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STRUCTURE OF (2,6-DIMETHYLPHENYL)DICYCLOPENTADIENYLTITANIUM(III)

G.J. OLTHOF * and F. VAN BOLHUIS
Laboratory of Structural Chemistry, The University, Zernikelaan, Paddepoel, Groningen (The Netherlands)

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Summary

An X-ray diffraction study of (2,6-dimethylphenyl)dicyclopentadienyltitanium has shown the two slightly staggered cyclopentadienyl ligands to be π-bonded to the titanium atom (average distance Ti—C 2.35 Å); the ring planes include an angle of 41.6°. The aryl ligand is σ-bonded to the titanium atom (Ti—C distance 2.18 Å). The short distance (2.55 Å) between Ti and one of the methyl hydrogen atoms suggests an interaction between the two atoms.

Introduction

In 1972 Teuben and De Liefde Meyer [1] reported the synthesis and properties of a series of compounds of general formula $(C_5H_5)_2TiR$, where R is an aryl group. An important property of most of these compounds is the formation of nitrogen complexes from solutions of the compounds and nitrogen gas (1 atm), but this reaction does not occur when R = 2,6-dimethylphenyl or 2,4,6-trimethylphenyl [2]. It was also found that the thermal stability of $(C_5H_5)_2TiR$ is enhanced if the aryl group R carries one or, better, two substituents in the *ortho* position [1]. These effects were thought to be due to shielding of the metal by the *ortho*-methyl substituents of R. We have investigated the structure of $(C_5H_5)_2Ti$(2,6-dimethylphenyl) by means of X-ray diffraction in order to verify this assumption.

Results and discussion

The structure of the molecule as found by our X-ray diffraction study is shown in Fig. 1. The bond lengths and angles are listed in Table 1. Fig. 1 and Table 1 show that both five-membered rings are π-bonded to the metal. The

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* To whom correspondence should be addressed.

TABLE I[a]

BOND LENGTHS AND ANGLES OF THE MOLECULE

(a) Bond distances (in Å)			
Ti—C(1)	2.178(7)	C(1)—C(2)	1.415(8)
Ti—C(9)	2.341(9)	C(2)—C(3)	1.393(9)
Ti—C(10)	2.328(9)	C(3)—C(4)	1.381(9)
Ti—C(11)	2.370(8)	C(4)—C(5)	1.385(9)
Ti—C(12)	2.387(8)	C(5)—C(6)	1.403(9)
Ti—C(13)	2.349(9)	C(6)—C(1)	1.407(8)
Ti—C(14)	2.351(10)	C(2)—C(7)	1.496(9)
Ti—C(15)	2.361(10)	C(6)—C(8)	1.521(9)
Ti—C(16)	2.352(9)	Ti—RC(II)[b]	2.030
Ti—C(17)	2.327(9)	Ti—RC(III)	2.030
Ti—C(18)	2.325(9)		
C(9)—C(10)	1.408(11)	C(14)—C(15)	1.367(14)
C(10)—C(11)	1.389(10)	C(15)—C(16)	1.374(11)
C(11)—C(12)	1.392(10)	C(16)—C(17)	1.371(13)
C(12)—C(13)	1.411(10)	C(17)—C(18)	1.384(12)
C(13)—C(9)	1.417(10)	C(18)—C(14)	1.384(17)
(b) Bond angles (in degrees)			
Ti—C(1)—C(2)	125.3(4)	C(1)—C(2)—C(3)	121.3(5)
Ti—C(1)—C(6)	118.2(4)	C(1)—C(2)—C(7)	120.0(6)
C(2)—C(1)—C(6)	116.4(5)	C(3)—C(2)—C(7)	118.7(5)
C(2)—C(3)—C(4)	120.9(6)	C(1)—C(6)—C(5)	121.8(5)
C(3)—C(4)—C(5)	119.4(6)	C(1)—C(6)—C(8)	121.0(5)
C(4)—C(5)—C(6)	120.0(5)	C(5)—C(6)—C(8)	117.1(5)
C(9)—C(10)—C(11)	108.5(6)	C(14)—C(15)—C(16)	108.6(8)
C(10)—C(11)—C(12)	108.6(6)	C(15)—C(16)—C(17)	107.7(7)
C(11)—C(12)—C(13)	108.2(6)	C(16)—C(17)—C(18)	108.5(7)
C(12)—C(13)—C(9)	107.4(6)	C(17)—C(18)—C(14)	107.1(9)
C(13)—C(9)—C(10)	107.3(6)	C(18)—C(14)—C(15)	108.1(8)
RC(II)—Ti—RC(III)	140.9	RC(II)—Ti—C(1)	109.3
RC(III)—Ti—C(1)	109.6		
(c) Some intra molecular distances (in Å)			
Ti—C(2)	3.210(8)	C(1)—C(11)	2.978(12)
Ti—C(6)	3.102(8)	C(1)—C(12)	3.179(12)
Ti—H(81)	2.55	C(1)—C(15)	3.078(11)
C(9)—C(18)	3.004(12)	C(1)—C(16)	3.055(10)

[a] Atoms are numbered according to Fig. 1; hydrogen atoms are numbered according to the carbon atom to which they are attached. Standard deviations in parentheses are in units of the last decimal place. [b] RC denotes Ring-Centroid. For definition of I, II and III, see Table 2.

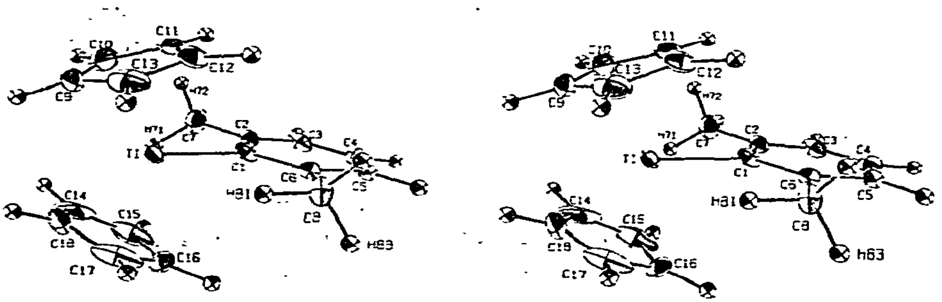

Fig. 1. Structure of the molecule.

distances of the carbon atoms of the rings II and III (definitions of the rings are given in Table 2(a)) from the Ti atom are similar to those found in other $(C_5H_5)_2TiR_{(n)}$ compounds; the average values for rings II and III being 2.355 and 2.343 Å, respectively. The rings are planar and quite regular; the bond angles are close to 108° and the C—C bond lengths lie in a narrow range for each ring, the average values being 1.403 and 1.376 Å for rings II and III, respectively. Table 2(b) gives the distances of the atoms from the least-squares planes of the rings; Ti lies 2.029 Å from the planes of both rings II and III. This distance is the same as was found in $(C_5H_5)_2TiBH_4$ [3] and $(C_5H_5)_2(CO)_2$ [4], but it is somewhat shorter than that observed in other compounds of the type $(C_5H_5)_2TiR_{(n)}$. From Table 2(c) it is seen that the dihedral angle between the ring planes is 41.6°, a rather small value. Table 1 shows the RC(II)—Ti—RC(III) angle to be 140.9°, and the Ti—RC(II) and the Ti—RC(III) distances to be 2.030 Å, indicating the ring planes to be slightly tilted with respect to the Ti—RC lines. The most interesting feature of the structure is the coordination of the aryl group at the Ti atom. The Ti—C(1) σ-bond length of 2.178(7) Å is in fairly good agreement with the values found for $(C_5H_5)_2TiC_4Ph_4$ [5] and $(PhCH_2)_4Ti$ [6], where the averaged Ti—C σ-bond distances are 2.157(5) and 2.14(3) Å, respectively.

The phenyl group is planar, but the metal atom and at least one of the carbon atoms of the methyl groups do not lie quite in the ring plane (see Table 2(b)). The C—C distances in the phenyl ring and the C—CH_3 distances are normal, but there are some deviations from the expected values of 120° for the

TABLE 2

BEST LEAST SQUARES PLANES [a]

(a) Equations of the planes

atoms	plane	*P*	*Q*	*R*	*S*
C(1) . . . C(6)	I	−0.6622	0.7081	0.2451	0.0594
C(9) . . . C(13)	II	−0.8676	0.3717	0.3302	1.9039
C(14) . . C(18)	III	−0.4351	0.8926	0.1181	−2.0960

(b) Distances of some atoms from the planes (in Å)

atoms	plane I	atoms	plane I	atoms	plane II	atoms	plane III
C(1)	−0.000	H(3)	−0.04	C(9)	0.012	C(14)	−0.003
C(2)	0.004	H(4)	−0.06	C(10)	−0.008	C(15)	0.001
C(3)	−0.002	H(5)	−0.02	C(11)	0.001	C(16)	0.001
C(4)	−0.004	H(71)	−0.64	C(12)	0.007	C(17)	−0.003
C(5)	0.008	H(72)	0.97	C(13)	−0.012	C(18)	0.003
C(6)	−0.006	H(73)	0.03	H(9)	0.02	H(14)	0.11
C(7)	0.038	H(81)	−0.15	H(10)	0.00	H(15)	0.01
C(8)	−0.011	H(82)	0.85	H(11)	−0.08	H(16)	0.04
Ti	−0.087	H(83)	−0.81	H(12)	−0.07	H(17)	0.06
				H(13)	−0.06	H(18)	−0.03
				Ti	−2.029	Ti	2.029

(c) Dihedral angles

I ∧ II : 23.3°; I ∧ III : 18.4°; II ∧ III : 41.6°

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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 axes system I, J and K, where I, J and K are unity vectors, with $I \parallel a$, $J \parallel b$ and $K \parallel c^*$.

bond angles. In particular, a significant distortion occurs around atom (C(1), as seen from Table 1(b). The small value for the endocyclic angle C(2)—C(1)—C(6) (116.4°) can be explained in terms of the electropositivity of the Ti atom [7]. The values for the Ti—C(1)—C(2) and the Ti—C(1)—C(6) bond angles, 125.3° and 118.2° respectively, could be accounted for in terms of a β-effect (resulting in a Ti—C(6) distance of 3.102 Å), similar to that in $(PhCH_2)_4Ti$ [5].

Perhaps the most remarkable feature of the structure is the close approach (2.55 Å) of one of the hydrogen atoms of the C(8)-methyl group, H(81), to the Ti atom, indicating some interaction of H(81) and Ti. A repulsive interaction (and an explanation of the difference between the Ti—C(1)—C(2) and Ti—C(1)—C(6) angles as mentioned above) does not seem likely in view of the enhancement of the stability of $(C_5H_5)_2TiR$ caused by methyl substituents in the *ortho* position(s) of R. (The short H(81)—Ti distance could be avoided by rotation of the methyl group around the C(6)—C(8) bond over 60°, but in that case two of the hydrogen atoms of this group would come within 2.1 Å of the cyclopentadienyl hydrogen atoms H(12) and H(16), respectively.) It seems likely, therefore, that the H(81)—Ti approach is of an attractive nature, causing the distortion around the C(1) atom and increasing the stability of the compound. It must be remarked, however, that the H(81)—Ti distance of 2.55 Å is still much longer than the Ti—H bridges (1.83 Å unrefined and 1.75 Å refined) in $(C_5H_5)_2$-TiH_2BH_2 [3]; it may be compared with the H—Pt approach of 2.4 Å found for a phenyl hydrogen in *trans* $PtCl_2(AsEt_3)(MeN{=}CHPh)$ [8] and with the hydrogen—metal approaches of about 2.6—2.9 Å which have been observed in some complexes of Ru, Rh and Pd [9].

From Fig. 1 and Table 1 it is seen that the structure is rather compact and that the position of the aryl group is fixed; movement of the aryl group in its plane (keeping the Ti—C(1) distance constant) is greatly hampered by the steric hindrance between the methyl groups and the cyclopentadienyl ligands. It seems plausible that a rearrangement of the three ligands around Ti, necessary for the accommodation of a fourth ligand (e.g. N_2), is not easy, which would

TABLE 3

DATA AND EXPERIMENTAL DETAILS OF THE STRUCTURE DETERMINATION OF (2,6-DIMETHYLPHENYL)$(C_5H_5)_2$Ti

Data	Experimental details
Monoclinic, space group $P2_1/n$	Weisenberg photographs of zero and higher layer lines
$a = 7.72(2)$ Å $b = 14.66(3)$ Å $c = 12.73(3)$ A $\beta = 101.01(6)°$ $T = -160°$C [10]	From *h0l* reflections of Weisenberg photograph of zero layer line (with $\lambda(Cu—K\alpha) = 1.5418$, $\lambda(Cu—K\alpha_1) = 1.5405$ and $\lambda(Cu—K\alpha_2) = 1.5443$ Å, and calibration with NaCl spots, $a(NaCl) = 5.64006$ Å), and observed optimalised diffractometer angles θ, ϕ and χ of 5 reflections (with $\lambda(Mo—K\bar{\alpha}) = 0.71069$ A)
$D_M = 1.33$ g cm^{-3} (20°C) $Z = 4$, D_X = 1.33 g cm^{-3} (—160°C)	Specific gravity by flotation method
2886 intensities	Automatic Nonius diffractometer, Zr filtered Mo-radiation, θ—2θ scan, $\sin(\theta)/\lambda < 0.597$ Å^{-1}. Reflections with I(net) < 0 were herafter discarded.
1944 independent *F(hkl)* values	Corrections for L.P. factors; no absorption correction ($\mu = 6.1$ cm^{-1}). Dimensions crystal: 0.015 — 0.035 cm

account for the non-existence of a nitrogen complex of (2,6-dimethylphenyl)dicyclopentadienyltitanium.

Experimental

$(C_5H_5)_2Ti(C_6H_3Me_2)$ was prepared as described in the literature [1]. Crystals suitable for X-ray diffraction were hard to obtain, since most were twinned along (101); only after several sublimations at 140—150°C (ca. 0.1 mmHg) were a few single crystals obtained. Because of the sensitivity of the compound towards air the crystals were mounted in capillaries. Crystallographic data are listed in Table 3.

The structure was solved by direct methods (use was made of the X-ray system). An *E*-map, based on the signs of the best set of Multan, revealed the Ti atom and 13 of the 18 C atoms. From a difference map made after a few cycles of isotropic least squares refinement of these atoms the remaining C atoms

TABLE 4. FINAL PARAMETERS

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

Atom	*x/a*	*y/b*	*z/c*	*B* (A^2)
Ti	0.27453(15) [a]	0.01466(7)	0.26194(9)	
C(1)	0.4136(8)	0.1222(4)	0.1938(4)	
C(2)	0.3745(8)	0.1518(4)	0.0861(5)	
C(3)	0.4760(9)	0.2182(4)	0.0482(5)	
C(4)	0.6179(8)	0.2579(4)	0.1150(5)	
C(5)	0.6592(8)	0.2315(4)	0.2214(5)	
C(6)	0.5593(8)	0.1636(4)	0.2598(5)	
C(7)	0.2197(9)	0.1127(5)	0.0108(5)	
C(8)	0.6137(8)	0.1372(4)	0.3770(5)	
C(9)	0.0126(9)	−0.0061(5)	0.3260(6)	
C(10)	−0.0251(9)	0.0492(5)	0.2341(6)	
C(11)	0.0617(9)	0.1319(4)	0.2565(6)	
C(12)	0.1563(9)	0.1295(4)	0.3611(6)	
C(13)	0.1298(10)	0.0435(5)	0.4049(6)	
C(14)	0.2603(13)	−0.1275(6)	0.1753(10)	
C(15)	0.4091(13)	−0.0853(5)	0.1562(6)	
C(16)	0.5243(9)	−0.0743(5)	0.2519(7)	
C(17)	0.4460(12)	−0.1099(5)	0.3308(6)	
C(18)	0.2812(12)	−0.1428(5)	0.2843(9)	
H(3)	0.4474	0.2385	−0.0349	0(1)
H(4)	0.7022	0.3070	0.0863	2(1)
H(5)	0.7711	0.2586	0.2766	1(1)
H(71)	0.2035	0.0395	0.0098	5(2)
H(72)	0.0887	0.1367	0.0146	7(2)
H(73)	0.1911	0.1346	−0.0717	7(2)
H(81)	0.5371	0.0791	0.3936	2(1)
H(82)	0.6056	0.1906	0.4343	6(2)
H(83)	0.7527	0.1209	0.3934	3(2)
H(9)	−0.0260	−0.0740	0.3451	5(2)
H(10)	−0.1122	0.0270	0.1619	5(2)
H(11)	0.0718	0.1890	0.2044	5(2)
H(12)	0.2471	0.1798	0.4020	3(1)
H(13)	0.1924	0.0209	0.4838	2(1)
H(14)	0.1341	−0.1413	0.1246	13(4)
H(15)	0.4066	−0.0693	0.0731	6(2)
H(16)	0.6519	−0.0415	0.2690	9(3)
H(17)	0.4978	−0.1081	0.4158	5(2)
H(18)	0.2018	−0.1757	0.3345	11(3)

TABLE 4

(b) Parameters U_{ij} (in 10^{-3} Å^2) of the temperature factor $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2ha^*kb^*U_{12}\ldots)]$

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
Ti	25.3(6)	10.0(5)	29.6(6)	2.4(10)	29.6(9)	2.7(10)
C(1)	28(4)	13(3)	12(3)	5(5)	5(5)	−6(5)
C(2)	23(3)	15(3)	21(3)	3(5)	17(5)	−2(5)
C(3)	35(4)	16(3)	22(3)	9(5)	26(5)	2(5)
C(4)	23(4)	21(3)	26(3)	4(5)	22(6)	6(5)
C(5)	18(3)	14(3)	25(3)	−3(5)	10(6)	−4(5)
C(6)	18(3)	16(3)	21(3)	3(5)	8(5)	−3(5)
C(7)	31(4)	30(4)	32(4)	−14(6)	−4(6)	5(6)
C(8)	26(4)	23(3)	25(3)	−16(5)	9(6)	−6(5)
C(9)	39(4)	18(4)	70(5)	−3(6)	73(8)	0(7)
C(10)	27(4)	37(4)	52(5)	2(6)	19(7)	−23(7)
C(11)	30(4)	22(4)	49(5)	20(6)	46(7)	14(6)
C(12)	36(4)	23(4)	39(4)	6(6)	36(7)	−26(6)
C(13)	49(5)	39(4)	35(4)	35(7)	55(7)	19(7)
C(14)	47(6)	33(5)	120(9)	52(9)	−61(13)	−94(11)
C(15)	83(7)	36(5)	31(4)	70(9)	44(9)	5(7)
C(16)	17(4)	27(4)	84(6)	4(6)	46(8)	−20(8)
C(17)	76(6)	43(5)	30(4)	81(9)	29(9)	23(7)
C(18)	43(5)	15(4)	122(9)	4(7)	87(12)	20(9)

[a] Standard deviations (in units of the last decimal place) are given in parentheses.

could be located. A difference map based on all, anisotropically refined, non-hydrogen atoms clearly showed the positions of the hydrogen atoms, which were at first isotropically refined. In the later stage of the refinement the hydrogen atoms were fixed at 1.08 Å from the corresponding C atom, without changing the observed C—H directions, only their B-values being refined. During the final refinement cycles we used the weighting scheme $w = [w_c^{-1} + 10^{-4}F^2 + 0.5 \sin(\theta)]^{-1}$, w_c being the weight based on counting statistics. The index $R = [\Sigma(\Delta F)^2/\Sigma(F_0)^2]^{1/2}$ and the index $R_w = [\Sigma w(\Delta F)^2/\Sigma w(F_0)^2]$ decreased to 0.093 and 0.088 respectively. The final coordinates and temperature factors and their standard deviations are listed in Table 4. A list of the observed and calculated structure factors is available from the authors on request.

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