SYNTHESES AND CRYSTAL STRUCTURES OF BIS[(TRIMETHYLSILYL)-TETRAMETHYLCYCLOPENTADIENYL]TITANIUM DICHLORIDE AND MONOCHLORIDE

Michal HORACEK[a1], Robert GYEPES[b1], Ivana CISAROVA[b2], Miroslav POLASEK[a2], Vojtech VARGA[a1] and Karel MACH[a1,]*

[a] *J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic; e-mail: [1] mach@jh-inst.cas.cz, [2] hanus@jh-inst.cas.cz*

[b] *Department of Inorganic Chemistry, Charles University, 128 40 Prague 2, Czech Republic; e-mail: [1] gyepes@prfdec.natur.cuni.cz, [2] cisarova@prfdec.natur.cuni.cz*

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 60th birthday.

(Trimethylsilyl)tetramethylcyclopentadiene (Cp′H) was obtained from the lithium salt of tetramethylcyclopentadiene and trimethylsilyl chloride. Bis[(trimethylsilyl)tetramethylcyclopentadienyl]titanium dichloride (**1**) and monochloride (**2**) were prepared by the generally known procedures. The X-ray crystal structures of **1** and **2** showed the placement of the bulky trimethylsilyl groups in side positions on opposite sides of the CE–Ti–CE planes. The steric congestion between the two chlorine atoms and two trimethylsilyl groups in **1** resulted in the nearly eclipsed conformation of the rings. Consequently, the steric hindrance between the methyl groups at the hinge position of the Cp′ ligands led to a decrease in the angle between the Cp′ ring planes by 4.8°, compared with the value of 44.6° in $(C_5Me_5)_2TiCl_2$. The titanocene skeleton in **2** is virtually the same as in $(C_5Me_5)_2TiCl$. The electronic effect of the trimethylsilyl group upon various properties of **1** and **2** appeared to be ambiguous. Based on the position of λ_{max} of electronic absorption bands of **1** the trimethylsilyl group exerted a stronger electron donation effect than the methyl group, however, the affinity of **2** to 2-methyltetrahydrofuran put the effect of the trimethylsilyl group close to that of hydrogen and the anisotropy of the EPR *g*-tensor of **2** close to that of the methyl group.

Key words: Titanium; Titanocene chlorides; (Trimethylsilyl)tetramethylcyclopentadienyl ligand; Crystal structures; Electronic effects of trimethylsilyl group.

Majority of homogeneous catalysts for polymerization of olefins are based on bent sandwich metallocene dichlorides of Group IVB elements (Ti, Zr, Hf) combined with aluminium alkyls or methylalumoxane[1–3] (MAO). The coordination capability of these

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* The author to whom correspondence should be addressed.

metals is strongly controlled by the substituents at the cyclopentadienyl ligands through their electronic and steric effects. Among the substituents, the methyl groups are known to act as effective electron donors via their induction and hyperconjugation effects[4,5]. In the methyl substituted titanocene dihalide series, $(C_5H_{5-n}Me_n)_2TiX_2$ (X = Cl, Br, I; n = 0–5), approximately regular increments per one methyl group were found in the decrease of the oxidation potential and the binding energies of the Ti(2p) inner shell electrons[6], the down-field shifts in ^{49}Ti NMR (ref.[7]), and the decrease of the lowest vertical ionization energy band in UPS spectra[8,9]. Conversely, the methyl groups increase the reduction potential and this is reflected in a decrease in the rates of reductive reactions[10,11]. A considerable steric congestion in the $(C_5Me_5)_2Ti$ compounds is reflected in about 9° smaller values of the angle between the least-squares planes of the cyclopentadienyl rings (ϕ) compared to those of the analogous $(C_5HMe_4)_2Ti$ compounds[12,13]. A smaller value of ϕ in the permethyltitanocene compounds diminishes the coordination space at the open side of the metallocene shell. Consequently, a strictly controlled mode of the coordination of substrates seems to cause the "enzymatic" selectivity of some catalytic reactions, for instance in the head-to-tail dimerization of terminal acetylenes[14,15]. On the other hand, the electron donation of methyl groups in most cases has a negative effect on the activity of the olefin polymerization catalysts[3].

The trimethylsilyl group is bulkier than the methyl group and its electronic effect at the metal has been found to be controversial, depending on the evaluated parameter. The reduction potential ($E_{1/2}^{\mathrm{red}}$) measured on a series of Cp'_2ZrCl_2 compounds increased in the series of substituents in the order $SiMe_3 < H < Me < Et$, thus qualifying the trimethylsilyl group to be an electron acceptor with respect to hydrogen[16]. This was compatible with the ease of the reduction of the $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ compounds increasing in the order of $n = 0 < 1 < 2$ (ref.[17]). In contrast, the binding energies of inner-shell electrons in the series of compounds $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ (n = 0–3) and $[C_5H_{5-n}(SiMe_3)_n]_2HfCl_2$ (n = 0 and 3) showed that the trimethylsilyl group is 1.25 times stronger electron donor than the methyl group[18]. The measurement of free energies of ionization of ruthenocene complexes also put the trimethylsilyl group to be a similar electron donor like the methyl group[19]. Absorption maxima of lowest energy transitions in the UV-VIS spectra of ring substituted titanocene dichlorides also indicated that the trimethylsilyl group is stronger electron donor than the methyl group[20].

This work describes the synthesis of $[C_5Me_4(SiMe_3)]_2TiCl_2$ (**1**) and $[C_5Me_4(SiMe_3)]_2TiCl$ (**2**), the first reported organometallic compounds of the $C_5Me_4(SiMe_3)$ ligand. The X-ray crystal structures of **1** and **2**, the electronic absorption spectrum of **1**, and the affinity of **2** towards 2-methyltetrahydrofuran (MTHF) and the magnitude of anisotropy of the EPR g-tensor of **2** give the first estimates of the steric and electronic effects of the trimethylsilyl group in highly methyl substituted metallocene compounds of Group IVB.

EXPERIMENTAL

The synthesis of $[C_5Me_4(SiMe_3)]_2TiCl_2$ (**1**) was carried out under argon atmosphere. The reduction of **1** to $[C_5Me_4(SiMe_3)]_2TiCl$ (**2**) as well as the purification, handling and the spectroscopic measurements of the latter were performed in vacuum. An all-sealed glass device equipped with breakable seals, an EPR sample tube and a couple of quartz cuvettes (*d* = 1.0 and 10 mm, Hellma) was used for the measurement of EPR and UV-VIS spectra. The adjustment of single crystals of **2** into the Lindemann glass capillaries for X-ray analysis and the preparation of KBr pellets for IR measurement was performed in a glovebox (Braun) under purified nitrogen. ^{1}H and ^{13}C NMR spectra were measured on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$ at 25 °C. Chemical shifts (given in the δ-scale) were referenced to the non-deuterated solvent signal. EPR spectra were registered on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of G.D.R., Berlin, Germany) in the X-band. *g*-Values were determined using a Mn^{2+} ($M_I = -1/2$ line) standard at $g = 1.9860$ and a proton magnetometer MJ-110 R (Radiopan, Poznan, Poland). Concentrations of the paramagnetic compounds were estimated from integrated first derivation spectra. Variable temperature unit STT-3 was used for the measurement in the range –130 to +20 °C. UV-VIS spectra were measured in the range 270–2 000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Mass spectra were measured on a JEOL D-100 spectrometer at 75 eV (only important mass peaks and peaks of intensity ≥5% are reported) using a direct inlet. Samples of **2** in capillaries were opened and inserted into the direct inlet under argon. Infrared spectra of **1** and **2** in KBr pellets were obtained on a UR-75 (Zeiss, Jena, Germany) and on a Mattson Galaxy 2020 spectrometer, respectively.

Chemicals

The solvents tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), hexane, and toluene were purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $(C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)]_2$ (ref.[21]). Fine magnesium turnings (Fluka, purum for Grignard reactions) were weighed and evacuated. Trimethylsilyl chloride (Aldrich) was transferred from the septum-sealed bottle by syringe under argon.

(Trimethylsilyl)tetramethylcyclopentadiene

Tetramethylcyclopentadiene (16.0 g, 131 mmol) was diluted with THF (400 ml) and 1.6 M BuLi in hexane (82 ml) was added under stirring. After one hour stirring of the homogeneous solution Me_3SiCl (16.7 ml, 132 mmol) was added and the mixture was stirred overnight. The solvents were evaporated and the residue (ca 50 ml) was washed with water (2 × 500 ml), dried with Na_2SO_4 and residual solvents were evaporated at reduced pressure. The product was distilled at reduced pressure (b.p. 96 °C/1 kPa). Yield 14.8 g (58%). GC-MS analysis revealed the presence of pure $C_5HMe_4(SiMe_3)$. Mass spectrum, *m/z* (%): 194 ($M^{+\bullet}$, 25), 179 (7), 121 (9), 120 (42), 119 (7), 105 (36), 91 (18), 79 (10), 77 (12), 74 (8), 73 (100), 59 (7), 45 (17), 43 (8). ^{1}H NMR spectrum: –0.016 s, 9 H ($SiMe_3$); 1.836 s, 6 H (2-Me and 3-Me); 1.952 s, 6 H (1-Me and 4-Me); 2.842 s, 1 H (H-5). ^{13}C NMR spectrum): –1.75 q, 3 C ($SiMe_3$); 11.08 q, 2 C (2-Me and 3-Me); 14.42 q, 2 C (1-Me and 4-Me); 55.40 d (C-5); 133.04 s, 2 C (C-1 and C-4); 135.29 s, 2 C (C-2 and C-3). IR spectrum (neat): 2 957 (s), 2 915 (s), 2 859 (s), 2 730 (w), 1 632 (m), 1 443 (s), 1 405 (m), 1 387 (m), 1 378 (m), 1 303 (m), 1 263 (s), 1 248 (vs), 1 220 (s), 1 179 (w), 1 125 (m), 1 110 (m), 1 048 (m), 1 023 (m), 985 (s), 953 (s), 920 (m), 844 (vs), 765 (m), 748 (s), 725 (m), 700 (s), 684 (s), 623 (vs), 560 (w), 550 (w), 485 (s).

$[C_5Me_4(SiMe_3)]_2TiCl_2$ (**1**)

Solution of 1.6 M butyllithium in hexane (47.4 ml) was added to $C_5HMe_4(SiMe_3)$ (14 g, 72 mmol) in THF (300 ml) and the mixture was stirred at ambient temperature for 2 h. In another vessel a pale blue slurry of crystalline $TiCl_3$. THF was prepared by adding 1.6 M butyllithium (48 ml) to a slurry of $TiCl_4$. THF made of $TiCl_4$ (4 ml, 36 mmol) and THF (50 ml). **Caution, the formation of a $TiCl_4$. THF adduct is a strongly exothermic reaction and requires cooling**. The lithium cyclopentadienide solution was then added under stirring and the mixture was refluxed for 40 h. Finally its volume was reduced to ca 200 ml and 15% aqueous HCl (200 ml) was added under stirring. After 1 h a brown crystalline solid was filtered off, washed twice with water and then with methanol until the washing was only slightly brown. The product was dried on air and crystallized from hot heptane. Recrystallization from heptane yielded 6.2 g (32%) of brown crystals. Mass spectrum (direct inlet, 75 eV), *m/z* (%): 504 ($M^{+\bullet}$, 1), 489 ($[M - Me]^+$, 3), 472 (5), 471 (13), 470 (12), 469 ($[M - Cl]^+$, 24), 433 ($[469 - HCl]^+$, 5), 361 (6), 333 (10), 331 (11), 315 (9), 314 (8), 313 (32), 312 (15), 311 ($[M - C_5Me_4(Me_3Si)]^+$, 41), 310 (6), 298 (9), 297 (11), 296 (13), 295 (11), 277 (9), 276 (10), 275 ($[311 - HCl]^+$, 18), 260 (6), 259 (7), 257 (7), 243 (5), 204 (5), 194 (17), 193 ($[C_5Me_4(Me_3Si)]^+$, 72), 191 (6), 178 (10), 177 (13), 175 (12), 168 (10), 166 (7), 163 (14), 161 (5), 151 (9), 137 (5), 133 (28), 120 (8), 119 (14), 105 (10), 97 (6), 91 (7), 83 (5), 74 (10), 73 ($[Me_3Si]^+$, 100), 59 (47), 45 (14), 43 (10), 41 (5), 36 (7), 28 (6), 18 (30). 17 (7). ^{1}H NMR spectrum: 0.279 s, 18 H ($SiMe_3$); 2.020 s, 12 H (Me); 2.176 s, 12 H (Me). ^{13}C NMR spectrum: 2.02 q, 6 C ($SiMe_3$); 12.52 q, 4 C; 16.40 q, 4 C; 128.94 s, 4 C; 135.69 s, 2 C; 137.00 s, 4 C. IR spectrum (KBr): 3 016 (m), 2 978 (m, sh), 2 958 (s), 2 896 (s), 2 861 (m, sh), 1 480 (s), 1 445 (m), 1 405 (m), 1 378 (s), 1 344 (s), 1 246 (vs), 1 126 (m), 1 025 (s), 990 (w), 954 (w), 841 (vs), 758 (s), 690 (m, sh), 685 (m), 637 (s), 628 (m), 613 (w), 582 (vw), 550 (vw), 429 (s). UV-VIS, nm (toluene, 23 °C): 475 > 570 (sh).

$[C_5Me_4(Me_3Si)]_2TiCl$ (**2**)

Compound **1** (0.250 g, 0.50 mmol) and Mg (0.006 g, 0.25 mmol) were heated in THF (6 ml) to 60 °C for 24 h. Brown colour of the solution turned to blue and all magnesium disappeared. The solvent was evaporated and the residue was extracted by hexane (10 ml). The extract was evaporated in a closed system and the residue was carefully extracted by condensing vapour of hexane. A trace of a brown impurity was removed by this way. The remaining crystalline blue product was dissolved in hexane to give a saturated solution. Slow cooling of the latter afforded blue crystals, yield 0.18 g (80%). These were used for the X-ray diffraction analysis, mass spectra measurement and, after dissolving in toluene, for UV-VIS and EPR measurements. Mass spectrum (direct inlet, 100 °C) *m/z* (%): 473 ($M_i^{+\bullet}$, 8), 472 ($M_i^{+\bullet}$, 20), 471 ($M_i^{+\bullet}$, 53), 470 ($M_i^{+\bullet}$, 47), 469 ($M^{+\bullet}$, 100), 468 (15), 467 (12), 454 ($[M - CH_3]^+$, 10), 434 (11), 433 ($[M - HCl]^+$, 20), 362 (8), 361 ($[433 - Me_3Si]^+$, 22), 359 (8), 278 (12), 277 (29), 276 (31), 275 ($[M - C_5Me_4(Me_3Si)]^+$, 60), 274 (11), 273 (14), 271 (12), 261 (9), 260 ($[275 - CH_3]^+$, 14), 259 (20), 258 (11), 257 (17), 245 (6), 243 (10), 204 (10), 168 ($[275 - Me_3Si, - Cl]^+$, 22), 167 (9), 166 (15), 74 (7), 73 ($[Me_3Si]$, 82), 59 (13). EPR spectrum (toluene, 23 °C): $g = 1.9537$, $\Delta H = 14$ G; (toluene, –130 °C): $g_1 = 1.9987$, $g_2 = 1.9822$, $g_3 = 1.8933$, $g_{av} = 1.958$. UV-VIS, nm (hexane): 360 (sh) >> 560 > 660 (sh).

X-Ray Structure Determination

A brown needle crystal of **1** was cut and its fragment was mounted onto a measuring rod in air. The blue crystal fragment of **2** was fixed into a Lindemann glass capillary under purified nitrogen in a glovebox (Braun) and was closed with a sealing wax. Diffraction data were collected on an Enraf–Nonius CAD-4 diffractometer at room temperature using graphite monochromated MoKα radiation (λ 0.71069 Å). The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions and refined riding on their attached carbon atoms. Calculations were performed by SHELX76 and SHELXL93 programs. Details of data collection and refinement are given in Table I. Positional parameters and isotropic thermal factors for titanocenes **1** and **2** are listed in Tables II and III, respectively. Selected bond distances

TABLE I
Crystallographic data for **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{24}H_{42}Cl_2Si_2Ti$	$C_{24}H_{42}ClSi_2Ti$
Molecular weight	505.56	470.11
Crystal system	monoclinic	triclinic
Space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a, Å	18.455(3)	8.5210(10)
b, Å	8.127(2)	9.1068(8)
c, Å	19.544(4)	19.151(2)
α, °	90	96.649970
β, °	110.44(2)	90.677(9)
γ, °	90	114.623(9)
V, $Å^3$	2 746.7(10)	1 338.9(2)
Z	4	2
d_{calc}, g cm^{-3}	1.223	1.166
μ(MoKα), mm^{-1}	0.603	0.517
F(000)	1 080	506
Crystal size	0.4 × 0.5 × 0.6	0.6 × 0.6 × 0.6
θ_{min}, θ_{max}, °	2.22, 24.98	1.07, 24.97
Range of indices (*hkl*)	–21 → +20, 0 → 9, 0 → 23	–10 → +9, 0 → 10, ±22
Reflections collected	2 487	4 701
Independent reflections	2 415 [*R*(int) = 0.0118]	4 701 [*R*(int) = 0.000]
Data, restraints, parameters	2 413, 0, 216	4 701, 0, 421
Goodness-of-fit on F^2	1.061	1.044
Final *R*1 values	0.0330	0.0368
$wR2$ [$I > 2\sigma(I)$]	0.0852	0.0974
*R*1 values (all data)	0.0476	0.0516
$wR2$ (all data)	0.0926	0.1060
Min. and max. residual density, e $Å^{-3}$	–0.292, 0.316	–0.537, 0.551

and bond angles are shown in Table IV. Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre. These and all other details concerning the structure determination are available from the authors (R. G., I. C.).

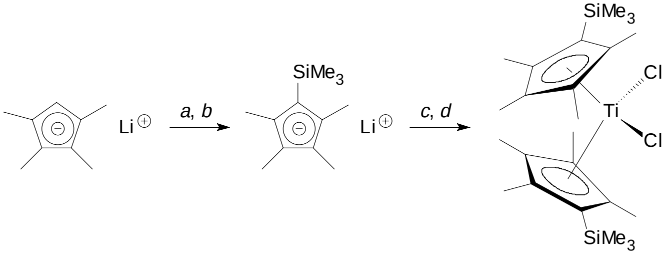
RESULTS AND DISCUSSION

The synthesis of **1** followed the steps generally used for the preparation of highly methyl substituted titanocene dichlorides (see Scheme 1). In spite of apprehension that the bulky trimethylsilyl group will be reluctant to react with the tetramethylcyclopentadienyl anion (step *a*), (trimethylsilyl)tetramethylcyclopentadiene was obtained in good yield after the reaction time of 16 h at ambient temperature. The crucial step of the synthesis, i.e. the reaction of $[C_5(SiMe_3)Me_4]^-Li^+$ with $TiCl_3$ in tetrahydrofuran (THF) required a longer reaction time at the reflux temperature than the permethylated titanocene dichloride (40 h against 25 h). The brown thin needle crystals of **1** were obtained in moderate yield.

The reduction of **1** to $[C_5(SiMe_3)Me_4]_2TiCl$ (**2**) was carried out by half of one equivalent of Mg in THF according to Eq. (*1*). Crystalline compound **2** was obtained in high yield.

$$2\ [C_5(SiMe_3)Me_4]_2TiCl_2 + Mg \longrightarrow 2\ [C_5(SiMe_3)Me_4]_2TiCl + MgCl_2 \quad (1)$$

The X-ray crystal structure analysis of **1** and **2** revealed that the compounds acquire the bent sandwich structures, common to Group IVB metallocene derivatives. The ORTEP drawing of **1** and the atom numbering scheme is shown in Fig. 1. The molecular structure of **1** is symmetrical with respect to a crystallographic twofold rotation axis which passes the Ti atom and bisects the Cl–Cl′ interconnection. The titanium atom is pseudotetrahedrally coordinated and the molecular planes defined by CE (centroid of the cyclopentadienyl ring), Ti and CE′, and by the Cl, Ti and Cl′ atoms are mutualy nearly perpendicular (88.8°). ORTEP drawing of **2** with the atom numbering scheme is



1

a) Me_3SiCl, THF; *b*) BuLi, THF-hexane; *c*) $TiCl_3$, reflux; *d*) HCl, air

SCHEME 1

depicted in Fig. 2. The titanium atom is trigonally coordinated by two Cp′ ligands and one chlorine atom. An approximate twofold symmetry of **2** with respect to the axis passing the Ti and Cl atoms is not explored crystallographically. Selected bond distances and important angles of **1** and **2** are listed in Table IV. The molecular structures

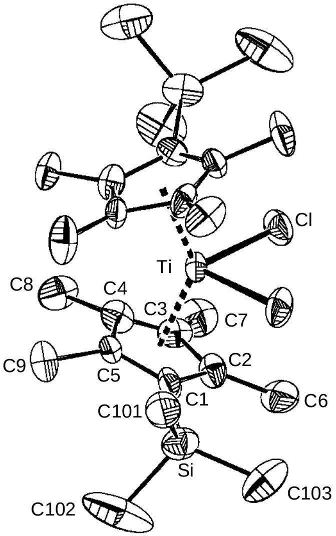


FIG. 1
ORTEP drawing of **1** with atom numbering scheme (ellipsoids are drawn at 30% probability level)

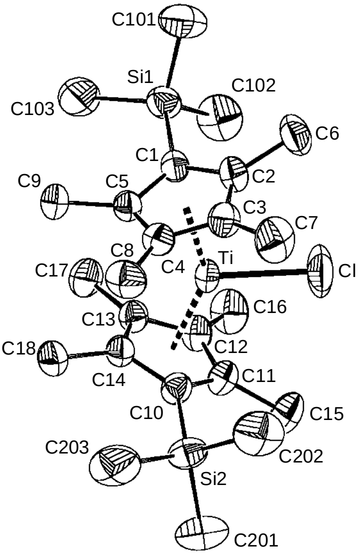


FIG. 2
ORTEP drawing of **2** with atom numbering scheme (ellipsoids are drawn at 30% probability level)

of **1** and **2** are most similar to the structures of $(C_5Me_5)_2TiCl_2$ (**3**) (ref.[22]) and $(C_5Me_5)_2TiCl$ (**4**) (ref.[23]). The main geometrical parameters of **1** and **2**, i.e., the Ti–CE distances and the CE–Ti–CE angles are the same as those of **3** and **4** within 0.01 Å and 1°, respectively. The Cl–Ti–Cl′ angle in **1** has virtually the same value as in **3**. The pseudotetrahedral coordination of the Ti atom in **1** and **3** brings about slightly longer Ti–C and Ti–Cl bonds and smaller CE–Ti–CE angles than in trigonally coordinated compounds **2** and **4** (Table IV).

The presence of bulky trimethylsilyl groups, however, induced minor structure variations between **1** and **2** and between both of them and both **3** and **4**. A large steric congestion introduced by the trimethylsilyl groups is largely relieved by their placement in side positions on opposite sides of the CE–Ti–CE planes (see Fig. 1 and Fig. 2), as it is known e.g., for bis(*tert*-butylcyclopentadienyl)titanium dichloride[24] or bis(isodicyclopentadienyl)titanium dichloride[25]. In **2**, the Cp′ rings are mutually staggered (the torsion angle C5, CE1, CE2, C14 is 33.1°) and the trimethylsilyl groups are in strictly

TABLE II
Atomic coordinates (. 10^4) and equivalent isotropic thermal parameters (. 10^3) for non-hydrogen atoms of **1**

Atom	*x*	*y*	*z*	$U_{eq}{}^a$, Å^2
Ti	0	1781(1)	2500	31(1)
Cl	–923(1)	3846(1)	2439(1)	51(1)
Si	1248(1)	1416(1)	1272(1)	53(1)
C1	299(1)	1153(2)	1423(1)	37(1)
C2	–359(1)	2219(3)	1204(1)	39(1)
C3	–993(1)	1365(3)	1275(1)	42(1)
C4	–741(1)	–217(3)	1554(1)	41(1)
C5	44(1)	–357(2)	1634(1)	38(1)
C6	–428(2)	3900(3)	874(2)	58(1)
C7	–1820(2)	1914(5)	1003(2)	62(1)
C8	–1284(2)	–1608(4)	1539(2)	61(1)
C9	463(2)	–1966(3)	1732(2)	57(1)
C101	2103(2)	927(5)	2089(2)	67(1)
C102	1219(3)	–58(9)	531(3)	101(2)
C103	1388(2)	3502(6)	939(3)	90(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor. Symmetry transformation used to generate equivalent atoms (Cl′, Si′, C(1′), etc.): –*x*, *y*, 1/2 –*z*.

opposite positions so that the carbon atoms C1, C10 and silicon atoms Si1 and Si2 form a plane with the deviation as little as 0.03 Å. In **1**, the congestion which arises from the presence of two chlorine atoms and two trimethylsilyl groups apparently causes that the rings are in a close-to-eclipsed conformation with the C2 and C2′ atoms close to the CE, Ti, CE′ plane. The torsion C2, CE, CE′, C2′ angle is 11.3°. The steric hindrance

TABLE III
Atomic coordinates (. 10^4) and equivalent isotropic thermal parameters (. 10^3) for non-hydrogen atoms of **2**

Atom	*x*	*y*	*z*	$U_{eq}{}^{a}$, Å^2
Ti	1102(1)	4422(1)	2472(1)	38(1)
Si1	–1620(1)	2186(1)	770(1)	52(1)
Si2	2664(1)	7251(1)	4218(1)	54(1)
Cl	3131(1)	3308(1)	2396(1)	97(1)
C1	–17(3)	4110(3)	1297(1)	42(1)
C2	1812(3)	4659(3)	1266(1)	47(1)
C3	2650(3)	6225(3)	1646(1)	49(1)
C4	1384(3)	6730(3)	1894(1)	45(1)
C5	–262(3)	5449(3)	1673(1)	42(1)
C6	2731(4)	3813(5)	834(2)	67(1)
C7	4582(4)	7237(5)	1717(2)	75(1)
C8	1742(5)	8429(3)	2220(2)	64(1)
C9	–1917(4)	5648(4)	1688(2)	54(1)
C10	1058(3)	5340(3)	3682(1)	43(1)
C11	1188(3)	3815(3)	3655(1)	46(1)
C12	–322(3)	2569(3)	3303(1)	45(1)
C13	–1442(3)	3267(3)	3120(1)	42(1)
C14	–616(3)	4961(3)	3362(1)	41(1)
C15	2587(5)	3512(5)	4013(2)	68(1)
C16	–714(5)	792(3)	3192(2)	66(1)
C17	–3280(3)	2314(4)	2832(2)	58(1)
C18	–1538(4)	6054(4)	3417(2)	55(1)
C101	–1179(6)	2271(6)	–179(2)	83(1)
C102	–1414(6)	386(4)	1052(3)	82(1)
C103	–3918(4)	1873(6)	835(2)	87(1)
C201	2838(7)	6861(6)	5141(2)	85(1)
C202	4826(5)	7916(6)	3850(2)	91(1)
C203	2034(8)	8989(5)	4274(3)	96(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

between the methyl groups close to the hinge position of the rings resulted in a smaller angle between the ring planes (ϕ) compared to that of **3** (39.7° against 44.6°). As a consequence, the ring plane is slightly tilted in an opposite direction than in **3** (the angle between the Ti–CE vector and the ring plane towards the hinge position is 89.0° for **3** and 91.3° for **1**). The trigonal coordination in **2** and **4** together with the absence of the chlorine-induced steric hindrance afforded very low values of the angle ϕ (35.8 and 36.4°, respectively) while the Ti–CE vectors were perpendicular to the ring planes within 0.2°. This allows us to conclude that the replacement of one methyl group in each of the C_5Me_5 ligands of **3** by the trimethylsilyl group should not induce a remarkable change in the energy levels of the frontier orbitals $1a_1$ and b_2 following from their dependence on the CE–Ti–CE angle[26], as changes in these angles are negligible (see Table IV). However, the influence of empty d-orbitals of the silicon atoms and of the

TABLE IV
Selected bond lengths (Å) and angles (°) for **1** and **2**

Atoms	**1**	**2**[a]	
		Bond lengths	
Ti–Cl	2.365(1)	2.340(1)	[a]
Ti–C1	2.408(2)	2.373(2)	2.377(2)
Ti–C2	2.411(2)	2.405(3)	2.401(3)
Ti–C3	2.478(2)	2.405(3)	2.411(3)
Ti–C4	2.482(2)	2.413(2)	2.411(2)
Ti–C5	2.446(2)	2.401(2)	2.398(2)
Ti–CE	2.128(2)	2.074(2)	2.073(2)
C–C(ring)$_{av}$	1.416(3)	1.419(4)	1.420(4)
C–C(Me)$_{av}$	1.499(4)	1.503(5)	1.500(5)
Si1–C1	1.889(2)	1.875(3)	1.877(3)
Si1–C(Me)$_{av}$	1.862(6)	1.862(5)	1.860(5)
		Bond angles	
CE–Ti–CE	137.6(5)	144.4(1)	–
Si1–C1–C2	127.8(7)	123.0(2)	122.1(2)
Si1–C1–C5	122.4(7)	130.2(2)	130.9(2)
C2–C1–C5	108.2(8)	105.6(2)	105.7(2)
ϕ[b]	39.8	35.8	–
Cl–Ti–Cl′	89.5(1)	–	–

[a] The second column for **2** concerns the atoms of the CE2 ring containing the C10–C14 atoms and Si2 (see Fig. 2). Only one set of data for **1** stems from the symmetry of the molecule. [b] Dihedral angle between least-squares planes of the cyclopentadienyl rings.

ring tilting from the perpendicuar position to the Ti–CE vector on the electronic structure of the titanocene complexes has not yet been investigated.

The overall electron donating/releasing effect of the trimethylsilyl group in **1** can be estimated from the comparison of positions of its electronic absorption bands with those of the methylated analogs. The data in Table V indicate that the methyl substituents shift the positions of the two absorption bands in visible region to longer wavelengths. The increments of the shift per one methyl group widely vary between the particular compounds and the assignment of the transitions is not known. In spite of it, the longest wavelengths of both the bands for **1** place the trimethylsilyl group to be the electron donor with a stronger effect than the methyl group.

The effect of the trimethylsilyl group has been also evaluated from the affinity of compound **2** to MTHF and from the anisotropy of its EPR *g*-tensor. The *g*-tensor components obtained in frozen glassy toluene and MTHF solutions for **2** and the highly methylated compounds $(C_5Me_5)_2TiCl$, $(C_5HMe_4)_2TiCl$, and $(C_5H_2Me_3)_2TiCl$ are collected in Table VI. The formation of the MTHF adduct, probably Cp'_2TiCl . MTHF, in the MTHF solution at room temperature and at –140 °C is also indicated.

The electron donation effect of methyl groups in titanocene monohalides results in their reluctance to form halogen-bridged dimers and in the loss of their affinity to MTHF with the increase in the number of methyl substituents at the cyclopentadienyl rings. The $(C_5H_{5-n}Me_n)_2TiCl$ compounds remain monomeric in the solid state and in toluene solution for $n \geq 3$ while they form dimers for $n = 0$–2 (refs[27–29]). In MTHF solution, the EPR evidence was obtained (see Table VI) that $(C_5H_2Me_3)_2TiCl$ partly coordinates MTHF at room temperature and this coordination is quantitative at –140 °C. $(C_5HMe_4)_2TiCl$ forms the MTHF adduct as a minor component only at –140 °C and $(C_5Me_5)_2TiCl$ does not coordinate MTHF even at –196 °C (ref.[30]). The solution of **2** in MTHF gave the EPR spectra which did not indicate the presence of either the dimer (a broad anisotropic spectrum of the electronic triplet state in frozen glassy solution[28,29]) or the MTHF adduct (*g*-value close to 1.98 in solution and a *g*-tensor of low anisotropy

TABLE V
Absorption maxima[a] (nm) in the UV-VIS spectra of ring-substituted titanocene dichlorides

Compound	λ_{max}	λ_{max}
$(C_2H_5)_2TiCl_2$	390	515
$(C_5H_2Me_3)_2TiCl_2$	400 (sh)	520
$(C_5HMe_4)_2TiCl_2$	440	520 (sh)
$(C_5Me_5)_2TiCl_2$	470	550 (sh)
$[C_5Me_4(SiMe_3)]_2TiCl_2$	475	570 (sh)

[a] sh shoulder.

Table VI
EPR parameters for **2** and methyl substituted titanocene chlorides

Compound	Solvent	Cp'_2TiCl					Cp'_2TiCl . MTHF			Data taken from
		g_{iso}	g_1	g_2	g_3	g_{av}	g_{iso}	g_3	g_{av}	
2	toluene	1.953	1.999	1.982	1.893	1.958	–	–	–	this work
	MTHF	1.953	1.996	1.980	1.897	1.958	no[a]	1.953	1.976	
$(C_5Me_5)_2TiCl$	toluene	1.957	1.999	1.984	1.889	1.956	–	–	–	ref.[30]
	MTHF	1.956	1.999	1.984	1.888	1.957	no	–	no	
$(C_5HMe_4)_2TiCl$	toluene	1.964	2.000	1.985	1.910	1.965	–	–	–	ref.[30]
	MTHF	1.964	2.000	1.984	1.909	1.964	no	1.954	1.979	
$(C_5H_2Me_3)_2TiCl$	toluene	1.965	2.001	1.986	1.915	1.967	–	–	–	ref.[30]
	MTHF	1.965	2.001	1.983	–	no	1.979	1.954	1.979	

[a] The absence of the species in MTHF solutions at room temperature (g_{iso}) or at –140 °C (g_{av}) is indicated by "no". The g_1 and g_2 tensor components of Cp'_2TiCl and Cp'_2TiCl . MTHF occur at virtually the same g-value and cannot be distinguished.

in glass[30]). The g-tensor of the $(C_5H_{5-n}Me_n)_2TiX$ (X = Cl, Br, I; n = 3–5) compounds in toluene glass showed that its high-field component (g_3) strongly depends on the number of methyl groups n whereas the g_1 and g_2 components remain constant[30]. The g-tensor of **2** in frozen toluene (g_1 = 1.999, g_2 = 1.982, g_3 = 1.893) agrees very well with that of $(C_5Me_5)_2TiCl$ (see Table VI) and thus, judging from this parameter, the effect of the trimethylsilyl group is similar to the electron donation effect of the methyl group. In MTHF solution, however, the $[C_5Me_4(SiMe_3)]_2TiCl$. MTHF adduct was present in frozen glass at –140 °C at a considerably higher abundance than in the solution of $(C_5HMe_4)_2TiCl$ at a similar overall concentration. It was completely absent at room temperature. This behaviour towards MTHF thus indicates that **2** is a weaker Lewis acid than $(C_5H_2Me_3)_2TiCl$, only slightly stronger than $(C_5HMe_4)_2TiCl$. This would classify the trimethylsilyl group to be a weaker electron donor than proton. These results and so far available literature data allow us to assume that the spectroscopic data, which are dependent on energy levels of particular molecular orbitals, usually put the effect of the trimethylsilyl group close to that of the methyl group whereas the overall molecular behaviour based on the chemical reactivity identifies the trimethylsilyl group to be an electron acceptor.

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