metal-organic papers

Dibromo(η^5,η^5-propane-2,2-diyldicyclopentadienyl)zirconium(IV)

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The title compound, [ZrBr$_2$(C$_{13}$H$_{24}$)], contains a pseudo-tetrahedral Zr^{IV} centre involving two η^5-bonded cyclopentadienyl rings [Zr—Cg = 2.1843 (12) Å; Cg is the centroid of a cyclopentadienyl ring] and two Br atoms [Zr—Br = 2.5828 (5) and 2.5879 (6) Å]. The angle $Cg1$—Zr—$Cg2$ is constrained to a value of 116.80 (5)° due to the presence of a short interannular 2,2-propylidene bridge. The Zr and Br atoms lie on a crystallographic mirror plane, which bisects the organic ligand.

Comment

Zirconocene complexes are broadly investigated as efficient olefin polymerization (Lee *et al.*, 2004) and co-polymerization catalysts (Jung *et al.*, 2005) or as very selective reagents in organic syntheses (Pool & Chirik, 2005). Both chemical and physical properties of these compounds can be easily modified by substitution at the cyclopentadienyl rings and many ring-substituted zirconocenes have been described. Incorporation of an interannular bridge connecting both cyclopentadienyl ligands leads to a broad class of complexes known as ansa-metallocenes. As part of an investigation of the influence of ring substitution on the properties of cyclopentadienyl complexes, the title compound, (I), was prepared, characterized spectroscopically and its structure determined

(I)
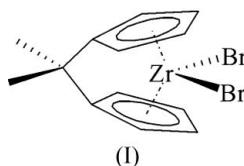
Compound (I) crystallizes in the space group $P2_1/m$. The molecule adopts C_s symmetry, with atoms C6–C8, Br1, Br2 and Zr1 located on a mirror plane bisecting the molecule. The bond distance Cg—Zr1 [2.1843 (12) Å; Cg is the centroid of the cyclopentadienyl ring] is similar to the value of 2.1914 (11) Å found in the analogous dichloro derivative [ZrCl$_2$(C$_{13}$H$_{24}$)] (Koch *et al.*, 2000). The Zr—Br distances [2.5828 (5) and 2.5879 (6) Å] are slightly shorter than those in dibromozirconocene, [ZrBr$_2$(C$_5$H$_5$)$_2$] [2.610 (3) and 2.611 (3) Å]. The angle $Cg1$—Zr1—$Cg2$ [116.80 (5)°] is significantly smaller than that observed in dibromo-zirconocene [129.3 (3) Å; Buhl *et al.*, 1996]. The most remarkable feature of the structure of (I) is the distortion of the bond angle C1—C6—C1($x, \frac{1}{2} - y, z$) to a value of 99.7 (3)°. These structural features are presumably due to the steric effect relating to the presence of the 2,2-propylidene bridge between the Cp ligands.
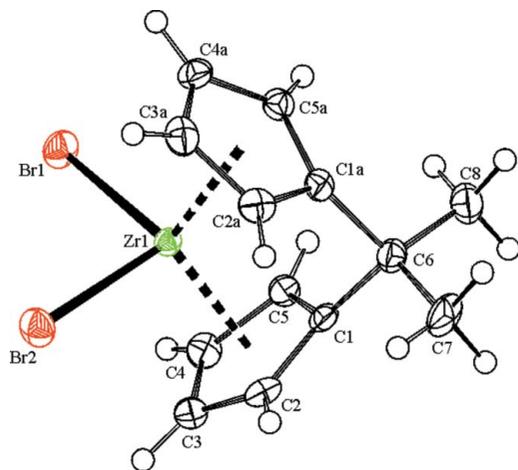
Figure 1
Perspective view of (I), shown with 50% probability displacement ellipsoids. [Symmetry code: (a) $x, \frac{1}{2} - y, z$.]

When the structural parameters of (I) and its dichloro analogue (Koch *et al.*, 2000) are compared, it is clear that replacing chloride with bromide ligands does not significantly affect the structure of the $[Zr(C_{13}H_{24})]^{2+}$ unit.

Experimental

Complex (I) was prepared by the reaction of the dichloro analogue (Nifant'ev & Ivchenko, 1997) with boron tribromide in dichloromethane. $[ZrCl_2(C_{13}H_{24})]$ (240 mg, 0.72 mmol) was dissolved in dichloromethane (20 ml) and boron tribromide (0.05 ml, 0.53 mmol) was added *via* a septum. The reaction mixture was stirred for 2 h at 298 K and the solvent was evaporated *in vacuo*. The solid residue was washed with pentane, dried in a vacuum and subsequently sublimed at 10^{-3} Pa and 450–470 K, yielding 260 mg (86%) of (I). Crystallization from hot chloroform yielded green crystals of (I) suitable for X-ray diffraction measurements. ^{1}H NMR (CDCl$_3$): δ 6.83 (*m*, 4H), 5.75 (*m*, 4H), 1.77 (*s*, 6H); ^{13}C NMR (CDCl$_3$): δ 123.2, 120.6, 106.9, 37.5, 23.9; IR (KBr disc, cm^{-1}): 3116 (*m*), 3081 (*m*), 1473 (*s*), 1457 (*m*), 1411 (*vs*), 1385 (*m*), 1371 (*m*), 1264 (*vs*), 1150 (*m*), 1079 (*s*), 1058 (*m*), 1043 (*vs*), 944 (*m*), 909 (*m*), 886 (*m*), 874 (*vs*), 868 (*s*), 835 (*s*), 819 (*vs*), 801 (*vs*), 748 (*vs*), 714 (*s*), 607 (*w*), 546 (*m*), 451 (*s*), 401 (*s*), 332 (*s*); UV–Vis (CH$_2$Cl$_2$, maxima at nm): 397, 305, 235.

Crystal data

$[ZrBr_2(C_{13}H_{14})]$	$D_x = 2.107$ Mg m^{-3}
$M_r = 421.28$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 7302
$a = 7.3360$ (3) Å	reflections
$b = 8.7470$ (4) Å	$\theta = 1–27.5°$
$c = 10.3500$ (3) Å	$\mu = 6.82$ mm^{-1}
$\beta = 90.763$ (2)°	$T = 150$ (2) K
$V = 664.08$ (5) Å^3	Needle, green
$Z = 2$	$0.14 \times 0.05 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	1635 independent reflections
φ and ω scans	1421 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian (Coppens, 1970)	$R_{int} = 0.056$
	$\theta_{max} = 27.5°$
$T_{min} = 0.398$, $T_{max} = 0.759$	$h = -9 \rightarrow 9$
11528 measured reflections	$k = -11 \rightarrow 11$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$+ 0.607P]$
$wR(F^2) = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
1635 reflections	$\Delta\rho_{max} = 0.81$ e Å^{-3}
82 parameters	$\Delta\rho_{min} = -0.73$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °)..

Zr1—Cg1	2.1843 (12)	Cg1—Zr1—Cg2	116.80 (5)
Zr1—Cg2	2.1843 (12)	Br1—Zr1—Br2	100.53 (2)
Zr1—Br1	2.5828 (5)	C1—C6—C1^i	99.7 (3)
Zr1—Br2	2.5879 (6)	C7—C6—C8	109.3 (4)
P_r1—C1—C6	14.34 (19)	P_r1—Cg1—Zr1	86.11 (12)
P_r1—P_r2	70.97 (17)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$. Cg1 and Cg2 are the centroids of the C1–C5 and C1^i–C5^i cyclopentadienyl rings, respectively; P_r1 is the ring plane defined by atoms C1–C5; (c) P_r2 is the ring plane defined by atoms C1^i–C5^i.

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* (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: *enCIFer* (Allen *et al.*, 2004).

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