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## Synthesis of Novel Alkaline Earth Metal Acetylides

Eva Baker

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## 1. Introduction:

### 1.1 General Remarks:

Not much is known about  $\sigma$ -bonded organometallic compounds of calcium, strontium, and barium due to their low solubility and high reactivity which makes them difficult to prepare and characterize.<sup>1</sup> In contrast,  $\text{RMgX}$  and  $\text{R}_2\text{Mg}$  ( $\text{R}$  = alkyl, aryl,  $\text{X}$  = halide) organomagnesium compounds have been proven to be extremely useful as synthetic reagents.<sup>2</sup> Thus, we aspired to develop good synthetic routes for the heavier alkaline earth metals so they too can be as useful. Already, many organometallic compounds of these metals are seen in applications with synthetic, polymer, and solid state chemistry,<sup>3</sup> further encouraging chemists to fully understand their nature.

As the library of organoalkaline-earth metal compounds begins to grow, fundamental questions, such as the metal-ligand bonding, can now be addressed. Further extension of the library of these target compounds critically depends on the development of simple, reproducible synthetic methods and the introduction of novel ligand and donor systems. As more compounds become available, understanding of their nature improves and the applications can be further developed and expanded.

This research paper focuses on a specific ligand group - the acetylides - to be connected in a  $\sigma$ -fashion to the heavy alkaline earth metals calcium, strontium, and barium. Acetylene ligands  $\text{HC}\equiv\text{CR}$  with  $\text{R}$  =  $\text{SiPh}_3$ ,  $\text{SiMe}_3$ , 4-

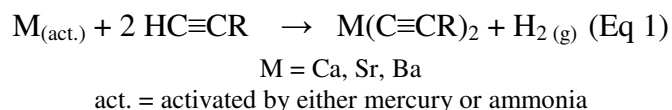
*t*BuC<sub>6</sub>H<sub>4</sub>, and *t*Bu are commercially available and were used in this work.

Variation of the R group on the acetylide provides control over the solubility properties of the target compounds and introduces varying degrees of steric bulk. Acetylene ligands are also attractive due to their acidic nature. With a pK<sub>a</sub> of about 20, acetylenes can be deprotonated with a variety of synthetic methodologies. Moreover, once the alkaline earth compounds are prepared and analyzed, they can be compared with the closely related alkali metal derivatives to obtain information about the metal-ligand bonding and the coordination chemistry of the ligands.

## 1.2 Synthetic Methods

Three specific methods of synthesis to form alkaline earth metal acetylides are direct metallation, transamination, and toluene elimination.

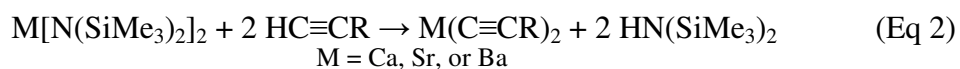
Direct metallation<sup>1</sup> (Eq 1) employing acetylenes is as follows:



This is the most straightforward route whereby the ligand is added directly to the metal and hydrogen gas is released, yielding the product. No work-up is necessary. However, the metals must be highly active and pure. This synthesis route works best for the most reactive metal, barium, while the less reactive strontium and calcium metals require reflux conditions. To improve metal reactivity, an increase of surface area by cutting the metal into very small pieces is advantageous. Other activation methods include the formation of an

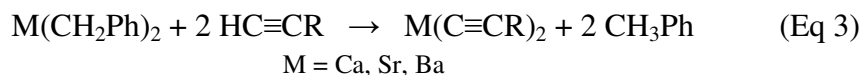
amalgam by addition of mercury or by solvation of the metals in dry, liquid ammonia. Although ammonia chemistry is the preferred method, due to its benign nature, the necessary reaction conditions are challenging. Ammonia gas is transferred from a gas tank to a three-necked round bottom flask containing sodium metal to remove trace amounts of moisture. The flask is kept at  $-78^{\circ}\text{C}$ , at which temperature gaseous ammonia condenses into a liquid. Once dried, this liquid is then vaporized, causing a build-up of pressure. With no other release option, the gas is transferred through a thin metal cannula into the receiving Schlenk tube, where it is again condensed using a dry-ice acetone bath. Since this process requires the condensation and vaporization of a gaseous compound, great care needs to be taken to avoid a pressure build-up which could lead to an explosion.

First used to prepare a family of heavy alkaline earth acetylides by David Green in our laboratory group,<sup>4</sup> transamination<sup>1</sup> (Eq 2) proves to be a facile and versatile synthetic route towards the acetylide target compounds.



Advantages of transamination include the good solubility properties of the alkaline earth metal amides,  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ , as well as the easy work-up since the amines are easily removed under vacuum. The largest drawbacks to this method are that the alkaline earth metal amides must be prepared first<sup>5</sup> and that transamination is limited to substrates with a higher acidity than  $\text{HN}(\text{SiMe}_3)_2$  to allow a forward reaction.

Alkaline earth metal acetylides may also be prepared by toluene elimination (Eq 3).<sup>1</sup>

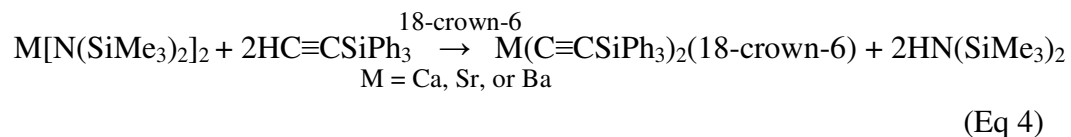


This reaction occurs rapidly because of the thermodynamic drive to form toluene,  $\text{CH}_3\text{Ph}$ , which can then easily be removed. Moreover, the  $\text{pK}_a$  difference between the acetylides and toluene is large, ensuring a smooth reaction. However, the benzyl derivatives of the alkaline earth metals must be first synthesized through a multi step procedure. Since the benzyl derivatives are relatively insoluble, the highly polar tetrahydrofuran (THF) must be used as the solvent. Due to the high basic nature of the dibenzyl derivatives, great care must be taken to avoid ether cleavage reactions.<sup>6</sup> Consequently, all reactions involving dibenzyl reagents in ethereal solvents are kept at  $-78^\circ\text{C}$ .

All of the above reactions require the use of donors to kinetically stabilize the target compound. The large sizes of the heavy alkaline earth metals require substantial ligand bulk or donor hapticity to afford sufficient kinetic stabilization of the molecules. Various crown ethers, such as 15-crown-5 and 18-crown-6, are attractive choices, due to effective metal-donor binding. However, ether cleavage can occur.<sup>6</sup> To prevent this undesired reaction, a low reaction temperature ( $-78^\circ\text{C}$ ) is required. However, at these low temperatures, reactions may take too long to complete. Another approach is the use of more robust systems such as nitrogen based donors like  $\text{N},\text{N},\text{N}',\text{N}'$ -tetramethylethylenediamine (TMEDA).

### 1.3 Previously Prepared Alkaline Earth Acetylides:

Triphenylsilyl acetylides of calcium, strontium, and barium have been prepared previously in our laboratory by David Green.<sup>4</sup> The synthetic method of choice was transamination (Eq 4).



The X-ray crystal structure of the calcium, strontium, and barium derivatives are shown in Figures 1-3, while pertinent geometrical features are summarized in Table 1.

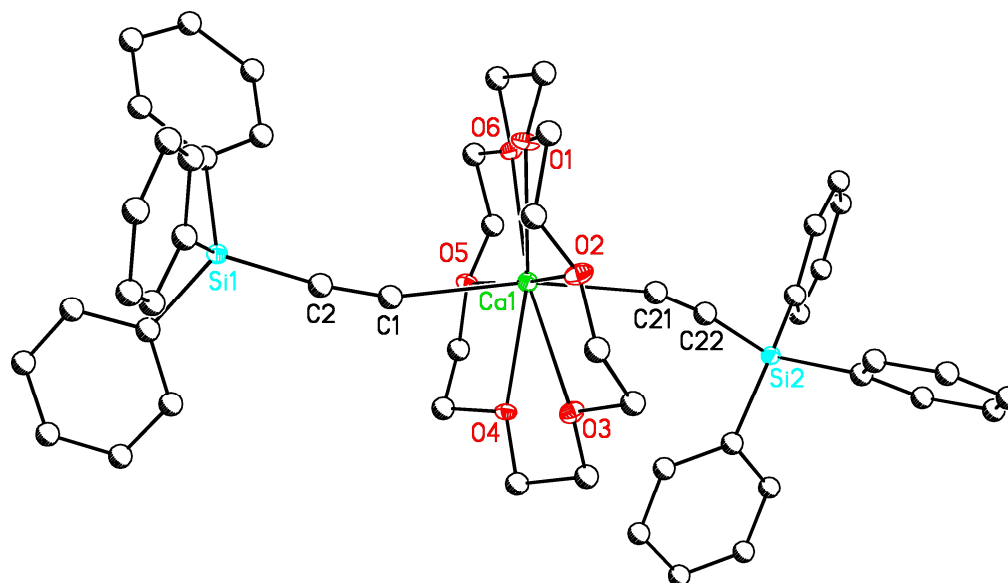


Figure 1: Crystal structure of  $\text{Ca}(\text{C}\equiv\text{CSiPh}_3)_2(18\text{-crown-6})$   
Hydrogen atoms have been omitted for clarity.

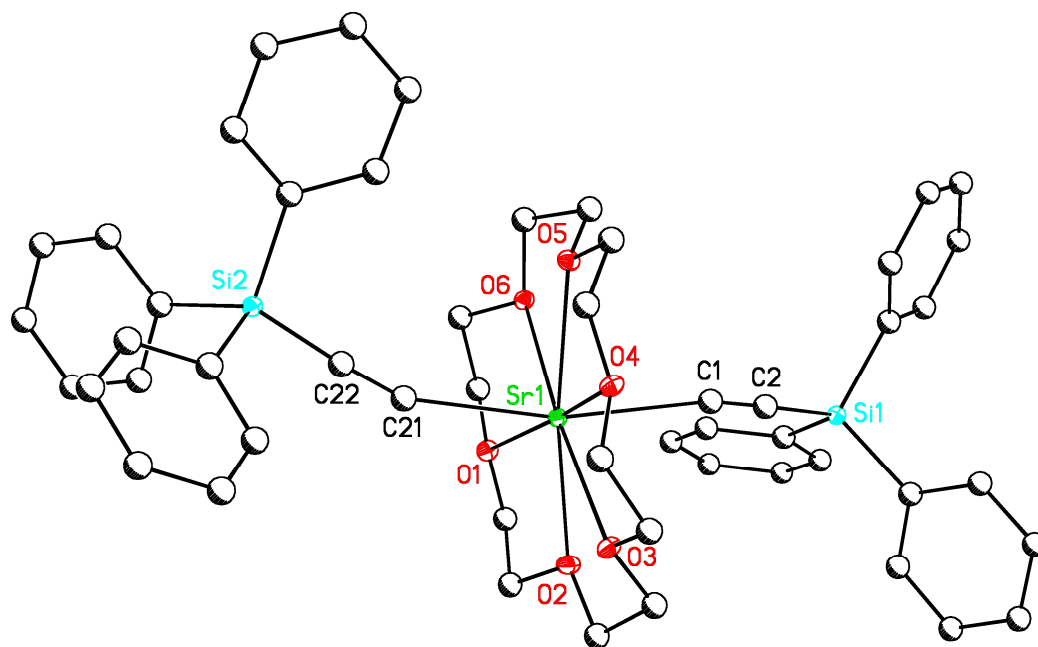


Figure 2: Crystal structure of Sr(C≡CSiPh<sub>3</sub>)<sub>2</sub>(18-crown-6)  
Hydrogen atoms have been omitted for clarity.

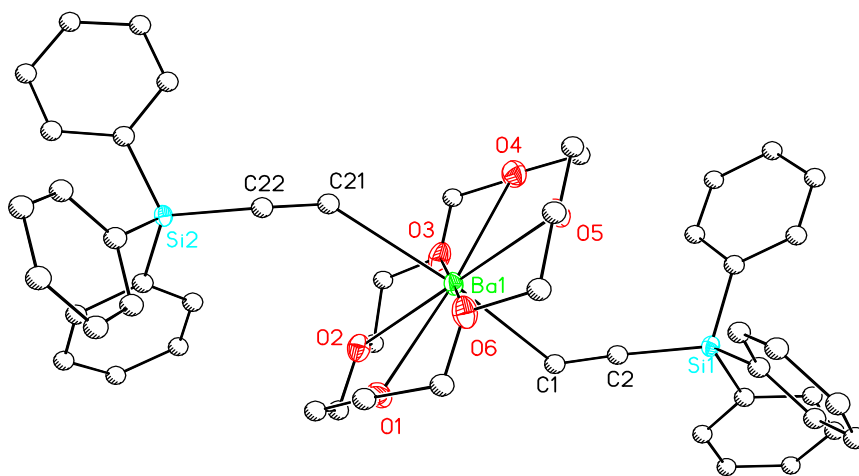
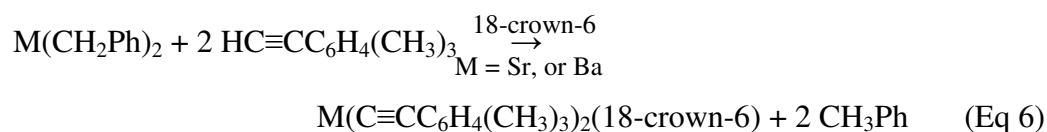
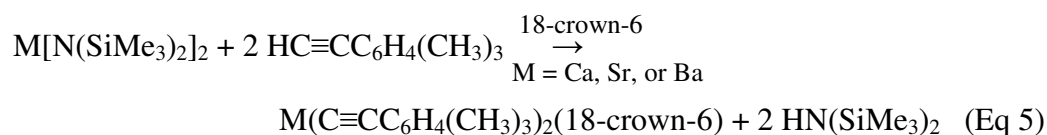


Figure 3: Crystal structure of Ba(C≡CSiPh<sub>3</sub>)<sub>2</sub>(18-crown-6)  
Hydrogen atoms and 2 THF have been omitted for clarity.

M	M-C	C≡C	C-M-C	C≡C-M
Ca	2.541 Å	1.232 Å	168.7°	163.2°
Sr	2.708 Å	1.212 Å	166.0°	159.3°
Ba	2.853 Å	1.230 Å	162.7°	134.0°

Table 1: Bond lengths and angles for  $M(\text{C}\equiv\text{CSiPh}_3)_2(18\text{-crown-6})$   
(values given are averages)

In order to investigate if the geometrical features observed in the triphenylsilyl acetylides depend on the ligand, a family of 4-*t*butylphenyl acetylides were prepared. Using both transamination (Eq 5) and toluene elimination (Eq 6), the strontium and barium derivatives were prepared by Jacob Alexander, from our laboratory group, in good yield and purity (Figures 4-5, Table 2).<sup>7</sup>



Again, 18-crown-6 was used as a donor. Unfortunately, despite repeated attempts, the calcium species, which was prepared by transamination, could not be analyzed by single crystal X-ray crystallography due to poor crystal quality.



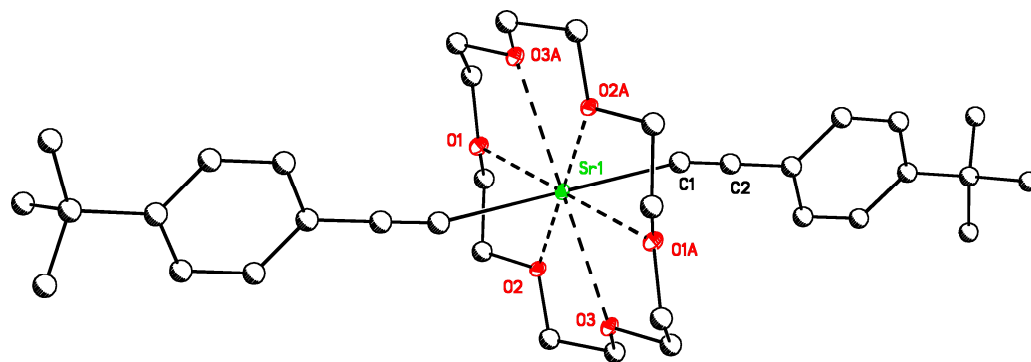


Figure 4: Crystal structure of  $\text{Sr}(\text{C}\equiv\text{CC}_6\text{H}_4t\text{Bu})_2(18\text{-crown-6})$   
Hydrogen atoms have been omitted for clarity.

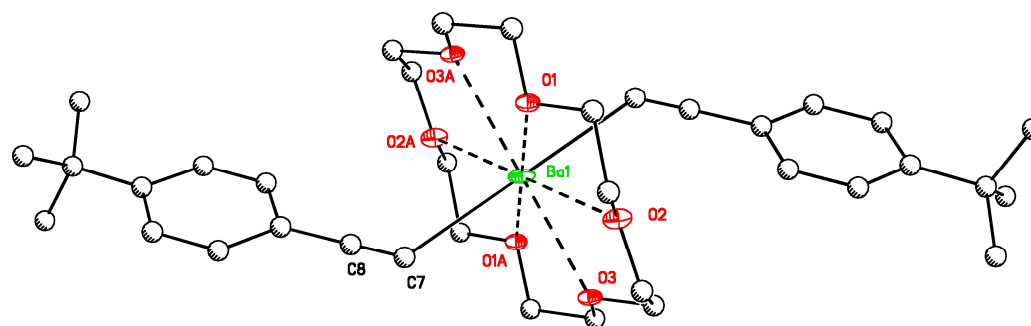


Figure 5: Crystal structure of  $\text{Ba}(\text{C}\equiv\text{CC}_6\text{H}_4t\text{Bu})_2(18\text{-crown-6})$   
Hydrogen atoms have been omitted for clarity. This compound displays disorder with three different orientations of the acetylide ligands. Shown is the major component.

M	M-C	C≡C	C-M-C	C≡C-M
Sr	2.70 Å	1.192 Å	180°	166.4°
Ba	2.85 Å	1.22 Å	180°	126.1° *

Table 2: Bond lengths and angles for  $\text{M}(\text{C}\equiv\text{CC}_6\text{H}_4t\text{Bu})_2(18\text{-crown-6})$  (values given are averages) \*This compound displays disorder, and only the C≡C-M angle for the major component is given.

The comparison of structural features in the two acetylide families reveals quite similar structural features. There is a smooth increase in the metal-ligand distance as one descends group 2 due to the increase in size of the metal. Both the C-M-C angle and M-C-C angle decrease upon descending the group for the triphenylsilyl series. According to the VSEPR theory, the M-C-C angle is expected to be 180° due to the *sp* hybridization of the triply bonded carbon. However, X-ray analysis of the acetylides revealed these to range from 126.1° to 166.4°. Several reasons may be responsible for this structural flexibility. The significant ionic character of the metal-ligand bond makes orbital control less important. Moreover, the *sp* hybrid orbital with its 50% *s*-character is not very directed, supporting the idea of easy deformation from ideal geometry. Indeed, bending at the *ipso* carbon atom is facile, as shown recently in density functional theory calculations, performed by our collaborator Professor M. McKee, Auburn University. He confirmed that energy differences between linear and bent geometries are as low as 10 kcal/mol.<sup>8</sup> However, many open questions remain to fully understand the metal-ligand bonding and properties of these novel compounds.

To further understand metal-ligand bonding in the acetylides, the heavier metal analogs need to be compared with the lighter metal analogs. To this effect, a series of magnesium acetylides was prepared. Pioneered by Weiss et al., two magnesium acetylides were prepared previously,  $\text{Mg}(\text{C}\equiv\text{CPh})_2(\text{TMEDA})_2$ <sup>9</sup> and  $\text{Mg}(\text{C}\equiv\text{C}i\text{Bu})_2(\text{TMEDA})_2$ ,<sup>10</sup> with apparently very

similar structural features. However, structural data for the latter were less reliable due to poor crystal quality.

To prepare the magnesium acetylides, Weiss et al. used  $\text{Ph}_2\text{Mg}$  as a starting material, which upon reaction with the acidic acetylene derivatives eliminated benzene (Eq 7).



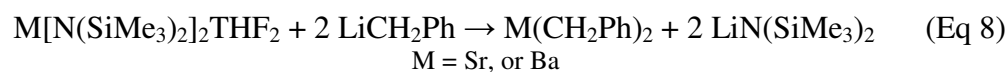
The structures of both of these compounds prove to have geometries which would be expected according to VSEPR theories. However, when analyzed with the heavier alkaline earth metal derivatives, a better understanding of periodic trends and how ligands and/or donors affect the geometry of these compounds can be realized. As a result, my honors thesis was concerned with the extension of this chemistry by introducing novel ligand systems to provide a better basis for the understanding of these alkaline earth metal species.

## 2. Novel Alkaline Earth Metal Acetylides:

### 2.1 Synthetic Methods:

The study of the heavy alkaline earth metals is challenging due to the high reactivity of the compounds. Consequently, strict inert gas conditions need to be maintained at all times. To verify that I mastered inert gas techniques, I began my project with the preparation of the known acetylides

$M(\text{C}\equiv\text{CSiPh}_3)_2$ (18-crown-6)  $M = \text{Ca}, \text{Sr}, \text{Ba}$  by transamination chemistry (Eq 4). In addition, resynthesizing the compounds proved that the synthetic method employed is reproducible, while enabling the further characterization of the organometallic species. In addition to the known pathway, transamination, I investigated toluene elimination for the preparation of these species. Toluene elimination is attractive since less acidic ligands may be employed. The starting materials for these reactions, dibenzylcalcium, strontium, and barium,  $M(\text{CH}_2\text{Ph})_2$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ), are not commercially available and need to be prepared. Dibenzylstrontium and barium are obtained by transmetallation chemistry (Eq 8), involving the treatment of the metal amides  $M[\text{N}(\text{SiMe}_3)_2]_2\text{THF}_2$  with two equivalents of benzyllithium. The resulting dibenzyl derivatives are obtained as red powders, while the resulting lithium amide remains in solution.



This synthetic method was published in 2000 by Harder for the barium derivative,<sup>11</sup> and subsequent work in our group allowed the clean, high yield preparation of the strontium species.<sup>6</sup> Despite numerous attempts, extension of this chemistry towards the calcium derivative failed due to our inability to separate the two solid reaction products. It was not until Harder's 2004 publication that the synthesis of dibenzylcalcium, by an entirely different route - salt elimination - became available (Eq 9).<sup>12</sup> However, our attempts to reproduce Harder's synthetic procedure were met with difficulties.

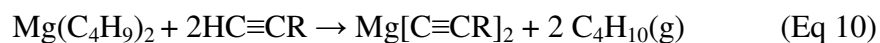


The preparation of dibenzylcalcium begins with the synthesis of  $\text{KCH}_2\text{Ph}$  by treatment of toluene,  $\text{CH}_3\text{Ph}$ , with a mixture of  $n\text{BuLi}$  and  $\text{KO}t\text{Bu}$ . These two latter reagents form a superbases complex 'LiKOR' where  $\text{R} = t\text{Bu}$ ,  $n\text{Bu}$ . This superbases has a high deprotonation ability, capable of deprotonating the methyl group on toluene. The reaction typically provides a very clean reagent in less than an hour. The byproduct,  $\text{LiO}t\text{Bu}$ , is easily separated from the potassium salt as it is soluble in the toluene layer whereas  $\text{KCH}_2\text{Ph}$  precipitates. The resulting red  $\text{KCH}_2\text{Ph}$  reagent is highly reactive.<sup>13</sup>

Once  $\text{KCH}_2\text{Ph}$  has been obtained in pure form, it can be reacted with commercially available  $\text{CaI}_2$ .  $\text{CaI}_2$  needs to be of very high purity. These two reagents then undergo a salt elimination reaction producing dibenzylcalcium and potassium iodide (Eq 9). The reaction proceeded cleanly, as seen by the formation of a white precipitate, presumably  $\text{KI}$ . Unfortunately, further work-up was very challenging, and  $\text{Ca}(\text{CH}_2\text{Ph})_2$  was obtained containing significant amounts of impurities. Repeated attempts preparing dibenzylcalcium did not afford pure starting material, and attempts to use this dibenzylcalcium as a starting material in reactions with the acetylides were not successful since the impurities were transferred into the product. Several attempts to slightly modify Harder's original procedure did not improve the situation. Future work will focus on the replacement of the originally used solvent, benzene, which solidifies at  $5^\circ\text{C}$ , by toluene, allowing for the storage of the mother liquor in the

freezer. Other attempts included the introduction of hexane into the benzene stock solutions in order to decrease the polarity of the solvent and promote product precipitation.

While still exploring synthetic routes towards dibenzylcalcium, we decided to also investigate the chemistry of magnesium acetylides to provide a family of lighter alkaline earth compounds to compare with the previously made heavier analogs. A reaction similar to the toluene elimination used to prepare  $M(C\equiv CR)_2(18\text{-crown-}6)$  ( $R = \text{SiPh}_3, 4\text{-}t\text{BuC}_6\text{H}_4$ ;  $M = \text{Sr}, \text{Ba}$ ), alkane elimination was used for this purpose. In contrast to the challenging preparation of dibenzylcalcium, dibutylmagnesium can be obtained commercially.



This reaction produces volatile butane gas, thereby forcing the reaction to proceed to the product side. In addition, having a volatile byproduct ensured a facile work-up. A closely related procedure, benzene elimination was used earlier by Weiss et al. to obtain Mg phenylacetylide<sup>9</sup> and Mg *t*butylacetylide<sup>10</sup> both with TMEDA as a donor. Various commercially available acetylides ( $\text{HC}\equiv\text{CSiPh}_3$ ,  $\text{HC}\equiv\text{CSiMe}_3$ ,  $\text{HC}\equiv\text{C}t\text{Bu}$ , and  $\text{HC}\equiv\text{CC}_6\text{H}_4t\text{Bu}$ ) and donors (THF, TMEDA, 15-crown-5) were used to study their influence on the structural features of the resulting compounds, resulting in the isolation and structural characterization of the five magnesium compounds **1-5** (Figures 6-10, Tables 3-7). Some of these reactions were carried out in the CHE 139 and CHE 422 laboratory setting.

To demonstrate that butane and benzene elimination afford identical products,  $\text{Mg}(\text{C}\equiv\text{C}t\text{Bu})_2(\text{TMEDA})_2$ , **1**, originally prepared and characterized by Weiss et al.,<sup>10</sup> was reproduced. The crystal structure of compound **1** is shown in Figure 6 and pertinent structural data are summarized in Table 3. The structural data for Weiss et al.'s compound and ours are identical, with our data containing a smaller estimated standard deviations due to data collection at low temperature.

## 2.2 Structural Features:

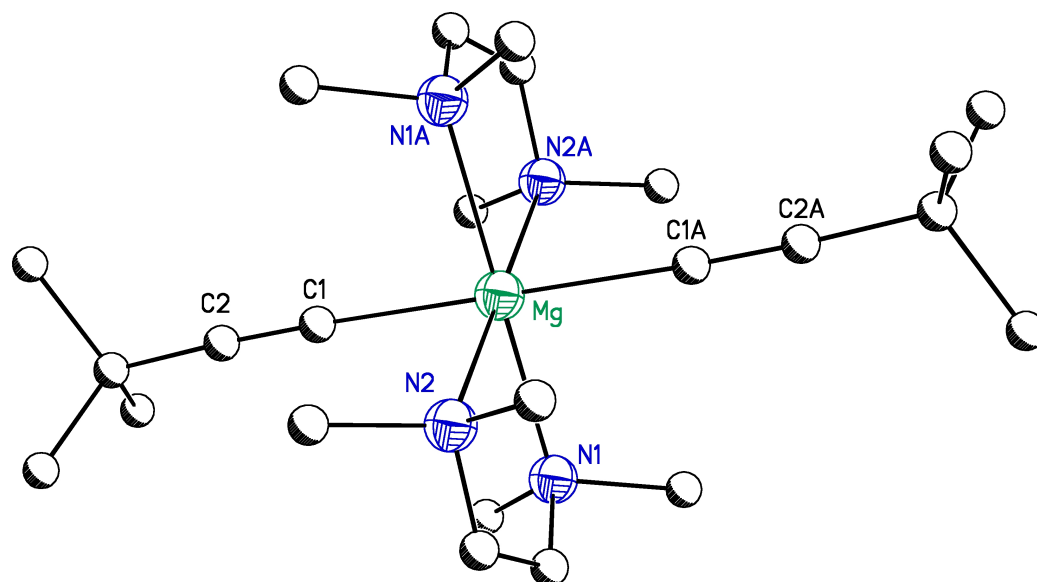


Figure 6: Crystal structure of  $\text{Mg}(\text{C}\equiv\text{C}t\text{Bu})_2(\text{TMEDA})_2$ , **1**  
Hydrogen atoms have been omitted for clarity.<sup>10</sup>

Bond Lengths (Å)		Bond Angles (°)	
Mg – N	2.288-2.359 (2.374(4)-2.382(6))	C1-Mg-N1	89.5 (89.8(2))
Mg – C	2.179 (2.175(4))	C1-Mg-N2	89.6 (90.1(2))
N – C	1.459 (1.371(8)-1.501(8))	C1-Mg-C1A	180.0
C1 ≡ C2	1.207 (1.207(5))	N1-Mg-N2	81.0 (88.2(2))
C2 – C3	1.465 (1.479(5))	Mg-C1≡C2	177.8 (175.6(4))

Table 3: Bond lengths and angles of  $\text{Mg}(\text{C}\equiv\text{C}t\text{Bu})_2(\text{TMEDA})_2$ , **1**

This is preliminary data, and is still being refined. Data in parentheses refers to the previously published bond lengths and angles reported by Weiss et al.<sup>10</sup>



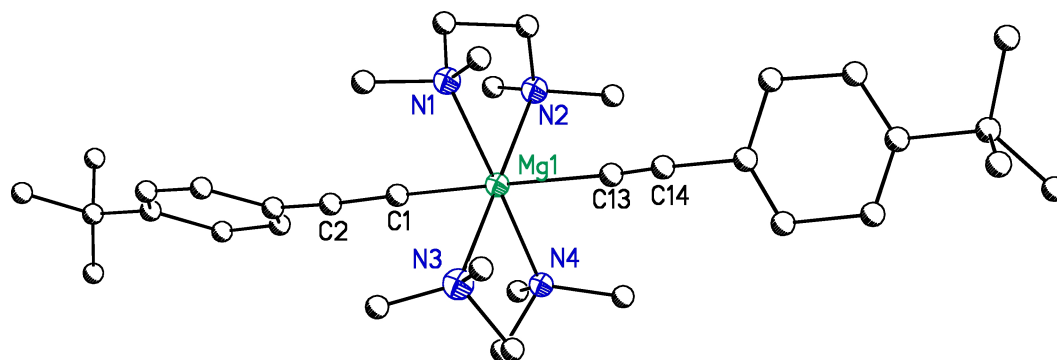


Figure 7: Crystal structure of  $\text{Mg}(\text{C}\equiv\text{CC}_6\text{H}_4t\text{Bu})_2(\text{TMEDA})_2$ , **2**<sup>14</sup>  
Hydrogen atoms have been omitted for clarity.

Bond Lengths (Å)		Bond Angles (°)	
Mg - N	2.30	C1-Mg-N1	89.2
Mg - C	2.203	C1-Mg-N2	91.0
N - C	1.40	C1-Mg-C13	178.8
C1 $\equiv$ C2	1.219	N-Mg-N	81.7
C2 - C3	1.50	Mg-C1 $\equiv$ C2	178.2

Table 4: Bond lengths and angles of  $\text{Mg}(\text{C}\equiv\text{CC}_6\text{H}_4t\text{Bu})_2(\text{TMEDA})_2$ , **2**

This is preliminary data, and is still being refined.

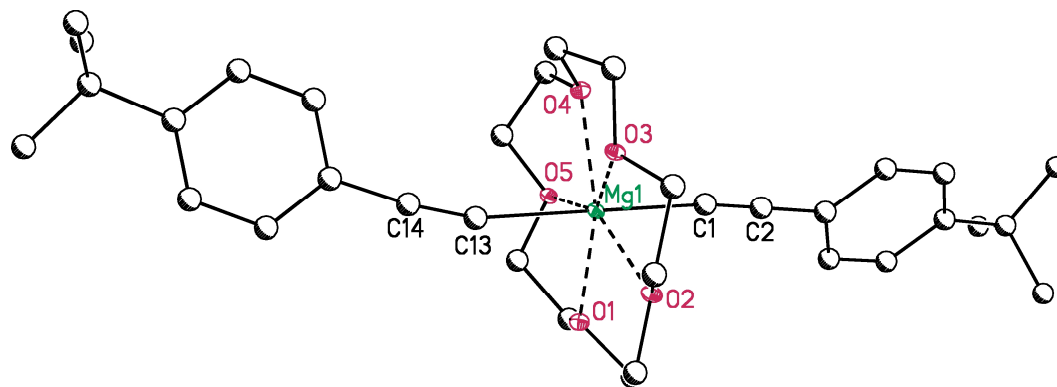


Figure 8: Crystal structure of  $\text{Mg}(\text{C}\equiv\text{CC}_6\text{H}_4\text{tBu})_2(15\text{-crown-5})$ , **3**<sup>14</sup>  
 Hydrogen atoms have been omitted for clarity.

Bond Lengths (Å)		Bond Angles (°)	
Mg - O	2.205(1)-2.252(1)	C1-Mg-O1	91.11(6)
Mg - C1	2.204(2)	C1-Mg-O	102.28(6)
O - C	1.422(2)-1.442(2)	C1-Mg-C13	174.17(7)
C1 $\equiv$ C2	1.219(2)	O-Mg-O	70.96(4)-146.84(5)
C2 - C3	1.445(2)	Mg-C1 $\equiv$ C2	172.69 (14)

Table 5: Bond lengths and angles of  $\text{Mg}(\text{C}\equiv\text{CC}_6\text{H}_4\text{tBu})_2(15\text{-crown-5})$ , **3**

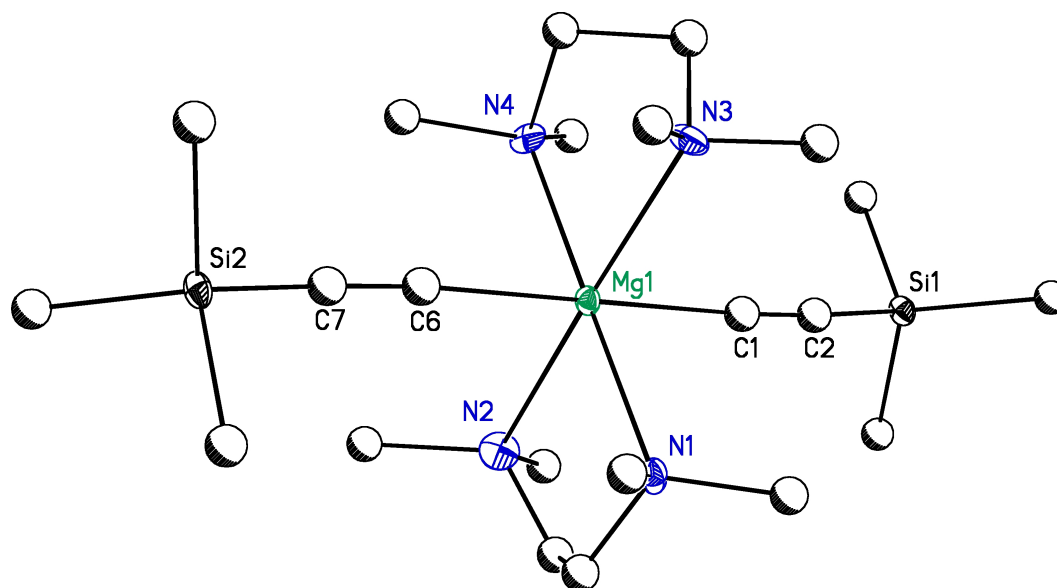


Figure 9: Crystal structure of  $\text{Mg}(\text{C}\equiv\text{CSiMe}_3)_2(\text{TMEDA})_2$ , **4**<sup>14</sup>  
Hydrogen atoms have been omitted for clarity.

Bond Lengths (Å)		Bond Angles (°)	
Mg - N	2.4	C-Mg-N	89.7
Mg - C1	2.2	C1-Mg-N	100
N - C	1.4	C1-Mg-C6	179.8
C $\equiv$ C	1.2	N-Mg-N	80.4
C - Si	1.8	Mg-C1 $\equiv$ C2	172

Table 6: Bond lengths and angles of  $\text{Mg}(\text{C}\equiv\text{CSiMe}_3)_2(\text{TMEDA})_2$ , **4**  
This is preliminary data, and is still being refined.

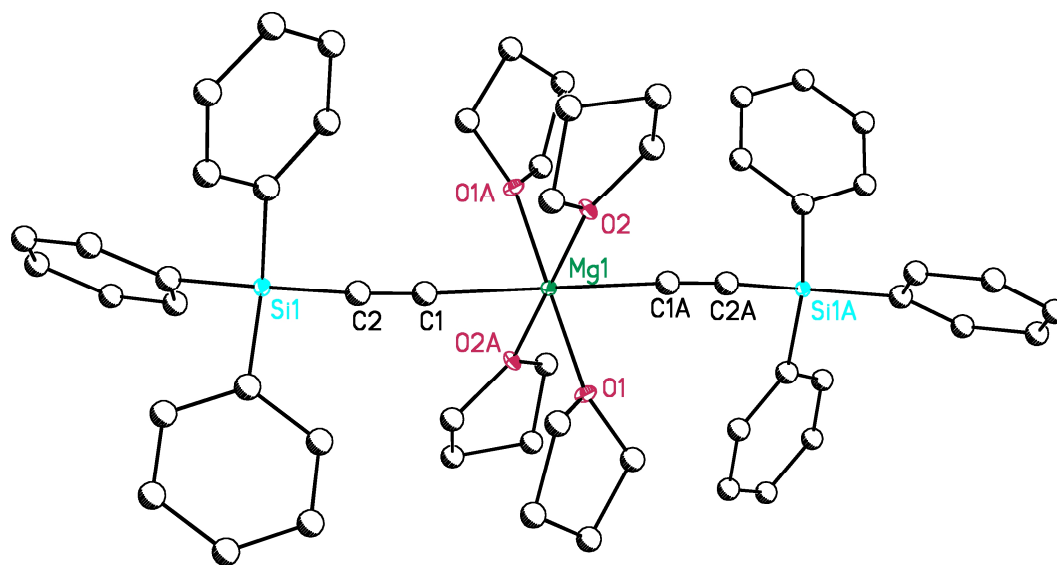


Figure 10: Crystal structure of  $\text{Mg}(\text{C}\equiv\text{CSiPh}_3)_2(\text{THF})_4$ , **5**<sup>14</sup>  
Hydrogen atoms have been omitted for clarity.

Bond Lengths (Å)		Bond Angles (°)	
Mg – O2	2.1394(9)	C1-Mg-O1	90.30(4)
Mg – C1	2.238(1)	C1-Mg-O2	89.03(4)
O – C	1.438(2)-1.459(2)	C1-Mg-C1A	179.999(1)
C1 ≡ C2	1.226(2)	O1-Mg-O2 / O1-Mg-O2A	90.24(4) / 89.76(4)
C2 – Si	1.819(2)	Mg-C1≡C2	173.3(1)

Table 7: Bond lengths and angles of  $\text{Mg}(\text{C}\equiv\text{CSiPh}_3)_2(\text{THF})_4$ , **5**

### 2.3 Analysis of Novel Acetylides:

Four of the five compounds display six coordinate metal centers, namely those containing TMEDA and THF ligands. Only compound **3** is seven coordinate with five coordination sites from the cyclic crown ether, 15-crown-5.

The overall molecular geometries in compounds **1**, **2**, **4**, and **5** are close to an ideal octahedral geometry. The perfect trans geometry in compounds **1** and **5** is geometrically mandated by an inversion center at the metal site. The C-M-C angles for compounds **2-4** are observed at 178.8° (**2**), 174.17(7)° (**3**), and 179.8° for compound **4**. Compound **5** also closely follows the ideal octahedral geometry since the four monodentate THF donors, which complete the metal coordination sphere, have O-M-O angles of 89.76(4)°, 89.76(4)°, 90.24(4)°, 90.24(4)°. However, deviations from ideal octahedral geometry can be caused by the bidentate TMEDA donor, with N-M-N angles smaller than the ideal 90° geometry with 81.00° for **1**, 81.7° in **2**, and 80.4° in **4**. Compound **3** is seven coordinate, with five Mg-O donor contacts from the crown ether. This structure approaches pentagonal bipyramidal geometry, as shown with O-Mg-O angles within the crown ether as narrow as 70.96(4)°.

Magnesium-carbon bond lengths in **1-5** lie in a narrow range with the shortest at 2.179Å for **1** with compounds **2-4** very close to 2.20Å, and **5** slightly elongated with 2.238(2)Å. It is interesting to note that the seven-coordinate **3** has Mg-C distances which are shorter than those for the six-coordinate **5**. Apparently, the steric demand of the ligand plays a major role, with the

sterically demanding triphenylsilyl ligand responsible for the Mg-C bond elongation. The similarity of metal-ligand bond lengths involving THF and crown ether coordinated compounds, despite an increase in coordination number, has been observed often in heavy alkaline earth metal chemistry. Virtually identical metal-ligand bond lengths occur in the eight coordinate Ba(Se-2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(18-crown-6) (3.23Å) and the six coordinate Ba(Se-2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub> (3.28Å).<sup>15</sup> The Mg-C≡C angles in compounds **1-5** are observed in the range from 172 to 178.2°. While the VSEPR theory suggests a perfectly linear arrangement for this moiety, the deviations in compounds **1-5** can be considered minor.

The comparison of the magnesium analogs with the heavier metal analogs illustrates significant differences. First, an increase in coordination number is observed upon descending the group. In fact, all known heavy alkaline earth metal acetylides are kinetically stabilized by 18-crown-6 coordination, with a coordination number of 8. Acetylides of the heavier alkaline earth metals are not stable if donors of lower hapticity, such as the bidentate TMEDA or the tridentate PMDTA,<sup>6</sup> are employed. It appears that complexes of this type may be prepared at low temperature, but upon warming to room temperature, they decompose as recognized by an observed color change.

The striking difference between the magnesium acetylides and the heavier conjugates is the deviation from a linear ligand arrangement geometry

of the latter. As shown in Figures 1-5, a significant decrease in C-M-C angles is observed as the group is descended (Tables 1 and 2). More dramatically, a decrease in the *ipso*-carbon atom angle (M-C $\equiv$ C) is observed for the heavier analogs with angles as narrow as 126°. With M-C $\equiv$ C angles ranging from 172°-178.2° for **1-5**, these values are in agreement with the linear geometry predicted by the VSEPR theory for a *sp* hybridized carbon atom. It is remarkable though that the ligand with the largest steric demand, C $\equiv$ CSiPh<sub>3</sub>, displays the smallest value, since one could assume that a strictly linear arrangement might afford the least degree of steric repulsion. A geometry closer to theoretical values for the magnesium compounds may be explained by the larger covalent bond contribution in these species, with consequently increased orbital control. Covalent character decreases significantly for the heavier alkaline earth species, with electrostatic interactions being the prominent forces in determining molecular geometries.

### 3. Conclusion and Remarks:

This work resulted in the preparation of two previously known acetylides M(C $\equiv$ CSiPh<sub>3</sub>)<sub>2</sub>(18-crown-6) (M = Sr, Ba) by a new synthetic strategy, toluene elimination. This method allows for the preparation of these materials in good yields and purity.

Extension of this method towards the calcium analogs was difficult, due to the problematic preparation of the dibenzylcalcium starting material. Future work will have to reexamine this synthetic procedure with careful evaluation of possible solvent systems and alternative methods of purification of the final product. Due to the highly reactive nature of the dibenzyl reagent, synthetic procedures need to be simple to avoid accidental exposure to moisture or air. Due to the success of toluene elimination for the strontium and barium acetylides and butyl and benzene elimination for the magnesium derivatives, there is a high likelihood that the corresponding reactions with dibenzylcalcium will produce the desired products.

The successful preparation of several magnesium acetylides allows for a nice trend comparison for the group 2 acetylides. The increasing degree of deviation from predicted VSEPR geometry upon descending the group of alkaline earth metals clearly points towards the role of orbital control, with the more covalent, lighter metal derivatives displaying values closest to the predicted geometry.

#### **4. Experimentals:**

All reactions were performed using standard dry box and Schlenk line techniques under the inert gases nitrogen or argon. Solvents including THF, toluene, benzene, and hexane were all distilled using a Na/K metal alloy and



then degassed twice by subsequent freezing, purging, and thawing cycles. All acetylenes were obtained commercially. All ligands, except triphenylsilylacetylene, are liquids, and were dried over calcium hydride, with subsequent distillation. Triphenylsilylacetylene is a powder, and was placed under vacuum before transfer into the dry box through a chamber which was purged three times with inert gas and vacuum cycles. Dibutylmagnesium (a statistical mixture of secondary butyl and *n*-butyl) was obtained commercially as a 1.0 M heptane solution, packaged under argon. The alkaline earth amides,  $M[N(\text{SiMe}_3)_2]_2[\text{THF}]_2$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ), were made according to the literature<sup>5</sup> as were dibenzylstrontium and barium<sup>16</sup> and benzylpotassium.<sup>13</sup>  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were collected on a Bruker DPX-300 spectrometer. Infrared spectra were obtained from a Perkin-Elmer Paragon 1000 FT-IR. Crystal data was collected on a Bruker SMART system.

**Ca(C $\equiv$ CSiPh<sub>3</sub>)<sub>2</sub>(18-crown-6):** (transamination)

Ca[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[THF]<sub>2</sub> (0.5 mmol, 0.28 g), HC $\equiv$ CSiPh<sub>3</sub> (1 mmol, 0.29 g), and 18-crown-6 (0.5 mmol, 0.14 g) were weighed out in the dry box. About 50 mL of degassed THF was evenly distributed between each of the three starting materials while stirring at room temperature. The calcium amide solution was placed in a dry ice-acetone bath (-78°C), while continuously stirring. The HC $\equiv$ CSiPh<sub>3</sub> solution was added dropwise then, followed by the 18-crown-6 solution. The resulting colorless solution was allowed to stir overnight at room temperature. This was then filtered, the volume reduced, and placed in the -23°C freezer. Colorless crystals were obtained within a few days. mp. 261°C;

yield 0.24 g (55%).  $^1\text{H}$  NMR (300 MHz, 25°C,  $[\text{D}_8]\text{THF}$ ):  $\delta = 3.58$  (s, 24H 18-crown-6), 7.15-7.81 (m, 30H,  $\text{Ph}_3\text{Si}$ ).  $^{13}\text{C}$  NMR (75 MHz, 25°C,  $\text{C}_6\text{D}_6$ ):  $\delta = 74.30$  (18-crown-6), 131.98 (Ph), 133.00 (Ph), 140.04 (Ph), 140.90 (Ph); IR ( $\text{cm}^{-1}$ ) (Nujol):  $\nu = 3854$  s, 3822 s, 3752 s, 3736 s, 3712 s, 3691 s, 3676 s, 3650 s, 3630 s, 3620 s, 3568 s, 3062 s, 3042 s, 2922 s, 1980 s, 1831 w/m, 1564 w/m, 1481 s, 1427 s, 1351 s, 1284 m, 1261 m, 1249 s, 1185 m, 1107 s, 1029 m, 997 m, 972 s, 846 m, 744 s, 705 s, 656 s, 617 m, 544 w/m.

**Ba(C $\equiv$ CSiPh $_3$ ) $_2$ (18-crown-6) and Sr(C $\equiv$ CSiPh $_3$ ) $_2$ (18-crown-6):**

(toluene elimination)

The proper stoichiometric amounts for a 0.5 mmol scale were used.  $\text{M}(\text{CH}_2\text{Ph})_2$  (M = Ba 0.16 g or Sr 0.14 g),  $\text{HC}\equiv\text{CSiPh}_3$  (1 mmol, 0.29 g), and 18-crown-6 (0.14 g) were weighed out in the dry box. 50 mL of degassed THF was distributed evenly between each of the three starting materials. The dibenzylbarium or dibenzylstrontium solution was placed in a dry ice-acetone bath (-78°C). The triphenylsilyl acetylene was added, dropwise. Next, the crown ether was added dropwise as well. The solutions were allowed to stir overnight, were then filtered over a celite padded filter frit, followed by the reduction of volume. Slow cooling in the -23°C freezer allowed for crystals to form. X-ray crystallography of the barium derivative revealed the same structure as is published.<sup>4</sup>

**Sr(C $\equiv$ CSiPh $_3$ ) $_2$ (18-crown-6):** mp. 269°C, yield 0.16 g (35%).  $^1\text{H}$  NMR (300 MHz, 25°C,  $[\text{D}_8]\text{THF}$ ):  $\delta = 3.62$  (s, 24H 18-crown-6), 7.10-7.80 (30H,  $\text{Ph}_3\text{Si}$ ).  $^{13}\text{C}$  NMR (75 MHz, 25°C,  $\text{C}_6\text{D}_6$ ):  $\delta = 70.16$  (18-crown-6), 110.23 (C $\equiv$ C),

127.44 (Ph), 129.09 (Ph), 130.68 (Ph), 136.42 (Ph), 136.87 (Ph); IR ( $\text{cm}^{-1}$ ) (Nujol):  $\nu = 3853$  s, 3750 m, 3675 m, 3648 m, 2284 w, 1969 m, 1829 w, 1772 w, 1733 w, 1716 w, 1698 w, 1684 w, 1670 w, 1636 w, 1616 w, 1558 w, 1540 w, 1521 w, 1506 w, 1427 m, 1350 m, 1285 w, 1248 w, 1186 w, 1101 s, 1039 w, 1020 w, 997 w, 969 m, 843 w, 746 w, 703 s, 654 w, 618 w.

**Ba(C $\equiv$ CSiPh $_3$ ) $_2$ (18-crown-6)•2 THF:** mp. 232°C.  $^1\text{H}$  NMR (300MHz, 25°C, C $_6$ D $_6$ ):  $\delta = 1.43$  (m, 8H, THF), 3.09 (s, 24H 18-crown-6), 3.58 (m, 8H, THF), 7.19-8.11 (30H, Ph $_3$ Si); IR ( $\text{cm}^{-1}$ ) (Nujol):  $\nu = 2930$  s, 1955 s, 1830 s, 1773 s, 1566 s, 1426 s, 1346 s, 1305 m/s, 1283 s, 1261 s, 1245 s, 1185 s, 1092 s, 1063 s, 1028 s, 997 m/s, 961 s, 911 s, 859 m, 828 s, 745 s, 703 s, 652 s, 617 m.

### **Dibenzylcalcium:**<sup>12</sup>

Benzylpotassium (68 mmol, 8.88 g) and calcium iodide (34 mmol, 9.99 g) were each dissolved separately in 70-80 mL of degassed THF, stirring until both were completely dissolved, upon which the calcium iodide solution was added dropwise to the benzylpotassium solution. The resulting solution was allowed to stir for 24 hours at room temperature, which resulted in a gradual color change from orange to red. When stirring was discontinued, the solution settled overnight into two layers with the top as a dark red liquid and the bottom a white precipitate, presumably KI. The top layer was decanted into a separate flask, and the solvent was removed under vacuum, resulting in a red oil. To optimize the yield, the white precipitate was washed twice with benzene. These washes were added to the flask containing the dibenzylcalcium oil. The resulting dibenzylcalcium benzene solution was concentrated by reducing the

volume under vacuum. The flask was then cooled slowly in the +5°C refrigerator, upon which small amounts of crystals formed. Analysis of the crystals by  $^1\text{H}$  NMR revealed many impurities.

**Magnesium Compounds  $\text{Mg}(\text{C}\equiv\text{C}t\text{Bu})_2(\text{TMEDA})_2$  **1**,**

**$\text{Mg}(\text{C}\equiv\text{CC}_6\text{H}_4t\text{Bu})_2(\text{TMEDA})_2$  **2**,  $\text{Mg}(\text{C}\equiv\text{CC}_6\text{H}_4t\text{Bu})_2(\text{15-crown-5})$  **3**,**

**$\text{Mg}(\text{C}\equiv\text{CSiMe}_3)_2(\text{TMEDA})_2$  **4**, and  $\text{Mg}(\text{C}\equiv\text{CSiPh}_3)_2(\text{THF})_4$  **5****

**General Procedure:**<sup>14</sup>

Dibutylmagnesium (2 mmol, 2 mL) was transferred by syringe into 30 mL of solvent, while stirring, followed by dropwise addition of 4 mmol of ligand by syringe. To this solution, stoichiometric amounts of donor were added, and the reaction stirred overnight. Work-up included the filtration of the resulting solutions and reduction of volume. The resulting clear solutions were placed in the refrigerator (7°C), and if no crystals formed within a few days, they were moved into the -23°C freezer.

**1:** Hexane was used as the solvent.  $\text{HC}\equiv\text{C}t\text{Bu}$  (0.49 mL), TMEDA (2 mmol, 0.30 mL). mp. 108-113°C; yield trace.  $^1\text{H}$  NMR (300 MHz, 25°C,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 1.11 (s, 18H,  $\text{CH}_3$ ), 1.48 (s, 24H, THF), 2.14 (t, 8H, THF).  $^{13}\text{C}$  NMR (75 MHz, 25°C,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 31.27 ( $\text{C}(\text{CH}_3)_3$ ), 33.41 ( $\text{CH}_3$ ), 46.65 (TMEDA), 58.07 (TMEDA).

**2:** Toluene was used as the solvent.  $\text{HC}\equiv\text{CC}_6\text{H}_4t\text{Bu}$  (0.71 mL), TMEDA (2 mmol, 0.20 mL). Yield trace.

**3:** Toluene was used as the solvent.  $\text{HC}\equiv\text{CC}_6\text{H}_4t\text{Bu}$  (0.71 mL), 15-crown-5 (1 mmol, 0.30 mL). mp. 185-190°C; yield 0.20 g (18%).  $^1\text{H}$  NMR (300 MHz,

25°C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.14 (s, CH<sub>3</sub>, 18H), 3.43 (t, 15-crown-5, 20H), 7.14-7.65 (m, C<sub>6</sub>H<sub>4</sub>, 8H). <sup>13</sup>C NMR (75 MHz, 25°C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 31.89 (CH<sub>3</sub>), 34.70 (C(CH<sub>3</sub>)<sub>3</sub>), 68.12 (15-crown-5), 107.98, 126.02, 131.75, 146.68 (C<sub>6</sub>H<sub>4</sub>).

**4:** Hexane was used as the solvent. HC≡CSiMe<sub>3</sub> (0.57 mL), TMEDA (2 mmol, 0.30 mL). mp. 115-120°C; yield 0.25 g (28%). <sup>1</sup>H NMR (300 MHz, 25°C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.35 (s, CH<sub>3</sub>, 18H), 2.16 (s, TMEDA, 24H), 2.32 (t, TMEDA, 8H). <sup>13</sup>C NMR (75 MHz, 25°C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 2.04 (CH<sub>3</sub>), 48.06 (TMEDA), 57.62 (TMEDA), 115.33 (C≡C).

**5:** THF was used as the solvent and donor. HC≡CSiPh<sub>3</sub> (1.14 g). mp. 170°C; yield 1.10 g (63%). <sup>1</sup>H NMR (300 MHz, 25°C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.40 (m, THF, 16H), 3.75 (t, THF, 16H), 7.26 (m, Ph, 18H), 8.07 (d, Ph, 12H). <sup>13</sup>C NMR (75 MHz, 25°C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 25.81 (THF), 69.09 (THF), 128.35, 129.70, 136.55, 137.88 (Ph).

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