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Note

Synthesis and structure of $Zr_2Cl_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$, an arene complex of zirconium(II)

F.A. Cotton* and W.A. Wojtczak

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843 (USA)

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Abstract

The title compound consists of two identical subunits, $(PMe_2Ph)Cl_2Zr(\eta^6\text{-}C_6H_5PMe_2)$, connected by the coordination of the phosphorus atom of each $(\eta^6\text{-}C_6H_5PMe_2)$ moiety to the zirconium atom of the other. There are two crystallographically distinct molecules, each on a $\bar{1}$ position, in the unit cell. In each a pyramidal *trans*-ZrP_2Cl_2 unit has an η^6-arene ring opposite and approximately parallel to the mean plane of the P_2Cl_2 set of atoms. The crystals are isotypic to those of the previously reported $Hf_2Br_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$. They are triclinic, $P\bar{1}$ with $a=9.172(2)$, $b=13.710(2)$, $c=15.458(1)$ Å, $\alpha=101.47(1)$, $\beta=91.74(1)$, $\gamma=98.21(1)°$, $V=1882.1(4)$ Å^3, $Z=2$. The Zr to carbon distances are in the range 2.29–2.52 Å, the mean Zr–Cl distance is 2.506[12] Å and the Zr–P distances are in the range 2.759(2)–2.771(2) Å.

Key words: Crystal structures; Zirconium complexes; Arene complexes

Introduction

A couple of years ago work in this laboratory was reported showing that the compounds $Zr_2I_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ and $Hf_2Br_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ can be prepared, and giving their structure and a description of the bonding [1]. We have carried out one more study to show that the same type of compound can be obtained even with the commonest Group 4 starting material, $ZrCl_4$.

Experimental

All manipulations were carried out under an argon atmosphere by using standard vacuum-line and Schlenk techniques. The solvents were freshly distilled under nitrogen from the appropriate drying reagent. $ZrCl_4$ and PMe_2Ph were purchased from Strem Chemicals, Inc. and used as received.

TABLE 1. Crystal data for $Zr_2Cl_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$

Formula	$Zr_2Cl_4P_4C_{32}H_{44}$
Formula weight	876.9
Space group	$P\bar{1}$ (No. 2)
Systematic absences	none
a (Å)	9.172(2)
b (Å)	13.710(2)
c (Å)	15.458(1)
α (°)	101.47(1)
β (°)	91.74(1)
γ (°)	98.21(1)
V (Å^3)	1882.1(4)
Z	2
D_{calc} (g/cm^3)	1.547
Crystal size (mm)	$0.10\times0.20\times0.15$
$\mu(K\alpha)$ (cm^{-1})	91.13 (Cu)
Data collection instrument	Rigaku AFC5R
Radiation monochromated (Å)	Cu Kα (1.54184)
Orientation reflections: no., range	25, $44\leqslant2\theta\leqslant58$
Temperature (°C)	21(±2)
Scan method	ω–2θ
Data collection range, 2θ (°)	$4\leqslant2\theta\leqslant115$
No. unique data, total with $F_o^2>3\sigma(F_o^2)$	4920, 3539
No parameters refined	379
Transmission factors: max., min.	1.000, 0.5361
R^a	0.04763
R_w^b	0.06676
Quality-of-fit indicator^c	1.291
Largest shift/e.s.d., final cycle	0.01
Largest peak (e/Å^3)	0.505

$^aR=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bR_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit$=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

Synthesis of $Zr_2Cl_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$

$ZrCl_4$ (0.233 g, 1.0 mmol), PMe_2Ph (0.29 ml, 2.04 mmol) and 2.0 M Na/Hg (1.2 ml, 2.4 mmol) were stirred vigorously in 20 ml of toluene. After 36 h of stirring the brown reaction solution was filtered through Celite (2 cm) into a Schlenk tube and layered with hexanes (30 ml). Crystallization occurred over a 2 week period with the appearance of small brown plates. The crystals were isolated by decantation. Yield *c.* 233 mg (26.6%).

X-ray crystallography

Crystal structure of $Zr_2Cl_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$

A small crystal ($0.10\times0.20\times0.15$ mm) was wedged inside a Lindemann capillary tube that had been previously purged with argon. The capillary was filled with

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*Author to whom correspondence should be addressed.

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TABLE 2. Positional and equivalent isotropic displacement parameters and their e.s.d.s for $Zr_2Cl_4(PMe_2Ph)_4$

Atom	x	y	z	B_{eq} (Å^2)
Zr(a)	0.30384(7)	0.96868(5)	0.85959(4)	3.24(1)
Cl(1a)	0.4936(2)	0.8770(2)	0.7817(1)	4.60(5)
Cl(2a)	0.0742(2)	0.8438(2)	0.8585(2)	4.80(5)
P(1a)	0.3669(2)	0.8737(2)	0.9947(1)	3 09(4)
P(2a)	0.2163(2)	0.9438(2)	0.6826(2)	3.73(5)
C(11a)	0.346(1)	0.7364(7)	0 9508(7	5.5(3)
C(12a)	0.2386(9)	0.8864(7)	1.0835(6)	4.8(2)
C(13a)	0.5458(8)	0.8977(6)	1.0536(5)	3.2(2)
C(14a)	0.6765(9)	0.9013(6)	1.0012(6)	3.6(2)
C(15a)	0.8145(8)	0.9021(7)	1.0388(6)	3.9(2)
C(16a)	0.8319(9)	0.8998(7)	1.1313(6)	4.2(2)
C(17a)	0.7014(9)	0.8593(6)	1.1722(6)	4.0(2)
C(18a)	0.5623(9)	0.8596(6)	1.1364(5)	3.7(2)
C(21a)	0.357(1)	0.9900(8)	0.6122(6)	5.6(2)
C(22a)	0.165(1)	0 8089(8)	0.6325(7)	6.0(3)
C(23a)	0.0561(9)	0.9996(7)	0.6560(5)	3.8(2)
C(24a)	0.068(1)	1 0804(7)	0.6142(6)	4.7(2)
C(25a)	−0.057(1)	1.1256(8)	0.6028(7)	5.5(3)
C(26a)	−0.193(1)	1.0891(9)	0.6299(7)	5.9(3)
C(27a)	−0.206(1)	1.0048(9)	0.6694(7)	5.9(3)
C(28a)	−0.082(1)	0.9616(8)	0.6826(6)	5.2(2)
Zr(b)	0.38203(7)	0.52128(5)	0.34393(4)	3.49(1)
Cl(1b)	0.1962(2)	0.6010(2)	0.4377(2)	5.35(6)
Cl(2b)	0.5184(3)	0.6541(2)	0.2725(2)	5.90(6)
P(1b)	0.5842(2)	0.6324(2)	0.4765(1)	3.45(5)
P(2b)	0.1579(3)	0.5276(2)	0.2229(2)	3.99(5)
C(11b)	0.559(1)	0.7652(7)	0.4941(7)	5.7(3)
C(12b)	0.778(1)	0.6366(9)	0.4468(6)	5.7(3)
C(13b)	0.5868(9)	0.6086(6)	0.5867(5)	3.7(2)
C(14b)	0.7133(9)	0.6570(6)	0.6509(6)	3.9(2)
C(15b)	0.708(1)	0.6564(7)	0.7388(7)	4.9(2)
C(16b)	0.578(1)	0.6088(7)	0.7727(6)	4.7(2)
C(17b)	0.442(1)	0.5970(8)	0.7168(6)	4.7(2)
C(18b)	0.4452(9)	0.5957(7)	0.6291(6)	4.1(2)
C(22b)	0.136(1)	0.6593(8)	0.2234(8)	6.3(3)
C(21b)	−0.028(1)	0.468(1)	0 2440(8)	6.7(3)
C(23b)	0.1767(9)	0.4757(7)	0 1082(6)	4.0(2)
C(24b)	0.287(1)	0.5221(8)	0 0622(6)	5.2(2)
C(25b)	0.311(1)	0.4798(9)	−0.0259(6)	5 9(3)
C(26b)	0.225(1)	0.3903(8)	−0.0690(7)	5 6(2)
C(27b)	0.117(1)	0.3419(8)	−0.0246(7)	5.7(3)
C(28b)	0.089(1)	0.3863(7)	0.0640(7)	5.1(2)

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: (4/3)-$[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

dried and degassed mineral oil, sealed at both ends with epoxy cement, and placed on the goniometer head of a Rigaku AFC5R diffractometer. Unit cell parameters were obtained by centering and indexing 25 randomly found reflections, refined by centering 25 reflections in the range $44 \leqslant 2\theta \leqslant 58$, and verified by axial photography. Three standard reflections were checked after every 250 intensity measurements, which showed no obvious change in crystal orientation, but a total of 34.1% decay during the data collection. The intensity data were corrected for Lorentz and polarization effects, anisotropic decay, and an empirical absorption correction based on azimuthal scans of seven reflections with their χ angles near 90°. The $R_{\rm int}$ for averaging equivalent intensity data was 0.0223. Since the $Zr_2Cl_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ structure is isotypic with that of $Hf_2Br_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$, the starting positions of the atoms were taken from the hafnium complex [1]. The final difference Fourier map was featureless with a highest peak height of 0.505 e/Å^3. The crystal data are listed in Table 1. Atomic positional parameters are given in Table 2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were omitted from the refined model.

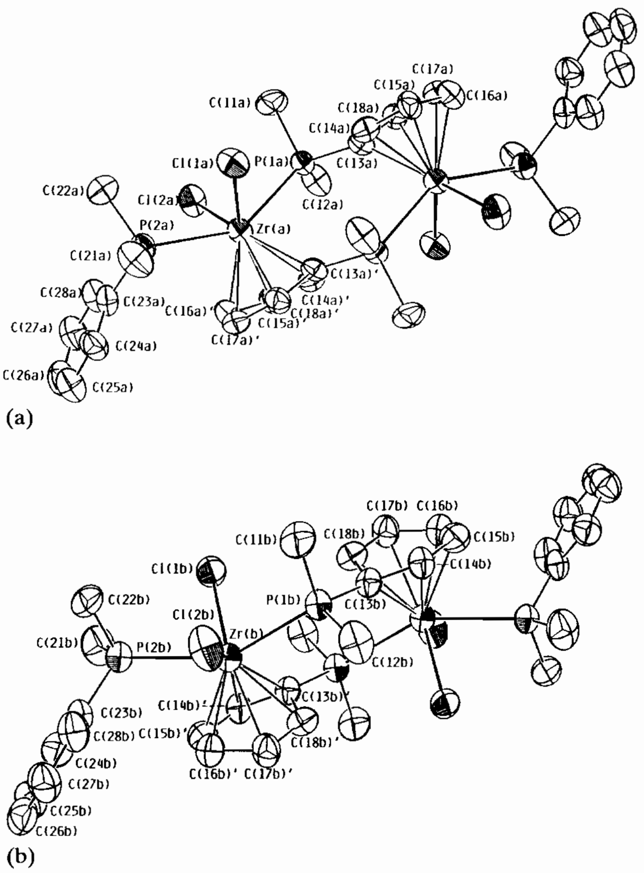

Fig. 1. (a) A side view of molecule **a**, (b) the same view of molecule **b**. Atoms are represented by their ellipsoids at the 50% level.

Results and discussion

There are two crystallographically distinct but virtually identical molecules, each residing on a center of inversion. These are shown with their atomic numbering schemes in Fig. 1 and the more important bond distances and angles are listed in Table 3.

The title compound is isotypic with the previously reported compound, $Hf_2Br_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$.

TABLE 3. Selected listing of bond distances (Å) and angles (°) for $Zr_2Cl_4(PMe_2Ph)_4$

Bond dıstances (Å)					
Zr(a)–Cl(1a)	2.491(2)	P(2a)–C(23a)	1.823(9)	Zr(b)–C(17b)′	2.52(1)
Zr(a)–Cl(2a)	2.515(2)	C(13a)–C(14a)	1.47(1)	Zr(b)–C(18b)′	2.492(9)
Zr(a)–P(1a)	2.760(2)	C(13a)–C(18a)	1.49(1)	P(1b)–C(11b)	1.84(1)
Zr(a)–P(2a)	2.768(2)	C(14a)–C(15a)	1.37(1)	P(1b)–C(12b)	1.842(9)
Zr(a)–C(13a)′	2.290(7)	C(15a)–C(16a)	1.44(1)	P(1b)–C(13b)	1.798(9)
Zr(a)–C(14a)′	2.490(8)	C(16a)–C(17a)	1.46(1)	P(2b)–C(22b)	1.84(1)
Zr(a)–C(15a)′	2.516(8)	C(17a)–C(18a)	1.38(1)	P(2b)–C(21b)	1.85(1)
Zr(a)–C(16a)′	2.32(1)	Zr(b)–Cl(1b)	2.500(3)	P(2b)–C(23b)	1.798(8)
Zr(a)–C(17a)′	2.509(9)	Zr(b)–Cl(2b)	2.517(3)	C(13b)–C(14b)	1.49(1)
Zr(a)–C(18a)′	2.484(8)	Zr(b)–P(1b)	2.771(2)	C(13b)–C(18b)	1.48(1)
P(1a)–C(11a)	1.850(9)	Zr(b)–P(2b)	2.759(2)	C(14b)–C(15b)	1.36(1)
P(1a)–C(12a)	1.833(9)	Zr(b)–C(13b)′	2.299(9)	C(15b)–C(16b)	1.44(1)
P(1a)–C(13a)	1.807(8)	Zr(b)–C(14b)′	2.494(9)	C(16b)–C(17b)	1.46(1)
P(2a)–C(21a)	1.84(1)	Zr(b)–C(15b)′	2.524(9)	C(17b)–C(18b)	1.35(1)
P(2a)–C(22a)	1.84(1)	Zr(b)–C(16b)′	2.348(9)		
Bond angles (°)					
Cl(1a)–Zr(a)–Cl(2a)	108.02(8)	P(1a)–C(13a)–C(14a)	117.6(6)	C(11b)–P(1b)–C(12b)	102.7(5)
Cl(1a)–Zr(a)–P(1a)	84.38(7)	P(1a)–C(13a)–C(18a)	118.9(6)	C(11b)–P(1b)–C(13b)	103.0(4)
Cl(1a)–Zr(a)–P(2a)	76.43(7)	C(14a)–C(13a)–C(18a)	115.3(7)	C(12b)–P(1b)–C(13b)	104.3(4)
Cl(2a)–Zr(a)–P(1a)	76.95(7)	C(13a)–C(14a)–C(15a)	121.1(8)	Zr(b)–P(2b)–C(22b)	110.1(3)
Cl(2a)–Zr(a)–P(2a)	82.46(7)	C(14a)–C(15a)–C(16a)	119.7(8)	Zr(b)–P(2b)–C(21b)	115.8(4)
P(1a)–Zr(a)–P(2a)	145.86(7)	C(15a)–C(16a)–C(17a)	116.8(7)	Zr(b)–P(2b)–C(23b)	118.4(3)
P(1a)–Zr(a)–C(13a)′	82 8(2)	C(16a)–C(17a)–C(18a)	120.4(8)	C(22b)–P(2b)–C(21b)	103.9(6)
Zr(a)–P(1a)–C(11a)′	109.1(4)	C(13a)–C(18a)–C(17a)	119.4(8)	C(22b)–P(2b)–C(23b)	103.4(5)
Zr(a)–P(1a)–C(12a)′	114.0(3)	P(2a)–C(23a)–C(24a)	121.9(6)	C(21b)–P(2b)–C(23b)	103.6(4)
Zr(a)–P(1a)–C(13a)′	122.5(3)	P(2a)–C(23a)–C(28a)	118.5(8)	Zr(b)′–C(13b)–P(1b)	138.4(4)
C(11a)–P(1a)–C(12a)	104.1(5)	Cl(1b)–Zr(b)–Cl(2b)	107.49(9)	P(1b)–C(13b)–C(14b)	119.8(6)
C(11a)–P(1a)–C(13a)	101.7(4)	Cl(1b)–Zr(b)–P(1b)	84.24(7)	P(1b)–C(13b)–C(18b)	118.2(6)
C(12a)–P(1a)–C(13a)	103.4(4)	Cl(1b)–Zr(b)–P(2b)	76.57(8)	C(14b)–C(13b)–C(18b)	113.0(7)
Zr(a)–P(2a)–C(21a)	115.7(3)	Cl(2b)–Zr(b)–P(1b)	76 24(7)	C(13b)–C(14b)–C(15b)	121.5(8)
Zr(a)–P(2a)–C(22a)	110.3(4)	Cl(2b)–Zr(b)–P(2b)	82.82(8)	C(14b)–C(15b)–C(16b)	120.7(8)
Zr(a)–P(2a)–C(23a)	117.3(3)	P(1b)–Zr(b)–P(2b)	145.79(8)	C(15b)–C(16b)–C(17b)	114.8(9)
C(21a)–P(2a)–C(22a)	104.4(5)	P(1b)–Zr(b)–C(13b)	83.3(2)	C(16b)–C(17b)–C(18b)	121.6(8)
C(21a)–P(2a)–C(23a)	103.6(5)	Zr(b)–P(1b)–C(11b)	108.9(3)	C(13b)–C(18b)–C(17b)	120.8(8)
C(22a)–P(2a)–C(23a)	104.1(5)	Zr(b)–P(1b)–C(12b)	113.9(3)	P(2b)–C(23b)–C(24b)	119.7(6)
Zr(a)′–C(13a)–P(1a)	137.8(4)	Zr(b)–P(1b)–C(13b)	121.9(3)	P(2b)–C(23b)–C(28b)	121.7(7)

Numbers in parentheses are e.s.d.s ın the least significant digits.

The packing of the molecules is substantially identical in the two types of crystal. The molecules are as similar as the changes from Hf to Zr and Br to Cl allow. The previously reported $Zr_2I_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ also has the same general molecular structure but the crystal packing is different and corresponds to a different space group symmetry.

The Zr–Cl and Zr–P bond lengths have the following ranges and average values: Zr–Cl, 2.491(2)–2.517(3), 2.506[12] Å, Zr–P, 2.759(1)–2.771(2), 2.764[6] Å. The C–C bond lengths of the zirconium bond phenyl groups have a range and average value of 1.37(1)–1.49(1) and 1.43[5] Å, respectively. For comparison, the range and average values at the C–C bound lengths of the η^6-phenyl in $Hf_2Br_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ and $Zr_2I_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ are 1.33(3)–1.48(3), 1.43[5] Å and 1.40(2)–1.49(3), 1.46[3] Å, respectively. The Zr–C bond lengths in $Zr_2Cl_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ cover a considerable range of 2.290(7) to 2.524(9) Å with an average value of 2.44[9] Å. The large variation of the C–C and Zr–C bond lengths is in accordance with the significant ring puckering, as shown in Fig. 1. Similar to the Hf/Br compound [1], carbon atoms 13(a, b) and 16(a, b) lie an average of 0.25[1] Å closer to the zirconium atom as calculated from a least-squares plane through carbon atoms 14(a, b), 15(a, b), 17(a, b) and 18(a, b). The non-planarity of the ring and large range for the Zr–C and C–C bond lengths suggest that there is considerable synergistic donor–acceptor bonding between the zirconium atoms and phenyl groups.

With the preparation of this molecule it would seem likely that all six molecules of the general formula $M_2X_4(\eta^6\text{-}C_6H_5PMe_2)_2(PMe_2Ph)_2$ are accessible, since the three now characterized include both an Hf and a Zr compound, and include all the halogens, Cl, Br and I.

Supplementary material

Full listing of bond lengths and angles, thermal displacement parameters, least-squares planes, unit cell diagrams (12 pages), and tables of observed and calculated structure factors (18 pages) are available from the author F.A.C.

Acknowledgement

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Reference

1 F.A. Cotton, P.A. Kibala, M. Shang and W.A. Wojtczak, *Organometallics, 10* (1991) 2626, and refs. therein.