which had $h = 3$. For the Se crystal 40 reflections were excluded using the above criteria, of these 32 had $h = 4$. In the Se crystal difference map peaks in the general plane of the Se atoms of the dimer indicated the possible nature of the major contributors to this twinning; there were peaks at Se–Se separations consistent with the displacements of the dimer unit along the Se---Se 3.2-Å vectors. Two sets of four Se positions (as if two more dimer units were interstitial with the main unit) were included in the refinement. These fractional Se atoms were constrained to map positions with isotropic B values set at 3, and the multiplicities were refined. One set (which had positions of approximately $x - 0.28$, y, z, of the main dimer) refined to an occupancy factor of 0.063. The other set (at $x - 0.16$, y, z) refined to an occupancy factor of 0.037. The inclusion of these traces of Se atoms led to a significant reduction of the highest difference map residual and, perhaps more significantly, produced a refinement with much more reasonable values for the isotropic thermal parameters of the N and C atoms. Inclusion of complete dimer units attached to these Se positions and parallel to the main dimer unit gave some additional improvement, but in view of the fact that the parallelism was arbitrary, this model was not used. Only the Se positions indicted by difference maps were used as outlined above.

Acknowledgment. Financial support at Guelph was provided by the Natural Sciences and Engineering Research Council of Canada and at Arkansas by the National Science Foundation (EPSCOR program) and the State of Arkansas.

Supplementary Material Available: Tables of structure solution and refinement data (S1), hydrogen atom coordinates (S2), bond lengths and angles (S3 and S4), and anisotropic thermal parameters (S5–S8) for the six structures reported (12 pages); listings of observed and calculated structure factors (101 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Approaches to Hexane-Soluble Cationic Organometallic Lewis Acids. Synthesis, Structure, and Reactivity of Titanocene Derivatives Containing Polysilylated Cyclopentadienyl Ligands

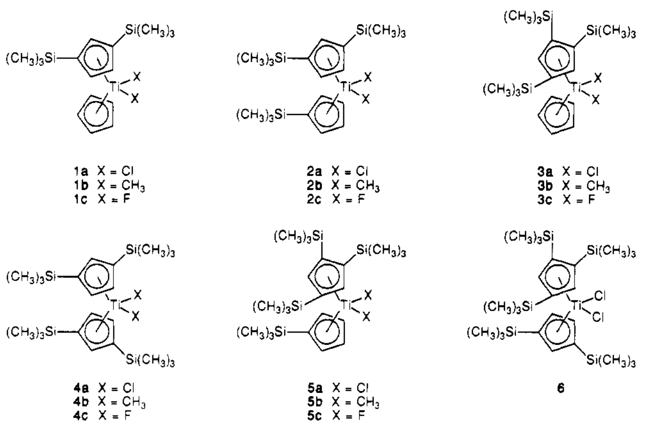
Charles H. Winter,* Xiao-Xing Zhou,[1] and Mary Jane Heeg

Received November 7, 1991

A series of titanocene dichloride derivatives was synthesized where the total trimethylsilyl substitution on the two cyclopentadienyl rings was 0, 2, 3, 4, and 5. Treatment of these complexes with methyllithium afforded 88–93% yields of the dimethyl derivatives, while reaction of the dichlorides with silver tetrafluoroborate afforded 45–57% yields of the difluoro derivatives. However, 1,1′,2,3′,4-pentakis(trimethylsilyl)titanocene dichloride afforded complex reaction mixtures upon treatment with either methyllithium or silver tetrafluoroborate. Complexes containing three and four trimethylsilyl groups afforded moderately stable cationic intermediates. The cationic complex derived from 1,1′,3,3′-tetrakis(trimethylsilyl)titanocene dichloride and silver tetrafluoroborate was the most stable and was partially characterized by ^{1}H, ^{19}F, and ^{13}C NMR and IR spectroscopy. The barrier to cyclopentadienyl rotation was examined for 1,1′,3,3′-tetrakis(trimethylsilyl)titanocene dichloride and 1,1′,3,3′-tetrakis(trimethylsilyl)titanocene difluoride and was found to be 8.9 ± 0.5 kcal/mol for both complexes. The X-ray crystal structures of 1,1′,3,3′-tetrakis(trimethylsilyl)titanocene difluoride and 1,1′,2,4-tetrakis(trimethylsilyl)titanocene difluoride were determined to probe for steric distortions. 1,1′,3,3′-Tetrakis(trimethylsilyl)titanocene difluoride crystallizes in the orthorhombic space group *Pbna* with $a = 8.788$ (9) Å, $b = 18.093$ (2) Å, $c = 18.585$ (2) Å, $V = 2954.8$ (9) Å^3, and $Z = 4$. 1,1′,2,4-Tetrakis(trimethylsilyl)titanocene difluoride crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.2476$ (5) Å, $b = 10.6838$ (15) Å, $c = 15.8842$ (19) Å, $\alpha = 106.754$ (10)°, $\beta = 96.727$ (8)°, $\gamma = 99.291$ (8)°, $V = 1456.9$ (3) Å^3, and $Z = 2$.

Transition metal complexes bearing bulky substituted cyclopentadienyl ligands often exhibit properties very different from those of the corresponding unsubstituted cyclopentadienyl analogues.[2,3] Although much of the chemistry of substituted cyclopentadienyl ligands has centered around the pentamethylcyclopentadienyl (Cp*) ligand,[3] other bulky cyclopentadienyl ligands have been employed.[4-10] Relatively little work has appeared concerning transition metal complexes containing silylated cyclopentadienyl ligands.[5-9] Initial investigations have clearly

Chart I



1a X = Cl
1b X = CH$_3$
1c X = F

2a X = Cl
2b X = CH$_3$
2c X = F

3a X = Cl
3b X = CH$_3$
3c X = F

4a X = Cl
4b X = CH$_3$
4c X = F

5a X = Cl
5b X = CH$_3$
5c X = F

6

---

(1) Wilfred Heller Fellow, 1991–1992.

(2) Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1386. Thomas, J. L. *Ibid.* **1973**, *95*, 1838. King, R. B.; Efraty, A. *Ibid.* **1972**, *94*, 3773. King, R. B.; Efraty, A.; Douglas, W. M. *J. Organomet. Chem.* **1973**, *56*, 345.

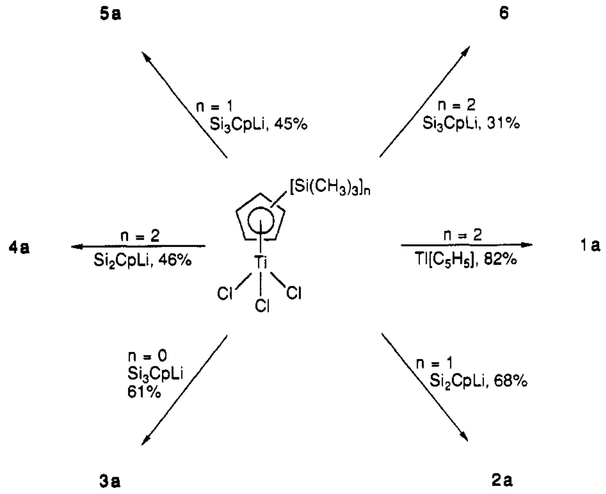
(3) For leading references, see: Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. Wolczanski, P. T.; Bercaw, J. E. *Ibid.* **1980**, *13*, 121. McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451. Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Ibid.* **1978**, *100*, 3939. Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *Ibid.* **1981**, *103*, 1265. Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *Ibid.* **1979**, *101*, 892. King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155. Schmid, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 3508. Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *Ibid.* **1985**, *107*, 8091.

(4) For leading references, see: Chambers, J. W.; Baskar, A. J.; Bott, S. G.; Atwood, J. L.; Rausch, M. D. *Organometallics* **1986**, *5*, 1635. Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4259. See also: Lorbeth, J.; Shin, S.-H.; Wocadlo, S.; Massa, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 735.

(5) For example, see: Jutzi, P.; Schlüter, E.; Krüger, C.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 994. Morley, C. P.; Jutzi, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1987**, *6*, 1084.

0020-1669/92/1331-1808$03.00/0

Scheme I. Synthesis of Titanocene Dichlorides **1a–6**



demonstrated that bis(trimethylsilyl)cyclopentadienyl (Si_2Cp) and tris(trimethylsilyl)cyclopentadienyl (Si_3Cp) ligands possess extremely large steric profiles, tend to promote the formation of monomeric complexes, and significantly increase the solubility of complexes in nonpolar solvents.

In connection with our studies of hexane-soluble organometallic Lewis acids,[11] we have been systematically exploring the chemistry of early transition metal complexes bearing bulky polysilylated cyclopentadienyl ligands. Our goal has been to prepare highly electrophilic cationic complexes that are soluble in the most nonpolar media (e.g., alkanes, perfluoroalkanes) in order to explore the coordination/activation of alkanes and related groups by the electrophilic metals. Through these investigations, most of the possible titanocene dichlorides containing two or more trimethylsilyl groups have been prepared. Such complexes offer a unique opportunity to examine the effects of extremely bulky groups upon the synthesis, structure, and reactivity of the titanocene skeleton. We now report the results of this investigation, which shows that five trimethylsilyl groups on the cyclopentadienyl ligands are sufficient to block substitution at the titanium–chlorine bonds. Moreover, the steric effects of the bulky groups enhance the kinetic stability of cationic complexes with tetrafluoroborate counterions, although not enough to prevent slow decomposition to the titanocene difluorides.

Table I. Selected Spectroscopic Data for **10** and **3c**

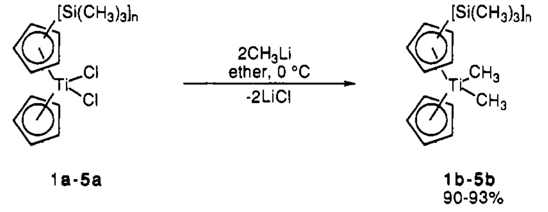
	10	3c
^{1}H NMR[a]	7.29 (s, C_5H_5) 7.13 (s, $C_5H_2(Si(CH_3)_3)_3$)	7.11 (s, $C_5H_2(Si(CH_3)_3)$) 6.36 (s, C_5H_5)
^{13}C{^{1}H} NMR[b]	146.31 (s, C-H) 143.89 (s, C-$Si(CH_3)_3$) 140.88 (s, C_5H_5) 138.75 (s, 2 C-H)	141.57 (s, C-H) 141.08 (s, 2 C-$Si(CH_3)_3$) 126.84 (s, 2 C-H) 118.61 (s, C_5H_5)
IR[c]	$\nu_{(B-F)}$ at 1126 (vs) 1108 (vs) 1084 (vs) 1060 (vs) 1036 (vs) 536 (w) 521 (w)	$\nu_{(Ti-F)}$ at 580 (vs) 548 (vs)

[a] δ in chloroform-*d* at 23 °C. [b] ppm in chloroform-*d* at 23 °C. [c] cm^{-1} in KBr.

Results

Preparation of Highly Soluble Titanocene Dichlorides. A series of titanocene derivatives (**1–6**) possessing enhanced solubility in nonpolar solvents was prepared with varying degrees of trimethylsilyl substitution through the use of cyclopentadienide, (trimethylsilyl)cyclopentadienide, 1,3-bis(trimethylsilyl)cyclopentadienide, 1,2,4-tris(trimethylsilyl)cyclopentadienide, and combinations thereof as ligands (Chart I). The syntheses of these complexes were straightforward and are summarized in Scheme I. Further preparative details can be found in the Experimental Section. Despite a number of attempts, we were unable to prepare 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)titanocene dichloride.

Preparation of Dimethyltitanocenes. The preparation of the dimethyl derivatives (dimethyltitanocene = dicyclopentadienyldimethyltitanium) was examined in order to have potential precursors to cationic complexes. Treatment of **1a–5a** with 2 equiv of methyllithium in ether at 0 °C (modified conditions for the formation of dimethyltitanocenes[16]) followed by workup afforded nearly quantitative yields of the dimethyltitanocenes **1b–5b** (eq 1). These complexes were pale orange crystalline solids and were



stable to air at ambient temperatures. Unlike dimethyltitanocene, which decomposes at room temperature, the silylated dimethyltitanocenes are thermally stable at 25 °C and can be stored at 0 °C for months without any decomposition. Curiously, treatment of **6** with methyllithium afforded a complex mixture of products, from which no clean material could be isolated. Apparently, the five trimethylsilyl groups in **6** effectively block substitution of the chlorines, which opens other reaction pathways that lead to decomposition (e.g., deprotonation, nucleophilic attack at Si, etc.).

---

(6) Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1190. Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *Ibid.* **1984**, 1082. Blake, P. C.; Lappert, M. F.; Taylor, R. G.; Atwood, J. L.; Hunter, W. E.; Zhang, H. *Ibid.* **1986**, 1394. Edelman, M. A.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *Inorg. Chim. Acta* **1987**, *139*, 185. See also: Harvey, S.; Raston, C. L.; Skelton, B. W.; White, A. H.; Lappert, M. F.; Srivastava, G. *J. Organomet. Chem.* **1987**, *328*, C1.

(7) (a) Duff, A. W.; Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Organomet. Chem.* **1985**, *293*, 271. (b) Antiñolo, 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) Antiñolo, A.; Bristow, G. S.; Campbell, G. K.; Duff, A. W.; Hitchcock, P. B.; Kamarudin, R. A.; Lappert, M. F.; Norton, R. J.; Sarjudeen, N.; Winterborn, D. J. W.; Atwood, J. L.; Hunter, W. E.; Zhang, H. *Polyhedron* **1989**, *8*, 1601. (d) Bohra, R.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1989**, 728.

(8) (a) Okuda, J. *J. Organomet. Chem.* **1990**, *397*, C37. (b) Okuda, J. *Chem. Ber.* **1989**, *122*, 1259. (c) Okuda, J. *J. Organomet. Chem.* **1989**, *367*, C1. (d) Okuda, J. *Ibid.* **1988**, *356*, C43. (e) Okuda, J. *Ibid.* **1988**, *353*, C1. (f) Okuda, J.; Herdtweck, E. *Chem. Ber.* **1988**, *121*, 1899. (g) Okuda, J. *J. Organomet. Chem.* **1987**, *333*, C41.

(9) (a) Miftakhov, M. S.; Tolstikov, G. A. *Zh. Obshch. Khim.* **1976**, *46*, 930. (b) Tolstikov, G. A.; Miftakhov, M. S.; Monakov, Y. B. *Ibid.* **1976**, *46*, 1778. (c) Jutzi, P.; Kuhn, M. *J. Organomet. Chem.* **1979**, *173*, 221.

(10) For leading references, see: Okuda, J. *J. Organomet. Chem.* **1990**, *385*, C39. See also: Venier, C. G.; Casserly, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 2808.

(11) (a) Winter, C. H.; Kampf, J. W.; Zhou, X.-X. *Acta Crystallogr.* **1990**, *C46*, 1231. (b) Winter, C. H.; Zhou, X.-X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210. (c) Winter, C. H.; Dobbs, D. A.; Zhou, X.-X. *J. Organomet. Chem.* **1991**, *403*, 145. (d) Winter, C. H.; Pirzad, S.; Cao, D. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1206. (e) Winter, C. H.; Zhou, X.-X.; Heeg, M. J. *Organometallics* **1991**, *10*, 3799.

(12) Klingert, B.; Sitek, F.; Rembold, M. Eur. Patent Appl. EP 256,981, 1988; *Chem. Abstr.* **1988**, *109*, 83442p.

(13) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156.

(14) Okuda, J.; Herdtweck, E. *Inorg. Chem.* **1991**, *30*, 1516. Okuda, J. *Chem. Ber.* **1990**, *123*, 87.

(15) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; 3rd ed.; p 514.

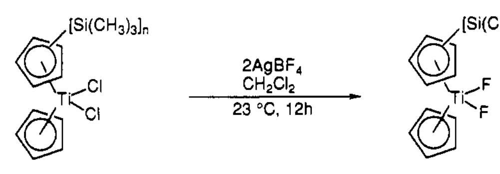
(16) Erskine, G. J.; Wilson, D. A.; McKowan, J. D. *J. Organomet. Chem.* **1976**, *114*, 119.

Table II. Selected Spectroscopic Data for **11** and **4c**

	11	**4c**
^{1}H NMR[a]	7.18 (t, *J* = 1.5 Hz, $C_5\mathit{H}H'_2(Si(CH_3)_3)_2$) 7.13 (d, *J* = 1.5 Hz, $C_5H\mathit{H}'_2(Si(CH_3)_3)_2$)	6.69 (s, $C_5H_2\mathit{H}'(Si(CH_3)_3)_2$) 6.55 (d, *J* = 1.5 Hz, $C_5\mathit{H}_2H'(Si(CH_3)_3)_2$)
$^{13}C\{^1H\}$ NMR[b]	141.24 (s, *C*–Si(CH$_3$)$_3$) 135.40 (s, Cp *C*–H) 131.34 (s, 2 Si$_2$Cp *C*H)	145.34 (s, Cp *C*–H) 132.96 (s, *C*–Si(CH$_3$)$_3$) 121.04 (s, 2 Si$_2$Cp *C*H)
^{19}F NMR[c]	−147.2 (broad s)	82.16 (s)
IR[d]	$\nu_{(B-F)}$ at 1145–1023 (vs) 535 (w) 523 (w)	$\nu_{(Ti-F)}$ at 573 (s) 554 (s)

[a] δ in chloroform-*d* at 23 °C. [b] ppm in chloroform-*d* at 23 °C. [c] δ in chloroform at 23 °C. [d] cm^{-1} in KBr.

Preparation of Cationic Complexes. Treatment of the dichlorides **2a**, **3a**, **4a**, and **5a** with 2–3 equiv of silver tetrafluoroborate in dichloromethane at ambient temperature afforded the difluorides **2c–5c**[17] in moderate yields upon extraction of the reaction residues with hexane (eq 2). The remainder of the material appeared to be insoluble decomposition products which could not be identified. Use of less than 2 equiv of silver tetrafluoroborate led to an inseparable mixture of dihalide complexes. It should be noted that **2a–5a** failed to react (starting material recovered) using a standard method for forming titanocene difluorides (e.g., titanocene dichloride, excess sodium fluoride in methanol[18]).

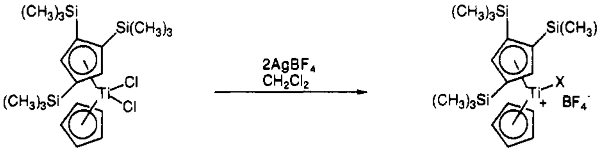


(2)

2a-5a

2a-5a
45-57%

While isolable cationic species were not obtained from **1a** and **2a**, the bulkier dichloride **3a** afforded a moderately stable cationic complex. Treatment of **3a** with silver tetrafluoroborate (2–3 equiv) in dichloromethane at ambient temperature, followed by filtration and removal of the solvent, afforded the cationic complex **10** as a light orange powder (eq 3). Table I gives selected NMR and IR data for complexes **10** and **3c**. In particular, the large downfield shifts experienced by the cyclopentadienyl protons and carbons, relative to **3c**, were diagnostic of a cationic complex. Furthermore, the infrared spectrum showed the presence of a tetrafluoroborate counterion.[19] For comparison, NaBF$_4$ showed a very strong absorption between 1070 and 1025 cm^{-1} and two medium absorptions at 547 and 517 cm^{-1}. Hence, the cationic nature of **10** was established. The tetrafluoroborate absorptions were not clear enough to establish or rule out direct bonding between titanium and a fluoride of tetrafluoroborate,[20] due to overlapping strong absorptions arising from the silylated cyclopentadienyl ligands. Complex **10** decomposed to **3c** over 6–8 h both in solution and in the solid state. Hence, further characterization was not possible.



(3)

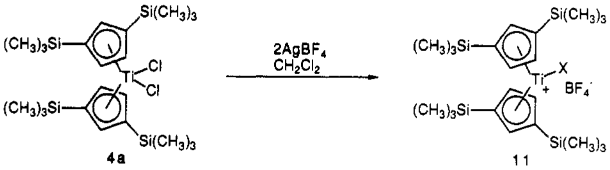
3a

10
X = Cl or F

Table III. Bond Lengths (Å) and Selected Angles (deg) for **4c**

Ti–F(1)	1.832 (2)	C(1)–C(2)	1.413 (4)
Ti–C(1)	2.408 (3)	C(1)–C(5)	1.409 (4)
Ti–C(2)	2.413 (3)	C(2)–C(3)	1.406 (4)
Ti–C(3)	2.437 (3)	C(3)–C(4)	1.422 (4)
Ti–C(4)	2.387 (3)	C(4)–C(5)	1.391 (4)
Ti–C(5)	2.390 (3)	Si(1)–C(1)	1.878 (3)
Si(1)–C(6)	1.838 (5)	Si(1)–C(7)	1.841 (5)
Si(1)–C(8)	1.852 (5)	Si(2)–C(3)	1.864 (3)
Si(2)–C(9)	1.863 (5)	Si(2)–C(10)	1.842 (5)
Si(2)–C(11)	1.838 (6)	Ti–Cp	2.087 (2)
Cp(1)–Ti–Cp(2)	133.79 (3)	F(1)–Ti–F(1)′	97.6 (2)
C(1)–C(5)–C(4)	109.9 (2)	C(1)–C(2)–C(3)	112.1 (2)
C(1)–C(2)–C(5)	104.4 (2)	C(3)–C(4)–C(5)	109.2 (2)
C(1)–Si(1)–C(6)	110.6 (2)	C(3)–Si(2)–C(9)	107.2 (2)
C(1)–Si(1)–C(7)	109.9 (2)	C(3)–Si(2)–C(10)	108.8 (2)
C(1)–Si(1)–C(8)	107.0 (2)	C(3)–Si(2)–C(11)	110.7 (2)
C(6)–Si(1)–C(7)	110.3 (2)	C(9)–Si(2)–C(10)	109.0 (3)
C(6)–Si(1)–C(8)	108.5 (2)	C(9)–Si(2)–C(11)	110.2 (3)
C(7)–Si(1)–C(8)	110.5 (2)	C(10)–Si(2)–C(11)	110.8 (3)

Complex **4a** afforded a cationic species that was qualitatively more stable than **10**. Treatment of **4a** with silver tetrafluoroborate (2–3 equiv) under conditions similar to the preparation of **10** afforded the cationic complex **11** as a light orange powder (eq 4). Table II gives selected NMR and IR data for **11** and **4c**.



(4)

4a

11
X = Cl or F

The large downfield shifts associated with the cyclopentadienyl protons and carbons of **11**, relative to **4c**, are consistent with a cationic formulation. The ^{19}F NMR spectrum of **11** showed a single broad resonance at δ −147.2, which is in the range expected for ionic tetrafluoroborate. There was no evidence for a Ti–F bond in **11** by ^{19}F NMR. For comparison, **4c** showed a singlet in the ^{19}F NMR at δ 81.16. The infrared spectrum revealed a broad, strong absorption from 1020 to 1150 cm^{-1}, which is assigned to tetrafluoroborate B–F stretches. Complex **11** slowly decomposed to **4c** and insoluble products both in solution and in the solid state, which complicated unambiguous analyses and precluded its further characterization.

Hindered Rotation of the Cyclopentadienyl Ligands. One measure of steric bulk is the barrier to cyclopentadienyl rotation, which is generally easily measured using dynamic NMR spectroscopy. Accordingly, the ^{1}H and ^{13}C NMR spectra of **4a**, **4c**, **5a**, and **6** were examined through the temperature range of −90 °C to +60 °C. Complexes **4a** and **4c** showed hindered rotation of the cyclopentadienyl ligands, with a rotational barrier of 8.9 ± 0.5 kcal/mol being obtained in dichloromethane-d_2 using standard dynamic NMR techniques.[21] Okuda has previously reported a rotational barrier of 8.9 kcal/mol for **4a**.[8] Surprisingly, no line broadening was observed in **5a** and **6** at any temperature in dichloromethane-d_2. The ^{1}H NMR spectrum of **6** in benzene-d_6 showed no changes upon heating at +60 °C. On the basis of the variable-temperature results and assuming typical values for peak separations, the barrier to cyclopentadienyl rotation in **5a** and **6** must be ≤8.9 kcal/mol or ≥17.0 kcal/mol.

Structures of 4c and 5c. We sought to examine the solid-state structures of titanocenes containing four and five trimethylsilyl groups, since unexpected trends in the hindered rotation of the cyclopentadienyl ligands were possibly present (e.g., $\Delta G^{\ddagger}$: 4 ≥

---

(17) For related reactions, see: Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556. Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. Seyan, A.; Samha, H.; Hodali, H. *Gazz. Chim. Ital.* **1990**, *120*, 527.

(18) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.

(19) For a discussion of Ti–F infrared spectra, see: Samuel, E.; Ferner, R.; Bigorgne, M. *Inorg. Chem.* **1973**, *12*, 881. Maslowsky, E., Jr.; Nakamoto, K. *Appl. Spectrosc.* **1971**, *25*, 187.

(20) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

(21) Sändstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; Chapter 7.

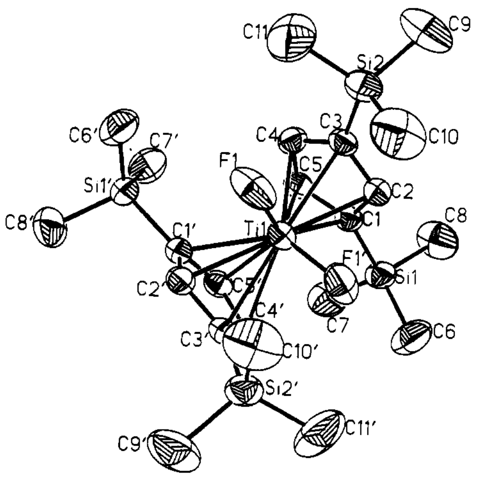


Figure 1. ORTEP view of **4c**. Thermal ellipsoids are at 50% probability.

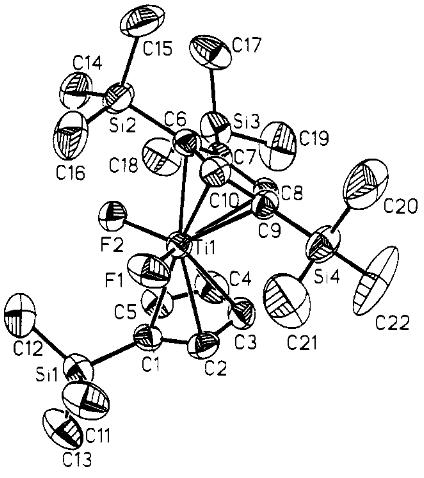


Figure 2. ORTEP view of **5c**. Thermal ellipsoids are at 50% probability.

5, 6). Ground-state steric congestion in **5** and **6** might lead to such perturbations in rotational barriers. Unfortunately, crystals of **5a**, **5b**, and **6** were soft and waxy and did not diffract well. This is probably a consequence of the large number of trimethylsilyl groups. However, this problem was circumvented with the difluorides **4c** and **5c**, which formed yellow crystals of suitable quality.

Figure 1 shows an ORTEP drawing of **4c**. Table III lists bond distances and selected bond angles. A C_2 axis existed, which made the two cyclopentadienyl ligands and fluorides identical. The cyclopentadienyl ligands were staggered, with the trimethylsilyl substituents situated to minimize interannular steric interactions. The cyclopentadienyl ligands were planar to ±0.012 Å. The titanium–carbon distances averaged 2.407 Å, and the Si_2Cp centroid–titanium distance was 2.087 (2) Å. The carbon–carbon distances averaged 1.408 Å. The cyclopentadienyl carbon–silicon distances were 1.878 (3) and 1.864 (3) Å, while the methyl silicon–carbon distances averaged 1.846 Å. The titanium–fluorine distance was 1.832 (2) Å. The cyclopentadienyl centroid–titanium–cyclopentadienyl centroid angle was 133.79 (3)°, and the fluorine–titanium–fluorine angle was 97.6 (2)°.

One measure of steric interactions in substituted cyclopentadienyl complexes is the degree to which the cyclopentadienyl substituents are bent out of the plane of the cyclopentadienyl ligand. In **4c**, Si(1) was bent out of the plane of the cyclopentadienyl ligand (away from titanium) by 6.6 (1)°. The corresponding value for Si(2) was 0.6 (1)°. The larger bending of Si(1) is consistent with its position in the more sterically crowded interannular position.

Figure 2 shows an ORTEP drawing of **5c**. Table IV lists bond distances and selected bond angles. The cyclopentadienyl ligands were staggered, with the trimethylsilyl substituents situated to minimize interannular steric interactions. The cyclopentadienyl ligands were planar to ±0.015 Å. The titanium–carbon distances averaged 2.404 Å (SiCp) and 2.403 Å (Si_3Cp), and the Si_3Cp centroid–titanium and SiCp centroid–titanium distances were 2.075 (3) and 2.084 (3) Å, respectively. The carbon–carbon bond distances averaged 1.411 Å (SiCp) and 1.424 Å (Si_3Cp). The cyclopentadienyl carbon–silicon bond distances averaged 1.876 Å, while the methyl carbon–silicon distances averaged 1.853 Å. The titanium–fluorine distance was 1.839 (2) Å. The cyclopentadienyl centroid–titanium–cyclopentadienyl centroid angle was 133.2°, and the fluorine–titanium–fluorine angle was 97.0°.

Table IV. Bond Lengths (Å) and Selected Angles (deg) for **5c**

Ti–F(1)	1.838 (2)	Si(2)–C(16)	1.862 (5)
Ti–F(2)	1.838 (2)	Si(3)–C(7)	1.876 (3)
Ti–C(1)	2.419 (3)	Si(3)–C(17)	1.881 (3)
Ti–C(2)	2.406 (3)	Si(3)–C(18)	1.856 (3)
Ti–C(3)	2.393 (4)	Si(3)–C(19)	1.835 (5)
Ti–C(4)	2.390 (3)	Si(4)–C(9)	1.873 (3)
Ti–C(5)	2.412 (2)	Si(4)–C(20)	1.867 (3)
Ti–C(6)	2.411 (3)	Si(4)–C(21)	1.810 (6)
Ti–C(7)	2.398 (3)	Si(4)–C(22)	1.818 (7)
Ti–C(8)	2.401 (3)	C(1)–C(2)	1.432 (5)
Ti–C(9)	2.408 (3)	C(1)–C(5)	1.417 (5)
Ti–C(10)	2.398 (2)	C(2)–C(3)	1.392 (6)
Si(1)–C(1)	1.874 (4)	C(3)–C(4)	1.418 (5)
Si(1)–C(11)	1.846 (4)	C(4)–C(5)	1.395 (6)
Si(1)–C(12)	1.874 (5)	C(6)–C(7)	1.448 (5)
Si(1)–C(13)	1.863 (3)	C(6)–C(10)	1.409 (4)
Si(2)–C(6)	1.882 (4)	C(7)–C(8)	1.427 (4)
Si(2)–C(14)	1.858 (3)	C(8)–C(9)	1.414 (4)
Si(2)–C(15)	1.868 (4)	C(9)–C(10)	1.423 (5)
Cp(1)–Ti	2.084 (3)	Cp(2)–Ti	2.075 (3)

F(1)–Ti–F(2)	97.0 (1)	Cp(1)–Ti–Cp(2)	133.2 (1)
Si(1)–C(1)–C(2)	126.4 (3)	C(7)–Si(3)–C(17)	108.1 (1)
Si(1)–C(1)–C(5)	128.7 (2)	C(7)–Si(3)–C(18)	114.5 (2)
Si(2)–C(6)–C(7)	133.3 (2)	C(7)–Si(3)–C(19)	106.9 (2)
Si(2)–C(6)–C(10)	120.3 (3)	C(7)–C(6)–C(10)	106.3 (3)
Si(3)–C(7)–C(6)	130.9 (2)	C(7)–C(8)–C(9)	111.1 (3)
Si(3)–C(7)–C(8)	122.0 (3)	C(8)–C(9)–C(10)	104.5 (3)
Si(4)–C(9)–C(8)	130.2 (3)	C(9)–Si(4)–C(20)	107.7 (2)
Si(4)–C(9)–C(10)	124.3 (2)	C(9)–Si(4)–C(21)	110.8 (2)
C(9)–Si(4)–C(22)	110.3 (2)	C(1)–Si(1)–C(11)	108.3 (2)
C(11)–Si(1)–C(12)	109.5 (2)	C(1)–Si(1)–C(12)	110.4 (2)
C(11)–Si(1)–C(13)	110.2 (2)	C(1)–Si(1)–C(13)	108.1 (2)
C(12)–Si(1)–C(13)	110.3 (2)	C(1)–C(2)–C(3)	109.5 (3)
C(14)–Si(2)–C(15)	109.1 (2)	C(1)–C(5)–C(4)	110.5 (3)
C(14)–Si(2)–C(16)	109.1 (2)	C(2)–C(1)–C(5)	104.9 (3)
C(15)–Si(2)–C(16)	110.2 (2)	C(2)–C(3)–C(4)	108.1 (3)
C(17)–Si(3)–C(18)	110.7 (2)	C(3)–C(4)–C(5)	107.0 (4)
C(17)–Si(3)–C(19)	108.9 (2)	C(6)–Si(2)–C(14)	115.2 (2)
C(18)–Si(3)–C(19)	107.6 (2)	C(6)–Si(2)–C(15)	106.2 (2)
C(20)–Si(4)–C(21)	107.7 (2)	C(6)–Si(2)–C(16)	106.9 (2)
C(20)–Si(4)–C(22)	109.1 (3)	C(6)–C(7)–C(8)	106.3 (2)
C(21)–Si(4)–C(22)	111.2 (3)	C(6)–C(10)–C(9)	111.7 (3)

In **5c**, Si(1) was bent out of the plane of the cyclopentadienyl ring toward the titanium atom by 1.0 (2)°, while Si(2) was bent toward the titanium atom by 1.2 (2)°. By contrast, Si(3) and Si(4) were bent out of the plane of the cyclopentadienyl ring, away from titanium, by 6.9 (2) and 6.7 (2)°, respectively. It is clear from these values that Si(3) and Si(4) are in the most sterically congested positions, while Si(1) and Si(2) are in the least congested environments.

The structure of **3a**, which we reported recently,[11a] provides a benchmark against which to compare the structures of **4c** and **5c**. Complex **3a** showed average titanium–carbon distances of 2.41 Å (Si_3Cp) and 2.39 Å, with titanium–cyclopentadienyl centroid distances of 2.076 Å (Si_3Cp) and 2.082 Å (Cp). The Cp–Ti–Cp′ angle was 129.7°, and the Cl–Ti–Cl′ angle was 92°. These values are similar to those found in **4c** and **5c**, which indicates that the extra bulky trimethylsilyl substituents do not induce noticeable structural distortions. Interestingly, **3a** showed a small distortion toward trihapto bonding in the Si_3Cp ligand, which appeared to arise from silicon–chlorine nonbonded repulsions. Such distortions are completely absent in **4c** and **5c**, probably due to the smaller size of fluorine versus chlorine. The structures of **4c** and **5c** represent the first titanocene difluorides to be structurally characterized. The titanium–fluorine bond lengths in **4c** (1.832 (2) Å) and **5c** (1.838 (2) Å)) are shorter than the sum of the covalent radii of titanium and fluorine (r(Ti^{4+}) = 0.68 Å,[15] r(F$^-$) = 1.36 Å[15]), perhaps as a result of ionic character in the titanium–fluorine bond. These bond lengths are similar to the related values in $K_3[Ti(O_2)(C_7H_3O_4N)F_2]\cdot 2H_2O$ (1.853, 1.861 Å),[22a] $Cp_2Ti(F)(OC_5(CF_3)_4)$ (1.838 Å),[22b] and *trans*-difluoro(tetraphenylporphyrinato)titanium(IV) (1.788 Å).[22c]

The geometries of **4c** and **5c** can be compared with several other relevant complexes whose structures have been determined. Lappert has reported the crystal structures of $(Si_2Cp)_2ZrX_2$ (X = F, Br).[7c] The orientation of the trimethylsilyl substituents in **4c** is very similar to that in the corresponding zirconocene difluoride and dibromide, which further substantiates the idea that the observed geometry is the one in which the bulky groups adopt the sterically least demanding orientation. Another useful comparison can be made with 1,1′,3,3′-tetrakis(*tert*-butyl)titanocene dichloride (**12**), whose structure was reported by Lemenovskii.[23] Interestingly, the titanium–carbon bonds in **12** averaged 2.437 Å, which is longer than the corresponding value (2.407 Å) in **4c**. This lengthening of the Ti–C bonds in **12**, relative to **4c**, may be attributed to the fact that *tert*-butyl groups are slightly more compact than trimethylsilyl groups, which leads to increased steric congestion about the metal center. Additionally, the smaller fluorines in **4c** should lead to diminished steric interactions relative to **12**.

Discussion

The series of complexes **1**–**6** provides insight into how the presence of extremely bulky cyclopentadienyl substituents affects the titanocene skeleton. While titanocene dichlorides containing up to five trimethylsilyl substituents were easily prepared, the yields became progressively poorer with increasing cyclopentadienyl substitution. It was not possible to prepare the complex containing six trimethylsilyl substituents, 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)titanocene dichloride. Apparently, a titanium(IV) center is too small to support two bulky Si_3Cp ligands. The effects of steric bulk were also apparent in the reactivity of **1a**–**6a**. For example, complexes **1a**–**5a** formed the dimethyl derivatives **1c**–**5c** and the difluoro derivatives **1b**–**5b** upon reaction with methyllithium and silver tetrafluoroborate, respectively. By contrast, treatment of **6** with either methyllithium or silver tetrafluoroborate led to complex reaction mixtures, from which tractable species could not be isolated. The five bulky trimethylsilyl groups kinetically probably protect the chlorines from substitution, which opens other reaction paths that lead to decomposition.

All of the neutral titanocene derivatives described herein exhibit enhanced solubilities in hexane, benzene, toluene, and similar nonpolar media due to the lipophilic nature of the trimethylsilyl groups. No attempt was made to quantify the solubilities. The beneficial effect of trimethylsilyl substitution was also manifested in the stability of the titanocene dichlorides toward silica gel. The silylated titanocene dichlorides and difluorides could be conveniently purified by column chromatography on silica gel using dichloromethane/hexane mixtures as the eluent. Organic impurities were easily removed by elution with hexane.

It is clear from the foregoing results that the presence of the extremely bulky trimethylsilyl groups does not provide sufficient kinetic stabilization to afford stable base-free titanocene cations with tetrafluoroborate as the counterion. Instead, fluoride abstraction occurs to give titanocene difluorides in moderate yields along with insoluble material. In the complexes containing four trimethylsilyl groups, cationic species could be isolated and partially characterized. However, even these complexes decompose slowly to the difluorides. Several other workers have documented fluoride abstraction reactions in attempting to prepare titanocene and zirconocene cations containing perfluoro element counterions.[17] The high bond strength of the titanium–fluorine linkage provides a strong driving force for abstraction of fluorine by the electrophilic metal center.

It was not possible to measure the barriers to cyclopentadienyl rotation in **5a** and **6** between −90 and +60 °C. Assuming −90 °C as the upper temperature limit to cyclopentadienyl rotation affords a barrier of ≤8.9 kcal/mol, while use of +60 °C affords a minimum barrier of ≥17.0 kcal/mol. If the rotational barriers for **5a** and **6** are assumed to be ≤8.9 kcal/mol, then this implies that increasing the number of bulky groups does not increase (possibly even reduces) the rotational barrier. While this may seem counterintuitive, Okuda has found that the rotational barrier in 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocene ($\Delta G^{\ddagger} = 11.0 \pm 0.5$ kcal/mol) is about the same as that of 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)ferrocene ($\Delta G^{\ddagger} = 11.0 \pm 0.5$ kcal/mol), due to incomplete cyclopentadienyl rotation in the more silylated ferrocene. We have previously cautioned that a similar rotational process is not possible in bent metallocene dihalides, because the enantiomeric structure needed to equivalence the sites is removed due to the 120–140° angle between the cyclopentadienyl ligands.[11c] Steric interactions between the interannular trimethylsilyl groups of **5a** and **6** may be substantial enough to produce barriers of ≥17.0 kcal/mol.

The crystal structures of **4c** and **5c** were determined to probe possible ground-state steric distortions that could rationalize the observed cyclopentadienyl rotational barrier trends. Both of these complexes exhibited essentially normal structural features for the titanocene skeleton, indicating that the trimethylsilyl groups do not induce significant ground-state distortions. Deformations due to silicon–halogen nonbonded interactions that were observed in **3a**[11a] were not present in the structures of **4c** and **5c**, apparently as a consequence of the smaller size of fluorine versus chlorine. It remains possible that an unusual trend in the cyclopentadienyl rotational barriers (i.e., **4a,c** > **5a**, **6**) is due to attenuated silicon–chlorine nonbonded contacts in **5a** and **6**, which has the effect of lengthening the average titanium–carbon bond, thus anomalously lowering the rotational barriers.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of argon or nitrogen using either a 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] Titanium tetrachloride was used as received from Aldrich.

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained on a General Electric QE-300 or GN-300 spectrometer in chloroform-*d*. 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)titanocene Dichloride (1a). A 50-mL Schlenk flask was charged with (bis(trimethylsilyl)cyclopentadienyl)titanium trichloride (0.931 g, 2.57 mmol), cyclopentadienylthallium (0.810 g, 3.10 mmol), benzene (20 mL), and a stir bar and was fitted with a reflux condenser. The mixture was refluxed for 10 h. After cooling to room temperature, the reaction solution was filtered through a 3-cm pad of Celite on a coarse glass frit. Removal of the solvent under reduced pressure, followed by crystallization from dichloromethane/hexane, afforded a deep red microcrystalline solid (0.824 g, 82%): mp 177–179 °C; IR (cm^{-1}, KBr) 3121 (m), 2956 (m), 2899 (m), 1637 (w), 1620 (w), 1447 (m), 1423 (w), 1408 (w), 1384 (m), 1327 (m), 1250 (s), 1211 (m), 1080 (s), 1027 (m), 937 (m), 921 (m), 909 (s), 836 (vs), 757 (s), 695 (m), 635 (m); ^{1}H NMR (CDCl$_3$, δ) 7.18 (d, J = 2.1 Hz, $C_5\mathit{H}_2H'(Si(CH_3)_3)_2$), 6.96 (t, J = 2.1 Hz, $C_5H_2\mathit{H}'(Si(CH_3)_3)_2$), 6.55 (s, $C_5\mathit{H}_5$), 0.27 (s, 2 $Si(CH_3)_3$); ^{13}C{^{1}H} NMR (CDCl$_3$,

---

[22] (a) Schwarzenbach, D. *Helv. Chim. Acta* **1972**, *55*, 2990. (b) Burk, M. J.; Staley, D. L.; Tumas, W. *J. Chem. Soc., Chem. Commun.* **1990**, 809. (c) Marchon, J.-C.; Latour, J.-M.; Grand, A.; Belakhovsky, M.; Loos, M.; Goulon, J. *Inorg. Chem.* **1990**, *29*, 57. For other Ti–F bond lengths, see: Penicaud, A.; Batail, P.; Bechgaard, K.; Sala-Pala, J. *Synth. Met.* **1988**, *22*, 201. Sheldrick, W. S. *J. Fluorine Chem.* **1975**, *4*, 415.

[23] Urazowski, I. F.; Ponomaryov, V. I.; Ellert, O. G.; Nifant'ev, I. E.; Lemenovskii, D. A. *J. Organomet. Chem.* **1988**, *356*, 181.

ppm) 135.88 (s, $\mathrm{Si_2Cp}$ *C*H), 132.55 (s, $\mathrm{Si_2Cp}$ *C*H), 131.84 (s, quat *C* $\mathrm{Si(CH_3)_3}$), 120.28 (s, $\mathrm{C_5H_5}$), −0.10 (s, 2 $\mathrm{Si(CH_3)_3}$). HRMS: calcd for $\mathrm{C_{16}H_{26}Cl_2Si_2Ti - CH_3}$, *m/e* 377.019478; found, *m/e* 377.0198. Anal. Calcd for $\mathrm{C_{16}H_{26}Cl_2Si_2Ti}$: C, 48.86; H, 6.66. Found: C, 48.76; H, 6.88.

Preparation of 1,1′,3-Tris(trimethylsilyl)titanocene Dichloride (2a). A 50-mL 3-necked round-bottomed flask was charged with (trimethylsilyl)cyclopentadiene (1.393 g, 10.10 mmol), tetrahydrofuran (10 mL), and a stir bar and was fitted with a reflux condenser. A 10.0 solution of *n*-butyllithium in hexane (1.1 mL, 11 mmol) was added by syringe, and the mixture was refluxed for 2 h. After the solution was cooled to room temperature, (bis(trimethylsilyl)cyclopentadienyl)titanium trichloride (3.978 g, 11.0 mol) was added under flow of argon, and the mixture was refluxed for 10 h. The volatiles were removed under reduced pressure, and the residue was extracted with hexane (100 mL). The red extract was applied to a 5-cm pad of silica gel on a coarse glass frit and was eluted with dichloromethane (30 mL). Removal of the solvent under reduced pressure and vacuum drying afforded an analytically pure red microcrystalline solid (3.202 g, 68%): mp 200–201 °C; IR ($\mathrm{cm^{-1}}$, KBr) 2954 (s), 2895 (m), 1454 (w), 1412 (m), 1385 (s), 1330 (w), 1316 (w), 1258 (s), 1248 (s), 1215 (w), 1190 (w), 1087 (s), 1042 (m), 938 (m), 931 (m), 921 (m), 911 (s), 904 (s), 839 (vs), 766 (m), 757 (s), 696 (m), 638 (s); ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 7.00 (d, *J* = 2.1 Hz, $\mathrm{C_5\mathit{H}_2H'(Si(CH_3)_3)_2}$), 6.94 (t, *J* = 2.1 Hz, $\mathrm{C_5H_2\mathit{H}'(Si(CH_3)_3)_2}$), 6.65 (t, *J* = 2.4 Hz, $\mathrm{C_5\mathit{H}_2H'_2Si(CH_3)_3}$), 6.54 (t, *J* = 2.4 Hz, $\mathrm{C_5H_2\mathit{H}'_2Si(CH_3)_3}$), 0.31 (s, $\mathrm{Si(C\mathit{H}_3)_3}$), 0.27 (s, 2 $\mathrm{Si(C\mathit{H}_3)_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, ppm) 134.50 (s, $\mathrm{Si_2Cp}$ *C*H), 134.07 (s, SiCp *C*–$\mathrm{Si(CH_3)_3}$)), 133.86 (s, SiCp *C*H), 133.71 (s, SiCp *C*H), 131.22 (s, $\mathrm{Si_2Cp}$ *C*–$\mathrm{Si(CH_3)_3}$)), 114.54 (s, $\mathrm{Si_2Cp}$ *C*H), 0.15 (s, $\mathrm{Si(\mathit{C}H_3)_3}$), 0.02 (s, 2 $\mathrm{Si(\mathit{C}H_3)_3}$). HRMS: calcd for $\mathrm{C_{19}H_{34}Cl_2Si_3Ti}$, *m/e* 464.08248; found, *m/e* 464.0822. Anal. Calcd for $\mathrm{C_{19}H_{34}Cl_2Si_3Ti}$: C, 49.02; H, 7.36. Found: C, 49.05; H, 7.36.

Preparation of 1,2,4-Tris(trimethylsilyl)titanocene Dichloride (3a). A 100-mL Schlenk flask was charged with 1,2,4-tris(trimethylsilyl)cyclopentadiene (1.278 g, 4.52 mmol), benzene (30 mL), and a stir bar and was fitted with a reflux condenser. A 10.0 M solution of *n*-butyllithium in hexane (0.46 mL, 4.6 mmol) was added via syringe, and the solution was refluxed for 1.5 h. After the solution was cooled to room temperature, cyclopentadienyltitanium trichloride (1.012 g, 4.61 mmol) was added under flow of argon, and the mixture was stirred at room temperature for 4 h. The volatiles were removed under reduced pressure, and the residue was extracted with hexane (50 mL). The deep red hexane extract was applied to a 5-cm pad of silica gel on a coarse glass frit and excess organic material was eluted with hexane (100 mL). Elution with dichloromethane (100 mL) gave a deep red band. Removal of the solvent under reduced pressure and vacuum drying afforded analytically pure **3a** (1.277 g, 61%): mp 122–123 °C; IR ($\mathrm{cm^{-1}}$, KBr) 3125 (w), 3106 (w), 3082 (w), 2955 (s), 2899 (m), 1448 (m), 1408 (m), 1385 (m), 1250 (vs), 1099 (s), 1028 (m), 1022 (m), 983 (s), 926 (s), 836 (vs), 759 (s), 694 (s), 642 (s); ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 7.29 (s, $\mathrm{C_5\mathit{H}_2(Si(CH_3)_3)_3}$), 6.53 (s, $\mathrm{C_5\mathit{H}_5}$), 0.35 (s, 2 $\mathrm{Si(C\mathit{H}_3)_3}$), 0.27 (s, $\mathrm{Si(C\mathit{H}_3)_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, ppm), 143.30 (s, 2 *C*–$\mathrm{Si(CH_3)_3}$), 142.26 (s, $\mathrm{Si_3Cp}$ *C*H), 130.41 (s, *C*–$\mathrm{Si(CH_3)_3}$), 120.24 (s, $\mathrm{\mathit{C}_5H_5}$), 1.16 (s, $\mathrm{Si(\mathit{C}H_3)_3}$), 0.15 (s, 2 $\mathrm{Si(\mathit{C}H_3)_3}$). HRMS: calcd for $\mathrm{C_{19}H_{34}Cl_2Si_3Ti}$, *m/e* 466.07953; found, *m/e* 466.0791. Anal. Calcd for $\mathrm{C_{19}H_{34}Cl_2Si_3Ti}$: C, 49.02; H, 7.36. Found: C, 49.10; H, 7.39.

Preparation of 1,1′,3,3′-Tetrakis(trimethylsilyl)titanocene Dichloride (4a). A 50-mL 3-necked round-bottomed flask was charged with bis(trimethylsilyl)cyclopentadiene (1.666 g, 7.93 mmol), tetrahydrofuran (10 mL), and a stir bar and was fitted with a reflux condenser. A 10.0 M solution of *n*-butyllithium in hexane (0.9 mL, 9.0 mmol) was added via syringe, and the mixture was refluxed for 5 h. After the solution was cooled to room temperature, (bis(trimethylsilyl)cyclopentadienyl)titanium trichloride (3.258 g, 9.00 mmol) was added under flow of argon, and the mixture was refluxed for 10 h. The volatiles were removed under reduced pressure, and the residue was extracted with hexane (25 mL). The red extract was applied to a 5-cm pad of silica gel on a coarse glass frit and was eluted with hexane (60 mL). Removal of the solvent under reduced pressure and vacuum drying afforded an analytically pure deep red crystalline solid (1.960 g, 46%): mp 192–193 °C (lit. mp 182–184 °C[9a]); IR ($\mathrm{cm^{-1}}$, KBr) 2960 (m), 2897 (m), 1453 (w), 1405 (m), 1385 (m), 1326 (w), 1271 (s), 1258 (s), 1250 (s), 1214 (w), 1089 (s), 1067 (w), 917 (s), 903 (m), 897 (m), 830 (vs), 749 (s), 690 (m), 634 (s); ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 7.12 (s, $\mathrm{C_5H_2\mathit{H}'(Si(CH_3)_3)_2}$), 6.37 (s, $\mathrm{C_5\mathit{H}_2H'(Si(CH_3)_3)_2}$), 0.33 (s, 4 $\mathrm{Si(CH_3)_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, ppm) 149.36 (s, 2 Cp *C*–H), 133.70 (s, $\mathrm{Si_2Cp}$ *CH*), 122.36 (s, 4 $\mathrm{Si_2Cp}$ *C*H), 0.22 (s, 4 $\mathrm{Si(\mathit{C}H_3)_3}$). HRMS: calcd for $\mathrm{C_{22}H_{42}Cl_2Si_4Ti}$, *m/e* 536.12200; found, *m/e* 536.1225.

Preparation of 1,1′,2,4-Tetrakis(trimethylsilyl)titanocene Dichloride (5a). A 50-mL 3-necked flask was charged with tris(trimethylsilyl)cyclopentadiene (1.399 g, 4.96 mmol), tetrahydrofuran (5 mL), and a stir bar and was fitted with a reflux condenser. A 10.0 M solution of *n*-butyllithium in hexane (0.55 mL, 5.5 mmol) was added via syringe, and the mixture was refluxed for 8 h. After the solution was cooled to room temperature, ((trimethylsilyl)cyclopentadienyl)titanium trichloride (1.584 g, 5.54 mmol) was added under flow of argon, and the mixture was refluxed for 10 h. The volatiles were removed under reduced pressure, and the residue was extracted with hexane. The red extract was applied to a 5-cm pad of silica gel on a coarse glass frit and was eluted with hexane (50 mL). Removal of the solvent under reduced pressure and vacuum drying afforded an analytically pure deep red crystalline solid (1.202 g, 45%): mp 159–160 °C; IR ($\mathrm{cm^{-1}}$, KBr) 2954 (s), 2899 (m), 1455 (w), 1442 (w), 1408 (m), 1385 (m), 1319 (w), 1251 (vs), 1190 (m), 1163 (w), 1105 (s), 1079 (m), 1045 (m), 988 (s), 932 (s), 924 (m), 908 (m), 903 (m), 895 (m), 839 (vs), 755 (s), 691 (s), 631 (s); ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 7.19 (s, $\mathrm{C_5\mathit{H}_2(Si(CH_3)_3)_3}$), 6.58 (s, $\mathrm{C_5\mathit{H}_2H'_2(Si(CH_3)_3))}$), 6.53 (m, $\mathrm{C_5H_2\mathit{H}'_2(Si(CH_3)_3))}$), 0.34 (s, 2 $\mathrm{Si(CH_3)_3}$), 0.32 (s, $\mathrm{Si(CH_3)_3}$), 0.27 (s, $\mathrm{Si(CH_3)_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, ppm) 142.35 (s, 2 *C*–$\mathrm{Si(CH_3)_3}$), 141.95 (s, $\mathrm{Si_3Cp}$ *C*H), 135.57 (s, SiCp *C*H), 134.43 (s, Cp *C*–$\mathrm{Si(CH_3)_3}$), 129.00 (s, Cp *C*–$\mathrm{Si(CH_3)_3}$), 111.98 (s, SiCp *C*H), 1.23 (s, 2 $\mathrm{Si(\mathit{C}H_3)_3}$), 0.32 (s, $\mathrm{Si(\mathit{C}H_3)_3}$), 0.24 (s, $\mathrm{Si(\mathit{C}H_3)_3}$). HRMS: calcd for $\mathrm{C_{22}H_{42}Cl_2Si_4Ti}$, *m/e* 536.12200; found, *m/e* 536.1225. Anal. Calcd for $\mathrm{C_{22}H_{42}Cl_2Si_4Ti}$: C, 49.14; H, 7.87. Found: C, 49.04; H, 8.31.

Preparation of 1,1′,2,3′,4-Pentakis(trimethylsilyl)titanocene Dichloride (6). A 50-mL 3-necked flask was charged with tris(trimethylsilyl)cyclopentadiene (1.320 g, 4.68 mmol), tetrahydrofuran (5 mL), and a stir bar and was fitted with a reflux condenser. A 10.0 M solution of *n*-butyllithium in hexane (0.52 mL, 5.2 mmol) was added via syringe, and the mixture was refluxed for 8 h. After the solution was cooled to room temperature, (bis(trimethylsilyl)cyclopentadienyl)titanium trichloride (1.810 g, 5.00 mmol) was added under flow of argon, and the mixture was refluxed for 10 h. The volatiles were removed under reduced pressure, and the residue was extracted with hexane (50 mL). The red extract was applied to a 5-cm pad of silica gel on a coarse glass frit and was eluted with hexane (30 mL). Removal of the solvent under reduced pressure and vacuum drying afforded an analytically pure deep red crystalline solid (0.880 g, 31%): mp 140–141 °C; IR ($\mathrm{cm^{-1}}$, KBr) 2952 (s), 2901 (m), 1634 (w), 1620 (w), 1407 (m), 1385 (m), 1285 (m), 1252 (vs), 1200 (w), 1189 (w), 1145 (w), 1096 (s), 985 (s), 930 (s), 917 (s), 830 (vs), 755 (s), 695 (s), 638 (s); ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 6.91 (t, *J* = 1.8 Hz, $\mathrm{C_5\mathit{H}H'_2(Si(CH_3)_3)_2}$), 6.58 (d, *J* = 1.8 Hz, $\mathrm{C_5H\mathit{H}'_2(Si(CH_3)_3)_2}$), 6.46 (s, $\mathrm{C_5\mathit{H}_2(Si(CH_3)_3)_3}$), 0.37 (s, $\mathrm{Si(C\mathit{H}_3)_3}$), 0.33 (s, 2 $\mathrm{Si(C\mathit{H}_3)_3}$), 0.23 (s, 2 $\mathrm{Si(C\mathit{H}_3)_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, ppm) 149.20 (s, 2 *C*–$\mathrm{Si(CH_3)_3}$), 145.03 (s, 2 *C*–$\mathrm{Si(CH_3)_3}$), 137.93 (s, SiCp *C*H), 134.39 (s, *C*–$\mathrm{Si(CH_3)_3}$), 132.50 (s, 2 SiCp *C*H), 118.43 (s, 2 SiCp *C*H), 1.50 (s, 2 $\mathrm{Si(\mathit{C}H_3)_3}$), 0.24 (s, 2 $\mathrm{Si(\mathit{C}H_3)_3}$), 0.20 (s, $\mathrm{Si(\mathit{C}H_3)_3}$). HRMS: calcd for $\mathrm{C_{25}H_{50}Cl_2Si_5Ti}$, *m/e* 608.16153; found, *m/e* 608.1610. Anal. Calcd for $\mathrm{C_{25}H_{50}Cl_2Si_5Ti}$: C, 49.23; H, 8.26. Found: C, 48.85; H, 8.45.

General Procedure for Preparation of the Dimethyltitanocenes. A Schlenk flask was charged with the appropriate titanocene dichloride (~1 mmol), diethyl ether (~15 mL), and a stir bar and was fitted with a rubber septum. The solution was cooled to −78 °C, and a 1.6 M solution of methyllithium in diethyl ether (~2.2 mmol) was added by syringe. The mixture was stirred at −78 °C for 0.5 h, and then it was warmed to room temperature and was stirred for an additional 0.5 h. The volatiles were removed under reduced pressure, and the residue was extracted with pentane (40 mL). Filtration of the pentane followed by removal of the volatiles at reduced pressure afforded the dimethyl derivatives as orange-yellow crystalline solids.

Dimethyl-1,3-bis(trimethylsilyl)titanocene (1b): mp 70–71 °C; IR ($\mathrm{cm^{-1}}$, KBr) 2957 (m), 2894 (m), 1385 (s), 1246 (s), 1086 (m), 1020 (w), 965 (w), 923 (m), 909 (w), 839 (vs), 812 (s), 756 (s), 690 (w), 631 (m); ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 7.32 (d, *J* = 1.8 Hz, $\mathrm{C_5\mathit{H}_2H'(Si(CH_3)_3)_2}$), 6.08 (s, $\mathrm{C_5H_5}$), 5.47 (s, $\mathrm{C_5H_2\mathit{H}'(Si(CH_3)_3)_2}$), 0.12 (s, 2 $\mathrm{Si(C\mathit{H}_3)_3}$), −0.12 (s, 2 $\mathrm{TiC\mathit{H}_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, ppm) 129.60 (s, $\mathrm{Si_2Cp}$ *C*H), 122.60 (s, *C*–$\mathrm{Si(CH_3)_3}$), 121.66 (s, $\mathrm{Si_2Cp}$ *C*H), 113.78 (s, $\mathrm{\mathit{C}_5H_5}$), 46.01 (s, 2 $\mathrm{Ti\mathit{C}H_3}$), 0.10 (s, 2 $\mathrm{Si(CH_3)_3}$). Anal. Calcd for $\mathrm{C_{18}H_{32}Si_2Ti}$: C, 61.33; H, 9.15. Found: C, 60.92; H, 8.80.

Dimethyl-1,1′,3-tris(trimethylsilyl)titanocene (2b): mp 79–80 °C; IR ($\mathrm{cm^{-1}}$, KBr) 2956 (s), 2897 (m), 1450 (m), 1404 (m), 1384 (m), 1332 (w), 1322 (w), 1249 (s), 1216 (m), 1188 (m), 1083 (s), 1043 (m), 923 (m), 905 (m), 835 (vs), 810 (s), 755 (s), 691 (m), 636 (m); ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 6.74 (d, *J* = 1.8 Hz, $\mathrm{C_5\mathit{H}_2H'(Si(CH_3)_3)_2}$), 6.39 (t, *J* = 2.4 Hz, $\mathrm{C_5\mathit{H}_2H'_2(Si(CH_3)_3))}$), 6.00 (t, *J* = 1.8 Hz, $\mathrm{C_5H_2\mathit{H}'(Si(CH_3)_3)_2}$), 5.71 (t, *J* = 2.4 Hz, $\mathrm{C_5H_2\mathit{H}'_2(Si(CH_3)_3))}$), 0.31 (s, $\mathrm{Si(CH_3)_3}$), 0.17 (s, 2 $\mathrm{Si(CH_3)_3}$), −0.10 (s, 2 $\mathrm{TiC\mathit{H}_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, ppm) 128.87 (s, quat *C*–$\mathrm{Si(CH_3)_3}$), 126.13 (s, $\mathrm{Si_2Cp}$ *C*H), 126.04 (s, 2 $\mathrm{Si_2Cp}$ *C*H), 125.23 (s, 2 $\mathrm{Si_2Cp}$ *C*–$\mathrm{Si(CH_3)_3}$), 123.28 (s, SiCp*C*H), 111.87 (s, SiCp *C*H), 44.83 (s, 2 $\mathrm{Ti\mathit{C}H_3}$), 0.40 (s, $\mathrm{Si(CH_3)_3}$), 0.17 (s, 2 $\mathrm{Si(CH_3)_3}$). HRMS: calcd for $\mathrm{C_{21}H_{40}Si_3TiCH_3}$, *m/e* 444.13710; found, *m/e* 444.1374. Anal. Calcd for $\mathrm{C_{21}H_{40}Si_3Ti}$: C, 59.39; H, 9.49. Found: C, 59.19; H, 9.53.

Dimethyl-1,2,4-tris(trimethylsilyl)titanocene (3b): mp 65–66 °C; IR (cm^{-1}, KBr), 3078 (w), 2958 (s), 2899 (m), 2797 (w), 1443 (m), 1408 (m), 1384 (m), 1324 (w), 1247 (vs), 1211 (w), 1151 (w), 1104 (s), 1020 (m), 997 (s), 937 (s), 895 (s), 836 (vs), 800 (vs), 752 (vs), 680 (s), 645 (s), 627 (s); ^1H NMR ($CDCl_3$, δ) 6.59 (s, $C_5H_2(Si(CH_3)_3)_3$), 6.09 (s, C_5H_5), 0.31 (s, 2 $Si(CH_3)_3$), 0.14 (s, $Si(CH_3)_3$), −0.06 (s, 2 $TiCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 134.14 (s, Si_3Cp *C*H), 131.32 (s, *C*–$Si(CH_3)_3$), 123.42 (s, *C*–$Si(CH_3)_3$), 114.04 (s, C_5H_5), 46.54 (s, 2 $TiCH_3$), 1.42 (s, 2 $Si(CH_3)_3$), 0.34 (s, $Si(CH_3)_3$). Anal. Calcd for $C_{21}H_{40}Si_3Ti$: C, 59.39; H, 9.49. Found: C, 59.48; H, 9.68.

Dimethyl-1,1′,3,3′-tetrakis(trimethylsilyl)titanocene (4b): mp 121–122 °C; IR (cm^{-1}, KBr) 2955 (s), 2897 (m), 1450 (m), 1401 (m), 1385 (s), 1327 (w), 1249 (s), 1216 (m), 1126 (m), 1087 (s), 1068 (w), 964 (w), 922 (s), 889 (w), 841 (vs), 821 (vs), 753 (s), 689 (s), 634 (s); ^1H NMR ($CDCl_3$, δ) 7.12 (t, *J* = 1.5 Hz, $C_5H_2H'(Si(CH_3)_3)_2$), 5.63 (d, *J* = 1.5 Hz, $C_5H_2H'(Si(CH_3)_3)_2$), 0.22 (s, 4 $Si(CH_3)_3$), −0.14 (s, 2 $TiCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 137.46 (s, Si_2Cp *C*H), 125.68 (s, *C*–$Si(CH_3)_3$), 117.01 (s, Si_2Cp *C*H), 44.27 (s, 2 $TiCH_3$), 0.22 (s, 4 $Si(CH_3)_3$). Anal. Calcd for $C_{24}H_{48}Si_4Ti$: C, 58.01; H, 9.74. Found: C, 57.49; H, 9.68.

Dimethyl-1,1′,2,4-tetrakis(trimethylsilyl)titanocene (5b): mp 91–92 °C; IR (cm^{-1}, KBr) 2960 (s), 2897 (m), 1444 (m), 1409 (m), 1381 (m), 1317 (w), 1251 (s), 1216 (w), 1185 (m), 1160 (w), 1104 (m), 1076 (w), 1048 (m), 998 (m), 936 (m), 904 (m), 859 (s), 834 (vs), 812 (vs), 753 (s), 692 (m), 639 (m); ^1H NMR ($CDCl_3$, δ) 6.50 (s, $C_5H_2(Si(CH_3)_3)_3$), 6.42 (t, *J* = 2.4 Hz, $C_5H_2H'_2(Si(CH_3)_3)$), 5.45 (t, *J* = 2.4 Hz, $C_5H_2H'_2(Si(CH_3)_3)$), 0.37 (s, $Si(CH_3)_3$), 0.27 (s, 2 $Si(CH_3)_3$), 0.12 (s, $Si(CH_3)_3$), −0.10 (s, 2 $TiCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 134.34 (s, SiCp *C*H), 131.36 (s, *C*–$Si(CH_3)_3$), 128.22 (s, *C*–$Si(CH_3)_3$), 124.98 (s, SiCp *C*H), 122.78 (s, *C*–$Si(CH_3)_3$), 109.10 (s, Si_2Cp *C*H), 44.75 (s, 2 $TiCH_3$), 1.37 (s, 2 $Si(CH_3)_3$), 0.57 (s, $Si(CH_3)_3$), 0.30 (s, $Si(CH_3)_3$). Anal. Calcd for $C_{24}H_{48}Si_4Ti$: C, 58.01; H, 9.74. Found: C, 57.69; H, 9.69.

General Preparation of the Titanocene Difluorides. A Schlenk flask was charged with the appropriate titanocene dichloride (~1 mmol), dichloromethane (~15 mL), silver tetrafluoroborate (~2.2 mmol), and a stir bar and was fitted with a rubber septum. The mixture was stirred for 12 h at room temperature. The volatiles were removed under reduced pressure, and the residue was extracted with pentane (50 mL). The light yellow pentane extract was applied to a 5-cm pad of silica gel on a coarse glass frit and was eluted with pentane (20 mL). Removal of the solvent under reduced pressure and vacuum drying afforded the titanocene difluorides as bright yellow solids.

1,1′,3-Tris(trimethylsilyl)titanocene difluoride (2c): mp 115–116 °C; IR (cm^{-1}, KBr) 2952 (m), 2898 (m), 1449 (w), 1409 (w), 1384 (m), 1252 (s), 1158 (w), 1100 (s), 1028 (w), 1019 (w), 993 (m), 933 (m), 903 (m), 835 (vs), 811 (vs), 765 (m), 756 (m), 692 (m), 643 (m), 628 (m), 602 (m), 588 (vs), 557 (s); ^1H NMR ($CDCl_3$, δ) 6.72 (s, $C_5H_2H'(Si(CH_3)_3)_2$), 6.67 (s, $C_5H_2H'(Si(CH_3)_3)_2$), 6.59 (t, *J* = 2.4 Hz, $C_5H_2H'_2Si(CH_3)_3$), 6.54 (t, *J* = 2.4 Hz, $C_5H_2H'_2Si(CH_3)_3$), 0.24 (s, 2 $Si(CH_3)_3$), 0.20 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 134.76 (s, Si_2Cp *C*H), 134.07 (s, SiCp *C*–$Si(CH_3)_3$), 129.96 (s, Si_2Cp *C*–$Si(CH_3)_3$), 129.44 (s, 2 Si_2Cp *C*H), 125.36 (s, SiCp *C*H), 113.76 (s, SiCp *C*H), −0.64 (s, 2 $Si(CH_3)_3$), −0.98 (s, $Si(CH_3)_3$). HRMS: calcd for $C_{19}H_{34}F_2Si_3Ti$, *m/e* 432.14157; found, *m/e* 432.1422. Anal. Calcd for $C_{19}H_{34}F_2Si_3Ti$: C, 52.75; H, 7.92. Found: C, 52.52; H, 8.12.

1,2,4-Tris(trimethylsilyl)titanocene difluoride (3c): mp 110–111 °C; IR (cm^{-1}, KBr) 3075 (m), 2949 (m), 2897 (m), 1456 (w), 1406 (m), 1386 (m), 1327 (w), 1246 (s), 1248 (vs), 1213 (m), 1180 (m), 1087 (s), 1062 (m), 1055 (m), 1042 (w), 942 (w), 922 (m), 912 (s), 897 (w), 878 (m), 838 (vs), 818 (vs), 761 (s), 751 (s), 692 (m), 637 (m), 627 (m), 604 (w), 580 (vs), 548 (vs); ^1H NMR ($CDCl_3$, δ) 7.11 (s, $C_5H_2(Si(CH_3)_3)_3$), 6.36 (s, C_5H_5), 0.32 (s, 2 $Si(CH_3)_3$), 0.32 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 141.57 (s, Si_3Cp *C*H), 141.08 (s, 2 *C*–$Si(CH_3)_3$), 126.84 (s, 2 *C*–H), 118.61 (s, C_5H_5), 0.76 (s, 2 $Si(CH_3)_3$), 0.01 (s, $Si(CH_3)_3$). HRMS: calcd for $C_{19}H_{34}F_2Si_3Ti$, *m/e* 432.14157; found, *m/e* 432.1423. Anal. Calcd for $C_{19}H_{34}F_2Si_3Ti$: C, 52.75; H, 7.92. Found: C, 53.05; H, 7.95.

1,1′,3,3′-Tetrakis(trimethylsilyl)titanocene difluoride (4c): mp 168–169 °C; IR (cm^{-1}, KBr) 3077 (w), 2952 (m), 2908 (w), 1456 (w), 1387 (s), 1324 (w), 1274 (m), 1243 (s), 1205 (w), 1092 (s), 1055 (w), 936 (m), 917 (s), 867 (m), 836 (vs), 754 (s), 692 (m), 635 (m), 573 (s), 554 (s); ^1H NMR ($CDCl_3$, δ) 6.69 (s, $C_5H_2H'(Si(CH_3)_3)_2$), 6.55 (d, *J* = 1.5 Hz, $C_5H_2H'(Si(CH_3)_3)_2$), 0.28 (s, 4 $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 145.34 (s, 2 Cp *C*–H), 132.96 (s, 4 *C*–$Si(CH_3)_3$), 121.04 (s, 4 Si_2Cp *C*H), −0.40 (s, 4 $Si(CH_3)_3$). HRMS: calcd for $C_{22}H_{42}F_2Si_4Ti$, *m/e* 504.18110; found, *m/e* 504.1819. Anal. Calcd for $C_{22}H_{42}F_2Si_4Ti$: C, 52.34; H, 8.39. Found: C, 52.33; H, 8.76.

1,1′,2,4-Tetrakis(trimethylsilyl)titanocene difluoride (5c): mp 97–98 °C; IR (cm^{-1}, KBr) 2958 (s), 2900 (m), 1448 (m), 1409 (m), 1394 (s), 1316 (w), 1251 (s), 1185 (m), 1162 (w), 1102 (s), 1074 (w), 1162 (w), 1045 (m), 994 (m), 934 (m), 909 (m), 839 (vs), 816 (vs), 762 (s), 694 (m), 633 (s), 585 (s), 560 (s); ^1H NMR ($CDCl_3$, δ) 7.06 (s, $C_5H_2(Si(CH_3)_3)$, 6.62 (s, $C_5H_2H'_2(Si(CH_3)_3)$), 6.25 (m, $C_5H_2H'_2(Si(CH_3)_3)$), 0.36 (s, $Si(CH_3)_3$), 0.32 (s, 2 $Si(CH_3)_3$), 0.22 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 141.32 (s, Si_3Cp *C*H), 140.22 (s, *C*–$Si(CH_3)_3$), 138.92 (s, *C*–$Si(CH_3)_3$), 133.17 (s, SiCp CH), 125.22 (s, *C*–$Si(CH_3)_3$), 110.72 (s, SiCp *C*H), 0.82 (s, 2 $Si(CH_3)_3$), −0.08 (s, $Si(CH_3)_3$), −0.68 (s, $Si(CH_3)_3$). HRMS: calcd for $C_{22}H_{42}F_2Si_4Ti$, *m/e* 504.18110; found, 504.1814. Anal. Calcd for $C_{22}H_{42}F_2Si_4Ti$: C, 52.34; H, 8.39. Found: C, 52.38; H, 8.40.

Table V. Crystallographic Data for **4c** and **5c**

	4c	**5c**
chem formula	$C_{22}H_{42}F_2Si_4Ti$	$C_{22}H_{42}F_2Si_4Ti$
fw	504.821	504.821
space group	*Pbna*	$P\bar{1}$
a, Å	8.788 (9)	9.2476 (5)
b, Å	18.093 (2)	10.6838 (15)
c, Å	18.585 (2)	15.8842 (19)
α, deg	90	106.754 (10)
β, deg	90	96.727 (8)
γ, deg	90	99.291 (8)
V, $Å^3$	2954.8 (9)	1456.9 (3)
Z	4	2
T, °C	20	20
ρ_{found}, $g\cdot cm^{-3}$	1.13	1.16
ρ_{calc}, $g\cdot cm^{-3}$	1.13 (1)	1.15 (1)
scan method	$\theta/2\theta$	$\theta/2\theta$
λ, Å	1.541 78	1.541 78
μ, cm^{-1}	4.33	42.5
transm coeff	0.764–0.845	0.648–0.196
$R(F_o)^a$	0.037	0.048
$R_w(F_o)^b$	0.036	0.062

[a] $R(F_o) = (\sum|\Delta F|)/(\sum|F_o|)$. [b] $R_w(F_o) = [(\sum|\Delta F|^2)/(\sum wF_o^2)]^{1/2}$.

Preparation of the Cationic Complex 10. A 50-mL Schlenk flask, equipped with a stir bar and rubber septum, was charged with **3a** (0.201 g, 0.433 mmol), silver tetrafluoroborate (0.178 g, 0.913 mmol), and dichloromethane (15 mL). The mixture was stirred at ambient temperature for 2 h, and then the reaction mixture was filtered through a 1-cm pad of Celite on a coarse glass frit. Hexane (20 mL) was added to the filtered solution, and the solution was placed in a −20 °C freezer. Complex **10** (~90–95% pure) precipitated over 2 days as an orange powder (0.072 g, 33% assuming $[(Si_3Cp)(Cp)TiF]^+BF_4^-$ stoichiometry). The compound slowly decomposed (6–8 h at ambient temperature) both in solution and in the solid state to afford **3c** as the sole tractable product. Hence, only partial characterization was possible. For spectral data, see Table I.

Preparation of the Cationic Complex 11. In a fashion similar to the preparation of **10**, treatment of **4a** (0.137 g, 0.256 mmol), silver tetrafluoroborate (0.105 g, 0.538 mmol), and dichloromethane (10 mL) afforded **11** (~90–95% pure) as a light orange powder (0.056 g, 38% assuming $[(Si_2Cp)_2TiF]^+BF_4^-$ stoichiometry). The compound slowly decomposed (10–12 h at ambient temperature) to **4c** both in solution and in the solid state but was qualitatively more stable than **10**. For spectral data, see Table II.

Determination of the Rotational Barrier for 4c. A 5-mm NMR tube was charged with **4c** (12.5 mg, 0.0248 mmol) and dichloromethane-d_2 (0.70 mL) and was fitted with a rubber septum. The tube was transferred to a −90 °C NMR probe. At this temperature, the cyclopentadienyl protons existed as a sharp singlet at δ 6.63 (1 H) and as a broad singlet as δ 6.53 (2 H, $\omega_{1/2}$ = 38.7 Hz). Upon warming of the sample to room temperature, the broad singlet became a sharp singlet. Using the peak width at half-height at −90 °C as an estimate of the peak separation at the low-temperature limit ($\Delta\nu$) for an AB system and using standard dynamic NMR equations for an AB system[21] affords a barrier of 8.9 ± 0.5 kcal/mol for cyclopentadienyl rotation. Complex **4a** exhibited identical behavior, while **5a** and **6** showed no line broadening of any resonances above the freezing point of dichloromethane-d_2. Taking −95 °C as the upper limit of the coalescence temperature for **5a** and **6**, using 20 Hz as for $\Delta\nu$ for the Si_3Cp ligand (a typical value[11c]), and assuming a simple AB exchange[21] for the Si_3Cp proton coalescence yields an upper limit of 8.9 kcal/mol for the rotational barriers.

X-ray Crystal Structure of 1,1′,3,3′-Tetrakis(trimethylsilyl)titanocene Difluoride (4c). The single-crystal diffraction experiment was performed at ambient temperature on a suitable clear yellow square rod of **4c** that was grown by sublimation at 120 °C (0.1 mm). Details of the data collection are given in Table V, while positional parameters are listed in

Table VI. Positional Parameters for **4c**

atom	*x*	*y*	*z*
Ti(1)	0.27880 (7)	0.25000	0.50000
F(1)	0.4160 (2)	0.2761 (1)	0.4303 (1)
Si(1)	0.0358 (1)	0.11756 (5)	0.61375 (4)
Si(2)	0.4713 (1)	0.11573 (5)	0.37474 (5)
C(1)	0.1280 (3)	0.1421 (2)	0.5257 (1)
C(2)	0.2711 (3)	0.1167 (1)	0.5014 (2)
C(3)	0.2991 (3)	0.1368 (1)	0.4295 (1)
C(4)	0.1659 (3)	0.1758 (2)	0.4082 (2)
C(5)	0.0638 (3)	0.1774 (2)	0.4654 (2)
C(6)	0.1692 (6)	0.1317 (3)	0.6886 (2)
C(7)	−0.1366 (5)	0.1738 (3)	0.6270 (2)
C(8)	−0.0134 (6)	0.0181 (3)	0.6094 (3)
C(9)	0.4586 (6)	0.0168 (3)	0.3476 (3)
C(10)	0.6417 (5)	0.1287 (3)	0.4311 (3)
C(11)	0.4793 (6)	0.1752 (4)	0.2946 (3)

Table VII. Positional Parameters for **5c**

atom	*x*	*y*	*z*
Ti(1)	0.26770 (7)	0.08278 (7)	0.24204 (4)
Si(1)	0.5392 (1)	0.2841 (1)	0.15085 (8)
Si(2)	0.3828 (2)	−0.1946 (1)	0.31185 (8)
Si(3)	−0.0055 (1)	−0.2557 (1)	0.15326 (8)
Si(4)	0.0971 (2)	0.2486 (1)	0.44571 (8)
F(1)	0.4322 (3)	0.1927 (3)	0.3206 (2)
F(2)	0.3655 (3)	−0.0385 (2)	0.1774 (2)
C(1)	0.3379 (4)	0.2242 (4)	0.1525 (3)
C(2)	0.2505 (5)	0.2897 (4)	0.2134 (3)
C(3)	0.1068 (5)	0.2131 (5)	0.1946 (3)
C(4)	0.0991 (5)	0.0980 (5)	0.1207 (3)
C(5)	0.2384 (5)	0.1077 (4)	0.0948 (3)
C(6)	0.2358 (4)	−0.0918 (4)	0.3105 (2)
C(7)	0.0997 (4)	−0.1083 (4)	0.2494 (2)
C(8)	0.0376 (4)	0.0057 (4)	0.2850 (2)
C(9)	0.1307 (4)	0.0953 (4)	0.3634 (2)
C(10)	0.2499 (4)	0.0307 (4)	0.3784 (2)
C(11)	0.6212 (6)	0.4139 (5)	0.2587 (3)
C(12)	0.6403 (6)	0.1427 (6)	0.1354 (4)
C(13)	0.5505 (6)	0.3558 (6)	0.0571 (3)
C(14)	0.3930 (6)	−0.3119 (5)	0.2014 (3)
C(15)	0.3393 (7)	−0.2920 (5)	0.3898 (4)
C(16)	0.5647 (5)	−0.0754 (6)	0.3571 (4)
C(17)	−0.0147 (6)	−0.4090 (5)	0.1897 (3)
C(18)	0.0724 (6)	−0.2790 (5)	0.0484 (3)
C(19)	−0.1948 (6)	−0.2276 (6)	0.1303 (4)
C(20)	0.0604 (8)	0.2059 (6)	0.5485 (3)
C(21)	0.2605 (8)	0.3818 (6)	0.4773 (4)
C(22)	−0.0644 (9)	0.3003 (8)	0.3998 (4)

Table VI. Cell constants were obtained from 25 high-angle ($2\theta > 40°$) reflections. During data collection, periodically remeasured standard reflections varied <3%. The orientation was checked midway through data collection by recentering. Absorption corrections were empirical, based upon a number of ψ scans.[24a] Neutral-atom scattering factors and corrections for anomalous dispersion were from ref 24b.

The structure was solved by heavy atom methods and was refined in a full matrix with the programs of SHELX-76.[24c] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in observed positions and were refined isotropically. No correction for secondary extinction was made. A C_2 axis existed, which made the two cyclopentadienyl ligands and fluorides identical. The titanium atom resided on a special position. The largest peak in a final difference Fourier map represented 0.36 e Å^{-3} and was near H(21). The experimental density was determined by flotation in aqueous potassium iodide. Figure 1 shows a perspective view of the molecule, while bond lengths and selected angles are given in Table III. Further data are contained in the supplementary material.

X-ray Crystal Structure of 1,1′,2,4-Tetrakis(trimethylsilyl)titanocene Difluoride (5c). The single-crystal diffraction experiment was performed at ambient temperature on a suitable clear yellow parallelepiped of **5c** that was grown by sublimation at 120 °C (0.1 mm). Details of the data collection are given in Table V, while the positional parameters are listed in Table VII. Cell constants were obtained from 25 high-angle ($2\theta > 40°$) reflections. The orientation was checked midway through data collection by recentering. Absorption corrections were empirical, based upon a number of ψ scans.[24a] Neutral-atom scattering factors and corrections for anomalous dispersion were from ref 24b.

The structure was solved by direct methods and refined in a full matrix with the programs of SHELX-76.[24c] All non-hydrogen atoms were refined ansiotropically; hydrogen atoms were placed in observed positions and were held invariant. No correction for secondary extinction was made. All atoms occupy general positions in the lattice. The largest peak in a final difference Fourier map represented 0.63 e Å^{-3}. The experimental density was determined by flotation in aqueous potassium iodide. Figure 2 shows a perspective view of the molecule, while bond lengths and selected angles are given in Table IV. Further data are contained in the supplementary material.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Supplementary Material Available: Tables S1–S9, listing thermal parameters, hydrogen positional parameters, least-squares planes, complete bond angles, and experimental crystallographic data for **4c** and **5c** (12 pages); Tables S10 and S11, listing calculated and observed structure factors for **4c** and **5c** (38 pages). Ordering information is given on any current masthead page.

---

(24) (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; Vol. IV. (c) Sheldrick, G. M. *SHELX-76*; University Chemical Laboratory: Cambridge, England, 1976.