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THE STRUCTURE OF THE CHLORO DERIVATIVE OF TITANOCENE, $[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$

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Summary

The crystal structure of the chloro derivative of titanocene has been determined by single-crystal X-ray analysis and shown to be $[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$. Each of the rings of a fulvalene ligand, C_5H_4—C_5H_4, is π-coordinated to one Ti. Furthermore, each Ti is coordinated by one π-C_5H_5 ligand and by two Cl atoms which bridge the two metal atoms. There is no Ti—Ti bond. The observed diamagnetism of the compound is tentatively ascribed to the coupling of the two metal atoms by the fulvalene ligand.

Introduction

The reaction of titanocene, $(C_{10}H_{10}Ti)_2$, with hydrogen chloride in the absence of air yields a purple product [1]. This product was isolated and characterized by Salzmann and Mosimann [2] who regarded it as an oligomer $[(C_5H_5)_2TiCl]_n$ ($n \approx 10$). Brintzinger and Bercaw [3], however, showed the composition to be $[(C_5H_5)(C_5H_4)TiCl]_2$, by analogy with that of titanocene $[(C_5H_5)(C_5H_4)TiH]_2$. For the latter compound a number of structures have been proposed, including a structure with two hydride bridges and one fulvalene, $C_{10}H_8$, ligand linking two $Ti(C_5H_5)$ units [3]. The presence of a fulvalene ligand in titanocene is supported by ^{13}C NMR spectroscopy [4].

Titanocene is diamagnetic; the diamagnetism has been ascribed to a Ti—Ti bond [2] or possibly to strong super-exchange through the hydride bridging ligands [5]. Salzmann and Mosimann [2] suggested that the chloride $[(C_5H_5)(C_5H_4)TiCl]_2$ is paramagnetic in solution, but our careful investigation, which shows that the solid compound is strictly diamagnetic, casts doubt on their proposal. In order to establish the structure of the compound, in particular the

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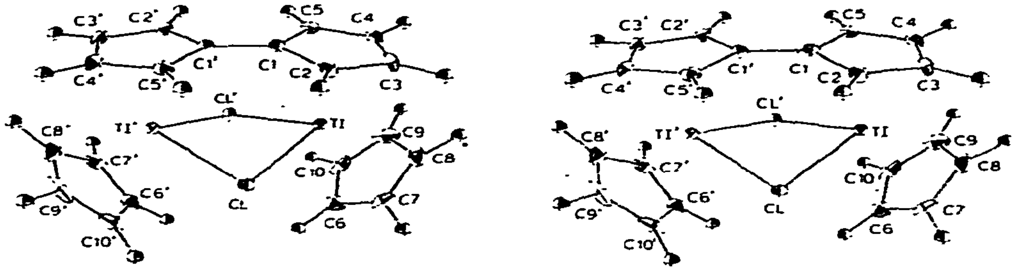

Fig. 1. Structure of the $[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$ molecule.

presence and nature of a fulvalene ligand and the possibility of a Ti—Ti bond, a study of its crystal structure by X-ray diffraction was undertaken.

Results and discussion

Our X-ray study shows that the compound consists of molecules of $[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$ (Fig. 1). The molecule contains a fulvalene ligand; each of the rings, I and I', of this ligand is π-coordinated to one Ti atom. Furthermore, each Ti atom is coordinated by one π-cyclopentadienyl ligand (rings II and II', respectively) and by two chlorine atoms bridging the two metals. The molecular symmetry is strictly C_2-2, but the deviations from C_{2v}-$mm2$ symmetry are rather small. Interatomic distances and angles are listed in Table 1.

The five-membered rings are all planar (Table 2), but the central carbon—carbon bond of the fulvalene ligand, C(1)—C(1)', makes an angle of 2.5° with the planes of each of the rings of this ligand. This angle, together with a minor twist around C(1)—C(1)', results in a dihedral angle of 5.32° between the two ring planes. The distances of the Ti atoms from the fulvalene rings (2.059 Å) and from the cyclopentadienyl rings (2.054 Å) have normal values, as have the Ti—C

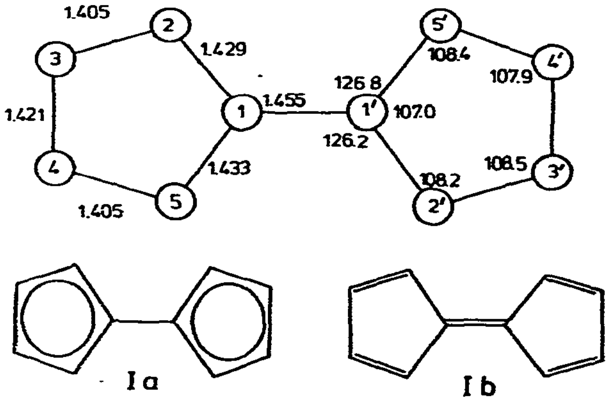

Fig. 2. Observed bond distances in Å (on the left) and bond angles (on the right) in the fulvalene ligand indicating contributions from resonance structures Ia and Ib.

TABLE 1

BOND DISTANCES IN Å AND ANGLES (°)[a]

Atoms	Bond length	Atoms	Bond length
Ti—Cl	2.514(1)	C(1)—C(1)'	1.455(6)
Ti—Cl'	2.524(1)	C(1)—C(2)	1.429(4)
Ti—C(1)	2.371(3)	C(2)—C(3)	1.405(4)
Ti—C(2)	2.388(3)	C(3)—C(4)	1.421(4)
Ti—C(3)	2.405(3)	C(4)—C(5)	1.405(4)
Ti—C(4)	2.395(3)	C(5)—C(1)	1.433(4)
Ti—C(5)	2.376(3)	C(6)—C(7)	1.398(5)
Ti—C(6)	2.369(3)	C(7)—C(8)	1.401(5)
Ti—C(7)	2.350(3)	C(8)—C(9)	1.420(6)
Ti—C(8)	2.369(3)	C(9)—C(10)	1.391(6)
Ti—C(9)	2.385(4)	C(10)—C(6)	1.407(5)
Ti—C(10)	2.407(4)		
Ti—R(I)	2.059 [b]	Ti—R(II)	2.054
Ti—Cl—Ti'	92.47(3)	C(1)'—C(1)—C(2)	126.21(26)
Cl—Ti—Cl'	81.29(4)	C(1)'—C(1)—C(5)	126.78(26)
C(6)—C(7)—C(8)	108.20(30)	C(1)—C(2)—C(3)	108.19(23)
C(7)—C(8)—C(9)	107.33(31)	C(2)—C(3)—C(4)	108.50(24)
C(8)—C(9)—C(10)	108.31(33)	C(3)—C(4)—C(5)	107.94(24)
C(9)—C(10)—C(6)	107.83(31)	C(4)—C(5)—C(1)	108.42(24)
C(10)—C(6)—C(7)	108.32(31)	C(5)—C(1)—C(2)	106.95(23)
R(I)—Ti—R(II)	134.42		

[a] In this and other tables atoms are numbered according to Fig. 1; hydrogen atoms are numbered as the carbon atoms to which they are linked. Standard deviations (in units of the last decimal place) are given in parentheses. [b] R(I) denotes the centroid of ring I (C(1)—C(5)), R(II) that of ring II (C(6)—C(10)).

TABLE 2

BEST LEAST-SQUARES PLANES

(a) Atoms	*Plane* [a]	*P*	*Q*	*R*	*S* (Å)
C(1)—C(5)	I	−0.0427	−0.0181	0.9989	−2.1339
C(6)—C(10)	II	0.6722	−0.0658	0.7375	3.2819

(b) Distances (Å) of some atoms from plane I

C(1)	0.001	C(1)'	0.062
C(2)	0.001	H(2)	−0.08
C(3)	−0.002	H(3)	0.04
C(4)	0.003	H(4)	−0.10
C(5)	−0.003	H(5)	0.00
Ti	2.059		

(c) Distances (Å) of some atoms from plane II

C(6)	−0.004	H(6)	−0.03
C(7)	−0.001	H(7)	0.12
C(8)	0.005	H(8)	−0.01
C(9)	−0.007	H(9)	0.15
C(10)	0.007	H(10)	−0.09
Ti	−2.054		

(d) Dihedral angles: $I \frown II$ *44.84°;* $I \frown I'$ *5.32°.*

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[a] The equations of the planes are $PI + QJ + RK = S$, where P, Q and R are direction cosines referred to the orthogonal unity vectors I, J and K with $I // a$, $J // b$ and $K // c$.

distances which average 2.387 Å for the fulvalene ligand and 2.376 Å for the cyclopentadienyls.

All bond angles in the five-membered rings are close to 108° (Table 1). The C—C distances in the cyclopentadienyl rings II show some spread about their average length of 1.403 Å. Despite their smaller standard deviations (due to smaller thermal motion), the spread in the C—C distances in the fulvalene rings I about their average (1.419 Å) is larger and, moreover, the variations are systematic (Fig. 2). This systematic variation in bond length (which in our opinion is significant) indicates some contribution of resonance structure Ib to the fulvalene ligand. This view is supported by the length of the central C—C bond (1.455 Å) which is much shorter than the central C—C bond in diphenyl (1.50 ± 1 Å, [6]) and derivatives (1.52 ± 1 Å, [7]). Central C—C bonds of about 1.45 Å were also found in the fulvalene ligands in other titanium complexes (Table 3), but in $(C_{10}H_8)_2Fe_2$ [9] the central C—C bonds are slightly longer (1.476(9) Å).

The R(I)—Ti—R(II) angle is 134.42° (R(I) and R(II) are the centres of rings I and II, respectively), while the dihedral angle between rings I and II coordinated at the same Ti atom is 44.8°. Similar values were found for the angle between the fulvalene and cyclopentadienyl rings in other titanium complexes [5,8]; they lie in the range of corresponding angles in numerous compounds containing $(C_5H_5)_2Ti$ groups. However, the dihedral angle between the two rings of the fulvalene ligand is considerably smaller than that in other fulvalene titanium complexes (Table 3). This is obviously due to the longer Ti—Ti distance in the compound studied by us; the Ti—Ti distance, in turn, is dependent on the nature of the other ligands bridging the two Ti atoms.

If the five-membered rings are regarded as five-electron donors, the normal electron-counting schemes lead to a 17-electron configuration for the metal centres in $(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2$. However, as stated, the compound is diamagnetic, as is titanocene [2] and other fulvalene titanium complexes [5]; (the hydroxo complex $[(C_{10}H_8)(C_5H_5)_2Ti_2(OH)_2 \cdot THF]$ has been reported as weakly paramagnetic [8]). Diamagnetism has been ascribed either to a Ti—Ti bond [2,5] or to strong super-exchange through the bridging hydride ligands [5]. For $(C_{10}H_8)(C_5H_5)_2TiCl_2$ the existence of a Ti—Ti bond may be excluded due to the long Ti—Ti distance (3.638 Å). In our opinion, strong super-exchange via the bridging chloride ligands is also unlikely, since the geometry of the Ti_2Cl_2 group is not very different from that in other organotitatium complexes with a 17-

TABLE 3

CENTRAL C—C BONDS AND DIHEDRAL ANGLES IN THE FULVALENE LIGANDS AND Ti—Ti DISTANCES IN SOME COMPOUNDS

$(C_{10}H_8)(C_5H_4X)_2Ti_2RR'$

X	R	R'	Central C—C bond (Å)	Dihedral angle (°)	Ti—Ti (Å)	Ref.
H	Cl	Cl	1.455	5.3	3.638	
H	H	H_2AlEt_2	1.45	12.5	3.374	5
H	OH	OH · THF	1.43	15.1	3.195	8
$AlEt_2H$	—	—	1.46	25.8	2.910	5

TABLE 4

GEOMETRY OF Ti_2Cl_2 GROUPS IN SOME ORGANOMETALLIC COMPOUNDS

Compound	Ti—$Cl_{av.}$ (Å)	Ti—Ti (Å)	∠Cl—Ti—Cl (°)	∠Ti—Cl—Ti (°)	Ref.
$[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$	2.519	3.638	81.29	92.47	
$[(C_5H_5)_2TiCl]_2$	2.546		$78.42_{av.}$		10
$[(CH_3C_5H_4)_2TiCl]_2$	2.537		$79.26_{av.}$		10
$[(C_8H_8)TiCl \cdot THF]_2$					11
molec. I	2.531	3.808	82.4	97.6	
molec. II	2.549	3.859	81.6	98.4	
$[(C_8H_8)TiCl]_4$					11
face I [a]	2.609	4.059	77.79	102.12	
faces II, III [a]	2.583	3.743	81.52	97.16	

[a] Faces of Ti_4Cl_4 hexahedron.

electron configuration of the metal (Table 4), which are all paramagnetic. While $[(C_8H_8)TiCl \cdot THF]_2$ and $[(C_8H_8)TiCl]_4$ obey the Curie—Weiss law (with one unpaired electron per Ti) [11], a weak antiferromagnetic interaction ($-J = 159$—186 cm^{-1}) between the two Ti atoms has been found for $[(C_5H_5)_2TiCl]_2$ [12]. While the Ti_2Cl_2 groups in $[(C_8H_8)TiCl \cdot THF]_2$ and $[(C_8H_8)TiCl]_4$ are (virtually) planar rhombs, they are somewhat bent in $[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$ due to the constraint on the distance between the Ti atoms caused by their coordination at one fulvalene ligand.

In view of the above it seems to us that the diamagnetism of $[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$ and other fulvalene titanium complexes is predominantly due to the fact that the fulvalene ligand couples the two metal atoms, rather than to super-exchange via other bridging ligands.

TABLE 5

CRYSTALLOGRAPHIC DATA AND EXPERIMENTAL DETAILS FOR THE STRUCTURE DETERMINATION OF $[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$

Orthorhombic space group *Fdd*2	Weissenberg photographs of zero and higher layer lines
a = 20.423(4) Å b = 21.928(5) Å c = 7.691(2) Å $\alpha = \beta = \gamma = 90°$ T = —160°C [13]	Least-squares refinement on observed optimalised diffractometer (Nonius, CAD-4) angles of 15 reflections, with $\lambda(Mo\text{-}K_{\alpha_1}) = 0.70926$ and $\lambda(Mo\text{-}K_{\alpha_2}) = 0.71354$ Å
D_M = 1.59 g/cm³ (20°C) $Z = 8[(C_{10}H_8)(C_5H_5)_2TiCl_2]$ D_X = 1.64 g/cm³ (—160°C)	Specific gravity by flotation method
2015 independent intensities	Automatic Nonius CAD-4 diffractometer, Zr filtered Mo-radiation, ω-scan, θ_{max} 35°. Reflections with $I_{net} < 0$ were hereafter discarded.
1955 *F(hkl)* values with $\|F\| > 3\,\sigma_c(\|F\|)$	Corrections for LP and absorption ([14]: crystal bounded by 14 planes, μ(Mo) = 12.66 cm^{-1}; correction factors between $\sqrt{1.35}$ and $\sqrt{1.52}$)

TABLE 6

FINAL ATOMIC PARAMETERS

(a) Coordinates and temperature parameters B of the hydrogen atoms (Å^2)

(b) Parameters U_{ij} (in 10^{-4} Å^2) of the temperature factor $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2\,ha^*kb^*U_{12} + 2\,ha^*lc^*U_{13} + 2kb^*lc^*U_{23})]$.

Atom	x/a	y/b	z/c	B	U_{11}	U_{22}	U_{33}	$2\,U_{12}$	$2\,U_{23}$	$2\,U_{13}$
Ti	0,08880(2)	−0,00646(2)	0,00000		86(2)	75(2)	87(2)	3(3)	−5(4)	−7(3)
Cl	0,00662(3)	0,07457(3)	0,07626(11)		109(2)	73(2)	129(3)	2(4)	−4(4)	−5(5)
C(1)	0,03558(13)	−0,00162(12)	−0,27362(36)		111(10)	105(10)	80(10)	−2(16)	12(18)	19(17)
C(2)	0,07961(13)	0,04894(12)	−0,26611(41)		133(10)	143(11)	108(12)	−40(17)	53(20)	33(20)
C(3)	0,14385(13)	0,02609(13)	−0,26039(47)		121(10)	151(11)	145(12)	−19(17)	49(23)	77(22)
C(4)	0,14098(13)	−0,03864(13)	−0,26331(44)		140(11)	175(12)	103(12)	60(18)	9(23)	67(21)
C(5)	0,07478(13)	−0,05580(12)	−0,27252(38)		156(11)	111(10)	88(12)	30(17)	−23(18)	12(19)
C(6)	0,11535(17)	0,00094(15)	0,29905(43)		229(15)	233(14)	117(12)	94(23)	22(22)	−52(23)
C(7)	0,15753(17)	0,03945(15)	0,20721(45)		244(15)	147(12)	199(15)	−44(22)	−13(20)	−198(25)
C(8)	0,19778(16)	0,00328(18)	0,10165(47)		113(15)	451(20)	180(15)	−74(25)	48(30)	−59(23)
C(9)	0,17923(19)	−0,05840(18)	0,12867(55)		307(17)	307(17)	264(18)	419(30)	−269(30)	−345(30)
C(10)	0,12933(17)	−0,05966(14)	0,25162(59)		271(15)	174(13)	293(18)	−80(24)	170(30)	−356(32)
H(2)	0,0641	0,0959	−0,2754	2,3(9)						
H(3)	0,1920	0,0461	−0,2484	4,2(12)						
H(4)	0,1797	−0,0720	−0,2739	6,0(16)						
H(5)	0,0561	−0,1019	−0,2761	2,2(9)						
H(6)	0,0763	0,0082	0,3916	2,9(22)						
H(7)	0,1685	0,0876	0,2144	5,9(16)						
H(8)	0,2364	0,0100	0,0075	6,8(18)						
H(9)	0,2037	−0,0905	0,0869	10,6(24)						
H(10)	0,1018	−0,0994	0,2910	7,0(17)						

Experimental

$[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$ was prepared by the method of Salzmann and Mosimann [2] and purified by sublimation at 270°C (0.1 mmHg). Magnetic measurements in the range 4—300 K (carried out by Mr. H. Druiven) showed the compound to be strictly diamagnetic.

Crystals suitable for X-ray diffraction were obtained by sublimation at 200—250°C (0.1 mmHg). The crystallographic data are listed in Table 5. Approximate coordinates of the Ti and Cl atoms were found from a Patterson synthesis. After isotropic refinement of the Ti and Cl parameters by least-squares techniques a difference map showed the positions of some of the carbon atoms. The remaining carbon atoms were found from a difference Fourier map calculated after isotropic refinement of Ti, Cl and C obtained from the previous map.

After anisotropic refinement of the "heavy" atoms hydrogen atoms were added to the model at 1.08 Å from the corresponding carbon atoms and isotropically refined. In the latter refinement cycles the lengths of the C—H bonds were constrained at 1.08 Å and their directions kept fixed so that only the B values of the hydrogen atoms were varied (in addition to the anisotropic parameters of the heavy atoms). From the two possible absolute configurations of the (non-centrosymmetric) crystal that giving best agreement of calculated and observed structure factors was selected. The final weighing scheme used is $w = (w_c^{-1} + EF^2 + J \sin \theta)^{-1}$ with $E = 3.10^{-6}$ and $J = 0.1$; $w_c = 1/\sigma_c^2(|F|)$ with $\sigma_c^2(|F|)$ being the variance based on counting statistics. The choice of E and J hardly affected the variation in $\langle w|\Delta F|^2\rangle$ as a function of $|F|$; their values were chosen such that the standard deviations in the parameters are minimal. The final residuals $R = (\Sigma|\Delta F|^2/\Sigma|F_o|^2)^{1/2} = 4.3\%$ and $R_w = (\Sigma w|\Delta F|^2/\Sigma w|F_o|^2)^{1/2} = 4.3\%$. The final coordinates and temperature factors and their standard deviations are listed in Table 6. A list of the observed and calculated structure factors is available on request.

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