Synthesis, Reactivity, and Molecular and Crystal Structures of some Trinuclear Diphenylphosphido-bridged Carbonyl Derivatives of Rhodium ‡

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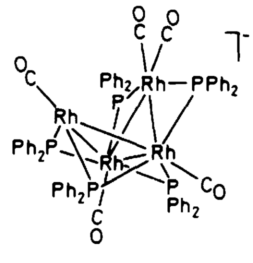
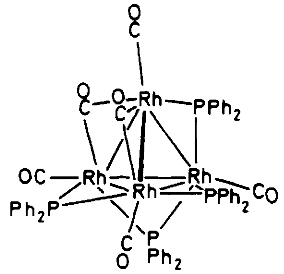
Reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with PPh_2H in benzene affords, in the presence of a base and under an atmosphere of CO, a yellow crystalline product, believed to be $[Rh_3(\mu\text{-}PPh_2)_3(CO)_9]$ and which degrades to an orange-red species, characterised as the heptacarbonyl $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$, on recrystallisation from methanol under CO at 15 °C. The same reaction in ethanol, also under an atmosphere of CO but in the absence of a base, gave an orange-red crystalline derivative established to be $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$. All three complexes are unstable under any atmosphere but CO and are readily and reversibly decarbonylated, with loss of PPh_2H as well in the case of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$, to a green crystalline species characterized as $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$. The latter condenses slowly in polar solvents to afford the tetranuclear cluster $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_4]$ while it reacts with Cl_2 to give the 50-electron species $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$. Crystal structure determinations on $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ [monoclinic, space group $P2_1/n$, a = 14.003(5), b = 17.471(5), c = 16.523(5) Å, β = 103.76(5)°, and Z = 4], $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ [monoclinic, space group $P2_1/c$, a = 18.16(1), b = 17.935(10), c = 13.119(10) Å, β = 103.5(1)°, and Z = 4], and $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ [monoclinic, space group $P2_1/c$, a = 12.515(5), b = 11.843(5), c = 37.102(5) Å, β = 94.6(1)°, and Z = 4] have revealed that addition of PPh_2H and/or CO to the pentacarbonyl compound is accompanied by an expansion of the Rh_3P_3 ring from an average Rh–Rh distance of 2.766 Å to one of 3.15 Å for $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ and one of 3.165 Å for $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$.

A limitation in the use of transition-metal cluster compounds as homogeneous catalysts is their tendency to fragment into mononuclear moieties under the reaction conditions commonly employed in catalytic processes. One way of overcoming this problem is to link the metal atoms of the cluster through stable non-fluxional bridging ligands such that the integrity of the metal cluster framework is essentially retained during a chemical reaction. One of the approaches that is being adopted in this respect involves the utilisation of face- or edge-bridging monodentate phosphorus, arsenic, or sulphur ligands to stabilise metal clusters and indeed a wide range of highly unusual clusters containing these bridging groups have been reported, *e.g.* $[Co_3(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_6]$,[1] $[Co_5(\mu\text{-}PMe_2)_3(\mu\text{-}CO)_3(CO)_8]$,[2] $[Fe_3(\mu_3\text{-}SBu^t)(\mu\text{-}SBu^t)(CO)_9]$,[3] $[Os_3(\mu_3\text{-}S)(\mu\text{-}H)_2(CO)_9]$,[4] $[Fe_3(\mu_3\text{-}PPh)(\mu\text{-}H)_2(CO)_9]$,[5] $[Co_3(\mu_3\text{-}PPh)(CO)_9]$,[6] $[Ru_3(\mu_3\text{-}AsPh)(\mu\text{-}H)_2(CO)_9]$,[7] $[Fe_4(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{10}]$,[8] and $[Ru_3Rh_2(\mu_4\text{-}PPh)(\mu\text{-}CO)(CO)_{12}]$.[9] Significantly $[Co_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)_2(CO)_8]$ has been found to homogeneously catalyse the hydroformylation of alkenes without any apparent fragmentation to mononuclear species.[10] As part of a programme investigating the potential of the diphenylphosphido-ligand, PPh_2, for stabilising homo- and heteronuclear metal cluster compounds of unusual geometry and stereochemistry [11–14] we have carried out a detailed examination of the reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with PPh_2H to find that it affords a range of unusual products, the formation and nature of which are dependent on the reaction conditions.[15–18] The results of the study of the reaction of these two species in the presence of a base are now described; some of these results have already been reported in preliminary communications.[15,18]



(1)



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Results and Discussion

It has been previously established that while the reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with SPh^- (1 : 2 mol ratio) in tetrahydrofuran (thf) affords the red dinuclear complex $[\{Rh(\mu\text{-}SPh)(CO)_2\}_2]$,[19] the corresponding reaction involving PPh_2^- produces an oligomeric species $[\{Rh(\mu\text{-}PPh_2)(CO)_2\}_n]$ where n is probably 3 or 4.[20] More recent investigations have revealed that if the latter reaction is carried out in the presence of a slight excess of PPh_2^-, the anionic species $[Rh_4(\mu\text{-}PPh_2)_5(CO)_5]^-$ (1) is formed,[21] a crystal structure determination on which revealed that the cluster adopts a butterfly structure with all five edges being bridged by a diphenylphosphido-group.[21]

We have now discovered that the reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with PPh_2^- is even more complex than that described above and that depending on the reaction conditions employed any one of a number of different cluster species can be produced. The complexity of this reaction is increased even further if PPh_2H is used as a source for the *in situ* generation of PPh_2^-.

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‡ *Supplementary data available* (No. SUP 23816, 75 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

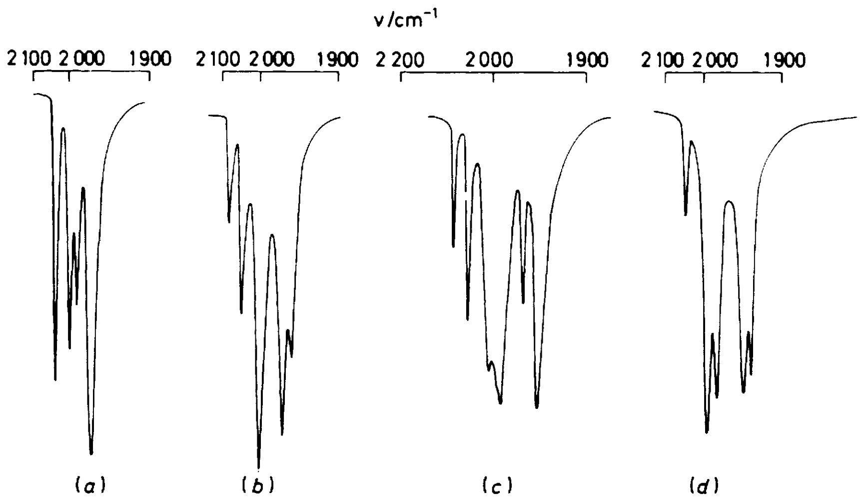

Figure 1. The solid-state i.r. spectra in the C−O stretching region of (*a*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, (*b*) $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$, (*c*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$, and (*d*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$

As reported earlier [17] the compound characterised by Hieber and Kummer [20] as $[\{Rh(\mu\text{-}PPh_2)(CO)_2\}_n]$ (n = 3 or 4) has in fact the stoicheiometry $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_4]$ (2) and can be readily synthesised by reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with PPh_2H (1 : 2 mol ratio) in benzene in the presence of a base such as $NHEt_2$. Although solutions of $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_4]$ are dark brown it was observed that the dropwise addition of the solution of PPh_2H to the solution containing $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ and $NHEt_2$ produced a bright green reaction mixture and that the latter only reverted to a dark brown colour after a substantial period of time. The green product was isolated pure by filtration of the solution to remove the $[NH_2Et_2]Cl$, subsequent freeze-drying of the benzene filtrate to afford a green residue, and rapid crystallisation of the latter from hexane at 0 °C. The solid state and solution i.r. spectra were found to exhibit identical and characteristic band patterns in the carbonyl stretching region comprising five peaks {ν(C−O): 2 043s, 2 013s, 2 000m, 1 992w, and 1 978vs cm^{-1} (Nujol mull) [Figure 1(*a*)]; 2 044s, 2 013s, 2 000ms, 1 993w, and 1 977vs cm^{-1} (C_6H_{12})}, the frequencies of which were indicative of the compound containing terminal carbonyls only, in contrast to $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_4]$,[17] while the elemental analyses were consistent with the complex having a stoicheiometry of either $[Rh_3(PPh_2)_3(CO)_5]$ or $[Rh_3(PPh_2)_3(CO)_6]$.

An *X*-ray crystallographic analysis has confirmed that the compound is the pentacarbonyl derivative $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ and the molecular geometry of this species is illustrated in Figure 2. The complex contains a triangular skeleton of rhodium atoms with each edge being bridged by a diphenylphosphido-ligand such that the rhodium-phosphorus framework adopts a half-chair geometry (Figure 3); the two PPh_2 groups co-ordinated to the unique rhodium atom, Rh(2), are essentially coplanar with the metal-atom plane [deviations of the **P** atoms from the Rh_3 plane are 0.29 and −0.29 Å for P(1) and P(2) respectively] while the third, co-ordinated to Rh(1) and Rh(3), is almost orthogonal with it, the dihedral angle between the planes P(3)Rh(1)Rh(3) and Rh(1)Rh(3)-Rh(2) being 97.2°. The Rh-Rh distances [Rh(1)−Rh(2), 2.793(1); Rh(1)—Rh(3), 2.698(1); Rh(2)−Rh(3), 2.806(1) Å] correspond with those normally associated with formal Rh−Rh bonds which is indicative of the Rh−P−Rh bridge bonding being of the *closed* type.* While two of the rhodium atoms each have two CO ligands terminally co-ordinated to them, the third, Rh(2), has a single terminal carbonyl group. The carbonyls on Rh(1) and Rh(3) are slightly staggered with respect to each other as revealed by the C(2)−Rh(1)−Rh(3)−C(5) torsion angle of −16.8° (see Figure 3). The Rh(2) adopts an essentially planar configuration which can be attributed to it being a ' 16-electron system '. A similar explanation will account for the Rh(2)−P(2) and Rh(2)−P(1) distances being shorter than those for Rh(3)−P(2) and Rh(1)−P(1). Interestingly a planar geometry is also observed for the unique rhodium atom in $[Rh_3Fe(\mu\text{-}PPh_2)_3(\mu\text{-}CO)_2(CO)_6]$.[13] The co-ordination unsaturation of Rh(2) can be attributed to the presence of a

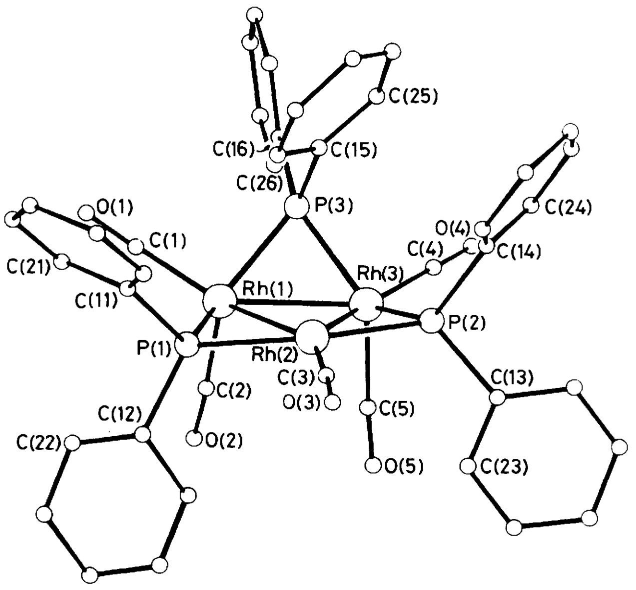

Figure 2. The molecular stereochemistry of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$

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* A *closed* M−P−M bridge bond is defined as the bond between two metal atoms, M, which are linked through a bridging phosphorus atom and in which the M−M distance corresponds with the range of distances found for formal M−M bonds. 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 M−M distance is appreciably larger than the range of distances observed for M−M bonds.

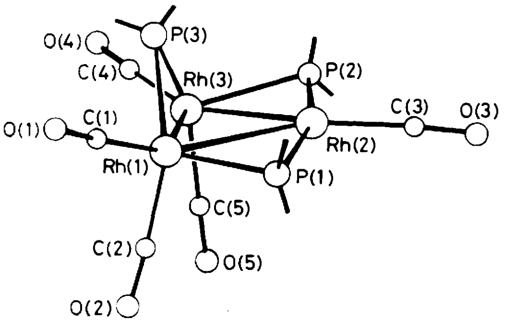
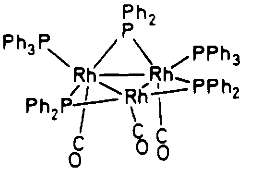


Figure 3. An alternative view of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ (phenyl groups omitted)



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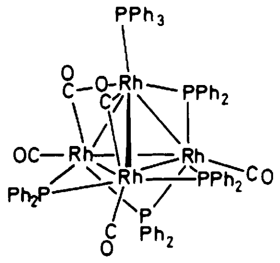


(4)

phenyl group on P(3) blocking a co-ordination site (Figure 2).

The thermal decomposition of $[RhH(CO)(PPh_3)_3]$ in nonane at 120 °C has recently been reported to yield trinuclear $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$ (3) in the absence of carbon monoxide[22] but tetranuclear $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_3(PPh_3)]$ (4) in the presence of a 1 : 1 mixture of CO and H_2 at 4 atm (*ca.* 40.5×10^4 Pa) pressure.[23] Not surprisingly the structures of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ and its PPh_3 substituted derivative $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$ are very similar with the average Rh–Rh distance in the former being slightly less than that in the latter. This indicates that the formation of trinuclear $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$ in preference to dinuclear *trans*-$[\{Rh(\mu\text{-}PPh_2)(CO)(PPh_3)\}_2]$ in the pyrolysis of $[RhH(CO)(PPh_3)_3]$ in the absence of CO cannot necessarily be attributed to steric interactions between the phenyl groups of the PPh_2 ligands and those of PPh_3 as initially proposed.[23]

Solutions of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ in benzene or toluene gradually turn brown over a period of time (at least 24 h) resulting from the conversion of this compound to the product referred to above and previously characterised as $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_4]$.[17] This condensation, which is far more rapid in polar solvents such as CH_2Cl_2, is irreversible and no evidence could be obtained for the formation of $[Rh_3(\mu\text{-}PPh)_3(CO)_5]$ by carbonylation of the tetranuclear compound.

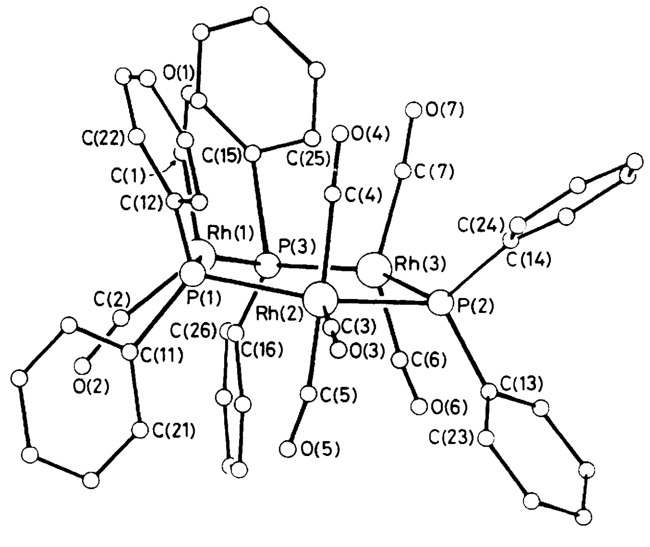
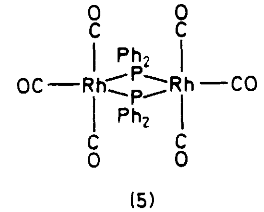


Figure 4. The molecular geometry of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$

Passage of carbon monoxide through a solution of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ results in a rapid colour change from green to yellow; this process is reversible and the colour of the solution reverts immediately to green on cessation of the carbon monoxide flow. The yellow product was isolated as a crystalline compound by evaporation of the dichloromethane from a solution of the compound in CH_2Cl_2–hexane under a stream of carbon monoxide. Elemental analyses were consistent with the formula $[\{Rh(PPh_2)(CO)_x\}_n]$ (x = 2 or 3; n = 2 or 3). The compound was found to be stable only in the presence of carbon monoxide, even in the solid state, and the yellow crystals rapidly transformed to green $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ under any other atmosphere. A molecular mass measurement to establish the value of n was thus not possible. Conversion of $[\{Rh(\mu\text{-}PPh_2)(CO)_x\}_n]$ to $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ in the solid state was found to be accompanied by a decrease in mass of 9.1% due to the loss of carbon monoxide. This corresponds to 1.2 carbonyl groups per rhodium atom, which is consistent with the yellow compound having the formulation $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$ and the conversion corresponding to equation (i). The solid-state i.r. spectrum of the compound exhibits

$$3[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n] \underset{+CO}{\overset{-CO}{\rightleftharpoons}} n[Rh_3(\mu\text{-}PPh_2)_3(CO)_5] \quad (i)$$

peaks in the C–O stretching region corresponding to terminal carbonyls only {ν(C–O): 2 075m, 2 042ms, 2 000s, 1 968s, and 1 958 (sh) cm^{-1} (Nujol mull) [Figure 1(*b*)]} while the yellow colour is indicative of the absence of direct metal–metal interactions. On this basis with n being either 2 or 3, the two most likely structures for the compound are those illustrated, (5) and (6). Although it is impossible to determine unequivocally whether the complex is di- or tri-nuclear, a number of factors point to it being the latter. In particular, as described below, $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ reacts readily and reversibly with carbon monoxide and PPh_2H to afford a trinuclear compound characterised by *X*-ray crystallography as $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ while, as also discussed below, recrystallisation of $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$ from methanol at −15 °C similarly leads to the separation of a trinuclear derivative, *viz.* $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$, which can be readily reconverted to $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$ by treatment with CO. Also, as reported above, the condensation of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ to the tetranuclear compound, $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_4]$ is a slow and irreversible process, as might be expected for one involving fragmentation of the Rh_3P_3 framework, whereas the conversion of $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$ to $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ is rapid, even in the solid state, which is more compatible with simple loss of carbon monoxide. Finally the dinuclear thiol complexes of the type $[\{Rh(\mu\text{-}SR)(CO)_2\}_2]$ (R = alkyl or aryl group) cannot be



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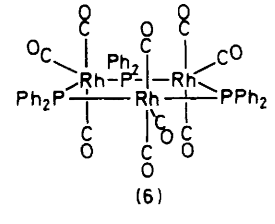

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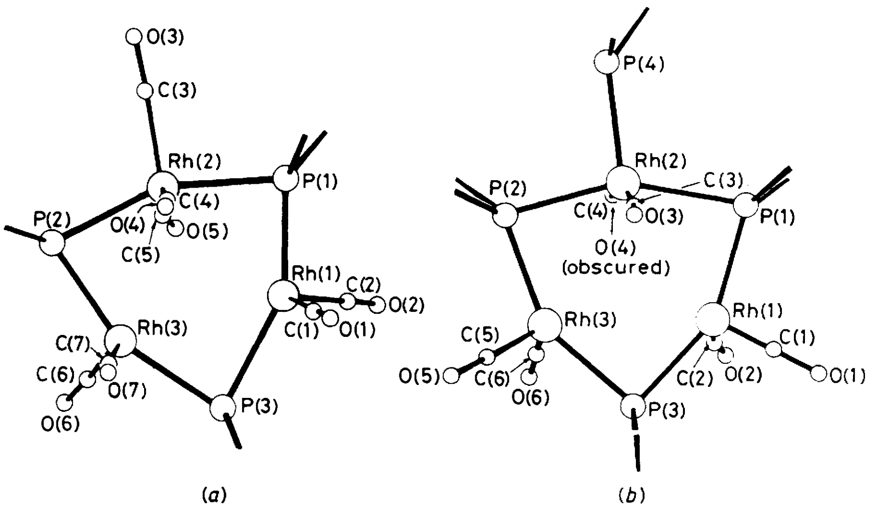


Figure 5. Plan view of (*a*) [$Rh_3(\mu\text{-}PPh_2)_3(CO)_7$] and (*b*) [$Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)$]

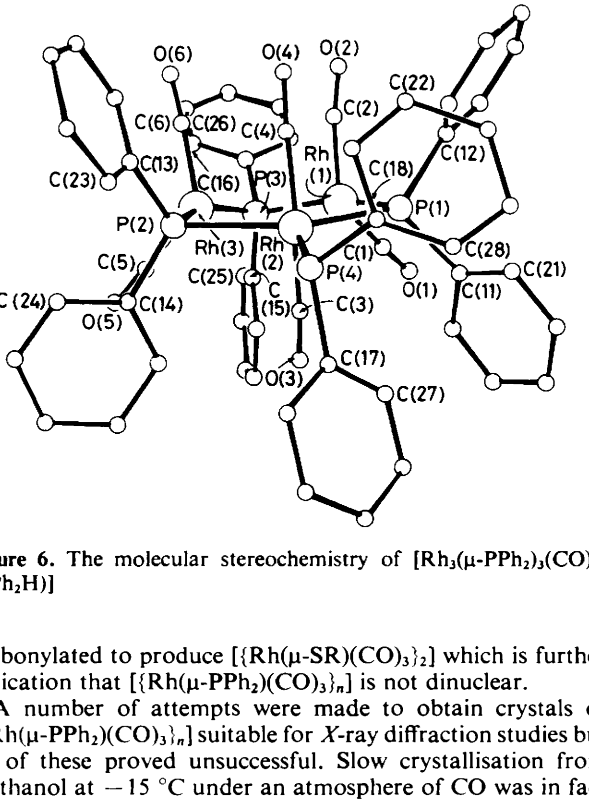


Figure 6. The molecular stereochemistry of [$Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)$]

carbonylated to produce [{$Rh(\mu\text{-}SR)(CO)_3$}$_2$] which is further indication that [{$Rh(\mu\text{-}PPh_2)(CO)_3$}$_n$] is not dinuclear.

A number of attempts were made to obtain crystals of [{$Rh(\mu\text{-}PPh_2)(CO)_3$}$_n$] suitable for *X*-ray diffraction studies but all of these proved unsuccessful. Slow crystallisation from methanol at −15 °C under an atmosphere of CO was in fact found to lead to the separation of well formed orange-red crystals, together with trace amounts of yellow needles of [{$Rh(\mu\text{-}PPh_2)(CO)_3$}$_n$], but these afforded a band pattern in the C–O stretching region of their solid-state i.r. spectrum different from that of [{$Rh(\mu\text{-}PPh_2)(CO)_3$}$_n$] {ν(C–O): 2 086m, 2 057ms, 2 012 (sh), 1 992s, 1 969m, and 1 953s cm^{-1} (Nujol mull) [Figure 1(*c*)]}. An *X*-ray crystallographic analysis established this compound to be a decarbonylation product of [{$Rh(\mu\text{-}PPh_2)(CO)_3$}$_n$] and to have the stoicheiometry [$Rh_3(\mu\text{-}PPh_2)_3(CO)_7$] (see later). This heptacarbonyl is unstable under any atmosphere but CO and readily degrades to the green pentacarbonyl derivative [$Rh_3(\mu\text{-}PPh_2)_3(CO)_5$]. It is also readily reconverted to [{$Rh(\mu\text{-}PPh_2)(CO)_3$}$_n$] by treatment with carbon monoxide.

[$Rh_3(\mu\text{-}PPh_2)_3(CO)_5$] was found to be susceptible also to nucleophilic attack by PPh_3 and PPh_2H in ethanol in the presence of CO to afford a product which in the case of the PPh_2H reaction was obtained far more readily by an alternative route involving the reaction of [{$Rh(\mu\text{-}Cl)(CO)_2$}$_2$] with a slight excess of PPh_2H in ethanol, under CO. The latter which readily separates from ethanolic solutions as orange-red crystals and is only stable, both in solution and the solid state under an atmosphere of CO, affords a solid-state i.r. spectrum containing peaks in the C–O stretching region corresponding to terminal carbonyls only {ν(C–O): 2 047m, 1 996s, 1 982s, 1 948s, and 1 938s cm^{-1} (Nujol mull) [Figure 1(*d*)]} and a ^{1}H n.m.r. spectrum exhibiting resonances readily assigned to phenyl hydrogens and a hydrogen directly bonded to a phosphorus atom. The elemental analysis for the compound indicated it to be a substituted derivative of [$Rh_3(\mu\text{-}PPh_2)_3(CO)_7$] and to have the stoicheiometry [$Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)$] which was confirmed by an *X*-ray crystallographic analysis of its dichloromethane solvate.

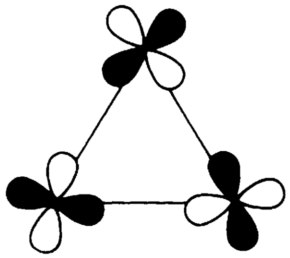
The molecular geometries of [$Rh_3(\mu\text{-}PPh_2)_3(CO)_7$] and [$Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)$] are very similar and are illustrated in Figures 4 and 5(*a*) and 5(*b*) and 6 respectively. For both compounds the three rhodium atoms are linked to each other through bridging PPh_2 ligands and, together with the three phosphorus atoms, occupy alternate vertices of near-planar six-membered rings (deviations from the least-squares planes range from 0.00(5) [P(2)] to 0.14(5) Å [Rh(3)] for [$Rh_3(\mu\text{-}PPh_2)_3(CO)_7$] and from 0.00(5) [P(1)] to 0.16(5) Å [P(2)] for [$Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)$]. While two of the rhodium atoms have two terminal carbonyl groups co-ordinated to them and adopt geometries intermediate between square planar and tetrahedral, the third has three terminal carbonyls bonded to it in the case of [$Rh_3(\mu\text{-}PPh_2)_3(CO)_7$] and a diphenylphosphine, as well as two carbonyl ligands, in the case of [$Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)$] and adopts a distorted trigonal-bipyramidal geometry in both complexes. In spite of a different co-ordination number for one of the rhodium atoms, the Rh_3P_3 rings in both species exhibit approximate three-fold symmetry {see Figures 4(*a*) and (*b*); the internal angles at the P atoms are 83(1), 85(1), and 85(1)° for [$Rh_3(\mu\text{-}PPh_2)_3(CO)_7$] and 83.3(1), 83.9(1), and 89.9(1)° for [$Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)$] while those at the rhodium atoms are 152(1), 155(1), and 155(1)° for the former compound and 150.8(1), 152.5(1), and 155.2(1)° for the latter}. The Rh–Rh distances are considerably longer than those normally associated with formal Rh–Rh bonds {[$Rh_3(\mu\text{-}PPh_2)_3(CO)_7$]: Rh(1)–

Table 1. Crystallographic and refinement data

Compound	$[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$	$[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$	$[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$
(*a*) Crystal data			
M	1 004.35	1 060.37	1 303.49
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	14.003(5)	18.16(1)	12.515(5)
b/Å	17.471(5)	17.935(10)	11.843(5)
c/Å	16.523(5)	13.119(10)	37.102(5)
β/°	103.76(5)	103.5(1)	94.6(1)
U/Å^3	3 926.3	4 154.8	5 481.4
Z	4	4	4
D_c/g cm^{-3}	1.70	1.695	1.58
$F(000)$	1 984	2 096	2 600
μ/mm^{-1}	1.36	1.22	9.68
(*b*) Data collection			
Radiation	Mo-K_α	Mo-K_α	Cu-K_α
λ/Å	0.7107	0.7107	1.5418
Crystal size/mm	0.32 × 0.2 × 0.12	0.08 × 0.08 × 0.07	0.1 × 0.07 × 0.07
Scan speed/° s^{-1}	0.03	0.03	0.04
Scan width/°	1.0	1.3	1.3
2θ max./°	46	36	120
N (reflections)	5 712	2 662	8 930
N (independent reflections)	5 346	1 023	5 587
Criterion	$I > \sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$
(*c*) Refinement			
R	0.067	0.134	0.111
R'	0.044	0.134	0.123
k	0.461		1.0
g	0		0.046
U_H/Å^2	0.11(1)		0.14(2)

Rh(2) = 3.124(11), Rh(1)–Rh(3) = 3.223(12), and Rh(2)–Rh(3) = 3.084(11) Å; $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$: Rh(1)–Rh(2) = 3.118(2), Rh(1)–Rh(3) = 3.246(2), and Rh(2)–Rh(3) = 3.130(2) Å} and are consistent with the Rh–P–Rh bridge bonding being more of the *open* type. A range of compounds of the type $[M_3(\mu\text{-}Y)_3L_n]$ (M = metal, Y = edge-bridging ligand such as PPh_2, L = neutral ligand such as CO or PPh_3; n = 3, 4, 6, or 9, *etc.*) with a planar M_3Y_3 skeleton is known but the metal–metal distances in these complexes, in contrast to those in $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ and $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ are short and correspond to *closed* M–Y–M bridge bonding.[1,24–33]

Similar to its parent heptacarbonyl, $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ is unstable under any atmosphere but CO and is readily decarbonylated, with loss of PPh_2H, to produce $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$. This process is a reversible one and an obvious intermediate in the formation of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ from the pentacarbonyl derivative, as well as in the formation of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ from the latter, is $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6]$. Although it has not been possible to isolate and structurally characterise this hexacarbonyl it is assumed that it will contain a Rh_3P_3 framework structurally analogous to that in $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, with Rh–Rh distances of the order of 2.75—2.80 Å on the basis that the Co_3P_3 skeleton in a corresponding tricobalt cluster, $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$, adopts a similar conformation and that the Co–Co distances in this complex are short, ranging from 2.514 to 2.673 Å and corresponding in a formal sense to Co–Co bonds.[34] Addition of two electrons to $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6]$, by co-ordination of a donor ligand, has thus resulted in a symmetric expansion of the Rh_3P_3 ring, together with an accompanying rearrangement to a planar configuration, through the apparent population of a molecular orbital which is antibonding with respect to the three rhodium atoms. The geometries of Rh(1)—Rh(3) for both $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ and $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ can be described as distorted pseudo-trigonal bipyramidal, distorted pseudo-octahedral, and distorted pseudo-trigonal bipyramidal respectively with appropriate metal hybrid orbitals being directed towards the centre of the trirhodium triangle. Overlap of these orbitals cannot give rise to a molecular orbital (m.o.) which is antibonding with respect to all three rhodium atoms, however, and the m.o. associated with the symmetric opening of the Rh_3P_3 ring probably results from interaction of metal *d* orbitals lying in the plane of the ring as illustrated below. Rives *et al.*[35] have considered a similar interaction in their m.o. description of compounds of the type $[M_3(\mu_3\text{-}Y)_2L_3]$ (M = Fe, Co, or Ni; Y = S or CO; L = $\eta^5\text{-}C_5H_5$ or 3CO].



Although the Rh–Rh distances in these compounds are appreciably longer than those associated with formal Rh–Rh bonds, they are still markedly shorter than those expected for a complete non-bonding metal–metal interaction. For instance the Fe–Fe distance in $[\{Fe(\mu\text{-}PPh_2)(CO)_3\}_2]^{2-}$ is 3.630(3)

Table 2. Fractional atomic co-ordinates of the non-hydrogen atoms (× 10^4) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
(*a*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$							
Rh(1)	1 255(0)	1 009(0)	9 244(0)	C(52)	2 844(9)	3 260(7)	11 306(7)
Rh(2)	2 493(0)	1 930(0)	8 559(0)	C(62)	2 535(7)	2 828(5)	10 565(6)
Rh(3)	2 799(0)	351(0)	8 801(0)	C(13)	4 892(5)	1 301(4)	8 509(4)
C(1)	−48(6)	779(4)	9 249(5)	C(23)	5 203(5)	1 730(4)	9 219(4)
O(1)	−843(4)	626(4)	9 226(4)	C(33)	6 205(5)	1 797(4)	9 609(5)
C(2)	1 902(5)	897(4)	10 384(5)	C(43)	6 882(6)	1 437(4)	9 257(5)
O(2)	2 207(5)	811(4)	11 078(4)	C(53)	6 594(6)	1 024(5)	8 568(5)
C(3)	2 909(5)	2 866(4)	8 334(5)	C(63)	5 587(5)	945(4)	8 161(5)
O(3)	3 201(5)	3 466(3)	8 239(4)	C(14)	3 481(5)	1 021(4)	6 996(4)
C(4)	3 181(5)	−631(5)	8 552(5)	C(24)	3 608(5)	297(4)	6 691(5)
O(4)	3 426(5)	−1 224(3)	8 407(4)	C(34)	3 538(6)	198(5)	5 838(5)
C(5)	3 714(5)	480(4)	9 870(5)	C(44)	3 348(6)	800(5)	5 315(5)
O(5)	4 271(4)	562(3)	10 477(3)	C(54)	3 214(6)	1 517(5)	5 611(5)
P(1)	1 273(1)	2 316(1)	9 157(1)	C(64)	3 295(5)	1 638(4)	6 456(4)
P(2)	3 574(1)	1 187(1)	8 095(1)	C(15)	928(4)	795(4)	6 990(4)
P(3)	1 216(1)	379(1)	8 020(1)	C(25)	1 079(5)	378(4)	6 314(4)
C(11)	145(5)	2 782(4)	8 595(4)	C(35)	851(5)	697(4)	5 522(5)
C(21)	−744(5)	2 593(4)	8 769(5)	C(45)	474(5)	1 419(5)	5 416(5)
C(31)	−1 602(6)	2 965(5)	8 350(5)	C(55)	334(5)	1 848(5)	6 070(5)
C(41)	−1 555(6)	3 527(5)	7 785(5)	C(65)	565(5)	1 545(4)	6 879(4)
C(51)	−689(6)	3 688(5)	7 577(5)	C(16)	494(5)	−509(4)	7 873(4)
C(61)	180(6)	3 322(4)	7 998(5)	C(26)	674(6)	−1 033(4)	8 515(5)
C(12)	1 586(5)	2 901(4)	10 085(4)	C(36)	116(6)	−1 712(5)	8 454(5)
C(22)	937(6)	3 385(5)	10 342(5)	C(46)	−565(6)	−1 851(5)	7 746(5)
C(32)	1 250(7)	3 842(5)	11 038(6)	C(56)	−778(7)	−1 339(5)	7 114(6)
C(42)	2 189(8)	3 789(6)	11 491(7)	C(66)	−259(5)	−645(5)	7 181(5)
(*b*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$							
Rh(1)	6 665(5)	4 990(6)	5 886(7)	C(32)	4 870(55)	3 115(33)	7 231(99)
Rh(2)	7 834(4)	4 169(4)	7 654(5)	C(42)	5 071(55)	2 724(33)	8 175(99)
Rh(3)	8 256(5)	4 384(5)	5 529(6)	C(52)	5 731(55)	2 911(33)	8 913(99)
P(1)	6 588(16)	4 625(15)	7 502(22)	C(62)	6 190(55)	3 490(33)	8 709(99)
P(2)	8 905(12)	3 810(11)	7 035(17)	C(13)	9 808(18)	4 181(26)	7 697(41)
P(3)	7 370(20)	5 187(19)	4 542(28)	C(23)	9 967(18)	4 263(26)	8 784(41)
C(1)	6 018(118)	4 283(62)	5 085(91)	C(33)	10 697(18)	4 451(26)	9 335(41)
O(1)	5 644(69)	3 749(45)	4 985(92)	C(43)	11 269(18)	4 556(26)	8 799(41)
C(2)	6 368(50)	5 967(15)	6 023(83)	C(53)	11 110(18)	4 474(26)	7 712(41)
O(2)	6 324(42)	6 580(13)	6 080(64)	C(63)	10 380(18)	4 286(26)	7 161(41)
C(3)	8 007(35)	3 914(33)	9 058(18)	C(14)	9 107(31)	2 825(15)	7 055(54)
O(3)	8 126(35)	3 756(33)	9 892(18)	C(24)	9 486(31)	2 573(15)	6 310(54)
C(4)	7 365(78)	3 348(42)	6 914(81)	C(34)	9 773(31)	1 849(15)	6 371(54)
O(4)	7 082(42)	2 817(25)	6 626(56)	C(44)	9 683(31)	1 377(15)	7 178(54)
C(5)	8 284(38)	5 104(18)	7 733(59)	C(54)	9 305(31)	1 629(15)	7 924(54)
O(5)	8 439(26)	5 702(13)	7 759(38)	C(64)	9 017(31)	2 353(15)	7 862(54)
C(6)	8 990(42)	5 099(43)	5 485(73)	C(15)	6 694(90)	4 714(51)	3 420(62)
O(6)	9 439(25)	5 487(27)	5 391(47)	C(25)	5 934(90)	4 505(51)	3 215(62)
C(7)	7 951(41)	3 510(25)	4 798(55)	C(35)	5 612(90)	4 108(51)	2 306(62)
O(7)	7 685(31)	3 001(20)	4 398(43)	C(45)	6 050(90)	3 920(51)	1 601(62)
C(11)	6 370(95)	5 460(38)	8 227(77)	C(55)	6 811(90)	4 129(51)	1 806(62)
C(21)	5 699(95)	5 807(38)	8 311(77)	C(65)	7 132(90)	4 526(51)	2 715(62)
C(31)	5 705(95)	6 316(38)	9 116(77)	C(16)	7 587(52)	6 133(27)	4 256(122)
C(41)	6 381(95)	6 477(38)	9 839(77)	C(26)	7 496(52)	6 449(27)	3 262(122)
C(51)	7 051(95)	6 130(38)	9 756(77)	C(36)	7 817(52)	7 141(27)	3 149(122)
C(61)	7 046(95)	5 621(38)	8 950(77)	C(46)	8 229(52)	7 518(27)	4 029(122)
C(12)	5 989(55)	3 880(33)	7 765(99)	C(56)	8 320(52)	7 203(27)	5 022(122)
C(22)	5 329(55)	3 693(33)	7 027(99)	C(66)	7 999(52)	6 510(27)	5 136(122)
(*c*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$							
Rh(1)	2 634(1)	−1 365(1)	3 637(0)	C(33)	2 452(8)	5 321(9)	3 171(2)
Rh(2)	3 452(1)	1 118(1)	3 706(0)	C(43)	1 863(8)	5 164(9)	2 840(2)
Rh(3)	972(1)	728(1)	3 674(0)	C(53)	1 309(8)	4 156(9)	2 768(2)
P(1)	4 329(3)	−653(3)	3 619(1)	C(63)	1 344(8)	3 305(9)	3 029(2)
P(2)	1 948(3)	2 364(3)	3 712(1)	C(13)	1 933(8)	3 462(9)	3 361(2)
P(3)	845(3)	−1 207(4)	3 747(1)	C(24)	915(8)	3 936(11)	4 112(3)
P(4)	4 800(3)	2 479(4)	3 834(1)	C(34)	782(8)	4 635(11)	4 407(3)
C(1)	2 858(14)	−2 538(14)	3 954(5)	C(44)	1 545(8)	4 633(11)	4 703(3)
O(1)	2 997(12)	−3 349(13)	4 116(4)	C(54)	2 440(8)	3 931(11)	4 703(3)
C(2)	2 303(12)	−1 489(12)	3 138(5)	C(64)	2 573(8)	3 231(11)	4 408(3)

Table 2 (*continued*)

(*c*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$ (*continued*)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
O(2)	2 166(12)	−1 689(12)	2 835(4)
C(3)	3 324(12)	683(13)	4 182(4)
O(3)	3 279(9)	478(10)	4 490(4)
C(4)	3 265(12)	1 255(12)	3 207(4)
O(4)	3 138(11)	1 288(11)	2 893(4)
C(5)	216(13)	1 031(14)	4 061(4)
O(5)	−381(13)	1 254(13)	4 279(4)
C(6)	519(13)	667(14)	3 192(5)
O(6)	77(14)	605(15)	2 911(5)
C(100)	3 083(36)	1 153(35)	1 161(12)
Cl(1)	4 467(14)	891(14)	1 275(4)
Cl(2)	2 345(14)	138(14)	974(5)
C(21)	6 492(8)	−738(10)	3 904(2)
C(31)	7 297(8)	−858(10)	4 184(2)
C(41)	7 040(8)	−1 220(10)	4 524(2)
C(51)	5 978(8)	−1 461(10)	4 585(2)
C(61)	5 173(8)	−1 340(10)	4 305(2)
C(11)	5 430(8)	−979(10)	3 964(2)
C(22)	5 462(8)	83(6)	3 034(3)
C(32)	5 936(8)	−81(6)	2 711(3)
C(42)	5 916(8)	−1 147(6)	2 550(3)
C(52)	5 421(8)	−2 047(6)	2 713(3)
C(62)	4 947(8)	−1 882(6)	3 037(3)
C(12)	4 967(8)	−817(6)	3 197(3)
C(23)	2 487(8)	4 469(9)	3 432(2)
C(14)	1 811(8)	3 234(11)	4 112(3)
C(25)	−310(8)	−2 446(9)	4 237(3)
C(35)	−551(8)	−2 772(9)	4 583(3)
C(45)	17(8)	−2 310(9)	4 887(3)
C(55)	826(8)	−1 522(9)	4 845(3)
C(65)	1 067(8)	−1 195(9)	4 499(3)
C(15)	499(8)	−1 657(9)	4 196(3)
C(26)	−1 133(9)	−1 476(8)	3 346(4)
C(36)	−1 900(9)	−2 078(8)	3 130(4)
C(46)	−1 666(9)	−3 160(8)	3 011(4)
C(56)	−666(9)	−3 641(8)	3 107(4)
C(66)	100(9)	−3 039(8)	3 323(4)
C(16)	−133(9)	−1 956(8)	3 442(4)
C(27)	5 821(11)	1 654(9)	4 479(4)
C(37)	6 324(11)	1 765(9)	4 826(4)
C(47)	6 374(11)	2 818(9)	4 995(4)
C(57)	5 921(11)	3 760(9)	4 816(4)
C(67)	5 417(11)	3 649(9)	4 469(4)
C(17)	5 367(11)	2 596(9)	4 300(4)
C(28)	6 935(9)	2 150(10)	3 681(3)
C(38)	7 778(9)	2 208(10)	3 457(3)
C(48)	7 624(9)	2 724(10)	3 119(3)
C(58)	6 627(9)	3 183(10)	3 005(3)
C(68)	5 784(9)	3 125(10)	3 229(3)
C(18)	5 938(9)	2 609(10)	3 567(3)

Å[36] while one of the Pt–Pt distances in $[Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$ is also 3.630(1) Å.[27] More significantly the average Fe–Fe distance in the planar six-membered ring complex $[Fe_3(\mu\text{-}SPh)_3Cl_6]^{3-}$ is *ca.* 4.40 Å.[37] In fact the average distance of 3.165 Å is very similar to the Rh–Rh distance in $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ (3.12 Å)[38] which has been reconciled in terms of the population of bridge-bonding orbitals which overall are bonding with respect to the rhodium atoms.[39] The Rh–P–Rh bond angles are also considerably less than the tetrahedral angle of 109° 28′, the geometry that might be expected for localised Rh–P bonding. The structural data for $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ are thus not inconsistent with a net bonding interaction, albeit probably weak, between the rhodium atoms in the compound. Interestingly, Summerville and Hoffmann[40] have proposed that the rhodium atoms in compounds of the type $[\{Rh(\mu\text{-}Y)(CO)_2\}_2]$ will preferentially adopt a square-planar geometry if the bridging groups are π donors and a tetrahedral geometry if they are not. The tendency for the rhodium atom in the $Rh(PPh_2)(CO)_2$ monomer to adopt the latter rather than the former geometry is presumably the reason for it giving rise to a number of oligomeric products in contrast to $Rh(SR)(CO)_2$ (R = alkyl or aryl group) which affords a dinuclear compound, $[\{Rh(\mu\text{-}SR)(CO)_2\}_2]$, only.*

The ready and reversible carbonylation of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ to $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$, the separation of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ together with $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$ on slow recrystallisation of the latter from methanol under CO, the separation of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ from alcoholic solutions of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ and PPh_2H under an atmosphere of CO and the ready decarbonylation of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$, with loss of PPh_2H to afford $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, can be readily reconciled in terms of the set of equilibria summarised in the Scheme.

$[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ was also found to be susceptible to electrophilic attack by halogens and with chlorine affords the 50-electron system $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$, also synthesised by reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with PPh_2H in benzene.[16]

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[43] 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 FT80A instrument in deuteriated solvents. Elemental analyses were obtained by Mr. M. Martin-Short, Microanalytical Laboratory, University of Natal, Pietermaritzburg, by the Analytical Laboratories of H. Malissa and G. Reuter, Engelskirchen, West Germany and by Elemental Microanalysis Ltd., Beaworthy, Devon.

Synthesis of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$.—A solution of PPh_2H (0.29 g, 1.5 mmol) in benzene (*ca.* 15 cm^3) was added dropwise to a stirred solution of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ (0.30 g, 0.75 mmol) and $NHEt_2$ (0.11 g, 1.5 mmol) in benzene (*ca.* 40 cm^3).

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* At the time of the submission of this paper two publications appeared in print describing the synthesis and structural characterisation of two isomers of $[\{Rh(\mu\text{-}PBu^t_2)(CO)_2\}_2]$ and of the trinuclear species $[Rh_3(\mu\text{-}PBu^t_2)_3(CO)_3]$ respectively.[41,42] Significantly neither of the two isomers of the dinuclear compound adopts a geometry in which both rhodium atoms are tetrahedral. In one isomer both rhodium atoms are square planar while in the other isomer one rhodium is square planar and the other tetrahedral. These results are not necessarily at variance with the proposals of Summerville and Hoffmann[40] and the formation of isomers of $[\{Rh(\mu\text{-}PBu^t_2)(CO)_2\}_2]$ containing at least one square-planar rhodium atom rather than an isomer in which both rhodiums are tetrahedral could well be related to the steric bulk of the t-butyl group. Steric factors could also account for the formation of $[Rh_3(\mu\text{-}PBu^t_2)_3(CO)_3]$ rather than $[Rh_3(\mu\text{-}PBu^t_2)_3(CO)_5]$ or $[Rh_3(\mu\text{-}PBu^t_2)_3(CO)_6]$ and for the formation of dinuclear as well as trinuclear products in the reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with $LiPBu^t_2$.

Table 3. Relevant bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) $[\mathrm{Rh_3(\mu\text{-}PPh_2)_3(CO)_5}]$

Rh(1) ··· Rh(2)	2.793(1)	Rh(3) ··· P(2)	2.295(2)	Rh(2) ··· C(3)	1.804(8)	P(1) ··· C(11)	1.822(6)
Rh(1) ··· Rh(3)	2.698(1)	Rh(3) ··· P(3)	2.285(2)	Rh(2) ··· P(1)	2.269(2)	P(1) ··· C(12)	1.808(7)
Rh(1) ··· C(1)	1.872(9)	C(1) ··· O(1)	1.137(10)	Rh(2) ··· P(2)	2.263(2)	P(2) ··· C(13)	1.820(6)
Rh(1) ··· C(2)	1.896(8)	C(2) ··· O(2)	1.135(10)	Rh(3) ··· C(4)	1.872(8)	P(2) ··· C(14)	1.812(7)
Rh(1) ··· P(1)	2.288(2)	C(3) ··· O(3)	1.150(10)	Rh(3) ··· C(5)	1.933(7)	P(3) ··· C(15)	1.807(7)
Rh(1) ··· P(3)	2.291(2)	C(4) ··· O(4)	1.135(10)			P(3) ··· C(16)	1.836(7)
Rh(2) ··· Rh(3)	2.806(1)	C(5) ··· O(5)	1.123(8)				

Rh(2)-Rh(1)-Rh(3)	61.4(0.0)	C(4)-Rh(3)-P(3)	100.6(0.2)	Rh(3)-Rh(2)-P(1)	109.6(0.1)	C(13)-P(2)-C(14)	102.7(0.3)
Rh(2)-Rh(1)-C(1)	145.6(0.2)	C(5)-Rh(3)-P(3)	149.0(0.3)	C(3)-Rh(2)-P(1)	97.7(0.3)	Rh(1)-P(3)-Rh(3)	72.3(0.1)
Rh(3)-Rh(1)-C(1)	139.0(0.2)	P(2)-Rh(3)-P(3)	102.2(0.1)	Rh(1)-Rh(2)-P(2)	109.6(0.1)	Rh(1)-P(3)-C(15)	126.2(0.2)
Rh(2)-Rh(1)-C(2)	105.4(0.2)	Rh(1)-C(1)-O(1)	177.5(0.7)	Rh(3)-Rh(2)-P(2)	52.5(0.1)	Rh(3)-P(3)-C(15)	120.7(0.2)
Rh(3)-Rh(1)-C(2)	90.1(0.3)	Rh(1)-C(2)-O(2)	173.6(0.7)	C(3)-Rh(2)-P(2)	100.1(0.3)	Rh(1)-P(3)-C(16)	114.8(0.2)
C(1)-Rh(1)-C(2)	102.1(0.3)	Rh(2)-C(3)-O(3)	176.0(0.7)	P(1)-Rh(2)-P(2)	162.1(0.1)	Rh(3)-P(3)-C(16)	119.1(0.2)
Rh(2)-Rh(1)-P(1)	51.9(0.1)	Rh(3)-C(4)-O(4)	179.0(0.6)	Rh(1)-Rh(3)-Rh(2)	61.0(0.0)	C(15)-P(3)-C(16)	102.9(0.3)
Rh(3)-Rh(1)-P(1)	112.8(0.1)	Rh(3)-C(5)-O(5)	177.6(0.7)	Rh(1)-Rh(3)-C(4)	137.6(0.3)	P(1)-C(11)-C(21)	120.1(0.5)
C(1)-Rh(1)-P(1)	103.9(0.2)	Rh(1)-P(1)-Rh(2)	75.6(0.1)	Rh(2)-Rh(3)-C(4)	155.8(0.3)	P(1)-C(11)-C(61)	119.9(0.6)
C(2)-Rh(1)-P(1)	98.9(0.2)	Rh(1)-P(1)-C(11)	117.2(0.2)	Rh(1)-Rh(3)-C(5)	95.9(0.2)	P(1)-C(12)-C(22)	124.2(0.5)
Rh(2)-Rh(1)-P(3)	78.9(0.1)	Rh(2)-P(1)-C(11)	124.2(0.3)	Rh(2)-Rh(3)-C(5)	93.5(0.2)	P(1)-C(12)-C(62)	116.2(0.6)
Rh(3)-Rh(1)-P(3)	53.8(0.0)	Rh(1)-P(1)-C(12)	121.0(0.2)	C(4)-Rh(3)-C(5)	98.4(0.3)	P(2)-C(13)-C(23)	118.0(0.5)
C(1)-Rh(1)-P(3)	94.7(0.2)	Rh(2)-P(1)-C(12)	118.7(0.3)	Rh(1)-Rh(3)-P(2)	111.9(0.1)	P(2)-C(13)-C(63)	122.8(0.5)
C(2)-Rh(1)-P(3)	137.1(0.2)	C(11)-P(1)-C(12)	100.7(0.3)	Rh(2)-Rh(3)-P(2)	51.5(0.0)	P(2)-C(14)-C(24)	121.6(0.5)
P(1)-Rh(1)-P(3)	115.0(0.1)	Rh(2)-P(2)-Rh(3)	76.0(0.1)	C(4)-Rh(3)-P(2)	106.0(0.3)	P(2)-C(14)-C(64)	118.6(0.5)
Rh(1)-Rh(2)-Rh(3)	57.6(0.0)	Rh(2)-P(2)-C(13)	120.6(0.2)	C(5)-Rh(3)-P(2)	95.7(0.2)	P(3)-C(15)-C(25)	120.2(0.5)
Rh(1)-Rh(2)-C(3)	150.2(0.3)	Rh(3)-P(2)-C(13)	116.0(0.2)	Rh(1)-Rh(3)-P(3)	54.0(0.0)	P(3)-C(15)-C(65)	119.5(0.5)
Rh(3)-Rh(2)-C(3)	151.0(0.3)	Rh(2)-P(2)-C(14)	122.5(0.2)	Rh(2)-Rh(3)-P(3)	78.7(0.0)	P(3)-C(16)-C(26)	117.7(0.5)
Rh(1)-Rh(2)-P(1)	52.5(0.0)	Rh(3)-P(2)-C(14)	118.6(0.2)			P(3)-C(16)-C(66)	122.9(0.5)

(*b*) $[\mathrm{Rh_3(\mu\text{-}PPh_2)_3(CO)_7}]$

Rh(1) ··· Rh(2)	3.124(11)	Rh(3) ··· C(6)	1.858(17)	Rh(2) ··· P(2)	2.365(23)	C(1) ··· O(1)	1.163(68)
Rh(1) ··· Rh(3)	3.223(12)	Rh(3) ··· C(7)	1.854(17)	Rh(2) ··· C(3)	1.851(16)	C(2) ··· O(2)	1.107(18)
Rh(1) ··· P(1)	2.254(30)	P(1) ··· C(11)	1.864(46)	Rh(2) ··· C(4)	1.857(18)	C(3) ··· O(3)	1.103(16)
Rh(1) ··· P(3)	2.434(37)	P(1) ··· C(12)	1.807(19)	Rh(2) ··· C(5)	1.858(17)	C(4) ··· O(4)	1.106(19)
Rh(1) ··· C(1)	1.875(22)	P(2) ··· C(13)	1.796(18)	Rh(3) ··· P(2)	2.294(22)	C(5) ··· O(5)	1.106(17)
Rh(1) ··· C(2)	1.854(18)	P(2) ··· C(14)	1.803(18)	Rh(3) ··· P(3)	2.318(35)	C(6) ··· O(6)	1.101(16)
Rh(2) ··· Rh(3)	3.084(11)	P(3) ··· C(15)	1.884(54)			C(7) ··· O(7)	1.105(17)
Rh(2) ··· P(1)	2.371(30)	P(3) ··· C(16)	1.801(20)				

Rh(2)-Rh(1)-Rh(3)	58.1(0.2)	P(2)-Rh(3)-C(6)	96.2(3.0)	Rh(3)-Rh(2)-C(3)	155.5(2.0)	Rh(1)-P(3)-C(16)	117.8(4.1)
Rh(2)-Rh(1)-P(1)	49.1(0.8)	P(3)-Rh(3)-C(6)	87.9(3.2)	P(1)-Rh(2)-C(3)	96.1(2.1)	Rh(3)-P(3)-C(16)	123.0(4.2)
Rh(3)-Rh(1)-P(1)	107.1(0.8)	Rh(1)-Rh(3)-C(7)	100.9(2.4)	P(2)-Rh(2)-C(3)	108.2(2.1)	C(15)-P(3)-C(16)	113.3(6.3)
Rh(2)-Rh(1)-P(3)	103.0(0.9)	Rh(2)-Rh(3)-C(7)	104.7(2.5)	Rh(1)-Rh(2)-C(4)	80.6(4.0)	Rh(1)-C(1)-O(1)	153.2(9.5)
Rh(3)-Rh(1)-P(3)	45.8(0.8)	P(2)-Rh(3)-C(7)	95.6(2.5)	Rh(3)-Rh(2)-C(4)	78.9(3.9)	Rh(1)-C(2)-O(2)	166.7(8.1)
P(1)-Rh(1)-P(3)	151.9(1.1)	P(3)-Rh(3)-C(7)	98.7(2.6)	P(1)-Rh(2)-C(4)	85.3(4.8)	Rh(2)-C(3)-O(3)	178.3(6.9)
Rh(2)-Rh(1)-C(1)	109.0(3.8)	C(6)-Rh(3)-C(7)	134.2(3.9)	P(2)-Rh(2)-C(4)	85.3(4.7)	Rh(2)-C(4)-O(4)	168.8(1.0)
Rh(3)-Rh(1)-C(1)	99.0(8.2)	Rh(1)-P(1)-Rh(2)	84.9(1.0)	C(3)-Rh(2)-C(4)	106.0(4.0)	Rh(2)-C(5)-O(5)	169.0(6.7)
P(1)-Rh(1)-C(1)	99.4(4.8)	Rh(1)-P(1)-C(11)	108.3(3.3)	Rh(1)-Rh(2)-C(5)	80.2(2.2)	Rh(3)-C(6)-O(6)	173.9(9.4)
P(3)-Rh(1)-C(1)	93.4(7.0)	Rh(2)-P(1)-C(11)	123.1(5.1)	Rh(3)-Rh(2)-C(5)	74.8(2.4)	Rh(3)-C(7)-O(7)	171.1(7.6)
Rh(2)-Rh(1)-C(2)	122.4(3.3)	Rh(1)-P(1)-C(12)	124.5(4.3)	P(1)-Rh(2)-C(5)	95.3(2.3)	P(1)-C(11)-C(21)	133.8(5.1)
Rh(3)-Rh(1)-C(2)	128.6(2.6)	Rh(2)-P(1)-C(12)	109.5(3.5)	P(2)-Rh(2)-C(5)	83.0(2.4)	P(1)-C(11)-C(61)	104.8(5.2)
P(1)-Rh(1)-C(2)	95.7(3.1)	C(11)-P(1)-C(12)	106.7(4.5)	C(3)-Rh(2)-C(5)	101.4(2.9)	P(1)-C(12)-C(22)	120.2(4.5)
P(3)-Rh(1)-C(2)	98.4(2.9)	Rh(2)-P(2)-Rh(3)	82.9(0.7)	C(4)-Rh(2)-C(5)	152.4(4.3)	P(1)-C(12)-C(62)	119.8(4.5)
C(1)-Rh(1)-C(2)	122.4(7.2)	Rh(2)-P(2)-C(13)	117.7(2.1)	Rh(1)-Rh(3)-Rh(2)	59.3(0.3)	P(2)-C(13)-C(23)	118.8(2.0)
Rh(1)-Rh(2)-Rh(3)	62.5(0.3)	Rh(3)-P(2)-C(13)	118.5(2.0)	Rh(1)-Rh(3)-P(2)	108.9(0.7)	P(2)-C(13)-C(63)	120.6(2.0)
Rh(1)-Rh(2)-P(1)	45.9(0.7)	Rh(2)-P(2)-C(14)	116.3(2.4)	Rh(2)-Rh(3)-P(2)	49.6(0.6)	P(2)-C(14)-C(24)	116.0(2.5)
Rh(3)-Rh(2)-P(1)	108.3(0.7)	Rh(3)-P(2)-C(14)	121.0(2.3)	Rh(1)-Rh(3)-P(3)	48.8(0.9)	P(2)-C(14)-C(64)	123.1(2.5)
Rh(1)-Rh(2)-P(2)	110.1(0.6)	C(13)-P(2)-C(14)	101.3(2.5)	Rh(2)-Rh(3)-P(3)	107.2(1.0)	P(3)-C(15)-C(25)	134.9(5.4)
Rh(3)-Rh(2)-P(2)	47.6(0.5)	Rh(1)-P(3)-Rh(3)	85.4(1.2)	P(2)-Rh(3)-P(3)	155.5(1.1)	P(3)-C(15)-C(65)	105.0(5.4)
P(1)-Rh(2)-P(2)	155.5(0.9)	Rh(1)-P(3)-C(15)	98.3(5.5)	Rh(1)-Rh(3)-C(6)	116.4(3.1)	P(3)-C(16)-C(26)	126.4(5.2)
Rh(1)-Rh(2)-C(3)	141.5(2.0)	Rh(3)-P(3)-C(15)	113.4(3.6)	Rh(2)-Rh(3)-C(6)	116.4(2.9)	P(3)-C(16)-C(66)	112.7(5.2)

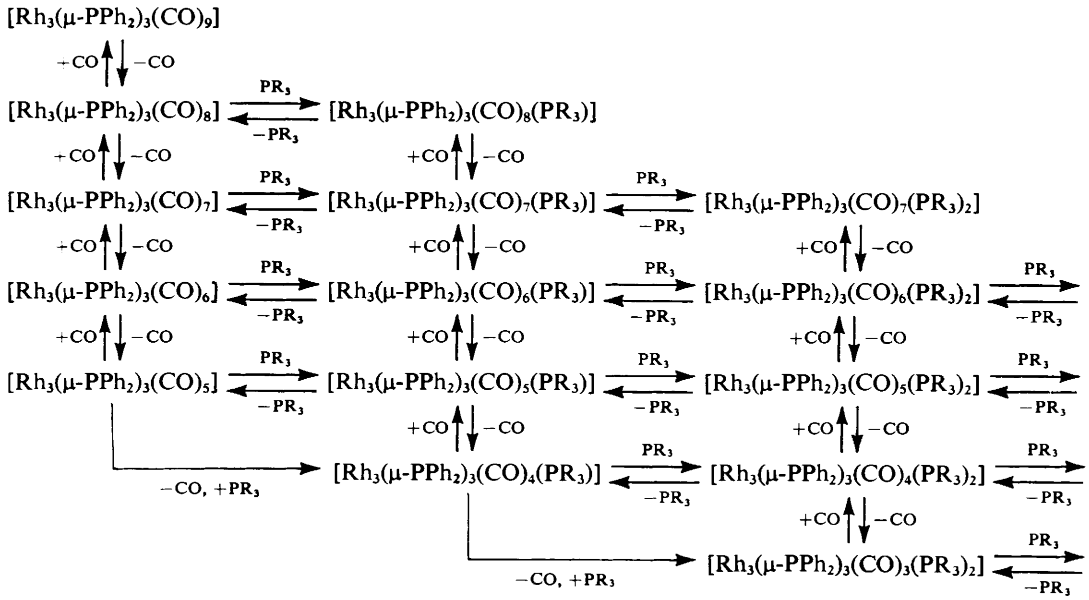
(*c*) $[\mathrm{Ru_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2}$

Rh(1) ··· Rh(2)	3.118(2)	P(1) ··· C(11)	1.847(10)	Rh(2) ··· P(2)	2.393(4)	C(1) ··· O(1)	1.139(23)
Rh(1) ··· Rh(3)	3.246(2)	P(1) ··· C(12)	1.822(11)	Rh(2) ··· P(4)	2.355(4)	C(2) ··· O(2)	1.147(23)
Rh(1) ··· P(1)	2.289(4)	P(2) ··· C(13)	1.840(10)	Rh(2) ··· C(3)	1.858(17)	C(3) ··· O(3)	1.174(21)
Rh(1) ··· P(3)	2.315(4)	P(2) ··· C(14)	1.827(12)	Rh(2) ··· C(4)	1.853(16)	C(4) ··· O(4)	1.165(22)
Rh(1) ··· C(1)	1.826(17)	P(3) ··· C(15)	1.831(11)	Rh(3) ··· P(2)	2.288(4)	C(5) ··· O(5)	1.172(24)
Rh(1) ··· C(2)	1.870(17)	P(3) ··· C(16)	1.829(12)	Rh(3) ··· P(3)	2.315(4)	C(6) ··· O(6)	1.143(25)
Rh(2) ··· Rh(3)	3.130(2)	P(4) ··· C(17)	1.821(14)	Rh(3) ··· C(5)	1.818(17)	C(100) ··· Cl(1)	1.777(48)
Rh(2) ··· P(1)	2.401(4)	P(4) ··· C(18)	1.806(13)	Rh(3) ··· C(6)	1.836(18)	C(100) ··· Cl(2)	1.637(46)

Table 3 (*continued*)

(*c*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$ (*continued*)

Rh(2)–Rh(1)–Rh(3)	58.9(0.0)	Rh(1)–Rh(3)–P(3)	45.5(0.1)	P(1)–Rh(2)–P(2)	155.2(0.1)	Rh(3)–P(2)–C(13)	125.5(0.4)
Rh(2)–Rh(1)–P(1)	49.9(0.1)	Rh(2)–Rh(3)–P(3)	102.7(0.1)	Rh(1)–Rh(2)–P(4)	152.6(0.1)	Rh(2)–P(2)–C(14)	118.7(0.4)
Rh(3)–Rh(1)–P(1)	108.5(0.1)	P(2)–Rh(3)–P(3)	150.8(0.1)	Rh(3)–Rh(2)–P(4)	143.2(0.1)	Rh(3)–P(2)–C(14)	116.3(0.4)
Rh(2)–Rh(1)–P(3)	103.0(0.1)	Rh(1)–Rh(3)–C(5)	124.1(0.5)	P(1)–Rh(2)–P(4)	107.3(0.1)	C(13)–P(2)–C(14)	100.4(0.5)
Rh(3)–Rh(1)–P(3)	45.5(0.1)	Rh(2)–Rh(3)–C(5)	121.3(0.5)	P(2)–Rh(2)–P(4)	97.3(0.1)	Rh(1)–P(3)–Rh(3)	89.0(0.1)
P(1)–Rh(1)–P(3)	152.5(0.1)	P(2)–Rh(3)–C(5)	95.4(0.5)	Rh(1)–Rh(2)–C(3)	76.3(0.5)	Rh(1)–P(3)–C(15)	116.1(0.4)
Rh(2)–Rh(1)–C(1)	129.2(0.5)	P(3)–Rh(3)–C(5)	93.3(0.5)	Rh(3)–Rh(2)–C(3)	80.4(0.5)	Rh(3)–P(3)–C(15)	114.7(0.4)
Rh(3)–Rh(1)–C(1)	128.3(0.6)	Rh(1)–Rh(3)–C(6)	94.4(0.5)	P(1)–Rh(2)–C(3)	87.8(0.5)	Rh(1)–P(3)–C(16)	117.4(0.4)
P(1)–Rh(1)–C(1)	101.8(0.6)	Rh(2)–Rh(3)–C(6)	105.7(0.5)	P(2)–Rh(2)–C(3)	92.0(0.5)	Rh(3)–P(3)–C(16)	117.2(0.4)
P(3)–Rh(1)–C(1)	92.8(0.6)	P(2)–Rh(3)–C(6)	102.4(0.5)	P(4)–Rh(2)–C(3)	96.5(0.5)	C(15)–P(3)–C(16)	103.0(0.5)
Rh(2)–Rh(1)–C(2)	101.5(0.4)	P(3)–Rh(3)–C(6)	93.2(0.5)	Rh(1)–Rh(2)–C(4)	89.2(0.4)	Rh(2)–P(4)–C(17)	117.5(0.4)
Rh(3)–Rh(1)–C(2)	90.6(0.5)	C(5)–Rh(3)–C(6)	129.7(0.7)	Rh(3)–Rh(2)–C(4)	86.0(0.5)	Rh(2)–P(4)–C(18)	122.1(0.4)
P(1)–Rh(1)–C(2)	97.5(0.5)	Rh(1)–P(1)–Rh(2)	83.3(0.1)	P(1)–Rh(2)–C(4)	87.9(0.5)	C(17)–P(4)–C(18)	104.5(0.6)
P(3)–Rh(1)–C(2)	92.4(0.5)	Rh(1)–P(1)–C(11)	123.0(0.4)	P(2)–Rh(2)–C(4)	85.4(0.5)	Rh(1)–C(1)–O(1)	172.0(1.6)
C(1)–Rh(1)–C(2)	126.0(0.7)	Rh(2)–P(1)–C(11)	114.4(0.4)	P(4)–Rh(2)–C(4)	100.0(0.5)	Rh(1)–C(2)–O(2)	171.6(1.4)
Rh(1)–Rh(2)–Rh(3)	62.6(0.0)	Rh(1)–P(1)–C(12)	117.2(0.3)	C(3)–Rh(2)–C(4)	163.5(0.7)	Rh(2)–C(3)–O(3)	175.2(1.3)
Rh(1)–Rh(2)–P(1)	46.8(0.1)	Rh(2)–P(1)–C(12)	116.5(0.3)	Rh(1)–Rh(3)–Rh(2)	58.5(0.0)	Rh(2)–C(4)–O(4)	176.9(1.3)
Rh(3)–Rh(2)–P(1)	109.2(0.1)	C(11)–P(1)–C(12)	102.7(0.5)	Rh(1)–Rh(3)–P(2)	108.0(0.1)	Rh(3)–C(5)–O(5)	171.3(1.5)
Rh(1)–Rh(2)–P(2)	109.2(0.1)	Rh(2)–P(2)–Rh(3)	83.9(0.1)	Rh(2)–Rh(3)–P(2)	49.5(0.1)	Rh(3)–C(6)–O(6)	169.0(1.7)
Rh(3)–Rh(2)–P(2)	46.6(0.1)	Rh(2)–P(2)–C(13)	113.1(0.4)			Cl(1)–C(100)–Cl(2)	118.6(2.6)



Scheme.

The colour of the solution changed rapidly from yellow to dark green and $[NH_2Et_2]Cl$ separated. After rapid filtration under a nitrogen atmosphere, the solvent was removed by freeze-drying to afford a green residue of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$. The compound was crystallised (rapidly) from hexane (yield: 0.3 g, 60%) (Found: C, 48.9; H, 3.0; P, 9.0. Calc. for $C_{41}H_{30}O_5P_3Rh_3$: C, 49.0; H, 3.0; P, 9.3%).

Synthesis of $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$ *from* $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$.—Carbon monoxide gas was passed through a solution of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ (0.50 g, 0.5 mmol) in hexane–dichloromethane (4 : 1) (*ca.* 20 cm^3). The solution rapidly turned yellow and, on evaporation of the CH_2Cl_2, yellow crystals of $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$ separated. The mother-liquor was decanted and the crystals washed repeatedly with very cold CO-saturated pentane, both operations being performed under CO. The crystals were dried under a stream of CO (yield: 0.4 g, 80%) (Found: C, 48.5; H, 2.8; P, 8.3. Calc. for $C_{15}H_{10}O_3PRh$: C, 48.4; H, 2.7; P, 8.3%).

Synthesis of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ *from* $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$.—$[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$ was dissolved in a minimum amount of CO-saturated methanol and the solution purged with CO and stored at −15 °C under an atmosphere of CO for several weeks. Orange-red crystals of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ separated together with trace quantities of yellow needles of $[\{Rh(\mu\text{-}PPh_2)(CO)_3\}_n]$. The mother-liquor was decanted and the crystals washed with very cold CO-saturated methanol and pentane and dried under a stream of CO. Separation of the orange-red crystals from the yellow needles was effected by mechanical means. The extreme instability of this compound, particularly in the absence of solvent, prevented its characterisation by elemental analysis.

Synthesis of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$.—A solution of PPh_2H (0.19 g, 1.0 mmol) in ethanol (*ca.* 5 cm^3) was added dropwise to a stirred solution of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ (0.2 g, 0.5 mmol) in ethanol (*ca.* 20 cm^3) and the reaction mixture allowed to stand at 0 °C. Orange microcrystals of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ which separated from the dark solution were isolated after 1 h under a stream of CO and washed repeatedly with CO-saturated pentane. The compound was dried under a stream of CO (yield: 0.26 g, 65%) (Found: C, 53.4; H, 3.5; P, 10.2; Rh, 26.0. Calc. for $C_{53}H_{41}O_5P_4Rh_3$: C, 53.4; H, 3.4; P, 10.4; Rh, 26.0%).

$[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$ was recrystallised as the dichloromethane solvate by slow passage of CO through a solution of the compound in CH_2Cl_2–ethanol (1 : 1).

X-*Ray Crystallography.*—*Crystal and intensity data.* Crystal data, data collection, and structure refinement details are summarised in Table 1. Crystals of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ and $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$ were handled at all times under an atmosphere of CO or in cold CO-saturated liquid paraffin and for the purposes of data collection were mounted enveloped in epoxy cement which itself had been prepared under a CO atmosphere. These precautions were not necessary in the case of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$. Preliminary photography established the space groups and gave the unit-cell parameters which were refined using 25 high-angle reflections measured on a Philips PW1100 diffractometer employing graphite-monochromated Mo-K_α radiation. Monitoring of reference reflections indicated crystal decomposition in the cases of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ and $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$; the fall-off in reference reflections intensity was enough in the case of the former to warrant applying a correction to the intensity data. Lorentz polarisation corrections were also applied but no allowance was made for absorption.

Structure determination and refinement. All calculations were carried out on a Burroughs B6800 computer at the University of South Africa using SHELX.[44] The structures were solved by conventional methods and refined with anisotropic Rh and P atoms and, for $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, carbonyl groups; all other atoms were isotropic. Phenyl rings were treated as rigid perfect hexagons (C–C, 1.395 Å): this constraint was removed during the last four cycles of least-squares refinement of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ but retained throughout the refinement of the other two structures. The high final value of R and somewhat poor definition of light-atom positions in $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ and to a lesser extent in $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$ may be ascribed to the indifferent quality of the available crystals of these compounds.

Convergence was considered complete when no shift to error ratio exceeded 1.0 e Å^{-3}; at this point difference maps of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$ and $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$ showed several peaks with heights between 1 and 2 e Å^{-3} associated with the heavy atoms; a final difference map of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ was essentially featureless. In the final stages of the analysis of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ and $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$ a weighting scheme $w = k/(\sigma^2F + gF^2)$[44] was employed: hydrogen atoms were included at calculated positions with a common thermal parameter. The diphenylphosphine hydrogen was not located. Fractional atomic co-ordinates are given in Table 2 while relevant bond lengths and angles are summarised in Table 3. Selected torsion angles and least-squares planes are presented in Table 4. Scattering factors were from ref. 45.

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Table 4. Selected torsion angles (°) and least-squares planes [distances of atoms (Å) from the planes are given in square brackets][a]

(*A*) Torsion angles

(*a*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$

C(1)–Rh(1)–Rh(3)–C(4)	−16.2
C(2)–Rh(1)–Rh(3)–C(5)	−16.8

(*b*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$[b]

C(1)–Rh(1)–Rh(3)–C(7)	−6.1
C(2)–Rh(1)–Rh(3)–C(6)	1.7

(*c*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]$

C(1)–Rh(1)–Rh(3)–C(5)	6.1
C(2)–Rh(1)–Rh(3)–C(6)	4.0

(*B*) Least-squares planes

(*a*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$

Atoms defining plane: Rh(1), Rh(2), Rh(3), P(1), and P(2)

$$6.2212x + 2.3110y + 12.4743z = 12.6729$$

[Rh(1), −0.13; Rh(2), 0.0; Rh(3), 0.13; P(1), 0.08; P(2), −0.08; C(1), −0.72; C(3), 0.20; C(4), −0.43]

(*b*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_7]$

Atoms defining plane: Rh(1), Rh(2), Rh(3), P(1), P(2), and P(3)

$$6.3187x + 15.2375y + 3.9911z = 14.2404$$

[Rh(1), −0.08; Rh(2), 0.12; Rh(3), −0.14; P(1), −0.04; P(2), 0.0; P(3), 0.13; C(3), 0.40; this last figure can be considered as approximate only]

(*c*) $[Rh_3(\mu\text{-}PPh_2)_3(CO)_6(PPh_2H)]\cdot CH_2Cl_2$

Atoms defining plane: Rh(1), Rh(2), Rh(3), P(1), P(2), and P(3)

$$0.8238x - 0.3488y + 36.6903z = 13.6998$$

[Rh(1), 0.14; Rh(2), −0.16; Rh(3), −0.09; P(1), 0.0; P(2), 0.16; P(3), −0.05; P(4), 0.68]

[a] E.s.d.s are 0.5° and 0.05 Å for angular and distance measurements. [b] Owing to the high e.s.d.s in the light-atom positions the torsion angles given under (*b*) here can be considered as approximate only.

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