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1,3-Di-t-butyl substituted cyclopentadienyl Titanium complexes. New structural aspects

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Abstract

$\mathrm{Cp}_2^{\star\star}\mathrm{TiCl}_2$ (I) was obtained by the reaction of TiCl_4 with $\mathrm{Cp}^{\star\star}\mathrm{Li}{=}\mathrm{C}_5\mathrm{H}_3(\mathrm{C}_4\mathrm{H}_9\text{-t})_2\mathrm{Li}$. Complex I was treated with potassium metal in pentane to give paramagnetic $\mathrm{Cp}_2^{\star\star}\mathrm{TiCl}$ (II) in high yield. The crystal structures of I and II were determined by X-ray crystallography. The molecules of both complexes are monomeric in crystals. Complex I: monoclinic, $B2/b$, a 21.069, b 19.387, c 6.560 Å, γ 94.25°, $R = 0.045$. Ti–Cl and Ti–C bond distances are 2.349 and 2.124 Å, on the average, respectively. Cl–Ti–Cl and $\mathrm{Cp}^{\star\star}$–Ti–$\mathrm{Tp}^{\star\star}$ angle values are 93.1 and 121°. Complex II: monoclinic, $P2/n$, a 13.497, b 13.441, c 7.207 Å, γ 86.48°, $R = 0.064$. Ti–Cl and Ti–C bond distances are 2.337 and 2.386 Å, on the average, respectively. $\mathrm{Cp}^{\star\star}$–Ti–$\mathrm{Cp}^{\star\star}$ angle value is 134.8°.

Results and discussion

The geometrical structure and properties of compounds can be explained in terms of the interaction of electronic and steric factors. In many cases these factors are antagonistic. Progress in the study of steric factors is largely dependent on the availability of suitable molecular models. The chemical community often has had to modify or change its views on chemical bonding, once new facts had come to light after the development and study of certain prominent molecular models.

Here we deal with some aspects of titanocene chemistry. We have synthesized and studied the structure of two novel titanocene derivatives, namely bis[η^5-1,3-di(t-butyl)cyclopentadienyl]titaniumdichloride (I) and similar titanocenemonochloride (II).

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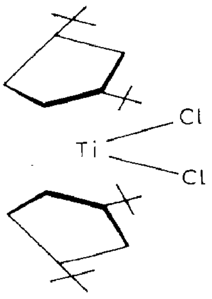
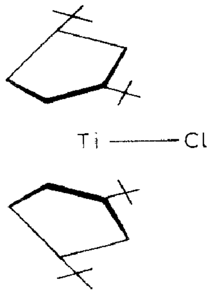
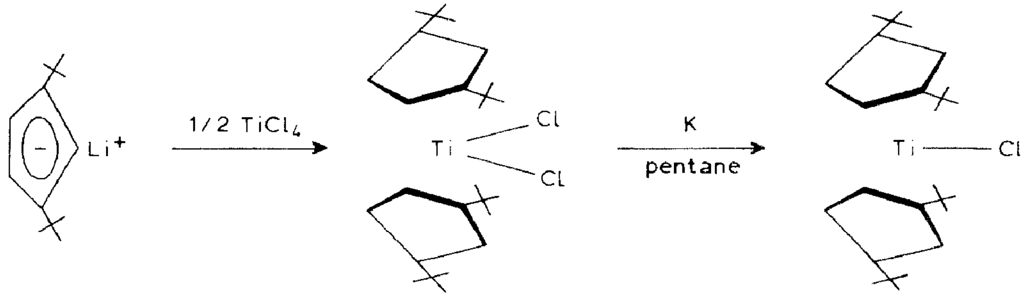


(I)



(II)

Dichloride (I) was obtained from the reaction of lithium 1,3-di-t-butylcyclopentadienide with $TiCl_4$, by the procedure generally used for other titanocene species.



The titanocene complex I was found to undergo smooth reduction with finely powdered potassium in pentane under ambient conditions to give a deep blue pentane solution of the paramagnetic complex II monochloride. The dichloride I is insoluble in pentane.

Introduction of two bulky t-butyl substituents into each cyclopentadienyl ring affects the molecular and crystal structures of compounds I and II. Their properties are also very different when compared with the more common titanocene derivatives without bulky substituents in the Cp rings. Both new complexes are highly soluble in aromatic hydrocarbons, in addition monochloride II is readily soluble in ethyl ether and pentane. The crystals suitable for X-ray analysis were isolated from $CHCl_3$ for I, and from pentane for II.

The molecular and crystal structures of I are shown in Figs. 1 and 2, respectively. The bond lengths and bond angles are collected in Tables 1 and 2.

We have compared the structural parameters of I with those of structurally analogous $(\eta^5\text{-}C_5H_4Me)_2TiCl_2$ (III) [1] *. The general configurations of the molecules I and III are very different, viz. Table 3. The only coincidence is Cl–Ti–Cl angle value being 93.1°. Ti–Cl and Ti–C average distances are substantially different and so are Cp–Ti–Cp angle values. For I Cp^{**}–Ti–Cp^{**} angle is 121°

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* We chose compound III for comparison because of the high degree of accuracy with which the structural parameters were obtained see in ref. 1.

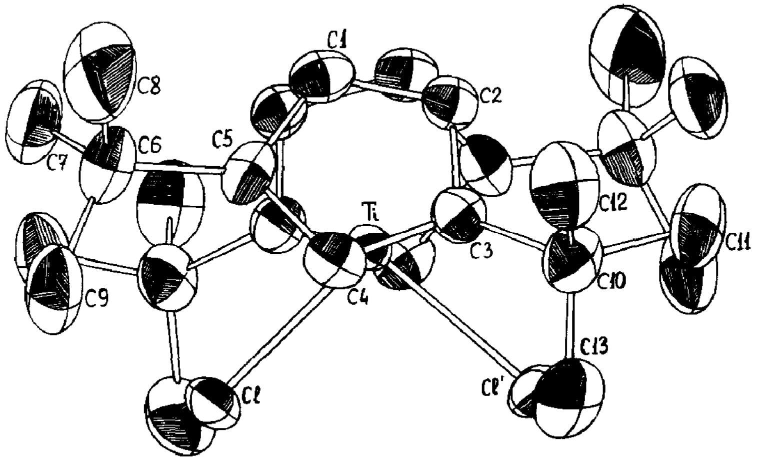


Fig. 1. Configuration of molecule I.

and that is the minimum value in the range of titanocene derivatives. Only $CH_2(C_5H_4)_2TiCl_2$ (IV), the complex with the shortest CH_2 bridge between substituted Cp rings shows aproximate value of 121.5° [2]. For the majority of titanocene derivatives this value ranges from 128 to 133° [3].

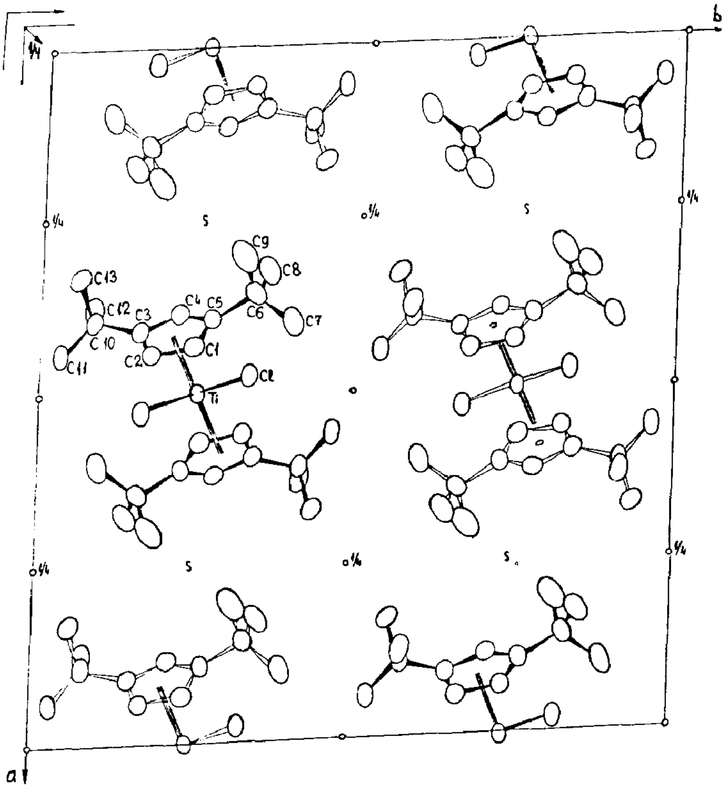


Fig. 2. The crystal structure of complex I projected along the *c* direction.

Table 1

Bond lengths *d* (Å) in I

Ti–Cl	2.349(1)		
Ti–C(1)	2.342(3)	C(1)–C(5)	1.413(4)
Ti–C(2)	2.347(3)	C(8)–C(9)	1.528(4)
Ti–C(3)	2.534(3)	C(9)–C(10)	1.520(5)
Ti–C(4)	2.488(3)	C(9)–C(11)	1.539(6)
Ti–C(5)	2.473(3)	C(9)–C(12)	1.513(7)
C(1)–C(2)	1.407(4)	C(13)–C(14)	1.514(5)
C(2)–C(3)	1.419(4)	C(13)–C(15)	1.540(5)
C(3)–C(4)	1.399(4)	C(13)–C(16)	1.533(5)
C(4)–C(5)	1.405(4)	C(6)–C(13)	1.522(4)

The most interesting feature of structure I is the unusually long average Ti–C distance, the same is true for complex II. Average Ti–C distance in I is 0.1 Å longer than any other Ti–C bond distance of all structurally studied titanocene compounds [3]. Thus, in III Ti–C average bond length is 0.14 Å shorter than that in I. Moreover, the compound I is characterized by significant deviations of each Ti–C bond distance from the average length value, and those deviations are substantially greater than in III.

Ti–Cl bond distances are similar for I, III, and II. It is noteworthy that this is despite the slight shortening of the Ti–Cl bond (0.012 Å) which is inherent in I, in contrast to III.

The Cp^{**} rings in I are practically planar. The deviations of carbon atoms from the mean square plane are between ±0.04 Å. But quaternary carbon atoms of t-butyl groups are bent from the mean square plane of the ring by 0.38 (C(6)) and 0.45 (C(10)) Å and the corresponding angles are 13.5 and 15.7° for C(5)–C(6) and

Table 2

Bond angles ω (°) in I [a]

C(1)–C(2)–C(3)	108.4(3)	C(2)–C(3)–C(10)	126.1(3)
C(2)–C(3)–C(4)	106.0(3)	C(4)–C(3)–C(10)	126.4(3)
C(3)–C(4)–C(5)	110.4(3)	C(1)–C(5)–C(6)	124.8(3)
C(4)–C(5)–C(1)	106.2(6)	C(4)–C(5)–C(6)	127.5(3)
C(5)–C(1)–C(2)	108.4(3)		
C(5)–C(6)–C(7)	112.5(3)	C(3)–C(10)–C(11)	113.1(3)
C(5)–C(6)–C(8)	112.1(3)	C(3)–C(10)–C(12)	103.7(3)
C(5)–C(6)–C(9)	105.5(3)	C(3)–C(10)–C(13)	112.1(3)
C(7)–C(6)–C(8)	108.7(3)	C(11)–C(10)–C(12)	107.5(3)
C(7)–C(6)–C(9)	110.3(4)	C(11)–C(10)–C(13)	110.9(3)
C(8)–C(6)–C(9)	108.1(4)	C(12)–C(10)–C(13)	109.1(3)
Cl–Ti–Cl′	93.1(5)		
Cp_c–Ti–Cp_c'	132.2(5)		
Cp_c–Ti–Cl	105.5(5)		
Cp_c–Ti–Cl′	106.9(5)		

[a] Cp_c is the centroid of corresponding cyclopentadienyl ligand.

Table 3

Important geometrical parameters in the sandwich complexes of Ti^{III} (I–VIII) and V^{III} (IX)

Compound	M–X (Å)	M–C (Å)	M–Cp[a] (Å)	XMX (°)	CpMCp (°)	Ref.
$[C_5H_3(Bu\text{-}t)_2]_2TiCl_2$ (I)	2.349	2.449	2.124	93.1	121.0	[b]
$[C_5H_3(Bu\text{-}t)_2]_2TiCl$ (II)	2.337	2.386	2.066	–	134.8	[b]
$[C_5H_4(Me)]_2TiCl_2$ (III)	2.361	2.307	2.067	93.15	130.2	1
$CH_2(C_5H_4)_2TiCl_2$ (IV)	2.34	2.40	2.05	97.1	121.5	2
$\{[C_5H_4(Me)]_2Ti\}_2(\mu\text{-}Cl)_2$ (V)	2.547	2.376	2.062	79.2	130.9	3, 4
$(C_5H_5)_2Ti(2,6\text{-}Me_{26}H_3)$ (VI)	2.18	2.35	[c]	–	138.4	5
$(C_5H_5)_2Ti\text{-}O\text{-}2,6(Bu\text{-}t)_2\text{-}4\text{-}MeC_6H_2$ (VII)	1.892	2.362	[c]	–	135.5	6
$(C_5Me_5)_2TiCl$ (VIII)	2.363	[c]	2.06	–	143.6	7
$(C_5H_5)_2VCl$ (IX)	2.390	2.28	1.946	–	139.5	9

[a] The distance between metal atom and the centroid of cyclopentadienyl ligand. [b] This work. [c] Not calculated.

C(3)–C(10) bonds respectively. Thus in I the Ti–η^5–Cp** bonds, compared with those in III, are weakened owing to strong steric repulsion by the substituted Cp**-rings. The situation may be regarded as a structure containing relatively ionic Ti–η^5–Cp** bonds. In this case Ti–Cl bonds must be strengthened because of the stronger interaction of the Ti Lewis acidic center with the σ- and $p\pi$-donor Cl atoms. The Ti–Cl bonds in I are, in fact, somewhat shorter than those in III. The average value for C–H bond distance is about 1.0 Å in I.

The shortest non-bonding contacts in I are as follows: Cl $\cdots$ C(3) 3.10, C(1) $\cdots$ C(1′) 2.91, C(1) $\cdots$ C(2′) 3.01, C(4) $\cdots$ C(8) 3.02, Cl $\cdots$ H 2.73, and H $\cdots$ H 2.23 Å. Intermolecular C $\cdots$ C distances in the lattice are greater than 3.6 Å.

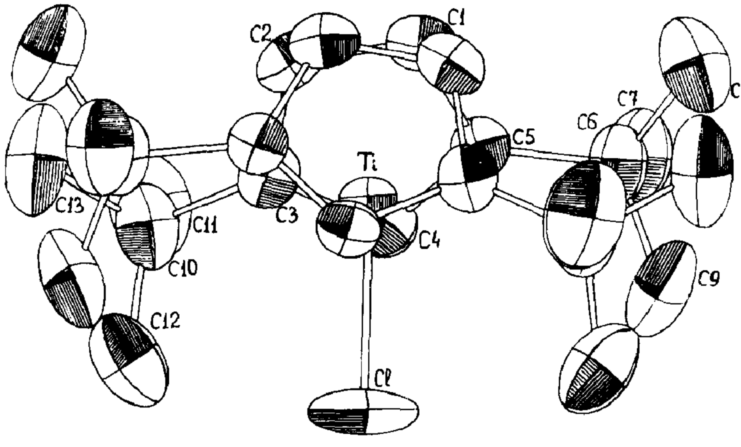


Fig. 3. Configuration of molecule II.

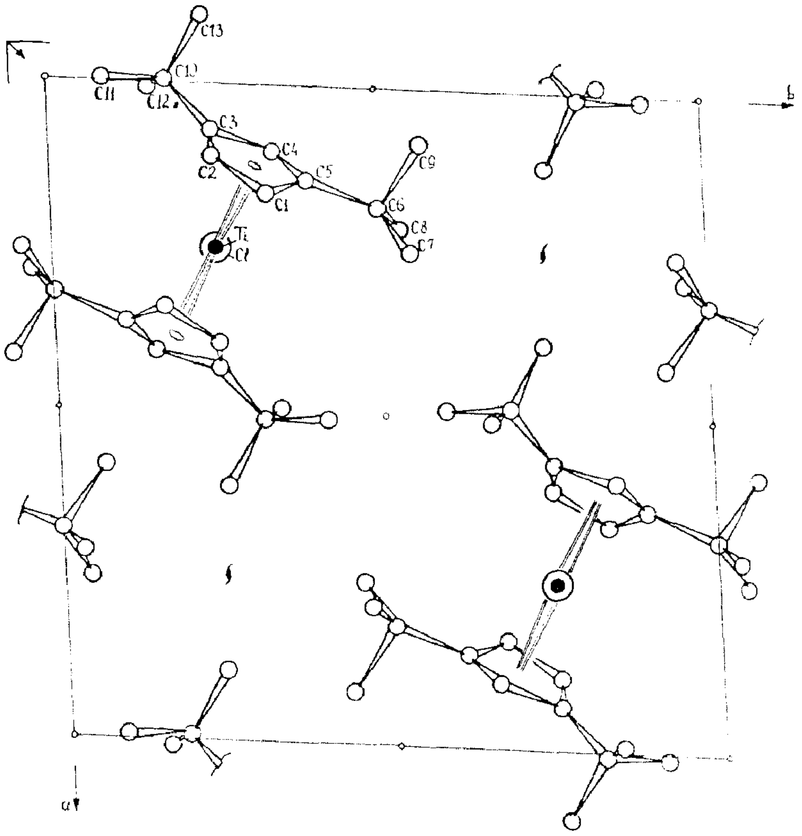
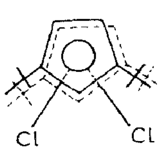
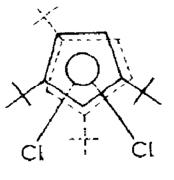


Fig. 4. The crystal structure of complex II projected along the *c* direction.

The nearly eclipsed sandwich moiety conformation in I is a unique feature of this molecule. Cp** rings are somewhat twisted, the torsion angle 28.5°, and t-butyl groups are practically overlapping, see Fig. 1. Thus rotamer **A**, observed in the solid state, is less strained than any other, for example **B**.



(A)



(B)

A priori a non predictable conformation arises and this is unprecedented. The steric interaction of the Cp** cycles gives the observed conformation, **A**. This is obvious because the same conformation is found in the structure of monochloride II, for which the angle of rotation about the Cp** ring axis of one ring relative to the other is 22.5°.

The crystal lattice of II is made up of monomeric Cp$_2^{**}$TiCl units, which is of interest because the majority of $(\eta^5\text{-Cp}')_2\text{Ti}^{\text{III}}\text{X}$ compounds, where X is monovalent acidic residue, are dimers in the solid state, viz. $\text{Cp}'_2\text{Ti}(\mu\text{-X})_2\text{TiCp}'_2$, see for example V in Table 3 [3,4].

The molecular and crystal structures of II are shown in Figs. 3 and 4, respectively.

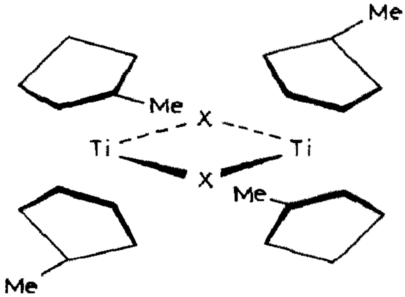
Up to now only a few monomeric compounds of this class were known, i.e. $Cp_2Ti(2,6\text{-}Me_2C_6H_3)$ (VI) [5], and $Cp_2TiO\text{-}[2,6(Bu\text{-}t)_2\text{-}4\text{-}MeC_6H_2]$ (VII) [6]. Clearly, dimerization is hindered here by the bulky residue that is σ-bonded to the Cp_2Ti moiety *. This is in sharp contrast to our complex II, and the newly synthesized $(\eta^5\text{-}C_5Me_5)_2TiCl$ (VIII) [7]. They are both monomeric due to the bulky groups in the Cp ligands.

The electron configuration of Ti in $(Cp'_2TiX)_n$ ($n = 1, 2$) is d^1 so that monomeric complexes II, VI, VII, and VIII, $n = 1$, are paramagnetic. We have studied the magnetic susceptibility of II in the range 77–297 K and obtained the effective magnetic moment. The observed value of 1.65 BM, which is close to the ideal value of 1.73 BM characteristic of isolated Ti^{III} ion [8], is not temperature dependent. This indicates that there is no spin interaction in the solid.

The resulting magnetic properties of the dimers $(Cp'_2TiX)_2$ are strongly dependent on the nature of bridging X groups. When X is halogen or alkoxy group, antiferromagnetic interaction of spinning Ti atoms is observed and causes the effective magnetic moment to become temperature dependent. With the temperature decrease, the magnetic susceptibility of the samples $(Cp'_2TiOR)_2$ and $(Cp'_2TiHal)_2$ is also decreasing. The compounds with NR_2, PR_2, and SR bridging groups are diamagnetic even at room temperature [4].

Of the dimeric complexes, the most accurate structural data were obtained for $[(C_5H_5)_2Ti(\mu\text{-}Cl)]_2$ and $[(MeC_5H_4)_2Ti(\mu\text{-}X)]_2$ (X = Cl, Br) (V). Their geometry indicates that there are close intramolecular non-valent contacts between atoms and that the dimers are strained. The strongest repulsions are between the hydrogens of the various sandwich moieties ($H_{Cp} \cdots H_{Cp'}$). The most important structural parameters of V are collected in Table 3.

Methyl groups in V do not cause any significant additional strain because they are situated in suitable conformational positions. We have shown here that the increase in the number and bulkiness of the substituents to Cp rings leads to the growth of the steric strain in the hypothetical dimers $(Cp_2^{**}TiCl)_2$. The two bulky t-butyl groups in each Cp ligand prevent the formation of the dimer. The same



(V)

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* Cp_2TiY complexes with Y being chelating ligands, are also monomeric, see [3]. These components are discussed elsewhere.

Table 4

Bond lengths *d* (Å) in II

Ti–Cl	2.337(1)		
Ti–C(1)	2.349(2)	C(1)–C(5)	1.407(3)
Ti–C(2)	2.371(2)	C(3)–C(10)	1.524(4)
Ti–C(3)	2.441(2)	C(10)–C(11)	1.529(4)
Ti–C(4)	2.386(2)	C(10)–C(12)	1.524(6)
Ti–C(5)	2.384(2)	C(10)–C(13)	1.519(5)
C(1)–C(2)	1.411(3)	C(5)–C(6)	1.518(3)
C(2)–C(3)	1.394(3)	C(6)–C(7)	1.531(4)
C(3)–C(4)	1.413(3)	C(6)–C(8)	1.528(5)
C(4)–C(5)	1.405(3)	C(6)–C(9)	1.532(6)

effect is observed for permethylated titanocene monochloride $(C_5Me_5)_2$TiCl, which is also monomeric when solid [7].

Crystals of II consist of monomeric molecules $\mathrm{Cp}_2^{\star\star}$TiCl, which possess a C_2 point symmetry group, with the Ti and Cl atoms on the axis. The $\mathrm{Cp}_2^{\star\star}$Ti moiety is a bent sandwich, with a dihedral angle of 134.8°. This value is close to that typical of a large variety of titanocene derivatives [3]. The bond distances and angle value of II are presented in Tables 4 and 5.

The geometry of the $\mathrm{Cp}^{\star\star}$ rings is quite typical, C–C distances are in the range 1.394–1.412 Å with a mean of 1.406 Å. The deviations of carbon atoms from the mean square plane are less than 0.014 Å (C(3)). Quaternary carbon carbon atoms of t-butyl groups C(6) and C(10) are deflected from this plane by 0.24 Å (C(6)) and 0.28 Å (C(10)), the corresponding angles are 8.8 and 10.0°. These angles are smaller than those in dichloride I.

The fact that the effective magnetic moment of II is not temperature dependent is in good agreement with its crystal structure, that of monomeric non-interacting $\mathrm{Cp}_2^{\star\star}$TiCl molecules. The observed magnetic moment differs slightly from pure spin magnitude, and is due to diamagnetic contaminations in crystalline samples of II which are highly reactive towards O_2 and H_2O.

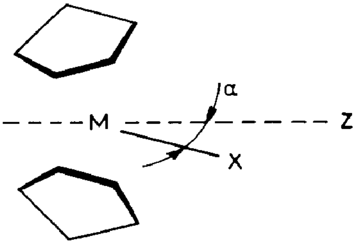
The determination of the molecular structures of II and VIII [7] was necessary to verify the predictions made on the basis of EHMO theory of the structures of

Table 5

Bond angles *ω* (°) in II

C(1)–C(2)–C(3)	109.0(2)	C(5)–C(6)–C(9)	110.4(3)
C(2)–C(3)–C(4)	106.0(2)	C(7)–C(6)–C(8)	107.8(3)
C(3)–C(4)–C(5)	110.5(2)	C(7)–C(6)–C(9)	108.3(3)
C(4)–C(5)–C(1)	105.8(2)	C(8)–C(6)–C(9)	110.4(3)
C(2)–C(1)–C(5)	108.7(2)	C(3)–C(10)–C(11)	107.3(3)
C(2)–C(3)–C(10)	128.4(3)	C(3)–C(10)–C(12)	112.6(3)
C(4)–C(3)–C(10)	124.7(3)	C(3)–C(10)–C(13)	112.0(3)
C(1)–C(5)–C(6)	128.0(3)	C(11)–C(10)–C(12)	110.2(4)
C(4)–C(5)–C(6)	125.4(3)	C(11)–C(10)–C(13)	107.6(3)
C(5)–C(6)–C(7)	108.5(3)	C(12)–C(10)–C(13)	107.1(4)
C(5)–C(6)–C(8)	111.4(3)		

coordinatively unsaturated bent-sandwich complexes of transition metals. With the exception of II and VIII, only one structurally characterized compound of formula Cp_2MCl that is monomeric when solid. It is Cp_2VCl (IX) [9]. The molecules of II, VIII, and IX possess C_2 symmetry. The fact that all these molecules have a C_2 axis comprising M–Cl bonds is of interest for the electronic theory of bent-sandwich complexes. More then ten years ago, on the basis of EHMO method it was assumed that there might be non-symmetrical Cp_2MX molecules without a C_2 axis *.



It was thought that the angle α might be in the range 30–60° [10]. The greatest possibility for such distortion was proposed for Cp_2MX molecules of either d^0, d^1, d^2 (low spin), or d^3 electronic configuration of the metal atom. Vanadocene monochloride, Cp_2VCl (VII), does not belong to this group, because it is a high-spin d^2 complex, and the distortion of its C_2 symmetry cannot be expected. Compounds II and VIII, with Ti d^1 central atom, are acceptable for comparison with the proposed model. It is obvious that the results of structural studies of II and VIII are in conflict with the calculated data, probably because of steric demands by the ligands which affect the molecular geometry of the Cp_2MX complexes.

Experimental

Preparation of $[(t\text{-}C_4H_9)_2C_5H_3]_2TiCl_2$ *(I)*

A 2.0 *N* hexane solution (275 ml) of n-BuLi (0.55 mol) was added dropwise under vigorous stirring to a mixture of 89 g (0.5 mol) di-t-butylcyclopentadiene, 200 ml benzene, and 100 ml dimethoxyethane. A solution of 47.5 g (0.25 mol) $TiCl_4$ in 200 ml hexane was then added dropwise to the mixture at 0 °C, and the mixture was stirred for 30 min and 100 ml chloroform, and 10 ml conc. hydrochloric acid was added. After removal of solvent by slow evaporation at room temperature, the resulting solid was washed with pentane until the washings became pale yellow. The product, I, was recrystallized from benzene. The yield was 35 g (30%) of I. Found: C, 63.99; H, 8.96; Cl, 14.99; Ti, 9.62; $C_{26}H_{42}Cl_2Ti$ calc.: C, 65.96; H, 8.94; Cl, 14.98; Ti, 10.20%. ^1H NMR (δ (ppm), $CDCl_3$): 1.27 s (36H); 6.11 d (4H); 6.65 t (2H); J 2.44 Hz.

Preparation of $[(t\text{-}C_4H_9)_2C_5H_3]_2TiCl$ *(II)*

A suspension of 5.0 g (10.6 mmol) of I and 1.0 g (25.6 mmol) of powdered potassium was stirred vigorously in 50 ml pentane for 5 h until the solution became

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* The structures of the monomeric complexes V and VI are not suited for the purpose of our discussion because of the great bulk of the moieties σ-bonded to Cp_2Ti residue. These σ-bonded groups affect the overall geometry of molecules V and VI.

Table 6

Coordinates ($\times 10^4$) of non-hydrogen atoms of I, with their thermal parameters

Atom	x	y	z	B_{eq} (Å^2)
Ti	5000	2500	1782(1)	2.2
Cl	4750(1)	3317(1)	−681(1)	3.2
C(1)	4308(2)	2442(2)	4582(5)	3.1
C(2)	4423(2)	1759(2)	4053(5)	3.0
C(3)	4089(1)	1585(2)	2224(5)	3.0
C(4)	3835(1)	2193(2)	1564(5)	3.0
C(5)	3926(2)	2713(2)	3049(5)	3.2
C(6)	3568(2)	3367(2)	3265(6)	4.3
C(7)	3992(2)	3979(2)	4040(8)	5.6
C(8)	3261(2)	3572(2)	1246(9)	6.1
C(9)	3041(3)	3180(3)	4777(10)	8.4
C(10)	3912(2)	857(2)	1442(6)	3.7
C(11)	4408(2)	354(2)	1924(7)	4.7
C(12)	3307(2)	627(2)	2653(7)	5.1
C(13)	3754(2)	849(2)	−839(7)	5.0

deep blue and most of the residue had dissolved. The clear solution was decanted and the solvent removed, to yield 4.1 g (94%) of II. Found: C, 70.07; H, 9.31; Cl, 7.90; Ti, 10.98; $C_{26}H_{42}ClTi$ calc.: C, 71.30; H, 9.67; Cl, 8.09; Ti, 10.94%. ESR spectrum: $g = 1.9495$, singlet ^{48}Ti.

X-ray study of I and II

The X-ray study was carried out with a Durrum automatic diffractometer, (Cu-K_α) radiation, graphite monochromator, at room temperature. The structures

Table 7

Coordinates ($\times 10^3$) of hydrogen atoms of I

Atom [a]	x	y	z
H(1)	448(2)	268(2)	583(5)
H(2)	467(2)	142(2)	489(5)
H(4)	360(1)	218(2)	41(5)
H(7A)	411(2)	386(2)	533(7)
H(7B)	372(2)	435(2)	452(7)
H(7C)	427(2)	420(2)	274(7)
H(8A)	301(2)	328(2)	84(6)
H(8B)	307(1)	400(1)	142(4)
H(9A)	285(2)	361(2)	516(6)
H(9B)	315(1)	301(1)	581(5)
H(9C)	278(1)	267(1)	452(4)
H(11A)	452(2)	37(2)	349(7)
H(11B)	429(2)	−13(2)	162(6)
H(11C)	481(2)	47(2)	108(6)
H(12A)	314(2)	18(2)	232(7)
H(12B)	347(2)	62(2)	419(6)
H(12C)	293(2)	93(2)	245(6)
H(13A)	160(1)	387(1)	387(4)
H(13B)	357(2)	26(2)	−134(6)
H(13C)	416(2)	92(2)	−177(6)

[a] The numbering of hydrogen atoms corresponds to that of the carbon atoms to which they are attached.

Table 8

Deflections of carbon atoms from m.s. planes of Cp** rings, defl. (Å) in I, ($17.084x + 4.977y - 3.231z = 7.097$) and the shortest non-bonded intramolecular contacts d (Å) in I

C(1)	0.001	C(6)	0.38
C(2)	−0.025	C(7)	−0.40
C(3)	0.041	C(8)	0.15
C(4)	−0.041	C(9)	1.86
C(5)	0.024	C(10)	0.45
Ti	−2.114	C(11)	0.01
Cl	−2.890	C(12)	1.99
		C(13)	−0.01
Cl···C(3)	3.095(6)	C(1)···C(1′)	2.907(8)
Cl···C(4)	3.167(7)	C(1)···C(2′)	3.011(9)
Cl···C(5)	3.175(7)	C(1)···C(7)	3.12(1)
C(4)···C(8)	3.02(1)	C(1)···C(9)	3.12(1)
C(4)···C(13)	3.04(1)	Ti···H(1)	2.90(4)
C(2)···C(11)	3.06(1)	Ti···H(2)	2.98(3)

were determined by direct method using the programs "Roentgen 75" [9].

[(t-C$_4$H$_9$)$_2$C$_5$H$_3$]$_2$TiCl$_2$ (I). Crystals of I are monoclinic, space group $B\ 2/b$, a 21.069(6), b 19.387(6), c 6.560(3) Å, γ 94.25(2)°, V 2672,5(8) Å^3, $M = 473.4$, d_{calc} 1.18 g/cm^3, $Z = 4$. 1447 unique reflections with $I \geqslant 2\sigma(I)$ were measured, w–$w/2w$ scan, up to $\sin\theta/\lambda = 0.600$, no absorption correction was applied. The structure was determined by a standard heavy atom method and refined by a least-squares procedure by full matrix anisotropic approximations to $R = 0.045$. 20 of the 21 independent hydrogen atoms were included in the refinement with fixed positional and isotropic thermal parameters.

The coordinates of non-hydrogen and hydrogen atoms, respectively are collected in Tables 6 and 7. In Tables 1 and 2 are listed the most important interatomic

Table 9

Coordinates ($\times 10^4$) of non-hydrogen atoms of II, with their thermal parameters

Atom	x	y	z	B_{eq} (Å^2)
Ti	2500	2500	2388(1)	2.3
Cl	2500	2500	−855(1)	6.4
C(1)	1637(2)	3367(2)	4779(4)	3.4
C(2)	1140(2)	2489(2)	4468(4)	3.5
C(3)	698(2)	2540(2)	2720(4)	3.4
C(4)	966(2)	3448(2)	1931(4)	3.3
C(5)	1527(2)	3976(2)	3196(4)	3.2
C(6)	1784(2)	5054(2)	2983(5)	4.4
C(7)	825(3)	5719(3)	3105(7)	6.0
C(8)	2473(3)	5364(3)	4533(7)	6.7
C(9)	2258(3)	5216(3)	1084(7)	7.0
C(10)	−72(2)	1879(2)	1911(6)	4.9
C(11)	+1091(3)	2418(3)	2200(8)	7.3
C(12)	98(4)	1660(4)	−143(8)	7.5
C(13)	−76(3)	881(3)	2899(9)	7.5

Table 10

Coordinates ($\times 10^3$) of hydrogen atoms of II

Atom[a]	x	y	z
H(1)	195(2)	344(2)	585(4)
H(2)	114(2)	196(2)	548(4)
H(3)	82(2)	373(2)	72(4)
H(4)	84(3)	649(3)	268(5)
H(5)	63(3)	563(3)	426(6)
H(6)	49(3)	552(2)	210(4)
H(7)	310(3)	492(3)	444(5)
H(8)	256(4)	607(3)	451(6)
H(9)	223(2)	524(2)	555(4)
H(10)	276(3)	480(3)	72(5)
H(11)	235(3)	588(3)	92(6)
H(12)	111(3)	704(3)	862(5)
H(13)	120(2)	755(2)	656(4)
H(14)	29(4)	223(4)	888(7)
H(15)	37(4)	760(4)	14(7)
H(16)	19(6)	877(7)	56(12)
H(17)	9(3)	90(3)	401(6)
H(18)	54(4)	954(3)	761(6)
H(19)	54(4)	41(3)	250(6)

[a] The numbering of hydrogen atoms corresponds to that of the carbon atoms to which they are attached.

distances and valent angle values. The deflections of carbon atoms from mean square (m.s.) planes of Cp** ligands and the shortest non-valent contacts in I are provided in Table 8.

$[(t\text{-}C_4H_9)_2C_5H_3]_2TiCl$ (II). Crystals of II are monoclinic, space group $P2/n$, a 13.497(2), b 13.441(2), c 7.207(2) Å, γ 86.48(2)°, V 1305.0(5) Å^3, $M = 438$, d_{calc} 1.12 g/cm^3, $Z = 2$. 1915 unique reflections with $I \geqslant 2\sigma(I)$ were measured up to $\sin\theta/\lambda = 0.600$, no absorption correction was applied. The structure was de-

Table 11

Deflections of carbon atoms from m.s. planes of Cp** rings, defl. (Å), in II ($-10.905x + 5.321y + 2.772z = 1.330$) and the shortest non-bonded intramolecular contacts d (Å) in II

C(1)	−0.002	C(6)	−0.24
C(2)	0.010	C(7)	−1.67
C(3)	−0.014	C(8)	−0.08
C(4)	0.013	C(9)	0.72
C(5)	0.007	C(10)	−0.28
Ti	2.064	C(11)	−1.76
Cl	2.963	C(12)	0.59
		C(13)	−0.03
Cl ··· C(4)	3.10(1)	C(1) ··· C(1′)	3.19(1)
C(4) ··· C(7)	3.16(1)	C(1) ··· C(2′)	3.16(1)
C(4) ··· C(9)	3.09(1)	C(2) ··· C(13)	3.01(1)
C(4) ··· C(11)	3.18(1)	Ti ··· H(1)	2.87(5)
C(4) ··· C(12)	3.12(1)	Ti ··· H(2)	3.00(5)
C(1) ··· C(8)	2.98(1)	Ti ··· H(3)	2.98(5)

termined by a standard heavy atom technique and refined by a least-squares procedure by full matrix anisotropic approximations to $R = 0.064$. 19 or the 21 independent hydrogen atoms were included in the refinement with fixed positional and isotropic thermal parameters. The coordinates of non-hydrogen and hydrogen atoms are presented in Tables 9 and 10, respectively. The most important interatomic distances and bond angles are listed in Tables 4 and 5. The deflections of carbon atoms from m.s. planes of Cp^{**} ligands and the shortest non-valent contacts in II are given in Table 11.

Magnetic susceptibility study of II

Magnetic susceptibility measurements of II were carried out by the Institute of General and Inorganic Chemistry of the Academy of Sciences, U.S.S.R. [8]. Static magnetic susceptibility of II was measured by use of the method of Faraday at temperatures between 77–297 K. These experiments were used to calculate the effective magnetic moment of II.

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