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Trichloro(η^5-1,2,3-trimethylcyclopentadienyl)-titanium(IV)

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The crystal structure of the title compound, [Ti(Me$_3$Cp)Cl$_3$], where Me$_3$Cp is 1,2,3-trimethylcyclopentadienyl (C$_8$H$_{11}$), was determined as part of our investigation of monocyclopentadienyltitanium(IV) trihalides. The title compound exhibits a three-legged piano-stool geometry. The Ti—ring distance is 2.0120 (7) Å.

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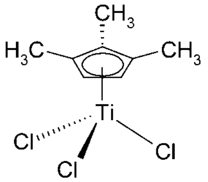
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.025
wR factor = 0.065
Data-to-parameter ratio = 22.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structure of the title compound, (I), a catalyst precursor for olefin polymerization, has been analysed.



(I)

Fig. 1 shows the η^5 coordination of the trimethyl-substituted cyclopentadienyl ring to the TiCl$_3$ moiety, which is akin to the structures of similar half-sandwich Cp′TiCl$_3$ complexes (Cp′ is a substituted cyclopentadienyl ligand).

The geometry around the Ti atom can be described as a three-legged piano-stool configuration, where the plane defined by the three Cl atoms and the plane of the cyclopentadienyl ring are almost parallel, with an angle of 0.77 (7)° between them. The distance between the Ti atom and the centre of the ring is longer than in [Ti(MeCp)Cl$_3$] [2.0042 (15) Å] and shorter than in [Ti(Me$_4$Cp)Cl$_3$] [2.0151 (17) Å] or [Ti(Me$_5$Cp)Cl$_3$] [2.0211 (7) Å] (Kirschbaum & Giolando, 1991; Pevec, 2003).

Two of the methyl C atoms, C6 and C7, are displaced slightly out of the ring plane, away from the TiCl$_3$ fragment (Table 1). The third C atom is displaced much less, with an angle of 0.34 (10)° between the ring plane and the C5—C8 bond. This fact can be attributed to the steric hindrance caused by the Cl atoms, where the Cl2$\cdots$C8 distance [3.608 (2) Å] is longer than the Cl2$\cdots$C7 and Cl3$\cdots$C6 distances [3.295 (2) and 3.340 (2) Å, respectively].

Experimental

The title compound was prepared according to the trimethylsilylation procedure of Cardoso *et al.* (1980). (1,2,3-Trimethylcyclopentadienyl)trimethylsilane, obtained from 1,2,3-trimethylcyclopentadienyllithium (Broussier *et al.*, 1997) and chlorotrimethylsilane, was reacted with titanium tetrachloride (2% excess) in toluene. After evaporation of volatiles, the resulting sticky brown product was purified by repeated vacuum sublimation, yielding 42% of a red–

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orange solid. Suitable crystals of (I) were obtained by sublimation at 10^{-3} Pa, at a temperature of 353 K. Spectroscopic analysis: ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 6.72 (*s*, 2H), 2.40 (*s*, 6H), 2.33 (*s*, 3H); ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 139.6, 137.2, 123.5, 16.2, 13.3; ^{49}Ti NMR ($CDCl_3$, δ, p.p.m,.): −225.1 (half-width 36.9 Hz); ^{47}Ti NMR ($CDCl_3$, δ, p.p.m,.): −491.4 (half-width 84.6 Hz). Elemental analysis, calculated for $C_8H_{11}Cl_3Ti$: C 36.75, H 4.24, Cl 40.68%; found: C 36.28, H 4.21, Cl 40.47%.

Crystal data

$[Ti(C_8H_{11})Cl_3]$
$M_r = 261.42$
Triclinic, $P\overline{1}$
$a = 6.6790$ (2) Å
$b = 8.3360$ (3) Å
$c = 10.7120$ (4) Å
$\alpha = 82.9070$ (19)°
$\beta = 83.340$ (2)°
$\gamma = 67.368$ (2)°
$V = 544.74$ (3) Å^3
$Z = 2$
$D_x = 1.594$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2345 reflections
$\theta = 1$–27.5°
$\mu = 1.47$ mm^{-1}
$T = 150$ (2) K
Prism, red
0.25 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: none
8461 measured reflections
2488 independent reflections
2291 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.6°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.065$
$S = 1.06$
2488 reflections
112 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 0.2233P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å,°).

Ti1—*Cg*1	2.0120 (7)	Ti1—Cl2	2.2369 (4)
Ti1—Cl1	2.2410 (5)	Ti1—Cl3	2.2412 (4)
*Cg*1—Ti1—Cl2	113.93 (3)	*Cg*1—Ti1—Cl3	115.38 (2)
Cl1—Ti1—Cl2	102.78 (2)	Cl1—Ti1—Cl3	103.30 (2)
*Cg*1—Ti1—Cl1	116.41 (3)	Cl2—Ti1—Cl3	103.31 (2)
P_r—C3—C6	3.59 (10)	P_r—C4—C7	3.18 (10)
P_r—C5—C8	0.34 (10)		

*Cg*1 is the centroid of the cyclopentadienyl ring and P_r is the ring plane defined by atoms C1–C5.

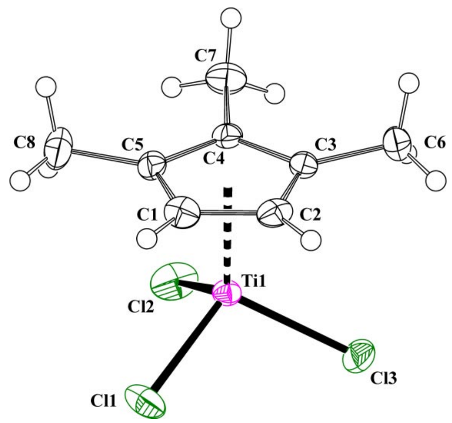

Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

All H atoms were positioned geometrically and refined 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* (Nonius, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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