Reactivity of SiMe2H Substituents in Permethylated Titanocene Complexes: Dehydrocoupling and Ethene Hydrosilylation

Michal Horáček,*,† Jiří Pinkas,† Róbert Gyepes,‡ Jiří Kubišta,† and Karel Mach†

J. Heyrovský Institute of Physical Chemistry of Academy of Sciences of the Czech Republic, v.v.i. Dolejškova 3, 182 23 Prague 8, Czech Republic, and Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

Received January 29, 2008

The complex [TiCl$_2${η^5-C$_5$Me$_4$(SiMe$_2$H)}$_2$] (**3**) was prepared by reacting the lithium salt of 2,3,4,5-tetramethyl-1-(dimethylsilyl)cyclopenta-2,4-diene (**1**) with [TiCl$_3$(THF)$_3$] followed by chlorination of the formed [TiCl{η^5-C$_5$Me$_4$(SiMe$_2$H)}$_2$] (**2**) with PbCl$_2$. The reduction of **3** with excess magnesium in THF in the presence of excess bis(trimethylsilyl)ethyne (btmse) afforded the bivalent metal *ansa* disilylene complex with π-coordinated btmse [Ti{η^5-C$_5$Me$_4$(SiMe$_2$)}$_2$(η^2-btmse)] (**4**). The dehydrocoupling of the SiMe$_2$H groups was accompanied by hydrogen transfer to the free btmse. Analogous reduction of **3** with magnesium in the presence of ethene gave a mixture of titanocene [Ti{η^5-C$_5$Me$_4$(SiMe$_2$Et)}$_2$] (**5**) and its ethene complex [Ti{η^5-C$_5$Me$_4$(SiMe$_2$Et)}$_2$(η^2-C$_2$H$_4$)] (**6**). The latter complex is however unstable in this mixture and rearranges with evolution of ethane to [Ti{η^5-C$_5$Me$_4$(SiMe$_2$Et)}{η^5:η^2-C$_5$Me$_4$(SiMe$_2$CH=CH$_2$)}] (**7**), which has its vinyl group attached by π-coordination to Ti(II). The chlorination of **4** by PbCl$_2$ yields *ansa*-[TiCl$_2${η^5-C$_5$Me$_4$(SiMe$_2$)}$_2$] (**8**), liberating the btmse ligand. Complex **8** is reduced with a half-equivalent of Mg to give *ansa*-[TiCl{η^5-C$_5$Me$_4$(SiMe$_2$)}$_2$] (**9**). Compounds **5**, **6**, and **7** were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectra. The crystal structures of complexes **3**, **4**, and **9** have been determined by X-ray crystallography.

Introduction

The transition metal-catalyzed hydrosilylation of unsaturated hydrocarbons[1] and the dehydrocoupling of hydrosilanes[2] are two of the more important synthetic reactions of organosilicon compounds. In contrast to late transition metal complexes, which are known to be efficient catalysts for selective hydrosilylation of unsaturated hydrocarbons even with tertiary silanes,[3] early transition metal alkyl or hydride compounds are usually less effective and catalyze competing hydrosilylation of alkenes and alkynes with primary and secondary silanes and dehydrocoupling of the silane compounds, facilitated by hydrogen transfer to the unsaturated hydrocarbons.[4] The silane dehydrocoupling both in the absence and in the presence of unsaturated hydrocarbons became the subject of a thorough investigation resulting in detection or isolation of metal intermediates related to the mechanism of the Si−Si bond formation.[5] The isolated titanocene and zirconocene (hydride)silyl reaction intermediates arising from oxidative addition of silanes to d^2 metallocene complexes[6] are compatible with the suggested σ-metathesis mechanism of dehydrocoupling of primary and secondary silanes.[7]

---

* To whom correspondence should be addressed. E-mail: horacek@jh-inst.cas.cz.

† Academy of Sciences of the Czech Republic.

‡ Charles University.

(1) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; p 1415. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; p 1479. (c) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000; pp 401–421. (d) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175–292. (e) Roy, A. K. *Adv. Organomet. Chem.* **2008**, *55*, 1–59.

(2) (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327–346. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359–1410. (c) Harrod, J. F. In *Inorganic and Organometallic Polymers with Special Properties*; Laine, R. M., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. 206, pp 87–98.

(3) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16–21. (b) Ruiz, J.; Bentz, P. O.; Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2709–2713. (c) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1987**, *52*, 4118–4121. (d) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127–3133. (e) Oro, L. A.; Fernandez, M. J.; Esteruelas, M. A.; Jimenez, M. S. *J. Mol. Catal.* **1986**, *37*, 151–156. (f) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128–2135. (g) Duckett, S. B.; Peruz, R. N. *Organometallics* **1992**, *11*, 90–98. (h) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151–2156.

(4) (a) Harrod, J. F. *Coord. Chem. Rev.* **2000**, *206–207*, 493–531. (b) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381–1387. (c) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564–8566. (d) Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095–1103. (e) Corey, J. Y.; Zhu, X.-H. *Organometallics* **1992**, *11*, 672–683. (f) Campbell, W. H.; Hilty, T. K.; Yurga, L. *Organometallics* **1989**, *8*, 2615–2618. (g) Ura, Y.; Hara, R.; Takahashi, T. *Chem. Lett.* **1998**, *3*, 195–196.

(5) (a) Samuel, E.; Harrod, J. F. *J. Am. Chem. Soc.* **1984**, *106*, 1859–1860. (b) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059–4066. (c) Samuel, E.; Mu, Y.; Harrod, J. F.; Dromzee, Y.; Jeannin, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3435–3439. (d) Woo, H. G.; Harrod, J. F.; Hénique, J.; Samuel, E. *Organometallics* **1993**, *12*, 2883–2885. (e) Hao, L.; Lebuis, A.-M.; Harrod, J. F. *Chem. Commun.* **1998**, 1089–1090. (f) Hao, L.; Woo, H.-G.; Lebuis, A.-M.; Mu, Y.; Shu, R.; Samuel, E.; Harrod, J. F. *Chem. Commun.* **1998**, 2013–2014. (g) Hao, L.; Harrod, J. F.; Lebuis, A.-M.; Mu, Y.; Shu, R.; Samuel, E.; Woo, H.-G. *Angew. Chem., Int. Ed.* **1998**, *37*, 3126–3129.

(6) (a) Spaltenstein, E.; Palma, P.; Kreutzer, K. A.; Willoughby, C. A.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 10308–10309. (b) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564–8566. (c) Kreutzer, K. A.; Fisher, R. A.; Davis, W. M.; Spaltenstein, E.; Buchwald, S. L. *Organometallics* **1991**, *10*, 4031–4035.

(7) (a) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22–29. (b) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047–7055. (c) Woo, H. G.; Heyn, R.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698–5707. (d) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *124*, 6814–6815.

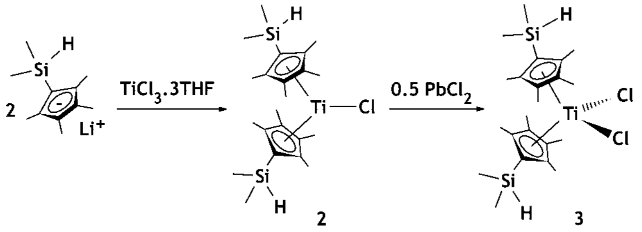
10.1021/om8000789 CCC: $40.75

The dimethylsilyl group is easily introduced onto cyclopentadienes by reacting their lithium salts with chlorodimethylsilane.[8] Using anionic cyclopentadiene species from C_5Br_6 and metals (Li, Mg), even hexakis(dimethylsilyl)cyclopentadiene and $[Li(C_5(SiMe_2H)_5(THF)]$ can be obtained.[9] Similarly, a series of complexes $(\eta^5\text{-}C_5Br_{5-n}(SiMe_2H)_n)Mn(CO)_3$ ($n = 1$–5) was also obtained.[10] The stability of the dimethylsilylated cyclopentadienyl compounds compared to the trimethylsilylated cyclopentadienyls, where the maximum trisubstituted ligand compounds are known,[11] shows that the $SiMe_2H$ group is much less space demanding. Of the early transition metal complexes the *ansa* titanocene, zirconocene, and hafnocene dichlorides are known having the bridging >SiMeH, >SiEtH, >SiPhH, and >Si(CH=CH_2)H groups. The hydrosilyl groups appeared to be sufficiently reactive to hydrosilylate vinyl- or allylsilane compounds under catalysis of a Pt catalyst.[12a,b] Analogous Pt-catalyzed hydrosilylation reactions were also exploited for anchoring the *ansa*-zirconocene dichlorides onto the silica surface.[12c]

A few early transition metal metallocene dichlorides containing the dimethylsilyl group attached to cyclopentadienyl[8b,13a] or indenyl ligands[13b] and CGC complexes $(\eta^5\text{-}C_5Me_4)SiMeHN(^tBu)MCl_2$ (M = Ti or Zr) were prepared.[13c,d] Among the known crystal structures of bis(2-dimethylsilyl)indenylzirconium dichloride,[13b] $[\{\eta^5\text{-}C_5Me_4(SiClMeH)\}TiCl_3]$,[13c] and $[\{\eta^5\text{-}C_5H_4(SiMe_2H)\}ZrCl_3]$[13a] only the last one showed an Si−H−Zr interaction, however, in the solid state only, enhancing the dimer formation. A strong agostic[14] interaction of the Si−H bond with the central metal atom,[15] which could activate the $SiMe_2H$ group in metallocene derivatives, has been observed so far in complexes where the Si−H bond was situated in the open shell of the bent metallocene, as in the zirconium d^0 complex $[ZrCl\{\eta^5\text{-}C_5H_5\}_2\{N(^tBu)(SiMe_2H)\}]$ with the $SiMe_2H$ group attached to zirconium[16] or in the d^2 titanium $[Ti\{\eta^5\text{-}C_5H_5\}_2\{\eta^2\text{-}^tBuC{\equiv}CSiMe_2H)]$ complex.[17]

Here we report for the first time the reactivity of Si−H bond(s) in $Ti\{\eta^5\text{-}C_5Me_4(SiMe_2H)\}_2$ derivatives toward their intramolecular dehydrocoupling or hydrosilylation reaction with ethene. Since the early transition metal-catalyzed silane dehydrocoupling or hydrosilylation reactions proceeded in a low-valent state of the metal,[4,5] we have investigated the reactions during the reduction of titanocene dichloride $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_2H)\}_2]$ with magnesium in THF in the presence of bis(trimethylsilyl)ethyne (btmse) or ethene. Both unsaturated hydrocarbons can stabilize the metal in the d^2 state,[18] btmse can act as a hydrogen acceptor,[19] thus facilitating the dehydrocoupling, and ethene serves as a probe for the hydrosilylation capability of the $SiMe_2H$ substituent.

Scheme 1



Results and Discussion

Synthesis of Titanocene Dichloride $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_2H)\}_2]$ (3). The new tetramethyl-substituted cyclopentadiene containing the Me_2SiH group $HC_5Me_4(SiMe_2H)$ (**1**) was prepared from 1,2,3,4-tetramethylcyclopentadienyllithium and chlorodimethylsilane in THF, as it is common for obtaining tetramethyl(trialkylsilyl)cyclopentadienes.[20] The titanocene dichloride $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_2H)\}_2]$ (**3**) was obtained in two steps from the lithium salt of **1** and $TiCl_3(THF)_3$ followed by chlorination of the resulting $[TiCl\{\eta^5\text{-}C_5Me_4(SiMe_2H)\}_2]$ (**2**) with $PbCl_2$ (Scheme 1).[21]

The dark blue compound **2** and red compound **3** were isolated under strictly anaerobic conditions and analyzed as usual for highly air-sensitive complexes (similarly sensitive compounds ref 22). Both compounds contain Si−H bonds, as evidenced from their infrared spectra, showing an intense absorption band of ν(Si−H) at 2129 cm^{-1} for **2** and at 2157 cm^{-1} for **3**. The bending vibration of the same bond was found at 890 cm^{-1} for **2** and at 882 cm^{-1} for **3** as a very strong band. The EI-MS spectra of both compounds are complex due to extensive loss of hydrogen atoms from the molecular ion followed by transfer to fragment ions. EI-MS spectra of **2** show the molecular ion pattern with the most abundant $[M - 4H]^+$ ion, which easily loses SiH_2Me_2 and further HCl. The molecular ion of **3** loses up to 3 H atoms and subsequently 2 HCl molecules, or competitively the whole Cp′ ligand. The paramagnetic compound **2** was characterized by its EPR spectra both in solution and in frozen glassy matrix and its electronic absorption spectra in solution. The spectra do not differ from the typical spectra of persubstituted titanocene chlorides[23] and are thus not indica-

---

(8) (a) Colomer, E.; Corriu, R. J. P.; Pleixats, R. *J. Organomet. Chem.* **1990**, *381*, C1–C6. (b) Cuenca, T.; Royo, P. *Coord. Chem. Rev.* **1999**, *193–195*, 447–498, and references therein.

(9) Sekiguchi, A.; Sugai, Y.; Ebata, K.; Kabuto, Ch.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 1144–1146.

(10) (a) Sünkel, K.; Hofmann, J. *Organometallics* **1992**, *11*, 3923–3925. (b) Sünkel, K.; Hofmann, J. *Chem. Ber.* **1993**, *126*, 1791–1795.

(11) (a) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1–17. (b) Winter, C. H.; Dobbs, D. A.; Zhou, X.-X. *J. Organomet. Chem.* **1991**, *403*, 145–151. (c) Winter, C. H.; Zhou, X.-X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210–214. (d) Winter, C. H.; Zhou, X.-X.; Heeg, M. J. *Inorg. Chem.* **1992**, *31*, 1808–1815.

(12) (a) Antinolo, A.; Fajardo, M.; Gómez-Ruiz, S.; López-Solera, I.; Otero, A.; Prashar, S. *Organometallics* **2004**, *23*, 4062–4069. (b) Gómez-Ruiz, S.; Prashar, S.; Fajardo, M.; Antinolo, A.; Otero, A.; Maestro, M. A.; Volkis, V.; Eisen, M. S.; Pastor, C. J. *Polyhedron* **2005**, *24*, 1298–1313. (c) Tian, J.; Soo-Ko, Y.; Metcalfe, R.; Feng, Y.; Collins, S. *Macromolecules* **2001**, *34*, 3120–3122.

(13) (a) Ciruelo, G.; Cuenca, T.; Gómez, R.; Gómez-Sal, P.; Martín, A. *J. Chem. Soc., Dalton Trans.* **2001**, 1657–1663. (b) Möller, A. C.; Heyn, R. H.; Blom, R.; Swang, O.; Görbitz, C. H.; Kopf, J. *Dalton Trans.* **2004**, 1578–1589. (c) Vázquez, A. B.; Royo, P.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *683*, 155–164. (d) Vázquez, A. B.; Royo, P. *J. Organomet. Chem.* **2003**, *671*, 172–178.

(14) (a) For definition of agostic interaction see, e.g.: Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408. (b) Braga, D.; Grepioni, F.; Tedesco, E.; Biradha, K.; Desiraju, G. R. *Organometallics* **1997**, *16*, 1846–1856. (c) Thakur, T. S.; Desiraju, G. R. *Chem. Commun.* **2006**, 552–554.

(15) Nikonov, G. I. *Adv. Organomet. Chem.* **2005**, *53*, 217–309.

(16) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 177–185.

(17) Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Rosenthal, U. *J. Am. Chem. Soc.* **1995**, *117*, 10399–10400.

(18) Horáček, M.; Kupfer, V.; Thewalt, U.; Štěpnička, P.; Polášek, M.; Mach, K. *Organometallics* **1999**, *18*, 3572–3578.

(19) Varga, V.; Mach, K.; Polášek, M.; Sedmera, P.; Hiller, J.; Thewalt, U.; Troyanov, S. I. *J. Organomet. Chem.* **1996**, *506*, 241–251.

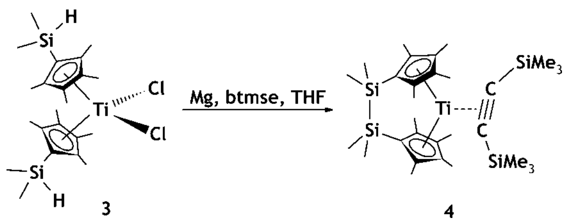
(20) Horáček, M.; Gyepes, R.; Císařová, I.; Polášek, M.; Varga, V.; Mach, K. *Collect. Czech. Chem. Commun.* **1996**, *61*, 1307–1320.

(21) Luinstra, G. A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1470–1471.

(22) Pinkas, J.; Lukešová, L.; Gyepes, R.; Císařová, I.; Lönnecke, P.; Kubišta, J.; Horáček, M.; Mach, K. *Organometallics* **2007**, *26*, 3100–3110.

(23) (a) Lukens, W. W.; Smith, M. R., III; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 1719–1728. (b) Mach, K.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1992**, 683–688.

Scheme 2

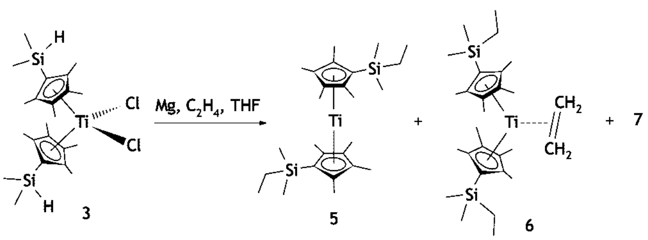


tive of the presence of the Si–H bonds. Compound **3** was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectra, displaying the chemical shifts of the Si–H group at δ_H 4.79 ppm and δ_{Si} at −25.96 ppm. Its composition and structure were further corroborated by single-crystal X-ray diffraction analysis.

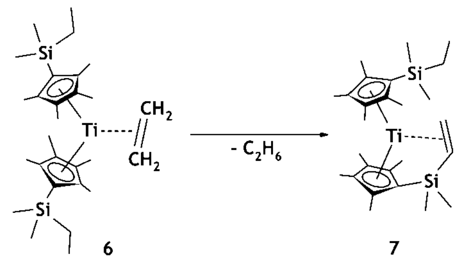
Preparation of *ansa*-[Ti{η^5-C$_5$Me$_4$(SiMe$_2$)}$_2$(η^2-btmse)] (4). The reduction of compound **3** with magnesium and excess btmse in THF afforded the η^2-btmse *ansa*-SiMe$_2$-SiMe$_2$–complex **4** in nearly quantitative yield (Scheme 2). The intramolecular dehydrocoupling of the SiMe$_2$H substituents was apparently facilitated by hydrogen transfer to the btmse ligand.[19] According to GC-MS analysis, volatiles distilled from the reaction residue contained 1,2-bis(trimethylsilyl)ethene, and even 1,2-bis(trimethylsilyl)ethane in addition to excess btmse and THF. The yellow compound **4** exhibited neither the valence nor the bending Si–H vibration in the infrared spectrum; however, the intense infrared bands typical of a SiMe$_2$ group at 1247 (s) cm^{-1} and 850 (vs) cm^{-1} and 831 (s) cm^{-1} were still present. The $\nu_{(C\equiv C)}$ valence vibration of the coordinated btmse occurred as three bands: 1643 (w), 1602 (m), 1568 (m). The appearance of these bands is similarly complex for [Ti{η^5-C$_5$Me$_4$(SiMe$_3$)}$_2$(η^2-btmse)] (1620 (sh), 1595 (m), 1560 (sh)),[18] [Ti{η^5-C$_5$Me$_4$(SiMe$_2{}^i$Pr)}$_2$(η^2-btmse)] (1634 (w), 1599 (s), 1562 (w)),[24] and [Ti(η^5-C$_5$Me$_5$)$_2$(η^2-btmse)] (1598 (m), 1563 (w))[25] and other less methylated titanocene complexes.[19] The reason for this complexity has not yet been elucidated. The EI-MS spectra did not show the molecular ion; instead, the base peak corresponding to the titanocene ion generated mostly by the thermal dissociation of the btmse molecule[26] was displayed. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra showed the fixed SiMe$_2$C$_5$Me$_4$ moiety and π-coordinated btmse ligand displaying δ_C at 248.27 ppm. This is comparable with the values for [Ti(η^5-C$_5$Me$_5$)$_2$(η^2-btmse)] (248.5 pp)[25] or [Ti{η^5-C$_5$Me$_4$(SiMe$_3$)}$_2$(η^2-btmse)] (246.4 ppm).[18] The structure of **4** is also corroborated by its electronic absorption spectrum, showing an absorption band at 920 nm. The presence of absorption band in the region 900–1000 nm is indicative of the titanocene complexes with one π-coordinated double or triple bond.[18,19,27] The structure of **4** was further established by X-ray diffraction analysis (see below).

The formation of **4** from **3** indicates that intermediately formed complex [Ti{η^5-C$_5$Me$_4$(SiMe$_2$H)}$_2$(η^2-btmse)] is unstable at a relatively low temperature. Similar hydrogen transfer to the leaving btmse was previously observed at temperatures of 150–200 °C under the formation of doubly tucked-in titanocene compounds.[19,27a–c] The only exception was the clean dissociation of btmse from [Ti{η^5-C$_5$Me$_4$(SiMe$_3$)}$_2$(η^2-btmse)] at 70 °C, yielding the thermally stable titanocene.[18]

Scheme 3



Scheme 4



Reduction-Induced Hydrosilylation of Ethene. An analogous reduction of **3** in the presence of excess ethene instead of btmse afforded a waxy noncrystallizing greenish-brown residue after evaporating the volatiles under vacuum and extraction with hexane. After dissolving in C$_6$D$_6$, it was investigated by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy in a flame-sealed NMR tube. The mixture measured after 6 h showed the presence of three components, all of them containing SiMe$_2$Et groups instead of SiMe$_2$H. They were paramagnetic titanocene [Ti{η^5-C$_5$Me$_4$(SiMe$_2$Et)}$_2$] (**5**), the titanocene complex with π-coordinated ethene [Ti{η^5-C$_5$Me$_4$(SiMe$_2$Et)}$_2$(η^2-C$_2$H$_4$)] (**6**), and a minor component [Ti{η^5-C$_5$Me$_4$(SiMe$_2$Et)}{η^5:η^2-C$_5$Me$_4$(SiMe$_2$CH=CH$_2$)}] (**7**) containing one dimethylsilylvinyl group with the vinyl π-coordinated to the metal (Scheme 3).

Surprisingly, complex **6** appeared to be unstable, and after 1 week keeping the sample tube at room temperature in darkness it completely rearranged into **7** with evolution of ethane (Scheme 4).

The concentration of **5** remained constant and the rearrangement of **6** to **7** did not generate any byproduct observable in the NMR spectra except for ethane, giving a single resonance at δ_H 0.79 ppm. The sample tube was consequently opened with a magnetic breaker in an evacuated glass device equipped with further breakable seals. Volatiles (C$_6$D$_6$ and C$_2$H$_6$) were distilled into a vessel cooled by liquid nitrogen, and ethane was determined by GC-MS of vapors after cooling volatiles to −30 °C. The residue was investigated by EI-MS spectroscopy. The mass spectra of the mixture of **5** and **7** was dominated by a complex peak pattern with the base peak *m/z* 460, which is attributable to the molecular ion of **7**, whereas the second most abundant peak at *m/z* 462 represents compound **5** (see analysis of the experimental data in the Supporting Information).

---

(24) Lukešová, L.; Pinkas, J.; Horáček, M.; Gyepes, R.; Kubišta, J.; Mach, K. *J. Organomet. Chem.* **2006**, *691*, 748–758.

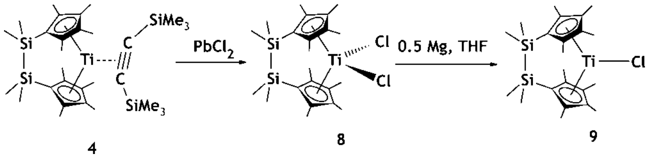
(25) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884–900, and references therein.

(26) Polášek, M.; Kubišta, J. *J. Organomet. Chem.* **2007**, *692*, 4073–4083.

(27) (a) Kupfer, V.; Thewalt, U.; Tišlerová, I.; Štěpnička, P.; Gyepes, R.; Kubišta, J.; Horáček, M.; Mach, K. *J. Organomet. Chem.* **2001**, *620*, 39–50. (b) Horáček, M.; Štěpnička, P.; Kubišta, J.; Gyepes, R.; Císařová, I.; Petrusová; L.; Mach, K. *J. Organomet. Chem.* **2002**, *658*, 235–241. (c) Horáček, M.; Štěpnička, P.; Gyepes, R.; Císařová, I.; Polášek, M.; Mach, K.; Pellny, P.-M.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **1999**, *121*, 10638–10639. (d) Pellny, P.-M.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Horáček, M.; Štěpnička, P.; Mach, K.; Rosenthal, U. *Organometallics* **2000**, *19*, 2816–2819. (e) Štěpnička, P.; Gyepes, R.; Císařová, I.; Horáček, M.; Kubišta, J.; Mach, K. *Organometallics* **1999**, *18*, 4869–4880.

(28) (a) Hitchcock, P. B.; Kerton, F. M.; Lawless, G. A. *J. Am. Chem. Soc.* **1998**, *120*, 10264–10265. (b) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2045–2046. (c) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087–5095. (d) Hanna, T.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 14688–14689.

Scheme 5



NMR Identification of Compounds 5–7. Compound **5** displayed a ^{1}H NMR spectrum consisting of two downfield shifted signals at 77.06 and 25.88 ppm and additional signals at 6.13, 5.73, and 5.14 ppm, which all showed thermally dependent paramagnetic shifts (see Supporting Information) similar to those found for titanocenes [Ti{η^5-$C_5Me_4(SiMe_3)$}$_2$],[18] [Ti{η^5-$C_5Me_4(SiMe_2{}^iPr)$}$_2$],[24] [Ti{η^5-$C_5Me_4(SiMe_2{}^tBu)$}$_2$],[28a] [Ti(η^5-C_5Me_5)$_2$],[28b,c] [Ti{η^5-$C_5Me_4({}^tBu)$}$_2$],[28d] and [Ti{η^5-$C_5Me_4({}^iPr)$}$_2$].[28d] The NMR spectra of **6** were obtained in a mixture with those of **7** (for additional NMR data see Supporting Information), which was initially a minor component only. However, with sample aging, it became the only diamagnetic component. The ^{1}H NMR spectrum of **6** clearly showed the presence of an ethyl group on the silicon atom, with chemical shifts for methylene (δ_H 0.49 ppm, δ_C 10.01 ppm) and methyl (δ_H 1.01 ppm, δ_C 8.04 ppm) groups within the expected region. The resonances of π-coordinated ethene δ_H 2.06 ppm and δ_C 104.26 ppm were close to those found in other known titanocene−ethene complexes: [Ti(η^5-C_5Me_5)$_2$(η^2-C_2H_4)] (δ_H 2.02 ppm and δ_C 105.1 ppm)[29] and [Ti{η^5-$C_5Me_4(SiMe_3)$}$_2$(η^2-C_2H_4)] (δ_H 2.34 ppm and δ_C 104.3 ppm).[18] The ^{1}H NMR spectrum of **7** after aging revealed the presence of one Et group (SiC*H*$_2$: δ_H 0.08–0.42 ppm and δ_C 9.06 ppm; SiCH$_2$*Me*: δ_H 0.88–0.95 ppm and δ_C 7.90 ppm) on one silicon atom and one vinyl group on the other one. The vinyl group was π-coordinated to the titanium atom (δ_H/δ_C [ppm]: CH= 0.78–0.87/89.23; =CH$_2$ 1.33 and 3.15/105.75). These resonances were very close to those found in [Ti{η^5-$C_5Me_4(SiMe_2CH{=}CH_2)$}{η^5:η^2-$C_5Me_4(SiMe_2CH{=}CH_2)$}] (δ_H/δ_C [ppm]: CH= 0.88/88.9 ppm; =CH$_2$ 1.37 and 3.25/105.5).[30] The coordination of the vinyl double bond to the metal decreases its $\nu_{(C=C)}$ vibration observed at 1901 and 1590 cm^{-1} for [TiCl$_2${η^5-$C_5Me_4(SiMe_2CH{=}CH_2)$}$_2$] into the region of bending CH vibrations (<1500 cm^{-1}), where it is hidden.

Reactions of *ansa* Complexes with a −SiMe$_2$−SiMe$_2$− Bridge. The above prepared *ansa* titanocene−btmse complex **4** served as a suitable starting material for preparing its other derivatives. The stoichiometric chlorination of **4** with PbCl$_2$ quantitatively afforded the known *ansa*-[TiCl$_2${η^5-$C_5Me_4(SiMe_2)$}$_2$] (**8**), previously prepared from the [HC$_5$Me$_4$(SiMe$_2$)]$_2$ ligand.[31] Compound **8** was fully characterized by current spectroscopic methods and single-crystal X-ray diffraction (see below). On the other hand, the reduction of **8** with a half-equivalent of magnesium cleanly gave the paramagnetic *ansa*-[TiCl{η^5-$C_5Me_4(SiMe_2)$}$_2$] (**9**) (Scheme 5).

Compound **9** displayed EPR and UV–vis spectra pertinent to persubstituted titanocene monochlorides,[23] the *g*-factor of its EPR spectrum being only slightly smaller than that of **2**. The crystal structure of **9** was determined (see below).

The synthesis of **8** from **3** in this way represents another case of synthesis of organometallic complexes via reactions proceeding on ligands within the complex.[32] In particular, it is another case of reactions triggered by the decrease of valency of the central atom. Previously, the pendant double bonds linked to cyclopentadienyl ligands of early transition metals were similarly stimulated to form cyclopentadienyl ring-tethered metallacyclopentanes.[33]

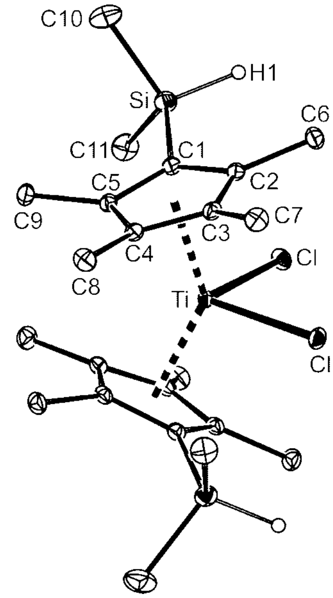


Figure 1. PLATON[40] drawing of **3** at the 30% probability level, with atom-labeling scheme. Hydrogen atoms except H1 on the silicon atoms are omitted for clarity.

Solid-State Structures. The titanocene dichloride complex **3** (Figure 1) and the *ansa* titanocene monochloride complex **9** (Figure 2) both crystallized in a monoclinic lattice (space group *C*2/*c*, no. 15).

The molecular structures of **3** and **9** are constrained by a crystallographic 2-fold rotation axis that bisects the Cl−Ti−Cl bond angle of **3** or passes through the Ti and Cl atoms of **9**. The essential molecular parameters of **3** and **9** are gathered in Table 1. In **3**, the bulky Me$_2$SiH groups are orientated in lateral positions with respect to the crystallographic 2-fold axis, as this arrangement helps to minimize their mutual repulsion. The hydrogen atoms at the Me$_2$SiH groups are oriented toward the open side of the titanocene shell. The Si−H bond length of 1.39(2) Å is slightly shorter than in [{η^5-$C_5Me_4(SiClMeH)$}-TiCl$_3$], where it is 1.43(2) Å, apparently due to the presence of the chlorine atom.[13c] In spite of a higher bulkiness of the SiMe$_3$ group, the molecular parameters for [TiCl$_2${η^5-$C_5Me_4(SiMe_3)$}$_2$], which has analogous placement of SiMe$_3$ groups,[20] and those for **3** are very similar. In compound **9**, the relative position of cyclopentadienyl rings is driven by the Si−Si bond, which is declined from the Cg,Ti,Cg plane (angle τ). A common interesting feature of both these crystal structures is the presence

---

(29) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136–1143.

(30) Lukešová, L.; Štěpnička, P.; Fejfarová, K.; Gyepes, R.; Císařová, I.; Horáček, M.; Kubišta, J.; Mach, K. *Organometallics* **2002**, *21*, 2639–2653.

(31) Xu, S.-S; Deng, X.-B.; Wang, B.-Q.; Zhou, X.-Z. *Acta Chim. Sinica* **1997**, *55*, 829–832; *Huaxue Xuebao* (*Chin.*)

(32) (a) Erker, G.; Kehr, G.; Fröhlich, R *J. Organomet. Chem.* **2004**, *689*, 1402–1412. (b) Nie, W. -L.; Erker, G.; Kehr, G.; Fröhlich, R. *Angew. Chem., Int.* **2004**, *43*, 310–313. (c) Hüerländer, N.; Kleigrewe, N.; Kehr, G.; Erker, G.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2002**, 2633–2642. (d) Knüppel, S.; Erker, G.; Fröhlich, R *Angew. Chem., Int. Ed.* **1999**, *38*, 1923–1926. (e) Bai, S.-D.; Wei, X.-H.; Guo, J.-P.; Liu, D.-S.; Zhou, Z.-Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 1926–1928.

(33) (a) Horáček, M.; Štěpnička, P.; Gyepes, R.; Císařová, I.; Tišlerová, I.; Zemánek, J.; Kubišta, J.; Mach, K. *Chem.−Eur. J.* **2000**, *6*, 2397–2408. (b) Waren, T. H.; Erker, G.; Fröhlich, R.; Wibbeling, B. *Organometallics* **2000**, *19*, 127–134. (c) Lukešová, L.; Štěpnička, P.; Fejfarová, K.; Gyepes, R.; Císařová, I.; Horáček, M.; Kubišta, J.; Mach, K. *Organometallics* **2002**, *21*, 2639–2653. (d) Licht, A. I.; Alt, H. G. *J. Organomet. Chem.* **2002**, *648*, 134–148.

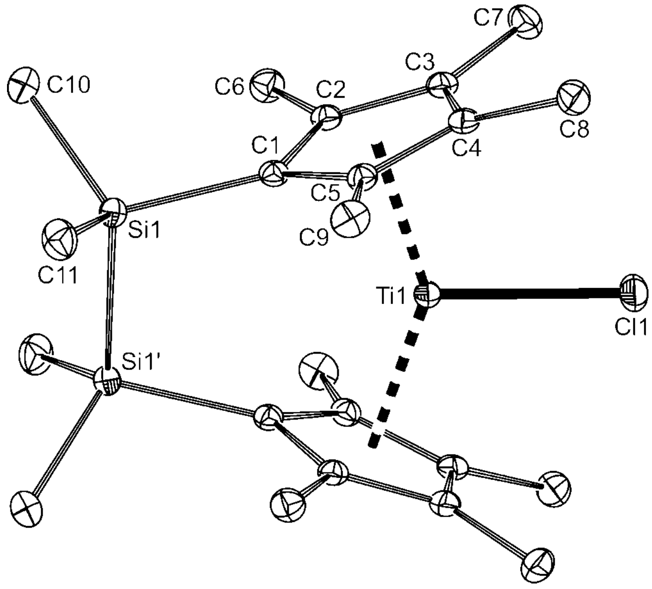


Figure 2. PLATON[40] drawing of **9** at the 30% probability level, with atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 3 and 9

3		9	
Ti−Cl	2.3668(5)	Ti−Cl	2.3561(10)
Ti−C(ring)	2.3896(19)−2.4931(19)	Ti−C(ring)	2.351(2)−2.418(2)
Si−H1	1.39(2)	Si−Si	2.3402(11)
Ti−Cg[a]	2.1248(8)	Ti−Cg[a]	2.0517(9)
Cg−Ti−Cg	137.48(3)	Cg−Ti−Cg	143.67(4)
Si−Cg−Cg′−Si′	164.27	Si−Cg−Cg′−Si′	11.29(2)
φ[b]	40.58(6)	φ[b]	39.89(6)
Cl−Ti−Cl	90.49(3)	τ[c]	14.60(8)

[a] Cg denotes the centroid of the corresponding cyclopentadienyl ring (C1, C2, C3, C4, C5). [b] Dihedral angle between the least-squares planes of the cyclopentadienyl rings. [c] Dihedral angle between the Si−Si−Ti plane and the Cg−Ti−Cg′ plane.

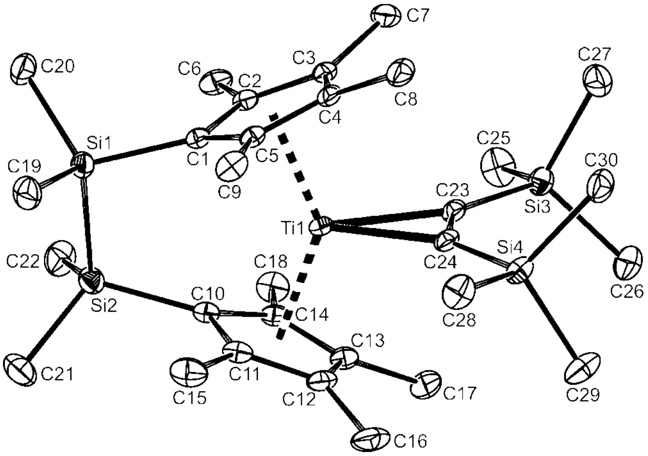


Figure 3. PLATON[40] drawing of **4** at the 30% probability level, with atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 4

Ti−C23	2.144(2)	Ti−C24	2.133(2)
C23−C24	1.309(3)	Si−Si	2.355(1)
Ti−C(ring)	2.370(2)−2.476(2)	Ti−Cg1[a]	2.113(1)
Ti−Cg2[b]	2.122(1)		
Cg1−Ti−Cg2	138.47(4)	C23−Ti−C24	35.63(7)
C1−Si−Si−C10	18.02(9)	Si3−C23−C24	137.76(16)
Si4−C24−C23	137.15(16)	φ[c]	43.71(7)
τ[d]	18.83(8)		

[a] Cg1 denotes the centroid of the cyclopentadienyl ring C1, C2, C3, C4, C5. [b] Cg denotes the centroid of the cyclopentadienyl ring C10, C11, C12, C13, C14. [c] Dihedral angle between the least-squares planes of the cyclopentadienyl rings. [d] Dihedral angle between the Si−Si−Ti plane and the Cg−Ti−Cg′ plane.

of Cp−Cp intermolecular $\pi-\pi$ stacking, generating "molecular chains" in [0 1 0] (see Supporting Information). Compound **4** crystallized in a triclinic lattice (space group $P\bar{1}$, no. 2), and its molecule is asymmetrical. Its graphical representation is given in Figure 3, and its important molecular parameters are listed in Table 2. Compared to parameters of **9** the bond lengths such as Ti−Cg, Ti−C(ring), and Si−Si are longer and angles φ and τ are larger, apparently as a result of accommodating the bulky btmse ligand. The geometry of the coordinated btmse and its average Ti−C bond length fall into the range found for other titanocene−btmse complexes.[18,19,27]

Conclusions

The investigation of reactivity of the $SiMe_2H$ substituent during the reduction of **3** revealed that the Si−H bonds are highly reactive when titanium(IV) is reduced to Ti(II), affording stable products **4** in the presence of btmse or **7** in the presence of ethene. Such reductions of $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$ have been reported to produce the stable compounds $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2(\eta^2\text{-btmse})]$ and $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2(\eta^2\text{-}C_2H_4)]$[18] and, without doubt analogous compounds, are formed as intermediates in the present case. Whereas btmse dissociated from $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2(\eta^2\text{-btmse})]$ unchanged at 70 °C, the dehydrocoupling reaction affording **4** gives evidence for a high reactivity of the Si−H bond in the coordination field of d^2 titanocene even at lower temperatures. In the presence of excess ethene the activated Si−H bonds enter the subsequent hydrosilylation reaction occurring with the coordinating ethene to give $SiMe_2Et$ groups. After its formation, titanocene **5** is further capable of coordinating an ethene molecule, as proved by the presence of **6**. The latter is apparently of relatively low stability, dissociating either to **5** when all ethene is removed or rearranging to the more stable **7** with elimination of ethane. The driving force for the latter process is the higher stability of the π-coordinated intramolecularly tethered vinyl group as well as the formation of ethane. Concerning the mechanisms of both of these reactions one has to consider an agostic interaction of the Si−H bond with the metal and an unprecedented insertion of ethene into this bond or the hydrogen transfer to btmse accompanied by the Si−Si bond formation, all within the ligand field of the metal. DFT calculations to examine the stability of titanocene $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_2H)\}_2$ in the ground and transition state are in progress.

Experimental Section

General Considerations. All manipulations including spectroscopic measurements were performed under high vacuum using all-sealed glass devices equipped with breakable seals or carried out under an argon atmosphere (organic ligands). ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ (INEPT technique) NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300, 75.4, and 59.6 MHz, respectively, in C_6D_6 solutions at 25 °C. Chemical shifts (δ/ppm) are reported relative to the residual solvent signal (δ_H 7.15) and to the solvent resonance (δ_C 128.00). The δ_{Si} values are related to tetramethylsilane as external standard. Standard NMR techniques such as APT, 1D NOESY, gCOSY, gHMQC, and gHMBC were used for detailed assignments of the signals. Methyl groups on cyclopentadiene or cyclopentadienyl rings are labeled α and β for the proximal or distal position with respect to the silyl substituent, respectively. EI-MS spectra were obtained on a VG-7070E double-focusing mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance higher than 7% and by important peaks of lower intensity. Crystals for EI-MS measurements, melting point determination, and X-ray analysis were placed in glass capillaries in a Labmaster 130 glovebox under purified nitrogen (mBraun, O_2 and H_2O concentrations lower than 1.0 ppm) and sealed with a flame. KBr pellets were prepared in the glovebox and placed in an air-protecting cuvette, and IR spectra were recorded on a Nicolet Avatar FTIR spectrometer in the range 400–4000 cm^{-1}. UV−near-IR and ESR measurements were performed using an all-sealed glass device with attached quartz cuvettes (Hellma) and a quartz ESR sample tube. UV−near-IR spectra were taken on a Varian Cary 17D spectrometer in the 300–2000 nm range. ESR spectra were measured on an ESR-220 spectrometer (Center for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-3 unit (Magnettech, Berlin, Germany) in the X-band. g-Values were determined using an Mn^{2+} standard at $g = 1.9860$ ($M_I = -½$line). An STT-3 variable-temperature unit was used for measurements in the range −143 to +23 °C.

Chemicals. The solvents tetrahydrofuran (THF), hexane, toluene, and benzene-d_6 were purified by conventional methods, dried by refluxing over $LiAlH_4$, and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)\{(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)\}_2]$.[34] Bis(trimethylsilyl)ethyne (btmse) (Aldrich) was degassed, stored as a solution of green dimeric titanocene for 4 h, and distilled into ampules. Magnesium turnings (purum for Grignard reactions) and $PbCl_2$ were obtained from Aldrich, weighed, and evacuated. Me_2SiHCl (Aldrich) and $TiCl_3(THF)_3$, prepared according to literature procedures,[35] were handled under nitrogen atmosphere. Butyllithium (LiBu) 1.6 M in hexane and $LiAlH_4$ were obtained from Aldrich and used as received. 1,2,3,4,-Tetramethylcyclopenta-1,3-diene (85%, remainder a mixture of isomers) was prepared as described.[36]

Preparation of $C_5HMe_4(SiMe_2H)$ (1). $C_5H_2Me_4$ (6.1 g, 50 mmol) was diluted with THF (300 mL), the solution was cooled to −18 °C, and 1.6 M LiBu in hexane (31.25 mL, 50.0 mmol) was added under stirring. A white precipitate was immediately formed. After 2 h of stirring at 0 °C $SiClHMe_2$ (5.2 g, 55.0 mmol) was slowly added by a syringe with vigorous stirring. The white precipitate dissolved to give a pale yellow solution. This was stirred for 1 h, and then all volatiles including an excess of $SiClHMe_2$ were vacuum evaporated. The remaining yellow oil was distilled at reduced pressure. The fraction distilling at 86 °C/2 Torr was 5-(dimethylsilyl)-1,2,3,4,-tetramethylcyclopenta-1,3-diene (**1**). Yield: 7.2 g (80%).

Data for **1** are as follows. ^1H NMR (C_6D_6, 298 K): −0.12 (d, $^3J_{HH} = 3.6$ Hz, 6H, Si*Me*$_2$H); 1.79 (d, $^5J_{HH} = 0.6$ Hz, 6H, β-*Me*, C_5Me_4); 1.90 (s, 6H, α-*Me*, C_5Me_4); 2.74 (br s, $\nu_{1/2} = 8.2$ Hz, 1H, C_5Me_4H); 4.23 (septuplet, $^3J_{HH} = 3.6$ Hz, 1H, $SiMe_2H$). $^{13}C\{^1H\}$ (C_6D_6, 298 K): −6.30 (Si*Me*$_2$H); 11.24, 13.81 (C_5Me_4); 53.11 (br, $\nu_{1/2} = 5.9$ Hz, *C*H, C_5Me_4H); 132.28, 135.65 (C_q, C_5Me_4). $^{29}Si\{^1H\}$ (C_6D_6, 298 K): −12.46 (*Si*Me$_2$H). EI-MS (60 °C): *m/z* (relative abundance, %) 181 (13), 180 ($M^{•+}$; 71), 165 ($[M - Me]^+$; 36), 149 (7), 123(10), 122 (28), 121 ($[C_5HMe_4]^+$;41), 120 ($[C_5Me_4]^+$; 55), 119 (15), 107 (33), 106 (16), 105 ($[C_5Me_4 - Me]^+$; 64), 91 (28), 79 (13), 77 (15), 75 (22), 74 (10), 73 ($[SiMe_3]^+$;100), 59 ($[SiMe_2H]^+$; 91), 43 (15), 41 (17), 39 (14). IR (neat; cm^{-1}): 2964 (s), 2913 (s), 2857 (s), 2115 (vs), 1635 (w), 1444 (m), 1380 (m), 1306 (w), 1248 (vs), 1220 (m), 1125 (m), 1111 (m), 1048 (m), 1024 (m), 987 (s), 953 (m), 899 (vs), 878 (vs), 836 (s), 802 (m), 771 (m), 735 (m), 707 (w), 669 (w), 648 (m), 631 (w), 556 (w), 497 (m), 487 (m).

Preparation of $[TiCl\{\eta^5\text{-}C_5Me_4(SiMe_2H)\}_2]$ (2). Compound **1** (7.2 g, 40 mmol) in diethyl ether (250 mL) was cooled to 0 °C, and 1.6 M LiBu in hexane (25.0 mL, 40 mmol) was added under stirring. A white voluminous precipitate was formed. After vigorous stirring for 1 h the precipitate was left to settle down, and the solution was removed. The white precipitate was washed by 50 mL of diethyl ether and dried under vacuum. The white powder of the lithium salt was dissolved in 100 mL of THF, and turquoise $TiCl_3(THF)_3$ (7.35 g, 20 mmol) was added. The mixture was vigorously stirred until the solution color turned dark blue (16 h). All volatiles were distilled off under vacuum, and the dark blue residue was extracted with 50 mL of hexane. The blue hexane solution was collected and concentrated. Cooling to −18 °C afforded dark blue crystals of **2**, which were dried in vacuum. Yield: 7.06 g (80%).

Data for **2** are as follows. Mp: 73 °C. EI-MS (70 °C): *m/z* (relative abundance, %) 441 ($M^{•+}$; 2), 440 (3), 439 ($[M - 2H]^+$; 7), 438 (6), 437 ($[M - 4H]^+$; 11), 385 (11), 384 (19), 383 ($[M - SiMe_2]^+$; 55), 382 (44), 381 ($[M - SiH_2Me_2]^+$; 100), 380 (16), 379 (17), 346 (17), 345 ($[M - SiH_2Me_2 - HCl]^+$; 44), 344 (12), 343 (25), 342 (7), 341 (12), 243 (12), 204 (19), 73 ($[SiMe_3]^+$; 11), 59 ($[SiMe_2H]^+$; 23). IR (KBr; cm^{-1}): 2973 (s), 2948 (s), 2907 (s), 2868 (w), 2129 (vs), 1479 (w), 1450 (w), 1409 (w), 1380 (m), 1350 (w), 1337 (m), 1248 (s), 1128 (w), 1025 (m), 890 (vs), 835 (s), 765 (m), 742 (w), 691 (w), 675 (m), 655 (m), 463 (m), 437 (s). ESR (toluene, 23 °C): $g = 1.965$, $\Delta H = 11$G. ESR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.985$, $g_3 = 1.912$, $g_{av} = 1.965$. UV–vis (hexane): 350 (sh) ≫ 553 > 650 (sh) nm. Anal. Calcd for $C_{22}H_{38}ClSi_2Ti$ (442.03): C, 59.78; H, 8.66. Found: C, 59.61; H, 8.70.

Preparation of $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_2H)\}_2]$ (3). Compound **2** (7.06 g, 16 mmol) was dissolved in THF (100 mL), and $PbCl_2$ (2.22 g, 8.0 mmol) was added under vigorous stirring. After 16 h of stirring the initial blue color of the solution turned dark red. Then, all volatiles were evaporated in vacuum, and a dark red residue was extracted with hexane. The hexane was replaced by toluene, from which red crystals of **3** were obtained by cooling to −18 °C. Yield: 6.66 g (88%). Data for **3** are as follows. Mp: 138 °C. ^1H NMR (C_6D_6): 0.35 (d, $^3J_{HH} = 3.9$ Hz, 12H, Si*Me*$_2$H); 1.75 (s, 12H, C_5Me_4, β-*Me*); 2.19 (s, 12H, C_5Me_4, α-*Me*); 4.79 (septuplet, $^3J_{HH} = 3.9$ Hz, 2H, $SiMe_2H$). $^{29}Si\{^1H\}$ (C_6D_6): −25.96 (*Si*Me$_2$H). EI-MS (160 °C): *m/z* (relative abundance, %) 478 (6), 476 ($M^{•+}$; 7), 475 (7), 474 (6), 473 ($[M - 3H]^+$; 7), 456 (6), 443 (13), 442 (19), 441 (37), 440 ($[M - HCl]^+$; 43), 439 (88), 438 (56), 437 ($[M - 3H - HCl]^+$; 100), 436 (19), 435 (18), 401 ($[M - 3H - 2HCl]^+$; 12), 300 (11), 299 (23), 298 (21), 297 ($[M - C_5Me_4(SiMe_2H)]^+$; 35), 296 (21), 295 (15), 180 (13), 179 ($[C_5Me_4(SiMe_2H)]^+$; 58), 178 (11), 119 (12), 73 ($[SiMe_3]^+$; 22), 59 ($[SiMe_2H]^+$; 21). IR (KBr; cm^{-1}): 2957 (s), 2909 (s), 2157 (vs), 1482 (m), 1440 (m), 1413 (w), 1390 (m), 1376 (s), 1365(w), 1342 (s), 1251 (s), 1245 (s), 1125 (m), 1025 (m), 882 (vs), 839 (s), 800 (w), 765 (s), 748 (w), 730 (w), 702 (w), 656 (m), 638 (w), 626 (w), 538 (w), 429 (m). Anal. Calcd for $C_{22}H_{38}Cl_2Si_2Ti$ (477.48): C, 55.34; H, 8.02. Found: C, 55.29; H, 7.97.

Preparation of $[Ti\{Me_4Si_2(\eta^5\text{-}C_5Me_4)_2\}\{\ \eta^2\text{-}Me_3SiC'CSiMe_3\}]$ (4). Compound **3** (1.9 g, 4.0 mmol) was mixed with excess Mg (0.2 g, 8 mmol) and btmsa (1.02 g, 6.0 mmol) in THF (50 mL), and the mixture was heated to 60 °C until its color turned from red, through blue (complex **2**), to orange (5 days). All volatiles were evaporated under vacuum at 60 °C, and the orange residue was extracted with hexane. The concentrated solution afforded after cooling to −18 °C orange crystals of **4**. Yield: 1.8 g (78%). Mp: 175 °C. ^1H NMR (C_6D_6): −0.01 (s, 18H, Si*Me*$_3$); 0.30 (s, 12H,

---

(34) Antropiusová, H.; Dosedlová, A.; Hanuš, V.; Mach, K. Transition Met. Chem. (London) **1981**, *6*, 90.

(35) Manzer, E. L. *Inorg. Synth.* **1982**, *21*, 135.

(36) Mach, K.; Varga, V.; Antropiusová, H.; Poláček, J. *J. Organomet. Chem.* **1987**, *333*, 205.

Table 3. Crystallographic Data and Data Collection and Structure Refinement Details 3, 9, and 4

	3	9	4
formula	$\mathrm{C_{22}H_{38}Cl_2Si_2Ti}$	$\mathrm{C_{22}H_{36}ClSi_2Ti}$	$\mathrm{C_{30}H_{54}Si_4Ti}$
mol wt	477.50	440.04	574.99
cryst syst	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*C*2/*c*	$P\bar{1}$
a (Å)	18.3852(11)	14.8534(4)	9.0743(2)
b (Å)	8.1284(3)	9.8688(4)	11.6767(4)
c (Å)	16.4522(10)	16.7163(7)	16.9712(5)
α (deg)	90.00	90.00	77.7294(14)
β (deg)	96.183(2)	109.387(3)	75.2076(16)
γ (deg)	90.00	90.00	75.1488(18)
V (Å^3); Z	2444.4(2); 4	2311.42(15); 4	1659.61(8); 2
D_{calcd} (g cm^{-3})	1.298	1.265	1.151
μ (mm^{-1})	0.673	0.594	0.419
color; habit	red; bar	blue; prism	orange; prism
cryst size (mm^3)	0.63 × 0.23 × 0.13	0.23 × 0.15 × 0.15	0.50 × 0.20 × 0.10
T (K)	150(2)	150(2)	150(2)
θ_{min}; θ_{max} (deg)	1.00; 27.48	2.52; 27.47	1.00; 29.13
range of *h*	−23→23	−19→19	−12→12
range of *k*	−7→10	−12→12	−15→16
range of *l*	−21→21	−21→21	−23→23
no. of diffrns collected	7346	15 548	31 599
no. of unique diffrns	2788	2653	8914
F(000)	1016	940	624
no. of params	133	126	334
$R(F)$; $R_{\mathrm{w}}(F^2)$ all data (%)	5.27; 8.22	6.26; 9.23	7.09; 10.70
GOF(F^2), all data	1.038	1.021	1.024
$R(F)$; $R_{\mathrm{w}}(F2)$ (I > 2σ(*I*))	3.60; 7.45	3.82; 8.29	4.40; 9.55
$\Delta\rho$ (e Å^{-3})	0.344; −0.301	0.519; −0.291	0.621; −0.294

Si*Me*$_2$); 1.24 (s, 12H, α-*Me*); 2.46 (s, 12H, *β*-*Me*). ^{13}C{^{1}H} ($\mathrm{C_6D_6}$): −0.06 (Si*Me*$_2$); 4.44 (Si*Me*$_3$); 14.34, 15.04 ($\mathrm{C_5}$*Me*$_4$); 116.64 (C_{ipso}, C_5Me$_4$); 126.98, 131.37 (C_5Me$_4$); 248.27 (*C*SiMe$_3$). ^{29}Si{^{1}H} ($\mathrm{C_6D_6}$): −17.64, −17.55 (*Si*Me$_3$ and *Si*Me$_2$). EI-MS (180 °C): *m*/*z* (relative abundance, %) 407 (14), 406 (48), 405 (86), 404 ([M − btmsa]$^+$; 100), 403 (42), 402 (43), 401 (17), 346 (7), 345 ([M − btmsa − SiMe$_2$H]$^+$; 13), 343 (9), 341 (8), 170 ([btmse]$^+$; 9), 157 (8), 156 (17), 155 ([btmse − Me]$^+$; 82), 73 ([SiMe$_3$]$^+$; 35), 59 ([SiMe$_2$H]$^+$; 20). IR (KBr; cm^{-1}): 2978 (s), 2949 (s), 2897 (s), 1643 (w), 1602 (m), 1568 (m), 1484 (w), 1454 (w), 1403 (w), 1381 (m), 1356 (w), 1340 (m), 1247 (s), 1132 (w), 1020 (m), 850 (vs), 831 (vs), 810 (s), 788 (m), 757 (m), 725 (w), 674 (w), 654 (m), 617 (w), 457 (m), 431 (m). UV−near IR (hexane): 395 (sh) ≫ 920 nm.The GC-MS analysis of volatiles revealed that in addition to btmsa 1,2-bis(trimethylsilyl)ethene and 1,2-bis(trimethylsilyl)-ethane were present. Anal. Calcd for $\mathrm{C_{30}H_{54}Si_4Ti}$ (574.96): C, 62.67; H, 9.47. Found: C, 62.56; H, 9.39.

Reduction of 3 in the Presence of Ethene: Formation of 5, 6, and 7. Compound **3** (0.31 g, 0.65 mmol) and magnesium (0.12 g, 5.0 mmol) were loaded into an ampule, and THF (20 mL) and subsequently ethene (5 mmol) were condensed in on a vacuum line at liquid nitrogen temperature. The ampule was then heated to 40 °C on a water bath until the solution changed its red color to dirty green. After another 1 h, when the color was not changing, the solution was separated into another ampule while volatiles (THF and ethene) were distilled back. The residue was extracted with hexane, the hexane was replaced with $\mathrm{C_6D_6}$, and about half of the concentrated solution was sealed with flame in an NMR sample tube. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra identified the presence of one paramagnetic product, one major diamagnetic product, and one minor diamagnetic product. The ^{1}H spectrum of the paramagnetic product can be assigned to [Ti{η^5-C$_5$Me$_4$(SiMe$_2$Et)}$_2$] (**5**) on the basis of comparison with the spectra of [Ti{η^5-C$_5$Me$_4$-(SiMe$_3$)}$_2$],[18] [Ti{η^5-C$_5$Me$_4$(SiMe$_2{}^i$Pr)}$_2$],[24] [Ti{η^5-C$_5$Me$_4$-(SiMe$_2{}^t$Bu)}$_2$],[28a] and [Ti(η^5-C$_5$Me$_5$)$_2$].[28b,c] The diamagnetic major product appeared to be the complex of [Ti{η^5-C$_5$Me$_4$(SiMe$_2$Et)}$_2$(η^2-C$_2$H$_4$)] (**6**) with π-coordinated ethene. The correct selection of resonances of **6** was corroborated by their disappearance after aging the sample for 1 week in darkness. Then, the resonances of the previous minor diamagnetic product increased in intensity and became the sole diamagnetic product obtained. This was assigned to [Ti{η^5-C$_5$Me$_4$(SiMe$_2$Et)}{η^5:η^2-C$_5$Me$_4$(SiMe$_2$CH=CH$_2$)}] (**7**). Simultaneously, one single resonance in the ^{1}H NMR and a single resonance in the ^{13}C NMR spectra were observed, which could be assigned to ethane. During this aging the intensity of resonances of **5** did not change. The NMR sample tube was opened under vacuum, and the solid product was collected and its EI-MS spectra were measured.

Data for a mixture of **5** and **7** are as follows. EI-MS (150 °C): *m*/*z* (relative abundance, %) 464 (16), 463 (34), 462 ([**5**]$^{\bullet+}$; 84), 461 (79), 460 ([**7**]$^{\cdot+}$; 100), 459 (24), 458 (20), 371 (12), 369 (14), 262 (11), 261 (11), 242 (15), 241 (23), 87 ([SiMe$_2$Et]$^+$; 14), 84 (16), 59 ([SiMe^{2}H]$^+$; 50).

Data for **5** are as follows. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 298 K): 5.14 ($\Delta\nu_{1/2}$ ≈21 Hz, 6H, SiCH$_2$*Me*); 5.78 ($\Delta\nu_{1/2}$ ≈ 52 Hz, 12H, Si*Me*$_2$); 6.13 ($\Delta\nu_{1/2}$ ≈ 180 Hz, 4H, SiC*H*$_2$Me); 25.88 ($\Delta\nu_{1/2}$ ≈ 100 Hz, 12H, C$_5$*Me*$_4$,); 77.06 ($\Delta\nu_{1/2}$ ≈ 200 Hz, 12H, C$_5$*Me*$_4$,).

Data for **6** are as follows. ^{1}H NMR ($\mathrm{C_6D_6}$): −0.19 (s, 12H, Si*Me*$_2$); 0.49 (q, $^3J_{\mathrm{HH}}$ = 7.8 Hz, 4H, SiC*H*$_2$); 1.01 (t, $^3J_{\mathrm{HH}}$ = 7.8 Hz, 6H, SiCH$_2$*Me*); 1.33 (s, 12H, C$_5$*Me*$_4$); 2.06 (s, 4H, C*H*$_2$=); 2.34 (s, 12H, C$_5$*Me*$_4$). ^{13}C{^{1}H} ($\mathrm{C_6D_6}$): −0.65 (Si*Me*$_2$); 8.04 (SiCH$_2$*Me*); 10.01 (Si*C*H$_2$Me); 12.00 15.69 (C$_5$*Me*$_4$); 104.26 (*C*H$_2$=); 123.80, 129.54, 132.13 (C_5Me$_4$).

Data for **7** are as follows. ^{1}H NMR ($\mathrm{C_6D_6}$): −0.60, −0.49, 0.02 (3 × s, 3 × 3H, Si*Me*$_2$); 0.08–0.42 (m, 2H, SiC*H*$_2$Me); 0.47 (s, 3H, C$_5$*Me*$_4$); 0.78–0.87 (partially overlapped, m, 1H, CH=CH$_2$); 0.85 (s, 3H, Si*Me*$_2$); 0.88–0.95 (m, 3H, SiCH$_2$*Me*); 0.98; 0.99; 1.10; 1.14 (4 × s, 4 × 3H, C$_5$*Me*$_4$); 1.33 (dd, $^2J_{\mathrm{HH}}$ = 3.9 Hz, $^3J_{\mathrm{HH}}$ = 10.8 Hz, H_{anti}, 1H, CH=CH$_2$); 1.49, 2.99 (2 × s, 2 × 3H, C$_5$*Me*$_4$); 3.15 (dd, $^2J_{\mathrm{HH}}$ = 3.9 Hz, $^3J_{\mathrm{HH}}$ = 12.3 Hz, 1H, H_{syn}, CH=C*H*$_2$); 3.29 (s, 3H, C$_5$*Me*$_4$). ^{13}C{^{1}H} ($\mathrm{C_6D_6}$): −1.33, −0.76, −0.03, 6.06 (Si*Me*$_2$); 7.90 (SiCH$_2$*Me*); 9.06 (Si*C*H$_2$Me); 10.65, 10.81, 11.31, 11.99, 12.49, 12.88, 16.51, 18.66 (C$_5$*Me*$_4$); 89.23 (*C*H=CH$_2$); 105.75 (CH=*C*H$_2$); 109.01, 121.24 (C_{ipso}); 122.60, 123.67, 123.72, 124.75, 126.77, 127.08, 131.50, 135.31 (C_5Me$_4$). ^{29}Si{^{1}H} ($\mathrm{C_6D_6}$): −22.98, −5.33 (*Si*Me$_2$Et and *Si*Me$_2$(CH=CH$_2$).

Preparation of [TiCl$_2${Me$_4$Si$_2$(η^5-C$_5$Me$_4$)$_2$}] (8). Compound **4** (1.15 g, 2.0 mmol) was dissolved in 50 mL of THF, and PbCl$_2$(0.55 g, 2.0 mmol) was added. The mixture was stirred at 60 °C while its color was changing from orange to red. After 2 h the solvent was evaporated under vacuum, and a red residue was extracted with hexane. Cooling of the hexane solution to −18 °C afforded a red crystalline material. This was recrystallized from toluene to give red crystals of **6**. Yield: 0.76 g (80%).

Data for **8** are as follows. ^{1}H NMR (C_6D_6): 0.36 (s, 12H, Si*Me*$_2$); 1.87 (s, 12H, α-*Me*); 2.13 (s, 12H, *β-Me*). ^{13}C{^{1}H} (C_6D_6): −0.06 (Si*Me*$_2$); 14.16, 16.43 (C_5Me_4); 122.25, 129.58, 141.12 (*C*$_5$Me$_4$). ^{29}Si{^{1}H} (C_6D_6): −12.32 (*Si*Me$_2$). EI-MS (160 °C): *m*/*z* (relative abundance, %) 478 (12), 477 (16), 476 (41), 475 (25), 474 ($M^{\bullet+}$; 52), 439 (10), 438 ($[M - HCl]^+$; 13), 437 (10), 298 (13), 296 ($[M - C_5Me_4SiMe_2]^+$; 18), 179 (12), 178 ($[C_5Me_4SiMe_2]^+$; 46), 177 (31), 163 (36), 119 ($[C_5Me_4 - H]^+$; 36), 105 (17), 97 (28), 91 (14), 83 (20), 73 ($[SiMe_3]^+$; 45), 59 ($[SiMe_2H]^+$; 100), 58 (14). IR (KBr; cm^{-1}): 2963 (s), 2906 (s), 1498 (w), 1468 (w), 1453 (w), 1407 (w), 1376 (s), 1364 (m), 1353 (w), 1335 (m), 1257 (vs), 1246 (s), 1180 (w), 1127 (w), 1092 (m), 1019 (s), 858 (w), 831 (vs), 816 (s), 796 (s), 770 (w), 743 (w), 694 (w), 679 (m), 660 (m), 464 (w), 439 (m), 424 (m). Anal. Calcd for $C_{22}H_{36}Cl_2Si_2Ti$ (475.47): C, 55.57; H, 7.63. Found: C, 55.48; H, 7.57.

Preparation of [Ti{Me$_4$Si$_2$(η^5-C$_5$Me$_4$)$_2$}Cl] (9). **8** (0.30 g, 0.63 mmol) was dissolved in 50 mL of THF, and Mg 0.0076 g (0.315 mmol) was added. The red mixture was stirred at 60 °C, until its color turned from red to blue (10 h). All volatiles (THF) were evaporated under vacuum, and a blue residue was extracted with toluene. The concentrated blue toluene solution afforded after cooling to 0 °C a blue precipitate of **9**. This was recrystallized from toluene to give dark blue crystals. Yield: 0.23 g (82%). Mp: 235 °C. EI-MS (direct inlet, 70 eV, 180 °C; *m*/*z* (relative abundance): 442 (11), 441 (29), 440 (37), 439 ($M^{\bullet+}$;86), 438 (49), 437 ($[M - H_2]^+$; 100), 436 (16), 435 (15), 424 ($[M - Me]^+$; 7), 423 (7), 422 (8), 421 (7), 401 (($[M - H_2 - HCl]^+$; 9), 73 (16), 59 (30). ESR (toluene, 23 °C): $g = 1.959$, $\Delta H = 11$ G. ESR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.985$, $g_3 = 1.896$, $g_{av} = 1.960$. IR (KBr; cm^{-1}): 2973 (s), 2947 (s), 2907 (s), 2891 (w), 1479 (w), 1449 (w), 1408 (w), 1380 (m), 1351 (w), 1329 (s), 1245 (s), 1129 (w), 1087 (w), 1021 (m), 857 (m), 829 (vs), 818 (s), 795 (s), 767 (m), 742 (w), 731 (w), 691 (w), 675 (m), 655 (m), 463 (m), 438 (vs). UV–vis (hexane, nm): $357 > 415$ (sh) $\gg 565 > 665$ (sh). Anal. Calcd for $C_{22}H_{36}ClSi_2Ti$ (440.01): C, 60.05; H, 8.25. Found: C, 59.94; H, 8.18.

X-ray Structure Determination. Crystal fragments of **3**, **4**, and **9** were fixed into Lindemann glass capillaries under nitrogen in a glovebox and were sealed with wax. Diffraction data were collected on a Nonius KappaCCD diffractometer and processed by the HKL program package.[37] The structures were solved by direct methods (SIR-92)[38] and refined by full-matrix least-squares on F^2 (SHELXL-97).[39] Relevant crystallographic data are given in Table 3. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. The hydrogen atoms residing on the silicon atoms for **3** were refined without any constraints, while all other hydrogen atoms were included in ideal positions.

Acknowledgment. This investigation was supported by GAČR (project no. 104/05/0474) and by the Ministry of Education, Youth and Sports (project no. LC06070).

Supporting Information Available: CIF file for the structures **3**, **4**, and **9**; dependence of chemical shifts of **5** on temperature; additional NMR data for compounds **6** and **7**, and isotope distribution of molecular ions of compounds **5** and **7** and its comparison with experimental values. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8000789

---

(37) HKL Denzo and Scalepack program package by Nonius: Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(38) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(39) Sheldrick, G. M. *SHELXL97*, *Program for Crystal Structure Refinement from Diffraction Data*; University of Göttingen: Göttingen, 1997.

(40) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2007.