i}Pr$_2$C$_6$H$_3$)CH}$_2$], with BeCl$_2$ in hexane quantitatively yields [L^1:Si=Si:L^1]BeCl$_2$, (**7**). Remarkably, compound **7** is the first example of a molecule containing a silicon−beryllium dative bond. The X-ray structure of **7** reveals that one silicon atom in [L^1:Si=Si:L^1] serves as a monodentate two-electron donor ligand for beryllium chloride, while the other silicon atom has a non-bonding electron pair.

In notable contrast to carbene ligand systems, the reactivity of BeCl$_2$ with diimine ligands is also explored. Sterically demanding diimines ([L^3 = {:N(2,6-^{i}Pr$_2$C$_6$H$_3$)CH}$_2$] and [L^4 = {:N(2, 4,6-Me$_3$C$_6$H$_2$)CH}$_2$] were used to prepare the corresponding beryllium chloride complexes, [L^3BeCl$_2$ (**8**) and L^4BeCl$_2$ (**9**)]. Reduction of **9** with potassium graphite yields a diimine-stabilized beryllium dimer containing a Be$_2$N$_2$ four-membered ring, [L^4Be]$_2$ (**10**).

INDEX WORDS: beryllium, N-heterocyclic carbene, stabilization, main group metal, reduction, sterically demanding ligands, hydroboration, hydrogenation, oxidation-state, computational analysis, mesityl, alkali earth metals, coordination

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DEDICATION

I dedicate this dissertation to my father, the late Robert J. Gilliard, Sr. and my mother, Linda C. Gilliard for their steadfast love, support, and encouragement.

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I thank God for grace, mercy, and favor which has allowed me to achieve at this level. I have made it to this milestone in life due to his many blessings.

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INTRODUCTION

1.1 Purpose of Study

Chemistry is the physical science that is concerned with the composition, structure, and properties of matter. The most fundamental concept in chemistry is the chemical bond.[1] There are a number of factors that affect the propensity of two atoms to form a chemical bond (i.e., solvent effects, attractive forces, electronics, sterics). Synthetic chemists are charged with reconciling these factors in order to prepare the necessary materials of the future. For many years, synthetic inorganic chemists have sought to prepare organometallic compounds (compounds containing at least one metal–carbon bond). These compounds are important components in drug discovery,[2] materials chemistry,[3] and catalysis.[4] Therefore, the synthesis of these novel molecules is essential to scientific advancement and technological discovery.

Currently, there is considerable interest in studying the chemistry of unstable or highly reactive molecules. The ability to trap, or stabilize reactive species, allows chemists to examine the properties of molecules that were previously inaccessible. Indeed, many of these compounds have unusual structures and exhibit novel reactivity. Fortunately, there has been remarkable progress in this area and a number of molecules that were once considered unstable laboratory curiosities can no longer be regarded as such. To this end, this research project explores the stabilization of highly reactive beryllium complexes using a class of organic bases known as N-heterocyclic carbenes.[5] This technique of carbene-stabilization stems from the successful isolation of a number of low oxidation state main group allotropes. A series of unprecedented molecules have been isolated that challenge conventional theories of structure and bonding.

Beryllium is one of the least studied elements on the Periodic Table due to the experimental challenges (i.e., obscure reactivity, high toxicity) one must overcome in the quest to isolate notable molecules. Indeed, the literature contains a limited number of structurally characterized compounds containing beryllium (the smallest metallic atom). Hence, we focus on developing synthetic strategies that facilitate the synthesis of novel highly reactive organoberyllium complexes. The experimental realization of such beryllium compounds provide valuable insight into the structure, bonding, and reactivity of an element whose properties has confused chemists for a number of years.

1.2 The History of Organometallic Chemistry

Organometallic chemistry is the branch of chemistry that concerns compounds containing a metal−carbon bond. The preparation of organometallic compounds typically involves traditional synthetic inorganic and organic techniques. Undergraduate chemistry textbooks tend to emphasize the well-known Grignard reagents, however, the field of organometallic chemistry extends much further than often acknowledged. The main group elements known as "metalloids" are generally accepted to reside at the boundary between metals and non-metals. Consequently, there is often ambiguity concerning the classification of a carbon−metalloid bond. Thayer proposed that compounds containing a carbon−metalloid bond, in which the metalloid is less electronegative than carbon, may also be considered organometallic.[6,7]

French chemist, Cadet de Gassicourt, prepared the first organometallic compound in 1760 by reacting potassium acetate with arsenic trioxide, generating a red fuming liquid known as "Cadet's fuming arsenical liquid".[8] The red liquid was later characterized by Robert Bunsen (a German chemist, widely known for the development of bunsen burners and the discovery of cesium and rubidium) as a mixture of tetramethyldiarsane $(CH_3)_2As{-}As(CH_3)_2$ (Figure 1a) and tetramethyldiarsane oxide $(CH_3)_2As(\mu\text{-}O)As(CH_3)_2$ (Figure 1b) (1837-1843).[9]

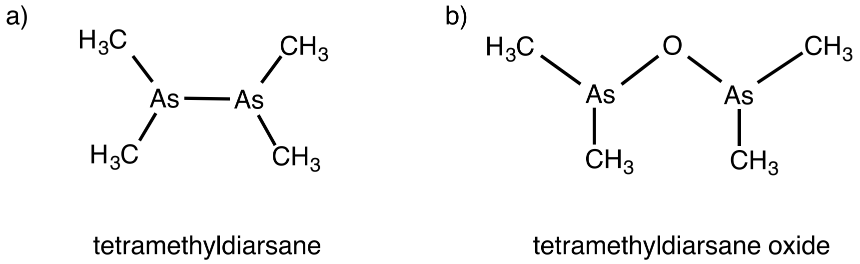


Figure 1. Cadet's "Fuming Liquid": a mixture of a and b.

Since arsenic is a metalloid, many consider W.C. Zeise's preparation of potassium trichloro(ethene)platinate(II), K[$C_2H_4PtCl_3$], to be the first organometallic compound (prepared in 1827).[10] The air-stable, yellow crystalline material was synthesized by refluxing $PtCl_4$ in ethanol. Zeise[11] proposed that the molecule contained an ethylene group, however, this was criticized by Liebig.[12] Though Birnbaum[9] confirmed the percent composition in 1868, it was in 1954 that X-ray crystallography was used to confirm that the structure contained an anionic fragment where the π-electrons of an η^2-ethylene ligand were bound to $PtCl_3$ (Figure 2).[13] Notably, Zeise's salt is the first transition metal π-complex (an olefin which uses its π-electrons to bond to a metal).

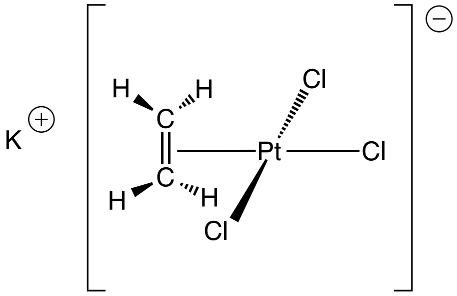
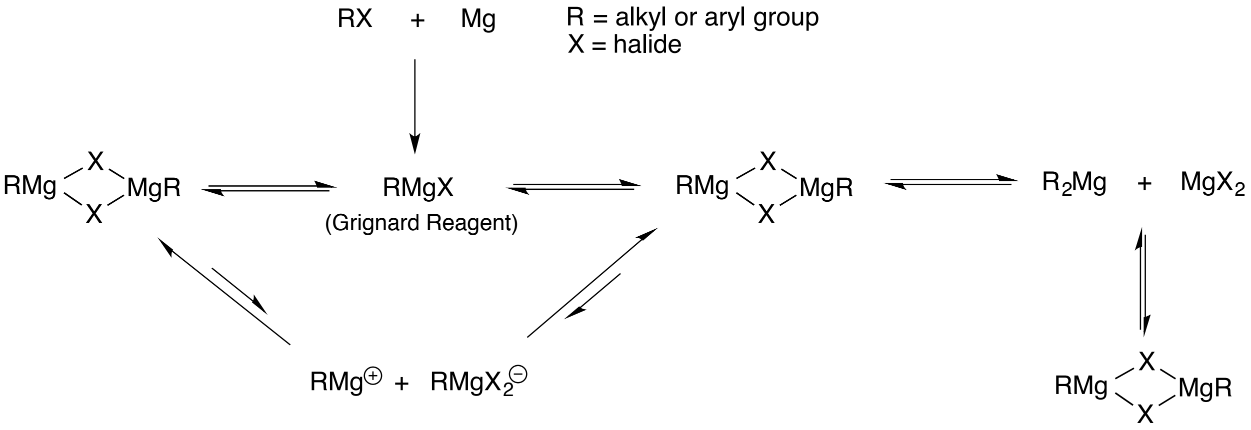


Figure 2. Zeise's salt.

Chemists became interested in main group chemistry when Edward Frankland synthesized the first organozinc compound, diethylzinc [$(C_2H_5)_2Zn$], by heating ethyl iodide in the presence of zinc metal.[14] Though zinc is a d-block element and resides in group 12, its electron configuration [Ar]$3d^{10}4s^2$ makes it a main group metal–it has a filled d-subshell. Organozinc compounds were the driving force for organometallic chemistry for a number of years until François Auguste Victor Grignard discovered organomagnesium compounds in 1900.[15] Grignard was awarded the 1912 Nobel Prize in Chemistry, along with Paul Sabatier, for pioneering discoveries that have advanced organic synthesis. These organomanesium compounds, now known as Grignard reagents, are prepared by the exothermic reaction of an alkyl or aryl halide with activated magnesium metal (activating magnesium involves heating magnesium metal under an inert atmosphere, usually nitrogen or argon, to remove the thin layer of magnesium oxide). In the chemical literature, Grignard reagents are represented by RMgX, however, in solution they exist in a complex Schlenk-type equilibrium (Scheme 1).[16]



Scheme 1. Schlenk-type equilibrium of Grignard reagents in solution.

An unexpected discovery in 1951 sparked the rapid development of organometallic chemistry as we know it today. Kealy and Pauson attempted to prepare fulvalene by the reaction of a Grignard reagent, cyclopentadienyl magnesium bromide, CpMgBr (Cp = C_5H_5), with anhydrous ferric chloride (Figure 3a).[17] Surprisingly, they did not isolate fulvalene, analytical methods suggested a compound with the molecular formula $FeC_{10}H_{10}$. The following year, Miller independently prepared the identical compound by the reaction of iron metal with cyclopentadiene (Figure 3b).[18] Miller proposed that the 10-electron complex consisted of two Cp ligands σ-bound to an iron center (Figure 3c). The five-membered ring in this compound did not undergo hydrogenation or Diels-Alder reactions which lead Fischer to doubt the structure proposed by Miller. Ultimately, Fischer and Wilkinson independently proposed that the Cp ligands were bound to the iron center in an unusual fashion using its six π-electrons.[19,20] Indeed, the p-orbitals on the Cp rings overlap with the d-orbitals of the metal to form an 18-electron "sandwich compound" (Figure 3d). The infrared spectrum reported by Wilkinson supported the structural assignment, only one C–H stretch was observed with zero dipole moment.[20] The structure was unambiguously confirmed by Dunitz using single crystal X-ray diffraction studies in 1956.[21] The sandwich compound is aromatic, therefore, Woodward suggested the name "ferrocene" to replace the formal name, dicyclopentadienyliron, because of similar reactivity when compared to benzene. Indeed, Friedel-Crafts acylation reactions of this compound were achieved. In general, any compound with the formula [M(C_5H_5)$_2$] are now known as "metallocenes"–a subset of a broader class of sandwich compounds.

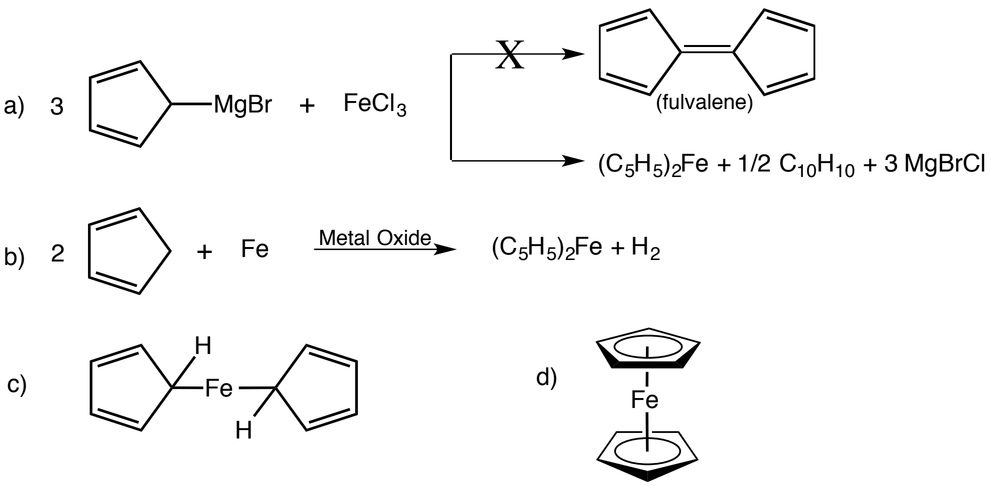


Figure 3. Synthesis and structure of ferrocene.

The field of organometallic chemistry is, arguably, one of the most exciting research areas in chemistry. Though the synthesis of organometallic compounds is often experimentally challenging, the structures of landmark, iconic compounds continue to be isolated. The discovery of these novel molecules has not only had major implications in materials chemistry and industrial catalysis but it has also provided a platform from which our knowledge of biological systems has been greatly enhanced.[22] One can certainly envision that organometallic chemistry will continue evolve and thrive in the future.

1.3 Air-sensitive Reagent Handling and Synthetic Techniques

Many organometallic reagents are sensitive to air and/or moisture (they readily decompose via hydrolysis). Therefore, special synthetic techniques are required to rid all reagents and equipment of water, preventing these decomposition processes. Glassware (syringes, round-bottom flasks, Schlenk tubes etc.) are typically dried in a 200 °C oven overnight or flame-dried for immediate use.[23] Organic solvents are dried, degassed, and freshly distilled prior to use in air-sensitive reactions. Indeed, a number of compounds containing metal−carbon bonds are inherently unstable in air. While some organic solvents require special drying agents such as calcium hydride (dichloromethane) and phosphorus pentoxide (chloroform, carbon tetrachloride), most common solvents (toluene, THF, hexane, diethyl ether) can be dried using sodium/benzophenone.[24] The observance of the dark blue/purple ketal radical formed from the reaction of sodium metal and benzophenone provides an easy and efficient means to quickly visualize if a particular solvent is dry.

Schlenk lines, named after German chemist Wilhelm Schlenk, and gloveboxes are common equipment employed in organometallic chemistry laboratories. Schlenk lines are specially designed dual manifold systems where one manifold is connected to a source of inert gas (usually nitrogen or argon), while the other is connected to a high vacuum pump. The gas is released through an oil bubbler, while solvent vapors are collected using a liquid nitrogen trap. Most Schlenk manifolds contain multiple lines that easily switch between inert-gas and vacuum using a two-way stopcock. Schlenk lines are essential for manipulating air- or moisture- sensitive compounds on the benchtop. In conjunction with standard Schlenk techniques, a glovebox (or drybox) is often used to transfer air-sensitive reagents, store chemicals, conduct experiments, and prepare samples for characterization.

Though special precautions are often necessary, a number of analytical methods are used to characterize organometallic compounds. Examples include nuclear magnetic resonance (NMR), infrared spectroscopy (IR), mass spectrometry (MS), ultraviolet-visible spectroscopy (UV-vis), electron paramagnetic resonance (EPR) or electron spin resonance (ESR), and elemental analysis (EA). The most important technique for the unambiguous characterization of organometallic compounds is X-ray crystallography. Single crystal X-ray diffraction is a powerful tool used for determining the molecular structure of a crystal. In order to use X-ray crystallography a single crystal of the molecule of interest must be obtained. Often this can be a "hit or miss proposition". Thus, chemists use a variety of methods to promote crystal growth (i.e., slow cooling, slow evaporation, saturation, vapor diffusion, liquid-liquid diffusion). During data collection, atoms cause a beam of X-rays to diffract into specific directions. Based on the intensity and angle of the diffracted beam, a three-dimensional picture of the electron density can be produced. From the electron density map, the position of atoms in the crystal can be determined as well as the composition of the chemical bonds (i.e., bond distance).

1.4 The Chemistry of the Groups 1 and 2

Organometallic chemists rely on the elements in group 1 (alkali metals) as they readily donate their electrons to facilitate further chemical transformations. These elements are highly reactive and the reactivity increases upon descending the group (from lithium to francium). The last element in group 1, francium, is rarely used as it is extremely reactive and radioactive. Alkali metals are soft and can be cut to expose a shiny surface which dulls in air due to oxidation. In each element, the valence electron configuration is ns^1 (where n is the period number). Alkali metals also emit distinctive colors when exposed to a flame, making identification relatively simple.[25] When an element is placed in a flame, heat (a form of energy) promotes the outermost electron to a higher energy level. Upon relaxation of the electron to the ground-state, energy is emitted in the form of light and corresponds to a particular wavelength (color) on the visible spectrum (lithium-red, sodium-yellow, potassium-lilac, rubidium-red, cesium-blue).

Several aspects of this research project would be impossible without using the elements in group 1. Lithium, sodium, and potassium serve as excellent reducing agents in a number of reactions. However, one of the most commonly employed reducing agents in organometallic synthetic procedures is potassium graphite (KC_8).[26] Potassium atoms insert or intercalate between the graphite sheets, hence, these types of molecules are called intercalation or lamellar compounds (lamellar originates from the latin word “lamella” meaning thin plate or layer). Potassium graphite is one of the strongest reducing agents known and is prepared by the solid-state charge transfer reaction of potassium metal with graphite at elevated temperatures (Figure 4a). Interestingly, once the potassium is absorbed into the graphite the color changes from black to gold (Figure 4b). Structurally, the potassium to potassium distance is twice the distance between the hexagons in the carbon framework of graphite. The space-filling model indicates that the potassium (purple spheres) are held between the well-separated (3.35 Å) layers of graphite (black spheres) via a guest-host interaction (Figure 4c).

a) $$K + 8\ C_{(graphite)} \xrightarrow{\Delta} KC_8$$

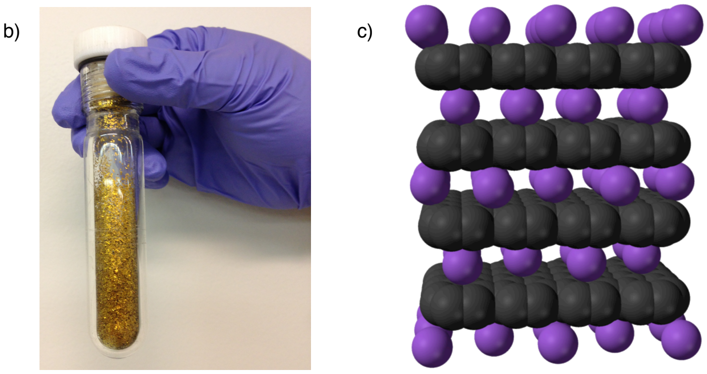
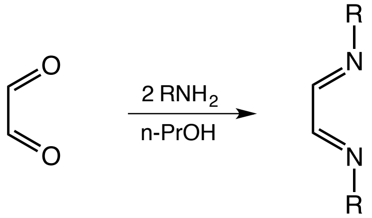


Figure 4. Potassium Graphite.

Regarding synthesis, the chemistry of group 2 (alkali earth metals) is dominated by magnesium, namely, the Grignard reagent (described in section 1.2). The metals in group 2 are harder and more dense than those in group 1. This is may be attributed to the additional valence electron on each atom, which leads to stronger metallic bonding than what is observed for the group 1 elements. Due to lower reduction potentials, alkali metal reductions are more common than their alkaline earth metal counterparts.[27-29] Three of the alkali earth metals give a characteristic color when heated in a flame (calcium-brick red, strontium-crimson, barium-green). Magnesium and beryllium do not give characteristic flame test colors due to their small atomic size.[30] The electrons are held more strongly to the nucleus essentially thwarting the transition of electrons which is the necessary process that facilitates the distinctive colors. The reactivity of beryllium is considered abnormal when compared to the heavier alkali earth metals (a detailed discussion of beryllium chemistry is provided in section 1.8).[31]

1.5 Diimine Ligands

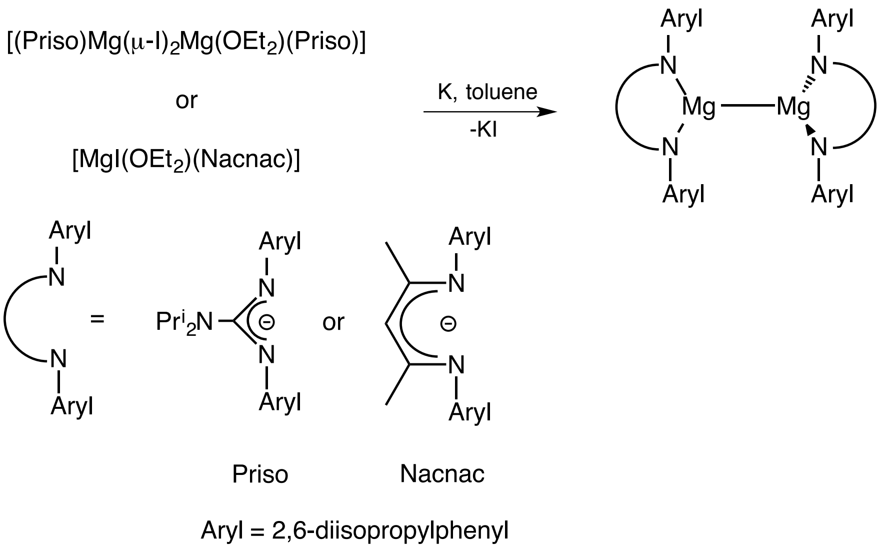
The purpose of this section is to provide background information on the fundamental properties of α-Diimine ligands (or 1,2-diketimine ligands), which were routinely employed in this research project. In general, diimines are organic compounds that contain two imine (RCH=NR) functionalities. These ligands are used as precursors to heterocyclic compounds, namely, N-heterocyclic carbenes. Diimines may be prepared by condensation reactions involving diketones and amines (Scheme 2).[32] A notable example is glyoxal-bis(mesitylimine), a bright yellow solid that is synthesized by the reaction of 2,4,6-trimethylaniline and glyoxal in *n*-propyl alcohol.



Scheme 2. Synthesis of diimine ligands.

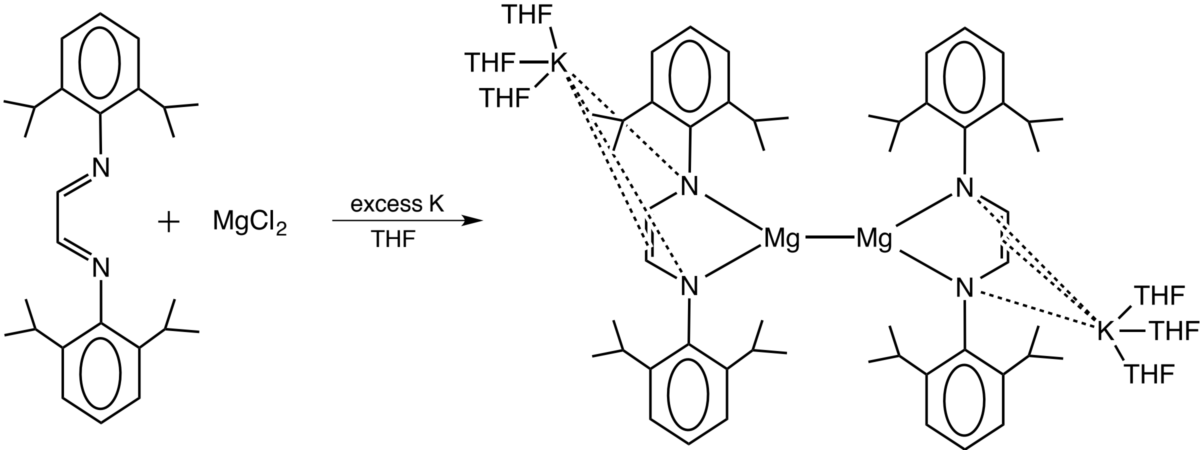
1.5.1 Utility of Diimines in Inorganic Chemistry

The tunable steric and electronic properties of the substituents of diimines make them useful in a number of reactions including the formation of metal−metal bonds. Diimines were initially used to prepare compounds containing Zn−Zn bonds,[33] however, this strategy was recently extended to magnesium.[34] Following the isolation of the first stable compounds containing Mg−Mg bonds (Scheme 3; R = $[(2,6\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{NC}(\mathrm{N}^i\mathrm{Pr}_2)\mathrm{N}(2,6\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)]^-$ or $\{[(2,6\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{NC}(\mathrm{Me})]_2\mathrm{CH}\}^-$),[35] Yang and Wu reported a similar reduction route using sterically demanding diimine ligands (Scheme 4; R = $2,6\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{NC}(\mathrm{Me})]_2{}^{2-}$).[34]



Scheme 3. Synthesis of RMg−MgR.

Potassium metal was added to a THF solution containing diimine ligand and magnesium chloride (3:1:1=K:$MgCl_2$:diimine). The reduction reaction proceeded and pink air- and moisture-sensitive crystals of **1** were obtained in 48% yield. Notably, while the priso and nacnac ligands are both formally anionic, the diimine ligand is dianionic (diimine ligands may be neutral, anionic, or dianionic based on the bonding situation).



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Scheme 4. Synthesis of [K(THF)$_3$]$_2$[RMg−MgR].

1.6 Evolution of Carbenes

Carbenes are neutral species containing divalent, two-electron donor carbon atoms, surrounded by six electrons. Attempts to prepare the simplest carbene, H_2C: (Figure 5), were reported by Dumas in 1835.[36] At that time of Dumas' report, the tetravalent nature of carbon was not established, consequently, the existence of carbenes was considered reasonable.[36]

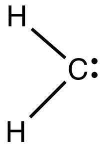


Figure 5. Methylene carbene.

Curtius[37] (1885) and Staudinger[38] (1912) demonstrated that carbenes could be generated from diazo compounds or ketones, as highly reactive intermediates. Their inherently unstable nature can be attributed to the six valence-electron shell, which defies the octet rule. In 1954, carbenes as transient species became popular when Doering discovered the cyclopropanation reaction.[39] Breslow[40] (1958) and Wanzlick[41] (1962) showed that the stability of carbenes could be significantly enhanced by the presence of amino substituents. However, they were unable to isolate a "free" monomeric carbene. Bertrand reported the synthesis of a (phosphino)(silyl)carbene in 1988.[42] In 1991, Arduengo reported the synthesis and structure of the first crystalline "free" (no metal bound to the C2 carbene center) carbene.[43] These fundamental discoveries led to the rapid development of carbene chemistry. It has now been well-established that carbenes have the ability to activate small molecules,[44] stabilize reactive species,[45-57] and serve as catalysts.[58] Nolan indicated that the σ-donating capability of NHCs is superior to their phosphorus congeners which makes them attractive for a wide range of applications.[59]

1.6.1 Spin Multiplicity of Carbenes

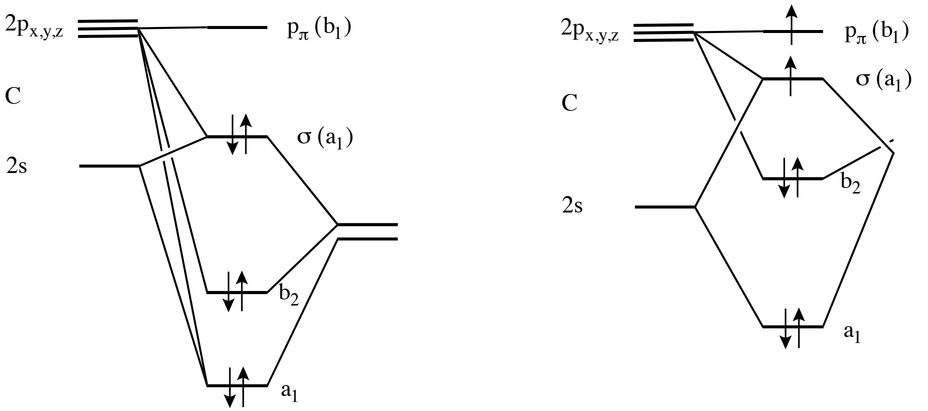
The ground state spin multiplicity of carbenes can be singlet (spin paired, S=0) or triplet (spin unpaired, S=1). Singlet carbenes are bent in geometry and contain an sp^2 hybridized orbital, an empty p orbital, and an electron pair in the sp^2 hybrid orbital. Due to the fact that singlet carbenes possess a filled and a vacant orbital, they have ambiphilic character (the ability to accept and donate electrons).[5] Triplet carbenes are linear and they contain an sp hybridized orbital at the carbene center and one unpaired electron in each p orbital. Therefore, triplet carbenes may be regarded as diradicals.

The reactivity of a carbene is determined by its ground state spin multiplicity, which is related to the relative energy of the σ and $p\pi$ orbitals. Hoffman determined that a value of 2.0 eV (large σ-$p\pi$ separation) is needed to promote a singlet ground state while a value below 1.5 eV (small σ-$p\pi$ separation) leads to a triplet state.[60]

1.6.2 Electronic Effects

Early developments in carbene chemistry revealed that the substituents adjacent to the carbene center directly influence the carbene's multiplicity.[61-66] More recent developments have confirmed that σ-electron-withdrawing groups favor the singlet state versus the triplet state.[67] Harrison[61,63] demonstrated that the ground state changes from triplet to singlet when the electropositive lithium substituents are replaced with hydrogen or fluorine. Based on the orbital diagrams, the σ-electron-withdrawing substituents inductively stabilize the σ-nonbonding orbital by increasing its s character and leaving the $p\pi$-orbital unaffected (Figure 6a).[5] Therefore, the σ-

pπ gap is increased and the singlet state is preferred. In notable contrast, σ-electron-donating groups constitute a small σ-pπ gap and the triplet state is favored (Figure 6b).



a) σ–electron-withdrawing substituents

b) σ–electron-donating substituents

Figure 6. Orbital diagram-inductive effects.

Mesomeric or resonance effects also play an important role in carbene stability and reactivity.[61,68,69] In most cases, mesomeric effects arise as a result of the interaction of the orbitals of the carbene carbon (s, pπ or px, py) with the p or π orbitals of the adjacent substituents. Depending on the substituents interacting with the carbene center (ED: π-electron-donating or EW: π-electron-withdrawing), drastic changes in reactivity may be observed. Carbenes of type (ED−C−ED) are predicted to be bent singlet carbenes (Figure 7a).[65-67,70-74] The symmetric combination of the lone pairs (b_1) on the ED groups interact with the empty pπ-orbital (increasing its energy). Since there is no significant change to the σ-orbital, the σ-pπ gap is increased and singlet sate is favored. The position of the σ-orbital and the non-symmetric combination of the lone pairs on the ED-substituents (a_2) are close in energy, their relative position depends on the electronegativity of the ED-group compared to carbon. Resonance donation of the ED-substituent lone pairs to the carbene center results in a polarized three-center four-electron π-system. The majority of (EW−C−EW) carbenes are predicted to be linear singlet carbenes (Figure 7b).[65-67,75,76] In this type of carbene, the symmetric combination of the substituents vacant orbitals interact with the p_y orbital. Notably, this interaction does not affect the p_x orbital. Consequently, the (p_x,p_y) degeneracy is broken making these carbenes have a singlet ground state even though they are linear.[65,66] This bonding situation results in a three-center two-electron π-system. Finally, quasi-linear carbenes (ED−C−EW) are comprised of both electron donating and electron withdrawing substituents (Figure 7c).[77] The electron pair on the ED-substituent interacts with the p_y orbital, while the EW-substituent's vacant orbital interacts with the p_x orbital. This type of bonding interaction contains ED−C and C−EW multiple bonds favoring the singlet state (the vacant p_y orbital is destabilized, while the filled p_x orbital is stabilized).

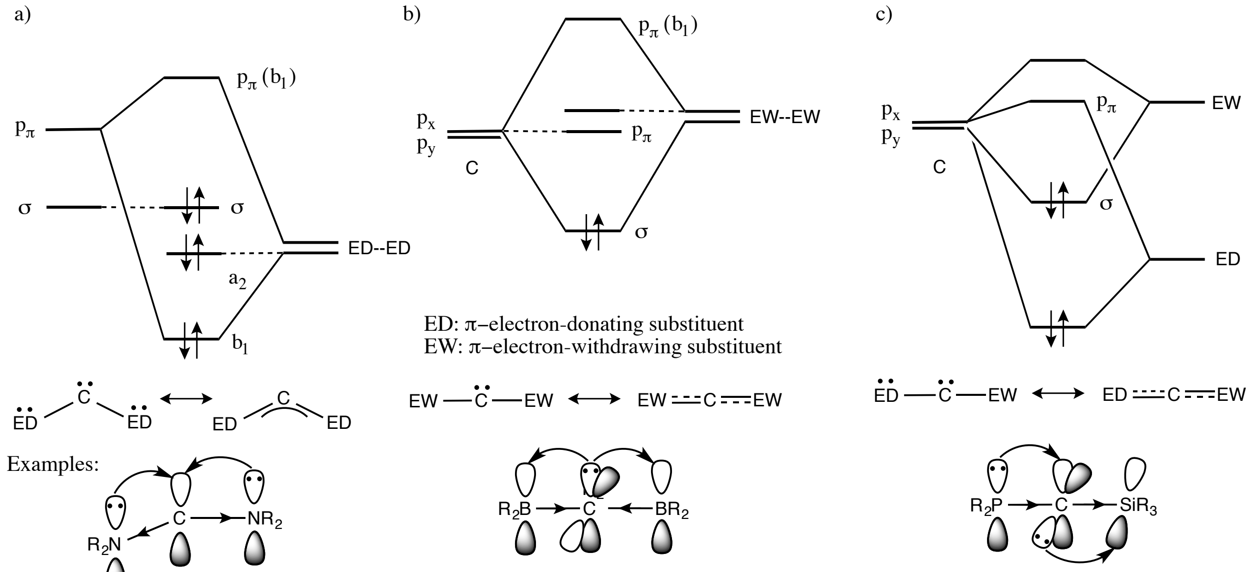


Figure 7. Orbital diagram-mesomeric effect.

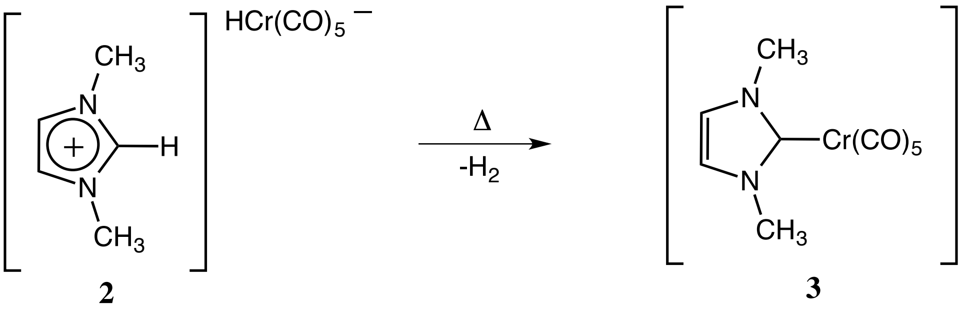
1.6.3 Steric Effects

The amount of steric shielding around the carbene center also influences reactivity. Bulky substituents provide kinetic stabilization, and if the electronic effects are minimal sterics can dictate the ground state multiplicity.

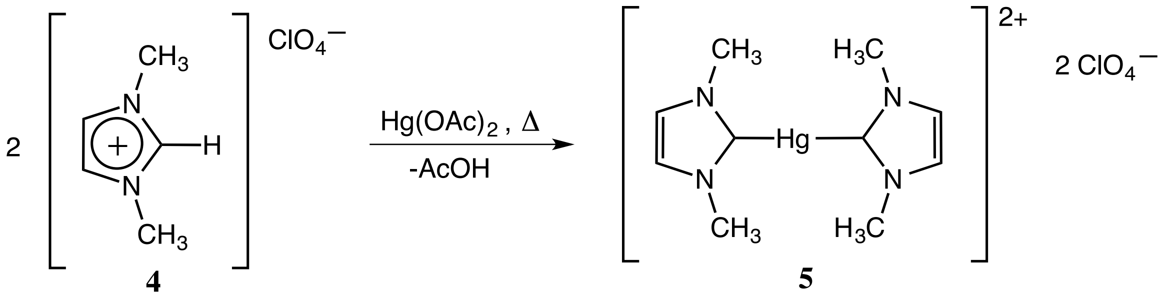
The electronic stabilization of the triplet state relative to the singlet state is maximized when the carbene frontier orbitals are degenerate (degenerate orbitals are ones that have the same energy), therefore, a linear geometry will favor the triplet state. This may be rationalized by the influence of the carbene bond angle on the ground-state spin multiplicity of the parent carbene. Below 90°, the energy of the singlet methylene drops below the energy of the triplet state.[68,69] In a similar fashion, increasing the steric bulk of the carbene substituents broaden the carbene bond angle and favors the triplet state.[78]

1.6.4 N-Heterocyclic Carbenes

N-heterocyclic carbenes (NHCs) are neutral species containing a divalent, two-electron donor carbon atom in a five-membered imidazole ring. Generally, NHC ligands are more stable and versatile than Fischer and Schrock carbenes.[79,80] The utilization of NHCs in transition metal chemistry dates back to the early work of Wanzlick[81] (1960) and Öfele[82] (1968). NHC-chromium (**3**) and -mercury (**5**) complexes were prepared by thermal extraction of hydrogen from the corresponding imidazolium salts (**2**) and **(4**) (Schemes 5 and 6).

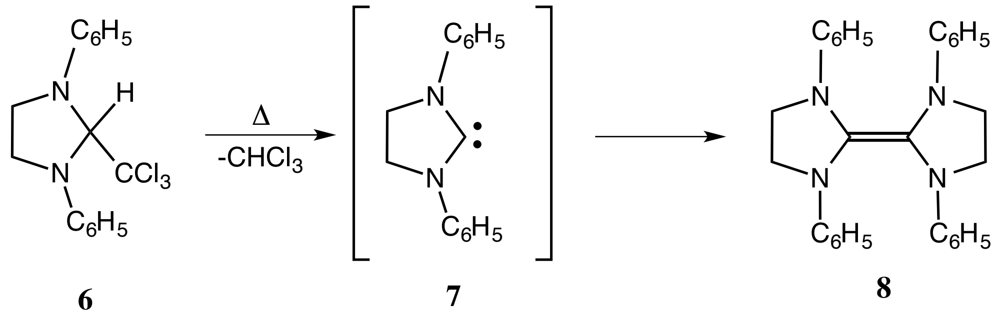


Scheme 5. Synthesis of NHC-chromium carbene complex.

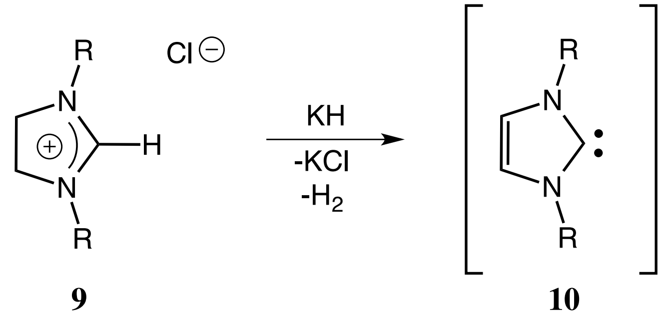


Scheme 6. Synthesis of NHC-mercury carbene complex.

Though these types of carbenes were being used as intermediates in transition metal chemistry, attempts to prepare the "free" NHC (no metal bound to the carbene center) failed (Scheme 7). Wanzlick realized that the stability of carbenes could be enhanced by the presence of amino substituents. Consequently, they attempted to prepare 1,3-diphenylimidazolidin-2-ylidene (**7**), by heating 1,3-diphenyl-2-trichloromethyl-imidazolidine (**6**) to thermally eliminate chloroform.[81] However, an electron-rich dimer was isolated, **8**. Though more recent experiments by Denk[83] suggest a modest equilibrium reaction between the NHC-precursor and the free carbene, initial cross-coupling experiments by Wanzlick did not give evidence of any such process. Subsequently, Wanzlick demonstrated that imidazolium salt precursors, **9**, could be deprotonated using potassium hydride to trap the corresponding imidazol-2-ylidenes, **10** (1970) (Scheme 8).[84,85]

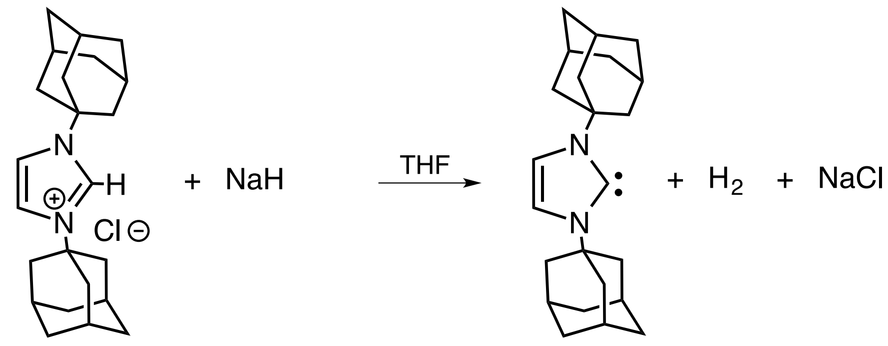


Scheme 7. Synthesis of Wanzlick NHC dimer.



Scheme 8. Deprotonation of NHC salt precursor.

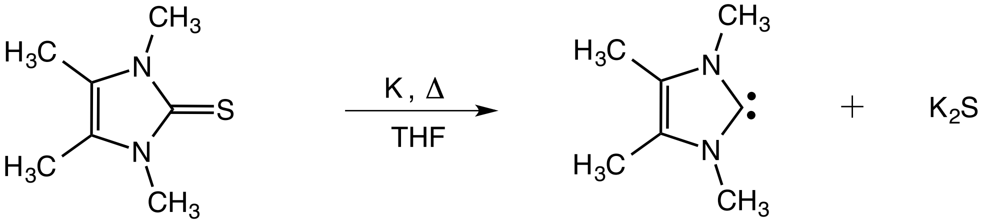
Ultimately, Arduengo prepared “A Stable Crystalline Carbene” two decades later (1991) (Scheme 9).[43] The product, **12**, was obtained in quantitative yield by reaction of 1,3,-di-1-adamantylimidazolium chloride, **11**, with sodium or potassium hydride in the presence of catalytic amounts of potassium *t*-butoxide. The crystalline carbene is thermally stable and melts at 240-241 °C without decomposition. Subsequently, Arduengo prepared NHCs with less bulky substituents demonstrating that the steric effects that were once believed to be responsible for the isolation of the “free” carbene is second to electronics.[32] Indeed, it is the donation of the nitrogen lone pairs into the empty p-orbital at the carbene center that is largely responsible for its remarkable stability.



11 **12**

Scheme 9. Synthesis of the a crystalline carbene.

In 1993, Kuhn reported a novel approach to prepare smaller alkyl substituted NHCs.[86] Imidazole-2-ylidenes were prepared by desulfurization of alkyl substituted imidazole-2-thione with potassium metal in boiling THF (Scheme 10). The synthesis of these alkyl-substitued NHCs provides further confirmation that electronic effects take precedence over sterics in these systems. Indeed, the stability of these carbenes is similar to their adamantyl-substituted congeners.

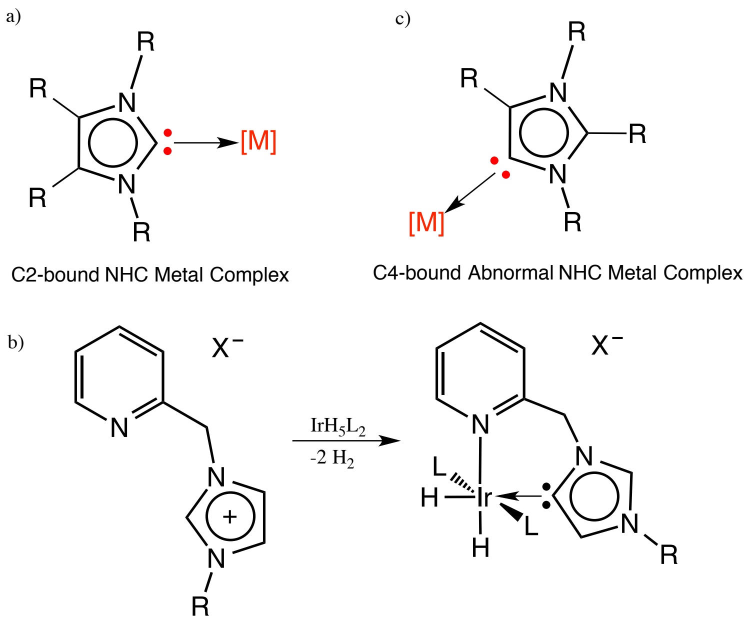


13 **14**

Scheme 10. Desulfurization of thiones.

1.6.5 Abnormal Carbenes

Normal carbenes (or NHCs) are those in which the carbene center is at the C2 position of the imidazole ring. Metals bind to NHCs to give η^1 complexes (Figure 8a). However, Crabtree synthesized iridium complexes (Figure 8b) where the iridium metal was bound to the carbene ligand the “wrong way”−to the C4 position of the heterocyclic ring (2001) (Figure 8c).[87]

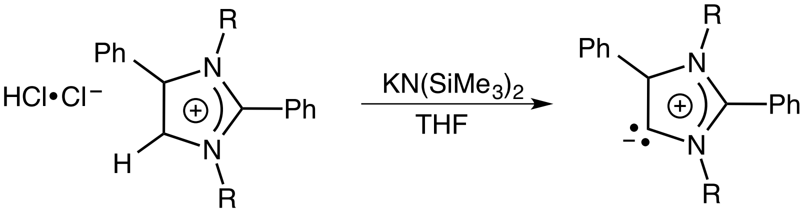


C2-bound NHC Metal Complex

C4-bound Abnormal NHC Metal Complex

Figure 8. C2 and C4 bound NHC-Metal Complexes.

Experimental and theoretical data suggest that abnormal carbenes (*a*NHCs) are stronger electron donor ligands than NHCs.[88-90] This was supported by Nolan who prepared *a*NHC-palladium complexes and reported significant catalytic activity in Heck reactions, whereas the comparable NHC-palladium complexes were catalytically inactive.[89] NHCs are classically prepared by deprotonation of imidazolium salt precursors. Computational analysis reveals that the pKa for the loss of the C4-bound proton is only nine units higher than the C2-bound proton.[91,92] Moreover, the parent *a*NHC is only 17 kcal mol^{-1} higher in energy than its NHC counterpart.[93] Therefore, it is reasonable that free *a*NHCs are viable synthetic targets. In 2009, Bertrand ultimately isolated the first example of a free *a*NHC, **16**, by capping the C2 position of the imidazole ring with a phenyl group and subsequently reacting the *a*NHC precursor, **15**, with sodium hexamethyldisilazide (Scheme 11; R = 2,6-diisopropylphenyl).[94] The ability of the abnormal carbene to act as a traditional two-electron donor carbene ligand was demonstrated in coordination reactions with AgCl and CO_2.[94]



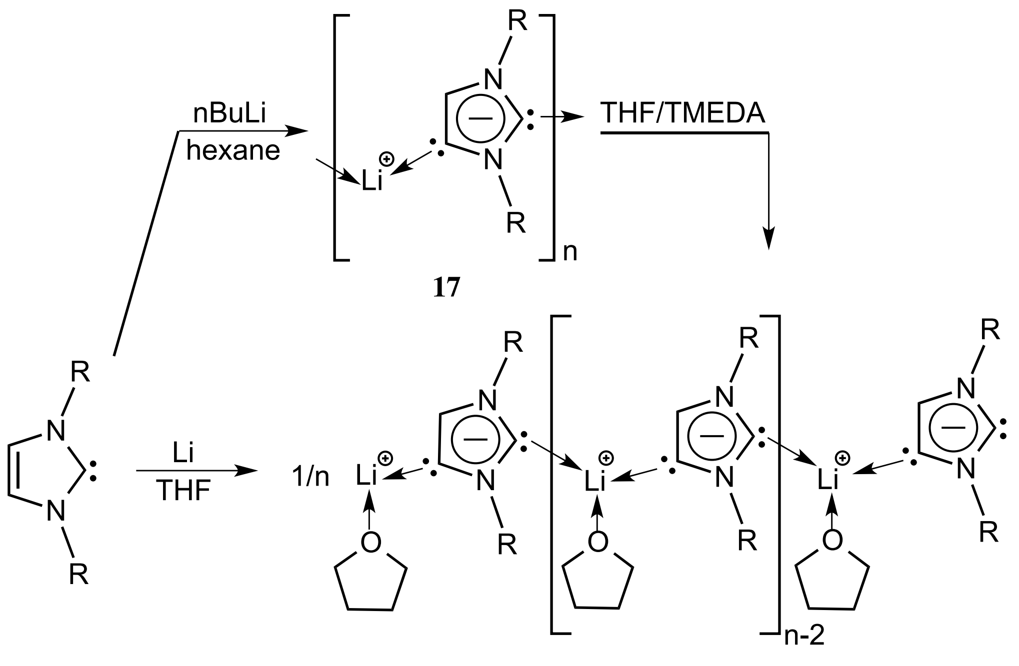
15

16

Scheme 11. Synthesis of a crystalline abnormal carbene.

1.6.6 Dicarbenes

NHCs and *a*NHCs have one carbene center (C2 and C4 positions, respectively) in their five-membered heterocyclic rings. In 2010, Robinson isolated the first anionic dicarbene (NHDC) in which there are two carbene centers (normal-C2 and abnormal-C4 position) in the same imidazole ring .[95] NHDC, **17**, is conveniently prepared in quantitative yield by the reaction of an NHC ligand with *n*-BuLi in hexane (Scheme 7; R = 2,6-diisopropylphenyl). Dissolution of NHDC in THF/TMEDA affords the polymeric NHDC, **18**, in which one THF molecule is coordinated to each lithium cation. Although the yield is lower, NHDC may also be obtained by the direct reaction of an NHC and lithium metal. The dicarbene nature is unambiguously exhibited in the formation of aluminum and boron adducts.[95]

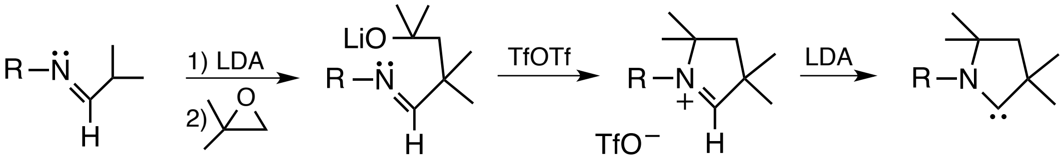


Scheme 12. Synthesis of anionic N-heterocyclic dicarbene.

1.6.7 Cyclic (Alkyl)(Amino)Carbenes

In notable contrast to N-heterocyclic carbenes, Bertrand synthesized cyclic(alkyl)(amino) carbenes (CAACs) which have one less electronegative amino substituent (2005).[96,97] The nitrogen atom is replaced by a strong σ-donor alkyl group making CAAC ligands more electron-rich than phosphines or NHCs. Structurally, the carbene center in CAACs reside in a unique steric environment. The presence of a quaternary carbon atom in the α-position shields the carbene center making CAACs substantially different from previously reported stable carbenes. Indeed, these ligands are reported to have superior σ-donating capability, however, they are weak π-acceptors.[97]

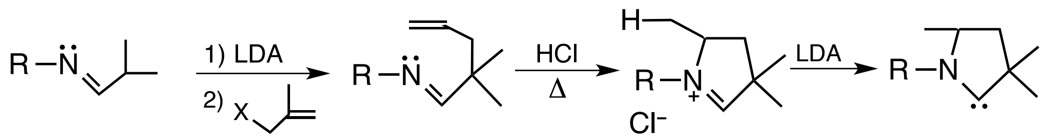
CAACs are prepared in a three-step synthesis (Scheme 13; R = 2,6-diisopropylphenyl). Reaction of the imine, **19**, with LDA (lithium diisopropylamide) affords the aza-allyl anion, which induces the ring opening of 1,2-epoxy-2-methylpropane to generate the alkoxide, **20**. Triflic anhydride (TfOTf) is added to a solution of **20** at −78 °C leading to the corresponding triflic derivative, which converts to the aldiminium salt, **21**, upon warming to room temperature. Finally, deprotonation with LDA affords the CAAC, **22**, as a white solid in 58% yield. The stability of CAACs are comparable to NHCs as they are stable in the solid-state and in solution for several weeks.



19 **20** **21** **22**

Scheme 13. Synthesis of Cyclic (Alkyl)(Amino)Carbenes.

Initially, the synthesis of CAACs only permitted the use of specific substituents, however, an alternate, more versatile, route was reported by Bertrand two years later.[98] The imine starting material (**23**) in this synthetic strategy can be conveniently prepared by reacting 2,6-diisopropylaniline with cyclohexane carboxaldehyde. Deprotonation of **23** with LDA affords the corresponding 1-aza-allyl anion, which readily reacts with 3-bromo-2-methylpropene at room temperature to form the alkenyl aldimine, **24**. Addition of an HCl/Et_2O solution to a toluene solution of **24**, at −78 °C, results in the immediate formation a white precipitate. Heating the mixture at 50 °C for 18 h generates the desired carbene precursor, **25**. Lastly, deprotonation with LDA gives the CAAC, **26**. Notably, the new synthetic route resulted in a significant improvement of the overall yield (88% vs. 48%).



23 **24** **25** **26**

Scheme 14. Improved synthesis of cyclic (alkyl)(amino)carbenes.

1.7 Carbene-Stabilization of Highly Reactive Molecules

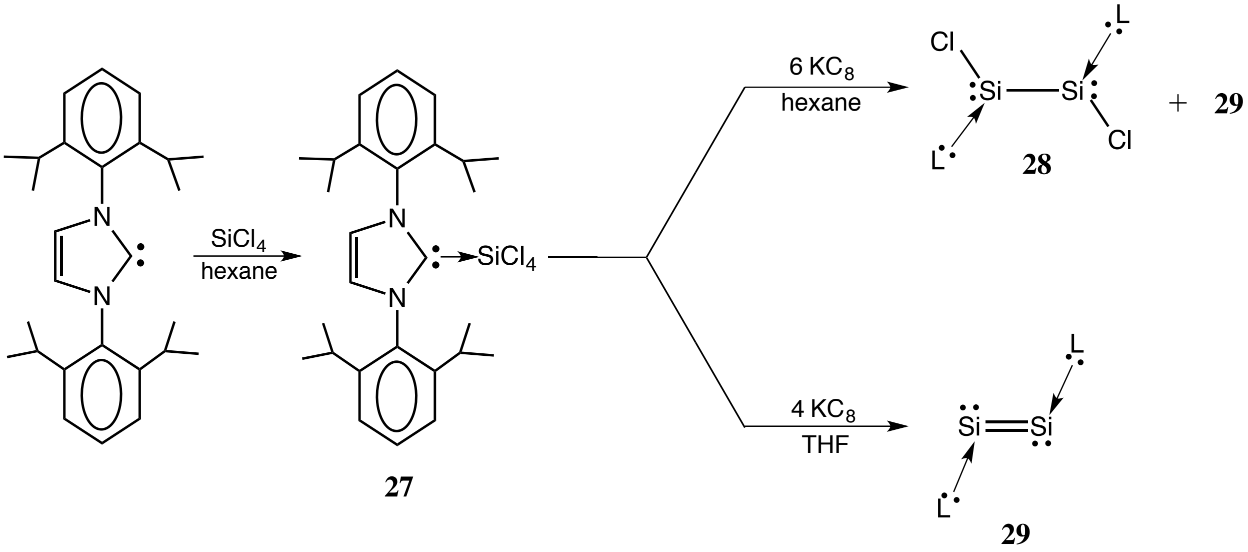
Arduengo's discovery of the first crystalline carbene invigorated the field of carbene chemistry. In recent years, synthetic inorganic chemists have utilized N-heterocyclic carbenes and CAACs to prepare a plethora of molecules that are considered to be highly reactive. The seminal report of carbene-stabilized disilicon demonstrates that NHCs can serve as efficient donor ligands for stabilizing reactive Si^0 species. This section will highlight recent discoveries that are related to the research project presented herein.

1.7.1 Carbene-Stabilized Disilicon

There is continuing interest in the synthesis and reactivity of low-valent silicon compounds. This is due, in part, to the experimental realization of novel structures and bonding motifs that often differ from the chemistry of carbon, its lighter congener. While $SiCl_4$ can accommodate ligands through coordination reactions (due to the hypervalent nature of silicon), the carbon atom in CCl_4 would exceed its valency and needs to lose a chlorine to form another bond.[56] The chemistry of C−C multiple bonds have been studied for more than two centuries, however, it was was West[99] (1981) and Sekiguchi[100] (2004) that prepared the first disilene (RSi=SiR) and disilyne (RSi≡SiR), respectively. Regarding the oxidation state of these molecules, the Si atoms in disilene reside in the formal oxidation state of (+2), while the Si atoms in disilyne are (+1), owing to the electronic contribution of the ligands (they are formally anionic).

It has been well-established that transition metals often reside in the formal oxidation state of zero, however, this is a rare occurrence for main group elements.[101,102] The study of highly reactive silicon(0) compounds is interesting since it has the potential to redefine the applications of silicon in synthetic chemistry. Typically, these reactive species are studied under specific reaction conditions that require expensive instrumentation and specialized techniques.[103] Indeed, diatomic Si_2 (having a triplet ground state) had only been studied in the gas phase and in argon matrices.[104]

Recently, our laboratory prepared diatomic silicon where both Si atoms are in the formal oxidation state of zero.[56] N-heterocyclic carbenes were employed in this chemistry as they are neutral ligands. These organic bases serve as ancillary ligands stabilizing the highly reactive :Si=Si: moiety. Carbene-stabilized disilicon [L:Si=Si:L, L=:C{N(2,6-^{i}Pr$_2$C$_6$H$_3$)CH}$_2$)] is prepared in a two-step complexation and reduction process (Scheme 15). Beginning with the sterically demanding NHC suspended in hexane, $SiCl_4$ is added to the mixture forming L:$SiCl_4$, (**27**). Potassium graphite reduction of the hypervalent silicon complex, **27** (1:6 ratio=**27**:KC_8), in hexane, affords a mixture of bis-silylene, **28** (major product, isolated as orange crystals), and disilicon, **29** (minor product, isolated as red crystals). Carbene-stabilized disilicon, **29**, may be exclusively isolated by potassium reduction of **27** with KC_8 in THF (1:4 ratio=**27**:KC_8).



Scheme 15. Synthesis of NHC-stabilized bis-silylene and disilicon.

Single Crystal X-ray diffraction studies of **28** reveal that the Si_2 core is protected by two sterically demanding NHC ligands. Both silicon atoms are in a three-coordinate trigonal planar environment and the formal oxidation state is (+1). The Si−Si bond distance is 2.393 Å, marginally longer than the sum of Si covalent radii (2.34 Å).[105] The disilicon molecule (**29**) features a Si=Si double bond (2.229 Å) which is expectedly shorter than the Si−Si single bond in (**28**). The Wiberg bond index (WBI) of 1.73 also supports the presence of a Si=Si double bond. In contrast to the geometry of previously reported disilenes which possess trigonal pyramidal or planar geometry, **29** is *trans*-bent with C−Si−Si angles of 93.37°. The research project presented herein sought to extend this technique of carbene-stabilization to group 2 in order to isolate highly reactive beryllium compounds.

1.8 Beryllium Chemistry

Beryllium (chemical symbol: Be) is the smallest metal atom and is one of the most understudied elements on the Periodic Table.[106-108] Although most well-known for its toxicity, beryllium has an array of properties that make it incredibly interesting. Residing in group 2 of the Periodic Table (atomic number 4), it is divalent and occurs in nature only in combination with other elements in minerals.[108] In its metallic form, beryllium is the lightest and most brittle of the alkaline earth metals.[108] Though the literature contains a paucity of structures containing beryllium, recently, there has been a growing interest in the chemistry involving this obscure element. This sections serves to introduce beryllium chemistry and highlight prominent achievements relating to the work in our laboratory.

1.8.1 The History of Beryllium

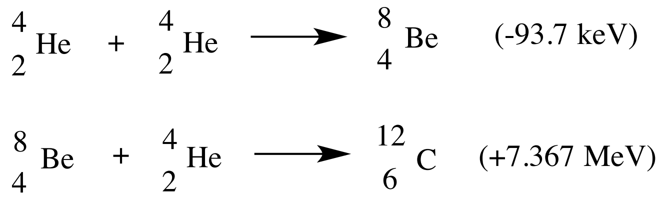
Beryllium was discovered in 1798 by French chemist, Louis-Nicolas Vauquelin, while analyzing beryl−a transparent mineral, beryllium aluminum cyclosilicate ($Be_3Al(SiO_3)_6$). Vauquelin reported that he found a "new earth" by dissolving aluminum hydroxide and beryl in a basic media.[108] Due to the sweet taste of some of its compounds Vanquelin named the new earth "glucinium" and it was given the chemical symbol "GI". The name "beryllium" (steming from Latin: Beryllus and French: Béry−meaning to be pale, in reference to the pale semiprecious gemstone beryl) was ultimately adopted by the French in 1957 and is still used today.[108]

Beryllium was independently isolated in its elemental form by Friedrich Wöhler[109] and Antoine Bussy[110] by the reaction of beryllium chloride and potassium metal (1828). Paul Lebeau obtained the first pure samples of elemental beryllium by electrolysis of a mixture of beryllium fluoride and sodium fluoride (1898).[111] The first commercial process for beryllium production was developed by Alfred Stock and Hans Goldschmidt (1932).[111] The method involved the electrolyzation of beryllium fluoride and barium, which causes beryllium to collect on a water-cooled iron cathode. Currently, beryllium is produced by the reduction of beryllium chloride with magnesium metal.

1.8.2 Applications of Beryllium

The low atomic number and very low absorption for X-rays makes beryllium ideal for a number of applications. One of the most important applications for beryllium is its utility in the construction of radiation windows for X-ray tubes. The transparency to energetic particles led to its use in beam pipes around the collision region in particle physics experiments. Indeed, beryllium is a component in all four main detector experiments at the Large Hardon Collider−the world's largest and most powerful particle collider.[112]

Beryllium is also relevant in nuclear applications acting as a neutron reflector in current power plants.[108] Beryllium foils are used in nuclear weapon designs as the outer layer of the plutonium pits in the primary stage of thermonuclear bombs. In space, beryllium mediated fusion reactions in old stars generate carbon through the "triple alpha process" (Scheme 16).[108] Two helium-4 nuclei (alpha particles) fuse into highly unstable beryllium-8 (−93.7 keV), which decay to reform helium-4.[113] However, under certain conditions, the reactive beryllium nuclei are formed at a faster rate than they decay. Therefore, beryllium-8 can fuse with additional alpha particles to form the stable carbon-12 atom (+7.367 MeV).[113]



$$^{4}_{2}\mathrm{He} + ^{4}_{2}\mathrm{He} \longrightarrow ^{8}_{4}\mathrm{Be} \quad (-93.7\ \mathrm{keV})$$

$$^{8}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He} \longrightarrow ^{12}_{6}\mathrm{C} \quad (+7.367\ \mathrm{MeV})$$

Scheme 16. Triple-alpha process.

Because of the light weight and stability of beryllium over a wide temperature range, it offers interesting mechanical, thermal, and electrical properties as well. In particular, mixing 2% beryllium into copper forms an alloy that is six times stronger than copper alone.[114] Beryllium-copper alloys have found utility in gyroscopes and magnetic resonance devices. It is noteworthy that the addition of 0.005% beryllium alloyed with liquid magnesium results in enhanced oxidation resistance and decreased flammability.[114] Such properties are convenient characteristics for military and aerospace applications.

An interesting new application for beryllium is in quantum computers. Beryllium ions may serve as processors, such a computer has already been built and has been tested for 160 different programs.[115] The system was successful and operated accurately 80% of the time. Based on this data, it is likely that larger computers with beryllium-based processing units will be realized in the future.[108]

1.8.3 Beryllium and Human Health

Beryllium is well-known for its toxicity and special precautions are required when working with the element, however, approximately 35 µg of beryllium is found in the human body.[116] This amount is not considered harmful, however, at increased levels beryllium can be detrimental. Due to the chemical similarities between beryllium and magnesium the human body has difficulty distinguishing between the two elements. Therefore, beryllium can displace magnesium from large biological molecules responsible for metabolic processes, causing them to malfunction.[116]

Beryllium dust is especially toxic and can cause berylliosis−a chronic pulmonary disease that is difficult to detect and can take months to years to manifest in the body. Beryllium compounds are characterized as Category 1 carcinogens and lung cancer is a possible result of prolonged exposure to beryllium dust.[116] There is essentially no viable treatment for beryllium related diseases and a third of patients die or are left severely disabled. Hence, anyone working with beryllium must remain vigilant in ensuring that proper precautions are upheld.

1.8.4 Reactivity of Beryllium

While beryllium and magnesium have some similarities as group 2 elements, beryllium is often excluded from reviews covering the chemistry of group 2 for a number of reasons. The unusual, and often obscure reactivity of beryllium compared to the heavier group 2 elements is often responsible for the omission. For example, beryllium chloride ($BeCl_2$) melts and boils at 405 °C and 520 °C, respectively.[117] In contrast, magnesium chloride ($MgCl_2$) melts at 714 °C and boils at 1412 °C. A high melting point is what one would expect for the strong forces resulting from positive and negative ions, however, the melting point of $BeCl_2$ is quite low. Moreover, the reaction of $BeCl_2$ with water results in a vigorous, exothermic reaction with the expulsion of HCl gas, while $MgCl_2$ has no visible reaction with water.[118] These differences are due to the propensity of beryllium to form covalent compounds instead of ionic compounds. Structurally, beryllium chloride is polymeric in the solid-state and forms electron-deficient three-centered two-electron bonds (Figure 9a).[119] In the vapor phase, $BeCl_2$ exist at equilibrium between a monomer (Figure 9b) and a dimer (Figure 9c). The small size of beryllium atom, coupled with the large charge density is mainly responsible for its unique reactivity profile.[30]

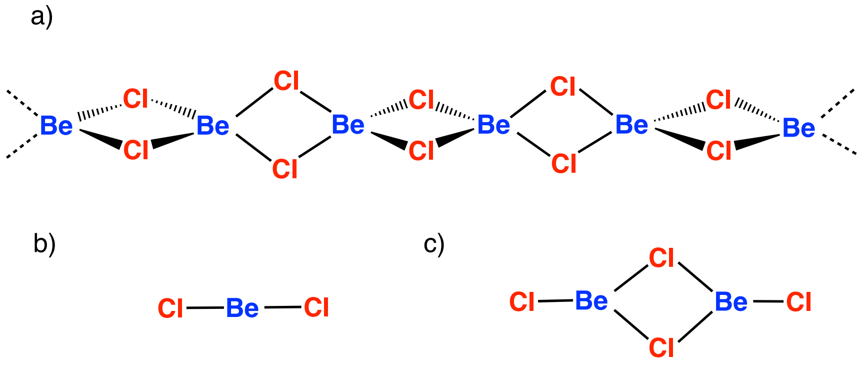


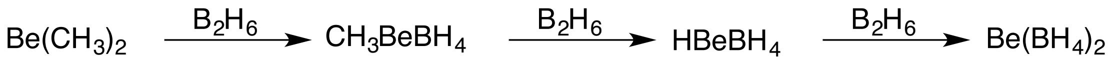
Figure 9. Structure of beryllium chloride.

1.9 Beryllium Borohydride

The study of beryllium borohydride and its derivatives date back to the seminal work of Burg and Schlesinger over seven decades ago.[120] While the molecular structure has remained a mystery, the synthesis was reported in 1940. The literature is riddled with contradictory reports regarding the analysis of this interesting compound.[121] Recent discoveries in our laboratory has reinvigorated discussions regarding the elusive gas-phase structure of the beryllium borohydride monomer. This sections serves to summarize the work chemists have done to elucidate the structural ambiguities surrounding this compound.

1.9.1 Synthesis of Beryllium Borohydride

Originally, beryllium borohydride, **30**, was synthesized by the sequential addition of excess borane to dimethylberyllium (Scheme 17).[120] The reaction proceeded in a series of steps and some of the intermediates are isolable. Beryllium borohydride exhibited some properties similar to aluminum borohydride−it inflames violently in air and reacts vigorously with water. In terms of physical properties, beryllium borohydride is less volatile than the aluminum congener and its melting point is at least 180 °C higher (the final melting point could not be determined due to decomposition).



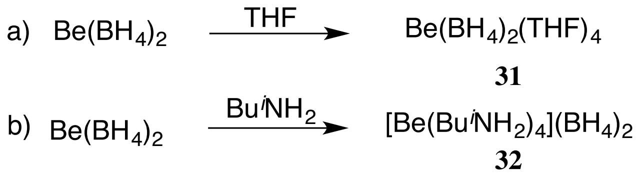
30

Scheme 17. Original synthesis of beryllium borohydride.

The original report by Burg and Schlesinger also explored reactions of beryllium borohydride with trimethylamine.[120] At −80 °C, $Be(BH_4)_2$ reacts with $N(CH_3)_3$ to form the corresponding coordination complex, $(BH_4)_2Be{:}N(CH_3)_3$. Upon exposure to air, this material burst in to a blue-white flame. At elevated temperatures, $(BH_4)_2Be{:}N(CH_3)_3$ decomposes to form $BH_3{:}N(CH_3)_3$ and $BeBH_5{:}N(CH_3)_3$.

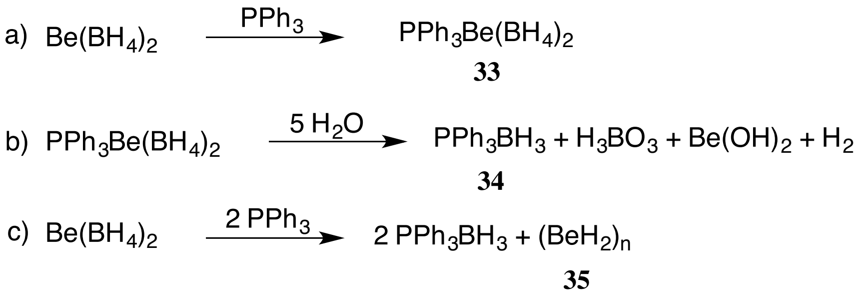
1.9.2 The First Beryllium Borohydride Complexes

Two decades after the synthesis of beryllium borohydride was reported, Coates began to study its coordination chemistry.[122,123] Beryllium borohydride is very soluble in THF and irreversibly reacts to form a chelate complex, **31** (Scheme 18a). Evaporation of excess THF yields a glassy material possibly due to the polymeric nature of the structure. The reaction of $Be(BH_4)_2$ with amines was also explored. It was determined that the reaction beryllium borohydride with isobutylamine yields a 4:1 adduct, **32** (Scheme 18b).[123]



Scheme 18. Reactions of beryllium borohydride with THF and amine.

Triphenylphosphine forms a stable borane adduct, therefore, it was of interest to examine its coordination chemistry with beryllium borohydride. Accordingly, $Be(BH_4)_2$ was added to a benzene solution of triphenylphosphine to form a 1:1 adduct, **33** (Scheme 19a). The monomeric adduct quantitatively undergoes hydrolysis in benzene to form a triphenylphosphine-borane adduct, **34** (Scheme 19b). Conversely, the triphenylphosphine-borane adduct is remarkably resistant to hydrolysis. Interestingly, pyrolysis of a mixture of beryllium borohydride with two equivalents of triphenylphosphine at 180 °C in a sealed tube (under nitrogen) resulted in the formation of a mixture of liquid and solid products (Scheme 19c). As Coates postulated, one of the products was easily identified as a stable triphenylphosphine-borane adduct while the other product was believed to be the highly reactive beryllium hydride, **35** (based on IR data).[123] Notably, it is believed that BeH_2 is not monomeric and no evidence for a stable Be−H bond is reported. However, it is suggested that beryllium hydride is irregular and polymeric in nature where each beryllium atom is bound to up to four other beryllium atoms by single hydrogen bridges (Be·H·Be, the dots represent a single electron or half bond). To date, there is still no structurally characterized example of a compound containing a terminal beryllium hydride with a stable Be−H single bond. In a subsequent report, more concrete evidence for polymeric beryllium hydride was reported.[124] The exchange of the hydrogens in $Be(BH_4)_2$ for deuterium proved that the bridging hydrides in polymeric $(BeH_2)_n$ originated from the $Be(BH_4)_2$ starting material. It is noteworthy that beryllium borohydride coordinates [(L:$Be(BH_4)_2$), L: = Et_2O, Me_3P, Et_3P, Me_3N, and Me_2NH] with other bases forming unstable liquids that are monomeric in benzene.



Scheme 19. Coordination chemistry with triphenylphosphine.

1.9.3 Solid-State Structure of Beryllium Borohydride

Since the synthesis of beryllium borohydride in 1940,[120] there have been a number of contradictory reports regarding its structure. Both bent and linear structures for the B−Be−B fragment have been proposed, and the suggestions on the position of the hydrogen atoms are numerous.[125] Lipscomb published the first crystallographic study regarding this molecule in 1971 with a more detailed report in 1972.[126,127] It was determined that the solid-state structure of beryllium borohydride (Figure 10a) consisted of helical polymers of $-BH_4Be-$ and $-BH_4-$ with a crystallographic polymeric unit (Figure 10b).[126] In the $-BH_4Be-$ unit, the Be---B distance is 1.918 Å, while each Be atom is linked to two remaining BH_4 units (also connected to two Be) at a Be---B distance of 2.001 Å. Half of the BH_4 units link beryllium atoms in the polymeric chain, while the remaining BH_4 units are linked to only one beryllium atom. There are only two hydrogens in the chemical formula $Be(BH_4)_2$ that are not involved in some degree of bonding to a beryllium center. The hexacoordinated beryllium atom is approximately trigonal prismatic.

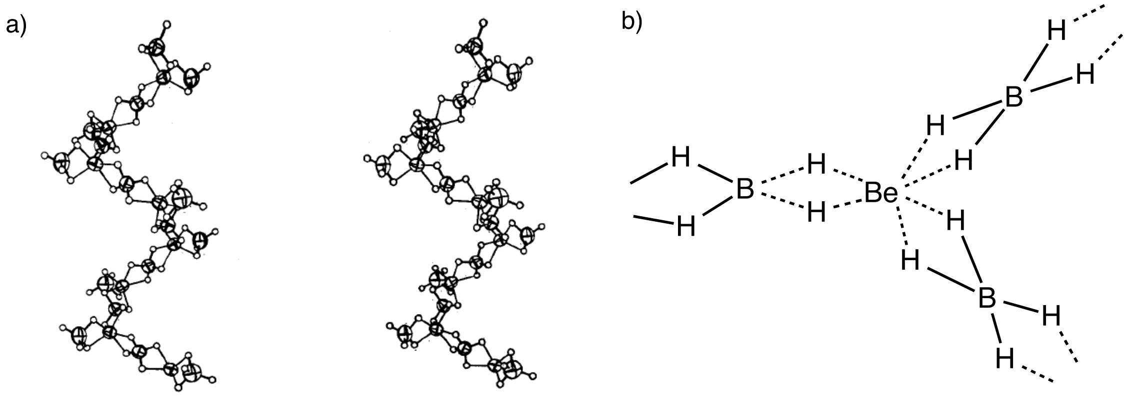


Figure 10. Structure and repeat unit of polymeric beryllium borohydride.

1.9.3 Gas-Phase Structure of Beryllium Borohydride Monomer

Several years after the report of the solid-state structure, despite significant effort, there was still no sufficient evidence concerning the gas-phase structure of monomeric beryllium borohydride. All uncontroversial beryllium borohydride structures [solid-state $Be(BH_4)_2$, $MeBe(BH_4)_2$, and $B_5H_{10}[BeBH_4]$ reveal the presence of double hydrogen bridges between beryllium and boron.[128] Theoretical studies for the gas-phase structure have favored double and triple hydrogen bridges with a linear B−Be−B moiety.[129-131] As many as nine different structures were proposed based on a variety of analytical methods. Gaines narrowed the possibilities based on gas-phase and solution ^{11}B and ^{1}H NMR of the $Be(BH_4)_2$ monomer.[128] Within each borohydride group rapid internal hydrogen exchange was observed on an NMR time scale. None of the previously proposed bent or triangular structures for the gas-phase $Be(BH_4)_2$ monomer were supported by their data. Based on their studies the gas-phase structure contains a linear B−Be−B fragment with the $Be(BH_4)_2$ molecule being highly fluxional (Figure 11). Therefore, the position of the hydrogen atoms was a point of continuing interest. To date, the gas-phase structure is still a mystery being studied by theoretical chemists.

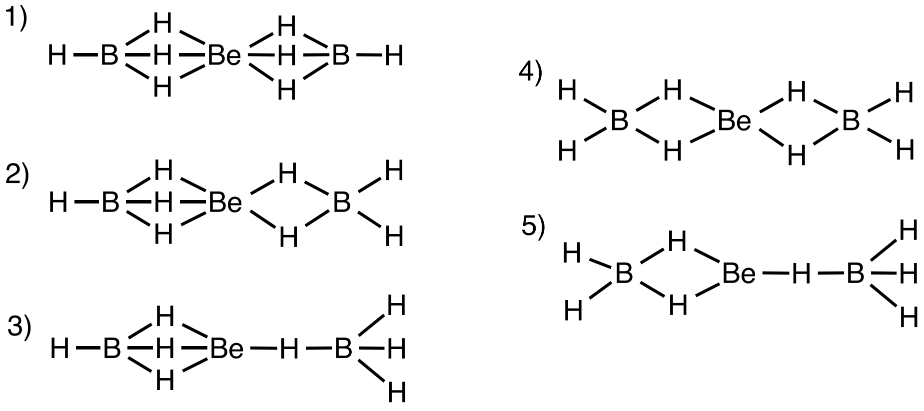


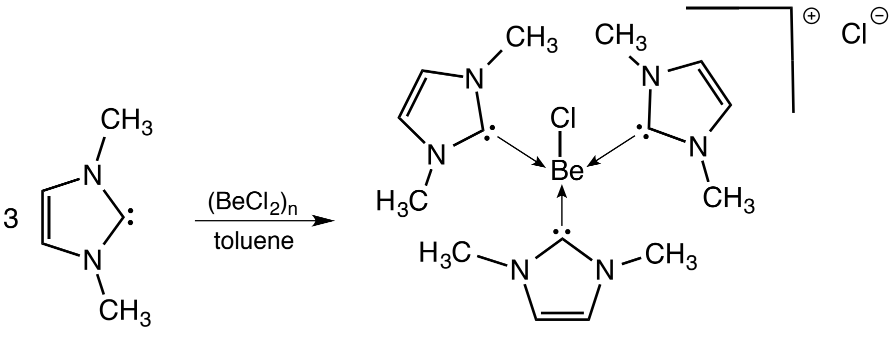
Figure 11. Proposed gas-phase structures of $Be(BH_4)_2$.

1.10 Beryllium and N-Heterocyclic Carbenes

The chemistry of beryllium and NHCs was virtually non-existent before Hermann's report of an ionic beryllium carbene complex (1995).[132] Since then, there have been several years of inactivity regarding NHC-beryllium chemistry, however, recently, a number of interesting molecules have been prepared. This section serves to highlight known NHC-beryllium complexes.

1.10.1 An Ionic Beryllium Carbene Complex

The first example of a beryllium carbene complex was prepared in 1995 by Herrmann (Scheme 20; L: $=:C\{N(CH_3)CH\}_2$).[132] The reaction of $(BeCl_2)_n$ with three equivalents of an NHC ligand resulted in the cleavage of the beryllium chloride polymer and the formation of an ionic beryllium carbene adduct, **36**. Compound **36** was isolated as an air- and temperature- sensitive solid in 73% yield. Structural analysis confirms that the nucleophilic carbene ligand splits the polymeric structure of $(BeCl_2)_n$ and causes heterolysis to afford the ionic complex. The Be−C bond distances (1.807 -1.882 Å) are in accord with previously reported examples of Be−C bonds (1.708-1.853 Å).[133-136] The beryllium atom resides in a distorted tetrahedral environment. Due to the sterically hindered beryllium center, attempts to coordinate a fourth carbene were unsuccessful and resulted in free NHC ligand in solution.[132]

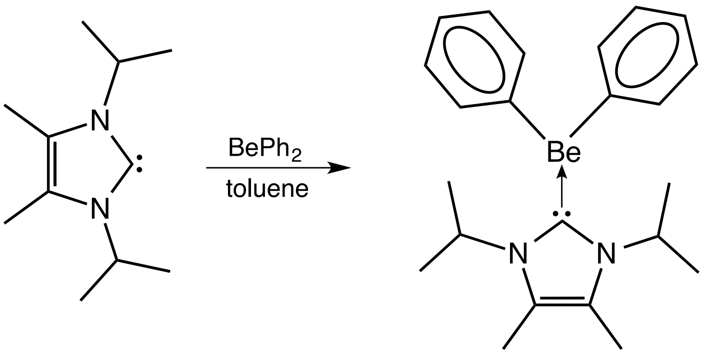


36

Scheme 20. Synthesis of [L:$_3$BeCl]$^+$Cl$^-$.

1.10.2 A Diorganoberyllium Carbene Complex

Gottfriedsen reported the first example of a diorganoberyllium carbene complex in 2006 (Scheme 21; L: =:C{N(^{i}Pr)CH}$_2$).[137] While the synthesis of diphenylberyllium was reported by Gilman in 1927, no X-ray structures were known of its Lewis base adduct.[138] The reaction of the stable NHC with diphenylberyllium in toluene afforded the nucleophilic carbene complex, **37**, as colorless crystals in 85% yield. The structure of **37** confirms the trigonal planar geometry of the beryllium atom. The Be–C$_{\text{carbene}}$ bond distance (1.807 Å) is in the range of the previously reported ionic beryllium carbene complex (1.807-1.822 Å).[132]



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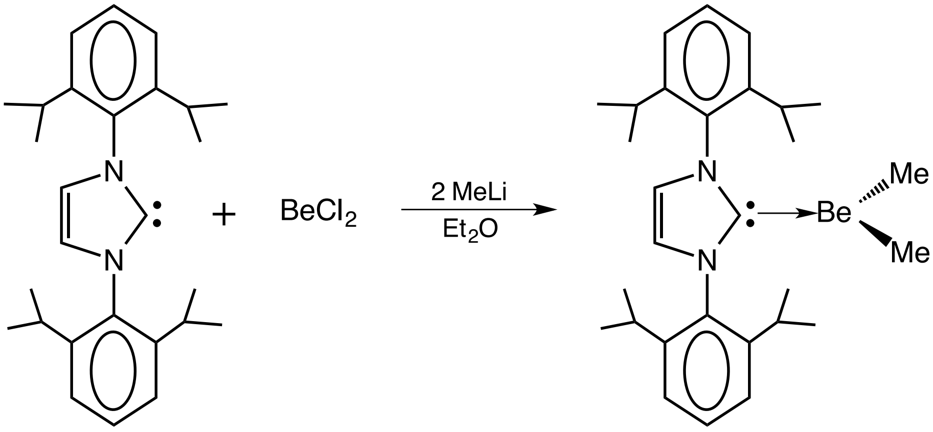
Scheme 21. Synthesis of L:BePh$_2$.

1.10.3 Beryllium-Induced Activation of an NHC Ligand

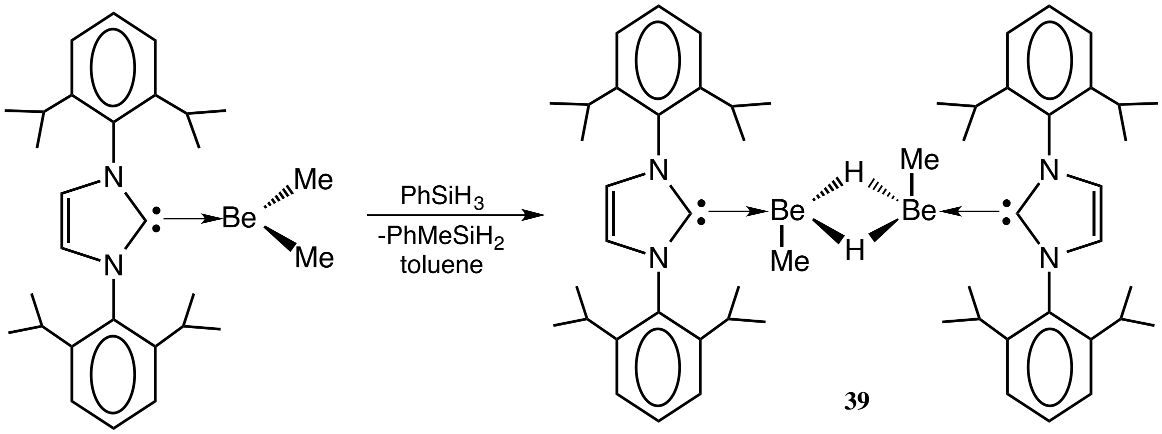
As previously discussed (section 1.9.2), BeH_2 is highly reactive and difficult to isolate. Recently, Hill attempted to prepare BeH_2 by the reaction of a sterically demanding NHC with polymeric $(BeH_2)_n$ in THF.[139] Although no reaction was observed, it led to some interesting chemistry. An ethereal suspension of a free NHC ligand and $BeCl_2$ was treated with methyllithium (1.6 M in diethyl ether) to afford the corresponding dimethylberyllium carbene complex, **38**, in 56% yield (Scheme 22). Similar to the diorganoberyllium complex, **37**, compound **38** is three-coordinate with trigonal planar geometry. One might envision that the elimination of methane from compound **38** might yield the first example of a stable terminal beryllium hydride.



38

Scheme 22. Synthesis of carbene dimethylberyllium.

The isolation of several magnesium hydrides was dependent upon phenylsilane acting as a reducing agent (hydride source).[140-142] Thus, compound **38** was dissolved in toluene and treated with two molar equivalents of $PhSiH_3$. Colorless crystals of **39**, a Be−H−Be dimeric adduct, were obtained in 78% yield (Scheme 23). Notably, compound **39** was the first example of a structurally characterized organoberyllium hydride (BeMeH). Though this compound is interesting, the terminal BeH_2 molecule was not realized. Accordingly, it is within reason that the removal of the remaining methyl groups could yield the target compound.



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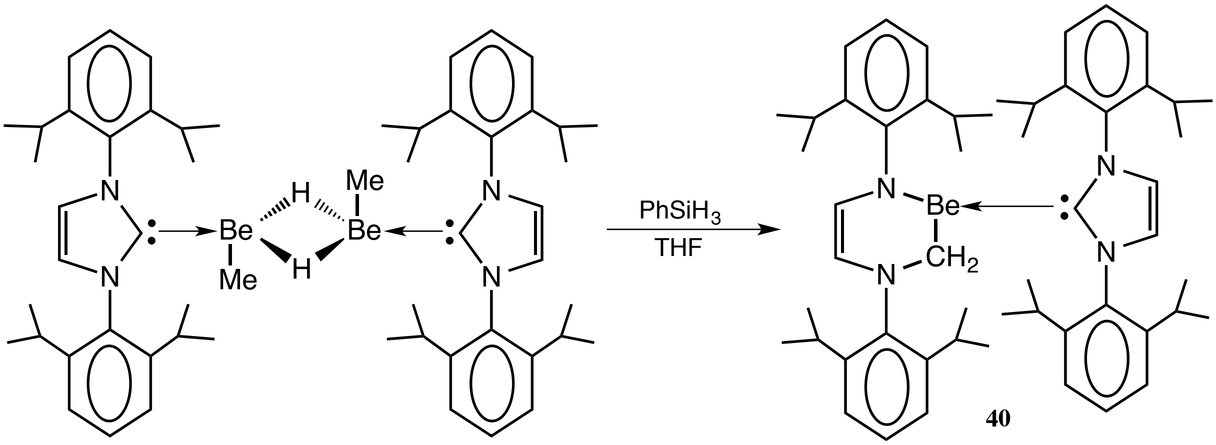
Scheme 23. Synthesis of carbene-complexed organoberyllium hydride.

Surprisingly, when compound **39** was allowed to react with one equivalent of phenylsilane for 6 hours at 80 °C, the symmetry of the molecule was broken giving an orange-red solution (Scheme 24). While phenylsilane was readily converted to the expected metathesis product, $PhMeSiH_2$, NMR suggested the presence of two inequivalent ligands. Indeed, the C−N bond of the NHC ligand had been activated and a BeH_2 unit was inserted (the σ and *π* systems of the imidazole ring were destroyed). The X-ray structure reveals that the three-coordinate beryllium atom is stabilized by a chelating dianionic amidoalkyl ligand and a sterically demanding NHC. The authors reason that the formation of compound **40** is promoted by the instability of the dihydridoberyllium center, during its interaction with phenylsilane.[139]

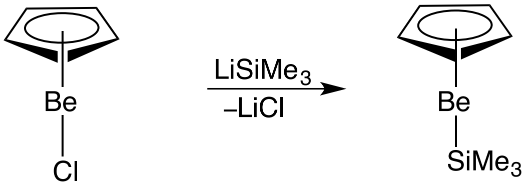


40

Scheme 24. Insertion of a BeH_2 into an NHC ligand.

1.11 Beryllium－Silicon Bonds

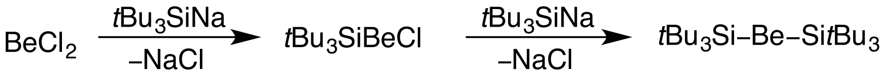
The literature contains few examples of compounds containing bonds between group 2 elements and silicon. Prior to 2003, beryllium－silicon chemistry was essentially nonexistent.[143] Compounds containing beryllium and silicon are now of interest in the semiconductor industry.[143] Hence, the study of compounds with novel Be−Si bonds are significant and may foster a better understanding of their utility. Saulys prepared the first structurally characterized compound containing a bond between beryllium and a group 14 element (other than carbon).[143] The reaction of $LiSiMe_3$ and CpBeCl in pentane yields $CpBe(SiMe_3)$, **41**, as air-sensitive colorless crystals. The ^{29}Si NMR shows a quintet at −27.31 ppm. The X-ray structure of **41** reveals that the Si atom is in a four-coordinate trigonal pyramidal environment. The three Be−Si−C bond angles average to 113.2° exceeding the ideal tetrahedral angle of 109.5°. Compound **41** has a Si−Be bond distance (2.185(2) Å) that is longer than the sum of the covalent radii (2.01 Å).



41

Scheme 25. Synthesis of $CpBe(SiMe_3)$.

Lerner prepared the second series of compounds containing Si−Be bonds.[144] The metathesis reaction of $BeCl_2$ with one equivalent of sodium supersilanide, tBu$_3$SiNa, in THF, led to the formation of **42** as an air- and moisture- sensitive solid, in 80% yield. Addition of an second equivalent of tBu$_3$SiNa in heptane followed by filtration resulted in a clear solution. Storage of the filtrate at −25 °C afforded colorless crystals of **43** in 80% yield. The Be−Si bond distance in **43** (2.1930 Å) is marginally longer than in **42** (2.185 Å).



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43

Scheme 26. Synthesis of tBu$_3$SiBeCl and Be(SitBu$_3$)$_2$.

CHAPTER 2

RESULTS AND DISCUSSIONS

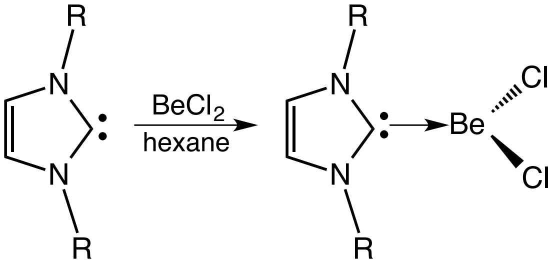
Our research group has rich history in the synthesis, structure, and reactivity of unusual main group molecules. Recents efforts have resulted in the stabilization of a number of highly reactive main group molecules using a class of organic bases known as N-heterocyclic carbenes.[45-56,145,146] Notably, neutral carbenes are in stark contrast to the classical, formally anionic, *m*-terphenyl ligands, and provide access to elements in the formal oxidation state of zero. The seminal report of the first diatomic main group allotrope (carbene-stabilized disilicon, section 1.7.1) invigorated this field.[56] The Si=Si double bond, coupled with the electron rich silicon atoms makes the Si(0) compound highly reactive. These types of molecules have long been studied in the gas phase and in argon matrices, however, isolation of these reactive species was deemed highly unlikely. While a series of main group allotropes containing group 13, 14, and 15 elements have now been synthesized (B_2, Si_2, Ge_2, Sn_2, P_2, As_2), notable structures containing lighter group 2 elements are still challenging.[50,55,56,147,148] Therefore, our laboratory continues to explore synthetic methods to extend the technique of *carbene-stabilization* to the lighter alkali earth metals. The experimental realization of these stable molecules provides a convenient method to study the reactivity of compounds that were previously inaccessible.

2.1 Carbene-Stabilized Beryllium Borohydride

While beryllium borohydride was first synthesized over seven decades ago, the structure of this compound is still being debated (section 1.9). The linear nature of the B—Be—B moiety is currently the accepted orientation, however, the location of the bridging hydrogen atoms is not established.[128] Metal borohydrides are currently of interest due to possible applications in alternative energy.[149-153] Among them, beryllium borohydride was analyzed as a hydrogen storage candidate.[149] Indeed, owing to the small size and high charge density of the beryllium atom, $Be(BH_4)_2$ has the highest hydrogen capacity of all metal borohydrides (20 wt%).[154] Herein, we provide clarity to the solid-state structure of monomeric beryllium borohydride and demonstrate that this molecule can be stabilized by sterically demanding N-heterocyclic carbene ligands.

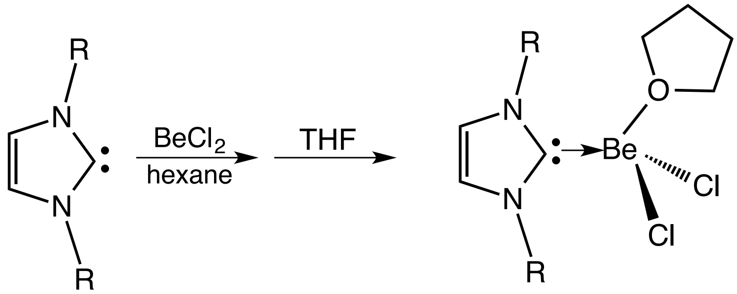
*2.1.1 Synthesis and Molecular Structures of (**1**), (**2**), (**3**), and (**4**)*

The addition of $BeCl_2$ to a slurry of L^1: in hexane resulted in the formation of a white precipitate (Scheme 27). The hexane solution was filtered and the remaining solvent was removed in vacuo. Compound **1** was isolated as colorless crystals from a warm toluene/ hexane solution. Compounds **2** and **3** were quantitatively prepared in a similar fashion, addition of THF in the reaction mixture or as a crystallization solvent results in their formation (Scheme 28). X-ray quality crystals of **2** and **3** may be obtained by cooling THF/hexane solutions to −20 °C in the freezer. The addition of 1,4-dioxane to **1** in the presence or absence of additional (non-coordinating) solvents gives **4** as colorless crystals in near quantitative yield (Scheme 29).



1 R= 2,6-diisopropylphenyl

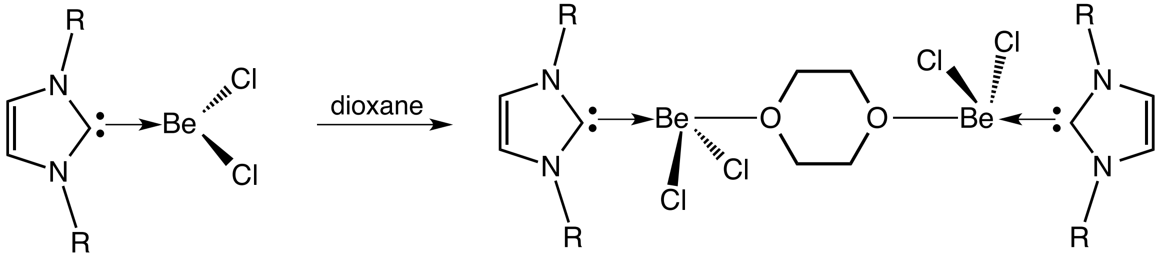
Scheme 27. Synthesis of (**1**).



2 R= 2,6-diisopropylphenyl

3 R= 2,4,6-trimethylphenyl

Scheme 28. Synthesis of (**2**) and (**3**).



4 R= 2,6-diisopropylphenyl

Scheme 29. Synthesis of (**4**).

Structural analysis of **1** reveals a three-coordinate beryllium atom in a trigonal planar environment (Figure 12). The $CBeCl_2$ plane is staggered with respect to the imidazole ring and has a Cl(1)—Be(1)—C(1)—N(1) torsion angle of 76°. The Be(1)—C(1) bond distance of 1.765(2) Å is in accord with previously reported Be—C_{carbene} bonds ranging from 1.707-1.822 Å.[132] The crystal structures of **2** and **3** feature four-coordinate beryllium atoms with tetrahedral geometry (Figures 13 and 14). While the Be(1)—C(1) bond in **1** is relatively short (1.765(2) Å), the Be(1)—C(1) bonds in **2** and **3** are elongated (1.843(3) and 1.848(4), respectively) due to the coordination of a THF molecule to the beryllium center. The C(1)—Be(1)—Cl(1) angles in **2** (108.11(15)°) and **3** (112.13(19)°) are expectedly smaller than in **1** (121.3(3)°) due to the increased coordination number of the beryllium atoms in the THF adducts. Single crystal X-ray diffraction studies of **4** reveal a carbene-beryllium chloride dimer linked by a dioxane molecule (Figure 15). The tetracoordinate beryllium atom resides in a tetrahedral environment with a C(1)—Be(1)—Cl(1) angle of 106.01(11)°, which falls in the range of those in **2** and **3** (108.11-112.13°). While the Be(1)—O(1) bonds in **2** and **3** are 1.697(3) Å and 1.698(4) Å, respectively, the Be(1)—O(1) in **4** is longer at 1.767(2) Å. This observation stems from the distorted nature of the dioxane molecule.

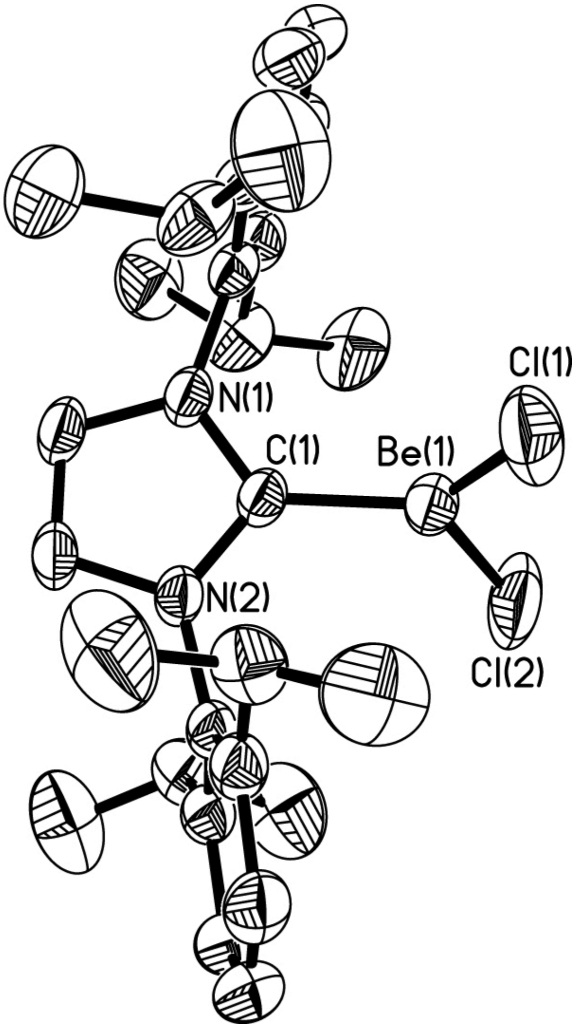


Figure 12. Molecular structure of (**1**).

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

Atoms	Distance	Atoms	Angle
Be(1)−C(1)	1.773(5)	C(1)−Be(1)−Cl(2)	120.4(4)
Be(1)−Cl(2)	1.844(9)	C(1)−Be(1)−Cl(1)	121.3(3)
Be(1)−C1(1)	1.881(6)	C(2)−Be(1)−Cl(1)	117.2(3)

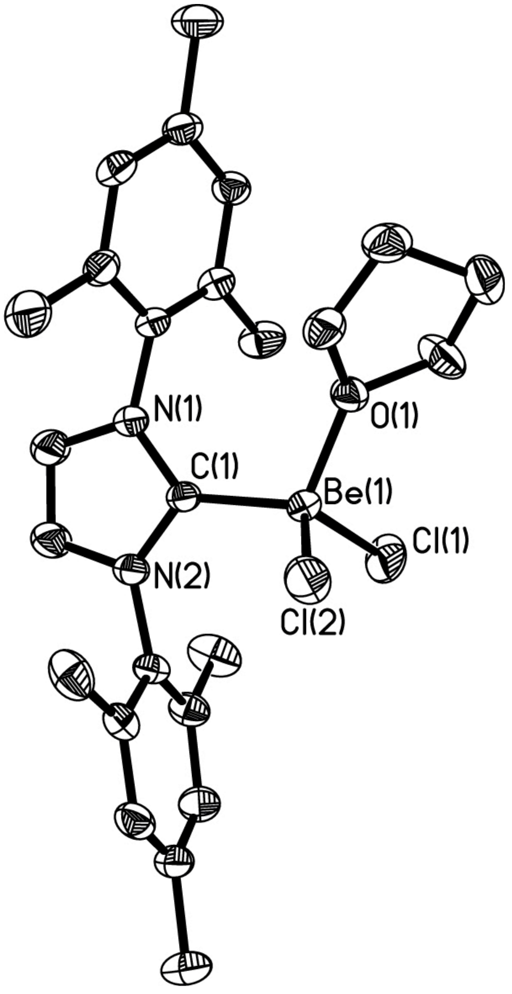


Figure 13. Molecular structure of (**2**).

Table 2. Selected bond lengths [Å] and angles [°] for **2**.

Atoms	Distance	Atoms	Angles
Be(1)−O(1)	1.697(3)	O(1)−Be(1)−C(1)	110.83(16)
Be(1)−C(1)	1.843(3)	O(1)−Be(1)−Cl(1)	105.84(14)
Be(1)−Cl(1)	1.989(3)	C(1)−Be(1)−Cl(1)	108.11(15)
Be(1)−Cl(2)	2.008(3)	O(1)−Be(1)−Cl(2)	104.92(15
		C(1)−Be(1)−Cl(2)	112.38(15)
		Cl(1)−Be(1)−Cl(2)	114.54(13)

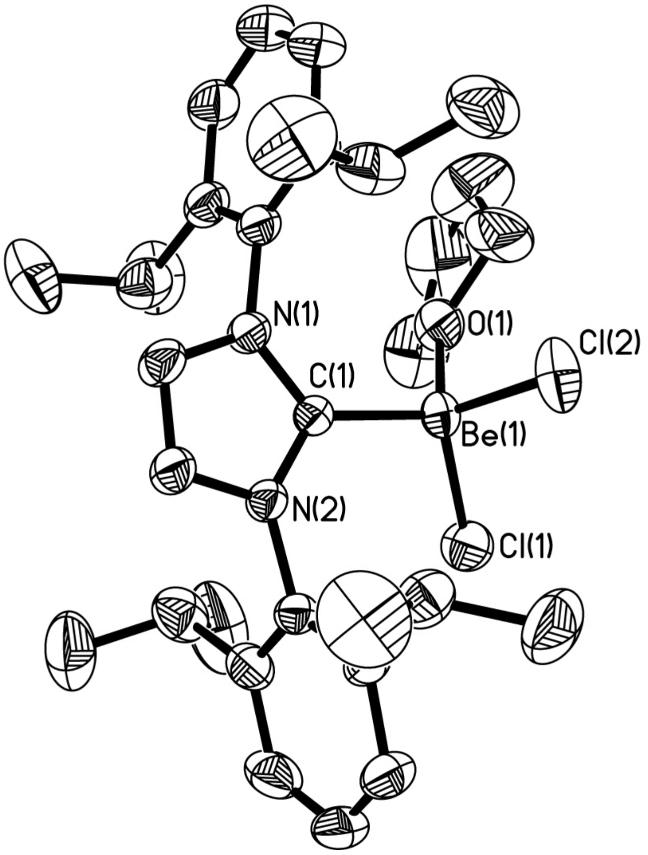


Figure 14. Molecular structure of (**3**).

Table 3. Selected bond lengths [Å] and angles [°] for **3**.

Atoms	Distance	Atoms	Angles
Be(1)−O(1)	1.698(4)	O(1)−Be(1)−C(1)	110.7(2)
Be(1)−C(1)	1.848(4)	O(1)−Be(1)−Cl(2)	106.96(19)
Be(1)−Cl(2)	2.000(4)	C(1)−Be(1)−Cl(2)	108.17(19)
Be(1)−Cl(1)	1.985(4)	O(1)−Be(1)−Cl(2)	106.6(2)
		C(1)−Be(1)−Cl(1)	112.13(19)
		Cl(2)−Be(1)−Cl(1)	112.17(18)

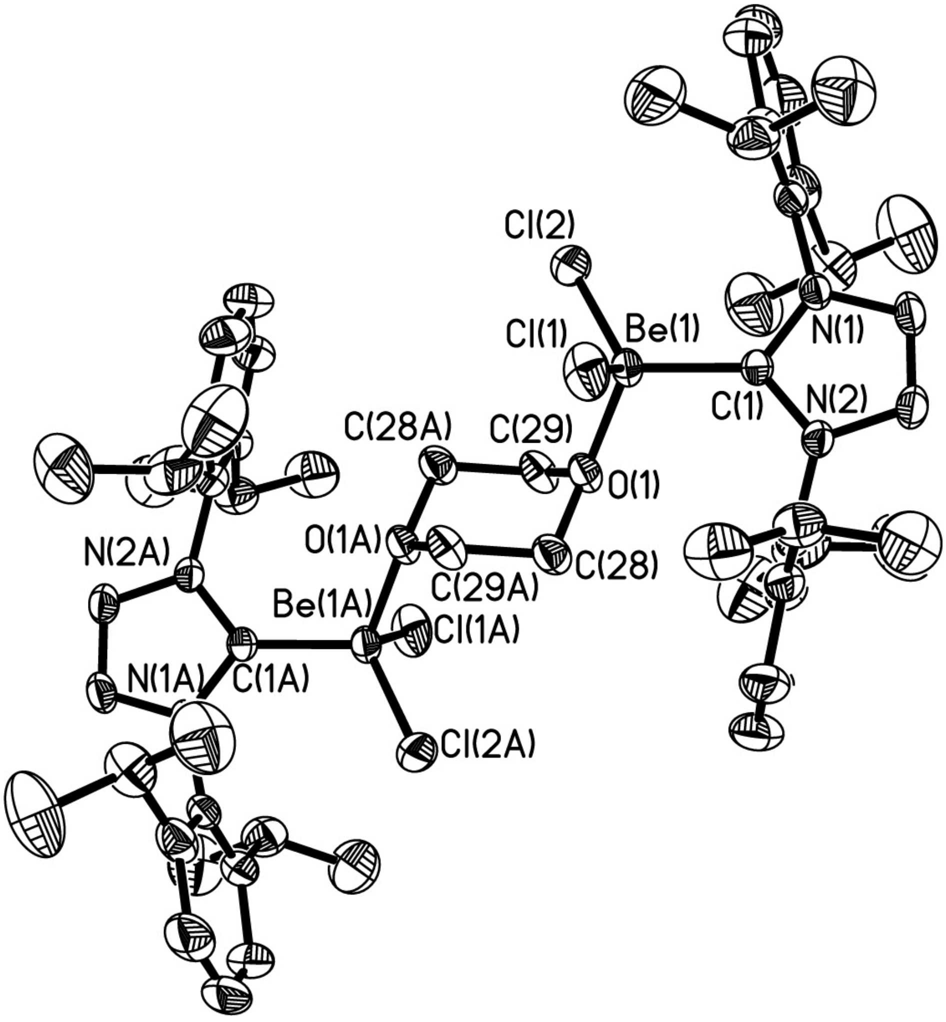


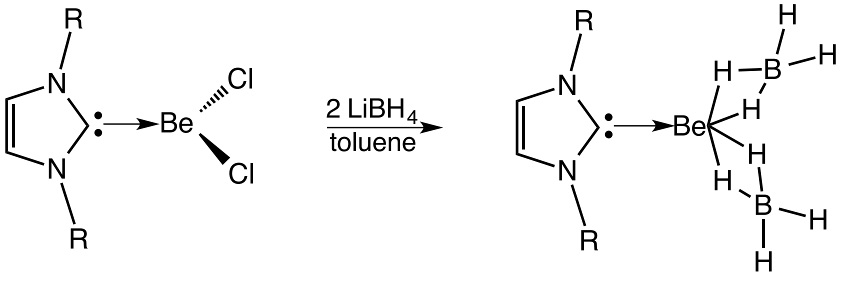
Figure 15. Molecular structure of (**4**).

Table 4. Selected bond lengths [Å] and angles [°] for **4**.

Atoms	Distance	Atoms	Angles
Be(1)−O(1)	1.767(2)	O(1)−Be(1)−C(1)	109.79(13)
Be(1)−C(1)	1.828(2)	O(1)−Be(1)−Cl(2)	106.74(11)
Be(1)−Cl(2)	1.963(2)	C(1)−Be(1)−Cl(2)	114.47(12)
Be(1)−Cl(1)	1.989(2)	O(1)−Be(1)−Cl(1)	105.50(11)
		C(1)−Be(1)−Cl(1)	106.01(11)
		Cl(2)−Be(1)−Cl(1)	113.96(11)

*2.1.2 Synthesis and Molecular Structure of (**5**)*

Recently, N-heterocyclic carbenes have found utility in the stabilization of alkali earth metal hydrides. For example, in the presence of a hydride source, the C−N bond of an NHC ligand in L:Be(Me)(μ-H_2)(Me)Be:L (L:=:C{N(2, 6-$^{i}Pr_2C_6H_3$)CH}$_2$) is activated with insertion of a BeH_2 unit (section 1.10.3).[139] NHC-complexed beryllium chloride (**1**) reacts with two molar equivalents of lithium borohydride in toluene to afford carbene-stabilized beryllium borohydride (**5**) as colorless prism-shaped crystals in 67.8% yield (Scheme 30). While previously reported beryllium borohydride derivatives are unstable and exhibit explosive reactivity with air and/or moisture, crystalline **5** can survive in air for three days without decomposition. Proton NMR resonances of the carbene backbone (C=C) in **1** and **5** show an expected slight downfield shift (6.39 to 6.42 ppm). The proton-coupled ^{11}B NMR resonances of the borohydride units in **5** give rise to a broad quintet at −31.2 ppm (THF-d_8), which is comparable to −42.0 ppm for lithium borohydride (THF-d_8). The proton resonance for the $[BH_4]^-$ units in the ^1H NMR spectrum overlap with the methyl groups on the carbene ligand, however, it can be visualized unambiguously as a singlet at 0.06 ppm in the $^1H\{^{11}B\}$ spectrum.



1

5 R= 2,6-diisoproypylphenyl

Scheme 30. Synthesis of (**5**).

Crystallographic studies of **5** display a five-coordinate beryllium center with distorted square-pyramidal geometry (Figure 16). The Be(1)–C(1) bond distance of 1.765(2) Å in compound **5** is comparable to those in compounds **1-4** and to the computed value (1.797 Å) in the simplified model compound L'Be$(BH_4)_2$ (L': :C{N(Ph)CH}$_2$). Each borohydride anion $[BH_4]^-$ is bound to the beryllium center through two bridging Be−H−B bonds. The Be---B distances in **5** are in accord with those in the highly reactive beryllium borohydride polymer [1.918(4)−2.001(4) Å]. Moreover, the B(1)−Be(1)−B(2) angle (121.7°) is slightly smaller than in Be$(BH_4)_2$ (123.5−124.8). This may be attributed to the coordination of the sterically demanding carbene ligand. In the $[BH_4]^-$ units of **5**, the B−H bond lengths average to 1.08 Å which comparable to that in the polymeric structure (1.13 Å). While the Wiberg bond indices (WBIs) of the Be−C (0.22) and Be−H (0.07-0.08) bonds are quite low, the WBIs of the B−H bonds in the borohydride units is significantly higher ranging from 0.87 to 0.99. This data is consistent with mainly ionic bonding character. Natural Bond Orbital analysis of **5** showed that the sum of the natural atomic charges for each borohydride unit is −0.83 and the natural charge of the beryllium atom is +1.53, suggesting dicationic character.

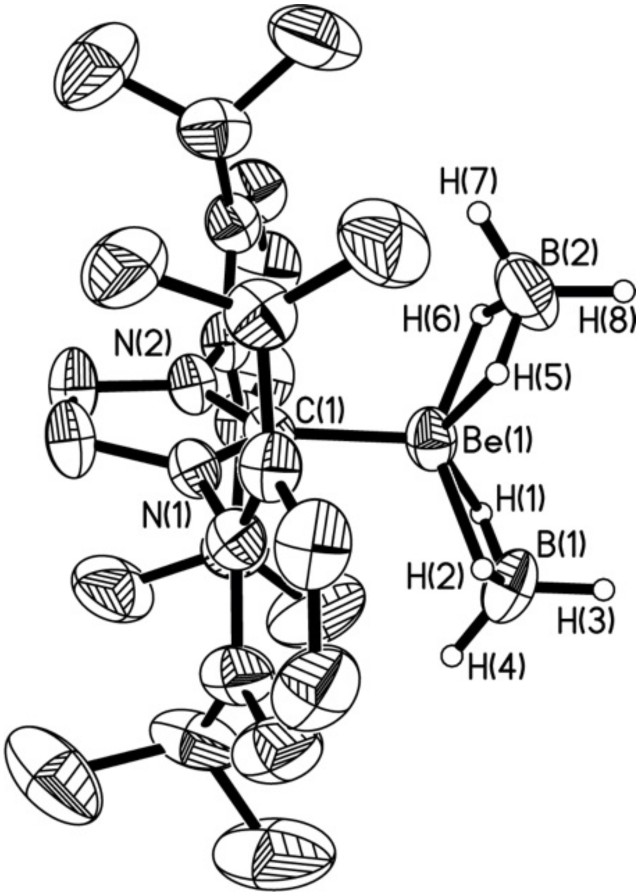


Figure 16. Molecular structure of (**5**).

Table 5. Selected bond lengths [Å] and angles [°] for **5**.

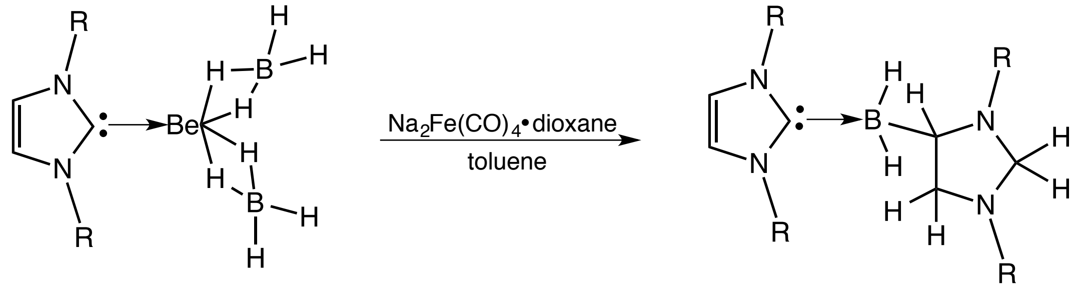
Atoms	Distance	Atoms	Angles
Be(1)−C(1)	1.765(2)	Be(1)−H(1)−B(1)	94.6(12)
Be(1)−H(1)	1.586(14)	Be(1)−H(2)−B(1)	94.9(14)
Be(1)−H(2)	1.549(19)	Be(1)−H(5)−B(2)	90.6(12)
Be(1)−H(5)	1.530(15)	Be(1)−H(6)−B(2)	91.1(13)
Be(1)−H(6)	1.571(19)		
B(1)−H(1)	1.03(2)		
B(1)−H(2)	1.07(2)		
B(1)−H(3)	1.045(17)		

2.2 Reactivity of Carbene-Stabilized Beryllium Borohydride

Beryllium borohydride derivatives are inherently unstable species.[120,122-124] Indeed, the trimethylamine adduct $[(CH_3)_3N{:}Be(BH_4)_2]$ of beryllium borohydride is reported to be pyrophoric, exhibiting a blue-white flame upon exposure to air.[120] Consequently, there is little known about the reactivity of these materials beyond the aforementioned coordination complexes (section 1.9.2 and 2.1.1). The study of beryllium borohydride derivatives may provide insight into the reactivity of other metal borohydrides which are currently being explored in hydrogen storage applications.[149] The chemistry of carbene-stabilized beryllium borohydride under reducing conditions is presented herein.

*2.2.1 Synthesis and Molecular Structure of (**6**)*

Recently, $Mg(BH_4)_2(pyrazine)_2$ was reported to undergo facile arene hydroboration.[155] Moreover, an imidazole was reduced to imidazolidine by the reaction of sodium borohydride and an osmium carbonyl compound.[156] To explore the reactivity of $L^1{:}Be(BH_4)_2$ under reducing conditions, disodium tetracarbonylferrate, $Na_2Fe(CO)_4{\cdot}dioxane$ (also know as Collman's reagent), was combined with **5** in toluene and allowed to react for 7 days. The reaction mixture was filtered and the solution was concentrated to yield crystalline **6** in 64.3% yield. The structure of **6** shows that the carbene backbone (C=C) was reduced via a classical hydroboration reaction. Additionally, the C2 carbene center underwent hydrogenation. It is noteworthy that lithium aluminum hydride has the ability to reduce C2 carbon atoms of imidazolinium salts.[32] Bertrand recently reported the splitting of H_2 at a nucleophilic carbene center.[44] However, the synthesis of **6** represents the first example of the "dual reduction" of both the C=C double bond and the C2 carbene center of the NHC imidazole ring. The two ^1H NMR resonances at 4.08 and 4.22 ppm are attributed to the two diastereotopic hydrogens at the reduced carbene center, which are consistent with similar C2 proton resonances in known imidazolidines (4.29 and 4.59 ppm).[32] The ^{11}B NMR spectrum further supports the “dual reduction” of the imidazole ring. While the BH_2 fragment is not visible in the proton NMR spectrum, the ^{11}B spectrum shows a broad singlet with shoulders at −25.5 ppm.



5

6 R= 2,6-diisoproypylphenyl

Scheme 31. Synthesis of (**6**).

X-ray structural analysis of **6** reveals that the B(1)−C(1) bond of 1.615(2) Å is slightly longer than those in N-heterocyclic carbene borane binuclear complexes ranging from 1.588(7)-1.602(7) Å (Figure 17).[145] The BH_2 unit is bridged between C(1) of a stabilizing NHC ligand and C(29) of a reduced carbene moiety. In comparison to the NHC imidazole C(2)=C(3) double bond of 1.327(2) Å, the C(29)−C(30) single bond of the reduced carbene is expectedly longer at 1.507(2) Å. The geminal hydrogen pairs at C(28), C(30) and B(1) and the hydrogen at C(29) were all located in the difference Fourier map.

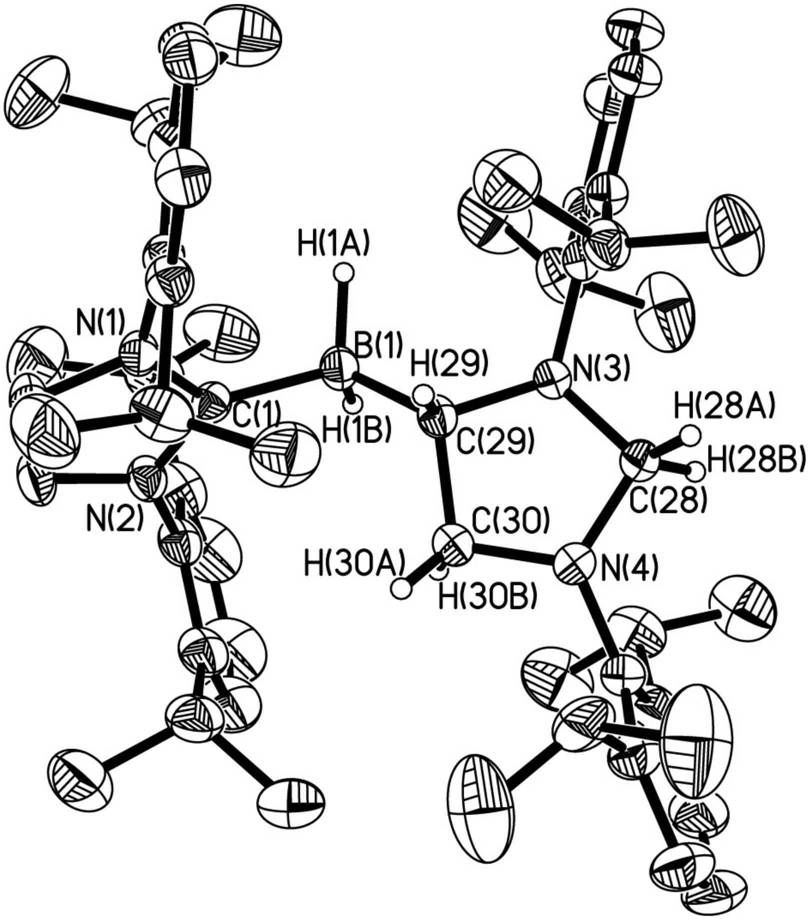


Figure 17. Molecular structure of (**6**).

Table 6. Selected bond lengths [Å] and angles [°] for **6**.

Atoms	Distance	Atoms	Angles
B(1)−C(1)	1.615(2)	C(1)−B(1)−C(29)	113.97(11)
B(1)−C(29)	1.614(2)	B(1)−C(29)−N3(1)	112.28(11)
C(2)−C(3)	1.327(2)	B(1)−C(1)−N(2)	126.98(12)
C(1)−N(1)	1.3550(16)		
C(1)−N(2)	1.3792(18)		
C(28)−N(4)	1.448(2)		
C(28)−N(3)	1.454(2)		

2.3 Disilicon-Complexed Beryllium Chloride

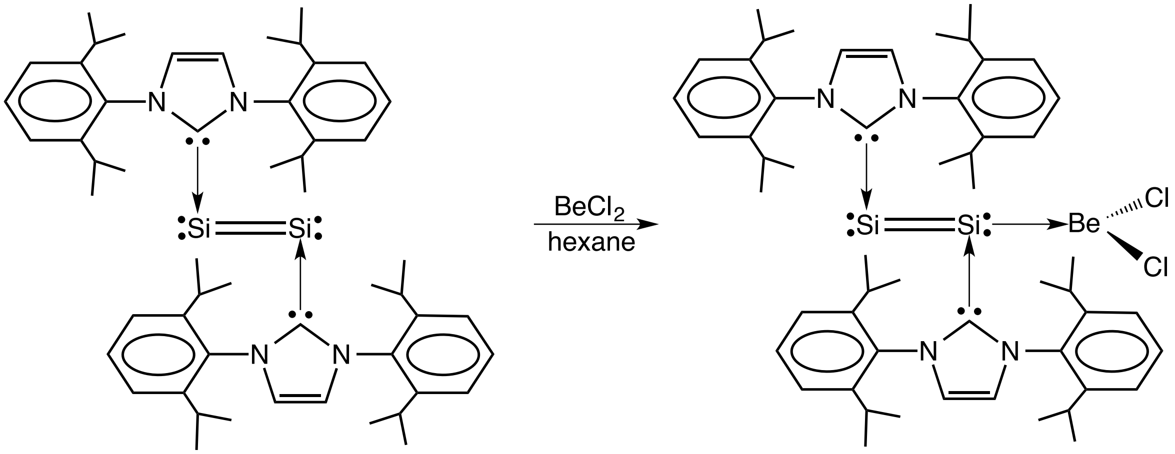
Early-late heteronuclear complexes have sparked interest due to possible applications in electronics and semiconducting industries.[143,157-164] In particular, beryllium doping of silicon via high-temperature evaporation and subsequent vapor deposition of Be metal onto Si wafers have been reported.[157,165,166] Group 2 element−silicon heteronulcear complexes are rare. In fact, there are only two reports of compounds containing Be−Si bonds.[143,144] Historically, silicon −beryllium chemistry has been marked by its ability to form covalent interactions with each other. Indeed, the first such compound, cyclopentadienyl(trimethylsilyl)beryllium CpBe($SiMe_3$), was prepared by the reaction of $LiSiMe_3$ and CpBeCl.[143]

N-Heterocyclic carbenes, as diverse sigma donors, have been utilized to stabilize a number of highly reactive main group molecules.[45-56,146,167] A prominent example from our laboratory is carbene-stabilized disilicon, the first zero-oxidation-state main group diatomic allotrope of elemental silicon (section 1.7.1).[56] This research project extensively studies reactions of NHC ligands (which contain a carbon electron pair) with $BeCl_2$. Might carbene-stabilized disilicon (containing silicon electron pairs) be used to study coordination chemistry with $BeCl_2$?

2.3.1 Synthesis and Molecular Structure of (7)

The reaction of carbene-stabilized disilicon, L:Si=Si:L [L: = :C{N(2,6-$^iPr_2C_6H_3$) CH}$_2$], with beryllium chloride quantitatively yields [L:Si=Si:L]$BeCl_2$ (**7**) (Scheme 32). Notably, **7** is a rare example of a compound containing a Si−Be bond. Moreover, this is the first example of a compound containing a Si−Be dative bond (or donor-acceptor bond). The ^{29}Si NMR resonance for disilicon is 224.5 ppm representing the two equivalent Si atoms. In notable contrast, the two

^{29}NMR peaks (229.5 and −25.9 ppm) are consistent with the unsymmetrical Si_2 moiety of **7**. Indeed, one of the silicon atoms possess a lone pair of electrons while the other silicon atom is using its electron pair to coordinate beryllium chloride.



7

Scheme 32. Synthesis of (**7**).

The X-ray structure of **7** demonstrates that the Si(1)=Si(2) bond (2.0000(14) Å) decreases upon the complexation of $BeCl_2$ [Si(1)=Si(2) in L:Si=Si:L: 2.294(11) Å] (Figure 18). The Si(1)−Be(1) bond in **7** (2.243(6)) is slightly longer that in $CpBe(SiMe_3)$ (2.185(2) Å) and *t*Bu_3Si −Be−Si*t*Bu_3 (2.185 Å).[143,144] This observation stems from the fact that dative bonds are typically longer and marginally weaker than their covalent counterpart. The *trans*-bent nature of carbene-stabilized disilicon is retained with an increase in the C(1)−Si(1)−Si(2) angle (101.84° vs. 93.37°). While the C(1)−Be(1) dative bond in **1** is 1.773(5), the comparable Si(1)−Be(1) dative bond (2.243(6)) in **7** is significantly longer, which is in accord with the increased atomic size of silicon compared to carbon.

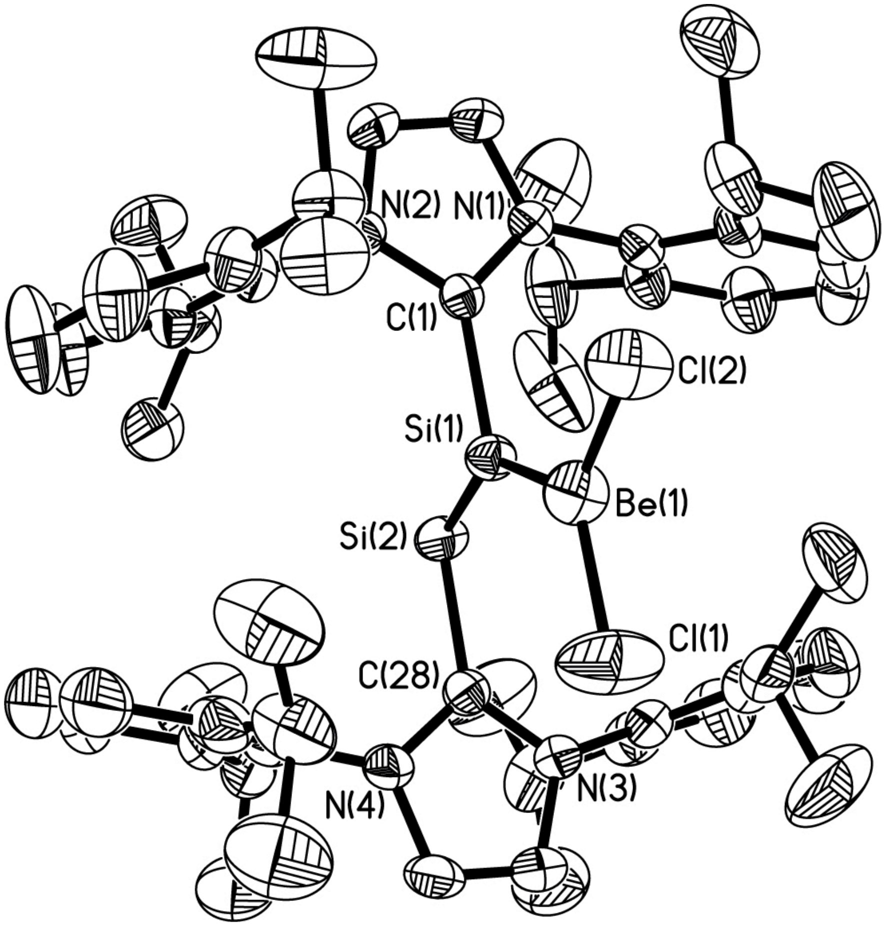


Figure 18. Molecular structure of (**7**).

Table 7. Selected bond lengths [Å] and angles [°] for **7**.

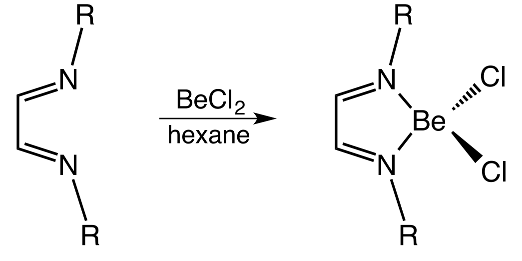
Atoms	Distance	Atoms	Angles
Si(1)−C(1)	1.937(3)	C(1)−Si(1)−Si(2)	101.84(10)
Si(1)−Si(2)	2.0000(14)	C(1)−Si(1)−Be(1)	114.88(18)
Si(1)−Be(1)	2.243(6)	Si(2)−Si(1)−Be(1)	143.08(17)
Si(2)−C(28)	1.930(3)	C(28)−Si(2)−Si(1)	96.69(11)
Be(1)−Cl(2)	1.907(6)	Cl(2)−Be(1)−Cl(1)	116.2(3)
Be(1)−Cl(1)	1.923(6)	Cl(2)−Be(1)−Si(1)	124.4(3)

2.4 Diimine-Stabilized Beryllium Dimer

After the discovery of the first compound containing a Mg−Mg bond, chemists sought to prepare the lighter Be−Be bond.[168] Though theoretical chemists have predicted that molecules containing Be−Be are stable species, synthetic chemists have had difficulty isolating such compounds.[169] Indeed, Jones reports that the reduction of nacnac and diimine beryllium halides result in ligand decomposition (C−H bond activation) and the deposition of beryllium metal.[168] The reaction mechanism may proceed through beryllium radical formation making the molecule highly unstable. We found that the reduction of diimine beryllium chlorides result in the formation of a novel beryllium dimer.

*2.4.1 Synthesis and Molecular Structure of (**8**) and (**9**)*

Computations have shown that a negatively charged ligand system may enhance the probability of isolating a compound containing a Be−Be bond.[170] Therefore, diimine ligands may be advantageous in this regard as they are easily reduced to form anionic or dianionic ligand systems. To this end, the sterically demanding diimine ligands were allowed to react with $BeCl_2$ in hexane to form compounds **8** and **9** in quantitative yield (Scheme 33). In contrast to N-heterocyclic carbenes (which use a carbon lone pair to bond to $BeCl_2$), these diimines use nitrogen lone pairs to complex $BeCl_2$.



8 R = 2,6-diisoproypylphenyl

9 R = 2,4,6-trimethylphenyl

Scheme 33. Synthesis of (**8**) and (**9**).

The X-ray crystal structure of **8** reveals that the diimine serves as a bidentate ligand for $BeCl_2$ (Figure 19). The four-coordinate beryllium atom resides in a distorted tetrahedral environment. While the Cl−Be−Cl angles in compounds **1-4** range from 112.17-114.54°, the Cl −Be−Cl angle in **8** slightly larger at 115.0°. The Be−N bond distances in **8** (1.795 and 1.802 Å) compare well with previously reported Be−N bonds in $(PhCN)_2BeCl_2$ (1.740 Å) and $(pyr)_2BeCl_2$ (1.741 Å).[171]

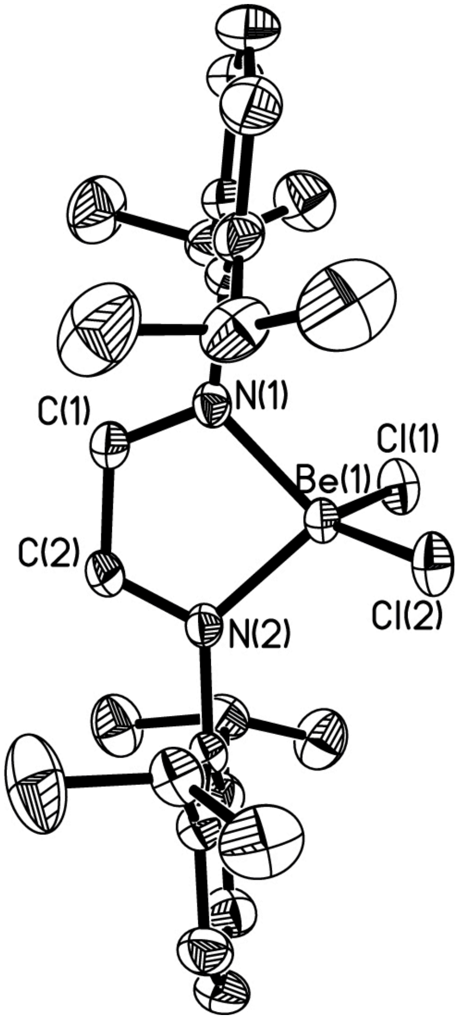


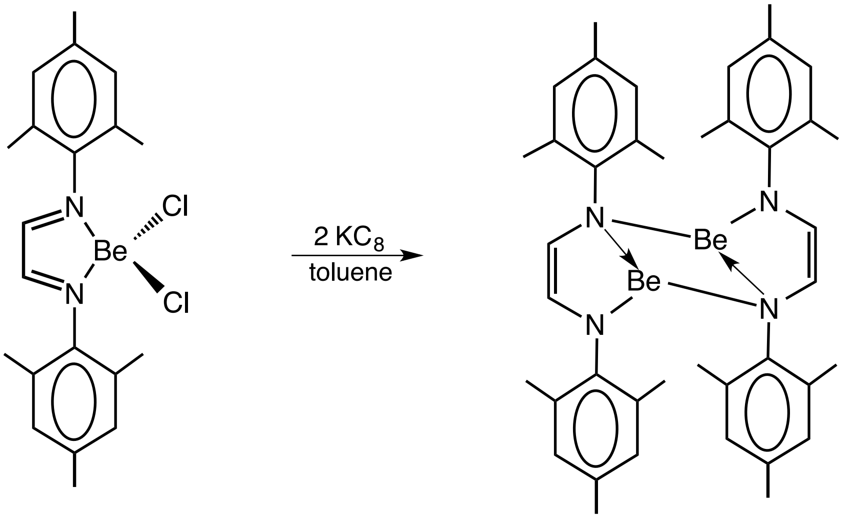
Figure 19. Molecular structure of (**8**).

Table 8. Selected bond lengths [Å] and angles [°] for **8**

Atoms	Distance	Atoms	Angle
Be(1)−N(2)	1.795(5)	N(2)−Be(1)−N(2)	89.4(2)
Be(1)−N(1)	1.802(5)	N(2)−Be(1)−Cl(2)	112.7(3)
Be(1)−C1(2)	1.955(5)	N(1)−Be(1)−Cl(1)	117.2(2)
Be(1)−C1(1)	1.953(5)	N(2)−Be(1)−Cl(1)	111.6(2)
C(1)−C(2)	1.467(4)	Cl(2)−Be(1)−Cl(1)	115.0(2)

*2.4.2 Synthesis and Molecular Structure of (**10**)*

Reduction of the diimine beryllium chloride complex (**9**) with two equivalents of KC_8 in toluene yields a novel beryllium dimer (**10**) (Scheme 34). Notably, the two chlorine atoms were removed and two diimine Be-units approach each other forming a Be_2N_2 four-membered ring.



10

Scheme 34. Synthesis of (**10**).

Single crystal X-ray diffraction studies of **10** reveal that each beryllium atom is three-coordinate adopting distorted trigonal planar geometry (Figure 20). Each beryllium atom contains one Be−N dative bond (1.720 Å) that is noticeably longer than the two Be−N covalent bonds (1.565 and 1.685 Å). This is consistent with the fact that dative bonds are typically longer and weaker than covalent bonds. Overall, the Be−N bonds (1.565, 1.685 and 1.720 Å) in **10** are comparable to those in **8** (1.795-1.802 Å). In the structure of compound **10**, one of the diimine ligands is essentially perpendicular to the other.

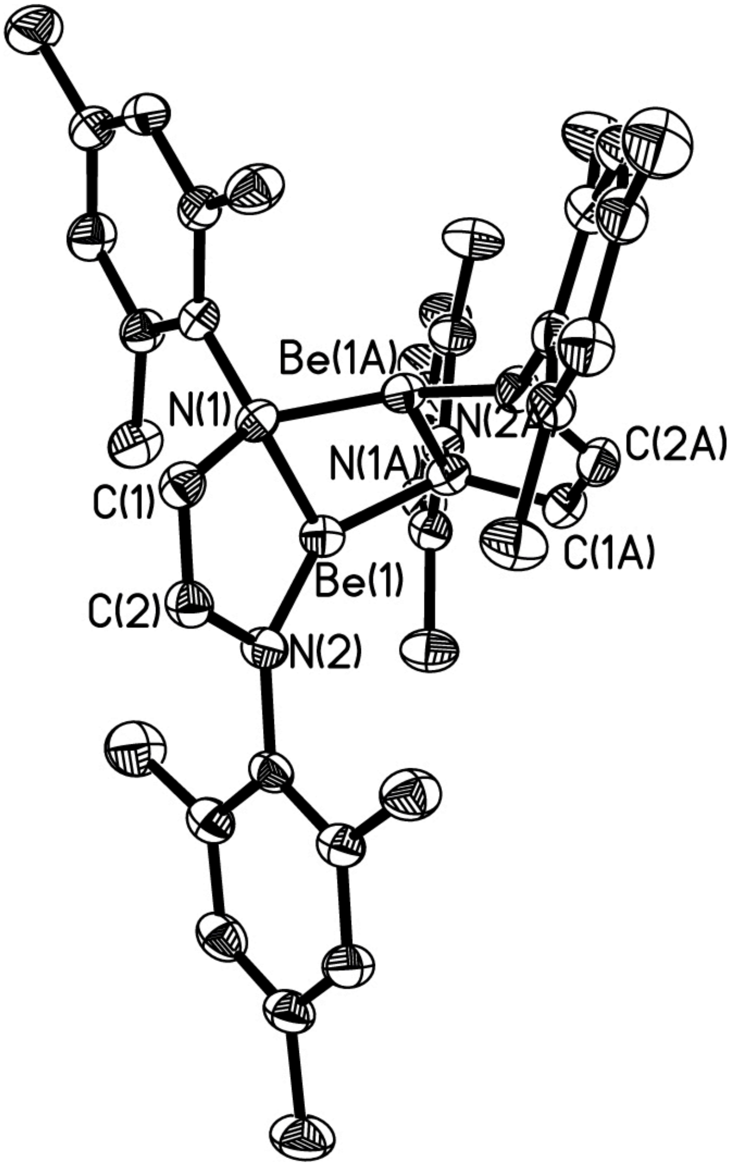


Figure 20. Molecular structure of (**10**).

Table 9. Selected bond lengths [Å] and angles [°] for **10**.

Atoms	Distance	Atoms	Angle
Be(1)－N(2)	1.565(3)	N(2)－Be(1)－N(1)#1	144.25(16)
Be(1)－N(1)#1	1.685(3)	N(2)－Be(1)－N(1)	103.80(14)
Be(1)－N(1)	1.720(3)	N(1)#1－Be(1)－N(1)	99.75(13)

CHAPTER 3

CONCLUSION

3.1 Concluding Remarks

The basic goal of my research project was to demonstrate that our *N-heterocyclic stabilization strategy* can be extended to stabilize highly reactive beryllium complexes. This proved challenging due to the peculiar reactivity of beryllium. Nevertheless, we isolated one of the most important organoberyllium compounds in recent years. Indeed, the synthesis of these types of novel molecules has made a significant contribution to inorganic chemistry.

The premier N-heterocyclic carbene ligand L^1: = :$C\{N(2, 6\text{-}{}^{i}Pr_2C_6H_3)CH\}_2$) employed in this research was previously shown to stabilize reactive species. In particular, the isolation of a series of stable diatomic molecules [(H)B=B(H), Si_2, P_2, As_2] inspired us to extend this carbene stabilization strategy to group 2 elements, namely beryllium. I found this research incredibly interesting as it led to the experimental realization of various novel molecules. Ultimately, I sought to isolate the first stable beryllium borohydride derivative. Indeed, lithium borohydride reduction of L^1:$BeCl_2$ afforded L^1:$Be(BH_4)_2$ (**5**). Compound **5**, represents the first structurally characterized molecule containing the highly reactive $Be(BH_4)_2$ moiety. Reaction of **5** with $Na_2Fe(CO)_4$·dioxane gave an unusual doubly reduced NHC ligand (**6**). Indeed, **6** contains a BH_2 unit which is bridged between an N-heterocyclic carbene and a reduced N-heterocyclic carbene moiety.

We also examined the reactivity of carbene-stabilized disilicon toward beryllium chloride. Addition of one equivalent $BeCl_2$ to [L^1:Si=Si:L^1] resulted in the formation of a novel coordination complex [L^1:Si=Si:L^1]$BeCl_2$ (**7**). One of the silicon atoms possess a lone pair of electrons while the other silicon atom is using its electron pair to coordinate beryllium chloride. Compound **7**, is the first example of a compound containing a silicon−beryllium dative bond.

The reactivity of $BeCl_2$ with sterically demanding diimine ligands was also explored. Compounds **8** and **9** were prepared quantitatively by the reaction of $BeCl_2$ with the corresponding diimine in hexane. Notably, reduction of **9** with two equivalents of KC_8 afforded a beryllium dimer containing a Be_2N_2 four-membered ring (**10**).

In conclusion, my research efforts have demonstrated that N-heterocyclic carbenes may be be used to stabilize highly reactive organoberyllium complexes. NHC-beryllium chemistry has only recently emerged, therefore, it is expected that a number of novel structures will be isolated in the future. Our laboratory continues to synthesize NHC-beryllium complexes in an effort to examine the structure, bonding, and reactivity of one of the least studied elements on the Periodic Table.

CHAPTER 4

EXPERIMENTAL

4.1 General Background

4.1.1 Techniques and Reagents

Apart from the synthesis of NHC precursors, all manipulations were performed using a combination of standard Schlenk techniques and an MBraun inert atmosphere (argon) glovebox. Diethyl ether, tetrahydrofuran, and hexane were dried at reflux over a mixture of sodium metal and benzophenone. Toluene was refluxed over sodium metal. To ensure minimal exposure to moisture or air, all solvents were freshly distilled from their corresponding mixtures immediately prior to use. Diethylzinc was used to test the MBraun glovebox for the presence of moisture. Any visible smoke from diethylzinc indicates that the glovebox atmosphere was not completely dry and regeneration was completed. Schlenk lines were protected under argon gas, which was first passed through copper-based purification and molecular sieve drying columns prior to use. Melting points were determined on a Haake Buchler MFB 595 802 C melting point apparatus.

Beryllium chloride (98.5%-purified by sublimation), silicon(IV) chloride, 1,4-dioxane, glyoxal (40% aqueous solution), potassium *tert*-butoxide, disodium tetracarbonyl ferrate dioxane complex, and graphite were purchased from Aldrich Chemical Company (Milwaukee, WI). 2,4,6-trimethylphenylaniline (97%) and 2,6-diisopropylphenylaniline (92%) was purchased from Acros Organics (New Jersey, NJ). Chloromethylethyl ether (96%) was purchased from TCI America (Montgomeryville, PA). Potassium metal and lithium borohydride (95%) was purchased from Strem Chemicals (Newburyport, MA). All reagents were used as received without further purification.

4.1.2 Instrumental Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer. ^{11}B and ^{29}Si NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer. The chemicals shifts were referenced to an external BF_3 and $SiMe_3$ standard for ^{11}B and ^{29}Si, respectively. Deuterated benzene (C_6D_6), tetrahydrofuran (THF-d_8), dichloromethane (CD_2Cl_2), and chloroform ($CDCl_3$) were used as solvents in NMR experiments. Elemental analyses were performed by Complete Analysis Laboratories, Inc. (Parsippany, NJ).

4.1.3 Single Crystal X-ray Diffraction Methods

Crystals suitable for X-ray crystallographic studies were mounted in glass capillaries in an argon-filled glovebox. The capillaries were sealed with silicon grease and removed from the glovebox where they were flamed sealed and covered with a small amount of wax. The X-ray intensity data were collected at room temperature on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the ω-scan technique. Solution refinement was performed using the SHELXTL 6.1 solution package. Data were corrected for polarization and Lorentz effects and integrated with the manufacturer's SAINT software. Data were corrected for absorption effects with the SADABS. Structures were solved using the SHELXTL 6.1 Software Package. Non-hydrogen atomic scattering factors were taken from literature tabulations. Non-hydrogen atoms were located from successive fourier map calculations and refined in anisotropic displacement parameters. Hydrogen atoms were allowed to ride on the carbon to which they are bonded assuming a C–H bond distance of 0.95 Å.

Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor on the carbon to which they are bonded.

4.2 Preparation of Starting Materials

4.2.1 Synthesis of glyoxal-bis-(2,6-diisopropylphenyl)imine.

This procedure was performed according to modified literature procedures for the synthesis of diimines.[32] A 40% aqueous solution of glyoxal (101.65 g, 0.70 mol) was added to a flask containing 2,6-diisopropylaniline (300.0 g, 1.56 mol) and 1000 mL of *n*-propanol. Next, 350 mL of *n*-propanol and 300 mL of water was added to the mixture and the solution was stirred for 16 hours, producing a yellow precipitate. 1200 mL of water was added to the reaction mixture which was stirred for 10 min. The mixture was filtered and dried in vacuo to give glyoxal-bis-(2,6-diisopropylphenyl)imine. The purity was confirmed by ^{1}H NMR.

4.2.2 Synthesis of 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride.

This procedure was performed in the fume-hood according to the published procedure.[32] Glyoxal-bis-(2,6-diisopropylphenyl)imine (200.0 g, 0.53 mol) was added to 1200 mL of THF. A 96% solution of chloromethylethyl ether (54.70 g, 0.56 mol) in 100 mL of THF and 6 mL of water were added to the flask and stirred for 16 hours. (Note: chloromethylethyl ether is a volatile lachrymator (substance which increases the flow of tears). Therefore, this reagents is handled in a well-ventilated fume hood. The solution was filtered to give 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride as a white powder. The purity was confirmed by ^{1}H NMR.

4.2.3 Synthesis of 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene.

1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride (25.0 g, 0.06 mol) was dried in vacuo in a Schlenk flask while stirring for 24 hours. It was transferred to a glovebox and potassium tert-butoxide (6.99 g, 0.062 mol) was added to it. Then 150 mL of dry THF was added to the flask and the mixture was stirred for 12 hours. The solvent was removed in vacuo and the residue was taken up in 150 mL of toluene. The mixture was heated until all solid dissolved. The solution was filtered through celite and all solvent was removed in vaccuo to give a pale yellow powder (19.38 g, 85% yield). Purity was confirmed by ^{1}H NMR.

4.2.4 Synthesis of glyoxal-bis-(2,4,6-trimethylphenyl)imine.

This procedure was performed according to modified literature procedures for the synthesis of diimines.[32] A 40% aqueous solution of glyoxal (78.82 g, 1.36 mol) was added to a flask containing 2,4,6-trimethylaniline (150.0 g, 1.11 mol) and 750 mL of *n*-propanol. Next, 350 mL of *n*-propanol and 300 mL of water was subsequently added and the solution was stirred for 16 hours, during which time a thick yellow precipitate formed. 1000 mL of water was added to the reaction mixture, which was filtered and dried in vacuo to give glyoxal-bis-(2,6-diisopropylphenyl)imine. The purity was confirmed by ^{1}H NMR.

4.2.5 Synthesis of 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride.

This procedure was performed in the fume-hood according to the published procedure.[32] Glyoxal-bis-(2,4,6-trimethylphenyl)imine (70.64 g, 0.24 mol) was added to 1200 mL of THF. A 96% solution of chloromethylethyl ether (25.76 g, 0.285 mol) in 100 mL of THF and 6 mL of water were added to the flask and stirred for 16 hours. (Note: chloromethylethyl ether is volatile, an irritant, and a lachrymator (substance which increases the flow of tears). Therefore, this reagents is handled in a well-ventilated fume hood. The solution was stirred for 16 hours and filtered to give a 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride as a white powder. The purity was confirmed by ^{1}H NMR.

4.2.6 Synthesis of 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene.

1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (20.0 g, 0.058 mol) was dried in vacuo in a Schlenk flask while stirring for 24 hours. It was transferred to a glovebox and potassium tert-butoxide (7.24 g, 0.064 mol) was added to it. Then 150 mL of dry THF was added to the flask and the mixture was stirred for 16 hours. The solvent was removed in vacuo and 200 mL of toluene was added to it. It was heated until all solid dissolved. The solution was filtered through celite and all solvent was removed in vaccuo to give a pale yellow powder (17.68 g, 90% yield). Purity was confirmed by ^{1}H NMR.

4.2.7 Synthesis of Potassium Graphite.

Graphite (25.64 g, 2.14 mol) was dried in an open house-made pressure tube/flask overnight in a 200 °C oven. The hot graphite was transferred to a glovebox and small pieces of freshly cut potassium metal (10.58 g, 0.27 mol) was added to the flask. It was heated until the mixture turned golden-brown (quantitative yield).

4.3 Synthesis of Carbene-Stabilized Beryllium Chlorides

*4.3.1 Synthesis of NHC-Beryllium Chloride (**1**)*

NHC carbene ligand (10 g, 25.73 mmol) was added to a flask containing 60 mL of hexane at ambient temperature. With stirring $BeCl_2$ (2.04 g, 23.01 mmol) was added into the flask. The mixture was stirred for 24 hours and then filtered. The residue was vacuumed yielding a white powder **1** (11.50 g, 95.6% yield). Compound **1** was recrystallized from a warm toluene solution to obtain X-ray quality colorless block crystals. Mp: gradually decomposed (>215 °C) then completely melts (267 °C). ^1H NMR (400 MHz, C_6D_6): δ 0.99 [d, 12H, $CH(C\mathit{H}_3)_2$], 1.42 [d, 12H, $CH(C\mathit{H}_3)_2$], 2.75 [m, 4H, $C\mathit{H}(CH_3)_2$], 6.39 [s, 2H, NC*H*], 7.05 [d, 4H, Ar-*H*], 7.17 [t, 2H, Ar-*H*]. Anal. Calculated(Experimental): C = 69.22%(68.96%), H = 7.75%(8.01%). Crystal Data for **1**: $C_{27}H_{36}N_2BeCl_2$, F.W. = 468.49, Monoclinic, P2(1)/n, a = 10.4308(9) Å, b = 18.1887(15) Å, c = 15.4186(13) Å, $\alpha = 90^{\circ}$, $\beta = 101.4190(10)^{\circ}$, $\gamma = 90^{\circ}$, $V = 2867.4(4)$ Å^3, Z = 4, $R1 = 0.0565$ for 2484 data ($I > 2\sigma(I)$), $wR2 = 0.1912$ (all data).

*4.3.2 Synthesis of NHC-Beryllium Chloride-THF Adduct (**2**)*

NHC carbene ligand (5 g, 16.42 mmol) was added to a flask containing 50 mL of hexane at ambient temperature. With stirring $BeCl_2$ (1.31 g, 16.42 mmol) was added into the flask. The mixture was stirred for 24 hours and then filtered. The residual solvent was removed in vacuo yielding a white powder. X-ray quality colorless block crystals of compound **2** (7.10 g, 95.0% yield) were obtained from a warm toluene/THF (2:1 ratio) solution. Mp: gradually decomposed (>204 °C) completely melts (258 °C). ^1H NMR (400 MHz, C_6D_6): δ 1.03 [d, 12H, $CH(C\mathit{H}_3)_2$], 1.11 [m, 4H, $C\mathit{H}_2CH_2O$], 1.46 [d, 12H, $CH(C\mathit{H}_3)_2$], 3.00 [m, 4H, $C\mathit{H}(CH_3)_2$], 3.59 [m, 4H, $OC\mathit{H}_2$], 6.46 [s, 2H, NC*H*], 7.09 [d, 4H, Ar-*H*], 7.18 [t, 2H, Ar-*H*]. Crystal Data for **2**:

$C_{38}H_{52}N_2OBeCl_2$, F.W. = 632.73, Orthorhombic, P2(1)2(1)2(1), a = 12.9799(6) Å, b = 15.6817(7) Å, c = 18.3157(8) Å, α= 90 °, β = 90 °, γ = 90 °, V = 2867.4(4) Å^3, Z = 4, $R1$ = 0.0474 for 5167 data ($I > 2\ \sigma(I)$), $wR2$ = 0.1425 (all data).

*4.3.3 Synthesis of NHC-Beryllium Chloride-THF Adduct (**3**)*

NHC carbene ligand (5 g, 12.90 mmol) was added to a flask containing 60 mL of hexane at ambient temperature. With stirring $BeCl_2$ (1.01 g, 12.90 mmol) was added into the flask. The mixture was stirred for 24 hours and then filtered. The residue was vacuumed yielding a white powder. X-ray quality colorless block crystals of compound **3** (6.66 g, 96.0% yield) was obtained from toluene/THF solution. Mp: 228 °C; ^{1}H NMR (400 MHz, C_6D_6): δ 1.52 [m, 4H, CH_2CH_2O], 2.51 [s, 6H, $C(CH_3)$], 2.67 [s, 12H, $C(CH_3)$], 4.10 [m, 4H, CH_2CH_2O], 6.44 [s, 2H, NC*H*], 7.62 [s, 4H, Ar-*H*]. Crystal Data for **3**: $C_{25}H_{32}N_2OBeCl_2$, F.W. = 456.45, Monoclinic, P2(1)/n, a = 10.5334(6) Å, b = 12.5444(7) Å, c = 19.4767(11) Å, α= 90 °, β = 100.5810(10) °, γ = 90 °, V = 2529.8(2) Å^3, Z = 4, $R1$ = 0.0491 for 3963 data ($I > 2\ \sigma(I)$), $wR2$ = 0.1604 (all data).

*4.3.4 Synthesis of NHC-Beryllium Chloride-Dioxane Complex (**4**)*

NHC carbene ligand (10 g, 25.73 mmol) was added to a flask containing 60 mL of hexane at ambient temperature. With stirring $BeCl_2$ (2.04 g, 23.01 mmol) was added into the flask. The mixture was stirred for 24 hours and then filtered. The residue was vacuumed yielding a white powder **1** (11.50 g, 95.6% yield). Dissolution of **1** in dioxane yields compound **4** as colorless block crystals. Mp: 254 °C; ^{1}H NMR (400 MHz, C_6D_6): δ 0.98 [d, 12H, $CH(CH_3)_2$], 1.42 [d, 12H, $CH(CH_3)_2$], 2.82 [m, 4H, $CH(CH_3)_2$], 3.40 [s, 8H, $C_4H_8O_2$], 6.38 [s, 2H, NC*H*], 7.06 [d, 4H, Ar-*H*], 7.18 [t, 2H, Ar-*H*].

Crystal Data for **4**: $C_{65}H_{88}N_2O_4BeCl_2$, F.W. = 1117.22, Monoclinic, P2(1)/n, a = 12.6855(7) Å, b = 14.4535(8) Å, c = 18.9074(11) Å, α= 90 °, β = 104.6930(1) °, γ = 90 °, V = 3353.3(3) $Å^3$, Z = 2, $R1$ = 0.0475 for 5426 data ($I > 2\sigma(I)$), $wR2$ = 0.1531 (all data).

4.4 Synthesis of Carbene-Stabilized Beryllium Borohydride

*4.4.1 Synthesis of NHC-Beryllium Borohydride, **(5)***

L:BeCl$_2$ (1.5 g, 3.20 mmol) was added to a flask containing 80 mL of toluene. LiBH$_4$ (0.14 g, 6.42 mmol) was added to the flask and the reaction was stirred for 48 hrs at ambient temperature leaving a white LiCl precipitate. The solution was filtered and the toluene was removed in vacuo leaving approximately 30 mL toluene. Cooling to -20 °C over one week gave X-ray quality colorless block crystals of **5** (0.93 g, 67.8% yield). Mp: 210-215 °C; ^{1}H NMR (400 MHz, C_6D_6): δ 0.95 [d, 12H, CH(C*H*$_3$)$_2$], 1.38 [d, 12H, CH(C*H*$_3$)$_2$], 2.83 [m, 4H, C*H*(CH$_3$)$_2$], 6.43 [s, 2H, NC*H*], 7.03 [d, 4H, Ar-*H*], 7.15 [t, 2H, Ar-*H*]; ^{1}H{11B} (500 MHz, THF-d$_8$): 0.06 [s, 8H, B*H*$_4$]; ^{11}B NMR (500 MHz, THF-d$_8$): δ -31.16 [quintet, 1B, *B*H$_4$]. Anal. Calculated(Experimental): C = 75.90%(75.65%), H 10.38%(10.42%). Crystal Data for **5**: $C_{27}H_{44}N_2B_2Be$, F.W. = 427.27, a = 10.4255(7) Å, b = 17.9488(11) Å, c = 15.9335(10) Å, α= 90^o, β = 98.5790(10) ^{o}, γ = 90 ^{o}, V = 2948.2(3) Å^3, Z = 4, $R1$ = 0.0527 for 3784 data ($I > 2\ \sigma(I)$), *wR2* = 0.1707

*4.4.2 Synthesis of Doubly Reduced NHC, (**6**)*

Crystals of **2** (2 g, 4.68 mmol) were added to a flask containing 50 mL of toluene. Na$_2$[Fe(CO)$_4$]•dioxane complex (1.62 g, 4.68 mmol) was added to the flask and the reaction was vigorously stirred at ambient temperature for 7 days. The reaction was filtered and the mother liquor was concentrated to 10 mL. Over several days **6** (1.16 g, 64.3% yield) was obtained as X-ray quality colorless prism and block shaped crystals. Mp: 243-250; ^{1}H NMR (400 MHz, C_6D_6): δ0.92-1.40 [m, 48H, CH(C*H*$_3$)$_2$], 1.82 [t, 1H, im-*H*], 2.55 [m, 2H, C*H*(CH$_3$)$_2$], 2.62 [m, 2H, C*H*(CH$_3$)$_2$], 3.15 [t, 1H, im-*H*], 3.29 [m, 1H, C*H*(CH$_3$)$_2$], 3.62 [m, 2H, C*H*(CH$_3$)$_2$], 3.88 [m, 1H, C*H*(CH_3)$_2$], 4.47 [m, 1H, im-*H*], 4.56 and 4.65 [s, 2H, NC*H*$_2$N], 6.23 [s, 2H, NC*H*], 6.93-7.25 [m, 12H, Ar-*H*]; ^{11}B NMR (500 MHz, THF-d$_8$): δ -25.5 [br. s with shoulders, 1B, *B*H_2]. Anal. calculated(Experimental): C = 81.79%(81.76%), H = 9.79%(9.97%)Crystal Data for **6**: $C_{54}H_{77}N_4B$, F.W. = 793.01, a = 12.4807(7) Å, b = 23.1679(12) Å, c = 17.7375(10) Å, α= 90°, β = 91.1000(10) °, γ = 90 °, V = 5127.9(5) Å^3, Z = 4, $R1$ = 0.0499 for 7051 data ($I > 2\ \sigma(I)$), $wR2$ = 0.1375 (all data).

4.5 Synthesis of Disilicon-Complexed Beryllium Chloride

4.5.1 Synthesis of Disilicon-Complexed Beryllium Chloride (7)

NHC-Stabilized disilicon (0.2 g, 0.24 mmol) was added to a flask containing 20 mL of hexane at ambient temperature. With stirring $BeCl_2$ (0.020 g, 0.24 mmol) was added into the flask. The mixture was stirred for 24 hours and the solvent was removed in vacuo yielding **7** (0.020 g, 95.0% yield) as an orange powder. Compound **7** was recrystallized from a warm toluene solution to obtain X-ray quality orange block crystals. Mp: 205 °C. ^{1}H NMR (400 MHz, THF-d8): 0.94 [d, 12H, $CH(CH_3)_2$], 0.99 [d, 12H, $CH(CH_3)_2$], 2.94 [m, 4H, $CH(CH_3)_2$], 6.94 [d, 4H, Ar-*H*], 7.15 [s, 2H, NC*H*], 7.21 [t, 2H, Ar-*H*]. ^{29}Si NMR (500 MHz, THF-d_8): δ229.1 Crystal Data for **7**: $C_{54}H_{72}N_4Si_2BeCl_2$, F.W. = 913.25, Monoclinic, P2(1)/c, a = 22.2461(14) Å, b = 14.4513(9) Å, c = 17.7211(11) Å, $\alpha = 90^{\circ}$, $\beta = 101.1860(10)^{\circ}$, $\gamma = 90^{\circ}$, $V = 5588.8(6)$ Å^3, Z = 4, $R1 = 0.0634$ for 4958 data ($I > 2\sigma(I)$), $wR2 = 0.1958$ (all data).

4.6 Synthesis of Diimine-Stabilized Beryllium Chlorides

*4.6.1 Synthesis of Diimine-Complexed Beryllium Chloride (**8**)*

Diimine ligand (3.00 g, 7.96 mmol) was added to a flask containing 50 mL of hexane at ambient temperature. With stirring $BeCl_2$ (0.63 g, 7.96 mmol) was added into the flask. The mixture was stirred for 24 hours and the solvent was removed in vacuo yielding **8** (3.73 g, 95.6% yield) as a yellow powder. Compound **8** was recrystallized from a warm toluene solution to obtain X-ray quality yellow needle crystals. Mp: (193°C) . ^1H NMR (400 MHz, C_6D_6): δ 1.18 [d, 24H, $CH(CH_3)_2$], 2.96 [s, 4H, $CH(CH_3)_2$], 7.08 [t, 2H, Ar-*H*], 7.15 [d, 4H, Ar-*H*], 8.10 [s, 2H, NC*H*]. Crystal Data for **8**: $C_{26}H_{36}N_2BeCl_2$, F.W. = 456.48, Monoclinic, P2(1)/n, a = 13.0253(13) Å, b = 16.0248(16) Å, c = 13.4297(13) Å, $\alpha = 90^{\circ}$, $\beta = 105.281(2)^{\circ}$, $\gamma = 90^{\circ}$, $V = 2704.0(5)$ Å^3, Z = 4, $R1 = 0.0554$ for 2424 data ($I > 2\sigma(I)$), $wR2 = 0.1258$ (all data).

*4.6.2 Synthesis of Diimine-Complexed Beryllium Chloride (**9**)*

Diimine ligand (3.00 g, 11.43 mmol) was added to a flask containing 50 mL of hexane at ambient temperature. With stirring, $BeCl_2$ (0.91 g, 11.43 mmol) was added into the flask. The mixture was stirred for 24 hours and the solvent was removed in vacuo yielding **9** (3.49 g, 96.2% yield) as an orange powder. Mp: 170 °C. ^1H NMR (400 MHz, C_6D_6): δ 2.13 [s, 12H, *ortho*-CH_3], 2.16 [s, 6H, *para*-CH_3], 6.78 [s, 4H, *meta*-C*H*], 8.07 [s, 2H, C*H*].

4.7 Synthesis of Diimine-Stabilized Beryllium Dimer

*4.7.1 Synthesis of Diimine-Stabilized Beryllium Dimer (**10**)*

Diimine-$BeCl_2$ complex (2.00 g, 25.73 mmol) was added to a flask containing 50 mL of toluene at ambient temperature. With stirring KC_8 (2.04 g, 23.01 mmol) was added into the flask. The mixture was stirred for 24 hours and the solvent was removed in vacuo yielding **10** (11.50 g, 48.2% yield) as a off-white powder. Mp: 215 °C . Crystal Data for **10**: $C_{40}H_{48}N_4Be_2$, F.W. = 602.84, Monoclinic, C2/c, a = 15.4075(10) Å, b = 17.0070(11) Å, c = 15.0456(10) Å, α= 90 ^{o}, β = 118.1460(10) ^{o}, γ = 90 ^{o}, V = 3476.3(4) Å^3, Z = 4, $R1$ = 0.0787 for 2271 data ($I > 2\sigma(I)$), $wR2$ = 0.1334 (all data).

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APPENDIX A

CRYSTALLOGRAPHIC DATA

Structural Data for L^1:BeCl$_2$ **1**

Table 10. Crystal data and structural refinement for **1**.

Empirical formula	$C_{27} H_{36} Be Cl_2 N_2$
Formula weight	468.49
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.4308(9) Å
	b = 18.1887(15) Å
	c = 15.4186(13) Å
	α = 90°
	β = 101.4190(10)°
	γ = 90°
Volume	2867.4(4) Å^3,
Calculated density	4, 1.085 Mg/m^3
Absorption coefficient	0.242 mm^{-1}
F(000)	1000
Crystal size	0.21 x 0.18 x 0.04 mm
Theta range for data collection	2.17 to 25.00°
Limiting indices	-12<=h<=12, -21<=k<=21, -18<=l<=18
Reflections collected / unique	30313 / 5043 [R(int) = 0.0613]
Completeness to theta =	25.00 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9904 and 0.9510
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	5043 / 143 / 355
Goodness-of-fit on F^2	1.006
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1431
R indices (all data)	R1 = 0.1284, wR2 = 0.1912
Largest diff. peak and hole	0.380 and -0.333 e. Å^{-3}

Table 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1**.

Atom	X	Y	Z	U(eq)
Be(1)	7503(5)	2564(3)	2621(3)	85(2)
Cl(1)	5821(1)	2148(1)	2462(1)	135(1)
Cl(2)	7978(7)	2988(4)	1644(4)	148(2)
Cl(2')	8432(8)	2702(4)	1654(4)	149(2)
N(1)	9131(2)	2200(1)	4246(2)	63(1)
N(2)	8709(2)	3349(1)	4128(1)	63(1)
C(1)	8466(3)	2703(2)	3692(2)	60(1)
C(2)	9790(3)	2530(2)	5012(2)	76(1)
C(3)	9533(3)	3248(2)	4938(2)	78(1)
C(4)	8187(3)	4061(2)	3819(2)	63(1)
C(5)	6907(3)	4226(2)	3892(2)	73(1)
C(6)	6503(4)	4951(2)	3674(2)	89(1)
C(7)	7316(5)	5449(2)	3392(3)	99(1)
C(8)	8534(4)	5258(2)	3299(2)	87(1)
C(9)	9012(3)	4551(2)	3507(2)	71(1)
C(10)	10382(4)	4354(2)	3400(2)	90(1)
C(11)	11396(4)	4787(3)	4043(4)	153(2)
C(12)	10571(5)	4480(3)	2460(3)	155(2)
C(13)	6005(4)	3682(2)	4197(2)	92(1)
C(14)	6033(6)	3751(3)	5180(3)	181(3)
C(15)	4616(4)	3720(3)	3653(4)	160(2)
C(16)	9138(3)	1416(2)	4078(2)	64(1)
C(17)	8170(3)	993(2)	4349(2)	80(1)
C(18)	8202(4)	244(2)	4189(3)	98(1)
C(19)	9148(5)	-59(2)	3793(3)	103(1)
C(20)	10082(4)	373(2)	3541(2)	88(1)
C(21)	10108(3)	1130(2)	3677(2)	68(1)
C(22)	11140(30)	1645(19)	3450(20)	98(9)
C(23)	12440(40)	1350(30)	3990(30)	126(11)
C(24)	11100(40)	1550(20)	2469(16)	127(10)
C(22')	11165(13)	1587(9)	3418(8)	76(4)
C(23')	12430(20)	1600(20)	4138(16)	129(7)
C(24')	11520(30)	1433(13)	2523(12)	162(8)
C(25)	7238(16)	1352(10)	4879(13)	92(4)
C(26)	7740(20)	1384(13)	5878(15)	115(4)
C(27)	5872(18)	1009(15)	4690(20)	169(6)
C(25')	6960(30)	1260(30)	4660(30)	99(9)
C(26')	7360(50)	1130(40)	5650(30)	120(11)
C(27')	5730(40)	810(40)	4310(40)	146(13)

Table 12. Bond lengths [Å] for **1**.

Atoms	Distance	Atoms	Distance
Be(1)-C(1)	1.773(5)	C(13)-C(14)	1.516(6)
Be(1)-Cl(2)	1.844(9)	C(13)-C(15)	1.526(5)
Be(1)-Cl(1)	1.881(6)	C(16)-C(21)	1.387(4)
Be(1)-Cl(2')	1.948(10)	C(16)-C(17)	1.398(5)
N(1)-C(1)	1.347(3)	C(17)-C(18)	1.386(5)
N(1)-C(2)	1.380(4)	C(17)-C(25')	1.509(19)
N(1)-C(16)	1.450(4)	C(17)-C(25)	1.535(10)
N(2)-C(1)	1.353(3)	C(18)-C(19)	1.374(6)
N(2)-C(3)	1.381(3)	C(19)-C(20)	1.366(5)
N(2)-C(4)	1.449(4)	C(20)-C(21)	1.393(5)
C(2)-C(3)	1.334(4)	C(21)-C(22')	1.497(10)
C(4)-C(5)	1.394(4)	C(21)-C(22)	1.516(18)
C(4)-C(9)	1.389(4)	C(22)-C(24)	1.521(16)
C(5)-C(6)	1.406(5)	C(22)-C(23)	1.543(17)
C(5)-C(13)	1.504(5)	C(22')-C(24')	1.524(10)
C(6)-C(7)	1.368(5)	C(22')-C(23')	1.547(11)
C(7)-C(8)	1.352(5)	C(25)-C(26)	1.526(9)
C(8)-C(9)	1.393(5)	C(25)-C(27)	1.529(10)
C(9)-C(10	1.513(5)	C(25')-C(26')	1.515(17)
C(10)-C(11)	1.517(5)	C(25')-C(27')	1.528(17)
C(10)-C(12)	1.518(5)		

Table 13. Bond angles [°] for **1**.

Atoms	Angle	Atoms	Angle
C(1)-Be(1)-Cl(2)	120.4(4)	C(4)-C(5)-C(13)	123.5(3)
C(1)-Be(1)-Cl(1)	121.3(3)	C(6)-C(5)-C(13)	121.1(3)
Cl(2)-Be(1)-Cl(1)	117.2(3)	C(7)-C(6)-C(5)	121.4(4)
C(1)-Be(1)-Cl(2')	114.7(4)	C(8)-C(7)-C(6)	121.2(4)
Cl(2)-Be(1)-Cl(2')	21.1(3)	C(7)-C(8)-C(9)	120.9(4)
Cl(1)-Be(1)-Cl(2')	123.0(3)	C(4)-C(9)-C(8)	116.9(3)
Cl(2')-Cl(2)-Be(1)	87.8(12)	C(4)-C(9)-C(10)	123.3(3)
C(1)-N(1)-C(2)	110.8(3)	C(8)-C(9)-C(10)	119.7(4)
C(1)-N(1)-C(16)	125.1(2)	C(11)-C(10)-C(9)	110.9(3)
C(2)-N(1)-C(16)	124.1(2)	C(11)-C(10)-C(12)	109.8(4)
C(1)-N(2)-C(3)	110.9(2)	C(9)-C(10)-C(12)	111.9(4)
C(1)-N(2)-C(4)	126.2(2)	C(5)-C(13)-C(14)	111.6(3)
C(3)-N(2)-C(4)	122.9(2)	C(5)-C(13)-C(15)	112.5(4)
N(1)-C(1)-N(2)	104.6(2)	C(14)-C(13)-C(15)	111.9(4)
N(1)-C(1)-Be(1)	128.3(3)	C(21)-C(16)-C(17)	124.1(3)
N(2)-C(1)-Be(1)	127.1(3)	C(21)-C(16)-N(1)	118.6(3)
N(1)-C(2)-C(3)	107.2(3)	C(17)-C(16)-N(1)	117.3(3)
N(2)-C(3)-C(2)	106.6(3)	C(18)-C(17)-C(16)	116.3(4)
C(5)-C(4)-C(9)	124.0(3)	C(18)-C(17)-C(25')	115(2)
C(5)-C(4)-N(2)	118.0(3)	C(16)-C(17)-C(25')	128(2)
C(9)-C(4)-N(2)	117.9(3)	C(18)-C(17)-C(25)	123.6(8)
C(4)-C(5)-C(6)	115.4(3)	C(16)-C(17)-C(25)	119.8(8)
C(25')-C(17)-C(25)	16.4(18)	C(21)-C(22)-C(23)	105(3)
C(17)-C(18)-C(19)	121.2(4)	C(24)-C(22)-C(23)	109.5(19)
C(20)-C(19)-C(18)	120.8(4)	C(21)-C(22')-C(24')	117.5(12)
C(21)-C(20)-C(19)	121.3(4)	C(21)-C(22')-C(23')	112.6(16)
C(16)-C(21)-C(20)	116.3(3	C(24')-C(22')-C(23')	109.1(10)
)C(16)-C(21)-C(22')	123.5(7)	C(26)-C(25)-C(17)	115.3(14)
C(20)-C(21)-C(22')	120.2(7)	C(26)-C(25)-C(27)	109.0(7)
C(16)-C(21)-C(22)	118.8(14)	C(17)-C(25)-C(27)	113.1(13)
C(20)-C(21)-C(22)	124.8(15)	C(17)-C(25')-C(26')	101(3)
C(22')-C(21)-C(22)	4.7(19)	C(17)-C(25')-C(27')	114(3)
C(21)-C(22)-C(24)	106(2)	C(26')-C(25')-C(27')	108.5(17)

Structural Data for L^2:BeCl$_2$·THF **2**

Table 14. Crystal data and structural refinement for **2**.

Empirical formula	C_{25} H_{32} Be Cl_2 N_2 O
Formula weight	456.44
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.5334(6) Å
	b = 12.5444(7) Å
	c = 19.4767(11) Å
	α = 90°
	β = 100.5810(10)°
	γ = 90°
Volume	2529.8(2) A^3
Z, Calculated density	4, 1.198 Mg/m^3
Absorption coefficient	0.275 mm^-1
F(000)	968
Crystal size	0.30 x 0.28 x 0.09 mm
Theta range for data collection	2.13 to 26.00°
Limiting indices	-12<=h<=12, -15<=k<=15, -24<=l<=24
Reflections collected / unique	28486 / 4967 [R(int) = 0.0217]
Completeness to theta = 26.00	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9757 and 0.9221
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4967 / 113 / 317
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1441
R indices (all data)	R1 = 0.0617, wR2 = 0.1604
Largest diff. peak and hole	0.485 and -0.355 e. Å^{-3}

Table 15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2**.

Atom	X	Y	Z	U(eq)
Be(1)	4392(2)	8776(2)	6288(1)	44(1)
Cl(1)	5877(1)	8068(1)	5977(1)	86(1)
Cl(2)	4729(1)	10283(1)	6619(1)	78(1)
N(1)	2762(2)	7345(1)	6941(1)	44(1)
N(2)	4584(2)	7665(1)	7582(1)	44(1)
C(1)	3863(2)	7921(2)	6953(1)	37(1)
C(2)	2804(2)	6760(2)	7545(1)	62(1)
C(3)	3953(2)	6964(2)	7947(1)	61(1)
C(4)	5854(2)	8054(2)	7888(1)	41(1)
C(5)	5947(2)	8991(2)	8277(1)	45(1)
C(6)	7165(2)	9299(2)	8612(1)	55(1)
C(7)	8253(2)	8700(2)	8580(1)	59(1)
C(8)	8113(2)	7773(2)	8201(1)	58(1)
C(9)	6920(2)	7424(2)	7845(1)	50(1)
C(10)	6805(3)	6386(2)	7448(2)	77(1)
C(11)	9573(3)	9055(3)	8964(2)	97(1)
C(12)	4779(3)	9638(2)	8347(1)	67(1)
C(13)	1644(2)	7302(2)	6388(1)	40(1)
C(14)	521(2)	7814(2)	6487(1)	48(1)
C(15)	-578(2)	7674(2)	5984(1)	51(1)
C(16)	-573(2)	7081(2)	5386(1)	48(1)
C(17)	575(2)	6602(2)	5298(1)	47(1)
C(18)	1695(2)	6686(2)	5800(1)	42(1)
C(19)	2897(2)	6091(2)	5719(2)	63(1)
C(20)	-1793(2)	6941(3)	4846(2)	73(1)
C(21)	494(3)	8510(3)	7120(2)	78(1)
O(1)	3219(1)	8873(1)	5566(1)	47(1)
C(22)	3526(18)	8850(20)	4877(7)	78(4)
C(23)	2239(17)	9150(15)	4438(7)	109(5)
C(24)	1973(8)	10107(7)	4914(4)	97(3)
C(25)	2211(13)	9701(11)	5595(5)	73(3)
C(22')	3374(19)	8650(20)	4839(8)	73(4)
C(23')	2431(17)	9327(16)	4343(7)	85(3)
C(24')	1378(6)	9491(7)	4798(3)	69(2)
C(25')	2065(12)	9470(12)	5495(4)	57(3)

Table 16. Bond lengths [Å] for **2**.

Atoms	Distance	Atoms	Distance
Be(1)-O(1)	1.697(3)	C(13)-C(18)	1.389(3)
Be(1)-C(1)	1.843(3)	C(13)-C(14)	1.391(3)
Be(1)-Cl(1)	1.989(3)	C(14)-C(15)	1.383(3)
Be(1)-Cl(2)	2.008(3)	C(14)-C(21)	1.516(3)
N(1)-C(1)	1.363(2)	C(15)-C(16)	1.383(3)
N(1)-C(2)	1.381(3)	C(16)-C(17)	1.389(3)
N(1)-C(13)	1.444(2)	C(16)-C(20)	1.513(3)
N(2)-C(1)	1.357(2)	C(17)-C(18)	1.391(3)
N(2)-C(3)	1.375(3)	C(18)-C(19)	1.502(3)
N(2)-C(4)	1.446(2)	O(1)-C(25')	1.413(13)
C(2)-C(3)	1.339(3)	O(1)-C(22)	1.438(14)
C(4)-C(9)	1.388(3)	O(1)-C(22')	1.482(15)
C(4)-C(5)	1.393(3)	O(1)-C(25)	1.494(13)
C(5)-C(6)	1.383(3)	C(22)-C(23)	1.512(13)
C(5)-C(12)	1.501(3)	C(23)-C(24)	1.574(14)
C(6)-C(7)	1.381(4)	C(24)-C(25)	1.400(11)
C(7)-C(8)	1.371(4)	C(22')-C(23')	1.509(13)
C(7)-C(11)	1.519(3)	C(23')-C(24')	1.556(12)
C(8)-C(9)	1.389(3)	C(24')-C(25')	1.417(10)
C(9)-C(10)	1.507(3)		

Table 17. Bond angles [°] for **2**.

Atoms	Angle	Atoms	Angle
O(1)-Be(1)-C(1)	110.83(16)	C(6)-C(7)-C(11)	120.7(3)
C(1)-Be(1)-Cl(1)	108.11(15)	C(7)-C(8)-C(9)	122.3(2)
O(1)-Be(1)-Cl(2)	104.92(15)	C(4)-C(9)-C(8)	117.3(2)
C(1)-Be(1)-Cl(2)	112.38(15)	C(4)-C(9)-C(10)	122.2(2)
Cl(1)-Be(1)-Cl(2)	114.54(13)	C(8)-C(9)-C(10)	120.6(2)
C(1)-N(1)-C(2)	111.91(17)	C(18)-C(13)-C(14)	122.24(19)
C(1)-N(1)-C(13)	127.41(17)	C(18)-C(13)-N(1)	119.09(18)
C(2)-N(1)-C(13)	120.68(17)	C(14)-C(13)-N(1)	118.49(19)
C(1)-N(2)-C(3)	112.05(17)	C(13)-C(18)-C(17)	117.71(19)
C(1)-N(2)-C(4)	127.82(17)	C(13)-C(18)-C(19)	121.52(19)
C(3)-N(2)-C(4)	120.13(17)	C(17)-C(18)-C(19)	120.7(2)
N(2)-C(1)-N(1)	102.84(16)	C(25')-O(1)-C(22)	105.0(6)
N(2)-C(1)-Be(1)	125.57(16)	C(25')-O(1)-C(22')	104.4(7)
N(1)-C(1)-Be(1)	131.46(16)	C(22)-O(1)-C(22')	11(2)
C(3)-C(2)-N(1)	106.3(2)	C(15)-C(14)-C(13)	117.8(2)
C(2)-C(3)-N(2)	106.9(2)	C(15)-C(16)-C(20)	120.9(2)
C(9)-C(4)-C(5)	122.45(19)	C(22')-O(1)-C(25)	111.6(7)
C(9)-C(4)-N(2)	118.77(18)	C(22')-C(23')-C(24')	99.4(11)
C(5)-C(4)-N(2)	118.40(18)	C(17)-C(16)-C(20)	120.8(2)
C(6)-C(5)-C(4)	117.3(2)	C(16)-C(17)-C(18)	121.7(2)
C(6)-C(5)-C(12)	120.8(2)	C(15)-C(16)-C(17)	118.35(19)
C(4)-C(5)-C(12)	121.9(2)	C(25')-O(1)-Be(1)	127.0(4)
N(2)-C(1)-N(1)	102.84(16)	C(22)-O(1)-Be(1)	121.2(7)
N(2)-C(1)-Be(1)	125.57(16)	C(22')-O(1)-Be(1)	126.0(7)
N(1)-C(1)-Be(1)	131.46(16)	C(25)-O(1)-Be(1)	115.6(4)
C(3)-C(2)-N(1)	106.3(2)	C(25')-C(24')-C(23')	104.6(8)
C(2)-C(3)-N(2)	106.9(2)	O(1)-C(25')-C(24')	112.4(7)
C(9)-C(4)-C(5)	122.45(19)	O(1)-C(22)-C(23)	100.9(10)
C(9)-C(4)-N(2)	118.77(18)	C(22)-C(23)-C(24)	95.6(11)
C(5)-C(4)-N(2)	118.40(18)	C(25)-C(24)-C(23)	105.1(8)
C(6)-C(5)-C(4)	117.3(2)	O(1)-C(22')-C(23')	109.5(10)
C(6)-C(5)-C(12)	120.8(2)	C(24)-C(25)-O(1)	102.8(8)
C(4)-C(5)-C(12)	121.9(2)	C(22)-O(1)-C(25)	109.6(7)
C(7)-C(6)-C(5)	122.2(2)	C(15)-C(14)-C(21)	120.7(2)
C(8)-C(7)-C(6)	118.5(2)	C(13)-C(14)-C(21)	121.5(2)
C(8)-C(7)-C(11)	120.8(3)	C(16)-C(15)-C(14)	122.2(2)
C(25')-O(1)-C(25)	14.1(9)		

Structural Data for L^1:$BeCl_2$·THF **3**

Table 18. Crystal data and structural refinement for **3**.

Empirical formula	$C_{38} H_{52} Be Cl_2 N_2 O$
Formula weight	632.73
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 12.9799(6) Å
	b = 15.6817(7) Å
	c = 18.3157(8) Å
	α = 90°
	β = 90°
	ɣ = 90°
Volume	3728.1(3) A^3
Z, Calculated density	4, 1.127 Mg/m^3
Absorption coefficient	0.204 mm^{-1}
F(000)	1360
Crystal size	0.32 x 0.25 x 0.12 mm
Theta range for data collection	2.04 to 25.35°
Limiting indices	-15<=h<=15, -18<=k<=18, -22<=l<=22
Reflections collected / unique	41664 / 6822 [R(int) = 0.0331]
Completeness to theta =	25.35 99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9759 and 0.9376
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6822 / 43 / 397
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.1278
R indices (all data)	R1 = 0.0677, wR2 = 0.1425
Absolute structure parameter	-0.02(7)
Largest diff. peak and hole	0.288 and -0.174 e. $Å^{-3}$

Table 19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3**.

Atom	X	Y	Z	U(eq)
Be(1)	5503(3)	6516(2)	-973(2)	57(1)
Cl(1)	4931(1)	6780(1)	6(1)	89(1)
Cl(2)	5321(1)	7483(1)	-1674(1)	99(1)
N(1)	5285(2)	5018(1)	-1893(1)	53(1)
N(2)	3919(2)	5295(1)	-1301(1)	50(1)
C(1)	4909(2)	5555(1)	-1378(1)	46(1)
C(2)	4554(2)	4447(2)	-2130(2)	66(1)
C(3)	3693(2)	4619(2)	-1759(2)	65(1)
C(4)	3160(2)	5594(2)	-774(1)	54(1)
C(5)	2491(2)	6243(2)	-979(2)	63(1)
C(6)	1739(3)	6467(2)	-468(2)	82(1)
C(7)	1671(3)	6068(3)	192(2)	92(1)
C(8)	2337(3)	5434(3)	371(2)	89(1)
C(9)	3123(2)	5174(2)	-110(2)	68(1)
C(10)	3858(3)	4468(2)	102(2)	90(1)
C(11)	3333(4)	3610(3)	138(4)	141(2)
C(12)	4420(5)	4643(4)	816(3)	165(3)
C(13)	2562(3)	6699(2)	-1700(2)	82(1)
C(14)	2478(5)	7661(3)	-1613(3)	143(2)
C(15)	1759(5)	6351(5)	-2242(3)	163(2)
C(16)	6339(2)	4978(2)	-2152(2)	56(1)
C(17)	6603(2)	5437(2)	-2773(2)	70(1)
C(18)	7607(3)	5347(3)	-3033(2)	91(1)
C(19)	8292(3)	4818(3)	-2686(2)	95(1)
C(20)	8012(2)	4369(2)	-2079(2)	85(1)
C(21)	7020(2)	4423(2)	-1793(2)	66(1)
C(22)	6686(3)	3874(2)	-1156(2)	82(1)
C(23)	7497(4)	3773(3)	-557(3)	128(2)
C(24)	6364(4)	2997(3)	-1405(3)	128(2)
C(25)	5831(3)	5985(3)	-3191(2)	90(1)
C(26)	6297(4)	6802(3)	-3495(2)	121(2)
C(27)	5326(5)	5481(4)	-3799(3)	154(2)
O(1)	6790(2)	6377(1)	-861(1)	79(1)
C(28)	7230(4)	6121(4)	-171(3)	132(2)
C(29)	8393(5)	6198(5)	-284(5)	174(3)
C(30)	8557(4)	6500(6)	-990(4)	175(3)
C(31)	7572(3)	6818(4)	-1268(3)	122(2)
C(32)	877(5)	3478(9)	-2106(5)	187(3)
C(33)	745(10)	2643(8)	-1862(9)	237(6)
C(34)	606(13)	2650(11)	-1200(9)	291(8)

Table 19 (cont.). Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3**.

Atom	X	Y	Z	U(eq)
C(35)	533(8)	3252(10)	-655(7)	227(4)
C(36)	633(6)	4039(8)	-934(8)	213(4)
C(37)	813(6)	4182(5)	-1645(7)	170(3)
C(38)	977(11)	3514(14)	-2834(7)	390(12)

Table 20. Bond lengths [Å] for **3**.

Atoms	Distance	Atoms	Distance
Be(1)-O(1)	1.698(4)	C(16)-C(17)	1.390(4)
Be(1)-C(1)	1.848(4)	C(17)-C(18)	1.395(5)
Be(1)-Cl(2)	2.000(4)	C(17)-C(25)	1.525(5)
Be(1)-Cl(1)	1.985(4)	C(18)-C(19)	1.372(6)
N(1)-C(1)	1.354(3)	C(19)-C(20)	1.365(5)
N(1)-C(2)	1.375(3)	C(20)-C(21)	1.392(4)
N(1)-C(16)	1.450(3)	C(21)-C(22)	1.514(5)
N(2)-C(1)	1.356(3)	C(22)-C(24)	1.508(6)
N(2)-C(3)	1.383(3)	C(22)-C(23)	1.529(6)
N(2)-C(4)	1.456(3)	C(25)-C(26)	1.523(5)
C(2)-C(3)	1.335(4)	C(25)-C(27)	1.515(6)
C(4)-C(9)	1.383(4)	O(1)-C(31)	1.436(5)
C(4)-C(5)	1.391(4)	O(1)-C(28)	1.443(5)
C(5)-C(6)	1.398(4)	C(28)-C(29)	1.529(8)
C(5)-C(13)	1.504(5)	C(29)-C(30)	1.392(9)
C(6)-C(7)	1.364(5)	C(30)-C(31)	1.465(8)
C(7)-C(8)	1.358(6)	C(32)-C(38)	1.341(11)
C(8)-C(9)	1.408(5)	C(32)-C(37)	1.393(10)
C(9)-C(10)	1.513(5)	C(32)-C(33)	1.394(12)
C(10)-C(11)	1.509(6)	C(33)-C(34)	1.227(14)
C(10)-C(12)	1.523(6)	C(34)-C(35)	1.377(14)
C(13)-C(15)	1.541(6)	C(35)-C(36)	1.342(11)
C(13)-C(14)	1.521(5)	C(36)-C(37)	1.341(11)
C(16)-C(21)	1.403(4)		

Table 21. Bond angles [°] for **3**.

Atoms	Angle	Atoms	Angle
O(1)-Be(1)-C(1)	110.7(2)	C(15)-C(13)-C(14)	111.8(4)
O(1)-Be(1)-Cl(2)	106.96(19)	C(21)-C(16)-C(17)	123.4(3)
C(1)-Be(1)-Cl(2)	108.17(19)	C(21)-C(16)-N(1)	117.9(2)
O(1)-Be(1)-Cl(1)	106.6(2)	C(17)-C(16)-N(1)	118.5(2)
C(1)-Be(1)-Cl(1)	112.13(19)	C(16)-C(17)-C(18)	117.2(3)
Cl(2)-Be(1)-Cl(1)	112.17(18)	C(16)-C(17)-C(25)	122.7(3)
C(1)-N(1)-C(2)	112.1(2)	C(18)-C(17)-C(25)	120.0(3)
C(1)-N(1)-C(16)	126.5(2)	C(19)-C(18)-C(17)	120.6(4)
C(2)-N(1)-C(16)	121.3(2)	C(20)-C(19)-C(18)	121.1(3)
C(1)-N(2)-C(3)	111.6(2)	C(19)-C(20)-C(21)	121.4(3)
C(1)-N(2)-C(4)	127.9(2)	C(20)-C(21)-C(16)	116.3(3)
C(3)-N(2)-C(4)	120.3(2)	C(20)-C(21)-C(22)	121.4(3)
N(1)-C(1)-N(2)	103.11(19)	C(16)-C(21)-C(22)	122.2(3)
N(1)-C(1)-Be(1)	129.5(2)	C(21)-C(22)-C(24)	111.4(3)
N(2)-C(1)-Be(1)	126.8(2)	C(21)-C(22)-C(23)	114.5(3)
C(3)-C(2)-N(1)	106.5(2)	C(24)-C(22)-C(23)	108.3(3)
C(2)-C(3)-N(2)	106.6(2)	C(17)-C(25)-C(26)	113.3(3)
C(9)-C(4)-C(5)	124.3(3)	C(17)-C(25)-C(27)	111.0(4)
C(9)-C(4)-N(2)	117.0(2)	C(26)-C(25)-C(27)	110.0(4)
C(5)-C(4)-N(2)	118.6(2)	C(31)-O(1)-C(28)	108.0(3)
C(4)-C(5)-C(6)	116.0(3)	C(31)-O(1)-Be(1)	124.7(3)
C(4)-C(5)-C(13)	123.2(3)	C(28)-O(1)-Be(1)	122.1(3)
C(6)-C(5)-C(13)	120.8(3)	O(1)-C(28)-C(29)	104.5(5)
C(7)-C(6)-C(5)	121.6(3)	C(30)-C(29)-C(28)	107.7(5)
C(8)-C(7)-C(6)	120.6(3)	C(29)-C(30)-C(31)	107.8(5)
C(7)-C(8)-C(9)	121.4(3)	O(1)-C(31)-C(30)	105.8(5)
C(4)-C(9)-C(8)	116.0(3)	C(38)-C(32)-C(37)	125.1(16)
C(4)-C(9)-C(10)	123.5(3)	C(38)-C(32)-C(33)	111.7(15)
C(8)-C(9)-C(10)	120.5(3)	C(37)-C(32)-C(33)	122.9(10)
C(9)-C(10)-C(11)	112.3(3)	C(34)-C(33)-C(32)	109.1(16)
C(9)-C(10)-C(12)	113.0(4)	C(33)-C(34)-C(35)	137(2)
C(11)-C(10)-C(12)	109.8(4)	C(36)-C(35)-C(34)	110.4(14)
C(5)-C(13)-C(15)	110.9(4)	C(35)-C(36)-C(37)	122.7(13)
C(5)-C(13)-C(14)	112.0(3)	C(32)-C(37)-C(36)	117.8(10)

Structural Data for L^1:$BeCl_2$·dioxane **4**

Table 22. Crystal data and structural refinement for **4**.

Empirical formula	$C_{65} H_{88} Be_2 Cl_4 N_4 O_2$
Formula weight	1117.22
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 12.6855(7) Å
	b = 14.4535(8) Å
	c = 18.9074(11) Å
	α = 90°
	β = 104.6930(10)°
	ɣ = 90°
Volume	3353.3(3) A^3
Z, Calculated density	2, 1.106 Mg/m^3
Absorption coefficient	0.219 mm^{-1}
F(000)	1196
Crystal size	0.28 x 0.25 x 0.11 mm
Theta range for data collection	2.18 to 27.88 deg.
Limiting indices	-16<=h<=16, -19<=k<=19, -24<=l<=24
Reflections collected / unique	43943 / 8003 [R(int) = 0.0300]
Completeness to theta =	27.88 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9764 and 0.9413
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8003 / 79 / 389
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.1324
R indices (all data)	R1 = 0.0761, wR2 = 0.1531
Largest diff. peak and hole	0.334 and -0.274 e. $Å^{-3}$

Table 23. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4**.

Atom	X	Y	Z	U(eq)
Be(1)	291(2)	5543(1)	1520(1)	46(1)
Cl(1)	1525(1)	4677(1)	1895(1)	79(1)
Cl(2)	-1122(1)	5074(1)	1608(1)	79(1)
N(1)	433(1)	6971(1)	2588(1)	43(1)
N(2)	1514(1)	7218(1)	1913(1)	43(1)
C(1)	699(1)	6645(1)	1984(1)	38(1)
C(2)	1073(2)	7719(1)	2882(1)	57(1)
C(3)	1748(2)	7874(1)	2460(1)	57(1)
C(4)	2035(1)	7230(1)	1318(1)	49(1)
C(5)	1492(2)	7680(1)	671(1)	64(1)
C(6)	2022(2)	7717(2)	118(1)	85(1)
C(7)	3027(3)	7340(2)	201(1)	90(1)
C(8)	3554(2)	6914(2)	839(1)	76(1)
C(9)	3073(2)	6847(1)	1426(1)	55(1)
C(10)	3679(2)	6421(2)	2138(1)	67(1)
C(11)	4260(2)	5521(2)	2034(2)	102(1)
C(12)	4493(2)	7124(2)	2588(2)	104(1)
C(13)	398(2)	8137(2)	580(2)	92(1)
C(14)	553(3)	9128(2)	872(2)	136(1)
C(15)	-311(3)	8150(2)	-207(2)	132(1)
C(16)	-459(1)	6677(1)	2887(1)	49(1)
C(17)	-1446(2)	7148(2)	2651(1)	68(1)
C(18)	-2268(2)	6894(2)	2978(2)	93(1)
C(19)	-2112(2)	6221(2)	3498(2)	102(1)
C(20)	-1138(2)	5777(2)	3715(1)	90(1)
C(21)	-268(2)	5991(1)	3416(1)	61(1)
C(22)	808(2)	5497(2)	3667(1)	76(1)
C(23)	1438(3)	5860(3)	4410(2)	125(1)
C(24)	687(3)	4448(2)	3685(2)	120(1)
C(25)	-1617(12)	7941(10)	2063(7)	80(3)
C(26)	-2110(20)	8799(13)	2337(12)	163(7)
C(27)	-2290(20)	7616(16)	1321(8)	138(5)
C(25')	-1660(13)	7813(13)	2076(10)	106(5)
C(26')	-1732(18)	8818(10)	2339(12)	131(5)
C(27')	-2713(18)	7587(17)	1494(12)	157(7)
O(1)	195(1)	5662(1)	576(1)	50(1)
C(28)	1048(2)	5364(1)	237(1)	57(1)
C(29)	-834(1)	5606(1)	35(1)	56(1)

Table 23 (cont.). Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4**.

Atom	X	Y	Z	U(eq)
C(30)	-4678(7)	5343(6)	-33(4)	106(2)
C(31)	-5694(7)	5205(8)	-471(6)	99(2)
C(32)	-5101(12)	6166(6)	-593(5)	292(6)
C(33)	-4179(7)	6139(6)	-155(4)	105(2)
C(34)	-3951(7)	5309(12)	381(6)	320(10)

Table 24. Bond lengths [Å] for **4**.

Atoms	Distance	Atoms	Distance
Be(1)-O(1)	1.767(2)	C(17)-C(25')	1.43(2)
Be(1)-C(1)	1.829(2)	C(17)-C(25)	1.574(15)
Be(1)-Cl(2)	1.963(2)	C(18)-C(19)	1.361(4)
Be(1)-Cl(1)	1.989(2)	C(19)-C(20)	1.360(4)
N(1)-C(1)	1.3540(18)	C(20)-C(21)	1.398(3)
N(1)-C(2)	1.381(2)	C(21)-C(22)	1.507(3)
N(1)-C(16)	1.451(2)	C(22)-C(23)	1.523(4)
N(2)-C(1)	1.3584(19)	C(22)-C(24)	1.525(4)
N(2)-C(3)	1.379(2)	C(25)-C(27)	1.518(11)
N(2)-C(4)	1.442(2)	C(25)-C(26)	1.538(10)
C(2)-C(3)	1.329(3)	C(25')-C(27')	1.535(13)
C(4)-C(9)	1.395(2)	C(25')-C(26')	1.546(11)
C(4)-C(5)	1.401(3)	O(1)-C(29)	1.443(2)
C(5)-C(6)	1.381(3)	O(1)-C(28)	1.455(2)
C(5)-C(13)	1.507(3)	C(28)-C(29)#1	1.495(3)
C(6)-C(7)	1.358(4)	C(29)-C(28)#1	1.495(3)
C(7)-C(8)	1.369(3)	C(30)-C(31)#2	1.237(15)
C(8)-C(9)	1.398(3)	C(30)-C(30)#2	1.311(15)
C(9)-C(10)	1.504(3)	C(30)-C(33)	1.360(11)
C(10)-C(11	1.532(3)	C(30)-C(31)	1.358(11)
C(10)-C(12)	1.541(4)	C(30)-C(32)	1.592(11)
C(13)-C(14)	1.530(4)	C(31)-C(30)#2	1.237(15)
C(13)-C(15)	1.531(4)	C(31)-C(32)	1.624(14)
C(16)-C(17)	1.395(3)	C(32)-C(33)	1.250(13)
C(16)-C(21)	1.384(3)	C(33)-C(34)	1.550(15)
C(17)-C(18)	1.389(3)		

Table 25. Bond angles [°] for **4**.

Atoms	Angle	Atoms	Angle
O(1)-Be(1)-C(1)	109.79(13)	C(21)-C(16)-N(1)	118.70(15)
O(1)-Be(1)-Cl(2)	106.74(11)	C(18)-C(17)-C(16)	116.3(2)
C(1)-Be(1)-Cl(2)	114.47(12)	C(18)-C(17)-C(25')	119.9(8)
O(1)-Be(1)-Cl(1)	105.50(11)	C(16)-C(17)-C(25')	123.7(8)
C(1)-Be(1)-Cl(1)	106.01(11)	C(18)-C(17)-C(25)	121.4(7)
Cl(2)-Be(1)-Cl(1)	113.96(11)	C(16)-C(17)-C(25)	122.2(6)
C(1)-N(1)-C(2)	111.42(13)	C(17)-C(18)-C(19)	121.4(2)
C(1)-N(1)-C(16)	127.77(12)	C(20)-C(19)-C(18)	120.6(2)
C(2)-N(1)-C(16)	120.58(13)	C(19)-C(20)-C(21)	121.6(3)
C(1)-N(2)-C(3)	111.66(13)	C(16)-C(21)-C(20)	116.1(2)
C(1)-N(2)-C(4)	126.57(13)	C(16)-C(21)-C(22)	123.10(17)
C(3)-N(2)-C(4)	121.55(13)	C(20)-C(21)-C(22)	120.8(2)
N(2)-C(1)-N(1)	103.32(12)	C(21)-C(22)-C(23)	110.4(2)
N(2)-C(1)-Be(1)	127.85(13)	C(21)-C(22)-C(24)	113.0(2)
N(1)-C(1)-Be(1)	127.34(13)	C(23)-C(22)-C(24)	110.8(2)
C(3)-C(2)-N(1)	107.04(14)	C(27)-C(25)-C(26)	112.5(11)
C(2)-C(3)-N(2)	106.56(14)	C(27)-C(25)-C(17)	111.9(12)
C(9)-C(4)-C(5)	123.26(16)	C(26)-C(25)-C(17)	110.1(14)
C(9)-C(4)-N(2)	118.89(15)	C(17)-C(25')-C(27')	111.5(15)
C(5)-C(4)-N(2)	117.74(16)	C(17)-C(25')-C(26')	113.8(13)
C(6)-C(5)-C(4)	116.9(2)	C(27')-C(25')-C(26')	108.6(12)
C(6)-C(5)-C(13)	120.5(2)	C(29)-O(1)-C(28)	108.15(12)
C(4)-C(5)-C(13)	122.53(18)	C(29)-O(1)-Be(1)	121.96(13)
C(7)-C(6)-C(5)	121.4(2)	C(28)-O(1)-Be(1)	123.21(13)
C(6)-C(7)-C(8)	121.1(2)	O(1)-C(28)-C(29)#1	109.78(14)
C(7)-C(8)-C(9)	121.1(2)	O(1)-C(29)-C(28)#1	110.46(15)
C(4)-C(9)-C(8)	116.29(19)	C(34)-C(30)-C(30)#2	110.1(16)
C(4)-C(9)-C(10)	122.89(16)	C(31)#2-C(30)-C(33)	124.7(9)
C(8)-C(9)-C(10)	120.77(18)	C(31)#2-C(30)-C(31)	119.5(8)
C(9)-C(10)-C(11)	112.76(19)	C(33)-C(30)-C(31)	115.5(10)
C(9)-C(10)-C(12)	110.03(19)	C(34)-C(30)-C(32)	128.0(11)
C(11)-C(10)-C(12)	110.7(2)	C(30)#2-C(30)-C(32)	121.0(12)
C(5)-C(13)-C(14)	109.9(3)	C(34)#2-C(31)-C(30)	116.4(18)
C(5)-C(13)-C(15)	114.4(2)	C(30)#2-C(31)-C(32)	123.9(8)
C(14)-C(13)-C(15)	109.2(2)	C(33)-C(32)-C(31)	105.6(7)
C(17)-C(16)-C(21)	123.95(18)	C(32)-C(33)-C(34)	116.4(9)
C(17)-C(16)-N(1)	117.24(17)		

Structural Data for L^2:$BeCl_2$ **5**

Table 26. Crystal data and structural refinement for **5**.

Empirical formula	C_{27} H_{44} B_2 Be N_2
Formula weight	427.27
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.4255(7) Å
	b = 17.9488(11) Å
	c = 15.9335(10) Å
	α = 90°
	β = 98.5790(10)°
	ɣ = 90°
Volume	2948.2(3) A^3
Z, Calculated density	4, 0.963 Mg/m^3
Absorption coefficient	0.053 mm^{-1}
F(000)	936
Crystal size	0.30 x 0.28 x 0.12 mm
Theta range for data collection	2.27 to 25.99 deg.
Limiting indices	-12<=h<=12, -22<=k<=22, -19<=l<=19
Reflections collected / unique	33973 / 5787 [R(int) = 0.0302]
Completeness to theta =	25.99 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9936 and 0.9841
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5787 / 6 / 321
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0527, wR2 = 0.1447
R indices (all data)	R1 = 0.0826, wR2 = 0.1707
Largest diff. peak and hole	0.164 and -0.150 e. $Å^3$

Table 27. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **5**.

Atom	X	Y	Z	U(eq)
Be(1)	2642(2)	2556(1)	2632(1)	66(1)
B(1)	826(3)	2234(2)	2440(2)	91(1)
B(2)	3595(4)	2753(2)	1694(2)	113(1)
N(1)	4114(1)	2141(1)	4186(1)	57(1)
N(2)	3703(1)	3303(1)	4116(1)	59(1)
C(1)	3481(1)	2664(1)	3672(1)	52(1)
C(2)	4727(2)	2456(1)	4926(1)	77(1)
C(3)	4468(2)	3181(1)	4883(1)	81(1)
C(4)	3180(2)	4028(1)	3850(1)	61(1)
C(5)	1912(2)	4185(1)	3963(1)	71(1)
C(6)	1483(2)	4910(1)	3760(2)	96(1)
C(7)	2280(3)	5426(1)	3466(2)	107(1)
C(8)	3501(3)	5244(1)	3349(1)	94(1)
C(9)	3997(2)	4537(1)	3534(1)	73(1)
C(10)	5376(2)	4358(1)	3414(2)	94(1)
C(11)	5653(4)	4555(2)	2530(2)	153(1)
C(12)	6328(3)	4755(2)	4076(2)	159(1)
C(13)	1043(2)	3625(1)	4304(2)	89(1)
C(14)	1211(3)	3657(2)	5277(2)	148(1)
C(15)	-379(2)	3698(2)	3911(3)	161(2)
C(16)	4097(2)	1350(1)	4011(1)	61(1)
C(17)	3122(2)	925(1)	4282(1)	82(1)
C(18)	3149(2)	166(1)	4125(2)	110(1)
C(19)	4092(3)	-140(1)	3727(2)	112(1)
C(20)	5043(2)	290(1)	3470(1)	94(1)
C(21)	5085(2)	1057(1)	3610(1)	66(1)
C(22)	6165(2)	1528(1)	3368(1)	79(1)
C(23)	7356(2)	1476(2)	4046(2)	129(1)
C(24)	6510(3)	1338(2)	2496(2)	134(1)
C(25)	2106(2)	1263(1)	4755(2)	110(1)
C(26)	772(3)	918(2)	4513(3)	194(2)
C(27)	2525(3)	1219(2)	5719(2)	167(2)

Table 28. Bond lengths [Å] for **5**.

Atoms	Distance	Atoms	Distance
Be(1)-H(2)	1.549(19)	C(4)-C(9)	1.393(2)
Be(1)-H(5)	1.530(15)	C(5)-C(6)	1.398(3)
Be(1)-H(6)	1.571(19)	C(5)-C(13)	1.508(3)
Be(1)-H(1)	1.586(14)	C(6)-C(7)	1.371(3)
Be(1)-C(1)	1.765(2)	C(7)-C(8)	1.354(3)
Be(1)-B(2)	1.947(4)	C(8)-C(9)	1.385(3)
Be(1)-B(1)	1.959(4)	C(9)-C(10)	1.513(3)
B(1)-H(3)	1.045(17)	C(10)-C(12)	1.514(3)
B(1)-H(1)	1.03(2)	C(10)-C(11)	1.521(3)
B(1)-H(4)	1.057(17)	C(13)-C(15)	1.526(3)
B(1)-H(2)	1.07(2)	C(13)-C(14)	1.535(4)
B(2)-H(7)	1.04(2)	C(16)-C(17)	1.391(2)
B(2)-H(8)	1.048(18)	C(16)-C(21)	1.393(2)
B(2)-H(6)	1.12(2)	C(17)-C(18)	1.386(3)
B(2)-H(5)	1.19(2)	C(17)-C(25)	1.515(3)
N(1)-C(1)	1.3511(17)	C(18)-C(19)	1.362(4)
N(1)-C(2)	1.376(2)	C(19)-C(20)	1.367(3)
N(1)-C(16)	1.4468(19)	C(20)-C(21)	1.394(3)
N(2)-C(1)	1.3497(18)	C(21)-C(22)	1.503(3)
N(2)-C(3)	1.374(2)	C(22)-C(24)	1.525(3)
N(2)-C(4)	1.4495(19)	C(22)-C(23)	1.522(3)
C(2)-C(3)	1.328(3)	C(25)-C(26)	1.518(4)
C(4)-C(5)	1.389(2)	C(25)-C(27)	1.536(4)

Table 29. Bond angles [°] for **5**.

Atoms	Angle	Atoms	Angle
H(2)-Be(1)-H(5)	94.1(11)	C(1)-N(1)-C(2)	110.87(13)
H(2)-Be(1)-H(6)	137.8(10)	C(1)-N(1)-C(16)	125.02(12)
H(5)-Be(1)-H(6)	72.6(11)	C(2)-N(1)-C(16)	124.03(13)
H(2)-Be(1)-H(1)	64.6(10)	C(1)-N(2)-C(3)	111.23(13)
H(5)-Be(1)-H(1)	132.1(11)	C(1)-N(2)-C(4)	125.62(12)
H(6)-Be(1)-H(1)	94.4(11)	C(3)-N(2)-C(4)	123.12(13)
H(2)-Be(1)-C(1)	111.4(8)	N(2)-C(1)-N(1)	104.03(12)
H(5)-Be(1)-C(1)	110.2(8)	N(2)-C(1)-Be(1)	127.44(12)
H(6)-Be(1)-C(1)	110.8(7)	N(1)-C(1)-Be(1)	128.42(13)
H(1)-Be(1)-C(1)	117.5(8)	C(3)-C(2)-N(1)	107.07(14)
H(2)-Be(1)-B(2)	119.7(7)	C(2)-C(3)-N(2)	106.80(15)
H(5)-Be(1)-B(2)	37.6(8)	C(5)-C(4)-C(9)	123.91(15)
H(6)-Be(1)-B(2)	35.1(8)	C(5)-C(4)-N(2)	117.91(15)
H(1)-Be(1)-B(2)	115.5(8)	C(9)-C(4)-N(2)	118.12(15)
C(1)-Be(1)-B(2)	117.51(18)	C(4)-C(5)-C(6)	115.92(19)
H(2)-Be(1)-B(1)	33.1(8)	C(4)-C(5)-C(13)	123.05(16)
H(5)-Be(1)-B(1)	115.4(8)	C(6)-C(5)-C(13)	121.00(18)
H(6)-Be(1)-B(1)	117.4(7)	C(7)-C(6)-C(5)	121.1(2)
H(1)-Be(1)-B(1)	31.5(8)	C(6)-C(7)-C(8)	121.0(2)
C(1)-Be(1)-B(1)	120.75(16)	C(7)-C(8)-C(9)	121.3(2)
B(2)-Be(1)-B(1)	121.73(19)	C(8)-C(9)-C(4)	116.69(19)
H(3)-B(1)-H(1)	107.4(18)	C(8)-C(9)-C(10)	119.90(19)
H(3)-B(1)-H(4)	124(2)	C(4)-C(9)-C(10)	123.38(16)
H(1)-B(1)-H(4)	104.6(18)	C(9)-C(10)-C(12)	110.39(17)
H(3)-B(1)-H(2)	110.2(18)	C(9)-C(10)-C(11)	112.6(2)
H(1)-B(1)-H(2)	105.7(14)	C(12)-C(10)-C(11)	109.9(2)
H(4)-B(1)-H(2)	103.7(18)	C(5)-C(13)-C(15)	113.2(2)
H(3)-B(1)-Be(1)	119.4(16)	C(5)-C(13)-C(14)	110.81(19)
H(1)-B(1)-Be(1)	53.8(8)	C(15)-C(13)-C(14)	111.6(2)
H(4)-B(1)-Be(1)	116.7(15)	C(17)-C(16)-C(21)	124.11(16)
H(2)-B(1)-Be(1)	52.0(10)	C(17)-C(16)-N(1)	117.78(15)
H(7)-B(2)-H(8)	122(2)	C(21)-C(16)-N(1)	118.06(14)
H(7)-B(2)-H(6)	105.7(18)	C(16)-C(17)-C(18)	116.6(2)
H(8)-B(2)-H(6)	110(2)	C(16)-C(17)-C(25)	122.19(18)
H(7)-B(2)-H(5)	103.6(18)	C(18)-C(17)-C(25)	121.2(2)
H(8)-B(2)-H(5)	109.6(19)	C(19)-C(18)-C(17)	121.1(2)
H(6)-B(2)-H(5)	105.4(12)	C(20)-C(19)-C(18)	121.2(2)
H(7)-B(2)-Be(1)	117.8(15)	C(19)-C(20)-C(21)	121.1(2)
H(8)-B(2)-Be(1)	120.4(18)	C(20)-C(21)-C(16)	115.94(18)
H(6)-B(2)-Be(1)	53.8(10)	C(20)-C(21)-C(22)	121.44(17)
H(5)-B(2)-Be(1)	51.8(7)	C(16)-C(21)-C(22)	122.58(15)

Table 29 (cont.). Bond angles [º] for **5**.

Atoms	Angle
C(21)-C(22)-C(24)	113.26(19)
C(21)-C(22)-C(23)	110.29(17)
C(24)-C(22)-C(23)	110.8(2)
C(17)-C(25)-C(26)	113.1(3)
C(17)-C(25)-C(27)	111.12(18)
C(26)-C(25)-C(27)	110.2(3)
B(1)-H(1)-Be(1)	94.6(12)
B(1)-H(2)-Be(1)	94.9(14)
B(2)-H(5)-Be(1)	90.6(11)
B(2)-H(6)-Be(1)	91.1(13)

Structural Data for L^2:$BeCl_2$ **6**

Table 30. Crystal data and structural refinement for **6**.

Empirical formula	$C_{54} H_{77} B N_4$
Formula weight	793.01
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 12.4807(7) Å
	b = 23.1679(12) Å
	c = 17.7375(10) Å
	α = 90°
	β = 91.1000(10)°
	ɣ = 90°
Volume	5127.9(5) A^3
Z, Calculated density	4, 1.027 Mg/m^3
Absorption coefficient	0.059 mm^{-1}
F(000)	1736
Crystal size	0.35 x 0.30 x 0.14 mm
Theta range for data collection	2.10 to 25.60°
Limiting indices	-15<=h<=15, -28<=k<=28, -21<=l<=21
Reflections collected / unique	57706 / 9641 [R(int) = 0.0328]
Completeness to theta =	25.60 99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9918 and 0.9797
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9641 / 161 / 617
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.1212
R indices (all data)	R1 = 0.0703, wR2 = 0.1375
Extinction coefficient	0.0066(5)
Largest diff. peak and hole	0.249 and -0.211 e. $Å^{-3}$

Table 31. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **6**.

Atom	X	Y	Z	U(eq)
B(1)	9910(1)	1655(1)	7340(1)	44(1)
N(2)	8533(1)	997(1)	8080(1)	47(1)
N(3)	11880(1)	1815(1)	6986(1)	39(1)
N(4)	12747(1)	1113(1)	7663(1)	49(1)
C(1)	9089(1)	1496(1)	8002(1)	39(1)
C(2)	7946(1)	1560(1)	8966(1)	57(1)
C(3)	7826(1)	1038(1)	8667(1)	60(1)
C(4)	8565(1)	500(1)	7586(1)	54(1)
C(5)	9127(2)	12(1)	7826(1)	65(1)
C(6)	9113(2)	-461(1)	7342(1)	96(1)
C(7)	8562(3)	-442(1)	6668(2)	117(1)
C(8)	8009(2)	38(1)	6456(1)	106(1)
C(9)	7981(2)	527(1)	6906(1)	72(1)
C(10)	7363(9)	1061(6)	6666(7)	84(3)
C(11)	6214(10)	1024(8)	6940(10)	133(4)
C(12)	7426(12)	1123(7)	5809(6)	124(3)
C(10')	7280(15)	1030(10)	6683(13)	93(6)
C(11')	6088(16)	886(13)	6686(17)	150(8)
C(12')	7482(17)	1354(14)	5946(16)	135(7)
C(13)	9691(2)	-33(1)	8589(1)	74(1)
C(14)	10781(2)	-332(1)	8565(2)	101(1)
C(15)	8968(2)	-348(1)	9144(1)	113(1)
C(16)	9023(1)	2430(1)	8723(1)	43(1)
C(17)	9633(1)	2534(1)	9376(1)	50(1)
C(18)	9823(1)	3108(1)	9567(1)	59(1)
C(19)	9438(1)	3549(1)	9128(1)	62(1)
C(20)	8850(1)	3436(1)	8484(1)	60(1)
C(21)	8614(1)	2873(1)	8263(1)	49(1)
C(22)	7911(1)	2758(1)	7574(1)	63(1)
C(23)	8187(2)	3149(1)	6910(1)	108(1)
C(24)	6728(2)	2801(1)	7774(2)	105(1)
C(25)	10078(2)	2054(1)	9880(1)	64(1)
C(26)	11298(2)	2052(1)	9898(1)	87(1)
C(27)	9645(2)	2099(1)	10676(1)	100(1)
C(28)	12937(1)	1566(1)	7119(1)	44(1)
C(29)	11154(1)	1646(1)	7604(1)	40(1)
C(30)	11599(1)	1057(1)	7786(1)	49(1)
C(31)	13382(1)	599(1)	7658(1)	49(1)
C(32)	13959(1)	474(1)	8324(1)	63(1)
C(33)	14586(2)	-20(1)	8350(1)	86(1)

Table 31 (cont.). Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **6**.

Atom	X	Y	Z	U(eq)
C(34)	14646(2)	-381(1)	7744(2)	95(1)
C(35)	14068(2)	-261(1)	7100(1)	81(1)
C(36)	13414(1)	225(1)	7041(1)	59(1)
C(37)	12757(2)	322(1)	6322(1)	73(1)
C(38)	13475(2)	389(1)	5642(1)	105(1)
C(39)	11932(2)	-156(1)	6190(2)	114(1)
C(40)	13946(8)	896(4)	8994(4)	95(3)
C(41)	14601(4)	1447(3)	8870(3)	114(2)
C(42)	14020(9)	658(4)	9775(3)	157(4)
C(40')	13800(9)	843(5)	9010(7)	79(3)
C(41')	14937(7)	1041(6)	9240(6)	147(5)
C(42')	13321(8)	507(5)	9622(5)	135(4)
C(43)	11819(1)	2384(1)	6679(1)	41(1)
C(44)	12203(1)	2872(1)	7068(1)	46(1)
C(45)	12105(1)	3411(1)	6723(1)	64(1)
C(46)	11645(2)	3473(1)	6021(1)	76(1)
C(47)	11274(2)	2996(1)	5646(1)	68(1)
C(48)	11347(1)	2445(1)	5955(1)	51(1)
C(49)	10957(2)	1926(1)	5516(1)	66(1)
C(50)	11823(2)	1725(1)	4987(1)	122(1)
C(51)	9901(2)	2026(1)	5098(2)	128(1)
C(52)	12708(1)	2842(1)	7852(1)	52(1)
C(53)	13864(2)	3055(1)	7856(1)	90(1)
C(54)	12045(2)	3177(1)	8415(1)	85(1)

Table 32. Bond lengths [Å] for **6**.

Atoms	Distance	Atoms	Distance
B(1)-H(1A)	1.138(13)	C(18)-C(19)	1.367(2)
B(1)-H(1B)	1.160(12)	C(19)-C(20)	1.372(2)
B(1)-C(29)	1.614(2)	C(20)-C(21)	1.391(2)
B(1)-C(1)	1.615(2)	C(21)-C(22)	1.515(2)
N(1)-C(1)	1.3550(16)	C(22)-C(23)	1.529(3)
N(1)-C(2)	1.3792(18)	C(22)-C(24)	1.528(3)
N(1)-C(16)	1.4502(17)	C(25)-C(27)	1.526(3)
N(2)-C(1)	1.3556(17)	C(25)-C(26)	1.523(3)
N(2)-C(3)	1.3819(19)	C(29)-C(30)	1.507(2)
N(2)-C(4)	1.4486(18)	C(31)-C(36)	1.397(2)
N(3)-C(43)	1.4302(16)	C(31)-C(32)	1.401(2)
N(3)-C(28)	1.4537(17)	C(32)-C(33)	1.386(3)
N(3)-C(29)	1.4875(16)	C(32)-C(40')	1.504(13)
N(4)-C(31)	1.4303(18)	C(32)-C(40)	1.540(8)
N(4)-C(28)	1.4480(18)	C(33)-C(34)	1.365(3)
N(4)-C(30)	1.4596(18)	C(34)-C(35)	1.368(3)
C(2)-C(3)	1.327(2)	C(35)-C(36)	1.392(2)
C(4)-C(5)	1.391(2)	C(36)-C(37)	1.520(2)
C(4)-C(9)	1.400(2)	C(37)-C(39)	1.529(3)
C(5)-C(6)	1.392(2)	C(37)-C(38)	1.525(3)
C(5)-C(13)	1.517(3)	C(40)-C(42)	1.492(7)
C(6)-C(7)	1.368(3)	C(40)-C(41)	1.535(8)
C(7)-C(8)	1.358(4)	C(40')-C(42')	1.472(10)
C(8)-C(9)	1.387(3)	C(40')-C(41')	1.540(11)
C(9)-C(10')	1.506(16)	C(43)-C(44)	1.404(2)
C(9)-C(10)	1.514(10)	C(43)-C(48)	1.408(2)
C(10)-C(11)	1.525(8)	C(44)-C(45)	1.396(2)
C(10)-C(12)	1.530(9)	C(44)-C(52)	1.517(2)
C(10')-C(12')	1.531(11)	C(45)-C(46)	1.368(3)
C(10')-C(11')	1.525(12)	C(46)-C(47)	1.366(3)
C(13)-C(14)	1.529(3)	C(47)-C(48)	1.391(2)
C(13)-C(15)	1.533(3)	C(48)-C(49)	1.507(2)
C(16)-C(21)	1.400(2)	C(49)-C(51)	1.518(3)
C(16)-C(17)	1.394(2)	C(49)-C(50)	1.519(3)
C(17)-C(18)	1.392(2)	C(52)-C(54)	1.522(2)
C(17)-C(25)	1.523(2)	C(52)-C(53)	1.524(2)

Table 33. Bond angles [°] for **6**.

Atoms	Angle	Atoms	Angle
H(1A)-B(1)-H(1B)	110.2(11)	C(9)-C(10')-C(11')	113.0(18)
H(1A)-B(1)-C(29)	109.5(8)	C(12')-C(10')-C(11')	106.7(14)
H(1B)-B(1)-C(29)	109.5(8)	C(5)-C(13)-C(14)	113.84(17)
H(1A)-B(1)-C(1)	107.4(8)	C(5)-C(13)-C(15)	109.74(19)
H(1B)-B(1)-C(1)	106.2(8)	C(14)-C(13)-C(15)	109.73(18)
C(29)-B(1)-C(1)	113.97(11)	C(21)-C(16)-C(17)	123.07(13)
C(1)-N(1)-C(2)	111.02(12)	C(21)-C(16)-N(1)	118.86(12)
C(1)-N(1)-C(16)	127.61(11)	C(17)-C(16)-N(1)	117.80(12)
C(2)-N(1)-C(16)	121.35(11)	C(18)-C(17)-C(16)	116.98(14)
C(1)-N(2)-C(3)	110.77(12)	C(18)-C(17)-C(25)	119.67(14)
C(1)-N(2)-C(4)	126.62(12)	C(16)-C(17)-C(25)	123.35(13)
C(3)-N(2)-C(4)	122.35(12)	C(19)-C(18)-C(17)	121.35(15)
C(43)-N(3)-C(28)	118.02(10)	C(18)-C(19)-C(20)	120.45(15)
C(43)-N(3)-C(29)	119.63(10)	C(19)-C(20)-C(21)	121.43(15)
C(28)-N(3)-C(29)	109.87(10)	C(16)-C(21)-C(20)	116.70(14)
C(31)-N(4)-C(28)	120.18(11)	C(16)-C(21)-C(22)	122.74(14)
C(31)-N(4)-C(30)	118.17(12)	C(20)-C(21)-C(22)	120.51(14)
C(28)-N(4)-C(30)	109.74(11)	C(21)-C(22)-C(23)	112.44(16)
N(1)-C(1)-N(2)	104.08(11)	C(21)-C(22)-C(24)	110.40(15)
N(1)-C(1)-B(1)	128.66(12)	C(23)-C(22)-C(24)	111.93(18)
N(2)-C(1)-B(1)	126.98(12)	C(27)-C(25)-C(26)	110.60(16)
C(3)-C(2)-N(1)	106.99(13)	C(27)-C(25)-C(17)	111.24(16)
C(2)-C(3)-N(2)	107.13(13)	C(26)-C(25)-C(17)	111.60(15)
C(5)-C(4)-C(9)	123.46(15)	N(4)-C(28)-N(3)	103.66(11)
C(5)-C(4)-N(2)	118.78(14)	N(3)-C(29)-C(30)	99.71(11)
C(9)-C(4)-N(2)	117.69(15)	N(3)-C(29)-B(1)	112.28(11)
C(4)-C(5)-C(6)	116.82(19)	C(30)-C(29)-B(1)	114.96(12)
C(4)-C(5)-C(13)	123.43(14)	N(4)-C(30)-C(29)	104.23(11)
C(6)-C(5)-C(13)	119.67(18)	C(36)-C(31)-C(32)	120.68(14)
C(7)-C(6)-C(5)	120.9(2)	C(36)-C(31)-N(4)	122.98(14)
C(6)-C(7)-C(8)	120.8(2)	C(32)-C(31)-N(4)	116.31(14)
C(7)-C(8)-C(9)	121.9(2)	C(33)-C(32)-C(31)	118.64(18)
C(8)-C(9)-C(4)	116.1(2)	C(33)-C(32)-C(40')	121.7(4)
C(8)-C(9)-C(10')	120.2(10)	C(31)-C(32)-C(40')	119.4(4)
C(4)-C(9)-C(10')	123.5(10)	C(33)-C(32)-C(40)	120.8(4)
C(8)-C(9)-C(10)	121.7(6)	C(31)-C(32)-C(40)	120.4(4)
C(4)-C(9)-C(10)	122.2(6)	C(34)-C(33)-C(32)	121.23(19)
C(9)-C(10)-C(11)	110.0(9)	C(35)-C(34)-C(33)	119.82(18)
C(9)-C(10)-C(12)	108.6(11)	C(34)-C(35)-C(36)	121.68(19)
C(11)-C(10)-C(12)	112.8(9)	C(35)-C(36)-C(31)	117.90(17)
C(9)-C(10')-C(12')	119.9(17)	C(35)-C(36)-C(37)	119.22(17)

Table 33 (cont.). Bond angles [º] for **6**.

Atoms	Angle	Atoms	Angle
C(31)-C(36)-C(37)	122.87(15)	C(43)-C(48)-C(49)	121.07(13)
C(45)-C(44)-C(52)	118.30(14)	C(48)-C(49)-C(51)	113.50(18)
C(43)-C(44)-C(52)	123.13(12)	C(48)-C(49)-C(50)	109.81(16)
C(46)-C(45)-C(44)	121.59(16)	C(51)-C(49)-C(50)	111.5(2)
C(45)-C(46)-C(47)	119.46(16)	C(54)-C(52)-C(44)	110.88(14)
C(46)-C(47)-C(48)	122.03(16)	C(54)-C(52)-C(53)	111.04(16)
C(47)-C(48)-C(43)	118.29(15)	C(44)-C(52)-C(53)	111.50(13)
C(47)-C(48)-C(49)	120.62(15)	C(32)-C(40')-C(42')	111.0(8)
C(42')-C(40')-C(41')	110.3(8)	C(32)-C(40')-C(41')	104.4(8)
C(44)-C(43)-C(48)	120.07(13)	C(36)-C(37)-C(38)	111.31(18)
C(44)-C(43)-N(3)	122.66(12)	C(36)-C(37)-C(39)	111.86(16)
C(48)-C(43)-N(3)	117.27(12)	C(32)-C(40)-C(41)	113.9(5)
C(45)-C(44)-C(43)	118.56(14)		

Structural Data for [L^1:Si=Si:L^1]$BeCl_2$ **7**

Table 34. Crystal data and structural refinement for **7**.

Empirical formula	C_{54} H_{72} Be Cl_2 N_4 Si_2
Formula weight	913.25
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 22.2461(14) Å
	b = 14.4513(9) Å
	c = 17.7211(11) Å
	α = 90°
	β = 101.1860(10)°.
	ɣ = 90°
Volume	5588.8(6) A^3
Z, Calculated density	4, 1.085 Mg/m^3
Absorption coefficient	0.195 mm^{-1}
F(000)	1960
Crystal size	0.30 x 0.24 x 0.08 mm
Theta range for data collection	2.16 to 25.00°
Limiting indices	-26<=h<=26, -17<=k<=17, -21<=l<=21
Reflections collected / unique	59014 / 9834 [R(int) = 0.0868]
Completeness to theta =	25.00 99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9846 and 0.9438
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9834 / 36 / 568
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0634, wR2 = 0.1540
R indices (all data)	R1 = 0.1403, wR2 = 0.1958
Largest diff. peak and hole	0.563 and -0.519 e. $Å^{-3}$

Table 35. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **7**.

Atom	X	Y	Z	U(eq)
Si(1)	2452(1)	10487(1)	2295(1)	53(1)
Si(2)	2485(1)	9050(1)	2710(1)	62(1)
Be(1)	2470(3)	11357(4)	1251(3)	80(2)
Cl(1)	2642(1)	10782(1)	338(1)	142(1)
Cl(2)	2304(1)	12652(1)	1186(1)	108(1)
N(1)	1747(1)	11332(2)	3392(2)	53(1)
N(2)	2718(1)	11565(2)	3742(1)	49(1)
N(3)	2295(1)	8070(2)	1206(2)	59(1)
N(4)	3253(1)	8310(2)	1665(2)	64(1)
C(1)	2294(2)	11163(2)	3181(2)	44(1)
C(2)	1841(2)	11814(3)	4081(2)	71(1)
C(3)	2440(2)	11957(3)	4290(2)	66(1)
C(4)	3376(2)	11544(2)	3819(2)	57(1)
C(5)	3699(2)	10848(3)	4264(2)	68(1)
C(6)	4329(2)	10881(4)	4369(3)	115(2)
C(7)	4622(2)	11569(5)	4058(4)	142(2)
C(8)	4302(2)	12254(4)	3628(3)	116(2)
C(9)	3662(2)	12264(3)	3499(2)	72(1)
C(10)	3306(2)	13043(3)	3050(2)	82(1)
C(11)	3614(2)	13419(3)	2410(3)	103(2)
C(12)	3201(3)	13838(4)	3576(3)	157(3)
C(13)	3383(2)	10103(3)	4642(2)	70(1)
C(14)	3373(3)	10332(3)	5484(3)	114(2)
C(15)	3662(2)	9148(3)	4595(3)	99(2)
C(16)	1149(2)	11044(3)	2988(2)	58(1)
C(17)	903(2)	10230(3)	3219(2)	72(1)
C(18)	325(2)	9980(3)	2824(3)	93(1)
C(19)	15(2)	10510(4)	2245(3)	105(2)
C(20)	257(2)	11313(4)	2044(3)	96(2)
C(21)	835(2)	11615(3)	2409(2)	71(1)
C(22)	1089(2)	12535(3)	2211(3)	94(1)
C(23)	977(3)	13283(4)	2790(4)	140(2)
C(24)	823(3)	12854(4)	1386(3)	140(2)
C(25)	1211(2)	9664(4)	3899(4)	114(2)
C(26)	1165(3)	8623(4)	3755(5)	192(4)
C(27)	917(4)	9894(6)	4589(4)	199(4)
C(28)	2682(2)	8488(2)	1800(2)	53(1)
C(29)	2626(2)	7668(3)	706(2)	75(1)
C(30)	3211(2)	7816(3)	986(2)	79(1)
C(31)	3823(2)	8453(3)	2211(3)	77(1)

Table 35 (cont.). Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **7**.

Atom	X	Y	Z	U(eq)
C(32)	3992(2)	7796(4)	2794(3)	89(1)
C(33)	4556(3)	7945(5)	3302(3)	119(2)
C(34)	4903(3)	8689(7)	3207(5)	145(3)
C(35)	4744(3)	9319(5)	2636(5)	136(3)
C(36)	4184(2)	9205(4)	2103(4)	99(2)
C(37)	4019(3)	9877(4)	1459(4)	120(2)
C(38)	4119(3)	10897(4)	1686(5)	177(3)
C(39)	4369(3)	9659(5)	803(4)	174(3)
C(40)	3616(2)	6951(3)	2884(3)	101(2)
C(41)	3603(4)	6707(4)	3716(4)	171(3)
C(42)	3839(3)	6131(4)	2468(4)	169(3)
C(43)	1648(2)	7884(3)	1170(2)	70(1)
C(44)	1501(2)	7069(4)	1515(3)	95(1)
C(45)	874(3)	6877(5)	1435(4)	137(2)
C(46)	440(3)	7444(7)	1056(6)	167(3)
C(47)	594(3)	8237(6)	720(4)	138(2)
C(48)	1214(2)	8484(4)	772(3)	92(1)
C(49)	1395(2)	9332(4)	392(3)	103(2)
C(50)	1406(4)	9138(5)	-470(3)	184(3)
C(51)	1002(3)	10191(4)	470(4)	182(3)
C(52)	1957(3)	6407(4)	1941(3)	108(2)
C(53)	1882(4)	6282(5)	2776(3)	172(3)
C(54)	1944(3)	5461(4)	1539(4)	161(3)

Table 36. Bond lengths [Å] for **7**.

Atoms	Distance	Atoms	Distance
Si(1)-C(1)	1.937(3)	C(17)-C(25)	1.507(6)
Si(1)-Si(2)	2.2000(14)	C(18)-C(19)	1.357(6)
Si(1)-Be(1)	2.243(6)	C(19)-C(20)	1.356(7)
Si(2)-C(28)	1.930(3)	C(20)-C(21)	1.392(6)
Be(1)-Cl(2)	1.907(6)	C(21)-C(22)	1.512(6)
Be(1)-Cl(1)	1.923(6)	C(22)-C(24)	1.537(6)
N(1)-C(1)	1.363(4)	C(22)-C(23)	1.543(7)
N(1)-C(2)	1.386(4)	C(25)-C(26)	1.526(8)
N(1)-C(16)	1.445(4)	C(25)-C(27)	1.530(9)
N(2)-C(1)	1.362(4)	C(29)-C(30)	1.317(5)
N(2)-C(3)	1.372(4)	C(31)-C(36)	1.386(6)
N(2)-C(4)	1.444(4)	C(31)-C(32)	1.400(6)
N(3)-C(28)	1.364(4)	C(32)-C(33)	1.413(6)
N(3)-C(29)	1.385(4)	C(32)-C(40)	1.505(7)
N(3)-C(43)	1.452(5)	C(33)-C(34)	1.353(9)
N(4)-C(28)	1.361(4)	C(34)-C(35)	1.357(9)
N(4)-C(30)	1.386(4)	C(35)-C(36)	1.419(8)
N(4)-C(31)	1.452(5)	C(36)-C(37)	1.489(8)
C(2)-C(3)	1.327(5)	C(37)-C(38)	1.532(7)
C(4)-C(9)	1.397(5)	C(37)-C(39)	1.553(8)
C(4)-C(5)	1.389(5)	C(40)-C(41)	1.523(7)
C(5)-C(6)	1.377(6)	C(40)-C(42)	1.528(7)
C(5)-C(13)	1.511(5)	C(43)-C(44)	1.396(6)
C(6)-C(7)	1.363(7)	C(43)-C(48)	1.385(6)
C(7)-C(8)	1.363(7)	C(44)-C(45)	1.400(7)
C(8)-C(9)	1.396(6)	C(44)-C(52)	1.489(7)
C(9)-C(10)	1.511(5)	C(45)-C(46)	1.344(10)
C(10)-C(12)	1.526(6)	C(46)-C(47)	1.366(10)
C(10)-C(11)	1.533(5)	C(47)-C(48)	1.410(7)
C(13)-C(15)	1.522(5)	C(48)-C(49)	1.490(7)
C(13)-C(14)	1.533(6)	C(49)-C(51)	1.541(7)
C(16)-C(17)	1.392(5)	C(49)-C(50)	1.558(7)
C(16)-C(21)	1.395(5)	C(52)-C(53)	1.532(7)
C(17)-C(18)	1.386(5)	C(52)-C(54)	1.539(7)

Table 37. Bond angles [°] for **7**.

Atoms	Angle	Atoms	Angle
C(1)-Si(1)-Si(2)	101.84(10)	C(15)-C(13)-C(14)	109.4(3)
C(1)-Si(1)-Be(1)	114.88(18)	C(17)-C(16)-C(21)	123.2(4)
Si(2)-Si(1)-Be(1)	143.08(17)	C(17)-C(16)-N(1)	118.3(3)
C(28)-Si(2)-Si(1)	96.69(11)	C(21)-C(16)-N(1)	118.4(3)
Cl(2)-Be(1)-Cl(1)	116.2(3)	C(16)-C(17)-C(18)	116.8(4)
Cl(2)-Be(1)-Si(1)	124.4(3)	C(16)-C(17)-C(25)	123.4(4)
Cl(1)-Be(1)-Si(1)	119.4(3)	C(18)-C(17)-C(25)	119.7(4)
C(1)-N(1)-C(2)	110.0(3)	C(19)-C(18)-C(17)	121.3(5)
C(1)-N(1)-C(16)	126.7(3)	C(20)-C(19)-C(18)	120.8(5)
C(2)-N(1)-C(16)	123.3(3)	C(19)-C(20)-C(21)	121.7(4)
C(1)-N(2)-C(3)	110.5(3)	C(20)-C(21)-C(16)	116.2(4)
C(1)-N(2)-C(4)	127.3(3)	C(20)-C(21)-C(22)	121.5(4)
C(3)-N(2)-C(4)	122.1(3)	C(16)-C(21)-C(22)	122.3(4)
C(28)-N(3)-C(29)	110.1(3)	C(21)-C(22)-C(24)	113.0(4)
C(28)-N(3)-C(43)	126.0(3)	C(21)-C(22)-C(23)	110.3(4)
C(29)-N(3)-C(43)	122.7(3)	C(24)-C(22)-C(23)	109.9(4)
C(28)-N(4)-C(30)	109.9(3)	C(17)-C(25)-C(26)	113.3(5)
C(28)-N(4)-C(31)	125.5(3)	C(17)-C(25)-C(27)	108.8(5)
C(30)-N(4)-C(31)	123.7(3)	C(26)-C(25)-C(27)	108.9(5)
N(2)-C(1)-N(1)	104.6(3)	N(3)-C(28)-N(4)	104.6(3)
N(2)-C(1)-Si(1)	126.8(2)	N(3)-C(28)-Si(2)	128.2(3)
N(1)-C(1)-Si(1)	128.7(2)	N(4)-C(28)-Si(2)	126.6(3)
C(3)-C(2)-N(1)	107.2(3)	C(30)-C(29)-N(3)	107.4(3)
C(2)-C(3)-N(2)	107.8(3)	C(29)-C(30)-N(4)	107.8(3)
C(9)-C(4)-C(5)	123.0(3)	C(36)-C(31)-C(32)	123.6(5)
C(9)-C(4)-N(2)	118.7(3)	C(36)-C(31)-N(4)	118.3(5)
C(5)-C(4)-N(2)	118.1(3)	C(32)-C(31)-N(4)	118.0(4)
C(6)-C(5)-C(4)	116.9(4)	C(31)-C(32)-C(33)	116.4(5)
C(6)-C(5)-C(13)	120.9(4)	C(31)-C(32)-C(40)	123.6(4)
C(4)-C(5)-C(13)	122.2(3)	C(33)-C(32)-C(40)	119.9(5)
C(5)-C(6)-C(7)	121.6(5)	C(34)-C(33)-C(32)	120.0(7)
C(8)-C(7)-C(6)	121.1(5)	C(33)-C(34)-C(35)	123.6(7)
C(7)-C(8)-C(9)	120.3(5)	C(34)-C(35)-C(36)	119.1(7)
C(4)-C(9)-C(8)	117.1(4)	C(31)-C(36)-C(35)	117.2(6)
C(4)-C(9)-C(10)	122.3(4)	C(31)-C(36)-C(37)	123.6(5)
C(8)-C(9)-C(10)	120.5(4)	C(35)-C(36)-C(37)	119.2(6)
C(9)-C(10)-C(12)	111.5(4)	C(36)-C(37)-C(38)	115.2(6)
C(9)-C(10)-C(11)	112.9(4)	C(36)-C(37)-C(39)	110.9(5)
C(12)-C(10)-C(11)	109.2(4)	C(38)-C(37)-C(39)	108.8(5)
C(5)-C(13)-C(15)	113.1(4)	C(32)-C(40)-C(41)	114.0(4)
C(5)-C(13)-C(14)	112.0(3)	C(32)-C(40)-C(42)	109.8(5)

Table 37 (cont.). Bond angles [º] for **7**.

Atoms	Angle	Atoms	Angle
C(41)-C(40)-C(42)	110.9(5)	C(43)-C(48)-C(47)	116.8(6)
C(44)-C(43)-C(48)	123.5(5)	C(43)-C(48)-C(49)	121.5(4)
C(44)-C(43)-N(3)	116.8(4)	C(47)-C(48)-C(49)	121.7(5)
C(48)-C(43)-N(3)	119.6(4)	C(48)-C(49)-C(51)	114.5(5)
C(43)-C(44)-C(45)	115.9(6)	C(48)-C(49)-C(50)	110.6(5)
C(43)-C(44)-C(52)	124.7(4)	C(51)-C(49)-C(50)	110.5(5)
C(45)-C(44)-C(52)	119.5(6)	C(44)-C(52)-C(53)	111.9(5)
C(46)-C(45)-C(44)	122.4(7)	C(44)-C(52)-C(54)	112.7(4)
C(45)-C(46)-C(47)	120.8(7)	C(53)-C(52)-C(54)	110.3(5)
C(46)-C(47)-C(48)	120.7(7)		

Structural Data for L^4:$BeCl_2$ **9**

Table 38. Crystal data and structural refinement for **9**.

Empirical formula	C_{26} H_{36} Be Cl_2 N_2
Formula weight	456.48
Temperature	273(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.0253(13) Å
	b = 16.0248(16) Å
	c = 13.4297(13) Å
	α = 90°
	β = 105.281(2)°
	ɣ = 90°
Volume	2704.0(5) A^3
Z, Calculated density	4, 1.121 Mg/m^3
Absorption coefficient	0.255 mm^{-1}
F(000)	976
Crystal size	0.19 x 0.07 x 0.04 mm
Theta range for data collection	2.02 to 25.00°
Limiting indices	-15<=h<=15, -19<=k<=19, -15<=l<=15
Reflections collected / unique	28649 / 4755 [R(int) = 0.1315]
Completeness to theta =	25.00 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9899 and 0.9532
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4755 / 0 / 280
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.0966
R indices (all data)	R1 = 0.1362, wR2 = 0.1258
Largest diff. peak and hole	0.210 and -0.162 e. $Å^{-3}$

Table 39. Atomic coordinates (x 104) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **9**.

Atom	X	Y	Z	U(eq)
Be(1)	2040(4)	2500(3)	5743(3)	43(1)
Cl(1)	895(1)	1910(1)	6135(1)	55(1)
Cl(2)	2833(1)	3290(1)	6769(1)	58(1)
N(1)	2803(2)	1748(2)	5240(2)	38(1)
N(2)	1590(2)	2950(2)	4479(2)	38(1)
C(1)	2574(3)	1805(2)	4269(2)	54(1)
C(2)	1890(3)	2512(2)	3826(2)	50(1)
C(3)	1013(3)	3717(2)	4150(2)	41(1)
C(4)	1610(3)	4443(2)	4163(2)	45(1)
C(5)	1037(3)	5166(2)	3860(3)	60(1)
C(6)	-64(3)	5178(3)	3575(3)	65(1)
C(7)	-617(3)	4447(3)	3575(3)	60(1)
C(8)	-101(3)	3690(2)	3854(2)	45(1)
C(9)	-719(3)	2886(2)	3790(3)	52(1)
C(10)	-1599(3)	2927(3)	4343(3)	79(1)
C(11)	-1172(3)	2626(3)	2656(3)	79(1)
C(12)	2816(3)	4434(2)	4454(3)	57(1)
C(13)	3304(3)	5147(3)	5178(4)	98(2)
C(14)	3232(3)	4424(3)	3501(3)	115(2)
C(15)	3493(3)	1073(2)	5744(2)	42(1)
C(16)	4550(3)	1296(3)	6217(3)	56(1)
C(17)	5203(3)	639(3)	6686(3)	77(1)
C(18)	4839(4)	-163(3)	6680(3)	83(1)
C(19)	3791(4)	-343(3)	6211(3)	71(1)
C(20)	3083(3)	274(2)	5727(3)	51(1)
C(21)	1928(3)	46(2)	5213(3)	60(1)
C(22)	1385(3)	-404(3)	5946(3)	86(1)
C(23)	1847(4)	-471(3)	4242(3)	99(2)
C(24)	4967(3)	2168(3)	6175(3)	75(1)
C(25)	5648(4)	2461(3)	7222(4)	136(2)
C(26)	5563(4)	2237(3)	5341(4)	138(2)

Table 40. Bond lengths [Å] for **9**.

Atoms	Distance	Atoms	Distance
Be(1)-N(2)	1.795(5)	C(9)-C(10)	1.523(5)
Be(1)-N(1)	1.802(5)	C(9)-C(11)	1.538(4)
Be(1)-Cl(2)	1.955(5)	C(12)-C(14)	1.515(5)
Be(1)-Cl(1)	1.953(5)	C(12)-C(13)	1.525(5)
N(1)-C(1)	1.262(4)	C(15)-C(20)	1.386(5)
N(1)-C(15)	1.455(4)	C(15)-C(16)	1.402(4)
N(2)-C(2)	1.262(4)	C(16)-C(17)	1.396(5)
N(2)-C(3)	1.447(4)	C(16)-C(24)	1.506(5)
C(1)-C(2)	1.467(4)	C(17)-C(18)	1.370(5)
C(3)-C(4)	1.398(4)	C(18)-C(19)	1.374(5)
C(3)-C(8)	1.400(4)	C(19)-C(20)	1.390(5)
C(4)-C(5)	1.380(5)	C(20)-C(21)	1.525(5)
C(4)-C(12)	1.516(5)	C(21)-C(23)	1.525(5)
C(5)-C(6)	1.383(5)	C(21)-C(22)	1.535(5)
C(6)-C(7)	1.375(5)	C(24)-C(26)	1.525(6)
C(7)-C(8)	1.390(4)	C(24)-C(25)	1.525(5)
C(8)-C(9)	1.509(5)		

Table 41. Bond angles [°] for **9**.

Atoms	Angle	Atoms	Angle
N(2)-Be(1)-N(1)	89.4(2)	C(3)-C(8)-C(9)	122.7(3)
N(2)-Be(1)-Cl(2)	112.7(3)	C(8)-C(9)-C(10)	113.2(3)
N(1)-Be(1)-Cl(2)	117.2(2)	C(8)-C(9)-C(11)	110.4(3)
N(2)-Be(1)-Cl(1)	111.6(2)	C(10)-C(9)-C(11)	110.6(3)
N(1)-Be(1)-Cl(1)	108.3(3)	C(14)-C(12)-C(4)	111.0(3)
Cl(2)-Be(1)-Cl(1)	115.0(2)	C(14)-C(12)-C(13)	111.4(3)
C(1)-N(1)-C(15)	118.9(3)	C(4)-C(12)-C(13)	112.7(3)
C(1)-N(1)-Be(1)	109.7(3)	C(20)-C(15)-C(16)	124.8(3)
C(15)-N(1)-Be(1)	131.0(2)	C(20)-C(15)-N(1)	119.4(3)
C(2)-N(2)-C(3)	119.5(3)	C(16)-C(15)-N(1)	115.7(3)
C(2)-N(2)-Be(1)	110.4(3)	C(15)-C(16)-C(17)	114.9(4)
C(3)-N(2)-Be(1)	130.0(2)	C(15)-C(16)-C(24)	122.7(3)
N(1)-C(1)-C(2)	115.3(3)	C(17)-C(16)-C(24)	122.3(4)
N(2)-C(2)-C(1)	114.5(3)	C(16)-C(17)-C(18)	122.5(4)
C(4)-C(3)-C(8)	124.1(3)	C(19)-C(18)-C(17)	120.0(4)
C(4)-C(3)-N(2)	117.5(3)	C(18)-C(19)-C(20)	121.4(4)
C(8)-C(3)-N(2)	118.5(3)	C(15)-C(20)-C(19)	116.4(4)
C(3)-C(4)-C(5)	116.1(3)	C(15)-C(20)-C(21)	123.9(3)
C(3)-C(4)-C(12)	122.0(3)	C(19)-C(20)-C(21)	119.7(4)
C(5)-C(4)-C(12)	121.8(3)	C(23)-C(21)-C(22)	110.6(3)
C(6)-C(5)-C(4)	122.2(4)	C(23)-C(21)-C(20)	110.8(3)
C(7)-C(6)-C(5)	119.6(4)	C(22)-C(21)-C(20)	112.9(3)
C(8)-C(7)-C(6)	121.8(4)	C(16)-C(24)-C(26)	110.6(4)
C(7)-C(8)-C(3)	116.2(3)	C(16)-C(24)-C(25)	112.3(4)
C(7)-C(8)-C(9)	121.1(3)	C(26)-C(24)-C(25)	111.7(4)

Structural Data for $[L^3\text{:Be}]_2$ **10**

Table 42. Crystal data and structural refinement for **10**.

Empirical formula	C_{40} H_{48} Be_2 N_4
Formula weight	602.84
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 15.4075(10) Å
	b = 17.0070(11) Å
	c = 15.0456(10) Å
	α = 90°
	β = 118.1460(10)°
	ɣ = 90°
Volume	3476.3(4) A^3
Z, Calculated density	4, 1.152 Mg/m^3
Absorption coefficient	0.066 mm^{-1}
F(000)	1296
Crystal size	0.19 x 0.15 x 0.08 mm
Theta range for data collection	1.92 to 26.00°
Limiting indices	-18<=h<=18, -20<=k<=20, -18<=l<=18
Reflections collected / unique	20090 / 3421 [R(int) = 0.0487]
Completeness to theta =	26.00 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9947 and 0.9875
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3421 / 0 / 214
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 = 0.1126
R indices (all data)	R1 = 0.0787, wR2 = 0.1334
Largest diff. peak and hole	0.201 and -0.188 e. $Å^{-3}$

Table 43. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **10**.

Atom	X	Y	Z	U(eq)
Be(1)	-54(2)	1771(1)	1783(2)	39(1)
N(1)	957(1)	1569(1)	2921(1)	39(1)
N(2)	334(1)	2393(1)	1289(1)	43(1)
C(1)	1656(1)	2116(1)	2875(1)	44(1)
C(2)	1307(1)	2529(1)	2028(1)	47(1)
C(3)	-50(1)	2824(1)	366(1)	41(1)
C(4)	-114(1)	2475(1)	-505(1)	50(1)
C(5)	-520(1)	2898(1)	-1399(1)	57(1)
C(6)	-853(1)	3660(1)	-1464(1)	54(1)
C(7)	-758(1)	4004(1)	-592(1)	53(1)
C(8)	-364(1)	3602(1)	321(1)	46(1)
C(9)	-279(2)	4002(1)	1251(2)	66(1)
C(10)	-1324(2)	4092(2)	-2459(2)	79(1)
C(11)	265(2)	1655(1)	-474(2)	79(1)
C(12)	1397(1)	809(1)	3353(1)	39(1)
C(13)	1354(1)	189(1)	2724(1)	46(1)
C(14)	1768(2)	-529(1)	3156(2)	55(1)
C(15)	2226(1)	-650(1)	4189(2)	52(1)
C(16)	2266(1)	-27(1)	4791(1)	50(1)
C(17)	1874(1)	707(1)	4401(1)	44(1)
C(18)	2011(2)	1376(1)	5109(1)	60(1)
C(19)	2697(2)	-1431(1)	4642(2)	76(1)
C(20)	896(2)	296(1)	1600(1)	61(1)

Table 44. Bond lengths [Å] for **10**.

Atoms	Distance	Atoms	Distance
Be(1)-N(2)	1.565(3)	C(5)-C(6)	1.380(3)
Be(1)-N(1)#1	1.685(3)	C(6)-C(7)	1.380(3)
Be(1)-N(1)	1.720(3)	C(6)-C(10)	1.510(3)
Be(1)-Be(1)#1	2.084(4)	C(7)-C(8)	1.393(2)
Be(1)-C(2)	2.338(3)	C(8)-C(9)	1.503(3)
N(1)-C(1)	1.449(2)	C(12)-C(13)	1.397(2)
N(1)-C(12)	1.462(2)	C(12)-C(17)	1.401(2)
N(1)-Be(1)#1	1.685(3)	C(13)-C(14)	1.389(2)
N(2)-C(3)	1.429(2)	C(13)-C(20)	1.504(2)
N(2)-C(2)	1.401(2)	C(14)-C(15)	1.386(3)
C(1)-C(2)	1.327(2)	C(15)-C(16)	1.377(3)
C(3)-C(4)	1.398(2)	C(15)-C(19)	1.513(3)
C(3)-C(8)	1.400(3)	C(16)-C(17)	1.391(2)
C(4)-C(5)	1.388(3)	C(17)-C(18)	1.504(2)
C(4)-C(11)	1.504(3)		

Table 45. Bond angles [°] for **10**.

Atoms	Angle	Atoms	Angle
N(2)-Be(1)-N(1)#1	144.25(16)	C(3)-C(4)-C(5)	119.22(18)
N(2)-Be(1)-N(1)	103.80(14)	C(3)-C(4)-C(11)	120.69(17)
N(1)#1-Be(1)-N(1)	99.75(13)	C(5)-C(4)-C(11)	120.08(18)
N(2)-Be(1)-Be(1)#1	129.07(12)	C(6)-C(5)-C(4)	122.55(18)
N(1)#1-Be(1)-Be(1)#1	53.04(11)	C(5)-C(6)-C(7)	117.52(17)
N(1)-Be(1)-Be(1)#1	51.49(10)	C(5)-C(6)-C(10)	121.1(2)
N(2)-Be(1)-C(2)	35.58(8)	C(7)-C(6)-C(10)	121.4(2)
N(1)#1-Be(1)-C(2)	149.57(14)	C(6)-C(7)-C(8)	122.08(19)
N(1)-Be(1)-C(2)	68.28(10)	C(3)-C(8)-C(7)	119.43(17)
Be(1)#1-Be(1)-C(2)	102.11(13)	C(3)-C(8)-C(9)	120.44(16)
C(1)-N(1)-C(12)	112.96(13)	C(7)-C(8)-C(9)	120.14(18)
C(1)-N(1)-Be(1)#1	127.37(13)	C(13)-C(12)-C(17)	120.12(15)
C(12)-N(1)-Be(1)#1	109.30(13)	C(13)-C(12)-N(1)	120.16(15)
C(1)-N(1)-Be(1)	99.68(12)	C(17)-C(12)-N(1)	119.71(14)
C(12)-N(1)-Be(1)	129.11(13)	C(12)-C(13)-C(14)	118.78(16)
Be(1)#1-N(1)-Be(1)	75.48(13)	C(12)-C(13)-C(20)	121.11(16)
C(3)-N(2)-C(2)	118.93(14)	C(14)-C(13)-C(20)	120.09(16)
C(3)-N(2)-Be(1)	137.15(14)	C(15)-C(14)-C(13)	122.28(17)
C(2)-N(2)-Be(1)	103.89(14)	C(14)-C(15)-C(16)	117.67(17)
C(2)-C(1)-N(1)	114.41(15)	C(14)-C(15)-C(19)	121.20(18)
C(1)-C(2)-N(2)	118.10(16)	C(16)-C(15)-C(19)	121.09(19)
C(1)-C(2)-Be(1)	77.61(12)	C(15)-C(16)-C(17)	122.55(17)
N(2)-C(2)-Be(1)	40.53(9)	C(16)-C(17)-C(12)	118.57(16)
C(4)-C(3)-C(8)	119.16(16)	C(16)-C(17)-C(18)	119.45(16)
C(4)-C(3)-N(2)	120.43(16)	C(12)-C(17)-C(18)	121.92(15)
C(8)-C(3)-N(2)	120.41(15)		

APPENDIX B

RESEARCH PUBLICATIONS

Co-Authored by Robert Jerard Gilliard, Jr.

1. Wang, Yuzhong; Yaoming, Xie; Abraham, Mariham Y.; Gilliard Jr., Robert J.; Wei, Pingrong; Schaefer III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Carbene-Stabilized Parent Phosphinidene" *Organometallics* **2010**, *132*, 14370-14372.

2. Wang, Yuzhong; Yaoming, Xie; Abraham, Mariham Y.; Gilliard Jr., Robert J.; Wei, Pingrong; Smith, Jared C.; Robinson, Gregory H. "From Anionic Dicarbenes to Abnormal Carbene-Borane Complexes" *Organometallics* **2012**, *131*, 791-793.

3. Gilliard Jr., Robert J.; Abraham, Mariham Y.; Wang, Yuzhong; Wei, Pingrong; Yaoming, Xie; Quillian, Brandon; Schaefer III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Carbene-Stabilized Beryllium Borohydride" *J. Am. Chem. Soc.* **2012**, *134*, 9953-9955.

4. Wang, Yuzhong; Yaoming, Xie; Abraham, Mariham Y.; Gilliard Jr., Robert J.; Wei, Pingrong; Schaefer III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "NHC-Stabilized Triorganozincates: Syntheses, Structures, and Transformation to Abnormal Carbene-Zinc Complexes" *Angew. Chem., Int. Ed.* **2012**, *51*,10173-10176.

5. Wang, Yuzhong; Abraham, Mariham Y.; Gilliard Jr., Robert J.; Sexton, Daniel R.; Wei, Pingrong; Robinson, Gregory H. "N-Heterocyclic Olefin-Stabilized Borenium Cations" *Organometallics* **2013**, *32*, 6639-6642.

6. Abraham, Mariham Y.; Wang, Yuzhong; Yaoming, Xie; Gilliard Jr., Robert J.; Wei, Pingrong; Vaccaro, Brian J.; Johnson, Michael K.; Schaefer III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Oxidation of Carbene-Stabilized Diarsenic: Diarsene Dications and Diarsenic Radical Cations" *J. Am. Chem. Soc.* **2013**, *135*, 2486-2488.