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Zirconium Compounds of Hexamethyldisiloxane. Synthesis and Structure of $(\eta^5\text{-}C_5H_5)_2Zr(CH_2SiMe_2OSiMe_3)_2$ and $(\eta^5\text{-}C_5Me_5)ZrCl_2(\eta^2\text{-}CH_2SiMe_2OSiMe_3)$ and Their Reactivity with Methyl Isocyanide

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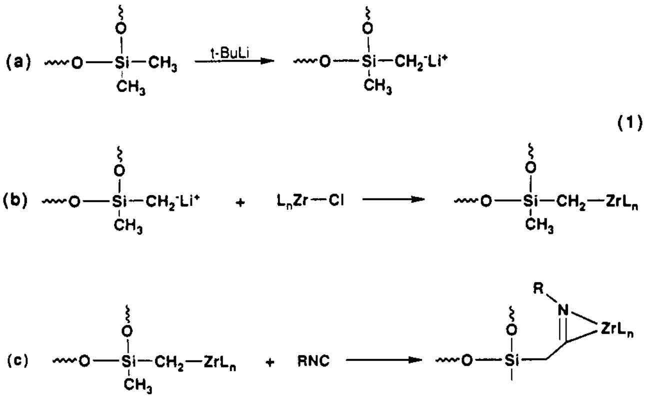
A preliminary investigation into the feasibility of using organozirconium reagents to functionalize the methyl groups of polydimethylsiloxanes is made. Hexamethyldisiloxane is deprotonated and then bound to Zr to give $Cp_2Zr(CH_2SiMe_2OSiMe_3)_2$ (**1**) and $Cp^*ZrCl_2(CH_2SiMe_2OSiMe_3)$ (**3**). These represent the first well-characterized compounds possessing methylsiloxane coordinated to zirconium. X-ray crystallography of **1** and **3** reveals a monodentate and a bidentate coordination mode, respectively, with **3** possessing an unexpected and very weak bond to the siloxane oxygen [Zr–O = 2.427 (3) Å]. This is among the longest Zr–O bonds known. Data for **1**: cell constants a = 8.330 (3) Å, b = 16.077 (6) Å, c = 10.710 (4) Å, β = 94.66 (1)°; space group $P2_1$; R = 0.0194, R_w = 0.0227. Data for **3**: cell constants a = 14.530 (2) Å, b = 8.417 (1) Å, c = 18.725 (4) Å, β = 106.62 (1)°; space group $P2_1/n$; R = 0.0318, R_w = 0.0372. Compounds **1** and **3** react readily with MeNC to yield insertion products.

Introduction

We have begun to explore the possibility of using organozirconium reagents to functionalize the methyl groups on polydimethylsiloxanes (PDMS's) $[Me_3Si\text{–}(OSiMe_2)_n\text{–}SiMe_3]$. PDMS's are currently prepared via the inexpensive "direct process" and have found wide use as lubricants and surfactants.[1] Conversion of some of the polymer methyl groups to more polar functionalities would lead to new and different properties for this class of compounds. The envisioned conversion would include deprotonation of a methyl group (a), ligation to zirconium (b), and functionalization of the bound methylene group (such as isonitrile insertion (eq 1)) (c). The first step (a), siloxy methyl deprotonation, has been previously demonstrated for hexamethyldisiloxane ($Me_3SiOSiMe_3$, HMDS) and octamethylcyclotetrasiloxane (D_4).[2] Since D_4 already serves as a feedstock for PDMS via anion-induced ring-opening polymerization,[3] modified D_4 would serve as a potential feedstock for functionalized PDMS's.



(1)

In this work we use HMDS as a model for beginning this study. This paper will discuss the first zirconium complexes of the $Me_3SiOSiMe_2CH_2^-$ ligand, the observed bonding modes of this siloxane ligand, and the isonitrile insertion chemistry of $Cp_2Zr(CH_2SiMe_2OSiMe_3)_2$ (**1**) and $Cp^*ZrCl_2(CH_2SiMe_2OSiMe_3)$ (**3**). Of particular interest is the unexpected observation of siloxane oxygen coordination to zirconium in **3**.

Experimental Section

General Comments. Ether and hexane were distilled from sodium/benzophenone under argon. Cp_2ZrCl_2, hexamethyldisiloxane, and *tert*-butyllithium (1.40 M in pentane) were purchased from the Aldrich Chemical Co. and used without further purification. $LiCH_2SiMe_2OSiMe_3$ (LiHMDS) was prepared and isolated via modification of a procedure described elsewhere.[2] Cp^*ZrCl_3 and methyl isocyanide were prepared as described elsewhere.[4,5] All syntheses and subsequent handling of compounds were conducted in anhydrous conditions under argon. Elemental analyses were performed by Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim, Germany. NMR spectra were measured with a General Electric OMEGA GN-300 300-MHz spectrometer. The ^{1}H-NMR chemical shifts are

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referenced to the residual proton peak of chloroform-d_1 at δ 7.26 vs TMS or the central peak of toluene-d_8 at δ 2.085 vs TMS, and the ^{13}C resonances are referred to the central peak of chloroform-d_1 at δ 77.70 vs TMS. Infrared spectra were measured as mineral oil mulls in the region 4000–300 cm^{-1} with a Nicolet 20-DX spectrophotometer equipped with a CsI beam splitter.

$LiCH_2SiMe_2OSiMe_3$ (LiHMDS). A flask was charged with HMDS (20.37 g, 125 mmol) and 100 mL of hexane. The solution was stirred and *tert*-butyllithium (66.0 mL, 92.4 mmol) was added rapidly via a syringe. After 6 days of stirring the reaction volume was reduced via trap to trap distillation until a large amount of white precipitate had formed. The precipitate was recovered via filtration, and the filtrate was further reduced in volume to yield two more crops of white solid. The crops were combined, washed with small amounts of cold hexane, and dried in vacuo (10.041 g, 64.6%). ^{1}H-NMR (toluene-d_8): δ 0.34 s ($SiMe_2$); δ 0.18 s ($SiMe_3$); δ −1.57 s ($SiCH_2$).

$Cp_2Zr(CH_2SiMe_2OSiMe_3)_2$ (1). A flask was charged with LiHMDS (2.29 g, 13.6 mmol), Cp_2ZrCl_2 (2.02 g, 6.92 mmol), and 65 mL of ether. The resulting mixture was stirred for 24 h to produce a white slurry. After solvent removal via trap to trap distillation, the product was extracted into 30 mL of hexane and the mixture was filtered to yield a clear colorless solution. The solution was reduced in volume to approximately 5 mL and cooled to −40 °C to yield 2.65 g of white crystals (impure by ^{1}H-NMR). Two further recrystallizations from minimal amounts of hexane afforded pure product (2.17 g). The original mother liquor was also concentrated to approximately 2 mL and cooled to yield another 0.48 g of pure product. The total yield was 2.65 g (71.2%). ^{1}H-NMR ($CDCl_3$): δ 6.18 s (Cp, 10 H); δ 0.12 s ($SiMe_3$, 9 H); δ 0.10 s (CH_2, 2 H); δ 0.03 s ($SiMe_2$, 6 H). IR (cm^{-1}): 1712 w, 1252 s, 1028 vs, 889 m, 843 s, 828 sh, 800 s, 757 m, 682 sh, 672 m, 627 m, 558 sh, 540 m, 434 m, 346 s. Anal. Calcd for $C_{22}H_{44}O_2Si_4Zr$: C, 48.56; H, 8.15; Si, 20.64. Found: C, 48.36; H, 8.10; Si, 20.26.

$Cp_2Zr(C(NMe)CH_2SiMe_2OSiMe_3)(CH_2SiMe_2OSiMe_3)$ (2). Methyl isocyanide (0.082 g, 2.00 mmol) was added to a hexane solution (40 mL) of 1 (0.495 g, 0.910 mmol), and the solution was stirred for 2 days. Solvent removal via trap to trap distillation yielded pure product as a clear yellow viscous liquid (0.513 g, 96.4% yield). ^{1}H-NMR ($CDCl_3$): δ 5.64 s (Cp, 10 H); δ 2.87 s (NMe, 3 H); δ 2.64 s ($NCCH_2$, 2 H); δ 0.24 s ($SiMe_2$, 6 H); δ 0.19 s ($SiMe_2$, 6 H); δ 0.17 s ($SiMe_3$, 18 H); δ −0.30 ($ZrCH_2$, 2 H). ^{13}C-NMR ($CDCl_3$): δ 236.52 (CN); δ 106.54 (Cp); δ 33.06 (CH_2, inserted); 31.37 (NMe); δ 14.30 (Zr–CH_2); δ 6.28, 3.05, 2.70, 2.51 (2 $SiMe_3$ and 2 $SiMe_2$). IR (cm^{-1}): 3104 w, 1690 w, 1621 s, 1581 sh, 1254 s, 1179 m, 1119 m, 1040 vs, 916 s, 841 s, 792 s, 758 m, 685 m, 668 m, 628 s, 541 s, 506 s, 431 m, 399 m, 330 s. Anal. Calcd for $C_{24}H_{47}NSi_4O_2Zr$: C, 49.26; H, 8.10; N, 2.39; Si, 19.20; Zr, 15.59. Found: C, 49.36; H, 8.18; N, 2.31; Si, 19.12; Zr, 15.47.

$Cp^*Zr(CH_2SiMe_2OSiMe_3)Cl_2$ (3). A solution of LiHMDS (1.444 g, 8.58 mmol) in 25 mL of ether was added over 1 h to a stirred slurry of Cp^*ZrCl_3 (2.855 g, 8.58 mmol) in 150 mL of ether. After the solution was stirred for 2 additional hours, the solvent was removed via trap to trap distillation. The product was extracted into 25 mL of hexane and separated from the LiCl salt via centrifugation. The LiCl was washed with 2 × 25 mL of hexane, and the washes were combined with the extract. The extract was concentrated to 30 mL and cooled to −40 °C to yield 0.23 g of yellow powder, recovered via filtration. This was shown to be mostly impure by ^{1}H-NMR and was discarded. The yellow filtrate was concentrated to approximately 1 mL and cooled to yield slightly impure yellow crystals. Recrystallization from 2 mL of hexane afforded pure product as yellow crystals (0.740 g, 18.8%). ^{1}H-NMR ($CDCl_3$): δ 1.99 s (Cp*, 15 H); δ 0.51 s ($SiMe_3$, 9 H); δ 0.44 s ($SiMe_2$, 6 H); δ 0.32 s (CH_2, 2 H). IR (cm^{-1}): 1323 w, 1256 s, 1248 sh, 1026 m, 902 s, 880 sh, 864 sh, 850 vs, 804 m, 762 m, 740 w, 688 vw, 674 w, 634 w, 559 m, 498 w, 433 m, 411 vw, 370 s, 364 sh, 336 s, 313 m. Anal. Calcd for $C_{16}H_{32}OCl_2Si_2Zr$: C, 41.89; H, 7.03. Found: C, 41.93; H, 6.94.

$Cp^*Zr(C(NMe)CH_2SiMe_2OSiMe_3)Cl_2$ (4). Methyl isocyanide (0.064 g, 1.56 mmol) was added to a pale yellow hexane solution (40 mL) of 3 (0.685 g, 1.49 mmol). The resulting clear orange solution darkened to brown as the reaction was stirred for 4 h. Solvent removal via trap to trap distillation yielded a pasty brown solid. The product was extracted into 5 mL of hexane, and the mixture was filtered and cooled to −40 °C to yield a dark brown noncrystalline solid. The solid was isolated by pipetting off the mother liquor and dried in vacuo to yield 0.305 g of pure product. The mother liquor was concentrated to approximately 2 mL and cooled to yield an additional 0.055 g of pure product. The total yield was 0.360 g (48.3%). ^{1}H-NMR ($CDCl_3$): δ 3.39 s (NMe, 3 H); δ 2.82 s (CH_2, 2 H); δ 2.01 s (Cp*, 15 H); δ 0.19 s ($SiMe_2$, 6 H); δ 0.06 s ($SiMe_3$, 9 H). ^{13}C-NMR ($CDCl_3$): δ 246.01 (CN); δ 123.08 (Cp*, ring); δ 35.84 (CH_2, inserted); δ 32.90 (NMe); δ 12.34 (Cp*, Me); δ 2.55, 2.44 ($SiMe_3$ and $SiMe_2$). IR (cm^{-1}): 1588 m, 1304 vw, 1258 s, 1197 w, 1108 w, 1057 s, 975 sh, 881 sh, 844 s, 802 m, 763 m, 753 m, 735 w, 687 m, 636 w, 535 w, 503 w, 428 m, 388 m, 341 m, 328 m, 320 m. Anal. Calcd for $C_{18}H_{35}Cl_2NOSi_2Zr$: C, 43.26; H, 7.06; N, 2.80; Cl, 14.19; Si, 11.24; Zr, 18.25. Found: C, 43.29; H, 6.96; N, 2.91; Cl, 14.28; Si, 11.18; Zr, 18.37.

Table I. Summary of Crystal Data and Intensity Collection for $Cp_2Zr(CH_2SiMe_2OSiMe_3)_2$ (1) and $Cp^*ZrCl_2(CH_2SiMe_2OSiMe_3)$ (3)

	1	3
formula	$C_{22}H_{44}ZrSi_4O_2$	$C_{16}H_{32}ZrCl_2Si_2O$
fw	544.15	458.73
a, Å	8.330 (3)	14.530 (2)
b, Å	16.077 (6)	8.417 (1)
c, Å	10.710 (4)	18.725 (4)
β, deg	94.66 (1)	106.62 (1)
V, Å^3	1429.61	2194.45
Z	2	4
d, g cm^{-3}	1.264	1.388
space group	$P2_1$	$P2_1/n$
cryst dimens, mm	0.25 × 0.25 × 0.25	0.35 × 0.35 × 0.35
temp, °C	−171	−154
λ(Mo Kα radiation), Å	0.710 69	0.710 69
linear abs coeff, cm^{-1}	5.569	8.457
receiving aperature, mm	3.0 × 4.0; 22.5 cm from cryst	3.0 × 4.0; 22.5 cm from cryst
take-off angle, deg	2.0	2.0
scan speed, deg min^{-1}	6.0 (in 2θ)	15.0 (in 2θ)
bkgd counts, s	4 (at each end)	3 (at each end)
2θ limits, deg	6–45	6–45
data collcd	$h,k\pm l$	$h,k\pm l$
no. of unique data	1935	2859
no. of unique data with $F_o^2 > 2.33\sigma(F_o^2)$	1917	2613
$R(F)$	0.0194	0.0318
$R_w(F)$	0.0227	0.0372

X-ray Structural Determinations. Pertinent data for the structures of compounds 1 and 3 are in Table I. The crystals were mounted on a computer-controlled Picker four-circle diffractometer equipped with a Furnas monochromator (HOG crystal) and cooled by a gaseous nitrogen cooling system. A systematic search of a limited hemisphere of reciprocal space for 1 located a set of diffraction maxima possessing monoclinic symmetry with extinctions corresponding to $P2_1$ or $p2_1/m$. Subsequent solution and refinement confirmed the correct choice to be the noncentrosymmetric $P2_1$. A similar search for 3 revealed diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/n$. Orientation matrices and accurate unit cell dimensions were determined at low temperatures from least-squares fits of 32 reflections (20° > 2θ > 30°) for both 1 and 3. Intensity data were collected by using the $\theta/2\theta$ scan method; four standard reflections, monitored every 300 reflection measurements, showed only statistical fluctuations for both compounds. No absorption correction was performed for either compound due to their small and roughly equal dimensions and the small value of their linear absorption coefficients. The intensities were corrected for Lorentz and polarization factors and scaled to give the number of independent data with $I > 2.33\sigma(I)$ indicated in Table I.

The initial locations of the Zr and Si atoms of 1 were determined via the Patterson heavy-atom method. The structure for 3 was solved by a combination of direct methods (MULTAN78) and Fourier techniques. All atoms, including hydrogens, were located for both compounds. The non-hydrogen atoms were refined anisotropically for both compounds. The hydrogen atoms for 1 were fixed at their idealized positions, and only their isotropic thermal parameters were refined. The hydrogen atoms for 3 were refined isotropically. Refinements converted to values for the conventional R indicies shown in Table I. The maximum residuals in the final difference Fourier synthesis for 1 and 3 were 0.42 and 0.45 e/Å^3, respectively. The weighting scheme used in the final calculations was of the form $w = 1/\sigma F^2$. Scattering factors were taken from ref 6. The scattering factors for Zr and Si were corrected for the real and imaginary parts of anomalous dispersion by using values from ref 6. All computations were carried out on a 386 PC using programs described elsewhere.[7] The positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table II, the atom-numbering schemes being shown in Figures 1 and 2 for compounds 1 and 3, respectively. Anisotropic thermal parameters for the non-hydrogen atoms and hydrogen atom coordinates and isotropic thermal parameters are listed in Tables IV and V (supplementary material) for compounds 1 and 3, respectively.

Table II. Coordinates (×10^4) and Equivalent Isotropic Temperature Factors for $Cp_2Zr(CH_2SiMe_2OSiMe_3)_2$[a] (1) and $Cp^*ZrCl_2(CH_2SiMe_2OSiMe_3)$[a] (3)

	x	*y*	*z*	*U*, Å^2
		Compound 1		
Zr(1)	2854.4 (4)	3487.3 (3)	2650.5 (3)	12
C(2)	1022 (5)	2459 (3)	3548 (4)	23
C(3)	1708 (5)	2051 (3)	2564 (4)	23
C(4)	3355 (5)	1941 (2)	2914 (4)	20
C(5)	3682 (5)	2290 (3)	4105 (4)	21
C(6)	2235 (6)	2599 (3)	4495 (4)	23
C(7)	950 (5)	3662 (3)	744 (4)	25
C(8)	2266 (6)	4159 (3)	530 (4)	28
C(9)	2321 (5)	4823 (3)	1386 (4)	27
C(10)	1025 (6)	4725 (3)	2125 (4)	23
C(11)	176 (5)	4020 (3)	1728 (4)	23
C(12)	3757 (5)	4353 (3)	4226 (4)	17
Si(13)	2563 (1)	4796 (1)	5440 (1)	15
C(14)	3564 (5)	4605 (3)	7040 (4)	25
C(15)	2273 (5)	5940 (3)	5222 (4)	24
O(16)	776 (3)	4351 (2)	5386 (2)	17
Si(17)	−1016 (1)	4468 (1)	5883 (1)	15
C(18)	−2130 (5)	5251 (3)	4879 (4)	21
C(19)	−2042 (4)	3446 (4)	5748 (4)	21
C(20)	−835 (5)	4825 (3)	7541 (4)	23
C(21)	5325 (4)	3377 (3)	1901 (3)	15
Si(22)	5735 (1)	2759 (1)	510 (1)	15
C(23)	7139 (5)	1883 (3)	937 (4)	23
C(24)	6642 (4)	3416 (4)	−680 (3)	21
O(25)	4035 (3)	2367 (2)	−152 (2)	17
Si(26)	3365 (1)	1727 (1)	−1257 (1)	17
C(27)	3226 (6)	669 (3)	−589 (4)	28
C(28)	1323 (6)	2073 (3)	−1880 (4)	30
C(29)	4740 (6)	1734 (3)	−2551 (4)	24
		Compound 3		
Zr(1)	5708.4 (3)	3541.7 (4)	8285.6 (2)	12
Cl(2)	6217 (1)	6191 (1)	8007 (1)	19
Cl(3)	4195 (1)	3189 (1)	8573 (1)	19
C(4)	6396 (3)	1517 (5)	9277 (2)	16
C(5)	6303 (3)	2913 (5)	9666 (2)	15
C(6)	6934 (3)	4069 (5)	9518 (2)	16
C(7)	7431 (3)	3357 (5)	9045 (2)	17
C(8)	7114 (3)	1766 (5)	8913 (2)	17
C(9)	5859 (3)	−15 (5)	9288 (3)	22
C(10)	5733 (3)	3067 (6)	10215 (3)	19
C(11)	7098 (4)	5707 (6)	9852 (3)	23
C(12)	8221 (3)	4100 (7)	8792 (3)	25
C(13)	7579 (3)	503 (6)	8567 (3)	24
C(14)	5729 (3)	1719 (6)	7404 (2)	23
Si(15)	4632 (1)	2361 (1)	6710 (1)	20
O(16)	4552 (2)	4160 (3)	7099 (1)	16
Si(17)	3856 (1)	5750 (1)	6769 (1)	16
C(18)	3709 (4)	6972 (6)	7554 (3)	24
C(19)	2658 (3)	5023 (7)	6224 (3)	28
C(20)	4439 (4)	6874 (7)	6166 (3)	29
C(21)	3566 (4)	1133 (6)	6701 (3)	31
C(22)	4721 (5)	2642 (8)	5746 (3)	33

[a] Estimated standard deviations are given in parentheses. Equivalent isotropic thermal parameters are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Results and Discussion

It has been reported earlier that *t*-BuLi deprotonates HMDS instead of cleaving an Si–O bond as do other alkyllithiums with siloxanes.[2] We have taken advantage of this fact to obtain $LiCH_2SiMe_2OSiMe_3$ (LiHMDS) as a pure white powder in good yield. This supplies us with a model for larger deprotonated polydimethylsiloxanes. With this ligand we can study the feasibility of further siloxane methyl group functionalization on a zirconium center.

We have prepared the first zirconium compounds of a deprotonated methylsiloxane ligand by reacting LiHMDS with Cp_2ZrCl_2 and Cp^*ZrCl_3 in ether (eqs 2 and 3). It is of interest to note that monosubstituted $Cp_2ZrCl(CH_2SiMe_3OSiMe_3)$ was not recovered upon combining equimolar amounts of Cp_2ZrCl_2 and LiHMDS. Attempts to do so via slow addition of an ether solution of LiHMDS to an ether slurry of Cp_2ZrCl_2 at room temperature yielded only 1 and unreacted Cp_2ZrCl_2, both recovered pure.

$$Cp_2ZrCl_2 + 2LiHMDS \xrightarrow{Et_2O} \underset{1}{Cp_2Zr(CH_2SiMe_2OSiMe_3)_2} + 2LiCl \qquad (2)$$

$$Cp^*ZrCl_3 + LiHMDS \xrightarrow{Et_2O} \underset{3}{Cp^*ZrCl_2(CH_2SiMe_2OSiMe_3)} + LiCl \qquad (3)$$

Both 1 and 3 were quite soluble in ether and hexane. Recrystallization from hexane at −40 °C yielded colorless and yellow crystals suitable for X-ray structure determination for 1 and 3, respectively.

Molecular Structures for 1 and 3. Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of 1 and 3 are presented in Table II; bond distances and angles are given in Table III. Perspective views showing the molecular geometry and the atom-numbering schemes for 1 and 3 are presented in Figures 1 and 2, respectively.

The molecular structure of 1 is that expected for a bent metallocene. The angle between the Zr–Cp(centroid) vectors is 132.1 (2)°, within the normal expected range.[8] The best description of the molecular structure of 3 is a capped pseudotetrahedron, with O(16) capping the face defined by atoms Cl2, Cl3, and C(14). The angle between the Zr to Cp* centroid and Zr–O vectors is 172.2 (1)°, with the O(16) atom displaced 1.79 Å below the plane defined by atoms Cl2, Cl3, C(14). The most interesting aspect of these structures involves the bonding mode of the $CH_2SiMe_2OSiMe_3$ ligand. The HMDS derived ligand is monodentate in 1 and bidentate in 3. The Zr–O bond length of 2.427 (3) Å in 3 is quite long. For example, the

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(6) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

(7) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

(8) This angle can vary from 148° in Cp_2MoH_2 to 126° in Cp_2ZrI_2. (a) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallgr., Sect. B: Crystallogr. Cryst. Chem.* **1974**, *B30*, 2290. (b) Guggenberger, L. J. *Inorg. Chem.* **1973**, *12*, 232. (c) Melmed, K. M.; Coucouvanis, D. L.; Lippard, S. J. *Ibid.* **1973**, *12*, 232.

Table III. Bond Distances (Å) and Angles (deg) for $Cp_2Zr(CH_2SiMe_2OSiMe_3)_2$ (1) and $Cp^*ZrCl_2(CH_2SiMe_2OSiMe_3)$ (3)

atoms		dist	atoms			angle
			Compound 1			
Zr(1)	C(2)–C(6)	2.495 (4)–2.536 (4)	C(12)	Zr(1)	C(21)	93.18 (14)
Zr(1)	C(7)–C(11)	2.498 (4)–2.559 (4)	O(16)	Si(13)	C(12)	110.24 (17)
Zr(1)	C(12)	2.268 (4)	O(16)	Si(13)	C(14)	107.18 (17)
Zr(1)	C(21)	2.276 (4)	O(16)	Si(13)	C(15)	108.41 (17)
Si(13)	O(16)	1.648 (3)	C(12)	Si(13)	C(14)	110.91 (20)
Si(13)	C(12)	1.843 (4)	C(12)	Si(13)	C(15)	111.36 (20)
Si(13)	C(14)	1.870 (4)	C(14)	Si(13)	C(15)	108.61 (21)
Si(13)	C(15)	1.867 (5)	O(16)	Si(17)	C(18)	108.46 (17)
Si(17)	O(16)	1.635 (3)	O(16)	Si(17)	C(19)	107.44 (17)
Si(17)	C(18)	1.854 (4)	O(16)	Si(17)	C(20)	109.91 (17)
Si(17)	C(19)	1.853 (6)	C(18)	Si(17)	C(19)	110.52 (19)
Si(17)	C(20)	1.861 (4)	C(18)	Si(17)	C(20)	110.03 (20)
Si(22)	O(25)	1.656 (3)	C(19)	Si(17)	C(20)	110.42 (19)
Si(22)	C(21)	1.845 (4)	O(25)	Si(22)	C(21)	110.03 (15)
Si(22)	C(23)	1.864 (5)	O(25)	Si(22)	C(23)	108.34 (19)
Si(22)	C(24)	1.862 (4)	O(25)	Si(22)	C(24)	107.67 (16)
Si(26)	O(25)	1.633 (3)	C(21)	Si(22)	C(23)	111.28 (19)
Si(26)	C(27)	1.852 (5)	C(21)	Si(22)	C(24)	111.04 (21)
Si(26)	C(28)	1.861 (5)	C(23)	Si(22)	C(24)	108.36 (20)
Si(26)	C(29)	1.868 (4)	O(25)	Si(26)	C(27)	109.07 (19)
C(2–6)	C(2–6)	1.390 (7)–1.404 (6)	O(25)	Si(26)	C(28)	108.65 (18)
C(7)–C(11)	C(7)–C(11)	1.384 (7)–1.405 (7)	O(25)	Si(26)	C(29)	109.86 (17)
			C(27)	Si(26)	C(28)	109.21 (23)
			C(27)	Si(26)	C(29)	110.71 (22)
			C(28)	Si(26)	C(29)	109.30 (21)
			Si(13)	O(16)	Si(17)	141.64 (18)
			Si(22)	O(25)	Si(26)	141.32 (18)
			C(2)–C(6)	C(2)–C(6)	C(2)–C(6)	107.8 (4)–108.5 (4)
			C(7)–C(11)	C(7)–C(11)	C(7)–C(11)	107.3 (4)–108.5 (4)
			Compound 3			
Zr(1)	C(4)–C(8)	2.505 (4)–2.562 (4)	Cl(2)	Zr(1)	Cl(3)	120.40 (4)
Zr(1)	Cl(2)	2.542 (1)	Cl(2)	Zr(1)	O(16)	77.42 (7)
Zr(1)	Cl(3)	2.428 (1)	Cl(2)	Zr(1)	C(14)	113.19 (14)
Zr(1)	O(16)	2.427 (3)	Cl(3)	Zr(1)	O(16)	78.19 (17)
Zr(1)	C(14)	2.260 (4)	Cl(3)	Zr(1)	C(14)	106.32 (13)
Si(15)	O(16)	1.699 (3)	O(16)	Zr(1)	C(14)	68.11 (13)
Si(15)	C(14)	1.827 (4)	Zr(1)	C(14)	Si(15)	97.36 (20)
Si(15)	C(21)	1.859 (5)	O(16)	Si(15)	C(14)	96.34 (17)
Si(15)	C(22)	1.862 (5)	O(16)	Si(15)	C(21)	109.91 (20)
Si(17)	O(16)	1.685 (3)	O(16)	Si(15)	C(22)	109.63 (22)
Si(17)	C(18)	1.855 (5)	C(14)	Si(15)	C(21)	113.38 (25)
Si(17)	C(19)	1.852 (5)	C(14)	Si(15)	C(22)	116.01 (25)
Si(17)	C(20)	1.853 (5)	C(21)	Si(15)	C(22)	110.60 (28)
C(4)–C(8)	C(4)–C(8)	1.409 (6)–1.425 (6)	C(16)	Si(17)	C(18)	110.03 (19)
C(9)–C(13)	C(9)–C(13)	1.498 (6)–1.510 (6)	C(16)	Si(17)	C(19)	108.13 (20)
			C(16)	Si(17)	C(20)	107.32 (20)
			C(18)	Si(17)	C(19)	108.49 (24)
			C(18)	Si(17)	C(20)	112.05 (25)
			C(19)	Si(17)	C(20)	110.75 (26)
			Zr(1)	O(16)	Si(15)	95.05 (12)
			Zr(1)	O(16)	Si(17)	133.79 (14)
			Si(15)	O(16)	Si(17)	131.10 (16)
			C(4)–C(8)	C(4)–C(8)	C(4)–C(8)	107.7 (3)–108.5 (3)

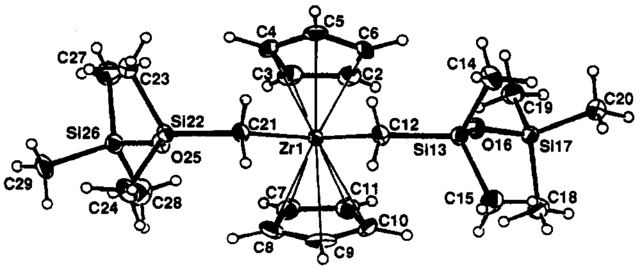

Figure 1. ORTEP diagram of $Cp_2Zr(CH_2SiMe_2OSiMe_3)_2$ (1).

Zr–O bond length to the η^2-acetyl ligand in $Cp_2Zr(COCH_3)(CH_3)$ is 2.290 (4) Å.[9] Shorter still are the Zr–O distances in such compounds as $Cp_2ZrCl[SOCN(CH_3)_2]$ (2.249 Å),[10] $Zr(acac)_4$ (2.198 Å),[11] $Zr[SOCN(C_2H_5)_2]_4$ (2.190 Å),[12] and $Cp_2ZrCl[OC(SiMe_3){=}CH(9\text{-anthryl})]$ (1.950 Å).[13] Average values for a Zr–O single and double bond are 2.2 and 1.95 Å, respectively.[14] The very long Zr–O bond length of 3 is similar to that of the THF adduct Zr(THF)(η^4-cot)(η-cot) (2.447 Å) from which THF is lost at room temperature.[15] The Si–O–Si bond angle of 131.10 (16)° in 3 is significantly less than the values observed in 1 (141.6 (2) and 141.3 (2)°) or in HMDS (149°).[16] The wide angle in HMDS has often been attributed to donation of oxygen

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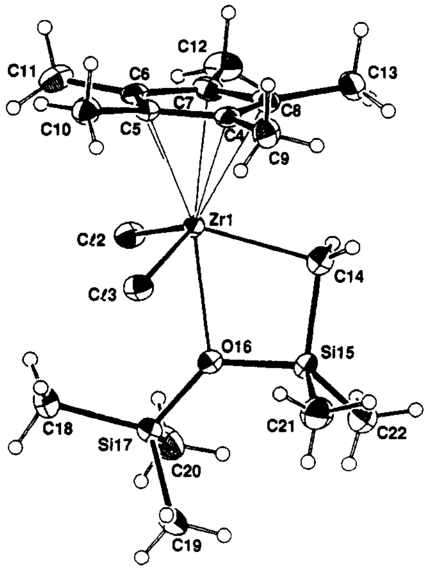
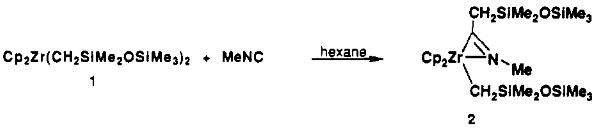


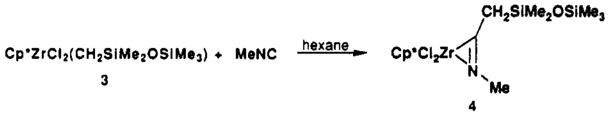
Figure 2. ORTEP diagram of $Cp^*ZrCl_2(CH_2SiMe_2OSiMe_3)$ (**3**).

lone pairs into the empty 3d orbitals on silicon.[17] The result is a weakening of the basicity of the O atom and a corresponding poor donor ability. This result is even more dramatic for amines, where tris(trimethylsilyl)amine shows no basic properties at all.[18] We were therefore surprised to find the oxygen of the deprotonated HMDS ligand in **3** bound to the zirconium atom. While weak donor ability may be a contributing factor to the long Zr–O bond length in **3**, it should also be mentioned that a decrease in this distance would require that the C(14)–Si(15)–O(16) bond angle be reduced significantly from the observed value of 96.3 (2)°, resulting in additional strain within the four-membered ZrCSiO ring. The closing down of the Si–O–Si bond angle in **3** relative to both **1** and HMDS may be indicative of less oxygen lone pair donation into silicon's 3d orbitals due to bonding with zirconium (the average Si–O bond length in **3** is 0.048 (3) Å longer than in **1**). However, it may also be due to a steric interaction between Cl2 and methyl group C(18) [this intramolecular contact is 0.192 Å less than the sum of the van der Waal's radius of Cl (1.75 Å) and a methyl group (2.0 Å)]. Given the very long Zr–O bond length in **3**, we prefer to view the oxygen coordination as a weak adduct. Compound **3** has a weak band at 498 cm^{-1} in its IR spectrum (not observed in the spectrum of **1**) which we tentatively assign to a Zr–O stretching mode.

Reactivity of 1 and 3 with Methyl Isocyanide. Compounds **1** and **3** react readily with methylisonitrile in hexane at room temperature to give the insertion products **2** and **4**, respectively (eqs 4 and 5). While neither **2** nor **4** could be characterized by X-ray diffraction, IR and NMR spectra support the conclusion that the isonitrile inserted into the Z–C bond. Both compounds **2** and **4** exhibit a strong band in their IR spectrum assignable to a C=N stretching mode (1621 and 1588 cm^{-1}, respectively). The η^2-iminoacyl coordination mode shown for **2** and **4** is supported by low-intensity singlets in their ^{13}C-NMR



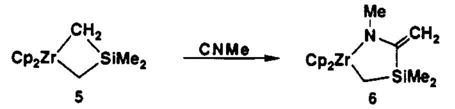
(4)



(5)

spectra at δ 236.52 and 246.01, respectively.[19] An η^2 coordination mode is also observed for related insertion products.[13,19] The "N-inside" configuration shown for **2** is not confirmed, but it is predicted by extended Huckel calculations.[20] The lack of oxygen coordination depicted in **4** is supported by the absence of the 498-cm^{-1} peak present in the IR spectrum of **3**. It is also reasonable to expect a lack of oxygen coordination in **4** upon η^2-iminoacyl formation given the length of the Zr–O bond in **3**.

Both compounds **2** and **4** possess a Si atom β to the bound iminoacyl C atom, a necessary requirement for a 1,2-silyl shift to occur. For example, Peterson and Berg observed that **5** reacted with MeNC to give **6** (eq 6).[19] The



(6)

two hydrogens of the exocyclic methylene of **6** are chemically inequivalent and therefore give a doublet of doublets in the ^1H-NMR spectrum. The absence of this splitting pattern in the ^1H-NMR of **2** and **4** verifies that CNMe insertion was not followed by an intramolecular 1,2-silyl shift. Refluxing both **2** and **4** in toluene for 24 h failed to induce any silyl shift, with **2** and **4** showing no and significant amounts of thermal decomposition, respectively.

Conclusions

Compounds **1** and **3** are the first examples isolated of a deprotonated methylsiloxane coordinated to a zirconium center. Although generally considered a very poor donor atom, the siloxane oxygen will weakly bind to zirconium if it is relatively uncrowded and electron deficient. Compounds **1** and **3** were prepared with the intent of further functionalization of the bound CH_2 group. These compounds readily insert isonitriles to yield η^2-iminoacyls which do not undergo an intramolecular 1,2-silyl shift.

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Supplementary Material Available: Tables of thermal parameters and hydrogen atom coordinates (Tables IV and V) (2 pages). Ordering information is given on any current masthead page.

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