THE DIMERIC STRUCTURE OF BIS(1,3-DIMETHYLCYCLOPENTADIENYL)TITANIUM(III) CHLORIDE

Karel MACH[a], Vojtech VARGA[a], Gunter SCHMID[b1], Jorg HILLER[b2] and Ulf THEWALT[b3]

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

[b] *Universitat Ulm, Sektion fur Rontgen- und Elektronenbeugung, D-89069 Ulm, Germany; e-mail: [1] guenter.schmid@chemie.uni-ulm.de, [2] joerg.hiller@chemie.uni-ulm.de, [3] ulf.thewalt@chemie.uni-ulm.de*

Received March 19, 1996
Accepted April 16, 1996

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

The X-ray crystal structure analysis of bis(1,3-dimethylcyclopentadienyl)titanium(III) chloride revealed that it is a centrosymmetric chlorine-bridged dimer $[(\eta^5\text{-}C_5H_3Me_2)_2Ti(\mu\text{-}Cl)]_2$ (**1**) with the Ti–Ti distance of 3.9155(8) Å. Its skeleton is virtually identical with those of the $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ and $[(\eta^5\text{-}C_5H_4Me)_2Ti(\mu\text{-}Cl)]_2$ dimers. The solution EPR study proved that **1** remains a dimer in toluene whereas it dissociates in 2-methyltetrahydrofuran (MTHF) to give $(\eta^5\text{-}C_5H_3Me_2)_2TiCl$. MTHF. The EPR spectra of frozen toluene solutions proved that **1** forms the triplet state whose *g*-tensor and zero-field splitting *D* are virtually the same as those of $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)]_2$.

Key words: Titanium; Titanocene(III) chloride, dimer; Crystal structure; Electron paramagnetic resonance.

The structure of titanocene halides Cp'_2TiX ($Cp' = \eta^5\text{-}C_5H_{5-n}Me_n$, $n = 0$–5; X = Cl, Br, I) in the solid state and in solutions is known for $n = 0$, 1, 3–5). The X-ray crystal analyses revealed halogen-bridged dimers for $n = 0$ and $n = 1$ (ref.[1]) whereas $(C_5HMe_4)_2TiCl$, $(C_5HMe_4)_2TiI$ (ref.[2]) and $(C_5Me_5)_2TiCl$ (ref.[3]) were established to be monomers. The EPR study of the series of compounds $(C_5H_2Me_3)_2TiX$, $(C_5HMe_4)_2TiX$ and $(C_5Me_5)_2TiX$ (X = Cl, Br, I) in the toluene solution and glass has proven that all the compounds are monomers at temperatures down to 77 K (ref.[4]). The solution EPR spectra of $[(C_5H_5)_2TiCl]_2$ and $[(C_5H_4Me)_2TiCl]_2$ in toluene gave low-intensity asymmetrical broad signals which were difficult to assign until recently, when the EPR spectrum of $[(C_5H_5)_2TiCl]_2$ in toluene glass was interpreted as arising from a dimer in the spin triplet state[5]. In 2-methyltetrahydrofuran (MTHF), however, the ESR spectra of the C_5H_5 and C_5H_4Me compounds indicated the presence of monomers with coordinated at least one molecule of MTHF (refs[4,6]). The $C_5H_2Me_3$, C_5HMe_4 and C_5Me_5 titanocene halides showed the increasing affinity to MTHF with decreasing number of methyl substituents and with decreasing temperature. Whereas $(C_5Me_5)_2TiCl$ in MTHF solution remained uncoordinated even at

77 K, $(C_5HMe_4)_2TiCl$ showed a small fraction of molecules with coordinated MTHF at –130 °C and $(C_5H_2Me_3)_2TiCl$ coordinated MTHF completely at –130 °C. In the MTHF solution, only $(C_5H_2Me_3)_2TiCl$ showed comparable amounts of the MTHF-coordinated and non-coordinated molecules at room temperature while others were non-coordinated[4]. Thus, in the series of the Cp'_2TiCl compounds bis(1,3-dimethylcyclopentadienyl)titanium(III) chloride, $(C_5H_3Me_2)_2TiCl$ (**1**), remained the last compound whose structure in the solid state and in solutions was unknown.

This work aims at the crystal structure determination of **1** by the X-ray diffraction method and at the EPR investigation of **1** in toluene and MTHF solutions.

EXPERIMENTAL

General Data and Methods

All operations with Ti(III) complexes were performed under vacuum in all-sealed devices equipped with magnetically breakable seals. A combined device equipped with a couple of quartz cuvettes (1 cm and 1 mm) and a quartz ESR tube was used for the UV-VIS and EPR measurements. UV-VIS spectra were measured in the range 280–2 000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). ESR 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 –140 to +20 °C. Samples in capillaries for MS analysis were opened and inserted into the direct inlet (90 °C) of a JEOL D-100 spectrometer under argon.

Chemicals

The solvents toluene, hexane, and MTHF were purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as a solution of dimeric titanocene $(\mu\text{-}C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)]_2$ (ref.[7]). Butyllithium (BuLi) 1.6 M solution in hexane (Chemetall, Frankfurt a.M., Germany) was distributed into ampoules under argon and then degassed and divided into ampoules for immediate use. Bis(1,3-dimethylcyclopentadienyl)titanium dichloride, $(C_5H_3Me_2)_2TiCl_2$, was prepared as described earlier[8].

Preparation of $[(C_5H_3Me_2)_2Ti(\mu\text{-}Cl)]_2$ (**1**)

$(C_5H_3Me_2)_2TiCl_2$ (0.60 g, 2 mmol) was dissolved in toluene (20 ml) and 1.6 M solution of BuLi in hexane (1.4 ml, 2.2 mmol) was added. The mixture was stirred at 60 °C for 5 h and then all volatiles were evaporated in vacuum. The residue was washed with hexane (10 ml) and this washing was discarded. The solid was repeatedly extracted with hexane (50 ml) in a closed system until a white solid of LiCl remained (ca 30 times). The whole extraction procedure was repeated with the yellow precipitate in order to separate traces of LiCl. An extracted solid was dissolved in hexane (80 ml) at 100 °C and the solution was very slowly cooled to room temperature. The crop of crystalline **1** was separated, washed with hexane and dried in vacuo. Yield of crystalline **1** was 0.20 g (40%). These crystals were used for X-ray crystal diffraction measurements and for preparing toluene and MTHF solutions. Mass spectrum, *m/z* (%): 269 ($M^{+\bullet}$, 58), 233 ($[M - HCl]^+$, 95), 231 ($[M - HCl - H_2]^+$, 100), 176 ($[M - (C_5H_3Me_2)]^+$, 38), 175 (25), 174 (23), 161 (11), 148 (16), 140 (30), 138 (17), 91 (33), 83 (31). Only the monomer **1** is present in the gas phase. EPR spectra (toluene, 23 °C): main species – broad signal $g = 1.98$, $\Delta H = 9$ mT; minor species $g = 1.964$, $\Delta H = 1.8$ mT and $g = 1.979$, $\Delta H = 0.4$ mT; (toluene, –130 °C): $g_{\|} = 1.999$, $g_{\perp} = 1.972$, $D = 0.0365$ cm^{-1}, $E \approx 0$, $g_{av} = 1.981$; (MTHF, 23 °C): $g = 1.979$, $\Delta H = 0.5$ mT, $a_{Ti} = 1.18$ mT; (MTHF, –140 °C): $g_1 = 1.994$, $g_2 = 1.980$, $g_3 = 1.963$, $g_{av} = 1.979$. UV-VIS spectra (nm), toluene: 463 > 670 > 810 (sh); MTHF: 463 >> 650 (sh).

Crystal Structure Determination of **1**

A plate-shaped yellow-green crystal of **1** was mounted into a Lindemann glass capillary in a glovebox (Braun) under the atmosphere of purified nitrogen. Diffraction intensities were collected on a Philips PW1100 four-circle diffractometer (graphite monochromator, MoKα radiation, $\lambda = 0.71069$ Å). The structure was solved by iterative symbolic addition[9] (ISA) and refined with full-matrix least-squares based on F^2 applying a variance-based weighting scheme (SHELXL93, ref.[10]). All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included in calculated positions and not refined. A torsion angle for the methyl groups was allowed to refine. Crystal and refinement data for **1** are summarized in Table I. The positional and isotropic equivalent temperature parameters of **1** are listed in Table II. The atomic positional parameters have been deposited with the Cambridge Crystallographic Data Centre. The supplementary material is available from the author (G. S.) either in printed form or in files on disk. The data are stored having the CIF and FCF standard of the International Union of Crystallography.

RESULTS AND DISCUSSION

The X-ray crystal diffraction analysis of $(C_5H_3Me_2)_2TiCl$ revealed that it forms a chlorine bridged centrosymmetric dimer. ORTEP drawing of **1** and atom numbering scheme is shown in Fig. 1. Selected bond distances and bond angles are summarized in Table III. The bridging skeleton is planar, however, the Ti–Cl and Ti–Cl′ bonds slightly differ in their length. This bridging arrangement is common with other dimeric titanocene chlorides $[(C_5H_4Me)_2Ti(\mu\text{-}Cl)]_2$ and $[(C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ (ref.[1]). The comparison of structure parameters of the titanocene chloride dimers in Table IV shows that their skeletons are practically identical, however, some shortening of the Ti–Ti distance from 3.943 Å and 3.968 Å for two independent molecules in the unit cell of $[(C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ to 3.926 Å for $[(C_5H_4Me)_2Ti(\mu\text{-}Cl)]_2$ and to 3.915 Å for **1** is well discernible. The orientation of methyl substituted cyclopentadienyl rings in titanocene chlorides is rather bizzare. The dimeric $[(C_5H_4Me)_2Ti(\mu\text{-}Cl)]_2$ has two C_5H_4Me ligands in nearly eclipsed conformation situated approximately perpendicularly to the Ti–Ti direction, each titanocene moiety on opposite side[1]. The $(C_5H_4Me)_2TiCl_2$ crystal contained the eclipsed ligands with methyl groups directed to the side of chlorine atoms[11]. The $(C_5HMe_4)_2TiCl_2$ and $(C_5HMe_4)_2TiCl$ have the staggered rings with protons occupying positions where the rings are inclined each to other[2]. Compound **1** shows another possibility, with pairs of the $C_5H_3Me_2$ ligands in opposite orientation at each titanocene moiety (Fig. 1). The bonding angles at the ring carbon atoms nicely demonstrate smaller angles at the carbon bearing the methyl groups (average 106.3°) compared with angles at the hydrogen-bearing carbon atoms (average 109.1°) (Table III). The CE1–

Ti–CE2 angle of 132.4(1)° is negligibly larger than in the other congeners (Table IV) and all of them do not differ from the CE–Ti–CE angles in titanocene dichlorides, e.g. 130.2° in $(C_5H_4Me)_2TiCl_2$ (ref.[11]) and 133.4° in $(C_5HMe_4)_2TiCl_2$ (ref.[2]). It is, however, much smaller than in monomeric titanocene monochlorides of trigonal coordination, e.g. $(C_5HMe_4)_2TiCl$ 139.1° (ref.[2]), $(C_5Me_5)_2TiCl$ 143.6° (ref.[3]). The magnitude of this angle does not imply any steric hindrance between the $C_5H_3Me_2$ ligands, however, the methyl substituents are deviated from the ring planes farther away from the titanium atom by 0.02–0.14 Å. This deviation is smaller than in congested highly methylated

TABLE I
Crystal and structure refinement data for $[(\eta^5\text{-}C_5H_3Me_2)_2TiCl]_2$ (**1**)

Empirical formula	$C_{28}H_{36}Cl_2Ti_2$
Molecular weight	539.27
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
a, Å	11.265(1)
b, Å	14.484(1)
c, Å	8.176(1)
β, °	97.69(1)
Volume, $Å^3$	1 322.0(2)
Z	2
d_{calc}, g/cm^3	1.355
Crystal dimensions, mm	0.8 × 0.3 × 0.15
μ, mm^{-1}	0.820
λ, Å	0.71069
Number and θ-range (°) of reflections for lattice parameter refinement	188; 12.7–17.7
Temperature, K	293(2)
Scan technique	$\omega/2\theta$
θ range for data collection, °	2.9 to 25.0
Reflections collected	2 302
Unique reflections, R_{int}	2 146, 0.01
Data, restraints, parameters	2 145, 0, 151
Final R_1, R_2 $[I > 2\sigma(I)]$	0.032, 0.073
Final R_1, R_2 (all data)	0.039, 0.095
Goodness-of-fit on F^2	1.102
Max. and min. heights in final $\Delta\rho$ map, $e/Å^3$	0.22(5), –0.26(5)

titanocene moieties[2,3,12]. Much shorter C–C bonds in the Cp rings of $[(C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ compared to those of $[(C_5H_4Me)_2Ti(\mu\text{-}Cl)]_2$ and **1** (Table IV) are due to the considerable libration motion of the C_5H_5 rings[1]. The Ti–Ti distance of 3.915 Å does not imply any direct Ti–Ti bond.

The structure of compound **1** in toluene solution was drawn from the EPR spectra of frozen glass at –140 °C. The saturated solution of **1** in toluene gave a very broad (ΔH = 9 mT) and asymmetrical signal of very low intensity at about g = 1.98 and weak and sharp signals at g = 1.979, ΔH = 0.4 mT and at g = 1.964, ΔH = 1.8 mT. This spectrum was very similar to the spectrum of $[(C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ (ref.[4]). These spectra are compatible with previous measurements of magnetic susceptibility of $[(C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ which indicated the antiferromagnetic interaction between the unpaired electrons of the Ti(III) ions[1] but they do not allow us to draw any conclusion concerning the structure of **1**. More informative EPR spectrum was obtained from the frozen glass of the toluene solution (see Fig. 2a). The spectrum displays a strong central signal and broad features

TABLE II
Atomic coordinates (. 10^4) and equivalent isotropic thermal parameters ($Å^2$. 10^3) for $[(\eta^5\text{-}C_5H_3Me_2)_2TiCl]_2$ (**1**)

Atom	x	y	z	U_{eq}[a]
Ti	–1227(1)	898(1)	–856(1)	30(1)
Cl	905(1)	836(1)	625(1)	37(1)
C1	–1563(2)	1786(2)	1541(3)	42(1)
C11	–640(3)	2389(2)	2517(4)	69(1)
C2	–1788(2)	851(2)	1866(3)	37(1)
C3	–2794(2)	549(2)	793(3)	40(1)
C31	–3406(3)	–366(2)	850(4)	64(1)
C4	–3163(2)	1293(2)	–242(3)	47(1)
C5	–2414(2)	2047(2)	225(3)	48(1)
C6	–714(3)	1992(2)	–2796(3)	49(1)
C61	–146(3)	2896(2)	–2249(5)	79(1)
C7	–1939(3)	1792(2)	–3207(3)	52(1)
C8	–2084(3)	862(2)	–3690(3)	50(1)
C81	–3223(3)	373(3)	–4288(4)	81(1)
C9	–927(3)	498(2)	–3618(3)	49(1)
C10	–99(2)	1180(2)	–3087(3)	47(1)

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

typical of the triplet state with an approximate cylindrical symmetry. This assignment to the triplet state was further confirmed by the observation of the $\Delta M_S = 2$ transition at approximately half value of the magnetic field. The origin of the strong central signal is not known. Samuel et al.[5] obtained a very similar EPR spectrum for $[(C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ and were first who assigned the broad features to a triplet state of the dimer. They suggested that the strong central part of the spectrum is due to the presence of a

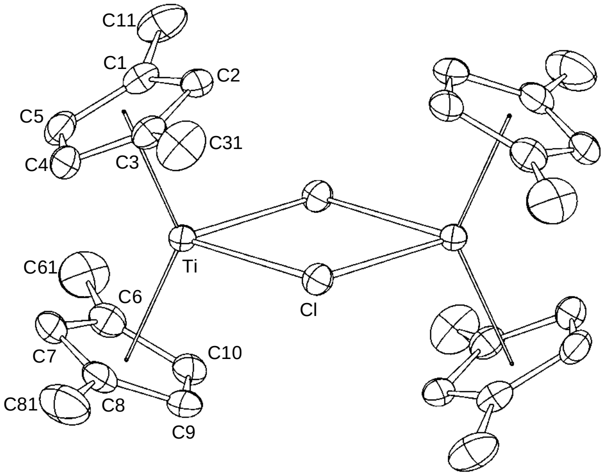

FIG. 1
ORTEP drawing of **1** with atom numbering scheme

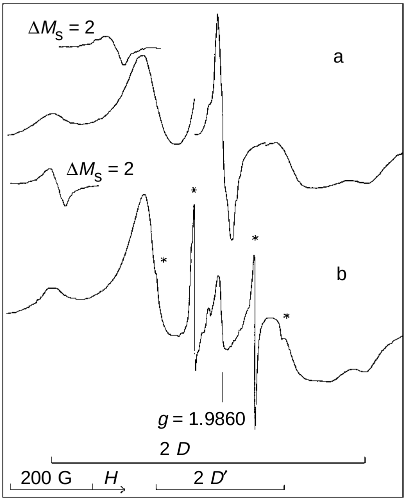

FIG. 2
EPR spectra of **1** in toluene glass at –140 °C: sample before sublimation in vacuum (a); sample of the residue after sublimation off about one half of the amount of **1** (b) (the signals of an impurity forming a triplet state are labelled by asterisk and its zero field splitting is denoted *D′*). Signals of $\Delta M_S = 2$ transitions are situated at arbitrary magnetic field; the central part of the spectrum *a* is attenuated by the factor 8

monomer which is in equilibrium with the dimer. Our attempts to purify **1** by the sublimation in vacuum led to the increase of the central signal. This brought us to the investigation of the less volatile sublimation fraction. The repeated sublimation was stopped when about one half of the sample was sublimed and the sublimation residue was dissolved in toluene. No differences in the yellow colour of the solutions and in the UV-VIS spectra of all the used samples were recognized, however, the EPR spectrum

TABLE III
Selected bond distances (Å) and angles (°) for **1**[a]

Atoms	Distances	Atoms	Distances
Ti–Cl	2.544(1)	Ti–Cl′	2.541(1)
Ti–C1	2.415(3)	Ti–C2	2.396(3)
Ti–C3	2.411(3)	Ti–C4	2.371(3)
Ti–C5	2.382(3)	Ti–C6	2.367(3)
Ti–C7	2.372(3)	Ti–C8	2.391(3)
Ti–C9	2.402(3)	Ti–C10	2.393(3)
Ti–CE1	2.074(3)	Ti–CE2	2.065(3)
C1–C2	1.415(3)	C2–C3	1.416(4)
C3–C4	1.401(4)	C4–C5	1.410(5)
C5–C1	1.399(5)	C1–C11	1.505(5)
C3–C31	1.499(5)	C6–C7	1.409(5)
C7–C8	1.413(5)	C8–C9	1.410(5)
C9–C10	1.384(5)	C10–C6	1.404(5)
C6–C61	1.500(6)	C8–C81	1.488(6)
Atoms	**Angles**	**Atoms**	**Angles**
Ti–Cl–Ti′	100.8(0)	Cl–Ti–Cl′	79.2(0)
CE1–Ti–CE2[b]	132.4(1)	C5–C1–C2	106.7(2)
C1–C2–C3	109.3(2)	C2–C3–C4	106.7(2)
C3–C4–C5	108.4(2)	C4–C5–C1	109.1(2)
C10–C6–C7	106.1(3)	C6–C7–C8	109.7(3)
C7–C8–C9	106.1(3)	C8–C9–C10	109.1(3)
C9–C10–C6	108.9(2)		

[a] Atoms Ti′, Cl′, C1′, etc. are related to atoms Ti, Cl, C1, respectively, etc., by the symmetry operation $-x$, $-y$, $-z$. [b] CE1 centroid of the C1–C5 ring; CE2 centroid of the C6–C10 ring.

of the toluene solution in frozen glass showed the absence of a strong central signal. Instead, the triplet state spectrum of **1** was accompanied by another, narrow triplet state spectrum with sharp lines (see Fig. 2b). The concentration of the species responsible for this new spectrum was estimated from the integrated records to be less than 5% of **1**.

The distance between the unpaired electrons forming the triplet state is inversely proportional to the zero field splitting parameter D which is derived from the outermost features of the spectra (Fig. 2). Particularly, the dipolar component of D (denoted D_d) is related to the distance between the electrons (R, Å) for the system of the cylindrical symmetry according to the relation[13] (*1*).

$$R = (0.65 g_{||}/D_d)^{1/3} \tag{1}$$

The contribution of a pseudodipolar component (D_e) to D ($D = D_d + D_e$) has been found to be low in most of dimeric titanium(III) complexes. A good agreement of the EPR values R and crystallographic distances d(Ti–Ti) were obtained for $[(C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2Zn$ (R = 6.80 Å; d(Ti–Ti) = 6.84 Å; ref.[14]), $[(C_5H_5)_2Ti(\mu\text{-}OMe)]_2$ (R = 3.38 Å; d(Ti–Ti) = 3.35 Å) and $[(C_5H_5)_2Ti(\mu\text{-}OEt)]_2$ (R = 3.33 Å; d(Ti–Ti) = 3.35 Å; ref.[5]), $[(C_5HMe_4)_2Ti(\mu\text{-}H)_2]_2Mg$ (R = 5.59 Å; d(Ti–Ti) = 5.57 Å; ref.[15]), and for $[(C_5HMe_4)_2Ti(\mu\text{-}OMe)_2]_2Mg$ (R = 6.43 Å; d(Ti–Ti) = 6.33 Å; ref.[16]). The EPR parameters for **1**: $g_{||} = 1.999$, $g_{\perp} = 1.972$, $D = 0.0365$ cm^{-1}, $E = 0$ correspond, according to Eq. (*1*), to R = 4.14 Å. This is in reasonable agreement

TABLE IV
Comparison of the structure parameters in the $[(C_5H_{5-n}Me_n)_2Ti(\mu\text{-}Cl)]_2$ (n = 0, 1, 2) compounds

Parameters	$n = 0^a$	$n = 1^a$	$n = 2$
Ti–Cl, Å	max. 2.558(2)	max. 2.566(2)	2.544(1)
	min. 2.534(2)	min. 2.526(2)	2.541(1)
Ti–CE, Å	max. 2.058	min. 2.074	2.074(3)
	min. 2.049	max. 2.043	2.065(3)
C–C(Cp), Å	av. 1.342(33)	av. 1.396(13)	1.406(9)
C–C(Me), Å	–	av. 1.537(9)	av. 1.498(6)
Ti–Ti, Å	3.943 and 3.968	3.926	3.9155(8)
Ti–Cl–Ti, °	101.2(1)–102.9(1)	100.7(0), 100.9(0)	100.8(0)
Cl–Ti–Cl, °	77.1(1)–78.6(1)	79.1(1), 79.3(1)	79.2(0)
CE–Ti–CE, °	131.2–133.4	130.9, 131.0	132.4(1)

[a] The data are taken from ref.[1].

with the crystallographic Ti–Ti distance which is equal to 3.9155(8) Å. It has to be noticed that the features of the triplet state spectrum are broad, and this precludes a more accurate determination of D and g-tensor components. This is probably due to only approximate cylindrical symmetry of the g-tensor. The calculation of R for $[(C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ by the formula for the rhombic g-tensor afforded a different value of R (3.58 Å; ref.[5]) although the value of D is consistent with that for **1**.

The impurity characterized by the narrow triplet state EPR spectrum was found to be more soluble in hexane. It was observed as blue spots when the sample of **1** was extracted by condensing hexane vapours. Its amount was, however, too low to be isolated and characterized. Its EPR parameters $g_{||} = 1.985$, $g_{\perp} = 1.978$, $D' = 0.01472$, $E' = 0$ correspond to $R = 5.58$ Å. This distance and the axial symmetry of the system indicate that it could be a trinuclear complex probably containing a tetrahedrally coordinating metal atom in the centre bridged through μ-H bonds to two titanocene species. Since the absence of other metals seems to be certain, the central atom could be only Ti(II). The disproportionation of $[(C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ during its sublimation was observed earlier and the presence of $(C_5H_5)_2TiCl_2$ was established in the most volatile sublimation fraction[1].

In MTHF solution, compound **1** coordinates one molecule of the solvent. This is apparent from the EPR spectrum which shows the parameters ($g = 1.979$, $\Delta H = 0.5$ mT, $a_{Ti} = 1.18$ mT) which are nearly identical with those found for the $(C_5H_5)_2TiCl$. MTHF complex[4,6]. The tetrahedrally coordinated Ti(III) atom gives a low anisotropy of the g-tensor ($g_1 = 1.994$, $g_2 = 1.980$, $g_3 = 1.963$) typical for all Cp'_2TiCl . MTHF complexes[4,6].

The above results allow us to conclude that compound **1** is stable as a dimer in the solid state and in non-polar solvents like toluene, and coordinates the Lewis bases of the strength of MTHF. A sample of **1** was prepared whose EPR spectrum in the frozen toluene glass did not show a strong signal near $g = 1.98$. This proved that this signal in other samples was due to impurities and not due to the presence of the equilibrium between the monomer and dimer of **1**.

This investigation was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. 440403). G. S. thanks the Studienstiftung des deutschen Volkes for a Promotionsstipendium.

REFERENCES

1. Jungst R., Sekutowski D., Davis J., Luly M., Stucky G.: Inorg. Chem. *16*, 1645 (1977).
2. Troyanov S. I., Rybakov V. B., Thewalt U., Varga V., Mach K.: J. Organomet. Chem. *447*, 221 (1993).
3. Pattiasina J. W., Heeres H. J., van Bolhuis F., Meetsma A., Teuben J. H., Spek A. L.: Organometallics *6*, 1004 (1987).
4. Mach K., Raynor J. B.: J. Chem. Soc., Dalton Trans. *1992*, 683.

5. Samuel E., Harrod J. F., Gourier D., Dromzee Y., Robert F., Jeannin Y.: Inorg. Chem. *31*, 3252 (1992).
6. Samuel E., Vedel J.: Organometallics *8*, 237 (1989).
7. Mach K., Antropiusova H., Hanus V., Dosedlova A.: Transition Met. Chem. *5*, 5 (1980).
8. Varga V., Mach K., Schmid G., Thewalt U.: J. Organomet. Chem. *475*, 127 (1994).
9. Bruggemann R., Debaerdemaeker T., Muller B., Schmid G., Thewalt U.: *Ulm-Programmsystem, 1. Jahrestagung der Deutschen Gesellschaft für Kristallografie, Mainz, June 9–12, 1992*. Abstr. p. 33.
10. Sheldrick G. M.: *SHELXL93. Program for the Refinement of Crystal Structures*. University of Gottingen, Gottingen 1993.
11. Petersen J. L., Dahl L. F.: J. Am. Chem. Soc. *97*, 6422 (1975).
12. McKenzie T. C., Sanner R. D., Bercaw J. E.: J. Organomet. Chem. *102*, 457 (1975).
13. Belford R. L., Chasteen N. D., So H., Tapscott R. E.: J. Am. Chem. Soc. *91*, 4675 (1969).
14. Gourier D., Vivien D., Samuel E.: J. Am. Chem. Soc. *107*, 7418 (1985).
15. Gyepes R., Mach K., Cisarova I., Loub J., Hiller J., Sindelar P.: J. Organomet. Chem. *497*, 33 (1995).
16. Gyepes R., Hiller J., Thewalt U., Polasek M., Sindelar P., Mach K.: J. Organomet. Chem., in press.