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Article

Lanthanum and Alkali Metal Coordination Chemistry of the Bis(dimethylphenylsilyl)amide Ligand

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The coordination chemistry of the bis(dimethylphenylsilyl)amide ligand, $[N(SiMe_2Ph)_2]^{1-}$, with sodium, potassium, and lanthanum has been investigated for comparison with the more commonly used $[N(SiMe_3)_2]^{1-}$ and $[N(SiHMe_2)_2]^{1-}$ ligands. $HN(SiMe_2Ph)_2$ reacts with KH to produce $KN(SiMe_2Ph)_2$, **1**, which crystallizes from toluene as the dimer $[KN(SiMe_2Ph)_2(C_7H_8)]_2$, **2**. The structure of **2** shows that the $[N(SiMe_2Ph)_2]^{1-}$ ligand can function as a polyhapto ligand with coordination from each phenyl group as well as the normal nitrogen ligation and agostic methyl interactions common in methylsilylamides. Each potassium in **2** is ligated by an η^4-toluene, two bridging nitrogen atoms, and an η^2-phenyl, an η^1-phenyl, and an η^1-methyl group. $KN(SiMe_2Ph)_2$ crystallizes from toluene in the presence of 18-crown-6 to make the monometallic complex (18-crown-6)$KN(SiMe_2Ph)_2$, **3**, in which $[N(SiMe_2Ph)_2]^{1-}$ functions as a simple monodentate ligand through nitrogen. The reaction of $HN(SiMe_2Ph)_2$ with NaH in THF at reflux for 2 days generates $Na[N(SiMe_2Ph)_2]$, **4**, which crystallizes as the solvated dimer $\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, **5**. A lanthanide metallocene derivative of $[N(SiMe_2Ph)_2]^{1-}$ was obtained by reaction of $K[N(SiMe_2Ph)_2]$ with $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$. Crystals of $(C_5Me_5)_2La[N(SiMe_2Ph)_2]$, **6**, show agostic interactions between lanthanum and methyl groups of each silyl substituent. The $[N(SiMe_3)_2]^{1-}$ analogue of **3**, (18-crown-6)$KN(SiMe_3)_2$, **7**, was also structurally characterized for comparison.

Introduction

Bulky silylamide ligands, $[N(SiR_3)_2]^{1-}$, have played an important role in the development of low coordinate chemistry for a variety of metals.[1−3] In the f element area, the most commonly used silylamide, $[N(SiMe_3)_2]^{1-}$, has provided rare examples of low coordinate complexes accessible for all the metals, typically in good yield.[3−6] $[N(SiMe_3)_2]^{1-}$ complexes of the lanthanides are structurally interesting[3−6] and have proven to be excellent precursors to a variety of other f element compounds.[3−9] The less sterically crowded $[N(SiHMe_2)_2]^{1-}$ [10−15] has also proven to be useful as a precursor and offers steric flexibility that can be used to advantage.

While the $[N(SiHMe_2)_2]^{1-}$ ligand provides a sterically smaller alternative to $[N(SiMe_3)_2]^{1-}$, silylamide ligands with greater steric bulk, such as $[N(SiMe_2Ph)_2]^{1-}$,[16−19] $\{N[SiMe_2(OSiMe_3)]_2\}^{1-}$,[16] $\{N[SiMe_2(OPh)]_2\}^{1-}$,[16] $[N(SiPh_3)_2]^{1-}$,[17]

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$[N(SiMePh_2)_2]^{1-}$,[20,21] and $[NR(SiMe_3)]^{1-}$ (R = Ph,[22] $C_6H_3{}^iPr_2$-2,6,[22,23] $SiMe_2{}^tBu$,[24] mesityl[24]), are not so readily available. None has been ligated to an f element to our knowledge.

This report addresses the use of the larger silylamide ligand bis(dimethylphenylsilyl)amide, $[N(SiMe_2Ph)_2]^{1-}$, in f element chemistry. A lithium salt of this amide, $Li_2[\mu\text{-}N(SiMe_2Ph)_2]_2$,[16] has been structurally characterized, and iron,[17] copper,[19] gallium,[18] and tin[25] derivatives have been made. Since in synthetic f element chemistry, lithium readily forms "ate" salt adducts,[26,27] sodium and potassium precursors are often preferred. We report here the synthesis and structural characterization of potassium and sodium salts of the $[N(SiMe_2Ph)_2]^{1-}$ ligand as well as the first f element complex of this silylamide. For the latter purpose, the favorable coordination environment of a bis(pentamethylcyclopentadienyl) system was used, and the tetraphenylborate salt, $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$,[28] was employed as an effective precursor.

Experimental Section

The manipulations described below were performed under nitrogen with the rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$[28] and $Y[N(SiMe_3)_2]_3$[29] were made according to the literature. KH and NaH were purchased from Aldrich and washed with hexanes before use. 18-Crown-6 was purchased from Aldrich and placed under vacuum overnight before use. Diphenyltetramethyldisilazane was purchased from Gelest and used as received. Solvents were sparged with argon and dried using GlassContour columns.[30] NMR solvents were dried over sodium potassium alloy, degassed, and vacuum transferred before use. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker 500 MHz and DRX 400 MHz spectrometers. Infrared spectra were recorded as thin-films obtained from benzene using an ASI ReactIR 1000 spectrometer.[31] Elemental analyses were performed by Desert Analytics (Tucson, AZ) or by complexometric titration.[32]

Synthesis of $KN(SiMe_2Ph)_2$, 1, $[KN(SiMe_2Ph)_2(C_7H_8)]_2$, 2, and (18-Crown-6)$KN(SiMe_2Ph)_2$, 3. $HN(SiMe_2Ph)_2$ (17.056 g, 59.73 mmol) was sparged with nitrogen and cannulated into a suspension of KH (2.706 g, 67.47 mmol) in ca. 200 mL of THF. Gas evolution was observed as the solution stirred under nitrogen. After 2 days, solvent was removed in vacuo, and the solids were extracted with toluene. Recrystallization from toluene and subsequent removal of solvent in vacuo gave **1** as a white powder (16.086 g, 83%). ^1H NMR (THF-d_8) δ 0.09 (s, 12 H, $N(Si\mathit{Me}_2Ph)_2$), 7.08 (t, 2H, p-$N(SiMe_2\mathit{Ph})_2$), 7.15 (t, 4H, m-$N(SiMe_2\mathit{Ph})_2$), 7.66 (d, 4H, o-$N(SiMe_2\mathit{Ph})_2$). ^{13}C NMR (THF-d_8) δ 5.9 ($N(Si\mathit{Me}_2Ph)_2$), 127.0 (p-$N(SiMe_2\mathit{Ph})_2$), 127.5 (m-$N(SiMe_2\mathit{Ph})_2$), 134.5 (o-$N(SiMe_2\mathit{Ph})_2$), 152.5 (i-$N(SiMe_2\mathit{Ph})_2$). ^1H NMR (C_6D_6) δ 0.29 (s, 12H, $N(Si\mathit{Me}_2Ph)_2$), 7.21 (m, 6H, $N(SiMe_2\mathit{Ph})_2$), 7.52 (d, 4H, o-$N(SiMe_2\mathit{Ph})_2$). ^{13}C NMR (C_6D_6) δ 6.1 ($N(Si\mathit{Me}_2Ph)_2$), 128.7 ($N(SiMe_2\mathit{Ph})_2$), 133.5 (o-$N(SiMe_2\mathit{Ph})_2$), 149.9 (i-$N(SiMe_2\mathit{Ph})_2$). Anal. Calcd for $C_{16}H_{22}Si_2NK$: C, 59.37; H, 6.80; N, 4.33. Found: C, 59.47; H 7.17; N, 4.33. IR 3069m, 3049w, 2957m, 2362m, 2343w, 1957w, 1891w, 1814w, 1772w, 1749w, 1718w, 1698w, 1687w, 1671w, 1652w, 1556w, 1525m, 1428m, 1251s, 1181s, 1116s, 1000s, 930s, 830s, 830s, 799s, 768s, 726m, 699s cm^{-1}. At −35 °C over 1−3 days, a concentrated sample of **1** in toluene produced colorless X-ray quality crystals of $[KN(SiMe_2Ph)_2(C_7H_8)]_2$, **2**, in the space group $C2/c$. Colorless X-ray quality crystals of **2** in the space group $P\bar{1}$ can be obtained from a concentrated sample of crude **1** in THF. A solution of **1** (110 mg, 0.34 mmol) and 18-crown-6 (91 mg, 0.34 mmol) in ca. 2 mL toluene at −35 °C, over 1−2 days, produced colorless crystals of (18-crown-6)$KN(SiMe_2Ph)_2$, **3**·1/2(C_7H_8).

Synthesis of $NaN(SiMe_2Ph)_2$, 4, and $\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, 5. $HN(SiMe_2Ph)_2$ (1.998 g, 7.00 mmol) was sparged with nitrogen and cannulated onto a suspension of NaH (0.207 g, 8.63 mmol) in ca. 30 mL of THF. The solution was heated at reflux under nitrogen for 2 days. The solvent was removed in vacuo and gummy off-white solids were extracted with toluene. The mixture was filtered, and the toluene was removed to give an off-white solid that was washed with a minimal amount of THF to leave a white solid. This was recrystallized from toluene at −35 °C over 1−3 days to form $\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, **5**. Crystals of **5** were crushed to a powder, dried under vacuum, and recrystallized from methylcyclohexane to give **4** as a white powder (1.739 g, 81%). ^1H NMR (THF-d_8) δ 0.09 (s, 12H, $N(Si\mathit{Me}_2Ph)_2$), 7.08 (t, 2H, p-$N(SiMe_2\mathit{Ph})_2$), 7.15 (t, 4H, m-$N(SiMe_2\mathit{Ph})_2$), 7.67 (d, 4H, o-$N(SiMe_2\mathit{Ph})_2$). ^{13}C NMR (THF-d_8) δ 5.9 ($N(Si\mathit{Me}_2Ph)_2$), 127.1 (p-$N(SiMe_2\mathit{Ph})_2$), 127.5 (m-$N(SiMe_2\mathit{Ph})_2$), 134.6 (o-$N(SiMe_2\mathit{Ph})_2$), 152.2 (i-$N(SiMe_2\mathit{Ph})_2$). ^1H NMR (C_6D_6) δ 0.36 (s, 12H, $N(Si\mathit{Me}_2Ph)_2$), 7.22 (m, 6H, $N(SiMe_2\mathit{Ph})_2$), 7.60 (d, 4H, o-$N(SiMe_2\mathit{Ph})_2$). ^{13}C NMR (C_6D_6) δ 5.7 ($N(Si\mathit{Me}_2Ph)_2$), 128.7, 128.8 ($N(SiMe_2\mathit{Ph})_2$), 133.5 (o-$N(SiMe_2\mathit{Ph})_2$), 145.0 (i-$N(SiMe_2\mathit{Ph})_2$). Anal. Calcd for $C_{16}H_{22}Si_2NNa$: C, 62.48; H, 7.21; N, 4.55. Found: C, 62.44; H 7.55; N, 4.05. IR 3366w, 3015m, 2953s, 2895m, 2358w, 2328w, 1957w, 1884w, 1818w, 1772w, 1749w, 1718w, 1648w, 1590m, 1556m, 1525m, 1428s, 1320m, 1301m, 1251s, 1177s, 1108s, 1050s, 1050s, 1000m, 925s, 845s, 799s, 741s, 699s cm^{-1}.

Synthesis of $(C_5Me_5)_2La[N(SiMe_2Ph)_2]$, 6. $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$ (53 mg, 0.07 mmol) and **1** (21 mg, 0.07 mmol) were combined in ca. 20 mL of toluene and allowed to stir overnight. The solution was filtered, and the solvent was removed in vacuo leaving a white powder. A concentrated solution of the solid in toluene produced colorless X-ray quality crystals over 1−3 days at −35 °C (42 mg, 93%). ^1H NMR (THF-d_8) δ 0.33 (s, 12H, $N(Si\mathit{Me}_2Ph)_2$), 1.97 (s, 30H $C_5\mathit{Me}_5$), 7.23 (m, 6H, $N(SiMe_2\mathit{Ph})_2$), 7.26 (d, 4H, o-$N(SiMe_2\mathit{Ph})_2$). ^{13}C NMR (THF-d_8) δ 3.0 ($N(Si\mathit{Me}_2Ph)_2$), 12.2 ($C_5\mathit{Me}_5$), 122.1 (C_5Me_5), 128.5, 129.3 ($N(SiMe_2\mathit{Ph})_2$), 134.6 (o-$N(SiMe_2\mathit{Ph})_2$), 144.6 (i-$N(SiMe_2\mathit{Ph})_2$). ^1H NMR (C_6D_6) δ 0.44 (s, 12H, $N(Si\mathit{Me}_2Ph)_2$), 2.00 (s, 30H $C_5\mathit{Me}_5$), 7.24 (m, 6H, $N(SiMe_2\mathit{Ph})_2$), 7.62 (d, 4H, o-$N(SiMe_2\mathit{Ph})_2$). ^{13}C NMR (C_6D_6) δ 3.0 ($N(Si\mathit{Me}_2Ph)_2$), 12.2 ($C_5\mathit{Me}_5$), 121.8 (C_5Me_5), 129.2, 129.7

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Table 1. X-ray Data Collection Parameters for $[KN(SiMe_2Ph)_2(C_7H_8)]_2$ (**2**), $\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$ (**5**), $(C_5Me_5)_2La[N(SiMe_2Ph)_2]$ (**6**), and (18-Crown-6)$KN(SiMe_3)_2$ (**7**)

	2	**5**	**6**	**7**
fw	831.52	759.24	693.88	463.81
T (K)	163(2)	163(2)	163(2)	163(2)
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	18.300(5)	11.143(20	10.7007(11)	9.3271(8)
b (Å)	13.331(4)	22.300(4)	14.9335(15)	10.6844(9)
c (Å)	20.992(6)	18.258(3)	21.830(2)	14.9957(12)
α (deg)	90	90	90	104.7620(10)
β (deg)	111.917(4)	103.521(3)	97.307(2)	98.9240(10)
γ (deg)	90	90	90	110.5980(10)
V (Å^3)	4751(2)	4411.1(14)	3460.1(6)	1302.30(19)
Z	4	4	4	2
ρ_{calcd} (Mg/m^3)	1.162	1.143	1.332	1.183
μ (mm^{-1})	0.332	0.188	1.328	0.325
R1 [$I > 2.0\sigma(I)$]	0.0316	0.0634	0.0183	0.0287
wR2 (all data)	0.0853	0.1994	0.0494	0.0792

(N(SiMe$_2$*Ph*)$_2$), 134.4 (*o*-N(SiMe$_2$*Ph*)$_2$), 144.3 (*i*-N(SiMe$_2$*Ph*)$_2$). Calcd for $C_{36}H_{52}Si_2NLa$: La, 20.02. Found: La, 19.8. IR 3367w, 3654w, 3632w, 3370w, 2957m, 2907m, 2856m, 2729w, 2366w, 2343w, 1993w, 1883w, 1816w, 1776w, 1552w, 1428s, 1378m, 1320w, 1247s, 1177s, 1015s, 930s, 834s, 811s, 772s, 718s, 699s cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for 2, 5, 6, and 7. X-ray crystallographic data were obtained by mounting a crystal on a glass fiber and transferring it to a Bruker CCD platform diffractometer. The SMART[33] program package was used to determine the unit cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[34] and SADABS[35] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[36] program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[37] for neutral atoms were used throughout the analysis. Crystallographic data appear in Table 1.

$[KN(SiMe_2Ph)_2(C_7H_8)]_2$, 2. A colorless crystal obtained from toluene of approximate dimensions 0.10 × 0.37 × 0.45 mm^3 was handled as described above. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that the centrosymmetric space group $C2/c$ was correct. Hydrogen atoms were located from a difference Fourier map and refined (x, y, z and U_{iso}). The molecule was located about an inversion center (Z = 4). At convergence, wR2 = 0.0853 and GOF = 1.035 for 364 variables refined against 5748 data. As a comparison for refinement on F, R1 = 0.0316 for those 4674 data with $I > 2.0\sigma(I)$.

A colorless crystal obtained from THF of approximate dimensions 0.22 × 0.25 × 0.30 mm^3 was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Hydrogen atoms were included using a riding model. There were two independent molecules of the formula unit present. One molecule was located in a general position, and the other was located about an inversion center (Z = 3). Least-squares analysis yielded wR2 = 0.2386 and GOF = 1.031 for 731 variables refined against 12488 data (0.80 Å). As a comparison for refinement on F, R1 = 0.0900 for those 7009 data with $I > 2.0\sigma(I)$.

$\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, 5. A colorless crystal of approximate dimensions 0.27 × 0.28 × 0.29 mm^3 was handled as described above. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ which was later determined to be correct. Hydrogen atoms were included using a riding model. Least-squares analysis yielded wR2 = 0.1994 and GOF = 1.028 for 451 variables refined against 8985 data (0.80 Å). As a comparison for refinement on F, R1 = 0.0634 for those 5134 data with $I > 2.0\sigma(I)$.

$(C_5Me_5)_2La[N(SiMe_2Ph)_2]$, 6. A colorless crystal of approximate dimensions 0.29 × 0.30 × 0.32 mm^3 was handled as described above. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ which was later determined to be correct. Hydrogen atoms were located from a difference Fourier map and refined (x, y, z and U_{iso}). At convergence, wR2 = 0.0494 and GOF = 1.044 for 569 variables refined against 8534 data. As a comparison for refinement on F, R1 = 0.0183 for those 7909 data with $I > 2.0\sigma(I)$.

(18-Crown-6)$KN(SiMe_3)_2$, 7. $Y[N(SiMe_3)_2]_3$ (73 mg, 0.13 mmol) in ca. 5 mL THF was added to 18-crown-6 (34 mg, 0.13 mmol) in ca. 5 mL THF with K (5 mg, 0.13 mmol) dropwise, and this mixture was allowed to stir overnight.[38] The solvent was then removed in vacuo. At −35 °C, over 1−3 days, a concentrated sample in diethyl ether produced colorless X-ray quality crystals. A colorless crystal of approximate dimensions 0.08 × 0.11 × 0.15 mm^3 was handled as described above. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0792 and GOF = 1.029 for 253 variables refined against 6291 data. As a comparison for refinement on F, R1 = 0.0287 for those 5614 data with $I > 2.0\sigma(I)$.

Results and Discussion

Synthesis. $KN(SiMe_2Ph)_2$, **1**, was readily synthesized on the gram scale by the addition of $HN(SiMe_2Ph)_2$ to excess KH in THF. A slight excess of KH was used to avoid the need to remove unreacted $HN(SiMe_2Ph)_2$, eq 1. Removal of THF, extraction with toluene, and filtration to separate excess KH gave a toluene solution that provided $KN(SiMe_2Ph)_2$, **1**, as an off white powder after removal of solvent.

$$HN(SiMe_2Ph)_2 + 1.1KH \rightarrow KN(SiMe_2Ph)_2 + H_2 \quad (1)$$

Compound **1** is soluble in THF and toluene, but it is only sparingly soluble in *n*-hexane.

Recrystallization of **1** from toluene gives the toluene complex $[KN(SiMe_2Ph)_2(C_7H_8)]_2$, **2**, Figure 1. Crystals of **2** were also obtained from crystallization of **1** from THF in

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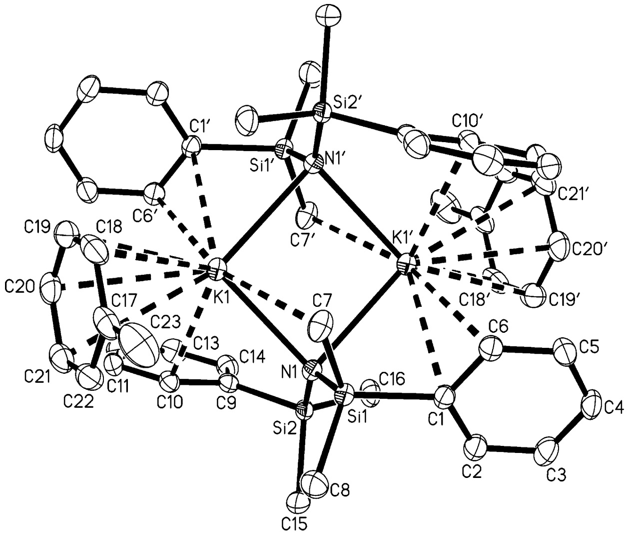


Figure 1. Thermal ellipsoid plot of $[KN(SiMe_2Ph)_2(C_7H_8)]_2$, **2**, with ellipsoids drawn at the 50% probability level.

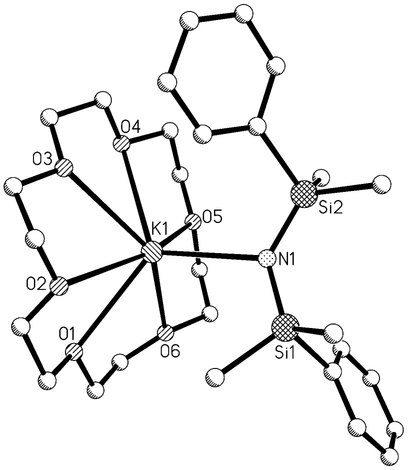


Figure 2. Ball and stick diagram of the structure of (18-crown-6)$KN(SiMe_2Ph)_2$, **3**.

the presence of toluene. In this case, **2** crystallized in a different space group containing two crystallographically independent molecules similar to that obtained from toluene. Crystallization of **1** in the presence of 18-crown-6 yielded (18-crown-6)$KN(SiMe_2Ph)_2$, **3**, Figure 2, which has a structure similar to that of the $[N(SiMe_3)_2]^{1-}$ analogue, (18-crown-6)$KN(SiMe_3)_2$, **7**, Figure 3.

In contrast to the synthesis of **1**, the analogous reaction of $HN(SiMe_2Ph)_2$ with NaH gave poor yields of the sodium salt. It was necessary to heat a THF slurry of NaH and $HN(SiMe_2Ph)_2$ at reflux for 2 days in order to get a significant yield, eq 2.

$$HN(SiMe_2Ph)_2 + 1.1NaH \rightarrow NaN(SiMe_2Ph)_2 + H_2 \quad (2)$$

Upon workup, an off-white gummy powder was obtained that could be purified by washing with THF and recrystallizing from toluene. This gave the solvated dimer $\{(THF)Na[\mu\text{-}\eta^1\text{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, **5**, Figure 4. Unsolvated $NaN(SiMe_2Ph)_2$, **4**, could be obtained by crushing crystals of **5**, drying under vacuum, and crystallizing from methylcyclohexane.

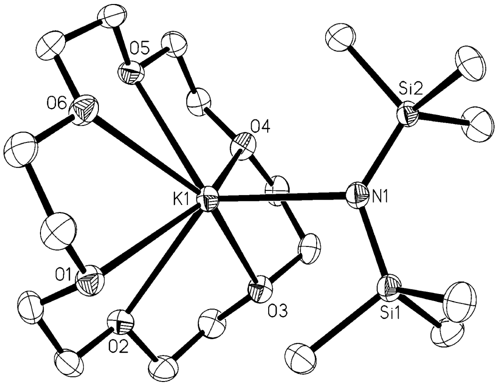


Figure 3. Thermal ellipsoid plot of (18-crown-6)$KN(SiMe_3)_2$, **7**, with ellipsoids drawn at the 50% probability level.

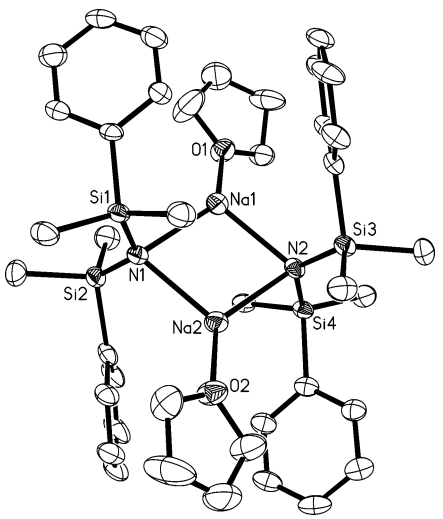


Figure 4. Thermal ellipsoid plot of $\{(THF)Na[\mu\text{-}\eta^1\text{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, **5**, with ellipsoids drawn at the 50% probability level.

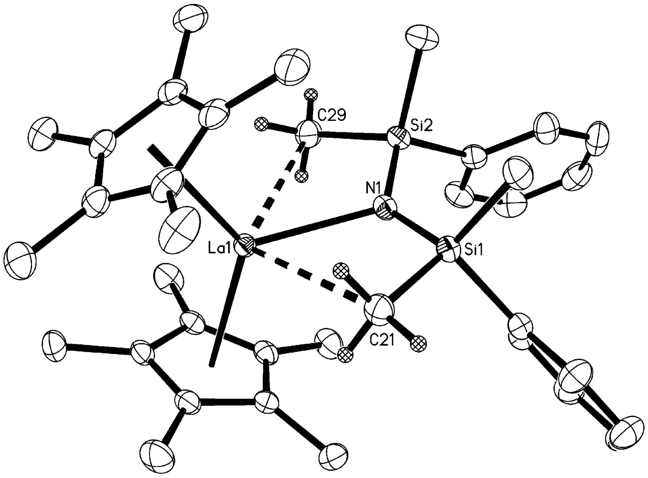
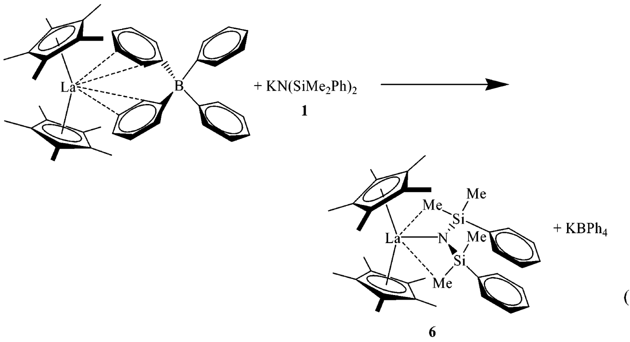


Figure 5. Thermal ellipsoid plot of $(C_5Me_5)_2La[N(SiMe_2Ph)_2]$, **6**, with ellipsoids drawn at the 50% probability level.

To examine the ligation of $[N(SiMe_2Ph)_2]^{1-}$ to a lanthanide in a typical coordination environment, **1** was added to $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$[28] to generate the metallocene complex, $(C_5Me_5)_2La[N(SiMe_2Ph)_2]$, **6**, eq 3, Figure 5. Although **6** could also be made from the reaction of **1** and $(C_5Me_5)_2LaCl_2K(THF)_2$,[39] a precursor to $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$, the reaction product failed to yield a product as



(3)

Table 2. Summary of Selected Bond Lengths (Å) and Angles (deg) for Compounds 2, **5**, **6**, and **7**

	$[KN(SiMe_2Ph)_2(C_7H_8)]_2$ (**2**)		
K(1)−N(1)	2.660(1)	N(1)−K(1)−N(1A)	93.28(4)
K(1)−N(1A)	2.874(1)	K(1)−N(1)−K(1A)	86.72(4)
K(1)−C(19)	3.241(2)	Si(1)−N(1)−Si(2)	132.06(7)
K(1)−C(7)	3.245(2)	Si(1)−N(1)−K(1)	105.87(5)
K(1)−C(10)	3.248(2)	Si(2)−N(1)−K(1)	116.79(6)
K(1)−C(1A)	3.265(2)	Si(1)−N(1)−K(1A)	94.48(5)
K(1)−C(20)	3.265(2)	Si(2)−N(1)−K(1A)	108.23(6)
K(1)−C(6A)	3.343(2)		
K(1)−C(18)	3.497(2)	Si(1)−N(1)	1.672(1)
K(1)−C(21)	3.532(2)	Si(2)−N(1)	1.672(1)
	$\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$ (**5**)		
Na(1)−O(1)	2.298(3)	N(1)−Na(1)−N(2)	99.91(12)
Na(1)−N(2)	2.399(4)	N(1)−Na(2)−N(2)	99.92(12)
Na(1)−N(1)	2.481(4)	O(1)−Na(1)−N(1)	135.17(13)
Na(2)−O(2)	2.302(3)	O(1)−Na(1)−N(2)	117.54(12)
Na(2)−N(1)	2.397(4)	O(2)−Na(2)−N(1)	119.94(13)
Na(2)−N(2)	2.483(3)	O(2)−Na(2)−N(2)	134.03(13)
Si(1)−N(1)	1.685(3)	Si(1)−N(1)−Si(2)	128.4(2)
Si(2)−N(1)	1.682(3)	Si(3)−N(2)−Si(4)	129.0(2)
Si(3)−N(2)	1.679(3)	Si(2)−N(1)−Na(2)	112.47(17)
Si(4)−N(2)	1.686(3)	Si(1)−N(1)−Na(2)	112.71(17)
Na(1)−C(22)	3.196	Si(2)−N(1)−Na(1)	106.04(16)
Na(2)−C(14)	3.190	Si(1)−N(1)−Na(1)	104.95(15)
		Si(3)−N(2)−Na(1)	114.13(17)
		Si(4)−N(2)−Na(1)	111.71(17)
Na(1)−N(1)−Na(2)	80.12(11)	Si(3)−N(2)−Na(2)	108.28(16)
Na(1)−N(2)−Na(2)	80.05(11)	Si(4)−N(2)−Na(2)	100.300(15)
	$(C_5Me_5)_2La[N(SiMe_2Ph)_2]$ (**6**)		
La(1)−Cnt(1)[a]	2.589	Cnt(1)−La(1)−Cnt(2)	130.9
La(1)−Cnt(2)[a]	2.549	Cnt(1)−La(1)−N(1)	116.9
La(1)−N(1)	2.446(1)	Cnt(2)−La(1)−N(1)	112.1
La(1)−C(21)	3.121(2)	Si(1)−N(1)−Si(2)	132.49(7)
La(1)−C(29)	3.388(2)	Si(1)−N(1)−La(1)	110.13(6)
La(1)−H(21A)	3.01(2)	Si(2)−N(1)−La(1)	116.07(6)
La(1)−H(21B)	2.86(2)	N(1)−Si(1)−C(21)	106.80(6)
La(1)−H(29A)	2.95(2)	N(1)−Si(1)−C(22)	116.55(7)
La(1)−H(29B)	3.46(2)	N(1)−Si(2)−C(29)	106.42(7)
Si(1)−N(1)	1.692(1)	N(1)−Si(2)−C(30)	113.39(7)
Si(2)−N(1)	1.703(1)		
	$(18\text{-Crown-}6)KN(SiMe_3)_2$ (**7**)		
K(1)−N(1)	2.760(1)	Si(1)−N(1)−Si(2)	130.47(6)
K(1)−O(1)	2.849(1)	Si(1)−N(1)−K(1)	110.54(4)
K(1)−O(2)	2.961(1)	Si(1)−N(1)−K(2)	116.85(5)
K(1)−O(3)	2.747(1)		
K(1)−O(4)	2.820(1)		
K(1)−O(5)	2.978(1)	Si(1)−N(1)	1.670(1)
K(1)−O(6)	2.895(1)	Si(2)−N(1)	1.665(1)

[a] Cnt(1) is the centroid of the C(1)−C(5) ring, and Cnt(2) is the centroid of the C(11)−C(15) ring.

pure as that in eq 3. This emphasizes the utility of the $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ complexes as synthetic precursors.[28,40, 41]

Structure. The crystal structures of **2**, **3**, **5**, and **6** show that the $[N(SiMe_2Ph)_2]^{1-}$ ligand can ligate metals in several ways. The most conventional structure obtained from this study is that of the crown ether complex, (18-crown-6)$KN(SiMe_2Ph)_2$,[42] **3**, Figure 2. Unfortunately, the crystallographic data were good enough only to determine connectivity for this complex. Its overall structure is analogous to that of the bis(trimethylsilyl) analogue, (18-crown-6)$KN(SiMe_3)_2$, **7**, Figure 3, a complex that did give crystals suitable for a detailed metrical analysis (Table 2).

The next most conventional structure arising from this study was the THF solvate of **4** which crystallizes as the dimer, $\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, **5**, Figure 4. This compound has known $[N(SiMe_3)_2]^{1-}$ analogues: $\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_3)_2]\}_2$,[43] **8**, and $(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_3)_2]_2K(THF)_2$,[44] **9**. However, in contrast to the similarity of complexes **3** and **7**, there are some interesting differences between the structure of **5** and those of **8** and **9** that highlight differences in $[N(SiMe_3)_2]^{1-}$ versus $[N(SiMe_2Ph)_2]^{1-}$ ligation.

In each of these compounds, **5**, **8**, and **9**, the sodium ion is three coordinate due to two bridging nitrogen atoms and a terminal THF. In **8** and **9**, the sodium adopts the expected trigonal planar geometry. However, in **5**, Na(1), N(1), N(2), and O(1) are not coplanar. In fact, O(1) is 0.942 Å (24.2°) out of the NaN_2 plane. The THF is oriented away from the phenyl substituents of the silyl groups as shown in Figure 6. This arrangement puts the ortho carbon atoms C(22) and C(14) within 3.2 Å of Na(1) and Na(2), respectively. This is on the long end of Na−C(arene) distances in the literature.[45,46] The closest analogues of **5** with a Na−C(arene) interaction are $Na[C(SiMe_3)_2(SiMe_2Ph)](TMEDA)$,[47] which has its shortest contacts at 2.934(3) and 2.965(3) Å, and $Na[C(SiMe_3)(SiMe_2Ph)_2](TMEDA)$,[47] which has 2.885(6) and 3.026(5) Å Na−C(arene) lengths. The long Na−C(arene) distance in **5** is notably longer than the shortest Na−C(arene) distance of the similar *trans*-$[Na\{\mu\text{-}N(SiMe_3)(SiMe_2Ph)\}]$,[48] which has a Na−C(arene) distance of 2.686(1) Å. In contrast, the Na−C(arene) distance is comparable to the Yb−C(arene) distance in $Yb(OC_6H_3Ph_2\text{-}2,6)_3(THF)_2$,[49] 2.978(6) Å, which is 3.130 Å when normalized to the radial size of Na.[50]

The Na_2N_2 unit in **5** is planar as it is in **8**, but it is a rectangle in **5** instead of the square found in **8**. The parallel Na(1)−N(1) and Na(2)−N(2) lengths in **5**, 2.481(4) and 2.483(3) Å, respectively, are longer than the Na(1)−N(2) and Na(2)−N(1) distances, 2.399(4) and 2.397(4) Å. In

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(39) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(40) (a) Evans, W. J.; Lee, D. S.; Lie, C.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 5517. (b) Evans, W. J.; Perotti, J. M.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 5204. (c) Evans, W. J.; Perotti, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 3894.

(41) Evans, W. J.; Nyce, G. W.; Forrestal, K. J.; Ziller, W. J. *Organometallics* **2002**, *20*, 1050.

(42) X-ray unit cell parameters for **3** follow: cryst syst, triclinic; space group, $P\bar{1}$; $a = 11.6717(14)$ Å; $b = 11.7444(14)$ Å; $c = 13.7456(17)$ Å; $\alpha = 87.787(2)°$; $\beta = 76.661(2)°$; $\gamma = 72.868(2)°$; V, 1751.2(4) Å^3; $Z = 2$; $\rho = 1.202$ Mg/m^3; final R indices [$I > 2\sigma(I) = 3548$ data], R1 = 0.1480, wR2 = 0.4101.

(43) Karl, M.; Seybert, G.; Harms, K.; Agarwal, S.; Maleika, R.; Stelter, W.; Greiner, A.; Heitz, W.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1301.

(44) Williard, P. G.; Nichols, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 9671.

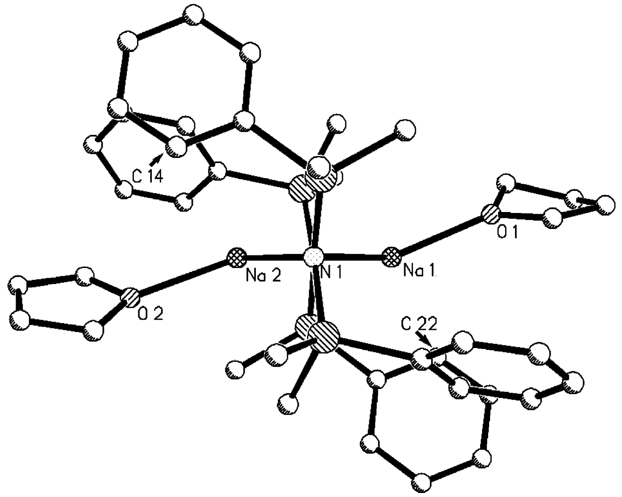

Figure 6. Ball and stick diagram of the structure of $\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, **5**, as seen down the N(1)···N(2) axis.

comparison, the Na−N distances in **8** are 2.398(2) and 2.399(2) Å. Complex **9** is not square due to its mixed metal composition and has a Na(1)−N(1) distance of 2.365(3) Å. Hence, **5** has two Na−N linkages that are significantly longer than usual. The 2.298(3) and 2.302(3) Å Na−O(THF) distances in **5** are comparable to those in **8** and **9**, 2.267(2) and 2.292(3) Å, respectively.

The structure of **5** can also be compared to its dimeric unsolvated lithium analogue, $Li_2[\mu\text{-}N(SiMe_2Ph)_2]_2$,[16] **10**. This complex has a square M_2N_2 unit with Li−N(SiMe$_2$Ph) distances in the narrow range 2.011(4)−2.035(4) Å. Addition of the 0.40 Å difference in ionic radii between four coordinate lithium and sodium[50] gives expected values for Na−N distances close to the short lengths observed in **5**. The structural description of **10** also includes a discussion of Li−C(phenyl) distances that range from 2.53 to 2.77 Å. Again, addition of 0.40 Å puts these in the range of the closest Na−C(phenyl) distances in **5**. In **10**, the C−C phenyl distances for carbons closest to lithium were found to be numerically longer than those distant from the metal, but if such a pattern existed in **5**, it was not discernible within the error limits of the data. Both **5** and **10** suggest that the phenyl group of the $[N(SiMe_2Ph)_2]^{1-}$ ligand can alter the structure compared to $[N(SiMe_3)_2]^{1-}$ complexes.

The structure of $(C_5Me_5)_2La[N(SiMe_2Ph)_2]$, **6**, Figure 5, can also be compared with that of $[N(SiMe_3)_2]^{1-}$ analogues, the $(C_5Me_5)_2Ln[N(SiMe_3)_2]$ complexes (Ln = Sm,[51] **11**; Y,[52,53] **12**; and U,[41] **13**). This provides a good estimate of the differences between $[N(SiMe_2Ph)_2]^{1-}$ and $[N(SiMe_3)_2]^{1-}$ in an f element coordination environment.

In each of the four structures, the nitrogen donor atom is located symmetrically in the metallocene wedge in the (C_5Me_5 ring centroid)−metal−(C_5Me_5 ring centroid) plane. The (C_5Me_5 ring centroid)−M−(C_5Me_5 ring centroid) angles for **6** and **11**−**13** are similar: 130.0°, 132.8°, 132.2°, and 132.4°, respectively. The metal−(C_5Me_5 ring centroid) distances for **6** are 2.589 and 2.549 Å. When values for **11** (2.479 and 2.470 Å), **12** (2.391 and 2.400 Å), and **13** (2.532 and 2.523 Å) are adjusted for the difference in ionic radius[50] and normalized to La, they are numerically smaller: 2.553 and 2.544 Å for **11**, 2.523 and 2.532 Å for **12**, and 2.539 and 2.519 Å for **13**, respectively. The M−N distance in **5**, 2.446(1) Å, is also longer than the values found in **11**, **12**, and **13** (2.301(3), 2.274(5), and 2.352(2) Å, respectively) when these are normalized to La: 2.375, 2.406, and 2.359 Å, respectively. These data are consistent with the larger size of $[N(SiMe_2Ph)_2]^{1-}$ versus $[N(SiMe_3)_2]^{1-}$. Another difference between **6** and **11**−**13** is that the arrangement of the two silicon atoms and lanthanum around nitrogen is not planar in **6**. Lanthanum is 0.563 Å (13.3°) out of the plane and oriented away from the phenyl groups. In contrast, in **11**, **12**, and **13**, each metal is coplanar with the NSi_2 plane. The planar structure had been attributed to interaction of the nitrogen lone pair with the lanthanide to give a shorter than expected Ln-N bond length. The longer La−N in **6** is consistent with the absence of this $LaNSi_2$ coplanarity.

Another difference in the structure of **6** is that a methyl carbon on *each* SiMe$_2$Ph group is oriented toward lanthanum. The La−C distances are 3.121(2) Å for C(21) and 3.388(2) Å for C(29). Refinement of hydrogens attached to these methyl groups gave distances to La of 2.86(2), 2.95(2), 3.01(2), and 3.46(2) Å for H(21B), H(29A), H(21A), and H(29B), respectively. These distances are comparable to the closest M−C(SiMe$_3$) distances in **11**−**13** (3.216, 2.970(6), and 3.197(4) Å, respectively) when normalized to La: 3.296, 3.110, and 3.197 Å, respectively. Metal−hydrogen distances were obtained in the structures of **11** and **12** (2.97 and 2.45 Å, respectively) with distances normalized to La of 3.05 and 2.59 Å, respectively. In **11**−**13**, however, only one methyl group per $[N(SiMe_3)_2]^{1-}$ ligand is oriented toward the metal. In **6**, both methyl groups are within the distances common for agostic interactions.

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(45) Smith, J. D. *Adv. Organomet. Chem.* **1998**, *43*, 267.

(46) For example, the following Na−C(arene) distances have been reported: 2.887 Å for Na(SiPh^{t}Bu$_2$) (Lerner, H.-W.; Scholz, S.; Bolte, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1638); 2.950 Å for $Na_4(HBEt_3)_4$-(mesitylene)$_2$ (Koster, R.; Schussler, W.; Boese, R.; Blaser, D. *Chem. Ber.* **1991**, *124*, 2259); 2.996 Å for Na[Ln(3,5-di-tert-butylpyrazolato)$_4$]-(C_7H_8) (Ln = Tb, Ho) (Deacon, G. B.; Delbridge, E. E.; Evans, D. J.; Harika, R.; Junk, P. C.; Skelton, B. W.; White, A. H. *Chem. Eur. J.* **2004**, *10*, 1193); 2.970 Å for $NaC(SiMe_3)_2(SiMe_2PPh_2)$ (Avent, A. G.; Bonafoux, D.; Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **2000**, 2183); 3.037 Å for Na-(C_6H_5Me)[$Me_3GaSi(SiMe_3)$] (Wochele, R.; Schwarz, W.; Klinkhammer, K. W.; Locke, K.; Weidlein, J. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1963); 3.100 Å for $(THF)_2Na(Ph_2N)_2Sm[N(SiMe_3)_2]_2$ (Karl, M.; Dashti-Mommertz, A.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 355); 3.120 Å for Na(SiPh^{t}Bu$_2$)(THF) (Lerner, H.-W.; Scholz, S.; Bolte, M.; Wagner, M. *Z. Anorg. Allg. Chem.* **2004**, *630*, 443); and 3.259 Å for Na[^{t}BuCuSi(SiMe$_3$)$_3$](C_7H_8) (Klinkhammer, K. W.; Klett, J.; Xiong, Y.; Yao, S. *Eur. J. Inorg. Chem.* **2003**, 3417).

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(50) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(51) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618.

(52) den Haan, K. H.; de Boer, J. L.; Teuben, J. H. *Organometallics* **1986**, *5*, 1726. Two crystallographically independent molecules of **12**; all distances and angles, unless otherwise noted, refer to "molecule 1."

(53) Klimper, M. G.; Görlitzer, H. W.; Tafipolsky, M.; Spiegler, M.; Scherer, W.; Anwander, R. *J. Organomet. Chem.* **2002**, *647*, 236.

Another measure of agostic interactions in silylamides is the distortion of N−Si−C angles. In **6**, the angles involving C(21) and C(29) are 106.80(6)° and 106.42(7)° compared to the values of 116.55(7)° and 113.39(7)° for the methyl carbons pointing away from the metal, C(22) and C(30), respectively.

The most unusual structure in this study was obtained when **1** was crystallized from toluene. This generated a dimer, $[KN(SiMe_2Ph)_2(C_7H_8)]_2$, **2**, Figure 1, in which toluene functions as a ligand. Complex **2** incorporates *all* of the interactions seen in the previous structures; i.e., phenyl and methyl carbons atoms of the $[N(SiMe_2Ph)_2]^{1-}$ ligand are oriented toward the metal as well as the main donor atom, the nitrogen. As in **5** and **10**, the M_2N_2 unit is planar, but in **2**, the M−N distances are even more disparate than in **5**. The 2.660(1) and 2.874(1) Å distances for K(1)−N(1) and K(1)−N(1′), respectively, can be compared to the values of 2.778 and 2.862 Å obtained by adding the 0.38 Å difference in ionic radii between potassium and sodium[50] to the values in **5**.

The next closest approach of a ligand atom to potassium in **2** involves the 3.231(2) Å K(1)−C(19) length of one of the carbon atoms of the toluene. Three other arene carbon atoms are located within 3.6 Å (C(20) 3.265(2) Å; C(18) 3.497(2) Å; C(21) 3.532(2) Å), and the other two ring carbons are found at longer distances, 3.764, and 3.755 Å. Hence, the coordination can be considered to be tetrahapto. The coordination of arenes to potassium cations is not unknown,[54−57] although the coordination of a free arene, such as toluene, is less common.[55] The K−C(arene) distances in **2** are within the range of K−C(arene) distances noted in the literature.[45,58] The K−C(arene) distance is shorter than the 2.978(6) Å Yb−C(arene) distance of $Yb(OC_6H_3Ph_2\text{-}2,6)_3(THF)_2$[49] which is 3.570 Å when normalized to the radial size of K.[50]

Both the methyl and phenyl substituents of the $[N(SiMe_2Ph)_2]^{1-}$ ligand have K−C distances similar to those in the coordinated toluene. Hence, *ipso* carbon C(1) and ring carbon C(6) of the phenyl ring are at distances from K(1′) of 3.265(2) Å and 3.343(2) Å, and the methyl carbon, C(7), is oriented toward K(1) at a distance of 3.245(2) Å. Phenyl carbon C(10) in the other phenyl substituent is oriented toward K(1) at a distance of 3.248(2) Å. With the four described K−C(phenyl) contacts, these four carbons combine to have a total of eight carbons oriented toward potassium in **2**. The shortest Na−C distance in **5**, 3.190 Å, when adjusted for the difference in ionic radius[50] and normalized to K, is 3.57 Å, which is much longer then the eight previously noted K−C bonds in **2**. The Na−N bond lengths in **5**, when adjusted for the difference in ionic radius[50] and normalized to K, are 2.777, 2.779, 2.861, and 2.863 Å, and they are intermediate between the K−N distances of 2.660(1) and 2.874(1) Å.

Unexpectedly, the crude product from a reaction forming **1** also crystallized from THF as a toluene adduct. Hence, even in the presence of a good donor solvent like THF, this toluene ligation is still obtainable. The crystals of **2** that were obtained from THF differed from those obtained from toluene in space group and in the fact that there were two independent molecules in the unit cell with one molecule located in a general position and the other located about an inversion center.[59] The molecule around the inversion center is isomorphous with the dimer obtained from the toluene solution. The other independent molecule is also analogous, but it has more variations in bond distances. The largest one involves the potassium−*ipso* phenyl carbon distance that was found to be 3.192(6) Å.

Conclusion

The potassium salt of the $[N(SiMe_2Ph)_2]^{1-}$ ligand can be readily obtained and is a good precursor for introducing this ligand into the coordination sphere of a lanthanide. The $[N(SiMe_2Ph)_2]^{1-}$ ligand appears to be sterically bulkier than the commonly used $[N(SiMe_3)_2]^{1-}$ amide. In a lanthanide metallocene environment, it coordinates with a slightly longer Ln−N bond and with two agostic methyl interactions rather than one. The $[N(SiMe_2Ph)_2]^{1-}$ ligand can coordinate to metals in a variety of ways. It can function as a simple monohapto ligand as in $(18\text{-crown-}6)KN(SiMe_2Ph)_2$, **3**. However, it can also engage in agostic interactions with its methyl ligands as well as the phenyl ligands. In $(C_5Me_5)_2La[N(SiMe_2Ph)_2]$, **6**, it is trihapto with one nitrogen and two methyl carbons, in $\{(THF)Na[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, **5**, and $\{Li[\mu\text{-}\eta^1{:}\eta^1\text{-}N(SiMe_2Ph)_2]\}_2$, **10**, it is trihapto with one nitrogen and two phenyl carbons, and in $[KN(SiMe_2Ph)_2(C_7H_8)]_2$, **2**, it is pentahapto with one nitrogen, three phenyl carbons, and one methyl carbon. The coordinative versatility of this ligand should make it an excellent choice when the normal modes of bonding of $[N(SiMe_3)_2]^{1-}$ are inadequate to give isolable fully characterizable complexes.

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Supporting Information Available: X-ray diffraction details (CIF) and X-ray data collection, structure solution, and refinement of compounds **2**, **3**, **5**, **6**, and **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(58) Typical K−C(arene) average distances in these complexes are 2.986 Å for $KBPh_4$;[57] 3.512 Å for $\{K[(C_5H_5)_2Nd(OC_6H_3Me_2\text{-}2,6)_2]\}_n$;[54] 3.300 Å for $K[Nd(OC_6H_3{}^iPr_2\text{-}2,6)_4]$;[55] 3.196 Å for $Ph_3CK(THF)(PMDTA)$ (Hoffmann, D.; Bauer, W.; von R. Schleyer, P.; Pieper, U.; Stalke, D. *Organometallics* **1993**, *12*, 1193); 3.275 Å for $[(C_6H_6)KOSiMe_2Ph]_4$ (Fuentes, G. R.; Coan, P. S.; Streib, W. E.; Caulton, K. G. *Polyhedron* **1991**, *10*, 2371); 3.369 Å for $Lu[CH(SiMe_3)_2]_3(\mu\text{-}Cl)K(C_7H_8)_2$;[56] and 3.28 and 3.193 Å for the C_6H_6 and phenyl rings, respectively, in $[K(C_6H_6)]\{K[C(SiMe_3)_2(SiMe_2Ph)]\}$ (Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2679).

(59) X-ray unit cell parameters for **2** crystallized from THF follow: cryst syst, triclinic; space group, $P\bar{1}$; $a = 11.334(5)$ Å; $b = 11.469(5)$ Å; $c = 28.841(12)$ Å; $\alpha = 88.759(7)°$; $\beta = 87.665(7)°$; $\gamma = 72.764(6)°$; V, 3557(2) Å^3; $Z = 3$; $\rho = 1.164$ Mg/m^3; final R indices [$I > 2\sigma(I)$ = 3548 data], R1 = 0.0900, wR2 = 0.2386.