**Titanium Complexes**

# A Five-Coordinate Homoleptic Organotitanium(III) Compound**

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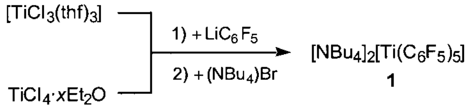
The term "homoleptic", as coined by Lappert for $[\{MR_x\}_n]^{q-}$ species ($q = 0, \pm1, \pm2,\ldots$), is a logical extension of the classical concept of "binary" compounds $E_nX_m$, used in traditional chemistry.[1] Both kinds of compounds are of fundamental importance: They are simple species whose stability, structure, and chemical properties are determined by a minimum number of factors: 1) the electronic and steric properties of a single type of atom X or group R, and 2) the electron configuration, charge, and size of the atom E or metal M. The latter set of factors is inextricably related to the oxidation state of a given element (E or M). In the realm of organotitanium chemistry, the five-coordinate species $[Ti^{IV}Me_5]^-$ has been isolated[2] and structurally characterized.[3] To the best of our knowledge, however, no related $[TiR_5]^{2-}$ species has yet been described containing titanium(III), a much less studied oxidation state for this metal. In fact, the only well-established homoleptic organotitanium(III) compounds conform to the $[TiR_2]^+$ ($R = C_5Me_5$),[4] $[TiR_3]$ ($R = C_5H_5$,[5] $CH(SiMe_3)_2$),[6] and $[TiR_4]^-$ ($R = C_6Cl_5$)[7] stoichiometries. We now report the synthesis and characterization of $[NBu_4]_2[Ti(C_6F_5)_5]$ ($d^1$, paramagnetic), containing discrete $[Ti^{III}(C_6F_5)_5]^{2-}$ units, which is an unprecedented formula for homoleptic organotitanium compounds.

The low-temperature reaction of a suspension of $TiCl_4{\cdot}x\,Et_2O$ in $Et_2O$ with $LiC_6F_5$ in the presence of $[NBu_4]Br$ proceeds with metal reduction and affords $[NBu_4]_2[Ti^{III}(C_6F_5)_5]$ (**1**) as an orange-red solid in moderate yield (Scheme 1). Compound **1** can alternatively be prepared under similar conditions from the titanium(III) complex $[TiCl_3(thf)_3]$. Note that the reaction of $[TiCl_3(thf)_3]$ with $LiC_6Cl_5$ has been reported to afford the four-coordinate compound $[Li(thf)_4][Ti^{III}(C_6Cl_5)_4]$.[7] Compound **1** is extremely air sensitive, both in solution and in the solid state. Solid **1** easily explodes under slight mechanical stress, for example, from percussion or a sharp temperature change. The IR spectrum shows only a weak absorption assignable to the X-sensitive vibration mode[8] of the $C_6F_5$ group at $801\ cm^{-1}$.



*Scheme 1.*

The crystal and molecular structures of **1** were established by X-ray diffraction. Two crystallographically independent $[Ti(C_6F_5)_5]^{2-}$ anions were found in the asymmetric unit of the crystal but, because of their similarity, we refer to only one of them (Figure 1). The Ti center is located in a heavily distorted trigonal-bipyramidal (*TBPY*-5) environment formed by five terminal, σ-bonded $C_6F_5$ ligands. The axial positions are defined by the $C_6F_5$ groups with the widest interligand angle (C(1)-Ti(1)-C(7) 164.6(2)°). The sum of the interligand $C_{eq}$-Ti-$C_{eq}$ angles is 359.3(3)°, that is, the equatorial plane shows no pyramidalization at the Ti atom. Although weaker $M{-}L_{ax}$ bonds would be expected for a $d^n$ (*TBPY*-5)-$ML_5$ species with $n < 5$,[9] no significant difference between the average values of $Ti{-}C_{ax}$ (226.2(8) pm) and $Ti{-}C_{eq}$ (223.1(7) pm) bond lengths can be observed in **1**. The mean Ti−C bond length (224.4(8) pm) is slightly longer than that observed in the homoleptic, tetrahedral anion $[Ti^{III}(C_6Cl_5)_4]^-$ (Ti−C 220.7(5) pm),[7] a fact that can be ascribed to the different coordination numbers in the two anionic species, as well as to their different global charges. Important angular deviations from ideal *TBPY*-5 geometry are observed in the Ti coordi-

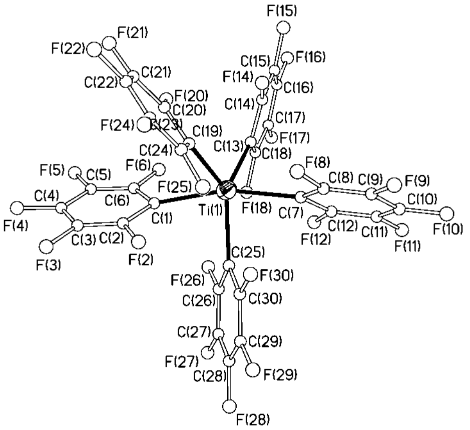


*Figure 1.* Thermal ellipsoid diagram (50% probability) of one of the two crystallographically independent $[Ti(C_6F_5)_5]^{2-}$ anions in **1**. Selected bond lengths [pm] and angles [°]: Ti(1)−C(1) 226.2(8), Ti(1)−C(7) 225.7(8), Ti(1)−C(13) 222.1(7), Ti(1)−C(19) 223.8(7), Ti(1)−C(25) 223.5(6); C(1)-Ti(1)-C(7) 164.6(2), C(1)-Ti(1)-C(13) 105.2(3), C(1)-Ti(1)-C(19) 79.4(3), C(1)-Ti(1)-C(25) 81.5(2), C(7)-Ti(1)-C(13) 86.5(3), C(7)-Ti(1)-C(19) 108.3(3), C(7)-Ti(1)-C(25) 83.4(3), C(13)-Ti(1)-C(19) 101.7(2), C(13)-Ti(1)-C(25) 129.6(3), C(19)-Ti(1)-C(25) 128.3(2).

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[**] This work was supported by the Spanish MCYT (DGI)/FEDER (Projects BQU2002-03997-CO2-02 and BQU2002-00554) and the Gobierno de Aragón (Grupo Consolidado: Química Inorgánica y de los Compuestos Organometálicos). The Gobierno de Aragón is also acknowledged for a grant to M.A.G.-M. We thank Dr. I. Ara for collecting the X-ray diffraction data.

Supporting information for this article (PDB files of the crystallographically independent anions and variable-temperature EPR spectrum of **1**) is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200460111

nation sphere. The equatorial $C_6F_5$ groups are tilted from the equatorial plane by between 28.5° and 47.3°, but they fail to arrange helically around the ideal axial direction, in contrast to the disposition adopted by the $C_6Cl_5$ groups in the related anions (*TBPY*-5-11)-$[M(C_6Cl_5)_3Cl_2]^-$ (M = Zr, Hf).[7a] Since the $C_{eq}$-Ti-$C_{eq}$ angle between the two like-rotated $C_6F_5$ rings (C(13)-Ti-C(19) 101.7(2)°) is significantly more acute than those between counterrotated rings (ca. 130°), an equatorial Y distortion occurs.[10] The axial $C_6F_5$ groups depart by about 17° from the normal to the equatorial plane: Axial C(1) leans toward the C(19)-Ti(1)-C(25) bisector, while axial C(7) leans to the bisector of C(13)-Ti(1)-C(25), resulting in acute $C_{ax}$-Ti(1)-C(25) angles of about 82° (reversed Berry distortion towards a so-called edge-bridged tetrahedron, with a precession angle of $\beta \approx 17°$).[10,11] The angular distortions in the $[Ti(C_6F_5)_5]^{2-}$ anion yield an approximate $C_{2v}$ local symmetry and can be jointly described as a "totally reversed Berry distortion" in which C(25) acts as the pivot substituent (Figure 2).

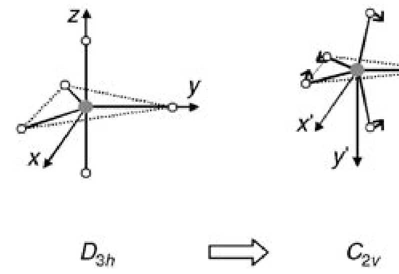

*Figure 2.* Schematic representation of the $Ti^{III}$ environment in **1** as a distortion of an ideal *TBPY*-5 geometry with the appropriate choice of reference frame in each case.

The stereochemistry of five-coordinate compounds has always been a difficult and controversial issue.[12] When purely electrostatic factors are considered, the *TBPY*-5 geometry is generally found to be more stable than the *SPY*-5 alternative.[13] However, in our case an idealized *TBPY*-5 geometry would lead to the orbitally degenerate electronic state $e''(xy,xz)^1$ (Figure 3),[14] which, according to the Jahn–Teller theorem, should be unstable.[15] On the other hand, detailed calculations at different levels of theory on homoleptic $[MR_5]^{q-}$ systems bearing purely σ-donor ligands (e.g., H or Me) point to the "non-VSEPR"[16] *SPY*-5 geometry as the most energetically favored.[3,11,16–18] These theoretical predictions were experimentally confirmed in a number of $d^0$ and $d^1$ species, such as $[Ta(CH_2C_6H_4)]$ ($d^0$),[19] $[TaMe_5]$ ($d^0$),[20] and $[MoMe_5]$ ($d^1$).[18] These results departing from simple VSEPR models apply for covalent, essentially nonpolar species.[16,21] The fact that $[Ti(C_6F_5)_5]^{2-}$ in **1** with a distorted *TBPY*-5 structure more closely resembles a transition state calculated[11] for the anion $[TiH_5]^-$ than the ground-state structure of this and the aforementioned organometallic compounds could be related to the polarity of the Ti–C bonds caused by the strongly electron withdrawing character of the $C_6F_5$ group.[22] It can be concluded that, on a simple VSEPR basis, both the high polarity of the Ti–C bond and the bulkiness of the $C_6F_5$ ligand would be expected to favor the *TBPY*-5 geometry. The significant deviations observed in the solid-state structure of **1** could be attributed to the Jahn–Teller effect, as well as to steric problems possibly encountered in arranging five highly anisotropic $C_6F_5$ ligands around the $Ti^{III}$ centre.

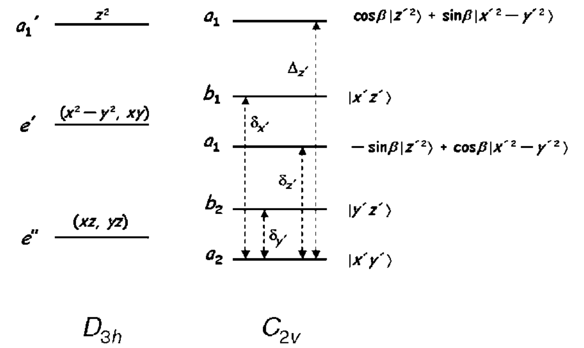

*Figure 3.* Energy level diagrams corresponding to a $[MR_5]^{q-}$ ($q = 0, \pm 1, \pm 2, \ldots$) species with ideal *TBPY*-5 geometry ($D_{3h}$) and with the lowering of symmetry experimentally observed in **1** ($C_{2v}$). The labels identify the primary character of the orbitals.

Variable-temperature EPR spectra (77.3 to 250 K) were measured on polycrystalline samples of **1**. The results obtained (Figure 4; see also Supporting Information) can be assigned to an $S = 1/2$ species with the following principal values of the $\tilde{g}$ tensor: $g_1 = 1.971(1)$, $g_2 = 1.871(1)$, and $g_3 = 1.771(1)$. These values denote a more markedly orthorhombic character than in the related[7] four-coordinate species $[Ti(C_6Cl_5)_4]^-$ and are also appreciably more shifted from the free-electron $g$ factor ($g_e = 2.0023$). The two crystallographically independent $Ti^{III}$ sites in **1** are sufficiently similar to give a single type of EPR signal (within its resolution limit). According to the molecular structure of the $[Ti(C_6F_5)_5]^{2-}$ anion and following the energy-level diagram given in Figure 3 for the $C_{2v}$ distortion of *TBPY*-5 geometry depicted in Figure 2, it is reasonable to assign the $a_2(x',y')^1$ configuration as the (orbitally nondegenerate) ground state.[23] The principal values of the $\tilde{g}$ tensor would be given, in this case, by Equation (1).

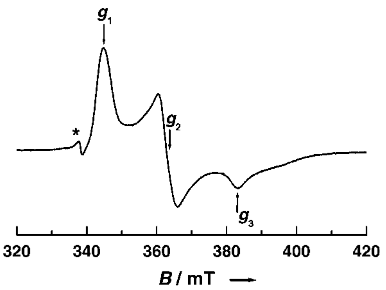

*Figure 4.* EPR spectrum of **1** at 77.3 K (X-band, polycrystalline sample). The asterisked signal at $g \approx 2.00$ is assigned to some spurious radical species.

$$g_{x'} = g_e - \frac{2\lambda}{\delta x'}, g_{y'} = g_e - \frac{2\lambda}{\delta y'}, g_{z'} = g_e - \left(\frac{\cos^2\beta}{\delta z'} + \frac{\sin^2\beta}{\Delta z'}\right) \qquad (1)$$

The energy differences are defined in Figure 3, $\lambda$ is the spin-orbit coupling parameter, and $\beta$ accounts for mixing between the $a_1$ orbitals. Starting from an ideal *TBPY*-5 geometry and considering the $C_{2v}$ distortion as a perturbation in a first order approximation ($\beta = \pi/3$), Equation (2) applies.

$$g_{z'} = g_e - \frac{2\lambda}{\delta z'} - \frac{6\lambda}{\Delta z'} \qquad (2)$$

In line with this reasoning, the assignments in Equation (3) can be made.

$$g_1 = g_{x'}, g_3 = g_{y'}, g_2 = g_{z'} \qquad (3)$$

In summary, $[NBu_4]_2[Ti(C_6F_5)_5]$ (**1**) is the first example of a $[TiR_5]^{2-}$ unit in organometallic chemistry. Precedents for this stoichiometry in coordination chemistry are also very rare, namely, $[TiX_5]^{2-}$ (X = F, Cl). No structural data are known for $K_2[TiCl_5]$,[24] and the salt $[NH_4]_2[TiF_5]$ was found to contain infinite chains of octahedral $[TiF_6]^{3-}$ units sharing fluoro ligands in *trans*-disposed vertices.[25] Compound **1** occupies a unique position not only in the organometallic but also in the coordination chemistry of titanium. Experimental work aiming to extend these results to the heavier Group 4 metals, Zr and Hf, is underway.

## Experimental Section

General working techniques are described in ref. [7]. **CAUTION**: **1** has been found to explode by percussion, and sometimes for no obvious reason.

**1**: Method A: $[TiCl_3(thf)_3]$[27] (1.60 g, 4.31 mmol) suspended in $Et_2O$ (15 $cm^3$) was added to a solution of $LiC_6F_5$[26] (ca. 26 mmol) in $Et_2O$ (50 $cm^3$) at −78 °C. The mixture was allowed to warm to −30 °C and, after addition of $[NBu_4]Br$ (1.40 g, 4.31 mmol), the temperature was allowed to rise to 0 °C. After 3 h of stirring at this temperature, an orange-red solid had precipitated, which was collected by filtration, washed with $Et_2O$ (3 × 3 $cm^3$), dried under vacuum, and extracted with $CH_2Cl_2$ (60 $cm^3$) at 0 °C. The extract was concentrated to about 15 $cm^3$, and slow diffusion of a $Et_2O$ layer (50 $cm^3$) at −30 °C yielded **1** as an orange-red microcrystalline solid (2.30 g, 1.68 mmol; 39 % yield based on the titanium precursor). Satisfactory elemental analysis. IR (KBr): $\tilde{\nu}$ = 1629 (m), 1533 (m), 1493 (s, $C_6F_5$), 1436 (vs), 1382 (w), 1369 (w), 1320 (w), 1237 (w), 1179 (w), 1108 (w), 1060 (m), 1041 (s), 979 (w), 946 (vs, $C_6F_5$: C–F),[8] 882 (w, $NBu_4^+$), 801 (w, $C_6F_5$: X-sensitive vibr.),[8] 741 (w, $NBu_4^+$), 713 (w), 593 (w), 480 $cm^{-1}$ (w).

Method B: A suspension of yellow $TiCl_4 \cdot x Et_2O$ in $Et_2O$ (prepared by mixing $TiCl_4$ (0.5 $cm^3$, 4.6 mmol) and $Et_2O$ (25 $cm^3$), both precooled at −78 °C) was added to a solution of $LiC_6F_5$[26] (ca. 30 mmol) in $Et_2O$ (60 $cm^3$) at −78 °C. Following the procedure described in Method A, including the addition of $[NBu_4]Br$ (1.47 g, 4.60 mmol) where appropriate, gave **1** in 34 % yield (2.13 g, 1.55 mmol).

Crystal data for **1**: $C_{62}H_{72}F_{25}N_2Ti$; monoclinic; space group $P2_1/c$; $a = 1876.0(2)$, $b = 2095.1(2)$, $c = 3225.3(4)$ pm, $\beta = 89.893(2)°$, $V = 12.677(3)$ $nm^3$; $Z = 8$; $T = 100(2)$ K; $\lambda = 71.073$ pm; abs. coeff. 0.249 $mm^{-1}$; range for data collection $1.09 < \theta < 25.05°$; reflns collected/unique: 69322/22367 ($R_{int} = 0.1417$); Bruker Smart CCD diffractometer. The crystallographic data were corrected for absorption with SADABS.[28] The structure was solved by direct methods, and refinement against $F^2$ with SHELXL-97[29] converged to final residual indices of $R_1 = 0.0668$, $wR_2 = 0.1325$ [$I > 2\sigma(I)$] and $R_1 = 0.1840$, $wR_2 = 0.1773$ (all data). GoF = 1.011. CCDC-233902 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

EPR spectra were recorded on a Bruker ESP380E spectrometer working in the X-band. Measurements at liquid-nitrogen temperature (77.3 K) were made in a quartz immersion Dewar vessel. A Bruker ERV4111T device was used for variable-temperature measurements. The microwave frequency was determined with a Hewlett-Packard HP5350B frequency counter, and the magnetic field strength with a Bruker ER035M gaussmeter.

Received: March 24, 2004
Revised: June 16, 2004

**Keywords:** EPR spectroscopy · fluorinated ligands · homoleptic compounds · metal–carbon bonds · titanium

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