The Synthesis, Reactivity, and Crystal and Molecular Structure of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$,† an Unusual 50-Electron Closed Trinuclear Cluster Derivative of Rhodium

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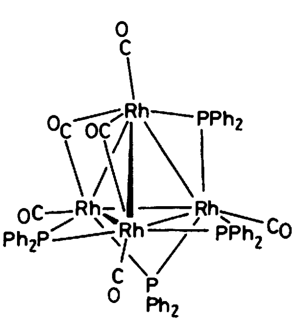
The reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with PPh_2H in benzene affords the mononuclear complex $[RhCl(CO)(PPh_2H)_2]$ for a molar ratio of 1 : 4 and the trinuclear derivative $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$, for a molar ratio of 1 : 2. The structure of the trinuclear derivative has been determined by *X*-ray crystallography. It crystallises in the monoclinic space group $P2_1/n$, with $a = 12.461(5)$, $b = 32.867(5)$, $c = 11.149(5)$ Å, $\beta = 99.29(1)°$, $Z = 4$, and $R = 0.085$. The metal atoms adopt a triangular configuration with each edge of the triangle being bridged by a diphenylphosphido-group as well as by either a chloro or a carbonyl group. In spite of this compound being a 50-electron system, all of the Rh–Rh distances correspond with those normally associated with a formal rhodium–rhodium bond. The chloro-groups in this compound can be extracted as radicals by the addition of NEt_2H, affording, in the presence of CO, $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, or displaced as chloride ions by treatment of the complex with $AgSbF_6$; the former reaction is a reversible process with dissolution of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ in CCl_4 resulting in the regeneration of the title complex. $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ is only moderately stable in solution and converts slowly to an insoluble species formulated as $[\{Rh(\mu\text{-}PPh_2)(\mu\text{-}Cl)(CO)\}_n]$.

It has been patented previously that treatment of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with PPh_2H in benzene leads to the formation of a product which on the basis of analytical and presumably spectroscopic data was proposed to be a tetranucleur rhodium complex of stoicheiometry $[Rh_4(\mu\text{-}PPh_2)_2(\mu\text{-}Cl)_4(CO)_4(PPh_2H)_2]$.[1] Tetranuclear compounds have also been reported to be formed in the reactions of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with PPh_2^-. In particular that involving a 1 : 2 molar ratio of these two species has been observed to afford a neutral product, initially believed to be $[\{Rh(\mu\text{-}PPh_2)(CO)_2\}_n]$ (n = 3 or 4),[2] but subsequently established to be $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_4]$ (1),[3] while that involving a slightly larger molar ratio than 1 : 2 has been shown to yield an anionic species structurally characterised as $[Rh_4(\mu\text{-}PPh_2)_5(CO)_5]^-$ (2).[4] As part of a programme investigating the potential of the diphenylphosphido-ligand, PPh_2^-, for stabilising homo- and hetero-nuclear metal cluster compounds of unusual geometry and stereochemistry [5-8] we have carried out a detailed examination of the reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with PPh_2H.[3,9-11] This study included a reinvestigation of the reaction of these two species in benzene in the absence of a base. It has now been established that this reaction affords at least three products, none of which was described in the initial patent. The results of this investigation are now reported here; some of these have already been described in a preliminary communication.[11]



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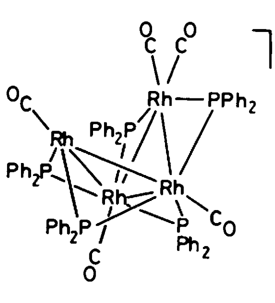

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Results and Discussion

Treatment of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with a four-fold molar amount of PPh_2H in benzene was found to result in the immediate liberation of carbon monoxide and, on addition of hexane, the separation from solution of a yellow crystalline compound characterised by means of elemental analysis and i.r. and n.m.r. spectroscopy [ν(C–O) 1 978 (C_6H_{12}) and 1 966 cm^{-1} (Nujol mull); ν($Rh–Cl_{terminal}$) 293 cm^{-1} (Nujol mull); δ(P–*H*) 5.08(br) p.p.m., relative to $SiMe_4$] as $[RhCl(CO)(PPh_2H)_2]$. The formation of this species is not unexpected, however, in view of the fact that the well documented complex *trans*-$[RhCl(CO)(PPh_3)_2]$ [12] is readily synthesised by reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with a stoicheiometric amount of PPh_3,[13] and on this basis it is presumed to have a *trans* structure similar to the latter.

A reduction in the molar ratio of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ to PPh_3 in the above reaction to 1 : 2 did not lead to a simple decrease in the yield of $[RhCl(CO)(PPh_2H)_2]$ but to the formation of a second product which could be isolated as orange crystals by addition of hexane to the reaction mixture. The elemental analysis and a molecular mass measurement were consistent with the stoicheiometry of the complex being $[Rh_3(PPh_2)_3Cl_2(CO)_4]$ while a conductivity measurement was indicative of it being neutral. The solid-state and solution i.r. spectra revealed the presence of both bridging and terminal carbonyl groups [ν(C–O) 2 033m, 2 015vs, and 1 822m cm^{-1} (Nujol mull); 2 033w, 2 015vs, and 1 822m cm^{-1} (C_6H_{12})] and

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† μ-Carbonyl-tricarbonyl-di-μ-chloro-tris(μ-diphenylphosphido)-*triangulo*-trirhodium.

Supplementary data available (No. SUP 23681, 39 pp.): structure factors, thermal parameters, H-atom co-ordinates, least-squares planes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Fractional atomic co-ordinates (× 10^5 for Rh atoms; × 10^4 for all other atoms) for the non-hydrogen atoms with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	18 313(7)	11 584(3)	27 348(8)	C(23)	1 571(17)	−326(6)	784(19)
Rh(2)	39 003(7)	9 370(3)	38 803(8)	C(24)	1 989(13)	−604(5)	1 554(15)
Rh(3)	32 036(7)	17 523(3)	36 895(8)	C(25)	2 721(15)	−505(6)	2 502(17)
P(1)	3 051(3)	724(1)	2 015(3)	C(26)	3 071(13)	−106(5)	2 711(15)
Cl(2)	3 954(3)	1 389(1)	5 679(3)	C(31)	388(10)	2 046(4)	3 237(11)
P(2)	1 401(3)	1 685(1)	3 979(3)	C(32)	698(11)	2 379(4)	2 631(12)
Cl(1)	2 248(3)	617(1)	4 418(3)	C(33)	−72(11)	2 653(4)	2 022(12)
P(3)	4 847(3)	1 485(1)	3 334(3)	C(34)	−1 141(14)	2 573(5)	2 011(15)
C(4)	2 401(9)	1 659(4)	2 004(11)	C(35)	−1 452(17)	2 220(6)	2 611(18)
O(4)	2 273(8)	1 819(3)	1 049(8)	C(36)	−682(12)	1 959(5)	3 221(14)
C(2)	4 996(11)	552(4)	4 164(12)	C(41)	1 061(10)	1 634(4)	5 496(11)
O(2)	5 682(9)	315(4)	4 269(12)	C(42)	811(14)	1 273(5)	5 994(16)
C(3)	3 497(11)	2 313(4)	3 787(12)	C(43)	613(15)	1 249(6)	7 217(18)
O(3)	3 662(9)	2 658(3)	3 808(10)	C(44)	691(16)	1 586(6)	7 825(19)
C(1)	478(13)	1 081(4)	1 701(12)	C(45)	916(16)	1 942(6)	7 419(19)
O(1)	−259(11)	1 094(4)	978(13)	C(46)	1 112(12)	1 982(5)	6 200(14)
Cl(20)	4 722(8)	5 019(3)	7 928(9)	C(51)	5 393(11)	1 526(4)	1 915(12)
Cl(10)	2 482(10)	4 909(4)	7 245(12)	C(52)	6 338(15)	1 317(6)	1 806(18)
Cl(30)	3 590(8)	4 403(3)	8 977(9)	C(53)	6 809(18)	1 387(7)	698(20)
C(100)	3 516(17)	4 895(6)	8 401(19)	C(54)	6 356(18)	1 645(7)	−91(21)
C(11)	3 649(10)	778(4)	650(11)	C(55)	5 398(19)	1 871(7)	9(21)
C(12)	4 585(12)	568(4)	541(13)	C(56)	4 924(14)	1 808(5)	1 070(16)
C(13)	4 999(14)	575(5)	−582(15)	C(61)	6 052(9)	1 623(4)	4 428(11)
C(14)	4 493(15)	805(6)	−1 518(17)	C(62)	6 329(12)	2 019(5)	4 561(14)
C(15)	3 546(16)	1 041(6)	−1 376(18)	C(63)	7 255(13)	2 152(5)	5 327(15)
C(16)	3 116(13)	1 017(5)	−303(14)	C(64)	7 889(15)	1 874(6)	5 957(17)
C(21)	2 709(10)	184(4)	1 902(11)	C(65)	7 715(17)	1 467(7)	5 793(19)
C(22)	1 947(13)	73(5)	892(15)	C(66)	6 754(15)	1 360(6)	5 001(17)

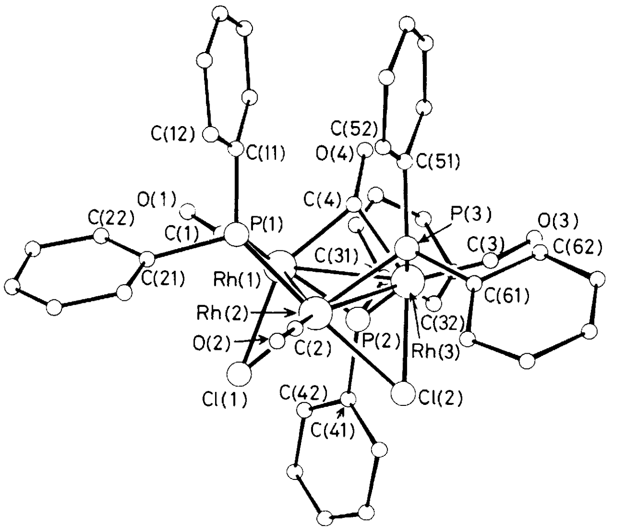

Figure 1. The molecular structure of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ showing the atom labelling used

that at least one of the chloro-groups was co-ordinated in the bridging mode [ν(Rh–$Cl_{bridging}$) 245 cm^{-1}]. With the aim of establishing unequivocally the structure of this obviously unusual compound, an *X*-ray crystallographic study was carried out.

Crystals suitable for *X*-ray analysis were obtained from dichloromethane–hexane by vapour diffusion techniques. The molecular geometry and crystal packing of the compound are illustrated in Figures 1 and 2 respectively while fractional atomic co-ordinates, selected bond lengths and angles, and torsion angles and least-squares planes are summarised in Tables 1, 2, and 3 respectively. The rhodium atoms adopt a triangular configuration with each of the Rh–Rh distances corresponding to those normally associated with a formal rhodium–rhodium bond [Rh(1)–Rh(2), 2.783(1); Rh(1)–Rh(3), 2.698(1); Rh(2)–Rh(3), 2.814(1) Å]. Each rhodium–rhodium edge is bridged by a diphenylphosphido-group * with two of the phosphorus atoms being *cis* disposed with respect to the trirhodium plane and the third *trans* disposed. Two of the rhodium–rhodium edges are also bridged by chloro-groups while the third and remaining edge is additionally bridged by a carbonyl ligand; this latter edge is appreciably shorter than the other two. The two RhPRhCl rings are puckered with the dihedral angles between the planes Rh(1)P(1)Rh(2) and Rh(1)Cl(1)Rh(2) and between the planes Rh(2)P(3)Rh(3) and Rh(2)Cl(2)Rh(3) being 100.2 and 100.6° respectively. The RhCRhP ring is similarly puckered with the dihedral angle between the planes Rh(1)C(4)Rh(3) and Rh(1)P(2)Rh(3) being 104.8°. The overall disposition of the ligands is such that the molecule contains an approximate plane of symmetry through Rh(2), P(2), C(2), and C(4). Interestingly the two proximate phenyl groups attached to P(1) and P(3), which are related by this plane of symmetry, are almost coplanar (the angle between the normals to the rings is 8.0°). The close contact between these rings (the distance separating their centroids is 3.9 Å) is also noteworthy.

Triangular metal cluster compounds in which all of the metal–metal distances correspond with those normally associated with metal–metal bonds are, in general, formally

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* The Rh–P–Rh bridge bonding can be considered as being of the *closed* type with a *closed* M–P–M bridge bond being defined as the bond between two metal atoms, M, which are linked through a bridging phosphorus atom and in which the metal–metal distance corresponds to a formal metal–metal bond. The bonding interaction between the metals may be direct, or through the bridging atom, or both. An *open* M–P–M bridge bond is one in which the metal–metal distance is appreciably larger than those associated with metal–metal bonds.

Table 2. Relevant bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Rh(1)–Rh(2)	2.783(1)	Rh(2)–P(1)	2.286(3)	Rh(3)–C(4)	2.004(12)	C(4)–O(4)	1.175(15)
Rh(1)–Rh(3)	2.698(1)	Rh(2)–Cl(2)	2.487(3)	Rh(3)–C(3)	1.879(15)	C(2)–O(2)	1.148(18)
Rh(1)–P(1)	2.322(3)	Rh(2)–Cl(1)	2.470(4)	P(1)–C(11)	1.808(14)	C(3)–O(3)	1.149(18)
Rh(1)–P(2)	2.335(3)	Rh(2)–P(3)	2.290(3)	P(1)–C(21)	1.823(12)	C(1)–O(1)	1.121(19)
Rh(1)–Cl(1)	2.576(3)	Rh(2)–C(2)	1.850(13)	P(2)–C(31)	1.829(12)	Cl(20)–C(100)	1.720(25)
Rh(1)–C(4)	2.016(12)	Rh(3)–Cl(2)	2.559(3)	P(2)–C(41)	1.817(14)	Cl(10)–C(100)	1.669(23)
Rh(1)–C(1)	1.900(14)	Rh(3)–P(2)	2.331(3)	P(3)–C(51)	1.825(15)	Cl(30)–C(100)	1.736(24)
Rh(2)–Rh(3)	2.814(1)	Rh(3)–P(3)	2.320(3)	P(3)–C(61)	1.832(11)		

Rh(2)–Rh(1)–Rh(3)	61.8(0.1)	Rh(1)–Rh(2)–P(3)	98.7(0.1)	P(3)–Rh(3)–C(3)	102.2(0.5)
Rh(2)–Rh(1)–P(1)	52.3(0.1)	Rh(3)–Rh(2)–P(3)	52.9(0.1)	C(4)–Rh(3)–C(3)	105.5(0.5)
Rh(3)–Rh(1)–P(1)	100.0(0.1)	P(1)–Rh(2)–P(3)	100.5(0.1)	Rh(1)–P(1)–Rh(2)	74.3(0.1)
Rh(2)–Rh(1)–P(2)	101.9(0.1)	Cl(2)–Rh(2)–P(3)	78.3(0.1)	Rh(1)–P(1)–C(11)	127.7(0.4)
Rh(3)–Rh(1)–P(2)	54.6(0.1)	Cl(1)–Rh(2)–P(3)	152.2(0.1)	Rh(2)–P(1)–C(11)	122.8(0.4)
P(1)–Rh(1)–P(2)	152.6(0.1)	Rh(1)–Rh(2)–C(2)	149.4(0.4)	Rh(1)–P(1)–C(21)	117.6(0.4)
Rh(2)–Rh(1)–Cl(1)	54.7(0.1)	Rh(3)–Rh(2)–C(2)	150.9(0.4)	Rh(2)–P(1)–C(21)	115.5(0.4)
Rh(3)–Rh(1)–Cl(1)	99.9(0.1)	P(1)–Rh(2)–C(2)	99.6(0.4)	C(11)–P(1)–C(21)	99.3(0.6)
P(1)–Rh(1)–Cl(1)	76.2(0.1)	Cl(2)–Rh(2)–C(2)	110.3(0.4)	Rh(2)–Cl(2)–Rh(3)	67.8(0.1)
P(2)–Rh(1)–Cl(1)	96.8(0.1)	Cl(1)–Rh(2)–C(2)	106.8(0.4)	Rh(1)–P(2)–Rh(3)	70.7(0.1)
Rh(2)–Rh(1)–C(4)	92.2(0.3)	P(3)–Rh(2)–C(2)	100.7(0.4)	Rh(1)–P(2)–C(31)	114.8(0.4)
Rh(3)–Rh(1)–C(4)	47.6(0.3)	Rh(1)–Rh(3)–Rh(2)	60.6(0.1)	Rh(3)–P(2)–C(31)	119.1(0.4)
P(1)–Rh(1)–C(4)	94.0(0.4)	Rh(1)–Rh(3)–Cl(2)	97.1(0.1)	Rh(1)–P(2)–C(41)	126.5(0.4)
P(2)–Rh(1)–C(4)	76.4(0.4)	Rh(2)–Rh(3)–Cl(2)	54.9(0.1)	Rh(3)–P(2)–C(41)	120.8(0.4)
Cl(1)–Rh(1)–C(4)	144.6(0.3)	Rh(1)–Rh(3)–P(2)	54.7(0.1)	C(31)–P(2)–C(41)	103.5(0.6)
Rh(2)–Rh(1)–C(1)	155.4(0.4)	Rh(2)–Rh(3)–P(2)	101.1(0.1)	Rh(1)–Cl(1)–Rh(2)	66.9(0.1)
Rh(3)–Rh(1)–C(1)	141.3(0.4)	Cl(2)–Rh(3)–P(2)	93.5(0.1)	Rh(2)–P(3)–Rh(3)	75.2(0.1)
P(1)–Rh(1)–C(1)	105.9(0.4)	Rh(1)–Rh(3)–P(3)	100.4(0.1)	Rh(2)–P(3)–C(51)	124.6(0.4)
P(2)–Rh(1)–C(1)	101.1(0.4)	Rh(2)–Rh(3)–P(3)	51.9(0.1)	Rh(3)–P(3)–C(51)	125.7(0.4)
Cl(1)–Rh(1)–C(1)	113.8(0.4)	Cl(2)–Rh(3)–P(3)	76.3(0.1)	Rh(2)–P(3)–C(61)	114.8(0.4)
C(4)–Rh(1)–C(1)	101.6(0.5)	P(2)–Rh(3)–P(3)	152.2(0.1)	Rh(3)–P(3)–C(61)	116.4(0.4)
Rh(1)–Rh(2)–Rh(3)	57.6(0.1)	Rh(1)–Rh(3)–C(4)	48.0(0.3)	C(51)–P(3)–C(61)	100.3(0.6)
Rh(1)–Rh(2)–P(1)	53.4(0.1)	Rh(2)–Rh(3)–C(4)	91.5(0.3)	Rh(1)–C(4)–Rh(3)	84.3(0.5)
Rh(3)–Rh(2)–P(1)	97.6(0.1)	Cl(2)–Rh(3)–C(4)	142.9(0.3)	Rh(1)–C(4)–O(4)	136.6(0.9)
Rh(1)–Rh(2)–Cl(2)	96.7(0.1)	P(2)–Rh(3)–C(4)	76.7(0.4)	Rh(3)–C(4)–O(4)	139.1(0.9)
Rh(3)–Rh(2)–Cl(2)	57.3(0.1)	P(3)–Rh(3)–C(4)	95.9(0.4)	Rh(2)–C(2)–O(2)	175.9(1.3)
P(1)–Rh(2)–Cl(2)	149.8(0.1)	Rh(1)–Rh(3)–C(3)	146.9(0.4)	Rh(3)–C(3)–O(3)	177.8(1.1)
Rh(1)–Rh(2)–Cl(1)	58.4(0.1)	Rh(2)–Rh(3)–C(3)	151.1(0.4)	Rh(1)–C(1)–O(1)	167.2(1.3)
Rh(3)–Rh(2)–Cl(1)	99.5(0.1)	Cl(2)–Rh(3)–C(3)	111.6(0.4)	Cl(20)–C(100)–Cl(10)	111.1(1.3)
P(1)–Rh(2)–Cl(1)	79.0(0.1)	P(2)–Rh(3)–C(3)	105.5(0.5)	Cl(20)–C(100)–Cl(30)	109.7(1.2)
Cl(2)–Rh(2)–Cl(1)	88.5(0.1)				

48-electron systems (or less) and as a consequence $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$, with its short Rh–Rh distances (see Table 4), is somewhat novel in that it can be considered as a 50-electron system based on each carbonyl ligand contributing two electrons to the metal-atom framework and each phosphido- and chloro-group, three. In fact, only two other trinuclear clusters with short metal–metal distances and which contain more than 48 skeleton electrons are known, *viz.* $[Co_3(\mu_3\text{-}PPh)(CO)_9]$,[14] a 49-electron system, and $[Co_3(\mu\text{-}SEt)_5(\mu\text{-}CO)(CO)_3]$,[15,16] a 50-electron complex; significantly the overall geometry of the latter is very similar to that of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$. It is apparent that the structure of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ cannot be reconciled with the 18-electron rule otherwise distances longer than those generally associated with formal Rh–Rh bonds would have been expected for at least one of the Rh–Rh edges. For instance $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$, another 50-electron system, has only two iron–iron distances which correspond to formal iron–iron bonds with the third distance being considerably longer [2.582(9), 2.609(10), and 3.371(10) Å].[17] Furthermore the addition of CO (or PPh_3) to $[MnFe_2(\mu_3\text{-}PPh)(\eta^5\text{-}C_5H_5)(CO)_8]$ leads to the successive opening of two of the manganese–iron bonds.[18] Interestingly $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$,[10] which is also a 50-electron system, and which similarly to $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ (see below) can be produced both formally and chemically from $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ has essentially equal but appreciably longer Rh–Rh distances than its parent,[9] as summarised in Table 4. On the other hand $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ has rhodium–rhodium distances which are essentially equal to those of the pentacarbonyl derivative and which, as described above, correspond to those normally associated with rhodium–rhodium bonds. The overall symmetries as well as the local symmetries of the rhodium atoms are different, however, for the two molecules. Theoretical studies are being carried out on these molecules to establish why the formal addition of four electrons to $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, through co-ordination of PPh_2H and CO, should lead to a symmetric opening of the Rh_3P_3 ring while the formal addition of a similar number of electrons through co-ordination of two Cl radicals and concomitant loss of carbon monoxide, has no apparent effect on the Rh–Rh distances.*

$[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ was found to degrade

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* The bonding in $[Co_3(\mu\text{-}SEt)_5(\mu\text{-}CO)(CO)_3]$ has been described previously in terms of a molecular orbital scheme based on each cobalt atom being approximately square pyramidal with respect to its neighbouring ligands and the cobalt–ligand σ-bonding consequentially involving the d_{xy}, the *s*, and the three *p* orbitals of each cobalt atom.[16] The four remaining *d* orbitals of each cobalt were utilised for constructing the molecular orbitals responsible for the Co–Co interactions. However, this scheme effectively considers the cobalt–sulphur bonding as being localised whereas the Co–S–Co bond angles [average 68.5(3)°] are considerably less than that expected for localised bonding.

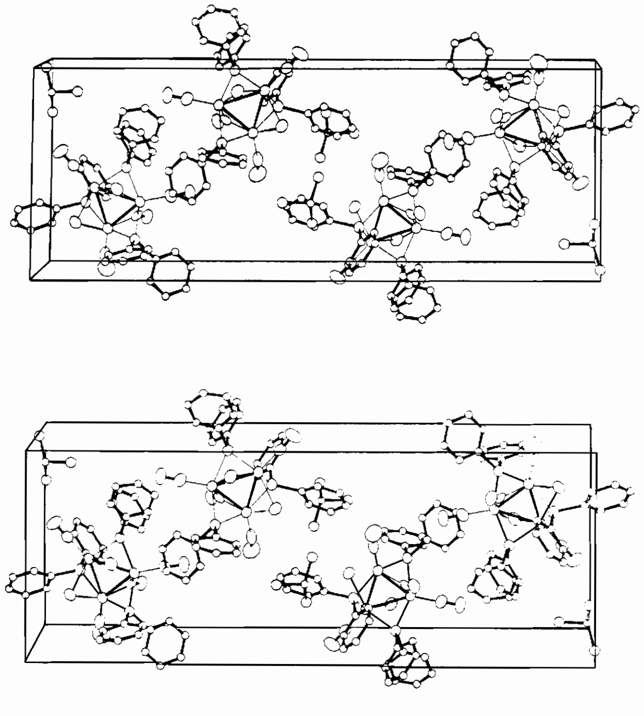


Figure 2. Crystal packing diagram of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$

Table 3. Selected torsion angles (°), least-squares plane, and dihedral angles (°) *

(*a*) Torsion angles

C(1)–Rh(1)–Rh(2)–C(2)	1.0
C(1)–Rh(1)–Rh(3)–C(3)	1.6
C(2)–Rh(2)–Rh(3)–C(3)	2.4

(*b*) Least-squares plane [distances of atoms (Å) from the plane are given in square brackets]

Plane: Rh(1), Rh(2), Rh(3)

$$-6.0743x - 2.7474y + 10.4404z = 1.4246$$

[P(1) −1.37, Cl(1) 1.65, P(2) 1.42, C(1) −0.23, O(1) −0.55, C(2) −0.26, O(2) −0.51, C(3) −0.23, O(3) −0.41, Cl(2) 1.72]

(*c*) Dihedral angles (°) between the planes

Rh(1),Rh(2),Rh(3)–Rh(1),P(1),Rh(2)	131.6
Rh(1),Rh(2),Rh(3)–Rh(1),Cl(1),Rh(2)	128.2
Rh(1),Rh(2),Rh(3)–Rh(2),P(3),Rh(3)	134.7
Rh(1),Rh(2),Rh(3)–Rh(2),Cl(2),Rh(3)	124.7
Rh(1),Rh(2),Rh(3)–Rh(1),C(4),Rh(3)	123.3
Rh(1),Rh(2),Rh(3)–Rh(1),P(2),Rh(3)	131.9
Rh(1),P(1),Rh(2)–Rh(1),Cl(1),Rh(2)	100.2
Rh(2),P(3),Rh(3)–Rh(2),Cl(2),Rh(3)	100.6
Rh(1),C(4),Rh(3)–Rh(1),P(2),Rh(3)	104.8

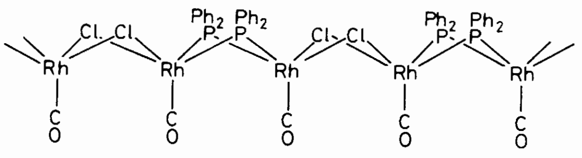
* E.s.d.s are 0.5° and 0.05 Å for angular and distance measurements.

Table 4. Comparison of Rh–Rh bond length (Å) data

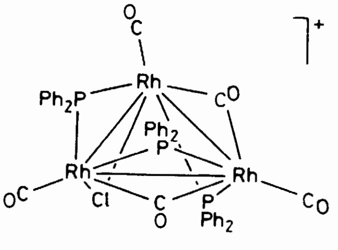
$[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$	$[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$	$[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$
2.698(1)	2.698(1)	3.09(1)
2.793(1)	2.783(1)	3.12(1)
2.806(1)	2.814(1)	3.23(1)

slowly in solution and in fact recrystallisation of this compound always led to the separation of a second product from solution which proved insoluble in all common organic solvents. As a result of this insolubility, this compound could not be isolated pure but elemental analysis indicated a stoicheiometry of $[\{Rh(PPh_2)Cl(CO)\}_n]$. The solid-state i.r. spectrum of the compound contains two peaks in the C–O stretching region at 2 064s and 2 054s cm^{-1} readily assigned to terminal carbonyl groups and a strong absorbance at 235 cm^{-1}, consistent with the chloro-group co-ordinating in the bridging mode. On the basis of the extreme insolubility of the compound, it is suggested that it is polymeric and has a chain-like structure, (3), illustrated below. The compound is presumably the same as that patented as $[Rh_4(\mu\text{-}PPh_2)_2(\mu\text{-}Cl)_4(CO)_4(PPh_2H)_2]$.[1]

It was anticipated that one of the chloro-groups in $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ should be readily displaced as chloride ions to afford, in the presence of carbon monoxide, the 48-electron system $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)(\mu\text{-}CO)_2(CO)_3]^+$ (4). Treatment of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ with a stoicheiometric amount of $AgSbF_6$ in the presence of CO was indeed observed to lead to a change in the colour of the reaction mixture from red to purple and the separation from solution of AgCl, but the product could not be isolated in sufficiently pure form for characterisation purposes. Addition of diethylamine to $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ was also found to lead to the extraction of the chloro-groups but effectively as radicals to produce in the presence of CO a green reaction mixture from which $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$[9] could be isolated. This process is a reversible one and dissolution of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ in CCl_4 resulted in the regeneration of the bridged chloro-compound. Not surprisingly this reaction could be accelerated by addition of chlorine to the carbon tetrachloride solution.

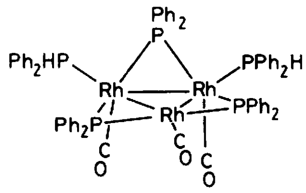


(3)



(4)

The phosphine hydrogens in $[RhCl(CO)(PPh_2H)_2]$ are labile and treatment of a solution of this complex with an equimolar amount of NEt_2H led to the rapid formation of a green-brown solution from which a green product could be isolated. As a result of the instability of this compound it could not be obtained sufficiently pure for characterisation purposes but it is believed to be $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_2H)_2]$ (5) on the basis of its green colour {both $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ and its triphenylphosphine-substituted derivative, $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$ are green [9,19]}, that its C–O stretching frequencies [ν(C–O) 1 985s and 1 955s cm^{-1} (Nujol mull)]



(5)

correspond with those of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$ [ν(C–O) 1 985s and 1 945s cm^{-1} (CH_2Cl_2)[19]], and the fact that reaction of $[RhCl(CO)(PPh_3)_2]$ with $KPPh_2$ or of $Na[Rh(CO)_2(PPh_3)_2]$ with PPh_2Cl produces $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$.[20]

Experimental

All reactions and manipulations were carried out under an atmosphere of nitrogen, using Schlenk-tube techniques, unless otherwise stated. Solvents were purified and dried using standard procedures. $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ was synthesised from $RhCl_3{\cdot}3H_2O$ using a literature method[21] while PPh_2H was obtained commercially and used without further purification. Infrared spectra were recorded on Perkin-Elmer 457 and 283 grating spectrophotometers while ^1H n.m.r. spectra were measured on a Varian FT 80A instrument in deuteriated solvents. Elemental analyses were obtained by Mr. M. Martin-Short, Microanalytical Laboratory, University of Natal, Pietermaritzburg, by Elemental Microanalysis Ltd., Beaworthy, Devon, and the Analytical Laboratories of H. Malissa and G. Reuter, Engelskirchen, West Germany.

Synthesis of $[RhCl(CO)(PPh_2H)_2]$.—A solution of PPh_2H (1.0 g, 5.26 mmol) in benzene (*ca.* 10 cm^3) was added dropwise to a stirred solution of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ (0.50 g, 1.28 mmol) in benzene (*ca.* 15 cm^3) at room temperature. On cessation of the liberation of carbon monoxide, hexane was added and the reaction mixture cooled to 4 °C and kept at this temperature for 24 h. The yellow crystals of $[RhCl(CO)(PPh_2H)_2]$ which separated were collected by filtration, washed with hexane, and dried *in vacuo* (yield: 1.1 g, 80%) [Found: C, 55.8; H, 4.1; Cl, 6.5; P, 11.5%; *M*, 641 (vapour pressure osmometry in benzene). Calc. for $C_{25}H_{22}ClOP_2Rh$: C, 55.7; H, 4.1; Cl, 6.6; P, 11.5%; *M*, 539].

Synthesis of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$.—A solution of PPh_2H (0.48 g, 2.56 mmol) in benzene (*ca.* 10 cm^3) was added dropwise to a stirred solution of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ (0.25 g, 1.28 mmol) in benzene (*ca.* 30 cm^3) at room temperature. Hexane was added after 30 min and the reaction mixture cooled to 4 °C and kept at this temperature for 24 h. The orange hair-like crystals of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ which separated were collected by filtration, washed with hexane, and dried *in vacuo*. Recrystallisation was effected from CH_2Cl_2–hexane (yield: 0.31 g, 70%) [Found: C, 45.8; H, 3.0; Cl, 6.6; P, 9.0%; *M*, 1 142 (vapour pressure osmometry in benzene). Calc. for $C_{40}H_{30}Cl_2O_4P_3Rh_3$: C, 45.8; H, 2.9; Cl, 6.8; P, 8.9%; *M*, 1 047].

Synthesis of $[\{Rh(\mu\text{-}PPh_2)(\mu\text{-}Cl)(CO)\}_n]$.—The mother-liquor from the synthesis of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ was evaporated to dryness under reduced pressure to afford $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ as an orange amorphous material which was redissolved in dichloromethane. After a number of days at room temperature, $[\{Rh(\mu\text{-}PPh_2)(\mu\text{-}Cl)(CO)\}_n]$ separated from the CH_2Cl_2 solution as an orange microcrystalline solid. This was collected by filtration, washed repeatedly with CH_2Cl_2 and hexane and dried *in vacuo* (Found: C, 40.2; H, 2.9; Cl, 10.4; P, 8.3; Rh, 27.6. Calc. for $C_{13}H_{10}ClOPRh$: C, 44.4; H, 2.9; Cl, 10.1; P, 8.8; Rh, 29.3%; sample impure, contains variable amounts of CH_2Cl_2).

X-Ray Crystallography.—Crystal and intensity data. Crystals of $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]{\cdot}CH_2Cl_2$ were obtained by crystallisation from dichloromethane–hexane. $C_{41}H_{32}Cl_4O_4P_3Rh_3$, $M = 1\,132.14$, Monoclinic, space group $P2_1/n$, $a = 12.461(5)$, $b = 32.867(5)$, $c = 11.149(5)$ Å, $\beta = 99.29(1)°$, $U = 4\,506.2$ Å^3 $D_m = 1.71(5)$, $Z = 4$, $D_c = 1.67$ g cm^{-3}, $F(000) = 2\,232$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 13.7$ cm^{-1}. Preliminary photography established the space group and gave the unit-cell parameters which were refined using 25 high-angle reflections measured on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation. The crystal used (dimensions 0.15 × 0.2 × 0.2 mm) showed no instability. Diffraction data were collected in the range $6 < 2\theta < 46°$ [out of 6 396 reflections collected, 6 250 independent reflections had $I > \sigma(I)$] and were corrected for Lorentz and polarization effects but not for absorption. The high value of *b* precluded the measurement of background levels and these were corrected for by using a background *vs.* θ curve based on measurements of systematically absent reflections; the rather high final *R* values reflect this slightly inadequate method.

Structure solution and refinement. All calculations were carried out on a Burroughs B6800 computer at the University of South Africa. The structure was solved by conventional heavy-atom techniques using SHELX.[22] Table 1 gives the fractional atomic co-ordinates of the non-hydrogen atoms while relevant bond lengths and angles are summarized in Table 2. Torsion angles and parameters defining relevant planes are included in Table 3. In three final least-squares cycles, in which a weighting scheme $w = k[\sigma^2(F)]$ was employed, all atoms except the phenyl carbons and dichloromethane solvent atoms were refined with anisotropic thermal parameters. Hydrogen atoms were positioned geometrically and given a common thermal parameter U_H. Refinement converged with $R = 0.085$ and $R' = 0.095$ and was considered complete when no shift–error ratio exceeded 1.0; k refined to 5.58 and U_H to 0.18(3) Å^2. The two chlorine atoms of the dichloromethane molecule were disordered about three sites and were therefore refined as three atoms with $\frac{2}{3}$ site occupancy factors. In a final difference map there were no significant (>1 e Å^{-3}) peaks associated with the $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$ molecules although several peaks with heights >2 e Å^{-3} were associated with the CH_2Cl_2 molecule. Scattering factors were taken from ref. 23.

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