10 highest peaks in the final difference Fourier techniques had electron densities ranging from 2.65 to 2.08 e/Å³ but were very close to or within the metal skeleton at positions that made no chemical sense.

Cyclopentadienylmetal Trichloride Formation versus Metallocene Dichloride Formation in the Reactions of Silylated Cyclopentadienes with Zirconium and Hafnium Chlorides. Crystal Structure of (1,3-Bis(trimethylsilyl)cyclopentadienyl)titanium Trichloride

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The reaction of zirconium and hafnium tetrachlorides with tris(trimethylsilyl)cyclopentadiene affords the monocyclopentadienyl complexes (1,3-bis(trimethylsilyl)cyclopentadienyl)zirconium trichloride (1, 73%) and (1,3-bis(trimethylsilyl)cyclopentadienyl)hafnium trichloride (2, 76%) in good isolated yields. The reaction of 1 with (1,3-bis(trimethylsilyl)cyclopentadienyl)lithium affords 1,1′,3,3′-tetrakis(trimethylsilyl)zirconocene dichloride (74%). In contrast to the preparations of 1 and 2, reaction of bis(trimethylsilyl)cyclopentadiene with zirconium and hafnium tetrachlorides affords 1,1′-bis(trimethylsilyl)zirconocene dichloride (5, 73%) and 1,1′-bis(trimethylsilyl)hafnocene dichloride (6, 76%). The reaction of (trimethylsilyl)cyclopentadiene with zirconium and hafnium tetrachlorides affords zirconocene dichloride (7, 91%) and hafnocene dichloride (8, 90%). The intermediacy of monocyclopentadienyl species in the preparation of the metallocene dichlorides is supported by the reaction of cyclopentadienylzirconium trichloride with (trimethylsilyl)cyclopentadiene to afford 7 (85%). Reaction of zirconium tetrachloride with 1 equiv of (trimethylsilyl)cyclopentadiene at 0 °C for 0.5 h affords 7 and cyclopentadienylzirconium trichloride in a (69 ± 2):(31 ± 2) ratio. The silyl group regiochemistry in 1 and 2 was established through an X-ray crystal structure determination of the titanium analogue (1,3-bis(trimethylsilyl)cyclopentadienyl)titanium trichloride (3). Complex 3 crystallizes in the orthorhombic space group *Pbnm* with *a* = 7.459 (3) Å, *b* = 11.799 (3) Å, *c* = 20.535 (3) Å, *V* = 1807.1 (9) Å³, and *Z* = 4.

Introduction

The reactions of titanium tetrachloride with silylated cyclopentadienes have been extensively investigated.[1] It has been clearly established that titanium tetrachloride reacts with 1 equiv of the silylated cyclopentadiene to afford the cyclopentadienyltitanium trichloride as the sole product under all conditions. Hence, this procedure represents a particularly efficient route to monocyclopentadienyltitanium complexes. As part of studies relating to the preparation of highly soluble organometallic Lewis acids,[2] we required convenient syntheses of monocyclopentadienylzirconium and -hafnium trichlorides, where the cyclopentadienyl ligand contained one or more trimethylsilyl groups. On the basis of the results with titanium, the reactions of zirconium and hafnium tetrachlorides with silylated cyclopentadienes potentially offered an efficient route to monocyclopentadienylzirconium and -hafnium complexes. However, such reactions had not been described.[3] We now wish to report that these re-

actions are unexpectedly complex. Zirconium and hafnium complexes containing a single 1,3-bis(trimethylsilyl)-cyclopentadienyl ligand are easily accessed by the regiospecific silyl cleavage reaction of tris(trimethylsilyl)cyclopentadiene with the metal tetrachloride. In contrast, the related reactions of bis(trimethylsilyl)cyclopentadiene and (trimethylsilyl)cyclopentadiene with zirconium and hafnium tetrachlorides afford the metallocene dichlorides.

Results

Preparation of Complexes. Reaction of tris(trimethylsilyl)cyclopentadiene[4a] with zirconium and hafnium tetrachlorides in dichloromethane at ambient temperature for 3–4 h affords (1,3-bis(trimethylsilyl)cyclopentadienyl)zirconium trichloride (73%, 1)[5] and (1,3-bis-(trimethylsilyl)cyclopentadienyl)hafnium trichloride (76%, 2) upon workup. Complexes 1 and 2 are isolated as moderately air-sensitive white powders, which are soluble
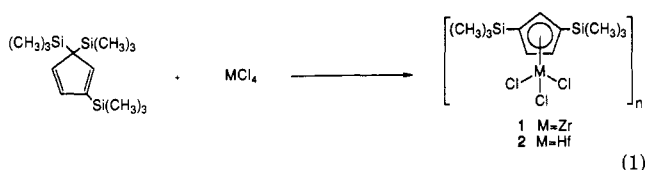
(1) (a) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156. (b) Krebs, K. W.; Engelhard, H.; Nischk, G. E. Ger. Offen. 1,959,322. (c) Jutzi, P.; Seufert, A. *J. Organomet. Chem.* **1979**, *169*, 373. (d) Jutzi, P.; Kuhn, M. *Ibid.* **1979**, *173*, 221. (e) Abel, E. W.; Moorhouse, S. *Ibid.* **1971**, *29*, 227.

(2) Winter, C. H.; Kampf, J.; Zhou, X.-X. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 1231.

(3) For related literature, see: Schore, N. E. *J. Am. Chem. Soc.* **1979**, *101*, 7410. Llinás, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37. Nief, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1988**, 770.

(4) (a) Jutzi, P.; Sauer, R. *J. Organomet. Chem.* **1973**, *50*, C29. (b) Miftakhov, M. S.; Tolstikov, G. A.; Lomakina, S. I. *Zh. Obshch. Khim.* **1976**, *46*, 2754. (c) Frisch, K. C. *J. Am. Chem. Soc.* **1953**, *75*, 6050.

(5) Duff, A. W.; Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G.; Segal, J. A. *J. Organomet. Chem.* **1985**, *293*, 271.
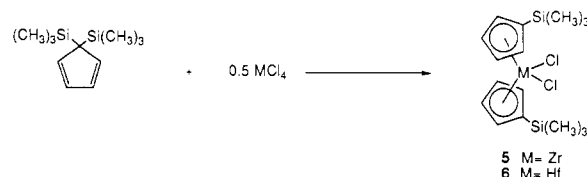
(1)

only in relatively polar solvents, such as acetone and tetrahydrofuran. This insolubility is consistent with a polymeric formulation, as has been observed for other monocyclopentadienylzirconium and -hafnium trichlorides.[6] Extended reaction of 1 and 2 with excess tris(trimethylsilyl)cyclopentadiene in refluxing toluene (30–40 h) does not result in the production of the complexes containing two 1,3-bis(trimethylsilyl)cyclopentadienyl ligands. The preparation of 1 and 2 is remarkable for several reasons. First, (bis(trimethylsilyl)-cyclopentadienyl)lithium reacts with zirconium tetrachloride at 0 °C to afford only the tetrakis(trimethylsilyl)zirconocene dichloride;[7b] complex 1 is not kinetically accessible by this route. Second, polysilylated cyclopentadienes are mixtures of readily interconverted isomers (by silatropic and sigmatropic shifts[4]) and the metal tetrachlorides react with only one of the possible isomers. Finally, the silyl cleavage reaction represents an efficient preparative procedure.
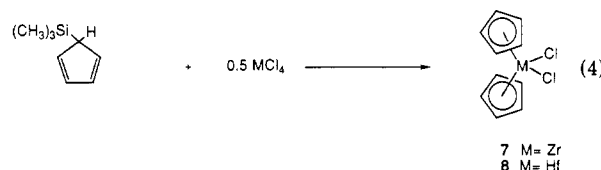
An important goal was to verify the silyl group regiochemistry in 1 and 2 (1,3 versus 1,2), since the regiochemistry could not be unambiguously assigned by ¹H NMR spectroscopy and suitable X-ray-quality crystals of 1 and 2 could not be grown. In addition to the crystal structure of the titanium analogue (1,3-bis(trimethylsilyl)cyclopentadienyl)titanium trichloride (3) described below, we have established the silyl regiochemistry through chemical synthesis. Reaction of 1 with (1,3-bis(trimethylsilyl)-cyclopentadienyl)lithium in toluene/tetrahydrofuran for 2 h (eq 2) afforded the known[8] 1,1′,3,3′-tetrakis(trimethylsilyl)zirconocene dichloride (4) in 74% yield after workup. Hence, the regiochemistry in 1 is exclusively 1,3.

(2)
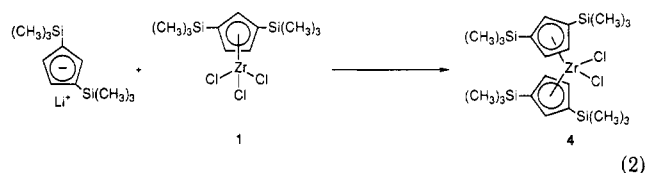
In contrast to the preparation of 1 and 2, the reaction of bis(trimethylsilyl)cyclopentadiene[4a] with zirconium and hafnium tetrachlorides in refluxing dichloromethane affords the known[7a,b,8] 1,1′-bis(trimethylsilyl)zirconocene dichloride (5, 73%) and 1,1′-bis(trimethylsilyl)hafnocene dichloride (6, 76%). Similarly, reaction of (trimethylsilyl)cyclopentadiene with zirconium and hafnium tetrachlorides affords zirconocene dichloride[7c] (7, 91%) and

(6) For selected examples, see: (a) Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; White, A. H. *Organometallics* **1984**, *3*, 18. (b) Wolczanski, P. T.; Bercaw, J. E. *Ibid.* **1982**, *1*, 793. (c) Erker, G.; Berg, K.; Treschanke, L.; Engel, K. *Inorg. Chem.* **1982**, *21*, 1277. (d) Wells, N. J.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1981**, *213*, C17. (e) Renaut, P.; Tainturier, G.; Gautheron, B. *Ibid.* **1978**, *148*, 35. (f) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood: Chichester, England, 1986; pp 33–40.

(7) (a) Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1980**, 476. (b) Antinolo, A.; Lappert, M. F.; Singh, A.; Winterborn, D. J. W.; Engelhardt, L. M.; Raston, C. L.; White, A. H.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1463. (c) Druce, P. M.; Kingston, P. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.

(8) Tolstikov, G. A.; Miftakhov, M. S.; Monakov, Y. B. *Zh. Obshch. Khim.* **1976**, *46*, 1778.

hafnocene dichloride[7c] (8, 90%) in good yield (eq 4).

(4)

These simple preparations of 5–8 should be compared with the more tedious traditional routes involving reaction of a cyclopentadienyllithium species with the metal tetrachloride.[7,8] The "double insertion" reactions in the preparation of 5–8 are in stark contrast to the related reactions with titanium tetrachloride, which afford only the mono-cyclopentadienyltitanium trichlorides, even under forcing conditions.[1a]

A logical intermediate in the preparation of the metallocene dichlorides is the monocyclopentadienylmetal trichloride. In support of this, reaction of cyclopentadienylzirconium trichloride (9) with (trimethylsilyl)cyclopentadiene in refluxing benzene for 18 h affords 7 in 85% yield (eq 5). This is consistent with the intermediacy of the monocyclopentadienylmetal trichlorides in the preparation of 5–8.

(5)
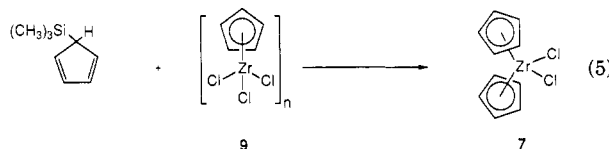
Given the facile preparations of 1 and 2, we wondered if it might be possible to kinetically control the addition of one (trimethylsilyl)cyclopentadiene to zirconium and hafnium tetrachlorides to afford the monocyclopentadienylmetal trichlorides. In order to explore this avenue, the reaction of zirconium tetrachloride with (trimethylsilyl)cyclopentadiene was monitored by ¹H NMR spectroscopy in dichloromethane-d₂ beginning at −80 °C (eq 6). No reaction was evident below −20 °C. However,

(6)
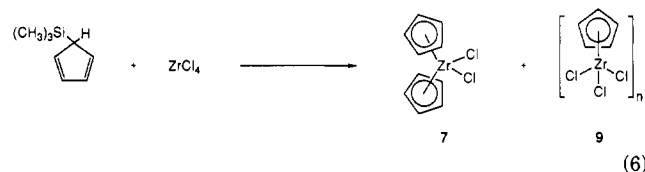
between −20 and 0 °C reaction began to occur. Cyclopentadienyl ¹H NMR resonances attributable to 7 (δ 6.50) and 9 (δ 6.85) slowly appeared. The only other new resonance observed was due to trimethylsilyl chloride (δ 0.42). The relative ratios of the products varied slightly upon warming, and the ¹H NMR chemical shifts varied slightly with temperature. After 0.5 h at 0 °C, the reaction was complete. The final ratio of 7:9 was (69 ± 2):(31 ± 2). From this experiment, it is clear that the addition of a second equivalent of (trimethylsilyl)cyclopentadiene to 9 is kinetically faster than the reaction of zirconium tetrachloride with (trimethylsilyl)cyclopentadiene. Hence, this approach does not represent an efficient preparative route to 9.
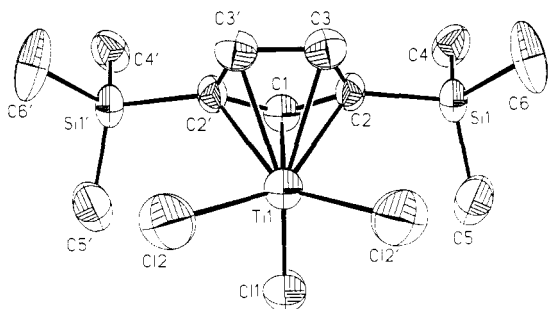
Table I. Experimental Crystallographic Data for 3

formula	$C_{11}H_{21}Cl_3Si_2Ti$
mol wt	363.72
cryst color, habit	orange-yellow square rods
cryst dimens, mm	0.42 × 0.30 × 0.18
cryst syst	orthorhombic
space group	*Pbnm*
cell dimens	
V, Å^3	1807.1 (9)
Z	4
calcd density, g cm^{-3}	1.337
scan method	$\theta/2\theta$
radiation	Mo Kα (λ = 0.710 73 Å)
diffractometer	Nicolet R3
monochromator	graphite cryst
scan range, deg	1.0 below Kα₁, 1.0 above Kα₂
scan rate, deg min^{-1}	2–5, variable
bkgd/scan time	0.5
2θ range, deg	6–50
total no. of data	1904
no. of obsd data, $I_o \geq 2.5\sigma(I)$	773
μ, cm^{-1}	10.28
transmissn coeff	0.959–0.640
$F(000)$	752
R, R_w	0.054, 0.052
w	σ_F^{-2}

Figure 1. Perspective view of 3.

Crystal Structure of (1,3-Bis(trimethylsilyl)cyclopentadienyl)titanium Trichloride (3).

In addition to the chemical characterization of 1 described above, the 1,3-silyl disposition was established through an X-ray crystal structure of the titanium analogue 3, whose preparation has been previously reported by Jutzi.[1d] X-ray data were collected under the conditions summarized in Table I. Bond lengths, bond angles, and positional parameters are summarized in Tables II and III. A perspective view of 3 is shown in Figure 1.

The structural features of 3 are normal. The average Ti–C bond length is 2.34 Å, the Ti–Cp centroid distance is 2.007 Å, and the Ti–Cl distances average 2.23 Å. These values can be compared with the related bond lengths in cyclopentadienyltitanium trichloride: average Ti–C, 2.30 Å; Ti–Cp centroid, 2.01 Å; average Ti–Cl, 2.22 Å.[6a] The angles about the titanium center are also normal and are essentially identical with those found in cyclopentadienyltitanium trichloride.

Discussion

The reaction of tris(trimethylsilyl)cyclopentadiene with zirconium and hafnium tetrachlorides represents a remarkably simple route to (1,3-bis(trimethylsilyl)cyclopentadienyl)metal trichlorides 1 and 2. This procedure provides an alternative to the use of (bis(trimethylsilyl)-cyclopentadienyl)lithium and may find general use in cases where the metal chloride is easily reduced or when the addition of a single bis(trimethylsilyl)cyclopentadienyl ligand is kinetically unfavorable. Complex 1 has been previously prepared through a route involving the reaction

Table II. Bond Lengths (Å) and Angles (deg) for 3^a

Ti(1)–Cl(1)	2.232 (3)	Si(1)–C(4)	1.843 (9)
Ti(1)–Cl(2)	2.229 (3)	Si(1)–C(5)	1.838 (13)
Ti(1)–C(1)	2.339 (11)	Si(1)–C(6)	1.861 (11)
Ti(1)–C(2)	2.338 (7)	C(1)–C(2)	1.399 (9)
Ti(1)–C(3)	2.342 (7)	C(2)–C(3)	1.429 (10)
Ti–Cp	2.007 (8)	C(3)–C(3)'	1.422 (14)
Si(1)–C(2)	1.890 (7)		

Cl(1)–Ti(1)–Cl(2)	102.0 (1)	C(3)–C(2)–Si(1)	125.7 (5)
Cl(2)–Ti(1)–Cl(2)'	102.6 (1)	C(2)–Si(1)–C(4)	105.7 (4)
Cl(1)–Ti(1)–Cp	115.3 (3)	C(2)–Si(1)–C(5)	110.4 (5)
Cl(2)–Ti(1)–Cp	116.4 (2)	C(2)–Si(1)–C(6)	107.7 (5)
C(1)–C(2)–C(3)	105.4 (7)	C(4)–Si(1)–C(5)	110.0 (6)
C(2)–C(3)–C(3)'	108.4 (6)	C(4)–Si(1)–C(6)	110.6 (7)
C(2)–C(1)–C(2)'	112.3 (7)	C(5)–Si(1)–C(6)	112.2 (8)
C(1)–C(2)–Si(1)	128.5 (6)		

^{a} Cp represents the centroid of the cyclopentadiene ring. Primed atoms are related through the crystallographic mirror at x, y, $^1/_4$.

Table III. Atomic Positional Parameters for 3

atom	x	y	z
Ti(1)	−0.4673 (3)	0.4884 (2)	0.75000
Cl(1)	−0.1689 (4)	0.5030 (3)	0.75000
Cl(2)	−0.5154 (4)	0.3742 (2)	0.6653 (1)
Si(1)	−0.4964 (4)	0.6835 (2)	0.89426 (9)
C(1)	−0.466 (2)	0.6866 (9)	0.75000
C(2)	−0.555 (1)	0.6513 (6)	0.8066 (3)
C(3)	−0.714 (1)	0.5957 (6)	0.7846 (3)
C(4)	−0.507 (2)	0.3839 (7)	0.9019 (5)
C(5)	−0.269 (2)	0.633 (1)	0.9131 (6)
C(6)	−0.669 (2)	0.615 (1)	0.9466 (6)

of bis(bis(trimethylsilyl)cyclopentadienyl)magnesium with zirconium tetrachloride in 77% yield.[5] We feel that our preparation of 1 is preferable to the magnesium route, as it is experimentally simpler and entails significantly fewer manipulations of air–sensitive reagents, while affording a similar yield. A drawback to our method is that it requires the preparation of tris(trimethylsilyl)cyclopentadiene, while the magnesium route only requires the availability of bis(trimethylsilyl)cyclopentadiene. We have found that after purification complexes 1 and 2 are soluble only in relatively polar solvents such as acetone. This is consistent with a polymeric formulation involving bridging chlorides, as has been found for related complexes.[6] Curiously, crude 1 and 2 are soluble in hexane and remain so until the hexane is removed. Apparently, their formation affords monomers or low oligomers; upon precipitation, the polymeric network forms and the complexes are no longer soluble in nonpolar solvents.

In contrast to the preparation of 1 and 2, reaction of mono- and bis(trimethylsilyl)cyclopentadiene with zirconium and hafnium tetrachlorides affords the metallocene dichlorides. These preparations of 5–8 are experimentally simpler than the standard preparations of metallocene dichlorides,[7,8] which entail the addition of cyclopentadienyllithium to the metal tetrachloride. While our method affords yields similar to those of the cyclopentadienyllithium routes, a drawback to it is that it requires the availability of the appropriate silylated cyclopentadienes. We have employed the reaction of functionalized (trimethylsilyl)cyclopentadienes with zirconium tetrachloride to prepare zirconocene dichlorides containing base-sensitive halocarbon substituents, which could not be introduced with use of standard cyclopentadienide methodology.[9] The behavior observed in the preparation of 5–8 is different from that of titanium tetrachloride, which affords cyclopentadienyltitanium trichlorides under

(9) Winter, C. H.; Pirzad, S. Unpublished results, Wayne State University, 1990.

all conditions.[1] The reactivity differences between the titanium, zirconium, and hafnium tetrachlorides may be due to the size differences between the metals and to the differences in Lewis acidities of the metal centers.

Unfortunately, it is not possibly to kinetically control the addition of a single (trimethylsilyl)cyclopentadiene to zirconium tetrachloride to cleanly afford **9**. The addition of a second equivalent of (trimethylsilyl)cyclopentadiene to **9** to afford **7** is kinetically faster than the formation of **9**. This is probably related to the low solubility of zirconium tetrachloride in dichloromethane. The bis(tetrahydrofuran) complex of zirconium tetrachloride, which is more soluble in dichloromethane, does not react cleanly with silylated cyclopentadienes.[9] However, several good synthetic routes to cyclopentadienylmetal trichlorides of zirconium and hafnium are available.[6] The exclusive formation of **1** and **2** must arise from the extremely large steric profile of the metal centers, which does not allow the approach of a second bulky tris(trimethylsilyl)cyclopentadiene.

The 1,3-silyl disposition in **1** and **2** was established through the reaction of **1** with (1,3-bis(trimethylsilyl)cyclopentadienyl)lithium to afford **4** in 74% yield. The crystal structure of the titanium complex **3** also confirmed the 1,3-silyl regiochemistry. The structural features of **3** are normal and are very similar to those of cyclopentadienyltitanium trichloride.

In summary, the reactions of a number of silylated cyclopentadienes with zirconium and hafnium tetrachlorides have been examined. With tris(trimethylsilyl)cyclopentadiene, the exclusive product is the (1,3-bis(trimethylsilyl)cyclopentadienyl)metal trichloride, while reactions with bis(trimethylsilyl)cyclopentadiene and (trimethylsilyl)cyclopentadiene afford the metallocene dichlorides. These reactions should prove to be extremely useful in organometallic synthesis. Elaboration of the complexes in this study to highly soluble cationic organometallic Lewis acids will be described in the near future.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of argon or nitrogen with use of either glovebox or Schlenk techniques. Tetrahydrofuran, diethyl ether, benzene, and toluene were distilled from purple solutions of sodium/benzophenone. Dichloromethane was distilled from calcium hydride. Hexane was distilled from sodium. NMR solvents were purified by vacuum transfer from activated 4-Å molecular sieves. The silylated cyclopentadienes were prepared according to the literature procedures.[4] Zirconium and hafnium tetrachloride were used as received from Aesar. Cyclopentadienylzirconium trichloride was purchased from Strem Chemical Co.

^{1}H NMR and ^{13}C$\{^1$H$\}$ NMR spectra were obtained on a General Electric QE-300 or GN-300 spectrometer in either benzene-d_6 or acetone-d_6. Infrared spectra were obtained on a Nicolet DX20 spectrophotometer using potassium bromide as the medium. Mass spectra were obtained on Kratos MS-50 or MS-80 spectrometers in the electron impact mode. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of (1,3-Bis(trimethylsilyl)cyclopentadienyl)zirconium Trichloride (1). A 50-mL Schlenk flask was charged with zirconium tetrachloride (0.500 g, 2.10 mmol), dichloromethane (10 mL), and a stirbar and was fitted with a rubber septum. Then tris(trimethylsilyl)cyclopentadiene (1.00 g, 3.50 mmol) was added by syringe. The mixture was stirred at ambient temperature for 3 h. The volatiles were removed under reduced pressure, and the residue was extracted with dichloromethane (50 mL). The extract was filtered through a 3-cm pad of Celite on a coarse glass frit, and hexane (300 mL) was added.

The layers were mixed by swirling, and the volume was reduced to 200 mL under reduced pressure. A white solid precipitated, which was collected on a medium frit and vacuum-dried (0.1 mm, 1 h) to afford **1** as a white microcrystalline solid (0.491 g, 73%): dec pt 140–150 °C; IR (cm^{-1}, KBr) 2956 (s), 2901 (m), 1448 (w), 1406 (w), 1385 (w), 1327 (w), 1248 (vs), 1211 (w), 1084 (s), 1060 (w), 928 (m), 916 (m), 869 (s), 838 (vs), 759 (s), 696 (m), 639 (s); ^{1}H NMR (acetone-d_6, δ) 6.84 (t, J = 1.8 Hz, C₅HH'_2(Si(CH₃)₃)₂), 6.76 (br s, C₅HH'_2(Si(CH₃)₃)₂), 0.29 (s, 2 Si(CH_3)₃); ^{13}C NMR (acetone-d_6, ppm) 133.35 (s, CSi(CH₃)₃), 132.55 (s, Cp CH), 127.48 (s, Cp CH), 0.22 (s, Si(CH₃)₃); HRMS calcd for C₁₁H₂₁Cl₃Si₂Zr M$^+$ – CH₃ 390.9026, found 390.9031. Anal. Calcd for C₁₁H₂₁Cl₃Si₂Zr: C, 32.46; H, 5.20. Found: C, 32.19; H, 5.68.

Preparation of (1,3-Bis(trimethylsilyl)cyclopentadienyl)hafnium Trichloride (2). A 50-mL Schlenk flask was charged with hafnium tetrachloride (0.548 g, 1.72 mmol), dichloromethane (12 mL), and a stirbar and was fitted with rubber septum. Then tris(trimethylsilyl)cyclopentadiene (0.467 g, 1.65 mmol) was added by syringe. The mixture was stirred at ambient temperature for 3 h. The volatiles were removed under reduced pressure, and the residue was extracted with dichloromethane (10 mL). Hexane (10 mL) was added, and the solution was filtered through a 3-cm pad of Celite on a coarse glass frit. The volatiles were removed from the clear, colorless filtrate under reduced pressure. Vacuum drying (0.1 mm, 1 h) afforded **2** as a white microcrystalline solid (0.618 g, 76%): mp 163–165 °C dec; IR (cm^{-1}, KBr) 2955 (s), 2900 (m), 1453 (w), 1406 (w), 1385 (w), 1329 (w), 1248 (vs), 1085 (s), 1060 (w), 929 (m), 922 (m), 872 (s), 837 (vs), 757 (s), 638 (w); ^{1}H NMR (acetone-d_6, δ) 6.71 (br s, C₅HH'_2(Si(CH₃)₃)₂), 6.64 (br s, C₅HH'_2(Si(CH₃)₃)₂), 0.29 (s, 2 Si(CH_3)₃); ^{13}C NMR (acetone-d_6, ppm) 131.19 (s, CSi(CH₃)₃), 130.90 (s, CpCH), 125.54 (s, CpCH), 0.29 (s, Si(CH₃)₃); HRMS calcd for C₁₁H₂₁Cl₃Si₂Hf M$^+$ – CH₃ 478.948 07, found 478.9475. Anal. Calcd for C₁₁H₂₁Cl₃Si₂Hf: C, 26.74; H, 4.28. Found: C, 27.08; H, 4.23.

Preparation of (1,3-Bis(trimethylsilyl)cyclopentadienyl)titanium Trichloride (3). A 30-mL Schlenk flask was charged with tris(trimethylsilyl)cyclopentadiene (0.864 g, 3.06 mmol), dichloromethane (10 mL), and a stirbar and was fitted with a rubber septum. Then titanium tetrachloride (0.335 mL, 3.06 mmol) was added via syringe and the solution was stirred at room temperatures for 0.25 h. The volatiles were removed under reduced pressure, and the residue was extracted with hexane (200 mL). The hexane extract was filtered through a 3-cm pad of Celite on a coarse glass frit to afford a bright yellow solution. Removal of the solvent under reduced pressure and vacuum drying (0.1 mm, 1 h) afforded **3** as a yellow-orange microcrystalline powder (0.882 g, 79%). An analytical sample was recrystallized from hexane: mp 126–128 °C (lit.[1d] mp 124–126 °C); IR (cm^{-1}, KBr) 3100 (w), 3077 (w), 2955 (s), 2899 (m), 1408 (m), 1395 (m), 1385 (m), 1251 (vs), 1086 (vs), 919 (s), 908 (s), 842 (vs), 740 (vs), 698 (s), 635 (s), 614 (m); ^{1}H NMR (benzene-d_6, δ) 7.24 (t, J = 1.7 Hz, C₅HH'_2(Si(CH₃)₃)₂), 6.72 (d, J = 1.7 Hz, C₅HH'_2(Si(CH₃)₃)₂), 0.20 (s, 2 Si(CH_3)₃); ^{13}C NMR (benzene-d_6, ppm) 146.01 (s, CSi(CH₃)₃), 135.30 (s, CpCH), 132.01 (s, CpCH), –0.72 (s, Si(CH₃)₃); HRMS calcd for C₁₁H₂₁Cl₃Si₂Ti M$^+$ – CH₃ 346.9492, found 346.9494. Anal. Calcd for C₁₁H₂₁Cl₃Si₂Ti: C, 36.32; H, 5.82. Found: C, 36.29; H, 5.83.

Preparation of 1,1′,3,3′-Tetrakis(trimethylsilyl)zirconocene Dichloride (4). A 100-mL Schlenk flask was charged with zirconium tetrachloride (0.573 g, 2.46 mmol), dichloromethane (20 mL), and a stirbar and was fitted with a septum. Then tris(trimethylsilyl)cyclopentadiene (0.730 g, 2.58 mmol) was added by syringe. The mixture was stirred at ambient temperature for 70 h. The volatiles were removed under reduced pressure to afford a tan powder. A separate 50-mL Schlenk flask was charged with bis(trimethylsilyl)cyclopentadiene (0.550 g, 2.61 mmol), toluene (10 mL), tetrahydrofuran (10 mL), and a stirbar and was fitted with a rubber septum. Then, a 10.0 M solution of butyllithium in hexane (0.25 mL, 2.5 mmol) was added by syringe. The mixture was stirred at ambient temperature for 0.5 h and was transferred by cannula to the flask containing crude **1**. The mixture was stirred at ambient temperature for 2.0 h. The volatiles were removed under reduced pressure, and the residue was extracted with hexane (50 mL). Filtration of the hexane, followed by removal of the volatiles at reduced pressure, afforded

a light yellow oily solid. Recrystallization of this solid from hexane gave 4 as a pure white microcrystalline solid (1.016 g, 74%): mp 184–185 °C (lit.[8] mp 180–181 °C); ^{1}H NMR (CDCl$_3$, δ) 7.01 (t, J = 2.1 Hz, C$_5$HH'$_2$(Si(CH$_3$)$_3$)$_2$), 6.44 (d, J = 2.1 Hz, C$_5$HH'$_2$-(Si(CH$_3$)$_3$)$_2$), 0.30 (s, Si(CH$_3$)$_3$). The spectral properties of this material were identical with those of material prepared by the literature method.[8]

Preparation of 1,1'-Bis(trimethylsilyl)zirconocene Dichloride (5). A 200-mL Schlenk flask was charged with zirconium tetrachloride (0.750 g, 3.22 mmol), benzene (15 mL), and a stirbar and was fitted with a condenser and a septum. Then bis(trimethylsilyl)cyclopentadiene (1.120 g, 5.33 mmol) was added by syringe. The mixture was refluxed for 10 h. The volatiles were removed under reduced pressure, and the residue was extracted with warm hexane (200 mL). The extract was filtered through a 3-cm pad of Celite on a coarse frit to afford a clear, colorless solution. Removing the volatiles under reduced pressure and vacuum drying (0.01 mm, 2 h) afforded 5 as a white microcrystalline solid (0.851 g, 73%): mp 137–138 °C (lit.[8] mp 130–131 °C); HRMS calcd for C$_{16}$H$_{26}$Cl$_2$Si$_2$Zr 435.996 37, found 435.9974.

Preparation of 1,1'-Bis(trimethylsilyl)hafnocene Dichloride (6). A 50-mL Schlenk flask was charged with hafnium tetrachloride (1.243 g, 3.89 mmol), dichloromethane (15 mL), and a stirbar. Then bis(trimethylsilyl)cyclopentadiene (1.309 g, 6.23 mmol) was added by syringe and the mixture was stirred at ambient temperature for 20 h. The solution was filtered through a 3-cm pad of Celite on a coarse glass frit. Hexane (200 mL) was added, and the mixture was again filtered through Celite. The volatiles were removed from the filtrate, and the residue was vacuum-dried (0.1 mm, 1 h) to afford 6 as a pure white microcrystalline solid (1.240 g, 76%): mp 126–128 °C (lit.[8] mp 125–127 °C); HRMS calcd for C$_{16}$H$_{26}$Cl$_2$HfSi$_2$ 524.0418, found 524.0414.

Preparation of Zirconocene Dichloride (7). A 100-mL Schlenk flask was charged with zirconium tetrachloride (0.750 g, 3.22 mmol), dichloromethane (15 mL), and a stirbar and was fitted with a condenser and a septum. Then (trimethylsilyl)cyclopentadiene (0.737 g, 5.33 mmol) was added by syringe and the mixture was refluxed for 20 h. The volatiles were removed under reduced pressure, and the residue was extracted with benzene (300 mL). The extract was filtered through a 3-cm pad of Celite on a coarse glass frit, and the volatiles were removed from the filtrate under reduced pressure. Vacuum drying (0.1 mm, 1 h) afforded 7 as a white crystalline solid (0.710 g, 91%): ^{1}H NMR (C$_6$D$_6$, δ) 5.84 (s, 2 C$_5$H$_5$) (7 (Aldrich) ^{1}H NMR (C$_6$D$_6$, δ) 5.84 (s)); HRMS calcd for C$_{10}$H$_{10}$Cl$_2$Zr 289.9202, found 289.9210.

Preparation of Hafnocene Dichloride (8). A 50-mL Schlenk flask was charged with hafnium tetrachloride (0.608 g, 1.90 mmol), dichloromethane (5 mL), and a stirbar and was fitted with a rubber septum. Then (trimethylsilyl)cyclopentadiene (0.500 g, 3.62 mmol) was added by syringe, and the mixture was refluxed for 24 h. The reaction mixture was filtered through a 3-cm pad of Celite on a coarse glass frit. Hexane (25 mL) was added to the filtrate, and the solution was filtered again through Celite. The volatiles were removed from the filtrate, and the residue was washed with hexane (10 mL). Vacuum drying (0.1 mm, 1 h) afforded 8 as a white crystalline solid (0.620 g, 90%): ^{1}H NMR (C$_6$D$_6$, δ) 5.77 (s, 2 C$_5$H$_5$) (8 (Aldrich) ^{1}H NMR (C$_6$D$_6$, δ) 5.77 (s)); HRMS calcd for C$_{10}$H$_{10}$Cl$_2$Hf 379.961 97, found 379.9616.

Reaction of Cyclopentadienylzirconium Trichloride with (Trimethylsilyl)cyclopentadiene. A 50-mL Schlenk flask was

charged with cyclopentadienylzirconium trichloride (0.576 g, 2.47 mmol), benzene (10 mL), and a stirbar and was fitted with a condenser and a rubber septum. Then (trimethylsilyl)cyclopentadiene (0.347 g, 2.51 mmol) was added by syringe, and the mixture was refluxed for 18 h. When it was cooled to ambient temperature, the reaction mixture was filtered through a 3-cm pad of Celite on a coarse glass frit. The volatiles were removed from the filtrate under reduced pressure. The residue was suspended in hexane (100 mL), and the product was collected on a fine glass frit. The product was washed with hexane (20 mL) and vacuum-dried (0.1 mm, 1 h) to afford 7 as a white solid (0.547 g, 85%). The complex was identified as above.

Reaction of Zirconium Tetrachloride with (Trimethylsilyl)cyclopentadiene. A 5-mm NMR tube was charged with zirconium tetrachloride (0.049 g, 0.21 mmol) and dichloromethane-d_2 (0.70 mL) and was capped with a septum. The tube was cooled to –78 °C, and (trimethylsilyl)cyclopentadiene (0.029 g, 0.21 mmol) was added by syringe. The tube was transferred to a –80 °C NMR probe. The probe was slowly warmed to 30 °C, and ^{1}H NMR spectra were recorded at 20 °C intervals. After 0.5 h at 0 °C, the reaction was complete by ^{1}H NMR spectroscopy: 7, δ 6.50 (69 ± 2%); 9, δ 6.85 (31 ± 2%). See text.

X-ray Structure Determination of (1,3-Bis(trimethylsilyl)cyclopentadienyl)titanium Trichloride (3). The single-crystal diffraction experiment was performed at ambient temperature on a suitable crystal grown from a dilute hexane solution at –20 °C. Details of the data collection are given in Table I. Cell constants were obtained from 25 high-angle (2θ > 20°) reflections. During data collection, periodically remeasured standard reflections varied 2%. The orientation was checked midway through data collection by recentering. Absorption corrections were empirical, based upon a number of ψ scans.[10a] Lp corrections were applied, and neutral atom scattering factors and corrections for anomalous dispersion were from ref 10b. One reflection, [200], was removed due to secondary extinction.

The structure was solved by Patterson methods and refined in a full matrix, minimizing $\sum w(F_0 - |F_c|)^2$.[10c] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in observed positions and were refined isotropically. Atoms Ti, Cl(1), and C(1) occupy a crystallographic mirror plane. The asymmetric unit contains a half–molecule. The largest peak in a final difference Fourier map represented 0.63 e Å^{-3}. Final positional parameters are given in Table III. Further data is contained in the supplementary material.

Supplementary Material Available: Tables of hydrogen parameters and anisotropic thermal parameters for 3 (2 pages); a list of calculated and observed structure factors for 3 (11 pages). Ordering information is given on any current masthead page.

(10) (a) Sheldrick, G. M. SHELXTL; University of Gottingen: Gottingen, Federal Republic of Germany, 1978. (b) Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds; Kynoch: Birmingham, England, 1974; Volume IV. (c) Sheldrick, G. M. SHELX-76; University Chemical Laboratory: Cambridge, England, 1976.