

The *ansa*-zirconocene [bis(η^5 -cyclopentadienyl)phenylphosphine]-dichloridozirconium(IV)

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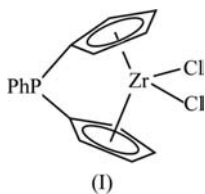
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In the title compound, $[\text{Zr}(\text{C}_{16}\text{H}_{13}\text{P})\text{Cl}_2]$, the geometry at the metal atom is distorted tetrahedral; the Cl—Zr—Cl angle is $101.490(16)^\circ$ and the cyclopentadienyl (Cp) centroids subtend an angle of $122.63(3)^\circ$ at the Zr atom. The P atom lies $0.474(3)$ and $0.496(3)$ Å out of the planes of the Cp rings. The C—P—C angle of $91.42(7)^\circ$ reflects the pincer effect of the two Cp rings. Three C—H \cdots Cl, one C—H \cdots P, one C—H \cdots π and one Cl \cdots P interaction link the molecules to form thick layers parallel to the *bc* plane.

Comment

Phosphorus-bridged *ansa*-metallocenes have attracted considerable interest as precursors for olefin polymerization catalysts. Anderson & Lin (1987, 1988) reported the synthesis of the title *ansa*-compound $[\text{PhP}(\eta^5\text{-C}_5\text{H}_4)_2]\text{ZrCl}_2$, (I). We are interested in novel donor-functionalized cycloheptatrienyl-cyclopentadienyl zirconium sandwich compounds, using zirconocenes as starting materials (Büschel *et al.*, 2009; Tamm, 2008; Tamm *et al.*, 2010). During these studies, we accidentally obtained single crystals of (I) that were suitable for X-ray diffraction studies. The molecular structure of (I) in the solid state is shown in Fig. 1.



The two Cl ligands and the centroids of the two cyclopentadienyl (Cp) ligands in (I) adopt a distorted tetrahedral arrangement about the Zr atom due to the presence of a PhP moiety as the bridging unit between the two carbocyclic fragments. The angle α subtended by the Cp centroids at the

metal atom is $122.63(3)^\circ$. The angle β between the Cp ring normals is $116.3(1)^\circ$, resulting in a value of 3.2° for the tilt angle γ [$\gamma = (\alpha - \beta)/2$]; the angles α , β and γ , which describe the bending of the *ansa*-zirconocene compound in more detail, are defined graphically in the second scheme, taken from Shin *et al.* (1999). As the tilt angle increases, the metal atom is displaced further towards the *ansa* bridge. The Cl1—Zr—Cl2 angle is $101.490(16)^\circ$, and the Zr—Cl bond lengths are $2.4224(4)$ and $2.4316(4)$ Å. The deviation from a symmetric η^5 -coordination towards a η^3 -coordination mode, associated with the tilting, is indicated by a range of 0.111 Å for the individual Zr—C_{Cp} bond lengths [$2.454(1)$ – $2.565(1)$ Å]. Distortion involving the P atom is also observed; it lies $0.474(3)$ Å out of the plane of the ring C1—C5 and $0.496(3)$ Å out of the plane of the ring C6—C10. The C6—P1—C1 angle, at $91.42(7)^\circ$, is considerably narrowed by the pincer effect of the two Cp rings [*cf.* C11—P1—C6 = $106.40(8)^\circ$ and C11—P1—C1 = $100.40(8)^\circ$].

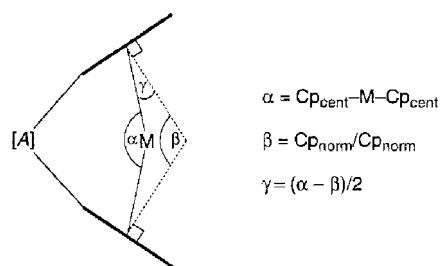


Table 2 collates related data for the compounds $[\text{PhP}(\text{C}_5\text{Me}_4)_2]\text{ZrCl}_2$, (II) (Shin *et al.*, 1999), and $[\text{MeP}(\text{C}_5\text{H}_4)_2]\text{ZrCl}_2$, (III) (Häp *et al.*, 1999). The closely related compound $[\text{MeP}(\text{C}_5\text{Me}_4)_2]\text{ZrCl}_2$ (Shin *et al.*, 1999) must be omitted from a detailed comparison because it suffers from disorder. Inspection of the supplementary material reveals that the reported space group is *C2/c*, with the Zr and P atoms lying on a twofold axis, and the methyl C atom is therefore disordered over two sites; the C_{Cp}—P—C_{Cp} angle seems improbably large at 107.8° . For comparison with systems lacking the bridging atom, the compound Cp_2ZrCl_2 , (IV), may be used, but the structure suffers somewhat from high *U* values (Corey *et al.*, 1995) of the Cp rings. Some more recent redeterminations at

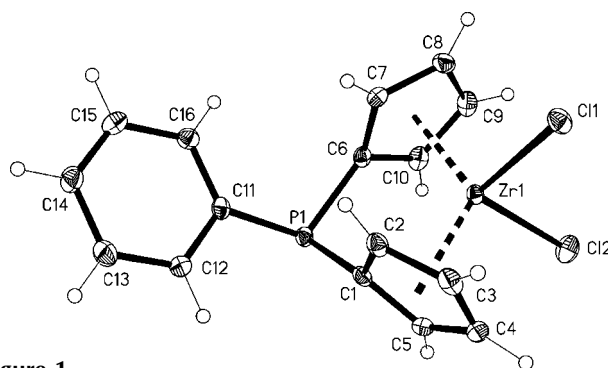


Figure 1
The molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

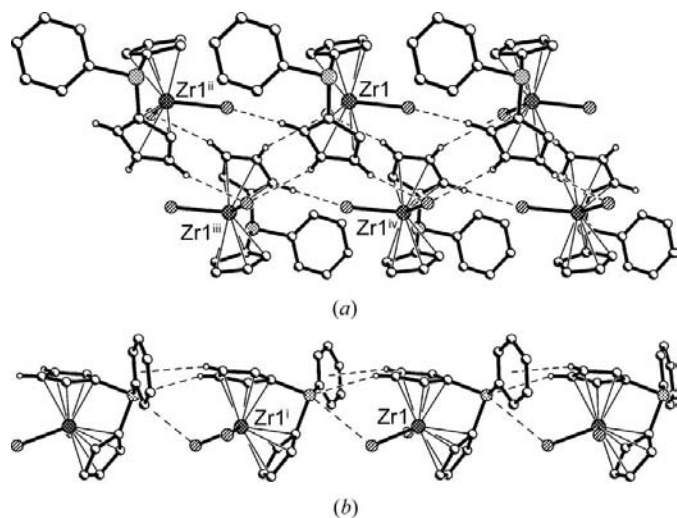


Figure 2
Packing diagrams for (I). (a) The three C—H...Cl contacts (thin dashed lines) connect the molecules to form double chains parallel to the *b* axis. The origin is at the bottom right, the *c* axis out of the paper, the *a* axis vertical and the *b* axis from right to left. (b) The three contacts C—H...P, C—H... π and Cl1...P (thin dashed lines) connect the molecules to form chains parallel to the *c* axis. The origin is at the bottom left, the *b* axis out of the paper, the *a* axis approximately vertical and the *c* axis from left to right. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. The symmetry codes are as in Table 1.

lower temperature can be found in the Cambridge Structural Database (Version 1.11; Allen, 2002), but suffer from various imperfections such as a lack of s.u. values. The complex Cp^*ZrCl_2 , (V) (Böhme & Rittmeister, 1998), is also adduced.

Table 2 indicates that the β angles are almost identical for all three compounds (I)–(III), so that the relative disposition of the Cp rings is also closely similar. Indeed, all three bending angles are very similar in (I) and (III). However, the α angle is significantly smaller in (I) than in (II), necessarily leading to a more pronounced tilting. The γ angle is largest for (II), also reflected in a larger deviation of (II) from a symmetric η^5 -coordination towards a η^3 -coordination mode [the range of Zr—C_{Cp} distances for (II) is 0.173 Å]. The Cl1—Zr—Cl2 angle in (I) [101.490 (19)°] is appreciably larger than that in (III), perhaps reflecting the differing spatial demands of methyl and phenyl groups at P, but the Zr—Cl bond lengths of both compounds are similar.

The unbridged complexes (IV) and (V), as expected, display larger values of α and (especially) β , somewhat lower Cl—Zr—Cl bond angles and a smaller range of Zr—C_{Cp} bond lengths, corresponding to more symmetric coordination of the Cp rings.

As would be expected, there are no unusually short intermolecular contacts in (I). Four weak hydrogen bonds are given in Table 1, of which we regard the H3...P1 interaction as borderline. There is also a C—H... π contact to the centroid of the phenyl ring, and finally a short Cl1...P1ⁱⁱⁱ contact of 3.5064 (7) Å (symmetry code as in Table 1). The molecules are connected by all these interactions to form thick layers parallel to the *bc* plane at $x \simeq \frac{1}{4}$ and $\frac{3}{4}$. However, the general view of such a layer is too complex to be useful. We therefore

present two separate packing diagrams. Fig. 2(a) shows that the three H...Cl contacts link the molecules to form double chains parallel to the *b* axis, whereas the other three contacts (Fig. 2b) form chains parallel to the *c* axis.

Experimental

The title *ansa*-zirconocene, (I), first synthesized by Anderson & Lin (1987, 1988), was obtained as a by-product during the attempted synthesis of a P-functionalized zirconocene. (LiC_5H_4)₂PPh (303 mg, 1.2 mmol) and ZrCl_4 (565 mg, 2.4 mmol; 2 equivalents) were placed in a Schlenk flask. Toluene (60 ml) was added and the mixture was cooled to 213 K, followed by the addition of tetrahydrofuran (1 ml). After warming to room temperature overnight, the yellow suspension was filtered through a plug of Celite. The solvent was removed *in vacuo* until approximately 3 ml remained. A yellow solid precipitated and was filtered off. The filtrate was cooled to 248 K. After 2 d, yellow crystals of (I) suitable for X-ray diffraction analysis were obtained.

Crystal data

$[\text{Zr}(\text{C}_{16}\text{H}_{13}\text{P})\text{Cl}_2]$	$V = 3038.44 (12) \text{ \AA}^3$
$M_r = 398.35$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 27.2712 (6) \text{ \AA}$	$\mu = 1.17 \text{ mm}^{-1}$
$b = 7.3272 (2) \text{ \AA}$	$T = 100 \text{ K}$
$c = 15.4592 (3) \text{ \AA}$	$0.16 \times 0.10 \times 0.07 \text{ mm}$
$\beta = 100.389 (2)^\circ$	

Data collection

Oxford Diffraction Xcalibur E diffractometer	31688 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	4641 independent reflections
$T_{\min} = 0.970$, $T_{\max} = 1.000$	3627 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	181 parameters
$wR(F^2) = 0.053$	H-atom parameters constrained
$S = 0.91$	$\Delta\rho_{\max} = 0.50 \text{ e \AA}^{-3}$
4641 reflections	$\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

C_g is the centroid of the C11–C16 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C9—H9...Cl1 ⁱ	0.95	2.84	3.7649 (18)	165
C8—H8...Cl1 ⁱⁱ	0.95	2.99	3.7520 (18)	138
C3—H3...P1 ⁱⁱⁱ	0.95	3.05	3.8416 (18)	142
C7—H7...Cl2 ^{iv}	0.95	2.92	3.7775 (18)	151
C4—H4...C _g ⁱⁱⁱ	0.95	2.80	3.656	150

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (iii) $x, -y + 1, z - \frac{1}{2}$; (iv) $x, y + 1, z$.

H atoms were introduced at calculated positions and refined using a riding model, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Table 2

 Selected dimensions (\AA , $^\circ$) of (I) and related structures.

 For references and definitions of angles, see *Comment*. Values not given explicitly in the original references were extracted or calculated from deposited material; s.u. values are thus not universally available. Cg is the centroid of a cyclopentadienyl (Cp) ring.

Compound	α	Cl–Zr–Cl	Zr–Cl	β	γ	Zr–Cg	Zr–C	Deviation of P from the Cp plane	C _{Cp} –P–C _{Cp}
(I)	122.63 (3)	101.490 (16)	2.4224 (4), 2.4316 (4)	116.3 (1)	3.2	2.2011 (8), 2.1919 (8)	2.454 (1)–2.565 (1), range 0.111	0.474 (3), 0.496 (3)	91.42 (7)
(II)	125.9	99.66 (8)	2.421 (2), 2.443 (2)	116.5	4.7	2.227, 2.223	2.435–2.608, range 0.173	0.528, 0.466	93.6
(III)	122.21	97.72 (3)	2.4374 (8), 2.4213 (7)	116.3	3.0	2.1981, 2.1957	2.465–2.551, range 0.086	0.406, 0.417	89.8
(IV)	126.3	95.4	2.462	130.9		2.262	2.512–2.579, range 0.067		
(V)	129.6, 129.5	97.0 (1), 97.1 (1)	2.444 (1)–2.450 (1)	126.7, 126.5		2.200–2.208	2.458–2.521, range 0.063		

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3332). Services for accessing these data are described at the back of the journal.

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