Alkyl−Silyl Complexes Free of Anionic π Ligands. Synthesis and Characterization of $(Me_3ECH_2)_3MSi(SiMe_3)_3$[†]

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We report here the synthesis and characterization of early-transition-metal complexes $(Me_3ECH_2)_3MSi(SiMe_3)_3$ (E = C, Si; M = Zr, Ti). These alkyl−silyl complexes, which are free of anionic π ligands such as cyclopentadienyl, were synthesized by the metathetic reactions of chlorotrialkyl complexes $(Me_3ECH_2)_3MCl$ with silyllithium reagent $LiSi(SiMe_3)_3(THF)_3$. The structures of $(Me_3ECH_2)_3TiSi(SiMe_3)_3$ [E = C (**1**), Si (**2**)] determined by X-ray diffraction show that the three alkyl groups on the metal centers are staggered with respect to the trimethylsilyl groups on the central silicon atoms.

Introduction

Transition-metal silyl chemistry has been a subject of enthusiastic study for four decades,[1] since the report in 1956 of the preparation of $Cp(CO)_2FeSiMe_3$,[1a] the first compound known to contain a transition metal−silicon bond. Early interest in the area was increased by the discovery of transition-metal-catalyzed olefin hydrosilation[1b] and subsequent work to elucidate the mechanism of oxidative addition of Si−H bonds to transition metal centers.[1c] The family of transition-metal silyl compounds is now quite large and includes almost all of the transition elements.[1d]

Late-transition-metal silyl chemistry quickly flourished; many low-valent, electron-rich transition-metal compounds are quite stable. The chemistry of electron-poor early-transition-metal silyl complexes is comparatively young. Research in the area has overwhelmingly concentrated on silyl complexes supported or stabilized by anionic π ligands such as cyclopentadienyl anions.[2] The few known Cp-free early-transition-metal silyl complexes usually contain carbonyls,[3] phosphines,[4] or alkoxy ancillary ligands.[5]

We report here the synthesis of a novel series of stable d^0 alkyl/silyl complexes of Group IV metals $(Me_3ECH_2)_3MSi(SiMe_3)_3$ (E = C, Si; M = Ti, Zr) that are free of anionic π or other ancillary ligands. To our knowledge, these are the first of their kind and represent a new class of metal silyl complexes. Preliminary results have been reported.[6a,b]

Results and Discussion

The reactions of the trialkylmetal chlorides $(Me_3ECH_2)_3MCl$[7] (E = C, Si; M = Ti, Zr) with the lithium silyl complex $LiSi(SiMe_3)_3(THF)_3$[8] in hexanes were

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[†] Dedicated to Professor Kenneth G. Caulton on the occasion of his 55th birthday.

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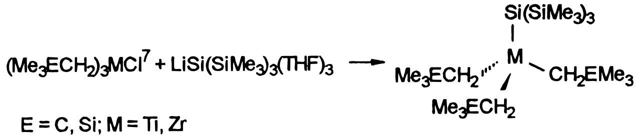
Scheme 1



found to produce trialkylmetal silyl complexes $(Me_3ECH_2)_3TiSi(SiMe_3)_3$ [E = C (**1**), Si (**2**)] and $(Me_3ECH_2)_3ZrSi(SiMe_3)_3$ [E = C (**3**), Si (**4**)] (Scheme 1). The reactions are almost instantaneous at 23 °C with the precipitation of LiCl. The four alkyl−silyl complexes are very soluble in nonpolar solvents such as hexanes. The products were purified by crystallization from hexanes or toluene. The metal silyl complexes are air- and moisture-sensitive and are photosensitive in solution. They are thermally stable in crystalline form, showing little or no degradation over several days in the dark at room temperature. Complex **3** could be sublimed in darkness at 40 °C ($<10^{-4}$ Torr) without significant decomposition. All four silyl complexes exhibit measurable decomposition in a few hours at room temperature in solution, though the zirconium complexes are significantly more stable than the titanium analogues.

Spectroscopic properties [^{1}H, ^{13}C{^{1}H}, and ^{1}H-gated-decoupled ^{13}C; also ^{1}H-^{29}Si heteronuclear correlation (HETCOR) NMR spectra for **2** and **4**] of the complexes are consistent with the structure assignments. The α-hydrogen and α-carbon NMR resonances of the Me_3CCH_2 ligands in the titanium complex **1** (^{1}H NMR, 2.50 ppm; ^{13}C NMR, 147.6 ppm) are significantly downfield shifted from those in the analogous zirconium complex **3** (^{1}H NMR: 1.63 ppm; ^{13}C NMR: 127.4 ppm). Similar downfield shifts are observed in the NMR resonances of the Me_3SiCH_2 ligands in **2** (^{1}H NMR, 2.96 ppm; ^{13}C NMR, 124.9 ppm) compared to those in **4** (^{1}H NMR, 1.57 ppm; ^{13}C NMR, 99.1 ppm). Such downfield shifts also exist in the α-hydrogen and α-carbon NMR resonances of $(Me_3CCH_2)_4Ti$[9] (^{1}H NMR, 2.22 ppm; ^{13}C NMR, 118.9 ppm) compared to those in $(Me_3CCH_2)_4Zr$[9] (^{1}H NMR, 1.41 ppm; ^{13}C NMR, 102.7 ppm).

The two titanium compounds **1** and **2** were also characterized by X-ray diffraction of single crystals grown by slow cooling of hexane solutions to −20 °C. The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. There are three unique but chemically equivalent molecules in a unit cell of **1**. The crystal data are listed in Table 1. Comparisons of selected analogous bond distances and angles in **1** and **2** are shown in Tables 2 and 3.

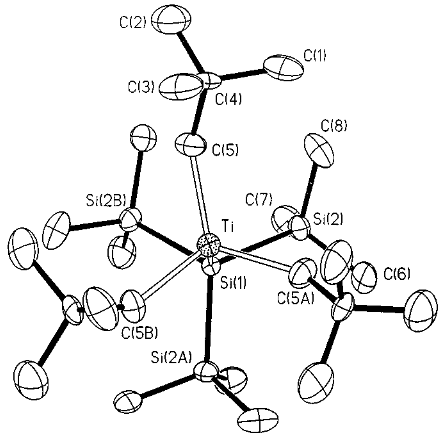


Figure 1. ORTEP diagram of $(Me_3CCH_2)_3TiSi(SiMe_3)_3$ (**1**). One of three symmetry-independent but chemically equivalent molecules is shown. Thermal ellipsoids are drawn at the 35% probability level.

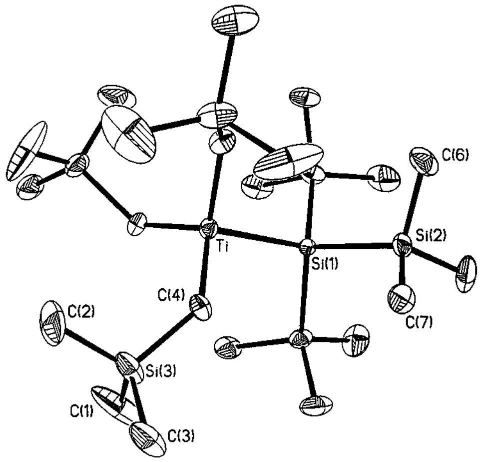


Figure 2. ORTEP diagram of $(Me_3SiCH_2)_3TiSi(SiMe_3)_3$ (**2**). Thermal ellipsoids are drawn at the 20% probability level.

Table 1. Crystal Data for 1 and 2

compd	**1**	**2**
formula	$C_{24}H_{60}Si_4Ti$	$C_{21}H_{60}Si_7Ti$
formula wt	509.0	557.22
cryst size (mm)	0.22 × 0.23 × 0.25	0.7 × 0.3 × 0.2
cryst syst	trigonal	trigonal
space grp	$P3$	$R3$
lattice params (Å)	$a = 16.383(3)$	$a = 16.278(2)$
	$c = 11.419(3)$	$c = 12.183(2)$
V (Å^3)	2654(1)	2795.7(8)
Z	3	3
density (calcd) (g/cm^3)	0.948	0.993
μ(Mo Kα) (mm^{-1})	0.383	0.462
F(000)	846	918
T (K)	229	174(2)
scan type	ω	ω
$2q_{max}$ (deg)	45.0	45.0
index ranges	$h, -k, \pm l$	$-h, k, \pm l$
unique reflns	3688	926
params varied	261	87
R indices	0.0736 (R_wF = 0.0847)	0.0389 (R_wF^2 = 0.1128)
goodness of fit	1.78 (on F)	1.003 (on F^2)

Each crystal structure reveals a 3-fold axis of symmetry along the Ti−Si bond. In each complex, the alkyl groups on the metal center are staggered with respect to the trimethylsilyl groups on the central silicon atom. The three alkyl and the silyl ligands present a pseudotetrahedral geometry around the metal centers. The angles between alkyl ligands, C5−Ti−C5A in **1** and C4−Ti−C4A in **2**, are 113.2(4)° (mean) and 112.4(2)°, respectively. The angles between alkyls and the silyl group (C−Ti−Si1) in **1** and **2** are 105.4(4)° (mean) and 106.3(2)°, respectively. In comparison, the C−M−C bond angles in some previously reported tetrahedral

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Table 2. Selected Interatomic Distances and Angles for 1

(a) Intramolecular Distances (Å)

Ti−Si(1)	2.594(7)	Si(1)−Si(2)	2.342(5)
Ti−C(5)	2.011(19)	Si(1′)−Si(2′)	2.348(4)
Ti′−Si(1′)	2.629(9)	Si(1″)−Si(2″)	2.354(5)
Ti′−C(5′)	2.034(18)	C(4)−C(5)	1.548(23)
Ti″−Si(1″)	2.624(8)	C(4′)−C(5′)	1.514(24)
Ti″−C(5″)	2.027(11)	C(4″)−C(5″)	1.510(19)

(b) Intramolecular Angles (deg)

Si(1)−Ti−C(5)	104.6(4)	C(1)−C(4)−C(5)	107.3(12)
C(5)−Ti−C(5A)	113.9(4)	C(2)−C(4)−C(5)	110.4(11)
Si(1′)−Ti′−C(5′)	105.8(4)	C(3)−C(4)−C(5)	110.3(15)
C(5′)−Ti′−C(5′A)	112.9(4)	Ti−C(5)−C(4)	141.3(10)
Si(1″)−Ti″−C(5″)	105.9(4)	C(1′)−C(4′)−C(5′)	109.4(21)
C(5″)−Ti″−C(5″A)	112.8(4)	C(2′)−C(4′)−C(5′)	109.0(15)
Ti−Si(1)−Si(2)	111.3(2)	C(3′)−C(4′)−C(5′)	113.8(18)
Si(2)−Si(1)−Si(2A)	107.6(2)	Ti′−C(5′)−C(4′)	142.5(15)
Ti′−Si(1′)−Si(2′)	110.6(2)	C(1″)−C(4″)−C(5″)	112.6(15)
Si(2′)−Si(1′)−Si(2C)	108.3(2)	C(2″)−C(4″)−C(5″)	110.6(12)
Ti″−Si(1″)−Si(2″)	110.6(2)	C(3″)−C(4″)−C(5″)	111.5(14)
Si(2″)−Si(1″)−Si(2E)	108.3(2)	Ti″−C(5″)−C(4″)	141.4(12)

Table 3. Selected Interatomic Distances and Angles for 2

(a) Intramolecular Distances (Å)

Ti−C(4)	2.041(8)	Si(2)−C(5)	1.890(12)
Ti−Si(1)	2.603(3)	Si(3)−C(2)	1.79(2)
Si(1)−Si(2)	2.341(2)	Si(3)−C(3)	1.847(12)
Si(2)−C(6)	1.866(9)	Si(3)−C(1)	1.82(2)
Si(2)−C(7)	1.857(11)	Si(3)−C(4)	1.854(8)

(b) Intramolecular Angles (deg)

C(4A)−Ti−C(4)	112.4(2)	C(5)−Si(2)−Si(1)	110.8(5)
C(4)−Ti−Si(1)	106.3(2)	C(2)−Si(3)−C(4)	110.0(9)
Si(2)−Si(1)−Si(2A)	108.04(8)	C(3)−Si(3)−C(4)	112.3(5)
Si(2)−Si(1)−Ti	110.87(8)	C(1)−Si(3)−C(4)	108.3(8)
C(6)−Si(2)−Si(1)	111.6(3)	Si(3)−Si(3)−C(4)	130.4(4)
C(7)−Si(2)−Si(1)	110.4(4)		

homoleptic complex ions are 105.9(3)−113.2(3)° in $[Y(CH_2SiMe_3)_4]^-$,[10a] 104.67(14)−112.00(14)° in $[In(CH_2SiMe_3)_4]^-$,[10b] and 107.3(5)−114.2(5)° in $[Lu(CMe_3)_4]^-$.[10c]

In both **1** and **2**, the coordination about the α-carbon atoms is greatly distorted from tetrahedral [Ti−C5−C4 angle of 141.7(12)° (mean) in **1** and Ti−C4−Si3 angle of 130.4(4)° in **2**]. Three primary possibilities to be considered that might contribute to this widening of the Ti−C−E angles are steric strain, some degree of double-bond nature between titanium and carbon, or an agostic interaction between the titanium center and one or more α-protons. Double-bond character is at least formally ruled out by the nature of the ligand; the α-carbon is four-coordinate and has no electrons to donate to an empty Ti dπ orbital. No evidence in favor of an agostic interaction is seen in ^1H or ^{13}C NMR spectra of **1** or **2** at −90, −50, or 23 °C. In addition, the crystal structure has a 3-fold axis of symmetry, which is not consistent with the assumption of one or two Ti−H agostic interactions in the crystalline molecule. The first possibility, that steric strain causes a widening of the Ti−C−E bond angle, is favored by analysis of the other nearby bond distances and angles.

The fact that, as stated above, the C−Ti−C angles in both complexes are wider than the C−Ti−Si angles may indicate that steric interaction among the alkyl ligands is greater than the interaction of each alkyl ligand with the silyl ligand. The greater Ti−Si bond distance seems to allow the $SiMe_3$ groups about the silicon to be relatively uncrowded; the bonding about the central silicon atom is not greatly distorted from tetrahedral [Ti−Si1−Si2 angle of 110.8(2)° (mean) in **1**; 110.87(8)° in **2**]. The shorter Ti−C bond may cause the three alkyl groups to interact and introduce steric strain, which may be relieved somewhat by the widening of the α-carbon atoms. This explanation is also consistent with the fact that the distortion is less pronounced in the (trimethylsilyl)methyl analogue **2** than in the neopentyl complex **1**; the longer C4−Si3 bond length in **2**, 1.854(8) Å, compared to the C5−C4 bond distance of 1.55(2) Å (mean) in **1**, may further reduce the steric crowding, allowing C−Ti−C angles in **2** to be closer to the ideal tetrahedral angle.

In comparison, the crystal structure of the similarly-arranged alkoxysilylzirconium compound $(Me_3CO)_3ZrSi(SiMe_3)_3$[5] shows a mean O−Zr−O angle of 111.4(4)° and a mean O−Zr−Si angle of 107.6(3)°. The Zr−O−C angle in the alkoxy complex [165(1)°] is larger than the mean Ti−C5−C4 angle [141.7(12)°] in **1** and Ti−C4−Si3 angle [130.4(4)°] in **2** and is consistent with the assumption of some degree of O(pπ)−Zr(dπ) bonding in $(Me_3CO)_3ZrSi(SiMe_3)_3$.[5]

The bonding in the $Si(SiMe_3)_3$ ligand itself is almost unperturbed by changing from Me_3CCH_2 ligands on the metal atoms in **1** to Me_3SiCH_2 ligands in **2**. The Ti−Si1 [2.618(8) Å (mean) in **1** and 2.603(3) Å in **2**] and Si1−Si2 bond lengths [2.348(5) Å (mean) in **1** and 2.341(2) Å in **2**] are nearly unchanged from complex **1** to **2**.

The unique silyl complexes $(Me_3ECH_2)_3MSi(SiMe_3)_3$ discussed here were prepared through the replacement of a chloride ligand (in trialkyl chloride complexes) by an anionic silyl ligand, a reaction analogous to the syntheses of homoleptic alkyl complexes of early transition metals such as $(RCH_2)_nM$ (M = Ti triad[9,11−13] and Cr,[13,14] $n = 4$; M = Nb, Ta, $n = 5$;[13,15,16] M = W, $n = 6$[13,17]). The steric crowding around the Ti and Zr centers in **1**−**4** perhaps makes the accommodation of no more than three alkyl ligands and one bulky silyl ligand in each complex possible. In comparison, the reactions of $(Me_3ECH_2)_3TaCl_2$ with *2 equiv* of $LiSiR_3$ led to the formation of $HSiR_3$ and four-coordinate complexes

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$(Me_3ECH_2)_2(Me_3ECH{=})TaSiR_3$ that have crystal structures[6] similar to those of **1** and **2**, giving a coordination sphere with no more than four ligands of this bulk.

Experimental Section

General Procedures. All manipulations were performed under dry nitrogen atmosphere with the use of either standard Schlenk techniques or a glovebox. All solvents were purified by distillation from potassium/benzophenone ketyl. Benzene-d_6 was dried over activated molecular sieves and stored under N_2. NMR spectra were recorded on a Bruker AC-250 or AMX-400 Fourier transform spectrometer and were referenced to solvents (residual protons in the ^1H spectra) or, in the ^{29}Si spectra, to TMS. $TiCl_4$ was converted into $TiCl_4(ether)_2$ and $TiCl_4(THF)_2$ before use.[18] $ZrCl_4$ (Strem) was purified by sublimation at ca. 170 °C (10^{-2} Torr). The anhydrous 1.0 M HCl/Et_2O solution was used as received from Aldrich. The elemental analyses were performed by Desert Analytics, Oneida Research Services, and E+R Microanalytical Laboratory. $(Me_3CCH_2)_4M$,[9] $(Me_3SiCH_2)_4Ti$,[11] $LiSi(SiMe_3)_3(THF)_3$,[8] $(Me_3CCH_2)_3ZrCl$,[7] and Me_3SiCH_2MgCl[19] were prepared by the literature methods.

Preparation of $(Me_3CCH_2)_3TiSi(SiMe_3)_3$ (1). A solution of 1.00 g (3.02 mmol) of $(Me_3CCH_2)_4Ti$ in 40 mL of ether at −25 °C was treated with 1 equiv of HCl (3.02 mL, 1.0 M in ether), added dropwise over 25 min. The reaction mixture was stirred for 1 h at room temperature to give $(Me_3CCH_2)_3TiCl$[7] and then cooled again to 0 °C before dropwise addition of a solution of $LiSi(SiMe_3)_3(THF)_3$ (1.42 g, 3.02 mmol) in hexanes. Stirring at room temperature for 1.5 h, filtration, and removal of volatiles afforded a black residue, which was extracted with hexanes and filtered. Crystallization from hexanes at −20 °C yielded orange-red hexagonal plates of pure **1** [0.212 g, 13.8% yield based on $(Me_3CCH_2)_4Ti$].[20] The product and the intermediate $(Me_3CCH_2)_3TiCl$[7] are somewhat photosensitive in solution, and light was excluded during the procedure: ^1H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 2.50 (s, 6H, $Me_3CC\mathit{H}_2$), 1.20 (s, 27H, Me_3CCH_2), 0.43 (s, 27H, $Si\mathit{Me}_3$); ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 147.6 ($Me_3C\mathit{C}H_2$, $^1J_{C-H} = 110.7$ Hz), 40.2 ($Me_3\mathit{C}CH_2$), 33.9 (Me_3CCH_2, $^1J_{C-H} = 123.2$ Hz), 3.6 ($Si\mathit{Me}_3$, $^1J_{C-H} = 119.5$ Hz); $^{29}Si\{^1H\}$ NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C) δ −8.1 ($Si(\mathit{Si}Me_3)_3$), −59.7 ($\mathit{Si}(SiMe_3)_3$). Anal. Calcd for $C_{24}H_{60}Si_4Ti$: C, 56.64; H, 11.88. Found: C, 56.27; H, 11.99.

Preparation of $(Me_3SiCH_2)_3TiSi(SiMe_3)_3$ (2). A solution of 0.692 g (1.74 mmol) of liquid $(Me_3SiCH_2)_4Ti$ in 30 mL of hexanes at −25 °C was treated with 1 equiv of HCl (1.7 mL, 1.0 M in ether), added dropwise over a 20-min period. The mixture was stirred at room temperature for 3.5 h and then cooled to −20 °C while volatiles were stripped off under vacuum to remove any remaining HCl.[7] The resulting yellow liquid was diluted with hexanes and stirred at −10 °C during dropwise addition of a solution of 0.821 g (1.74 mmol) of $LiSi(SiMe_3)_3(THF)_3$ in hexanes and ether. Volatiles were again removed under vacuum, leaving a black residue. Extraction with hexanes, filtration of the resulting dark red-brown solution, and recrystallization from hexanes at −20 °C yielded large dark red crystals of **2** [0.328 g, 33.9% yield based on $(Me_3SiCH_2)_4Ti$].[20] Like the neopentyl analogue **1**, **2** is photosensitive in solution, and light was excluded from the reaction vessel. ^1H NMR assignments were confirmed by $^1H{-}^{29}Si$ HETCOR spectra: ^1H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 2.96 (s, 6H, $Me_3SiC\mathit{H}_2$), 0.40 (s, 27H, $Si(Si\mathit{Me}_3)_3$), 0.24 (s, 27H, Me_3SiCH_2); ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 124.9 ($Me_3Si\mathit{C}H_2$, $^1J_{C-H} = 105.5$ Hz), 3.5 ($Si(Si\mathit{Me}_3)_3$, $^1J_{C-H} = 119.1$ Hz), 2.6 (Me_3SiCH_2, $^1J_{C-H} = 118.4$ Hz); $^{29}Si\{^1H\}$ NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C) δ −3.1 ($CH_2\mathit{Si}Me_3$), −8.1 ($Si(\mathit{Si}Me_3)_3$), −37.0 ($\mathit{Si}(SiMe_3)_3$). Anal. Calcd for $C_{21}H_{60}Si_7Ti$: C, 45.27; H, 10.85. Found: C, 45.16; H, 10.61.

Preparation of $(Me_3CCH_2)_3ZrSi(SiMe_3)_3$ (3). A yellow solution of $(Me_3CCH_2)_3ZrCl$ (2.08 mmol) in ether was prepared *in situ* from $(Me_3CCH_2)_4Zr$ and anhydrous HCl by the previously described method[7b] and then cooled and stirred at 0 °C. $LiSi(SiMe_3)_3(THF)_3$ (0.977 g, 2.07 mmol) in 20 mL of ether at 0 °C was added dropwise to the pale yellow $(Me_3CCH_2)_3ZrCl$, immediately producing a darker yellow color. The solution was stirred at 22 °C for 3 h after the end of the addition and then filtered. Volatiles were stripped under vacuum, and the brown residue was extracted with hexanes and filtered to remove LiCl. Removal of hexanes yielded 0.64 g of crude product $(Me_3CCH_2)_3ZrSi(SiMe_3)_3$ [56% yield based on $(Me_3CCH_2)_4Zr$]. The crude product was purified by crystallization from toluene at −30 °C: ^1H NMR (benzene-d_6, 250 MHz, 23 °C) δ 1.63 (s, 6H, $Me_3CC\mathit{H}_2$), 1.19 (s, 27H, Me_3CCH_2), 0.43 (s, 27H, $Si\mathit{Me}_3$); $^{13}C\{^1H\}$ NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 127.4 ($Me_3C\mathit{C}H_2$, $^1J_{C-H} = 102.2$ Hz), 37.9 ($Me_3\mathit{C}CH_2$), 34.7 (Me_3CCH_2, $^1J_{C-H} = 124.3$ Hz), 4.2 ($Si\mathit{Me}_3$, $^1J_{C-H} = 119.5$ Hz); $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.5 MHz, 23 °C) δ −7.64 ($Si(\mathit{Si}Me_3)_3$), −85.8 ($\mathit{Si}(SiMe_3)_3$). Anal. Calcd for $C_{24}H_{60}Si_4Zr$: C, 52.19; H, 10.95. Found: C, 52.01; H, 10.73.

Preparation of $(Me_3SiCH_2)_3ZrSi(SiMe_3)_3$ (4). A mixture of 1.83 g (7.87 mmol) of $ZrCl_4$ in 20 mL of ether was stirred at room temperature for several hours to produce a fine slurry and then cooled to 0 °C before dropwise addition of 3 equiv of Me_3SiCH_2MgCl (24 mmol, 18.2 mL of 1.3 M Me_3SiCH_2MgCl/ether solution).[7] The reaction mixture was stirred for 18 h at 0 °C and then filtered cold, via cannula, into a solution of 3.69 g (7.83 mmol) of $LiSi(SiMe_3)_3(THF)_3$ in 20 mL of ether at 0 °C. A bright yellow color appeared immediately upon addition. The reaction solution was stirred for 3 h at 0 °C. Filtration, removal of volatiles, extraction of the residue with hexane, and filtration gave a crude yellow product. The NMR of the crude product showed it was almost pure **4**. Subsequent recrystallization yielded several irregular crystal aggregates of **4** (0.245 g, 5.6% based on $ZrCl_4$).[20] ^1H NMR assignments were confirmed by ^1H-^{29}Si HETCOR spectra: ^1H NMR (benzene-d_6, 250 MHz, 23 °C) δ 1.57 (s, 6H, $Me_3SiC\mathit{H}_2$), 0.41 (s, 27H, $Si(Si\mathit{Me}_3)_3$), 0.24 (s, 27H, Me_3SiCH_2); $^{13}C\{^1H\}$ NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 99.1 ($Me_3Si\mathit{C}H_2$, $^1J_{C-H} = 102.5$ Hz), 4.3 ($Si(Si\mathit{Me}_3)_3$, $^1J_{C-H} = 118.4$ Hz), 2.9 (Me_3SiCH_2, $^1J_{C-H} = 119.6$ Hz); $^{29}Si\{^1H\}$ NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C) δ −3.8 ($CH_2\mathit{Si}Me_3$), −7.6 ($Si(\mathit{Si}Me_3)_3$), −75.7 ($\mathit{Si}(SiMe_3)_3$). Anal. Calcd for $C_{21}H_{60}Si_7Zr$: C, 42.00; H, 10.07. Found: C, 41.69; H, 9.59.

X-ray Crystal Structure Determination of 1.[21] Crystal, data collection, and refinement parameters are given in Table 1. A suitable crystal was selected and mounted in a thin-walled, nitrogen-flushed glass capillary. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \le 2\theta \le 24°$).

The unit parameters, equivalent reflections, and systematic absences in the diffraction data are consistent with the trigonal space groups $P3$, $P\bar{3}$, $P321$, $P3m1$, $P\bar{3}m1$, $P312$, $P31m$, and $P\bar{3}1m$. The E-statistics, the calculated Z, and the absence of a molecular 2-fold axis or mirror plane strongly suggested the noncentrosymmetric space group, $P3$. The other space-group possibilities were also thoroughly explored but were found to yield chemically bizarre results. The structure was solved with the use of the direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Absorption corrections were ignored (μ = 3.83 cm^{-1}). Three unique, but chemically equivalent, compound molecules were located, each on a 3-fold axis, in the

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[18] Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

[19] Whitmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 481.

[20] The NMR studies of the reactions of $(Me_3ECH_2)_3MCl$ with $LiSi(SiMe_3)_3$ show the conversion to be nearly quantitative. However, the products were found to be very soluble in nonpolar solvents (hexanes) and polar solvents (ether).

[21] The crystal structures of **1** and **2** were determined at the University of Delaware and the University of Tennessee, respectively.

asymmetric unit. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL PLUS (4.2) program library (Sheldrick, G. Siemens XRD, Madison, WI).

X-ray Crystal Structure Determination of 2.[21] The crystal structure was obtained at 173 K on a Siemens R3m/V diffractometer fitted with a Nicolet LT-2 low-temperature device. A suitable crystal was coated with Paratone oil (Exxon) and mounted under a stream of nitrogen. The compound was found to crystallize in the trigonal system. The unit parameters, equivalent reflections, and systematic absences in the diffraction data were consistent with the space groups $R3$ and $R\bar{3}$. The *E*-statistics and calculated *Z* strongly suggested the chiral space group $R3$. The other possibility was also explored but yielded chemically unreasonable results. Of 926 reflections collected, all were determined to be unique. The structure was solved by direct methods with the use of the Siemens SHELXTL 93 (Version 5.0) proprietary software package. All non-hydrogen atoms were located from successive Fourier maps and refined by full-matrix least-squares methods on F^2 to R (R_wF^2) = 3.89 (10.83)%. All atoms except hydrogen were anisotropically refined. The hydrogen atoms were placed in calculated positions and introduced into the refinement as fixed contributors with isotropic U values of 0.08 Å^2. Crystal data for **2** are summarized in Table 1.

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Supporting Information Available: Complete lists of the crystallographic data for **1** and **2** (15 pages). Ordering information is given on any current masthead page.

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