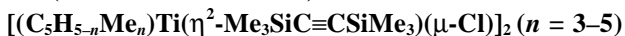


SYNTHESIS AND CRYSTAL STRUCTURES OF DIMERIC TITANIUM(II) BIS(TRIMETHYLSILYL)ACETYLENE COMPLEXES

Jörg HILLER^{a1}, Ulf THEWALT^{a2,*}, Jaroslav PODLAHA^b, Vladimír HANUS^{c1}
and Karel MACH^{c2,*}

^a *Sektion für Röntgen- und Elektronenbeugung, Universität Ulm, 89069 Ulm, Germany; e-mail:*

¹ *joerg.hiller@chemie.uni-ulm.de, ² ulf.thewalt@chemie.uni-ulm.de*

^b *Department of Inorganic Chemistry, Charles University, 128 40 Prague 2, Czech Republic;
e-mail: podlaha@prfdec.natur.cuni.cz*

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

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Crystalline Ti(II) complexes $[(C_5H_{5-n}Me_n)Ti(\eta^2-Me_3SiC\equiv CSiMe_3)(\mu-Cl)]_2$ ($n = 3-5$) (**1-3**) were prepared by reduction of the appropriate cyclopentadienyltitanium trichlorides $(C_5H_{5-n}Me_n)TiCl_3$ in tetrahydrofuran by one equivalent of magnesium in the presence of at least one equivalent of bis(trimethylsilyl)acetylene. The X-ray structure analyses of **1-3** revealed that all compounds form chlorine-bridged centrosymmetric dimers.

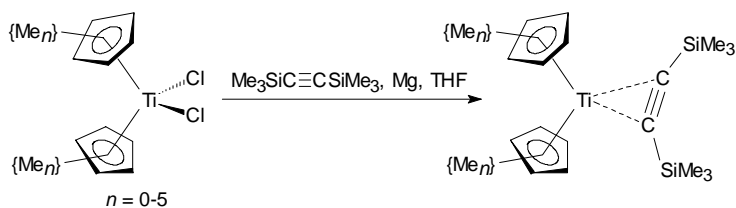
Key words: Sandwich complexes; Metallocenes; Titanocenes; Cyclopentadienyltitanium(II) complexes; Chlorine-bridged complexes; Bis(trimethylsilyl)acetylene ligand; Crystal structures.

Titanium compounds containing the Cp_2Ti^{II} fragment are usually stabilized by coordination of π - or lone-pair electron donor ligands which are able to accommodate the Ti^{II} d^2 electrons in a low-energy empty orbital¹⁻³. Among the π -coordinated acetylene complexes⁴⁻⁷, those containing bis(trimethylsilyl)acetylene ($Me_3SiC\equiv CSiMe_3$ or BTMSA) are thermally stable and in most cases, crystalline compounds⁸⁻¹¹. They are generally prepared¹¹ by the reduction of titanocene dichlorides $(C_5H_{5-n}Me_n)_2TiCl_2$ ($n = 0-5$) using Mg in tetrahydrofuran (THF) in the presence of BTMSA (Scheme 1).

Recent thorough investigation of this reaction, however, disclosed that reactivity of the BTMSA complexes towards excess magnesium depends on the number of methyl substituents at the cyclopentadienyl rings. For $n = 0-2$, a two-fold or larger molar excess of Mg and BTMSA leads to the Ti-Mg complexes containing perpendicularly

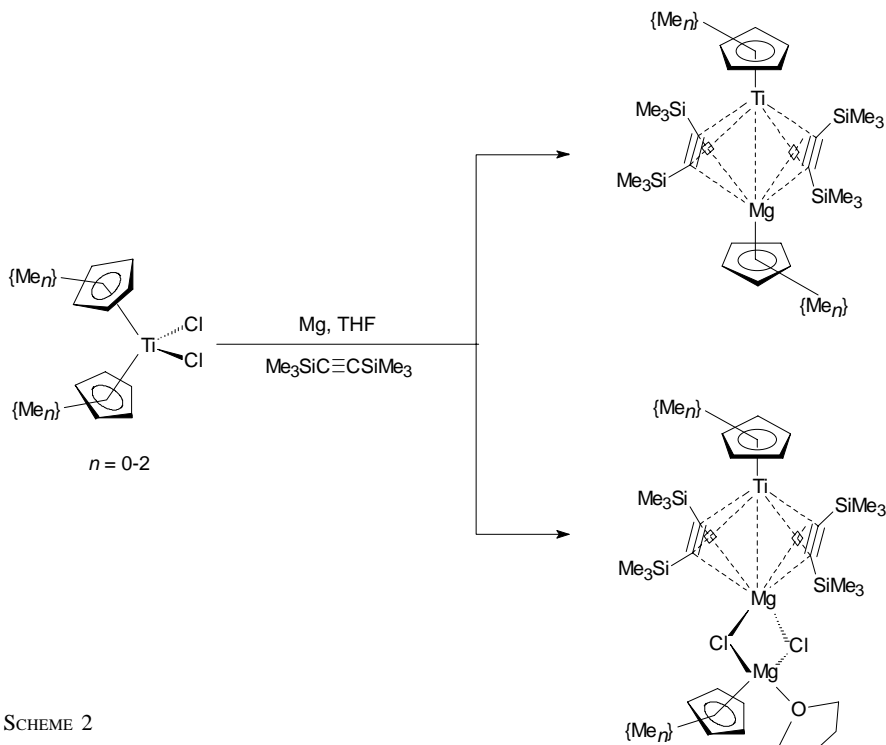
* The author to whom correspondence should be addressed.

bridging BTMSA ligands $[(C_5H_{5-n}Me_n)Ti(\mu-\eta^2:\eta^2-Me_3SiC\equiv CSiMe_3)_2Mg(C_5H_{5-n}Me_n)]$ and/or $[(C_5H_{5-n}Me_n)Ti(\mu-\eta^2:\eta^2-Me_3SiC\equiv CSiMe_3)_2Mg(\mu-Cl)_2Mg(C_5H_{5-n}Me_n)(THF)]$ (refs^{12,13}) (see Scheme 2).



SCHEME 1

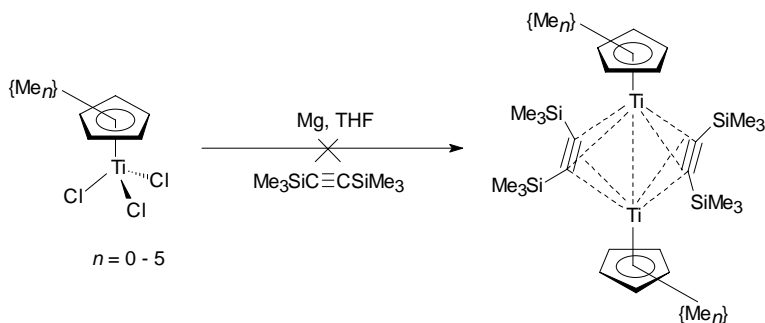
In contrast, the $[(C_5H_{5-n}Me_n)_2Ti(\eta^2-Me_3SiC\equiv CSiMe_3)_2]$ complexes for $n = 3-5$ do not react with magnesium¹¹.



SCHEME 2

These results brought us to the idea that replacement of the titanocene dichlorides in the reaction of Scheme 1 by the $(C_5H_{5-n}Me_n)TiCl_3$ compounds may lead to titanium complexes of the type $[(C_5H_{5-n}Me_n)Ti(\mu-\eta^2:\eta^2-Me_3SiC\equiv CSiMe_3)_2]$, analogues of the above Ti-Mg complexes (Scheme 3).

Moreover, at a Ti : Mg molar ratio equal to 1 : 1, intermediates of the composition $(C_5H_{5-n}Me_n)TiCl \cdot BTMSA$ should be obtained. The preparation and X-ray crystal structures of these complexes for $n = 3-5$ are described in this paper.



SCHEME 3

EXPERIMENTAL

General Data and Methods

All manipulations with reagents, syntheses, and most of the spectroscopic measurements were carried out under vacuum using all-sealed glass devices equipped with breakable seals. Electron impact mass spectra were measured on a JEOL D-100 spectrometer at 75 eV (only important mass peaks and peaks of intensity not below 5% are reported). Samples in capillaries were opened and inserted into the direct inlet under argon. Single crystals of **1-3** were adjusted into capillaries for the X-ray measurement and KBr pellets of **1** and **3** were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen. The pellets were measured in an air-protecting cuvette on a Mattson Galaxy 2020 IR spectrometer. 1H and ^{13}C NMR spectra of **2** and **3** were measured on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in C_6D_6 at 25 °C. Chemical shifts (δ) were referenced to the solvent signal (δ_H 7.15 ppm, δ_C 128.0 ppm). UV-VIS spectra were measured in the range 280–2400 nm on a Varian Cary 17D spectrometer using all sealed-quartz cuvettes (Hellma) ($d = 0.1$ and 1.0 cm). Electron dispersive X-ray analyses (EDX) were carried out on a Zeiss DSM-962 scanning electron microscope equipped with an EDAX PV9800 analyzer. Acceleration voltage of 25 kV was used. EDX measurements serve for qualitative and semi-quantitative analyses of the contents (>2%) of chemical elements with atomic number higher than 6.

Chemicals

The solvents THF, hexane, toluene, and benzene- d_6 were purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as degassed solutions of dimeric titanocene $(C_{10}H_8)(C_5H_5)_2Ti(\mu-H)_2$ (ref.¹⁴). The solvents were distilled therefrom under vacuum. Bis(trimethylsilyl)acetylene (BTMSA) (Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h and distilled into ampoules under vacuum. Magnesium turnings (Fluka, purum for Grignard reactions) were evacuated before use. Titanocene dichlorides $(C_5H_{5-n}Me_n)_2TiCl_2$ ($n = 0-5$) (ref.¹⁵) were finally purified by crystallization from toluene. Monocyclopentadienyltitanium trichlorides $(C_5H_{5-n}Me_n)TiCl_3$ ($n = 0-5$) were prepared by reacting $TiCl_4$ with the titanocene dichlorides¹⁵. A solution of $TiCl_4$ (0.45 ml, 4.1 mmol) in *m*-xylene (4 ml) was added to an evacuated ampoule containing $(C_5H_{5-n}Me_n)_2TiCl_2$ (4 mmol). The

ampoule was sealed off and heated to 140 °C for 4 h. After cooling to room temperature, the solvent and traces of TiCl_4 were distilled off at 100 °C into a trap cooled by liquid nitrogen. The yellow to orange products of $(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$ were sublimed under high vacuum into an ampoule cooled with an ice–water slurry. Yields of the products were not determined; judging from a negligible amount of the sublimation residue the yields were at least 95% (7.6 mmol).

Preparation of $[(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{Ti}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\mu\text{-Cl})_2]_2$ ($n = 3\text{--}5$) (**1–3**)

BTMSA (2.2 ml, 10 mmol) and THF (30 ml) were distilled onto Mg turnings (0.185 g, 7.6 mmol) and $(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$ ($n = 3\text{--}5$) (7.6 mmol) was added from an attached ampoule by washing it with condensed vapours of THF. The mixture was stirred overnight with a magnetic stirrer at room temperature whereas the color changed from yellow-orange to green. The magnesium metal was consumed only partly. After another 24 h of stirring all magnesium had disappeared and homogeneous dark brown solutions were obtained. The solvent and excess of BTMSA were evaporated in vacuum at 60 °C. The brown residue was repeatedly extracted with hexane until the extracts were nearly colourless. The subsequent extraction with toluene afforded a brown solution which, on slow cooling from 50 °C to room temperature, afforded a crop of brown crystals. Repeated crystallizations from the mother liquor yielded further crops of the crystals of **1–3**. These were, however, contaminated by MgCl_2 . The yields were generally low, decreasing strongly from **3** to **1**.

$[(\text{Me}_3\text{Cp})\text{Ti}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\mu\text{-Cl})_2]$ (**1**). Yield 0.04 g (1.5% related to $(\text{Me}_3\text{Cp})\text{TiCl}_3$). Mass spectrum (direct inlet, 150–160 °C), m/z (%): 720 (M^+ , 0.05), 550 ($[\text{M} - \text{C}_2(\text{SiMe}_3)_2]^+$, 1.2), 380 ($[\text{M} - 2\text{C}_2(\text{SiMe}_3)_2]^+$, 6.5), 360 (7.5), 262 (6.2), 193 (5.0), 192 (30.0), 191 (17.0), 190 (78.5), 189 (14.2), 188 (14.2), 157 (8.1), 156 (17.5), 155 (100), 154 (5.0), 153 (5.2), 152 (5.2), 97 (8.3), 91 (5.0), 83 (5.6), 73 (28), 70 (11.0). IR spectrum (cm^{-1}), KBr: 2 970 (s), 2 900 (m), 1 619 (m), 1 456 (w), 1 398 (w), 1 369 (w), 1 240 (s), 1 020 (w), 880 (s), 854 (s), 838 (vs), 788 (m), 750 (m), 688 (w), 650 (m), 622 (w), 587 (w), 481 (w), 457 (w), 425 (m). EDX spectrum ($\text{K}\alpha$): Ti : Si : Cl ratio approximately 1 : 2 : 1. NMR and UV-VIS spectra were not measured.

$[(\text{Me}_4\text{Cp})\text{Ti}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\mu\text{-Cl})_2]$ (**2**). Yield: 0.2 g (7.0%, related to $(\text{Me}_4\text{Cp})\text{TiCl}_3$). Mass spectrum (direct inlet, 100–150 °C), m/z (%): dissociation to the monomer is indicated by ions m/z 374 ($\text{M}/2^+$) and 204 $[(\text{M}/2) - \text{C}_2(\text{SiMe}_3)_2]^+$; total loss of BTMSA from the dimeric molecule is indicated by ions m/z 408 $[(\text{Me}_4\text{Cp})_2\text{Ti}_2\text{Cl}_2]^+$, m/z 290 $[(\text{Me}_4\text{Cp})_2\text{Ti}]^+$ and m/z 239 $[(\text{Me}_4\text{Cp})\text{TiCl}_2]^+$. ^1H NMR spectrum: 0.038 s, 36 H (SiMe_3); 1.940 s, 12 H (1-Me, 4-Me); 2.086 s, 12 H (2-Me, 3-Me); 7.150 s, 2 H ($\text{Me}_4\text{C}_5\text{H}$). ^{13}C NMR spectrum: 1.18 q, 12 C (SiMe_3); 12.94 q, 4 C; 15.82 q, 4 C; 115.94 d, 2 C; 127.01 s, 4 C; 129.03 s, 4 C; 263.97 s, 4 C. UV-VIS spectrum (nm), toluene, 20 °C: 335 (sh) > 405 (sh) > 800 nm. IR and EDX spectra were not measured.

$[(\text{C}_5\text{Me}_5)\text{Ti}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\mu\text{-Cl})_2]$ (**3**). Yield 0.5 g (17% related to $(\text{C}_5\text{Me}_5)\text{TiCl}_3$). Mass spectrum (direct inlet, 150–200 °C), m/z (%): 388 ($[\text{M}/2]^+$, 10), 253 ($[\text{M}/2 - \text{C}_5\text{Me}_5]^+$, 3), 221 (7), 220 (38), 219 (24), 218 ($[\text{M}/2 - \text{C}_2(\text{SiMe}_3)_2]^+$, 100), 217 (20), 216 (15), 215 (5), 213 (8), 170 (7), 157 (6), 156 (13), 155 (76), 119 (5), 73 (14), 70 (6). IR spectrum (cm^{-1}), KBr: 2 955 (s), 2 901 (s), 1 595 (s), 1 454 (w), 1 434 (w), 1 402 (w), 1 377 (m), 1 244 (s), 1 020 (w), 875 (sh), 856 (vs), 838 (vs), 752 (s), 687 (w), 650 (m), 621 (w), 584 (w), 476 (m), 426 (m). ^1H NMR spectrum: 0.070 s, 36 H (SiMe_3); 2.078 s, 30 H (Me). ^{13}C NMR spectrum: 1.74 q, 12 C (SiMe_3); 13.82 q, 10 C (Me); 100.87 s, 10 C (Cp); 264.65 s, 4 C ($\text{C}\equiv\text{C}$). UV-VIS spectrum (nm), toluene, 20 °C: 350 (sh) > 390 (sh) >> 800 nm. EDX spectrum ($\text{K}\alpha$): Ti : Si : Cl ratio approximately 1 : 2 : 1.

Attempted Preparation of $[(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{Ti}(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)_2]$ ($n = 0\text{--}5$)

The procedure was the same as that for **1–3** except that an excess of magnesium (0.74 g, 30.4 mmol) was used. The yellow-orange colour of the THF solutions of $(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$ turned rapidly to

green, brown and finally to dark green. The solvent was distilled off in vacuum and the dark residue was extracted with hexane. The dark brown solutions were separated from crystalline residues (probably impure MgCl_2). After evaporation of hexane, dark brown, amorphous, extremely hexane-soluble materials were obtained. The high solubility precluded purification on the basis of different solubilities or by fractional crystallization. NMR and MS spectra revealed the presence of various products among which the expected complexes could hardly be identified. Only for $n = 5$, crystals of **3** separated from the reaction solution in the yield of 0.05 g (1.7%).

Crystal Structure Analyses of **1**, **2**, and **3**

Selected crystal fragments of **1**, **2**, and **3** were mounted into Lindemann glass capillaries under purified nitrogen in a glovebox Labmaster 130 (mBraun) and sealed by wax. All X-ray measurements were performed at room temperature on a Philips PW1100 single crystal diffractometer (graphite monochromator, $\text{MoK}\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$). The intensity data were collected by $2\theta/\omega$ scans and were corrected for the Lorentz and polarization effects. No absorption corrections were applied. The structures were solved by iterative symbolic addition (ISA) (ref.¹⁶) and refined with full matrix least-squares methods based on F^2 applying variance-based weighting schemes (SHELXL93, ref.¹⁷). The cyclopentadienyl hydrogens were included at their calculated positions and the methyl hydrogens were refined using a riding model. The crystallographic data are summarized in Table I. Atomic coordinates and isotropic and anisotropic thermal parameters as well as further details concerning the crystal structure analyses of **1**, **2** and **3** are available upon request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, by quoting the deposition numbers CSD-406991 (**1**), CSD-406992 (**2**) and CSD-406993 (**3**). The data are stored having the CIF and FCF standard of the International Union of Crystallography.

RESULTS AND DISCUSSION

The reduction of $(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$ ($n = 0-5$) by a four-fold molar excess of magnesium in THF in the presence of BTMSA did not lead to the isolation of the expected compounds $[(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{Ti}(\mu\text{-}\eta^2\text{-}\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSi Me}_3)]_2$ of Scheme 3. Generally, intractable mixtures of highly hexane-soluble products were obtained except for $n = 5$ where, in addition, a very low yield of the $[(\text{C}_5\text{Me}_5)\text{Ti}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\mu\text{-Cl})]_2$ (**3**) (*vide infra*) crystallized out from a warm hexane extract of the solid residue after evaporation of THF *in vacuo*.

In contrast, treatment of the $(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$ ($n = 0-5$) compounds with one equivalent of Mg results in smooth isolation of crystalline products $[(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{Ti}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\mu\text{-Cl})]_2$ for $n = 3-5$ (**1-3**) which are apparently formed according to Scheme 4.

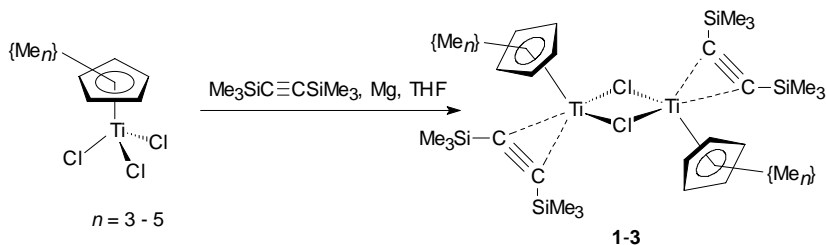
Yields of **1-3** strongly decrease with decreasing number of Me substituents, from 17% for **3** to 1.5% for **1**. The major products are present in the fraction highly soluble in hexane and in an amorphous insoluble solid, and were not isolated. The systems for $n = 0-2$ afford mixtures of the latter products only.

The structures of compounds **1-3** were determined by X-ray diffraction (*vide infra*). The presence of Ti : Si : Cl in the approximate atom ratio 1 : 2 : 1 and the absence of Mg was found by EDX measurements. Infrared spectra of **1** and **3** showed absorption

TABLE I
Crystal and structure refinement data for 1, 2 and 3

Parameter	1	2	3
Chemical formula	C ₃₂ H ₅₈ Cl ₂ Si ₄ Ti ₂	C ₃₄ H ₆₂ Cl ₂ Si ₄ Ti ₂	C ₃₆ H ₆₆ Cl ₂ Si ₄ Ti ₂
Molecular weight	721.84	749.90	777.95
Crystal system	triclinic	monoclinic	triclinic
Space group	<i>PI</i> , No. 2	<i>P2₁/c</i> , No. 14	<i>PI</i> , No. 2
<i>a</i> , Å	9.403(5)	13.600(1)	9.745(4)
<i>b</i> , Å	10.721(3)	16.6240(1)	10.260(4)
<i>c</i> , Å	11.441(3)	10.205(1)	13.680(3)
α , °	80.90(3)	90	102.71(3)
β , °	72.29(3)	110.809(7)	97.40(3)
γ , °	69.03(3)	90	119.08(2)
<i>V</i> , Å ³	1 024.4(7)	2 156.7(3)	1 120.7(7)
<i>Z</i>	1	2	1
<i>d</i> _{calc.} , g cm ⁻³	1.170	1.155	1.153
μ (MoK α), mm ⁻¹	0.656	0.626	0.604
<i>F</i> (000), e	384	800	416
Crystal colour	brown	brown	brown
Crystal habit	platelet	platelet	platelet
Crystal size, mm	0.8 × 0.4 × 0.2	0.6 × 0.5 × 0.4	0.5 × 0.5 × 0.3
θ_{\min} , θ_{\max} , °	3.42, 25.05	3.20, 25.00	3.18, 25.00
Range of indices (<i>h,k,l</i>)	-10→11, -12→12, 0→13	-16→15, 0→19, 0→12	-11→11, -12→11, 0→16
Reflections collected	3 571	4 021	3 943
Independent reflections	3 571 [<i>R</i> _{int} = 0.0000]	3 791 [<i>R</i> _{int} = 0.012]	3 775 [<i>R</i> _{int} = 0.041]
Data, restraints, parameters	3 571, 0, 181	3 791, 0, 190	3 775, 0, 199
Goodness-of-fit on <i>F</i> ²	1.112	1.046	1.127
<i>R</i> 1, <i>wR</i> 2 (all data)	0.061, 0.152	0.083, 0.254	0.073, 0.123
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.042, 0.142	0.063, 0.222	0.051, 0.114
Max. and min. residual density, e Å ⁻³	0.43; -0.54	0.72; -0.79	0.29; -0.29

bands typical of the $C_5H_2Me_3(1,2,3-Me_3)$ and C_5Me_5 ligands and bands of the π -coordinated BTMSA ligand: the intense $SiMe_3$ bands at $1\,244\text{ cm}^{-1}$ and in the $750\text{--}850\text{ cm}^{-1}$ region and a strongly red-shifted stretching vibration of the $C\equiv C$ bond. The latter occurred at $1\,619\text{ cm}^{-1}$ for **1** and at $1\,595\text{ cm}^{-1}$ for **3**. These values indicate that the BTMSA ligand is π -bonded by virtually the same strength as in the $(C_5H_{5-n}Me_n)_2Ti(\eta^2-Me_3SiC\equiv CSiMe_3)$ complexes where the $\nu(C\equiv C)$ bands were quoted¹¹ at $1\,627\text{ cm}^{-1}$ for $n = 3$ and at $1\,598\text{ cm}^{-1}$ for $n = 5$. ^{13}C NMR chemical shifts of the acetylenic carbon atoms also indicate strong coordination of the BTMSA ligand. The down-field shifts to $\delta\,263.97$ ppm for **2** and 264.65 ppm for **3** are considerably larger than those found in the $(C_5H_{5-n}Me_n)_2Ti(\eta^2-Me_3SiC\equiv CSiMe_3)$ complexes¹¹ ($n = 4$, 248.35 ppm and $n = 5$, 248.51 ppm) and in the dimethylsilylene-bridged *ansa*-complexes¹⁸ $Me_2Si(C_5H_4)_2Ti(\eta^2-Me_3SiC\equiv CSiMe_3)$ (248.93 ppm) and $Me_2Si(C_5Me_4)_2Ti(\eta^2-Me_3SiC\equiv CSiMe_3)$ (254.86 ppm). The comparison of the δ values for the compounds of these three types shows that the substitution by methyl groups at the cyclopentadienyl rings induces relatively small down-field shifts whereas the differences between the three types of compounds are large. The explanation of the latter effect is not straightforward. The electron-donating effect of the methyl groups undoubtedly decreases the Lewis acidity at the metal atom and causes a small down-field shift of the d values^{11,19}, but this contrasts with a large shift in the same direction induced by an overall electron releasing effect of the chlorine atoms. The observed extremely large ^{13}C NMR down-field shifts would classify the coordinated BTMSA as a four-electron ligand^{20,21}. Compounds **1–3** are silent in EPR spectroscopy. This is compatible with the formal Ti(II) valency which follows from the nature of bonds linking the ligands to the Ti atom (*vide infra*, X-ray structures).



SCHEME 4

X-Ray Crystal Structure Description

The X-ray crystal diffraction analyses of **1**, **2** and **3** revealed that all compounds form centrosymmetric dimers of the same structural type. Compounds **1–3** have (except for differing numbers of methyl groups) the same overall molecular structure. The structures and atom numbering schemes of compounds **1** and **2** are shown in Figs 1 and 2, respectively. The cyclopentadienyl ring in **3** is labelled in the same way as in compound **2**, with methyl C70 attached to C7. Selected bond distances and angles are listed

in Table II. Each Ti atom is coordinated by one η^5 -bonded methylated cyclopentadienyl ligand, one η^2 -bonded BTMSA ligand, and two bridging chlorine atoms. The geometry of the central Ti_2Cl_2 moiety is close to regular square. The distances from the carbon atoms of the cyclopentadienyl rings or their centroids (CE) to the Ti atom are the same for all compounds within the experimental error. The deviation of the cyclopentadienyl rings atoms from the least-squares plane is less than 0.01 Å and the methyl substituents are mostly displaced from the ring plane away from the Ti atom (maximum deviations from the plane are those of C30: **1**, 0.062 Å; **2**, 0.129 Å; **3**, 0.153 Å). The C1–C2 distance in the BTMSA ligands is close to 1.30 Å and the SiMe₃ substituents are bent away from Ti with the C–C–Si angles in the range 139.5(3)–142.1(2)°. These bond lengths are practically the same as in the $(C_5H_{5-n}Me_n)_2Ti(\eta^2-Me_3SiC\equiv CSiMe_3)$ ($n = 4$ and 5) compounds^{10,11}; the angles are, however, slightly larger compared to *ca* 135–136° in the latter compounds. The steric interaction between the methyl groups of the cyclopentadienyl ligand and the BTMSA ligand which is attached to the same Ti atom

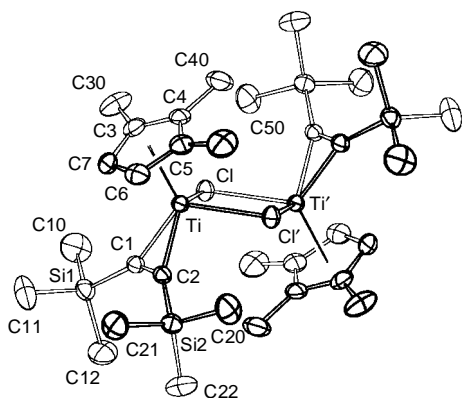


FIG. 1
ORTEP drawing of compound **1** at the 30% probability level with atom labelling scheme

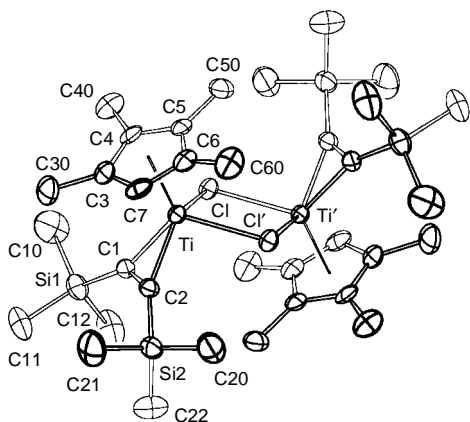


FIG. 2
ORTEP drawing of compound **2** at the 30% probability level with atom labelling scheme

TABLE II
Selected interatomic distances (Å) and angles (°) for **1**, **2** and **3**

Atoms	1	2	3
		Distances	
Ti-Ti'	3.689(1)	3.704(1)	3.743(1)
Ti-Cl	2.474(1)	2.481(1)	2.492(1)
Ti-Cl'	2.479(1)	2.485(1)	2.485(1)
Ti-C1	2.037(3)	2.051(5)	2.044(3)
Ti-C2	2.039(3)	2.047(5)	2.057(3)
Ti-C3	2.387(3)	2.362(5)	2.355(4)
Ti-C4	2.410(3)	2.380(4)	2.370(4)
Ti-C5	2.377(3)	2.387(5)	2.369(4)
Ti-C6	2.309(3)	2.372(5)	2.367(4)
Ti-C7	2.320(3)	2.338(5)	2.354(4)
Ti-C(ring) _{av}	2.36 ± 0.04	2.37 ± 0.02	2.363 ± 0.008
Ti-CE ^a	2.037(4)	2.042(5)	2.042(5)
C1-C2	1.302(4)	1.318(7)	1.309(5)
C1-Si1	1.848(3)	1.857(5)	1.867(4)
Si1-C(Me) _{av}	1.858 ± 0.008	1.86 ± 0.01	1.861 ± 0.006
C2-Si2	1.854(3)	1.840(5)	1.853(4)
Si2-C(Me) _{av}	1.860 ± 0.006	1.85 ± 0.01	1.864 ± 0.004
C-C(ring) _{av}	1.40 ± 0.01	1.41 ± 0.01	1.40 ± 0.02
C(ring)-C(Me) _{av}	1.508 ± 0.007	1.498 ± 0.003	1.510 ± 0.006
		Angles	
Cl-Ti-Cl'	83.73(5)	83.51(5)	82.46(5)
Cl-Ti-C1	93.92(10)	93.67(14)	94.10(10)
Cl-Ti-C2	119.26(9)	119.86(14)	119.90(11)
Cl-Ti-CE ^a	117.0(1)	116.6(2)	115.9(1)
Cl'-Ti-C1	119.20(9)	118.91(14)	120.46(11)
Cl'-Ti-C2	93.21(9)	93.49(14)	95.30(10)
Cl'-Ti-CE ^a	117.0(1)	117.7(2)	117.1(1)
C1-Ti-C2	37.24(13)	37.5(2)	37.23(14)
C1-Ti-CE ^a	117.6(1)	117.6(2)	117.5(2)
C2-Ti-CE ^a	117.9(1)	117.4(2)	117.9(2)
Ti-Cl-Ti'	96.27(5)	96.49(5)	97.54(5)
Ti-C1-Si1	146.4(2)	148.6(3)	148.4(2)
Ti-C1-C2	71.5(2)	71.0(3)	71.9(2)

TABLE II
(Continued)

Atoms	1	2	3
		Angles	
Si1–C1–C2	142.1(2)	140.2(4)	139.5(3)
Ti–C2–C1	71.3(2)	71.4(3)	70.8(2)
Ti–C2–Si2	146.5(2)	146.8(3)	147.1(2)
Si2–C2–C1	142.1(2)	141.7(4)	141.8(3)

^a Pseudoatom CE denotes the centroids of the C₅H_{5-n}Me_n ligands.

is probably responsible for the deviation of the Si atoms from the plane defined by the Ti, C1, and C2 atoms. In **1**, where the methyl groups at the C6 and C7 atoms are absent, the Si atoms are inclined to the cyclopentadienyl ligand by *ca* 0.07 Å, in **3** they are declined by *ca* 0.09 Å. This is probably accompanied by a small change in the orientation of the cyclopentadienyl ring plane with respect to the bridging plane. The dihedral angle between these planes is 40.6° in **1**, 38.5° in **2**, and 36.7° in **3**. The largest significant difference in the structural parameters occurs in the Ti–Cl bond lengths. The average distance is 2.476 Å in **1**, 2.483 Å in **2** and 2.488 Å in **3**. These differences and small variations in the bridging skeleton angles result in distinct differences in the Ti–T' distances, from 3.689(1) Å for **1** to 3.743(1) Å for **3**. This effect can be attributed to the electron-donating effect of the methyl groups which decreases the Lewis acidity at the titanium atom and thus weakens the Ti–Cl bonds.

Well-characterized monocyclopentadienyl compounds of Ti(II) are very rare²². Those relevant to compounds **1–3** are [(η⁵:η¹-C₅Me₄SiMe₂NR)Ti(diene)] complexes²³ and [(C₅H₅)TiCl(dmpe)₂] (dmpe, 1,2-bis(dimethylphosphino)ethane), [(C₅Me₅)Ti(BH₄)(dmpe)] or [(C₅Me₅)Ti(BH₄)(trimpsti)] (trimpsti, *tert*-butyltris[(dimethylphosphino)methyl]silane) (ref.²⁴). All of them are, however, monomeric and structurally rather different. All these compounds behave either as catalysts for oligomerization of ethylene or as their precursors. The investigation of the catalytic activity of compound **3** in combination with methylalumoxane towards ethylene and propylene is to be undertaken.

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