

The bis(η^5 -cyclopentadienyl)methyl-zirconium(IV) methyltris(pentafluorophenyl)borate ion pair

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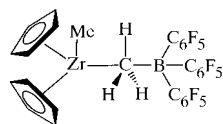
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The title complex, $[\text{Zr}(\text{CH}_3)(\text{C}_5\text{H}_5)_2][\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]$, crystallizes as an ion pair linked through an unsymmetrical methyl bridge. The bridging Zr—Me distance [2.556 (2) Å] is significantly longer than the terminal Zr—Me distance [2.251 (3) Å], while the Zr—C—B angle approaches linearity [169.1 (2)°].

Comment

Cationic zirconocene alkyl species of the general type $[(\text{C}_5\text{R}_5)_2\text{ZrR}']^+$ (C_5R_5 = cyclopentadienyl or substituted cyclopentadienyl, R' = hydrocarbyl) are the active species in $(\text{C}_5\text{R}_5)_2\text{ZrX}_2$ -based olefin polymerization catalysts (*i.e.* metallocene catalysts) (Guram & Jordan, 1995). Marks and coworkers have shown that $[(\text{C}_5\text{R}_5)_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ ion pairs can be generated by the reaction of $(\text{C}_5\text{R}_5)_2\text{ZrMe}_2$ with $\text{B}(\text{C}_6\text{F}_5)_3$ (Yang *et al.*, 1994). These ion pairs adopt methyl-bridged structures, *i.e.* $[(\text{C}_5\text{R}_5)_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$. In the course of our studies of the reactivity of $[(\text{C}_5\text{R}_5)_2\text{ZrR}']^+$ species (Dagorne *et al.*, 1997), we have crystallized $[\text{Cp}_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$, (I), which is the simplest member of this series.



(I)

Complex (I) consists of an ion pair joined through a bridging methyl group (Fig. 1). Selected bond distances and angles are presented in Table 1. The structural features of (I) are similar to those of other $[(\text{C}_5\text{R}_5)_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{H}_5)_3]$ complexes [$\text{C}_5\text{R}_5 = \eta^5\text{-C}_5\text{H}_3\text{Me}_2\text{-1,2}$, (II), $\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}$, (III), and $\eta^5\text{-C}_5\text{Me}_5$, (IV) (Yang *et al.*, 1994)]. The cation in (I) adopts a normal 'bent-sandwich' structure in which the angle between the cyclopentadienyl ligand planes is 131.1 (2)°. The Zr—Me(terminal) distance [2.251 (3) Å] is 0.303 (4) Å shorter

than the Zr—Me(bridging) separation [2.556 (2) Å], while the B—Me distance [1.667 (3) Å] is typical of a B—C σ -bond (Odom, 1982). The structure of (I) is very similar to that of (II), with the largest difference being in the Zr—C—B angle [169.10 (16) and 161.8 (2)°, respectively]. The increased bending of the Zr—C—B angle in (II) is likely due to steric interactions between the $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ anion and one of the $\text{C}_5\text{H}_3\text{Me}_2\text{-1,2}$ ligands. The Zr—Me(bridging) distance in (I) [2.556 (2) Å] is similar to that in (II) [2.549 (3) Å], but shorter than those in (III) and (IV) [2.625 (5) and 2.640 (7) Å]. Similarly, the Zr—C(Cp) distances in (I) are shorter than those in (II)–(IV) [average: 2.489 (2) in (I), 2.500 (2) in (II), 2.516 (3) in (III) and 2.537 (3) Å in (IV)]. The shorter Zr—Me and Zr—C(Cp) distances in (I) reflect the lower steric requirements of C_5H_5^- versus substituted Cp^- ligands. There are two close Zr...H contacts to the H atoms on the bridging methyl group in (I). These separations [average 2.38 (2) Å] are longer than those in (II) [average 2.24 (3) Å] and exceed the Zr...H $_{\beta}$ distance (2.16 Å) in the β -agostic complex $[(\text{MeC}_5\text{H}_4)_2\text{Zr}(\text{CH}_2\text{CH}_3)\text{PMe}_3][\text{BPh}_4]$ (Jordan *et al.*, 1990). The influence of the charge on the structure of the metallocene unit of (I) can be assessed by comparison of the structures of (I) and the neutral precursor Cp_2ZrMe_2 , (V) (Hunter *et al.*, 1983). Due to the increased electrophilic character of (I), the Zr—Me(terminal) and Zr—C(Cp) distances in (I) [2.251 (3) and average of 2.499 (15) Å, respectively] are shorter than the corresponding distances in (V) [2.277 (5) and 2.525 (12) Å]. The metric parameters for the $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ anion in (I) are very similar to those found for the anions in (II)–(IV).

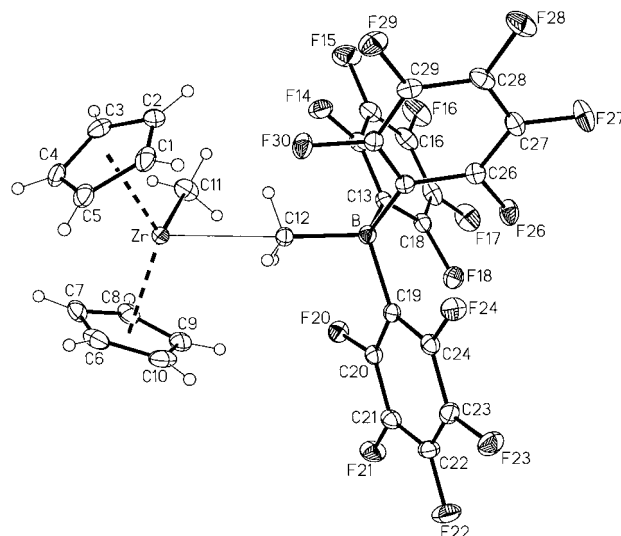


Figure 1

Perspective view of (I) with 30% probability displacement ellipsoids.

Experimental

$[\text{Cp}_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$, (I), was prepared by treatment of Cp_2ZrMe_2 (10 mg, 0.03 mmol) with $\text{B}(\text{C}_6\text{F}_5)_3$ (13 mg, 0.027 mmol) in $\text{C}_6\text{D}_5\text{Cl}$ at 298 K. Complex (I) crystallized as colorless blocks upon slow evaporation of the solvent at 233 K.

Crystal data

[Zr(CH ₃)(C ₅ H ₅) ₂](C ₁₉ H ₃ BF ₁₅)	$D_x = 1.845 \text{ Mg m}^{-3}$
$M_r = 763.46$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 5844 reflections
$a = 12.1506 (7) \text{ \AA}$	$\theta = 2-26^\circ$
$b = 15.4040 (9) \text{ \AA}$	$\mu = 0.525 \text{ mm}^{-1}$
$c = 15.5477 (9) \text{ \AA}$	$T = 183 (2) \text{ K}$
$\beta = 109.199 (1)^\circ$	Block, colorless
$V = 2748.2 (3) \text{ \AA}^3$	$0.38 \times 0.36 \times 0.32 \text{ mm}$
$Z = 4$	

Data collection

CCD area-detector diffractometer	4409 reflections with $I > 2\sigma(I)$
ϕ and ω scans	$R_{\text{int}} = 0.021$
Absorption correction: empirical (SADABS; Blessing, 1995)	$\theta_{\text{max}} = 26.37^\circ$
$T_{\text{min}} = 0.826$, $T_{\text{max}} = 0.850$	$h = -15 \rightarrow 14$
13 008 measured reflections	$k = -18 \rightarrow 18$
5534 independent reflections	$l = -19 \rightarrow 19$
	Intensity decay: <1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.0434P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.002$	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
5534 reflections	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$
488 parameters	
All H-atom parameters refined	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cnt1 and *Cnt2* are the centroids of the C1–C5 and C6–C10 rings, respectively.

Zr– <i>Cnt1</i>	2.195 (2)	Zr–C11	2.251 (3)
Zr– <i>Cnt2</i>	2.198 (2)	Zr–C12	2.556 (2)
<i>Cnt1</i> –Zr– <i>Cnt2</i>	131.1 (9)	<i>Cnt2</i> –Zr–C11	104.0 (8)
<i>Cnt1</i> –Zr–C11	103.8 (8)	<i>Cnt2</i> –Zr–C12	110.0 (9)
<i>Cnt1</i> –Zr–C12	110.5 (9)	C11–Zr–C12	87.70 (9)

The C–H distances are in the range 0.86 (3)–1.00 (2) \AA and U_{iso} values for H atoms range from 0.031 (6) to 0.074 (10) \AA^2 .

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SHELXTL (Sheldrick, 1997a); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997b); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1249). Services for accessing these data are described at the back of the journal.

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