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**Structural Characterization of a Substituted Derivative of  $\text{Ru}_3(\text{CO})_{12}$ :  
1,2,3,1-Bis $\{\mu$ -[Bis(diphenylphosphino)methane]- $P,P'$ }-1,1,2,2,2,3,3,3-octacarbonyl-  
triangulo-triruthenium(0) Acetone Solvate**

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**Abstract**

$\text{Ru}_3(\text{CO})_8\{(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2\}_2 \cdot n(\text{CH}_3)_2\text{CO}$  ( $n \approx 2$ ), orthorhombic,  $Pca2_1$ ,  $a = 21.371(5)$ ,  $b = 15.655(2)$ ,  $c = 18.242(4)$  Å,  $V = 6103$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calc}} = 1.537$ ,  $d_{\text{exp}} = 1.54$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 8.8$  cm<sup>-1</sup>. The structure was solved from a Patterson synthesis and refined to a final  $R$  of 0.051 for 3830 reflections. The complex is derived from  $\text{Ru}_3(\text{CO})_{12}$  by substitution of four equatorial carbonyl ligands by the P atoms of two edge-bridging bis(diphenylphosphino)-methane ligands. Metal–metal bonds within the metal framework are 2.826 (2), 2.833 (2) and 2.858 (2) Å.

**Introduction**

Several tridentate phosphine ligands have recently been designed to prevent cluster degradation under hard reaction conditions (de Boer, van Doorn & Masters, 1978; Arduini, Bahsoun, Osborn & Voelker, 1980). Such ligands were also found efficient in a template synthesis of clusters (Osborn & Stanley, 1980). However, the reaction of these tripod ligands with

$\text{Ru}_3(\text{CO})_{12}$  gave poor yields of the capped products; This was attributed to the fact that the capped product is derived from axial substitution, whereas equatorial substitutions are generally easier with phosphines (Arduini *et al.*, 1980).

We recently suggested an alternative way to retain the cluster frame by using an edge-bridging ligand such as bis(diphenylphosphino)methane (dppm): reaction of this ligand with  $\text{Ru}_3(\text{CO})_{12}$  gave good yields of the new complex  $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$  (Lavigne & Bonnet, 1981). We now report the X ray structural determination of this species.

**Experimental**

Suitable crystals for the complex were grown from a  $\frac{1}{3}$  acetone/ethanol mixture as red, lozenge-based parallelepiped platelets:  $\text{Ru}_3(\text{CO})_8(\text{dppm})_2 \cdot n(\text{CH}_3)_2\text{CO}$  ( $n \approx 2$ ).

Although the presence of acetone molecules in the lattice was unambiguously determined by mass spectrometry and <sup>1</sup>H NMR spectroscopy, the precise number of such molecules could not be accurately determined from analytical results.

	C (%)	H (%)	$d_{\text{calc}}$
	(calc.)	(calc.)	( $\text{g cm}^{-3}$ )
$\text{Ru}_3(\text{CO})_8(\text{dppm})_2$	53.70	3.39	1.411
$\text{Ru}_3(\text{CO})_8(\text{dppm})_2 \cdot (\text{CH}_3)_2\text{CO}$	54.05	3.69	1.474
$\text{Ru}_3(\text{CO})_8(\text{dppm})_2 \cdot 2(\text{CH}_3)_2\text{CO}$	54.39	3.96	1.537
	C (%)	H (%)	$d_{\text{exp}}$
	(exp.)	(exp.)	( $\text{g cm}^{-3}$ )
	53.30	3.78	1.54

Preliminary photographic data revealed that these crystals belong to the orthorhombic system and show systematic extinctions ( $0kl, l = 2n + 1; h0l, h = 2n + 1$ ) consistent with space groups  $Pca2_1$  (No. 29) and  $Pcam$  (No. 49). (Further evidence for the noncentrosymmetric group  $Pca2_1$  was obtained from statistical tests on  $E$  values.)

Cell constants were obtained from a least-squares fit to the setting angles of 25 reflections [ $24^\circ < 2\theta(\text{Mo}) < 26^\circ$ ] chosen from diverse regions of reciprocal space.

These cell constants and other pertinent data are given in the *Abstract*. 4360 reflections were collected at 294 K on an Enraf-Nonius CAD-4 diffractometer [Mo  $K\alpha$  radiation from a monochromator;  $\omega/2\theta$  scan technique, scan width  $1.5^\circ$  ( $\omega$ ), scan speed  $0.03^\circ \text{ s}^{-1}$  ( $\omega$ ); background measured for 12.5 s at the beginning and end of each scan]; take-off angle  $3^\circ$ ;  $2\theta$  limits  $4\text{--}45^\circ$ ; standard reflections (no significant deviations): 12,0,0; 10,0,5; 10,2,4; 094].

After processing the data, using a value of  $p = 0.03$  (Mosset, Bonnet & Galy, 1977), only those unique reflections having  $F_o^2 > 3\sigma(F_o^2)$  were used in subsequent calculations.

### Structure solution and refinement

Atomic scattering factors were taken from Cromer & Waber's (1974a) tabulation for all atoms except H, for which the values of Stewart, Davidson & Simpson (1965) were used. Anomalous-dispersion terms for Ru and P atoms were included in  $F_c$  (Cromer & Waber, 1974b).

The structure was solved by the heavy-atom technique. The three Ru atoms were located from a conventional Patterson synthesis. The positions of the remaining nonhydrogen atoms were obtained through the usual combination of full-matrix least-squares refinement and difference Fourier syntheses. Refinement of an isotropic model including 25 independent atoms and eight rigid groups (C atoms in phenyl rings were constrained to  $D_{6h}$  symmetry; C—C = 1.395 Å) converged to  $R = 0.064$  and  $R_w = 0.095$ . At this stage, H atoms were introduced and fixed in idealized positions (C—H = 0.95 Å); isotropic thermal parameters assigned to H atoms were taken as  $1 \text{ \AA}^2$  greater than those of their neighbouring C atoms. Anisotropic thermal parameters were used for 25

independent atoms. The final full-matrix least-squares refinement, involving 322 variables and 3830 observations, converged to  $R = 0.051$  and  $R_w = 0.082$ .\*

At this stage, a careful search was made in order to locate acetone molecules in the lattice. Several peaks were indeed observed in a Fourier difference map.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36779 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters for the non-group atoms of  $\text{Ru}_3(\text{CO})_8(\text{dppm})_2 \cdot 2(\text{CH}_3)_2\text{CO}$*

Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}$ ( $\text{\AA}^2$ )
Ru(1)	0.14735 (6)	0.22449 (8)	0	2.41 (6)
Ru(2)	0.03449 (6)	0.14741 (8)	0.0463 (1)	2.51 (6)
Ru(3)	0.04074 (6)	0.32808 (8)	0.0250 (1)	3.09 (7)
P(1)	0.2092 (2)	0.1046 (3)	0.0109 (3)	2.7 (2)
P(2)	0.0778 (2)	0.0133 (3)	0.0285 (3)	2.7 (2)
P(3)	0.0998 (2)	0.4522 (3)	0.0261 (3)	3.2 (2)
P(4)	0.2016 (2)	0.3421 (3)	−0.0472 (3)	3.0 (2)
C(1)	0.1741 (9)	0.261 (1)	0.097 (1)	3.7 (10)
O(1)	0.1923 (7)	0.2821 (9)	0.1525 (8)	4.9 (8)
C(2)	0.0787 (9)	0.152 (1)	0.139 (1)	3.3 (9)
O(2)	0.0990 (6)	0.1500 (9)	0.1970 (8)	4.6 (8)
C(3)	0.047 (1)	0.326 (1)	0.131 (1)	5.0 (10)
O(3)	0.0436 (9)	0.331 (1)	0.1932 (10)	8.2 (8)
C(4)	0.1163 (9)	0.175 (1)	−0.092 (1)	3.5 (9)
O(4)	0.1035 (7)	0.1463 (9)	−0.1457 (7)	4.1 (7)
C(5)	−0.0075 (9)	0.148 (1)	−0.048 (1)	3.5 (9)
O(5)	−0.0388 (7)	0.1463 (10)	−0.0989 (8)	5.1 (8)
C(6)	0.356 (9)	0.315 (1)	−0.079 (1)	3.4 (9)
O(6)	0.0282 (7)	0.3138 (10)	−0.1408 (9)	5.2 (8)
C(7)	−0.0432 (9)	0.121 (1)	0.091 (1)	4.0 (9)
O(7)	−0.0882 (7)	0.107 (1)	0.1188 (10)	8.1 (9)
C(8)	−0.0412 (10)	0.385 (1)	0.032 (1)	5.8 (10)
O(8)	−0.0860 (7)	0.418 (1)	0.036 (1)	10.7 (10)
C(9)	0.1611 (7)	0.011 (1)	0.040 (1)	3.3 (8)
C(10)	0.1846 (7)	0.436 (1)	0.011 (1)	3.3 (8)
H(1)	0.169	0.002	0.092	
H(2)	0.177	−0.038	0.015	
H(3)	0.205	0.431	0.057	
H(4)	0.202	0.487	−0.012	

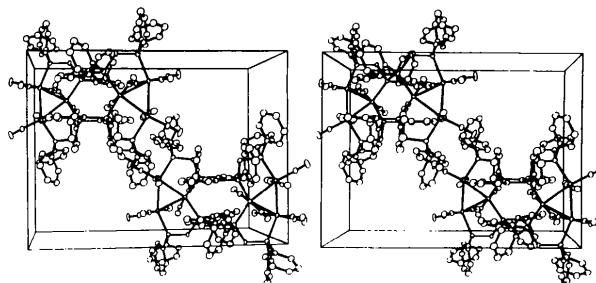


Fig. 1. Stereoscopic view showing the molecular packing.

Table 2. *Derived parameters for the rigid-group atoms*

$x_c$ ,  $y_c$  and  $z_c$  are the fractional coordinates of the origin of the rigid group. The rigid-group orientation angles  $\delta$ ,  $\varepsilon$  and  $\eta$  (radians) have been defined by La Placa & Ibers (1965).

	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )		$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
C(11)	0.2540 (5)	0.0670 (7)	-0.0692 (6)	2.9 (3)	C(35)	0.0847 (6)	0.5362 (7)	-0.0383 (6)	3.5 (4)
C(12)	0.2687 (6)	0.1278 (6)	-0.1221 (7)	3.7 (4)	C(36)	0.0488 (6)	0.5198 (7)	-0.1003 (7)	5.4 (5)
C(13)	0.3104 (6)	0.1077 (8)	-0.1781 (6)	5.3 (5)	C(37)	0.0412 (6)	0.5828 (9)	-0.1534 (6)	6.1 (6)
C(14)	0.3374 (6)	0.0268 (9)	-0.1812 (7)	5.8 (5)	C(38)	0.0696 (7)	0.6622 (8)	-0.1444 (7)	6.1 (5)
C(15)	0.3226 (6)	-0.0340 (7)	-0.1283 (8)	6.5 (6)	C(39)	0.1055 (7)	0.6785 (6)	-0.0823 (8)	5.8 (5)
C(16)	0.2809 (6)	-0.0139 (7)	-0.0723 (7)	5.4 (5)	C(40)	0.1131 (6)	0.6155 (8)	-0.0293 (6)	5.7 (5)
H(12)	0.2503 (8)	0.1830 (7)	-0.1200 (10)	4.8	H(36)	0.0294 (9)	0.4656 (8)	-0.106 (1)	6.2
H(13)	0.3205 (9)	0.149 (1)	-0.2142 (8)	6.5	H(37)	0.0167 (9)	0.572 (1)	-0.1958 (8)	7.0
H(14)	0.3658 (8)	0.013 (1)	-0.2194 (9)	6.9	H(38)	0.064 (1)	0.705 (1)	-0.1806 (9)	7.1
H(15)	0.3410 (9)	-0.0892 (8)	-0.130 (1)	7.3	H(39)	0.1249 (10)	0.7327 (8)	-0.076 (1)	6.7
H(16)	0.2709 (9)	-0.0554 (9)	0.0361 (9)	7.0	H(40)	0.1376 (9)	0.627 (1)	0.0131 (8)	6.5
C(17)	0.2733 (5)	0.1097 (8)	0.0797 (6)	3.4 (4)	C(41)	0.0953 (6)	0.5047 (8)	0.1152 (6)	3.5 (4)
C(18)	0.2625 (5)	0.0904 (8)	0.1531 (7)	4.9 (5)	C(42)	0.1431 (4)	0.5031 (9)	0.1670 (8)	6.1 (5)
C(19)	0.3119 (7)	0.0904 (9)	0.2027 (6)	6.3 (5)	C(43)	0.1325 (6)	0.5346 (10)	0.2373 (7)	6.7 (6)
C(20)	0.3722 (6)	0.1097 (9)	0.1789 (8)	6.1 (5)	C(44)	0.0741 (6)	0.5677 (9)	0.2556 (6)	5.6 (5)
C(21)	0.3830 (5)	0.1291 (9)	0.1056 (8)	6.8 (6)	C(45)	0.0264 (5)	0.5693 (8)	0.2038 (7)	5.4 (5)
C(22)	0.3335 (6)	0.1291 (9)	0.0559 (6)	5.3 (5)	C(46)	0.0370 (5)	0.5378 (8)	0.1336 (6)	4.1 (4)
H(18)	0.2213 (6)	0.077 (1)	0.1693 (9)	5.9	H(42)	0.1829 (5)	0.480 (1)	0.154 (1)	7.0
H(19)	0.3045 (9)	0.077 (1)	0.2528 (6)	6.9	H(43)	0.1651 (7)	0.533 (1)	0.2727 (9)	8.1
H(20)	0.4059 (7)	0.110 (1)	0.2128 (10)	7.2	H(44)	0.0669 (9)	0.589 (1)	0.3036 (6)	7.0
H(21)	0.4241 (5)	0.142 (1)	0.089 (1)	7.5	H(45)	-0.0135 (6)	0.592 (1)	0.2163 (10)	6.4
H(22)	0.3409 (9)	0.142 (1)	0.0059 (7)	6.5	H(46)	0.0044 (6)	0.539 (1)	0.0982 (8)	5.5
C(23)	0.0622 (6)	-0.0371 (8)	-0.0581 (6)	3.6 (4)	C(47)	0.2861 (5)	0.3403 (8)	-0.0456 (7)	3.3 (4)
C(24)	0.1082 (4)	-0.0469 (8)	-0.1115 (7)	4.5 (5)	C(48)	0.3156 (6)	0.3398 (9)	0.0224 (6)	5.8 (5)
C(25)	0.0935 (6)	-0.0855 (9)	-0.1780 (6)	5.3 (5)	C(49)	0.3806 (6)	0.3387 (9)	0.0265 (7)	7.3 (6)
C(26)	0.0328 (6)	-0.1141 (8)	-0.1912 (6)	5.5 (5)	C(50)	0.4161 (5)	0.3381 (9)	-0.0374 (9)	7.6 (7)
C(27)	-0.0131 (5)	-0.1042 (8)	-0.1378 (8)	5.4 (5)	C(51)	0.3866 (6)	0.3385 (10)	-0.1054 (7)	7.2 (6)
C(28)	0.0016 (5)	-0.0657 (8)	-0.0712 (7)	5.3 (5)	C(52)	0.3216 (7)	0.3396 (9)	-0.1095 (6)	5.6 (5)
H(24)	0.1495 (5)	-0.027 (1)	-0.1025 (10)	5.6	H(48)	0.2913 (9)	0.340 (1)	0.0661 (7)	6.8
H(25)	0.1248 (7)	-0.092 (1)	-0.2145 (8)	6.4	H(49)	0.4008 (9)	0.338 (1)	0.0729 (8)	7.7
H(26)	0.0228 (9)	-0.140 (1)	-0.2366 (7)	6.7	H(50)	0.4605 (5)	0.337 (1)	-0.035 (1)	7.8
H(27)	-0.0545 (5)	-0.124 (1)	-0.147 (1)	6.3	H(51)	0.4108 (9)	0.338 (1)	-0.1491 (9)	7.7
H(28)	-0.0298 (7)	-0.059 (1)	-0.0348 (9)	6.5	H(52)	0.3014 (9)	0.340 (1)	-0.1559 (7)	6.3
C(29)	0.0601 (5)	-0.0687 (7)	0.0937 (6)	3.2 (3)	C(53)	0.1886 (6)	0.3826 (8)	-0.1406 (6)	3.2 (3)
C(30)	0.0402 (5)	-0.0464 (6)	0.1638 (6)	3.3 (3)	C(54)	0.1899 (6)	0.4699 (7)	-0.1551 (7)	5.2 (5)
C(31)	0.0319 (6)	-0.1094 (8)	0.2168 (5)	5.1 (5)	C(55)	0.1784 (7)	0.4996 (7)	-0.2257 (9)	8.3 (7)
C(32)	0.0435 (7)	-0.1946 (7)	0.1997 (7)	6.4 (5)	C(56)	0.1654 (7)	0.442 (1)	-0.2818 (6)	8.2 (7)
C(33)	0.0634 (7)	-0.2168 (6)	0.1296 (8)	7.3 (6)	C(57)	0.1641 (7)	0.3546 (9)	-0.2672 (6)	7.0 (6)
C(34)	0.0717 (6)	-0.1538 (8)	0.0766 (6)	5.5 (5)	C(58)	0.1756 (6)	0.3250 (6)	-0.1966 (7)	5.0 (5)
H(30)	0.0323 (8)	0.0117 (6)	0.1755 (9)	4.4	H(54)	0.1988 (10)	0.5092 (9)	-0.1168 (9)	6.1
H(31)	0.0183 (9)	-0.094 (1)	0.2646 (6)	5.9	H(55)	0.179 (1)	0.5591 (8)	-0.236 (1)	8.0
H(32)	0.0379 (10)	-0.2376 (9)	0.2358 (9)	6.6	H(56)	0.158 (1)	0.462 (1)	-0.3300 (7)	8.6
H(33)	0.071 (1)	-0.2750 (6)	0.118 (1)	8.0	H(57)	0.155 (1)	0.315 (1)	-0.3055 (8)	7.4
H(34)	0.0853 (9)	-0.169 (1)	0.0288 (7)	6.1	H(58)	0.1747 (10)	0.2654 (6)	-0.187 (1)	5.8

## Rigid-group parameters

Group	$x_c$	$y_c$	$z_c$	$\delta$	$\varepsilon$	$\eta$
$\varphi$ (1)	0.2957 (4)	0.0469 (6)	-0.1252 (5)	0.748 (8)	-2.678 (8)	2.254 (9)
$\varphi$ (2)	0.3227 (4)	0.1097 (5)	0.1293 (6)	1.699 (8)	2.944 (7)	-1.375 (8)
$\varphi$ (3)	0.0475 (4)	-0.0756 (5)	-0.1246 (5)	-0.922 (10)	-2.494 (7)	2.070 (10)
$\varphi$ (4)	0.0518 (4)	-0.1316 (6)	0.1467 (5)	0.031 (8)	2.867 (7)	-1.268 (8)
$\varphi$ (5)	0.0772 (4)	0.5992 (6)	-0.0913 (5)	2.945 (9)	-2.801 (8)	2.100 (9)
$\varphi$ (6)	0.0847 (4)	0.5362 (5)	0.1854 (5)	-2.17 (1)	2.406 (7)	-1.16 (1)
$\varphi$ (7)	0.3511 (5)	0.3391 (5)	-0.0415 (6)	1.558 (9)	-2.671 (8)	-1.57 (1)
$\varphi$ (8)	0.1770 (4)	0.4123 (7)	-0.2112 (6)	-0.87 (3)	-1.858 (8)	0.74 (3)

Their maximum magnitude was  $\frac{2}{3}$  of a standard C atom in a previous Fourier synthesis. All these peaks were found close to the axes (0.75, 0.25,  $z$ ) and (0.25, 0.75,

$z$ ). Moreover, a careful examination of molecular packing within the unit cell (Fig. 1) revealed the presence of cylindrical holes (approximate diameter,

Table 3. *Interatomic distances (Å) with e.s.d.'s for Ru<sub>3</sub>(CO)<sub>8</sub>(dppm)<sub>2</sub>·2(CH<sub>3</sub>)<sub>2</sub>CO*

Ru—Ru			
Ru(1)—Ru(2)	2.826 (2)	Ru(2)—Ru(3)	2.858 (2)
Ru(1)—Ru(3)	2.833 (2)		
Ru—C and Ru...O (axial)			
Ru(1)—C(1)	1.94 (2)	Ru(1)...O(1)	3.08 (1)
Ru(2)—C(2)	1.95 (2)	Ru(2)...O(2)	3.07 (1)
Ru(3)—C(3)	1.94 (2)	Ru(3)...O(3)	3.07 (1)
Ru(1)—C(4)	1.96 (2)	Ru(1)...O(4)	3.07 (1)
Ru(2)—C(5)	1.94 (2)	Ru(2)...O(5)	3.08 (1)
Ru(3)—C(6)	1.92 (2)	Ru(3)...O(6)	3.04 (2)
Average	1.941 [5]*	Average	3.069 [5]*
Ru—C and Ru...O (equatorial)			
Ru(2)—C(7)	1.90 (2)	Ru(2)...O(7)	3.01 (1)
Ru(3)—C(8)	1.97 (2)	Ru(3)...O(8)	3.06 (1)
C—O (axial)			
C(1)—O(1)	1.14 (2)	C(4)—O(4)	1.12 (2)
C(2)—O(2)	1.14 (2)	C(5)—O(5)	1.14 (2)
C(3)—O(3)	1.14 (2)	C(6)—O(6)	1.13 (2)
C—O equatorial			
C(7)—O(7)	1.10 (2)	C(8)—O(8)	1.09 (2)
Ru—P			
Ru(1)—P(1)	2.304 (4)	Ru(2)—P(2)	2.317 (4)
Ru(1)—P(4)	2.341 (5)	Ru(3)—P(3)	2.318 (4)
P—C			
P(1)—C(9)	1.87 (1)	P(3)—C(10)	1.85 (2)
P(1)—C(11)	1.84 (1)	P(3)—C(35)	1.79 (1)
P(1)—C(17)	1.86 (1)	P(3)—C(41)	1.82 (1)
P(2)—C(9)	1.79 (2)	P(4)—C(10)	1.85 (2)
P(2)—C(23)	1.80 (1)	P(4)—C(47)	1.80 (1)
P(2)—C(29)	1.79 (1)	P(4)—C(53)	1.84 (1)

\* Error estimates shown in square brackets for average distances,  $\bar{d}$ , are the exterior estimates of the precision of the average value given by  $[\sum n(\bar{d} - d)^2 / (n^2 - n)]^{1/2}$ .

6 Å), centred on these axes. Such features strongly suggested that solvent molecules were trapped in these holes. The absence of reliable bonding distances between the residual peaks was indicative of an intricate disorder of these acetone molecules and prevented any further crystallographic treatment. Consequently, the crystal structure determination does not allow determination of the accurate number of solvent molecules in the lattice and so there is no proof of a stoichiometric amount.

All calculations were performed on a CII IRIS 80 computer, at the Centre Universitaire de Calcul de Toulouse. In addition to various local programs, modified versions of the following were used: A. Zalkin's *FORDAP* Fourier summation program; J. A. Ibers's *NUCLS* full-matrix least-squares program [modified from *ORFLS* (Busing, Martin & Levy, 1962)]; *ORFFE* error function program (Busing,

Table 4. *Selected bond angles (°) with e.s.d.'s for Ru<sub>3</sub>(CO)<sub>8</sub>(dppm)<sub>2</sub>·2(CH<sub>3</sub>)<sub>2</sub>CO*

Metal triangle			
Ru(1)—Ru(2)—Ru(3)	59.80 (4)	Ru(2)—Ru(1)—Ru(3)	60.66 (5)
Ru(1)—Ru(3)—Ru(2)	59.54 (4)		
Ru(1) environment			
C(1)—Ru(1)—Ru(2)	96.0 (5)	C(4)—Ru(1)—Ru(2)	78.2 (5)
C(1)—Ru(1)—Ru(3)	85.6 (6)	C(4)—Ru(1)—Ru(3)	95.2 (5)
C(1)—Ru(1)—P(1)	89.4 (6)	C(4)—Ru(1)—P(1)	87.0 (5)
C(1)—Ru(1)—P(4)	87.7 (5)	C(4)—Ru(1)—P(4)	99.5 (5)
P(1)—Ru(1)—Ru(2)	96.7 (1)		
P(1)—Ru(1)—P(4)	112.8 (2)		
P(4)—Ru(1)—Ru(3)	90.4 (1)		
Ru(2) environment			
C(2)—Ru(2)—Ru(1)	80.2 (5)	C(5)—Ru(2)—Ru(1)	97.3 (1)
C(2)—Ru(2)—Ru(3)	93.3 (5)	C(5)—Ru(2)—Ru(3)	83.9 (5)
C(2)—Ru(2)—C(7)	93.1 (8)	C(5)—Ru(2)—C(7)	88.9 (8)
C(2)—Ru(2)—P(2)	87.9 (5)	C(5)—Ru(2)—P(2)	93.9 (6)
P(2)—Ru(2)—Ru(1)	90.2 (1)		
P(2)—Ru(2)—C(7)	102.1 (6)		
C(7)—Ru(2)—Ru(3)	108.6 (6)		
Ru(3) environment			
C(3)—Ru(3)—Ru(1)	95.7 (6)	C(6)—Ru(3)—Ru(1)	79.8 (5)
C(3)—Ru(3)—Ru(2)	81.4 (6)	C(6)—Ru(3)—Ru(2)	91.3 (5)
C(3)—Ru(3)—C(8)	89.8 (9)	C(6)—Ru(3)—C(8)	93.8 (9)
C(3)—Ru(3)—P(3)	88.3 (7)	C(6)—Ru(3)—P(3)	97.6 (6)
P(3)—Ru(3)—Ru(1)	92.5 (1)		
P(3)—Ru(3)—C(8)	96.2 (6)		
C(8)—Ru(3)—Ru(2)	113.2 (6)		

Martin & Levy, 1964); and Johnson's (1965) *ORTEP* program.

A list of atomic coordinates and thermal parameters is presented in Table 1 for non-group atoms and in Table 2 for rigid-group atoms. Selected interatomic distances are listed in Table 3; bond angles are in Table 4.

## Results and discussion

Fig. 1 shows the molecular packing within the unit cell and reveals the presence of cylindrical holes in the lattice. These cavities are filled with disordered acetone molecules, as pointed out above.

The complex Ru<sub>3</sub>(CO)<sub>8</sub>(dppm)<sub>2</sub> is derived from Ru<sub>3</sub>(CO)<sub>12</sub> (Churchill, Hollander & Hutchinson, 1977) by substitution of four equatorial carbonyl groups by the P atoms of two edge-bridging dppm ligands (Fig. 2). The triangular framework of metal atoms involves (i) two 'supported' metal—metal bonds: Ru(1)—Ru(2) 2.826 (2) and Ru(1)—Ru(3) 2.833 (2) Å, and (ii) an 'unsupported' bond: Ru(2)—Ru(3) 2.858 (2) Å.

The latter bond length is closely related to those found in the parent molecule Ru<sub>3</sub>(CO)<sub>12</sub> [Ru—Ru: 2.8595 (4), 2.8518 (4), 2.8512 (4) Å (Churchill *et al.*, 1977)], while a shortening of both supported bond lengths is observed.

This shortening is probably of little chemical significance, since the reverse tendency was previously found in a closely related structure involving bis-

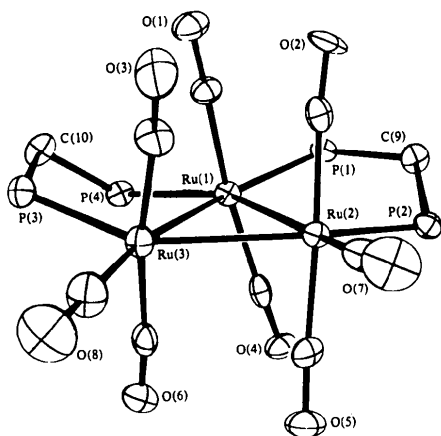


Fig. 2. Geometry and labeling of the complex  $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ ; phenyl rings on P atoms have been omitted for clarity.

(dimethylarsino)tetrafluorobutene as a ligand (Roberts & Trotter, 1970). The difficulty of rationalizing the variations of metal–metal bond lengths in substituted clusters probably arises from the competition between several steric and electronic factors which can act in opposite ways. Both these influences are discussed below.

### (1) Electronic influence

Since ligands of acceptor strength lower than that of a CO group are less efficient at removing  $\pi$  antibonding electron density from the metal cluster,  $M-M$  bonds would be expected to be longer than those involving only CO ligands (Roberts & Trotter, 1971). Although this influence is currently mentioned (Forbes, Goodhand, Jones & Hamor, 1979), it is not prevailing in the present case.

Moreover, the additional antibonding electron density in the substituted derivative might be expected to participate in an increased  $\pi$  back bonding with the remaining CO ligands. Nevertheless, the mean values  $\text{Ru}-\text{C}$  (axial) 1.941[5] and  $\text{Ru}\cdots\text{O}$  (axial) 3.069 [5] Å show no significant variation relative to the corresponding interatomic distances in  $\text{Ru}_3(\text{CO})_{12}$  [ $\text{Ru}-\text{C}$  (axial) 1.942 [4],  $\text{Ru}\cdots\text{O}$  (axial) 3.071 [3] Å].

### (2) Steric influence

The steric influence is often considered as the prevailing factor determining metal–metal bond-length variations. For instance, the steric hindrance of bulky phosphine groups  $\text{P}(\text{OCH}_3)_3$  or  $\text{PPh}_3$  was previously found to account for a lengthening of adjacent  $M-M$  bonds (Benfield, Johnson, Raithby & Sheldrick, 1978; Forbes *et al.*, 1979).

In the case of a bidentate bridging ligand, the bite angle would be expected to have an influence on the

Table 5. Dihedral angles ( $^\circ$ ) related to Newman projections along the metal–metal vectors

$[\text{Ru}(1)\text{Ru}(2)\text{P}(1)]/[\text{Ru}(1)\text{Ru}(2)\text{P}(2)]$	−15.8 (2)
$[\text{Ru}(1)\text{Ru}(2)\text{C}(1)]/[\text{Ru}(1)\text{Ru}(2)\text{C}(2)]$	−18.1 (7)
$[\text{Ru}(1)\text{Ru}(2)\text{C}(5)]/[\text{Ru}(1)\text{Ru}(2)\text{C}(4)]$	24.3 (7)
$[\text{Ru}(1)\text{Ru}(3)\text{P}(3)]/[\text{Ru}(1)\text{Ru}(3)\text{P}(4)]$	21.9 (2)
$[\text{Ru}(1)\text{Ru}(3)\text{C}(1)]/[\text{Ru}(1)\text{Ru}(3)\text{C}(3)]$	−22.8 (8)
$[\text{Ru}(1)\text{Ru}(3)\text{C}(4)]/[\text{Ru}(1)\text{Ru}(3)\text{C}(6)]$	−24.2 (7)
$[\text{Ru}(2)\text{Ru}(3)\text{C}(7)]/[\text{Ru}(2)\text{Ru}(3)\text{C}(8)]$	17.0 (10)
$[\text{Ru}(2)\text{Ru}(3)\text{C}(2)]/[\text{Ru}(2)\text{Ru}(3)\text{C}(3)]$	−25.2 (8)
$[\text{Ru}(2)\text{Ru}(3)\text{C}(5)]/[\text{Ru}(2)\text{Ru}(3)\text{C}(6)]$	−24.7 (8)

metal–metal separation. In contrast to ligands having a rigid frame (Roberts, Penfold & Trotter, 1970), bis(diphenylphosphino)methane is known to accommodate a wide range of metal–metal distances in binuclear species (Cowie & Dwight, 1980; Mays, Prest & Raithby, 1980; Cowie & Southern, 1980). This accommodation is related to the possibility of internal rotational conformations (Cotton, 1976) which allow the ligand to fit the accurate bite angle.

An additional distortion occurs in the present case, since  $\text{Ru}-\text{P}$  bonds are not coplanar; the P atoms are significantly out of the equatorial plane of the metal triangle: P(1)  $-0.332$  (5), P(2)  $+0.303$  (5), P(3)  $-0.596$  (5), P(4)  $+0.285$  (5) Å. These deviations induce slight rotations of the octahedral basis set of the three metal atoms relative to  $\text{Ru}_3(\text{CO})_{12}$ . Newman projections along the metal–metal vectors show that axial carbonyl ligands are no longer eclipsed, but exhibit a slightly staggered conformation, as shown in Table 5. The resulting reduction of van der Waals repulsions between these CO ligands would result in the slight decrease of metal–metal bond distances in comparison with those of  $\text{Ru}_3(\text{CO})_{12}$ .

As we are writing this paper, first attempts to clarify the effects of carbonyl substitution in several metal clusters have now been reported in a review by Benfield & Johnson (1981).

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**Structure of a Tetrairidium Cluster with a Bridging diop Ligand: 2,3- $\mu$ -[(+)-4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane]-(*P,P'*)-2,3;3,4;4,2-tri- $\mu$ -carbonyl-1,1,1,2,3,4,4-heptacarbonyl-tetrahedro-tetrairidium**

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### Abstract

The crystal structure of Ir<sub>4</sub>(CO)<sub>10</sub>{(+)-diop}, C<sub>41</sub>H<sub>32</sub>Ir<sub>4</sub>O<sub>12</sub>P<sub>2</sub>, has been determined. The cluster crystallizes in the space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, with *a* = 12.009 (3), *b* = 16.943 (6) and *c* = 20.823 (8) Å. The structure was refined to *R*<sub>1</sub> = 0.045 and *R*<sub>2</sub> = 0.052 for 1875 reflections. The diop ligand adopts an unusual configuration and bridges two Ir atoms, forming an eight-membered ring  $\square\text{Ir}-\text{Ir}-\text{P}-\text{C}_4-\text{P}\square$ . Ir atoms edge-bridged by carbonyl ligands have a mean Ir–Ir distance of 2.764 (2) Å, which is significantly longer than the mean Ir–Ir distance of 2.723 (2) Å for non-carbonyl-bridged atoms.

### Introduction

Many transition-metal complexes involving diop [4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane] have been used as catalysts for asymmetric synthesis (Balavoine, Brunie & Kagan, 1980; Balavoine, Dang, Eskenazi & Kagan, 1980; Botteghi *et al.*, 1977; Consiglio, 1976, 1977; Glaser & Blumenfeld, 1977). The configuration of this ligand in several mononuclear transition-metal complexes has been determined by X-ray methods (Balavoine, Brunie & Kagan, 1980; Brunie, Mazam, Langlois & Kagan, 1976; Gramlich & Consiglio, 1979; Knowles, Vineyard, Sabacky & Stults, 1979). In all of these, diop acts as a chelating ligand and exhibits only slight conformational changes, with the  $\square\text{metal}-\text{P}-\text{C}_4-\text{P}\square$

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