Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chlorobis(η^5-cyclopentadienyl)methoxytitanium

Dorothy H. Gibson,* Yan Ding, Mark S. Mashuta and John F. Richardson

Department of Chemistry and Center for Chemical Catalysis, University of Louisville, Louisville, KY 40292, USA

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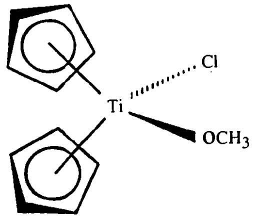
Abstract

The title compound, [TiCl(C$_5$H$_5$)$_2$(CH$_3$O)], is a 'bent metallocene' structural type typically found in Cp$_2MXY$ complexes. The Ti—O—C bond angle of 141.4 (3)° is significantly greater than the corresponding angle in the ethoxy analog, resulting in a shortened O—Ti bond and indicating greater π character of the O—Ti bond of the title compound.

Comment

In the course of our work on the chemistry of compounds with bridging ethyleneoxy ligands bound to titanocene and zirconocene fragments (Gibson, Franco & Ding, 1995), we have sought to compare the properties of compounds bearing simple alkoxy ligands with those having related bridging ligands. The title compound, (I), has been prepared and characterized for this purpose.



(I)

If the vectors from Ti to the centroids of the two Cp rings are considered together with the bonds to O and Cl, then the geometry about the Ti atom can be described as distorted tetrahedral. The related compound with an ethoxy ligand bound to Ti has been structurally characterized at 148 K (Huffman, Moloy, Marsella & Caulton, 1980) and has closely similar geometry about the Ti atom. The Ti(1)—O(1)—C(1) bond angle is more obtuse in (I) [141.4 (3)°] than in the ethoxy analog [133.2 (2)°]. As would be expected from this larger bond angle, the Ti(1)—O(1) bond is slightly shorter at 1.839 (2) Å than in the ethoxy analog [1.855 (2) Å]. Also, the O(1)—C(1) bond is significantly shortened in (I) [1.367 (4) compared with 1.415 (4) Å] and the Ti(1)—Cl(1) bond in (I) is slightly longer than in the ethoxy analog [2.412 (1) compared with 2.405(1) Å]. These altered structural parameters suggest that the

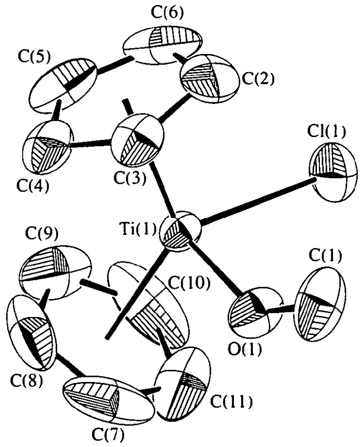


Fig. 1. View of the molecular structure of (I), showing the atom-numbering scheme with 50% probability displacement ellipsoids. H atoms are omitted for clarity.

extent of π bonding of the methoxy O atom to Ti is enhanced relative to that of the ethoxy derivative.

Both Cp rings are clearly disordered but a suitable model could not be refined. There are no close contacts between molecules.

Experimental

A sample of (I) was synthesized by the reaction of Cp_2TiCl_2 with methanol in the presence of triethylamine (molar ratio 1:2:1) for 1 h at 323 K. (I) was recrystallized from toluene.

Crystal data

[TiCl(C_5H_5)$_2$(CH_3O)]
$M_r = 244.58$
Orthorhombic
Pbca
$a = 14.630\,(4)$ Å
$b = 12.616\,(3)$ Å
$c = 11.709\,(3)$ Å
$V = 2161.2\,(8)$ Å^3
$Z = 8$
$D_x = 1.503$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15$–$18°$
$\mu = 1.001$ mm^{-1}
$T = 295$ K
Block
0.50 × 0.46 × 0.43 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.92$, $T_{max} = 1.00$
2671 measured reflections
2670 independent reflections

1717 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.02$
$\theta_{max} = 27.02°$
$h = -16 \rightarrow 0$
$k = 0 \rightarrow 18$
$l = -14 \rightarrow 0$
3 standard reflections frequency: 60 min intensity decay: 1.58%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.040$
$S = 2.13$
1717 reflections
128 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 2.90×10^{-7}
Atomic scattering factors from Cromer (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ti(1)	0.82442 (4)	0.17172 (5)	0.62155 (5)	2.22 (1)
Cl(1)	0.81445 (8)	0.04904 (8)	0.46413 (9)	4.43 (3)
O(1)	0.8619 (2)	0.0698 (2)	0.7237 (2)	3.49 (6)
C(1)	0.9366 (3)	0.0102 (3)	0.7524 (4)	4.81 (11)
C(2)	0.9776 (3)	0.1959 (3)	0.5565 (4)	4.71 (11)
C(3)	0.9729 (2)	0.2424 (3)	0.6648 (3)	3.51 (9)
C(4)	0.9111 (3)	0.3258 (3)	0.6581 (3)	3.68 (9)
C(5)	0.8812 (3)	0.3350 (3)	0.5447 (4)	4.66 (11)
C(6)	0.9216 (3)	0.2549 (5)	0.4832 (4)	5.40 (12)
C(7)	0.7051 (3)	0.1807 (7)	0.7592 (5)	6.64 (16)
C(8)	0.7169 (3)	0.2781 (5)	0.7202 (6)	5.98 (15)
C(9)	0.6892 (3)	0.2792 (5)	0.6074 (6)	6.40 (16)
C(10)	0.6636 (3)	0.1799 (7)	0.5801 (5)	7.26 (17)
C(11)	0.6739 (3)	0.1186 (4)	0.6741 (8)	7.31 (17)

Table 2. *Selected geometric parameters (Å, °)*

Ti(1)—O(1)	1.839 (2)	Ti(1)—*M*(1)*	2.088
Ti(1)—Cl(1)	2.412 (1)	Ti(1)—*M*(2)*	2.093
O(1)—C(1)	1.367 (4)		
Cl(1)—Ti(1)—O(1)	93.80 (9)	Cl(1)—Ti(1)—*M*(2)	106.3
O(1)—Ti(1)—*M*(1)	109.6	*M*(1)—Ti(1)—*M*(2)	130.8
O(1)—Ti(1)—*M*(2)	105.0	Ti(1)—O(1)—C(1)	141.4 (3)
Cl(1)—Ti(1)—*M*(1)	105.0		

* *M*(1) and *M*(2) are the centroids of the planes containing C(2)–C(6) and C(7)–C(11), respectively.

The structure was solved using heavy-atom Patterson methods and expanded using Fourier synthesis techniques. All non-H atoms were refined anisotropically. H atoms were located from ΔF maps but not refined. The C—H bond range is 0.94–1.21 Å with $B_{eq} = 1.2$ times that of the parent atom. Atomic scattering factors were corrected for anomalous-dispersion effects.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SAPI*91 (Yao, Zheng, Qian, Han, Gu & Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SX1010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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