Journal of Organometallic Chemistry, 447 (1993) 221-225

JOM 23196

Crystal and molecular structure of bis(tetramethylcyclopentadienyl)titanium halides, $(C_5HMe_4)_2TiCl$, $(C_5HMe_4)_2TiI$ and $(C_5HMe_4)_2TiCl_2$

Sergei I. Troyanov and Viktor B. Rybakov
Department of Chemistry, Moscow State University, 119899 Moscow (Russian Federation)

Ulf Thewalt
Department of X-ray and Electron Diffraction, University of Ulm, Oberer Eselsberg, W-7900 Ulm (Germany)

Vojtech Varga and Karel Mach
J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, 182 23 Prague 8 (Czechoslovakia)

(Received July 29, 1992)

Abstract

X-ray analysis of $(C_5HMe_4)_2TiCl$ (I), $(C_5HMe_4)_2TiI$ (II) and $(C_5HMe_4)_2TiCl_2$ (III) revealed that their overall geometry is very similar to that of permethylated $(C_5Me_5)_2TiCl$ (IV) and $(C_5Me_5)_2TiCl_2$ (V) complexes. The general structural difference between the C_5Me_5 and C_5HMe_4 bent sandwich compounds is a larger CE-Ti-CE angle (by approx. 4°; CE is the centroid of the Cp ring) in the latter compounds which apparently results from a release of steric strain in the C_5Me_5 derivatives upon replacement of Me groups by hydrogen atoms in positions of close approach of cyclopentadienyl rings. Another difference lies in a shift of the Ti atom from the symmetrical position with respect to the C_5HMe_4 ring towards the top of the dihedral angle. Comparison of structures I and II shows that the nature of the halogen atom does not affect the CE-Ti-CE angle in the titanocene skeleton.

1. Introduction

The exploitation of the pentamethylcyclopentadienyl ligand has given rise to a new titanocene chemistry based on enhanced reactivity of C_5Me_5 methyl groups, and this diversity has been enriched further by introducing a series of methylated titanocene dihalides $\overline{Cp}_2TiX_2$ ($\overline{Cp} = C_5H_{5-n}Me_n$, $n = 0$–5; X = Cl, Br, I) [1,2] as starting materials. In the titanocene monohalide series $\overline{Cp}_2TiX$, it is known that the number of Me groups controls their dimeric or monomeric nature, both in the solid state and in solution. The solid C_5H_5 and C_5H_4Me derivatives consist of dimers bridged by two halogen atoms [3] whereas the solid $(C_5Me_5)_2TiCl$ is monomeric [4]. In solution, the C_5H_5 and C_5H_4Me compounds form dimers [5] or monomeric solvates with polar solvents [6] whereas the $C_5H_2Me_3$, C_5HMe_4 and C_5Me_5 compounds are monomeric [4,7]. The electron donating effect of Me groups has been shown gradually to change the reactivity of $\overline{Cp}TiCl_3$ compounds towards ethylaluminium compounds and to give a smooth correlation of rate constants and ESR parameters of the resulting $\overline{Cp}TiAl_2Cl_{8-x}Et_x$ ($x = 0$–4) complexes with the number of Me groups [2]. On the other hand, similar correlations of ESR parameters in the series of the $\overline{Cp}_2Ti(\mu\text{-}Cl)_2AlCl_{2-x}Et_x$ ($x = 0$–2) complexes gave strongly deviated values for the C_5Me_5 complexes [8]. Also correlations of UPS ionization band energies in the series of $\overline{Cp}_2TiX_2$ [9] and $\overline{Cp}_2TiX$ compounds [10] indicated that constant increments of energy per Me group were strongly deviated for the permethylated members of the series. All these deviations as well as some unexpected differences in the catalytic properties

---

Correspondence to: Dr. S.I. Troyanov.

0022-328X/93/$6.00

of the C_5HMe_4 and C_5Me_5 titanocene derivatives [11–15] were in the C_5Me_5 complexes tentatively ascribed to steric hindrance.

To rationalize differences in steric effects between the C_5HMe_4 and C_5Me_5 derivatives we have undertaken the task of comparing solid state structures of some relevant titanocene halide compounds. Here we report crystal structures of $(C_5HMe_4)_2TiCl$ (I), $(C_5HMe_4)_2TiI$ (II) and $(C_5HMe_4)_2TiCl_2$ (III) to add to the crystal structures of $(C_5Me_5)_2TiCl$ (IV) [4], $(C_5Me_5)_2TiCl_2$ (V) [16] and $(C_5H_5)_2TiCl_2$ [17] which are known.

2. Experimental details

All manipulations with titanocene monohalides and their solutions were performed on a high-vacuum line equipped with metal valves and in glass apparatus using breakable seals.

$(C_5HMe_4)_2TiCl_2$ was prepared by the usual procedure [2]. Fine red crystals of needle shape were obtained by crystallization from toluene. $(C_5HMe_4)_2TiCl$ was prepared by boiling a mixture of $(C_5HMe_4)_2TiCl_2$ (0.36 g, 1 mmol) with fine crystalline $LiAlH_4$ (Chemetall) (0.15 g, 4 mmol) in toluene (50 ml) under argon. The mixture was cooled rapidly to room temperature when the red colour of the refluxing solution turned to blue (usually after 1–2 h). Toluene was replaced by hexane and the clear blue solution was poured away from traces of $LiAlH_4$ and LiCl. The hexane was distilled *in vacuo* into an attached ampoule and the fine crystalline product was washed with condensing vapours of hexane; the brown or reddish-brown washings were removed and hexane from the mother liquor was used to dissolve the pure crystalline product.

$(C_5HMe_4)_2TiI$ was prepared according to a procedure based on halogen exchange between $(C_5HMe_4)_2$-TiCl and LiI [4]. LiI was prepared by adding iodine to n-BuLi in hexane (1.6 M, Chemetall) with stirring. The white sediment was washed repeatedly with hexane and dried *in vacuo*. $(C_5HMe_4)_2TiCl$ (*ca.* 0.5 mmol) was dissolved in diethyl ether (20 ml) and the solution was mixed with LiI powder (*ca.* 4 mmol). After stirring overnight the dark green solution was evaporated *in vacuo* and the solid was extracted with hexane. The hexane solution was evaporated *in vacuo* to dryness and the solid was extracted with condensing hexane vapours. This was repeated once more with the washings obtained; the crystalline remainder after evaporation of hexane did not then show the presence of white particles (LiI, LiCl). The purity of all compounds was checked by mass spectrometry (JEOL, JMS D-100, 75 eV, direct inlet, dosing of Ti^{III} compounds under argon): $(C_5HMe_4)_2TiI$ ($M^{\cdot +}$ m/e 417) contained less than 3% of $(C_5HMe_4)_2TiCl$ ($M^{\cdot +}$ m/e 325).

2.1. X-ray structure determination

Single crystals of titanocene monohalides were grown from saturated hexane solutions by slow cooling. The selected crystals were mounted into glass capillar-

TABLE 1. Crystal data and details of the structure analysis for I–III

	I	II	III
Crystal data			
Chem. formula	$(C_5HMe_4)_2TiCl$	$(C_5HMe_4)_2TiI$	$(C_5HMe_4)_2TiCl_2$
Mol. wt.	325.76	417.21	361.19
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2/n$	$P2_1/n$	$C2/c$
a (Å)	15.490(3)	12.493(4)	16.334(4)
b (Å)	7.527(2)	11.276(2)	6.938(2)
c (Å)	15.588(2)	12.944(4)	16.939(4)
β (°)	100.67(2)	102.03(2)	110.67(5)
V (Å^3)	1786.1	1783.5	1796.1
Z	4	4	4
D (calc.) (g cm^{-3})	1.211	1.554	1.336
μ(Mo Kα) (cm^{-1})	6.1	21.8	7.0
Crystal size (mm)	0.15 × 0.3 × 0.3	0.4 × 0.5 × 0.5	0.1 × 0.2 × 0.2
Data collection and refinement			
θ_{max} (°)	25	25	24
Total data	3538	3314	1397
Obs. data ($F^2 \geq n\sigma(F^2)$)	1835 ($n = 3$)	2542 ($n = 3$)	1298 ($n = 2$)
No. of variables	183	202	96
R	0.071	0.048	0.063
R_w	0.078	0.061	0.072

ies under argon in a glove-box. Crystals of $(C_5HMe_4)_2TiCl_2$ were grown from toluene solution in air; long needle crystals were cut to suitable sizes. Diffraction data for $(C_5HMe_4)_2TiCl$ (**I**) and $(C_5HMe_4)_2TiI$ (**II**) were collected on an Enraf–Nonius CAD4 diffractometer (Mo Kα radiation, graphite monochromator, ω scan mode, room temperature). Empirical correction was applied using the program DIFABS for **I** and scanning data for 8 reflections for **II**. The structures were solved by a combination of direct method and Fourier difference techniques. Both structures were refined by the full-matrix-least-squares technique in anisotropic approximation. All calculations were with SDP programs. Data for $(C_5HMe_4)_2TiCl_2$ (**III**) were obtained on a Philips PW-1100 diffractometer (Mo Kα radiation, graphite monochromator, room temperature). The position of the Ti atom was obtained from a Patterson map and of the other non-hydrogen atoms from ΔF maps. The highest peak in the final ΔF map was 0.4 e Å^{-3}. Calculations were with the SHELX76 package [18]. Positions of hydrogen atoms were not determined for all the compounds.

Crystal data and details of the structure analysis for **I–III** are summarized in Table 1. Atom coordinates and thermal parameters are deposited in the Cambridge Crystallographic Data Centre *. Important bond distances and valence angles are listed in Table 2.

3. Results and discussion

The overall molecular geometry of $(C_5HMe_4)_2TiCl$ (**I**) and $(C_5HMe_4)_2TiI$ (**II**) is similar to that of $(C_5Me_5)_2TiCl$ (**IV**) [4]. Both compounds are monomeric and the titanium atom is in a planar pseudotrigonal coordination. Two C_5HMe_4 ligands form a bent sandwich which is typical for all titanocene derivatives [19]. The crystal structure of **I** contains two crystallographically independent $(C_5HMe_4)_2TiCl$ molecules possessing nearly the same geometry. Both molecules of **I** have a two-fold symmetry with Ti and Cl atoms located on the axis (Fig. 1). Molecules of $(C_5HMe_4)_2TiI$ (**II**) have a non-crystallographic two-fold symmetry.

A close inspection of titanocene parts of structures **I** and **IV** reveals several conformable features: the Cp* ligands are planar within 0.01 Å and are in staggered conformation. All methyl groups in **I** and **II**, and all except those attached to C(5) and C(10) in **IV** **, are bent slightly out of the ring plane and further away from the titanium atom. The difference in geometry of

---

* Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

** Carbon atoms in **IV** which occupy the same positions in $\overline{Cp}$ rings as C(H) atoms in **I–III** are denoted C(5) and C(10) (C(2) and C(10) in the orginal work [4]).

TABLE 2. Selected interatomic distances (Å) and angles (°) for **I–III**

	$(C_5HMe_4)_2TiCl$	[a]	$(C_5HMe_4)_2TiI$	[b]	$(C_5HMe_4)_2TiCl_2$
Bond distances					
Ti(1)–X(1)	2.318(4)	2.316(4)	2.759(2)		2.344(2)
Ti(1)–CE(1)	2.030	2.032	2.055	2.058	2.109
Ti(1)–C(1)	2.339(8)	2.359(7)	2.371(9)	2.38(1)	2.387(5)
Ti(1)–C(2)	2.377(9)	2.383(6)	2.42(1)	2.42(1)	2.484(5)
Ti(1)–C(3)	2.393(7)	2.396(8)	2.44(1)	2.42(1)	2.475(6)
Ti(1)–C(4)	2.331(7)	2.343(8)	2.370(9)	2.37(1)	2.413(6)
Ti(1)–C(5)	2.307(8)	2.310(8)	2.324(8)	2.31(1)	2.356(6)
C(1)–C(2)	1.41(1)	1.40(1)	1.41(1)	1.40(1)	1.429(7)
C(1)–C(5)	1.39(1)	1.42(1)	1.43(1)	1.44(1)	1.389(8)
C(2)–C(3)	1.40(1)	1.40(1)	1.43(1)	1.41(1)	1.366(8)
C(3)–C(4)	1.36(1)	1.41(1)	1.42(1)	1.40(1)	1.421(8)
C(4)–C(5)	1.40(1)	1.40(1)	1.42(1)	1.38(1)	1.416(8)
C(1)–C(11)	1.52(1)	1.51(1)	1.49(1)	1.46(1)	1.519(9)
C(2)–C(21)	1.54(2)	1.53(1)	1.49(1)	1.53(1)	1.516(9)
C(3)–C(31)	1.54(1)	1.53(1)	1.49(1)	1.51(1)	1.53(1)
C(4)–C(41)	1.56(1)	1.54(1)	1.49(2)	1.51(1)	1.52(1)
Angles					
CE(1)–Ti(1)–CE(1′)	139.0	139.2	139.3		133.4
CE(1)–Ti(1)–X(1)	110.5	110.4	110.1	110.6	106.0
CE(1)–Ti(1)–X(1′)					105.2
Cl–Ti–Cl′					94.2(1)

[a] The distances and angles for the second independent $(C_5HMe_4)_2TiCl$ molecule concern Ti(2), Cl(2), C(6)–C(10), and C(61)–C(91) atoms.
[b] The values for the C(6)–C(10), C(61)–C(91) atoms are from the same $(C_5HMe_4)_2TiI$ molecule.

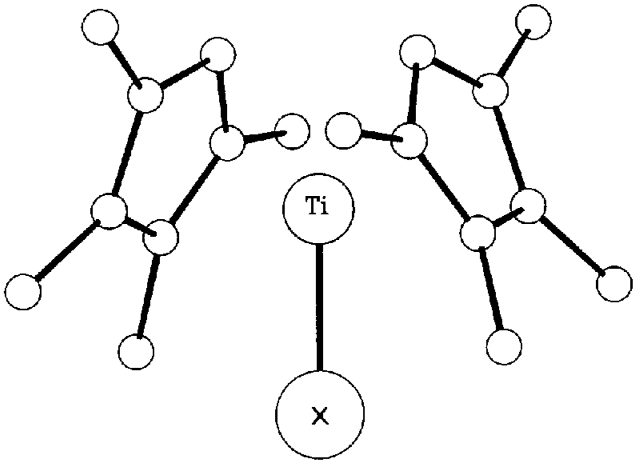

Fig. 1. Molecular geometry of $(C_5HMe_4)_2TiX$, X = Cl, I; H atoms are not shown. Carbon atoms of $\overline{Cp}$-rings bearing H atoms are referred to as C(5) and C(10) in the text. This is correct for **II**, while for **I** this notation corresponds to C(5) and C(5′) atoms in one independent molecule and C(10) and C(10′) in another.

molecules **I** and **IV** arises from the presence of Me groups at carbons C(5), C(10) in **IV** which occupy positions where both $\overline{Cp}$ rings closely approach each other. These methyl groups repel each other so that they are bent as much as 0.4 Å out of the ring plane [4]. In **I**, the carbon atoms C(5) and C(10) bearing hydrogen atoms occupy the positions of close approach of $\overline{Cp}$ rings. The absence of Me groups from them results in a higher inclination of the $\overline{Cp}$ planes (CE–Ti–CE 139.1°, CE: centroid of the $\overline{Cp}$ ring) and in shorter average Ti–C(ring) distance (2.35 Å) in **I** compared with **IV** (CE–Ti–CE 143.6°, Ti–C(ring)$_{av}$ 2.39 Å) (see Table 3).

Another important difference between **I** and **IV** lies in the position of the Ti atom with respect to the $\overline{Cp}$ ligands. While in **IV** all the Ti–C(ring) distances have approximately the same value, in **I** these distances differ by at the most 0.1 Å depending on their position, those to C(5) and C(10) being the shortest. It means that the Ti atom in **I** is shifted inside the dihedral angle of the $\overline{Cp}$ ligands. The Ti–Cl bond lengths in **I** and **IV** differ considerably. The short Ti–Cl bond length in **I** (2.32 Å) apparently reflects the absence of steric hindrance whereas the longer Ti–Cl bond in **IV** was explained by steric crowding resulting from the less inclined position of the permethylated $\overline{Cp}$ rings. Somewhat surprisingly the chlorine atom in **I** exerts an intense temperature motion in the direction parallel to $\overline{Cp}$ planes while the more distant chlorine atom in **IV** shows much lower amplitude of temperature motion [4]. This can also be tentatively explained by the difference in free space between $\overline{Cp}$ ligands at the open side of the sandwich structures.

The structure of **II** does not differ from that of **I** except that the Ti–I bond length is appropriately longer and the iodine atom does not show any enhanced thermal motion. The latter effect is apparently caused by non-valence interaction of Cp rings with the iodine atom; this type of interaction is probably much weaker in the chloro derivative **I**. On the other hand, crystallographic effective volumes of **I** and **II** are virtually the same (see Table 1). It implies that the geometry of the titanocene skeleton is influenced only slightly by the size of the halogen atom (packing mode effects can also contribute).

Molecules of $(C_5HMe_4)_2TiCl_2$ (**III**) contain the titanium atom in a pseudotetrahedral environment, located on a two-fold axis bisecting the CE–Ti–CE and Cl–Ti–Cl angles. The C_5HMe_4 rings are in staggered conformation and their non-methylated carbon atoms C(5) and C(10) occupy positions where the $\overline{Cp}$ rings are close to each other. Comparison of Ti^{IV} complexes **III** and $(C_5Me_5)_2TiCl_2$ (**V**) (see Table 2), shows that the changes concerning the geometry of titanocene skeletons are essentially the same as for the corresponding Ti^{III} complexes, however, Ti–Cl distances and Cl–Ti–Cl angles do not practically differ.

From the data collected in Table 3 for the relevant Ti^{IV} and Ti^{III} compounds it can be concluded that both the average Ti–C(ring) distances and the CE–Ti–CE

TABLE 3. Some geometrical features of $\overline{Cp}_2TiX$ and $\overline{Cp}_2TiCl_2$ molecules

Compound	No.	Average distance (Å)			Average angle (°)		Ref.
		Ti–X	Ti–C	Ti–CE	CE–Ti–CE	Cl–Ti–Cl	
$(C_5HMe_4)_2TiCl$	**I**	2.317	2.35	2.03	139.1		[a]
$(C_5HMe_4)_2TiI$	**II**	2.759	2.38	2.06	139.3		[a]
$(C_5Me_5)_2TiCl$	**IV**	2.363	2.39	2.06	143.6		4
$(C_5HMe_4)_2TiCl_2$	**III**	2.344	2.42	2.11	133.4	94.2	[a]
$(C_5Me_5)_2TiCl_2$	**V**	2.349	2.44	2.13	137.4	92.9	16
$(C_5H_5)_2TiCl_2$	**VI**	2.364	2.37	2.06	131.0	94.5	17

[a] This work.

angle increase on going from the Ti^{III} to Ti^{IV} compounds. Both also increase with increasing number of Me substituents, however, the difference between the values for the C_5Me_5 and C_5HMe_4 compounds is higher than for the C_5HMe_4 and C_5H_5 compounds. It means that the strain in the permethylated titanocene moiety is largely released in the C_5HMe_4 derivatives. The remarkable shift of the titanium atom towards the top of the dihedral angle of the $\overline{Cp}$ rings has been found in all the C_5HMe_4 compounds listed in Table 3 whereas in the C_5Me_5 and C_5H_5 derivatives **IV**, **V** and **VI** and in dimeric $[(C_5H_5)_2TiCl]_2$ [3] it was located centrally with respect to $\overline{Cp}$ ligands. The analogous shift of zirconium atom was also observed in $(C_5HMe_4)_2Zr(\sigma\text{-phenyl})Cl$ [12] with a maximum difference in the Zr–C(ring) distances of 0.15 Å, virtually the same as for **III**. These results suggest that the conformation of C_5HMe_4 ligands with the non-methylated carbon atoms in approaching positions of $\overline{Cp}$ rings is a general phenomenon in bent sandwich transition metal complexes, controlled sterically. These results offer an explanation for a large increase in the anisotropy of the EPR *g*-tensor between $(C_5HMe_4)_2TiCl$ and $(C_5Me_5)_2TiCl$ because of increasing energy of the $1a_1$ orbital, which is occupied by a d^1 electron, with increasing value of the CE-Ti-CE angle [7]. On the other hand, the equal CE–Ti–CE angles found for **I** and **II** refute the previous suggestion that the increase in anisotropy of the *g*-tensor on going from the Cl to I derivatives is due to change of the CE–Ti–CE angle. The results also imply that differences in reactivity and physico-chemical properties of titanocene derivatives when going from the C_5Me_5 to C_5HMe_4 ligands [8–15] need not arise exclusively from the change in the CE–Ti–CE angle but also from the different ligand field around the titanium atom resulting from its position asymmetric to C_5HMe_4 ligands. The latter effect should be taken into account when computing the dependence of orbital energies in titanocene complexes on the CE–Ti–CE angle by more accurate methods than previously [20].

References

1 W. C. Finch, E. V. Anslyn and R. H. Grubbs, *J. Am. Chem. Soc., 110* (1988) 2406.

2 K. Mach, H. Antropiusová, V. Varga and J. Poláček, *J. Organomet. Chem., 333* (1987) 205.

3 R. Jungst, D. Sekutowski, J. Davis, M. Luly and G. Stucky, *Inorg. Chem., 16* (1977) 1645.

4 J. W. Pattiasina, H. J. Heeres, F. van Bolhuis, A. Meetsma, J. H. Teuben and A. L. Spek, *Organometallics, 6* (1987) 1004.

5 R. S. P. Coutts, P. C. Wailes and R. L. Martin, *J. Organomet. Chem., 47* (1973) 375.

6 E. Samuel and J. Vedel, *Organometallics, 8* (1989) 23.

7 K. Mach and J. B. Raynor, *J. Chem. Soc., Dalton Trans.,* (1992) 683.

8 K. Mach and V. Varga, *J. Organomet. Chem., 347* (1988) 85.

9 T. Vondrák, K. Mach and V. Varga, *J. Organomet. Chem., 367* (1989) 69.

10 T. Vondrák, K. Mach and V. Varga, *Organometallics*, in press.

11 P. Courtot, R. Pichon, Y. Raoult and J. Y. Salaün, *J. Organomet. Chem., 327* (1987) C1.

12 P. Courtot, R. Pichon, J. Y. Salaün and L. Toupet, *Can. J. Chem., 69* (1991) 661.

13 H. Akita, H. Yasuda, K. Nagasuma and A. Nakamura, *Bull. Chem. Soc. Jpn., 56* (1983) 554.

14 H. Akita, H. Yasuda and A. Nakamura, *Bull. Chem. Soc. Jpn., 57* (1984) 480.

15 K. Mach, H. Antropiusová, V. Varga and V. Hanuš, *J. Organomet. Chem., 358* (1988) 123.

16 T. C. McKenzie, R. D. Sanner and J. E. Bercaw, *J. Organomet. Chem., 102* (1975) 457.

17 A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina, R. Ropal and I. Bernal, *Can. J. Chem., 53* (1975) 1622.

18 G. M. Sheldrick, *SHELX76 Program System*, Göttingen, unpublished.

19 D. Cozak and M. Melnik, *Coord. Chem. Rev., 74* (1986) 53.

20 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc., 98* (1976) 1729.