Synthesis and Structure of the First Fullerene Complex of Titanium $Cp_2Ti(\eta^2\text{-}C_{60})$

V. V. Burlakov,[a] A. V. Usatov,[a] K. A. Lyssenko,[a] M. Yu. Antipin,[a] Yu. N. Novikov,[a] and V. B. Shur*[a]

Keywords: Fullerenes / Titanium / Complexes / X-ray analysis

The first fullerene complex of titanium $Cp_2Ti(\eta^2\text{-}C_{60})$ has been synthesized by reaction of the bis(trimethylsilyl)acetylene complex of titanocene $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with an equimolar amount of fullerene-60 in toluene at room temperature under argon. An X-ray diffraction study of the complex has shown that it has the structure of a titanacyclopropane derivative.

Recent studies have revealed the ability of fullerenes to form complexes with transition metal compounds.[1,2] The majority of studies in this exciting area have been conducted on C_{60} for which a large number of complexes with different transition metals have been prepared and structurally characterized. Among fullerene complexes, the least studied ones are those of the Group IVB metals. Thus, for zirconium, the only available data on complexation with fullerenes concern the work on the hydrozirconation of C_{60} with Cp_2ZrHCl.[3,4] For titanium and hafnium, no fullerene complexes have previously been described.

In the present communication, we wish to report on the synthesis and structure of the first fullerene complex of titanium $Cp_2Ti(\eta^2\text{-}C_{60})$ **(1)**, which is readily obtained from the reaction of the bis(trimethylsilyl)acetylene complex of titanocene $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with an equimolar amount of fullerene-60 in toluene at room temperature under argon.

The isolated complex is a black crystalline solid which is poorly soluble in aromatic hydrocarbons. According to elemental analysis and X-ray diffraction data (see below), crystals of the complex contain one molecule of toluene per molecule of **1**. The molecular structure of $\mathbf{1}\cdot C_6H_5CH_3$ is shown in Figure 1. Selected bond lengths and angles for $\mathbf{1}\cdot C_6H_5CH_3$ are given in Table 1. The complex is a bis(η^5-cyclopentadienyl)titanium derivative in which the $(\eta^5\text{-}C_5H_5)_2Ti$ unit is bound to the olefinic C(1)−C(2) bond at the 6:6 ring junction of the fullerene core in an η^2-fashion. Such a mode of bonding is typical of fullerene complexes with transition metal compounds.

The coordination to titanium results in a significant elongation of the fullerene C(1)−C(2) bond. The length of this bond in **1** is 1.507(6) Å which is considerably greater than the corresponding C−C distance in free C_{60} (1.38 Å)[1] and is close to the values characteristic of the endocyclic C−C single bonds of cyclopropane [1.510(2) Å][7] and its heteroanalogues [e. g. 1.484(3) Å in thiirane,[8,9] 1.502(5) Å in phosphirane[8,10]]. Thus, complex **1** has the structure of a titanacyclopropane derivative.

A similar η^2-coordination of the olefin molecule with a titanium atom has been found in the previously described ethylene complex of permethyltitanocene $Cp^*{}_2Ti(\eta^2\text{-}C_2H_4)$.[8] However, the length of the coordinated C−C bond of the olefin ligand in this complex [1.438(5) Å] is noticeably smaller than that in complex **1**.

The influence of the complexation to titanium on the geometry of the C_{60} moiety is manifested not only in the elongation of the C(1)−C(2) bond but also in the lengthening of the other C−C bonds formed by the C(1) and C(2) atoms. As can be seen from Table 1, the C(1)−C(6), C(1)−C(9), C(2)−C(3) and C(2)−C(12) bond lengths in the molecule of **1** span the range of 1.478(6)−1.492(6) Å (av. 1.486 Å) while the average C−C distance at the other 5:6 ring junctions is 1.467 Å (1.45 Å in free fullerene[1]). The average C−C bond length at the 6:6 ring junctions in complex **1** [excluding the C(1)−C(2) bond] is 1.393 Å which is close to that in free C_{60} (1.38 Å[1]). Due to coordination by the Cp_2Ti unit, the C(1) and C(2) atoms of the fullerene ligand deviate from the planes of the corresponding 5- and 6-membered rings (by ca. 0.19 Å), as a result of which these rings acquire an envelope and a flattened sofa conformation, respectively. The other 5- and 6-membered cycles in the C_{60} moiety are planar within 0.005 Å. The distortion of the fullerene core in **1** can also be demonstrated by the comparison of its "radii" in different directions. Thus, the distances from the centroid of the C_{60} ligand[11] to the C(1) and C(2) atoms bonded to titanium are 3.75 Å whereas the corresponding average distance to the other carbon atoms of C_{60} is significantly shorter (3.540 Å).

The geometry of the bent sandwich in **1** is not exceptional. The planes of the $\eta^5\text{-}C_5H_5$ rings form a dihedral angle of 48.2°. The titanium atom and the coordinated C(1)−C(2) bond of the fullerene are located in the bisector plane of this dihedral angle. The distance from the titanium to the centroids of the $\eta^5\text{-}C_5H_5$ ligands is 2.06 Å. The Ti(1)−C(1) and Ti(1)−C(2) bond lengths are virtually identical [2.304(4) and 2.295(5) Å]. The Ti(1)−C(1)−C(2)

---

[a] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
Vavilov St. 28, Moscow 117813, Russia
Fax: (internat.) + 7-095/135-5085
E-mail: vbshur@ineos.ac.ru

$$Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3) + C_{60} \longrightarrow Cp_2Ti(\eta^2\text{-}C_{60}) + Me_3SiC_2SiMe_3$$

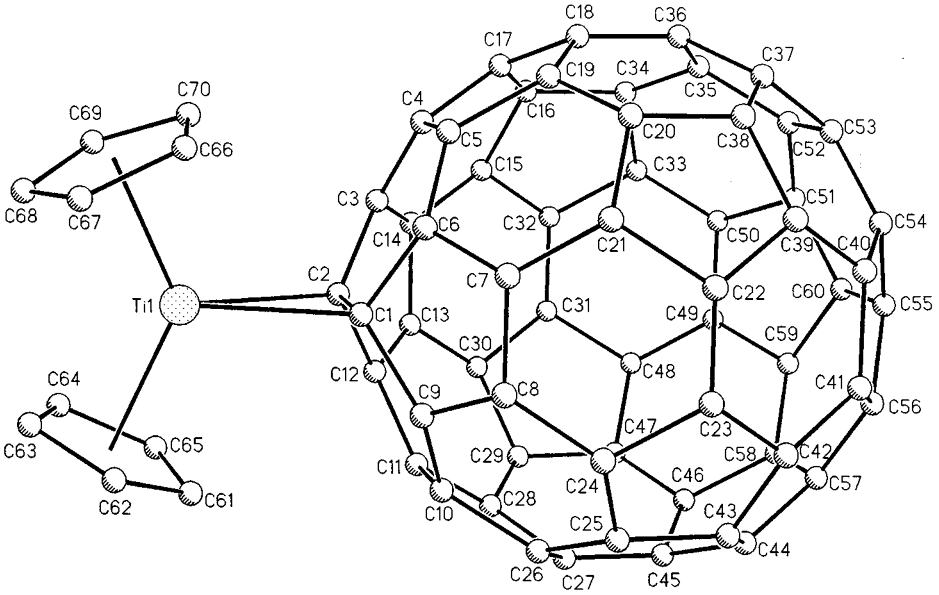

Figure 1. Molecular structure of complex **1** in the solid state

Table 1. Selected bond lengths [Å] and angles [°] for **1**·$C_6H_5CH_3$

Bond lengths			
Ti(1)−C(1)	2.304(4)	Ti(1)−C(68)	2.404(5)
Ti(1)−C(2)	2.295(5)	Ti(1)−C(69)	2.395(5)
Ti(1)−C(61)	2.367(6)	Ti(1)−C(70)	2.380(5)
Ti(1)−C(62)	2.384(6)	C(1)−C(2)	1.507(6)
Ti(1)−C(63)	2.378(6)	C(1)−C(6)	1.492(6)
Ti(1)−C(64)	2.349(6)	C(1)−C(9)	1.485(6)
Ti(1)−C(65)	2.352(5)	C(2)−C(3)	1.478(6)
Ti(1)−C(66)	2.361(5)	C(2)−C(12)	1.488(6)
Ti(1)−C(67)	2.345(5)		
Bond angles			
C(1)−Ti(1)−C(2)	38.3(2)	Cp(1)−Ti(1)−C(2)	114.4(7)
Ti(1)−C(1)−C(2)	70.5(2)	Cp(2)−Ti(1)−C(1)	111.6(7)
Ti(1)−C(2)−C(1)	71.2(2)	Cp(2)−Ti(1)−C(2)	115.3(7)
Ti(1)−C(1)−C(6)	123.1(3)	C(2)−C(1)−C(6)	115.5(4)
Ti(1)−C(1)−C(9)	125.0(3)	C(2)−C(1)−C(9)	117.8(4)
Ti(1)−C(2)−C(3)	123.9(3)	C(6)−C(1)−C(9)	102.6(4)
Ti(1)−C(2)−C(12)	124.1(3)	C(1)−C(2)−C(3)	117.3(4)
Cp(1)−Ti(1)−Cp(2)[a]	130.9(7)	C(1)−C(2)−C(12)	115.3(4)
Cp(1)−Ti(1)−C(1)	111.2(7)	C(3)−C(2)−C(12)	102.8(4)

[a] Cp(1) and Cp(2) are the centroids of Cp rings C(61)−C(65) and C(66)−C(70), respectively.

and Ti(1)−C(2)−C(1) bond angles are 70.5(2) and 71.2(2)°, respectively. The mutual orientation of the η^5-C_5H_5 rings closely corresponds to a staggered conformation. The average C−C bond length in the η^5-C_5H_5 groups is 1.386 Å.

Analysis of the atomic anisotropic displacement parameters of **1** was performed using the THMA-11 program.[12] The agreement between the experimental U_{ij} values and those calculated from the rigid-body LTS model[13] is characterized by a high value of the R_u factor (0.25), while the same value calculated in the segmented-rigid approximation for the (η^2-C_{60})Ti moiety was found to be rather low (0.095). Thus, the metallofullerene fragment in **1** can be correctly analyzed in terms of the LTS approximation and the high value of R_u for the whole molecule is probably caused by the significant libration motion of the η^5-C_5H_5 ligands. Analysis of the rigid-body LTS tensors for the (η^2-C_{60})Ti unit revealed that its libration motion is highly anisotropic. The eigenvalues of the libration tensor (L) are 17.3, 6.0 and 4.8 deg^2 and its maximum eigenvalue (L_1) is observed along the axis with the minimum moment of inertia, which coincides with the C_2 symmetry axis of the molecule. Taking into account that the L_1 value is rather low we can conclude that the barrier of the rotation for the C_{60} moiety in the crystal structure of **1**·$C_6H_5CH_3$ is high.

The crystal packing of **1** can be described as corrugated layers parallel to the *bc* crystallographic plane with the solvate toluene molecules between the layers. The shortest distance between the centroids of the C_{60} cores within the layers is 9.816 Å, while the corresponding distance between the layers is 10.29 Å. It is noteworthy that the distance within the layers is considerably shorter than in the crystal structure of free fullerene-60 (10.02 Å)[14] and the Van der Waal's radius of C_{60} (10.18 Å).[15]

Experimental Section

Experiments were carried out under argon with careful exclusion of air and moisture. Toluene was purified in the usual manner and freshly distilled before use over sodium under an atmosphere of argon. The starting acetylene complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ was prepared by the method described in refs.[5,6]

Synthesis of $Cp_2Ti(\eta^2\text{-}C_{60})$ (1): Fullerene-60 (0.101 g, 0.14 mmol) was dissolved in 50 mL of toluene and to the resulting violet solution was added a solution of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (0.055 g, 0.16 mmol) in toluene (5 mL). The reaction mixture was filtered and then kept overnight at room temperature under argon. During the course of the reaction, the colour of the mixture turned dark brown/green and within 24 h black crystals of $\mathbf{1}\cdot C_6H_5CH_3$ were precipitated. The solution was decanted, the crystals were washed with a small amount of toluene and dried at 20°C in a stream of argon. The yield of $\mathbf{1}\cdot C_6H_5CH_3$ was 0.04 g (29%). − $C_{77}H_{18}Ti$ (990.81): calcd. C 93.34, H 1.83; found C 93.34, H 1.75.

X-ray Structure Determination of 1: Crystals of $\mathbf{1}\cdot C_6H_5CH_3$ are monoclinic, space group $P2_1/c$, $a = 15.951(5)$ Å, $b = 13.678(4)$ Å, $c = 19.313(6)$ Å, $\beta = 108.11(2)°$, $V = 4005(2)$ Å^3, $d_{calc.} = 1.643\ g\cdot cm^{-3}$, $Z = 4$. Intensities of 6329 reflections ($R_{int} = 0.0174$) were measured at 150 K on a Siemens P3 automated diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å, balanced filter, $\theta - 2\theta$ scan, $\theta \leq 24°$). The structure was solved by direct methods and refined by full-matrix least squares against F^2 in the anisotropic (H-atoms isotropic) approximation. All hydrogen atoms were located from the electron density difference synthesis and were included in the refinement using the rigid motion model. The refinement converged to $wR_2 = 0.2254$ and $GOF = 1.115$ for 6329 independent reflections $\{R_1 = 0.0757$ was calculated against F for 4699 observed reflections with $I > 2\sigma(I)\}$. The number of refined parameters was 706. The final difference electron density map showed a maximum of 0.368 and a minimum of −0.642 eÅ^{-3}. All calculations were performed using SHELXTL PLUS 5.0 on an IBM PC/AT. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC-127616. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by grants from the Russian Foundation for Basic Research (Project codes 99−03−33008, 99−03−32893, 97−03−33783) and the Russian State Research Programme “Fullerenes and Atomic Clusters” (Project code 4-1-98).

---

[1] A. L. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123−2165.

[2] V. I. Sokolov, V. V. Bashilov, *Platinum Metals Rev.* **1998**, *42*, 18−24.

[3] S. Ballenweg, R. Gleiter, W. Krätschmer, *Tetrahedron Lett.* **1993**, *34*, 3737−3739.

[4] S. Ballenweg, R. Gleiter, W. Krätschmer, *J. Chem. Soc., Chem. Commun.* **1994**, 2269−2270.

[5] V. V. Burlakov, U. Rosenthal, P. V. Petrovskii, V. B. Shur, M. E. Vol′pin, *Metalloorg. Khim.* **1988**, *1*, 953−954 [*Organomet. Chem. USSR* **1988**, *1*, 526−527 (Engl. Transl.)].

[6] V. V. Burlakov, A. V. Polyakov, A. I. Yanovsky, Yu. T. Struchkov, V. B. Shur, M. E. Vol′pin, U. Rosenthal, H. Görls, *J. Organomet. Chem.* **1994**, *476*, 197−206.

[7] L. V. Vilkov, V. S. Mastryukov, N. I.Sadova, *Determination of the Geometrical Structure of Free Molecules*, Mir Publishers, Moscow, **1983**.

[8] S. A. Cohen, P. R. Auburn, J. E. Bercaw, *J. Am. Chem. Soc.* **1983**, *105*, 1136−1143.

[9] K. Okiye, C. Hirose, D. G. Lister, J. Sheridan, *J. Chem. Phys. Lett.* **1974**, *24*, 111.

[10] M. T. Bowers, R. A. Beaudet, H. Goldwhite, R. Tang, *J. Am. Chem. Soc.* **1969**, *91*, 17−20.

[11] The position of the centroid of the fullerene ligand in **1** was calculated without taking the C(1)−C(2) and the opposite C(55)−C(60) bonds into account.

[12] T. Maverick, K. N. Tueblood, *Thermal motion analysis program THMA-11*, Zurich, **1987**.

[13] T. Maverick, J. D. Dunitz, *Mol. Phys.* **1987**, *62*, 451−459.

[14] P. W. Stephens, D. Cox, J. W. Lauher, L. Mihaly, J. B. Wiley, P. Allemand, A. Hirsch, K. Holczer, Q. Li, J. D. Tompson, F. Wudl, *Nature*, **1992**, *355*, 4145−4147.

[15] Yu. L. Slovokhotov, I. V. Moskaleva, V. I. Shil′nikov, E. F. Valeev, Yu. N. Novikov, A. I. Yanovsky, Yu. T. Struchkov, *Mol. Mat.* **1996**, *8*, 117−124.

Received July 5, 1999
[I99239]