

## The first structurally characterised homoleptic $\sigma$ -organotitanium(III) compound

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The paramagnetic [EPR,  $S = 1/2$ ,  $d^1$ ;  $g_{av} = 1.959(2)$ ] organotitanate(III) anion  $[\text{Ti}^{\text{III}}(\text{C}_6\text{Cl}_5)_4]^-$  has been found to be a mononuclear species with nearly tetrahedral geometry (X-ray).

The organometallic chemistry of titanium has been the subject of extensive investigation for nearly half a century,<sup>1</sup> especially because of its relevance in relation to various industrially-appelling catalytic processes, including the classic Ziegler–Natta polymerisation of 1-alkenes.<sup>2</sup> In the latter process, both  $\text{TiCl}_4$  and  $\text{TiCl}_3$  have been widely used as catalysts in combination with different polyalkylaluminium derivatives presumably giving  $\text{Ti}^{\text{III}}\text{-C}(\sigma\text{-alkyl})$  sites which act as active polymerisation centres.<sup>†</sup> In spite of this, the organometallic chemistry of  $\text{Ti}^{\text{III}}$  ( $d^1$ ) is in no way as developed as that of  $\text{Ti}^{\text{IV}}$  ( $d^0$ ). This is especially true for homoleptic  $\sigma$ -organotitanium species not containing the Cp ring or any other ancillary ligand. Thus, the rational choice of suitable R organic groups preventing  $\beta$ -H elimination (R = alkyl or aryl) has allowed the isolation of a fair number of homoleptic  $\sigma$ -organotitanium(IV) species of formula  $[\text{TiR}_4]$ .<sup>4,5</sup> However, the application of the same principle to  $\text{Ti}^{\text{III}}$  has rendered discouraging results.<sup>5–7</sup> Only the salt  $\text{Li}[\text{Ti}(\text{C}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_4\text{-}4\text{thf}]^8$  and the neutral species  $[\text{TiR}_3]$  [R =  $\text{CH}_2\text{SiMe}_3$ <sup>7e</sup> or  $\text{CH}(\text{SiMe}_3)_2$ <sup>7g</sup>] could be isolated. To the best of our knowledge, however, no structural information is available for this important class of compounds.

The arylation of  $[\text{TiCl}_3(\text{thf})_3]$  with  $\text{LiC}_6\text{Cl}_5$  in  $\text{Et}_2\text{O}$  at low temperature leads to the formation of  $[\text{Li}(\text{thf})_4][\text{Ti}(\text{C}_6\text{Cl}_5)_4]$  (**1**), which can be isolated as a yellow solid in moderate yield.<sup>‡</sup> Complex **1** is extremely air- and moisture-sensitive and rapidly pales during short exposure to air. It also decomposes in an Ar atmosphere, both in solution and in the solid state, if the temperature is allowed to rise above 0 °C. Notwithstanding this instability, it has been possible to characterise **1** by analytical and spectroscopic methods (IR, MS and EPR).

The EPR spectrum of a powder sample of **1** consists of an orthorhombic signal with no hyperfine structure, which is assignable to an  $S = 1/2$  entity with  $g_x = 1.985(2)$ ,  $g_y = 1.955(2)$ ,  $g_z = 1.936(2)$ ;  $g_{av} = 1.959(2)$ .<sup>§</sup> These values are in keeping with those usually found for  $\text{Ti}^{\text{III}}$  molecular species both in polycrystalline samples<sup>12</sup> and in frozen solutions.<sup>13</sup>

The crystallisation of **1** in  $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$  mixtures resulted in partial thf replacement by  $\text{Et}_2\text{O}$  giving crystals of  $[\text{Li}(\text{thf})_2(\text{OEt}_2)_2][\text{Ti}(\text{C}_6\text{Cl}_5)_4\cdot\text{CH}_2\text{Cl}_2]$  (**1'**)<sup>¶</sup> which have been studied by X-ray diffraction methods.<sup>||</sup> The solid-state structure of **1'** consists of the separate ions  $[\text{Li}(\text{thf})_2(\text{OEt}_2)_2]^+$  (Fig. 1) and  $[\text{Ti}(\text{C}_6\text{Cl}_5)_4]^-$  (Fig. 2) together with interstitial  $\text{CH}_2\text{Cl}_2$  molecules. Both the cation and the anion have crystallographic  $C_2$  symmetry. The short-range, local geometry around the  $\text{Li}^+$  ion is nearly tetrahedral as is usually found in the related  $[\text{Li}(\text{thf})_4]^+$  cation.<sup>15</sup> There is no significant difference between the Li–O distances irrespective of the cyclic or open-chain nature of the attached ether molecule. The central core of the anion  $[\text{Ti}(\text{C}_6\text{Cl}_5)_4]^-$  (Fig. 2) can also be described as slightly distorted tetrahedral. The two crystallographically independent Ti–C bond distances are identical [220.7(5) pm] and compare well with those found in heteroleptic ( $\sigma$ -aryl)titanium(III) derivatives

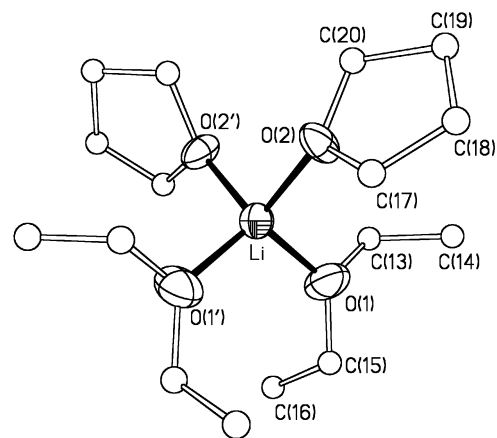


Fig. 1 Thermal ellipsoid diagram of the cation  $[\text{Li}(\text{thf})_2(\text{OEt}_2)_2]^+$  as found in **1'**. Selected distances [pm] and angles [°]: Li–O(1) 194.2(8), Li–O(2) 192.3(9); O(1)–Li–O(1') 116.8(7), O(1)–Li–O(2) 112.11(19), O(1)–Li–O(2') 105.52(18), O(2)–Li–O(2') 104.1(6).

regardless of their specific coordination number, as for instance:  $[\text{Li}(\text{tmen})_2][\text{TiPh}_2(\text{N}^i\text{Pr}_2)_2]$  [Ti–C 217.3(5) and 221.0(5) pm],<sup>16</sup>  $[\text{TiCp}_2(\text{C}_6\text{H}_3\text{Me}_2\text{-}2,6)]$  [Ti–C 217.8(7) pm],<sup>17</sup>  $[\text{TiCp}_2(\text{C}_6\text{H}_4\text{Me-}4)_2(\mu\text{-N}_2)]$  [Ti–C 221.6(7) pm]<sup>18</sup> and  $[\text{Ti}(\text{acacen-}\kappa^2\text{O},\kappa^2\text{N})(\text{C}_6\text{H}_2\text{Me}_3\text{-}2,4,6)]$  [Ti–C 222(2) pm; acacen =  $N,N'$ -ethylenebis(acetylacetonate iminato) dianion].<sup>19</sup> The C–Ti–C angles [ranging from 97.9(2)° to 116.8(2)°] deviate from the ideal tetrahedral value in such a way that the short-range, local geometry for the Ti centre can be described as being rigorously  $D_{2d}$ .

In contrast to the small distortions observed in the closest coordination sphere of  $\text{Ti}^{\text{III}}$  in **1'**, the long-range coordination environment is highly distorted as reflected in the orthorhombic

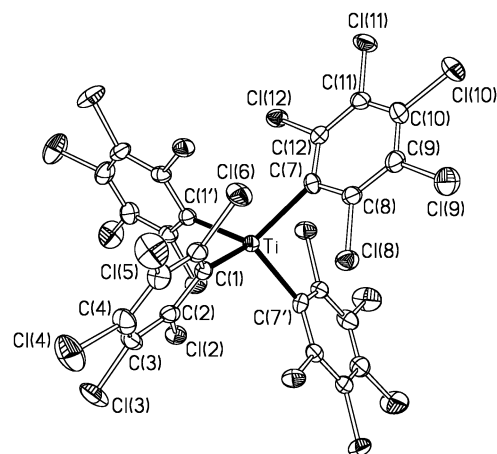


Fig. 2 Thermal ellipsoid diagram of the anion  $[\text{Ti}(\text{C}_6\text{Cl}_5)_4]^-$  as found in **1'**. Selected distances [pm] and angles [°]: Ti–C(1) 220.7(5), Ti–C(7) 220.7(4), Ti...Cl(2) 304.99(14), Ti...Cl(6) 377.30(15), Ti...Cl(8) 312.55(15), Ti...Cl(12) 370.43(16); C(1)–Ti–C(1') 98.5(2), C(1)–Ti–C(7) 116.8(2), C(1)–Ti–C(7') 114.0(2), C(7)–Ti–C(7') 97.9(2).

character of the  $g$  tensor (see above). The main source of distortion is the marked swing of the  $C_6Cl_5$  rings on each *ipso*-C atom. As a result of this, the  $Ti-C_{ipso}-C_{ortho}$  angles are dissimilar within each ring [ring 1:  $113.0(3)^\circ$  vs.  $133.8(3)^\circ$ ; ring 2:  $114.8(3)^\circ$  vs.  $131.5(3)^\circ$ ] as are the corresponding *ortho*-Cl...Ti distances [ring 1:  $304.99(14)$  vs.  $377.30(15)$  pm; ring 2:  $312.55(15)$  vs.  $370.43(16)$  pm]. All the *ortho*-Cl...Ti distances are too long to denote the existence of a bonding interaction. The  $C_6Cl_5$  group has been assigned a similar electronic effect to that of the widely used  $C_6F_5$  group, when acting as substituents in simple organic compounds.<sup>20</sup> From our experience, however, the two  $C_6X_5$  groups ( $X = F$  or  $Cl$ ) show remarkable differences in their organotransition metal chemistry.<sup>11</sup> Thus,  $C_6Cl_5$  has allowed unusual metal oxidation states such as Pt(III),<sup>21</sup> Rh(II)<sup>22</sup> and Ir(II)<sup>23</sup> to stabilise, which is a situation that is not found in the  $C_6F_5$  group. Additionally, the presence of *ortho*-Cl substituents enable  $C_6Cl_5$  to act both as a standard terminal ( $\kappa^1-C$ ) and as a poor chelating ligand ( $\kappa C, \kappa C^2$ ). This makes the  $C_6Cl_5$  group a particularly flexible ligand, which is able to match various metal geometries and oxidation states, as evidenced in the  $[M(C_6Cl_5)_4]^{n-}$  ( $n = 0, 1, 2$ ;  $M = Pt,^{24} Cr^{25}$ ) series for which no  $C_6F_5$  counterparts are known. These dissimilarities must necessarily depend on different electronic and steric properties that have been previously overlooked.

Further studies aiming to learn more about the chemical behaviour of the highly unusual  $Ti^{III}$  species **1** are currently in progress.

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## Notes and references

† It is also known that  $\beta$ - $TiCl_3$  is able, on its own, to promote the polymerisation of ethene and 1-propene without the need of polyalkylaluminium derivatives.<sup>3</sup>

‡ *Experimental procedure*: A precooled suspension of  $[TiCl_3(thf)_3]^9$  (2.37 g, 6.40 mmol) in  $Et_2O$  ( $15\text{ cm}^3$ ) was slowly added *via* cannula to a solution of  $LiC_6Cl_5^{10}$  (ca. 32 mmol) in  $Et_2O$  ( $70\text{ cm}^3$ ) at  $-78^\circ\text{C}$ . The mixture was allowed to warm to  $0^\circ\text{C}$  and was stirred in an ice bath for 3.5 h. By then, an orange solid had formed, which was filtered off and treated with  $CH_2Cl_2$  ( $70\text{ cm}^3$ ) at  $0^\circ\text{C}$ . The extract was evaporated to dryness and the resulting residue was redissolved in  $thf$  ( $10\text{ cm}^3$ ) and filtered. The diffusion of  $Et_2O$  ( $50\text{ cm}^3$ ) overlaid on the preceding solution at  $-30^\circ\text{C}$  caused the crystallisation of **1** as an orange solid that turned yellow when vacuum dried; yield: 2.76 g (2.06 mmol, 32%); elemental anal. found: C 36.59, H 2.26;  $C_{40}H_{32}Cl_{20}LiO_4Ti$  requires: C 35.84, H 2.40%; IR (KBr;  $cm^{-1}$ ): 1507m, 1461m, 1312s, 1283vs, 1224m, 1141m, 1063s, 1043s, 887m (thf), 827vs ( $C_6Cl_5$ : X-sensitive vibr.)<sup>11</sup> and 666vs; MS (FAB<sup>-</sup>):  $m/z$  1036  $[Ti(C_6Cl_5)_4]^-$ , 824  $[Ti(C_6Cl_5)_3Cl]^-$  and 577  $[Ti(C_6Cl_5)_2Cl]^-$ .

§ EPR spectra were measured at room temperature using a Bruker ESP380E spectrometer. The presence of a narrow, isotropic signal at  $g = 2.00$  (peak to peak distance 0.8 mT) is also observed in the EPR spectrum of **1**. Considering that the intensity of this additional signal depends on the ageing of each sample and in view of its spectral properties, it is logical to ascribe it to some decomposition radical species.

¶ Attempts to crystallise **1** in  $thf$ - $n$ -hexane mixtures gave only poor quality crystals with weak diffracted data from which the connectivity of the atoms could be established but not a detailed and satisfactory analysis.

|| *Crystal data for 1*:  $C_{41}H_{38}Cl_{22}LiO_4Ti$ ,  $M = 1429.45$ , monoclinic, space group  $C2/c$  (no. 15),  $a = 1674.8(5)$ ,  $b = 1915.46(15)$ ,  $c = 1758.0(2)$  pm,  $\beta = 91.58(3)^\circ$ ,  $V = 5.6376(18)\text{ nm}^3$ ,  $Z = 4$ ,  $D_c = 1.684\text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 1.235\text{ mm}^{-1}$ ,  $F(000) = 2860$ ,  $T = 150(2)\text{ K}$ , Enraf-Nonius CAD4 diffractometer, graphite-monochromated Mo-K $\alpha$  radiation,  $\lambda = 71.073\text{ pm}$ ,  $\omega$  scans, data collection range  $4.0 < 2\theta < 50.0^\circ$ , measured absorption correction based on  $\psi$  scans, 4548 intensity data collected, 4368 unique ( $R_{int} = 0.0281$ ), 4367 of which were used in all calculations. The structure was solved by Patterson and Fourier methods and refined anisotropically by full-matrix least squares on  $F^2$  (program SHELXL 93)<sup>14</sup> to final values of  $R_1 = 0.0484$  and  $wR_2 = 0.1202$  [for 3363 data with  $I > 2\sigma(I)$ ] and  $R_1 = 0.0761$  and  $wR_2 = 0.1385$  (all data) for 313 parameters.  $\Delta\rho = 675\text{ e nm}^{-3}$  ( $711\text{ e nm}^{-3}$ ).

CCDC reference number 172710. See <http://www.rsc.org/suppdata/cc/b1/b111127b/> for crystallographic data in CIF or other electronic form.

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