Titanium–Magnesium-Assisted Scission of 1,4-Bis(trimethylsilyl)-1,3-butadiyne: Synthesis and Structure of a Titanium(III) Tweezer Complex, [(η5-C5HMe4)2Ti(η1-C≡CSiMe3)2][Mg(THF)Cl]

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The reaction of $(C_5HMe_4)_2TiCl_2$ with Mg in THF in the presence of $Me_3SiC≡CC≡CSiMe_3$ afforded the bimetallic $Ti^{III}–Mg$ tweezer complex $[(η^5-C_5HMe_4)_2Ti(η^1-C≡CSiMe_3)_2][Mg(THF)-Cl]$ (1). Complex 1 crystallizes in the monoclinic space group $P2_1/c$ with $a = 19.510(6)$ Å, $b = 10.103(4)$ Å, $c = 19.817(7)$ Å, $β = 112.50(2)°$, $Z = 4$, and $V = 3608.6$ Å^3. The Mg atom is embedded between the C≡C bonds in a π-bonding position at an average Mg–C distance of 2.275 Å to the inner and 2.463 Å to the outer carbon atoms.

Our permanent interest in the catalytic properties of low-valent titanium complexes led us to study the conditions for the preparation and stabilization of titanocene species $(C_5H_{5-n}Me_n)_2Ti^{II}$ ($n = 0, 1, 3–5$).[1] Thermally stable titanocene (Ti^{II}) complexes are generally obtained by the reduction of the corresponding titanocene dichlorides with Mg in THF in the presence of π or lone-pair electron donor ligands, which are able to partly accommodate the Ti d^2 electrons in a low-energy empty orbital. In this way, the $Cp_2Ti(CO)_2$ ($Cp = η^5-C_5H_5$),[2a] $(C_5Me_5)_2Ti(CO)_2$,[2b] $Cp_2Ti(CO)PMe_3$,[3] $Cp_2Ti(PMe_3)_2$,[4] $Cp_2Ti(PMe_3)(RC≡CR)$,[5] $(C_5Me_5)_2Ti(CH_2=CH_2)$,[6] $Cp_2Ti(CO)(RC≡CR)$,[7] and $Cp_2Ti(RC≡CR)$[8] complexes were prepared. Well-defined complexes of the last type were obtained with bis(trimethylsilyl)acetylene, where the acetylene was classified as a four-electron ligand.[9] The homologous 1,4-bis(trimethylsilyl)-1,3-butadiyne (BSD),[10] which is known to be an extremely stable diyne, can afford, analogously

to other 1,3-diynes, a variety of metal complexes differing in their bonding modes (Chart I). Among the listed structural types, the titanium complex of type IV has been prepared. The complex containing a bridging $μ$-(1-3-η): $(2-4-η)$-1,4-diphenyl-*trans,trans*-1,3-butadiene ligand was obtained from titanocene(III) chloride and sodium in the presence of 1,4-diphenyl-1,3-butadiyne (DBD).[11] The DBD–Pt complexes DBD·Pt(PR$_3$)$_2$ and DBD·(Pt(PR$_3$)$_2$)$_2$[12] belong to types I and III, respectively, and the BSD complex of type II was found for permethylcalcocene, $(C_5Me_5)_2Ca·BSD$.[13] In addition, BSD forms complexes with iron carbonyls,[14] $CpCo(CO)_2$,[15] and $Co_2(CO)_8$.[16] In the last case, the $Co_2(CO)_6·BSD$ complex induces the cyclotrimerization of BSD to tris((trimethylsilyl)ethynyl)tris(trimethylsilyl)benzenes. Pt and Rh complexes catalyze the hydrosilylation of BSD; the regioselectivity of the addition is indicative of the formation of a metallacyclopropene intermediate of type I.[17] Recently, the scission of BSD has been reported to be induced by $Cp_2Ti(Me_3-SiC≡CSiMe_3)$, yielding dimeric $(Cp_2TiC≡CSiMe_3)_2$.[18]

We have attempted to prepare a titanocene–BSD complex using $(C_5HMe_4)_2TiCl_2/BSD/Mg$ in THF, anticipating structure IV as most probable. However, instead of a BSD complex we obtained an unexpected titanocene diacetylide "tweezer"[19] complex (1) containing the embed-

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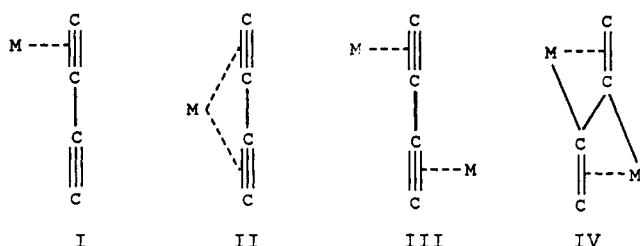
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Chart I

I   II   III   IV

ded [Mg(THF)Cl] species. Here we report the procedure for its synthesis, its crystal structure, and other characteristics.

Experimental Section

General Data. Manipulation with all reagents, synthesis, and spectroscopic measurements were carried out under vacuum using all-sealed devices equipped with breakable seals. The solvents THF, hexane, toluene, and 2-methyltetrahydrofuran (MTHF) were purified by conventional methods, dried by refluxing over $LiAlH_4$, and stored as solutions of dimeric titanocene $(C_{10}H_8)[(C_5H_5)TiH]_2$.[20] 1,4-Bis(trimethylsilyl)-1,3-butadiyne (BSD) was synthesized from hexachlorobutadiene, trimethylsilyl chloride, and magnesium:[10] IR (Nujol, cm^{-1}) 2064 vs, $\nu(C\equiv C)$. No impurities were found by MS and NMR analyses. Magnesium turnings (Fluka, purum for Grignard reactions) were activated by performing the synthesis of 1 with a large excess of nonactivated magnesium. In this case, a long irreproducible induction period was observed. Product 1 was worked up as described below, and the activated Mg turnings were washed with THF and dried in vacuo. $(C_5HMe_4)_2TiCl_2$ was prepared according to the literature procedure.[21] The EPR spectra of solutions of 1 were measured on an ERS-220 spectrometer (ZWG, Berlin) equipped with a proton magnetometer and a variable-temperature unit. Measurements were performed at room temperature and, for toluene and MTHF solutions, also in a glassy state at –120 °C. UV–vis spectra were measured in the range 270–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Samples in capillaries for MS analysis were opened and inserted into the direct inlet of a JEOL D-100 spectrometer under argon. Infrared spectra were recorded on a UR-75 instrument (Zeiss, Jena, Germany). Samples in Nujol mulls were prepared by grinding between rough glass plates under argon. ^1H and ^{13}C NMR spectra were measured on a Varian VXR-400 spectrometer.

Preparation of [(C$_5$HMe$_4$)$_2$Ti(C≡CSiMe$_3$)$_2$][Mg(THF)Cl] (1). $(C_5HMe_4)_2TiCl_2$ (0.18 g, 0.5 mmol) and 1,4-bis(trimethylsilyl)-1,3-butadiyne (BSD) (0.11 g, 0.55 mmol) were dissolved in 50 mL of THF and the solution was poured onto activated magnesium turnings (ca. 0.1 g). The reaction began immediately, as demonstrated by the color turning from red to blue; later, it turned to dirty green and finally to orange-brown. The reaction in a stirred mixture was complete within 2 h. The solution was separated from the magnesium pieces, and THF was evaporated in vacuo. The brown residue was repeatedly extracted with hexane to yield a yellow-brown solution. Brown crystals separated from a concentrated solution upon cooling. The mother liquor was decanted off, the crystals were dissolved in hexane, and the product was recrystallized by the same procedure. The yield of crystalline product was 0.12 g (0.2 mmol, 40% based on titanium). Anal. Calcd for $C_{32}H_{52}ClOSi_2MgTi$: C, 62.34; H, 8.50. Found: C, 61.56; H, 8.27. IR (Nujol, cm^{-1}): 1930 ($\nu(C\equiv C)$), 1020 (ν-(C—O), THF). EPR (toluene, 20 °C): $g = 1.9935$, $\Delta H_{pp} = 2.5$

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G, $a_{Ti} = 7.3$ G. EPR (toluene, –120 °C): $g_1 = 2.0015$, $g_2 = 1.9938$, $g_3 = 1.9876$, $g_{av} = 1.9943$. UV–vis (hexane, λ_{max} in nm (intensity)): 380 (vs), 400 (vs), 550 (w), 740 (vw). MS (direct inlet, 75 eV): decomposition at 220 °C.

Attempted Scission of BSD in the Presence of (C$_5$HMe$_4$)$_2$-Ti(Me$_3$SiC≡CSiMe$_3$). $(C_5HMe_4)_2Ti(Me_3SiC\equiv CSiMe_3)$ was prepared analogously to $(C_5Me_5)_2Ti(Me_3SiC\equiv CSiMe_3)$.[9b] (C$_5$-HMe$_4$)$_2$TiCl$_2$ (0.36 g, 1 mmol), Mg turnings (0.2 g, 8 mmol), degassed bis(trimethylsilyl)acetylene (0.5 mL, 2 mmol), and dry degassed tetrahydrofuran (THF) (30 mL) were charged into an evacuated ampule and stirred at room temperature for 20 h. All volatiles were removed under vacuum at 60 °C, and the yellow residue was extracted with hexane. Yellow crystals were obtained by cooling of the concentrated solution (the yield of crystals was 0.15 g (33%)). The mother liquor was evaporated, and the residue was extracted by condensing hexane vapor on the solid: first 1 mL of the extract was discarded; the other portion was evaporated and yielded 0.25 g (54%) of yellow product. The overall yield was 0.40 g (87%). Both products gave identical NMR and MS spectra attributable to $(C_5HMe_4)_2Ti(Me_3SiC\equiv CSiMe_3)$. ^1H NMR (400 MHz, C$_6D_6$, 25 °C): δ –0.049 (s, 18 H), 1.301 (s, 12 H, 1-Me, 4-Me), 2.116 (s, 12 H, 2-Me, 3-Me), 5.093 (s, 2 H, 5-H). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 3.46 (q, 6 C), 13.50 (q, 4 C, 1-Me, 4-Me), 13.57 (q, 4 C, 2-Me, 3-Me), 113.00 (d, 2 C, C-5), 121.53 (s, 4 C, C-1, C-4), 125.02 (s, 4 C, C-2, C-3), 248.35 (s, 2 C, C≡C). MS (direct inlet, 50–90 °C; m/z (relative intensity)): 460 (M$^+$, not seen), 290 (43), 275 (2), 170 (7), 155 (100), 121 (2). Anal. Calcd for $C_{28}H_{44}Si_2Ti$: C, 67.78; H, 9.63. Found: C, 67.65; H, 9.49.

The solution of $(C_5HMe_4)_2Ti(Me_3SiC\equiv CSiMe_3)$ in hexane (0.1 M, 5 mL) was added to finely crystalline BSD (60 mg, 0.3 mmol) under vacuum, and the mixture was heated to 70 °C for 6 h in a sealed ampule. The reaction mixture turned slightly brownish compared to the untreated solution of $(C_5HMe_4)_2Ti(Me_3-SiC\equiv CSiMe_3)$. The mixture was evaporated, and the residue was carefully extracted by condensing hexane vapor on the solid. A trace of very soluble brown product was extracted first, followed by BSD. The yellow residue was, according to NMR and MS spectra, the unchanged $(C_5HMe_4)_2Ti(Me_3SiC\equiv CSiMe_3)$. The brown product was not isolated in a pure state because of its low amount. It cannot be $[(C_5HMe_4)_2Ti(C\equiv CSiMe_3)]_2$ because its high solubility in hexane is at variance with the low solubility of $[Cp_2Ti(C\equiv CSiMe_3)]_2$[18,22] and moderate solubility of (C$_5$HMe$_4$)$_2$-Ti(Me$_3$SiC≡CSiMe$_3$) (vide supra). In contrast, the preparation of $[Cp_2Ti(C\equiv CSiMe_3)]_2$ from $Cp_2Ti(Me_3SiC\equiv CSiMe_3)$ and BSD at room temperature, repeated by us according to ref 18, was found to be reproducible.

X-ray Crystal Structure Determination of 1. A brown rhombic platelet approximately 0.15 × 0.30 × 0.30 mm was mounted in a glass capillary under argon. Experimental details and crystal data for 1 are listed in Table I. The structure was solved (SDP) by a combination of direct methods and Fourier difference techniques and refined by the full-matrix least-squares method with anisotropic thermal parameters for all the non-hydrogen atoms. The positions of the H atoms were partly determined from a ΔF map and were partly calculated. All the H atoms were included in the structure factor calculations but not refined. The final positional and thermal parameters are given in Table II. Selected bond distances and angles are listed in Table III. Tables of anisotropic thermal parameters, complete bond distances, and valence angles have been deposited as supplementary material.

Results and Discussion

The reaction of $(C_5HMe_4)_2TiCl_2$ with activated Mg in THF in the presence of 1,4-bis(trimethylsilyl)-1,3-butadiyne (BSD) afforded an orange-brown solution characterized by a single EPR signal at $g = 1.9935$. After evaporation of THF the residue was extracted with hexane. Light brown crystals of 1 were isolated from the concentrated solution by cooling. The X-ray crystallographic study

Table I. Crystallographic Data for Complex 1

formula	$C_{32}H_{52}ClOSi_2MgTi$
fw	616.57
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	19.510(6)
b, Å	10.103(4)
c, Å	19.817(7)
β, deg	112.50(2)
V, Å^3	3608.6
Z	4
d_{calcd}, g cm^{-3}	1.135
μ(Mo Kα), cm^{-1}	3.97
cryst size, mm	0.15 × 0.30 × 0.30
temp, °C	20
diffractometer	Enraf-Nonius CAD4
radiation (λ, Å)	0.710 69
θ_{max}, deg	22
scan method	ω
no. of data collected	4442
no. of data with $I \geq 3\sigma(I)$	2370
no. of variables	343
R	0.050
R_w	0.054

Table II. Atomic Coordinates and B_{eq} Values (Å^2) for 1

atom	x	y	z	B_{eq}
Ti	0.15889(7)	0.0856(2)	0.69702(7)	3.49(3)
Cl	0.4202(1)	−0.0651(3)	0.8443(1)	5.80(6)
Si(1)	0.2524(2)	−0.1794(3)	0.9401(1)	6.23(8)
Si(2)	0.3989(1)	0.3619(3)	0.7553(1)	5.53(7)
Mg	0.3224(1)	0.0689(3)	0.8323(1)	3.90(6)
O	0.3659(3)	0.1777(6)	0.9260(3)	5.1(2)
C(1)	0.2070(4)	−0.0175(8)	0.8005(4)	3.8(2)
C(2)	0.2337(4)	−0.0719(9)	0.8597(4)	4.1(2)
C(3)	0.3517(5)	−0.180(1)	0.9984(5)	9.2(4)
C(4)	0.1965(5)	−0.114(2)	0.9920(5)	9.8(5)
C(5)	0.222(1)	−0.347(1)	0.9086(7)	10.2(7)
C(6)	0.2616(4)	0.1963(7)	0.7321(4)	3.4(2)
C(7)	0.3204(4)	0.2564(8)	0.7516(4)	3.8(2)
C(8)	0.3729(5)	0.440(1)	0.6645(5)	8.6(3)
C(9)	0.4835(5)	0.270(1)	0.7817(7)	11.7(5)
C(10)	0.4094(7)	0.499(1)	0.8211(6)	11.9(5)
C(11)	0.1181(4)	−0.1127(8)	0.6283(5)	5.3(2)
C(12)	0.1956(4)	−0.1271(8)	0.6599(4)	4.2(2)
C(13)	0.2286(4)	−0.0288(8)	0.6317(4)	4.5(2)
C(14)	0.1717(4)	0.0503(9)	0.5830(4)	4.9(2)
C(15)	0.1052(4)	−0.0038(9)	0.5801(5)	5.6(3)
C(16)	0.0627(4)	0.253(1)	0.6484(5)	6.3(3)
C(17)	0.1160(4)	0.3045(9)	0.7106(5)	5.5(2)
C(18)	0.1150(5)	0.226(1)	0.7689(4)	6.3(3)
C(19)	0.0606(4)	0.124(1)	0.7404(5)	7.3(3)
C(20)	0.0309(4)	0.142(1)	0.6663(6)	7.6(3)
C(21)	0.4412(5)	0.164(1)	0.9777(5)	8.3(3)
C(22)	0.4590(6)	0.295(1)	1.0144(6)	9.2(4)
C(23)	0.3926(6)	0.357(1)	1.0090(6)	10.4(4)
C(24)	0.3314(5)	0.281(1)	0.9493(5)	9.8(4)
C(111)	0.0646(5)	−0.2065(9)	0.6392(5)	7.8(3)
C(121)	0.2388(5)	−0.2406(8)	0.7069(4)	5.9(3)
C(131)	0.3090(4)	−0.0193(9)	0.6424(4)	5.8(2)
C(141)	0.1816(5)	0.1615(9)	0.5360(4)	7.0(3)
C(161)	0.0356(7)	0.312(1)	0.5738(6)	11.5(5)
C(171)	0.1564(5)	0.4351(9)	0.7148(7)	10.2(4)
C(181)	0.1465(8)	0.251(1)	0.8450(7)	11.6(5)
C(191)	0.0393(5)	0.026(1)	0.7858(6)	12.3(4)

Table III. Selected Bond Distances (Å) and Angles (deg) for 1[a]

Ti–C(1)	2.167(7)	Mg–Cl	2.276(4)
Ti–C(6)	2.164(7)	Mg–C(1)	2.269(8)
Ti–C(11)	2.382(8)	Mg–C(2)	2.456(9)
Ti–C(12)	2.465(8)	Mg–C(6)	2.281(7)
Ti–C(13)	2.493(9)	Mg–C(7)	2.469(9)
Ti–C(14)	2.393(9)	Mg–O	2.042(6)
Ti–C(15)	2.329(9)	Si(1)–C(2)	1.847(8)
Ti–CE(1)[b]	2.095	Si(1)–C(3)	1.837(9)
Ti–C(16)	2.433(9)	Si(1)–C(4)	1.88(1)
Ti–C(17)	2.415(9)	Si(1)–C(5)	1.83(1)
Ti–C(18)	2.39(1)	Si(2)–C(7)	1.844(8)
Ti–C(19)	2.41(1)	Si(2)–C(8)	1.85(1)
Ti–C(20)	2.401(9)	Si(2)–C(9)	1.79(1)
Ti–CE(2)	2.099	Si(2)–C(10)	1.86(1)
C(1)–C(2)	1.22(1)	C(6)–C(7)	1.22(1)
CE(1)–Ti–CE(2)	134.8		
C(1)–Ti–C(6)	86.1(3)	C(2)–Mg–C(6)	110.1(3)
Ti–C(1)–C(2)	178.0(7)	C(2)–Mg–C(7)	138.5(2)
C(1)–C(2)–Si(1)	165.4(7)	C(2)–Mg–Cl	105.4(2)
Ti–C(6)–C(7)	178.6(7)	C(2)–Mg–O	101.1(3)
C(6)–C(7)–Si(2)	164.6(7)	C(6)–Mg–C(7)	29.5(2)
C(1)–Mg–C(2)	29.5(2)	C(6)–Mg–Cl	124.2(3)
C(1)–Mg–C(6)	81.1(3)	C(6)–Mg–O	112.6(3)
C(1)–Mg–C(7)	110.3(3)	C(7)–Mg–Cl	109.2(2)
C(1)–Mg–Cl	120.3(2)	C(7)–Mg–O	94.2(3)
C(1)–Mg–O	118.8(3)	Cl–Mg–O	100.7(2)

[a] The C–C distances in cyclopentadienyl rings are in the range 1.37–1.42 Å (average 1.40 Å), and C–C(Me) distances in C_5HMe_4 ligands are 1.42–1.52 Å (average 1.49 Å). [b] CE is the centroid of the C_5HMe_4 ligand.
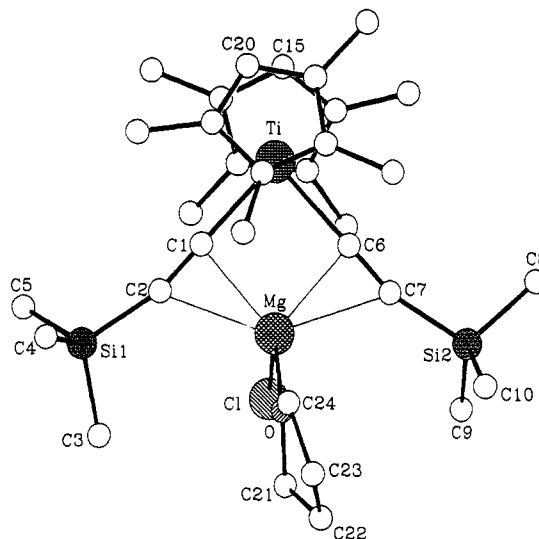

Figure 1. PLUTO drawing of $[(C_5HMe_4)_2Ti(C\equiv CSiMe_3)_2]$-$[Mg(THF)Cl]$ (1) with the atom-numbering scheme (carbon atoms of Me groups adjacent to ring carbon atoms C(11)–C(19) are denoted C(111)–C(191); hydrogen atoms are omitted for clarity).

established that compound 1 is $[(C_5HMe_4)_2Ti(\eta^1\text{-}C$ $\equiv CSiMe_3)_2][Mg(THF)Cl]$ with pseudotetrahedrally coordinated Ti and Mg atoms. A PLUTO drawing of 1 is shown in Figure 1. The titanium atom is π-bonded to two C_5HMe_4 ligands and σ-bonded to two (trimethylsilyl)-ethynyl groups. The C_5HMe_4 ligands are in a staggered configuration with the carbon atoms C(15) and C(20), bearing the hydrogen atoms, in positions where the C_5-HMe_4 ligands closely approach each other. The magnesium atom is located between the two arms of a tweezer formed by the acetylide groups in a π-bond manner and

bonded to one chlorine atom and to the oxygen atom of THF. The Ti and the acetylide carbon atoms lie in one plane with a maximum deviation of 0.04 Å. The magnesium atom is displaced from this plane by only 0.36 Å to the side of the chlorine atom.

The structure of 1 can be compared with that of the Ti(IV) tweezer complex $(C_5H_4SiMe_3)_2Ti(\sigma\text{-}C\equiv CSi\text{-}Me_3)_2\cdot FeCl_2$ (2) synthesized and characterized by Lang et al.[23] Although the cyclopentadienyl ligands and embedded metal chlorides are different and 1 contains Ti(III) (vide infra) and 2 Ti(IV), the geometries of both complexes are

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very similar. Both the CE–Ti–CE (CE = centroid of the cyclopentadiene ring) and (σ-C)–Ti–(σ-C) angles in **1** and **2** are practically the same (134.8 and 86.1° for **1** and 134.2 and 85.4° for **2**). The Ti—C≡C fragments are practically linear (average 178.3°) in **1**, whereas they are distinctly bent in **2** (171°), but the deviations from linearity in the C≡C—Si fragments (165 versus 163°) are practically the same. The Ti–(σ-C) bonds are slightly longer for **1** (2.165 Å) than for **2** (2.07 Å); this can be accounted for in terms of a larger radius of Ti(III) compared to that of Ti(IV) and some negative charge delocalization over the acetylenic bonds. In another Ti(III) complex, [Cp$_2$Ti(η^1-C≡CSi-Me$_3$)]$_2$[18,22] (**3**), the Ti–(σ-C) bond length was 2.06 Å; however, the acetylide groups were π-bonded to the other Ti atom and no charge was delocalized over these bonds. The C≡C bond lengths in **1** (1.22 Å), **2** (1.20 Å),[23] and **3** (1.25 Å)[22] differ only slightly.

The Ti–Mg distance of 3.21 Å does not imply any direct Ti–Mg bonding interaction. The position of the Mg atom between the acetylide fragments allows us to suggest that a π-bonding interaction is present. The average Mg–C bonding distances to the inner carbon atoms C(1) and C(6) (2.27 Å) and to the outer ones C(2) and C(7) (2.46 Å) are close to the known Mg–(π-C) bond lengths in crystalline Cp$_2$Mg (2.30 Å),[24a] CpMgBr·TMEDA (2.55 Å),[24b] and (η^5-indenyl)$_2$Mg (2.26 Å).[24c] The nature of bonding in such compounds is subject to discussion;[25] according to ab initio calculations[25c] the interaction of the 3s and the 3p orbitals of Mg with π-orbitals of ligands should result in negative charge delocalization over the π-ligands. The distances Mg–Cl (2.28 Å) and Mg–O(THF) (2.04 Å) have ordinary values for the tetrahedrally coordinated Mg atom.[26]
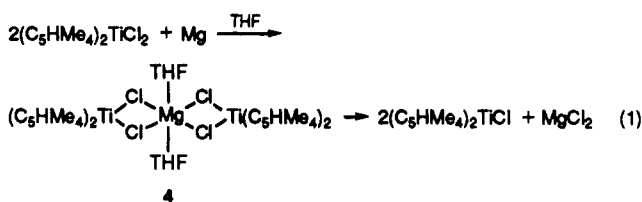
A variety of titanocene complexes with embedded transition-metal compounds, (C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSi-Me$_3$)$_2$·CuCl,[23] (C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CPh)$_2$·Ni(CO),[27] Cp$_2$-Ti(C≡CPh)$_2$·Ni(CO),[28] and Cp$_2$Ti(C≡CPh)$_2$·Pt(PR$_3$),[29] obviously belong to the same structural type. All of them were prepared by the reaction of (C$_5$H$_4$SiMe$_3$)$_2$Ti-(C≡CSiMe$_3$)$_2$[30] or Cp$_2$Ti(C≡CPh)$_2$ complexes[31] with stable transition-metal compounds, and their properties indicated that they contain Ti(IV).

Solutions of **1** in hexane, THF, toluene, and MTHF exhibited a single EPR signal at g = 1.9935 and ΔH_{pp} = 2.5 G with a($^{47/49}$Ti) = 7.3 G, and frozen toluene and MTHF solutions gave the same rhombic **g** tensor (g_1 = 2.0015, g_2 = 1.9938, g_3 = 1.9876 (g_{av} = 1.9943)). These results prove that **1** contains a Ti(III) atom and hence the complex can be formulated as the ionic complex [(C$_5$HMe$_4$)$_2$-Ti(C≡CSiMe$_3$)$_2$]$^-$[Mg(THF)Cl]$^+$. One of the highest g values known so far for titanocene derivatives (cf. (C$_5$-HMe$_4$)$_2$Ti(η^3-1-methylallyl), g = 1.9921; (C$_5$HMe$_4$)$_2$TiAlH$_4$,
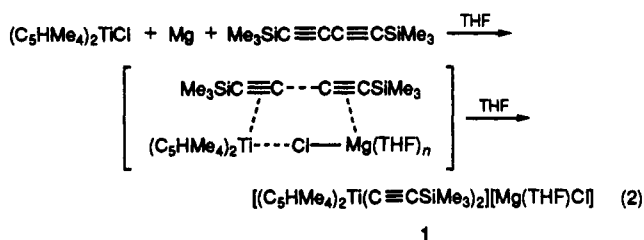
g = 1.9867, a_{Ti} = 5 G)[32] and the low anisotropy of the **g** tensor is in accord with the delocalization of the unpaired electron density over the anionic moiety with tetrahedrally coordinated Ti(III).

The EPR investigation of the reacting system revealed the formation of (C$_5$HMe$_4$)$_2$TiCl, whose EPR spectrum (g = 1.9630, ΔH = 13 G) was very similar to that recently described.[33] At the beginning of the reduction, a weak single line at g = 1.9795 and ΔH_{pp} = 3.5 G was also transiently observed, which could be assigned to [(C$_5$-HMe$_4$)$_2$Ti(μ-Cl)$_2$]$_2$Mg(THF)$_2$ (**4**) on the basis of the anticipated reaction products and its g value, which is close to that of a recently described cyclopentadienyl analogue.[34] The EPR signal of (C$_5$HMe$_4$)$_2$TiCl then decayed to yield the signal of **1**.

The reaction pathway to **1** can be envisaged in the following steps. The reduction of (C$_5$HMe$_4$)$_2$TiCl$_2$ to (C$_5$-HMe$_4$)$_2$TiCl is probably accompanied by transient formation of the Ti–Mg complex **4**, which disappears before the formation of (C$_5$HMe$_4$)$_2$TiCl is complete (eq 1).

$$2(C_5HMe_4)_2TiCl_2 + Mg \xrightarrow{THF}$$

$$(C_5HMe_4)_2Ti\overset{Cl}{\underset{Cl}{<}}\overset{Cl}{\underset{THF}{\overset{THF}{Mg}}}\overset{Cl}{\underset{Cl}{>}}Ti(C_5HMe_4)_2 \longrightarrow 2(C_5HMe_4)_2TiCl + MgCl_2 \quad (1)$$

4

Complex **4** must be unstable, since (C$_5$HMe$_4$)$_2$TiCl is monomeric and does not coordinate electron donors.[33] The formation of **1** apparently requires the active role of Mg in the dissociation process. The cleavage of BSD and oxidative addition of its fragments probably occurs immediately after the reduction of Ti(III) to Ti(II) in a transient complex involving the (C$_5$HMe$_4$)$_2$Ti^{II} and Mg^I-Cl(THF)$_n$ species and the π-coordinated BSD (eq 2). The successive C–C bond rupture and the rearrangement yielding **1** should not require the intermediate formation of (C$_5$HMe$_4$)$_2$TiC≡CSiMe$_3$ and Me$_3$SiC≡CMgCl(THF)$_n$ as constituents of **1**.

$$(C_5HMe_4)_2TiCl + Mg + Me_3SiC≡CC≡CSiMe_3 \xrightarrow{THF}$$

$$\left[\begin{array}{c} Me_3SiC≡C\text{---}C≡CSiMe_3 \\ \diagup \qquad\qquad \diagdown \\ (C_5HMe_4)_2Ti\text{----}Cl\text{----}Mg(THF)_n \end{array} \right] \xrightarrow{THF}$$

$$[(C_5HMe_4)_2Ti(C≡CSiMe_3)_2][Mg(THF)Cl] \quad (2)$$

1

The active participation of Mg in the process of BSD scission is at variance with the recent discovery that Cp$_2$-Ti(Me$_3$SiC≡CSiMe$_3$) alone induces the BSD scission, affording **3** quantitatively at room temperature.[18] However, analogous experiments performed by us showed that (C$_5$HMe$_4$)$_2$Ti(Me$_3$SiC≡CSiMe$_3$) and BSD did not react up to 70 °C, whereas compound **3** was prepared reproducibly at room temperature. This result can be accounted for by the electron-donating effect of Me groups at the Cp rings as well as by their steric effect, both effects increasing the stability of (C$_5$HMe$_4$)$_2$Ti(Me$_3$SiC≡CSiMe$_3$) compared

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to $Cp_2Ti(Me_3SiC\equiv CSiMe_3)$. As a result, the proposed intermediate of type IV[18] (Chart I) cannot be obtained as a precursor of $(C_5HMe_4)_2TiC\equiv CSiMe_3$ or its dimer. This conclusion, however, does not imply that a $(C_5HMe_4)_2Ti^{II}$ species nonstabilized by ligands at the onset of formation is not able to cleave the C–C bond in BSD in the absence of magnesium.

The cleavage of BSD was also induced in the presence of $(C_5Me_5)_2TiCl_2$, and the tweezer structure of the product was indicated by its EPR spectrum at $g = 1.9932$ with $\Delta H = 2.5$ G and $a_{Ti} = 7.4$ G. Further research is directed to study the influence of Me substituents at the $C_5H_{5-n}Me_n$ ($n = 0$–5) ligands on the cleaving ability of the corresponding titanocene species and the role of magnesium in the formation of complexes analogous to 1.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, and valence angles (4 pages). Ordering information is given on any current masthead page.

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