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Direct proof of the molecular structure of dimeric titanocene; the X-ray structure of μ-(η^5 : η^5-fulvalene)-di-(μ-hydrido)-bis(η^5-cyclopentadienyltitanium) · 1.5benzene *

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Abstract

The dimeric titanocene crystallizes as a benzene solvate with molar ratio 1:1.5. The crystals are monoclinic, space group $P2_1/n$ with $Z = 4$ and lattice parameters $a = 5.978(4)$, $b = 14.541(6)$, $c = 26.963(8)$ Å and $\beta = 92.11(2)°$. In the series of $(C_{10}H_8)[(C_5H_5)TiX]_2$ complexes, where X = H, H/Cl (1:1), Cl or OH, the dihydrido complex has the shortest Ti–Ti distance (2.989 Å) and largest dihedral angle between the planes of C_5H_4 rings of the fulvalene ligand (17.7°).

Introduction

Bright green titanocene was first reported in 1956 to be obtained from the reaction of $TiCl_2$ with cyclopentadienylsodium [1]. The same material was later obtained by reduction of Cp_2TiCl_2 ($Cp = C_5H_5$) with sodium naphthalene in tetrahydrofuran [2] or with sodium metal in hydrocarbons [3,4], or by hydrogenolysis of Cp_2TiMe_2 [5]. Its chemical properties were, however, at variance with the expected chemical behaviour of monomeric titanocene and the structure of the compound was subject to extensive discussion [6]. Strong evidence for the dimeric structure with one bridging fulvalene ligand and two hydride bridges was given by Brintzinger and Bercaw [7] and the fulvalene ligand was established by an X-ray crystallographic study of the compound arising from interaction of this compound with triethylaluminium [8]. The compound was reliably assigned to μ-(η^5 : η^5-

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fulvalene)-di-(μ-hydrido)-bis(η^5-cyclopentadienyltitanium) on the base of the ^{13}C NMR spectrum [9] and from the X-ray study of its di-(μ-hydroxyl) derivative prepared by hydrolysis of dimeric titanocene [10]. Later, the X-ray study of a purple product arising from the reaction of dimeric titanocene with HCl revealed that it is its di-(μ-Cl) derivative [11]. The mixed(μ-hydrido)-(μ-chloro) complex was also prepared [12] and its X-ray structure was determined [13]. The ^1H NMR evidence for the presence of bridging hydride ligands in dimeric titanocene was obtained at −60°C [14]. Attempts to determine its structure directly by X-ray crystallographic study have been unsuccessful until now [8,10].

Here we report the crystal and molecular structure of the dimeric titanocene containing 1.5 equiv. of benzene of crystallization.

Experimental

Preparation of crystalline μ-(η^5 : η^5-fulvalene)-di-(μ-hydrido)-bis(η^5-cyclopentadienyltitanium) · 1.5benzene (I)

Dimeric titanocene was prepared by the procedure described elsewhere [15]. A mixture of Cp_2TiCl_2 (1 g, 4 mmol) and $LiAlH_4$ (0.6 g, 16 mmol) in mesitylene was heated to boil under argon until the solution turned bright green (after approx. 1 h). Mesitylene was distilled off *in vacuo* and a green product was extracted with benzene from a black residue. The green microcrystalline material (0.85 g, 90% of theory) was obtained by evaporation of benzene *in vacuo*. It was further purified by repeated extraction (four times) with 7 ml of benzene and the remaining complex was then dissolved in benzene to give a saturated solution at 30°C. Long needle crystals of I were grown from this solution after standing for 1 month at room temperature. The largest crystals were separated in a vacuum-argon glove box. The crystals were mounted into Pyrex capillaries and sealed.

Crystal structure determination of I

Diffraction data for a crystal of the size 0.18 × 0.18 × 0.60 mm were collected on a CAD-4 four-circle diffractometer (Mo-K_α radiation, graphite monochromator, ω-scan, $\theta_{max} = 25°$) at 293 K. The unit cell of $(C_{10}H_8)[(C_5H_5)TiH]_2 \cdot 1.5C_6H_6$ (I) is monoclinic, $a = 5.978(4)$, $b = 14.541(6)$, $c = 26.963(8)$ Å, $\beta = 92.11(2)°$, space group $P2_1/n$, $Z = 4$, $V = 2342$ Å^3, $d_{calc.} = 1.342$ g cm^{-3}. A total of 4753 independent reflections were measured; 2485 reflections with $I \geq 3\sigma(I)$ were used for solution of the structure by automatic analysis of Patterson function (SHELX-86) and subsequent partial structure expansion. Positions of the carbon atoms of the benzene molecules of crystallization and bridging hydrogen atoms were located by means of subsequent difference Fourier syntheses. Positions of all other hydrogen atoms were calculated using a HYDRO program (SDP). The structure of I contains two types of molecules of benzene of crystallization: one is situated in a general position, the centre of the other molecule is placed in the centre of inversion at (0.5, 0, 0). The benzene molecules are strongly disordered, vibrating in their planes with turning to 30°. The multiplicities of carbon atoms for the two vibration positions are 0.8, 0.2 and 0.7, 0.3, respectively. The atom coordinates were refined by full-matrix least-squares methods in anisotropic approximation for Ti and C atoms of dimeric titanocene, in isotropic approximation for bridging H atoms and

Table 1

Positional and equivalent isotropic thermal parameters for dimeric titanocene in I

Atom	x	y	z	B (Å^2)
Ti(1)	0.0257(1)	0.17645(6)	0.21821(3)	2.72(1)
Ti(2)	0.0865(1)	0.17383(6)	0.32871(3)	2.70(1)
C(1)	0.1721(7)	0.3141(3)	0.2456(2)	3.18(9)
C(2)	−0.0291(8)	0.3356(3)	0.2178(2)	3.9(1)
C(3)	0.000(1)	0.3119(4)	0.1689(2)	5.0(1)
C(4)	0.219(1)	0.2776(4)	0.1647(2)	5.0(1)
C(5)	0.3240(8)	0.2784(3)	0.2113(2)	3.9(1)
C(6)	0.2018(7)	0.3128(3)	0.2985(2)	3.10(9)
C(7)	0.0346(8)	0.3319(3)	0.3334(2)	3.8(1)
C(8)	0.1180(9)	0.3068(3)	0.3804(2)	4.4(1)
C(9)	0.3346(9)	0.2720(4)	0.3751(2)	4.4(1)
C(10)	0.3871(8)	0.2750(3)	0.3260(2)	3.7(1)
C(11)	−0.046(1)	0.0155(3)	0.2121(2)	4.9(1)
C(12)	−0.2533(9)	0.0598(4)	0.2086(2)	5.2(1)
C(13)	−0.2589(9)	0.1115(4)	0.1668(2)	5.2(1)
C(14)	−0.060(1)	0.1019(4)	0.1426(2)	4.9(1)
C(15)	0.0712(9)	0.0425(4)	0.1714(2)	5.2(1)
C(16)	0.061(1)	0.0114(4)	0.3389(2)	6.0(1)
C(17)	0.183(1)	0.0457(4)	0.3778(2)	6.1(1)
C(18)	0.052(1)	0.1015(4)	0.4056(2)	5.5(1)
C(19)	−0.1593(9)	0.1023(4)	0.3818(2)	5.4(1)
C(20)	−0.151(1)	0.0460(4)	0.3415(2)	5.7(1)
H(1)	−0.075(7)	0.181(3)	0.275(2)	2(1)
H(2)	0.170(7)	0.132(3)	0.271(1)	1.3(9)

C atoms of the solvate benzene molecules, and with fixed $B_H = 3.5$ Å^2 for all other H atoms to give $R = 0.041$, $R_w = 0.043$. The atom coordinates for dimeric titanocene are listed in Table 1; the full list of atom coordinates is deposited in the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK. Selected bond distances are given in Table 2.

Table 2

Selected bond distances (Å) [a] for dimeric titanocene in I

Ti(1)–Ti(2)	2.989(1)	C(1)–C(6)	1.430(6)
Ti(1)–C(1)	2.296(4)	Ti(2)–C(6)	2.295(4)
Ti(1)–C(2)	2.338(5)	Ti(2)–C(7)	2.323(5)
Ti(1)–C(3)	2.378(5)	Ti(2)–C(8)	2.387(5)
Ti(1)–C(4)	2.387(6)	Ti(2)–C(9)	2.381(5)
Ti(1)–C(5)	2.332(5)	Ti(2)–C(10)	2.325(5)
Ti(1)–C(11)	2.384(5)	Ti(2)–C(16)	2.383(5)
Ti(1)–C(12)	2.386(6)	Ti(2)–C(17)	2.345(6)
Ti(1)–C(13)	2.352(5)	Ti(2)–C(18)	2.340(5)
Ti(1)–C(14)	2.348(5)	Ti(2)–C(19)	2.333(6)
Ti(1)–C(15)	2.342(5)	Ti(2)–C(20)	2.371(6)
Ti(1)–H(1)	1.67(4)	Ti(2)–H(1)	1.71(4)
Ti(1)–H(2)	1.76(4)	Ti(2)–H(2)	1.76(4)

[a] The average C–C distance in C_5H_5 rings is 1.37 Å; for the C–C distances in C_5H_4 rings see Fig. 3.

Results and discussion

The structure of dimeric titanocene in I and the atom numbering are shown in Fig. 1. Titanium atoms are bound through a fulvalene dianion and through two hydride bridges which are symmetrical within standard deviations. The molecule exhibits an approximate C_{2v}–$mm2$ noncrystallographic symmetry with two mutually perpendicular planes σ_1 and σ_2 containing C(1), C(6), Ti(1), Ti(2) and H(1), H(2) atoms, respectively, and a two-fold axis bisecting the C(1)–C(6) and Ti(1)–Ti(2) interatomic distances. All five-membered rings are planar with maximum deviation of 0.08 Å observed for the C(1)–C(5) ring. The fulvalene ligand is bent and its C_5H_4 rings are perpendicular to the σ_1 molecular plane. The angles between the C(1)–C(6) bond and the planes of C_5H_4 rings amount to nearly 9°; the dihedral angle between the ring planes is 17.7°. The lines connecting centroids of the C_5H_5 and C_5H_4 rings with titanium atoms are not perpendicular to the ring planes. The differences in the Ti–C bond lengths are remarkably larger for the C_5H_4 rings with the shortest Ti–C distances to C(1) and C(6) atoms (2.30 Å) and the longest distances to C(3), C(4), C(8) and C(9) atoms (on average 2.38 Å). The projection of dimeric titanocene in the Ti–Ti direction (Fig. 2) shows that bridging H atoms lie lower than the titanium atoms, farther from the fulvalene ligand. The dihedral angle between the planes containing titanium atoms and H(1) and H(2), respectively, amounts to 137°. This projection also reveals that the fulvalene rings are eclipsed while the C_5H_5 rings are slightly staggered. The C_5H_5 and C_5H_4 rings are in staggered position.

The X-ray structure of I with good accuracy ($R = 0.041$) allows us to compare geometrical parameters in the series of di-(μ-H), (μ-H) (μ-Cl) and di-(μ-Cl) compounds and with other dititanium fulvalene compounds (see Table 3). It follows from the data of Table 3 that the geometrical parameters primarily depend on the Ti–Ti distance. In the above series, this distance is the shortest for I, which apparently reflects the smallest size and lowest electronegativity of hydrogen among the bridging atoms, and becomes longer on going to di-(μ-Cl) compounds. The values of the Ti–H–Ti and H–Ti–H angles are also extreme compared to other molecules containing two equal bridging atoms. The shortening of the Ti–Ti distance is accompanied by an increase in the dihedral angle between the fulvalene

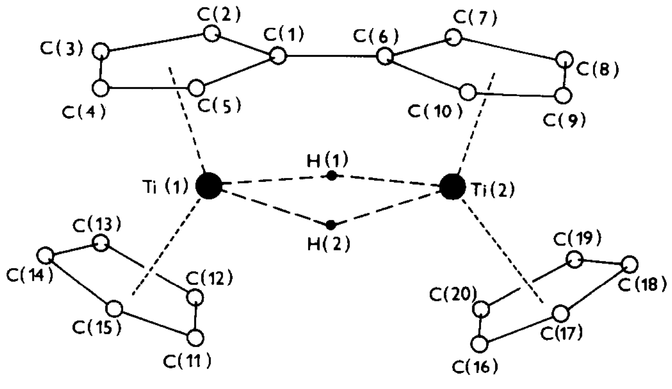

Fig. 1. Structure of dimeric titanocene and the atom numbering scheme.

Table 3

Geometrical parameters in dititanium fulvalene $(C_{10}H_8)[(C_5H_5)TiX]_2$ complexes

Compound	Interatomic distances (Å)					Angles (°) [a]				References
	Ti–Ti	Ti–C(fulv)	Ti–C(Cp)	Ti–X	C_1–C_6	α	β	θ	ω	
$Cp_2Ti_2(C_{10}H_8)(H)_2 \cdot 1.5C_6H_6$	2.989	2.30–2.39	2.36	1.71	1.43	57	120	138.6	17.7	This work
$Cp_2Ti_2(C_{10}H_8)(H)(Cl)$	3.125	2.32–2.39	2.36	2.17	1.45	92	93	137.3	15.6	13
				2.49			77.6	137.3	15.6	13
$Cp_2Ti_2(C_{10}H_8)(Cl)_2$	3.638	2.37–2.40	2.38	2.52	1.46	81.3	92.5	135.2	5.3	11
$Cp_2Ti_2(C_{10}H_8)(OH)_2 \cdot$thf	3.195	2.34–2.47 [b]	2.41 [b]	2.07	1.43	75.4	100.7	135.1	15.1	10
$Cp_2Ti_2(C_{10}H_8)(H)(H_2AlEt_2)$	3.374	2.33–2.39	2.35	1.80	1.45	–	138	134.1	12.5	8

[a] α, angle X–Ti–X; β, angle Ti–X–Ti; θ, dihedral angle between C_5H_5 and C_5H_4 planes; ω, dihedral angle between C_5H_4 planes. [b] Large error values for the Ti–C distances make the comparison with other structures unreliable.

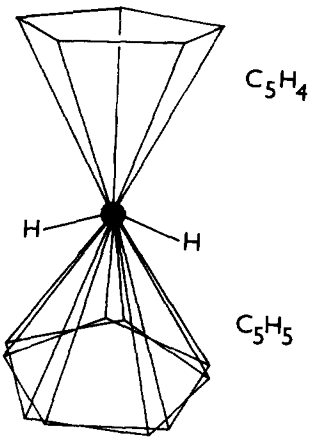

Fig. 2. Projection of the dimeric titanocene molecule in the Ti–Ti direction.

ring planes (ω), a decrease in the dihedral angle between the C_5H_5 and C_5H_4 planes (θ), by a slight shortening of Ti–C(C_5H_5) and by a considerable shortening of Ti–C(C_5H_4) bonds (see above for some bonds). The dependence of ω on the Ti–Ti distance is further extended in $(C_{10}H_8)[(C_5H_4)TiHAlEt_2]_2$, a dititanium fulvalene complex bridged through two η^1-cyclopentadienylaluminium hydride bridges [8]. These bridges give rise to the shortest Ti–Ti distance (2.910 Å) known so far, corresponding to the largest ω = 25.8° in the dititanium fulvalene complexes.

The strained structure of the dititanium fulvalene moiety also induces considerable changes in the configuration of the fulvalene dianion (see Fig. 3). Generally all C–C bonds in all five-membered rings in I are slightly shorter compared to the di-(μ-Cl) compound [11], however, remarkably shorter distances are observed for the C(2)–C(3), C(4)–C(5), C(7)–C(8) and C(9)–C(10) bonds in addition to the C(1)–C(6) bond whose lengths in different complexes are compared in Table 3. Reasons for this shortening of particular C–C bonds and for other changes of geometrical parameters are to be sought in both the steric and electronic effects induced by bridging atoms.

The Ti–Ti distance near 3.0 Å can suggest the presence of some direct Ti–Ti interaction, however, no systematic measurements of magnetic susceptibility *versus* temperature for the fulvalene compounds listed in Table 3 have been carried out

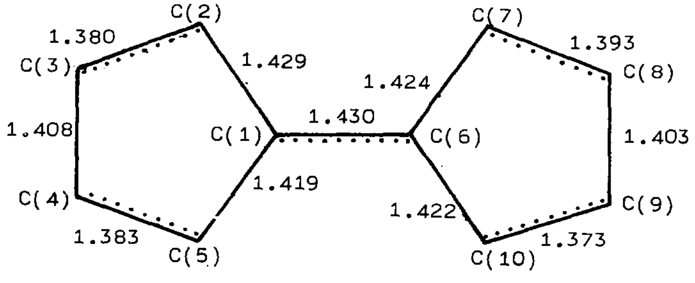

Fig. 3. Bond lengths in the fulvalene ligand of I.

to correlate their behaviour with the Ti–Ti distance. The compounds are essentially diamagnetic at ambient temperature which suggests that Ti^{III} *d* electrons are paired to give the singlet state. However, the temperature dependence of magnetic susceptibility for the di-(μ-Cl) complex revealed the presence of a thermally accessible triplet state [16] and thermally induced chemical shifts in the ^1H NMR spectra of dimeric titanocene also indicated the presence of increasing population (very low) of the triplet state with increasing temperature [14].

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