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Difluoro(η^5,η^5-propane-2,2-diyldicyclopentadienyl)titanium(IV)

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Key indicators

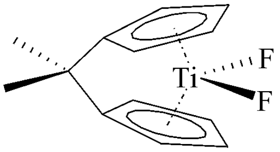
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.030
wR factor = 0.087
Data-to-parameter ratio = 16.9

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

In the title compound, $[Ti(C_{13}H_{14})F_2]$, the coordination polyhedron around the Ti atom is a distorted tetrahedron defined by the centroids of the cyclopentadienyl rings and the two F atoms. The Ti–ring centroid (Cg) distances are 2.0558 (7) and 2.0567 (8) Å. The presence of a short carbon bridge linking the cyclopentadienyl rings constrains the Cg—Ti—Cg angle to a value of 121.50 (3)°.

Comment

Metallocene complexes of general formula MX_2Cp_2 (Cp is the cyclopentadienyl ligand, M is an early transition metal, and X is a halide or an alkyl) have attracted considerable attention as a result of their applications as olefin polymerization catalysts (Alt & Köppl, 2000) and reagents for organic synthesis (Rosenthal *et al.*, 2003), and because of their biological activity (Tacke *et al.*, 2004). The physical and chemical properties of these compounds can be further modified either by changing the X ligand or by the introduction of various substituents into the cyclopentadienyl ligand. Complexes in which the two five-membered rings are attached to each other *via* an interannular bridge (*e.g.* methylene), the so-called ansa-metallocenes, are used for stereospecific polymerization of propene (Shaltout *et al.*, 1995). As a part of a broad investigation of metallocene complexes of early transition metals, the title titanium fluoride ansa-complex, $TiF_2[(C_5H_4)_2C(CH_3)_2]$, (I), has been prepared and structurally characterized (Fig. 1).



(I)

The titanium–ring centroid ($Cg1$ and $Cg2$, referring to the C1- and C6-containing rings, respectively) distances [Ti1—$Cg1$ = 2.0558 (7) Å and Ti1—$Cg2$ = 2.0567 (8) Å] are close to the value [2.0575 (14) and 2.0574 (14)Å; Koch *et al.*, 2000] found for the analogous dichloride complex $TiCl_2[(C_5H_4)_2C(CH_3)_2]$, (II). The Ti1—F bond lengths in (I), of 1.8565 (9) and 1.8648 (9) Å, are similar to those in $TiF_2[(C_5H_4)_2C_2(CH_3)_4]$ [1.8536 (13) and 1.8553 (14) Å; Edwards *et al.*, 1995].

The $Cg1$—Ti1—$Cg2$ and F1—Ti1—F2 bond angles in (I) are 121.50 (3) and 99.24 (4)°, respectively. The relatively small value of the Cg—Ti1—Cg angle in (I) compared with the equivalent angle in titanocene dichloride (131°; Clearfield *et al.*, 1975), is caused by the presence of the short 2,2-propyl-

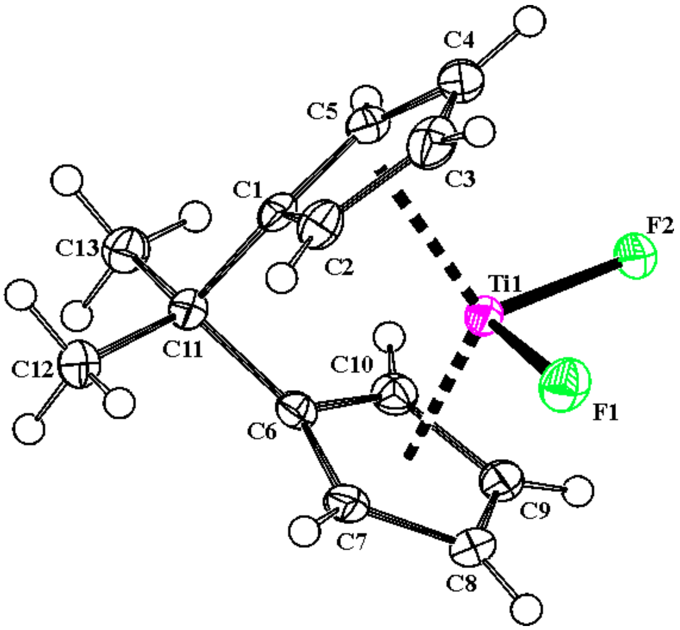


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms), with Ti—*Cg* bonds indicated by dashed lines.

idene bridge between the Cp ligands. The bond angles involving the bridging C atoms in (I) are distorted from their ideal tetrahedral values by the influence of η^5-coordination of the Cp rings to the central metal atom (Zachmanoglou *et al.*, 2002). The C1—C11—C6 and C12—C11—C13 angles are 97.16 (11) and 110.11 (13)°, respectively. The short ansa-bridge unit in (I) results in a dihedral angle of 65.76 (9)° between the mean ring planes. The Cp ring C—C bond distances in (I) are normal and no significant ring puckering was observed.

Experimental

Compound (I) was prepared from the chloride derivative (II) (Shaltout *et al.*, 1995) by reaction with Me_3SnF in toluene. Starting complex (II) (0.22 g, 0.76 mmol) was dissolved in dry toluene (60 ml) and freshly sublimed Me_3SnF (0.28 g, 1.53 mmol) was added. The suspension was stirred for 3 h at 353 K until all the Me_3SnF had been dissolved. The orange-coloured solution was then cooled to room temperature and stirred overnight. Toluene was evaporated *in vacuo* leaving a yellow solid, which was washed twice with dry hexane (20 ml) to remove Me_3SnCl and subsequently dried *in vacuo* [yield 93%, m.p. 520–540 K (decomposition)]. Upon cooling of a saturated chloroform solution to 270 K, orange crystals of (I) suitable for X-ray diffraction measurements crystallized. ^1H NMR ($CDCl_3$, p.p.m.): δ 6.55 (*s*, 4H), 5.74 (*t*, 4H), 1.97 (*s*, 6H); ^{13}C NMR ($CDCl_3$, p.p.m.): δ 128.0, 119.3, 109.8, 38.0, 24.0; IR (KBr disc, cm^{-1}): 3119 (*w*), 3096 (*m*), 3086 (*m*), 2964 (*m*), 2925 (*m*), 1274 (*m*), 1262 (*m*), 1101 (*s*), 1044 (*s*), 875 (*w*), 828 (*s*), 813 (*s*), 739 (*s*), 607 (*m*), 597 (*s*), 591 (*s*), 571 (*s*); Raman (quartz capillary, cm^{-1}): 3118 (*m*), 3111 (*s*), 3096 (*m*), 3085 (*w*), 2984 (*m*), 2958 (*w*), 2953 (*w*), 2929 (*m*), 1468 (*m*), 1391 (*m*), 1276 (*w*), 1153 (*s*), 1076 (*m*), 880 (*m*), 816 (*m*), 550 (*m*), 453 (*s*), 428 (*m*), 367 (*s*), 290 (*s*), 240 (*s*), 188 (*s*), 85 (*s*).

Crystal data

$[Ti(C_{13}H_{14})F_2]$
$M_r = 256.14$
Monoclinic, $P2_1/n$
$a = 7.9700\ (2)$ Å
$b = 14.3740\ (3)$ Å
$c = 9.5750\ (2)$ Å
$\beta = 100.3350\ (15)^\circ$
$V = 1079.12\ (4)$ Å^3
$Z = 4$
$D_x = 1.577$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2549 reflections
$\theta = 1$–27.5°
$\mu = 0.79$ mm^{-1}
$T = 150\ (2)$ K
Prism, orange
0.25 × 0.25 × 0.14 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: none
17813 measured reflections
2478 independent reflections
2163 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 27.5^\circ$
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 18$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.087$
$S = 0.99$
2478 reflections
147 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.5257P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.43$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

*Cg*1 is the centroid of the cyclopentadienyl ring C1–C5. *Cg*2 is the centroid of the cyclopentadienyl ring C6–C10. P_r1 is the ring plane defined by atoms C1–C5. P_r2 is the ring plane defined by atoms C6–C10.

Ti1—*Cg*1	2.0558 (7)	*Cg*1—Ti1—*Cg*2	121.50 (3)
Ti1—*Cg*2	2.0567 (8)	F1—Ti1—F2	99.24 (4)
Ti1—F1	1.8565 (10)	C1—C11—C6	97.15 (12)
Ti1—F2	1.8648 (9)	C12—C11—C13	110.11 (13)
P_r1—C1—C11	15.14 (10)	P_r2—C6—C11	16.31 (10)
P_r1—*Cg*1—Ti1	85.99 (7)	P_r2—*Cg*2—Ti1	86.74 (7)
P_r1—P_r2	65.76 (9)		

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