Organometallics **1997,** *16,* 4185−4191

Activation of the (Trimethylsilyl)tetramethylcyclopentadienyl Ligand in the $[C_5Me_4(SiMe_3)]_2TiCl_2$/Mg System, Yielding Intramolecular Si−CH$_2$−Mg and Si−CH$_2$−Ti Bonds. Molecular Structures of $\{[\eta^5\text{-}C_5Me_4SiMe_2(\mu\text{-}CH_2\{Mg,Mg\})][\eta^5\text{-}C_5Me_4(SiMe_3)]Ti^{III}(\mu\text{-}H)_2Mg(THF)\}_2$ and $[\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2][\eta^5\text{-}C_5Me_4(SiMe_3)]Ti^{III}$

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Received March 3, 1997[⊗]

The reduction of $[C_5Me_4(SiMe_3)]_2TiCl_2$ by excess Mg in THF yields the paramagnetic compound $\{[\eta^5\text{-}C_5Me_4SiMe_2(\mu\text{-}CH_2\{Mg,Mg\})][\eta^5\text{-}C_5Me_4(SiMe_3)]Ti^{III}(\mu\text{-}H)_2Mg(THF)\}_2$ (**3**). In the presence of $Me_3SiC{\equiv}CSiMe_3$ the same system affords the paramagnetic compound $[\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2][\eta^5\text{-}C_5Me_4(SiMe_3)]Ti^{III}$ (**4**) in 75% yield. The crystal structures of **3** and **4** reveal that one $SiMe_3$ group in each of the compounds has been activated by hydrogen abstraction. In centrosymmetric dimer **3**, two titanocene−magnesium hydride-bridged units are held together by two methylene groups which link the two Mg atoms via a two-electron−three-center Mg−C−Mg bond. In the mononuclear **4**, a regular Ti−CH$_2$ σ-bond (2.204(5) Å) binds the central Ti atom to the $\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2$ ligand.

Introduction

Activation of sp^2 and sp^3 C−H bonds in titanocene derivatives occurs at the onset of formation of Ti(II) species under the action of reducing agents. The Ti(II) d^2 electrons either are accommodated in a suitable ligand having low-energy empty orbitals, such as acetylenes,[1] phosphanes,[2] and carbon monoxide,[3] or induce hydrogen transfer from one of the cyclopentadienyl ligands to the central Ti atom, to give a titanocene hydride moiety,[4] or to a leaving alkyl radical with the elimination of a hydrocarbon molecule while new bridging Ti−C bonds are generated.[5] Another possibility is the formation of a new ligand which accommodates the d electrons.[6] The solid-state structures of the following products of particular reaction modes are known: $[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2][(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)]_2$,[4a] $[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_2Me_3)_2][(\eta^5\text{-}C_5H_2Me_3)Ti(\mu\text{-}H)]_2$,[1b] $[\mu\text{-}\eta^3{:}\eta^4\text{-}C_5HMe_2(CH_2)_2][(\eta^5\text{-}C_5HMe_4)Ti(\mu\text{-}H)]_2$,[4b] $[(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Ti(PMe_3)]_2$,[5a] $[(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_3Ti_2(THF)]$,[5b] $[(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)(\eta^5\text{-}C_5Me_5)Ti]$,[5c] and $[(\eta^1{:}\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5HMe_4)Ti]_2$ and $[(\eta^1{:}\eta^5\text{-}C_5HMe_3)(\eta^5\text{-}C_5H_2Me_3)Ti]_2$.[5d] The equilibrium between $(\eta^5\text{-}C_5Me_5)_2Ti$ and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4CH_2)TiH$ has also been well-established.[4c,d] In the Ti(II) compounds $(\eta^3{:}\eta^4\text{-}C_5Me_3(CH_2)_2)(\eta^5\text{-}C_5Me_5)Ti$[6a] and $(\eta^3{:}\eta^4\text{-}C_5HMe_2(CH_2)_2)(\eta^5\text{-}C_5HMe_4)Ti$[6b] the allyl diene ligands likely accommodate the d^2 electrons and thus minimize the energy of the complexes.[6c] The mode by which the above complexes are stabilized depends on the structure of the precursor, the nature of the leaving groups, and the electron density at the cyclopentadienyl ligands and the central metal atom. Provided the precursor type and the leaving group are given, the reactivity of a Ti(II) intermediate can be controlled through the electron donation effect of methyl substituents at the cyclopentadienyl rings and, for the tetra- and pentamethylated compounds, also by steric effects.[1,7] In contrast, the effect of the trimethylsilyl group in metallocene compounds appears to be controversial, depending on the

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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S0276-7333(97)00178-7 CCC: $14.00

investigated property or the measured parameter.[8] Recently we have synthesized $[C_5Me_4(SiMe_3)]_2TiCl_2$ (**1**) and $[C_5Me_4(SiMe_3)]_2TiCl$ (**2**) and have confirmed the ambigous behavior of the $SiMe_3$ group. On the basis of the red shift of electronic absorption bands of **1** compared to those of $(C_5Me_5)_2TiCl_2$, the $SiMe_3$ group exerts a stronger electron donation effect than the Me group. The affinity of **2** toward 2-methyltetrahydrofuran, however, puts the effect of the $SiMe_3$ group close to that of hydrogen.[9] In further attempts to prepare the dimeric Ti−Mg hydride complex $[C_5Me_4(SiMe_3)]_2Ti(\mu\text{-}H)_2Mg(THF)(\mu\text{-}Cl)]_2$ and the bis(trimethylsilyl)acetylene complex $[C_5Me_4(SiMe_3)]_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$, unexpected products have been obtained in high yields, showing an unusual reactivity of the $SiMe_3$ group. The preparative procedures, some properties, and X-ray structures of the new compounds are reported herein.

Experimental Section

General Data. Reduction of $[C_5Me_4(SiMe_3)]_2TiCl_2$ (**1**), workup of the products and their purification, handling, and spectroscopic measurements were performed under vacuum conditions using all-sealed glass devices equipped with breakable seals. EPR spectra were recorded on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences, Berlin, Germany) in the X-band; g values were determined using an Mn^{2+} ($M_I = -{}^1/_2$ line) standard at $g = 1.9860$ and an MJ-110 R proton magnetometer (Radiopan, Poznan, Poland). Concentrations of the paramagnetic compounds were estimated from integrated first-derivative spectra. An STT-3 variable-temperature unit was used for measurements in the range −140 to +20 °C. UV−vis spectra in the range 280−2000 nm were obtained on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). EI-MS spectra were measured on a VG-7070E mass spectrometer at 70 eV (only important mass peaks and peaks of intensity above 5% are reported). Samples in capillaries were opened and inserted into the direct inlet under argon. GC−MS analyses were carried out on a Hewlett-Packard gas chromatograph (5890 series II) equipped with a capillary column SPB-1 (length 30 m; Supelco) and a mass spectrometric detector (5971 A). KBr pellets were prepared in a Labmaster 130 glovebox (mBraun) under purified nitrogen and were measured in an air-protecting cuvette on a Mattson Galaxy 2020 infrared spectrometer. Electron dispersive X-ray analyses (EDX) were carried out on a Zeiss DSM-962 scanning electron microscope equipped with an EDAX PV9800 analyzer. An acceleration voltage of 25 kV was used. Melting points were determined in sealed glass capillaries under nitrogen and are uncorrected.

Chemicals. The solvents THF, hexane, and toluene were purified by conventional methods, dried by refluxing over $LiAlH_4$, and stored as solutions of the dimeric titanocene $(C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)]_2$. Bis(trimethylsilyl)acetylene (BTMSA, Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h, and distilled into ampules. Magnesium turnings (Fluka, purum for Grignard reactions) were used as received. The synthesis of $[C_5Me_4(SiMe_3)]_2TiCl_2$ (**1**) from $[C_5Me_4(SiMe_3)]Li$ and freshly prepared $TiCl_3$ has been carried out under argon, as recently reported.[9]

Preparation of $\{[\eta^5\text{-}C_5Me_4SiMe_2(\mu\text{-}CH_2\{Mg,Mg\})][\eta^5\text{-}C_5Me_4(SiMe_3)]Ti^{III}(\mu\text{-}H)_2Mg(THF)\}_2$ (3). Crystalline **1** (1.1 g, 2.0 mmol) and Mg turnings (0.5 g, 20 mmol) were charged into an ampule equipped with a magnetic stirrer and an EPR sample tube. The ampule was evacuated, and THF (30 mL) was distilled in. After it was stirred for 2 h at room temperature, the solution turned blue. Its EPR spectrum showed mainly a broad line ($\Delta H = 14$ G) at $g = 1.954$, which indicated the presence of $[C_5(SiMe_3)Me_4]_2TiCl$ (**2**).[9] Finally the mixture was heated to 60 °C for 6 h. The resulting blue solution afforded an EPR spectrum consisting of the triplet splitting (1:2:1) $a = 7.4$ G at $g = 1.9905$, whereas the signal of **2** disappeared. The solution was separated from magnesium, THF was evaporated, and a dark turquoise residue was repeatedly extracted by hexane to give a pale blue solution. Slow cooling of the concentrated solution afforded blue prisms of **3**. Yield: 0.9 g (85%). EPR (toluene, 23 °C): $g = 1.9905$, $a_H = 7.4$ G, $a_{Ti} = 6.5$ G. EPR (toluene, −140 °C): $g_1 = 2.002$, $g_2 = 1.991$, $g_3 = 1.983$, $g_{av} = 1.992$; A_3(1:2:1) = 12 G. UV/vis (toluene, nm): 360 ≫ 590. EI-MS (direct inlet, 70 eV, 100−220 °C; m/e (%)): decomposition. IR (KBr, cm^{-1}): 2951 (s), 2901 (s), 1452 (w), 1379 (w), 1325 (m), 1246 (vs), 1200 (s, b), 1128 (w), 1022 (m), 907 (m), 833 (vs), 801 (s), 756 (m), 714 (m), 683 (w), 652 (w), 633 (w), 519 (w). Anal. Calcd for $C_{56}H_{102}O_2Si_4Mg_2Ti_2$: C, 63.2; H, 9.7. Found: C, 62.9; H, 9.8.

Preparation of $[\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2][\eta^5\text{-}C_5Me_4SiMe_3]Ti^{III}$ (4). Crystalline **1** (1.1 g, 2.0 mmol) and Mg turnings (0.5 g, 20 mmol) were charged into an ampule, and BTMSA (1 mL, 4.5 mmol) and THF (30 mL) were subsequently distilled in on a vacuum line. The mixture was frozen by liquid nitrogen, the ampule was sealed off, and the mixture was then heated with stirring to 60 °C for 8 h. The resulting greenish yellow solution was separated from unreacted magnesium and evaporated under vacuum. The volatiles were collected for GC−MS analysis. It revealed, besides THF, the presence of only BTMSA. The green residue was extracted by hexane to give a dark green solution. Cooling of the solution afforded blue crystals of **3** (0.04 g), which were separated. The mother liquor was partially evaporated, and the solution was cooled to −18 °C for 3 days. Additional blue crystals crystallized out (<0.01 g). The yellow-green mother liquor was separated and evaporated to dryness under vacuum. The solid was extracted by condensing hexane vapor to give a clear light green solution, whereas traces of a white solid remained on the glass walls. Cooling of the solution afforded a light green crystalline material, which was separated and recrystallized from hexane. Well-shaped crystals were selected for the X-ray structure determination. Yield of light green crystals of **4**: 0.65 g (75%). Mp: 125 °C. EPR (toluene, 23 °C): $g = 1.9593$, $\Delta H = 15$ G. EPR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.984$, $g_3 = 1.889$, $g_{av} = 1.957$. UV/vis (hexane, nm): 320 ≫ 460 > 600. IR (KBr, cm^{-1}): 2949 (s), 2903 (s), 1479 (w), 1445 (m), 1406 (w), 1377 (m), 1329 (s), 1246 (s), 1126 (w), 1022 (m), 843 (vs), 789 (s), 756 (s), 685 (m), 669 (m), 633 (m), 573 (w), 519 (w), 469 (m), 428 (m). EI-MS (direct inlet, 70 eV, 80−90 °C; m/e (%)): 433 ($M^{\bullet+}$, 100), 432 (23), 431 (25), 430 (7), 429 (11), 427 (6), 418 (8), 417 (5), 361 (34), 360 (15), 359 (23), 358 (6), 357 (8), 355 (5), 343 (5), 341 (6), 339 (5), 289 (8), 287 (9), 285 (5), 73 (16). Anal. Calcd for $C_{24}H_{41}Si_2Ti$: C, 66.5; H, 9.5. Found: C, 66.3; H, 9.6.

Preparation of $[C_5Me_4(SiMe_3)]_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ (6) at Low Temperature. Crystalline **1** (1.1 g, 2.0 mmol) was dissolved in a mixture of THF (30 mL) and BTMSA (4 mL, 18 mmol). Activated Mg turnings from the previous experiment (0.5 g, 20 mmol) were added, and the mixture was vigorously shaken. The brown color of the solution turned to blue within ca. 5 min, and the ampule was put into the refrigerator overnight. Then, while it was cooled below 0 °C, the solution was separated from magnesium and THF was evaporated. The dark residue was extracted by hexane to give a dark yellow solution. Its evaporation gave a solidified oil. The EPR spectrum of the hexane solution gave the signals attributable to compounds **3** and **4**. The integrated areas of the signals gave estimates of concentrations to be less than 5% for **3** and

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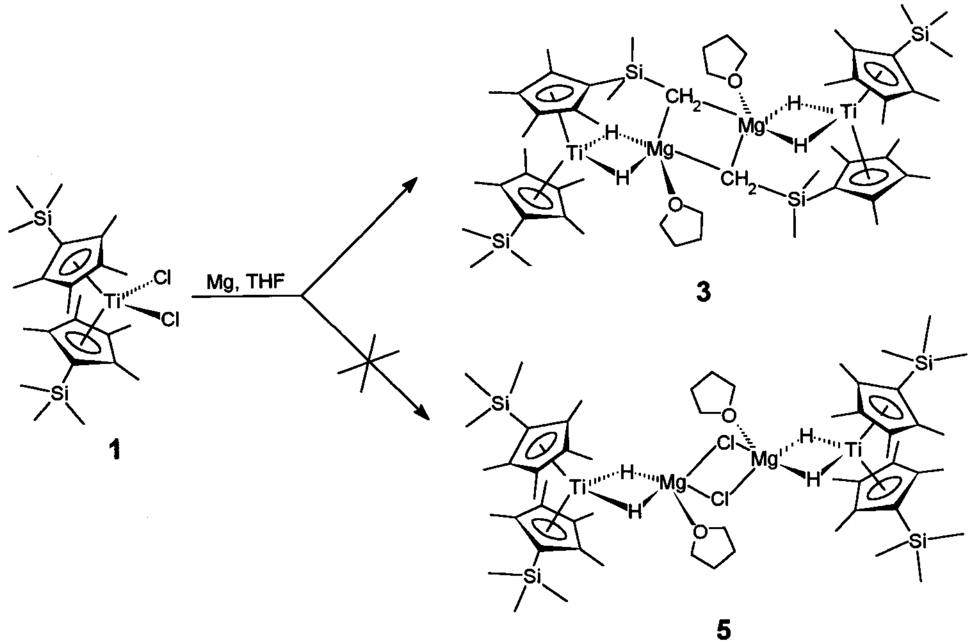
Table 1. Crystallographic Data and Experimental Details for 3 and 4

	3	4
mol formula	$C_{56}H_{102}Mg_2O_2Si_4Ti_2$	$C_{24}H_{41}Si_2Ti$
mol wt	1064.14	433.65
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
cell consts		
a, Å	11.0926(6)	8.9594(4)
b, Å	15.7011(14)	10.3092(6)
c, Å	18.3627(7)	14.0961(8)
α, deg	90	87.153(5)
β, deg	106.301(4)	82.584(5)
γ, deg	90	79.009(5)
V, Å^3	3069.6(4)	1266.98(12)
Z	2	2
d_{calcd}, g cm^{-3}	1.151	1.137
F(000)	1156	470
μ(Mo Kα), mm^{-1}	0.395	0.439
cryst dimens, mm	0.6 × 0.5 × 0.2	0.5 × 0.5 × 0.4
θ_{min}, θ_{max}, deg	3.22, 25.02	3.30, 25.02
range of indices (hkl)	−13 to +12, 0−18, 0−21	−10 to +10, −12 to +12, 0−16
no. of rflns collcd	5860	4627
no. of indepdt rflns	5397 (R(int) = 0.0691)	4463 (R(int) = 0.0181)
no. of data/restraints/params	5386/0/306	4456/0/244
goodness of fit on F^2	1.129	1.139
final R indices ($I > 2\sigma(I)$)	R1 = 0.0826, wR2 = 0.1866	R1=0.0647, wR2=0.1823
R indices (all data)	R1 = 0.1390, wR2 = 0.2308	R1 = 0.0724, wR2 = 0.2890
min, max resid density, e Å^{-3}	−0.268, 0.675	−0.362, 0.438

Scheme 1



less than 10% of **4** of the overall initial Ti concentration. The UV−vis−near-IR spectrum gave a single band in the near-IR region at λ_{max} 940 nm in addition to a band at 600 nm, apparently arising from the overlap of the bands of **3** and **4**. The band at 940 nm is indicative of the presence of **6** (compounds $(C_5H_{5-n}Me_n)_2TiCl_2/Mg/THF/Me_3SiC{\equiv}CSiMe_3$ (n = 0−5), λ_{max} 915−1060 nm, $\epsilon = 10^2$ cm^2 mmol^{-1}).[1b] Heating of the hexane solution to 60 °C led to a decrease of the intensity of this band to about half. Standing at room temperature overnight, however, restored the initial intensity of the band. The EPR signals of **3** and **4** did not change. Further, the hexane was replaced by THF and excess Mg turnings were added. After the mixture was heated to 60 °C for 3 h and worked up with hexane, the UV−vis spectrum did not show the band at 940 nm. The intensity of the EPR signal of **4** considerably increased compared to that of **3**.

X-ray Crystal Structure Analyses of 3 and 4. A dark blue crystal fragment of **3** and a green crystal fragment of **4** were mounted into Lindemann glass capillaries under purified nitrogen in a glovebox (mBraun Labmaster 130) that were sealed by wax. The X-ray measurements were carried out on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at room temperature. The intensity data were collected by $2\theta/\omega$ scans and were corrected for the Lorentz and polarization effects. No absorption corrections were applied. The structures were solved by Patterson and Fourier methods, which revealed the locations of the non-hydrogen atoms. The atomic coordinates and anisotropic thermal parameters were refined using the SHELX-76 program.[10] The final refinements were performed by the full-matrix least-squares method on all unique F_o^2 data using the SHELXL-93 program.[11] In **3** the carbon atoms of

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the trimethylsilyl group (C(61), C(62), C(63)) were found to be disordered. They appear in two different positions and were therefore refined as split atoms (C(61) and C(61A), etc.) with occupancy factors of 0.642 and 0.358 for the two rotamers. The hydrogen atoms H(1) and H(2) were clearly located in a difference electron density map and were refined isotropically. Contributions of the hydrogen atoms of the methylene groups and all other hydrogen atoms were included using a riding model. The PC ULM package[10] was used for further calculations. Crystal data and details on the data collection and refinement are given in Table 1.

Results and Discussion

Reduction of $[C_5Me_4(SiMe_3)]_2TiCl_2$ (1) by Mg in THF. The reduction of $[C_5Me_4(SiMe_3)]_2TiCl_2$ (**1**) by excess magnesium turnings in THF affords the blue crystalline compound $\{[\eta^5\text{-}C_5Me_4SiMe_2(\mu\text{-}CH_2\{Mg,Mg\})][\eta^5\text{-}C_5Me_4(SiMe_3)]Ti^{III}(\mu\text{-}H)_2Mg(THF)\}_2$ (**3**) as the only isolable titanium-containing product (Scheme 1). The EPR spectra of the reacting system revealed the transient formation of $[C_5Me_4(SiMe_3)]_2TiCl$[9] (**2**) and finally the presence of only one product, characterized by the triplet splitting (1:2:1) $a = 7.4$ G at $g = 1.9905$ and low-intensity satellite spectra reflecting the coupling of the Ti(III) d^1 electron to the ^{49}Ti and ^{47}Ti isotopes (natural abundances 5.5% and 7.7%), $a_{Ti(7/2)} = a_{Ti(5/2)} = 6.5$ G. The values of the g factor, triplet splitting (7.4 G), and a_{Ti} coupling are very close to the parameters of the $[(\eta^5\text{-}C_5H_{5-n}Me_n)_2Ti(\mu\text{-}H)_2Mg(OEt_2)(\mu\text{-}X)]_2$ ($n = 0-5$; X = Cl, Br) complexes, whose X-ray structures have been determined for $n = 4$ and X = Cl, Br.[12] The triplet splitting has been assigned to the coupling of the Ti(III) d^1 electron with two equivalent hydrogen nuclei in the hydride bridges,[13] binding a titanocene moiety to the magnesium atom. The presence of the hydride bridges in **3** was further corroborated by a broad and intense absorption band at 1330 cm^{-1} attributable to the vibration of bridging hydride bonds. Such absorption bands have been observed in the dimeric titanocenes $[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2][(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)]_2$[14] and $[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_2Me_3)_2][\eta^5\text{-}(C_5H_2Me_3)Ti(\mu\text{-}H)]_2$[1b] at 1227 and 1206 cm^{-1}, respectively. On the basis of these results, compound **3** was provisionally assigned to the structure **5** (Scheme 1), containing bridging chloride ligands between the two magnesium atoms.[15] However, the EDX measurements showed the absence of chlorine atoms in **3** and thus made the assignment to **5** impossible. Light was shed on the structure by an X-ray single-crystal analysis, which revealed that the dimerization of the titanocene hydride−magnesium hydride complex is accomplished via two electron-deficient Mg−C−Mg bonds.

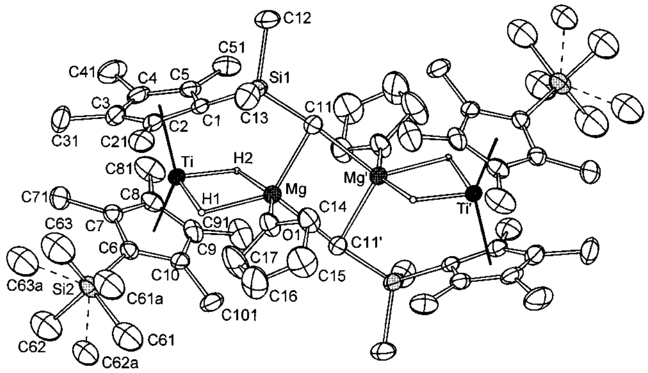

Figure 1. ORTEP drawing of **3** with ellipsoids drawn at the 30% probability level.

Table 2. Selected Bond Distances and Bond Angles for 3

(a) Bond Distances (Å)

Ti−CE(1)	2.114(6)	Ti−CE(2)	2.097(6)
Ti−C(1)	2.398(6)	Ti−C(2)	2.432(6)
Ti−C(3)	2.487(6)	Ti−C(4)	2.461(6)
Ti−C(5)	2.398(6)	Ti−C(6)	2.397(6)
Ti−C(7)	2.406(6)	Ti−C(8)	2.435(6)
Ti−C(9)	2.445(6)	Ti−C(10)	2.412(6)
Ti−H(1)	1.83(5)	Ti−H(2)	1.67(7)
Mg−H(1)	1.96(5)	Mg−H(2)	2.01(7)
Mg−O(1)	2.141(5)	Mg−C(11)	2.227(6)
Mg−C(11)′	2.348(6)	Si(1)−C(1)	1.875(6)
Si(1)−C(11)	1.850(6)	Si(1)−C(12)	1.879(7)
Si(1)−C(13)	1.871(8)	Si(2)−C(6)	1.859(6)

(b) Bond Angles (deg)

H(1)−Ti−H(2)	80(3)	H(1)−Mg−H(2)	70(2)
C(11)−Mg−C(11)′	101.0(2)	Mg−C(11)−Mg′	79.0(3)
Si(1)−C(11)−Mg	95.7(3)	Si(1)−C(11)−Mg′	174.5(3)
C(11)−Si(1)−C(1)	113.5(3)	C(11)−Si(1)−C(12)	112.0(3)
C(11)−Si(1)−C(13)	108.5(3)	O−Mg−C(11)	99.3(2)
O−Mg−C(11)′	94.1(2)	CE(1)−Ti−CE(2)	143.5(2)

Molecular Structure of $\{[\eta^5\text{-}C_5Me_4SiMe_2(\mu\text{-}CH_2\{Mg,Mg\})][\eta^5\text{-}C_5Me_4(SiMe_3)]Ti^{III}(\mu\text{-}H)_2Mg(THF)\}_2$ (3). The crystal structure of **3** with the atom-numbering scheme is shown in Figure 1. The pseudotetrahedrally coordinated Ti(III) atom is linked to a pentacoordinated Mg(II) atom directly *via* two hydride bridges and, remotely, *via* the magnesium−methylene Mg−C11 bond. The methylene group is attached to the dimethylsilylene substituent of the bridging cyclopentadienyl ligand. Its carbon atom is pentacoordinated, since it binds two magnesium atoms of both monomeric units of the centrosymmetric dimer. The magnesium atoms are coordinated in a rather irregular way by two hydride ligands, two methylene carbon atoms, and one oxygen atom of the THF ligand.

Selected geometric parameters of **3** are listed in Table 2. The Ti−CE(1) (CE(1) = centroid of the C(1)−C(5) ring) distance is only ca. 0.01 Å longer than the Ti−CE(2) (CE(2) = centroid of the C(6)−C(10) ring) distance, and both of them fall in the range of Ti−CE distances observed in compounds **1** and **2**. The CE(1)−Ti−CE(2) angle of 143.5(2)° is close to that of **2** (144.4(1)°),[9] and the angle between the normals of the least-squares planes of the cyclopentadienyl rings, $\phi = 145.8°$, is even larger than that in **2**. The Ti−H bonds are ca. 0.2 Å shorter than the Mg−H bonds, and both are in the ranges of values observed in the aforementioned dimeric hydrides $[(\eta^5\text{-}C_5HMe_4)_2Ti(\mu\text{-}H)_2Mg(OEt_2)(\mu\text{-}X)]_2$ (X = Cl, Br)[12] and in the trinuclear $[(C_5H_{5-n}Me_n)_2Ti(\mu\text{-}H)_2]_2Mg$ ($n = 3-5$) complexes.[16] The bridging hydride skeleton is bent toward the side of the non-bridged $C_5Me_4SiMe_3$ ligand so that the angle between

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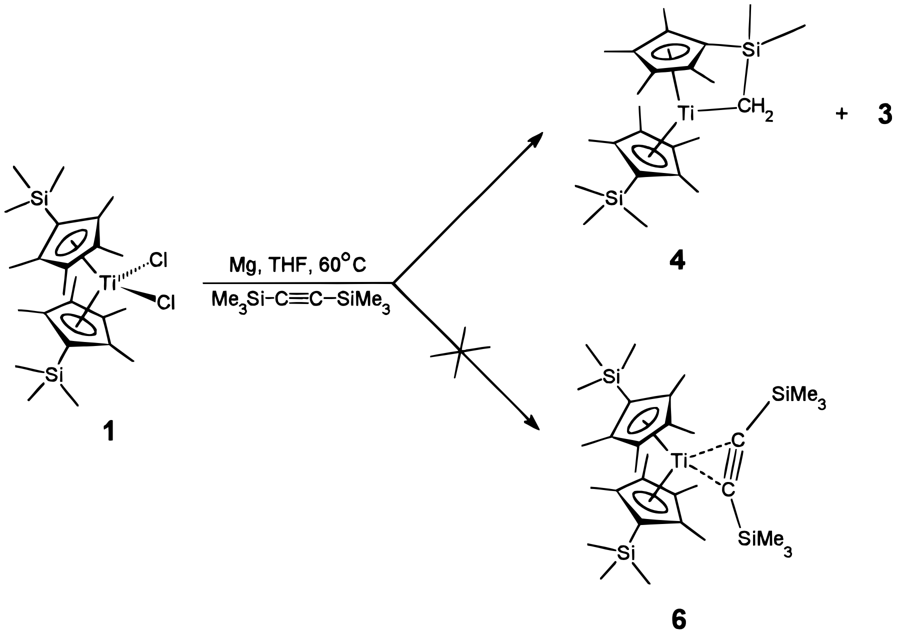
[15] The X-ray structure of $[(\eta^5\text{-}C_5HMe_4)_2Ti(\mu\text{-}H)_2Mg(THF)(\mu\text{-}Cl)]_2$ (obtained from the $(C_5HMe_4)_2TiCl_2$/Mg/THF system, has been communicated: Horáček, M.; Gyepes, R.; Varga, V.; Císařová, I.; Mach, K. XIth FECHEM Conference on Organometallic Chemistry, Parma, Italy, Sept 1995; Abstracts, P89, p 137.

Scheme 2



normals of the H1,Ti,H2 and H1,Mg,H2 planes amounts to about 165°. The SiMe$_3$ group of the nonbridging C$_5$Me$_4$(SiMe$_3$) ligand is disordered. This disorder can be described as a superposition of two rotamers. The Si(2) atom is displaced from the ring plane toward the Ti atom by 0.30 Å, whereas the Si(1) atom of the bridging silylene group is declined from the ring plane farther away from the Ti atom by 0.51 Å. The Si(1)-C(11) bond is shorter by ca. 0.02 Å than the other Si(1)−C bonds. The Mg−C(11) bond (2.227(6) Å) is remarkably shorter than the bridging Mg−C(11)′ bond (2.348(6) Å). The geometry of the bridges is further determined by the bridging angles Mg−C(11)−Mg′ = 79.0(3)° and C(11)−Mg−C(11)′ = 101.0(2)°. The structure of the three-center−two-electron Mg−C−Mg bond is known in dialkylmagnesium polymers [MgMe$_2$]$_n$,[17b] [MgEt$_2$]$_n$,[17c] and [MgPh$_2$]$_n$,[17d] in the [Mg(p-tolyl)$_2$(THF)]$_2$ dimer,[17d] and in the [Ph$_2$MgPh$_2$MgPh$_2$]$^{2-}$ [17e] and [Et$_2$Mg-Et$_2$MgEt$_2$]$^{2-}$ complex dianions.[17f] The two Mg−μ-C bonds in the Mg−C−Mg bridge are either equal or slightly different, with bond lengths in the range 2.24−2.36 Å. The bridging angles Mg−C−Mg and C−Mg−C span the values 73.2−77.7 and 102.5−114.4°, respectively. The values of the relevant angles in **3** are slightly outside the ranges mentioned, likely as a result of bulkiness of the titanocene moiety linked to the magnesium hydride species.

The metal atoms Ti, Mg, Ti′, and Mg′ form a planar zigzag structure with a Ti−Mg−Mg′ angle of 141.8(2)°. The hydride atoms H(1) and H(2) lie on one side, deviating by 0.21 and 0.17 Å from the plane of the metal atoms, and the oxygen of THF is on the other side, toward the methylene bridge, 0.30 Å away from the plane. The Mg−O distance of 2.141(5) Å falls into the range of distances found in organomagnesium−THF complexes.[17a] The least-squares plane of the THF ring is inclined toward the other monomeric unit. The Ti−Mg and Mg−Mg′ distances are 2.945(2) and 2.912(4) Å, respectively, both outside the range of bonding interaction.

Reduction of (C$_5$Me$_4$SiMe$_3$)$_2$TiCl$_2$ (1) by Mg in THF/Me$_3$SiC≡CSiMe$_3$. The presence of bis(trimethylsilyl)acetylene does not lead to the formation of the expected diamagnetic complex [C$_5$Me$_4$(SiMe$_3$)]$_2$Ti[η^2-C$_2$(SiMe$_3$)$_2$] (**6**) at 60 °C, as it is common in the (C$_5$H$_{5-n}$Me$_n$)$_2$TiCl$_2$/Mg/THF/Me$_3$SiC≡CSiMe$_3$ (n = 0−5) systems, which afford the (C$_5$H$_{5-n}$Me$_n$)$_2$Ti[η^2-C$_2$(SiMe$_3$)$_2$] complexes in quantitative yields.[1b] Instead, the paramagnetic light green product **4** has been obtained in a yield of 75% in addition to a small amount of **3** (~10%) (Scheme 2). The infrared spectrum of **4** shows the presence of an SiMe$_3$ group (835 and 1244 cm^{-1}) and the absence of any absorption in the region 1500−2000 cm^{-1} which could indicate the presence of a π-coordinated triple bond.[1] The EPR spectrum in a frozen toluene glass gives a strongly anisotropic **g** tensor of a trigonally coordinated Ti(III) compound resembling the spectra of monomeric titanocene halides[18a,b] or (C$_5$Me$_5$)$_2$-TiMe,[18b] (C$_5$HMe$_4$)$_2$TiMe,[5d] (C$_5$Me$_5$)$_2$TiCH$_2$CMe$_3$,[18c] or [(η^1:η^5-C$_5$Me$_4$CH$_2$)(η^5-C$_5$Me$_5$)Ti].[6c] The X-ray crystal structure determination shows that both chlorine ligands have been released from **1** and one hydrogen atom has been abstracted from one SiMe$_3$ group to give [η^5:η^1-C$_5$Me$_4$SiMe$_2$CH$_2$][η^5-C$_5$Me$_4$(SiMe$_3$)]Ti^{III}, where the dimethylsilylene group is σ-bonded to Ti(III) *via* a bridging methylene group. The GC−MS analysis of volatiles from the reaction mixture proved that bis(trimethylsi-

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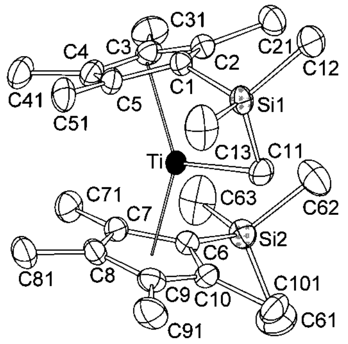

Figure 2. ORTEP drawing of **4** with ellipsoids drawn at the 30% probability level.

Table 3. Selected Bond Distances and Angles for 4

(a) Bond Distances (Å)			
Ti-C(11)	2.204(5)	Ti−C(1)	2.330(4)
Ti−C(2)	2.371(5)	Ti−C(3)	2.461(5)
Ti−C(4)	2.461(5)	Ti−C(5)	2.354(5)
Ti−C(6)	2.363(5)	Ti−C(7)	2.382(4)
Ti−C(8)	2.411(5)	Ti−C(9)	2.410(5)
Ti−C(10)	2.386(5)	Ti−CE(1)	2.068(5)
Ti−CE(2)	2.060(5)	Si(1)−C(1)	1.876(5)
Si(1)−C(11)	1.836(5)	Si(1)−C(12)	1.869(5)
Si(1)−C(13)	1.864(7)	$(Si(2)-C)_{av}$	1.863(7)
(b) Bond Angles (deg)			
CE(1)−Ti−CE(2)	146.1(2)	Ti−C(11)−Si(1)	97.9(2)
CE(1)−Ti−C(11)	103.6(2)	CE(2)−Ti−C(11)	109.6(2)
C(11)−Si(1)−C(1)	93.1(2)	C(11)−Si(1)−C(13)	111.3(3)
C(11)−Si(1)−C(12)	118.4(3)	C(13)−Si(1)−C(12)	106.3(3)
C(13)−Si(1)−C(1)	113.9(3)	C(12)−Si(1)−C(1)	113.9(2)

lyl)acetylene remained unchanged. This is in contrast to the thermolysis of $(C_5Me_5)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$, affording the allyl diene complex $[\eta^3{:}\eta^4\text{-}C_5Me_3(CH_2)_2)](\eta^5\text{-}C_5Me_5)Ti$[6a] and a mixture of cis and trans isomers of bis(trimethylsilyl)ethene.[1b] The acceptor of the hydrogen was not identified; it is not a titanium compound since compound **3**, the eventual hydrogen acceptor, is obtained in only ca. 10% yield for the BTMSA/Ti molar ratio 2 and its content further decreases with a larger excess of BTMSA.

Molecular Structure of $[\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2][\eta^5\text{-}C_5Me_4(SiMe_3)]Ti^{III}$ (4). The X-ray crystal structure of **4** is shown in Figure 2. Important bond distances and valence angles of **4** are given in Table 3. The central Ti(III) atom is η^5-bonded to two cyclopentadienyl rings and σ-bonded to a methylene group acting as a bridge to the Si atom. The Ti−CE(1) and Ti−CE(2) (CE(1) = centroid of the C(1)−C(5) ring, CE(2) = centroid of the C(6)−C(10) ring) distances are virtually equal and do not differ from the values typical of $(C_5Me_5)_2Ti$ derivatives. The C−C bonds in both rings and the bond distances between ring carbon atoms and Me carbon atoms are equal within narrow limits, close to the errors of the measurements. The Ti−C(11) σ-bond length of 2.204(5) Å is comparable with the Ti−C(sp^3) distances 2.231(5) Å in $(C_5Me_5)_2TiCH_2CMe_3$[18c] and 2.281(14) Å in $[(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)(\eta^5\text{-}C_5Me_5)Ti]$.[5c] The bridging Si(1)−C(11) bond is remarkably shorter (by 0.03−0.04 Å) than the other Si(1)−C and Si(2)−C bonds. The bent-titanocene structure of **4** shows a large CE(1)−Ti−CE(2) angle of 146.1(2)°. The angle between the normals of the least-squares planes of the cyclopentadienyl rings $\phi = 149.8°$. This angle is larger than the analogous angle in the trigonal Ti(III) complexes $[C_5Me_4(SiMe_3)]_2TiCl$[9] and $(C_5Me_5)_2TiCH_2CMe_3$[18c] and in **3**. The Ti−C(11) vector is slightly inclined toward the bridging cyclopentadienyl ligand, as the CE(1)−Ti−C(11) angle is smaller (103.6°) than the CE(2)−Ti−C(11) angle (109.6°). The bridging C(11) and Si(1) atoms deviate from the CE(1),Ti,CE(2) plane to the side opposite to Si(2). The $Ti-CH_2-SiMe_2-$ structural arrangement is known only for the Ti(IV) 1-sila-3-titanacyclobutane compound $Me_2Si(C_5H_4)_2Ti(CH_2)_2SiMe_2$, where the Ti−$CH_2$ bond lengths are 2.175(4) and 2.148(6) Å and Si−CH_2 bond lengths are 1.868(4) and 1.869(4) Å.[19]

Mechanistic Considerations. The reaction pathways to both **3** and **4** involve the reduction of **1** to $[C_5Me_4(SiMe_3)]_2TiCl$ (**2**). The formation of **2** is indicated by a transient blue color of the THF solution (λ_{max} = 560 nm) and by an EPR signal at $g = 1.953$ ($\Delta H = 14$ G).[9] Then, the EPR signals of **3** and **4** grow in intensity while that of **2** diminishes. In the absence of BTMSA, the transient formation of chlorine-bridged **5** on the pathway from **2** to **3** cannot be excluded, since the EPR spectra of both compounds are nearly identical.[12,15] The final blue product of the reaction, however, always showed the absence of chlorine. The source of hydrogen supplied to form the hydride bridges as well as the acceptor of hydrogen evolved from the $SiMe_3$ group are unknown. Even if the hydrogen atom from the $SiMe_3$ group is transferred to one Ti−H−Mg bond of **3**, the hydrogen for the other bridging bond should come from another source. Of two possible sources, the titanocene moiety or THF, a titanocene product arising from the hydrogen abstraction has not been found. The investigation of the $CpTiCl_3$/Mg/THF-d_8 system led to the conclusion that hydrogen is abstracted from the cyclopentadienyl ligand.[13b] However, this can hardly be the case in the present system, which does not contain sp^2 C−H bonds. Hence, the source of hydrogen for **3** has to be sought in the Mg/THF system. Coupling reactions of THF induced by the Mg/transition-metal system are known.[20]

The role of bis(trimethylsilyl)acetylene in the formation of **4** has been rationalized by several experiments. Although the formation of $[C_5Me_4(SiMe_3)]_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ (**6**) has not been observed in the experiment carried out at 60 °C, the reduction of $[C_5Me_4(SiMe_3)]_2TiCl$ (**2**) at 0 °C in the presence of a 9-fold excess of BTMSA afforded a dark yellow oil containing, according to EPR measurements, less than 10% of **4** and less than 5% of **3**. The overwhelming presence of the yellow compound **6** has been inferred from the presence of the absorption band at 940 nm, whose presence in the region 915−1060 nm is typical of all the $(C_5H_{5-n}Me_n)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ ($n = 0{-}5$) compounds.[1b] Heating of this mixture in hexane to 60 °C in a closed system resulted in the decrease in concentration of **6**, whereas cooling to room temperature reversibly restored the initial concentration of **6**. Compounds **3** and **4** remained in unchanged amounts. Heating of the initial sample of crude **6** with Mg in THF for 3 h at 60 °C resulted in complete conversion of **6** to **4**, whereas the amount of **3** remained unchanged. Heating of **3** with BTMSA up to 100 °C for 8 h did not produce **4** at all. These experiments point to the crucial intermediate formation of **6**, which further reacts with magnesium to give **4**. On the other hand, compound **3** is not the precursor of **4**. As compound **6**

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cannot be separated from the mixture with **3** and **4**, more effort will be paid to obtaining pure **6**, likely by using a higher excess of BTMSA and a lower reaction temperature. It is our aim to use compound **6** as a precursor for the thermal generation of the titanocene $[C_5Me_4(SiMe_3)]_2Ti$ species to follow the previous studies on the equilibria of $(C_5Me_5)_2Ti$ and $(C_5HMe_4)_2Ti$ species with their hydride isomers and on the hydrogen elimination thereof.

Conclusions. Although the mechanisms of the formation of **3** and **4** remain unknown, the structures of both compounds indicate that the hydrogen abstraction from the trimethylsilyl substituent at the otherwise methylated cyclopentadienyl ligand is feasible. The formation of compound **4** further shows that hydrogen abstraction from the $SiMe_3$ group is preferred compared to that from the methyl substituent. The suggested insertion of dipolar substrates into the Ti−CH_2− σ-bond of **4** will lead to an easy synthesis of titanocene Ti(III) bridged and nonbridged derivatives in a straightforward way.

Acknowledgment. This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. A4040711), by the Grant Agency of the Czech Republic (Grant No. 203/96/0948), and by the Volkswagen Stiftung. The Grant Agency of the Czech Republic (Grant No. 203/96/0111) sponsored an access to the Cambridge Structure Data Base. We thank Mrs. G. Dörfner for the EDX measurements.

Supporting Information Available: Tables of crystal data, atomic coordinates, isotropic and anisotropic thermal parameters, bond distances, valence angles, least-squares planes and atomic deviations therefrom, and important intermolecular contacts and figures giving views of the unit cell for **3** and **4** (29 pages). Ordering information is given on any current masthead page.

OM9701783