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Bis(triphenylphosphine)iminium Tetra-μ_3-carbonyl-undecacarbonylchloro-*octahedro*-hexarhodium

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Abstract. $[\{(C_6H_5)_3P\}_2N][Rh_6(CO)_{15}Cl]$, M_r = 1611.63, monoclinic, $P2_1/n$, a = 16.167 (4), b = 10.186 (2), c = 33.424 (7) Å, β = 99.94 (2)°, V = 5422 (2) Å^3, Z = 4, D_x = 1.974 g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 19.0 cm^{-1}, $F(000)$ = 3120, T = 296 K, $R(F)$ = 0.0378 for 5144 observed reflections and 595 least-squares parameters. The six Rh atoms form an octahedral cluster with μ_3-carbonyl groups capping the four opposing sides of the octahedron. The carbonyl stereochemistry is derived from $Rh_6(CO)_{16}$ by the replacement of one terminal CO group by a Cl ligand. The mean Rh—Rh bond distance is 2.753 (1) Å. The two Rh—Rh bonds approximately opposite to the Rh—Cl bond are unusually short: 2.731 (1) and 2.740 (1) Å.

Experimental. Black crystals, grown from dichloromethane and hexane, were obtained in the reaction of $Rh_4(CO)_{12}$ with PPNCl [PPN^+ = bis(triphenylphosphine)iminium] in THF. A crystal of dimensions 0.15 × 0.15 × 0.36 mm was used for data collection on a Nicolet *R*3*m* diffractometer with graphite monochromator and ω scans. Lattice parameters were determined from least-squares fit of 25 reflections ($20 \le 2\theta \le 25°$). No absorption correction was applied (μ = 19.0 cm^{-1}). Data were measured to $2\theta_{max} = 46°$ ($h = \pm 18$, $k = +12$, $l = +36$). Three standard reflections ($\bar{7}39$, 157 and $\bar{3}$,3,18), for 8199 reflections collected, showed less than 2% decay. Of 7536 unique reflections (R_{int} = 3.12%), 5144 were observed with $F_o > 5\sigma(F_o)$ (2392 unobserved reflections). Direct-methods (*SOLV*; Sheldrick, 1985) structure solution and least-squares refinement of 595 parameters were performed with all non-H atoms anisotropic, all H atoms calculated (C—H = 0.960 Å, $U = 1.2U$ for attached C), and phenyl rings constrained as rigid planar hexagons (C—C = 1.395 Å). $R(F)$ = 3.78%, $wR(F)$ = 4.27% [w^{-1} =

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Rh(1)	7978 (1)	4183 (1)	1527 (1)	41 (1)
Rh(2)	7506 (1)	1564 (1)	1520 (1)	45 (1)
Rh(3)	6327 (1)	3515 (1)	1520 (1)	45 (1)
Rh(4)	7982 (1)	2656 (1)	846 (1)	40 (1)
Rh(5)	6813 (1)	4643 (1)	843 (1)	43 (1)
Rh(6)	6332 (1)	2033 (1)	826 (1)	45 (1)
P(1)	2180 (1)	2144 (2)	1868 (1)	36 (1)
P(2)	2112 (1)	764 (2)	1071 (1)	39 (1)
N(1)	2094 (4)	1026 (7)	1535 (2)	37 (3)
Cl(1)	9084 (2)	3809 (3)	588 (1)	80 (1)
O(1)	9433 (4)	2114 (7)	1543 (2)	65 (3)
C(1)	8749 (5)	2416 (9)	1414 (2)	49 (3)
O(2)	5672 (4)	641 (7)	1538 (2)	81 (3)
C(2)	6127 (5)	1400 (9)	1425 (3)	57 (3)
O(3)	6857 (4)	3193 (6)	23 (2)	58 (2)
C(3)	6987 (5)	3200 (8)	376 (2)	47 (3)
O(4)	6732 (4)	6514 (6)	1572 (2)	70 (3)
C(4)	6854 (5)	5474 (8)	1457 (3)	52 (3)
O(5)	8562 (4)	4475 (8)	2438 (2)	80 (3)
C(5)	8335 (5)	4366 (9)	2105 (2)	51 (3)
O(6)	9246 (4)	6143 (7)	1347 (2)	78 (3)
C(6)	8770 (5)	5406 (9)	1403 (3)	55 (3)
O(7)	7939 (5)	1296 (8)	2431 (2)	90 (3)
C(7)	7764 (6)	1390 (9)	2089 (3)	63 (4)
O(8)	7948 (5)	−1261 (7)	1375 (3)	108 (4)
C(8)	7779 (6)	−213 (9)	1424 (3)	66 (4)
O(9)	6421 (4)	3520 (8)	2429 (2)	82 (3)
C(9)	6377 (5)	3546 (9)	2084 (3)	58 (3)
O(10)	4601 (5)	4381 (10)	1353 (2)	109 (4)
C(10)	5135 (6)	4085 (10)	1402 (3)	63 (4)
O(11)	8332 (5)	226 (7)	401 (2)	91 (3)
C(11)	8230 (5)	1126 (8)	579 (3)	54 (3)
O(12)	5138 (5)	5723 (8)	430 (2)	101 (4)
C(12)	5748 (6)	5302 (10)	585 (3)	65 (4)
O(13)	7767 (5)	6889 (7)	537 (2)	86 (3)
C(13)	7418 (7)	6028 (11)	640 (3)	58 (4)
O(14)	4549 (4)	2563 (8)	400 (2)	94 (3)
C(14)	5206 (7)	2341 (11)	568 (3)	57 (4)
O(15)	6342 (5)	−687 (7)	468 (3)	106 (4)
C(15)	6349 (5)	314 (10)	598 (3)	60 (4)
C(21)	3879 (3)	1700 (5)	2027 (1)	45 (3)
C(22)	4670	1608	2270	55 (3)
C(23)	4761	1821	2688	61 (4)
C(24)	4061	2126	2862	54 (3)
C(25)	3270	2218	2619	44 (3)
C(26)	3179	2005	2202	33 (3)
C(31)	2766 (3)	4641 (5)	1744 (2)	46 (3)
C(32)	2703	5872	1558	61 (4)
C(33)	1961	6236	1304	60 (4)
C(34)	1283	5370	1235	54 (3)
C(35)	1346	4139	1421	45 (3)
C(36)	2088	3775	1675	35 (3)
C(41)	1046 (3)	720 (4)	2219 (2)	47 (3)
C(42)	421	559	2455	60 (4)
C(43)	128	1642	2645	58 (4)
C(44)	459	2885	2598	64 (4)

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Table 1 (*cont.*)

	x	*y*	*z*	U_{eq}
C(45)	1085	3047	2362	47 (3)
C(46)	1378	1964	2173	36 (3)
C(51)	1264 (3)	−1064 (6)	539 (2)	56 (3)
C(52)	594	−1902	399	66 (4)
C(53)	−85	−1977	604	70 (4)
C(54)	−94	−1215	950	65 (4)
C(55)	576	−377	1090	46 (3)
C(56)	1255	−302	885	41 (3)
C(61)	1279 (3)	2570 (5)	520 (2)	52 (3)
C(62)	1227	3750	305	59 (4)
C(63)	1933	4552	328	54 (3)
C(64)	2692	4173	566	54 (3)
C(65)	2744	2993	780	49 (3)
C(66)	2038	2192	758	36 (3)
C(71)	3355 (4)	−43 (6)	640 (1)	58 (3)
C(72)	4064	−761	589	69 (4)
C(73)	4481	−1528	907	73 (4)
C(74)	4188	−1577	1276	66 (4)
C(75)	3478	−860	1326	51 (3)
C(76)	3062	−92	1009	41 (3)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* $[Rh_6(CO)_{19}Cl]^-$

Rh(1)—Rh(2)	2.774 (1)	Rh(1)—Rh(3)	2.751 (1)
Rh(1)—Rh(4)	2.757 (1)	Rh(1)—Rh(5)	2.740 (1)
Rh(2)—Rh(3)	2.753 (1)	Rh(2)—Rh(4)	2.740 (1)
Rh(2)—Rh(6)	2.773 (1)	Rh(3)—Rh(5)	2.771 (1)
Rh(3)—Rh(6)	2.768 (1)	Rh(4)—Rh(5)	2.768 (1)
Rh(4)—Rh(6)	2.731 (1)	Rh(4)—Cl(1)	2.413 (1)
Rh(5)—Rh(6)	2.767 (1)	P(1)—N(1)	1.583 (1)
P(2)—N(1)	1.578 (1)		

Rh(2)—Rh(1)—Rh(3)	59.8 (1)	Rh(2)—Rh(1)—Rh(4)	59.4 (1)
Rh(3)—Rh(1)—Rh(4)	89.7 (1)	Rh(2)—Rh(1)—Rh(5)	90.5 (1)
Rh(3)—Rh(1)—Rh(5)	60.6 (1)	Rh(4)—Rh(1)—Rh(5)	60.5 (1)
Rh(1)—Rh(2)—Rh(3)	59.7 (1)	Rh(1)—Rh(2)—Rh(4)	60.0 (1)
Rh(3)—Rh(2)—Rh(4)	90.0 (1)	Rh(1)—Rh(2)—Rh(6)	89.3 (1)
Rh(3)—Rh(2)—Rh(6)	60.1 (1)	Rh(4)—Rh(2)—Rh(6)	59.4 (1)
Rh(1)—Rh(3)—Rh(2)	60.5 (1)	Rh(1)—Rh(3)—Rh(5)	59.5 (1)
Rh(2)—Rh(3)—Rh(5)	90.3 (1)	Rh(1)—Rh(3)—Rh(6)	89.9 (1)
Rh(2)—Rh(3)—Rh(6)	60.3 (1)	Rh(5)—Rh(3)—Rh(6)	59.9 (1)
Rh(1)—Rh(4)—Rh(2)	60.6 (1)	Rh(1)—Rh(4)—Rh(5)	59.5 (1)
Rh(2)—Rh(4)—Rh(5)	90.7 (1)	Rh(1)—Rh(4)—Rh(6)	90.5 (1)
Rh(2)—Rh(4)—Rh(6)	60.9 (1)	Rh(5)—Rh(4)—Rh(6)	60.4 (1)
Rh(1)—Rh(4)—Cl(1)	97.3 (1)	Rh(2)—Rh(4)—Cl(1)	145.1 (1)
Rh(5)—Rh(4)—Cl(1)	100.8 (1)	Rh(6)—Rh(4)—Cl(1)	151.9 (1)
Rh(1)—Rh(5)—Rh(3)	59.9 (1)	Rh(1)—Rh(5)—Rh(4)	60.1 (1)
Rh(3)—Rh(5)—Rh(4)	89.0 (1)	Rh(1)—Rh(5)—Rh(6)	90.1 (1)
Rh(3)—Rh(5)—Rh(6)	60.0 (1)	Rh(4)—Rh(5)—Rh(6)	59.1 (1)
Rh(2)—Rh(6)—Rh(3)	59.6 (1)	Rh(2)—Rh(6)—Rh(4)	59.7 (1)
Rh(3)—Rh(6)—Rh(4)	89.8 (1)	Rh(2)—Rh(6)—Rh(5)	90.0 (1)
Rh(3)—Rh(6)—Rh(5)	60.1 (1)	Rh(4)—Rh(6)—Rh(5)	60.4 (1)
P(1)—N(1)—P(2)	143.1 (1)		

$\sigma^2(F_o) + gF_o^2$, $g = 0.001$], $S = 1.028$; $(\Delta/\sigma)_{max} = 0.398$; $\Delta\rho_{max} = 0.805$, $\Delta\rho_{min} = -0.685$ e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). *SHELXTL* programs (Sheldrick, 1985) were used for computations.

Atomic coordinates and isotropic thermal parameters are given in Table 1.* Selected bond lengths and bond angles are given in Table 2. Fig. 1 shows the structure of the anion and Fig. 2 the packing.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55421 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0574]

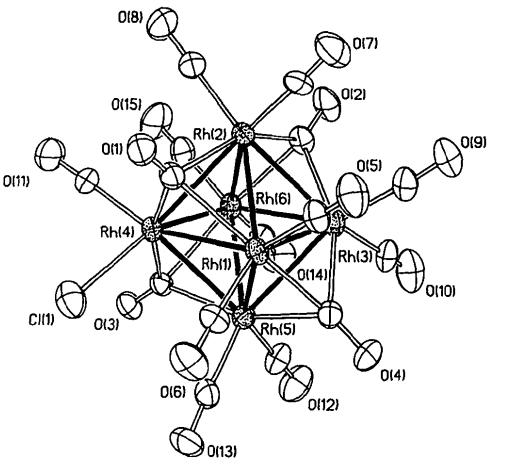

Fig. 1. Structure of the $[Rh_6(CO)_{19}Cl]^-$ anion.

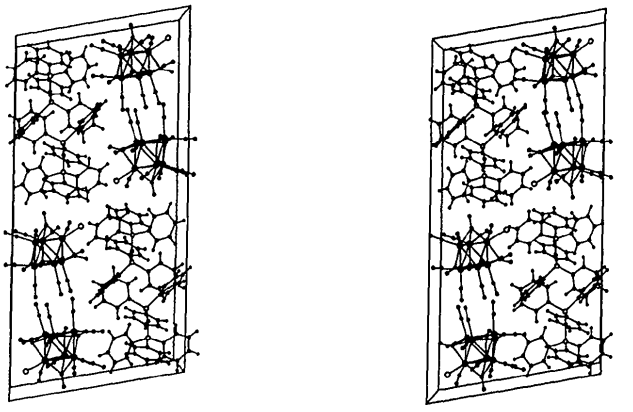

Fig. 2. Unit-cell packing diagram for $PPN[Rh_6(CO)_{19}Cl]$ as viewed down the *b* axis.

Related literature. Two related Rh cage structures have been reported by Ciani, Sironi, Chini & Martinengo (1981) containing COEt and Co(OMe) instead of Cl. Albano, Bellon & Sanson (1970) reported the structure of the iodide as the $(^nBu)_4N^+$ salt.

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