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Syntheses of Titanium and Zirconium Chlorotrialkyl Complexes and Crystal Structure of Chlorotrineopentylzirconium Containing Unusual Linear Symmetric Metal−Chloride Polymeric Chains

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We have been investigating titanium and zirconium alkyl silyl complexes $(Me_3ECH_2)_3M{-}SiR_3$ (M = Ti, Zr; E = C, Si),[1] which are prepared by the reactions of trialkyl chloride complexes $(Me_3ECH_2)_3MCl$ (M = Ti, E = C, **1**; Si, **2**; M = Zr, E = C, **3**; Si, **4**) with a silyl anion. These group 4 trialkyl halide complexes are potential precursors to other trialkyl complexes. $(Me_3CCH_2)_3ZrCl$ (**3**) was first synthesized by Wengrovius and Schrock through the reaction of $(Me_3CCH_2)_2Mg$ and $(Me_3CCH_2)_2ZrCl_2(Et_2O)$ and isolated by sublimation as a yellow solid containing a small percentage of $(Me_3CCH_2)_4Zr$.[2] **3** was the only known group 4 trialkyl halide complex, and this method for synthesizing **3** was the only one known for over a decade. We subsequently developed several new methods to prepare **3** in high yields.[3a] Recently, Hughes and Kingsley reported the formation of neopentylchloro complexes $(Me_3CCH_2)_xMCl_{4-x}$ (M, Ti, Zr; x = 1−3) through comproportionation reactions between $(Me_3CCH_2)_4M$ and MCl_4.[3b] We have also prepared and characterized new trialkyl halide complexes **2** and **4** and developed a new method to produce **1**. The syntheses of **1**−**4**, the characterization of the new complexes **2** and **4**, and the crystal structure of $(Me_3CCH_2)_3ZrCl$ (**3**) with unusual linear and symmetric polymeric −Zr−Cl−Zr−Cl− chains are presented here. We report as well improved syntheses of tetraalkyl complexes $(Me_3ECH_2)_4Ti$ (E = C, **5**;[4a] Si, **6**[4b]) which are used as precursors to **1** and **2**. Preliminary results have been reported.[3a]

Results and Discussion

Syntheses of Titanium and Zirconium Trialkyl Chloride Complexes. $(Me_3ECH_2)_3MCl$ (M = Ti, E = C, **1**; E = Si, **2**; M = Zr, E = Si, **4**) were prepared by the reactions outlined in eqs 1−3.

$$(Me_3ECH_2)_4Ti + HCl \rightarrow (Me_3ECH_2)_3TiCl\ (E = C,\ \mathbf{1};\ Si,\ \mathbf{2}) + Me_4E \quad (1)$$

$$ZrCl_4 + 3Me_3SiCH_2Li \rightarrow (Me_3SiCH_2)_3ZrCl\ (\mathbf{4}) + 3LiCl \quad (2)$$

$$ZrCl_4 + 3Me_3SiCH_2MgCl \rightarrow (Me_3SiCH_2)_3ZrCl\ (\mathbf{4}) + 3MgCl_2 \quad (3)$$

Attempts to synthesize the titanium compounds **1** and **2** directly through the metathesis of $TiCl_4$ and Me_3ECH_2Li failed to give high yields, probably because of the tendency of Ti(IV) to be easily reduced by reducing agents such as Me_3ECH_2Li. The successful method of producing **1** and **2** in this study was by treatment of the tetraalkyl precursor with dry HCl in ether solution.

Equations 2 and 3 are equally good methods of producing **4**; the reaction in eq 2 may be preferable because the reaction with Me_3SiCH_2MgCl produces copious amounts of $MgCl_2$, which makes filtration of the product somewhat more difficult. Compounds **1**, **2**, and **4** are photosensitive and thermally unstable. They were usually prepared in situ and used in the synthesis of the trialkyl silyl complexes $(Me_3ECH_2)_3M{-}SiR_3$.[1] These thermally unstable complexes **1**, **2**, and **4** were identified by their ^1H and ^{13}C NMR and by their subsequent reactions with $LiSiR_3$ to form $(Me_3ECH_2)_3M{-}SiR_3$.

We have developed four syntheses for $(Me_3CCH_2)_3Zr{-}Cl$ (**3**) which are more convenient and give higher yields.[3a] These syntheses are summarized in eqs 4−7.

$$ZrCl_4 + 3Me_3CCH_2Li^{5c} \rightarrow (Me_3CCH_2)_3Zr{-}Cl\ (\mathbf{3}) + 3LiCl (4)^{3a}$$

$$ZrCl_4 + 3Me_3CCH_2MgCl^{5d} \rightarrow (Me_3CCH_2)_3Zr{-}Cl\ (\mathbf{3}) + 3MgCl_2 \quad (5)$$

$$^1/_4ZrCl_4 + {}^3/_4(Me_3CCH_2)_4Zr\ (\mathbf{7}) \rightarrow (Me_3CCH_2)_3Zr{-}Cl\ (\mathbf{3}) \quad (6)^{3a}$$

$$(Me_3CCH_2)_4Zr\ (\mathbf{7}) + HCl \rightarrow (Me_3CCH_2)_3Zr{-}Cl\ (\mathbf{3}) + CMe_4 \quad (7)^{3a}$$

Compound **3** could be purified by sublimation (up to 60 °C, 0.01 Torr) or crystalization. Sublimation caused significant loss through decomposition of **3**. A small amount of $(Me_3CCH_2)_4Zr$ (**7**) was usually present in the product and was not separated by sublimation. In fact, because **3** decomposed at a higher rate during sublimation, sublimation actually increased the percentage of **7** in a sample. For most purposes, a small percentage of **7** did not pose a problem, as it was usually removed in a later synthetic step.[1a,b] The comproportionation reaction in eq 6 represents the most atom-efficient synthesis; there was no waste of mass. If a very pure sample was needed (>99% conversion of **7** to **3**), the synthesis in eq 7, monitored by NMR spectroscopy, was preferred, although more than one addition of HCl was often required for complete conversion.

Solid **3** deteriorates fairly rapidly under room light and decomposes more slowly at room temperature in darkness, with noticeable darkening of the yellow crystals in 1 day or less.

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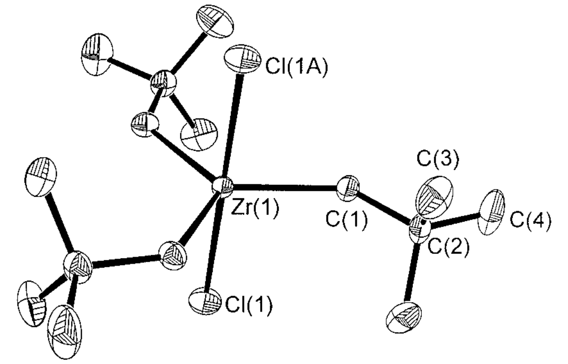


Figure 1. ORTEP diagram of **3** showing the trigonal bipyramidal structure around a Zr atom (thermal ellipsoids drawn at the 50% probability level).

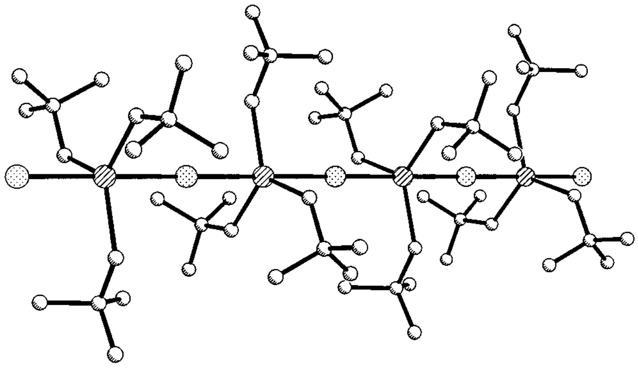
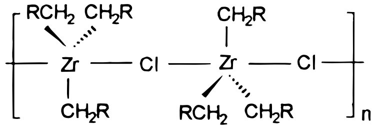


Figure 2. Diagram of a linear symmetric polymeric chain in the crystal of **3**.

Chart 1



(R = Me_3C)

The compound decomposes much more quickly in solution at room temperature.

Crystal Structure of 3. We were surprised to find that **3** crystallizes from hexanes in linear polymeric chains with the unit cell $-Cl-Zr(CH_2CMe_3)_3-Cl-Zr(CH_2CMe_3)_3-$ (Chart 1), as shown in the ORTEP diagram in Figures 1 and 2. The chloride bridges are linear and symmetric, with a Zr−Cl−Zr bond angle of 180° and all Zr−Cl bond distances equal, 2.547 Å. Four parallel polymeric chains occupy the four edges of a unit cell in a direction parallel to the *c* axis. Table 1 lists the crystal data and results of analyses. Interatomic distances and intramolecular bond angles are listed in Tables 2 and 3, respectively.

Table 1. Crystal Data for **3**[a]

formula (formula weight)	$C_{15}H_{33}ClZr$ (340.1)
crystal size (mm)	0.7 × 0.4 × 0.35
crystal system	hexagonal
space group	$P6_3/m$
lattice parameters	$a = b = 10.1250(10)$ Å; $c = 10.189(3)$ Å
V (Å^3)	904.5(4)
Z	2
density (calc) (g/cm^3)	1.249
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)
μ (Mo Kα) (cm^{-1})	7.31
F(000)	360
temp (°C)	−100(2)
scan type	ω
$2\theta_{max}$ (deg)	45.0
index ranges	$\pm h,k,l$
no. of unique reflections	422
no. of parameters varied	32
R indices[b]	0.0317 ($R_wF = 0.0571$)
goodness of fit (GOF)	1.04 (on F)

[a] See supplementary material in ref 3a for a complete list of crystallographic data. [b] $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$; $R_wF = (\Sigma[w(F_0 - F_c)^2]/\Sigma[w(F_0)^2])^{1/2}$.

Table 2. Interatomic Distances (Å) in **3**

Zr(1)−Cl(1)	2.547(1)	Zr(1)−C(1)	2.199(4)
Zr(1)−Cl(1A)	2.547(1)	Zr(1)−C(1A)	2.199(3)
Zr(1)−C(1B)	2.198(1)	Cl(1)−Zr(1A)	2.547(1)
C(1)−C(2)	1.515(7)	C(2)−C(3)	1.516(4)
C(2)−C(4)	1.513(7)	C(2)−C(3A)	1.516(4)

Table 3. Intramolecular Bond Angles (deg) in **3**

Cl(1)−Zr(1)−C(1)	90.0	Cl(1)−Zr(1)−Cl(1A)	180.0
C(1)−Zr(1)−Cl(1A)	90.0	Cl(1)−Zr(1)−C(1A)	90.0
C(1)−Zr(1)−C(1A)	120.0	Cl(1A)−Zr(1)−C(1A)	90.0
Cl(1)−Zr(1)−C(1B)	90.0	C(1)−Zr(1)−C(1B)	120.0
Cl(1A)−Zr(1)−C(1B)	90.0	C(1A)−Zr(1)−C(1B)	120.0
Zr(1)−Cl(1)−Zr(1A)	180.0	Zr(1)−C(1)−C(2)	130.5(2)
C(1)−C(2)−C(3)	108.1(3)	C(1)−C(2)−C(4)	112.0(4)
C(3)−C(2)−C(4)	109.3(3)	C(1)−C(2)−C(3A)	108.1(3)
C(3)−C(2)−C(3A)	109.9(4)	C(4)−C(2)−C(3A)	109.3(3)

Halide-bridged transition metal complexes are common; bridging halide ligands between two metal atoms normally have M−X−M angles around 109°, consistent with sp^3 hybridization of the halide bridge. Some linear chloride-bridged compounds have previously been reported for late transition metal complexes with d^n electron configuration. Symmetric or nonsymmetric chains with linear dinuclear −X−M−M−X−M−M− moieties[6] have been observed in d^n complexes $Ru_2(O_2CCH_3)_4Cl\cdot 2H_2O$ and $Ru_2(O_2CCH_2CH_3)_4Cl$,[6a] $M'_4[Pt_2(P_2O_5H_2)_4X]\cdot nH_2O$ ($M' = K, NH_4$; X = Cl, Br,),[6b] and $M_2(CH_3CS_2)_4I$ (M = Ni,[6c] Pt[6d]). Polymeric chains with linear symmetric chloride bridges are rare, however. There are a few examples of linear symmetric chains of the type −X−M−X−M−,[7] where M is a metal with d^n electron configuration. $Tl_2Mn^{III}F_5\cdot H_2O$ is reported to crystallize with symmetric linear chains of $-F-Mn^{III}F_4-F-Mn^{III}F_4-$ and with hydrogen bonds between the H_2O molecules and fluorine atoms.[7a] $CdCl_5(denH_3)$ (den = diethylenetriamine) forms a two-dimensional network of linear symmetric $-Cl-CdCl_4-Cl-CdCl_4-$ chains.[7b] To our knowledge, though, **3** is the first example of linear symmetric −X−M−X−M− chains in a d^0 metal complex.

In the crystal structure of **3**, the ligands around each zirconium atom are arranged in a trigonal bipyramid. The Cl−Zr−Cl and

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Zr−Cl−Zr bond angles are 180.0°, as defined by the crystallographic symmetry. Each metal center is coplanar with the three surrounding carbon atoms. This plane is exactly perpendicular to the linear −Cl−Zr−Cl−Zr− axis (C−Zr−Cl angles of 90.0° as defined by symmetry). The neopentyl groups on each metal center are arranged in a pinwheel structure, with the ligands on neighboring metal atoms staggered (Figure 2), as would be expected for the lowest-energy arrangement.

All the Zr−Cl bonding distances are equal, 2.547(1) Å. In comparison, $ZrCl_4$, which is reported to adopt a $-ZrCl_2-(\mu\text{-}Cl)_2-ZrCl_2-(\mu\text{-}Cl)_2-$ chain structure[8] has two different bridging Zr−Cl bond lengths [2.498(2) and 2.655(2) Å] and a terminal Zr−Cl bonding distance of 2.307(2) Å. The Zr−Cl bonding distance in **3** is much longer than the terminal Zr−Cl in $ZrCl_4$ and intermediate in length between the two bridging distances. It is not clear why the molecules of **3** polymerize in crystallization to form the linear symmetric chains.

Syntheses of $(Me_3ECH_2)_4Ti$ (E = C, 5; Si, 6).[11,12] These previously known tetraalkyl complexes are important precursors to other titanium complexes and solid-state materials.[13] In the current study, **5** and **6** were prepared as precursors to **1** and **2** through the reactions of $TiCl_4{\cdot}2THF$ with Me_3CCH_2Li and Me_3SiCH_2MgCl, respectively. The procedures here are improvements over literature methods.[4a,b,9d,13a] The THF adduct of $TiCl_4$,[10] much less volatile and easier to handle than the corrosive liquid $TiCl_4$, was preferred over pure liquid $TiCl_4$ in our syntheses of the titanium complexes.

In conclusion, we have prepared the new trialkyl chloride complexes $(Me_3SiCH_2)_3MCl$ (M = Ti, **2**; Zr, **4**) and presented the improved syntheses of **1** and **3** as well as tetraalkyl complexes $(Me_3ECH_2)_4Ti$ (**5**, **6**). These compounds are important precursors to group 4 metal complexes. The novel linear symmetric chain with the −Cl−Zr−Cl−Zr− unit in the solid-state structure of the d^0 complex **3** perhaps shows the tendency of the molecules to reduce electron deficiency at the metal centers through polymerization.

Experimental Section

General Procedures. All manipulations were performed under dry nitrogen or argon atmosphere with the use of either a glovebox or standard Schlenk techniques. Glassware was first oven-dried at 120 °C and then usually flame-dried under vacuum before use. Failure to flame-dry glassware generally resulted in lower yields. As the compounds are all somewhat photosensitive, hood lights were kept off during all syntheses.

All solvents were purified by distillation from potassium/benzophenone ketyl and stored under dry nitrogen. 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, at 23 °C unless otherwise noted; shifts were referenced to solvents (residual proton peak).

$ZrCl_4$ was sublimed at 170 °C before use. In reactions using solid $ZrCl_4$, stirring the solid in the reaction solvent at room temperature for at least 1 h before addition of other reagents produced a fine, homogeneous slurry with a large surface area of $ZrCl_4$. Me_3CCH_2Li,[5c] Me_3CCH_2MgCl,[5d] Me_3SiCH_2Li,[2a] and Me_3SiCH_2MgCl[5b] are prepared according to the literature methods. Anhydrous HCl, 1.0 M in ether (Aldrich), was used as received.

Compounds **1**−**8** are all somewhat thermally unstable at room temperature and were stored when necessary under nitrogen in a freezer at <-15 °C.

Preparation of $(Me_3CCH_2)_3TiCl$ (1, Eq 1). To a solution of **5** (100 mg, 0.3 mmol) in ether at −30 °C was added dropwise a slight excess of HCl (1.1 equiv, 0.33 mL of 1.0 M HCl/ether). Solvent was pumped away at −40 °C. The residue was dissolved in cold toluene-d_8 and an NMR spectrum taken at −40 °C, showing almost complete conversion of **5** into **1**: ^1H NMR (toluene−d_8, 400 MHz, −40 °C) δ 2.58 (CH_2), 1.08 (CMe_3); $^{13}C\{^1H\}$ NMR (toluene-d_8, 100 MHz, −40 °C) δ 125.2 (CH_2, J_{C-H} = 114.2 Hz), 38.1 (CMe_3), 33.1 (CMe_3, J_{C-H}, = 124.8 Hz). The compound is unstable at room temperature and was usually generated in situ in subsequent synthesis of $(Me_3CCH_2)_3Ti-Si(SiMe_3)_3$.[1]

Preparation of $(Me_3SiCH_2)_3TiCl$ (2, Eq 1). A solution of 0.69 g (1.7 mmol) of **6** in hexane at −20 °C was added with 1 equiv of HCl (1.7 mL, 1.0 M in ether) dropwise. The reaction flask was allowed to warm slowly. An NMR spectrum taken 4 h after HCl addition showed almost complete conversion of **6** into **2**. Solvent was removed at −20 °C, leaving viscous, sticky yellow liquid **2** which could then be used in situ in the following synthesis of, e.g., $(Me_3SiCH_2)_3Ti-SiR_3$.[1b] Although solutions of **2** are stable for short periods at room temperature, neat liquid **2** deteriorates rapidly above 0 °C: ^1H NMR (benzene-d_6, 250 MHz, 23 °C) δ 2.82 (CH_2), 0.17 ($SiMe_3$); $^{13}C\{^1H\}$ NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 109.2 (CH_2), 1.71 ($SiMe_3$).

Preparation of $(Me_3CCH_2)_3ZrCl$ (3). (a) From $ZrCl_4$ and $3Me_3CCH_2Li$ (Eq 4). A solution of 2.00 g (25.6 mmol) of Me_3CCH_2Li in a mixture of hexanes (10 mL) and ether (10 mL) at 0 °C was added dropwise over a period of 15 min to a rapidly stirred slurry of $ZrCl_4$ (2.40 g, 10.3 mmol, 20% excess) in 10 mL of ether, also at 0 °C. The mixture was stirred at room temperature overnight. The cloudy brown mixture was filtered, and solvent was removed under vacuum. Sublimation of the brown residue at 60 °C yielded 1.15 g (3.38 mmol, 40% yield based on Me_3CCH_2Li) of yellow **3** containing a small amount of $(Me_3CCH_2)_4Zr$ (**7**): ^1H NMR (benzene-d_6, 250 MHz, 23 °C) δ 1.54 (CH_2), 1.09 (CMe_3); $^{13}C\{^1H\}$ NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 103.5 (CH_2), 35.5 (CMe_3), 34.3 (CMe_3); IR (KBr pellet, 23 °C, cm^{-1}) 2950 (vs), 2704 (m), 1468 (vs), 1357 (s), 1219 (vs), 1082 (m), 928 (m), 911 (m), 740 (s), 523 (vs).

(b) From $ZrCl_4$ and $3Me_3CCH_2MgCl$ (Eq 5). A slurry of 0.629 g (2.70 mmol) of $ZrCl_4$ in ether was cooled to 0 °C and treated with 3 equiv of Me_3CCH_2MgCl (10 mL, 0.81 M in ether) added dropwise over 30 min. The reaction mixture was stirred at 0 °C for 18 h. Ether was removed under vacuum and the residue extracted with hexane to dissolve **3**. Filtration and removal of solvent yielded yellow solid of **3** (0.630 mg, 1.85 mmol, 69% yield) containing a small amount of $(Me_3CCH_2)_4Zr$.

(c) From $ZrCl_4$ and $3(Me_3CCH_2)_4Zr$ (Eq 6). A solution of 7.214 g (19.2 mmol) of $(Me_3CCH_2)_4Zr$ in 75 mL of ether at 0 °C was added dropwise over a period of 20 min to a suspension of $ZrCl_4$ (1.491 g, 6.40 mmol) in 75 mL of ether, also at 0 °C. The mixture was stirred at −2 °C for 18 h. The solvent was removed by vacuum to give 8.24 g (24.2 mmol, 95% yield) of yellow solid **3** containing a small amount of **7**.

(d) From $(Me_3CCH_2)_4Zr$ and HCl (Eq 7). A solution of 0.192 g of $(Me_3CCH_2)_4Zr$ (**7**, 0.511 mmol), in 2 mL of ether was cooled to −78 °C. Over a 15-min period, 5.11 mL of 0.10 M HCl/Et_2O solution (0.511 mmol HCl) prepared from 1.0 M HCl/Et_2O (Aldrich) was added dropwise to the stirring solution of **7**. The pale yellow solution was warmed slowly to room temperature over a 5-h period with constant

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(11) For related group 5 pentaalkyl $M(CH_2R)_5$ and alkyl alkylidene $(RCH_2)_3M{=}CHR$ complexes, see, e.g.: (a) Schrock, R. R.; Meakin, P. *J. Am. Chem. Soc.* **1974**, *96*, 5288. (b) Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796. (c) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359. (d) Wu, Y.-D.; Chan, K. W. K.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 9259. (e) Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746.

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stirring. Solvent was removed under vacuum to yield a yellow solid containing 92 mol % of **3** by NMR.

This reaction was always monitored by NMR spectroscopy; after solvent and any residual HCl were removed under vacuum, the completeness of the conversion was calculated from integration of the NMR resonances of **3** and **7**, and more HCl was added if needed. It was possible to achieve over 99% conversion into **3** provided that care was taken to avoid thermal and photolytic decomposition.

Preparation of $(Me_3SiCH_2)_3ZrCl$ (4). (a) From $ZrCl_4$ and $3Me_3SiCH_2Li$ (Eq 2). A solution of 3.64 g of Me_3SiCH_2Li (38.7 mmol) in 25 mL of ether at 0 °C was added in small portions over a 40-min period to a rapidly stirred slurry of $ZrCl_4$ (2.998 g, 12.86 mmol) in 25 mL of ether, also at 0 °C. The reaction mixture was left stirring at 0 °C for 6 h. The remaining solution was then filtered and the solvent stripped off under vacuum, leaving unstable solid **4**, which was then used in subsequent synthesis of $(Me_3SiCH_2)_3Zr-Si(SiMe_3)_3$:[1b] ^1H NMR (toluene-d_8, 400 MHz, 27 °C) δ 1.46 (CH_2), 0.18 (SiMe_3); ^{13}C $\{^1H\}$ NMR (toluene-d_8, 100 MHz, 27 °C) δ 80.6 (CH$_2$), 2.3 (SiMe_3).

(b) From $ZrCl_4$ and $3Me_3SiCH_2MgCl$ (Eq 3). A 0.834-g sample of $ZrCl_4$ in 30 mL of Et_2O was stirred at room temperature for several hours to produce a fine slurry. The slurry was cooled to 0 °C and stirred rapidly during dropwise addition of 6.3 mL of Me_3SiCH_2MgCl (1.7 M in Et_2O, 11 mmol) over a period of 30 min. The pale yellow reaction mixture was stirred at 0 °C for 9 h and then filtered directly into a solution of $LiSi(SiMe_3)_3$ to make $(Me_3SiCH_2)_3Zr-Si(SiMe_3)_3$.[1b]

Crystal Structure Determination of 3. The crystal structure was obtained at 173 K on a Siemens R3m/V diffractometer fitted with a Nicolet LT-2 lot 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 hexagonal system. The unit parameters, equivalent reflections, *E*-statistics and systematic absences in the diffraction data suggested the space group $P6_3/m$. Of 1341 reflections, 364 were determined to be unique. The Zr atom was located by the Patterson method, and all remaining non-hydrogen atoms were located and refined anisotropically. Successive full-matrix least-squares refinements converged the structure to $R(R_w) = 3.18(5.93)\%$. The hydrogen atoms on the methyl groups were located from a Fourier map. The two hydrogen atoms on the CH_2 group were fixed in calculated, idealized positions [$d(C-H) = 0.96$ Å]. These hydrogen atoms were not refined. Crystal data for **3** are summarized in Table 1; interatomic distances and intramolecular bond angles are listed in Tables 2 and 3, respectively.

Preparation of $(Me_3CCH_2)_4Ti$ (5).[13a] The reaction flask was wrapped in aluminum foil. A slurry of $TiCl_4 \cdot 2OR_2$ (2.97 g, 8.9 mmol) in 15 mL of hexane was cooled to −78 °C with stirring.[14b] A solution of Me_3CCH_2Li (2.77 g, 35.5 mmol) in a mixture of hexane and ether, also at −78 °C, was added dropwise over a 1.5-h period. The reaction solution was allowed to warm slowly to 23 °C over a 2-h period and then stirred for 4 h. Filtration of the dark gray-brown solution, removal of volatiles under vacuum, and sublimation of the residue at 40−50 °C under vacuum yielded 1.88 g (5.7 mmol) of clean yellow solid **5**, 64% based on $TiCl_4$.

Preparation of $(Me_3SiCH_2)_4Ti$ (6). All operations were carried out under reduced light, with the hood lights off and the reaction flask wrapped in foil. A solution of $TiCl_4 \cdot 2OR_2$ (0.717 g, 2.14 mmol) in ether was chilled to −20 °C and treated with 5.3 mL of Me_3SiCH_2MgCl solution (1.70 M in ether, 8.57 mmol) added dropwise over 90 min. The reaction solution was allowed to warm to 23 °C over 1 h and then stirred 6 h at 23 °C. Filtration of the dark solution, removal of volatiles under vacuum at −5 °C, and extraction of the dark brown, oily residue with hexanes gave a golden yellow solution. Evaporation of hexanes under vacuum at −5 °C left 0.69 g of **6** as a golden yellow, viscous liquid, 80% yield based on $TiCl_4$.[14a] Neat liquid **6** decomposes under room light and deteriorates in hours at room temperature: ^1H NMR (benzene−d_6, 250 MHz, 23 °C) δ 2.26 (CH_2), 0.19 (SiMe_3); ^{13}C $\{^1H\}$ NMR (benzene−d_6, 62.9 MHz, 23 °C) δ 97.5 (CH$_2$), 2.3 (SiMe_3).

Preparation of $(Me_3SiCH_2)_4Zr$ (8). This compound was first prepared by the reaction of $ZrCl_4$ with Me_3SiCH_2Li in 89% crude yield.[4b] It was prepared in this study by the Grignard reagent Me_3SiCH_2MgCl, and its NMR characterization is reported. A slurry of 0.851 g (3.65 mmol) of $ZrCl_4$ in 50 mL of ether was cooled to −20 °C and stirred rapidly during addition of 4 equiv of Me_3SiCH_2MgCl (20.0 mL, 0.73 M in ether), added dropwise over 1 h. The reaction temperature was kept below −7 °C during the addition. The pale tan reaction mixture was then warmed to 23 °C and stirred for 24 h. Hexanes were added, and the yellow-tan solution was filtered. The beige $MgCl_2$ precipitate was washed with several portions of hexane. Removal of solvent from the filtrate left **8** (1.20 g, 2.73 mmol, 75% yield) as a viscous yellow liquid: ^1H NMR (toluene−d_8, 400 MHz, 27 °C) δ 1.10 (CH_2), 0.20 (SiMe_3); ^{13}C $\{^1H\}$ NMR (toluene−d_8, 100 MHz, 27 °C) δ 75.8 (CH$_2$), 2.7 (SiMe_3).

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(14) (a) Attempts to obtain reliable percent yields were unsuccessful due to the difficulty of completely removing the solvent and the rapid decomposition of the neat compounds at room temperature. Only approximate yields could be obtained. (b) We initially attempted to make the ether adduct of $TiCl_4$ by adding ether to a hexane solution of $TiCl_4$. However, the ether adduct was volatile and melted near room temperature. It was redissolved in hexane and added THF to give a bright yellow powder of a mixture, $TiCl_4 \cdot 2OR_2$, containing about 25 mol % Et_2O and 75 mol % THF by NMR. This powder did not melt at room temperature. The average molar mass of this mixture, 335 g/mol, was used in all calculations.