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Reactions of Hypersilyl Potassium with Rare-Earth Metal Bis(Trimethylsilylamides): Addition versus Peripheral Deprotonation

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The scope of hypersilyl potassium, KHyp [Hyp = $Si(SiMe_3)_3$], as a silylation or deprotonation agent for some rare-earth bis(trimethylsilyl)amides has been explored. Thus, the reaction with $Yb\{N(SiMe_3)_2\}_2$ affords the addition product $[K][YbHyp\{N(SiMe_3)_2\}_2]$ (**2**) in high yield, which contains a three-coordinate ytterbium atom, therefore representing the first example of a lanthanide silyl with a coordination number lower than 6. In contrast, deprotonation on the periphery is observed with the tris(amides) $Ln\{N(SiMe_3)_2\}_3$ (Ln = Y, Yb) and compounds of the type $[K][CH_2Si(Me)_2N(SiMe_3)Ln\{N(SiMe_3)_2\}_2]$ (Ln = Y (**3**), Yb (**4**)) are isolated. Crystallization of **3** from a mixture of benzene and heptane afforded the bis(benzene) solvate $[(C_6H_6)_2K][CH_2Si(Me)_2N(SiMe_3)Y\{N(SiMe_3)_2\}_2]$ (**3a**). The reaction between the strong bases ^{n}BuLi/tetramethylenediamine (TMEDA) or ^{t}BuLi with $Y\{N(SiMe_3)_2\}_3$ or $Yb\{N(SiMe_3)_2\}_3$ yielded the deprotonation product $[(tmeda)Li][CH_2Si(Me)_2N(SiMe_3)Y\{N(SiMe_3)_2\}_2]$ (**6**) and the reduction product $[LiYb\{N(SiMe_3)_2\}_3]$ (**7**), respectively. Instead of the expected bimetallic product, the reaction between YbI_2 and 2 equiv of **3** gave the neutral complex $[Y\{CH_2Si(Me)_2N(SiMe_3)\}\{N(SiMe_3)_2\}(thf)]$ (**8**) in good yield. The compounds have been characterized by melting point, elemental analysis, IR spectroscopy, and X-ray crystallography and for selected species by ^1H, ^{13}C, ^{29}Si, and ^{171}Yb NMR spectroscopy. For **3a** and **4**, the nature of the bonding between the carbanionic centers and the lanthanide and potassium cations was studied by density functional theory calculations.

Introduction

The use of charged π-donor ligands and the principle of steric saturation by associated neutral σ-donors or the addition of anionic ligands have dominated chemistry of rare-earth metal organyls[1] for some decades. More recently, however, there has been a growing interest in low-coordinate σ-bonded lanthanide complexes with bulky substituted organyls[2] or bonding to the heavier group 14 elements,[3] the latter still being quite unexplored. Furthermore, the avoidance of coordinating solvents often leads to novel structures and unusual rare-earth metal−ligand interactions. Examples of the latter include agostic-type interactions[4] with alkyl-substituted ligands[5] or metal−π-arene interactions[6] in aryl-substituted ligand systems.[7] In contrast to the growing number of well-characterized σ-bonded rare earth organyls,[2]

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there are only few structurally authenticated lanthanide silyls.[8,9] Part of the interest in these compounds is due to their proposed role in the dehydropolymerization of primary silanes[10] or in the transfer of organyl groups to hydrosilanes.[11] According to recent quantum-chemical calculations,[12] compounds with Ln−Si bonds (Ln = rare-earth metal) might also play a role as active species in the lanthanide-based hydrosilylation of alkenes.[13]

We are interested in the synthesis of “Cp-free” lanthanide silyls with low-coordinate metal atoms that might serve as model compounds for reactivity studies in the above-mentioned catalytic processes. In this paper the scope of hypersilyl potassium, KHyp [Hyp = $Si(SiMe_3)_3$] (**1**), as a silylation or deprotonation agent for some rare earth bis(trimethylsilyl)amides is explored.[14]

Experimental Section

General Procedures. All manipulations were performed by using standard Schlenk techniques under an inert atmosphere of purified argon and solvents freshly distilled from Na wire or $LiAlH_4$. The compounds $YbI_2(thf)_4$[15a] $Yb\{N(SiMe_3)_2\}_3$, $Y\{N(SiMe_3)_2\}_3$,[15b] and $Si(SiMe_3)_4$[15c] were synthesized according to known literature procedures. Donor-free $Yb\{N(SiMe_3)_2\}_2$ was obtained by thermal desolvation of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$.[15d] NMR spectra were recorded on Bruker AM200, AC250, or AM400 instruments and referenced to solvent resonances (^1H, ^{13}C) or $[YbCp^*_2(thf)_2]$.[16] IR spectra (Nujol mull, CsBr plates) have been obtained in the range 4000−200 cm^{-1} with a Perkin-Elmer paragon 1000 PC spectrometer. Melting points were determined under Ar atmosphere in sealed glass tubes.

[KHyp] (1). According to ref 17 a suspension of $Si(SiMe_3)_4$ (10.3 g, 32.1 mmol) and KO*t*Bu (3.75 g, 33.4 mmol) in 25 mL of THF was stirred for 6 h, whereafter all volatile materials were removed under reduced pressure from the resulting deep yellow solution. The remaining solid was heated to 55 °C in a vacuum for 4 h. The crust of the obtained material was broken up, and heating in a vacuum was continued for another 1 h. The resulting gray pyrophoric powder was recrystallized from a benzene/*n*-heptane (1:2) mixture to afford big colorless crystals of **1** in 52% yield (4.79 g, 16.7 mmol). ^1H, ^{13}C, and ^{29}Si NMR spectroscopic data are in accordance with the published values.[18]

$[KYbHyp\{N(SiMe_3)_2\}_2]$ (2). A solution of KHyp (0.45 g, 1.57 mmol) in 10 mL of a benzene/*n*-heptane mixture was added at ambient temperature to $Yb\{N(SiMe_3)_2\}_2$ (0.78 g, 1.58 mmol) in 10 mL of *n*-pentane, and stirring was continued for 2 h. *n*-Pentane and part of the benzene was removed under reduced pressure to incipient crystallization, whereafter the precipitate was redissolved by warming with a heat gun. Stirring was then discontinued, and the solution was cooled to room temperature over several hours to give large deep orange crystals of **2**, which were suitable for X-ray crystallographic studies. A further crop of crystals was obtained by workup of the mother liquor. Yield: 1.01 g (1.29 mmol, 82%). Mp: crystals gradually darken above ca. 195 °C and decompose to a black liquid above 245 °C. ^1H NMR (250.1 MHz, benzene-d_6): δ 0.19 (s, 36H, $N(SiMe_3)_2$), 0.57 (s, 27H, $Si(SiMe_3)_3$). ^{13}C NMR (62.9 MHz, benzene-d_6): δ 6.5 (s, $^1J_{SiC}$ = 52.3 Hz, $N(SiMe_3)_2$), 6.7 (s, $^1J_{SiC}$ = 41.0 Hz, $Si(SiMe_3)_3$). ^{29}Si NMR (39.8 MHz, benzene-d_6): δ −148.6 (s, $^1J_{SiYb}$ = 716.1, $^1J_{SiSi}$ = 27.9 Hz, $\mathit{Si}(SiMe_3)_3$), −13.9 (s, $^1J_{SiC}$ = 52.2, $^2J_{SiYb}$ = 5.0 Hz, $N(\mathit{Si}Me_3)_2$), −4.7 (s, $^1J_{SiC}$ = 40.5, $^1J_{SiSi}$ = 27.9, $^2J_{SiYb}$ = 8.9 Hz, $Si(\mathit{Si}Me_3)_3$). ^{171}Yb NMR (70.1 MHz, benzene-d_6): δ 1057 (s, $w_{1/2}$ = 100 Hz). IR (Nujol, cm^{-1}): 1253 sh, 1244 vs, 1237 sh, 1224 sh, 1025 vs br, 864 vs, 822 vs br, 758 s, 743 s, 724 s, 667 s, 619 s, 605 m, 580 m, 466 w, 437 m, 430 m. Anal. Calcd for $C_{21}H_{63}KN_2Si_8Yb$: C, 32.31; H, 8.13; N, 3.59. Found: C, 31.88; H, 8.07; N, 3.63.

$[K][CH_2Si(Me)_2)N(SiMe_3)Y\{N(SiMe_3)_2\}_2]$ (3) and **$[K(C_6H_6)_2][CH_2Si(Me)_2)N(SiMe_3)Y\{N(SiMe_3)_2\}_2]$ (3a).** A solution of KHyp (1.08 g, 3.77 mmol) and $Y\{N(SiMe_3)_2\}_3$ (2.15 g, 3.77 mmol) in 30 mL of toluene was stirred at ambient temperature for 5 d, whereafter all volatile materials were removed under reduced pressure. The remaining solid was extracted two times with 10 mL of *n*-pentane and was dried under vacuum to afford the solvent-free product **3** as a white powder in 80% yield (1.83 g). Colorless needles of the solvate **3a**, which were suitable for X-ray crystallographic studies, were grown from a *n*-heptane/benzene (20:1) mixture at −60 °C. Because crystals of **3a** rapidly loose coordinated benzene, the following characterization was performed with the

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Table 1. Selected Crystallographic Data for Compounds **2**, **3a**, **4**, and **6**−**8a**

param	**2**	**3a**	**4**
formula	$C_{21}H_{63}KN_2Si_8Yb$	$C_{30}H_{65}KN_3Si_6Y$	$C_{18}H_{53}KN_3Si_6Yb$
molecular mass	780.6	764.4	692.3
color, habit	orange, block	colorless, needle	pale yellow, block
cryst size (mm)	0.50 × 0.40 × 0.35	0.55 × 0.15 × 0.10	0.40 × 0.35 × 0.30
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	21.048(5)	9.950(4)	11.715(2)
b (Å)	12.557(2)	11.856(5)	16.888(3)
c (Å)	17.440(4)	19.285(6)	19.192(3)
α (deg)		82.05(3)	67.365(13)
β (deg)	115.260(12)	84.44(3)	80.343(14)
γ (deg)		82.38(3)	77.379(14)
V (Å^3)	4168.4(16)	2226.1(14)	3405.1(10)
Z	4	2	4^b
d_{calc} (g/cm^3)	1.244	1.140	1.350
μ (cm^{-1})	25.86	15.86	30.91
2θ range (deg)	2−56	3−52	4−55
collcd data	10 213	9287	16 380
unique data/R$_{int}$	9953/0.049	8750/0.046	15 616/0.047
data with $I > 2\sigma(I)$ (N_o)	7135	6378	12 470
no. of params (N_p)	322	485	646
no. of restraints	0	19	31
R1 ($I > 2\sigma(I)$)^c	0.030	0.051	0.040
wR2 (all data)^d	0.071	0.119	0.096
GOF^e	0.881	1.175	1.166
resid dens (e/Å^3)	1.52/−1.48	0.37/−0.39	1.61/−1.22

param	**6**	**7**	**8**
formula	$C_{24}H_{69}LiN_5Si_6Y$	$C_{18}H_{54}LiN_3Si_6Yb$	$C_{16}H_{43}N_2OSi_4Y$
molecular mass	692.2	661.2	480.8
color, habit	colorless, block	orange-red, prism	colorless, plate
cryst size (mm)	0.75 × 0.70 × 0.45	0.40 × 0.35 × 0.30	0.55 × 0.30 × 0.15
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	12.265(4)	8.850(2)	11.232(4)
b (Å)	13.418(5)	11.720(3)	20.641(6)
c (Å)	13.450(5)	16.363(4)	11.872(3)
α (deg)	93.53(2)	96.46(2)	
β (deg)	99.65(2)	95.80(2)	99.03(2)
γ (deg)	100.15(2)	102.32(2)	
V (Å^3)	2138.5(13)	1633.9(7)	2718.2(13)
Z	2	2	4
d_{calc} (g/cm^3)	1.075	1.344	1.175
μ (cm^{-1})	15.51	30.92	23.28
2θ range (deg)	2−54	3−55	4−50
collcd data	9764	7967	5135
unique data/R$_{int}$	9324/0.052	7483/0.041	4722/0.085
data with $I > 2\sigma(I)$ (N_o)	6926	6148	2142
no. of params (N_p)	367	281	230
no. of restraints	0	0	5
R1 ($I > 2\sigma(I)$)^c	0.053	0.033	0.046
wR2 (all data)^d	0.126	0.082	0.100
GOF^e	1.198	0.963	0.736
resid dens (e/Å^3)	0.68/−0.60	1.18/−1.14	0.37/−0.33

[a] All data were collected at either 203 K (**8**) or 173 K (all other compounds), using Mo Kα (λ = 0.710 73 Å) radiation. [b] Two independent molecules. [c] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [e] $GOF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

solvent-free compound. Mp: partly melts above ca. 145 °C and decomposes with gas evolution above 255 °C. ^{1}H NMR (250.1 MHz, benzene-d_6): δ −1.27 (d, $^2J_{HY}$ = 2.6 Hz, 2H, YCH$_2$), 0.13 (s, 6H, SiMe$_2$), 0.56 (s, 9H, NSiMe$_3$), 0.57 (s, 36H, N(SiMe$_3$)$_2$). ^{13}C NMR (62.9 MHz, benzene-d_6): δ 5.9 (q, $^1J_{CH}$ = 116.5, $^1J_{SiC}$ = 52.9 Hz, N(SiMe$_3$)$_2$), 6.1 (q, $^1J_{CH}$ = 116.5, $^1J_{SiC}$ = 53.4 Hz, NSiMe$_3$), 8.2 (qd, $^1J_{CH}$ = 115.7, $^3J_{YC}$ = 1.8, $^1J_{SiC}$ = 50.0 Hz, SiMe$_2$), 23.6 (td, $^1J_{CH}$ = 120.2, $^1J_{YC}$ = 22.9 Hz, YCH$_2$). ^{29}Si NMR (79.5 MHz, benzene-d_6): δ −26.1 (d, $^2J_{SiY}$ = 3.9 Hz, SiMe$_2$), −13.5 (s, NSiMe$_3$), −12.0 (s, $^1J_{SiC}$ = 52.8 Hz, N(SiMe$_3$)$_2$). IR (Nujol, cm^{-1}): 1262 sh, 1249 vs, 1084 m, 991 vs, 956 vs, 883 sh, 863 sh, 831 vs br, 774 s, 754 s, 718 ms, 681 sh, 661 s, 611 sh, 601 s, 425 m, 397 ms. Anal. Calcd for $C_{18}H_{53}KN_3Si_6Y$: C, 35.55; H, 8.78; N, 6.91. Found: C, 34.99; H, 8.58; N, 6.88.

[K][CH$_2$Si(Me$_2$)N(SiMe$_3$)Yb{N(SiMe$_3$)$_2$}$_2$] (4). A solution of KHyp (0.31 g, 1.09 mmol) and Yb{N(SiMe$_3$)$_2$}$_3$ (0.71 g, 1.09 mmol) in 30 mL of toluene was stirred at ambient temperature for 5 d, whereafter all volatile materials were removed under reduced pressure. Crystallization from hot *n*-heptane afforded a mixture of pale yellow **4** (ca. 90%) and purple KYb{N(SiMe$_3$)$_2$}$_3$ (**5**) (ca. 10%) as crystalline material. Some of the crystals were isolated and examined by X-ray crystallography. The remaining material was purified by repeated crystallization at −20 °C from a *n*-pentane/toluene (3:1) mixture to give analytically pure **4** as pale yellow crystals. Yield: 0.22 g (0.32 mmol, 29%). Mp: decomposes above 150 °C. Anal. Calcd for $C_{18}H_{53}KN_3Si_6Yb$: C, 31.23; H, 7.72; N, 6.07. Found: C, 30.98; H, 7.65; N, 6.10.

[Li(tmeda)][$CH_2Si(Me)_2)N(SiMe_3)Y\{N(SiMe_3)_2\}_2$] (6). A 2.5 M solution of ^{n}BuLi in hexanes (1.18 mL, 2.95 mmol) was added to a stirred suspension of $Y\{N(SiMe_3)_2\}_3$ (1.59 g, 2.79 mmol) and TMEDA (0.44 mL, 2.95 mmol) in 15 mL of *n*-heptane. The mixture was heated to 50 °C for 4 h, and the resulting solution was cooled in a 0 °C fridge overnight. A colorless crystalline precipitate was obtained in 76% yield (1.47 g, 2.12 mmol). Mp: 295−297 °C (dec). ^{1}H NMR (250.1 MHz, benzene-d_6): δ −0.40 (s br, 2H, YCH_2), 0.44 (s, 6H, $SiMe_2$), 0.48 (s, 9H, $NSiMe_3$), 0.51 (s, 36H, $N(SiMe_3)_2$), 1.65 (s, 12H, NMe_2), 1.69 (s, 4H, NCH_2). ^{13}C NMR (62.9 MHz, benzene-d_6): δ 6.0 (s, $N(SiMe_3)_2$), 6.4 (s, $NSiMe_3$), 8.0 (d, $^3J_{YC}$ = 1.5 Hz, $SiMe_2$), 22.2 (d, $^1J_{YC}$ = 24.4 Hz, YCH_2), 46.0 (s, NMe_2), 56.6 (s, NCH_2). ^{29}Si NMR (79.5 MHz, benzene-d_6): δ −26.2 (d, $^2J_{SiY}$ = 3.4 Hz, $SiMe_2$), −13.4 (s, $NSiMe_3$), −12.0 (s, $N(SiMe_3)_2$). Anal. Calcd for $C_{24}H_{69}LiN_5Si_6Y$: C, 41.64; H, 10.05; N, 10.12. Found: C, 41.33; H, 9.98; N, 10.15.

[$LiYb\{N(SiMe_3)_2\}_3$] (7). With stirring, a 1.6 M solution of ^{t}BuLi in *n*-pentane (0.80 mL, 1.28 mmol) was added to a solution of $Yb\{N(SiMe_3)_2\}_3$ (0.78. g, 1.19 mmol) in 30 mL of *n*-heptane. Stirring was continued for 16 h, whereafter approximately half of the solvent was removed under reduced pressure. Storage of the resulting red solution in a −60 °C fridge overnight afforded deep orange crystals of **7** in 67% yield (0.53 g, 0.80 mmol). ^{1}H NMR (250.1 MHz, benzene-d_6): δ 0.11 (s, 36H, bridging $N(SiMe_3)_2$), 0.21 (s, 18H, terminal $N(SiMe_3)_2$). ^{13}C NMR (62.9 MHz, benzene-d_6): δ 5.1 (s, bridging $N(SiMe_3)_2$), 5.7 (s br, terminal $N(SiMe_3)_2$). ^{171}Yb NMR (70.1 MHz, benzene-d_6): δ 853 (s, $w_{1/2}$ = 230 Hz). Anal. Calcd for $C_{18}H_{54}LiN_3Si_6Yb$: C, 32.70; H, 8.23; N, 6.36. Found: C, 32.25; H, 8.18; N, 6.34.

[$Y\{CH_2Si(Me)_2)N(SiMe_3)\}\{N(SiMe_3)_2\}_2$(thf)] (8). $YbI_2(thf)_4$ (0.66 g, 0.92 mmol) was added with stirring at 0 °C to a solution of **3** (1.12 g, 1.84 mmol) in 30 mL of THF, and stirring was continued at ambient temperature for 3 h, whereafter all volatile materials were removed under reduced pressure. The remaining solid was extracted with 15 mL of *n*-pentane, solid byproducts were separated by centrifugation, and the resulting orange solution was stored in a −60 °C fridge. After 5 d a crop of pale yellow crystals was collected. Yield: 0.63 g (1.31 mmol, 71%). ^{1}H NMR (250.1 MHz, benzene-d_6): δ −0.13 (t, $^2J_{HY}$ = 1.4 Hz, 2H, YCH_2), 0.36 (s, 18H, $N(SiMe_3)_2$), 0.37 (s, 9H, $NSiMe_3$), 0.37 + 0.38 (2× s, 6H, $SiMe_2$), 0.89 (m, 4H, THF), 3.90 (m br, 4H, THF). ^{13}C NMR (62.9 MHz, benzene-d_6): δ 5.7 (s, $N(SiMe_3)_2$), 6.0 (s, $NSiMe_3$), 8.1 (s, $SiMe_2$), 53.2 (t, $^1J_{YC}$ = 24.4 Hz, YCH_2); the THF signals could not be detected. Anal. Calcd for $C_{16}H_{43}N_2OSi_4Y$: C, 39.97; H, 9.01; N, 5.83. Found: C, 39.15; H, 8.58; N, 5.88.

X-ray Crystallography. X-ray-quality crystals were obtained as described in the Experimental Section. Crystals were removed from Schlenk tubes and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected, attached to a glass fiber, and instantly placed in a low-temperature N_2-stream.[19a] All data were collected at 173 or 203 K (**8**) using either a Siemens P4 (**2**, **7**, **8**) or a rebuild Syntex $P2_1$/Siemens P3 (**3a**, **4**, **6**) diffractometer. Crystal data are given in Table 1. Calculations were performed with the SHELXTL PC 5.03[19b] and SHELXL-97[19c] program system installed on a local PC. The structures were solved by direct methods and refined on F_o^2 by full-matrix least-squares refinement. An absorption correction was applied by using semiempirical ψ-scans. Anisotropic thermal parameters were included for all non-hydrogen atoms. In **3a**, the disorder in one bis(trimethylsilyl)amido ligand was modeled with split postions (sof = 0.67/0.33 for N3, Si5, Si6, C51−C63/N3a, Si5a, Si6a, C51a−C63a) and SADI restraints for equivalent Y−N, N−Si, and Si−C distances. The carbon atoms of a rotationally disordered benzene ring (sof = 0.5 for C81−C86/C81a−C86a) were constrained to regular hexagons. In **4**, two disordered trimethylsilyl groups in the independent molecule 2 were refined with split positions (sof = 0.50/0.50 for Si2*, C21*−C23*, C61*−C63*/Si2a*, C24*−C26*, C64*−C66*) and SADI restraints for equivalent N−Si and Si−C distances. In **8**, the ethylene bridge of a disordered tetrahydrofuran molecule was modeled with split positions (sof = 0.65/0.35 for C54, C55/C54a, C55a), isotropic displacement parameters, and SADI restraints for the corresponding C−O and C−C distances. Positions and isotropic thermal parameters for H atoms in CH_2 groups bonded to Y (**3a**, **6**, **8**) and Yb (**4**) were allowed to refine freely. All other H atoms were placed geometrically and refined using a riding model, including free rotation of methyl groups and variable isotropic displacement parameters. Final R values are listed in Table 1. Important bond parameters are given in Figures 1−6 and in Table 2. Further details are provided in the Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-614768 (**2**), -614769 (**3a**), and -614770 (**4**) and CCDC-614771−614773 (**6**−**8**). Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax +(44)-1223−336−033; e-mail deposit@ccdc.cam.ac.uk).

Computational Details

The Gaussian 03[20] package was used for all energy and frequency calculations. The energies of the model compounds were minimized, starting from the crystallographically determined geometries, using density functional theory (DFT) with the functional B3PW91.[21a,b] Quasi-relativistic pseudopotentials of the Stuttgart/Bonn group have been employed for the heavier atoms silicon (N = 10)[21c] and yttrium (N = 28),[21d] where N denotes the number of core electrons. The corresponding optimized valence basis sets were taken from the literature[21c,d] and were additionally augmented by polarization

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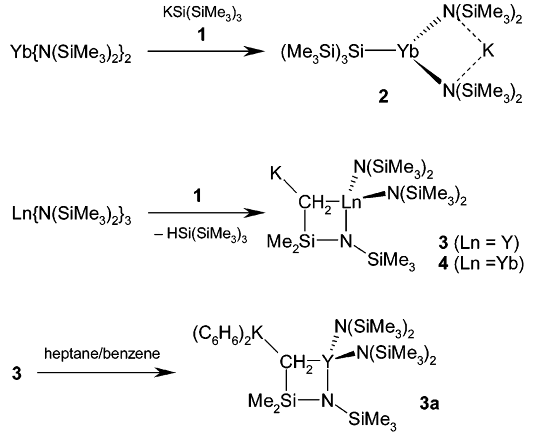
Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **3a**, **3M**, **4**, **4M**, and **6**

				4 (Ln = Yb, M = K)		
param	**3a** (Ln = Y, M = K)	**3M** (Ln = Y, M = K)	**6** (Ln = Y, M = Li)	**molecule 1**	**molecule 2**	**4M** (Ln = Y, M = K)
M−C11	3.000(4)	2.905	2.154(7)	3.022(6)	3.057(6)	2.887
M−N3				3.050(4)	2.978(5)	2.837
Ln−C11	2.449(4)	2.462	2.503(4)	2.360(5)	2.403(5)	2.424
Ln−N1	2.222(3)	2.266	2.231(3)	2.194(4)	2.181(4)	2.259
Ln−N2	2.291(3)	2.292	2.260(3)	2.231(4)	2.228(4)	2.269
Ln−N3	2.288(4)	2.300	2.259(3)	2.276(4)	2.270(4)	2.374
Ln···Si1	2.9581(16)	2.992	2.9676(13)	2.9284(14)	2.9490(14)	3.009
Si1−C11	1.835(4)	1.861	1.831(4)	1.860(5)	1.858(6)	1.875
Si1−C12	1.889(4)	1.912	1.884(4)	1.881(6)	1.870(6)	1.896
Si1−C13	1.886(4)	1.910	1.891(4)	1.879(6)	1.879(6)	1.921
N1−Si1	1.721(3)	1.730	1.711(3)	1.733(4)	1.719(4)	1.743
N1−Si2	1.696(3)	1.726	1.697(3)	1.706(4)	1.746(5)	1.732
N2−Si3	1.712(3)	1.730	1.707(3)	1.716(4)	1.710(4)	1.740
N2−Si4	1.697(3)	1.730	1.718(3)	1.701(4)	1.717(4)	1.728
N3−Si5	1.722(3)	1.728	1.703(3)	1.713(4)	1.717(5)	1.740
N3−Si6	1.720(3)	1.731	1.710(3)	1.720(4)	1.728(5)	1.739
N(1)−Ln−N(2)	110.14(11)	114.2	110.01(10)	112.44(15)	112.08(16)	116.9
N(1)−Ln−N(3)	118.63(13)	119.9	121.55(11)	121.75(15)	117.75(17)	117.4
N(2)−Ln−N(3)	125.03(14)	121.8	117.47(10)	122.27(14)	125.71(15)	122.5
C(11)−Ln−N(1)	73.17(12)	73.3	72.73(12)	74.70(16)	73.91(17)	73.1
C(11)−Ln−N(2)	117.29(12)	113.4	129.93(12)	111.34(17)	109.80(17)	110.8
C(11)−Ln−N(3)	100.30(17)	101.2	98.85(12)	100.98(16)	103.48(19)	101.5
Ln−C(11)−Si(1)	86.07(14)	86.4	84.92(15)	87.03(19)	86.6(2)	87.9
Ln−N(1)−Si(1)	96.39(14)	96.0	96.76(14)	95.72(18)	97.54(19)	96.7
N(1)−Si(1)−C(11)	103.32(16)	103.7	105.21(16)	100.6(2)	101.0(2)	101.0
M−C(11)−Ln	176.37(18)	174.8	176.0(3)	92.03(16)	87.78(18)	87.1
M−C(11)−Si(1)	94.40(14)	92.7	93.6(2)	99.6(2)	98.3(2)	99.0

Scheme 1. Synthesis of Compounds **2**−**4**



functions, namely an f-function for Y and a d-function for Si. The basis set 6-31G*, as implemented in the Gaussian program, was used for carbon, hydrogen, nitrogen, and oxygen atoms. Frequency calculations were done to verify that the geometries are true minima on the potential-energy surface. The natural bond orbital analysis employed the Gaussian 03 adaptation of the NBO program.[21e]

Results and Discussion

Syntheses. The preparation of compounds **2**−**4** is summarized in Scheme 1. The required starting material, donor solvent-free hypersilyl potassium (**1**),[18] was prepared by thermally induced desolvation of KHyp(thf)$_x$ which itself is easily accessible from tetrakis(trimethylsilyl)silane and potassium *tert*-butoxide.[17]

The reaction of **1** with Yb{N(SiMe$_3$)$_2$}$_2$ in a benzene/*n*-heptane mixture afforded deep orange crystals of the adduct [K][YbHyp{N(SiMe$_3$)$_2$}$_2$] (**2**) in good yield (82%). A quite different result is found for the reaction of **1** with bis(trimethylsilyl)amides of the trivalent rare earth metals (Ln{N(SiMe$_3$)$_2$}$_3$ with Ln = Y, Yb). Herein no addition or substitution reaction occurs, which is obviously because of the steric interference with the third amido substituent. As a consequence, peripheral deprotonation and formation of σ-donor-free ate complexes with the composition [K][CH$_2$-Si(Me)$_2$N(SiMe$_3$)Ln{N(SiMe$_3$)$_2$}$_2$] (Ln = Y (**3**), Yb (**4**)) is observed. A side product in the synthesis of **4** is the ytterbate(II) KYb{N(SiMe$_3$)$_2$}$_3$ (**5**) that could not be obtained in a pure form, however.[22] Crystallization of **3** from an *n*-heptane/benzene (20:1) mixture at −60 °C gave the benzene solvate [(C$_6$H$_6$)$_2$K][CH$_2$Si(Me)$_2$N(SiMe$_3$)Y{N(SiMe$_3$)$_2$}$_2$] (**3a**). Ionic products similar to **3**, **3a**, and **4** have been obtained earlier by deprotonation of transition metal[23] or rare-earth metal bis(trimethylsilyl)amides[24] with bases such as LiN(SiMe$_3$)$_2$, NaN(SiMe$_3$)$_2$, KH, or Li^{n}Bu. Donor-stabilized compounds of the type [(donor)M^{I}][CH$_2$Si(Me)$_2$N(SiMe$_3$)-M^{III}{N(SiMe$_3$)$_2$}$_2$] [with (donor)M^{I}/M^{III} = (12-crown-4)$_2$Na/Ti,[23a] (12-crown-4)Li/Ti,[23c] and (thf$_3$)Na/Ln, where Ln = Sc, Yb[24]], which are closely related to **3a** (and **6**; see below), have been structurally characterized by the Dehnicke group. In addition, related neutral complexes with the [CH$_2$Si(Me)$_2$N(SiMe$_3$)]$^{2-}$ moiety were obtained by C−H σ-bond metathesis or γ-elimination reactions.[25]

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(22) A preliminary X-ray structure determination on a hand-picked purple crystal of **5** clearly proved its constitution. However, accurate structural parameters could not be obrtained due to the extremely poor crystal quality. Cell data: triclinic, $P\bar{1}$, $a = 8.656(4)$ Å, $b = 11.249(7)$ Å, $c = 19.380(16)$ Å, $\beta = 111.65(5)°$, $V = 1751(2)$ Å^3.

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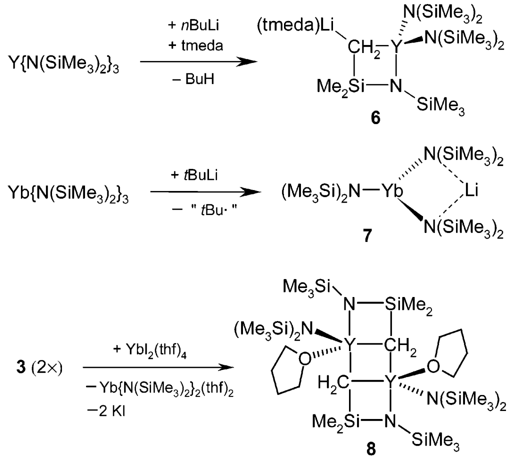
Scheme 2. Synthesis of Compounds **6**−**8**



Compounds **2**−**4** are highly air sensitive, especially **2**, which instantly burns on contact with air. With the exception of **3a**, which rapidly loses coordinated solvent at ambient temperature, they show considerable thermal stability, with decomposition points in the range 145−195 °C. Solutions of **2** and **3a** in benzene-d_6 are stable for weeks.

The previous results prompted us to investigate the use of bases different from **1** or $NaN(SiMe_3)_2$[24] for the deprotonation of Ln(III) bis(trimethylsilyl)amides (Scheme 2). Thus, reaction of $Y\{N(SiMe_3)_2\}_3$ with ^nBuLi in the presence of 1 equiv of tetramethylenediammine (TMEDA) gave colorless crystals of $[(tmeda)Li][CH_2Si(Me)_2N(SiMe_3)Y\{N(SiMe_3)_2\}_2]$ (**6**) in good yield. A rather different reaction is observed between $Yb\{N(SiMe_3)_2\}_3$ and ^tBuLi. In contrast to the formation of **4**, the stronger reducing power of ^tBuLi, compared with KHyp, leads to reduction of the Yb(III) precursor and formation of the ytterbate(II) $[LiYb\{N(SiMe_3)_2\}_3]$ (**7**) in high yield.

With the intention in mind to synthesize a heterobimetallic compound with two different lanthanide metals in distinguishable oxidation states, we have examined the reaction between YbI_2 and 2 equiv of $[K][CH_2Si(Me)_2N(SiMe_3)Y\{N(SiMe_3)_2\}_2]$ in THF as solvent. However, the reaction proceeds not only with elimination of KI but also with the concomitant formation of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$. The identity of the latter was proven by ^{171}Yb NMR spectroscopy (δ 680 at 298 K in benzene-d_6; cf. δ 683 at 294 K in toluene[15d]). Instead of the expected bimetallic product the neutral complex $[Y\{CH_2Si(Me)_2N(SiMe_3)\}\{N(SiMe_3)_2\}(thf)]$ (**8**) is isolated in good yield (Scheme 2).

Structural Studies. In the solid-state structure of the adduct **2** (Figure 1), a polymeric chain structure is observed in which the potassium cations connect adjacent ytterbate anions $[YbHyp\{N(SiMe_3)_2\}_2]^-$ via K−N and K···C interactions. The central feature is a four-membered planar $KYbN_2$ ring with the sum of the endocyclic angles being 359.97°. With a mean value of 2.909(3) Å, the K−N distances are significantly longer than the corresponding bonds in the dimer $[KN(SiMe_3)_2]_2$ (average 2.787(3) Å),[26] which also contains quasi-2-coordinate metal atoms. The longer bonds can be explained in terms of a competition of the softer Lewis acid K^+ with the harder Lewis acid Yb^{2+} for electron density. In the anionic part, the ytterbium atom shows a trigonal planar coordination by Si1 of the silyl and N1 and N2 of the silylamido ligands. Despite the low coordination number, the Yb−Si1 bond length of 3.0387(10) Å is practically identical with or slightly shorter than the Yb−Si distances in the 6-coordinate complexes $[YbCp^*Hyp(thf)_2]$ (3.032(3) Å)[8e] and $[Yb(SiPh_3)_2(thf)_4]$ (3.158(2) Å).[8d] The mean Yb−N distance of 2.373(3) Å may be compared with the corresponding values in the ytterbates $[K_2Zr_2(O^iPr)_9(thf)_3][Yb\{N(SiMe_3)_2\}_3]$ (2.355(6) Å),[27] $[NaYb\{N(SiMe_3)_2\}_3]$ ($Yb-N_{bridging} = 2.46(2)$ Å, $Yb-N_{terminal} = 2.38(2)$ Å),[28] and $[LiYb\{N(SiMe_3)_2\}_3]$ (**7**) ($Yb-N_{bridging} = 2.426(3)$ Å, $Yb-N_{terminal} = 2.309(3)$ Å; see below) as well as in the neutral dimer $[Yb_2\{N(SiMe_3)_2\}_4]$ ($Yb-N_{bridging} = 2.502(3)$ Å, $Yb-N_{terminal} = 2.305(3)$ Å).[29] Shorter bonds are observed in the 3-coordinate heteroleptic complex $[Yb_2\{N(SiMe_3)_2\}_2\{\mu\text{-}OC^tBu_3\}_2]$ (2.330(6) Å)[30] and in two tetraphenylborate supported species $[Yb\{N(SiMe_3)_2\}(BPh_4)(thf)_n]$ ($n = 0$, 1) (2.262(6), 2.314(2) Å).[31]

The trigonal-planar coordination of the ytterbium center leaves room for two additional intramolecular Yb···C contacts of 2.854(4) and 2.885(4) Å to the trimethylsilyl carbon atoms C31 and C51. The presence of these agostic interactions[4,32] is also indicated by small Yb−N−Si−C torsion angles of 8.9 or 12.8° for the involved carbon atoms and by the different Yb−N−Si angles for the interacting (average 102.2°) and for the noninteracting trimethylsilyl groups (average 123.6°). Notably, the acute Yb−N−Si angles lead to relatively short Yb···Si3 and Yb···Si5 contacts of 3.1907(11) and 3.2050(11) Å, respectively, which are only ca. 5% longer than the Yb−Si1 bond.

Recent experimental[5g] and theoretical[33] work has shown that unusual structural features and the occurrence of weak

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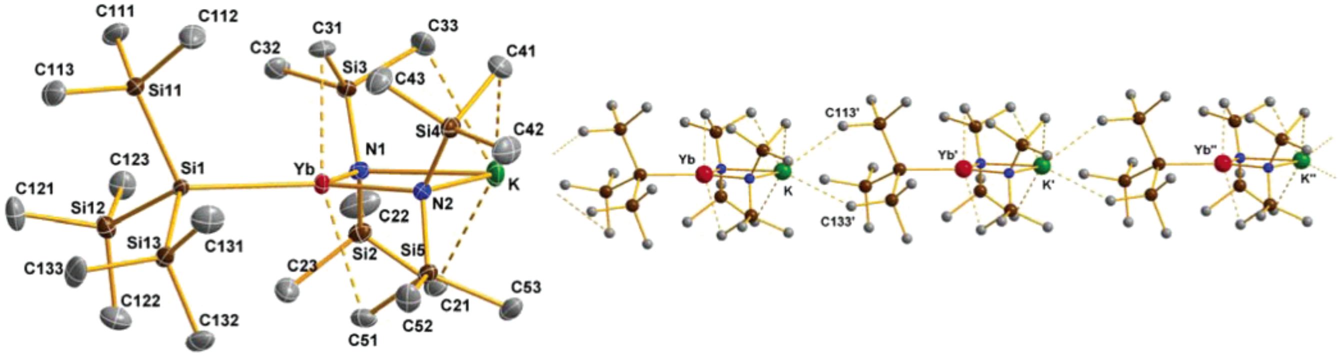

Figure 1. Molecular (left) and solid-state structure (right) of **2** with thermal ellipsoids set to 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles (deg), and intermolecular contacts (Å): K−N1 = 2.906(3), K−N2 = 2.911(3), K⋯C21 = 3.262(4), K⋯C33 = 3.498(4), K⋯C41 = 3.278(4), K⋯Yb = 3.7282(11), Yb−N1 = 2.368(3), Yb−N2 = 2.377(3), Yb−Si1 = 3.0386(10), Yb⋯Si3 = 3.1907(11), Yb⋯Si5 = 3.2050(11), Yb⋯C31 = 2.854(4), Yb⋯C51 = 2.885(4), N1−Si2 = 1.737(3), N1−Si3 = 1.701(3), N2−Si4 = 1.727(3), N2−Si5 = 1.700(3), Si1−Si13 = 2.3250(13), Si1−Si11 = 2.3581(13), Si1−Si12 = 2.3791(14), Si3−C31 = 1.926(4), Si3−C32 = 1.866(4), Si3−C33 = 1.887(4), Si5−C51 = 1.925(4), Si5−C52 = 1.871(4), Si5−C53 = 1.882(4); N1−K−N2 = 79.02(8), N1−Yb−N2 = 102.52(10), N1−Yb−Si1 = 128.55(7), N2−Yb−Si1 = 128.92(7), Yb−N1−K = 89.35(8), Yb−N2−K = 89.08(8), Yb−N1−Si2 = 125.08(14), Yb−N1−Si3 = 102.04(12), Yb−N2−Si4 = 122.10(13), Yb−N2−Si5 = 102.39(12); K⋯C133′ = 3.449(4), K⋯C113′ = 3.498(4) (symmetry operation: *x*, *y* − 1, *z*).

Ln⋯C interactions in lanthanide bis(trimethylsilyl)amides and the related bis(trimethylsilyl)methanides may be attributed to the establishment of *β*-Si−C agostic interactions between the electron-deficient metal atom and the alkyl substituents. These experiments and calculations also suggest that attractive interactions with the *γ*-C−H bonds are not important. Evidence for the presence of Yb⋯*β*-Si−C interactions in **2** is provided by a substantial elongation of the agostic Si−C bonds, which amounts to 0.049 Å for Si3−C31 and 0.048 Å for Si5−C51 (the average nonagostic Si−C distance in these groups is 1.877 Å). Another notable feature is the shortening of the N−Si bonds for the agostic trimethylsilyl groups (N1−Si3 = 1.701(3), N2−Si5 = 1.700(3) Å) compared to the nonagostic ones (N1−Si2 = 1.737(3), N2−Si4 = 1.727(3) Å). The shorter distances are most probably a result of increased back-bonding from the N lone pair into suitable acceptor orbitals, in particular σ^*_{SiC} orbitals.[5h] Finally, it should be noted that intra- and intermolecular M⋯C interactions in the range 3.262(4)−3.498(4) Å are also observed between the potassium cation and trimethylsilyl carbon atoms.

The structures of the deprotonation product **3a** and the closely related complex **6** are shown in Figures 2 and 4, respectively. In the solid state, the compounds are composed of contact ion pairs consisting of anionic $[\mathrm{Y\{N(SiMe_3)_2\}_2\{CH_2Si(Me)_2N(SiMe_3)\}}]^-$ and cationic $[\mathrm{K(C_6H_6)_2}]^+$ (**3a**) or $[\mathrm{Li(tmeda)}]^+$ (**6**) moieties. Each yttrium atom shows a very distorted tetrahedral coordination, with interligand angles in the range 73.17(12)−125.03(14)° (**3a**) or 72.73(12)−129.93(12)° (**6**), by two nitrogen atoms (N2, N3) of monodentate silylamido ligands as well as N1 and C11 of a deprotonated $\mathrm{NSiMe_3}$ group. The latter is part of a four-membered almost planar azasilayttracyclobutan ring [Y−C11−Si1−N1 = 9.2° (**3a**), 5.8° (**6**)]. With slightly different mean values of 2.290(4) Å (**3a**) and 2.260(3) Å (**6**), the Y−N distances to the terminal $\mathrm{N(SiMe_3)_2}$ ligands are at the long end of the usual 2.22−2.28 Å range found in other bis(trimethylsilyl)amides containing a 4-coordinate yttrium atom.[34] However, significantly shorter distances of 2.222(3) Å (**3a**) and 2.231(3) Å (**6**) are observed for the endocyclic Y−N bonds. The carbanionic C11 atom shows a distorted trigonal bipyramidal coordination, the axial and equatorial positions being occupied by Y, K/Li [with K−C11−Y = 176.37(18) and Li−C11−Y = 176.0(3)], and the two H atoms and Si1, respectively. The Y−C11 bond in **3a** (2.449(4) Å) is significantly shorter than that in **6** (2.503(4) Å).

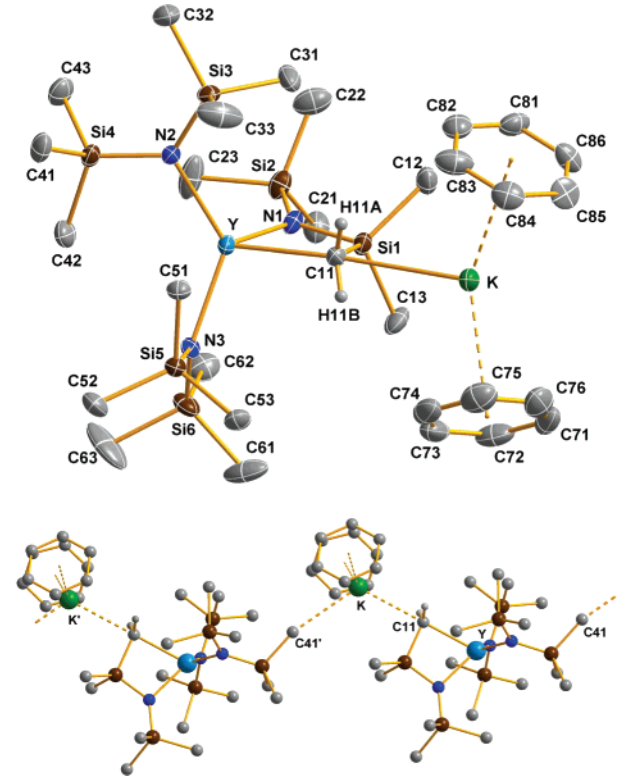

Figure 2. Molecular (top) and solid-state structure (bottom) of **3a** with thermal ellipsoids set to 30% probability. Hydrogen atoms, with the exception of the $\mathrm{YCH_2}$ ones, and disordered groups have been omitted for clarity. Selected bond lengths, intermolecular contacts (Å), and bond angles (deg) (see also Table 2): K⋯C71 = 3.378(5), K⋯C72 = 3.312(5), K⋯C73 = 3.231(5), K⋯C74 = 3.197(5), K⋯C75 = 3.271(5), K⋯C76 = 3.359(5), K⋯C81 = 3.380(13), K⋯C82 = 3.337(12), K⋯C83 = 3.243(14), K⋯C84 = 3.192(16), K⋯C85 = 3.236(15), K⋯C86 = 3.330(14), K⋯X1 = 2.997, K⋯X2 = 2.979 [X1/X2 = centroids of the C71→C76/C81→C86 rings]; X1⋯K⋯X2 = 129.1, X1⋯K−C11 = 111.4, X2⋯K−C11 = 107.0; K⋯C41′ = 3.228(4) (symmetry operation: *x*, *y* − 1, *z*).

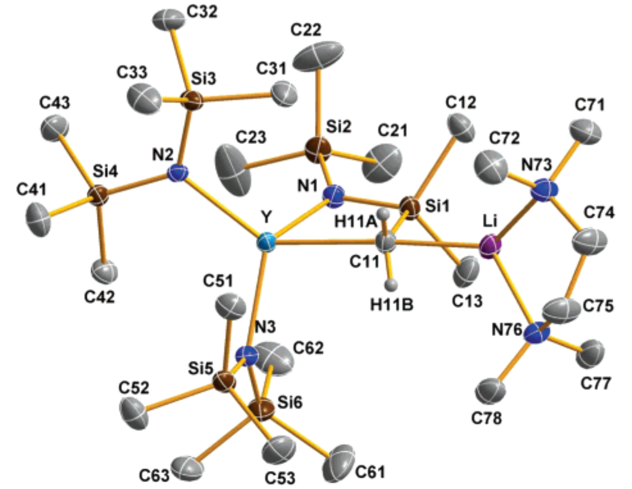

Figure 3. Molecular structure of **6** with thermal ellipsoids set to 30% probability. Only hydrogen atoms bonded to the deprotonated $SiMe_3$ group are shown for clarity. Selected bond lengths (Å) and angles (deg) (see also Table 2): Li−N73 = 2.042(7), Li−N76 = 2.035(6); N73−Li−N76 = 90.4(3), C11−Li−N73 = 132.6(3), C11−Li−N76 = 124.3(3).

The longer distance in the latter reflects the competitive bonding between the hard Lewis base RCH_2^- and the hard Lewis acid Y^{3+} on one side and the soft or hard Lewis acid K^+ or Li^+ on the other side. Typical Y−C bonds in 4-coordinate yttriates (e.g. $[Li(OEt_2)_3][Y\{CH(SiMe_3)_3\}Cl]$, 2.423(7) Å;[35a] $[Y(CH_2SiMe_3)_4]^-$, average 2.405(9) Å[35b]) are slightly shorter. In **3a**, the potassium cation exhibits a pseudotetrahedral coordination by the carbanionic carbon atom (K−C11 = 3.000(4) Å), the centroids of two benzene rings, and one intermolecular agostic contact to a trimethylsilyl carbon atom (K···C41′ = 3.228(4) Å). The mean K···C distances of 3.289 Å to the η^6-bonded benzene rings are unexceptional.[36] In **6**, a trigonal pyramidal coordination of the lithium cation by the carbanionic center (Li−C11 = 2.154(7) Å) and the chelating tmeda donor atoms is observed (Li−N73 = 2.042(7) Å, Li−N76 = 2.035(6) Å).

A rather complicated solid-state structure is observed for the donor-free deprotonation product **4**. Similar to the structures of **3a** and **6**, the ytterbium atom binds to two nitrogen atoms (N2, N3) of monodentate bis(trimethylsilyl)amido ligands as well as to N1 and C11 of a bidentate $\{CH_2Si(Me)_2N(SiMe_3)\}$ group, thus forming again a four-membered metallacycle. Two independent molecular units, one of them is shown in Figure 4 (top), are connected via agostic interactions between the potassium cations and trimethylsilyl carbon atoms (K*···C33 = 3.245(7) Å, K···C33* = 3.504(6) Å; atoms in the second independent molecule are marked by an asterisk). Two free coordination sides, indicated by dotted arrows in Figure 4 (bottom), are used for a further linkage (K···C = 3.458(7)/3.530(6) Å), thus resulting in a polymeric layer structure. In addition, there are several intramolecular agostic K···C interactions in the range 3.158(7)−3.450(6) Å. In contrast to the structures of **3a** and **6**, each potassium cation within one of the two independent units interacts not only with the carbanionic center C11 but also with the nitrogen atom N3 of one terminal $N(SiMe_3)_2$ ligand. As a consequence an average Yb−C−K angle close to 90° is observed (Yb−C11−K = 92.03(16)°, Yb*−C11*−K* = 87.78(18)°; cf. mean Y−C−M = 176.2° in **3a** and **6**). There are significant differences between the two independent molecular units. Thus, the K−N3 bonds are shorter in molecule 2 than in molecule 1 (K−N3 = 3.050(4) Å, K*−N3* = 2.978(5) Å), whereas the K−C11 distances are longer in the former (K−C11 = 3.022(6) Å, K*−C11* = 3.057(6) Å). With 2.360(5) Å the Yb−C11 bond is considerably shorter than the Yb*−C11* bond of 2.403(5) Å. This is probably due to the fact that the carbanionic center C11* in molecule 2 shows an additional, however relatively long interaction (3.445(5) Å) to the

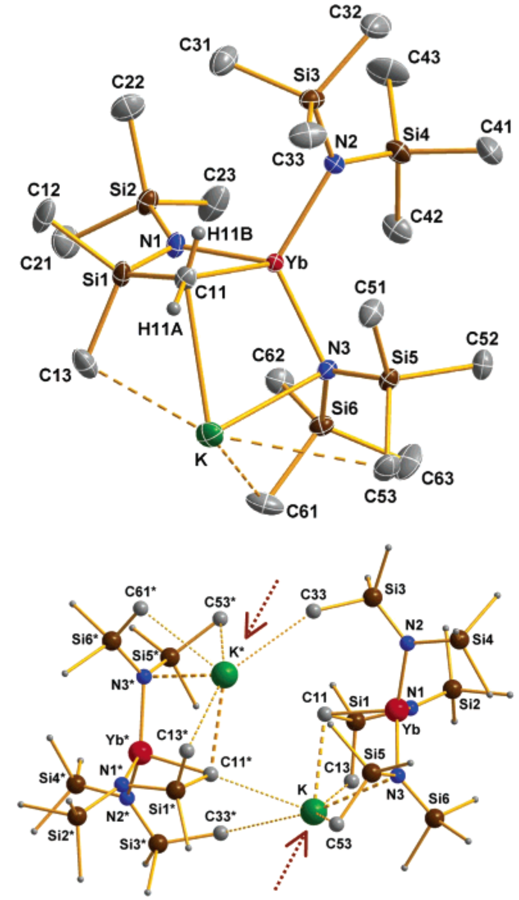

Figure 4. One of the two independent molecular units (top) and solid-state structure (bottom) of **4** with thermal ellipsoids set to 30% probability. Only hydrogen atoms bonded to the deprotonated $SiMe_3$ group are shown for clarity (top). Selected intra- and intermolecular K···C contacts (Å) (see also Table 2): K···C11 = 3.022(6), K···C11* = 3.445(5), K···C13 = 3.313(7), K···C33* = 3.504(6), K···C53 = 3.450(6), K···C61 = 3.158(7), K*···C11* = 3.057(6), K*···C13* = 3.356(7), K*···C33 = 3.245(7), K*···C53* = 3.354(8), K*···C61* = 3.203(16), K···C31*′ = 3.530(6), K*···C41″ = 3.458(7) [symmetry operations: $-x$, $2-y$, $-z$ (prime); $-x$, $1-y$, $-z$ (double prime)].

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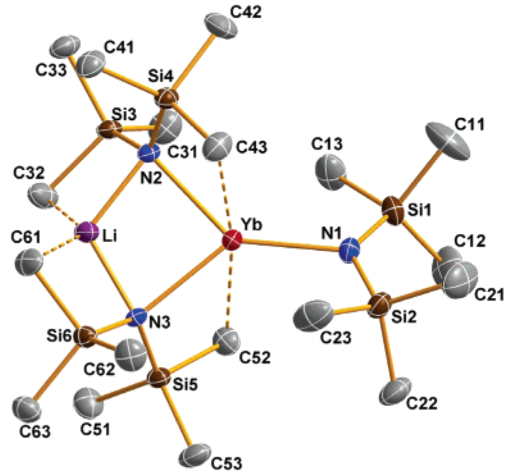

Figure 5. Molecular structure of **7** with thermal ellipsoids set to 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Li−N2 = 1.998(7), Li−N3 = 1.994(7), Li···C32 = 2.362(9), Li···C61 = 2.420(8), Li···Yb = 2.873(7), Yb−N1 = 2.309(3), Yb−N2 = 2.420(3), Yb−N3 = 2.431(3), Yb···C43 = 2.801(5), Yb···C52 = 2.847(5), Yb···Si4 = 3.1806(13), Yb···Si5 = 3.2031(13), N1−Si1 = 1.663(4), N1−Si2 = 1.669(3), N2−Si3 = 1.702(3), N2−Si4 = 1.691(3), N3−Si5 = 1.696(3), N3−Si6 = 1.699(3), Si4−C41 = 1.862(5), Si4−C42 = 1.849(4), Si4−C43 = 1.888(5), Si5−C51 = 1.862(5), Si5−C52 = 1.877(4), Si5−C53 = 1.854(4); N3−Li−N2 = 112.7(3), N1−Yb−N2 = 138.21(11), N1−Yb−N3 = 135.22(11), N2−Yb−N3 = 86.48(10), Li−N2−Yb = 80.5(2), Li−N3−Yb = 80.3(2), Si1−N1−Yb = 116.36(17), Si2−N1−Yb = 115.52(17), Si3−N2−Yb = 131.19(17), Si4−N2−Yb = 99.83(14), Si5−N3−Yb = 100.29(14), Si6−N3−Yb = 132.14(16).

potassium atom K in molecule 1. The mean Yb−C11 distance of 2.382 Å in **4** is significantly shorter than the average Y−C11 bond of 2.476 Å observed for **3a** and **6**, taking into account the different ionic radius values for Y^{3+} (0.90) and Yb^{3+} (0.868).[37] These variations can be explained by a change in hybridization at the carbon atom C11 (see below) and the presence of differently solvated countercations. The Yb−C11 distance is close to the values reported for the donor-stabilized compound $[(thf_3)Na][CH_2Si(Me)_2N(SiMe_3)Yb\{N(SiMe_3)_2\}_2]$ (2.386(11) Å)[24] and the 4-coordinate ytterbate $[Li(thf)_3][Yb\{CH(SiMe_3)_3\}Cl]$ (2.38(2) Å).[38]

The solid-state structure of the ytterbate **7** shows monomeric units (Figure 5) with a 3-coordinate ytterbium atom. Two silylamido ligands bridge the lithium and ytterbium cations while the third is terminally coordinated to the latter. The central four-membered Li−Yb−N2−N3 ring is essentially planar with the sum of the endocyclic angles being 359.98°. With 2.309(3) Å, the Yb−N1 bond to the terminal ligand is considerably shorter than those to the bridging amido groups (Yb−N2 = 2.420(3) Å, Yb−N3 = 2.431(3) Å). The trigonal-planar coordination of the ytterbium cation is augmented by two additional intramolecular Yb···C contacts of 2.801(5) and 2.847(5) Å to the trimethylsilyl carbon atoms C43 and C52. Evidence for the presence of agostic interactions is also provided by small Yb−N−Si−C torsion angles of 17.8 or 16.3° for the involved carbon atoms, by the different Yb−N−Si angles to the interacting (average 100.1°) and to the noninteracting trimethylsilyl groups (average 123.8°), and by a significant elongation of the corresponding Si−C bonds.

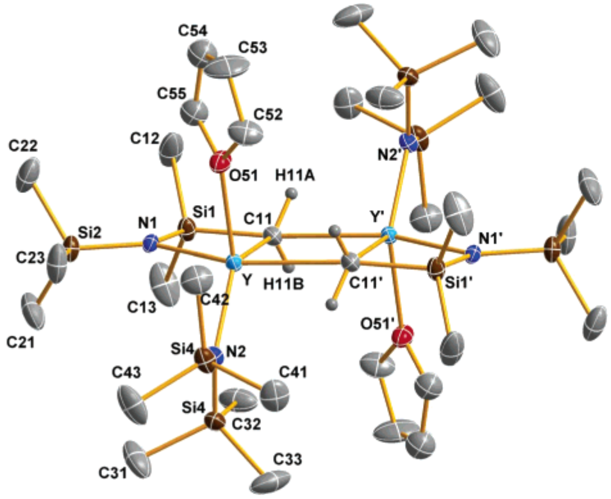

Figure 6. Molecular structure of **8** with thermal ellipsoids set to 30% probability. Hydrogen atoms, with the exception of the YCH_2 ones, and disordered groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y−N1 = 2.254(4), Y−N2 = 2.286(4), Y−C11 = 2.589(6), Y−C11′ = 2.587(6), Y−O51 = 2.404(4), Y···Y′ = 3.7421(13), N1−Si1 = 1.711(4), N1−Si2 = 1.725(4), N2−Si3 = 1.704(4), N2−Si4 = 1.724(5), Si1−C11 = 1.881(6); N1−Y−C11′ = 157.30(17), N2−Y−O51 = 124.49(16), N2−Y−C11 = 132.21(18), O51−Y−C11 = 103.30(17), N1−Y−N2 = 106.44(15), N1−Y−O51 = 89.42(15), N1−Y−C11 = 70.84(16), N2−Y−C11′ = 92.81(16), O51−Y−C11′ = 89.41(18), C11−Y−C11′ = 87.4(2), Y−N1−Si1 = 100.59(19), N1−Si1−C11 = 103.3(2), Y−C11−Si1 = 85.2(2), Y−C11−Y′ = 92.6(2) (symmetry operation: 1 − *x*, 1 − *y*, 1 − *z*).

With a mean value of 1.996(7) Å, the Li−N bonds to the quasi-2-coordinate lithium cation are identical within experimental error to the corresponding distances in the trimer $[LiN(SiMe_3)_2]_3$ (average 2.005(13) Å).[39] In addition, the steric and electronic unsaturation of the Li cation gives rise to two further intramolecular agostic contacts (Li···C32 = 2.362(9) Å, Li···C61 = 2.420(8) Å), thus affording a distorted tetrahedral coordination with interligand angles in the range 81.0−131.8°. In contrast to the structurally related heavier alkali-metal compounds $[NaYb\{N(SiMe_3)_2\}_3]$,[28] $[KSm\{N(SiMe_3)_2\}_3]$,[27] and **1** no additional short intermolecular M···C contacts are observed in **7**. Moreover, regarding the almost identical ionic radius values of Yb^{2+} and Ca^{2+}, it is not surpring that **7** is isostructural to the recently reported $[LiCa\{N(SiMe_3)_2\}_3]$.[40]

The structure of the dimeric centrosymmetric complex **8** is shown in Figure 6. It consists of two $[YN(SiMe_3)_2(thf)]^{2+}$ fragments bridged by two $[CH_2Si(Me)_2N(SiMe_3)]^{2-}$ units. The most prominent feature is a ladderlike structure with two central (Y−C11/Y′−C11′) and two outer (N1−Si1/N1′−Si1′) rugs. These are part of two symmetry-related four-membered and almost planar azasilayttracyclobutan rings (Y−C11−Si1−N1 = 1.8°). With an interplanar angle of 6.1°, the latter are almost coplanar to the central crystallographically required, planar Y_2C_2 ring. In the asymmetric unit, the

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Table 3. ^{171}Yb NMR Parameters for Compounds **2** and **7**, Other Yb^{II} Silyls, Selected Yb^{II} Organyls, and Amides

compound	solvent/T (K)	δ (ppm)	$w_{1/2}$ (Hz)[a]	ref
		Yb^{II} Silyls		
[KYbHyp{N(SiMe$_3$)$_2$}$_2$] (**2**)	benzene-d_6/298	1057	100	
[Yb(Hyp)$_2$(thf)$_x$]	b	875	[b]	8e
[Yb(Si(SiMe$_3$)$_2$SiMe$_2$Pph)$_2$(thf)$_2$][c]	benzene-d_6/298	928	40	14
[Yb(Cp*)(Hyp)(thf)$_2$]	toluene/298	421	[b]	8e
		Yb^{II} Organyls		
[Yb{CH(SiMe$_3$)$_2$}$_2$(OEt$_2$)$_2$]	Et$_2$O/304	904	500	41
[Yb(Dpp)$_2$(thf)$_2$][d]	THF-d_8/298	927	<15	7c
		Yb^{II} Amides		
[Yb{N(SiMe$_3$)$_2$}$_2$(OEt$_2$)$_2$]	Et$_2$O/193	614	70	42
[Yb{N(SiMe$_3$)$_2$}$_2$(thf)$_2$]	toluene/294	683	300	15d
[Yb$_2${N(SiMe$_3$)$_2$}$_4$]	toluene/263	796	90	42
[LiYb{N(SiMe$_3$)$_2$}$_3$] (**7**)	benzene-d_6/298	853	220	
[NaYb{N(SiMe$_3$)$_2$}$_3$]	toluene/193	947	190	42

[a] Signal width at half-height (Hz). [b] Value not published. [c] Pph = 2′,3′,4′,5′,6′-pentamethylbiphen-2-yl. [d] Dpp = 2,6-Ph$_2$C$_6$H$_3$.

yttrium atom shows a distorted trigonal bipyramidal coordination, with the equatorial positions beiing occupied by C11 of the bidentate [N(SiMe$_3$)SiMe$_2$CH$_2$]$^{2-}$ group, N2 of the terminal N(SiMe$_3$)$_2$ amido ligand, and O51 of the neutral donor THF. The coordination sphere is completed by the apically bonded atoms N2 of the deprotonated N(SiMe$_3$)$_2$ group and C11′ of the symmetry-related bidentate ligand, the enclosed angle N2−Y−C11′ being 157.30(17)°. In the central Y$_2$C$_2$ square, the two bridging carbon atoms are symmetrically placed between the two Y atoms within experimental error (Y−C11 = 2.589(6) Å, Y−C11′ = 2.587(6) Å). With 2.286(4) Å, the Yb−N2 bond to the terminal amido ligand is slightly shorter than the endocyclic one (Yb−N1 = 2.254(4) Å).

NMR-Spectroscopic Characterization. The diamagnetic compounds **2**, **3**, and **6**−**8** were characterized by ^{1}H, ^{13}C, ^{29}Si (**2**, **3**, **6** only), and ^{171}Yb (**2** only) NMR spectroscopy in C$_6$D$_6$ solution. As expected, two sets of signals are observed for the N(SiMe$_3$)$_2$ and Si(SiMe$_3$)$_3$ groups in the ^{1}H and ^{13}C NMR spectra of **2** with corresponding $^1J(^{13}\mathrm{C}-^{29}\mathrm{Si})$ coupling constants of 52.3 and 41.0 Hz in the latter. The ^{29}Si NMR spectrum comprises three resonances at δ −148.6, −13.9, and −4.7, the first assigned to *Si*(SiMe$_3$)$_3$ showing satellites with $^1J(^{29}\mathrm{Si}-^{171}\mathrm{Yb})$ = 716 and $^1J(^{29}\mathrm{Si}-^{29}\mathrm{Si})$ = 27.9 Hz, the second {N(*Si*Me$_3$)$_2$} displaying $^1J(^{29}\mathrm{Si}-^{13}\mathrm{C})$ = 52.2 and $^2J(^{29}\mathrm{Si}-^{171}\mathrm{Yb})$ = 5.0 Hz, and the last {Si(*Si*Me$_3$)$_3$} revealing $^2J(^{29}\mathrm{Si}-^{171}\mathrm{Yb})$ = 8.9 Hz and confirming the previously measured $^1J(^{29}\mathrm{Si}-^{13}\mathrm{C})$ and $^1J(^{29}\mathrm{Si}-^{29}\mathrm{Si})$ coupling. The $^1J(^{29}\mathrm{Si}-^{171}\mathrm{Yb})$ coupling of 716 Hz may be compared with the corresponding values in the silyls [Yb(Cp*)(Hyp)(thf)$_2$] (**A**)[8e] and [Yb(Si(SiMe$_3$)$_2$SiMe$_2$Pph)$_2$(thf)$_2$] (Pph = 2′,3′,4′,5′,6′-pentamethylbiphen-2-yl)[14] (**B**), which are 829 and 728 Hz, respectively. The ^{29}Si NMR chemical shift for the central metal-bound silicon atom in **2** (−148.6 ppm) lies somewhere in the middle of the values reported for **A** (−158.3 ppm) and **B** (−140.5 ppm) and is considerably smaller than the −185.7 ppm found in dimeric donor-free potassium hypersilyl.[18] In the ^{171}Yb NMR spectra of **2** and **7** single resonances are observed at δ 1057 and δ 853, respectively. Table 3 gives an overview of ^{171}Yb NMR chemical shifts for known Yb^{II} silyls and selected Yb^{II} organyls and Yb^{II} amides. The following trends are noteworthy. (i) Chemical shifts for Yb^{II} silyls are observed in the same range as for Yb^{II} organyls, whereas resonances for Yb^{II} amides are moved to higher field by ca. 250 ppm. (ii) The formation of ate complexes of the type MYbR$_3$ (M = Li, Na, K) is accompanied by a significant downfield shift for the ^{171}Yb NMR signal.

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3a** and **6** (values in braces) in C$_6$D$_6$ solution are in accordance with the solid-state structures. Therefore, they each show three signals for the N(SiMe$_3$)$_2$, NSiMe$_3$, and NSiMe$_2$ fragments, respectively. In addition, doublets for the metal-bound CH$_2$ group are observed in the ^{1}H NMR at δ −1.27 {−0.40} with $^2J(^1\mathrm{H}-^{89}\mathrm{Y})$ = 2.6 Hz {not detectable in **6**} and in the ^{13}C{^{1}H} NMR spectrum at δ 23.6 {22.2} with $^1J(^{89}\mathrm{Y}-^{13}\mathrm{C})$ = 22.9 {24.4} Hz. A comparison of these values with the corresponding parameters in other yttrium alkyls, which contain either trimethylsilylmethyl (e.g. [Y(CH$_2$SiMe$_3$)$_3$(thf)$_2$], $^1J_{\mathrm{YC}}$ = 35.7 Hz)[43] or bis(trimethylsilyl)methyl substituents (e.g. Y{CH(SiMe$_3$)$_2$}$_3$, $^1J_{\mathrm{YC}}$ = 30.3 Hz),[5e] shows that the $^1J_{\mathrm{CY}}$ coupling is unusually small. Comparable small $^1J_{\mathrm{YC}}$ coupling constants below 30 Hz are typical for binuclear yttrium compounds with bridging alkyl groups (e.g. [Y(C$_5$Me$_5$)(O-2,6-^{t}Bu$_2$C$_6$H$_3$)(μ-Me)]$_2$,[44] $^1J_{\mathrm{YC}}$ = 28 Hz; [Y(C$_5$H$_4$SiEt$_3$)$_2$(μ-Me)]$_2$,[45] $^1J_{\mathrm{YC}}$ = 25 Hz).

Additional information about the bonding situation in the central metallacycle of **3a** and **6** is provided by the evaluation of further coupling constants. Besides the small value for $^1J_{\mathrm{YC}}$, several other findings are remarkable: an observable $^3J(^{89}\mathrm{Y}-^{13}\mathrm{C})$ coupling to the SiMe$_2$ group (1.8 Hz) {1.5 Hz}, which seems to be the first of this kind, a relatively large $^2J(^{89}\mathrm{Y}-^{29}\mathrm{Si})$ coupling of 3.9 {3.4} Hz,[46] and finally a $^1J(^{13}\mathrm{C}-^1\mathrm{H})$ coupling of 120.2 Hz {not determined in **6**}. The latter is ca. 20−30 Hz larger than the corresponding coupling in other Y−CH$_2$SiMe$_3$ or Y−CH(SiMe$_3$)$_2$ compounds (e.g. Y{CH(SiMe$_3$)$_2$}$_3$, $^1J_{\mathrm{CH}}$ = 92.5 Hz;[5e] Y(CH$_2$SiMe$_3$)(DAC)

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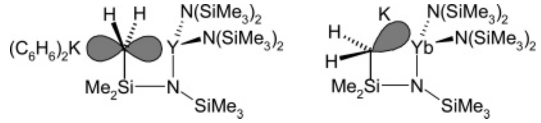
with DAC = deprotonated 4,13-diaza-18-crown-6,[47] $^1J_{CH}$ = 102 Hz). These observations are in accordance with a high s character for the bonding in the CH_2Si fragment (i.e. sp^2 hybridization) and a high p contribution for the lone pair at C11 which interacts with the yttrium and potassium cations (see below).

For **7**, the observation of two sets of signals in a 1:2 ratio in the ^1H and ^{13}C NMR spectra confirms the presence of terminal and bridging $N(SiMe_3)_2$ groups in solution and is therefore in accordance with the solid-state structure.

In **8**, the signals for the yttrium-bound CH_2 group are found in the ^1H NMR spectrum at δ −0.13 with $^2J(^1H-^{89}Y) = 1.4$ Hz and in the $^{13}C\{^1H\}$ NMR spectrum at δ 53.2 with $^1J(^{89}Y-^{13}C) = 24.4$ Hz, respectively. The multiplicity of the observed triplets is in agreement with the presence of dimeric units with bridging $[CH_2Si(Me)_2N(SiMe_3)]^{2-}$ ligands in solution.

DFT Calculations. To further understand the bonding situation in compounds **3a** and **6** on one side and compound **4** on the other side, which feature average Ln−C−K/Li angles close to 180 and 90°, respectively, density functional theory (DFT) calculations were undertaken. The calculations were performed on $[K(C_6H_6)_2][CH_2Si(Me)_2N(SiMe_3)Y\{N(SiMe_3)_2\}_2]$ (**3M**) or $[K][CH_2Si(Me)_2N(SiMe_3)Y\{N(SiMe_3)_2\}_2]$ (**4M**) model systems, using the B3PW91 functional, 6-31G* basis sets, and Stuttgart type pseudopotentials for atoms Y, K, and Si. To allow for a better comparison of both models, the ytterbium atom in **4** was replaced by yttrium in **4M**. Important bond parameters of the energy-minimized structures are summarized in Table 2. Taking into account the difference in the ionic radii for Y^{3+} and Yb^{3+}, the calculated bond lengths and angles are in reasonable agreement with the experimental values. According to the results of a natural bond orbital (NBO) analysis, the bonding between the yttrium or potassium atoms and the ligand carbon or nitrogen atoms is dominated by Coulomb interactions. High positive and negative natural population analysis (NPA) charges are calculated for the atoms Y [+1.83 (**3M**); +1.71 (**4M**)], K (+0.92; +0.98), endocyclic Si1 (+1.93; +1.97), and N1 (−1.66; −1.66), N2 (−1.68; −1.68), N3 (−1.68; −1.68), or C11 (−1.65; −1.64), respectively. Not surprisingly, the bonding between K and C11 is essentially ionic, as is indicated by the low Wiberg bond indices[21f] of 0.05 (**3M**) and 0.03 (**4M**). Although ionic contributions still dominate, covalent bond orders are higher for the Y−C11 (0.30; 0.41), the endocyclic Y−N1 (0.42; 0.46), and the exocyclic Y−N2 (0.38; 0.42) or Y−N3 (0.39; 0.36) bonds. Despite the considerable charge separation, much higher covalent bond orders are observed for the Si1−C11 (0.80; 0.76) and N1−Si1 (0.75; 0.73) bonds.

Scheme 3. Different Bonding Modes in Compounds **3a** and **4**



According to the NBO analysis, the negative charge on C11 is mainly concentrated in a lone pair with the following natural atomic orbitals contributions: s (5.0%), p (95.0%) (**3M**); s (26.6%), p (73.4%) (**4M**). For the model **3M** and the experimental compounds **3a** and **6**, these results may be interpreted in terms of a high p character for the lone pair on C11 that interacts with the lanthanide and alkali-metal cations (Scheme 3, left)[48] and a high s contribution for the bonding in the CH_2Si fragment (i.e. sp^2 hybridization). The latter is supported by the length of the calculated and experimentally observed endocyclic Si1−C11 bonds which are approximately 0.05 A shorter than the mean exocyclic Si1−C12 or Si1−C13 bonds and by the evaluation of the $^1J_{CH}$ coupling constant for **3a** (see above). For **4M** and **4**, the bonding in the CH_2Si fragment is best described by assuming a more conventional sp^3 hybridization at C11 (Scheme 3, right).

Conclusion

Our primary goal, the synthesis of compounds with Ln−Si bonds and low-coordinate lanthanide atoms by using potassium hypersilyl as silylation agent, has been achieved only in the case of the reaction with ytterbium(II) bis(trimethylsilyl)amide. Instead of the expected substitution products, deprotonation of trimethylsilyl groups is observed for reactions between potassium hypersilyl and lanthanide(III) bis(trimethylsilyl)amides. Aggregation behavior and bonding of the obtained metalation products strongly depends on the presence or absence of additional coordinating solvents. Future work will focus on the reactivity of these compounds.

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Supporting Information Available: Figures of ^{29}Si and ^{171}Yb NMR spectra for **2** and X-ray data (CIF) for **2**, **3a**, **4**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) Typical values for other known $^2J_{Y(C)Si}$ coupling constants are found below 2.3 Hz. There seem to be no reports of an observable $^2J_{Y(N)Si}$ coupling. Notably, a relatively high $^2J_{Y(O)Si}$ coupling of 7.7 Hz was measured in the alkoxide $[Y(\mu\text{-}OSiPh_3)(OSiPh_3)_2]_2$ only for the terminal $OSiPh_3$ groups and not for the bridging ones, which has been explained by the larger Y−O−Si angle (higher s character!) in the former. See: Coan, P. S.; Hubert-Pfalzgraf, L. G.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 1262.

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