

with N...S distances from 3.29 (9) to 3.38 (1) Å and favourable C—N...S angles (Table 4). There are also a few hydrogen bonds with the PF<sub>6</sub><sup>-</sup> ions with N...F distances from 3.00 (1) to 3.14 (1) Å.

The authors are grateful to the Medical Research Council of Canada for financial support.

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*Acta Cryst.* (1990). **C46**, 576–578

## 1,2,2,3,3,1-Tri- $\mu$ -carbonyl-1,2,2,3,3,4,4,4-octacarbonyl-1-(triisopropylphosphine)-tetrahedro-tetrarhodium(0)

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(Received 22 June 1989; accepted 14 July 1989)

**Abstract.** [Rh<sub>4</sub>(CO)<sub>11</sub>{P(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>}], *M<sub>r</sub>* = 879.9, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 11.057 (4), *b* = 15.660 (17), *c* = 17.248 (6) Å,  $\beta$  = 74.44 (1)°, *V* = 2877.1 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 2.031 g cm<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.7107 Å,  $\mu$  = 22.8 cm<sup>-1</sup>, *F*(000) = 1696, *T* = 293 K, *R* = 0.068 for 2978 observed reflections with *F* > 4 $\sigma$ (*F*). The Rh atoms form a nearly regular tetrahedron, with Rh—Rh bond lengths in the range 2.692–2.795 (2) Å. The carbonyls retain the C<sub>3v</sub> arrangement displayed by the parent [Rh<sub>4</sub>(CO)<sub>12</sub>] cluster, with three occupying bridging positions about the basal plane of the metal-atom tetrahedron. The phosphine ligand is coordinated in a basal axial position.

**Introduction.** The crystal structures of phosphine-substituted tetrahedral tetrarhodium clusters have been reported previously; for example, those of [Rh<sub>4</sub>(CO)<sub>10</sub>(PPh<sub>3</sub>)<sub>2</sub>] and [Rh<sub>4</sub>(CO)<sub>9</sub>{P(OPh)<sub>3</sub>}<sub>3</sub>] (Heaton, Longhetti, Mingos, Briant, Minshall, Théobald, Garlaschelli & Sartorelli, 1981), and [Rh<sub>4</sub>(CO)<sub>8</sub>{P(OPh)<sub>3</sub>}<sub>4</sub>] (Ciani, Garlaschelli, Manassero, Sartorelli & Albano, 1977). However, no examples of phosphine mono-substituted tetrahedral clusters have been described, so the X-ray crystal structure determination of [Rh<sub>4</sub>(CO)<sub>11</sub>{P(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>}] was undertaken.

**Experimental.** Dark red tabular air-stable crystals of the compound were prepared from dichloromethane/heptane (Iggo & Jackson, 1988); crystal size 0.35 × 0.30 × 0.15 mm. Approximate cell dimensions and space-group determination by preliminary Weissenberg photography. Intensity data recorded on a Stoe Stadi-2 2-circle diffractometer. 20 *h*0*l* reflections, 5 < 2 $\theta$  < 30°, used to determine exact cell parameters, except for *b*, which was determined by the positions of higher 0*k*0 reflections. Crystal mounted along unique *b* axis, data collected in 17 layers. 2 $\theta_{\min}$  = 4°, 2 $\theta_{\max}$  = 40°, 0 ≤ *h* ≤ 12, 0 ≤ *k* ≤ 16, -19 ≤ *l* ≤ 19, 4305 reflection intensities measured,  $\omega$ -scan mode, merging to 3755 unique. One standard reflection on each layer, measured after every 25th reflection; maximum variation in intensity 3%. Empirical absorption correction applied, transmission factors 1.0–0.65. Data reduction performed by program *STOE* (Gould & Taylor, 1986), Rh-atom positions found by automatic Patterson search procedure of *SHELX86* (Sheldrick, 1986) and used to phase subsequent Fourier syntheses using *SHELX76* (Sheldrick, 1976), revealing all other non-H-atom positions. Least-squares refinement with *SHELX76* converged at *R* = 0.068 for 2978 reflections with *F* > 4 $\sigma$ (*F*), *wR* = 0.070,  $w = 1/[\sigma^2(F) + 0.001436F^2]$ . All non-H atoms allowed anisotropic vibration param-

Table 1. Fractional coordinates of non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Rh(1)	0.23966 (10)	0.22295 (7)	0.29096 (6)	0.0264 (6)
Rh(2)	0.13688 (11)	0.34527 (7)	0.40667 (6)	0.0304 (6)
Rh(3)	0.09261 (11)	0.17798 (7)	0.44413 (6)	0.0332 (7)
Rh(4)	-0.01233 (11)	0.25386 (8)	0.33752 (7)	0.0355 (7)
P(1)	0.4621 (4)	0.2025 (3)	0.2597 (2)	0.0337 (21)
C(1)	0.2416 (15)	0.2075 (10)	0.1824 (10)	0.0437 (95)
O(1)	0.2354 (14)	0.1971 (10)	0.1177 (7)	0.0851 (100)
C(2)	0.2449 (13)	0.3548 (10)	0.2847 (8)	0.0316 (82)
O(2)	0.2781 (11)	0.4100 (7)	0.2391 (6)	0.0451 (64)
C(3)	0.0352 (18)	0.4460 (11)	0.4048 (9)	0.0511 (108)
O(3)	-0.0249 (14)	0.5015 (8)	0.4040 (8)	0.0891 (110)
C(4)	0.2613 (17)	0.3945 (10)	0.4535 (8)	0.0470 (99)
O(4)	0.3265 (15)	0.4269 (9)	0.4839 (7)	0.0868 (101)
C(5)	0.0277 (14)	0.2863 (10)	0.5131 (8)	0.0372 (88)
O(5)	-0.0372 (11)	0.3052 (7)	0.5759 (6)	0.0543 (74)
C(6)	-0.0543 (20)	0.1092 (12)	0.4848 (9)	0.0588 (119)
O(6)	-0.1405 (15)	0.0696 (10)	0.5083 (10)	0.0999 (120)
C(7)	0.1906 (17)	0.1345 (11)	0.5124 (9)	0.0488 (103)
O(7)	0.2446 (13)	0.1054 (10)	0.5541 (7)	0.0811 (99)
C(8)	0.1821 (16)	0.1042 (11)	0.3376 (9)	0.0435 (99)
O(8)	0.1829 (13)	0.0337 (8)	0.3231 (7)	0.0658 (86)
C(9)	-0.1665 (17)	0.2904 (14)	0.4167 (11)	0.0609 (119)
O(9)	-0.2541 (13)	0.3152 (12)	0.4616 (8)	0.0957 (116)
C(10)	-0.0633 (18)	0.1482 (13)	0.2937 (11)	0.0610 (118)
O(10)	-0.0998 (16)	0.0891 (10)	0.2742 (10)	0.1142 (131)
C(11)	-0.0081 (17)	0.3291 (11)	0.2476 (10)	0.0494 (99)
O(11)	-0.0064 (12)	0.3727 (9)	0.1943 (8)	0.0746 (92)
C(12)	0.5279 (17)	0.1720 (12)	0.3445 (10)	0.0569 (112)
C(13)	0.4897 (17)	0.2310 (15)	0.4120 (10)	0.0757 (140)
C(14)	0.4908 (19)	0.0800 (11)	0.3758 (12)	0.0703 (128)
C(15)	0.5424 (14)	0.3040 (10)	0.2230 (9)	0.0423 (91)
C(16)	0.6817 (17)	0.3175 (12)	0.2276 (12)	0.0682 (128)
C(17)	0.5351 (19)	0.3266 (11)	0.1373 (10)	0.0610 (119)
C(18)	0.5253 (16)	0.1255 (10)	0.1755 (10)	0.0486 (102)
C(19)	0.6672 (17)	0.1049 (13)	0.1597 (12)	0.0685 (130)
C(20)	0.4515 (18)	0.0455 (12)	0.1802 (12)	0.0738 (136)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

Rh(1)—Rh(2)	2.780 (3)	P(1)—C(12)	1.861 (18)
Rh(1)—Rh(3)	2.795 (3)	P(1)—C(15)	1.847 (16)
Rh(1)—Rh(4)	2.728 (3)	P(1)—C(18)	1.873 (17)
Rh(2)—Rh(3)	2.711 (3)	C(1)—O(1)	1.146 (22)
Rh(2)—Rh(4)	2.692 (3)	C(2)—O(2)	1.159 (18)
Rh(3)—Rh(4)	2.699 (3)	C(3)—O(3)	1.096 (23)
		C(4)—O(4)	1.119 (22)
		C(5)—O(5)	1.165 (19)
Rh(1)—P(1)	2.394 (5)	C(6)—O(6)	1.117 (25)
Rh(1)—C(1)	1.883 (17)	C(7)—O(7)	1.146 (22)
Rh(1)—C(2)	2.068 (15)	C(8)—O(8)	1.132 (21)
Rh(1)—C(8)	2.058 (17)	C(9)—O(9)	1.135 (25)
Rh(2)—C(2)	2.128 (15)	C(10)—O(10)	1.098 (26)
Rh(2)—C(3)	1.943 (18)	C(11)—O(11)	1.142 (23)
Rh(2)—C(4)	1.933 (16)	C(12)—C(13)	1.458 (27)
Rh(2)—C(5)	2.120 (15)	C(12)—C(14)	1.555 (27)
Rh(3)—C(5)	2.086 (15)	C(15)—C(16)	1.579 (25)
Rh(3)—C(6)	1.919 (19)	C(15)—C(17)	1.543 (24)
Rh(3)—C(7)	1.925 (18)	C(18)—C(19)	1.553 (26)
Rh(3)—C(8)	2.171 (17)	C(18)—C(20)	1.485 (26)
Rh(4)—C(9)	1.962 (20)		
Rh(4)—C(10)	1.964 (19)		
Rh(4)—C(11)	1.938 (18)		

All C—H bonds constrained to ideal tetrahedral geometry, with bond length = 1.08  $\text{\AA}$ .

Rh(2)—Rh(1)—Rh(3)	58.19 (4)	Rh(1)—C(1)—O(1)	176.0 (15)
Rh(2)—Rh(1)—Rh(4)	58.52 (4)	Rh(1)—C(2)—O(2)	83.0 (5)
Rh(3)—Rh(1)—Rh(4)	58.49 (4)	Rh(1)—C(2)—O(2)	141.2 (12)
Rh(1)—Rh(2)—Rh(3)	61.19 (4)	Rh(2)—C(2)—O(2)	135.6 (16)
Rh(1)—Rh(2)—Rh(4)	59.78 (4)	Rh(2)—C(3)—O(3)	178.1 (17)
Rh(3)—Rh(2)—Rh(4)	59.93 (4)	Rh(2)—C(4)—O(4)	174.8 (15)
Rh(1)—Rh(3)—Rh(2)	60.61 (4)	Rh(2)—C(5)—O(5)	80.3 (5)
Rh(1)—Rh(3)—Rh(4)	59.51 (4)	Rh(2)—C(5)—O(5)	139.4 (12)
Rh(2)—Rh(3)—Rh(4)	59.69 (4)	Rh(3)—C(5)—O(5)	140.3 (12)
		Rh(3)—C(6)—O(6)	179.4 (18)
		Rh(3)—C(7)—O(7)	176.6 (16)
Rh(1)—Rh(4)—Rh(2)	61.70 (4)	Rh(1)—C(8)—O(8)	82.7 (6)
Rh(1)—Rh(4)—Rh(3)	62.01 (4)	Rh(1)—C(8)—O(8)	144.3 (14)
Rh(2)—Rh(4)—Rh(3)	60.38 (4)	Rh(3)—C(8)—O(8)	132.9 (13)
		Rh(4)—C(9)—O(9)	176.9 (18)
Rh(1)—P(1)—C(12)	116.9 (6)	Rh(4)—C(10)—O(10)	174.5 (18)
Rh(1)—P(1)—C(15)	109.4 (5)	Rh(4)—C(11)—O(11)	179.1 (16)
Rh(1)—P(1)—C(18)	114.1 (5)		
C(12)—P(1)—C(15)	103.7 (8)		
C(12)—P(1)—C(18)	107.5 (8)		
C(15)—P(1)—C(18)	104.0 (7)		

eters, H atoms in calculated positions (C—H = 1.08  $\text{\AA}$ ) to give ideal tetrahedral geometry in the phosphine ligand, with  $U = 0.08 \text{\AA}^2$ . Final difference synthesis showed max. and min. heights of 2.0 and  $-3.2 e \text{\AA}^{-3}$ , associated with electron density in the metal cluster framework. Maximum parameter shift/e.s.d. in final round of refinement = 0.116. Scattering factors for all atoms and  $f'$  and  $f''$  values for Rh atoms from *International Tables for X-ray Crystallography* (1974), all calculations performed on an IBM3083 computer. Diagram produced by ORTEP (Johnson, 1981).

**Discussion.** Atom parameters are given in Table 1, and selected bond lengths and angles are given in Table 2.\* As shown in Fig. 1, the molecule consists of a tetrahedron of Rh atoms, coordinated by 11 carbonyl groups, eight of which are terminal and three of which bridge the edges of the tetrahedral basal plane. The structure is thus related to that of the parent compound  $[\text{Rh}_4(\text{CO})_{12}]$  (Wei, 1969), with

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52426 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

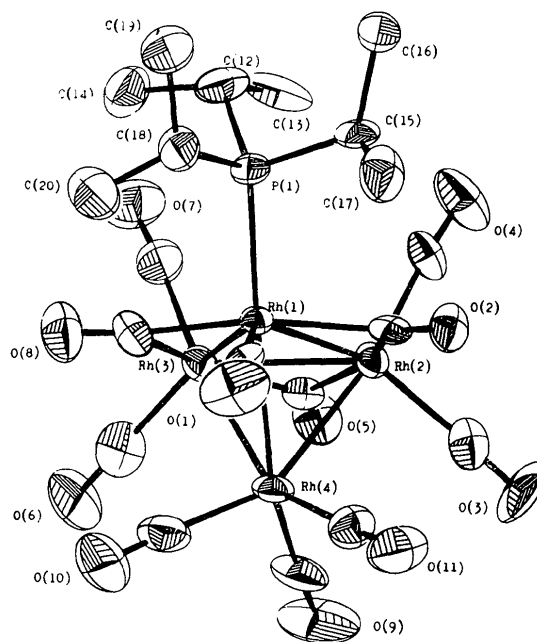


Fig. 1. Structure of the title compound. H atoms omitted for clarity. Diagram produced by ORTEP (Johnson, 1981), with ellipsoids at the 50% probability level.

one basal axial carbonyl in the C<sub>3v</sub> arrangement replaced by the phosphine ligand.

The Rh—Rh bond lengths range from 2.692 to 2.795 (2) Å, mean value 2.734 Å, and this is in good agreement with the corresponding lengths in [Rh<sub>4</sub>(CO)<sub>12</sub>] (mean value 2.732 Å) (Wei, 1969), [Rh<sub>4</sub>(CO)<sub>10</sub>(PPh<sub>3</sub>)<sub>2</sub>] (mean value 2.729 Å), [Rh<sub>4</sub>(CO)<sub>9</sub>{P(OPh)<sub>3</sub>}<sub>3</sub>] (mean value 2.706 Å) (Heaton *et al.*, 1981) and [Rh<sub>4</sub>(CO)<sub>8</sub>{P(OPh)<sub>3</sub>}<sub>4</sub>] (mean value 2.720 Å) (Ciani, Garlaschelli, Manassero, Sartorelli & Albano, 1977). The three longest Rh—Rh bond lengths are those involving Rh(1), the substituted atom, showing the back-bonding effect of the phosphine ligand. The Rh—P distance is quite long at 2.394 (2) Å, but this may be expected as the aliphatic isopropyl groups make this phosphine ligand more bulky than, for example, PPh<sub>3</sub> {Rh—P bond lengths in [Rh<sub>4</sub>(CO)<sub>10</sub>(PPh<sub>3</sub>)<sub>2</sub>] are 2.337 (4) and 2.341 (3) Å}.

In [Rh<sub>4</sub>(CO)<sub>10</sub>(PPh<sub>3</sub>)<sub>2</sub>] (Heaton *et al.*, 1981), one phosphine ligand is coordinated in a basal axial position, the other in a basal equatorial position. The basal axial positioning of the phosphine ligand in the title compound indicates that this is the site of first substitution.

The author acknowledges the SERC for the award of a studentship, and Dr Marjorie M. Harding for help and encouragement.

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*Acta Cryst.* (1990). **C46**, 578–581

## Structure of Carbonatobis(histamine)cobalt(III) Chloride Monohydrate

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(Received 22 December 1987; accepted 27 June 1989)

**Abstract.** Bis[4-(2-aminoethyl)imidazole-*N*<sup>3</sup>,*N*<sup>8</sup>]- (carbonato-*O,O'*)cobalt(III) chloride monohydrate, [Co(CO<sub>3</sub>)(C<sub>5</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>]Cl·H<sub>2</sub>O, *M<sub>r</sub>* = 394.71, triclinic, *P* $\bar{1}$ , *a* = 9.712 (3), *b* = 15.556 (5), *c* = 7.192 (3) Å,  $\alpha$  = 92.24 (3),  $\beta$  = 128.14 (2),  $\gamma$  = 106.69 (3)°, *V* = 784.1 (4) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.663 (1), *D<sub>x</sub>* =

1.672 Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$ ,  $\mu = 1.339 \text{ mm}^{-1}$ , *F*(000) = 408, room temperature, *R* = 0.030 for 1950 observed reflections. The histamine molecules and carbonate ion each act as bidentate ligands. The imidazole rings of the histamine molecules are coordinated in *trans* positions. The short O···O distance within the bidentate carbonate ligand results in the distortion of the coordination sphere,

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