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Structure of fac-Tricarbonyl[bis(2-diphenylphosphinoethyl)phenylphosphine]-tungsten(0)

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Abstract. $[W(CO)_3\{PhP(C_2H_4PPh_2)_2\}]$, $[W(CO)_3(C_{34}H_{33}P_3)]$, $M_r = 801\cdot8$, monoclinic, $P2_1/n$ $a = 12\cdot052$ (4), $b = 18\cdot761$ (4), $c = 15\cdot174$ (6) Å, $\beta = 106\cdot77$ (3)°, $V = 3285$ (2) Å^3, $Z = 4$, $D_m = 1\cdot61$ (3), $D_x = 1\cdot62$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot7093$ Å, $\mu = 37\cdot7$ cm^{-1}, $F(000) = 1592$, $T = 298$ K, $R = 0\cdot026$ for 4345 observed reflections. The title compound was prepared from $W(CO)_6$ and $PhP(C_2H_4PPh_2)_2$ in n-decane. The three homologues, $M(CO)_3[PhP(C_2H_4PPh_2)_2]$, $M = $ Cr, Mo and W, have similar molecular structure and the Mo and W analogues are isomorphous.

Introduction. The tritertiary phosphine, bis(2-diphenylphosphinoethyl)phenylphosphine (pf-pf-pf), can react with suitable metals under different conditions to form monoligate monometallic, biligate monometallic, triligate monometallic, biligate bimetallic, triligate bimetallic and triligate trimetallic complexes (King, Kapoor & Kapoor, 1971). For the derivatives of metal carbonyls of Group VIb, the three triligate monometallic complexes $M(CO)_3$-(pf-pf-pf), $M = $ Cr, Mo, and W, have been reported (Chatt & Watson, 1961; King, Kapoor & Kapoor, 1971; Favas, Kepert, Skelton & White, 1980). However, the crystal structure of the W complex has not, as yet, been published. In order to compare the structures and as part of a structural study on the derivatives of the metal carbonyls (Ueng & Hwang, 1991; Ueng & Leu, 1991), the crystal structure analysis of the title compound was undertaken.

Experimental. The title compound was prepared by refluxing stoichiometric amounts of $W(CO)_6$ and $PhP(C_2H_4PPh_2)_2$ in purified n-decane under nitrogen for *ca* 5 h. The reaction medium for the thermolytic substitution reaction is n-decane instead of xylene or

decalin which have been previously reported (King, Kapoor & Kapoor, 1971; Favas, Kepert, Skelton & White, 1980). Crystal was prepared from CH_2Cl_2/n-hexane by the diffusion method, crystal dimensions $0\cdot08 \times 0\cdot50 \times 0\cdot50$ mm. D_m by flotation. CAD-4 diffractometer. Unit cell from 25 reflections, 2θ range $17\cdot80$ to $23\cdot06°$. $\theta/2\theta$ mode with θ scan width $= (0\cdot65 + 0\cdot35\tan\theta)°$. Mo $K\alpha$ radiation. Three standard reflections were monitored every 2 h: variation on I $\leq 4\%$. 6189 reflections measured ($1\cdot0 \leq \theta \leq 49\cdot8°$; h, k, l: -14 to 13, 0 to 22, 0 to 18, respectively), 5776 unique ($R_{int} = 0\cdot012$), giving 4345 observed with $I \geq 2\cdot0\sigma(I)$. Absorption corrections were made according to experimental ψ rotation (max., min. transmission factors $= 0\cdot464$, $0\cdot999$). Structure solved by heavy-atom method. Positions of H atoms of phenyl groups were calculated after isotropic refinement, the others found in difference Fourier map. $(\Delta/\sigma)_{max} = 0\cdot10$. Peaks in final ΔF map $0\cdot870$ to $-0\cdot550$ e Å^{-3}. Secondary-extinction coefficient $0\cdot451$ (8) (length in μm). $w = 1/\sigma^2(F_o)$, with $\sigma(F_o)$ from counting statistics. The quantity minimized was $\sum w(KF_o - F_c)^2$, final R, wR and S are $0\cdot026$, $0\cdot020$, and $1\cdot49$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computing programs: *NRCVAX* (Gabe & Lee, 1981) package and *ORTEP* from *Structure Determination Package* (Enraf–Nonius, 1979).

Discussion. Atomic positional parameters are given in Table 1† and selected bond lengths and bond angles of the title compound are listed in Table 2. The molecular structure is shown in Fig. 1.

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and full bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53925 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å²)
W	0·18765 (2)	0·66619 (1)	0·10511 (1)	2·359 (8)
P1	0·3899 (1)	0·67470 (7)	0·20407 (8)	2·87 (6)
P2	0·1658 (1)	0·61936 (6)	0·25310 (9)	2·80 (6)
P3	0·1987 (1)	0·79595 (6)	0·14841 (9)	2·75 (6)
C1	0·0189 (4)	0·6661 (3)	0·0428 (3)	3·9 (3)
C2	0·2141 (4)	0·6891 (2)	−0·0134 (3)	3·4 (2)
C3	0·2041 (4)	0·5654 (2)	0·0772 (3)	3·3 (2)
C4	0·4038 (4)	0·6377 (2)	0·3197 (3)	3·7 (3)
C5	0·3075 (4)	0·5850 (2)	0·3196 (3)	3·4 (2)
C6	0·4336 (4)	0·7681 (3)	0·2312 (3)	3·8 (3)
C7	0·3332 (4)	0·8116 (2)	0·2442 (3)	3·6 (2)
C1A	0·5138 (4)	0·6373 (2)	0·1725 (3)	3·0 (2)
C2A	0·4965 (4)	0·5991 (2)	0·0931 (3)	3·5 (3)
C3A	0·5903 (5)	0·5726 (3)	0·0673 (4)	4·6 (3)
C4A	0·7007 (5)	0·5834 (3)	0·1208 (4)	5·1 (3)
C5A	0·7180 (5)	0·6202 (3)	0·2014 (4)	5·9 (4)
C6A	0·6260 (5)	0·6468 (3)	0·2278 (4)	4·9 (3)
C1B	0·0703 (4)	0·5434 (2)	0·2532 (3)	2·9 (2)
C2B	0·0555 (5)	0·5184 (2)	0·3352 (3)	3·7 (3)
C3B	−0·0190 (5)	0·4621 (3)	0·3363 (4)	4·3 (3)
C4B	−0·0790 (5)	0·4303 (2)	0·2547 (4)	4·2 (3)
C5B	−0·0652 (5)	0·4533 (3)	0·1738 (4)	4·5 (3)
C6B	0·0094 (4)	0·5098 (2)	0·1728 (3)	3·8 (3)
C1C	0·1212 (4)	0·6777 (2)	0·3343 (3)	3·2 (2)
C2C	0·0093 (5)	0·7040 (2)	−0·3030 (4)	4·1 (3)
C3C	−0·0350 (5)	0·7452 (3)	0·3593 (4)	5·6 (4)
C4C	0·0320 (6)	0·7612 (3)	0·4447 (5)	7·3 (4)
C5C	0·1420 (6)	0·7385 (3)	0·4758 (4)	7·4 (4)
C6C	0·1895 (5)	0·6951 (3)	0·4211 (4)	5·6 (3)
C1D	0·0886 (4)	0·8411 (2)	0·1904 (3)	3·0 (2)
C2D	−0·0282 (4)	0·8308 (3)	0·1425 (3)	3·9 (3)
C3D	−0·1150 (5)	0·8668 (3)	0·1684 (4)	5·2 (3)
C4D	−0·0842 (5)	0·9139 (3)	0·2416 (4)	5·2 (3)
C5D	0·0292 (5)	0·9238 (3)	0·2889 (4)	5·1 (3)
C6D	0·1162 (5)	0·8885 (2)	0·2643 (3)	4·0 (3)
C1E	0·2138 (4)	0·8600 (2)	0·0618 (3)	2·9 (2)
C2E	0·1477 (4)	0·9208 (2)	0·0378 (3)	3·6 (3)
C3E	0·1645 (5)	0·9672 (2)	−0·0283 (3)	4·1 (3)
C4E	0·2505 (5)	0·9561 (3)	−0·0693 (4)	4·3 (3)
C5E	0·3193 (5)	0·8964 (3)	−0·0457 (3)	4·3 (3)
C6E	0·3018 (4)	0·8485 (2)	0·0187 (3)	3·5 (3)
O1	−0·0793 (3)	0·6665 (2)	0·0047 (3)	6·7 (2)
O2	0·2256 (3)	0·6977 (2)	−0·0867 (2)	5·3 (2)
O3	0·2212 (3)	0·5070 (2)	0·0577 (2)	5·3 (2)

Table 2. *Selected bond lengths (Å) and angles (°)*

M—P(1)	2·472 (2)	M—C(1)	1·980 (5)
M—P(2)	2·495 (2)	M—C(2)	1·962 (4)
M—P(3)	2·515 (1)	M—C(3)	1·961 (4)
C(1)—O(1)	1·158 (6)	P(1)—C(4)	1·849 (5)
C(2)—O(2)	1·171 (6)	P(1)—C(6)	1·842 (5)
C(3)—O(3)	1·168 (5)	P(2)—C(5)	1·831 (5)
C(4)—C(5)	1·525 (7)	P(3)—C(7)	1·862 (5)
C(6)—C(7)	1·519 (7)		

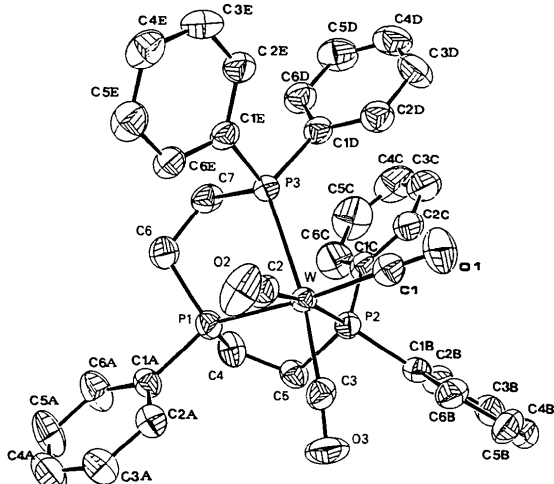|			
P(1)—M—P(2)	79·48 (5)	P(2)—M—C(1)	94·0 (2)
P(1)—M—P(3)	79·05 (4)	P(2)—M—C(3)	84·2 (1)
P(2)—M—P(3)	96·73 (4)	P(3)—M—C(1)	95·5 (1)
C(1)—M—C(2)	88·8 (2)	P(3)—M—C(2)	91·0 (1)
C(1)—M—C(3)	92·9 (2)	P(1)—M—C(1)	170·8 (1)
C(2)—M—C(3)	87·7 (2)	P(2)—M—C(2)	171·6 (1)
P(1)—M—C(2)	98·7 (2)	P(3)—M—C(3)	171·5 (1)
P(1)—M—C(3)	92·9 (1)		

Fig. 1. Molecular structure with atom-numbering scheme.

The molecule consists of a central W atom bonded to three carbonyl groups and three P atoms of the tritertiary phosphine. The coordination around the metal is a distorted octahedron with the twelve *cis* bond angles from 79·05 (4) to 98·7 (2)°, the three axial bond angles being 170·8 (1), 171·5 (1) and 171·6 (1)° and the three dihedral angles among the three mutually perpendicular least-squares planes, P(1)—P(2)—C(1)—C(2), P(1)—P(3)—C(1)—C(3) and P(2)—P(3)—C((2)—C(3), being 81·04 (7), 98·10(8) and 99·60 (7)°. Because the CO group *trans* to another CO group is easily replaced in the thermolytic substitution reaction, the geometry around the tritertiary phosphine is facial rather than meridional. Distortion of the title compound from the ideal octahedron geometry is largely due to the formation of the two fused chelate rings formed by the tridentate phosphine. The three Mo—P lengths are significantly different [2·472 (2), 2·495 (2) and 2·515 (1) Å] from each other. The shorter distance associated with the central P(1) atom relative to the peripheral P(2) and P(3) is a consequence of the lower degree of phenyl substitution. The small but significant difference among the three W—CO bond lengths [1·980 (5), 1·962 (4) and 1·961 (4) Å] complementarily reflects the nonequality of the W—P bond lengths. Owing to less sensitivity for the C—O bond length, the difference among the three C—O bond lengths is not obvious.

Among three homologous complexes of W, Mo and Cr, the M—P and the M—C bond lengths and the bite angles, ∠P—M—P, of the Cr complex are smaller than those of the Mo and W ones. This may be due to the relatively small radius of Cr. Except for the above differences, the structures of the three complexes are similar (Favas, Kepert, Skelton & White, 1980). Among the three complexes, the Mo and W homologues are isomorphous as indicated from their crystal data but the Cr complex is not isomorphous with the Mo or W.

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Structure of (2-Phenoxybenzoato)triphenyltin

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Abstract. [$Sn(C_{13}H_9O_3)(C_6H_5)_3$], $M_r = 563.24$, monoclinic, $P2_1/n$, $a = 15.447$ (3), $b = 10.172$ (1), $c = 17.271$ (4) Å, $\beta = 109.01$ (1)°, $V = 2565.6$ (7) Å^3, $Z = 4$, $D_x = 1.46$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 10.25$ cm^{-1}, $F(000) = 1136$, $T = 298$ K, $R = 0.032$ for 3051 $|F_o| \geq 4\sigma|F_o|$ reflections. The four-coordinate Sn atom exists in a distorted tetrahedral environment.

Introduction. Both steric and electronic factors determine whether a triphenyltin benzoate will adopt a monomeric or a polymeric structure. Four-coordinate structures are generally adopted by the esters of those benzoic acids whose pK_a values exceed 3·0 (Molloy, Blunden & Hill, 1988). Steric factors dominate when the acid carries an *ortho* substituent, as for carboxylate-bridged (2-chlorobenzoato)-triphenyltin (Holmes, Day, Chandrasekhar, Vollano & Holmes, 1986). (2-Methoxybenzoato)triphenyltin (Vollano, Day, Rau, Chandrasekhar & Holmes, 1984) is a four-coordinate molecule, and the present study of the 2-phenoxybenzoato analogue was carried out to ascertain whether replacing the methyl group by the more bulky phenyl group would lead to structural differences.

Experimental. Triphenyltin hydroxide (0·11 g, 0·3 mmol) and 2-phenoxybenzoic acid (0·11 g,

0·5 mmol) were dissolved in a small volume of 80% aqueous ethanol and the mixture refluxed for 1 h. Slow evaporation of the clear solution over a day afforded colorless prismatic crystals.

A crystal measuring 0·08 × 0·16 × 0·20 mm was mounted on a Nicolet *R3m/V* diffractometer for the diffraction study. Unit-cell dimensions were measured from 21 selected strong $5.05 \leq 2\theta \leq 17.33°$ reflections and intensity data were collected at room temperature (298 K) using the ω-scan mode. The data set was processed with a profile-fitting procedure (Diamond, 1969) and corrected for absorption (Kopfmann & Huber, 1968) (transmission factors 0·848 to 0·920). The maximum 2θ angle was 50°, with *hkl* ranges $h\ 0\ to\ 19$, $k\ 0\ to\ 13$ and $l\ -21$ to 21; 4469 reflections were collected, of which 3051 had $|F_o| \geq 4\sigma|F_o|$. Two standard reflections ($22\bar{2}$, $\bar{2}14$) monitored after every 125 data showed an intensity variation of ± 2%. The structure was solved by the heavy-atom method and refined (on F) by full-matrix least squares with anisotropic temperature factors for all non-H atoms. The H atoms of the phenyl groups were generated geometrically (C—H = 0·96 Å) and assigned an isotropic temperature factor of 0·08 Å^2. Computations were performed on a DEC Micro-VAX II computer with the *SHELXTL-Plus* program package (Sheldrick, 1985). Analytical expressions of atomic scattering factors were used, and anomalous-dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1974, Vol.

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