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THE CRYSTAL AND MOLECULAR STRUCTURE OF PENTAMETHYLCYCLOPENTADIENYL(CYCLOPENTADIENYL)TITANIUM DICHLORIDE

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SUMMARY

An X-ray study of $(C_5H_5)[(CH_3)_5C_5]TiCl_2$ has shown that the coordination of ligands in the molecule is that of a distorted tetrahedron with two staggered five-membered rings π-bonded to titanium [$(Ti\text{–}C)_{av.}$ 2.40 Å]. The cyclopentadienyl rings are tilted at an angle of 130° and the two σ-bonded Cl atoms are separated by an average distance of 2.33 Å. The Cl–Ti–Cl bond angle is equal to 94.8°.

INTRODUCTION

Pentamethylcyclopentadienyl(cyclopentadienyl)titanium dichloride belongs to the class of tetra-coordinated titanium compounds containing ordinary covalent M–Cl bonds and π-metal–ring bonds.

The aim of this study was to determine the conformation of this rather strained molecule.

EXPERIMENTAL

$(C_5H_5)[(CH_3)_5C_5]TiCl_2$ was obtained by the interaction of $(CH_3)_5C_5TiCl_3$ with sodium cyclopentadienide in tetrahydrofuran [1]. The substance was recrystallized from a mixture (1/1) of petroleum ether and benzene as dark-red irregular octahedra (m.p. 186–188°). Crystallographic data: $a=9.84$ (2), $b=11.29$ (3), $c=12.88$ (3) Å, $D_m=1.44$, $D_c=1.487$ g·cm^{-3}; $Z=4$; space group $Pna2_1$.

The X-ray intensities recorded by a de Young–Bouman camera (λ(Mo), multiple film technique, $hk0$–$hk5$) were estimated visually and converted to $F^2(hkl)$ values by applying the usual Lorentz and polarization corrections.

The structure was solved by the heavy atom method and refined by a full-matrix isotropic least squares analysis to give a value of $R=0.083$ for 585 non-zero independent reflections.

RESULTS AND DISCUSSION

The atomic and isotropic temperature parameters are listed in Table 1. The molecular geometry is given in Fig. 1. The two staggered rings are π-bonded to the

TABLE 1

ATOMIC AND ISOTROPIC TEMPERATURE PARAMETERS FOR PENTAMETHYLCYCLOPENTADIENYL(CYCLOPENTADIENYL)TITANIUM DICHLORIDE

	x/a	*y/b*	*z/c*	*B*
Ti	0.1033	0.0246	−0.0009	3.4
Cl(1)	0.1335	0.1545	0.1383	4.0
Cl(2)	0.1623	0.1625	−0.1269	3.8
C(1)	−0.096	−0.024	−0.097	3.6
C(2)	−0.116	0.093	−0.053	3.6
C(3)	−0.120	0.081	0.056	4.2
C(4)	−0.103	−0.043	0.079	4.1
C(5)	−0.086	−0.107	−0.015	3.5
C(6)	0.188	−0.168	−0.057	3.6
C(7)	0.284	−0.085	−0.092	4.2
C(8)	0.344	−0.015	−0.016	3.8
C(9)	0.295	−0.065	0.076	4.2
C(10)	0.200	−0.158	0.054	4.1
C(11)	0.454	0.075	0.007	4.3
C(12)	0.308	−0.068	0.193	4.1
C(13)	0.123	−0.236	0.129	4.0
C(14)	0.133	−0.267	−0.123	3.8
C(15)	0.350	−0.049	−0.193	4.2

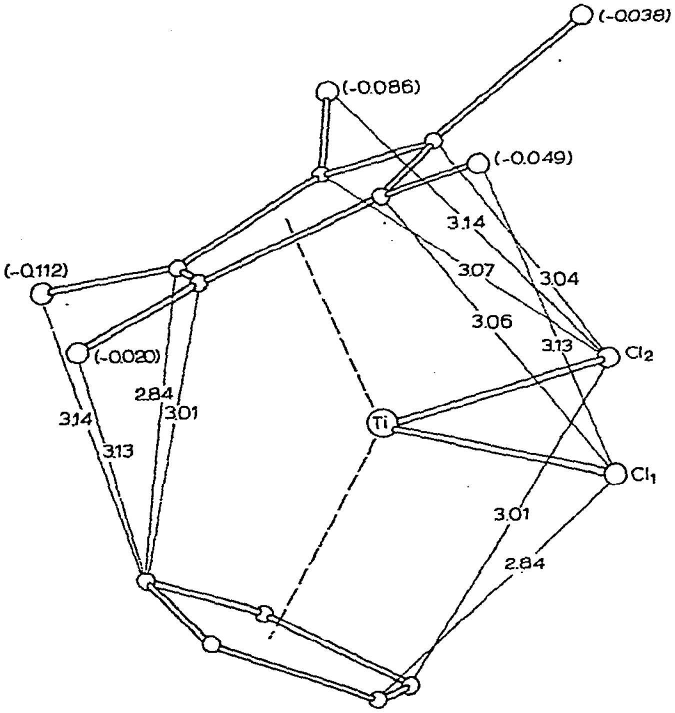

Fig. 1.

titanium atom with an average Ti–C distance of 2.40(2) Å (2.39 Å for ring I and 2.41 Å for ring II), their planes making an angle (φ) of 130(1.7)°. The distances of Ti atom from plane (I) and plane (II) respectively are 2.06(2) Å and 2.09(2) Å. The five-membered rings are planar (the maximum out-of-plane deviation being less than 0.015 Å); standard deviation in C–C lengths $= \pm 0.023$ Å; $(C\text{–}C)_{av.}^{ring} = 1.42(1)$ Å; Ti–Cl distances: Ti–Cl(1)=2.334(8) Å, Ti–Cl(2)=2.323(8) Å (av. 2.33 Å). Bond angles: Cl(1)–Ti–Cl(2) 94.8(0.9), Cl(1)–Ti–Cp(I)=103.6(1.3), Cl(1)–Ti–Cp(II) 111.7(1.6), Cl(2)–Ti–Cp(I) 108.4(1.3), Cl(2)–Ti–Cp(II) 124.6(1.6)°. (Cp=Cyclopentadienyl (centre).)

The spread in $C\text{–}CH_3$ distances extends from 1.50 to 1.52 Å (av. 1.51 Å). The methyl groups are out of plane (0.04–0.11 Å) and to one side of it with the result that the molecule is rather strained. The minimum distance between the C atoms of both rings is equal to 2.84 Å and Cl(1) and one of the ring carbon atoms are at the same short distance (see Fig. 1). These distances (and other short intramolecular distances) probably determine the molecular conformation.

Steric strains in the left-hand side of the molecule (see Fig. 1) caused by the repulsive forces between the carbon atoms of both rings are balanced by the steric strains due to the rigidity of the Cl–Ti–Cl angle and the repulsive forces between the Cl and C atoms. The intramolecular Cl–Cl distance of 3.43 Å is equal to double the Van der Waals radius for Cl.

Virtually the same structural parameters were found in the related structure of dicyclopentadienyltitanium dichloride[2]: staggered conformation, $\varphi = 129.5°$, Cl–Ti–Cl 95.2°, Ti–Cl=2.36 Å and Ti–C=2.44 Å.

In contrast, there is a considerable difference between our reported data (and those of Tkachev and Atomyan[2]) with the data obtained from an electron diffraction study of $(C_5H_5)_2TiCl_2$ by Ronova and Alekseev[3] who found that dicyclopentadienyltitanium dichloride has an eclipsed conformation, the planes of the cyclopentadienyl rings being tilted at an angle of 122° with the Cl–Ti–Cl bond angle being 100° and the Ti–Cl distance equal to 2.24 Å. The shortest distance between the carbon atoms of the neighbouring rings is equal to 2.62 Å, while the shortest C–Cl distances are 2.95 and 3.24 Å, and the Cl–Cl (intramolecular) distance is 3.43 Å. The most surprising feature of the structure described by Ronova and Alekseev is not the difference in the mutual rotation of the planes of the cyclopentadienyl rings (eclipsed conformation) but the very short intramolecular C–C distance (2.62 Å) and the irregular distribution of the steric strains in the molecule.

The available data on other four-coordinated cyclopentadienyltitanium compounds show that the difference in the angle φ (the tilt of the cyclopentadienyl planes) lies in the range 129–136° [4–9] and is apparently determined by steric effects.

With $(C_5H_5)[(CH_3)_5C_5]TiCl_2$, methylation of one of the Cp rings gives rise to additional strains which cause appreciable out-of-plane deviations for several of the CH_3 groups.

In this respect, an X-ray study of the fully methylated derivative recently synthesised[10] would be of particular interest.

The molecules in the crystal are held together by Van der Waals forces, the shortest intermolecular distances corresponding to normal Van der Waals contacts.

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