

the large number of unsaturated centres in these molecules, there are no notably short contacts (<4 Å) between any of these centres in adjacent molecules, and the solid compounds do not undergo spontaneous polymerization reactions. The observed intensity decay during data collection is probably due to decomposition involving loss of 4-vinylpyridine ligands.

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Structural Characterization of Zr₂Cl₈(PPh₃)₂

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Abstract. Octachlorobis(triphenylphosphane)dizirconium(IV), [Zr₂Cl₈(C₁₈H₁₅P)₂], *M_r* = 990.65, monoclinic, *P*2₁/*c*, *a* = 11.526 (3), *b* = 17.530 (4), *c* = 20.628 (5) Å, β = 106.03 (2)°, *V* = 4006 (3) Å³, *Z* = 4, *D_x* = 1.643 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 11.6 cm⁻¹, *F*(000) = 1968, *T* = 294 K, *R* = 0.048 for 3059 unique observed reflections. The molecule is dinuclear with two Zr atoms bridged by three Cl ligands forming a triangular face perpendicular to the Zr–Zr axis. The Zr–Zr distance is 3.649 (2) Å. The Zr–Cl_{bridge} distances range from 2.582 (3) to 2.612 (3) Å with a mean value of 2.594 (6) Å. The mean Zr–Cl_{bridge}–Zr angle is 89.4 (2)°. The coordination sphere around the first Zr atom is completed by two Cl ligands and two PPh₃ ligands mutually *trans* to each other. The two Cl ligands and two P atoms of the PPh₃ ligands form a distorted square parallel to the plane of the three bridging chlorides. The Zr–Cl_{trans} distances are 2.381 (3) and 2.386 (3) Å, and the Zr–P_{trans} distances are 2.824 (2) and 2.855 (2) Å. The Cl_{trans}–Zr–Cl_{trans} angle is 111.7 (1)° and the P_{trans}–Zr–P_{trans} angle is 134.98 (9)°. Octahedral coordination around the second Zr atom is completed with three terminal Cl

ligands with Zr–Cl_{term} distances ranging from 2.337 (3) to 2.343 (3) Å with a mean value of 2.340 (2) Å.

Introduction. In our laboratory we have been actively investigating coordination compounds of Group IV metals with halides and phosphines, especially those of the type *cis,cis*-*M*₂Cl₆(PR₃)₄, where *M* = Zr and Hf, that contain metal–metal bonds (Cotton, Diebold & Kibala, 1988; Cotton, Kibala & Wojtczak, 1990). The title complex was accidentally synthesized during an attempt to prepare a PPh₃ analog of the *M*₂Cl₆(PR₃)₄ species. We have later prepared Zr₂Cl₈(PPh₃)₂ by reacting directly ZrCl₄ with PPh₃. Because the compound exhibits rather unusual geometry we report this work here.

Experimental. The compound was prepared by refluxing stoichiometric amounts of ZrCl₄ and PPh₃ under argon in toluene. X-ray-quality crystals were obtained upon cooling of the reaction mixture. The quality of the crystals was confirmed by polarized light microscopy. A light-yellow irregularly shaped crystal, 0.45 × 0.40 × 0.40 mm, was mounted in a capillary under argon. Unit-cell dimensions were determined from least-squares analysis of 25 reflec-

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tions with $20 < 2\theta < 30^\circ$. Laue class and the unit-cell dimensions were confirmed with axial photographs. Intensity data were collected to $(\sin\theta)/\lambda = 0.538 \text{ \AA}^{-1}$ ($0 \leq h \leq 13$; $0 \leq k \leq 19$; $-23 \leq l \leq 23$) at variable scan speeds ($3\text{--}30^\circ \text{ min}^{-1}$), which depended on a pre-scan count with a skip option, using the moving-crystal/moving-counter technique, $\omega\text{--}2\theta$ scans, on a Nicolet P3/F equivalent diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Three standard reflections (344 , $27\bar{4}$ and $17\bar{3}$), measured every 100 reflections, decreased 46.7% over 97.3 h of data collection. The decay was corrected for by the use of an isotropic decay correction. Data were corrected for Lorentz and polarization effects. Absorption and extinction corrections were not applied. 5542 reflections were measured, 4519 found unique ($R_{\text{int}} = 0.02$) and 3059 with $F_o^2 > 3\sigma(F_o^2)$ considered observed.

Positions of Zr, Cl, and P atoms were determined by direct methods using *SHELXS86* (Sheldrick, 1986) and subjected to alternating full-matrix least-squares refinements and difference Fourier maps employing the Enraf–Nonius (1979) *Structure Determination Package* to reveal the rest of the molecule. $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ was minimized, where $w = 1/\sigma^2(|F_o|)$. All atoms were refined anisotropically for a total of 433 variables with H atoms not included. The final $R = 0.049$, $wR = 0.061$, and $S = 1.19$. At convergence, $(\Delta/\sigma)_{\text{max}} = 0.01$, $(\Delta\rho)_{\text{max}} = 0.49$ and $(\Delta\rho)_{\text{min}} = -0.65 \text{ e \AA}^{-3}$ on final difference Fourier map. Atomic scattering factors, including anomalous-dispersion correction, were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The positional and equivalent isotropic displacement parameters are given in Table 1. The structure is depicted in Fig. 1 where the atom-numbering scheme is also defined. A unit-cell diagram is shown in Fig. 2. Selected important interatomic bond distances and angles are given in Table 2.*

Very few Group IV complexes with metal–metal bonds are known. The first structurally characterized zirconium halide-phosphine complex containing a single Zr–Zr bond, $\text{Zr}_2\text{Cl}_6(\text{PBu}_3)_4$, was reported in 1981 (Wengrovius, Schrock & Day, 1981). The compound was of the edge-sharing bi-octahedral type. Structures of PMe_2Ph and PEt_3 derivatives were described in 1988 (Cotton, Diebold & Kibala, 1988)

Table 1. *Positional and equivalent isotropic displacement parameters and their estimated standard deviations for $\text{Zr}_2\text{Cl}_6(\text{PPh}_3)_2$*

$$B_{\text{eq}} = (1/3)[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}].$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Zr(1)	0.25825 (8)	0.24052 (5)	0.49496 (4)	2.31 (2)
Zr(2)	0.50257 (9)	0.33880 (6)	0.44834 (5)	3.17 (2)
Cl(1)	0.1403 (2)	0.2910 (2)	0.5632 (1)	3.23 (6)
Cl(2)	0.2073 (3)	0.1109 (1)	0.4646 (1)	3.45 (6)
Cl(3)	0.3680 (3)	0.3693 (2)	0.5267 (1)	3.59 (6)
Cl(4)	0.2901 (2)	0.2874 (2)	0.3825 (1)	3.55 (6)
Cl(5)	0.4819 (2)	0.2071 (2)	0.5014 (1)	3.45 (6)
Cl(6)	0.5804 (3)	0.2808 (2)	0.3673 (1)	5.06 (8)
Cl(7)	0.4650 (3)	0.4601 (2)	0.3996 (2)	5.69 (9)
Cl(8)	0.6782 (3)	0.3651 (2)	0.5346 (1)	4.72 (7)
P(1)	0.0242 (2)	0.2584 (2)	0.4068 (1)	2.41 (5)
P(2)	0.3549 (2)	0.1755 (2)	0.6257 (1)	2.61 (6)
C(11)	-0.0047 (9)	0.2331 (6)	0.3173 (5)	2.9 (2)
C(12)	0.064 (1)	0.1786 (7)	0.2978 (5)	4.0 (3)
C(13)	0.041 (1)	0.1578 (8)	0.2294 (5)	4.9 (3)
C(14)	-0.054 (1)	0.1901 (8)	0.1826 (5)	5.6 (3)
C(15)	-0.122 (2)	0.245 (1)	0.2014 (6)	8.8 (5)
C(16)	-0.100 (1)	0.2670 (9)	0.2714 (6)	6.6 (4)
C(21)	-0.0243 (9)	0.3567 (6)	0.4057 (4)	2.8 (2)
C(22)	-0.142 (1)	0.3762 (6)	0.4036 (6)	5.0 (3)
C(23)	-0.179 (1)	0.4542 (7)	0.3982 (7)	6.5 (4)
C(24)	-0.095 (1)	0.5098 (7)	0.4001 (6)	5.7 (3)
C(25)	0.024 (1)	0.4901 (7)	0.4043 (7)	5.8 (4)
C(26)	0.060 (1)	0.4142 (6)	0.4071 (6)	4.9 (3)
C(31)	-0.0866 (9)	0.2002 (6)	0.4334 (5)	2.8 (2)
C(32)	-0.1248 (9)	0.2220 (6)	0.4900 (5)	3.5 (3)
C(33)	-0.2026 (9)	0.1751 (7)	0.5128 (5)	3.9 (3)
C(34)	-0.240 (1)	0.1050 (7)	0.4801 (6)	5.3 (3)
C(35)	-0.199 (1)	0.0835 (7)	0.4256 (7)	6.3 (4)
C(36)	-0.122 (1)	0.1312 (6)	0.4013 (6)	4.7 (3)
C(41)	0.2493 (9)	0.1229 (6)	0.6608 (5)	3.0 (2)
C(42)	0.131 (1)	0.1135 (6)	0.6235 (6)	4.4 (3)
C(43)	0.047 (1)	0.0720 (7)	0.6496 (6)	5.3 (3)
C(44)	0.093 (1)	0.0401 (7)	0.7155 (6)	5.2 (3)
C(45)	0.211 (1)	0.0513 (8)	0.7525 (5)	5.0 (3)
C(46)	0.291 (1)	0.0917 (7)	0.7260 (5)	4.5 (3)
C(51)	0.4803 (9)	0.1106 (5)	0.6396 (5)	2.9 (2)
C(52)	0.476 (1)	0.0512 (6)	0.5926 (5)	3.2 (2)
C(53)	0.574 (1)	0.0018 (6)	0.5986 (5)	4.0 (3)
C(54)	0.677 (1)	0.0111 (6)	0.6511 (5)	4.2 (3)
C(55)	0.683 (1)	0.0681 (7)	0.7001 (6)	4.9 (3)
C(56)	0.585 (1)	0.1181 (6)	0.6939 (5)	3.9 (3)
C(61)	0.4109 (9)	0.2554 (6)	0.6829 (4)	3.1 (2)
C(62)	0.5141 (9)	0.2933 (6)	0.6769 (5)	3.6 (3)
C(63)	0.553 (1)	0.3621 (7)	0.7155 (6)	4.8 (3)
C(64)	0.488 (1)	0.3877 (7)	0.7578 (6)	5.3 (3)
C(65)	0.381 (1)	0.3496 (7)	0.7607 (6)	4.7 (3)
C(66)	0.343 (1)	0.2832 (6)	0.7238 (5)	3.7 (3)

* Lists of structure factors, anisotropic thermal parameters and complete bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53376 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

as well as the structure of $\text{Zr}_2\text{Cl}_6(\text{dppe})_2$; where dppe = 1,2-bis(diphenylphosphino)ethane. Recently, a hafnium complex with a single metal–metal bond, $\text{Hf}_2\text{Cl}_6(\text{PMe}_2\text{Ph})_4$, has also been characterized (Cotton, Kibala & Wojtczak, 1990). In all these complexes the phosphine ligands are *cis* to each other. Reasons for that arrangement are not well understood. To explore the possibility that steric factors are responsible for the *cis* arrangement of the phosphine ligands we decided to use the bulky PPh_3 ligand in an attempt to prepare the *trans* isomer of $\text{Zr}_2\text{Cl}_6(\text{PPh}_3)_4$. However, under the conditions employed the reaction did not take place and only

Zr₂Cl₈(PPh₃)₂ was isolated. The compound was subsequently prepared in nearly quantitative yield by refluxing ZrCl₄ and PPh₃ in toluene under argon.

The compound we report here is dinuclear with two Zr atoms bridged by three Cl ligands. Each Zr atom has a very different coordination sphere. The geometry around the first Zr atom is best described as 'four against three' with two Cl ligands and two P atoms of the PPh₃ ligands, mutually *trans* to each other, in a nearly square arrangement parallel to the triangular face of the three bridging Cl ligands. The coordination sphere around the second atom is completed with three terminal Cl ligands to give a distorted octahedron. The long Zr—Zr distance, 3.649 (2) Å, indicates lack of metal-to-metal bonding further evidenced by the mean Zr—Cl_{bridge}—Zr angle of 89.4 (2)°. The Zr—Cl distances vary widely with the mean Zr—Cl_{bridge} distance 2.594 (6) Å, the mean Zr—Cl_{term(sq)} 2.384 (3) Å, and the mean Zr—Cl_{term(oct)} 2.340 (2) Å.

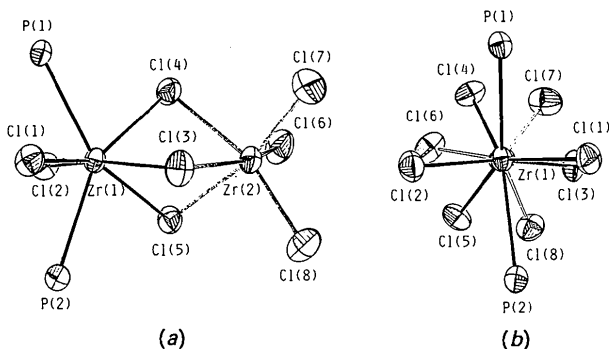


Fig. 1. ORTEP (Johnson, 1965) drawing of the core of the Zr₂Cl₈(PPh₃)₂ molecule. Atoms are represented by displacement ellipsoids at the 50% level. C atoms omitted for clarity. (a) A view with the Zr—Zr axis parallel to the plane of drawing. (b) A view with the Zr—Zr axis perpendicular to the plane of drawing.

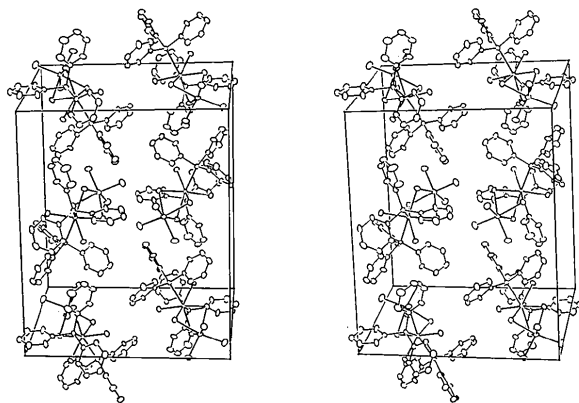


Fig. 2. Unit-cell diagram for Zr₂Cl₈(PPh₃)₂. Atoms are represented by displacement ellipsoids at the 20% level. Axis orientation: *b* across, *c* down, *a* towards viewer.

Table 2. Selected interatomic bond distances (Å) and angles (°) for Zr₂Cl₈(PPh₃)₂; e.s.d.'s in the least significant digits are given in parentheses

Zr(1)	Zr(2)	3.649 (2)	Zr(1)	P(2)	2.855 (2)		
Zr(1)	Cl(1)	2.381 (3)	Zr(2)	Cl(3)	2.586 (3)		
Zr(1)	Cl(2)	2.386 (3)	Zr(2)	Cl(4)	2.612 (3)		
Zr(1)	Cl(3)	2.582 (3)	Zr(2)	Cl(5)	2.593 (3)		
Zr(1)	Cl(4)	2.582 (3)	Zr(2)	Cl(6)	2.337 (3)		
Zr(1)	Cl(5)	2.611 (3)	Zr(2)	Cl(7)	2.340 (3)		
Zr(1)	P(1)	2.824 (2)	Zr(2)	Cl(8)	2.343 (3)		
Cl(1)	Zr(1)	Cl(2)	111.7 (1)	P(1)	Zr(1)	P(2)	134.98 (9)
Cl(1)	Zr(1)	Cl(3)	81.1 (1)	Cl(3)	Zr(2)	Cl(4)	76.02 (9)
Cl(1)	Zr(1)	Cl(4)	131.26 (9)	Cl(3)	Zr(2)	Cl(5)	77.26 (9)
Cl(1)	Zr(1)	Cl(5)	140.34 (8)	Cl(3)	Zr(2)	Cl(6)	162.2 (1)
Cl(1)	Zr(1)	P(1)	74.91 (8)	Cl(3)	Zr(2)	Cl(7)	90.5 (1)
Cl(1)	Zr(1)	P(2)	74.18 (8)	Cl(3)	Zr(2)	Cl(8)	91.5 (1)
Cl(2)	Zr(1)	Cl(3)	165.2 (1)	Cl(4)	Zr(2)	Cl(5)	74.36 (8)
Cl(2)	Zr(1)	Cl(4)	98.8 (1)	Cl(4)	Zr(2)	Cl(6)	88.1 (1)
Cl(2)	Zr(1)	Cl(5)	88.2 (1)	Cl(4)	Zr(2)	Cl(7)	93.1 (1)
Cl(2)	Zr(1)	P(1)	79.33 (8)	Cl(4)	Zr(2)	Cl(8)	162.3 (1)
Cl(2)	Zr(1)	P(2)	82.61 (8)	Cl(5)	Zr(2)	Cl(6)	90.8 (1)
Cl(3)	Zr(1)	Cl(4)	76.60 (9)	Cl(5)	Zr(2)	Cl(7)	164.2 (1)
Cl(3)	Zr(1)	Cl(5)	77.02 (9)	Cl(5)	Zr(2)	Cl(8)	90.9 (1)
Cl(3)	Zr(1)	P(1)	112.33 (8)	Cl(6)	Zr(2)	Cl(7)	98.6 (1)
Cl(3)	Zr(1)	P(2)	94.22 (8)	Cl(6)	Zr(2)	Cl(8)	102.0 (1)
Cl(4)	Zr(1)	Cl(5)	74.56 (9)	Cl(7)	Zr(2)	Cl(8)	99.6 (1)
Cl(4)	Zr(1)	P(1)	74.54 (8)	Zr(1)	Cl(3)	Zr(2)	89.85 (9)
Cl(4)	Zr(1)	P(2)	149.39 (9)	Zr(1)	Cl(4)	Zr(2)	89.29 (7)
Cl(5)	Zr(1)	P(1)	144.31 (9)	Zr(1)	Cl(5)	Zr(2)	89.05 (9)
Cl(5)	Zr(1)	P(2)	74.92 (9)				

We suggest that in the first step ZrCl₄ reacts with two equivalents of PPh₃ to give *trans*-ZrCl₄(PPh₃)₂ (Gordon & Wallbridge, 1986) which, in turn, reacts with another ZrCl₄ to give Zr₂Cl₈(PPh₃)₂. Such a reaction scheme explains why both PPh₃ ligands are located on just one Zr center and are *trans* to each other. We further suggest that the unusual geometry of the complex results from the known tendency of Zr to attain higher coordination numbers. In Zr₂Cl₈(PPh₃)₂ there are thirteen metal-to-ligand bonds as opposed to twelve in simple edge-sharing bioctahedral complexes.

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