

poorly defined, but consistent with the known *trans* configuration of the pyridine N atoms in the structure of dpyam (Johnson & Jacobson, 1973). The sulfate anion is also disordered about a centre of symmetry, with a SOF = 0.5. The O atoms can be separated into two poorly defined interpenetrating tetrahedra. The uncoordinated water molecule is also disordered, SOF = 0.5.

The square-based pyramidal distorted trigonal bipyramidal $\text{CuN}_4\text{N}'$ chromophore (I) has been observed previously in the cations of $[\text{Cu}(\text{bpy})_2(\text{NH}_3)][\text{BF}_4]_2$ (Stephens, 1972) ($\tau = 0.77$) and $[\text{Cu}(\text{bpy})_2(\text{NCS})][\text{BF}_4]$ (Tyagi & Hathaway, 1981) ($\tau = 0.60$) and in a series of cation distortion isomers of the $[\text{Cu}(\text{bpy})_2\text{Cl}]^+$ cation (Harrison *et al.*, 1981) ($\tau = 1.0-0.60$). These have been used to suggest a structural pathway from a regular trigonal bipyramidal ($\tau = 1.0$) to a distorted square-based pyramidal ($\tau = 0.0$) stereochemistry (Hathaway, 1984) and suggest that (I) forms a point in a more extensive ($\tau = 0.31$) structural pathway for the $\text{CuN}_4\text{N}'$ chromophore.

The ESR spectrum of (I) is isotropic, $g_i = 2.083$, and gives no information on the electronic ground state of the copper(II) ion, due to the misalignment of the local molecular axes (Hathaway, 1984) of the two differently orientated $\text{CuN}_4\text{N}'$ chromophores ($2\gamma = 90^\circ$) in (I). The electronic reflectance spectrum of (I) has two almost equally intense peaks at 10 630 and 14 230 cm^{-1} , $\Delta E = 3\ 600\ \text{cm}^{-1}$, consistent with its stereochemistry, and similar to the electronic spectra of the comparable structure in the series of cation distortion isomers of the $[\text{Cu}(\text{bpy})_2\text{Cl}]^{2+}$ cation (Harrison *et al.*, 1981).

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References

- ADDISON, A. W., NAGESWARA RAO, T., REEDIJK, J., VAN RIJN, J. & VERSCHOOR, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DAVIES, E. K. (1980). *CHEM-X*. Molecular graphics program developed and distributed by Chemical Design Ltd, Oxford.
- FULLER, C. C. & JACOBSON, R. A. (1981). *Inorg. Chim. Acta*, **48**, 191–197.
- HARRISON, W. D., KENNEDY, D. M., POWER, M., SHEAHAN, R. & HATHAWAY, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1556–1564.
- HATHAWAY, B. J. (1984). *Struct. Bonding (Berlin)*, **57**, 55–118.
- HATHAWAY, B. J. (1987). *Comprehensive Coordination Chemistry. The Synthesis, Reactions, Properties & Applications of Coordination Compounds*. Editor in Chief G. WILKINSON, FRS; Executive Editors R. D. GILLARD & J. A. MCCLEVERTY, Vol. 5, section 53, pp. 533–774. Oxford: Pergamon Press.
- HENRICK, K. (1980). *PUBTAB*. Program to prepare and print crystallographic tables for publication.
- JOHNSON, J. E. & JACOBSON, R. A. (1973). *Acta Cryst.* **B29**, 1669–1674.
- RAY, N. & HATHAWAY, B. J. (1978). *Acta Cryst.* **B34**, 3224–3229.
- ROBERTS, P. & SHELDRIK, G. M. (1979). *XANADU*. Program for the calculation of crystallographic data. Univ of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEPHENS, F. S. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1350–1353.
- TYAGI, S. & HATHAWAY, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2029–2033.

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Structural Characterization of Two Hafnium(IV) Complexes, $\text{HfCl}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2) \cdot 2\text{C}_7\text{H}_8$ and $\text{HfCl}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)$

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Abstract. (1) [1,2-Bis(diphenylphosphino)ethane-*P,P'*)]tetrachlorohafnium(IV) bistoluene solvate,

$[\text{HfCl}_4(\text{C}_{26}\text{H}_{24}\text{P}_2)] \cdot 2\text{C}_7\text{H}_8$, $M_r = 903.01$, monoclinic, $C2/c$, $a = 11.340$ (3), $b = 18.243$ (6), $c = 19.661$ (3) Å, $\beta = 103.96$ (2)°, $V = 3947$ (3) Å³, $Z = 4$, $D_x = 1.519\ \text{g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu =$

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30.0 cm⁻¹, $F(000) = 1800$, $T = 294$ K, $R = 0.035$ for 2079 observed reflections. (2) [1,3-Bis(diphenylphosphino)propane-*P,P'*)]tetrachlorohafnium(IV), [HfCl₄(C₂₇H₂₆P₂)], $M_r = 732.76$, monoclinic, $P2_1/n$, $a = 12.596$ (5), $b = 14.117$ (2), $c = 17.028$ (4) Å, $\beta = 109.91$ (2)°, $V = 2847$ (3) Å³, $Z = 4$, $D_x = 1.710$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 41.4$ cm⁻¹, $F(000) = 1432$, $T = 294$ K, $R = 0.049$ for 1509 observed reflections. In both compounds the coordination around Hf is distorted octahedral with P atoms *cis* to each other forming five- or six-membered chelate rings. The mean Hf—Cl and Hf—P distances are 2.374 (1) and 2.808 (2) Å, and 2.372 (15) and 2.823 (2) Å for (1) and (2), respectively. In both compounds the Hf—Cl distances for the Cl atoms *trans* to the P atoms are somewhat shorter than the other Hf—Cl distances. The P—Hf—P angles for (1) and (2) are 74.80 (5) and 78.5 (2)°, respectively, consistent with the size of the chelate rings.

Introduction. During the course of a synthetic program directed towards systematic investigation of coordination compounds of Group IV metals with halides and phosphines, especially those that contain metal-metal bonds, we have synthesized and structurally characterized two adducts of hafnium tetrachloride with bis(diphenylphosphino)ethane, HfCl₄(dppe).2(toluene), and 1,3-bis(diphenylphosphino)propane, HfCl₄(dppp). Due to the paucity of structural information on complexes of this type we report this work here.

Experimental. Both compounds were synthesized by reacting stoichiometric amounts of hafnium tetrachloride and the appropriate phosphine in toluene at room temperature. The resulting solutions were layered with hexanes and allowed to stand for several days to give colorless X-ray-quality crystals. The crystals were sealed with epoxy cement in glass capillaries. Intensity data for (1) were collected at variable scan speeds (3–30° min⁻¹), which depended on a pre-scan count with a skip option, using the moving-crystal/moving-counter technique. Three standard reflections ($\bar{2}08$, $\bar{3}\bar{5}\bar{1}$ and $\bar{2}02$) were measured every 100 reflections and displayed an average decrease of 30.3% during data collection. This decay was corrected for by the use of an isotropic decay correction. Data were corrected for Lorentz and polarization effects, and for absorption effects based on ψ scans using the empirical method of North, Phillips & Matthews (1968). At the beginning of the data collection for (2) six azimuthal scans were collected and later used to correct for absorption. Intensity data were collected at constant speed of 8° min⁻¹ with a variable number of scans (max. = 3), which was determined on the basis of optimum counting statis-

Table 1. *Crystallographic data for (1) and (2)*

| | | |
|--|--|--|
| Systematic absences | $hkl: h + k = 2n + 1$ $h0l: k = 2n + 1$ | $h0l: h + k = 2n + 1$ $0k0: k = 2n + 1$ |
| Crystal size, mm | 0.55 × 0.45 × 0.45 | 0.35 × 0.20 × 0.15 |
| Data collection instrument | Syntex P3 | Rigaku AFC5R |
| Orientation reflections | 25, 20 < 2θ < 30 | 25, 20 < 2θ < 30 |
| Scan method | ω -2θ | ω -2θ |
| Data collection range, ° | 4 ≤ 2θ ≤ 45 | 4 ≤ 2θ ≤ 40 |
| h, k, l , ranges | 0 ≤ h ≤ 12 0 ≤ k ≤ 19 -20 ≤ l ≤ 20 | 0 ≤ h ≤ 14 0 ≤ k ≤ 15 -18 ≤ l ≤ 18 |
| Number of unique data (total) | 2410 | 2225 |
| with $F_o^2 > 3\sigma(F_o^2)$ | 2079 | 1509 |
| Number of parameters refined | 213 | 307 |
| Transmission factors | | |
| T_{\max}, T_{\min} | 0.999, 0.848 | 0.999, 0.576 |
| R | 0.03531 | 0.04890 |
| wR^* | 0.04788 | 0.05658 |
| S | 1.030 | 1.235 |
| Largest shift/e.s.d., final cycle, $(\Delta/\sigma)_{\max}$ | 0.09 | 0.03 |
| $(\Delta\rho)_{\max}, (\Delta\rho)_{\min}$, e Å ⁻³ | 0.54, -0.40 | 1.38, -0.54 |

* $w = 1/\sigma^2(F_o)$.

tics [$F/\sigma(F) = 30$], using the moving-crystal/moving-counter technique. Three standard reflections ($\bar{5}\bar{4}\bar{1}$, $4\bar{6}\bar{6}$ and $\bar{2}\bar{8}\bar{1}$), measured every 150 reflections, displayed an average decrease of 64.3% during the data collection. This decay was corrected for by the use of an isotropic decay correction. Data were corrected for Lorentz and polarization effects. All other information relating to data collection and structure refinement of (1) and (2) is summarized in Table 1. In each case the positions of Hf, P and Cl atoms were determined by direct methods (*SHELXS86*, Sheldrick, 1986) and the remainder of the atoms were located and refined by alternating difference Fourier maps and least-squares cycles employing the Enraf-Nonius (1979) *Structure Determination Package (SDP)*. Atomic scattering factors were those of *SDP*. All atoms were refined anisotropically. H atoms were not included. The final difference Fourier map for (2) showed five peaks near hafnium of height between 1.33 and 0.91 e Å⁻³. The remaining peaks were randomly located and had heights of < 0.85 e Å⁻³. No disorder or other non-routine problems arose for either of the compounds.

Discussion. The positional and equivalent isotropic displacement parameters for (1) and (2) are given in Table 2, while Table 3 presents selected interatomic bond distances and angles.* The structures of the hafnium tetrachloride-phosphine adducts are depicted in Figs. 1 and 2 where the atom-numbering

* Lists of structure factors, anisotropic thermal parameters and complete bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53374 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional and equivalent isotropic displacement parameters and their estimated standard deviations

$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_j.$$

| | x | y | z | $B_{eq}(\text{\AA}^2)$ |
|---|-------------|-------------|-------------|------------------------|
| HfCl₄(dppe).2C₇H₈ | | | | |
| Hf | 0-000 | 0-24198 (2) | 0-250 | 3-226 (8) |
| Cl(1) | 0-0141 (2) | 0-2175 (1) | 0-1331 (1) | 4-84 (5) |
| Cl(2) | 0-1677 (2) | 0-3229 (1) | 0-2762 (1) | 5-87 (6) |
| P(1) | -0-1527 (2) | 0-1197 (1) | 0-21394 (9) | 3-11 (4) |
| C(10) | -0-0517 (7) | 0-0407 (4) | 0-2159 (4) | 3-6 (2) |
| C(11) | -0-2528 (7) | 0-1168 (4) | 0-1258 (4) | 3-6 (2) |
| C(12) | -0-2710 (8) | 0-0515 (5) | 0-0877 (4) | 4-6 (2) |
| C(13) | -0-3505 (8) | 0-0509 (6) | 0-0212 (4) | 5-6 (2) |
| C(14) | -0-4098 (9) | 0-1141 (6) | -0-0078 (5) | 5-9 (2) |
| C(15) | -0-3931 (9) | 0-1767 (6) | 0-0309 (5) | 6-4 (3) |
| C(16) | -0-3147 (9) | 0-1796 (5) | 0-0988 (5) | 5-4 (2) |
| C(21) | -0-2535 (7) | 0-0966 (4) | 0-2698 (3) | 3-5 (2) |
| C(22) | -0-3096 (7) | 0-1551 (5) | 0-2959 (4) | 4-6 (2) |
| C(23) | -0-3943 (8) | 0-1416 (5) | 0-3354 (4) | 5-1 (2) |
| C(24) | -0-4223 (8) | 0-0708 (6) | 0-3505 (4) | 5-3 (2) |
| C(25) | -0-3656 (9) | 0-0134 (5) | 0-3250 (5) | 6-2 (2) |
| C(26) | -0-2789 (8) | 0-0253 (5) | 0-2855 (5) | 5-3 (2) |
| C(51) | 0-589 (1) | 0-4048 (9) | 1-0348 (8) | 11-4 (4) |
| C(52) | 0-4791 (9) | 0-3816 (6) | 1-0593 (6) | 7-2 (3) |
| C(53) | 0-491 (1) | 0-3673 (5) | 1-1317 (5) | 6-2 (2) |
| C(54) | 0-388 (1) | 0-3467 (6) | 1-1525 (6) | 7-3 (3) |
| C(55) | 0-277 (1) | 0-3383 (6) | 1-1048 (6) | 7-4 (3) |
| C(56) | 0-269 (1) | 0-3494 (7) | 1-0357 (7) | 8-0 (3) |
| C(57) | 0-369 (1) | 0-3725 (6) | 1-0108 (5) | 7-1 (3) |
| HfCl₄(dppp) | | | | |
| Hf | 0-46628 (8) | 0-14695 (6) | 0-13519 (5) | 3-80 (2) |
| Cl(1) | 0-4186 (5) | 0-3118 (4) | 0-1309 (3) | 5-2 (2) |
| Cl(2) | 0-4823 (6) | 0-1351 (4) | 0-0028 (3) | 6-8 (2) |
| Cl(3) | 0-5547 (5) | -0-0025 (3) | 0-1838 (3) | 5-3 (2) |
| Cl(4) | 0-2776 (5) | 0-1039 (4) | 0-1132 (4) | 7-7 (2) |
| P(1) | 0-6816 (5) | 0-2324 (4) | 0-1881 (3) | 3-9 (1) |
| P(2) | 0-5149 (5) | 0-1582 (4) | 0-3096 (3) | 3-8 (1) |
| C(111) | 0-809 (1) | 0-166 (1) | 0-197 (1) | 4-7 (5) |
| C(112) | 0-913 (2) | 0-210 (2) | 0-242 (1) | 8-9 (8) |
| C(113) | 1-012 (2) | 0-163 (2) | 0-243 (2) | 10 (1) |
| C(114) | 1-007 (2) | 0-071 (2) | 0-203 (1) | 8-4 (8) |
| C(115) | 0-905 (2) | 0-032 (1) | 0-163 (1) | 7-3 (7) |
| C(116) | 0-798 (2) | 0-081 (1) | 0-159 (1) | 6-0 (6) |
| C(121) | 0-683 (1) | 0-323 (1) | 0-110 (1) | 3-6 (5) |
| C(122) | 0-645 (2) | 0-418 (1) | 0-120 (1) | 6-2 (7) |
| C(123) | 0-634 (2) | 0-486 (2) | 0-052 (1) | 7-6 (8) |
| C(124) | 0-659 (2) | 0-457 (2) | -0-015 (2) | 8-4 (8) |
| C(125) | 0-702 (2) | 0-364 (2) | -0-023 (1) | 8-8 (8) |
| C(126) | 0-711 (2) | 0-294 (2) | 0-041 (1) | 6-9 (6) |
| C(131) | 0-706 (2) | 0-303 (1) | 0-283 (1) | 4-9 (6) |
| C(211) | 0-461 (2) | 0-053 (1) | 0-343 (1) | 4-3 (5) |
| C(212) | 0-532 (2) | -0-027 (1) | 0-383 (1) | 6-0 (7) |
| C(213) | 0-481 (2) | -0-113 (1) | 0-399 (1) | 6-3 (6) |
| C(214) | 0-368 (2) | -0-114 (1) | 0-383 (1) | 5-8 (6) |
| C(215) | 0-297 (2) | -0-036 (1) | 0-346 (1) | 6-0 (7) |
| C(216) | 0-345 (2) | 0-044 (1) | 0-327 (1) | 4-4 (6) |
| C(221) | 0-462 (2) | 0-251 (1) | 0-358 (1) | 3-7 (5) |
| C(222) | 0-353 (2) | 0-290 (1) | 0-316 (1) | 5-4 (6) |
| C(223) | 0-306 (2) | 0-358 (1) | 0-357 (1) | 6-4 (6) |
| C(224) | 0-374 (2) | 0-382 (1) | 0-441 (1) | 6-8 (6) |
| C(225) | 0-482 (2) | 0-342 (1) | 0-481 (1) | 6-3 (7) |
| C(226) | 0-522 (2) | 0-278 (1) | 0-439 (1) | 5-4 (6) |
| C(231) | 0-669 (2) | 0-150 (1) | 0-363 (1) | 4-3 (5) |
| C(300) | 0-738 (2) | 0-241 (1) | 0-365 (1) | 4-7 (6) |

schemes are also defined. Unit-cell diagrams are shown in Figs. 3 and 4.

Little structural information has been available for simple MX_4 adducts ($M = \text{Zr, Hf}$ and $X = \text{F, Cl, Br, I}$) with mono- or bidentate phosphines. Although

Table 3. Selected bond distances (\AA) and angles ($^\circ$); the numbers in parentheses are e.s.d.'s in the least significant digits

| | | | | | | | |
|---|--------|-----------|------------|--------|-----------|--------|-----------|
| HfCl₄(dppe).2C₇H₈ | | | | | | | |
| Hf | Cl(1) | 2-384 (2) | P(1) | C(11) | 1-828 (7) | | |
| Hf | Cl(2) | 2-364 (2) | P(1) | C(21) | 1-815 (8) | | |
| Hf | P(1) | 2-808 (2) | C(10) | C(10) | 1-555 (9) | | |
| P(1) | C(10) | 1-836 (8) | | | | | |
| HfCl₄(dppp) | | | | | | | |
| Hf | Cl(1) | 2-398 (5) | P(1) | C(121) | 1-85 (2) | | |
| Hf | Cl(2) | 2-336 (6) | P(1) | C(131) | 1-83 (2) | | |
| Hf | Cl(3) | 2-398 (5) | P(2) | C(211) | 1-81 (2) | | |
| Hf | Cl(4) | 2-357 (7) | P(2) | C(221) | 1-80 (2) | | |
| Hf | P(1) | 2-821 (6) | P(2) | C(231) | 1-85 (2) | | |
| Hf | P(2) | 2-825 (5) | C(131) | C(300) | 1-57 (3) | | |
| P(1) | C(111) | 1-82 (2) | C(231) | C(300) | 1-55 (3) | | |
| HfCl₄(dppe).2C₇H₈ | | | | | | | |
| Cl(1) | Hf | Cl(1)' | 158-44 (8) | P(1) | Hf | P(1)' | 74-80 (5) |
| Cl(1) | Hf | Cl(2) | 95-11 (9) | Hf | P(1) | C(10) | 106-0 (2) |
| Cl(1) | Hf | Cl(2)' | 98-31 (8) | Hf | P(1) | C(11) | 117-8 (3) |
| Cl(1) | Hf | P(1) | 77-81 (7) | Hf | P(1) | C(21) | 118-2 (2) |
| Cl(1) | Hf | P(1)' | 85-07 (7) | C(10) | P(1) | C(11) | 103-8 (3) |
| Cl(2) | Hf | Cl(2)' | 102-74 (8) | C(10) | P(1) | C(21) | 106-6 (4) |
| Cl(2) | Hf | P(1)' | 164-95 (7) | C(11) | P(1) | C(21) | 103-2 (3) |
| Cl(2) | Hf | P(1) | 91-50 (7) | P(1) | C(10) | C(10)' | 110-8 (5) |
| HfCl₄(dppp) | | | | | | | |
| Cl(1) | Hf | Cl(2) | 98-2 (2) | Hf | P(1) | C(111) | 122-0 (6) |
| Cl(1) | Hf | Cl(3) | 161-2 (2) | Hf | P(1) | C(121) | 108-1 (5) |
| Cl(1) | Hf | Cl(4) | 91-0 (2) | Hf | P(1) | C(131) | 111-7 (8) |
| Cl(1) | Hf | P(1) | 78-4 (2) | C(111) | P(1) | C(121) | 101-2 (9) |
| Cl(1) | Hf | P(2) | 86-6 (2) | C(111) | P(1) | C(131) | 109-1 (9) |
| Cl(2) | Hf | Cl(3) | 95-0 (2) | C(121) | P(1) | C(131) | 102-5 (8) |
| Cl(2) | Hf | Cl(4) | 104-0 (2) | Hf | P(2) | C(211) | 108-6 (6) |
| Cl(2) | Hf | P(1) | 87-1 (2) | Hf | P(2) | C(221) | 122-9 (5) |
| Cl(2) | Hf | P(2) | 163-6 (2) | Hf | P(2) | C(231) | 109-3 (7) |
| Cl(3) | Hf | Cl(4) | 98-8 (2) | C(211) | P(2) | C(221) | 102 (1) |
| Cl(3) | Hf | P(1) | 89-0 (2) | C(211) | P(2) | C(231) | 103-8 (8) |
| Cl(3) | Hf | P(2) | 77-2 (2) | C(221) | P(2) | C(231) | 108-2 (8) |
| Cl(4) | Hf | P(1) | 165-7 (2) | P(1) | C(131) | C(300) | 113 (1) |
| Cl(4) | Hf | P(2) | 91-6 (2) | P(2) | C(231) | C(300) | 116 (1) |
| P(1) | Hf | P(2) | 78-5 (2) | C(131) | C(300) | C(231) | 118 (1) |

several Zr and Hf tetrahalide adducts with such phosphines have been synthesized they have been characterized only by elemental analyses and/or spectroscopic techniques. The earliest report appeared in 1965 and described the synthesis of several compounds of formula $MCl_4(LL)$, where $M = \text{Zr, Hf}$, and $LL = \text{dppe}$ [1,2-bis(diphenylphosphino)ethane] and dpae [1,2-bis(diphenylarsino)ethane], as well as those of formula $\text{ZrBr}_4(LL)$ (Ray & Westland, 1965). In 1979 the synthesis of $\text{ZrCl}_4(\text{dmpe})_2$ [$\text{dmpe} = 1,2\text{-bis(dimethylphosphino)ethane}$] was reported (Beatty, Datta & Wreford, 1979), and later the synthesis of the hafnium analog (Fischer & Wreford, 1980). The last two compounds were used as starting materials for the synthesis of numerous organometallic species of which $\text{ZrMe}_4(\text{dmpe})_2$ and $\text{Zr}(\text{CH}_2\text{Ph})_4(\text{dmpe})$ were structurally characterized (Girolami, Wilkinson, Thornton-Pett & Hursthouse, 1984). Adducts of formula ZrCl_4L_2 ($L = \text{PR}_3$; $R = \text{Et, Pr}$ and $n\text{-Bu}$) (Wengrovius, Schrock & Day, 1980) have been mentioned but

are not well characterized. Synthesis of ZrCl₄(dbpe) [dbpe = 1,2-bis(di-*n*-butylphosphino)ethane] was also reported (Gordon & Wallbridge, 1986).

The two compounds reported here are the first structurally characterized examples of simple, six-coordinate Hf tetrahalide adducts with phosphines. The structures of the two compounds are fundamentally similar except for the size of the chelate ring. In (1) the five-membered ring has a twisted envelope conformation while in (2) the six-membered ring exhibits a twisted boat conformation. The Hf—Cl distances for the Cl atoms *trans* to the P atoms are somewhat shorter and have a mean value of 2.364 (2) and 2.346 (10) Å for (1) and (2), respectively. The values for other Hf—Cl distances are 2.384 (4) and 2.398 (5) Å, respectively for (1) and (2). The mean Hf—P distances are 2.808 (2) and 2.823 (2) Å for (1)

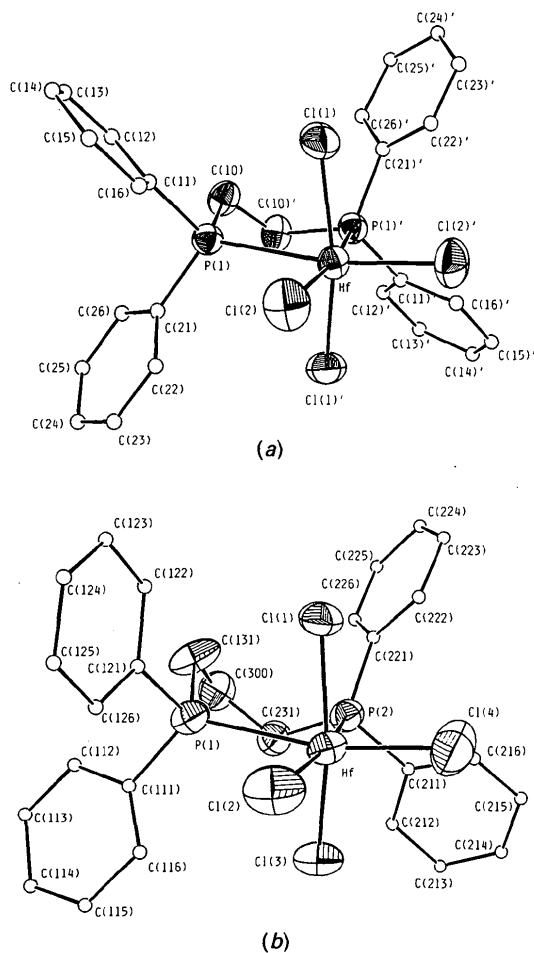


Fig. 1. ORTEP (Johnson, 1965) drawing of the HfCl₄(dppe) fragment of (a) compound (1) and (b) compound (2). HfCl₄(dppe) is located on the twofold symmetry axis. Atoms are represented by displacement ellipsoids at the 50% level. The C atoms are given arbitrary displacement parameters for clarity.

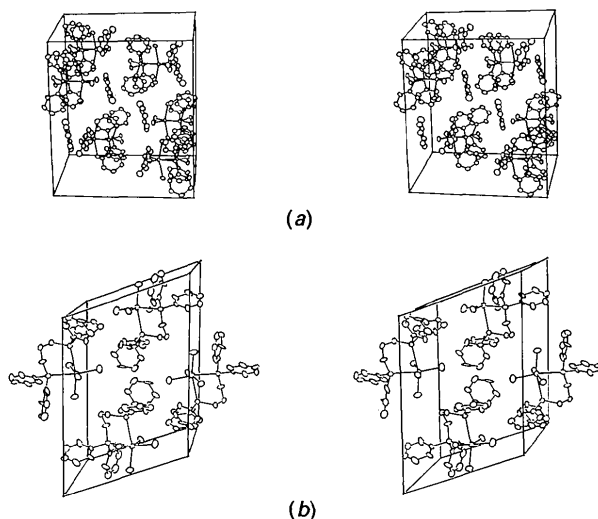


Fig. 2. (a) Unit-cell diagram for (1) and (b) unit-cell diagram for (2). Atoms are represented by displacement ellipsoids at the 20% level. (1) *b* across, *c* down, *a* towards viewer; (2) *a* across, *b* down, *c* towards viewer.

and (2), respectively. The P—Hf—P angle of 78.5° for (2) compared with 74.80 (5)° for (1) is consistent with the larger chelate ring size. The Hf—P bond distances for (1) and (2) compare well with those found in ZrMe₄(dmpe)₂ and Zr(CH₂Ph)₄(dmpe) (Girolami, Wilkinson, Thornton-Pett & Hursthouse, 1984), but the P—Hf—P angle for (1) is about 5° larger.

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References

- BEATTY, R. P., DATTA, S. & WREFORD, S. S. (1979). *Inorg. Chem.* **18**, 3139–3145.
- Enraf-Nonius (1979). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
- FISCHER, M. B. & WREFORD, S. S. (1980). *J. Organomet. Chem.* **188**, 353–366.
- GIROLAMI, G. S., WILKINSON, G., THORNTON-PETT, M. & HURSTHOUSE, M. B. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2789–2794.
- GORDON, D. & WALLBRIDGE, M. G. H. (1986). *Inorg. Chim. Acta*, **111**, 77–81.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- RAY, T. C. & WESTLAND, A. D. (1965). *Inorg. Chem.* **4**, 1501–1504.
- SHELDRIK, G. M. (1986). SHELX86. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
- WENGROVIUS, J. H., SCHROCK, R. R. & DAY, C. S. (1980). *Inorg. Chem.* **20**, 1844–1849.