

Tribromo(η^5 -1,2,3-trimethylcyclopentadienyl)-
titanium(IV)Milan Erben,^{a*} Ivana Císařová,^b
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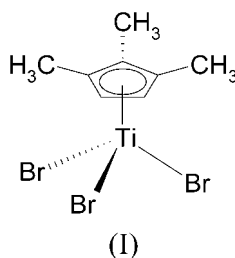
Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.026
 wR factor = 0.064
Data-to-parameter ratio = 23.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The crystal structure of the title compound, $[\text{TiBr}_3(\text{Me}_3\text{Cp})]$, where Me_3Cp is 1,2,3-trimethylcyclopentadienyl (C_8H_{11}), has been determined. The molecule has a typical piano-stool structure in which one η^5 -bonded trimethylcyclopentadienyl ring and three bromide ligands occupy the pseudo-tetrahedral coordination sites around the titanium(IV) centre. The Ti–ring distance is 2.0162 (16) Å.

Comment

Monocyclopentadienyl–titanium(IV) complexes of the general formula $\text{Cp}'\text{TiX}_3$ have been intensively studied for their catalytic activity towards olefin polymerization (Ewen, 2000). It is well known that the properties of these catalysts can be modified, both by introducing various substituents on the cyclopentadienyl ring (Cp) and by replacement of the X ligand. Kaminsky *et al.* (2002) tested the catalytic activity of a series of Cp-methylated titanium(IV) trichlorides and trifluorides and showed that replacing chlorides with fluorides can lead to higher activity. We prepared a series of $\text{Cp}'\text{TiX}_3$ (Cp' is a substituted cyclopentadienyl ring and $X = \text{Cl}, \text{Br}$ or I) half-sandwich complexes in the framework of a broad investigation of these catalytically active compounds (Erben, Ružička *et al.*, 2004). For this purpose, we have synthesized the title compound, (I), and analysed its crystal structure.



The title compound has the expected three-legged piano-stool structure (Fig. 1), where the angle between the plane defined by the three Br atoms and the Cp ring plane is 0.97 (14)°. The distance between the Ti atom and the centre of the Cp ring [2.0162 (16) Å] is slightly longer than in the corresponding chloride derivative [2.0120 (7) Å; Erben, Císařová *et al.*, 2004] and shorter than in the indenyl complex IndTiBr_3 [2.033 (4) Å; Shaw & Bollinger, 1999]. The Ti–Br distances are similar to those observed for IndTiBr_3 and significantly shorter than in the bis(cyclopentadienyl) compound Cp_2TiBr_2 [2.533 (2) and 2.5343 (18) Å; Jones & Thone, 1994]. Two of the methyl C atoms (C6 and C7) are displaced out of the Cp-ring plane, away from the titanium centre while the third methyl C atom (C8) is displaced much less (Table 1). This observation can be explained on the basis

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of the steric hindrance between Br atoms and methyl groups, where the Br1···C6 and Br2···C7 distances [3.440 (4) and 3.377 (4) Å, respectively] are shorter than the Br2···C8 distance [3.721 (4) Å].

Experimental

The title compound was prepared from Me₃CpTiCl₃ (Erben, Císařová *et al.*, 2004) and boron tribromide in dichloromethane solution. Me₃CpTiCl₃ (0.39 g, 14.9 mmol) was dissolved in dichloromethane (30 ml) and BBr₃ (0.41 g, 15.8 mmol) was added *via* a septum. The colour of the yellow–orange solution immediately changed to red. After stirring for 20 min at room temperature, the volatiles were removed in a vacuum. The resulting red solid was sublimed in a vacuum giving a dark-red product (0.57 g, 97%). Suitable crystals of (I) were obtained by sublimation at 10^{−3} Pa and 373 K. Spectroscopic analysis: ¹H NMR (CDCl₃, p.p.m.): 6.86 (s, 2H), 2.41 (s, 6H), 2.43 (s, 3H); ¹³C NMR (CDCl₃, p.p.m.): 140.1, 137.3, 123.2, 17.5, 14.7; ⁴⁹Ti NMR (CDCl₃, p.p.m., referenced to ⁴⁹TiCl₄): 49.0 (half-width: 46.4 Hz); ⁴⁷Ti NMR (CDCl₃, p.p.m., referenced to ⁴⁹TiCl₄): −218.3 (half-width: 125.6 Hz). UV–VIS (*n*-hexane, maxima at nm): 327, 437. Elemental analysis calculated for C₈H₁₁Br₃Ti: C 24.34, H 2.81%; found: C 23.97, H 2.77%.

Crystal data

[TiBr ₃ (C ₈ H ₁₁)]	Z = 2
M _r = 394.80	D _x = 2.239 Mg m ^{−3}
Triclinic, P $\bar{1}$	Mo K α radiation
a = 6.8210 (3) Å	Cell parameters from 6322 reflections
b = 8.5280 (3) Å	θ = 1–27.5°
c = 11.0770 (3) Å	μ = 10.91 mm ^{−1}
α = 92.547 (2)°	T = 150 (2) K
β = 95.901 (2)°	Prism, red
γ = 113.3971 (17)°	0.40 × 0.25 × 0.18 mm
V = 585.66 (4) Å ³	

Data collection

Nonius KappaCCD area-detector diffractometer	2681 independent reflections
ϕ and ω scans	2362 reflections with $I > 2\sigma(I)$
Absorption correction: by Gaussian integration (Coppens, 1970)	R _{int} = 0.042
T _{min} = 0.075, T _{max} = 0.301	θ_{max} = 27.5°
9260 measured reflections	h = −8 → 8
	k = −11 → 11
	l = −14 → 14

Refinement

Refinement on F ²	$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 0.5446P]$
R[F ² > 2 $\sigma(F^2)$] = 0.026	where $P = (F_o^2 + 2F_c^2)/3$
wR(F ²) = 0.064	(Δ/σ) _{max} < 0.001
S = 1.07	$\Delta\rho_{max}$ = 0.80 e Å ^{−3}
2681 reflections	$\Delta\rho_{min}$ = −0.70 e Å ^{−3}
113 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0120 (8)

Table 1

Selected geometric parameters (Å, °).

Ti1–Cg	2.0162 (16)	Ti1–Br2	2.3880 (6)
Ti1–Br1	2.3877 (6)	Ti1–Br3	2.3937 (6)
Cg–Ti1–Br1	116.04 (5)	Br1–Ti1–Br2	102.71 (2)
Cg–Ti1–Br2	114.32 (4)	Br2–Ti1–Br3	101.87 (2)
Cg–Ti1–Br3	116.61 (4)	Br3–Ti1–Br1	103.30 (2)
P _r –C3–C6	3.9 (2)	P _r –C4–C7	4.5 (2)
P _r –C5–C8	0.8 (2)		

Notes: (a) Cg is the centroid of the cyclopentadienyl ring; (b) P_r is the ring plane defined by atoms C1–C5.

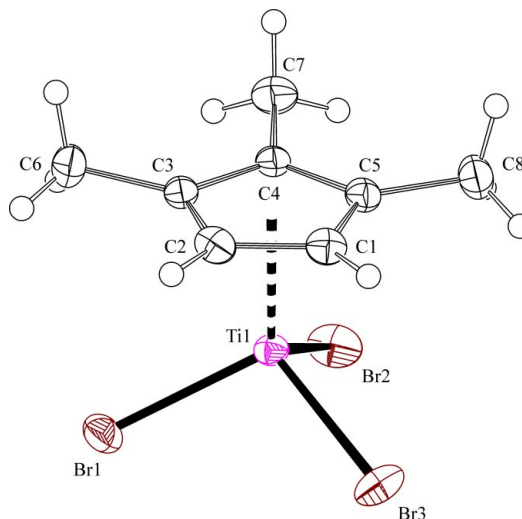


Figure 1

The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

All H atoms were positioned geometrically and refined as riding on their parent C atoms, with C–H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for cyclopentadienyl H atoms, and C–H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

Data collection: COLLECT (Hooft, 1998) and DENZO (Otwinowski & Minor, 1997); cell refinement: COLLECT and DENZO; data reduction: COLLECT and DENZO; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97.

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