# METAL-ORGANIC COMPOUNDS

*Acta Cryst.* (1994). C**50**, 1662–1664

## Two Zirconium(IV) Complexes, $[Zr_2Cl_8(PMe_3)_4]$ and *trans*-$[ZrI_4(PMe_2Ph)_2]$

F. Albert Cotton* and William A. Wojtczak

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

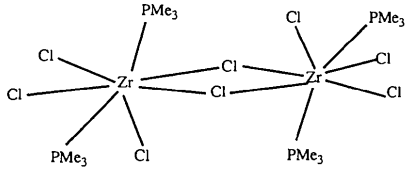
(*Received* 1 *October* 1993; *accepted* 12 *April* 1994)

### Abstract

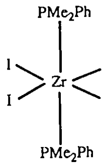
The crystal and molecular structures of di-$\mu$-chloro-bis-[trichlorobis(trimethylphosphine)zirconium(IV)], $[Zr_2Cl_8(C_3H_9P)_4]$ (1), and *trans*-bis(dimethylphenylphosphine)tetraiodozirconium(IV), *trans*-$[ZrI_4(C_8H_{11}P)_2]$ (2), have been determined. Compound (1) is dinuclear with Zr atoms bridged by two Cl atoms, forming the shared edge of the bipolyhedral structure. The coordination geometry around each of the seven-coordinate $Zr^{IV}$ atoms is best described as face-capped octahedral. The capping $PMe_3$ ligands are bound to the Zr atoms through the triangular faces formed by the terminal Cl atoms. In (2), the coordination geometry of the Zr atom is octahedral with the $PMe_2Ph$ ligands *trans* to each other.

### Comment

We have been actively investigating the coordination compounds of the Group IVA metals with halide atoms and phosphine ligands, particularly those of the edge-sharing bioctahedral type $M_2X_6(PR_3)_4$ ($M$ = Ti, Zr or Hf; $X$ = Cl or I) (Cotton, Diebold & Kabala, 1988; Cotton, Kibala & Wojtczak, 1990; Cotton, Shang & Wojtczak, 1991; Cotton & Wojtczak, 1993). During the synthesis of $M_2X_6(PR_3)_4$ compounds, by reduction of $MX_4$ and addition of phosphine, we obtained the title compounds in low yields. We later prepared compounds (1) and (2) in good yields by reacting $ZrX_4$ ($X$ = Cl or I) directly with $PMe_3$ and $PMe_2Ph$. While the reactions to prepare (1) and (2) are similar, the two products are quite different. *trans*-$[ZrI_4(PMe_2Ph)_2]$, (2), retains a mononuclear structure, but $[Zr_2Cl_8(PMe_3)_4]$, (1), is dinuclear and can be viewed as a dimerization product of two $ZrCl_4(PMe_3)_2$ molecules. Factors contributing to the greater stability of the dinuclear structure of (1) over the mononuclear $ZrCl_4(PMe_3)_2$ may be (*a*) the good bridging ability of Cl atoms, (*b*) the small size of the $PMe_3$ ligands, (*c*) the large size of Zr atoms, and (*d*) the formation of an additional Zr—Cl bond in (1).



(1)



(2)

Very little structural data are available for high-valent coordination compounds of the Group IVA metals containing only phosphine and halide ligands. In fact, $[HfCl_4(LL)]$, $LL$ = dppe [1,2-bis(diphenylphosphino)-ethane] and dppp [1,3-bis(diphenylphosphino)propane], and $[Zr_2Cl_8(PPh_3)_2]$ (Cotton, Kibala & Wojtczak, 1991;

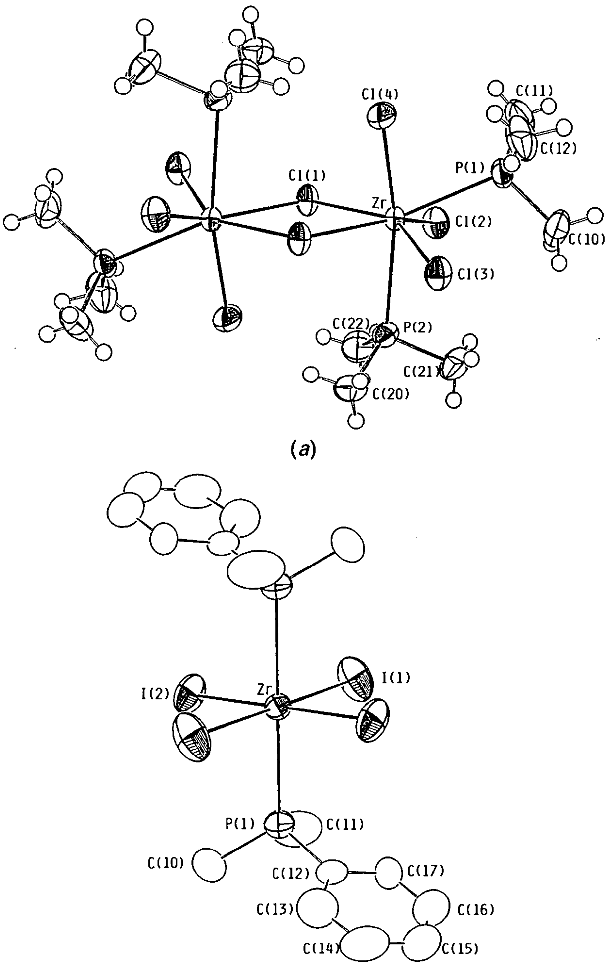


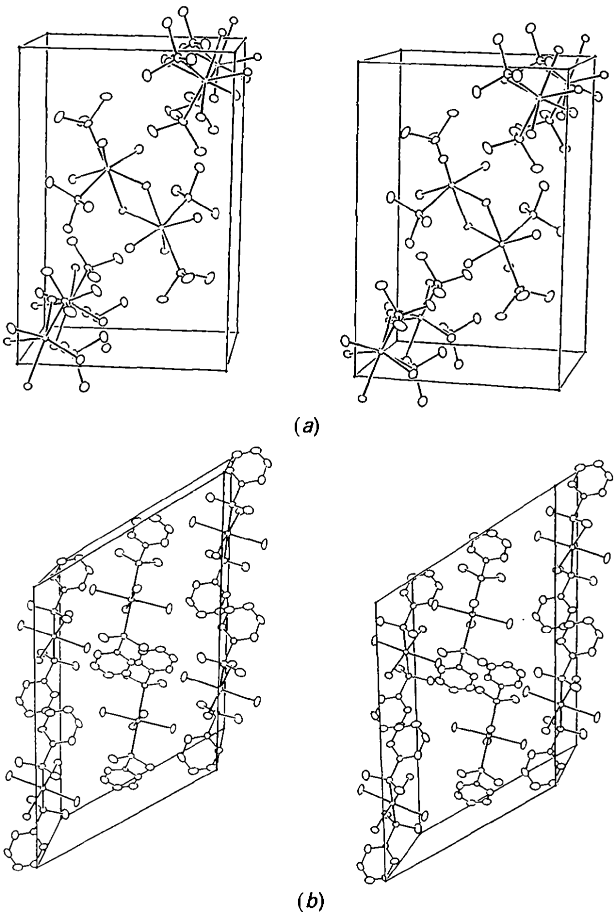
Fig. 1. *ORTEP* (Johnson, 1965) drawing of (*a*) $[Zr_2Cl_8(PMe_3)_4]$ (1) and (*b*) *trans*-$[ZrI_4(PMe_2Ph)_2]$ (2). Both (1) and (2) reside on crystallographic inversion centers. Atoms are represented by displacement ellipsoids at the 50% level. H atoms of (1) were given arbitrary displacement parameters for clarity.

*Acta Crystallographica Section C*
ISSN 0108-2701 ©1994

Cotton & Kibala, 1991) are the only other compounds of this type to have been structurally characterized.

The crystal structure of (1) comprises isolated $[Zr_2Cl_8(PMe_3)_4]$ bipolyhedra formed by Cl—Cl edge-sharing between $ZrCl_5(PMe_3)_2$ face-capped octahedra (Figs. 1*a* and 2*a*). The $Zr^{IV}$ atoms are seven coordinate. A $PMe_3$ ligand resides over each of the triangular faces formed by the three terminal Cl atoms of the $ZrCl_5(PMe_3)$ units. This produces a face-capped octahedral geometry around the Zr atoms. The average Zr—Cl bridge and Zr—Cl terminal distances of 2.659 (17) and 2.431 (4) Å, respectively, are similar to those reported for $[Zr_2Cl_8(PPh_3)_2]$ (Cotton & Kibala, 1991). The Hf—Cl terminal bond distances in the $[HfCl_4(LL)]$ compounds (Cotton, Kibala & Wojtczak, 1991) are approximately 0.05 Å shorter than in (1). This is consistent with the slightly smaller size of $Hf^{IV}$, compared to $Zr^{IV}$, as a result of the lanthanide contraction.

*trans*-$[ZrI_4(PMe_2Ph)_2]$, (2), has octahedral geometry (Figs. 1*b* and 2*b*) with I—Zr—I and I—Zr—P angles very near the ideal octahedral value of 90°. The Zr—I and Zr—P distances are 0.02–0.03 Å shorter than those reported for the $Zr^{III}$ compound $[Zr_2I_6(PMe_2Ph)_4]$ (Cotton, Shang & Wojtczak, 1991). However, this is not unexpected since $Zr^{IV}$ has a smaller radius than $Zr^{III}$.


(*a*)

(*b*)

Fig. 2. (*a*) Unit-cell diagram for (1) (*c* across, *a* down, *b* towards viewer) and (*b*) unit-cell diagram for (2) (*c* across, *b* down, *a* towards viewer). Atoms are represented by displacement ellipsoids at the 20% level.

## Experimental

Compound (1) was obtained from the reaction of $ZrCl_4$ with two equivalents of $PMe_3$ in 20 ml of benzene. X-ray quality crystals were grown by layering the benzene solution with 30 ml of hexanes. Compound (2) was synthesized by stirring together $ZrI_4$ and two equivalents of $PMe_2Ph$ in 25 ml of benzene. Crystals were obtained one week after layering the reaction solution with 20 ml of hexanes. Crystals of (1) and (2) were wedged inside capillary tubes that were previously filled with dried and degassed mineral. The tubes were then sealed at both ends with epoxy cement.

### Compound (1)

*Crystal data*

$[Zr_2Cl_8(C_3H_9P)_4]$
$M_r = 770.4$
Monoclinic
$P2_1/n$
$a = 8.220$ (1) Å
$b = 16.579$ (2) Å
$c = 11.192$ (1) Å
$\beta = 93.40$ (1)°
$V = 1522.55$ (29) Å$^3$
$Z = 2$
$D_x = 1.680$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13$–$16°$
$\mu = 1.594$ mm$^{-1}$
$T = 294$ K
Block
0.25 × 0.20 × 0.20 mm
Brown

*Data collection*

Syntex *P*3/*F* diffractometer
$\omega$–$2\theta$ scans
Absorption correction: $\psi$ scans at $\chi = 90°$
$T_{min} = 0.851$, $T_{max} = 0.997$
1892 measured reflections
1640 independent reflections
1395 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$

$R_{int} = 0.021$
$\theta_{max} = 23°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 19$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 100 reflections intensity variation: −36.4% overall

*Refinement*

Refinement on *F*
$R = 0.029$
$wR = 0.038$
$S = 0.801$
1395 reflections
172 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.02$

$\Delta\rho_{max} = 0.31$ e Å$^{-3}$
$\Delta\rho_{min} = -0.31$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for* (1)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Zr | 0.03610 (7) | 0.09081 (3) | 0.13616 (4) | 2.16 (1) |
| Cl(1) | 0.1338 (2) | −0.05301 (9) | 0.0670 (1) | 2.88 (3) |
| Cl(2) | 0.1697 (2) | 0.0430 (1) | 0.3228 (1) | 3.56 (3) |

| | | | | |
|---|---|---|---|---|
| Cl(3) | −0.1827 (2) | 0.18930 (9) | 0.1397 (1) | 3.44 (3) |
| Cl(4) | 0.2346 (2) | 0.1424 (1) | 0.0033 (1) | 4.53 (4) |
| P(1) | 0.1686 (2) | 0.2256 (1) | 0.2477 (1) | 3.13 (3) |
| P(2) | −0.2130 (2) | 0.0099 (1) | 0.2493 (1) | 2.97 (3) |
| C(10) | 0.0698 (9) | 0.2524 (5) | 0.3822 (6) | 4.9 (2) |
| C(11) | 0.3831 (8) | 0.2198 (5) | 0.2962 (7) | 5.3 (2) |
| C(12) | 0.158 (1) | 0.3168 (4) | 0.1587 (7) | 5.6 (2) |
| C(20) | −0.4153 (8) | 0.0047 (5) | 0.1742 (6) | 4.5 (2) |
| C(21) | −0.2515 (9) | 0.0649 (5) | 0.3854 (6) | 4.8 (2) |
| C(22) | −0.1719 (9) | −0.0909 (4) | 0.3048 (6) | 4.6 (2) |

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

| | | | |
|---|---|---|---|
| Zr—Cl(1) | 2.646 (2) | Zr—Cl(4) | 2.427 (2) |
| Zr—Cl(1)′ | 2.671 (1) | Zr—P(1) | 2.752 (2) |
| Zr—Cl(2) | 2.434 (2) | Zr—P(2) | 2.811 (2) |
| Zr—Cl(3) | 2.431 (2) | | |
| Cl(1)—Zr—Cl(1)′ | 72.06 (5) | Cl(2)—Zr—Cl(3) | 120.08 (6) |
| Cl(1)—Zr—Cl(2) | 80.11 (5) | Cl(2)—Zr—Cl(4) | 110.78 (6) |
| Cl(1)—Zr—Cl(3) | 147.94 (5) | Cl(2)—Zr—P(1) | 74.27 (5) |
| Cl(1)—Zr—Cl(4) | 84.93 (5) | Cl(2)—Zr—P(2) | 76.22 (5) |
| Cl(1)—Zr—P(1) | 138.18 (5) | Cl(3)—Zr—Cl(4) | 107.37 (6) |
| Cl(1)—Zr—P(2) | 86.75 (5) | Cl(3)—Zr—P(1) | 73.79 (5) |
| Cl(1)′—Zr—Cl(2) | 147.19 (5) | Cl(3)—Zr—P(2) | 75.74 (5) |
| Cl(1)′—Zr—Cl(3) | 79.73 (5) | Cl(4)—Zr—P(1) | 74.31 (5) |
| Cl(1)′—Zr—Cl(4) | 84.13 (5) | Cl(4)—Zr—P(2) | 167.96 (5) |
| Cl(1)′—Zr—P(1) | 138.53 (5) | P(1)—Zr—P(2) | 117.55 (5) |
| Cl(1)′—Zr—P(2) | 85.04 (5) | Zr—Cl(1)—Zr′ | 107.94 (5) |

## Compound (2)

### *Crystal data*

$[ZrI_4(C_8H_{11}P)_2]$
$M_r = 875.1$
Monoclinic
$C2/c$
$a = 20.598$ (4) Å
$b = 9.431$ (1) Å
$c = 15.307$ (3) Å
$\beta = 122.06$ (1)°
$V = 2520.05$ (79) Å$^3$
$Z = 4$
$D_x = 2.306$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.5$–17°
$\mu = 5.405$ mm$^{-1}$
$T = 294$ K
Irregular
0.70 × 0.50 × 0.50 mm
Orange

### *Data collection*

Syntex *P*3/*F* diffractometer
$\omega$–$2\theta$ scans
Absorption correction: $\psi$ scans at $\chi = 90°$
$T_{\min} = 0.798$, $T_{\max} = 0.999$
1776 measured reflections
1602 independent reflections
1403 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$

$R_{\rm int} = 0.030$
$\theta_{\max} = 23°$
$h = -23 \rightarrow 23$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 100 reflections intensity variation: −26% overall

### *Refinement*

Refinement on *F*
$R = 0.040$
$wR = 0.062$
$S = 1.423$
1403 reflections
106 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} < 0.01$

$\Delta\rho_{\max} = 0.36$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.49$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for* (2)

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{\rm eq}$ |
|---|---|---|---|---|
| Zr | 1/4 | 1/4 | 1/2 | 2.81 (2) |
| I(1) | 0.13660 (5) | 0.20192 (9) | 0.29510 (5) | 6.10 (2) |
| I(2) | 0.21079 (4) | −0.00381 (7) | 0.55428 (5) | 5.22 (2) |
| P(1) | 0.3508 (1) | 0.0844 (3) | 0.4760 (2) | 3.59 (5) |
| C(10) | 0.4249 (7) | −0.001 (1) | 0.5951 (9) | 6.8 (3) |
| C(11) | 0.3063 (6) | −0.065 (1) | 0.3845 (8) | 6.0 (3) |
| C(12) | 0.4016 (4) | 0.184 (1) | 0.4306 (5) | 3.5 (2) |
| C(13) | 0.4695 (5) | 0.254 (1) | 0.5008 (7) | 4.5 (2) |
| C(14) | 0.5066 (6) | 0.335 (1) | 0.4660 (9) | 6.5 (3) |
| C(15) | 0.4791 (5) | 0.354 (1) | 0.3648 (8) | 6.0 (3) |
| C(16) | 0.4139 (6) | 0.287 (1) | 0.2955 (7) | 6.1 (3) |
| C(17) | 0.3724 (6) | 0.200 (1) | 0.3241 (8) | 5.9 (3) |

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

| | | | |
|---|---|---|---|
| Zr—I(1) | 2.7787 (6) | Zr—P(1) | 2.774 (3) |
| Zr—I(2) | 2.7902 (7) | | |
| I(1)—Zr—I(2) | 89.62 (2) | I(1)—Zr—P(1)′ | 90.10 (4) |
| I(1)—Zr—I(2)′ | 90.38 (2) | I(2)—Zr—P(1) | 84.93 (6) |
| I(1)—Zr—P(1) | 89.90 (4) | I(2)—Zr—P(1)′ | 95.07 (6) |

The space group of (1) was determined unambiguously from the systematic absences (0*k*0 absent if $k = 2n + 1$; *h*01 absent if $h + 1 = 2n + 1$) as $P2_1/n$ (No. 14). The space group of (2) ($C2/c$, No. 15) was assumed initially and later confirmed by the successful refinement of the structure. H atoms of (1) were located from the difference Fourier map following the complete anisotropic refinement of all the atoms. The H atoms were refined isotropically with fixed displacement parameters of $1.3B_{\rm eq}$ of the corresponding C atoms. Data collection and cell refinement for (1) and (2): Nicolet–Syntex *P*3/*F* software. Data reduction and other calculations: *SDP* package (Enraf–Nonius, 1979). Structure solutions: direct methods in *SHELXS*86 (Sheldrick, 1986). Molecular graphics: *ORTEP* (Johnson, 1965).

We thank the Robert A. Welch Foundation for support under grant A494.

---

Lists of structure factors, anisotropic displacement parameters and complete geometry for (1) have been deposited with the IUCr (Reference: HR1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

---

## References

Cotton, F. A., Diebold, M. P. & Kibala, P. A. (1988). *Inorg. Chem.* **27**, 799–804.

Cotton, F. A. & Kibala, P. A. (1991). *Acta Cryst.* C**47**, 270–272.

Cotton, F. A., Kibala, P. A. & Wojtczak, W. A. (1990). *Inorg. Chim. Acta*, **17**, 1–3.

Cotton, F. A., Kibala, P. A. & Wojtczak, W. A. (1991). *Acta Cryst.* C**47**, 89–92.

Cotton, F. A., Shang, M. & Wojtczak, W. A. (1991). *Inorg. Chem.* **30**, 3670–3675.

Cotton, F. A. & Wojtczak, W. A. (1993). *Gazz. Chim. Ital.* **123**, 499–507.

Enraf–Nonius (1979). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.