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Synthesis and Characterization of Group 4 Amido Silyl Complexes Free of Anionic π-Ligands

Zhongzhi Wu, Jonathan B. Diminnie, and Ziling Xue*

Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996-1600

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A series of early-transition-metal silyl complexes free of anionic π-ligands such as cyclopentadienyl (Cp = η^5-C_5H_5) have been synthesized. These Cp-free complexes $(Me_2N)_3MSi(SiMe_3)_3$ [M = Zr (**1**), Hf (**2**)], $(Me_2N)_3TiSiPh_2Bu^t$ (**3**), $(Me_2N)_3ZrSiPh_2Bu^t\cdot 0.5THF$ (**4**), $(Me_2N)_3HfSiPh_2Bu^t\cdot n$THF [$n$ = 0.5 (**5a**), 1 (**5b**)], and $(Me_2N)_2[(Me_3Si)_2N]ZrSiR_3$ [$SiR_3 = Si(SiMe_3)_3$ (**7**), $SiPh_2Bu^t$ (**8**)] were prepared by metathetic reactions of chloro triamido complexes $(Me_2N)_3MCl$ (M = Ti, Zr, Hf) or $(Me_2N)_2[(Me_3Si)_2N]ZrCl$ (**6**) with silyllithium reagents $Li(THF)_3Si(SiMe_3)_3$ or $Li(THF)_3SiPh_2Bu^t$. The structures of **1**, **3**, **4**, **5b**, and **8** have been determined by X-ray crystallography and show that **1**, **3**, and **8** adopt a distorted tetrahedral coordination geometry while **4** and **5b** have a distorted trigonal bipyramidal geometry around the metal. The unit cell parameters are as follows. **1**: space group $R3c$, $a = 15.505(2)$ Å, $c = 19.308(4)$ Å, $V = 4019.9(13)$ Å^3, $Z = 6$. **3**: space group $P2_1$, $a = 8.633(5)$ Å, $b = 14.790(7)$ Å, $c = 9.388(4)$ Å, $\beta = 92.44(4)°$, $V = 1197.6(10)$ Å^3, $Z = 2$. **4**: space group $Pbca$, $a = 16.538(9)$ Å, $b = 17.282(7)$ Å, $c = 18.566(8)$ Å, $V = 5306(4)$ Å^3, $Z = 8$. **5b**: space group $Pna2_1$, $a = 17.463(6)$ Å, $b = 9.453(3)$ Å, $c = 17.800(6)$ Å, $V = 2938(2)$ Å^3, $Z = 4$. **8**: space group $Pca2_1$, $a = 19.775(5)$ Å, $b = 10.182(2)$ Å, $c = 15.752(5)$ Å, $V = 3172(2)$ Å^3, $Z = 4$. The M−Si bond distances for **1**, **3**, **4**, **5b**, and **8** are 2.781(2), 2.635(2), 2.803(2), 2.807(4), and 2.860(2) Å, respectively. The Zr−Si bond in **8**, to our knowledge, is the longest reported Zr−Si bond.

Introduction

Early-transition-metal silyl complexes are becoming increasingly important in organometallic chemistry.[1,2] The reactivity of these complexes in, e.g., insertion reactions,[3,4] silane dehydropolymerizations,[1,2,5] and hydrosilation of alkenes and alkynes[6] has been extensively studied in the past decade. However, much of early-transition-metal silyl chemistry involves complexes containing cyclopentadienyl (Cp) ligands. Few d° Cp-free silyl complexes of the early transition metals have been reported.[3c,7−10] We recently synthesized a series of Cp-free d^0 alkyl, alkylidene, and alkylidyne silyl complexes of group 4, 5, and 6 metals.[7] It was found that, among these complexes, only those with the bulky ligand $Si(SiMe_3)_3$ are thermally stable.

Recently, the reaction of $Ti(NMe_2)_4$ with SiH_4 was found to produce a mixture of titanium silicides and nitride.[11] The mechanistic pathway involved in this reaction is, however, not clear. We have synthesized stable silyl complexes $(Me_2N)_3MSiR_3$ (R = silyl, alkyl) as models for $(Me_2N)_3MSiH_3$, which are possible intermediates in the reactions of $(Me_2N)_4M$ (M = Ti, Zr, Hf) with SiH_4. Although one example of a Cp-free group 4 amido silyl complex has been previously reported,[12] no structural information on this complex is available. In this paper

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we report the synthesis and characterization of a series of new group 4 amido silyl complexes $(Me_2N)_3MSi(SiMe_3)_3$ (M = Zr, Hf), $(Me_2N)_3TiSiPh_2Bu^t$, $(Me_2N)_3ZrSiPh_2Bu^t\cdot0.5THF$, $(Me_2N)_3HfSiPh_2Bu^t\cdot n$THF ($n$ = 0.5, 1), and $(Me_2N)_2[(Me_3Si)_2N]ZrSiR_3$ [$SiR_3 = Si(SiMe_3)_3$, $SiPh_2Bu^t$].

Experimental Section

General Procedures. All manipulations were performed under a dry nitrogen atmosphere with the use of either standard Schlenk techniques or a glovebox. All solvents were purified by distillation from potassium/benzophenone ketyl. $ZrCl_4$ and $HfCl_4$ (Strem) were purified by sublimation. $TiCl_4$ was converted into $TiCl_4(THF)_2$ before use.[13] $LiNMe_2$ and $LiN(SiMe_3)_2$ (Aldrich) were used as received. $Li(THF)_3Si(SiMe_3)_3$ and $Li(THF)_3SiPh_2Bu^t$ were prepared according to the literature procedures.[14,15] Benzene-d_6 was dried over activated molecular sieves and stored under nitrogen. NMR spectra were recorded on a Bruker AC-250 or AMX-400 Fourier transform spectrometer and were referenced to solvents (residual protons in the ^{1}H spectra) or, in the ^{29}Si spectra, to $SiMe_4$. The elemental analyses were performed by the E+R Microanalytical Laboratory (1259 Route 46, Parsippany, NJ 07054-4909).

Preparation of $(Me_2N)_3ZrSi(SiMe_3)_3$ (1). A white slurry of $ZrCl_4$ (1.00 g, 4.29 mmol) in 30 mL of THF at −30 °C was treated with 3 equiv of $LiNMe_2$ (0.66 g, 12.9 mmol) in 20 mL of THF. After being stirred for 6 h at room temperature, the reaction mixture was cooled to −30 °C, and 1 equiv of $Li(THF)_3Si(SiMe_3)_3$ (2.02 g, 4.29 mmol) in 20 mL of THF was added over 30 min. The yellow reaction solution was then slowly warmed to room temperature. Stirring at room temperature for 3 h and removal of volatiles afforded a yellow solid. Extraction of the solid with hexanes, followed by filtration and crystallization at −20 °C, yielded pale-yellow crystals of **1** (1.21 g, 60% yield). ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C): δ 2.94 (s, 18H, N*Me*$_2$), 0.39 (s, 27H, Si*Me*$_3$). ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C): δ 40.2 (N*Me*$_2$), 5.1 (Si*Me*$_3$). ^{29}Si{^{1}H} NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ −4.4 [Si(*Si*Me$_3$)$_3$], −124.6 [*Si*(SiMe$_3$)$_3$]. Anal. Calcd for $C_{15}H_{45}N_3Si_4Zr$: C, 38.24; H, 9.65. Found: C, 38.14; H, 9.54.

Preparation of $(Me_2N)_3HfSi(SiMe_3)_3$ (2). Complex **2** was prepared by a procedure similar to that for the preparation of **1** and isolated as pale-yellow crystals (yield 56%). ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C): δ 2.94 (s, 18H, N*Me*$_2$), 0.39 (s, 27H, Si*Me*$_3$). ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C): δ 38.9 (N*Me*$_2$), 5.2 (Si*Me*$_3$). ^{29}Si{^{1}H} NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ −2.1 [Si(*Si*Me$_3$)$_3$], −103.5 [*Si*(SiMe$_3$)$_3$]. Anal. Calcd for $C_{15}H_{45}N_3Si_4Hf$: C, 32.27; H, 8.12. Found: C, 32.12; H, 8.12.

Preparation of $(Me_2N)_3TiSiPh_2Bu^t$ (3). To a yellow slurry of $TiCl_4(THF)_2$ (1.00 g, 2.99 mmol) in 20 mL of THF was added dropwise with stirring 3 equiv of $LiNMe_2$ (0.458 g, 9.02 mmol) in 20 mL of THF at −30 °C. After being stirred for 12 h at room temperature, the reaction mixture was cooled to −50 °C, and 1 equiv of $Li(THF)_3SiPh_2Bu^t$ (1.38 g, 2.99 mmol) in 20 mL of THF was added over 30 min. The reaction solution immediately turned dark-green. After 3 h of stirring for −20 °C, the volatiles were removed to give a black solid. Extraction with hexanes, followed by filtration and crystallization at −20 °C, yielded dark-green crystals of **3** (0.62 g, yield 49%). ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C): δ 7.68−7.20 (m, 10H, C$_6$*H*$_5$), 3.06 (s, 18H, N*Me*$_2$), 1.22 (s, 9H, C*Me*$_3$). ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C): δ 144.5, 136.8, 127.3, 127.1 (*C*$_6$H$_5$), 42.9 (N*Me*$_2$), 30.1 (C*Me*$_3$), 22.3 (*C*Me$_3$). ^{29}Si{^{1}H} NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ 17.8 (*Si*Ph$_2$Bu^t). Anal. Calcd for $C_{22}H_{37}N_3SiTi$: C, 62.98; H, 8.89. Found: C, 62.77; H, 8.85.

Preparation of $(Me_2N)_3ZrSiPh_2Bu^t\cdot0.5THF$ (4). To a white slurry of $ZrCl_4$ (3.00 g, 12.9 mmol) in 20 mL of THF was added dropwise with stirring 3 equiv of $LiNMe_2$ (1.97 g, 38.6 mmol) in 20 mL of THF at −10 °C. After being stirred for 12 h at room temperature, the reaction mixture was cooled to −30 °C, and 1 equiv of $Li(THF)_3SiPh_2Bu^t$ (5.97 g, 12.9 mmol) in 20 mL of THF was added over 30 min. The reaction solution immediately turned bright yellow. After 3 h of stirring at −20 °C, the volatiles were removed to give a yellow solid. Extraction with pentane, followed by filtration and crystallization at −20 °C, yielded yellow crystals of **4** (4.85 g, yield 76%). A satisfactory elemental analysis of **4** could not be obtained as the complex is unstable at room temperature. The structure assignment for **4** was thus made from spectroscopic data and X-ray crystallography. ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C): δ 7.70−7.19 (m, 10H, C$_6$*H*$_5$), 3.51 (m, 2H, OC*H*$_2$CH$_2$), 2.82 (s, 18H, N*Me*$_2$), 1.38 (m, 2H, OCH$_2$C*H*$_2$), 1.26 (s, 9H, C*Me*$_3$). ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C): δ 145.2, 136.9, 127.3, 127.0 (*C*$_6$H$_5$), 67.9 (O*C*H$_2$CH$_2$), 40.5 (N*Me*$_2$), 30.2 (C*Me*$_3$), 25.7 (OCH$_2$*C*H$_2$), 21.8 (*C*Me$_3$). ^{29}Si{^{1}H} NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ 19.6 (*Si*Ph$_2$Bu^t).

Preparation of $(Me_2N)_3HfSiPh_2Bu^t\cdot n$THF [$n$ = 0.5 (5a), 1 (5b)]. Complex **5** was prepared by a procedure similar to that for the preparation of **4** and isolated as yellow crystals (yield 59%). A satisfactory elemental analysis of **5** could not be obtained as the complex is unstable at room temperature. Analysis by X-ray crystallography showed that the unit cell in **5a** is similar to that in **4**.[16] ^{1}H NMR for **5a** (benzene-d_6, 250.1 MHz, 23 °C): δ 7.71−7.18 (m, 10H, C$_6$*H*$_5$), 3.48 (m, 2H, OC*H*$_2$CH$_2$), 2.83 (s, 18H, N*Me*$_2$), 1.34 (m, 2H, OCH$_2$C*H*$_2$), 1.29 (s, 9H, C*Me*$_3$). ^{13}C NMR for **5a** (benzene-d_6, 62.9 MHz, 23 °C): δ 145.7, 137.1, 127.3, 127.0 (*C*$_6$H$_5$), 68.0 (O*C*H$_2$CH$_2$), 39.3 (N*Me*$_2$), 30.3 (C*Me*$_3$), 25.6 (OCH$_2$*C*H$_2$), 23.0 (*C*Me$_3$). ^{29}Si{^{1}H} NMR for **5a** (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ 46.8 (*Si*Ph$_2$Bu^t).

The structure of **5b** has been determined by X-ray crystallography.

Preparation of $(Me_2N)_2[(Me_3Si)_2N]ZrCl$ (6). A slurry of $ZrCl_4$ (3.00 g, 12.9 mmol) in 20 mL of THF was treated with 2 equiv of $LiNMe_2$ (1.32 g, 25.9 mmol), and the reaction mixture was stirred for 4 h at room temperature. At this time, 1 equiv of $LiN(SiMe_3)_2$ (2.15 g, 12.9 mmol) in 10 mL of THF was added. The reaction mixture was stirred overnight at room temperature, and the solvent was than removed by vacuum. The yellow residue was extracted with hexane, and the solution was concentrated and cooled to −18 °C for 24 h, yielding pale-yellow crystals of **6** (3.80 g, 79%). ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C): δ 3.08 (s, 12H, N*Me*$_2$), 0.33 (s, 18H, NSi*Me*$_3$). ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C): δ 45.5 (N*Me*$_2$), 3.7 (NSi*Me*$_3$). ^{29}Si{^{1}H} NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ −4.4 (N*Si*Me$_3$). Anal. Calcd for $C_{10}H_{30}N_3ClSi_2Zr$: C, 32.01; H, 8.06. Found: C, 31.66; H, 7.76.

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(16) The unit cell constants for **5a** have been obtained: orthorhombic, a = 16.583(4) Å, b = 17.299(5) Å, c = 18.570(4) Å, V = 5327(2) Å^3.

Table 1. Crystallographic Data for **1**, **3**, **4**, **5b**, and **8**

	1	**3**	**4**	**5b**	**8**
formula	$C_{15}H_{45}N_3Si_4Zr$	$C_{22}H_{37}N_3SiTi$	$C_{24}H_{41}N_3O_{0.5}SiZr$	$C_{26}H_{45}N_3OSiHf$	$C_{26}H_{49}N_3Si_3Zr$
fw	471.12	419.54	498.92	622.23	579.17
color	pale-yellow	dark-green	yellow	pale-yellow	pale-yellow
cryst size, mm	0.46 × 0.36 × 0.24	0.48 × 0.38 × 0.24	0.56 × 0.50 × 0.48	0.60 × 0.45 × 0.24	0.48 × 0.45 × 0.40
T, °C	−100(2)	−100(2)	−100(2)	−100(2)	−100(2)
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	rhombohedral	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$R3c$	$P2_1$	$Pbca$	$Pna2_1$	$Pca2_1$
a, Å	15.505(2)	8.633(5)	16.538(9)	17.463(6)	19.775(5)
b, Å	15.505(2)	14.790(7)	17.282(7)	9.453(3)	10.182(2)
c, Å	19.308(4)	9.388(4)	18.566(8)	17.800(6)	15.752(5)
α, deg	90	90	90	90	90
β, deg	90	92.44(4)	90	90	90
γ, deg	120	90	90	90	90
V, Å^3	4019.9(13)	1197.6(10)	5306(4)	2938(2)	3172(2)
Z	6	2	8	4	4
D_{calc}, g/cm^3	1.168	1.163	1.249	1.407	1.213
μ(MoKα), cm^{-1}	5.92	4.18	4.76	36.11	4.78
R1 (wR2)[a]	0.0354 (0.0820)	0.0417 (0.1125)	0.0414 (0.1206)	0.0271 (0.0590)	0.0293 (0.0680)
goodness of fit	1.049	1.005	1.031	1.056	1.031

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2])^{1/2}$.

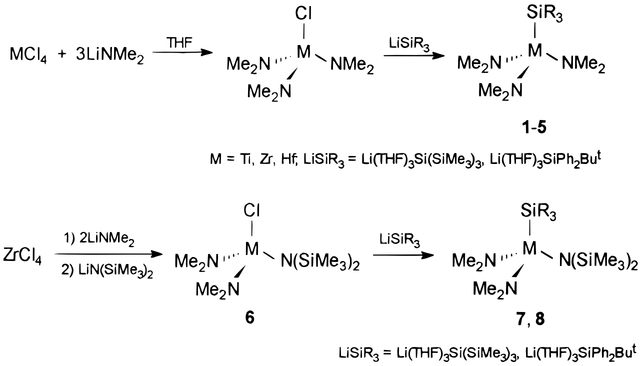
Preparation of $(Me_2N)_2[(Me_3Si)_2N]ZrSi(SiMe_3)_3$ (7). A solution of **6** (0.36 g, 0.96 mmol) in 5 mL of benzene was treated with 1 equiv of $Li(THF)_3Si(SiMe_3)_3$ (0.45 g, 0.96 mmol) at room temperature. The reaction mixture was stirred for 30 min, and the solvent was removed in vacuo. The yellow residue was extracted with pentane, and the solution was concentrated and cooled to −18 °C to afford pale-yellow crystals of **7** (0.32 g, 57%). ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C): δ 2.94 (s, 12H, N*Me*$_2$), 0.41 [s, 27H, Si(Si*Me*$_3$)$_3$], 0.29 (s, 18H, NSi*Me*$_3$). ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C): δ 40.9 (N*Me*$_2$), 5.6 [Si(Si*Me*$_3$)$_3$], 5.1 (NSi*Me*$_3$). ^{29}Si{^{1}H} NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ −3.8 (N*Si*Me$_3$), −5.4 [Si(*Si*Me$_3$)$_3$], −121.3 [*Si*(SiMe$_3$)$_3$]. Anal. Calcd for $C_{19}H_{57}N_3Si_6Zr$: C, 38.85; H, 9.78. Found: C, 38.51; H, 9.51.

Preparation of $(Me_2N)_2[(Me_3Si)_2N]ZrSiPh_2Bu^t$ (8). A solution of **6** (0.50 g, 1.3 mmol) in 10 mL of toluene was treated with 1 equiv of $Li(THF)_3SiPhBu^t$ (0.62 g, 1.3 mmol) at room temperature. The reaction mixture was stirred for 30 min, and the solvent was removed under vacuum. The yellow-orange residue was extracted with pentane, and the solution was concentrated and cooled to −18 °C to afford bright-yellow crystals of **8** (0.36 g, 47%). ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C): δ 2.89 (s, 12H, N*Me*$_2$), 1.22 (s, 9H, SiC*Me*$_3$), 0.16 (s, 18H, NSi*Me*$_3$). ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C): δ 144.9, 137.2, 127.5, 127.3 (Ph), 41.3 (N*Me*$_2$), 31.0 (SiC*Me*$_3$), 22.7 (Si*C*Me$_3$), 4.6 (NSi*Me*$_3$). ^{29}Si{^{1}H} NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ 18.1 (*Si*Ph$_2$Bu^t), −4.8 (N*Si*Me$_3$). Anal. Calcd for $C_{26}H_{49}N_3Si_3Zr$: C, 53.92; H, 8.53. Found: C, 54.44; H, 9.04.

Decomposition of 1−5 by H_2O. A 50 mg sample of **1** was placed in an NMR tube and dissolved in benzene-d_6 containing 1 equiv of H_2O at room temperature. After 4 h, white ZrO_2 had precipitated in the NMR tube. NMR spectra of the supernatant solution showed it to be a mixture of $Zr(NMe_2)_4$,[17] $HSi(SiMe_3)_3$, and $HNMe_2$. The reactions of **2**−**5** with H_2O gave similar results.

X-ray Crystal Structure Determinations of 1, 3, 4, 5b, and 8. Crystal data and a summary of intensity data collection parameters for **1**, **3**, **4**, **5b**, and **8** are given in Table 1. The crystal structures of **1**, **3**, **4**, **5b**, and **8** were determined on a Siemens R3m/V diffractometer equipped with a graphite-monochromated Mo source (Kα radiation, 0.710 73 Å) and fitted with a Nicolet LT-2 low-temperature device. Suitable crystals were coated with Paratone oil (Exxon) and mounted under a stream of nitrogen at 173 K. The unit cell parameters and orientation matrix were determined from a least-squares fit of the orientation of at least 30 reflections obtained from a rotation photograph and an automatic peak search routine. The structures were solved by direct methods. Non-hydrogen atoms were anisotropically refined except for those of the disordered THF molecule in **4**. All hydrogen atoms were placed in calculated positions and introduced into the refinement as fixed contributors with an isotropic U value of 0.08 Å^2. All calculations were performed using the Siemens SHELXTL 93 (version 5.0) proprietary software package.

Scheme 1



Results and Discussion

Synthesis and Spectroscopic Properties of 1−8. Complexes **1**−**5** were prepared by the reactions of $(Me_2N)_3MCl$ (M = Ti,[12] Zr, Hf) with $Li(THF)_3Si(SiMe_3)_3$ or $Li(THF)_3SiPh_2Bu^t$ in THF (Scheme 1); $(Me_2N)_3MCl$ were generated in situ by reactions of 3 equiv of $LiNMe_2$ with MCl_4 in THF. Complexes **7** and **8** were synthesized by the reactions of $(Me_2N)_2[(Me_3Si)_2N]ZrCl$ (**6**) with $Li(THF)_3Si(SiMe_3)_3$ and $Li(THF)_3SiPh_2Bu^t$, respectively, in THF (Scheme 1). The new chloro triamido complex **6** was prepared from $ZrCl_4$, $LiNMe_2$, and $LiN(SiMe_3)_2$ in a 1:2:1 ratio in THF. All the complexes are extremely air- and moisture-sensitive. It is interesting to note that when **1**−**5** were treated with 1 equiv of H_2O, tetraamido complexes $M(NMe_2)_4$ (M = Ti, Zr, or Hf) were produced along with silanes [$HSi(SiMe_3)_3$, $HSiPh_2Bu^t$], $HNMe_2$, and metal oxides (TiO_2, ZrO_2, HfO_2) (eq 1). Treating **1**−**5** with excess H_2O results in the complete decomposition of these complexes to produce the corresponding silanes, $HNMe_2$, and MO_2.

$$(Me_2N)_3MSiR_3 + H_2O \longrightarrow 1/2\ MO_2 + HNMe_2 + HSiR_3 + 1/2\ M(NMe_2)_4 \quad (1)$$

$R_3 = (SiMe_3)_3$, M = Zr, **1**; Hf, **2**;

$R_3 = Ph_2Bu^t$, M = Ti, **3**; $Zr(THF)_{0.5}$, **4**; $Hf(THF)_{0.5}$, **5**.

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(17) Chisholm, M. H.; Hammond, C. E.; Huffman, J. C. *Polyhedron* **1988**, *7*, 2515.

Complexes **1**, **2**, **7**, and **8** are thermally stable in both the solid state and solution. While **3**−**5** containing $SiPh_2Bu^t$ ligands can be stored indefinitely as crystalline solids at −20 °C, they tend to decompose over days at room temperature to give $HSiPh_2Bu^t$ and unidentified metal-containing species. This is probably due to the fact that complexes **3**−**5** containing $SiPh_2Bu^t$ ligands are more sterically unsaturated than **1**, **2**, **7**, and **8** containing the bulky $Si(SiMe_3)_3$ ligands. This is also consistent with the observation that trialkyl silyl complexes $R_3MSi(SiMe_3)_3$ ($R = CH_2CMe_3$, CH_2SiMe_3; M = Ti, Zr) are thermally stable at room temperature[7a,b] while no stable alkyl complexes containing $SiPh_2Bu^t$ ligands have yet been isolated. The isolation of **3**−**5** suggests that the stabilization of these complexes may be attributed to the strong electronegative donor nature of the amido ligands and the partial p(π)−d(π) bonds between the amido ligands and the metal centers.[17]

Spectroscopic properties [^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR] of the complexes are consistent with the structure assignments. The ^1H and $^{13}C\{^1H\}$ NMR resonances of the $Si(SiMe_3)_3$ ligand in **1**, **2**, and **7** resemble those observed for other group 4 $Si(SiMe_3)_3$ derivatives such as alkyl and alkoxide silyl complexes.[3c,7] However, the tertiary silicon NMR resonances of the M-*Si*$(SiMe_3)_3$ ligands in **1** (−124.6 ppm), **2** (−103.5 ppm), and **7** (−121.3 ppm) are significantly upfield shifted from those in the alkyl silyl complexes $(Me_3CCH_2)_3ZrSi(SiMe_3)_3$ (−85.8 ppm)[7b] and $(Me_3SiCH_2)_3ZrSi(SiMe_3)_3$ (−75.7 ppm)[7b] but are close to the corresponding values for $(Me_3CO)_3MSi(SiMe_3)_3$ [M = Zr (−115.82 ppm), Hf (−103.47 ppm)].[3c] The upfield shifts of the tertiary silicon NMR resonances in **1**, **2**, and **7** can be attributed to the p(π)−d(π) bonding between the lone pairs on the amido ligands and the metal centers. To our knowledge, few group 4 metal silyl complexes containing $SiPh_2Bu^t$ ligands have been reported and are available for comparison of ^{29}Si NMR.[10,18] The ^{29}Si NMR signals of **3** (17.8 ppm), **4** (19.6 ppm), **5** (46.8 ppm), and **8** (18.1 ppm) are downfield shifted compared to that (7.54 ppm) of $Li(THF)_3SiPh_2Bu^t$.[15] However, compared to the ^{29}Si chemical shift of $(Me_3SiO)_2Zr(SiPh_2Bu^t)Cl\cdot 2THF$ (49.6 ppm),[10] those of the Zr complexes **4** and **8** are upfield shifted.

It is interesting to note that **4** and **5** contain coordinated THF molecules whereas **3** is isolated solvent free. This perhaps is the result of the smaller size of the Ti(IV) ion in comparison to Zr(IV) and Hf(IV) ions. The chemical shifts of the THF molecule in **4** and **5** are found to be close to those of free THF, indicating a very weak bonding interaction between the THF molecule and metal center. This also suggests that complexes **4** and **5** are less sterically crowded compared to **1** and **2**, containing bulkier $Si(SiMe_3)_3$ ligands. The coordinated THF molecules in **4** and **5** are found to be labile, and the coordination of **5** with one-half or one coordinated THF has been observed. Replacing one of the NMe_2 ligands in **4** with a bulky $N(SiMe_3)_2$ ligand led to the THF-free complex **8**.

Solid-State Structures of 1, 3, 4, 5b, and 8. Complexes **1**, **3**, **4**, **5b**, and **8** have been characterized by X-ray crystallography. The molecular structure of **1** is shown in Figure 1. Selected bond distances and angles are listed in Table 2. In the structure of **1**, there is a crystallographically imposed 3-fold rotation axis along the Zr−Si bond with the three amido ligands on Zr staggered with respect to the trimethylsilyl groups on the tertiary silicon atom. The Zr atom exhibits a pseudotetrahedral geometry around the metal center. The Si−Zr−N [106.1(2)°] and N−Zr−N [112.6(2)°] angles are very close to those observed in tetrahedral alkyl silyl complexes $(Me_3CCH_2)_3TiSi(SiMe_3)_3$ [105.4(4) and 113.2(4)°],[7b] $(Me_3SiCH_2)_3TiSi(SiMe_3)_3$ [106.4(2) and 113.0(7)°],[7b] and $(Me_3CCH_2)_3ZrSi(SiMe_3)_3$ [105.6(8) and 113.0(7)°][19] and the alkoxide silyl complex $(Me_3CO)_3MSi(SiMe_3)_3$ [107.6(3) and 111.4(4)°].[3c]

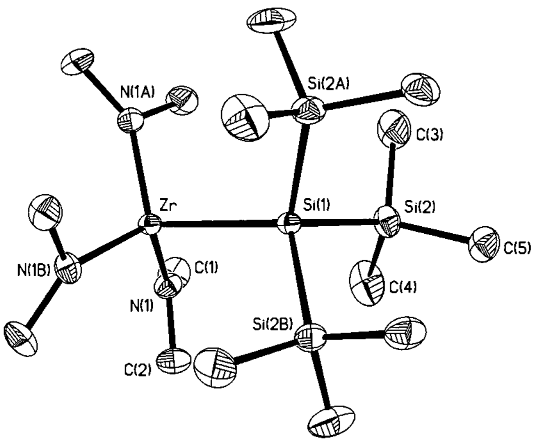

Figure 1. ORTEP view of the molecular structure of $(Me_2N)_3ZrSi(SiMe_3)_3$ (**1**), showing 50% thermal ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Zr−N(1)	2.018(7)	C(1)−N(1)	1.434(11)
Zr−Si(1)	2.784(4)	C(2)−N(1)	1.466(11)
Si(1)−Si(2)	2.334(3)	C(3)−Si(2)	1.842(10)
Si(2)−Si(4)	1.861(10)	C(5)−Si(2)	1.914(11)
N(1)−Zr−N(1A)	112.6(2)	Zr−N(1)−C(1)	137.9(6)
N(1)−Zr−Si(1)	106.1(2)	Zr−N(1)−C(2)	110.8(5)
Zr−Si(1)−Si(2)	112.61(12)	Si(1)−Si(2)−C(3)	111.8(3)
C(1)−N(1)−C(2)	111.3(7)	Si(1)−Si(2)−C(5)	109.0(4)
Si(1)−Si(2)−C(4)	114.1(3)	Si(2)−Si(1)−Si(2A)	106.16(13)

The Zr−N bond distance of 2.018(7) Å in **1** is similar to the terminal Zr−N bonds found in other Zr(IV) amido complexes[17,20] and is consistent with the presence of strong p(π)−d(π) bonding between the Zr center and Me_2N ligands.[17] The Zr−Si bond distance of 2.784(4) Å in **1** is slightly longer than the corresponding distances in the more sterically congested complexes $(Me_3CCH_2)_3ZrSi(SiMe_3)_3$ [2.74(2) Å][19] and $(Me_3CO)_3MSi(SiMe_3)_3$ [2.753(4) Å].[3c] The reason for the lengthening of the Zr−Si bond in **1** is not clear.

An ORTEP view of **3** is shown in Figure 2. Selected bond distances and angles are listed in Table 3. In the structure of **3**, the Ti atom is bonded to one $SiPh_2Bu^t$ and three Me_2N ligands to give a four-coordinated metal complex with the amido and

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(18) $Cp_2Zr(SiPh_2Bu^t)Cl$ was reported to be generated in situ in the reaction of $Cp_2ZrCl_2 + Li(THF)_3SiPh_2Bu^t$ with 2,6-dimethylphenyl isocyanide but could not be isolated: Honda, T.; Satoh, S.; Mori, M. *Organometallics* **1995**, *14*, 1548.

(19) Wu, Z.; McAlexander, L. H.; Diminnie, J. B.; Xue, Z. *Organometallics* **1998**, *17*, 4853.

(20) Some representative Zr−N bond lengths for Zr(IV) amide complexes follow. (a) 2.06 Å, $(Me_2N)_2Zr(\mu\text{-}NBu^t)_2Zr(NMe_2)_2$: Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030. (b) 2.06 Å, *rac*-$[C_2H_4(C_9H_6)_2]Zr(NMe_2)_2$: Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024. (c) 2.07 Å, *rac*-$[SiMe_2(C_9H_6)]_2Zr(NMe_2)_2$: 2.04 Å, $[\mu\text{-}SiMe_2(C_9H_6)_2]Zr_2(NMe_2)_6$: Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4038. (d) 2.07 Å, $[(Me_3Si)_2N]_3ZrCl$: Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Rarthby, P. R. *J. Chem. Soc., Dalton Trans* **1980**, 2000. (e) 2.08 Å, $[(Me_3Si)_2N]_3ZrMe$: Bradley, D. C.; Chudzynska, H.; Becker-Dirks, J. D.; Hursthouse, M. B.; Ibrahim, A. A.; Montevalli, M.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 1423. (f) 2.068 Å, $(Me_2N)_3Zr(\mu\text{-}NMe_2)_2Zr(NMe_2)_3$.[17] (g) 2.023 Å, $(Me_2N)_2ZrCl_2(THF)_2$; 2.032 Å, $(Et_2N)_2ZrCl_2(THF)_2$: Brenner, S.; Kempe, R.; Arndt, P. *Z. Anorg. Allg. Chem.* **1995**, *621*, 2021. (h) 2.060 Å, $(Me_2N)_3Zr(\mu\text{-}NMe_2)(\mu\text{-}Cl)_2Zr(NMe_2)_2(THF)$; 2.034 Å, $Cl(Me_2N)_2Zr(\mu\text{-}NMe_2)(\mu\text{-}Cl)_2Zr(NMe_2)_2(THF)$: Wu, Z.; Diminnie, J. B.; Xue, Z. *Inorg. Chem.* **1998**, *37*, 2570.

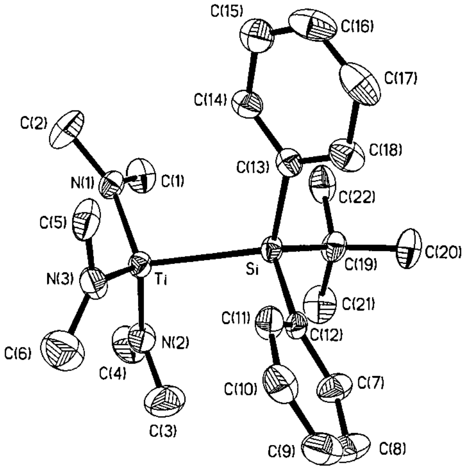

Figure 2. ORTEP view of the molecular structure of $(Me_2N)_3TiSiPh_2Bu^t$ (**3**), showing 50% thermal ellipsoids.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3**

Ti−N(1)	1.897(5)	N(1)−C(1)	1.454(8)
Ti−N(2)	1.868(5)	N(1)−C(2)	1.454(9)
Ti−N(3)	1.884(5)	N(2)−C(3)	1.457(9)
Ti−Si	2.635(2)	N(2)−C(4)	1.459(9)
N(3)−C(5)	1.456(8)	Si−C(12)	1.893(6)
N(3)−C(6)	1.442(9)	Si−C(13)	1.920(6)
Si−C(19)	1.931(6)		
Si−Ti−N(1)	108.3(2)	Ti−Si−C(12)	105.9(2)
Si−Ti−N(2)	104.3(2)	Ti−Si−C(13)	111.3(2)
Si−Ti−N(3)	101.3(2)	Ti−Si−C(19)	118.1(2)
N(1)−Ti−N(2)	114.2(2)	Ti−N(1)−C(1)	115.1(4)
N(1)−Ti−N(3)	113.4(2)	Ti−N(1)−C(2)	133.8(5)
N(2)−Ti−N(3)	113.9(2)	C(1)−N(1)−C(2)	111.0(6)
Ti−N(2)−C(3)	113.5(5)	Ti−N(3)−C(5)	115.9(4)
Ti−N(2)−C(4)	135.0(5)	Ti−N(3)−C(6)	131.9(5)
C(3)−N(2)−C(4)	111.5(6)	C(5)−N(3)−C(6)	112.1(6)

$SiPh_2Bu^t$ ligands staggered with respect to each other. The geometry around Ti is a distorted tetrahedron with a mean Si−Ti−N angle of 104.6(2)° and a mean N−Ti−N angle of 113.8(2)°. These bond angles are close to those found in **1** but different from those in $(Me_2N)_3TiCl$ [Cl−Ti−N = 113.3(2)° and N−Ti−N = 105.4(2)°].[21] The average Ti−N bond distance of 1.883(5) Å is slightly longer than that in $(Me_2N)_3TiCl$ [1.866(4) Å],[21] consistent with the fact that complex **3** is more sterically crowded than $(Me_2N)_3TiCl$. As in the structure of **1**, the Ti−Si bond distance of 2.635(2) Å is slightly longer than those in the more crowded alkyl silyl complexes $(Me_3CCH_2)_3TiSi(SiMe_3)_3$ [2.618(8) Å] and $(Me_3CCH_2)_3TiSi(SiMe_3)_3$ [2.603(3) Å].[7b]

An ORTEP view of **4** is shown in Figure 3. Selected bond distances and angles are listed in Table 4. In the solid-state structure of **4**, there is one disordered THF molecule between two back-to-back $(Me_2N)_3ZrSiPh_2Bu^t$ molecules. Each Zr atom is coordinated by three Me_2N ligands, one $SiPh_2Bu^t$ group, and a THF molecule to form a distorted trigonal bipyramidal geometry with the axial Si−Zr−O angle [172.3(2)°] near 180°. The angles from the Si−Zr vector to the equatorial Me_2N ligands range from 94.41(12) to 100.52(11)°, and are smaller than those in **1** and **3**. The O−Zr−N angles range from 78.6(2) to 85.7(2)°.

The average Zr−N bond distance of 2.021(4) Å is similar to that found in **1**. The Zr−Si bond distance of 2.803(2) Å is longer than those in **1**, $(Me_3CCH_2)_3ZrSi(SiMe_3)_3$ [2.74(2) Å],[19] and $(Me_3CO)_3MSi(SiMe_3)_3$ [2.753(4) Å][3c] and is close to those in $Cp_2Zr(SiPh_3)Cl$ [2.813(3) Å][22] and $Cp_2Zr(SiMe_3)(S_2CNEt_2)$ [2.815(1) Å][23] but is shorter than that found in the six-coordinate complex $(Me_3SiO)_2Zr(SiPh_2Bu^t)Cl{\cdot}2THF$ [2.848(3) Å].[10] The longer Zr−Si bond in **4** compared to that in **1** is probably due to the presence of the trans-coordinated THF molecule. The Zr−O(THF) bond distance of 2.532(8) Å is significantly longer than normal Zr(IV)-O(THF) bond distances, as observed in $(Me_2N)ZrCl_2(THF)_2$ [2.342(2) and 2.330(2) Å],[20g] $(Me_2N)_3Zr(\mu\text{-Cl})_2(\mu\text{-NMe}_2)Zr(NMe_2)_2(THF)$ [2.244(4) Å],[20h] $(Me_2N)_2ClZr(\mu\text{-Cl})_2(\mu\text{-NMe}_2)Zr(NMe_2)_2(THF)$ [2.249(3) Å], and $(Me_2N)(THF)Cl_2Zr(\mu\text{-Cl})_2Li(THF)_2$ [2.322(4) Å],[20h] indicating a very weak interaction between the Zr atom and THF molecule. This is consistent with chemical shifts of the THF ligand in **4** that are close to those of free THF.

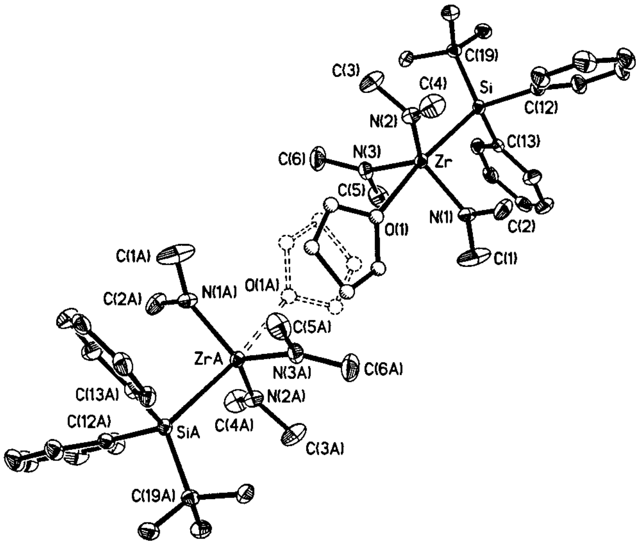

Figure 3. ORTEP view of the molecular structure of $(Me_2N)_3ZrSiPh_2Bu^t{\cdot}0.5THF$ (**4**), showing 50% thermal ellipsoids.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **4**

Zr−N(1)	2.004(4)	N(1)−C(1)	1.437(7)
Zr−N(2)	2.034(4)	N(1)−C(2)	1.441(6)
Zr−N(3)	2.026(4)	N(2)−C(3)	1.441(6)
Zr−Si	2.803(2)	N(2)−C(4)	1.441(6)
Zr−O(1)	2.532(8)	N(3)−C(5)	1.445(7)
Si−C(12)	1.918(5)	N(3)−C(6)	1.427(6)
Si−C(13)	1.908(5)	Si−C(19)	1.938(5)
Si−Zr−N(1)	94.41(12)	Zr−Si−C(12)	111.9(2)
Si−Zr−N(2)	102.11(11)	Zr−Si−C(13)	108.46(14)
Si−Zr−N(3)	100.52(11)	Zr−Si−C(19)	117.8(2)
O(1)−Zr−Si	172.3(2)	Zr−N(1)−C(1)	136.0(4)
O(1)−Zr−N(1)	78.6(2)	Zr−N(1)−C(2)	113.1(3)
O(1)−Zr−N(2)	78.7(2)	Zr−N(2)−C(3)	111.2(3)
O(1)−Zr−N(3)	85.7(2)	Zr−N(2)−C(4)	138.9(4)
N(1)−Zr−N(2)	119.3(2)	Zr−N(3)−C(5)	112.5(3)
N(1)−Zr−N(3)	116.1(2)	Zr−N(3)−C(6)	137.5(4)
N(2)−Zr−N(3)	117.3(2)	C(1)−N(1)−C(2)	110.9(5)
C(3)−N(2)−C(4)	109.9(4)	C(5)−N(3)−C(6)	110.0(5)

The hafnium complex $(Me_2N)_3HfSiPh_2Bu^t{\cdot}n$THF [$n$ = 0.5 (**5a**) or 1 (**5b**)] was found to crystallize with one-half or one coordinated THF ligand. The unit cell parameters of **5a** are similar to those of **4**,[16] indicating that **4** and **5a** are isostructural. The structure of **5b** was determined. An ORTEP view of **5b** is shown in Figure 4. Selected bond distances and angles are given in Table 5. **5b** adopts a distorted trigonal bipyramidal geometry,

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(21) Dick, D. G.; Rousseau, R.; Stephan, D. W. *Can. J. Chem.* **1991**, *69*, 357.

(22) Muir, K. J. *J. Chem. Soc. A* **1971**, 2663.

(23) Tilley, T. D. *Organometallics* **1985**, *4*, 1452.

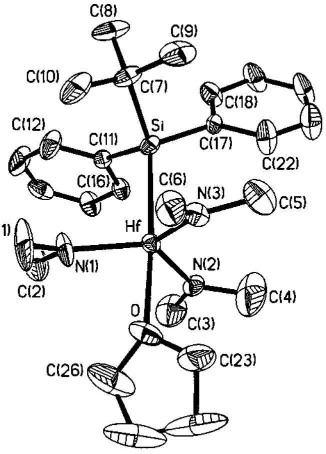

Figure 4. ORTEP view of the molecular structure of (Me$_2$N)$_3$HfSiPh$_2$-Bu^t·THF (**5b**), showing 35% thermal ellipsoids.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **5b**

Hf−N(1)	2.019(9)	N(1)−C(1)	1.42(2)
Hf−N(2)	2.030(9)	N(1)−C(2)	1.45(2)
Hf−N(3)	2.022(8)	N(2)−C(3)	1.41(2)
Hf−Si	2.807(4)	N(2)−C(4)	1.41(2)
Hf−O	2.390(9)	N(3)−C(5)	1.45(2)
Si−C(7)	1.933(11)	N(3)−C(6)	1.47(2)
Si−C(11)	1.925(11)	Si−C(17)	1.918(12)
Si−Hf−N(1)	93.1(4)	Hf−Si−C(12)	114.4(4)
Si−Hf−N(2)	94.1(3)	Hf−Si−C(13)	107.3(3)
Si−Hf−N(3)	99.3(3)	Hf−Si−C(19)	119.6(3)
O−Hf−Si	176.5(3)	Hf−N(1)−C(1)	125.6(10)
O−Hf−N(1)	83.5(5)	Hf−N(1)−C(2)	122.9(9)
O−Hf−N(2)	88.3(4)	Hf−N(2)−C(3)	127.2(9)
O−Hf−N(3)	81.8(4)	Hf−N(2)−C(4)	124.7(10)
N(1)−Hf−N(2)	118.0(4)	Hf−N(3)−C(5)	126.8(8)
N(1)−Hf−N(3)	121.2(4)	Hf−N(3)−C(6)	124.1(8)
N(2)−Hf−N(3)	118.1(4)	C(1)−N(1)−C(2)	111.3(11)
C(3)−N(2)−C(4)	108.0(11)	C(5)−N(3)−C(6)	109.0(9)

as observed in **4**. The bond distances and angles in **5b** are close to those found in **4** except that the Hf−O bond [2.390(9) Å] is shorter than that in **4**. The Hf−Si bond [2.807(4) Å] in **5b** is longer than those in Cp*Hf[Si(SiMe$_3$)$_3$]Cl$_2$ [2.748(4) Å],[24] CpCp*Hf[SiH(SiMe$_3$)$_2$]H [2.744(1) Å],[25] and CpCp*Hf(SiH$_2$-Ph)Cl [2.729(3) Å][26] but is shorter than those in the crowded complex CpCp*Hf[Si(SiMe$_3$)$_3$]Cl [2.881(4) and 2.888(4) Å].[26]

An ORTEP view of **8** is shown in Figure 5. Selected bond distances and angles are listed in Table 6. In **8**, the Zr atom is bonded to one (Me$_3$Si)$_2$N and one SiPh$_2$Bu^t and two Me$_2$N ligands to form a distorted tetrahedral geometry. It is interesting to note that, in contrast to the staggered conformation in the structures of **1**, **3**, and **4**, in **8**, the three amido ligands in **8** are nearly eclipsed with respect to the SiPh$_2$Bu^t ligand (Figure 6). This is perhaps the result of a larger steric repulsion between the (Me$_3$Si)$_2$N and SiPh$_2$Bu^t ligands. The three Si−Zr−N angles are significantly different; the Si−Zr−N(SiMe$_3$)$_2$ angle [120.17(14)°] is larger than the Si−Zr−NMe$_2$ angles [97.55(14) and 115.48(14)°]. The N−Zr−N angles [108.4(2) and 109.6(2)°] between Me$_2$N and (Me$_3$Si)$_2$N ligands are also larger than that [103.2(2)°] between the two Me$_2$N ligands. The Zr−N(3)−Si(2) (proximal) angle [113.5(3)°] and the Zr−N(3)−Si(3) (distal) angle [124.9(3)°] are close to those in Zr(IV) complexes containing the (Me$_3$Si)$_2$N ligand.[20d,e]

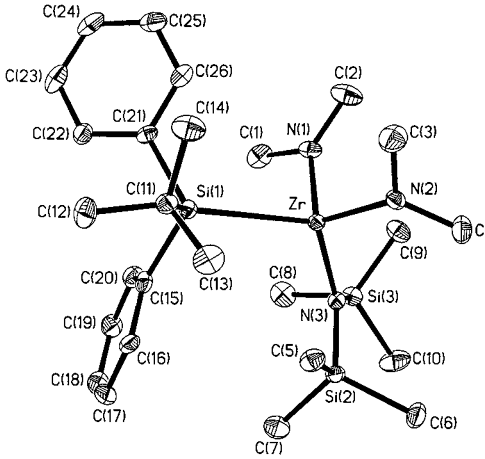

Figure 5. ORTEP view of the molecular structure of (Me$_2$N)$_2$[(Me$_3$-Si)$_2$N]ZrSiPh$_2$Bu^t (**8**), showing 35% thermal ellipsoids.

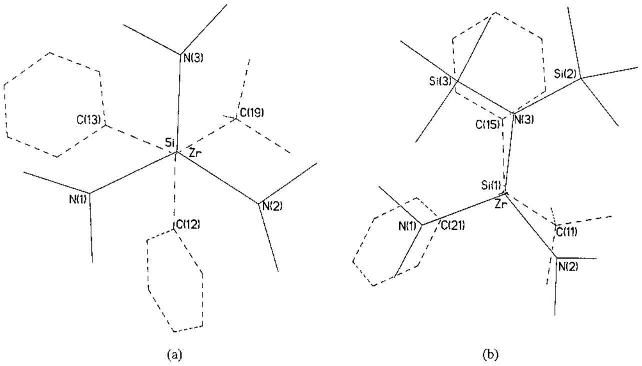

Figure 6. (a) View of the molecular structure of (Me$_2$N)$_3$ZrSiPh$_2$Bu^t·0.5THF (**4**) along the Zr−Si bond. The THF ligand was omitted for clarity. (b) View of the molecular structure of (Me$_2$N)$_2$[(Me$_3$Si)$_2$N]-ZrSiPh$_2$Bu^t (**8**) along the Zr−Si bond.

Table 6. Selected Bond Distances (Å) and Angles (deg) for **8**

Zr−N(1)	2.014(5)	N(1)−C(1)	1.466(8)
Zr−N(2)	2.001(5)	N(1)−C(2)	1.442(8)
Zr−N(3)	2.087(5)	N(2)−C(3)	1.467(8)
Zr−Si(1)	2.860(2)	N(2)−C(4)	1.453(7)
Si(1)−C(11)	1.922(6)	N(3)−Si(2)	1.732(5)
Si(1)−C(15)	1.923(6)	N(3)−Si(3)	1.739(5)
Si(1)−C(21)	1.906(6)		
Si(1)−Zr−N(1)	97.55(14)	Zr−Si−C(11)	123.2(2)
Si(1)−Zr−N(2)	115.48(14)	Zr−Si−C(15)	102.1(2)
Si(1)−Zr−N(3)	120.17(14)	Zr−Si−C(21)	110.4(2)
N(1)−Zr−N(2)	103.2(2)	Zr−N(3)−Si(2)	113.5(3)
N(1)−Zr−N(3)	108.4(2)	Zr−N(3)−Si(3)	124.9(3)
N(2)−Zr−N(3)	109.6(2)	Si(2)−N(3)−Si(3)	121.6(3)
C(11)−Si(1)−C(15)	110.6(3)	Zr−N(1)−C(1)	113.1(4)
C(11)−Si(1)−C(21)	103.8(3)	Zr−N(1)−C(2)	134.5(5)
C(15)−Si(1)−C(21)	105.6(3)	Zr−N(2)−C(3)	118.1(4)
Zr−N(2)−C(4)	129.3(4)		

The Zr−N(SiMe$_3$)$_2$ bond distance of 2.087(4) Å in **8** is slightly longer than the Zr−NMe$_2$ bond distances [ranging from 2.001(5) to 2.034(4) Å] in **1**, **4**, and **8** but is close to that [2.080(5) Å] in MeZr[N(SiMe$_3$)$_2$]$_3$.[20e] The Zr−Si bond distance of 2.860(2) Å in **8** is longer than those found in **1**, **4**, and other known Zr(IV) silyl complexes.[3c,10,19,22,23,27] To our knowledge, the Zr−Si bond in **8** is the longest reported Zr−Si bond. The

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lengthening of the Zr−Si bond in **8** perhaps can be attributed to the steric repulsion from the bulky $(Me_3Si)_2N$ ligand.

Conclusions

In summary, a series of Cp-free d^0 group 4 amido silyl complexes have been synthesized and characterized. These complexes add to the relatively new family of Cp-free group 4 silyl complexes. The spectroscopic properties and structural features of these complexes suggest that the $p(\pi)-d(\pi)$ interactions between amido ligands and metal centers can stabilize coordinatively unsaturated and electronically deficient silyl complexes.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, thermal parameters, and bond lengths and angles for **1**, **3**, **4**, **5b**, and **8** (26 pages). Ordering information is given on any current masthead page.

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