

Synthesis and structures of paramagnetic binuclear (η^8 -1,4-bis(trimethylsilyl)cyclooctatetraenide)titanium(III) chlorides

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Received 11 November 1998

Abstract

The reaction between equimolar quantities of $\text{TiCl}_3(\text{THF})_3$ and 1,4-bis(trimethylsilyl)cyclooctatetraene dianion (COT'') yields a mixture of $(\text{COT}'')_2\text{Ti}$ (**1**), $[(\text{COT}'')\text{Ti}]_2(\mu\text{-Cl})_3$ (**2**) and $[(\text{COT}'')\text{Ti}(\mu\text{-Cl})_2](\text{THF})$ (**3**). Crystalline **2** and **3** were isolated on the basis of different solubility in hexane. Their X-ray diffraction analyses revealed dimeric structures linked by chlorine bridges. In **3**, only one of the Ti atoms coordinates one molecule of THF. The mixed-valency Ti(III)/Ti(IV) compound **2** shows an ESR spectrum typical of mononuclear $(\text{COT}'')\text{Ti}(\text{III})$ complexes. The ESR spectra of **3** in toluene or 2-methyltetrahydrofuran glasses prove the triplet state of coupled Ti(III) d^1 electrons. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Bis(trimethylsilyl)cyclooctatetraene dianion; Binuclear complexes; Chloride bridges; Crystal structure; ESR spectra

1. Introduction

An easy and cheap access to 1,4-bis(trimethylsilyl)cyclooctatetraene dianion (COT'') [1] opened its wide application in synthesis of new complexes of early transition metals and lanthanides [2] although the electronic and steric effects of the SiMe_3 groups are not perspicuous. From the practical point of view, COT'' complexes are generally more soluble than analogous cyclooctatetraene (COT) complexes. In the crystal lattice, the COT'' ligand is, usually at variance with COT, firmly fixed, which is essential for good quality X-ray crystal structure determination. From the chemical point of view, the comparison is available in early transition metal series where complexes of the $(\text{COT}'')_2\text{M}$ and $(\text{COT}'')\text{MCl}_2$ type are available for both the ligands. The $(\text{COT}'')_2\text{M}$ ($\text{M} = \text{Ti}$ [3a], Zr [3a] and Hf

[3b]) complexes as well as the $(\text{COT})_2\text{M}$ ($\text{M} = \text{Ti}$ [4a–d], Zr [3b, 4e,f], and Hf [4g,h]) complexes possess η^8 - and η^4 -coordinated COT'' ligands. Of the $(\text{COT})\text{MCl}_2$ complexes, $(\text{COT})\text{ZrCl}_2$ [5] and $(\text{COT})\text{HfCl}_2$ [4g, 5] are easily obtainable by the synproportionation of $(\text{COT})_2\text{M}$ and MCl_4 compounds. They form either monomeric THF solvates $(\text{COT})\text{MCl}_2(\text{THF})$ or, in the absence of THF, the $[(\text{COT})\text{MCl}(\mu\text{-Cl})_2]$ dimers [5]. Such a dimer is analogously obtained from $(\text{COT}'')_2\text{Zr}$ and ZrCl_4 [5]. The $[(\text{COT})\text{ZrCl}(\mu\text{-Cl})_2]$ compound has been used as a starting material for syntheses of borohydride complexes [6a] and bis(trimethylsilyl)methyl complexes [6b] which both showed interesting rearrangements. The titanium compounds $(\text{COT})\text{MCl}_2$ and $(\text{COT}'')\text{TiCl}_2$ are not known. Instead, the Ti(III) compounds $[(\text{COT})\text{TiCl}]_4$ or $[(\text{COT})\text{TiCl}(\text{THF})_2]$ [7] have been prepared and used to synthesize $(\text{COT})\text{Ti}(\text{III})$ allyl derivatives [8] or the Ti(II) complex $[(\text{COT})\text{Ti}]_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3]$ [9]. Analogous $(\text{COT}'')\text{TiCl}$ compounds are not yet known, although examples of dimeric lanthanide complexes of this type have been described [10].

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Here we report the synthesis, crystal structures and EPR spectra of two dimeric (COT^{''})Ti(III) chlorides.

2. Experimental

2.1. General data and methods

Synthesis, purification and crystallization procedures and measurements of EPR and UV–NIR spectra in solutions were carried out in evacuated all-sealed glass devices equipped with magnetically breakable seals. A combined device equipped with a pair of quartz cuvettes (Hellma, $d = 1$ cm and 1 mm) and a quartz ESR tube was used for UV–NIR and ESR measurements. ESR spectra were measured on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnetech, Berlin, Germany) in the X-band. g -Values were determined using an Mn²⁺ ($M_1 = -1/2$ line) standard at $g = 1.9860$. The concentrations of the paramagnetic compounds were determined by double integration of the first derivative spectra. A variable temperature unit STT-3 was used for measurements in the range 102–296 K. NMR spectra were obtained on a Varian UNITY Inova 400 spectrometer (¹H-, ¹³C-, and ²⁹Si- 399.95, 100.58, and 79.46 MHz, respectively) in C₆D₆ at 25°C. Chemical shifts (given in the δ scale) were referenced to the solvent signal ($\delta_{\text{H}} 7.15$ ppm, $\delta_{\text{C}} 128.0$ ppm) and to a solution of SiMe₄ in C₆D₆ as the external reference. UV–NIR absorption spectra were taken on a Varian Cary 17D in the range 280–2200 nm. EI MS spectra were measured on a VG-7070E double-focusing mass spectrometer (70 eV, 50 $\mu\text{Å}$, 50–200°C). Samples in capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance not below 5% and by important peaks of lower intensity. IR spectra were registered on a Mattson Galaxy 2020 and Specord 75 IR (Carl Zeiss, Jena, FRG). KBr pellets were prepared from estimated amounts of solid samples in a glovebox under purified nitrogen and were measured under nitrogen atmosphere in a closed cell.

2.2. Chemicals

The solvents THF, 2-methyltetrahydrofuran (MTHF), hexane and toluene were purified by conventional methods, dried by refluxing over LiAlH₄ and stored as solutions of dimeric titanocene (C₁₀H₈)[(C₅H₅)Ti(μ -H)]₂ [11]. 5,8-Bis(trimethyl-silyl)-cycloocta-1,3,6-triene was prepared from 1,5-cyclooctadiene as described elsewhere [1b]. TiCl₄ (enzymes intern.) was degassed, refluxed with copper wire for 2 h, and distributed into ampoules by vacuum distillation.

n-Butyllithium (BuLi) in hexane (1.6 M) (Aldrich) was handled by syringe technique under argon. TiCl₃ was obtained by adding BuLi in hexane (1.6 M, 6.0 ml) to TiCl₄ (1.0 ml, 9.0 mmol) in 50 ml of THF under stirring. The mixture was refluxed for 30 min and the resulting brown precipitate was washed several times with THF and finally recrystallized from hot THF to give 2.4 g (6.5 mmol) of crystalline pale blue TiCl₃(THF)₃.

2.3. Reaction of [1,4-bis(trimethylsilyl)cyclooctatetraene]²⁻[2Li⁺] with TiCl₃(THF)₃

A total of 2.25 g of 1,4-bis(trimethylsilyl)cyclooctatriene (9 mmol) was dissolved in 50 ml of THF, and *n*-BuLi in hexane (1.6 M, 11.5 ml) was added. After stirring for 4 h at room temperature (r.t.) a golden yellow solution of (COT^{''})²⁻(2Li⁺) was obtained. This was slowly added to a stirred suspension of TiCl₃(THF)₃ (3.3 g, 9.0 mmol) in 40 ml of THF. Finally, the mixture was refluxed for 10 h to give a dark brown–red solution. The solvents were evaporated and a brown–red residue was successively extracted by hexane. A slow extraction by condensing hexane vapour afforded a brown–red solution of **1**, which was separated. The subsequent extraction by hexane yielded moderately soluble yellow crystalline **2**. The solid residue, nearly insoluble in hexane, was extracted by toluene to give a green solution of **3**. Compound **1** was isolated by evaporating hexane from the most soluble fraction as a reddish–brown oil which according to ¹H- and ¹³C-NMR spectra was identical with COT₂Ti [3a]. A paramagnetic compound **2** was identified by single crystal X-ray analysis to be (COT^{''}Ti)₂(μ -Cl)₃. A paramagnetic compound **3** crystallized from concentrated toluene solution as aggregates of pale green crystals. Its composition as [COT^{''}Ti(μ -Cl)]₂(THF) follows from the X-ray crystal structure determination.

[1,4-(SiMe₃)₂C₈H₆]₂Ti (**1**). Yield 0.73 g (15%). ¹H-NMR: δ 0.36 (s, 18H, 2 \times SiMe₃), 0.89 (s, 18H, 2 \times SiMe₃), 6.02 (m, 2H), 6.21 (m, 2H), 6.49 (m, 2H), 6.63 (s, 2H), 6.72 (s, 2H), 7.00 (m, 2H) all CH of ring. ¹³C-NMR: δ 0.43 (s, 2 \times SiMe₃), 0.89 (s, 2 \times SiMe₃), 100.4 (s, 2CH), 102.3 (s, 2CH), 103.9 (s, 2CH), 108.0 (s, 2CSi), 112.2 (s, 2CH), 112.4 (s, 2CH), 114.2 (s, 2CH), 121.0 (s, 2CSi). EI MS (direct inlet 70 eV, 145°C; m/z (%)): 544 (M⁺, 5), 471(6), 447(8), 446(16), 298(13), 297(23), 296(67), 295(10), 294(8), 248(5), 160(19), 145(12), 135((7), 74(8), 73(100), 45(13). (cf. Ref. [3a]).

{ $[\eta^8$ -1,4-(SiMe₃)₂C₈H₆]₂Ti}₂(μ -Cl)₃ (**2**). Yield 0.94 g (30%). EI MS (direct inlet 70 eV, 70–230°C): dec., ions of COT^{''}, (COT^{''}TiCl)₂, COT^{''}TiCl, COT^{''}TiCl₂ and non identified m/z 535 and 437 and others. EPR (toluene, 22°C): single line $g_{\text{iso}} = 1.987$, $\Delta H = 0.7$ mT, poorly discernible $a_{\text{Ti}} = 0.72$ mT; (toluene, –140°C: $g_{\parallel} =$

2.003, $g_{\perp} = 1.981$, $g_{av} = 1.988$ (see Fig. 1). UV–NIR (hexane, nm): 395 ~ 440(sh) > 2210. IR (KBr, cm^{-1}): 3040 (w), 2949 (m), 2901 (w), 1498 (w), 1475 (w), 1406 (w), 1354 (w), 1249 (s), 1035 (m), 989 (w), 900 (m), 837 (vs), 779 (w), 760 (m), 690 (w), 634 (m). $\{[\eta^{8-1,4}(\text{SiMe}_3)_2\text{C}_8\text{H}_6]\text{Ti}(\mu\text{-Cl})_2(\text{THF})\}_2$ (**3**). Yield 1.65 g (50%). EI MS (direct inlet, 70 eV, 60–220°C): liberation of mainly THF (m/z 72); (230°C; m/z (%): 662($[\text{M-THF}]^+$, 0.2), 334(6), 333(20), 332(15), 331($[(\text{M-THF})/2]^+$, 40), 248($[\text{COT}''^+]$, 13), 207(8), 161(9), 160(48), 159(11), 145(32), 135(24), 95(6), 93(18), 83(8), 75(9), 74(22), 73(100), 59(10), 45(37), 43(17). UV–NIR (hexane, nm): 410(sh); absorption increases from 1000 nm to shorter wavelengths. IR (KBr, cm^{-1}): 3038 (w), 2953 (m), 2895 (w), 1593 (vw), 1473 (w), 1446 (w), 1408 (w), 1354 (w), 1319 (w), 1248 (s), 1037 (m), 991 (w), 910 (w), 837 (vs), 787 (w), 761 (m), 688 (m), 638 (m), 543 (w). ESPR (toluene, 22°C): $g = 1.96$, $\Delta H = 21$ mT, a very broad line of low intensity further broadens with lowering of the temperature; (toluene, -140°C): $D = 0.04216$ cm^{-1} , $E = 0.00232$ cm^{-1} , $g_z = 1.985$, $g_y = 1.951$, $g_x = 1.972$, $g_{av} = 1.969$ (a triplet state of rhombic symmetry); (MTHF, -140°C): the triplet spectrum shows slightly doubled z - and x -features. It can be interpreted as the presence of two very similar species *I* and *II*. They have the same g -tensor $g_z = 1.985$, $g_y = 1.945$, $g_x = 1.972$, $g_{av} = 1.967$, $ID = 0.04100$ cm^{-1} , $E = 0.00222$ cm^{-1} , *II* $D = 0.03974$ cm^{-1} , $E = 0.00264$ cm^{-1} .

Complex **3** after high vacuum at 100°C —ESPR (toluene, -140°C): $D = 0.04711$ cm^{-1} , $E = 0$, $g_{\parallel} = 1.995$, $g_{\perp} = 1.955$, $g_{av} = 1.968$ (broad lines, triplet state of axial symmetry).

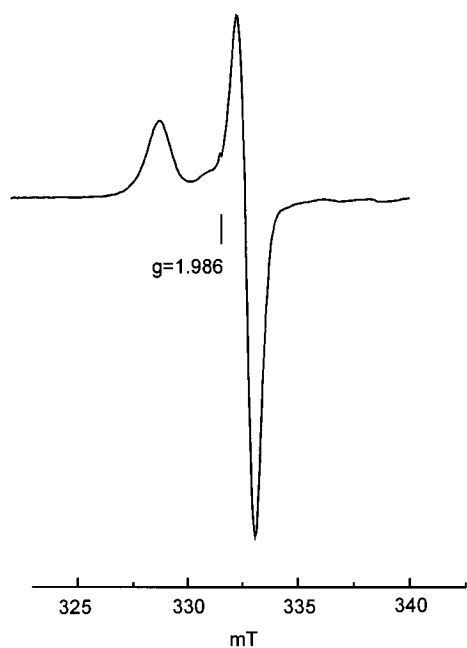


Fig. 1. ESR spectrum of **2** in frozen toluene glass at -140°C .

2.4. Alternative preparation of **2**

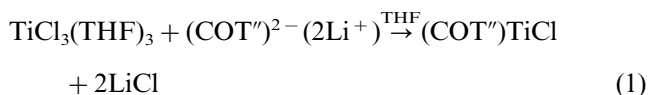
A total of 3.27g (6 mmol) of $\text{COT}''_2\text{Ti}$ was dissolved in 40 ml of hexane and 0.5 ml (4.5 mmol) of TiCl_4 was added. A yellow crystalline material gradually precipitated from a brown solution. The mixture was stirred for 3 h at r.t. Then, the brown solution of largely $\text{COT}''_2\text{Ti}$ was removed and the yellow crystalline solid was washed with hexane. Crystallization from warm toluene solution afforded yellow crystals of **2**. Yield 3.1 g (100% on TiCl_4).

2.5. Crystallography

A dark-yellow almost cube-shaped fragment of **2** and a pale green irregular fragment of **3** were fixed in Lindenmann glass capillaries under purified nitrogen in a Labmaster 130 (mBraun) glovebox. The capillaries were closed with sealing wax. The X-ray measurements were carried out at r.t. The diffraction data were collected on a STOE IPDS Imaging Plate System using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). The structures were solved using the Patterson method [12]. The refinement was performed with full matrix least-squares method based on F^2 (SHELXL93 [13]). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions. One trimethylsilyl group in **3** was strongly disordered. Nevertheless, its methyl C atoms were refined anisotropically because the directions of the long axes of their vibration ellipsoids are consistent with the rotation of the SiMe_3 group around the $\text{C}_{\text{ring}}\text{-Si}$ axis. Crystal data, details of data collection and refinement are given in Table 1. All atomic coordinates, thermal parameters, bond lengths and angles for **2** and **3** are available together with further details concerning the crystal structure analyses upon request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldhafen, by quoting the deposition numbers CSD-410382 (compound **2**) and CSD-410383 (compound **3**).

3. Results and discussion

The synthetic approach to $(\text{COT}''\text{TiCl})$ type compounds follows the procedure developed for obtaining $[(\text{COT})\text{TiCl}]_4$ or $[(\text{COT})\text{TiCl}(\text{THF})_2]$ [7]. It should consist of a stoichiometric reaction between $\text{TiCl}_3(\text{THF})_3$ and the alkali metal salt of COT'' (Eq. (1)).



Unfortunately, the reaction would proceed in the outlined way only if $\text{TiCl}_3(\text{THF})_3$ was always in excess

Table 1
Crystallographic data for **2** and **3**

	2	3
Crystal data		
Chemical formula	C ₂₈ H ₄₈ Cl ₃ Si ₄ Ti ₂	C ₃₂ H ₅₆ Cl ₂ OSi ₄ Ti ₂
Molecular weight (g mol ⁻¹)	699.17	735.83
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> (Å)	7.1945(14)	11.827(2)
<i>b</i> (Å)	13.761(2)	13.933(2)
<i>c</i> (Å)	18.366(4)	23.864(4)
α (°)	94.24(2)	90
β (°)	93.60(2)	97.13(2)
γ (°)	92.21(2)	90
<i>V</i> (Å ³)	1808.1(6)	3902.0(12)
<i>Z</i>	2	4
<i>D</i> _{calc.} (g cm ⁻³)	1.284	1.253
μ (Mo–K α)(cm ⁻¹)	8.13	6.92
<i>F</i> (000)	734	1560
Crystal size (mm ³)	0.51 × 0.62 × 0.65	0.46 × 0.62 × 0.65
Data collection		
<i>T</i> (K)	293(2)	293(2)
θ_{\min} , θ_{\max} (°)	1.92, 24.21	1.70, 24.19
Range of <i>hkl</i> indices	–7:7, –15:15, –21:20	–13:13, –15:15, –27:26
Reflections collected	11617	24623
Independent reflections	5368	5954
Data/restraints/parameters	5368/0/334	5953/0/370
Goodness-of-fit on <i>F</i> ²	0.885	0.894
Final <i>R</i> indices	<i>R</i> ₁ = 0.0444, [<i>I</i> > 2 σ (<i>I</i>)] <i>wR</i> ₂ = 0.1034	<i>R</i> ₁ = 0.0550, <i>wR</i> ₂ = 0.1352
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0766, <i>wR</i> ₂ = 0.1136	<i>R</i> ₁ = 0.0979, <i>wR</i> ₂ = 0.1557
Min., max. residual density	–0.424, 0.701	–0.373, 0.378

with respect to (COT^{''})²⁻. To conduct the reaction under this condition is practically impossible because TiCl₃(THF)₃ is low-soluble in THF. Even very slow dropwise addition of (COT^{''})²⁻(2Li⁺) in THF to the suspension of TiCl₃(THF)₃ in THF results in a brown coloured solution. The brown product was isolated as a reddish–brown oil. The compound was identified as [1,4-(SiMe₃)₂C₈H₆]₂Ti (**1**) [3a] on the basis of its EI MS, ¹H- and ¹³C-NMR spectra. Its easy formation means that the reductive electron transfer is faster than the ligand metathesis. This undesired product is easily separated from other products by careful extraction of the evaporated reaction residue with hexane since it is extremely soluble. A subsequent extensive extraction of the residue with hexane affords yellow, moderately soluble {[η^8 -1,4-(SiMe₃)₂C₈H₆]Ti}₂(μ -Cl)₃ (**2**). Finally, an exhaustive extraction by hexane for ca. 3 weeks gives pale green almost insoluble {[η^8 -1,4-(SiMe₃)₂C₈H₆]Ti(μ -Cl)}₂(THF) (**3**). Structures of **2** and **3** were established by single-crystal X-ray diffraction analysis (vide infra) to be dimers containing three and two equivalent bridg-

ing chlorine atoms, respectively. The actual products arising from reaction (1) are summarized in Scheme 1.

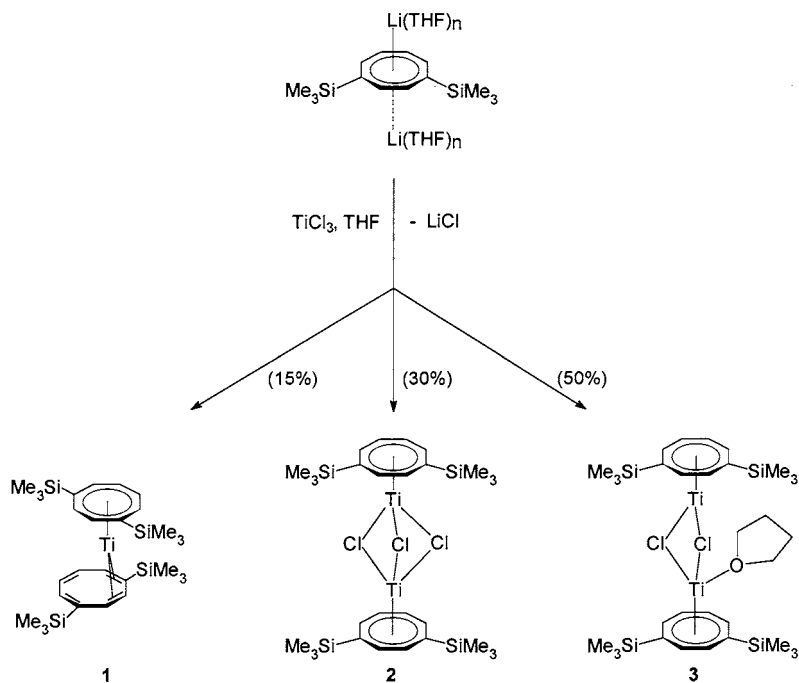
Spectroscopic data for **2** and **3** are compatible with their crystal structures. The presence of three bridging chlorine atoms in **2** requires one titanium atom to be Ti(IV) and the other Ti(III). The compound does not dissociate when dissolved in non-polar solvents as no colour change occurs, and the presence of a mixed-valency complex is corroborated by a strong charge-transfer band near 2000 nm. The ESR spectra of **2** in toluene solution ($\Delta H = 0.7$ mT, $a_{\text{Ti}} = 0.72$ mT) and toluene glass are typical of mononuclear COT^{''}Ti(III) species, showing *g*-tensor of axial symmetry with $g_{\parallel} > g_{\perp}$ (Fig. 1) (cf. Ref. [14] for (COT)TiR; R = cyclopentadienyl, indenyl and fluorenyl). The exchange of the Ti valency within the dimer has to be slow compared with the EPR relaxation time since no unusual line broadening is observed upon cooling. The compound dissociates on evaporation in the direct inlet of the MS spectrometer. The most natural [COT^{''}TiCl₂]⁺ and [COT^{''}TiCl]⁺ species are present among the fragment ions. The presence of a large variety of other ions whose abundances change with increasing temperature, however, indicates a complex thermolytic pattern.

Compound **3** is a dimer of two Ti(III) COT^{''}TiCl species with one of them bearing an additional THF molecule. The EI MS spectra proved that the THF molecule is released by warming to 80°C in vacuo. At temperatures above 170°C the MS spectra show the fragmentation pattern dominated by the dissociation of the dimer. The presence of *m/z* 662 indicates that at least a part of the dimeric molecules is present in the gas phase.

The ESR spectra of the frozen toluene solution (Fig. 2) prove that the Ti(III) d¹ electrons have unpaired electron spins. The triplet state spectrum (Fig. 2, upper spectrum) shows a rhombic *g*-tensor resulting from the presence of asymmetrically placed THF molecule. The zero-field splitting $D = 0.04216$ cm⁻¹ corresponds to the distance (*R*) between the unpaired electrons of 3.43 Å if the experimental value of *D* is taken for calculation of *R* instead of the dipolar contribution (*D*_d) in Eq. (2) [15]. This value is by 0.22 Å smaller than the crystallographic distance d(Ti–Ti) (vide infra).

$$D_d = (-\beta^2/3R^3)[2g_z^2 + (g_y^2 + g_x^2)/2] \quad (2)$$

This may result from neglecting the pseudodipolar contribution (*D*_e) ($D = D_d + D_e$). A similar discrepancy between d(Ti–Ti) and *R* was found in [(C₅H₅)₂Ti(μ -Cl)]₂ [15] and [(1,3-Me₂C₅H₃)₂Ti(μ -Cl)]₂ [16]. After warming solid **3** to 100°C under dynamic vacuum, the brown green residue dissolved in toluene gave a somewhat different ESR spectrum. In frozen glass at –140°C the spectrum displayed broader lines corresponding to a tensor of axial symmetry and a larger zero-field splitting. This change is compatible with a release of THF



accompanied by shortening of the Ti–Ti distance. The linewidth and the appearance of this spectrum is very similar to the spectra of $[(C_5H_5)_2Ti(\mu-Cl)]_2$ [15] and $[(1,3-Me_2C_5H_3)_2Ti(\mu-Cl)]_2$ [16]. On the other hand, compound **3** in frozen MTHF solution gives a rhombic g -tensor with doubled z - and x -features. The D -values derived from the z -features are slightly smaller than the D -value of **3** in toluene glass. This may be accounted for the two species solvated by MTHF. The dissociation into monomeric compound, e.g. $COT''TiCl(MTHF)_n$ ($n = 1$ or 2) was not noticed in the ESR spectra either at r.t. or at $-140^\circ C$.

3.1. Crystal structures of **2** and **3**

The common feature of molecular structures of both the molecules is an *eclipsed* conformation of COT'' ligands.

The molecule **2** (Fig. 3), being in a general position in the triclinic unit cell, is ca. symmetrical with respect to the plane bisecting the COT'' ligands and containing both Ti atoms and one Cl atom and to the plane defined by the three chlorine atoms. A closer inspection of molecular parameters (Table 2) shows that the two Ti atoms differ in bond lengths to the attached ligands, the bonds of Ti(1) being longer. The difference in the Ti–CE (CE-centroid of the COT'' ring) distances ranges the estimated S.D. limits, however, the Ti(1)–Cl bonds are longer by ca. 0.02 \AA . This may allow us to consider Ti(2) as a more acidic Ti(IV) and Ti(1) as Ti(III). The Ti–Ti distance of $3.349(1) \text{ \AA}$ is short enough for a contribution of a through-space interaction between the

titanium atoms, however, the bridging chlorine bonds are by far the main links. The *eclipsed* conformation of the COT'' ligands is responsible for differences between the Cl(2) atom and two ca. equivalent Cl(1) and Cl(3) atoms. The Ti–Cl(2) bonds are shorter by ca. 0.3 \AA and the Ti(1)–Cl(2)–Ti(2) angle is larger by 1.0° than the corresponding distances and angles involving the other two chlorine atoms. Moreover, the dihedral angle between planes defined by the Ti atoms and chlorine

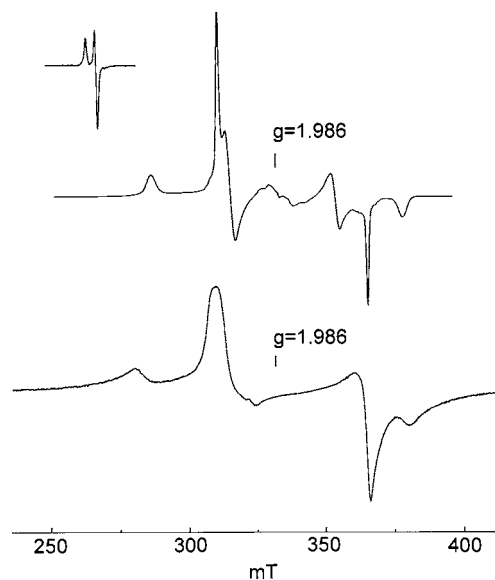


Fig. 2. ESR spectra in frozen toluene glass at $-140^\circ C$ of **3** (upper spectrum) and of **3** after THF was removed in dynamic vacuum (lower spectrum).

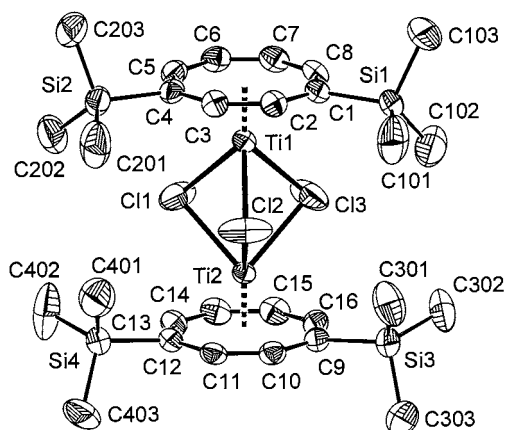


Fig. 3. ORTEP representation of **2** with thermal ellipsoids drawn at 30% probability level and atom numbering scheme.

atoms (Cl(1) and Cl(3)) is smaller (117.7°) than the angles between these planes and the plane involving Cl(2) (120.9 and 121.4°). The plane of the three chlorine atoms and the least-squares planes of COT' rings deviate from the parallel orientation by only 0.6° . The COT' ligands are parallel within 1.2° .

In complex **3**, the bridging chlorine atoms and the THF ligand are placed asymmetrically with respect to the eclipsed COT' ligands and the ring plane of THF ligand is irregularly distorted (Fig. 4). The bridging Ti–Cl bonds are shorter for the Ti(1) atom (av. $2.474(2)$ Å) than those for the Ti(2) atom (av. $2.540(2)$ Å) which bears the THF ligand. The system of bridging bonds is bent because of the presence of coordinated THF molecule (Fig. 5). The dihedral angle between planes defined by the Ti(1), Cl(1) and Cl(2) atoms and the Ti(2), Cl(1) and Cl(2) atoms is 35.4° and the Ti–Cl–Ti angles are larger (av. 93.25°) than the Cl–Ti–Cl angles (av. 81.53°). The THF ligand is loosely coordinated to the Ti(2) atom with a Ti–O bond length of $2.345(4)$ Å. Weakness of the bond follows from the comparison with the Ti–O bond lengths in $[(C_5H_5)TiCl_2(THF)]$ ($2.065(4)$ Å) and $[(C_5H_5)TiCl_2(THF)_2]$ ($2.241(4)$ and $2.275(4)$ Å) [17]. The distance of O(1) to Ti(1) of $2.976(5)$ Å may induce only a weak coulombic interaction. The coordination of THF brings about a marginal prolongation of the Ti(2)–CE(2) distance compared to Ti(1)–CE(1) ($1.510(5)$ vs. $1.495(5)$ Å). The least-squares planes of the COT' rings incline each to the other by the sides not containing the SiMe₃ groups, forming the dihedral angle of 6.1° . The COT' rings in both **2** and **3** are planar with maximum deviation of carbon atoms from the least-squares plane 0.02 Å, however, the bonding angles at the carbon atoms bearing SiMe₃ groups are markedly smaller (129.6 – 130.9°) than other ring angles (134.9 – 138.0°) (see Table 2). The silicon atoms lie almost exactly in the least-squares planes of the COT' rings. The Ti–Ti distance of $3.647(1)$ Å is close to the

Ti–Ti distance in $(\mu-\eta^5:\eta^5-C_{10}H_8)[(\eta^5-C_5H_5)Ti(\mu-Cl)]_2$ (3.638 Å) [18] or the $[(\eta^5-C_5H_5-n-Me_n)Ti(Me_3SiC\equiv CSiMe_3)(\mu-Cl)]_2$ ($n = 3-5$) complexes ($3.689(1)$ – $3.743(1)$ Å) [19], shorter than the Ti–Ti distance in titanocene chloride dimers, e.g. $[(\eta^5-C_5H_5-n-Me_n)_2Ti(\mu-Cl)]_2$ ($n = 0-2$; 3.915 – 3.968 Å) [16,20], and longer than in $[\eta^5-C_5Me_4Ph)TiCl(\mu-Cl)]_2$ ($3.345(11)$ Å)

Table 2
Selected bond distances (Å) and bond angles ($^\circ$) for **2** and **3**

	2	3
Bond distances (Å)		
Ti(1)–C _{ring} (av) ^a	2.362(4)	2.365(5)
Ti(2)–C _{ring} (av) ^a	2.357(4)	2.372(5)
Ti(1)–CE(1)	1.495(4)	1.495(5)
Ti(2)–CE(2)	1.485(4)	1.510(5)
Ti(1)–Cl(1)	2.4985(14)	2.474(2)
Ti(1)–Cl(2)	2.465(2)	2.480(2)
Ti(1)–Cl(3)	2.4985(14)	–
Ti(2)–Cl(1)	2.4783(14)	2.549(2)
Ti(2)–Cl(2)	2.4452(14)	2.532(2)
Ti(2)–Cl(3)	2.481(2)	–
Ti(2)–O(1)	–	2.345(4)
C _{ring} –C _{ring} (av) ^a	1.400(6)	1.403(7)
Nonbonding distances (Å)		
Ti(1)–Ti(2)	3.3491(12)	3.647(1)
Ti(1)–O(1)	–	2.976(5)
Cl(1)–Cl(2)	3.163(2)	–
Cl(1)–Cl(3)	3.152(2)	–
Cl(2)–Cl(3)	3.173(2)	–
Bond angles ($^\circ$)		
Cl(1)–Ti(1)–Cl(2)	79.16(6)	81.76(5)
Cl(1)–Ti(1)–Cl(3)	78.21(6)	–
Cl(2)–Ti(1)–Cl(3)	79.47(6)	–
Cl(1)–Ti(2)–Cl(2)	79.93(5)	79.30(5)
Cl(1)–Ti(2)–Cl(3)	78.93(6)	–
Cl(2)–Ti(2)–Cl(3)	80.19(6)	–
Ti(1)–Cl(1)–Ti(2)	84.59(4)	93.12(5)
Ti(1)–Cl(2)–Ti(2)	86.02(5)	93.38(6)
Ti(1)–Cl(3)–Ti(2)	84.53(5)	–
C(1)–C(2)–C(3)	137.9(4)	138.0(5)
C(1)–C(8)–C(7)	137.1(4)	136.6(5)
C(2)–C(1)–C(8)	130.1(4)	130.6(5)
C(2)–C(3)–C(4)	136.9(4)	136.9(5)
C(3)–C(4)–C(5)	130.8(4)	130.7(5)
C(4)–C(5)–C(6)	136.9(4)	136.3(5)
C(5)–C(6)–C(7)	135.5(4)	135.6(5)
C(6)–C(7)–C(8)	134.9(4)	135.4(5)
C(9)–C(10)–C(11)	137.4(4)	137.9(5)
C(9)–C(16)–C(15)	137.1(4)	137.4(5)
C(10)–C(9)–C(16)	130.9(4)	130.0(5)
C(10)–C(11)–C(12)	136.9(4)	137.6(5)
C(11)–C(12)–C(13)	130.5(4)	129.6(5)
C(12)–C(13)–C(14)	137.3(4)	137.8(5)
C(13)–C(14)–C(15)	135.2(4)	135.3(5)
C(14)–C(15)–C(16)	134.6(4)	134.4(5)
ϕ^b	1.2	6.1

^a Estimated S.D. appropriate to Ti–C or C–C bonds.

^b The angle between the least-squares planes of the COT' rings.

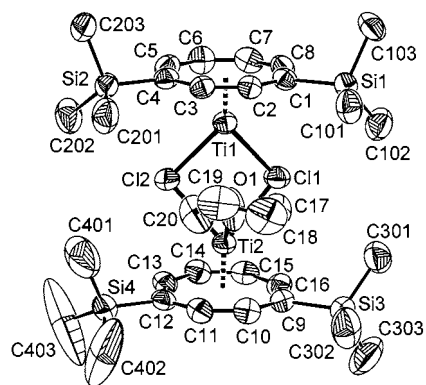


Fig. 4. ORTEP representation of **3** with thermal ellipsoids drawn at 30% probability level and atom numbering scheme.

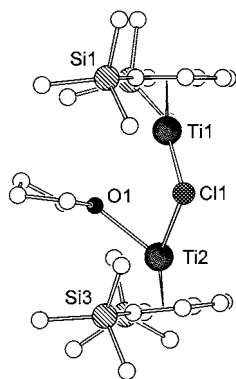


Fig. 5. PLUTO view of **3** in the Cl(1)–Cl(2) direction.

and $[\eta^5\text{-C}_5\text{Bn}_5\text{TiCl}(\mu\text{-Cl})_2]$ (Bn = benzyl; 3.374(2) Å) complexes [21]. An example of this structure type is known from lanthanide chemistry: the crystal structure of $[\text{COT}^*\text{Sc}(\mu\text{-Cl})_2](\text{THF})$ resembles that of **3** in all structural details [10].

The exploitation of **2** and **3** as starting materials for syntheses of titanium(II) complexes is under way.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (grant no. 203/96/0948), and by the Volkswagen Stiftung. The Grant Agency of the Czech Republic (grant no. 203/96/0111) also sponsored access to the Cambridge Structure Data Base.

References

[1] (a) N.C. Burton, F.G.N. Cloke, P.B. Hitchcock, H.C. de Lemos, A.A. Sameh, *J. Chem. Soc. Chem. Commun.* (1989) 1462. (b)

N.C. Burton, F.G.N. Cloke, S.C.P. Joseph, H. Karamallakis, A.A. Sameh, *J. Organomet. Chem.* 462 (1993) 39. (c) U. Killiman, R. Herbst-Irmer, D. Stalke, F.T. Edelmann, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1618. (d) P. Poremba, H.-G. Schmidt, M. Noltemeyer, F.T. Edelmann, *Organometallics* 17 (1998) 986.

[2] Recent reviews: (a) F.G.N. Cloke, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 4, Pergamon, Oxford, 1995, Ch. 13. (b) F.T. Edelmann, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 4, Pergamon, Oxford, 1995, Ch. 2.

[3] (a) F.G.N. Cloke, J.C. Green, P.B. Hitchcock, S.C.P. Joseph, P. Mountford, N. Kaltsoyannis, A. McCamley, *J. Chem. Soc. Dalton Trans.* (1994) 2867. (b) P. Berno, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Chem. Soc. Dalton Trans.* (1991) 3085.

[4] (a) H. Breil, G. Wilke, *Angew. Chem. Int. Ed. Engl.* 5 (1966) 898. (b) H. Dietrich, M. Soltwisch, *Angew. Chem. Int. Ed. Engl.* 8 (1969) 765. (c) J. Schwartz, J.E. Sadler, *J. Chem. Soc. Chem. Commun.* (1973) 172. (d) L. Hocks, R. Hubin, J. Goffart, *J. Organomet. Chem.* 104 (1976) 199. (e) D.M. Rogers, S.R. Wilson, G.S. Girolami, *Organometallics* 10 (1991) 2419. (f) H.-J. Kablitz, G. Wilke, *J. Organomet. Chem.* 51 (1973) 241. (g) H.-J. Kablitz, R. Kallweit, G. Wilke, *J. Organomet. Chem.* 44 (1972) C49. (h) H. Lehmkuhl, S. Kintopf, K. Mehler, *J. Organomet. Chem.* 46 (1972) C1.

[5] P. Berno, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Chem. Soc. Dalton Trans.* (1991) 3093.

[6] (a) S.C.P. Joseph, F.G.N. Cloke, C.J. Cardin, P.B. Hitchcock, *Organometallics* 14 (1995) 3566. (b) F.G.N. Cloke, P.B. Hitchcock, S.C.P. Joseph, *J. Chem. Soc. Chem. Commun.* (1994) 1207.

[7] H.R. van der Wal, F. Overzet, H.O. van Oven, J.L. de Boer, H.J. de Liefde-Meijer, F. Jellinek, *J. Organomet. Chem.* 92 (1975) 329.

[8] H.K. Hofstee, C.J. Groeneboom, H.O. van Oven, H.J. de Liefde-Meijer, *J. Organomet. Chem.* 85 (1975) 193.

[9] M. Horáček, J. Hiller, U. Thewalt, P. Štěpnička, K. Mach, *J. Organomet. Chem.* 571 (1998) 77.

[10] N.C. Burton, F.G.N. Cloke, P.B. Hitchcock, H.C. de Lemos, A.A. Sameh, *J. Chem. Soc. Chem. Commun.* (1989) 1462.

[11] H. Antropiusová, A. Dosedlová, V. Hanuš, K. Mach, *Transit. Met. Chem.* 6 (1981) 90.

[12] G.M. Sheldrick, Z. Dauter, K.S. Wilson, H. Hope, L.C. Sieker, *Acta Crystallogr. Ser. D* 49 (1993) 18.

[13] G.M. Sheldrick, *SHELXL-93*, Program for crystal structure refinement, University of Göttingen, Germany, 1993.

[14] (a) E. Samuel, G. Labauze, D. Vivien, *J. Chem. Soc. Dalton Trans.* (1979) 956. (b) E. Samuel, G. Labauze, D. Vivien, *J. Chem. Soc. Dalton Trans.* (1981) 2353.

[15] E. Samuel, J.F. Harrod, D. Gourrier, Y. Dromzee, F. Robert, Y. Jeannin, *Inorg. Chem.* 31 (1992) 3252.

[16] K. Mach, V. Varga, G. Schmid, J. Hiller, U. Thewalt, *Collect. Czech. Chem. Commun.* 61 (1996) 1285.

[17] S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Am. Chem. Soc.* 105 (1983) 7295.

[18] G.J. Olthof, *J. Organomet. Chem.* 128 (1977) 367.

[19] J. Hiller, U. Thewalt, J. Podlaha, V. Hanuš, K. Mach, *Collect. Czech. Chem. Commun.* 62 (1997) 1551.

[20] R. Jungst, D. Sekutowski, J. Davies, M. Luly, G. Stucky, *Inorg. Chem.* 16 (1977) 1645.

[21] G. Schmid, U. Thewalt, P. Sedmera, V. Hanuš, K. Mach, *Collect. Czech. Chem. Commun.* 63 (1998) 636.