Crystal and Molecular Structure of Tetra-μ_3-carbonyl-octacarbonyl-tetrakis(triphenyl phosphite)-*octahedro*-hexarhodium †

By **Gianfranco Ciani** * and **Mario Manassero**, Centro del C.N.R. di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Istituto di Chimica Generale dell'Università, Via G.Venezian 21, 20133 Milano, Italy
Vincenzo G. Albano, Istituto Chimico ' G. Ciamician ' dell'Università, Via F. Selmi 2, 40126 Bologna, Italy

The title compound, $[Rh_6(\mu_3\text{-}CO)_4(CO)_8\{P(OPh)_3\}_4]$, crystallises in the orthorhombic space group *Aba*2 with cell dimensions a = 19.654(5), b = 21.474(7), c = 19.955(4) Å, and Z = 4. The structure determination is based on 3 478 independent X-ray counter data, refinement being carried out by blocked matrix least squares to a conventional R value of 0.038. The molecule contains a slightly distorted octahedral cluster, with a mean Rh–Rh bond length of 2.789 Å. The ligand stereochemistry is derived from that of the parent $[Rh_6(CO)_{16}]$ species, with four terminal CO groups substituted by triphenyl phosphite ligands, bound to four ' equatorial ' coplanar rhodium atoms (mean Rh–P 2.265 Å). The Rh–C and C–O bond lengths for the terminal CO groups have mean values 1.88 and 1.14 Å respectively. The four triple-bridging carbonyls are slightly but significantly asymmetric, showing shorter bonds to the Rh atoms bearing the phosphite ligands (mean Rh–C 2.16 *vs.* 2.24 Å).

THE reaction of $[Rh_6(CO)_{16}]$ with triphenyl phosphite, $P(OPh)_3$, gives various substituted species, but the maximum number of phosphite groups seems to be four, even when using a large excess of the entering nucleophile.[1] In this paper we report the complete results of a single-crystal X-ray investigation on $[Rh_6(CO)_{12}\{P(OPh)_3\}_4]$; a preliminary account of the synthesis and structural characterisation has already appeared.[1] It was of particular interest to establish which of the carbonyl groups undergo substitution and to ascertain a possible rearrangement of the remaining groups with respect to the parent $[Rh_6(CO)_{16}]$ species.[2] We have examined whether steric reasons could prevent higher substitution with $P(OPh)_3$ ligands. The bond parameters are discussed in comparison with those of the related species $[Rh_6(CO)_{16}]$,[2] $[Rh_6(CO)_{15}I]^-$,[3] $[Rh_6(CO)_{14}(\eta\text{-}C_3H_5)]^-$,[4] and of the dimeric $[Rh_{12}(CO)_{30}]^{2-}$.[5]

EXPERIMENTAL

Crystal Data.—$C_{84}H_{60}O_{24}P_4Rh_6$, M = 2 194.7, Orthorhombic, a = 19.654(5), b = 21.474(7), c = 19.955(4) Å, U = 8 422.0 Å^3, D_m = 1.75(2) g cm^{-3}, Z = 4, D_c = 1.73 g cm^{-3}, $F(000)$ = 4 344, possible space groups *Aba*2 (no. 41) or *Cmca* (no. 64), Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 12.7 cm^{-1}.

Intensity Measurements.—The crystal was mounted on a Philips PW 1100 four-circle automatic diffractometer. The intensity data were collected by the θ—2θ method, using graphite monochromated Mo-K_α radiation, for $6 < 2\theta < 54°$. The reflections were measured with a scan width of 1.0° at a scan speed of 0.04° s^{-1}, the backgrounds being measured at each side of the scan range for half of the peak-scanning time. The total number of collected reflections was 5 007. Three standard reflections, measured every 60 min, showed no crystal decay. The integrated intensities were corrected for Lorentz and polarisation effects but not for absorption. After rejection of all data having $\sigma(I)/I > 0.26$ a set of 3 478 independent reflections was obtained and used in the structure solution and refinement.

Structure Solution and Refinement.—The structure solution was based on a three-dimensional Patterson map, which showed the presence of the metal-atom octahedron, lying either on a two-fold axis in the non-centrosymmetric *Aba*2 group, or on a 2/*m* crystallographic special position in the corresponding centrosymmetric group *Acam* (non-standard setting of *Cmca*). After a preliminary refinement of the metal-atom parameters in the latter space group, a successive difference-Fourier map showed double images for the ligand atoms, especially for the heavier P atoms, related by the mirror plane. The refinement was therefore continued assuming as space group the non-centrosymmetric *Aba*2. All the non-hydrogen atoms were located by successive difference-Fourier maps.

The refinement was carried out by the least-squares method in the block-diagonal approximation. The phenyl groups of the $P(OPh)_3$ ligands were treated as rigid bodies (D_{6h} symmetry, C–C 1.392 Å). Anisotropic temperature factors were assigned to all atoms except to the phenyl-carbon atoms. The phenyl-hydrogen atoms were not refined, but after each cycle of refinement they were located in their ideal positions (C–H 1.08 Å) and their contribution was introduced into the structure-factor calculations (assigning them isotropic thermal parameters equal to those of the corresponding carbon atoms). At this stage anomalous scattering was also taken into account (for Rh and P) and two refinements were made in order to establish the correct structural enantiomorph. In the better case the final values of R and R' were 0.038 and 0.049 respectively. Weighting was assigned according to the formula $w = 1/(A + BF_o + CF_o^2)$ where, in the final stages of refinement, A = 5.6, B = 0.02, and $C = 9 \times 10^{-4}$, chosen on the basis of an analysis of $\Sigma w(F_o - k|F_c|)^2$. Atomic scattering factors were taken from ref. 6 for the non-hydrogen atoms, and from ref. 7 for hydrogen. Corrections for both the real and imaginary parts of the anomalous dispersion were taken from ref. 8. The final difference-Fourier synthesis was flat except for some residual peaks not exceeding 0.9 e Å^{-3}, near to the metal atoms.

Atomic positional parameters are reported in Table 1. Temperature factors and observed and calculated structure factors are given in Supplementary Publication No. SUP

† 1,2,3;1,4,5;2,5,6;3,4,6-Tetra-μ_3-carbonyl-1,1,2,3,4,5,6,6-octacarbonyl-2,3,4,5-tetrakis(triphenyl phosphite)-*octahedro*-hexarhodium.

TABLE 1

Final atomic positional parameters * for $[Rh_6(CO)_{12}\{P(OPh)_3\}_4]$

Atom	x	y	z
Rh(1)	−8 897(3)	−4 378(3)	−9 568(5)
Rh(2)	−4 878(3)	8 132(3)	−9 888(5)
Rh(3)	0	0	0
Rh(4)	0	0	−19 422(5)
P(1)	−1 888(1)	−431(1)	−1 528(1)
P(2)	−465(1)	1 745(1)	−465(1)
C(1)	−1 201(5)	−1 097(4)	−444(5)
O(1)	−1 396(4)	−1 508(4)	−137(4)
C(2)	−1 099(5)	1 146(4)	−1 604(5)
O(2)	−1 402(4)	1 383(3)	−2 029(4)
C(3)	−320(5)	−535(5)	680(5)
O(3)	−527(5)	−822(4)	1 114(4)
C(4)	−644(5)	178(5)	−2 626(4)
O(4)	−989(4)	271(4)	−3 065(4)
C(5)	−352(5)	−963(4)	−1 677(4)
O(5)	−497(4)	−1 384(3)	−2 035(3)
C(6)	−1 057(5)	322(4)	−232(4)
O(6)	−1 486(4)	438(3)	150(3)
O(11)	−1 889(4)	−751(3)	−2 249(3)
O(12)	−2 536(4)	−784(3)	−1 233(3)
O(13)	−2 152(3)	257(3)	−1 715(4)
O(21)	9(3)	2 274(2)	−782(3)
O(22)	−197(4)	1 723(3)	285(3)
O(23)	−1 155(3)	2 144(3)	−426(4)
C(111)	−2 186(7)	−1 289(4)	−2 473(5)
C(112)	−1 990(5)	−1 871(5)	−2 232(4)
C(113)	−2 253(6)	−2 409(4)	−2 522(6)
C(114)	−2 711(7)	−2 366(4)	−3 052(5)
C(115)	−2 906(5)	−1 785(5)	−3 292(4)
C(116)	−2 644(6)	−1 246(4)	−3 002(6)
C(121)	−2 777(4)	−756(4)	−586(3)
C(122)	−3 015(5)	−1 317(3)	−326(4)
C(123)	−3 304(5)	−1 334(3)	309(4)
C(124)	−3 357(4)	−790(4)	685(3)
C(125)	−3 119(5)	−230(3)	425(4)
C(126)	−2 829(5)	−212(3)	−210(4)
C(131)	−2 728(4)	375(6)	−2 100(5)
C(132)	−2 677(4)	438(5)	−2 792(5)
C(133)	−3 248(6)	598(3)	−3 168(4)
C(134)	−3 870(4)	694(6)	−2 851(5)
C(135)	−3 921(4)	631(5)	−2 159(5)
C(136)	−3 350(6)	472(3)	−1 783(4)
C(211)	−200(6)	2 781(4)	−1 164(5)
C(212)	−309(3)	3 355(5)	−859(4)
C(213)	−523(5)	3 862(4)	−1 239(5)
C(214)	−629(6)	3 794(4)	−1 925(5)
C(215)	−521(3)	3 220(5)	−2 231(4)
C(216)	−306(5)	2 713(4)	−1 850(5)
C(221)	−117(5)	2 228(3)	706(4)
C(222)	−630(3)	2 387(4)	1 156(4)
C(223)	−545(4)	2 893(4)	1 584(4)
C(224)	52(5)	3 241(3)	1 561(4)
C(225)	564(3)	3 082(4)	1 111(4)
C(226)	479(4)	2 576(4)	683(4)
C(231)	−1 805(3)	1 959(5)	−356(4)
C(232)	−2 034(3)	1 679(4)	231(4)
C(233)	−2 715(4)	1 513(4)	296(3)
C(234)	−3 168(3)	1 627(5)	−225(4)
C(235)	−2 939(3)	1 906(4)	−813(4)
C(236)	−2 258(4)	2 072(4)	−878(3)
H(112)	−1 661	−1 902	−1 851
H(113)	−2 112	−2 827	−2 349
H(114)	−2 899	−2 753	−3 260
H(115)	−3 235	−1 753	−3 672
H(116)	−2 784	−828	−3 175
H(122)	−2 977	−1 707	−596
H(123)	−3 475	−1 737	496
H(124)	−3 564	−802	1 143
H(125)	−3 156	161	696
H(126)	−2 657	190	−396
H(132)	−2 230	369	−3 020
H(133)	−3 211	644	−3 665
H(134)	−4 280	809	−3 120
H(135)	−4 368	701	−1 931
H(136)	−3 387	427	−1 285
H(212)	−232	3 404	−366
H(213)	−600	4 275	−1 019
H(214)	−782	4 159	−2 198
H(215)	−597	3 172	−2 723
H(216)	−228	2 301	−2 069
H(222)	−1 058	2 138	1 173
H(223)	−912	3 008	1 908
H(224)	113	3 605	1 869
H(225)	994	3 332	1 095
H(226)	848	2 462	360
H(232)	−1 708	1 599	607
H(233)	−2 879	1 313	719
H(234)	−3 657	1 508	−178
H(235)	−3 264	1 987	−1 188
H(236)	−2 093	2 273	−1 300

* Parameters are $\times 10^5$ for Rh and $\times 10^4$ for other atoms; estimated standard deviations are in parentheses.

22928 (15 pp.).* All the computations were performed on an UNIVAC 1108 computer at the computing centre of Milan University with local programs.

RESULTS AND DISCUSSION

The crystal structure consists of discrete molecules packed as shown in Figure 1, with the apical axis coincident with the two-fold crystallographic axis *c*.

The $Rh_6(CO)_{12}P_4$ moiety, of idealised S_4 symmetry, is shown in Figure 2. The molecule consists of a slightly distorted octahedral cluster of metal atoms, bearing 12 carbonyl groups and four $P(OPh)_3$ ligands; the ligand arrangement is derived from that of the parent $[Rh_6(CO)_{16}]$, by the substitution of four terminal CO groups by triphenyl phosphite ligands, which are bound to the four 'equatorial' rhodium atoms, alternately above and below the same Rh_4 plane. The bond parameters are reported in Table 2.

The Rh–Rh bond lengths, in the range 2.754—2.826(1) Å, have a mean value of 2.789 Å, comparable with that found in $[Rh_6(CO)_{16}]$ (2.78 Å) [2] and somewhat higher than those of the anionic species $[Rh_6(CO)_{15}I]^-$ (2.75 Å),[3] $[Rh_6(CO)_{14}(\eta\text{-}C_3H_5)]^-$ (2.75 Å),[4] and $[Rh_{12}(CO)_{30}]^{2-}$ (2.77 Å).[5] The metal-atom octahedron is somewhat distorted and slightly contracted along the C_2 axis, the Rh(3) ··· Rh(4) diagonal being *ca.* 0.10 Å shorter than the other two. We ascribe these distortions to the steric effect of the bulky phosphite ligands. The four faces not capped by μ_3-CO groups bear three axial ligands (two CO and one phosphite), one per metal atom, approximately perpendicular to them (mean Rh–Rh–C and Rh–Rh–P angles, 97.4 and 102.3°): within each of these four faces, the two edges involving the rhodium atom bearing the axial phosphite group are significantly longer than the third one, due to the phosphite–carbonyl repulsions which are greater than the carbonyl–carbonyl ones. The corresponding Rh–Rh bond lengths, averaged on the whole cluster, are 2.806 (eight edges) *vs.* 2.754 Å (four edges).

The Rh–P bond lengths (mean 2.265 Å) are comparable with other similar interactions, *e.g.* in $[Rh_4(CO)_8\{P$-

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

$(OPh)_3\}_4$] (mean 2.23 Å) [1] and in $[Rh_4(CO)_8(Ph_2PCH_2PPh_2)_2]$ (mean 2.30 Å).[9]

The Rh–C and C–O bond lengths for the terminal CO groups have mean values of 1.88 and 1.14 Å respectively, shorter than the others (1.86 *vs.* 1.90 Å). The Rh–C and C–O bonds for the face-bridging carbonyls have overall mean values of 2.19 and 1.18 Å, but the bridges are significantly, although only slightly, asymmetric: the

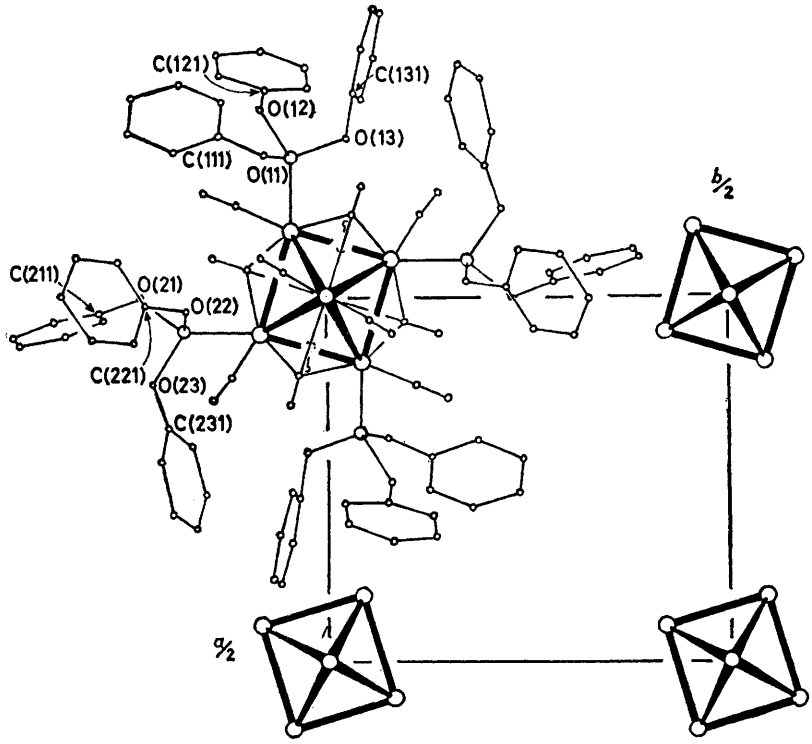

FIGURE 1 View of the packing down the *c* axis

similar to the corresponding values found in other octahedral carbonyl clusters of rhodium. However, the metal–carbon bond lengths for the CO groups bound to Rh(1) and Rh(2), which bear the phosphite ligands, are

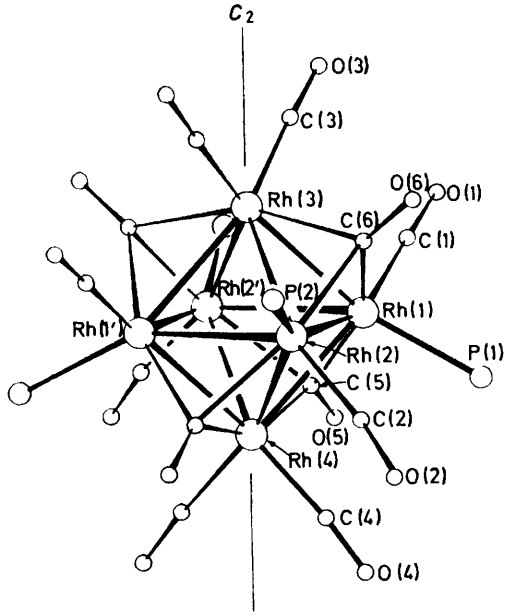

FIGURE 2 View of the $Rh_6(CO)_{12}P_4$ moiety of the molecule, showing atom numbering

Rh(1,2)–C bonds are again shorter than the Rh(3,4)–C bonds (mean 2.16 *vs.* 2.24 Å). These shortenings, common for terminal and bridging carbonyls, are associated with the presence on Rh(1) and Rh(2) of the triphenyl phosphite ligands. A possible explanation could be that the $P(OPh)_3$ groups are poorer π acceptors than CO and, as a consequence, these metal atoms exhibit a better π back donation toward the carbonyls than the other metal atoms. A similar asymmetry effect is observed also in $[Rh_6(CO)_{15}I]^-$,[3] and in $[Rh_6(CO)_{14}(\eta\text{-}C_3H_5)]^-$,[4] both species showing shorter Rh–C (bridging) bonds for the metal atoms bearing the poor π-acceptor iodide and η-allyl ligands (mean 2.08 *vs.* 2.21 Å in the former, and 2.03 *vs.* 2.29 Å in the latter species).

An interesting feature concerns the location and number of the substituent groups. Steric reasons seem to prevent the presence of two $P(OPh)_3$ ligands on the same metal atom; moreover, it seems also unlikely that two such groups can be bound on adjacent metal atoms, perpendicularly to the same triangular face of the cluster (see above). This leaves only two possible isomers with four substituents, namely, that experimentally observed and another obtained, for instance, by exchange of the phosphite containing P(1) with CO(4). This second case, of lower symmetry, with four $P(OPh)_3$ groups bound to all the metal atoms of two adjacent cluster faces, probably implies greater steric repulsions.

TABLE 2

Interatomic distances (Å) and angles (°) for $[Rh_6(CO)_{12}\{P(OPh)_3\}_4]$

(*a*) Distances

Rh(1)–Rh(2)	2.801(1)	C(1)–O(1)	1.140(14)
Rh(1)–Rh(2′)	2.826(1)	C(2)–O(2)	1.154(13)
Rh(1)–Rh(3)	2.754(1)	C(3)–O(3)	1.139(14)
Rh(1)–Rh(4)	2.794(1)	C(4)–O(4)	1.126(13)
Rh(2)–Rh(3)	2.804(1)	C(5)–O(5)	1.186(12)
Rh(2)–Rh(4)	2.755(1)	C(6)–O(6)	1.165(12)
Rh(1) · · · Rh(1′)	3.971(1)	P(1)–O(11)	1.595(8)
Rh(2) · · · Rh(2′)	3.984(1)	P(1)–O(12)	1.594(8)
Rh(3) · · · Rh(4)	3.876(1)	P(1)–O(13)	1.611(8)
Rh(1)–P(1)	2.271(3)	P(2)–O(21)	1.601(7)
Rh(2)–P(2)	2.259(3)	P(2)–O(22)	1.588(8)
		P(2)–O(23)	1.606(7)
Rh(1)–C(1)	1.852(10)		
Rh(2)–C(2)	1.862(10)	O(11)–C(111)	1.371(13)
Rh(3)–C(3)	1.888(11)	O(12)–C(121)	1.376(11)
Rh(4)–C(4)	1.902(10)	O(13)–C(131)	1.392(13)
Rh(1)–C(5)	2.112(10)	O(21)–C(211)	1.391(12)
Rh(2′)–C(5)	2.172(10)	O(22)–C(221)	1.382(11)
Rh(4)–C(5)	2.245(10)	O(23)–C(231)	1.345(10)
Rh(1)–C(6)	2.205(10)		
Rh(2)–C(6)	2.155(10)		
Rh(3)–C(6)	2.238(10)		

(*b*) Angles

Rh(1)–C(1)–O(1)	179.0(10)	Rh(1′)–Rh(2)–P(2)	102.9(1)
Rh(2)–C(2)–O(2)	170.9(9)	Rh(3)–Rh(2)–P(2)	102.7(1)
Rh(3)–C(3)–O(3)	175.2(10)	Rh(1)–Rh(2)–P(2)	147.7(1)
Rh(4)–C(4)–O(4)	174.8(9)	P(1)–Rh(1)–C(1)	89.7(3)
Rh(1)–C(5)–O(5)	134.2(8)	P(2)–Rh(2)–C(2)	88.7(3)
Rh(2′)–C(5)–O(5)	132.6(8)	C(3)–Rh(3)–C(3′)	88.1(5)
Rh(4)–C(5)–O(5)	129.3(7)	C(4)–Rh(4)–C(4′)	88.2(4)
Rh(1)–C(5)–Rh(2′)	82.5(3)	Rh(1)–P(1)–O(11)	116.8(3)
Rh(1)–C(5)–Rh(4)	79.7(3)	Rh(1)–P(1)–O(12)	120.2(3)
Rh(2′)–C(5)–Rh(4)	77.1(3)	Rh(1)–P(1)–O(13)	113.6(3)
Rh(1)–C(6)–O(6)	134.1(8)	Rh(2)–P(2)–O(21)	117.2(3)
Rh(2)–C(6)–O(6)	136.9(8)	Rh(2)–P(2)–O(22)	114.6(3)
Rh(3)–C(6)–O(6)	127.1(7)	Rh(2)–P(2)–O(23)	118.6(3)
Rh(1)–C(6)–Rh(2)	79.9(3)	P(1)–O(11)–C(111)	131.1(7)
Rh(1)–C(6)–Rh(3)	76.6(3)	P(1)–O(12)–C(121)	126.9(7)
Rh(2)–C(6)–Rh(3)	79.3(3)	P(1)–O(13)–C(131)	123.9(7)
Rh(2′)–Rh(1)–C(1)	96.4(3)	P(2)–O(21)–C(211)	126.8(7)
Rh(3)–Rh(1)–C(1)	95.1(3)	P(2)–O(22)–C(221)	126.0(6)
Rh(2)–Rh(1)–C(1)	147.1(3)	P(2)–O(23)–C(231)	130.5(7)
Rh(1)–Rh(2)–C(2)	101.6(3)	O(11)–P(1)–O(12)	97.3(4)
Rh(4)–Rh(2)–C(2)	90.7(3)	O(11)–P(1)–O(13)	100.7(4)
Rh(1′)–Rh(2)–C(2)	138.0(3)	O(12)–P(1)–O(13)	105.4(4)
Rh(1)–Rh(3)–C(3)	94.5(3)	O(21)–P(2)–O(22)	101.6(4)
Rh(2′)–Rh(3)–C(3)	103.9(3)	O(21)–P(2)–O(23)	97.6(4)
Rh(1)–Rh(4)–C(4)	99.0(3)	O(22)–P(2)–O(23)	104.5(4)
Rh(2)–Rh(4)–C(4)	97.8(3)		
Rh(2)–Rh(1)–P(1)	103.1(1)		
Rh(4)–Rh(1)–P(1)	100.7(1)		
Rh(2′)–Rh(1)–P(1)	145.0(1)		

The replacement of four terminal CO groups with triphenyl phosphite ligands creates an overcrowded ligand arrangement on the cluster surface. This can be seen by considering the values of the non-bonding intramolecular interactions: there are numerous contacts between the CO groups and the oxygen atoms of the phosphite ligands, the shortest being a (OC) · · · (OPh) distance of 2.82 Å. Another indication comes from the values of the C–Rh–C angles for the pairs of terminally bonded carbonyl groups, which are smaller in the present case (mean 88°) than in $[Rh_6(CO)_{15}I]^-$ (mean 94°),[3] in $[Rh_6(CO)_{14}(\eta\text{-}C_3H_5)]^-$ (mean 96°),[4] and in $[Rh_{12}(CO)_{30}]^{2-}$ (mean 95°).[5] These steric arguments can explain the difficulty of obtaining more highly substituted species with $P(OPh)_3$.

Finally, the triphenyl phosphite ligands show P–O and O–Ph bond lengths (means 1.60 and 1.38 Å) comparable with previously reported data;[10] the bond angles are also as normally found for these ligands.

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