

Serendipitous Synthesis of $[\eta^5\text{-}1,2,4,5,6\text{-Pentakis(trimethylsilyl)cyclohexadienyl}](\eta^5\text{-cyclopentadienyl)titanium(II)$ and Its 4-Alkyl Derivatives

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Received September 25, 1995[⊗]

The titanium–magnesium complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}][\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_2(\text{SiMe}_3)_2](\eta^5\text{-C}_5\text{H}_5)\text{Mg}]$ (**1**) containing perpendicularly bridging bis(trimethylsilyl)acetylene ligands reacts with excess (trimethylsilyl)ethyne to give mainly $(\eta^5\text{-}1,2,4,5,6\text{-pentakis(trimethylsilyl)cyclohexadienyl}](\eta^5\text{-cyclopentadienyl)titanium(II)$ (**2**). The X-ray crystal structure of **2** showed that the SiMe₃ group at C(6) is in an exo-position and that the planes of the Cp ring and of the diene part of the Chx ring are nearly parallel. The dihedral angle 4.9° between these planes is mainly due to tilting of the cyclohexadienyl ring by the C(1) and C(5) side toward the titanium atom. Analogous reactions of **1** with *tert*-butylethyne, cyclohexylethyne, 1-hexyne, and phenylethyne afforded $(\eta^5\text{-}1,2,5,6\text{-tetrakis(trimethylsilyl)cyclohexadienyl}](\eta^5\text{-cyclopentadienyl)titanium(II)$ derivatives **3–6** containing the 1-alkyne substituent at C(4).

Introduction

η^5 -Cyclohexadienyl complexes are widely accessible by nucleophilic addition of H[−] or R[−] to $[(\text{arene})\text{M}(\text{L})]^+$ complexes, e.g., for L = arene and M = Mn, Fe, Re, Ru,^{1a} Rh, Ir, Ru,^{1b} and Fe,^{1c} for L = cyclopentadienyl and M = Fe, Co, Rh^{2a} and Ru,^{2b} for L = (CO)₄ and M = V,^{3a} and for L = (CO)₃ and M = Mn,^{3b} Rh,^{3c} and Re.^{3d} An alternative access is based on the hydrogen abstraction from η^4 -cyclohexadiene e.g., in the carbonyl complexes of Fe^{4ab} and Mn.^{4c}

The mechanisms of the formation of metal η^5 -cyclohexadienyl complexes were thoroughly reviewed.⁵ Direct metathetical synthesis from transition-metal halides and main group metal cyclohexadienide salts is generally applicable using the stable 6,6'-dimethyl-

cyclohexadienyl anion (Dmchx).⁶ In this way, bis($\eta^5\text{-}6,6'\text{-dimethylcyclohexadienyl}$)metal (Dmchx)₂M complexes were obtained for Ti, V, Cr, Fe,^{7a} and Mo.^{7b} Of the titanium complexes, so far only (Dmchx)₂Ti, (Dmchx)₂Ti(PF₃), and (Dmchx)₂Ti(CO) have been described and the X-ray crystal structure of the carbonyl complex has been determined.^{7a} The η^5 -cyclohexadienyl complexes are closely related to both the η^5 -cyclopentadienyl (Cp) and open U-shaped η^5 -pentadienyl complexes by structural features, and their chemical properties classify them as intermediate compounds between both types of metallocenes. Therefore, they were included in a comprehensive review on transition-metal η^5 -pentadienyl complexes emphasizing the comparison of open metallocenes and metallocenes.⁸ It is of interest that contrary to all other transition metal elements 14-electron titanocene and zirconocene compounds have only recently been characterized as open 1,5-bis(trimethylsilyl)pentadienyl derivatives.⁹

Here we report an unusual synthesis of half-open 14-electron $(\eta^5\text{-}1,2,4,5,6\text{-pentasubstituted cyclohexadienyl}](\eta^5\text{-cyclopentadienyl)titanium(II)$ compounds, whose cyclohexadienyl ligands are generated from acetylenic precursors at the $(\eta^5\text{-cyclopentadienyl)titanium(II)}$ moiety. These transient species arise from the Ti–Mg complex containing two perpendicularly bridging bis(trimethylsilyl)acetylene ligands, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}][\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_2(\text{SiMe}_3)_2](\eta^5\text{-C}_5\text{H}_5)\text{Mg}]$ ¹⁰ (**1**), upon interaction with 1-alkynes.

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[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1996.

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Experimental Section

General Data. Manipulation with all air-sensitive reagents, synthesis, isolation, and spectroscopic measurements were carried out under vacuum using all-sealed glass devices equipped with breakable seals. The solvents THF, hexane, toluene, and benzene-d6 (95.5% atom % D) (all Aldrich) were dried by refluxing over LiAlH4 and stored as solutions of dimeric titanocene,11 (C10H8)[(C5H5)TiH]2, under metal valves on a high-vacuum line. Terminal acetylenes (trimethylsilyl)ethyne, tert-butylethyne, 1-hexyne, cyclohexylethyne, and phenylethyne (Aldrich) were purified by vacuum distillation and by storing for several hours as solutions of the dimeric titanocene. Then they were distilled into storage ampules on a vacuum line. The compound [(eta5-C5H5)Ti][mu-eta2:eta2-C2(SiMe3)2]2-[(eta5-C5H5)Mg] (1) was obtained from the reduction of (C5H5)2TiCl2 by excess magnesium in the presence of at least 2 equiv of bis(trimethylsilyl)acetylene.10 1H and 13C NMR spectra were measured on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in C6D6 at 25 °C. Samples were referenced to the solvent signal (deltaH 7.15, deltaC 128.00 ppm). The assignment of spectra is based on results of APT, COSY, delay-COSY, HOM2DJ, and HETCOR experiments. ESR spectra were recorded on an ERS-220 spectrometer (German Academy of Sciences, Berlin) in the X-band at room temperature. Infrared spectra of hexane solutions were registered on a UR-75 instrument (Zeiss, Jena, Germany) using KBr cuvettes filled under argon. KBr pellets of crystalline 2 were prepared under purified nitrogen in a glovebox (Braun) and were measured in an air-protecting cuvette on a Mattson Galaxy 2020 IR spectrometer. UV-vis spectra were recorded on a Varian Cary 17D spectrometer in the range 270-2000 nm using all-sealed quartz cells (Hellma). Elemental analyses were carried out only for crystalline products of high purity.

Preparation of [eta5-C6H2(SiMe3)5](eta5-C5H5)TiII (2). (Trimethylsilyl)acetylene (1.5 mL, 10 mmol) was added to a solution of [(C5H5)Ti][mu-eta2:eta2-C2(SiMe3)2]2[Mg(C5H5)] (1) (1.5 mmol) in toluene (15 mL). The red color of the solution changed immediately to brown-green. After 2 h of stirring at room temperature, all volatiles were evaporated at a maximum 60 °C under vacuum into a trap cooled by liquid nitrogen. The residue was extracted with 20 mL of hexane. The solution was separated, and its volume was reduced to 5 mL. The clear solution was transferred to a multiarm crystallization vessel. Slow crystallization of 2 was induced by slight cooling of the arm used for condensing solvent. The resulting polycrystalline solid was washed by condensing hexane vapors until washings were bright green. The remainder was dissolved in hexane, and the procedure was repeated. The bright green crystals were dried in vacuum and collected. The yield of crystalline 2 was 0.41 g (50%). The mother liquor contained another portion of 2 (ca. 20-30% of the overall titanium content), but its isolation was not effective. 2: EI-MS (direct inlet, 80-130 °C, m/z (%)) 552 (M+, 3.5), 479 (100), 407 (3), 327 (12), 311 (19), 113 (21), 73 (59); analysis, 552.2357, error +3.7 x 10^-3 for C26H52Si5Ti, 479.1905, error +1.7 x 10^-3 for C23H43Si4Ti, 327.0876, error +2.4 x 10^-3 for C14H27Si3Ti, 311.0564, error +2.3 x 10^-3 for C13H23Si3Ti, 279.1396, error +2.5 x 10^-3 for C14H27Si3; 1H NMR and 13C NMR spectra are listed in Tables 1 and 2, respectively; IR (KBr) 2951 (s), 2899 (s), 1447 (m), 1402 (s), 1246 (vs), 1150 (m), 1107 (s), 1055 (m), 1013 (m), 949 (m), 837 (vs), 785 (s), 748 (s), 681 (s), 635(s), 588 (w), 580 (w), 511 (m), 500 (m), 478 (m), 442 (w), 419 (m) cm^-1; IR (hexane) 1262 (sh) in addition to the bands found in KBr (within +/- 3 cm^-1); UV-vis (hexane, 23 °C) 318, 350 sh, 412, 565, 813 nm; EDAX (Kalpha) Ti:Si ratio 1:4-6. Anal. Calcd for C26H52Si5Ti: C, 56.5; H, 9.5. Found: C, 56.8; H, 9.6.

Table 1. 1H NMR Data (delta) for Compounds 2-6a

Table with 6 columns: group, multiplicity, 2, 3b, 4b, 5b, 6b. Rows include Cp, sp3-CH, sp2-CH, and SiMe3d with various chemical shifts and multiplicities.

a 400 MHz, 25 °C, C6D6. b Additional signals of substituents from the terminal acetylene are as follows. 3: 1.148 (s, 9H, t-Bu). 4: 0.484 (dm, J = 12.4 Hz, Hbeta-eq), 0.692 (ddd, J = 12.6, 12.4, 12.0, 3.4 Hz, Hbeta-ax), 1.046 (m, Hbeta-ax), 1.072 (m, Hgamma-ax), 1.313 (m, Hgamma-ax), 1.545 (m, Hgamma-eq), 1.583 (m, Hbeta-eq), 1.704 (dddd, J = 13.0, 13.0, 12.8, 3.6, Hbeta-ax), 1.811 (m, Hgamma-eq), 2.247 (dddd, J = 12.0, 11.6, 3.2, 3.2 Hz, Halpha), 2.562 (dm, J = 13.0 Hz, Hbeta-eq). Long-range coupling between the proton at 5.381 ppm and protons at 2.247 ppm (Halpha) and 0.692 ppm (Hbeta-ax) was detected by delay-COSY. 5: 0.901 (t, 3 H, J = 7.0 Hz, Me), 1.315 (m, 2 H-gamma), 1.361 (m, H-beta), 1.584 (m, H-beta), 1.834 (ddd, J = 14.2, 11.2, 5.2 Hz, H-alpha), 2.660 (ddd, J = 14.2, 10.9, 4.8 Hz, H-alpha). Long-range coupling between the proton at 5.099 ppm and alpha-protons of the side chain (2.660 and 1.834 ppm) was detected by delay-COSY. 6: 6.906 (2H, m, Ph-ortho), 6.944 (1 H, m, Ph-para), 7.073 (2 H, m, Ph-meta). c 5 H. d 9 H if not otherwise stated. e 18 H.

Table 2. 13C NMR Data (delta) for Compounds 2-6a

Table with 6 columns: group, multiplicity, 2, 3b, 4b, 5b, 6b. Rows include Cp, sp3-CH, sp2-CH, sp2-C, and SiMe3 with various chemical shifts and multiplicities.

a 100 MHz, 25 °C, C6D6. b Additional signals of substituents from the terminal acetylene are as follows. 3: 34.53 (q, 3C, Me), 38.35 (s). 4: 26.42 (t, C-delta), 27.70 (t, C-gamma), 27.83 (t, C-gamma), 34.54 (t, C-beta), 39.15 (t, C-beta), 46.47 (d, C-alpha). 5: 14.18 (q, C-delta), 23.35 (t, C-gamma), 34.65 (t, C-beta), 38.43 (t, C-alpha). 6: 126.09 (d, Ph-para), 127.83 (d, 2 C, Ph-meta), 129.36 (d, 2 C, Ph-ortho), 146.48 (s, Ph-ippo). c 5 C. d 2 C. e 3 C. f 6 C.

Preparation of [eta5-C6H2(tert-C4H9)(SiMe3)4](eta5-C5H5)Ti (3). The same procedure as for 2 afforded 0.18 g (22%) of green crystalline solid. The overall production of 3 was estimated to be more than 60%, but its purification by crystallization was extremely difficult due to high solubility in hexane of 3 and byproducts. 3: EI-MS (direct inlet, 80-130 °C, m/z (%)) 536 (M+, 4), 479 (2), 463 (100), 311 (13), 295 (7), 279 (15), 113 (24), 73 (70); analysis, 536.2618, error +0.7 x 10^-3 for C27H52Si4Ti, 463.2148, error +0.4 x 10^-3 for C24H43Si3Ti, 311.1125, error +0.5 x 10^-3 for C15H27Si2Ti; 1H NMR and 13C NMR spectra are given in Tables 1 and 2, respectively; IR (hexane) 1246 (vs), 1200 (m), 1150 (w), 1106 (m), 1058 (w), 1013 (s), 942 (s), 888 (m,sh), 836 (vs), 790 (s), 772 (s), 750 (s), 684 (m), 642 (m), 584 (w), 574 (w), 515 (w), 436 (w); UV-vis (hexane, 23 °C) 315 sh, 415 sh, 580, 840 sh, nm. Anal. Calcd for C27H52Si4Ti: C, 60.4; H, 9.5. Found: C, 60.8; H, 9.7.

Preparation of [eta5-C6H2(C6H11)(SiMe3)4](eta5-C5H5)Ti (4). The same procedure as for 2 afforded a green waxy solid which crystallized on cooling to -18 °C. The yield of the green waxy solid was ca. 0.4 g (50%). The portion of 4 remaining in the mother liquor was estimated to be another 10-20%. 4: EI-MS (direct inlet, 80-130 °C, m/z (%)) 562 (M+, 4), 479 (2), 463 (100), 311 (13), 295 (7), 279 (15), 113 (24), 73 (70); 1H NMR and 13C NMR spectra are collected in Tables 1 and 2, respectively; IR (hexane) 1262 (m, sh), 1248 (s), 1150 (w), 1106 (s), 1058 (w), 1013 (s), 961 (m), 889 (m, sh), 870 (s, sh), 838 (vs), 787 (s), 777 (s), 750 (s), 682 (m), 637 (m), 583 (w), 510

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Table 3. EPR Parameters of Presumed Ti(III)–Mg Tweezer Complexes
[Cp₂Ti(η¹-C≡CR)₂]⁻[Mg(C≡CR)]⁺ ^a

compd	R	<i>g</i>	<i>a</i> _H (G)	<i>a</i> _{Ti} (G)
2a	SiMe ₃	1.9920	0	8.6
	SiMe ₃ ^b	1.9935	0	7.3
3a	<i>t</i> -C ₄ H ₉	1.9907	0	9.3
4a	<i>c</i> -C ₆ H ₁₁	1.9912	2.7 (triplet)	9.2
5a	<i>n</i> -C ₄ H ₉	1.9912	2.3 (quintuplet)	9.0
6a	phenyl	1.9916	0	8.8

^a Solutions in hexane, 23 °C. ^b Parameters for [(C₅HMe₄)₂Ti(η¹-C≡CSiMe₃)₂]⁻[Mg(THF)Cl]⁺ (toluene, 20 °C).¹²

(m), 478 (w), 458 (w), 438 (w); UV–vis (hexane, 23°C) 350 sh, 410, 575, 865 nm.

Preparation of [η⁵-C₆H₂(*n*-C₄H₉)(SiMe₃)₄](η⁵-C₅H₅)Ti (5). The same procedure as for **2** afforded a dirty green waxy solid. Yield: 0.16 g (20%). **5**: EI-MS (direct inlet, 80–100°C, *m/z* (%) 536 (M⁺, 2.5), 463 (100), 461 (30), 309 (11); IR (hexane) 1260 (s, sh), 1246 (vs), 1150 (w), 1116 (s), 1050 (w), 1011 (s), 962 (s), 840 (vs), 787 (s), 778 (s, sh), 750 (s), 683 (s), 636 (s), 510 (m); ¹H NMR and ¹³C NMR spectra are described in Tables 1 and 2, respectively. The presence of impurities was discernible from both the NMR spectra and UV–vis spectra. The latter showed the absorption bands of **5** at 570 and 860 nm as shoulders on the background increasing in intensity to shorter wavelengths.

Preparation of [η⁵-C₆H₂(C₆H₅)(SiMe₃)₄](η⁵-C₅H₅)Ti (6). The same procedure as for **2** gave a green waxy solid. Yield: 0.14 g (16%). **6**: EI-MS (direct inlet, 130–140 °C, *m/z* (%) 556 (M⁺, 3), 483 (100), 411 (4), 331 (9), 315 (18), 113 (18), 73 (the sample contained triphenylbenzene (*m/z* 306, M⁺) and mainly tris(trimethylsilyl)phenylbenzene (*m/z* 370, M⁺ not observed, 355, 339, 283, 267) which contributed to the intensity of *m/z* 73 in the spectrum of **6**); ¹H NMR and ¹³C NMR spectra are reported in Tables 1 and 2, respectively; IR (hexane) 1597 (m), 1265 (m, sh), 1250 (s), 1148 (w), 1108 (s), 1060 (w), 1013 (w), 960 (m), 896 (m, sh), 843 (vs), 792 (s), 784 (s), 755 (s), 703 (s), 676 (m), 640 (w), 584 (w), 450 (w), 417 (w); UV–vis (hexane, 23°C) 315, 360 sh, 420, 580, 860 nm.

Paramagnetic Byproducts. Mother liquors from crystallization of **2–6** were diluted by hexane, and their EPR spectra were measured at room temperature. The spectra revealed the presence of one major type of paramagnetic products which were denoted **2a–6a**. Their EPR parameters are collected in Table 3. High *g*-values 1.9907–1.9920, narrow line widths Δ*H*_{pp} = 1.5–3.0 G, and *a*_{Ti} = 8.6–9.3 G are close to the parameters found for the Ti^{III}–Mg tweezer complex [(η⁵-C₅HMe₄)₂Ti(η¹-C≡CSiMe₃)₂]⁻[Mg(THF)Cl]⁺ (toluene, 22 °C: *g* = 1.9935, Δ*H*_{pp} = 2.0 G, *a*_{Ti} = 7.3 G).¹² Therefore the byproducts are proposed to be the [(η⁵-C₅H₅)₂Ti(η¹-C≡CR)₂]⁻[Mg(C≡CR)]⁺ complexes with acetylide groups derived from the corresponding 1-alkynes. The hyperfine splittings observed in the spectra of **4a** (triplet) and **5a** (quintuplet) (Table 3) are consistent with the coupling to 2 and 4 equivalent protons on the α-carbon atoms of the substituents at two equivalent acetylide tweezer arms. This coupling has been recently observed in the [(η⁵-C₅Me₅)₂Ti(η¹-C≡CR)₂]⁻[Mg(C≡CR)]⁺ complexes generated in the (η⁵-C₅Me₅)₂TiCl₂/*i*-PrMgCl/THF/1-alkyne catalytic systems for linear head-to-tail dimerization of 1-alkynes or by the interaction of [(C₅Me₅)₂Ti(η¹-C≡CSiMe₃)₂]⁻[Mg(THF)Cl]⁺ with the above mentioned 1-alkynes.¹³

Organic Byproducts. Volatiles from the reaction mixture for obtaining **2** were distilled in vacuum at a maximum temperature 60 °C overnight into a trap cooled by liquid nitrogen. Then, most of hexane was pumped off. GC MS of the distillate revealed a mixture of two isomers of tris-

Table 4. Crystallographic Data for 2

formula	C ₂₆ H ₅₂ Si ₅ Ti
fw	553.00
cryst color, habit	green, irregular
cryst dimens (mm)	0.3 × 0.4 × 0.6
cryst system	monoclinic
space group	P2 ₁ /c, No. 14
<i>a</i> (Å)	10.400(9)
<i>b</i> (Å)	32.693(22)
<i>c</i> (Å)	10.415(10)
β (deg)	110.80(5)
Z	4
<i>V</i> (Å ³)	3311(7)
<i>D</i> _{calc} (g·cm ⁻³)	1.11
μ(Mo Kα), (cm ⁻¹)	4.06
2θ _{max} (deg)	48
tot. no. of reflns	4521
no. of unique reflns	4036
reflcs with <i>F</i> _o ≥ 2σ(<i>F</i> _o)	3014
no. of params refined	292
residuals: <i>R</i> , <i>R</i> _w ^a	0.053, 0.057
resid density (e/Å ³)	-0.25 to +0.31

^a For the 3014 reflections with *F*_o ≥ 2σ(*F*_o); 2θ ≤ 48°.

(trimethylsilyl)benzene, apparently 1,2,4- and 1,3,5-isomers. By analogy with the titanium-catalyzed cyclotrimerization of 1-alkynes¹⁴ the unsymmetrical isomer should be prevailing. In addition, tetrakis(trimethylsilyl)benzene was also detected in a comparable quantity. This was isolated by liquid column chromatography as a crystalline solid and identified to be the 1,2,4,5-isomer by comparing its EI-MS and ¹H and ¹³C NMR spectra with the authentic compound.¹⁵ Volatiles from the reaction mixture for obtaining **4** were distilled off under vacuum at room temperature, the residue was dissolved in a minimum amount of hexane, and **4** was crystallized out. The main portion of the mother liquor was quenched by water, the organic products were extracted by hexane and the solvent was evaporated. The resulting white solid was analyzed by MS from direct inlet. The main product was tris(trimethylsilyl)cyclohexylbenzene: EI-MS (direct inlet, 130–150 °C, *m/z* (%) 376 (M⁺), 361, 345, 289, 279, and 273. Peaks attributable to tris(cyclohexyl)benzene were also registered (*m/z* 324 M⁺ and fragment ions). Both types of organic byproducts were detected as impurities in the mass spectrum of **6** (see above).

X-ray Single-Crystal Analysis of 2. A crystal fragment was mounted into a Lindemann glass capillary under purified nitrogen in a glovebox (Braun) and was sealed by wax. The X-ray measurements were carried out on a Phillips PW 1100 four-circle diffractometer. Intensity data were collected by the θ/2θ method using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at room temperature. The positions of the Ti and Si atoms were determined by the Patterson method. Atomic coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined by the least-squares method. Hydrogen atoms were constrained to idealized geometries with a C–H distance of 1.08 Å. The PC ULM package¹⁶ was used for all calculations. Crystallographic data for **2** are listed in Table 4. Atomic coordinates of non-hydrogen atoms are given in Table 5.

Results and Discussion

Addition of a 7-fold excess of 1-alkynes to [(η⁵-C₅H₅)Ti][μ-η²:η²-C₂(SiMe₃)₂]₂[(η⁵-C₅H₅)Mg] (**1**) in toluene re-

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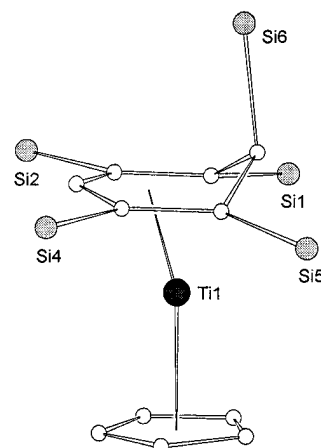
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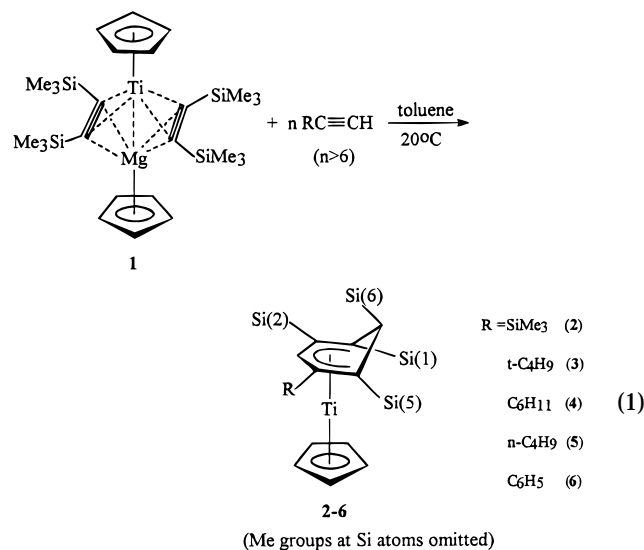
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Table 5. Atomic Coordinates and Equivalent Isotropic Temperature Factors (\AA^2) for Complex **2**

atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ti(1)	0.1203(1)	0.1144(1)	0.2086(1)	0.033(1)
C(1)	0.1776(4)	0.1173(1)	0.4181(4)	0.033(1)
Si(1)	0.3178(1)	0.0853(1)	0.5402(1)	0.040(1)
C(11)	0.2782(6)	0.0300(2)	0.4958(6)	0.062(1)
C(12)	0.3366(6)	0.0888(2)	0.7270(5)	0.062(1)
C(13)	0.4909(5)	0.0956(2)	0.5282(6)	0.059(1)
C(2)	0.1750(4)	0.1595(1)	0.3744(4)	0.032(1)
Si(2)	0.3089(1)	0.2010(1)	0.4411(1)	0.051(1)
C(21)	0.4144(6)	0.1952(2)	0.6288(5)	0.086(1)
C(22)	0.4269(7)	0.2046(2)	0.3429(7)	0.081(1)
C(23)	0.2217(7)	0.2517(2)	0.4229(7)	0.084(1)
C(3)	0.0515(4)	0.1735(2)	0.2672(4)	0.032(1)
C(4)	-0.0666(4)	0.1497(2)	0.1863(4)	0.033(1)
Si(4)	-0.1993(1)	0.1787(1)	0.0455(1)	0.044(1)
C(41)	-0.1833(7)	0.2339(2)	0.0909(8)	0.097(1)
C(42)	-0.1788(7)	0.1742(3)	-0.1240(5)	0.067(1)
C(43)	-0.3790(5)	0.1641(2)	0.0243(6)	0.066(1)
C(5)	-0.0692(4)	0.1063(1)	0.2289(4)	0.030(1)
Si(5)	-0.1889(1)	0.0637(1)	0.1481(1)	0.047(1)
C(51)	-0.2449(7)	0.0621(2)	-0.0452(5)	0.079(1)
C(52)	-0.3490(5)	0.0610(2)	0.1927(6)	0.073(1)
C(53)	-0.0993(6)	0.0146(2)	0.2153(5)	0.062(1)
C(6)	0.0264(4)	0.1002(1)	0.3830(4)	0.029(1)
Si(6)	-0.0578(1)	0.1247(1)	0.5033(1)	0.035(1)
C(61)	-0.2195(5)	0.1532(2)	0.4141(5)	0.044(1)
C(62)	-0.0994(6)	0.0803(2)	0.5970(5)	0.050(1)
C(63)	0.0547(6)	0.1617(2)	0.6307(5)	0.063(1)
C(70)	0.3125(7)	0.1113(3)	0.1379(7)	0.086(1)
C(80)	0.2083(9)	0.1275(3)	0.0312(8)	0.063(1)
C(90)	0.1075(8)	0.0982(3)	-0.0160(6)	0.081(1)
C(100)	0.1487(9)	0.0635(3)	0.0627(9)	0.090(1)
C(110)	0.2793(9)	0.0722(3)	0.1593(7)	0.048(1)

**Figure 1.** View of the PLUTO plot of **2** with methyl groups omitted for clarity.

sulted in a rapid reaction yielding 4-alkyl derivatives of $[\eta^5\text{-}1,2,5,6\text{-tetrakis(trimethylsilyl)cyclohexadienyl}](\eta^5\text{-cyclopentadienyl})\text{titanium(II)}$ (**2–6**) as the main products (eq 1). The common structure of products **2–6**



obtained from the reaction of **1** with (trimethylsilyl)ethyne, *tert*-butylethyne, cyclohexylethyne, 1-hexyne, and phenylethyne, respectively, follows from the X-ray crystal structure of **2** (Figure 1), the consistent assignment of ^1H (Table 1) and ^{13}C NMR spectra (Table 2) of all the compounds, and common features in their MS, IR, and UV-vis spectra. The crystal structure determination of **2** revealed that it is $(\eta^5\text{-}1,2,4,5,6\text{-pentakis(trimethylsilyl)cyclohexadienyl})(\eta^5\text{-cyclopentadienyl})\text{titanium(II)}$, the first structurally characterized 14-electron half-open titanocene. Compounds **2–6** are

thermally robust and can be sublimed in high vacuum without decomposition. They appeared to be unreactive toward all the above 1-alkynes, BTMSA, THF, 2,2'-bipyridyl, ethylene, and carbon monoxide under ambient pressure and temperature. The compounds are very highly soluble in hexane, and their purification by fractional crystallization from organic and organometallic byproducts is extremely difficult. Well-resolved NMR spectra obtained at ambient temperature prove the diamagnetism of the compounds.

The ^1H and ^{13}C NMR spectra of **2–6** showed the presence of one cyclopentadienyl (Cp) ligand and one pentasubstituted cyclohexadienyl (Chx) ligand, the latter arising from the cross-cycloaddition of two molecules of bis(trimethylsilyl)acetylene (BTMSA) and one molecule of 1-alkyne. The spectra of the Chx ligands showed the presence of one SiMe_3 group and one proton on the sp^3 carbon atom C(6), three other SiMe_3 groups, one substituent identical with that contained in 1-alkyne, one proton on an sp^2 carbon atom, and four quaternary sp^2 carbon atoms. In **2**, the pairs of quaternary sp^2 carbon atoms C(1) and C(5) and C(2) and C(4) were equivalent whereas in **3–6** all the carbon atoms were different. The spatial proximity of the substituent R and the sp^2 C–H proton was inferred from the appropriate delay-COSY cross peaks for **4** and **5** (see footnote to Table 1). However, no such proof could be obtained for **3** and **6** because of the absence of protons at the C_α atoms of substituents. It is interesting to note that all protons and carbons of cyclohexyl substituent in **4** were magnetically nonequivalent; this phenomenon was also observed for the two α -protons in **5** but was entirely absent for the phenyl protons in **6**.

The analogous structure of **2** and **3–6** is further supported by the common features of their EI-MS fragmentation patterns. The molecular ions most easily lose one SiMe_3 radical (m/z 73) (probably from the C(6) atom), and the formed ions release either silaisobutylene (m/z 72) (minor pathway) or the fragment m/z 152, $\text{C}_9\text{H}_{16}\text{Si}$ (major pathway). The latter pathway involves a transfer of the CH_2SiMe_3 group from the six-membered ring to the C_5H_5 ring, and the adduct $\text{C}_9\text{H}_{16}\text{Si}$, probably (trimethylsilyl)cyclohexadiene, is eliminated from the titanium-containing ion. The remaining ion in this fragmentation pathway is apparently $[\text{C}_5\text{H}_2\text{-(SiMe}_3)_2\text{R}]\text{Ti}^+$, where R is the substituent from the corresponding 1-alkyne. The transfer of a larger ring

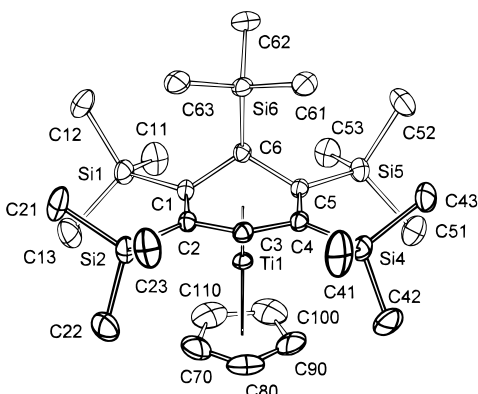


Figure 2. ORTEP drawing of **2**, with ellipsoids drawn at the 50% probability level.

carbon atom to a smaller ring is well-known for, e.g., (η^7 -cycloheptatrienyl)(η^5 -cyclopentadienyl)titanium.¹⁷

The infrared spectra of **2–6** are dominated by strong absorption bands of trimethylsilyl groups and afford no much information. It is worthwhile to mention strong bands at 1011–1013 cm^{-1} and at 1105–1116 cm^{-1} occurring in the spectra of all the compounds. The former can be assigned to the Cp ligand, and the latter to the Chx ligands.¹⁸ The absence of an absorption band at 2800 cm^{-1} confirms the absence of the C–H bond in the *exo*-position at the carbon atom C(6).^{3d} The electronic absorption spectra show the presence of two intense absorption bands in regions 565–580 nm and 813–870 nm which should belong to metal-to-ligand CT transitions. Their molar extinction coefficients are estimated to be higher than 10² L·cm·mol⁻¹. This is consistent with a strong metal–ligand orbital mixing which is facilitated by a small separation between the HOMO and LUMO orbitals in the Chx ligand.⁸ The absorption bands of the longest wavelength (813–860 nm) reached the extreme of 813 nm for **2** (electron-withdrawing SiMe₃ group), but the differences between the alkyl derivatives **3–6** were low (840–860 nm). The intense bands at shorter wavelengths were discernible in high-purity compounds **2**, **3**, and **6**; in other cases they were partly or completely overshadowed by an intense absorption of a brown impurity.

Crystal Structure of [η^5 -C₆H₂(SiMe₃)₅](η^5 -C₅H₅)-Ti^{II} (2**).** The ORTEP drawing of **2** with the atom numbering scheme is shown in Figure 2. Selected bond lengths and bond angles are listed in Table 6. The molecule has no symmetry element due to the distortion of the Chx ligand and a partly staggered conformation of the Chx and Cp ligands. Five sp² carbon atoms of the Chx ring form a least-squares plane with a maximum atom deviation of 0.035 Å. The sp³ carbon atom C(6) is 0.653 Å above this plane and the attached trimethylsilyl group is oriented in the *exo*-position. The dihedral angle between the ring plane and the plane

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for [η^5 -C₆H₂(SiMe₃)₅](η^5 -C₅H₅)Ti^{II} (2**)**

(a) Bond Distances (Å)			
Ti(1)–C(1)	2.050(4)	C(1)–C(2)	1.451(6)
Ti(1)–C(2)	2.186(4)	C(2)–C(3)	1.443(6)
Ti(1)–C(3)	2.218(5)	C(3)–C(4)	1.445(6)
Ti(1)–C(4)	2.200(4)	C(4)–C(5)	1.490(6)
Ti(1)–C(5)	2.073(4)	C(5)–C(6)	1.572(6)
Ti(1)–CE(1)	1.582(4)	C(1)–C(6)	1.585(6)
Ti(1)–C(Cp) _{av}	2.355(12)	Ti(1)–CE(2)	2.047(9)
C(1–5)–Si(1–5) _{av}	1.875(9)	C(6)–Si(6)	1.937(4)
Si(1–6)–C(Me) _{av}	1.872(4)		
(b) Bond Angles (deg)			
CE(1)–Ti(1)–CE(2)	164.7(1)	Si(1)–C(1)–C(2)	131.8(3)
C(1)–C(2)–C(3)	117.1(4)	Si(1)–C(1)–C(6)	115.4(3)
C(2)–C(3)–C(4)	128.3(4)	C(1)–C(2)–Si(2)	129.7(3)
C(2)–C(1)–C(6)	110.9(3)	Si(2)–C(2)–C(3)	113.2(3)
C(3)–C(4)–C(5)	116.1(4)	C(3)–C(4)–Si(4)	115.0(3)
C(4)–C(5)–C(6)	110.7(3)	Si(4)–C(4)–C(5)	128.9(3)
C(1)–C(6)–C(5)	114.0(3)	C(4)–C(5)–Si(5)	131.2(3)
C(1)–C(6)–Si(6)	110.2(3)	Si(5)–C(5)–C(6)	116.5(3)
C(5)–C(6)–Si(6)	109.9(3)		

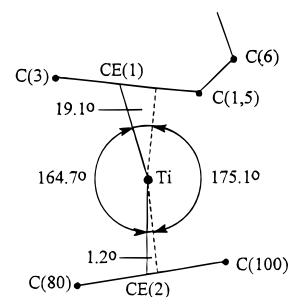


Figure 3. Schematic representation of angles around the Ti atom in **2** (dotted lines, normals to least-squares planes of Chx and Cp ligands).

through the C(1), C(6), and C(5) atoms is 48.6°. The silicon atoms Si(1)–Si(5) lie significantly out of the ring plane, and these atoms are directed toward the Ti atom. The largest declination from the plane was found for Si(1) and Si(5) (ca. 0.2 Å). The Chx ligand is tilted toward the titanium atom by the side bearing the sp³ carbon atom C(6) (vide infra). The cyclopentadienyl (Cp) ring defines the least-squares plane with maximum carbon atom deviation from the plane of only 0.004 Å. The Ti–C(100) bond is the shortest one (2.343(9) Å), and this corresponds to the tilt of the ring plane to the titanium atom by 1.2°. The planes of the Chx and Cp rings are thus inclined to each other, and the dihedral angle between them is 4.9°. Since the center CE(1) of the atoms of the dienyl fragment of the Chx ligand (C(1)–C(5)) is located close to C(3), the angle between the Ti–CE(1) connection and the normal to the Chx plane is as large as 19.1°. It accounts for the discrepancy between the values of the CE(1)–Ti–CE(2) angle (164.7°) and the angle of normal vectors to both the planes (175.1°) (Figure 3).

The average values of important bond lengths in **2** are compared with the values for (Dmchx)₂Ti(CO)^{7a} (**7**) and similar compounds (Cp)Ti(Dmp)(PEt₃) (Dmp = η^5 -2,4-dimethylpentadienyl),²⁰ (Cp)Ti(Chx) (Chx = η^7 -cycloheptatrienyl),²¹ and (Cp)Ti(Cot) (Cot = η^8 -cyclooctatetraene dianion)²² in Table 7. It shows that the Ti–C_n distance to a larger ring or Dmp is generally

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(18) A strong band at 1012–1015 cm^{-1} has been assigned to δ or γ (C–H) vibrations of the Cp ligand in titanocene dihalides;¹⁹ however, we have observed a strong absorption band at 1020 cm^{-1} for (C₅Me₃)₂-TiCl₂ and this has to be assigned to a ring vibration. In **2–6** both the assignments are possible for absorption bands of pentasubstituted cyclohexadienyl ligand at 1106–1116 cm^{-1} .

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Table 7. Average Values of Ti–C and C–C Bond Lengths and Ti–Ring Distances (Ti–R) in **2 and Related Compounds (Å)^a**

	Ti–C _{Cp}	Ti–C _n	C–C _{Cp}	C–C _n	Ti–R _{Cp}	Ti–R _n ref
2	2.355	2.145	1.374	1.457	2.046	1.495
7		2.331		1.392		1.911 7a
(Cp)Ti(Dmp)	2.346	2.240				21
(Cp)Ti(Chx)	2.321	2.194	1.396	1.397	1.994	1.490 20
(Cp)Ti(Cot)	2.353	2.323	1.396	1.395	2.030	1.439 22

^a The distances pertinent to the Cp ligand are denoted "Cp"; those to the other ligand "n"; Ti–R is the normal distance from the least-squares plane of the ring to the Ti atom.

shorter than Ti–C_{Cp} and that except for (Cp)Ti(Cot) the Ti–C bonds shorten as the C–C bonds lengthen in the pertinent ligand and vice versa. These effects are most prominent in **2**, where, however, the data for the Cp ring distances exert large anisotropic thermal parameters. This is probably due to the ring libration around the axis perpendicular to the ring plane. A similar effect was observed for both rings in (Cp)Ti(Chx)²¹ and in (Cp)Ti(Cot),²² where the libration shortening of the Ti–C and C–C bonds was estimated to be in the range of 0.01 Å. The C–C_{Cp} and Ti–C_{Cp} bond lengths in **2** were not corrected for this effect; however, it should not differ much from the above figure. The anisotropic thermal parameters for the carbon atoms of Chx ring are ca. 3× smaller and do not show a remarkable directional dependence. The Ti–C_n bonds in **2** are thus reliably shorter by about 0.2 Å than the Ti–C_{Cp} bonds, which is the largest difference among the compounds listed in Table 7. In contrast, the average π -bond length in the Chx ring C(1)–C(5) [(C–C)_{av} 1.457(6) Å] is by far the longest. The average length for the outer bonds C(1)–C(2) and C(4)–C(5) (1.470 Å) is longer than the average of the corresponding inner bonds (1.444 Å), which is at variance to the situation in **7**,^{7a} [(Dmchx)Mo(CO)₂]₂,^{7b} and in most metal–pentadienyl compounds.⁸ This can be due to an electron-releasing effect of the SiMe₃ groups at the C(1) and C(5) atoms, inducing a partial trianionic form of the dienyl ligand.²³ The inner angle C(2)–C(3)–C(4) (128.3°) of the Chx ligand is much larger than the angles C(1)–C(2)–C(3) (117.1°) and C(3)–C(4)–C(5) (116.1°), and this is again the opposite situation to that in **7** and in other above mentioned compounds.⁸ The C–Si bond lengths from the ring carbon atoms C(1), C(2), and C(5) as well as all the Si–C bonds to Me groups fall into the range 1.857–1.891 Å. The average values with errors typical of the particular bond type are given in Table 6. The C(6)–Si(6) bond is remarkably longer than others, and hence its value of 1.937(4) Å was not included into the set of averaged bond lengths.

The structure of **2** differs from that of **7** also by the direction of the ring tilt with respect to the titanium atom. In contrast to **2**, the Dmchx ring side bearing the sp³ carbon atom is tilted farther away from the titanium atom.^{7a} The analogous tilting was also found, e.g., in the crystal structure of η^5 -cyclohexadienyl complexes [(η^5 -C₅Me₅)Ir(η^5 -C₆H₆CH₂NO₂)] [BF₄],^{1b} (η^5 -C₆H₂(Me)(CMe₃)₂O)Rh(PPh₃)₂,^{3c} (η^5 -C₆H₇)Mn(CO)₃,²⁴ and

(η^5 -C₆H₇)Co[P(C₆H₁₁)₂CH₂]₂.²⁵ This direction of ring tilt is also common in partly methyl-substituted Cp rings where the unsubstituted part of the ring is at closer distance to the metal than the substituted one.²⁶ In the titanium complexes, this was recently observed for (η^5 -C₅HMe₄)₂Ti^{III} and –Ti^{IV} halides²⁷ and the isodicyclopentadienyl complex (η^5 -C₁₀H₁₁)Ti[(μ -Cl)AlCl₂]₂.²⁸ The opposite ring tilt in **2** cannot be attributed to a bonding interaction between the Ti atom and the Si(1) and Si(5) atoms, remarkably declined from the Chx ring plane toward the Ti atom, because their distance from the titanium atom is as large as 3.466 and 3.471 Å, respectively. More likely, the direction of the C–Si bonds is induced by the orbital hybridization at C(1) and C(5) resulting from an envelope folding of the Chx ligand.

A low dihedral angle between the Chx and Cp ring planes (ϕ 4.9°) classifies **2** to be a pseudometallocene with parallel ligand planes. The angle ϕ was found to deviate only slightly from zero in crystal structures of titanocene-like compounds (Cp)Ti(Chx),²¹ (Cp)Ti(Cot),²² (Cp*)Ti(Chx) (Cp* = η^5 -C₅Me₅), and (Cp*)Ti(Cot),²⁹ where the parallel orientation of rings is stabilized by the presence of one larger ring. The values of ϕ were 2.1, 1.9, 3.9, and 1.6°, respectively. The large value of ϕ in (Cp*)Ti(Chx) indicates that a steric congestion due to the methyl substituents in Cp* ring has no influence on the parallel orientation of the rings. Thus, crystal packing effects are probably responsible for the observed deviations from parallel structures in the above examples as well as in **2**.

Reactions between **1 and 1-Alkynes.** Compound **1** was found to be stable toward the internal acetylenes although it induced their slow cyclotrimerization.^{10b} In contrast, it rapidly reacted with 1-alkynes yielding a mixture of products. Compounds **2–6** were always the main products whose yields were estimated to be between 60–80% although the isolated yields were, due to difficult purification, much lower. The other identified products were tris(trimethylsilyl)alkylbenzenes and the cyclotrimers of 1-alkynes. Minor amounts of 1-alkynes remained unreacted. EPR evidence was obtained (see Table 3) for the presence of paramagnetic Ti^{III} byproducts, presumably Ti–Mg tweezer complexes of the type [(Cp)₂Ti(η^1 -C≡CR)₂][–][Mg(C≡CR)]⁺.

A possible reaction pathway leading to **2–6** is proposed in Scheme 1. It involves the cleavage of **1** by 1-alkyne yielding (Cp)MgC≡CR and a transient bis[η^2 -C₂(SiMe₃)₂](cyclopentadienyl)titanium(II) hydride complex which rearranges with intramolecular hydrogen transfer to give a titanacyclopentadiene skeleton.³⁰ As follows from the structure of **2**, the insertion of 1-alkyne into the Ti–C bond is controlled by a greater steric congestion at the SiMe₃ group compared to the (Cp)Ti moiety. The titanacycloheptatriene ring contraction accompanied by the change of σ - to π -bonding mode of Ti(II) to the cyclohexadienyl ligand accomplishes the

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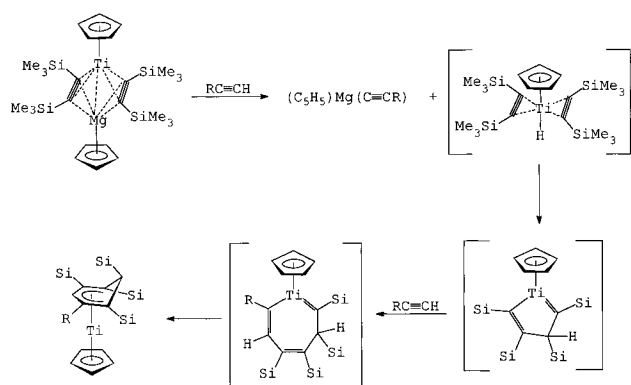
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Scheme 1



formation of **2–6**. It is noteworthy that the proposed mechanism involves the oxidative addition followed by reductive elimination steps between Ti^{II} and Ti^{IV} as it is generally accepted for the cyclotrimerizations of acetylenes¹⁴ and butadiene.³³ An alternative [2 + 2 +

(30) Bis(trimethylsilyl)acetylene (BTMSA) is reluctant to cyclotrimerize because of steric crowding in the products; however, the titanium-catalyzed cross-additions to conjugated double-bond systems are known.³¹ The (Cp)₂Ti(η²-BTMSA) complex does not react with excess BTMSA to give a titanacyclopentadiene derivative.³² The formation of the titanacyclopentadiene skeleton in the present case is enabled by the hydrogen transfer forming thus an sp³ carbon atom in the carbon chain and by the absence of steric hindrance at the (Cp)Ti moiety.

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2] cyclotrimerization (for reviews see ref 34a,b) of 2 molecules of Me₃SiC≡CSiMe₃ with HC≡CSiMe₃ is improbable to proceed without participation of a Ti–H moiety. Furthermore, the subsequent hydride addition to thus formed pentakis(trimethylsilyl)benzene would not account for the formation of only one isomer of the cyclohexadienyl ligand.

Tris(trimethylsilyl)alkylbenzenes formed as main byproducts probably originate in a side reaction of the intermediate titanacycloheptatriene (Scheme 1). It can be visualized as a transfer of one SiMe₃ group to titanium which leads to a rapid elimination of C₆H₂R-(SiMe₃)₃ and the formation of a highly reactive (Cp)Ti-(SiMe₃) species. The combination of the latter with a released (Cp)MgC≡CR in the presence of 1-alkyne may lead to the Ti(III) paramagnetic byproducts of the above suggested tweezer nature. Very low amounts of tri-alkylbenzenes were probably obtained by the catalytic cyclotrimerization of 1-alkynes catalyzed by **1** before it decomposed to give **2**.

Acknowledgment. This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. 440403), by the Grant Agency of the Czech Republic (Grant No. 203/93/0143), and by the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of complete atomic positional and thermal parameters, anisotropic thermal parameters, bond distances, valence angles, least-squares planes and atomic deviations therefrom, and important intermolecular contacts and figures showing views of the unit cell (13 pages). Ordering information is given on any current masthead page.

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