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Novel Synthetic Routes Toward the Alkaline-Earth Metal Amides

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1. Introduction:

1.1. General Remarks:

Until recently, the majority of Group II organoalkaline-earth metal chemistry focused on the magnesium-based “Grignard” reagents. The heavier congeners had been less extensively studied, due to the electropositive nature and large radii of its metals, which contributed to the difficulty in synthesizing and characterizing the targeted organoalkaline-earth metal complexes.[1, 2] In the late 1900’s, the scope of the research dedicated to these compounds was mainly limited to cyclopentadienyl systems, particularly the synthesis of $Ae(C_5H_5)_2$ (Ae = Ca, Sr, Ba, Figure 1) and *in situ* products.[3,4]

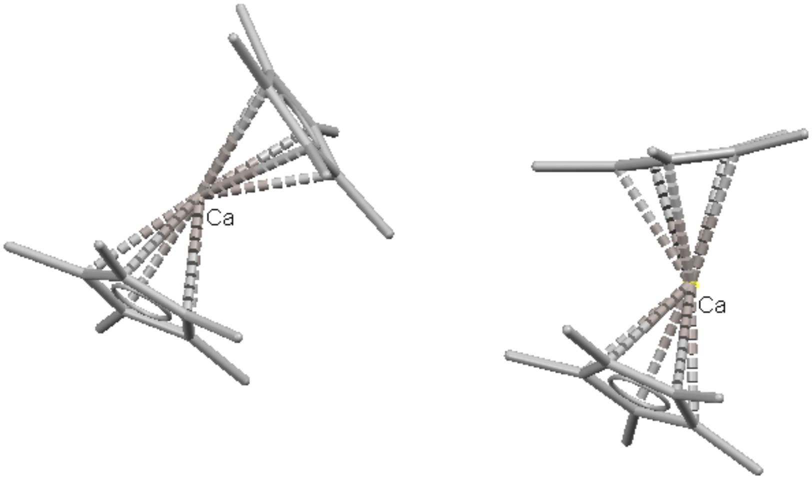


Fig. 1: The x-ray crystallographic molecular structure of $Ca(C_5H_5)_2$. Hydrogen atoms are omitted for clarity. The oligomerization of compounds of this nature is a common problem in alkaline-earth metal chemistry.[4]

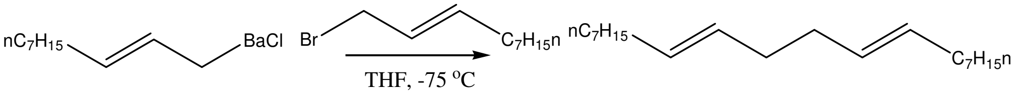
The isolation and characterization of organometallic alkaline-earth metal compounds was made difficult due to their high reactivity and tendency to form oligomeric and polymeric species, contributing to their low solubility. Recent developments in synthetic routes, as well as the use of sterically hindered ligands and neutral co-ligands, which coordinatively saturate the metal center and decrease the coordination number, coupled with an increase in potential applications have driven the chemistry of the heavier alkaline-earth metals to the forefront of main group chemistry and have led to an expansion of the library of their compounds.

Organoalkaline-earth metal complexes are desired for their potential use in synthetic, polymer, and solid-state applications, particularly metal organic chemical vapor deposition (MOCVD).[5] Further progress in this area of chemistry critically depends on facile, reproducible synthetic routes toward the target compounds.

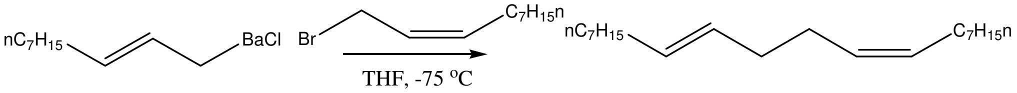
1.2 Applications of Organoalkaline-Earth Metal Complexes:

1.2.1 Synthetic Applications:

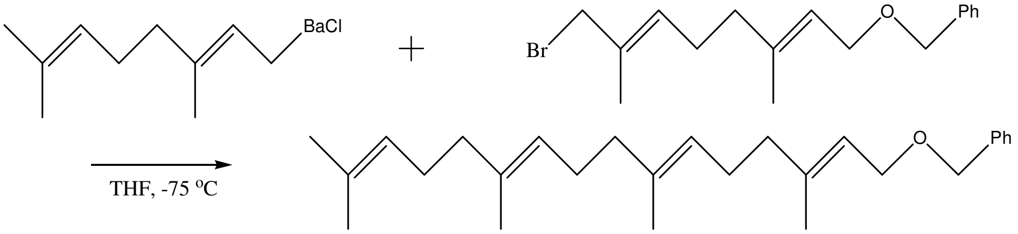
The desirability of the magnesium-based “Grignard” reagents can be attributed to their usefulness in synthetic chemistry, particularly for their ability to form new carbon-carbon bonds. Recently, Yamamoto et al. showed that allyl barium halide complexes of the form, $R_1R_2C{=}CHCH_2BaCl$, can be used in the regio- and stereo-selective allylation of carbonyl compounds in yields of up to 98% with an α-selectivity of up to 99%.[5] When used in the dimerization of allylic halides, barium metal has regio- and stereo-selectivities of 89-96%. Additionally, alkylbarium reagents (see Equations 1-4 for example) have been used in the syntheses of unsymmetrical dienes.[6] In each instance, the double bonded geometry of the starting allylic halide is maintained.



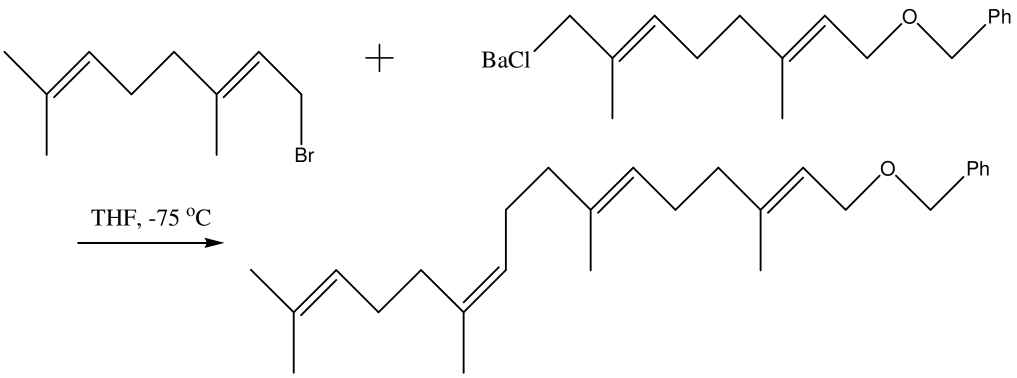
Eqn. 1: The reaction of (E)-2-decenylbarium and (E)-2-decenylbromide in THF at –75 °C to give the corresponding (E,E)-diene in 83 % yield.



Eqn. 2: The reaction of (E)-2-decenylbarium and (Z)-2-decenylbromide in THF at –75 °C to give the corresponding (E,Z)-diene in 87 % yield.



Eqn. 3: The reaction of a geranylbarium reagent with a primary allylic bromide in THF at –75 °C to give the benzyl ether of geranylgeranol in 81 % yield.



Eqn. 4: The reaction of an allylic barium reagent with neryl bromide in THF at –75 °C to give the benzyl geranylgeranyl ether in 60 % yield.

1.2.2 Polymer Chemistry:

1.2.2.1 Olefin Polymerization:

Organoalkaline-earth metal complexes are also desired for their ability to function as polymerization initiators, particularly in the anionic living polymerization of styrene. [7, 8] Calcium dimers, of the form (Ca(Me_3Si-fluorenyl)((*o*-dimethylamino)benzyl)$)_2$ (Figure 2) have been shown to act as initiators in the anionic polymerization of styrene. Alternatively, complexes of the form Ae(9-hypersilyl-fluorenyl$)_2$(thf$)_2$ (Ae = Ca, Sr, Figure 3), amongst others, have been studied as potential polymerization initiators.[8] Future work in this branch of organoalkaline-earth metal chemistry is focused on complexes that show an improvement of the syndiotacticity of the resulting polymer.[7]

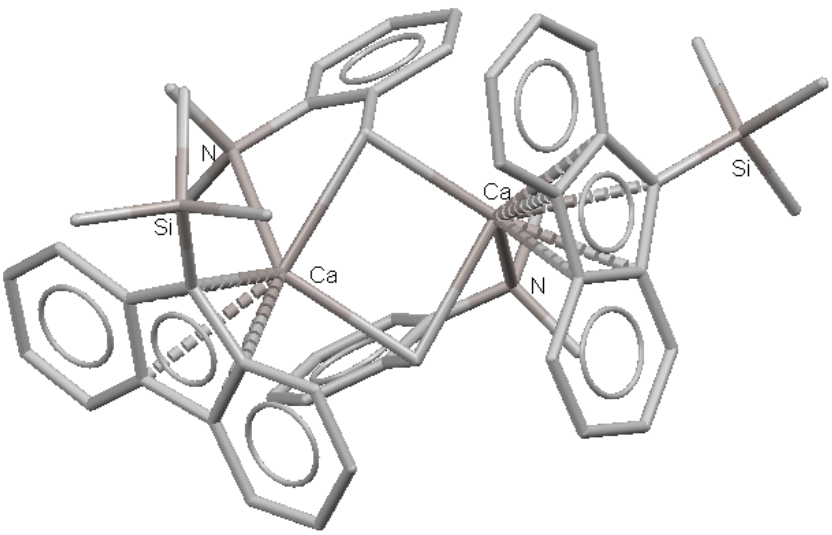


Fig. 2: The x-ray crystallographic molecular structure of (Ca(Me_3Si-fluorenyl)((*o*-dimethylamino)benzyl))$_2$. Hydrogen atoms are omitted for clarity.[7]

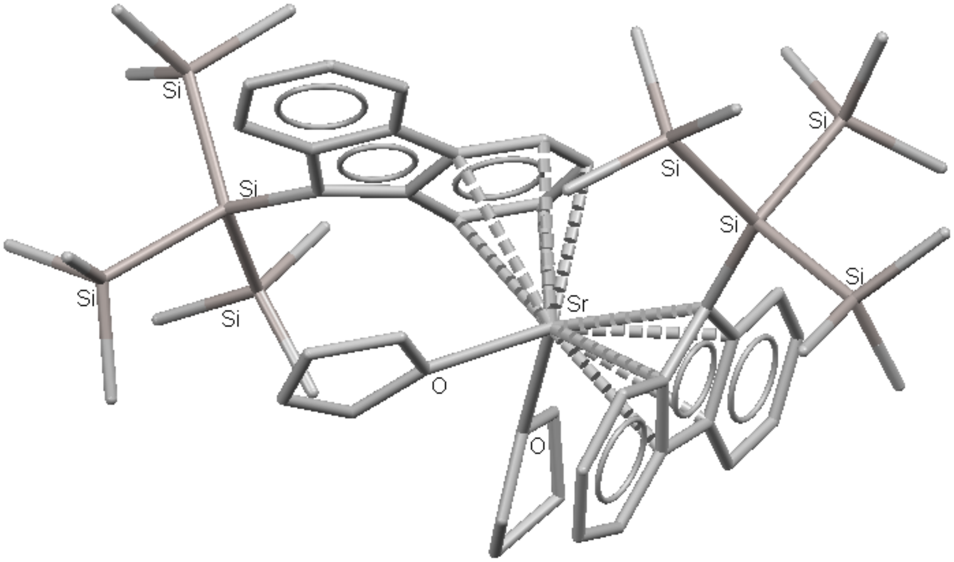


Fig. 3: The x-ray crystallographic molecular structure of Sr(9-hypersilyl-fluorenyl)$_2$(thf)$_2$. This is an example of the complexes being studied as polymerization initiators. The calcium analog is isostructural. Hydrogen atoms are omitted for clarity.[8]

1.2.2.2 Polymerization of Cyclic Esters:

Biocompatible and biodegradable aliphatic polyesters are desired for their potential medicinal and pharmaceutical applications. However, the catalytic process that leads to their formation leaves trace residues of the catalyst, necessitating the use of biocompatible catalysts. In this respect, organomagnesium and –calcium derivates (Figure 4) are currently being explored as potential catalysts/initiators in the polymerization of cyclic esters to afford biocompatible polylactides.[9] Currently, polymeric cyclic esters, based on D, L-lactide and ε-caprolactone are used in tissue engineering and as re-absorbable medical sutures.[10]

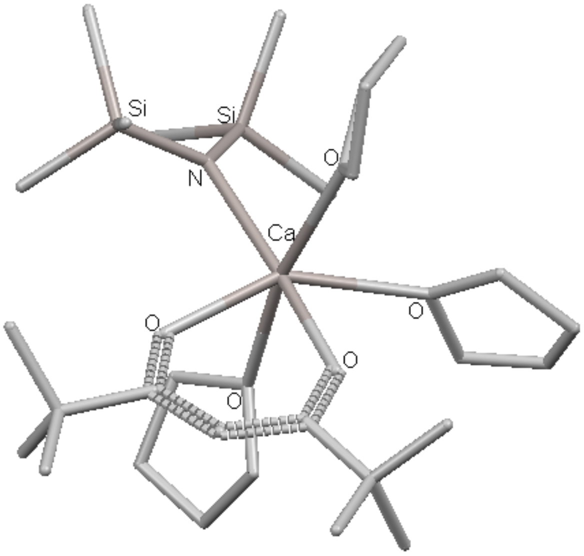


Fig. 4: The x-ray crystallographic molecular structure of $Ca((NSiMe_3)_2(O_2C_3H(^tBu)_2))(thf)_3$, one of the derivatives being explored in the production of biocompatible polylactides. Hydrogen atoms are omitted for clarity.[10]

1.2.3 Precursors for Metal Organic Chemical Vapor Deposition:

While the synthetic and polymerization potential of the heavier organoalkaline earth metal complexes is promising, complexes of this nature are also desired as precursor materials for MOCVD (metal organic chemical vapor deposition). MOCVD requires a volatile, metal-based precursor for the formation of thin films on a substrate surface. The process, which has several modifications, generally requires that a metal-based precursor be delivered to the CVD reactor.

Once the precursor is vaporized, it is transported *via* vapor phase to the heated substrate where it physisorbs and then chemisorbs, removing the organic ligands from the precursor and depositing the metal onto the substrate. More than one homometallic metal-based precursor is needed when mixed-metal films are desired.

The CVD method is preferred for the formation of thin films because it allows for conformal coverage of the substrate. Preferably, low temperature deposition is conducted, a process associated with a high level of compositional control when mixed-metal films are being constructed.[11, 12] The conformal coverage afforded by the CVD method allows for the production of films with specific spatial requirements. For example, the $AeTiO_3$ thin films (Ae = Sr, Ba), which will later be discussed in more detail, have required dimensions of $0.15 \times 0.35 \times 1.0\ \mu m^3$ with a minimum spacing of 1 μm.[13]

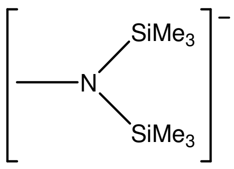
There is considerable interest in the precursors of Group II metals because their films have many technologically important properties. For example, $YBa_2Cu_3O_x$ (x= 6 or 7) is used to manufacture coils that are used in high magnetic fields for applications such as superconducting magnetic energy storage (SMES). [14] The doping of $LaMnO_3$ films with 20-40% of the Mn positions replaced with calcium or strontium causes the thin-film material to transition from a high-temperature paramagnetic insulator to a low-temperature ferromagnetic metal that exhibits high colossal magneto resistance, with applications in the development of magnetic recording heads.[15, 16] Ferroelectric films of the form $BaTiO_3$ and $SrTiO_3$ (BST Films) are desirable for their applications in electro-optic devices, integrated optics and photo detectors.[17] Additionally, BST Films are the dielectric material of choice for the cell capacitor of Dynamic Random Access Memory circuits (DRAMs) because they offer large dielectric constants with small dielectric loss and leakage current.[13]

In order to be suitable for MOCVD, a precursor must meet certain criteria. The precursor must have high volatility, which is a function of the molecular weight and lattice energy of the target compound. The molecular weight and the lattice energy of the compound can be modulated by using bulky ligands that saturate the coordination sphere of the metal, suppressing oligomerization. The target compound must also have a suitable balance between stability and reactivity. It must be stable up to the delivery temperature; however, it must also be reactive enough to decompose under mild conditions. Currently, some ferroelectric films such as $BaTiO_3$ require precursors with deposition temperatures of up to 600 ˚C.

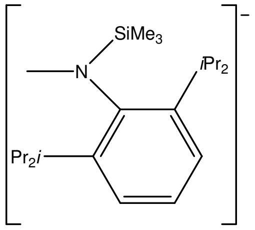
1.3 The Pursuit of Novel Classes of Alkaline-Earth Metal Amides:

1.3.1 Aryl Substituted Silyl Amides:

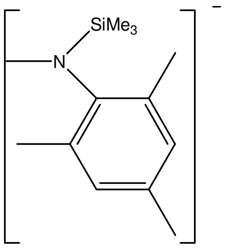
Heavy organoalkaline-earth metal compounds are highly reactive. Previous work has employed the use of sterically demanding ligands to kinetically stabilize the metal center, as demonstrated with the bulky $(N(SiMe_3)_2)^-$ ligand (Scheme 1A), which has been used to successfully synthesize alkaline-earth metal bis(bis(trimethylsilyl))amides.



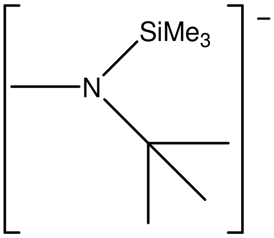
A: Bistrimethylsilyl Amido



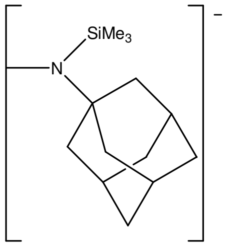
B: Trimethylsilyl Diip Amido



C: Trimethylsilyl Mesityl Amido



D: Trimethylsilyl *Tert*-Butyl Amido



E: Trimethylsilyl Adamantyl Amido

Scheme 1: The structure of the amido ligands that have been previously used in alkaline-earth metal chemistry (A-C) and the structure of the amido ligands that were used toward the alkyl amides (D-E).

These amides are thermally quite stable and exhibit excellent solubility in a range of solvent systems.[18, 19] While these amides have proven to be excellent starting materials, their use as MOCVD precursors is limited because of their tendency toward N-Si bond cleavage that may occur under high temperature or acidic condictions.[20] The silyl cleavage often leads to silicon incorporation in the final solid state material, reducing its usefulness in many electronic applications. An ideal precursor would be free of silyl groups altogether to avoid silicon contamination of the final product.[21]

Further developments in organoalkaline-earth metal amido chemistry (Scheme 1B and 1C) conducted in the Ruhlandt-Senge laboratory resulted in the synthesis of aryl substituted alkaline-earth metal silyl amides.[22, 23] The aryl substituted silyl amides are monomeric in nature and show an increase in volatility with reduced Si-N bond cleavage tendencies. Steric saturation of the metal centers was achieved by agostic interactions. Agostic interactions, which can thermodynamically stabilize the metal center, are weak bonding interactions between a metal and a C-H group on the ligand or donor.[24]

Effective further stabilization is possible through metal-π interactions, but specific ligand design is needed to position ligands for an effective metal-π stabilization.

Previously, the alkaline-earth metal aryl amides were prepared in our laboratory *via* salt metathesis reactions.[22] Alternatively, redox transmetallation/ligand exchange, pioneered by Deacon et al., [25, 26] is being explored as a new synthetic route toward the aryl amides based on the similarity between the divalent rare earth metals Yb^{2+}, Eu^{2+}, and Sm^{2+} with Ca^{2+} and Sr^{2+}. The feasibility of this route will be explored by preparing $Ae(N(2,6\text{-}^{i}Pr_2C_6H_3)(SiMe_3))_2(thf)_2$ (Ae = Ca, Sr, Ba).

While exploring redox transmetallation/ligand exchange using Ph_3Bi, we encountered three modifications of triphenylbismuth. Two of the modifications, crystallized in the C2/*c* and C2 space group, were previously known, but a third modification in the P2(1)/*c* space group was obtained fortuitously from redox transmetallation/ligand exchange studies. Since current work in our research group focuses on triphenylbismuth as a redox transmetallation agent, providing a benign alternative to the classic toxic organomercurial reagent, we were interested to study the different Ph_3Bi morphologies. The development of sustainable benign synthetic procedures that are technologically relevant is the driving force behind green chemistry. [27-29] A greater understanding of the solid-state properties of each of the modifications of triphenylbismuth may increase its potential applications in this particular field.

1.3.2 Alkyl Substituted Silyl Amides:

We are interested to prepare alkyl substituted alkaline-earth metal silyl amides due to their potential in synthetic and materials chemistry. Replacement of aryl groups in the aryl substituted silyl amides by an alkyl moiety will provide a new family of alkaline-earth metal amides with potential applications in synthetic and materials chemistry. The use of sterically demanding ligands and neutral donors/co-ligands can force monomeric species to form. Currently, F. Fleil and S. Harder synthesized the only known alkyl substituted alkaline-earth metal amide in 2005 (Figure 5). [30]

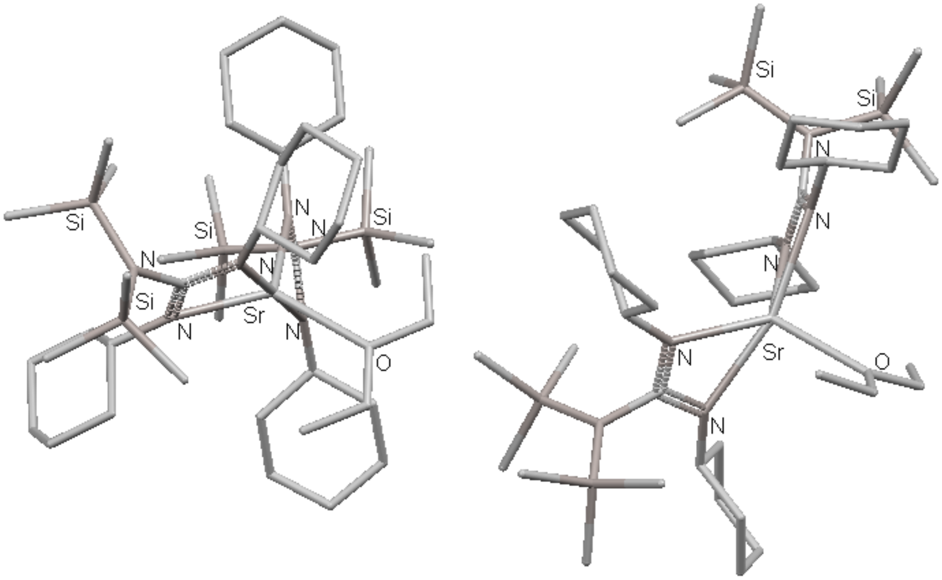


Fig. 5: The x-ray crystallographic molecular structure of (Sr(Cy)NC((N(SiMe$_3$)$_2$)N(Cy))$_2$. Hydrogen atoms are omitted for clarity.[30]

In 2006, Kemp et al. reported the ^{1}H-NMR analysis of an N-*tert*-butyl-trimethylsilyl substituted amide, but detailed analytical data remain elusive.[31]

Alkyl substituted alkaline-earth metal silyl amides were pursued using the sterically demanding N-*tert*-butyl-trimethylsilylamido (Scheme 1D) and N-adamantyl-trimethylsilylamido (Scheme 1E) ligands in combination with heavier Group II metals. The synthesis of the highly reactive target compounds was attempted using a variety of synthetic strategies, including salt metathesis, transamination, toluene elimination, and redox transmetallation/ligand exchange reactions. Details on each synthetic route will be discussed below in greater detail.

1.3.3 Primary Alkaline-Earth Metal Amides:

Aside from preparing alkyl substituted silyl amides, I was interested to prepare primary amides with the ultimate goal to eliminate the requirement for silyl substituted ligand systems. To this effect, the primary amine H_2N-Diip was employed. To date, primary amides of the heavy alkaline-earth metals remains as elusive as the alkyl substituted secondary amides, with examples limited to an intra-molecularly stabilized amido species.[32]

The preparation of primary amides will address several areas of concern: the compound will be free of silyl groups and thus will not lead to silicon contamination of the final product. Moreover, primary amides will display low molecular weight and thus the propensity for higher volatility, adding to the attractive nature of a potential CVD precursor.

Transamination reactions utilizing alkaline-earth metal bis(thf) bis(bis(trimethylsilyl))amides of magnesium, calcium, strontium, and barium were explored as a potential synthetic route toward the silyl-free primary amides. The synthesis of a primary alkaline-earth metal amide using the bis(thf) bis(bis(trimethylsilyl))amides and HMPA, a strong Lewis base was also explored. In this instance, the target compound would be highly volatile, however, it would not be silicon free. The results from this method will help elucidate whether or not the treatment of an alkaline-earth metal silyl amide will lead to the abstraction of a trimethylsilyl group.

1.4 Synthetic Methodologies:

Four synthetic routes, presented in Table 1, were explored toward the synthesis of the alkyl substituted alkaline-earth metal silyl amide target molecules: transamination (Equation 5), toluene elimination (Equation 6), salt metathesis (Equation 7-8), and redox transmetallation/ligand using a Ph_3Bi/Hg activator-catalyst (Equation 9). Each method has its own unique requirements and drawbacks that must be taken into consideration.

Synthetic Method	**Reaction Equation**
Transamination (Route A)	$Ae(N(SiMe_3)_2)_2(thf)_2 + 2\ HNRSiMe_3 \rightarrow Ae(NR(SiMe_3))_2(thf)_2 + 2\ HN(SiMe_3)_2$ (Eqn. 5)
Toluene Elimination (Route B)	$Ae(Bn)_2 + 2\ HNRSiMe_3 \rightarrow 2\ Tol + Ae(NR(SiMe_3))_2$ (Eqn. 6)
Salt Metathesis (Route C)	$HNRSiMe_3 + KH \rightarrow H_2 + KNRSiMe_3$ (Eqn. 7) $2KNRSiMe_3 + AeI_2 \rightarrow 2KI + Ae(NRSiMe_3)_2$ (Eqn. 8)
Redox Transmetallation-Ligand Exchange (Route D)	$Ae_{act.} + 2HNRSiMe_3 + Hg + Ph_3Bi \rightarrow Ae(NRSiMe_3)_2$ (Eqn. 9)

Table 1: The synthetic routes explored toward the alkaline-earth metal silyl amides. R = Adamantyl, ^{t}Butyl, Diip. Ae = Ca, Sr, Ba.

1.4.1 Transamination (Route A):

Transamination has been used extensively for the preparation of aryloxides, thiolates, selenolates and alkynes. The transamination reaction takes advantage of the availability and solubility of the alkaline-earth metal bis(thf) bis(bis(trimethylsily))amides.[33] In order for the reaction to proceed, the acidity of the starting amine must be higher then that of the liberated $HN(SiMe_3)_2$ (HMDS). While successful if conducted carefully, highly acidic substrates have been observed to cause N-Si bond cleavage[20], narrowing the p*K*a range of possible starting amines. N-*tert*-butyl-trimethylsilylamine, N-adamantyl-trimethylsilylamine and 2,6-Diisopropylaniline display p*K*a values of 28, 29, and 25 while that of HMDS is 30. Even that the p*K*a difference between the ligands and HMDS is small, it should be significant enough to enable a forward reaction. An additional advantage of this route is the easy removal of HMDS under vacuum (BP = 125 °C).

1.4.2 Toluene Elimination (Route B):

Toluene elimination makes use of alkaline-earth metal dibenzyl complexes, $Ae(Bn)_2$ (Ae = Ca, Sr, Ba). Similar requirements as discussed for transamination apply here; the substrate needs to display higher acidity than the liberated toluene (Equation 6). With the acidity of toluene (p*K*a 43) lower than that of HMDS, a larger range of substrates can be used. Adding to the attractive nature of the process, toluene can be easily removed by application of vacuum.

Drawbacks of the reaction include the high reactivity and low solubility of the dibenzyl starting materials. Even when stored under inert conditions, the dibenzyl complexes begin to decompose over a period of 24-48 hours. Moreover, the highly polar solvent THF must be used to achieve homogenous reaction conditions. The highly basic nature of the reagents lead to THF cleavage at temperatures above –40 °C.

1.4.3 Salt-Metathesis (Route C):

The salt metathesis method involves the reaction of potassium amide with an alkaline-earth metal halide. The potassium amide is typically prepared by metallation involving treatment of amine with potassium hydride. The formation of the potassium amide is driven forward by the evolution of hydrogen gas. The alkaline-earth metal iodides are then combined with the *in situ* prepared potassium amides, a reaction typically leading to the clean precipitation of KI. The combination of a potassium amide and a alkaline-earth metal iodide has been shown to provide best results, since good solubility of the alkaline-earth metal iodides is paired with low solubility of KI.

1.4.4 Redox Transmetallation/Ligand Exchange (Route D):

The redox transmetallation/ligand exchange reaction scheme has been used extensively in rare earth metal chemistry utilizing organomercurial reagents. Similarities in coordination number (CN) and ionic radii (r) between calcium (Ca^{2+}, CN = 8, r = 1.14 Å) and strontium (Sr^{2+}, CN = 8, r = 1.32 Å) with the divalent rare earth cations ytterbium (Yb^{2+}, CN = 8, r = 1.16 Å), europium (Eu^{2+}, CN = 8, r = 1.32 Å), and samarium (Sm^{2+}, CN = 8, r = 1.36 Å) has prompted the use of this synthetic route towards the alkyl and aryl substituted alkaline-earth metal silyl amides.[34] With the classical redox transmetallation/ligand exchange relying on organomercurials, the more negative redox potentials of the alkaline-earth metals as compared to the rare earth metals allowed the use of the less potent, but benign transmetallating agent, Ph_3Bi. Initial attempts described here still relied on Hg activation of the metal, but more recent results obtained by M. Gillett-Kunnath in our group suggest that under proper conditions the reaction proceeds in the absence of Hg.[35]

Reflux conditions or an ultrasound water bath with a frequency of 40 kHz and a temperature of 54 ºC were used to activate the metal. Current studies in our laboratory are geared to identify the reaction mechanism.

1.5 Coordinative Saturation of the Alkaline-Earth Metals:

Coordinative saturation is difficult to achieve for the heavy alkaline-earth metals because the large metal cations require a combination of sterically demanding ligands and Lewis bases. Multi-dentate bases, such as the nitrogen-based N,N,N',N'-tetramethylethylenediamine (TMEDA, Figure 6) and N,N,N’,N”,N’-pentamethyldiethylenetriamine (PMDTA, Figures 7) are exceptionally well suited to provide coordinative saturation. Other commonly used donors include tetrahydrofuran (THF, Figure 8) and hexamethylphosphoramide (HMPA, Figure 9).

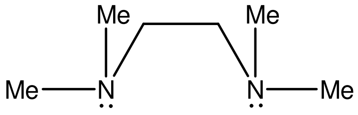


Fig. 6: TMEDA

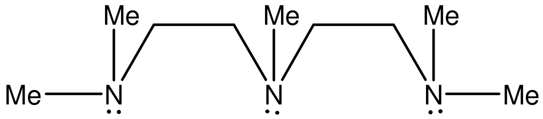


Fig. 7: PMDTA

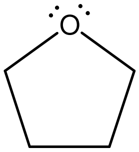


Fig. 8: THF

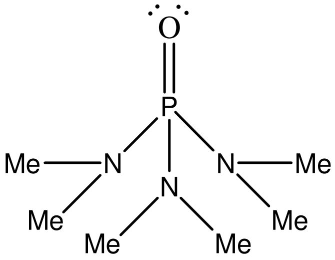


Fig. 9: HMPA

THF and HMPA are effective Lewis bases. For each, the oxygen atom acts as an electron donor, with HMPA being a stronger Lewis base than THF as the result of greater electron density at the oxygen atom. Additionally, HMPA is less sterically hindered and can be described as acting like a "torpedo" when functioning as a Lewis base.

The electron donating capacity of the nitrogen atoms in TMEDA and PMDTA is slightly reduced due to steric hindrance. However, unlike THF or HMPA that are monodentate donors, the multi-dentate nature of TMEDA and PMDTA allows preferential coordination through the chelate effect, with the coordination of the multi-dentate donors driven by entropic effects.

2. Alkyl Substituted Alkaline-Earth Metal Silyl Amides:

2.1 Ligand Choice:

Two different ligand systems, N-*tert*-butyl-trimethylsilylamine HN(^{t}Butyl)(SiMe$_3$) (Figure 10) and N-adamantyl-trimethylsilylamine HN(Adamantyl)(SiMe$_3$) (Figure 11) were chosen for their easy availability and steric bulk. The size of each ligand can potentially saturate the coordination sphere of the metal, avoiding the formation of aggregates. It is expected that the anticipated coordination number of calcium, strontium, and barium amides can be as low as three or four if sterically demanding ligands or multi-dentate bases are being introduced.[36]

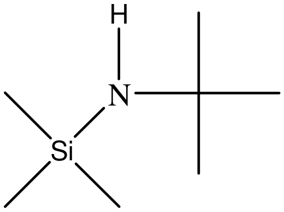


Fig. 10: HN(^{t}Butyl)(SiMe$_3$)

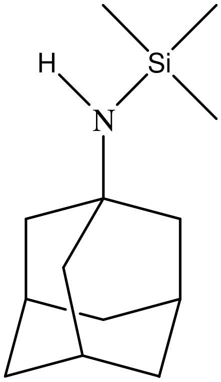


Fig. 11: HN(Adamantyl)(SiMe$_3$)

HN(^{t}Butyl)(SiMe$_3$) is available commercially. Lappert et al. have previously used it in the synthesis of lithium, sodium and potassium amides. These compounds display a trimeric structural motif (Figure 12).[37, 38]

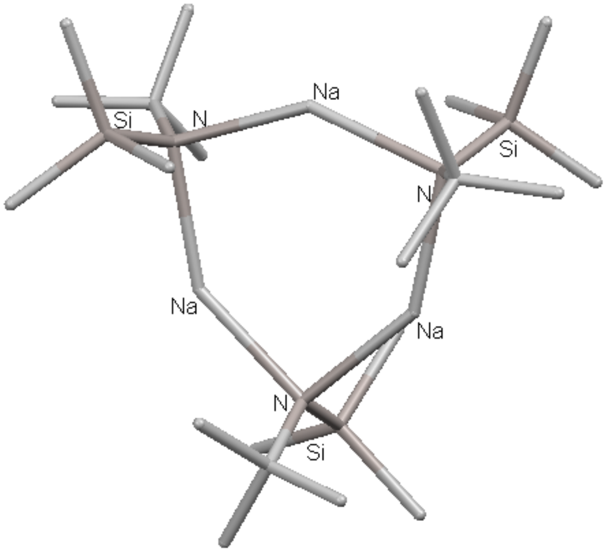


Fig. 12: The x-ray crystallographic molecular structure of $(Na(N(SiMe_3)(^tButyl)))_3$. Hydrogen atoms are omitted for clarity.[37]

The only prior alkaline-earth metal derivative prepared using this ligand is a highly unusual lithium-potassium-magnesium heterotrimetallic amide, of the form $(Li_2K_2Mg_2(^tBu(Me_2(H_2C)Si)N)_4)$ (Figure 13).[39] Aside from ^{1}H-NMR evidence for a calcium amide, no heavy alkaline-earth metal derivatives using this ligand system are available.[31]

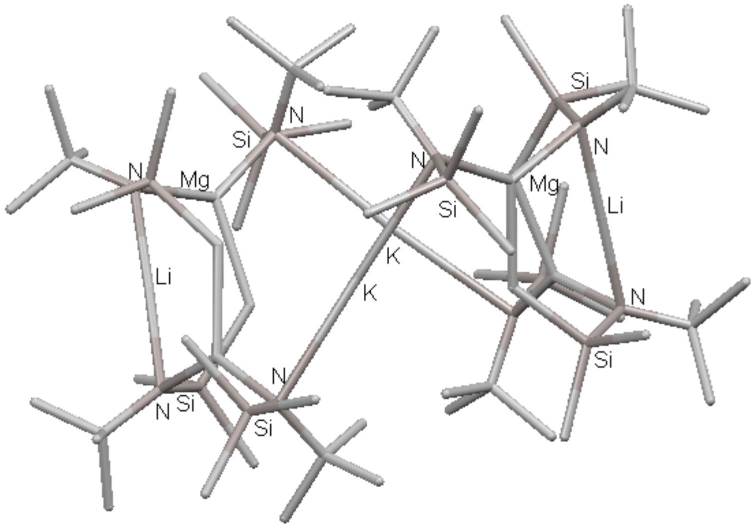


Fig. 13: The x-ray crystallographic molecular structure of ($Li_2K_2Mg_2(^tBu(Me_2(H_2C)Si)N)_4$). Hydrogen atoms are omitted for clarity.[39]

Previously, the closely related HN(Ad)($SiMe_3$) ligand system has been used to prepare a trimeric lithium amide[40] (Figure 14).

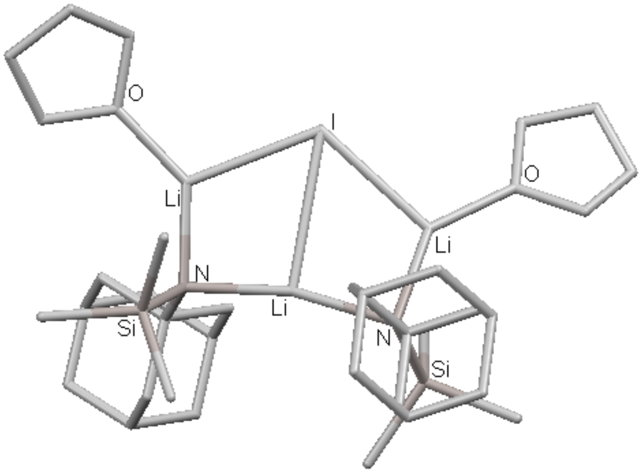


Fig. 14: The x-ray crystallographic molecular structure of ($Li_3(\mu_3$-I)(N(Ad)($SiMe_3$))$_2$(thf)$_2$). Hydrogen atoms are omitted for clarity.[40]

Alkaline-earth metal compounds utilizing this ligand system are limited to a magnesium derivative, Mg(N(Ad)($SiMe_3$))$_2$(Et_2O), reported in 2005.[41]

HN(Ad)($SiMe_3$) is prepared *via* straightforward metathesis, as illustrated in Equations 10-11.[42]

H_2NAd + *n*-ButylLi → LiN(H)Ad + Butane (Eqn. 10)

LiN(H)Ad + $ClSiMe_3$ → $HNAdSiMe_3$ + LiCl (Eqn. 11)

Lithiation of the primary amine H_2NAd with *n*-ButylLi (Eq. 10) followed by treatment of the resulting amide with chlorotrimethylsilane gives the product. The resulting LiCl can be easily separated by filtration. The ligand is purified by distillation. The boiling point of the amine is 110-115 °C at ambient pressure, affording the amine as a colorless oil in yields of 75-80%.

2.2 Preparation of Alkyl Silyl Amides:

Attempts toward the target compounds were made using routes A, B, C, and D of Table 1 with slight modification to account for the volatile nature of HN(^{t}Butyl)($SiMe_3$). For example, reflux conditions, which are typically utilized in the transamination reaction to remove the $HN(SiMe_3)_2$ as it forms, were avoided. The only instance where reaction conditions were unchanged from Table 1 was for the redox transmetallation/ligand exchange using both HN(Adamantly)($SiMe_3$) and HN(^{t}Butyl)($SiMe_3$), in which reflux conditions are required to activate the metal. The remaining synthetic routes, salt-metathesis and toluene elimination were conducted at –78 °C in a dry-ice/acetone bath.

Initial transamination reactions (Method A), conducted at room temperature did not proceed as planned. In order to avoid reflux conditions, $HN(SiMe_3)_2$ was not removed from the reaction mixture, possibly contributing to an incomplete reaction. In fact, ^{1}H-NMR analysis only revealed the presence of the starting amine. Since the volatility of the ligand precluded the use of more forcing reaction conditions, alternative synthetic routes were explored.

Redox transmetallation/ligand exchange reactions (Method D) were examined as a possible synthetic route toward the target compounds. Based on recent results in the Ruhlandt-Senge laboratory indicating the potential of Ph_3Bi as a redox transmetallation agent, this route was employed toward the target compounds. While we were unable to isolate the target compounds, possibly the result of extended reflux conditions and consequent decomposition of the potentially thermally labile products, novel modifications of Ph_3Bi were obtained. This work is described in detail below. Alternatively, the conditions utilized may not have provided sufficient metal activation thus preventing the reaction from proceeding. Future work will utilize sonication to activate the alkaline-earth metal. To further increase the metal surface area, metal filings will be used. To introduce milder reaction conditions, amines will only be added after metal activation has taken place. In this case, the reaction may be conducted at lower temperatures.

Two other synthetic routes, salt-metathesis and toluene elimination, were examined. In each instance, the reaction temperature was lowered from room temperature to –78 °C, as achieved using a dry-ice acetone bath. Toluene elimination (Method B) depends on the use of highly reactive alkaline-earth metal dibenzyl reagents. The high reactivity of these requires their fresh synthesis. Initial attempts using reagents that had been stored in the dry box for a few days failed. ^{1}H-NMR analysis of the final reaction indicated the presence of toluene in combination with free amine, suggesting either the hydrolysis of the dibenzyl reagent during storage or the hydrolysis of the target amine by inadvertent introduction of water. Future work will utilize freshly prepared dibenzyl derivatives, short reaction times at low temperature, and stringent exclusion of water and air.

As mentioned above, salt-metathesis (Method C) was explored as well. While the target compounds have not been obtained, this route appears to be most promising. The synthesis entails treatment of potassium amide with alkaline-earth metal iodide at –78 °C. Micro-crystals were obtained upon cooling to

–23 °C. These crystals will be analyzed *via* single crystal x-ray diffraction using an intense x-ray beam, as available at the CHESS synchrotron source at Cornell University. Attempts to grow bigger crystals are ongoing.

3. Aryl Substituted Silyl Amides:

3.1 Starting Amine:

Recent results in the Ruhlandt-Senge laboratory indicate the superior potential of the redox transmetallation/ligand exchange route utilizing Ph_3Bi as a redox transmetallation agent, allowing the convenient high yield preparation of the heavy alkaline-earth metal bis(bis(trimethylsilyl))amides in the absence of toxic mercury and its compounds.[35] In here, I am describing the extension of this method toward the preparation of the sterically more demanding $(N(Diip)(SiMe_3))^-$ alkaline-earth metal amides. These compounds have been prepared previously by W. Vargas in the Ruhlandt-Senge laboratory (Figure 15).[22]

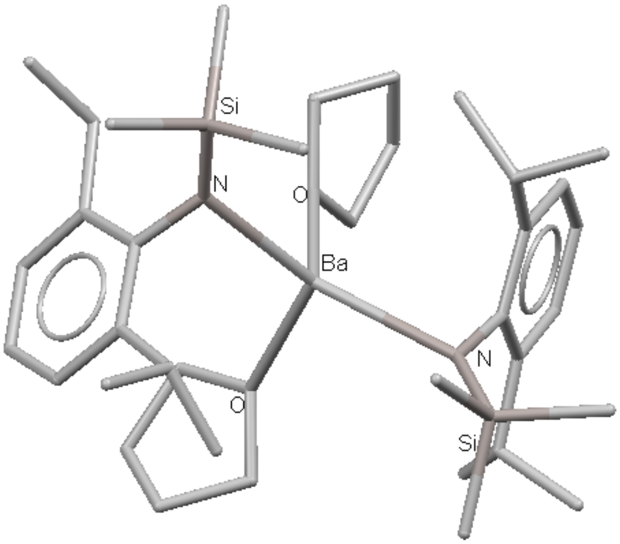


Fig. 15: The x-ray crystallographic molecular structure of $Ba(Diip)(SiMe_3))_2(thf)_2$. Hydrogen atoms are omitted for clarity.[22]

While the magnesium analog was obtained *via* alkane elimination using (n-Butyl)$_2$Mg, this route is not applicable for the heavier analogs. Instead, the heavier alkaline-earth metal derivatives were prepared *via* salt-metathesis, or for the barium species (Figure 15, above), *via* direct metallation after activation of the metal by solvation in anhydrous ammonia. Redox transmetallation/ligand exchange will provide a synthetic route without working with condensed gases (NH_3) and toxic mercury and its compounds while providing an economic alternative to the expensive, ultra-pure alkaline-earth metal iodides.

3.2 Synthetic Methods:

Redox transmetallation/ligand exchange was employed using cut metal pieces as well as metal filings. The metal was then activated using a Hg/Ph_3Bi catalyst/activator and reflux conditions. In each of the cases, the mixture using metal pieces was refluxed for 14-21 days. The mixture containing the metal filings was kept in a sonication bath for 7-14 days. The sonication bath operates at a frequency of 40 kHz and heats the water to 54 °C.

Significant differences were observed using both methods. While only Ph_3Bi was recovered if metal pieces and extended reflux (21 days for Ca, 17 days for Sr, and 14 days for Ba) was applied, the combination of sonication and metal filing proved more promising, resulting in the preparation of $Ba(N(Diip)(SiMe_3))_2(thf)_2$. The molecular structure of the previously reported compound was confirmed *via* x-ray crystallography by performing a unit cell check. At this time, the extension towards calcium and strontium analogs is being attempted. Furthermore, optimization to improve the yields of the barium target compound is underway. With the combination of metal shavings and sonication shown to be very effective for barium, this approach will be used toward the calcium and strontium derivatives.

4. Primary Alkaline-Earth Metal Amides:

Alkaline-earth metal amides that have been well characterized are almost exclusively limited to secondary amides. In this chapter, attempts to prepare a group of primary amides will be described. Amide ligands will be from H_2N-Diip, a sterically demanding aryl amide. Importantly, silyl substituents are absent, enhancing the potential of these compounds as CVD precursors since silicon contamination is not possible. As noted above, silicon contamination is highly detrimental to the use of silyl amides as CVD precursor materials.

Interestingly, all amide ligands in known alkaline-earth complexes carry a silyl substituent. Replacement of one silyl group to migrate from the well described $Ae(N(SiMe_3)_2)_2$ amides to $Ae(N(Aryl)(SiMe_3))_2$ have been successful in our group with aryl substituents being Mesityl or Diip.[21, 23] Replacing aryl by alkyl substituents have been more challenging (see above). The only known molecular structure for a primary amide was reported in 2004 by Hill et al.[32] This amide, $(Ca(NDiipCCH_3)_2CH)(\mu\text{-}NH(CH_2)_2OCH_3))_2$ is stabilized using intra-molecular coordination in conjunction with a very bulky ligand.

4.1 Synthetic Routes Toward Primary Amides:

Two synthetic opportunities exist for the preparation of primary amides, use of a primary amine, 2,6-diisopropylaniline or desilylation reactions utilizing the strong Lewis base, HMPA. Desilylation presents an attractive option to these compounds, however, prior evidence is limited to the removal of a trimethylsilyl functional group from a ligand to form an alkaline-earth metal organometallic (Equation 12).[43] The reaction is conducted in the presence of *n*-ButylLi and [18]-c-6 at room temperature using THF as the solvent.

$$Ba(O^tBu)_2 + 2HCPh_2SiMe_3 \rightarrow [Ba(CHPh_2)_2([18]\text{-}c\text{-}6] + 2SiMe_3O^tBu \quad \text{(Eqn. 12)}$$

Desilylation to prepare the primary amides relies on freshly distilled HMPA. The strongly basic oxygen anion seems to abstract the $SiMe_3$ moiety. The highly hygroscopic nature of HMPA requires it to be freshly distilled to prevent the hydrolysis reaction.

The only prior work done with the heavier congeners of the Group II alkaline-earth metals toward primary amides involved the synthesis of a heteroleptic calcium amide using a 2,6-diisopropylaniline substituted β-diketiminato ligand and 2,6-diisopropylaniline (Figure 16).[44]

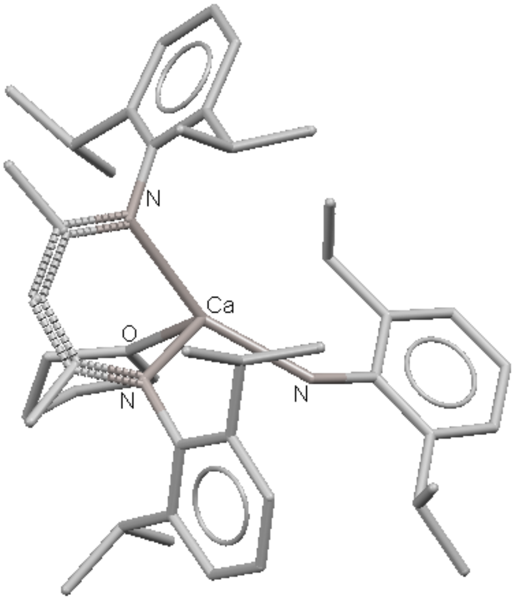


Fig. 16: The molecular structure of Ca((β-diketiminato)(NHDiip))(thf). Hydrogen atoms are omitted for clarity.[44]

Aside from the calcium compound displayed above, there have been no other structures reported with 2,6-diisopropylaniline and the heavier alkaline-earth metals.

Previously, this amine was used in the synthesis of a heteroleptic magnesium trimer, $Mg_3(\mu\text{-NHDipp})_4(N(SiMe_3)_2)_2$ (Figure 17).[45]

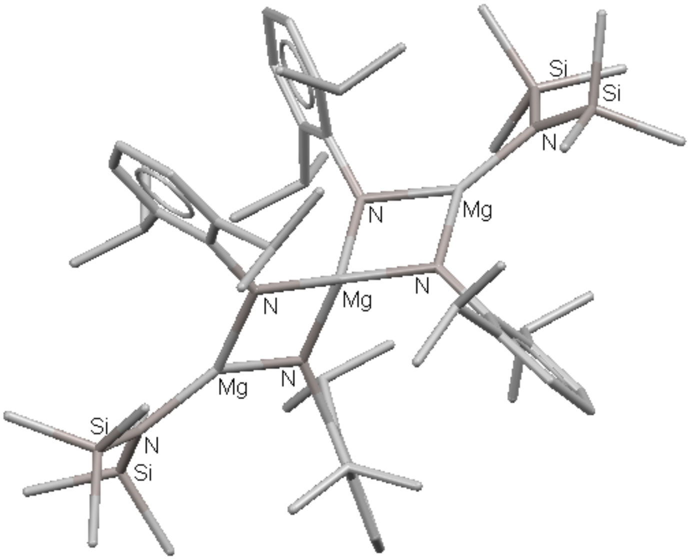


Fig. 17: The molecular structure of $Mg_3(\mu\text{-NHDiip})_4(N(SiMe_3)_2)_2$. Hydrogen atoms are omitted for clarity.[45]

4.2 Synthetic Methods:

The synthesis of the primary amides was attempted using two synthetic routes. The first synthetic route was transamination using the bis(thf) bis(bis(trimethylsilyl))amides and 2,6-diisopropylaniline (Method A). The second route involved desilylation of the bis(thf) bis(bis(trimethylsilyl))amides by HMPA, a strong Lewis base.

4.3 Remarks and Conclusions:

Application of transamination did not afford the target compounds; ^{1}H-NMR data of the reaction mixtures indicated the presence of neutral amine starting material. Several explanations are possible to rationalize this observation. First, perhaps no reaction took place based on the difference in p*K*a between H_2N-Diip (25) and $HN(SiMe_3)_2$ (30). While H_2N-Diip is slightly more acidic than $HN(SiMe_3)_2$ the difference might not be sufficient for a smooth reaction. Alternatively, the presence of the neutral starting amine may be a consequence of hydrolysis by inadvertent introduction of water or air.

Desilylation, which was explored toward the synthesis of the silicon-free silyl amides is still in the early stages of exploration. Initial results indicate that when the calcium amide was treated with a 2.5 equivalent excess of HMPA, the calcium metal center coordinated HMPA and THF. Future work in this synthetic route will explore the effect of various amounts of HMPA.

5. An Investigation of the Modifications of Triphenylbismuth:

Studies on redox transmetallation/ligand exchange reactions utilizing Ph_3Bi as the transmetallating agent suggest this route as an attractive alternative to alkaline-earth metal bis(bis(trimethylsilyl))amides.[35] This route has the capacity to replace the toxic organomercurial reagents that have been previously used. Based on the success of this route for the preparation of $Ae(N(SiMe_3)_2)_2$ (Ae = Ca, Sr, Ba), attempts were made to extend the route, as desribed above, to the preparation of substituted amides of the form $Ae(NR(SiMe_3))_2$ (Ae = Ca, Sr, Ba) where R is an aryl or an alkyl group.

Ph_3Bi is a benign reagent that has solid-state applications as a constituent in warheads and as an anti-fungal agent.[46, 47] It is also being explored as a reagent in solvent-free green chemistry toward the synthesis of bismuth containing compounds.[27-29]

Attempts to prepare the target compounds utilizing Ph_3Bi did not afford the amides, and Ph_3Bi was isolated unaltered. Curiously, the Ph_3Bi isolated from the redox transmetallation/ligand exchange attempts displayed two different polymorphs, one crystallizing in the space group C2/*c*, the other in space group P2(1)/*c*. Ph_3Bi is obtained commercially in the C2 space group.

5.1 Single Crystal X-Ray Diffraction Studies:

Single crystal x-ray diffraction studies were performed on each of the modifications of triphenylbismuth to analyze for the differences between the modifications. The molecular structure of the C2/*c* modification is shown below (Figure 18)[48].

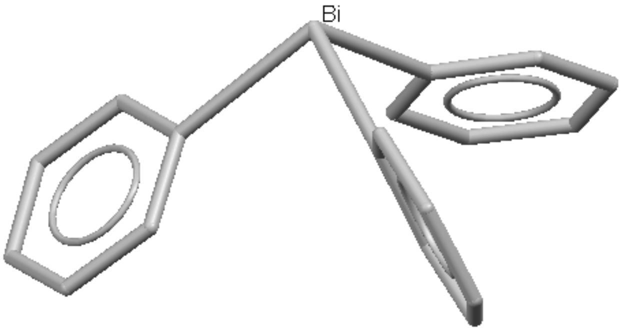


Fig. 18: The molecular structure of the C2/*c* modification of triphenylbismuth. Bi-C = 2.26Å and C-Bi-C = 94.7º, indicating a distorted tetrahedral geometry.[48]

Previously, the C2/*c* modification of triphenylbismuth was analyzed via single crystal x-ray diffraction on two occasions.[48, 49] The physical property data for each study is presented in Table 2. The study performed by Hawley and Ferguson[49] was conducted at room temperature. The Weitze[48] study was conducted at –130 ºC.

Space Group	**C2/*c***[49]	**C2/*c***[48]
Morphology	Colorless blocks	Colorless blocks
a (Å)	27.515(6)	27.70(3)
b (Å)	5.728(2)	5.82(2)
c (Å)	20.273(5)	20.45(3)
β (°)	114.30	114.48
V (Å^3)	2912.1	3000.0

Table 2: The unit cell data for the previously analyzed C2/*c* modifications. $\alpha = \gamma = 90°$.

The unit cell and physical property data for the C2 and P2(1)/*c* modifications of triphenylbismuth is presented in Table 3. This study was conducted at –175 ºC

Space Group	**C2**	**P2(1)/*c***
Morphology	Colorless Needles	Colorless Plates
a (Å)	20.23(3)	15.35(15)
b (Å)	5.73(8)	11.26(11)
c (Å)	13.29(19)	18.42(18)
β (°)	109.74(2)	110.58(2)
V (Å^3)	1452.15	2969.33

Table 3: The unit cell and physical property data for all observed modifications of triphenylbismuth. α = γ = 90°.

The Bi-C bond lengths for the experimentally determined P2(1)/*c* and C2 modification are presented in Table 4. The bond lengths from the previously studied C2/*c* modification are presented in Table 5.

Bond	**P2(1)/*c***	**C2**
Bi-C^1	2.253(3)	2.256(8)
Bi-C^7	2.245(3)	2.294(8)
Bi-C^{13}	2.252(3)	2.307(8)

Table 4: The experimentally determined Bi-C bond lengths for the two modifications of triphenylbismuth. All values are in Å.

Bond	**C2/*c*[49]**	**C2/*c*[48]**
Bi-C^1	2.21(2)	2.237(7)
Bi-C^7	2.25(2)	2.268(8)
Bi-C^{13}	2.25(3)	2.273(8)

Table 5: The previously determined Bi-C bond lengths for the C2/*c* modification of triphenylbismuth. All values are in Å.

The C-Bi-C angles for the experimentally determined P2(1)/*c* and C2 modification are presented in Table 6. The bond angles from the previously studied C2/*c* modification are presented in Table 7.

Bond Angle	P2(1)/*c*	C2
C^{1}-Bi-C^{13}	93.4(7)	91.5(3)
C^{1}-Bi-C^{7}	95.4(7)	92.5(3)
C^{13}-Bi-C^{7}	94.7(3)	92.1(3)

Table 6: The experimentally determined C-Bi-C bond angles for the P2(1)/*c* and C2 modifications of triphenylbismuth. All values are in degrees.

Bond Angle	C2/*c*[48]	C2/*c*[49]
C^{1}-Bi-C^{13}	92(1)	94.3(2)
C^{1}-Bi-C^{7}	96(1)	92.7(2)
C^{13}-Bi-C^{7}	94(1)	94.7(3)

Table 7: The previously determined C-Bi-C bond angles for the C2/*c* modification of triphenylbismuth. All values are in degrees.

The packing patterns for each modification of triphenylbismuth are presented in Figures 19-21.

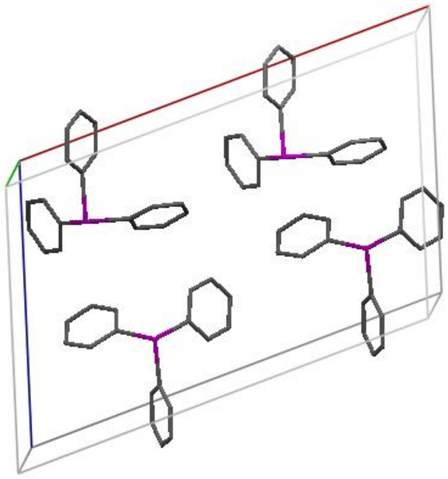


Fig. 19: The packing pattern for the C2 modification of triphenylbismuth.

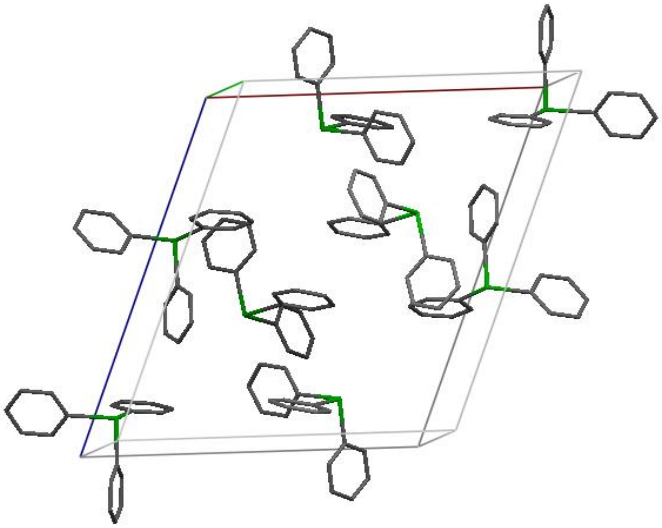


Fig. 20: The packing pattern for the P2(1)/*c* modification of triphenylbismuth.

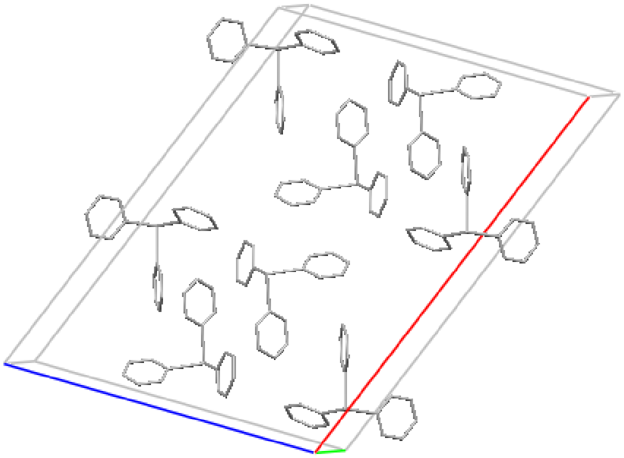


Fig. 21: The packing pattern for the C2/*c* modification of triphenylbismuth.

5.2 X-Ray Powder Diffraction Studies:

Thermally dependent x-ray powder diffraction studies of the three modifications of triphenylbismuth were conducted at low and elevated temperatures. The x-ray powder diffraction data for each modification is shown in Figures 22-24.

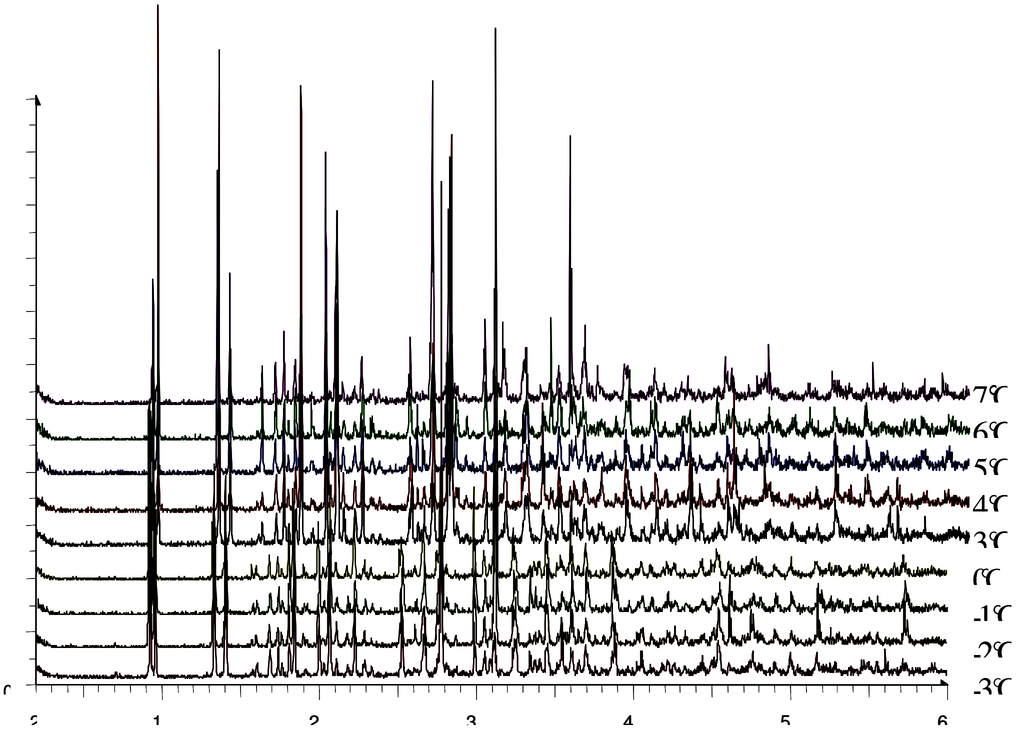


Fig. 22: The thermal x-ray powder diffraction data for the C2 modification of triphenylbismuth. The temperature range is from –30 °C to 70 °C.

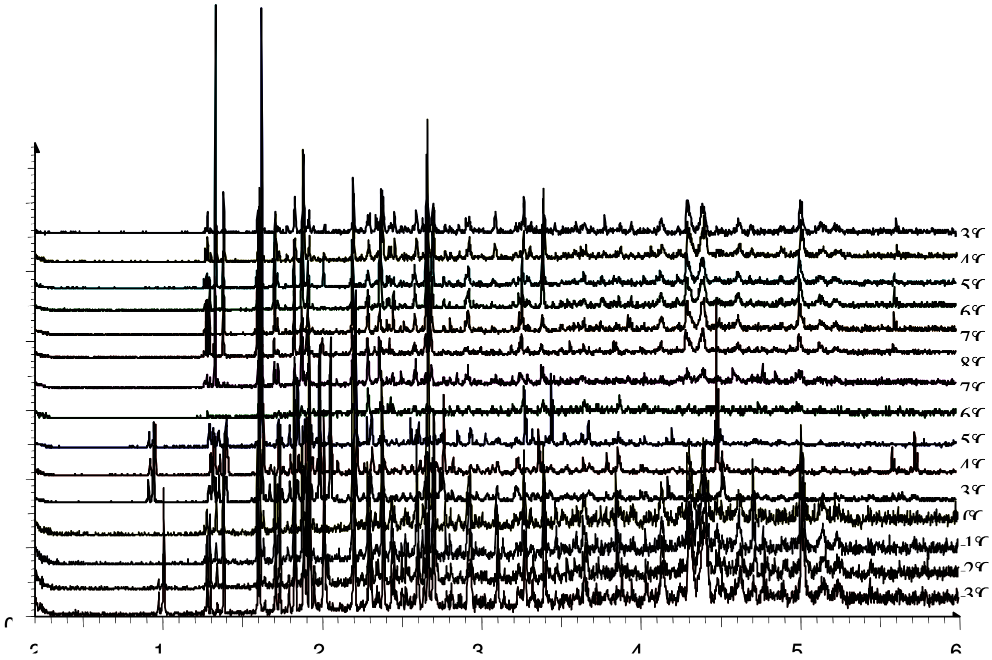


Fig. 23: The thermal x-ray powder diffraction data for the C2/*c* modification of triphenylbismuth. The temperature range is from –30 °C to 80 °C and then back to 30 °C.

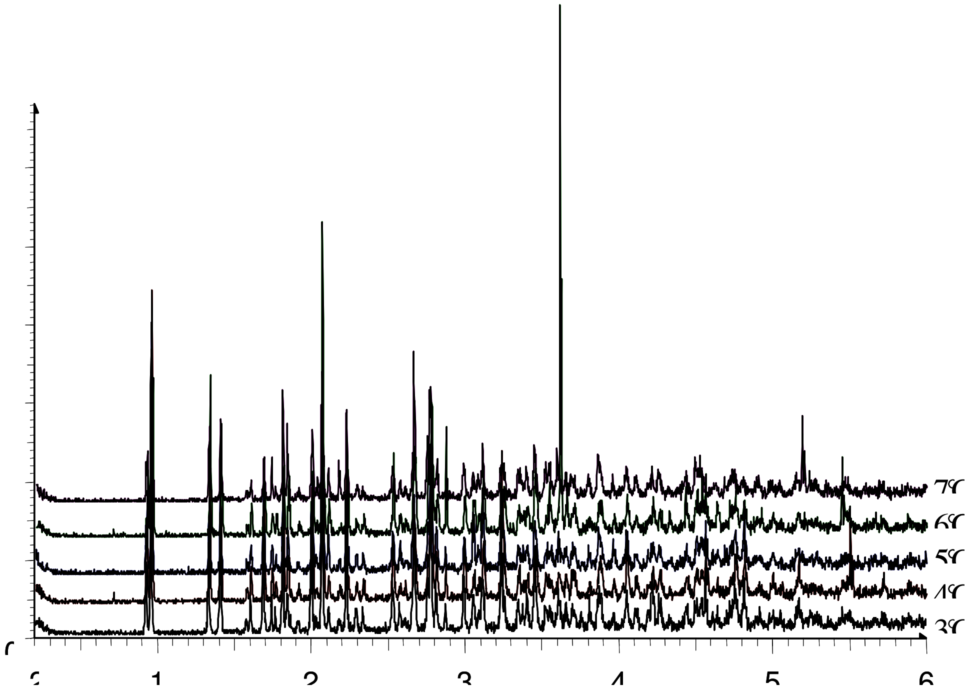


Figure 24: The thermal x-ray powder diffraction data for the P2(1)/*c* modification of triphenylbismuth. The temperature range is from 30 °C to 70 °C.

The three modifications of triphenylbismuth were analyzed using single crystal x-ray diffraction and temperature dependent x-ray powder diffraction to analyze for possible phase transitions. The geometrical data as obtained from single crystal data is almost identical for each modification.

The temperature dependent x-ray powder diffraction data indicates that at elevated temperatures, the samples sublime. The pattern profile at 50 ºC for the C2/*c* modification and 60 ºC for the P2(1)/*c* modification are indicative of the sample stage, indicating sublimation of the sample. Additionally, at 40 ºC for the C2 modification, the change in the pattern indicates a possible phase change, a result that needs to be further investigated by differential scanning calorimetry.

6. Experimental Section:

6.1 General Considerations:

The high reactivity of the alkaline-earth metals and the target complexes requires the use of inert gas (nitrogen or argon atmosphere) conditions. Consequently, all manipulations were carried out using Schlenk-line techniques or a Braun Labmaster dry-box. Solvents were dried and distilled prior to use over a sodium/potassium alloy, followed by three freeze-pump-thaw cycles. Alternatively, solvents were collected from a Vacuum Atmosphere solvent system. N-*tert*-Butyl-trimethylsilylamine was obtained commercially and dried by distillation over KOH. N-adamantylamine was obtained commercially and either dried under vacuum or recrystallized from dry toluene. N-Adamantyl-trimethylsilylamine was prepared according to modified literature procedures.[42]

n-ButylLi, the alkaline-earth metal iodides and triphenylbismuth were obtained commercially and used as received. 2,6-Diisopropylaniline was purchased and dried by distillation over calcium hydride prior to use. KH in a mineral oil dispersion was also purchased and washed with hexane prior to use.

HMPA, TMEDA, and PMDTA were purchased and dried by distillation over calcium hydride prior to use. Mercury was purchased, cleaned *via* filtration and stored in the dry-box.

The alkaline-earth metal bis[bis(trimethylsily)]amides and dibenzyl complexes were synthesized according to literature procedures.[32, 35, 50]

^{1}H-NMR spectra were recorded on a Bruker DPX-300 spectrometer. The NMR spectra were recorded in C_6D_6 at room temperature and referenced to residual solvent resonances.

X-ray crystallographic data was collected using a Siemens SMART system, equipped with 3-circle goniometer and APEX-I CCD detector. Low temperature collections were made possible using a custom built low temperature device from Professor H. Hope (UC Davis). In each collection, monochromated Mo K_α radiation (λ = 0.71073 Å) was used. The data sets nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different ϕ angle, and each exposure covering 0.3° in ω. Repeating the initial frames at the end of the data collection and analyzing the duplicate reflections monitored crystal decay.[51]

X-ray crystallographic studies were conducted by removing the x-ray quality crystals from the Schlenk-tube under a stream of nitrogen and immediately covering them with a layer of viscous hydrocarbon oil. Using a microscope equipped with a polarizing lens, a suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature liquid nitrogen stream of the diffractometer.[52]

X-ray powder diffraction data was collected using a Bruker-AXS D8 Advance automated diffractometer equipped with a TTK 450 heating stage using Cu K_α radiation. The powder was placed in the sample holder, which also acted as the heating system. The step size was 0.02° in 2θ, and the heating rate and cooling rate from room temperature to –30° C and 80° C was 0.5 °C/s. The delay time between reaching the set temperature and measuring the diffraction pattern was 5 minutes. All temperature readings were collected under vacuum.[53]

6.2 Amine Syntheses:

The starting amines, HN(Ad)($SiMe_3$) and HN(Diip)($SiMe_3$) were prepared according to modified literature procedures.[42] The modifications included the use of approximately 10 mL of THF prior to the addition of $ClSiMe_3$ and purification by distillation under vacuum.

HN(Adamantyl)($SiMe_3$):

1-Adamantylamine, 7.65 g (50 mmol) was dissolved in ~250 mL degassed toluene in a 500 mL round-bottom flask equipped with a stir-bar and rubber septum. The solution was placed in an ice bath and 23 mL (50 mmol + 20% excess) n-ButylLi was added *via* glass syringe. THF was added to the reaction mixture until it became bright yellow (approximately 10-15 mL). $ClSiMe_3$, 6.35 mL (50 mmol) was added to the reaction mixture. The reaction was stirred overnight, filtered, and distilled under vacuum, yielding 8.72 g, 77% $HN(Ad)(SiMe_3)$ as a colorless oil. ^{1}H-NMR (C_6D_6), δ (ppm): 1.54, 1.64, 1.95 (s, 15H, Ad); 0.16 (s, 9H, $-SiMe_3$).

$HN(Diip)(SiMe_3)$:

2,6-Diip, 9.43 mL (50 mmol) was added *via* syringe to hexane (250 mL) in a 500 mL round-bottom flask equipped with gas inlet and stir-bar. The flask was cooled in an ice bath. n-ButylLi, 22 mL (50 mmol + 20 % excess) was added *via* syringe to the mixture. THF was added to the mixture until a bright yellow color was obtained (approximately 10 mL). $ClSiMe_3$, 6.35 mL (50 mmol) was added to the mixture via syringe. The following day, the solution was filtered, the solvent was removed under vacuum and the resulting oil was distilled. In some cases, multiple distillations were performed until a colorless oil is obtained. ^{1}H-NMR (C_6D_6), δ (ppm): 7.1 (*mult.*-2H); 7.09 (*p*-H); 3.46 (sept., 2H, -CH); 1.2 (d, 12H, $-CH_3$); 0.11 (s, 9H, $-SiMe_3$).

6.3 General Syntheses:

The following procedures were used to execute the previously mentioned synthetic routes:

Salt Metathesis:

Potassium hydride (2 mmol) was suspended in 20 mL THF. The starting amines, $HNRSiMe_3$ (R = ^{t}Butyl, Adamantyl) (2 mmol) dissolved in 10 mL THF were added *via* cannula. After addition, bubbles, presumably hydrogen were observed. The cloudy, brown reaction mixture was stirred overnight. The following day, the solution was clear and lighter in color. It was added *via* cannula to the alkaline-earth metal iodide (1 mmol, CaI_2, SrI_2, BaI_2) in 20 mL THF cooled to –78 °C using a dry-ice/acetone bath. Almost immediately after addition, a white precipitate was observed. The reaction mixture was stirred overnight. The following day, a light yellow solution with a white precipitate was observed. In some cases, the respective donor was added the third day and the solution was stirred for 30-60 minutes. No visible changes were observed. Otherwise, the reaction mixture was filtered cold, concentrated, and cooled to –23 °C to initiate the formation of crystals. In each instance, the solution was clear and dark yellow.

Transamination:

Bis(thf) bis[bis(trimethylsilyl)]amides of calcium, strontium, and barium (2 mmol) were dissolved in 25 mL toluene giving a light yellow solution. The starting amines, H_2N-Diip or $HNRSiMe_3$ (R = ^{t}Butyl, Adamantyl) (4 mmol) dissolved in 15 mL toluene were added *via* cannula. After addition of the amines, no visible changes were observed. In the case of the H_2Ndiip, the reaction mixture was heated to reflux overnight, cooled to room temperature, filtered, concentrated and cooled to –23 °C to promote the formation of crystals. In all other instances the mixture was stirred overnight, filtered, concentrated, and cooled to –23 °C to promote the formation of crystals. In each instance after work-up, a light yellow solution was observed.

Toluene Elimination:

The alkaline-earth metal dibenzyl compounds of calcium, strontium, and barium (3 mmol) were dissolved in 25 mL THF and cooled to –78 °C using a dry-ice/acetone bath giving a dark red solution. The starting amines, $HNRSiMe_3$ (R = ^{t}Butyl, Adamantyl) (6 mmol) dissolved in 15 mL THF were cooled to –78 °C using a dry-ice/acetone bath for 5 minutes prior to addition and then added *via* cannula. No visible changes were observed and the reaction mixture was still dark red in color. The reaction mixture was left to stir overnight in the dry-ice/acetone bath. The following day the solution was bright red in color. After warming to room temperature, the reaction mixture was concentrated and cooled to –23 °C to promote the formation of crystals.

Redox Transmetallation/Ligand Exchange:

The starting amine, $HNRSiMe_3$ (R = ^{t}Butyl, Adamantyl, Diip) (3.6 mmol), alkaline-earth metal (4.0 mmol), triphenylbismuth (1.2 mmol) and 1 drop of mercury were dissolved in 40 mL of THF.

A. *Reflux Activation:*

The reaction mixture was held for 14-21 days, extracted with hexane, concentrated, and cooled to –23 °C to promote the formation of crystals. Activation of the metal was observed when the solution became black in color. The presence of dark yellow traces of solution on the Schlenk-tube walls was used as an indicator that a forward reaction occurred. Although the solution dark yellow traces were observed, the solution was primarily dark.

B. *Sonication Activation:*

The reaction mixture was sonicated for 7-10 days, filtered, extracted with hexane, and cooled to –23 °C to promote the formation of crystals. The same indicator was used to determine if a forward reaction occurred. Syntheses were also attempted using sonication activation without the use of mercury.

Reactions of bis[bis(trimethylsilyl)]amides with HMPA:

The bis(thf) bis(bis(trimethylsilyl))amides for calcium, strontium and barium (2.5 mmol) were dissolved in 25 mL hexane. To this resulting solution, 2.5 equivalents (6.25 mmol) of HMPA were added *via* syringe, resulting in a color darkening. The reaction mixture was concentrated and cooled to –10 °C to promote the formation of crystals.

6.4 Specific Syntheses:

$Ca[N(^{t}Butyl)(SiMe_3)]_2(tmeda)$:

$HN(^{t}Butyl)(SiMe_3)$, 0.31 g (2 mmol) is dissolved in 20 mL THF. The solution is added *via* cannula to 0.08 g (2 mmol) KH dissolved in 20 mL THF. Gas formation (hydrogen) is observed leading into a light grey solution. Stirring overnight, the solution retains the same color, but is slightly clearer. The reaction mixture is added *via* cannula to 0.29 g (1 mmol) CaI_2 in 20 mL THF that is cooled to –78 °C using a dry-ice/acetone bath. After the solution is added, the formation of precipitate is observed upon removal of the Schlenk-tube from the cold bath. The reaction mixture is stirred overnight, affording a clear, yellow solution and white precipitate. 1.8 mL (1 mmol) TMEDA is added *via* plastic syringe. The reaction is stirred for 30 minutes at room temperature. The solution is filtered, concentrated to ~ 18 mL and stored at –23 °C to promote the formation of crystals. After approximately 48 hours, colorless, block crystals are obtained. A second crop of crystals was obtained by cooling the mother liquor to –10 °C. Analysis is in progress.

$Sr[N(^{t}Butyl)(SiMe_3)]_2(tmeda)$:

$HN(^{t}Butyl)(SiMe_3)$, 0.31 g (2 mmol) are dissolved in 15 mL THF. The solution is added *via* cannula to 0.08 g (2 mmol) KH dissolved in 25 mL THF. Bubbles (hydrogen) and a light grey solution are observed. After stirring overnight the color is retained, but the solution is slightly clearer. The reaction mixture is added *via* cannula to 0.34 g (1 mmol) SrI_2 in 20 mL THF that is cooled to –78 °C using a dry-ice/acetone bath. After the solution is added, the formation of precipitate is observed upon removal of the Schlenk-tube from the cold bath. The reaction mixture is stirred overnight, affording a clear, yellow solution and white precipitate. 1.8 mL (1 mmol) TMEDA is added *via* plastic syringe. The reaction is stirred for 1 h at room temperature. The solution is filtered, concentrated to ~15 mL and stored at –23 °C to promote the formation of crystals. After approximately 3 days, colorless, block crystals are obtained. Analysis is in progress.

$Ba[N(2,6\text{-}^iPr2C_6H_3)(SiMe_3)]_2(thf)_2$:

Barium metal filings, 0.56 g (4 mmol), 0.53 g (1.2 mmol) triphenylbismuth, 0.92 g (3.6 mmol) $HN(Diip)(SiMe_3)$, and 1 drop of Hg are placed in a 100 mL Schlenk-tube equipped with stir-bar. 35 mL THF is added to the mixture *via* cannula, affording a colorless solution with metal filings. The rubber septum is replaced with a glass stopper and the Schlenk-tube is placed in a sonication bath. The reaction mixture is sonicated during the day, between 9:00am to 6:00pm and allowed to sit in the deactivated sonication bath at night. The following day, the reaction mixture becomes black in color. After a sonication period of 6 days, the Schlenk-tube is removed from the sonication bath and the solvent is removed under vacuum. 40 mL of hexane is added giving a black solution with a visible black solid that does not redissolve. The mixture is allowed to stir overnight. The following day the reaction is filtered and concentrated to ~15 mL giving a dark brown solution. The solution is stored at

–23 °C to promote the formation of crystals. After approximately 48 h, crystals are obtained. Analysis is in progress.

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