

Heavy Alkali Metal Amides: Role of Secondary Interactions in Metal Stabilization

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Received September 4, 2009

The coordination chemistry of the bis(diphenylmethylsilyl)amine ligand, HN(SiMePh₂)₂, with the heavy alkali metals potassium and rubidium has been investigated to study its effect on the structure of the resulting compounds. The compounds exhibit extensive intra- and intermolecular M—π interactions, creating 1-D coordination polymers, [K{N(SiMePh₂)₂}]_∞ (1) and [Rb{N(SiMePh₂)₂}]_∞ (3). This motif is maintained in the presence of tetrahydrofuran (THF), as seen in [K{N(SiMePh₂)₂}thf]_∞ (2). In contrast, use of the tridentate PMDTA allows isolation of a monomeric species, K(pmdta)N(SiMePh₂)₂ (4), which exhibits both agostic and M—π interactions. The incorporation of macrocyclic 18-crown-6, results in the formation of a rare non-metal bound amido species, {[K(18-crown-6)N(SiMePh₂)₂]_∞ (5), stabilized by M—π interactions from adjacent [N(SiMePh₂)₂][−] ligands propagating 1-D coordination polymers.

Introduction

Alkali metal amides have vividly demonstrated their significant utility as proton abstractors and versatile ligand transfer reagents. The vast majority of work has focused on lithium derivatives.^{1–15} In contrast, much less is known for the heavier metal congeners, likely a result of more difficult synthetic access because of increased reactivity, and less straightforward starting materials (as compared to the commercially available organolithium solutions). Furthermore,

the high reactivity of the compounds limits solvent choice and/or reaction conditions, a factor further aggravated by the compounds' tendency toward aggregation, and thus limited solubility in non-polar solvents.

The lack of information on heavy alkali metal amides is in stark contrast to the increasing utility of the reagents in synthetic applications, such as salt metathesis chemistry involving alkaline earth metal iodides, or metal exchange reactions.¹⁶

In analogy to organolithium chemistry, a key factor in the reactivity, and thus utility of the heavy alkali metal amides in synthetic chemistry, is a clear understanding of structure–function relations. Even with limited data on hand, it is clear that ligand size, the presence and/or nature of a co-ligand, and the metal size play a major role in determining the reactivity of the compounds.¹⁷

By far, the best studied amido system is based on the [N(SiMe₃)₂][−] ligand.^{18,19} Limited data focused on the replacement of the methyl or trimethylsilyl groups by alkyl and aryl substituents has demonstrated a profound effect on the

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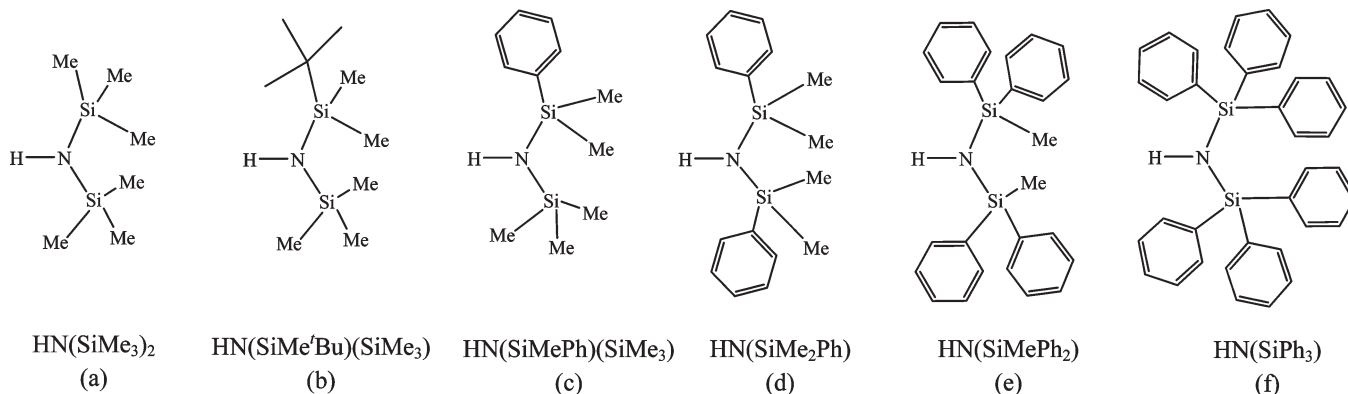


Figure 1. Comparison of amine ligand bulkiness relative to silyl substituent size.

structure and reactivity of the respective alkali metal compounds (Figure 1),^{19–27} but more work is needed to obtain a consistent picture. These ligands, **a–f**, increase in steric bulk as methyl groups are replaced by more bulky alkyl or aryl substituents, and their effect on the overall geometry and coordination patterns for alkali metals is summarized below. Comprehensive data for ligand **e** is provided in here, while chemistry based on ligand **f** is limited to [Li(12-crown-4)]₂[N(SiPh₃)₂]·THF (tetrahydrofuran, THF).²⁷

Heavy alkali metal complexes based on aryl and alkyl substituted silylamides **a–d** (Figure 1) display a dimeric M₂N₂ motif, with a formal metal coordination number of two (Figure 2), as first reported for [KN(SiMe₃)₂]₂ in 1990.¹⁹ The dimeric formulation is based on the inability of these ligands to sterically saturate the metal's coordination spheres in the compounds monomeric form.

As an alternative to oligomerization, the coordination of neutral co-ligands has been effective in achieving steric coordination for large s-block metal centers. Depending on the size and hapticity of the co-ligands, either monomeric (such as in the presence of crown ethers) or dimeric species have been observed (in the presence of thf).^{25,26a} Importantly, independent of the presence of co-ligands, secondary interactions including agostic M···H–C or metal–π interactions are frequently observed as a means to provide further steric saturation of the large metal centers.

The dimeric core is consistent for ligands **a–d**, where agostic interactions from the methyl groups are prevalent (Li–Cs). However, as arene substituents are introduced (**e**, **f**), increased steric bulk, and the capacity for metal–π interactions has a profound effect on the chemistry of the complexes.

First introduced in the late 1980s, HN(SiMePh₂)₂ (**e**) and HN(SiPh₃)₂ (**f**) have demonstrated their ability to prevent aggregation, as shown with Li(thf)₂N(SiMePh₂)₂, Li(12-crown-4)₂N(SiMePh₂)₂, and [Li(12-crown-4)]₂[N(SiPh₃)₂]·THF.^{26,27} Noteworthy, these species do not display secondary interactions (agostic, π), as attributed to the small ionic radii of the Li atom. No data are available for the heavier alkali metals.

To study the effects of metal and ligand size, and the presence of aryl groups capable of M–π interactions on the

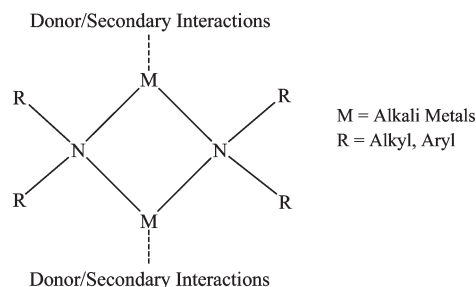


Figure 2. Alkali Metal M₂N₂ core.

structure of the resulting compounds, the HN(SiMePh₂)₂ ligand was used to prepare a family of heavy alkali metal compounds. To examine the effect of neutral co-ligands on the extent of M–π interactions, the compounds were prepared in the absence and presence of various donors, including monodentate THF, tridentate PMDTA (*N'*, *N'*, *N''*, *N''*, *N'''*-pentamethyldiethylenetriamine), and the hexadentate macrocycle 18-crown-6. This allowed isolation of a series of polymeric alkali amides, [K{N(SiMePh₂)₂}]_∞ (**1**), [K{N(SiMePh₂)₂}thf]_∞ (**2**), and [Rb{N(SiMePh₂)₂}]_∞ (**3**), a monomeric species, K(pmdta)N(SiMePh₂)₂ (**4**), as well as a rare example of a non-metal bound amido species, {[K(18-crown-6)N(SiMePh₂)₂]}_∞ (**5**).

Experimental Details

General Procedures. All reactions were carried out under strict inert gas conditions using a Braun Labmaster 100 drybox and/or modified Schlenk techniques. The solvents, including hexanes, toluene, benzene, and THF, were dried over Vac. Atm. Co. dri-solv solvent purifier system and degassed just prior to use. A 30% suspension of KH in mineral oil was washed with hexanes several times to remove the oil, and then the KH was dried in vacuo. KO^tBu and RbO^tBu were synthesized according to literature procedures.²⁸ Commercially available HN(SiMePh₂)₂ and 18-crown-6 were recrystallized prior to use. PMDTA was dried over CaH₂ and distilled prior to use. *n*-Butyllithium (1.6 M solution of a statistical mixture of *n*- and *sec*-butyllithium, *n*Bu/*s*BuLi, in hexane) was obtained from a commercial source and used as received. IR spectra were obtained as a Nujol mull on a Nicolet IR200 spectrometer. ¹H NMR and ¹³C NMR were recorded on a Bruker DPX-300 spectrometer at 25 °C in C₆D₆ and referenced to residual solvent peaks. Melting points were collected in sealed capillary tubes

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Table 1. Crystallographic Data for Compounds 1–5

	1	3	2	4	5
formula	KNSi ₂ C ₂₆ H ₂₆	RbNSi ₂ C ₂₆ H ₂₆	KNOSi ₂ C ₃₀ H ₃₄	KN ₄ Si ₂ C ₃₅ H ₄₉	KNO ₆ Si ₂ C ₃₈ H ₅₀
fw	447.76	494.13	519.86	621.06	712.07
<i>a</i> (Å)	16.166(2)	15.257(3)	11.349(2)	10.4872(7)	20.613(3)
<i>b</i> (Å)	10.144(2)	10.136(2)	17.238(2)	17.5643(11)	8.6680(10)
<i>c</i> (Å)	14.864(2)	15.984(3)	14.884(2)	19.7578(13)	22.354(3)
<i>a</i> (deg)	90	90	90	90	90
<i>b</i> (deg)	104.171(3)	103.66(3)	110.148(2)	94.505(10)	112.638(4)
<i>g</i> (deg)	90	90	90	90	90
<i>V</i> (Å ³)	2363.4(6)	2401.9(8)	2733.8(6)	3628.1(4)	3686.3(8)
<i>Z</i>	4	4	4	4	4
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>d</i> _{calc} (mg/m ³)	1.258	1.366	1.263	1.137	1.283
<i>μ</i> (mm ⁻¹)	0.339	2.174	0.306	0.241	0.255
<i>T</i> (K)	95(2)	95(2)	97(2)	96(2)	96(2)
2θ range (deg)	2.39–28.36	1.37–29.72	1.88–28.39	2.37 to 28.31	2.58 to 28.42
independent reflns	5895	6844	6815	9001	4599
no. of params	271	271	316	379	219
R1, wR2 (all data) ^a	0.0390, 0.0931	0.0340, 0.0690	0.0425, 0.0943	0.0660, 0.1315	0.0439, 0.0905
R1, wR2 (> 2σ) ^b	0.0335, 0.0931	0.0264, 0.0650	0.0362, 0.0902	0.0501, 0.1397	0.0337, 0.0875

$$^a \text{Mo K}\alpha (\lambda = 0.71073 \text{ \AA}). \quad ^b R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; \quad wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

and are uncorrected. Because of the pyrophoric nature of these compounds, satisfactory elemental analysis could not be obtained. This is a well-established problem with alkali and alkaline earth organometallics.^{5,29}

Single-Crystal X-ray Diffraction Studies. X-ray quality crystals for compounds 1–5 were grown as described below. The crystals were removed from the Schlenk tube under a stream of N₂ and immediately covered with a layer of viscous hydrocarbon oil (Infineum). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.³⁰ The intensity data sets for all compounds were collected using a Bruker SMART system, complete with a 3-circle goniometer and an APEX-CCD detector. Data for compounds 1–5 were collected at 95, 95, 97, 96, 96 K, respectively, using a custom built low-temperature device from Professor H. Hope (UC Davis). Further data collection, structure solution, and refinement details have been reported previously.^{31,32} Crystallographic data (excluding structure factors) for the structures reported herein (Table 1) have been deposited in the Cambridge Crystallographic Data Center (CCDC deposition numbers 744719–744723). CIF files can be obtained from the CCDC free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

[K{N(SiMePh₂)₂}]_∞ (1). To a stirred solution of KH (8 mmol, 0.32 g) in THF (30 mL) at 0 °C, HN(SiMePh₂)₂ (1 mmol, 0.41 g) in 10 mL of THF was added dropwise, and the reaction was allowed to stir until completion (cessation of hydrogen evolution). The solvent was removed, and the powder subsequently washed with hexane. The powder was redissolved in benzene. The resulting colorless solution was filtered using a Celite padded filter frit. Suitable crystals (colorless plates) deposited at room temperature within a few days. Yield: 0.38 g, 85%. Mp: 131–135 °C. ¹H NMR (300 MHz, 25 °C, C₆D₆): δH = 0.83 (s, 6H, -SiCH₃Ph₂), 7.26 (m, 8H, *o*-CH), 7.57 (m, 4H, *p*-CH), 7.82 (m, 8H, *m*-CH). ¹³C NMR (300 MHz, 25 °C, C₆D₆): δC = 4.89 (-SiCH₃Ph₂), 129.9 (*m*-CH), 135.1 (*p*-CH), 139.4 (*o*-CH), 149.2 (*i*-C). IR (cm⁻¹): ν 3188 m, 2968 m, 2722 m, 2354 w, 2337 w, 1952 w, 1893 w, 1806 w 1304 m, 1146 s, 1035 w, 732 w.

[Rb{N(SiMePh₂)₂}]_∞ (3). To a stirred solution of RbO⁺Bu (1 mmol, 0.16 g) in hexane (30 mL) at 0 °C, *n*BuLi (1 mmol, 0.61 mL) was added. To this suspension, HN(SiMePh₂)₂ (1 mmol, 0.41 g) in 10 mL of THF was added dropwise, and the reaction was allowed to stir for 24 h. The supernatant was removed via cannula, and the precipitate redissolved in a toluene/THF mixture. The resulting colorless solution was filtered using a Celite padded filter frit. Suitable crystals (colorless rods) deposited at room temperature. Yield: 0.29 g, 58%. Mp: 149–153 °C. ¹H NMR (300 MHz, 25 °C, C₆D₆): δH = 0.85 (s, 6H, -SiCH₃Ph₂), 7.25 (m, 8H, *o*-CH), 7.54 (m, 4H, *p*-CH), 8.04 (m, 8H, *m*-CH). ¹³C NMR (300 MHz, 25 °C, C₆D₆): δC = 4.91 (-SiCH₃Ph₂), 129.2(*m*-CH), 134.7 (*p*-CH), 138.3 (*o*-CH), 148.8 (*i*-C). IR (cm⁻¹): ν 3185 m, 2968 m, 2719 m, 2675 w, 2354 w, 2337 w, 1960 w, 1898 w, 1810 w 1565 m, 1304 m, 1146 s, 1094 w, 732 w.

[K{N(SiMePh₂)₂}thf]_∞ (2). To a stirred solution of KH (8 mmol, 0.32 g) in THF (30 mL) at 0 °C, HN(SiMePh₂)₂ (1 mmol, 0.41 g) in 10 mL of THF was added dropwise, and the reaction was allowed to stir until completion (cessation of hydrogen evolution). Solvent was removed, and the powder was subsequently washed with hexane. The solid residue was redissolved in benzene, and filtered using a Celite padded filter frit. The resulting colorless solution was layered with 5 mL of THF. Suitable crystals (colorless plates) grew at room temperature within a few days. Yield: 0.23 g, 44%. Mp: 119–123 °C. ¹H NMR (300 MHz, 25 °C, C₆D₆): δH = 0.815 (s, 6H, -SiCH₃Ph₂), 1.38 (m, 2H, THF), 3.44 (m, 2H, THF), 7.26 (m, 8H, *o*-CH), 7.57 (m, 4H, *p*-CH), 7.82 (m, 8H, *m*-CH). ¹³C NMR (300 MHz, 25 °C, C₆D₆): δC = 4.90 (-SiCH₃Ph₂), 26.2 (THF), 68.9 (THF), 129.9(*m*-CH), 135.1 (*p*-CH), 139.4 (*o*-CH), 149.2 (*i*-C). IR (cm⁻¹): ν 3423 w, 3188 m, 2975 s 2965 m, 2724 m, 2354 w, 2334 w, 1967 w, 1953 w, 1896 w, 1806 w, 1726 s, 1461 s, 1305 m, 1184 s, 1146 s, 1035 w, 732 w.

K(pmdta)N(SiMePh₂)₂ (4). To a stirred solution of KO⁺Bu (2 mmol, 0.22 g) in hexane (40 mL) at 0 °C, *n*BuLi (2 mmol, 1.22 mL) was added. To this suspension, HN(SiMePh₂)₂ (2 mmol, 0.82 g) in 10 mL of hexane was added. PMDTA (3.5 mmol, 0.73 mL) was added dropwise, and the reaction was allowed to stir for 24 h. The supernatant was removed via cannula, and the precipitate redissolved in hot toluene and filtered using a Celite padded filter frit. Suitable crystals (colorless plates) were grown at -23 °C. Yield: 0.67 g, 0.52%. Mp: 112–115 °C. ¹H NMR (300 MHz, 25 °C, C₆D₆): δH = 0.87 (s, 6H, -SiCH₃Ph₂), 1.40 (s, 3H, -CH₃, PMDTA), 1.69 (s, 8H, -CH₂, PMDTA), 1.74 (s, 12H, -CH₃, PMDTA), 7.24 (m, 8H, *o*-CH), 7.54 (m, 4H, *p*-CH), 8.02 (m, 8H, *m*-CH). ¹³C NMR (300 MHz, 25 °C, C₆D₆): δC = 4.91

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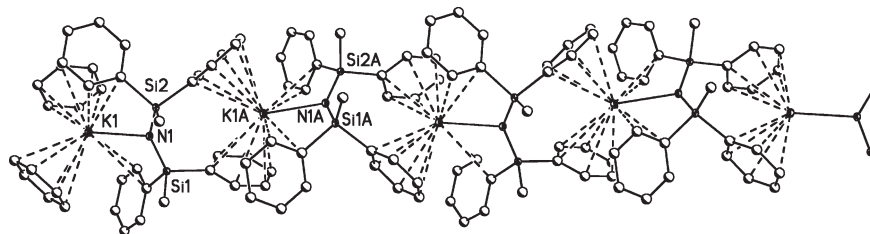


Figure 3. Structure of propagated 1-D coordination polymer $[K\{N(SiMePh_2)_2\}]_\infty$ (**1**). Hydrogen atoms removed for clarity.

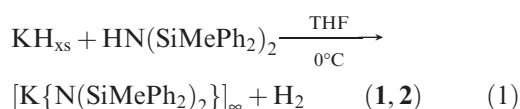
(-SiCH₃Ph₂), 41.5 (-N(CH₃)₂, PMDTA), 45.4 (-NCH₃, PMDTA), 56.1 (-CH₂, PMDTA), 57.3 (-CH₂, PMDTA), 129.9(*m*-CH), 135.4 (*p*-CH), 139.9 (*o*-CH), 149.7 (*i*-C). IR(cm⁻¹): ν 3188 m, 2967 m, 2850 m, 2768 m, 2360 w, w, 1952 s, 1893 s, 1829 s 1771 s, 1304 m, 1160 s, 1094 w, 1033 s, 788 s, 732 w.

[K(18-C-6)N(SiMePh₂)₂]_∞ (5). To a stirred solution of KO^tBu (2 mmol, 0.22 g) in hexane (40 mL) at 0 °C was added *n*BuLi (2 mmol, 1.22 mL). To this suspension, HN(SiMePh₂)₂ (2 mmol, 0.82 g) in 10 mL of hexane and 18-crown-6 (2 mmol, 0.52 g) in 10 mL of hexane were added dropwise, and the reaction was allowed to stir for 24 h. The supernatant was removed via cannula, and the white precipitate was redissolved in THF and filtered using a Celite padded filter frit. Suitable crystals (colorless plates) deposited at -23 °C within a few days. Yield: 0.87 g, 62%. Mp: 179–183 °C. ¹H NMR (300 MHz, 25 °C, C₆D₆): δ H = 0.47 (s, 6H, -SiCH₃Ph₂), 3.17 (s, 24H, 18-C-6), 7.32 (m, 8H, *o*-CH), 7.56 (m, 4H, *p*-CH), 8.12 (m, 8H, *m*-CH). ¹³C NMR (300 MHz, 25 °C, C₆D₆): δ C = 4.90 (-SiCH₃Ph₂), 69.4(18-C-6), 129.9(*m*-CH), 135.1 (*p*-CH), 139.4 (*o*-CH), 149.2 (*i*-C). IR(cm⁻¹): ν 3403 w, 3162 w, 2958 s, 2716 m, 2667 m, 2377 w, 2346 w, 2275 w, 1565 w, 1343 m, 1192 s, 967 s, 861 s, 788 s, 730 s, 449 w.

Results

Synthetic Aspects. Potassium amides are important starting materials in a number of synthetic strategies, including salt metathesis or metal exchange reactions.¹⁶ En route to preparing KN(SiMePh₂)₂, we encountered significant synthetic difficulties. Applications of conventional, stoichiometric reaction conditions were met with unreliable, low product yields, providing a likely rationale on the lack of data for this bulky silylamide. Accordingly, reaction conditions were modified, as outlined below.

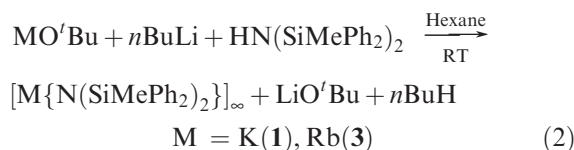
$[K\{N(SiMePh_2)_2\}]_\infty$ (**1**) and $[K\{N(SiMePh_2)_2\}thf]_\infty$ (**2**) were obtained by the treatment of HN(SiMePh₂)₂ with KH in THF (eq 1) at low temperatures (0°) to avoid potential ether cleavage reactions. Excess KH and extended reaction times (2–3 days) were necessary to obtain acceptable product yields, as attributed to the sterically demanding nature of the ligand (Figure 1). Upon removal of THF under vacuum, products were washed with hexane to remove unreacted ligand.²⁵ The resulting powders, were redissolved in benzene, and filtered to ensure removal of any excess KH. In the case of compound **2**, THF, was added to the benzene solution. Both compounds crystallized at room temperature.



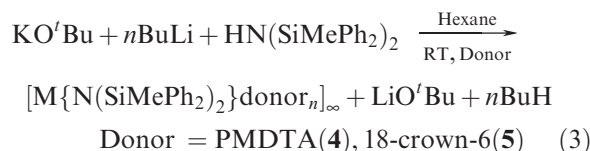
The potassium and rubidium analogues $[Rb\{N(SiMePh_2)_2\}]_\infty$ (**3**), $\{[K(18\text{-crown-6})N(SiMePh_2)_2]\}_\infty$ (**5**), and $K(pmdta)N(SiMePh_2)_2$ (**4**) were prepared using superbase

conditions, involving the treatment of the amine with a mixture of an organolithium and heavy alkali metal alkoxide (eq 2).⁷ This methodology has been used extensively because of easily available starting materials. A significant advantage of this route is the ability to use non-polar solvents, which allows for room temperature operations while avoiding potential ether cleavage reactions.

The reaction products are insoluble in hexane, and typically precipitate as white powders, allowing their easy separation from the soluble side products. Recrystallization from a toluene/THF mixture at room temperature afforded compound **3**, $[Rb\{N(SiMePh_2)_2\}]_\infty$.



In the presence of neutral co-ligands (eq 3), such as the tridentate, PMDTA, the initially insoluble products were redissolved in hot toluene prior to filtration affording $K(pmdta)N(SiMePh_2)_2$ (**4**). In compound **5**, hexadentate 18-crown-6 was dissolved in hexane, and added to the reaction mixture. The insoluble reaction products were redissolved in THF and filtered. Both compounds crystallized at -23 °C.



Structural Aspects. Compounds **1**, **2**, and **3** crystallize at room temperature as unique 1-D coordination polymers, propagated by both intra- and intermolecular metal π -interactions ($M-C(\pi)$) between the phenyl substituents of the bound and neighboring ligands and the large metal centers. In the isostructural compounds **1** (Figure 3) and **3** (Figure 4), aside from the metal–ligand bond, the metal centers are fully encapsulated by these interactions. Compound **4** (Figure 6) crystallizes as a discrete monomer because of the presence of PMDTA, while $\{[K(18\text{-crown-6})N(SiMePh_2)_2]\}_\infty$ (**5**) crystallizes as a rare example of a non-metal bound amido species owing to the strong affinity of 18-crown-6 to potassium metal (Figure 7).

The large ionic radii of heavy s-block metals frequently lead to the presence of agostic interactions ($M \cdots H-C$) from alkyl substituents in addition to metal– π (arene) interactions from either phenyl substituents or the

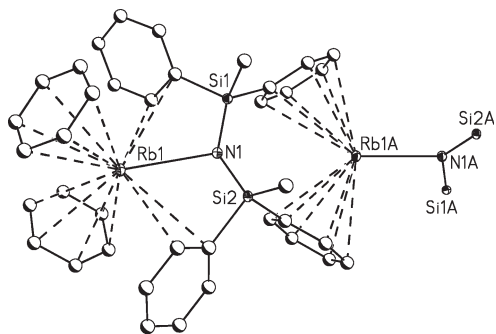


Figure 4. Structure of $[\text{Rb}\{\text{N}(\text{SiMePh}_2)_2\}]_\infty$ (**3**). Hydrogen atoms removed for clarity.

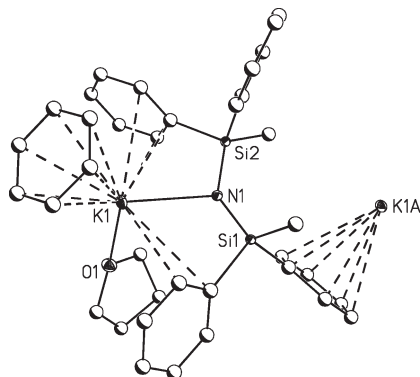


Figure 5. Structure of 1-D coordination polymer $[\text{K}\{\text{N}(\text{SiMePh}_2)_2\}\text{thf}]_\infty$ (**2**). Hydrogen atoms removed for clarity.

presence of aromatic solvents.^{19–25,33–35} Analysis of a family of select heavy alkali metal amides (Table 2) demonstrates that the extent and type of secondary interactions in these compounds depends on the steric demand and substitution pattern of the ligand, the ionic radii of the metal center, and the presence/absence of donor.

As shown in Figure 1, the overall steric demand of the ligand and its ability to shield the metal center increases dramatically by replacing a silyl bound methyl group by a phenyl substituent. The bulky nature of the $\text{HN}(\text{SiMePh}_2)_2$ and its capacity for metal– π interactions prevents dimerization. The ligand orients itself for maximizing metal– π interactions, as indicated by ligand geometry (Figures 3–7). Metal– π interactions typically increase in number as the metal size increases, which is well established for both amido and aryloxo ligands.^{19–25,34,35}

Cut-off values for $\text{M}—\text{C}(\pi)$ contacts ($\text{K}—\text{C}(\pi)$ is 3.57, $\text{Rb}—\pi = 3.62 \text{ \AA}$) ($\text{CN} = 6$, $\text{K} = 1.38$, $\text{Rb} = 1.52 \text{ \AA}$)^{1,35–39} applied in here are in line with previous work, as reported for a series of alkali/alkaline earth metal, alkali aryloxides, alkali/germanium, and alkali/rare earth metal

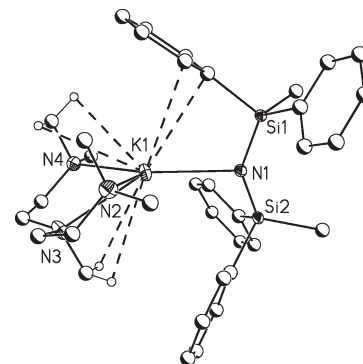


Figure 6. Structure of 1-D coordination polymer $\text{K}(\text{pmdta})\text{N}(\text{SiMePh}_2)_2$ (**4**). Hydrogen atoms removed for clarity.

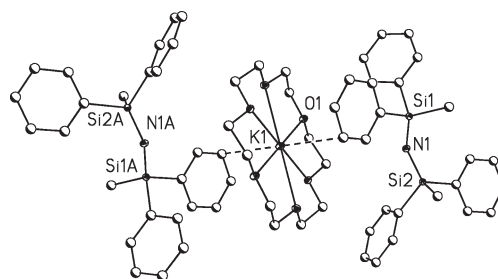


Figure 7. Structure of 1-D coordination polymer $\{[\text{K}(18\text{-crown-6})\text{N}(\text{SiMePh}_2)_2]\}_\infty$ (**5**). Hydrogen atoms removed for clarity.

aryloxo complexes, alkali metal thio- and selenolate terphenyl derivatives, as well as previously reported amido species ($\text{K}—\text{C}(\pi) = 2.775(4)–3.587(2) \text{ \AA}$; $\text{Rb}—\text{C}(\pi) = 3.198(3)–3.642(3) \text{ \AA}$).^{19–25,34–39}

Attesting to the overall strength of $\text{M}—\pi$ versus $\text{M}—\text{co-ligand}$ interactions, thermogravimetric analysis (TGA) studies performed by our group on a series of heterobimetallic alkali/alkaline earth metal aryloxides indicated that despite donor loss, aggregation was not observed; rather, the co-ligand free compounds with an increased degree of $\text{M}—\pi$ interactions were obtained.³⁴

Similar to the reaction products obtained in co-ligand free environments, these observations are in line with experimental and theoretical studies on $\text{K}^+—\text{C}(\pi)$ interactions that have been found to be strong noncovalent binding forces, even in aqueous solutions.^{40–45} These studies concluded that potassium interacts preferably with aromatic systems, including benzene and phenyl substituents, over H_2O coordination thus showcasing the overall ability of these interactions to saturate metal centers and affect geometrical parameters.

In $[\text{K}\{\text{N}(\text{SiMePh}_2)_2\}]_\infty$ (**1**) the $\text{K}—\text{N}$ bond distance of 2.735(6) \AA is similar to that of $[\text{K}\{\text{N}(\text{SiMePh}_2)_2\}\text{thf}]_\infty$ (**2**), (2.737(2) \AA), however slightly longer than in $\text{K}(\text{pmdta})\text{N}(\text{SiMePh}_2)_2$ (**4**), (2.726(2) \AA). The short $\text{K}—\text{N}$ bond in **4** is

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Table 2. Selected Bond Lengths and Secondary Interactions for Potassium Amides^a

ligand	M—N (Å) (av.)	N—Si (Å) (av.)	Si—N—Si (deg)	M—C(π) (Å) (av.)		M···H—C (agostic interactions) (Å) (av.)		structure
				intra	inter	intra	inter	
[K(N(SiMe ₃) ₂) ₂] ¹⁹	2.786(3)	1.682(4)	129.18(18)			3.232	NR	dimer
[KN(SiMe ₃) ₂](Bu-C ₆ H ₅) ₂ ²⁰	2.784(1)	1.669(1)	133.89(7)	3.384(2) η^6	NR	3.381	NR	dimer
[KN(SiMe ₃) ₂ (C ₇ H ₈) ₂] ²¹	2.773(3)	1.674(3)	133.8(2)	NR	NR	NR	NR	dimer
[KN(SiMe ₃) ₂ (Bu)(SiMe ₃) ₂] ²³	2.774(1)	1.682(1)	131.56(6)			3.375(2)	NR	dimer
[K(<i>trans</i> -N-(SiMe ₂ Ph)(SiMe ₃)) ₂] _{∞} ²⁴	2.793(2)	1.672(1)	133.49(13)	3.443(2) η^4	3.285(3) η^3	NR	NR	dimer
[K(N(SiMe ₂ Ph) ₂)(C ₇ H ₈) ₂] ²⁵	2.660(1)	1.672(1)	132.06(7)	3.330(2) η^6	NR		NR	dimer
[K(N(SiMePh ₂) ₂) ₂] _{∞} ¹	2.735(6)	1.663(2)	132.45(7)	3.333(3) η^2	3.313(4) η^6		NR	dimer
[K(N(SiMePh ₂) ₂)(thf)] _{∞} ²	2.738(2)	1.660(2)	136.83(8)	3.410(3) η^2	3.387(4) η^6		NR	dimer
KN(SiMePh ₂) ₂ (pmdta), (4)	2.726(2)	1.653(2)	136.81(10)	3.305(3) η^2		3.251(2)		1-D coord. polymer
{[K(18-crown-6)N(SiMePh ₂) ₂]} _{∞} ⁵		1.649(2)	135.56(9)		3.172(3) η^1			monomer
[Rb(N(SiMePh ₂) ₂) ₂] _{∞} ³	3.035(3)	1.644(3)	132.49(9)	3.353(4) η^2	3.426(4) η^6			1-D coord. polymer

^a NR = not reported.

a clear indication to the importance of the K— π bond, as compound **4** displays a formal coordination number of four, compared to one in **1**. Table 2 compares the relevant bond lengths in similar potassium silyl-substituted amides.

Curiously, upon comparison, compound **1** has a Si—N—Si angle of 132.45(7)°, while for compounds **2** and **4**, the angles widen to 136.83(8)° and 136.81(10)°, respectively; thus the Si—N—Si angle opens as co-ligands coordinate to the metal center. In an attempt to maximize the possible number of both intra- and intermolecular K—C(π) interactions, the ligand orients itself by narrowing the Si—N—Si angle, allowing the phenyl groups to approach the metal center. Two phenyl groups from the metal-bound ligand are oriented toward the metal center, each is involved in two K— η^2 -C(π) intramolecular contacts (3.176(3) and 3.518(3), and 3.226(2) and 3.414(2) Å). The remaining phenyl groups face away from the metal center to completely envelop the exposed side of the neighboring metal in two K— η^6 -C(π) intermolecular contacts, with distances ranging from 3.182(3) to 3.447(2) Å, thus creating a 1-D coordination polymer (Figure 3). All M—C(π) distances are summarized in Table 3.

A stark contrast to this structural motif and a demonstration of ligand bulk on the aggregation properties of potassium amides can be found in the smaller but closely related [KN(SiMe₂Ph)₂(C₇H₈)₂]₂.²⁵ As a result, the cone angle of the ligand is smaller and its ability to enable K—C(π) interactions is significantly reduced. Accordingly, a dimeric structure of the type K₂N₂ is observed, showcasing the effect that the extra phenyl group (instead of methyl) has on the metal saturation. Subsequently, toluene solvent molecules are found to be coordinating to each potassium, with K— η^4 -C(arene) values ranging from 3.231(2)—3.532(2) Å. In addition, both methyl groups and the phenyl ring are oriented toward the metal center offering additional metal—C(π) and agostic interactions (Table 2).

Despite the ionic radii of Rb being slightly larger than K (1.38 vs 1.52 Å, CN = 6),³⁶ [Rb{N(SiMePh₂)₂}] _{∞} (**3**) is isostructural to **1**, with the same number of metal— π interactions ranging from 3.174(3) to 3.564(3) Å for intramolecular Rb— η^2 -C(arene) to 3.253(4) to 3.619(3) Å for Rb— η^6 -C intermolecular interactions (Figure 4) again suggesting that metal— π interactions are a key factor for circumventing dimer formation. While the longer Rb—N bond of 3.033(3) Å is consistent with a larger metal ionic radii, the Si—N—Si angle of 132.49(9)° is comparable to that of [K{N(SiMePh₂)₂}] _{∞} (**1**) (132.45(7)°) (Table 2).

Analysis of compounds **1** and **3** suggests that the large ionic radii of the alkali metals require the presence of secondary interactions to stabilize the metal centers, even in the presence of donors. To evaluate the strength of these interactions, three different co-ligands, 18-crown-6, known to coordinate favorably to potassium, in addition to THF, and the nitrogen based donor, tridentate PMDTA, were employed.

The presence of THF during recrystallization afforded [K{N(SiMePh₂)₂}(thf)] _{∞} (**2**), where despite THF coordination, a 1-D coordination polymer is maintained (Figure 5). The K—N bond length of 2.738(2) is close to that of compound **1**, but the N—Si bonds lengthen as one of the K— η^6 -C intermolecularly coordinated phenyl

Table 3. Metal–Carbon Distances (Å) for Metal– π Interactions in **1–5**

M–C(π) (Å)	M = K				M = Rb	
	1	2	4	5	3	
intramolecular	M–C(7)	3.518(3)	3.573(2)	3.249(3)		3.564(3)
	M–C(8)	3.176(3)	3.331(4)	3.362(3)		3.174(3)
	M–C(20)	3.414(2)	3.235(2)			3.493(3)
	M–C(21)	3.226(2)	3.502(2)			3.188(4)
intermolecular	M–C(1)	3.436(2)	3.299(3)			3.619(3)
	M–C(2)	3.447(2)	3.384(3)			3.578(3)
	M–C(3)	3.378(4)	3.485(4)		3.172(3)	3.385(5)
	M–C(4)	3.248(3)	3.484(4)			3.253(4)
	M–C(5)	3.182(3)	3.388(3)			3.262(3)
	M–C(6)	3.281(3)	3.285(3)			3.414(4)
	M–C(14)	3.308(2)				3.470(3)
	M–C(15)	3.258(3)				3.369(3)
	M–C(16)	3.282(3)				3.385(5)
	M–C(17)	3.315(4)				3.439(5)
	M–C(18)	3.315(4)				3.457(4)
	M–C(19)	3.311(3)				3.487(3)

groups is replaced by a THF molecule. Despite the presence of coordinated donor, M–C(π) interactions continue to aid in saturating the metal centers. M–C(π) interactions for compound **2** range from 3.235(2)–3.573(2) Å for the phenyl groups that are oriented toward the metal center. Only one phenyl group is involved in intermolecular K– η^6 -C interactions with contacts ranging from 3.285(3)–3.485(4) Å. This lowers the number of overall metal– π interactions from 16 in **1** to 10 in **2**, consistent with a K– η^6 -C(π) coordination replaced by a THF co-ligand.

Upon employment of PMDTA, compound **4**, K-(pmdta)N(SiMePh₂)₂, crystallizes as a monomeric species, with one PMDTA molecule saturating the exposed metal coordination sphere. The K–N(lig) bond length is 2.726(2) Å, while the Si–N–Si angle is 136.81(10)° (Figure 6). Interestingly, coordination of the tridentate donor does not prevent metal– π interactions, as intramolecular K– η^2 -C(arene) interactions (3.249(3) and 3.362(3) Å) are maintained (Table 3). Furthermore, several agostic interactions from the PMDTA donor, ranging from 3.169(3) to 3.332(2) Å arise to saturate the metal center. The agostic interactions for **4** are within range for those found in smaller alkyl substituted ligands as summarized in Table 2.

Use of 18-crown-6 gives rise to a rare structure type, a non-metal-coordinated amide. This scenario, along with separated amido ions is very unusual. In **5**, no metal–nitrogen interaction is observed, rather the amide orients itself to allow for a single metal– π interaction to a ligand aryl ring, and formation of 1-D coordination polymer (Figure 7) occurs. The distance for the only K–C(π) interaction is 3.172(3) Å, well within range of accepted K–C(π) interactions. A similar structural motif is observed in [K(18-crown-6)N(Ph)₂] where the ligand orients itself so as to maximize metal– π interactions between the phenyl ring and the potassium metal in lieu of a metal–nitrogen bond.⁴⁶ This leads to intermolecular K– η^6 -C(π) interactions ranging from 3.180(4)–3.391(4) Å under formation of a 1-D polymer.

The motif observed in **5** is in contrast to the separated ion motif in [Li(12-crown-4)₂N(SiPh₃)₂]·THF, where the combination of the smaller metal Li (CN = 6, Li = 0.76, K = 1.38 Å) with the increasing number of phenyl groups on the ligand, leads to complete ion separation.^{27,36} A recent example from this lab further illustrates the delicate balance between the formation of contact versus separated ions with [Mg{N(Diip)(SiMe₃)}hmpa₃][N-(Diip)(SiMe₃)] (Diip = 2,6-diisopropylphenyl) where one amido group is metal-bound while the other one is non-coordinated.⁴⁷

Crown ether coordination to alkali metal amides does not necessarily lead to ion separation as seen by the addition of crown ether to the potassium amides based on the smaller -N(SiMe₃)₂ and -N(SiMe₂Ph)₂ ligands. In these cases, the monomeric species K(18-crown-6)-[N(SiMe₃)₂] and K(18-crown-6)[N(SiMe₂Ph)₂] are obtained.²⁵ As typical for crown ether coordinated monomers, the metal is dislocated slightly from the plane of the crown ether toward the ligand, in the above examples ligand metal coordination is prevented, and no secondary interactions are observed.

Not unexpectedly, the N–Si bond in **5** is rather short (1.649(2)Å). Further, the Si–N–Si angle widens to 135.56(9)°, a trend consistent with [Li(12-crown-4)₂][N-(SiPh₃)₂]·THF and [Mg{N(Diip)(SiMe₃)}hmpa₃][N-(Diip)(SiMe₃)].^{27,47} The shorter N–Si bonds and wider angles are consistent with the negative charge being distributed throughout the free amido ion, and the lower coordination number on nitrogen; this observation is in line with [K(18-crown-6)N(Ph)₂].⁴⁶

Conclusion

Careful consideration of synthetic conditions as well as use of co-ligands has allowed the isolation of a series of heavy alkali bis(diphenylmethylsilyl)amido species. The steric bulk of the ligand greatly impacts overall compound geometry, allowing compounds to deviate from the well established M₂N₂ dimer core for silyl-based amines. This is due to the emergence of extensive intra- and inter M– π interactions from the phenyl substituents of the HN(SiMePh₂)₂ ligand. These interactions arise even in the presence of neutral co-ligands. These findings are in accordance with both experimental and theoretical studies of the strength of these interactions even in aqueous solutions.

In addition, use of the macrocyclic 18-crown-6, combined with the HN(SiMePh₂)₂, has resulted in the isolation of a rare heavy alkali amido species where instead of K–N ligand interaction, the crown-ether coordinated potassium exhibits π -interaction to a phenyl group in the ligand. Further studies of this species will shed light on the implications of structure–function relationships and ion association.

Acknowledgment. The authors gratefully acknowledge support from the National Science Foundation (CHE 0753807). K.D. was supported by Graz University of Technology. Purchase of the X-ray diffraction equipment was made possible with grants from the National Science Foundation (CHE-9527858 and CHE-0234912), Syracuse University, and the W. M. Keck Foundation.

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