Complexes of Rhodium(I) with Carbon Monoxide, Bis(diphenylphosphino)methane, or Bis(diphenylarsino)methane, and Various Anionic Ligands

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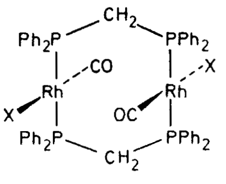
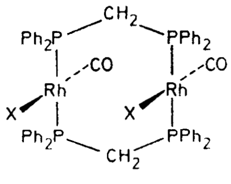
Complexes of rhodium(I) with carbon monoxide, bis(diphenylphosphino)methane (dppm), or the arsine analogue (dpam), and a variety of anionic ligands are described, and the natures of each of the novel complexes are compared with those of known complexes containing terminal or bridging chloro-ligands. In solution in acetone–methanol and in the presence of halide ions (X = Cl^-, Br^-, or I^-) cationic dinuclear 'A-frame' complexes $[Rh_2(\mu\text{-}X)(CO)_2L_2]^+$ and $[Rh_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2L_2]^+$ (L = dppm or dpam) are readily formed. In the presence of the pseudohalide ions (Z = CN^- or SCN^-) the neutral complexes $[Rh_2Z_2(CO)_4L_2]$ are initially formed. The cyano-complexes readily dissociate one (dppm) or two (dpam) moles of CO respectively. When Z is OCN^- or N_3^- the products are dinuclear dicarbonyl complexes $[Rh_2Z_2(CO)_2L_2]$.

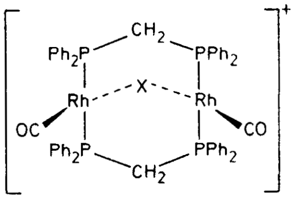
THE neutral complex *trans*-$[Rh_2Cl_2(CO)_2(dppm)_2]$ [1a; X = Cl; dppm = bis(diphenylphosphino)methane] is isomorphous with the analogous arsine (dpam) complex, and contains terminal chloro- and carbonyl ligands and mutally *trans* bridging diphosphine ligands.[1] The complex cation, $[Rh_2Cl(CO)_2(dppm)_2]^+$ has terminal carbonyl ligands and bridging dppm ligands. However, in this case the chloro-ligand bridges the rhodium atoms (2; X = Cl).[2,3] Complex (2) reversibly adds carbon monoxide,[3] or other two-electron donor ligands,[4,5] at the bridging position opposite to the chloro-ligand with concomitant formation of a metal–metal bond (*e.g.* 3; X = Cl). Attack by chloride ion on complex (3) and loss of one carbonyl ligand affords *cis*-$[Rh_2Cl_2(CO)_2(dppm)_2]$, (1b; X = Cl).[3,4] A related cationic complex of iridium(I), $[Ir_2Cl(\mu\text{-}CO)_2(CO)_2(dppm)_2]^+$ is asymmetric.[3] The structure (4a) was initially proposed,[3] but recent evidence suggests that the complex may be instead structure (4b).[6]



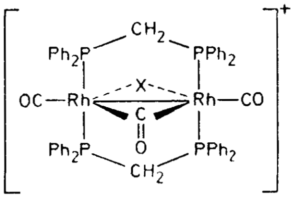
(1a)



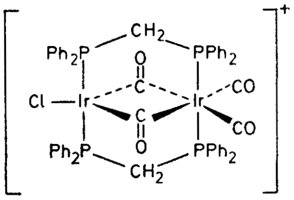
(1b)



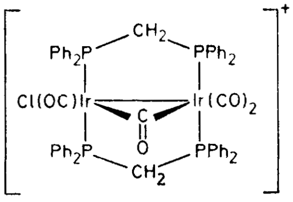
(2)



(3)



(4a)



(4b)

Complex (2) (X = Cl) is an active catalyst for the hydrogenation of alkenes or alkynes.[3,7] In order to ascertain the effect of changing the bridging ligand on the catalytic activity of (2) it was first necessary to synthesise a variety of complexes related to (1)—(4) but containing ligands other than chlorine. Herein complexes with bromo-, iodo-, azido-, cyano-, thiocyanato-, cyanato-, or acetato-ligands are described and compared with the known chloro-complexes.

EXPERIMENTAL

Initially all manipulations were performed in dry, dioxygen-free solutions. These precautions were later found to be frequently redundant: the products are not water sensitive, and only interaction of the iodo- and cyano-complexes with dioxygen has so far been observed.

Molecular weights were determined by osmometry using dibromomethane as solvent. Frequently samples were of low solubility in this or other suitable solvents, and some results are consequently of lower quality than would normally be desired. Such results should be regarded only as supporting evidence for proposed structures.

(a) *Preparation of* $[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dppm)_2]X$ {X = Br, $[RhBr_2(CO)_2]$, or BPh_4} *and the Analogous Arsine Complexes*.—(1). A mixture of KBr (1.054 g, 8.86 mmol) and $[Rh_2Cl_2(cod)_2]$ (0.372 g, 0.754 mmol) (cod = cyclo-octa-1,5-diene) in methanol (25 cm^3) and acetone (25 cm^3) was stirred under an atmosphere of CO. After 90 min dppm (0.514 g, 1.469 mmol) was added and the mixture was stirred (4 h) under a stream of CO. A yellow precipitate formed which was removed by filtration, washed successively with water and diethyl ether, and then recrystallised from dichloromethane to yield, as bright yellow crystals, $[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dppm)_2]Br$ (0.744 g, 83%) (Found: C, 51.5; H, 3.7; Br, 14.6. Calc.: C, 52.25; H, 3.6; Br, 13.1%). The product was slightly to very soluble in acetone, ethanol, dichloromethane, or diethyl ether to form yellow, conducting solutions (Λ_M = 108 S cm^2 mol^{-1}; 0.565 × 10^{-3} mol dm^{-3} in acetone). The yellow arsine analogue, $[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dpam)_2]Br$, was synthesised in a similar manner (Found: C, 45.5; H, 3.1; As, 21.8; Br, 11.7. Calc.: C, 45.7; H, 3.2; As, 21.5; Br, 11.5%).

A solution of the dppm complex in dichloromethane under an atmosphere of dinitrogen became redder over 2 days. The solvent was allowed to slowly evaporate to yield, as dark red-brown crystals, $[Rh_2Br_2(\mu\text{-}CO)(CO)(dppm)_2]$.[*] Reaction of CO with this product regenerated the original tricarbonyl cationic complex.

(2). When the above preparation was performed with a different stoicheiometry the product obtained was yellow crystals of $[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dppm)_2][RhBr_2(CO)_2]$ (Found: C, 44.7; H, 3.1%. *M* 1 306. Calc.: C, 45.3; H, 3.0%. *M* 1 457).

(3). Reaction of $[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dppm)_2]Br$ with an excess of $Na[BPh_4]$ in methanol–acetone gave yellow crystals of $[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dppm)_2][BPh_4]$ (Found: C, 63.3; H, 4.4; Br, 6.2%. *M* 1 694. Calc.: C, 63.4; H, 4.4; Br, 5.5%. *M* 1 458). The arsine analogue was similarly synthesised (Found: C, 56.5; H, 3.9. Calc.: C, 56.6; H, 3.95%).

In solution in dichloromethane under an atmosphere of dinitrogen, the above product very slowly (days) dissociates one mole of CO to form orange crystals of $[Rh_2(\mu\text{-}Br)(CO)_2(dppm)_2][BPh_4]$ (Found: C, 61.9; H, 4.4; P, 8.5. Calc.: C, 63.8; H, 4.5; P, 8.7%). A solution of the material in acetone was conducting ($\Lambda_M = 96$ S cm^2 mol^{-1}; 0.44×10^{-3} mol dm^{-3}). Under identical conditions the analogous arsine complex was rapidly formed (Found: C, 56.9; H, 4.1%. *M* 1 662. Calc.: C, 56.85; H, 4.0%. *M* 1 606).

(b) *Preparation of* $[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(dppm)_2]I$, *and the Arsine Analogue.*—In a procedure similar to (a)1 above, reaction of $K[RhI_2(CO)_2]$ with an equimolar amount of dppm in solution in acetone–methanol (1 : 1) gave, as bright yellow crystals, $[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(dppm)_2]I$ (0.582 g, 93%) (Found: C, 47.85; H, 3.4; I, 19.6. Calc.: C, 48.5; H, 3.4; I, 19.3%). The product was a 1 : 1 electrolyte in acetone solution ($\Lambda_M = 99$ S cm^2 mol^{-1}; 0.57×10^{-3} mol dm^{-3}). The product was sensitive to air both in solution and in the solid state, yielding a dark green material. In solution in dichloromethane and under a stream of dinitrogen the complex did not lose CO within 2 days, and was recovered unchanged.

The arsine analogue, $[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(dpam)_2]I$, was also synthesised and recrystallised from dichloromethane as deep orange crystals (Found: C, 42.6; H, 2.9; As, 19.9; I, 17.3. Calc.: C, 42.8; H, 3.0; As, 20.1; I, 17.05%). In solution in dichloromethane under a stream of dinitrogen the complex reversibly dissociated CO to yield $[Rh_2I_2(\mu\text{-}CO)(CO)(dpam)_2]$ [*] (Found: C, 42.6; H, 3.1; As, 19.9; I, 16.6. Calc.: C, 42.8; H, 3.0; As, 20.5; I, 17.4%). Reaction of CO with this product regenerated the cationic tricarbonyl complex above.

(c) *Preparation of* $[Rh_2(CN)_2(CO)_n(dppm)_2]$ ($n = 3,4$), *and the Arsine Analogues.*—A solution of $K[CN]$ (0.108 g, 1.659 mmol) and $[Rh_2Cl_2(cod)_2]$ (0.214 g, 0.434 mmol) in acetone (20 cm^3) and methanol (20 cm^3) was stirred under one atmosphere of CO (5 min), and subsequently dppm (0.340 g, 0.885 mmol) was added. The blood-red solution was stirred (12 h) during which a vermillion precipitate of $[Rh_2(CN)_2(CO)_4(dppm)_2]$ (0.186 g, 40%) developed (Found: C, 59.0; H, 4.1; N, 2.6%. *M* 967. Calc.: C, 59.1; H, 3.9; N, 2.5%. *M* 1 139). A solution of the material in acetone was non-conducting.

Dissolution of the material in dichloromethane and subsequent evaporation of the solvent under a stream of dinitrogen gave, as an impure red-brown powder, $[Rh_2(CN)_2(CO)_3(dppm)_2]$ (Found: C, 56.9; H, 4.0; N, 2.4. Calc.: C, 59.5; H, 4.0; N, 2.5%).

The red arsine analogue, $[Rh(CN)_2(CO)_4(dpam)_2]$, was prepared in a similar manner, but in methanol alone as solvent (Found: C, 50.9; H, 3.45; N, 2.3%. *M* 1 362. Calc.: C, 51.5; H, 3.4; N, 2.1%. *M* 1 314). Under a stream of dinitrogen and in solution in dichloromethane this complex dissociated two moles of carbon monoxide to yield, as a dark purple powder, $[Rh_2(CN)_2(CO)_2(dpam)_2]$ (Found: C, 49.8; H, 3.6; N, 2.1. Calc.: C, 51.5; H, 3.5; N, 2.2%).

Recrystallisation of either the dppm or dpam tetracarbonyl complex from acetone gave the bis(acetone) complex $[Rh_2(CN)_2(CO)_4(dppm)_2]\cdot 2(CH_3)_2CO$ (Found: C, 59.9; H, 4.7; N, 2.15. Calc.: C, 59.3; H, 4.5; N, 2.2%); $[Rh_2(CN)_2(CO)_4(dpam)_2]\cdot 2(CH_3)_2CO$ (Found: C, 51.0; H, 4.0; N, 1.9%. *M* 1 553. Calc.: C, 52.05; H, 3.95; N, 2.0%. *M* 1 431).

(d) *Preparation of* $[Rh_2(NCS)_2(CO)_4(dppm)_2]$, *and the Arsine Analogue.*—A mixture of $K[SCN]$ (0.459 g, 4.723 mmol) and $[Rh_2Cl_2(cod)_2]$ (0.235 g, 0.476 mmol) in acetone (20 cm^3) and methanol (20 cm^3) was stirred (30 min) under an atmosphere of CO, and dppm (0.368 g, 0.958 mmol) was subsequently added. A bright golden yellow precipitate of $[Rh_2(NCS)_2(CO)_4(dppm)_2]$ (0.511 g, 94%) formed. The material was purified by washing with successive aliquots of water, methanol, and diethyl ether (Found: C, 56.1; H, 4.0; N, 2.4; S, 5.2. Calc.: C, 55.9; H, 3.7; N, 2.3; S, 5.3%). The material was of very low solubility in appropriate solvents, thus precluding determination of the molecular weight. The arsine analogue, $[Rh_2(NCS)_2(CO)_4(dpam)_2]$ was similarly prepared (Found: C, 49.5; H, 3.5; N, 2.0; S, 4.5. Calc. C, 48.8; H, 3.2; N, 2.0; S, 4.65%).

(e) *Preparation of* $[Rh_2(NCO)_2(CO)_2(dppm)_2]$, *and the Arsine Analogue.*—Using a procedure similar to (d) above $[Rh_2(NCO)_2(CO)_2(dppm)_2]$ was synthesised and then recrystallised from dichloromethane as a red-orange microcrystalline powder (Found: C, 58.1; H, 4.0; N, 2.4. Calc.: C, 58.2; H, 4.0; N, 2.5%). The red arsine analogue $[Rh_2(NCO)_2(CO)_2(dpam)_2]$ was similarly prepared (Found: C, 49.6; H, 3.4; N, 2.1; As, 23.2. Calc.: C, 50.3; H, 3.4; N, 2.2; As, 23.8%).

(f) *Preparation of* $[Rh_2Cl(N_3)(CO)_2(dppm)_2]$.—A solution of $Na[N_3]$ (0.202 g, 3.11 mmol) and $[Rh_2Cl_2(cod)_2]$ (0.205 g, 0.416 mmol) in acetone (35 cm^3) and methanol (35 cm^3) was stirred (1 h) under an atmosphere of CO. Subsequently dppm (0.317 g, 0.826 mmol) was added, at which the yellow solution became progressively redder.

When the solution was reduced in volume under CO the product was a red powder which analysed as $[Rh_2Cl(N_3)(CO)_2(dppm)_2]$ (Found: C, 56.55; H, 4.1; N, 3.9. Calc.: C, 56.4; H, 4.0; N, 3.8%) and which formed a weakly conducting solution in acetone ($\Lambda_M = 41$ S cm^2 mol^{-1}; 0.15×10^{-3} mol dm^{-3}).

(g) *Attempted Synthesis of* $[Rh_2(O_2CCH_3)(CO)_3(dppm)_2][BPh_4]$.—A mixture of $Na[O_2CCH_3]$ (0.323 g, 3.94 mmol) and $[Rh_2Cl_2(cod)_2]$ (0.274 g, 0.556 mmol) in methanol (20 cm^3) and acetone (20 cm^3) was stirred (10 min) under an atmosphere of CO, and dppm (0.423 g, 1.102 mmol) was subsequently added. The dark brown-red solution so formed was stirred (18 h) under CO, and $Na[BPh_4]$ (0.390 g, 1.14 mmol) was subsequently added. After *ca.* 1 h an unidentified brown material (0.217 g) had precipitated (Found: C,

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[*] A similar material, to which this structure has been assigned, has been synthesised independently (M. Cowie and S. K. Dwight, unpublished work).

60.9; H, 4.2%. M 1 156. Calc. for $[Rh_2(O_2CCH_3)(CO)_3(dppm)_2][BPh_4]$: C, 66.0; H, 4.7%. M 1 437). A solution of the material in acetone was conducting ($\Lambda_M = 81$ S cm^2 mol^{-1}; 10^{-3} mol dm^{-3}).

Spectra were obtained using the following instruments: Bruker HFX 90 and WP 80 (^1H and ^{31}P n.m.r.); Perkin-Elmer 283 (i.r.). Elemental analyses were performed by the microanalytical service of the University of Alberta Department of Chemistry and by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany.

RESULTS AND DISCUSSION

(a) *Halogeno-complexes*.—Reactions of the dicarbonyldihalogenorhodate(I) ions, $[Rh(CO)_2X_2]^-$ (X = Cl, Br, or I), with dppm (or dpam) under an atmosphere of CO gave in each case the halogeno- and carbonyl-bridged complex cation, (3; X = Cl, Br, or I) [equation (1)]. Subsequent reactions with $Na[BPh_4]$ gave complexes (5) [equation (2)]. Thus, in these cases, the behaviour of the bromo- or iodo-systems is entirely analogous to that of the known chloro-complex.[3] Unlike the chloro-complex, however, complex (3; X = I) does not lose one mole of CO in an atmosphere of dinitrogen, or under vacuum, or by attack of iodide ion [equation (3)]. Also, compared to $[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dppm)_2]Cl$, complex (3; X = Br) is more stable and remains fully ionised in solution during determination of its molecular weight. However, under a stream of dinitrogen the bromo-complex does very slowly lose 1 mol of CO to form $[Rh_2Br_2(\mu\text{-}CO)(CO)(dppm)_2]$ (see footnote on previous page), for which no analogous chloro-complex has been observed. Under a stream of dinitrogen the corresponding tetraphenylborate complex (5; X = Br) loses one mole of CO to afford (2; X = Br), in a manner analogous to the chloro-complex, but much more slowly (days). Other differences between these complexes include the much greater solubility of the bromo-complex compared to the chloro-analogue.

$$2[Rh(CO)_2X_2]^- + 2\,dppm \longrightarrow \underset{(3)}{[Rh_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(dppm)_2]X} + 2X^- + CO \quad (1)$$

$$\underset{(3)}{[Rh_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(dppm)_2]X} + Na[BPh_4] \longrightarrow NaX + \underset{(5)}{[Rh_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(dppm)_2][BPh_4]} \quad (2)$$

$$\underset{(3)}{[Rh_2X(CO)_3(dppm)_2]X} \xrightleftharpoons[+CO]{-CO} \underset{(1b)}{[Rh_2X_2(CO)_2(dppm)_2]} \quad (3)$$

The structures within series of complexes (3) or (5) (X = Cl, Br, or I) are very similar, as evidenced by the spectroscopic properties. The i.r. spectra (Table 1) in each case show bands assigned to both terminal and bridging carbonyl ligands, of similar values for each halogeno-complex. The ^{31}P n.m.r. spectra (Table 2) are also similar for each halogeno-complex. In each case a second-order spectrum is observed, with a small relative chemical shift and a similar fine structure. The separations of the major features of the spectra are so similar as to indicate a very similar value for the interaction between the rhodium atoms [$|^1J(Rh\text{–}Rh)|$] and for the short- and long-range phosphorus–phosphorus coupling constants, with a very low dependence upon the nature of the halogen bridging the rhodium atoms.

An explanation for the relative lability of the carbonyl ligands of (3; X = Cl, Br, or I) is as follows. The reversible loss of one carbonyl ligand from (3; X = Cl) has been shown by labelling experiments to occur in a two-step process [equation (4)]; the ligand ultimately dissociated is one of the terminal carbonyl ligands and not the carbonyl ligand originally in the bridging position.[3] An X-ray crystallographic analysis of (3; X = Cl) has

TABLE 1

Infrared spectra [a]

Complex	CO bands	Other bands
trans-$[Rh_2Cl_2(CO)_2(dppm)_2]$ [b]	1 968	
cis-$[Rh_2Cl_2(CO)_2(dppm)_2]$ [b]	1 971	
$[Rh_2(\mu\text{-}Cl)(CO)_2(dppm)_2]^+$ [b]	1 997, 1 978	
$[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dppm)_2]^+$ [b]	1 992, 1 977, 1 863	
$[Rh_2(\mu\text{-}Br)(CO)_2(dppm)_2]^+$	1 998, 1 978	
$[Rh_2(\mu\text{-}Br)(CO)_2(dpam)_2]^+$	1 997, 1 980	
$[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dppm)_2]^+$	1 998, 1 983, 1 864	
$[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dpam)_2]^+$	1 996, 1 956, 1 865	
$[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(dppm)_2]^+$	1 996, 1 980, 1 863	
$[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(dpam)_2]^+$	1 992, 1 958, 1 863	
$[Ru_2I(\mu\text{-}I)(\mu\text{-}CO)(CO)(dpam)_2]$ [d]	1 942, 1 827	
$[Rh_2(NCS)_2(CO)_4(dppm)_2]$	1 992	2 073 [ν(RhN≡CS)] 830 [ν(RhNC–S)]
$[Rh_2(NCS)_2(CO)_4(dpam)_2]$	1 991	2 072 [ν(RhN≡CS)] 837 [ν(RhNC–S)]
$[Rh_2(NCO)_2(CO)_2(dppm)_2]$	1 968	2 238 [ν(RhNCO)] 593 [δ(OCN)]
$[Rh_2(NCO)_2(CO)_2(dpam)_2]$	1 969	2 238 [ν(RhNCO)] 590 [δ(OCN)]
$[Rh_2(CN)_2(CO)_4(dppm)_2]$	1 996	2 100 [ν(RhCN)]
$[Rh_2(CN)_2(CO)_4(dppm)_2]\cdot 2(CH_3)_2CO$	1 985	2 090 [ν(RhCN)] 1 713 [$RhO{=}C(CH_3)_2$]
$[Rh_2(^{13}CN)_2(CO)_4(dppm)_2]$	1 991	2 058 [ν(RhCN)]
$[Rh_2(CN)_2(\mu\text{-}CO)(CO)_2(dppm)_2]$	1 962, 1 816	2 100 [ν(RhCN)]
$[Rh_2(^{13}CN)_2(\mu\text{-}CO)(CO)_2(dppm)_2]$	1 960, 1 812	2 056 [ν(RhCN)]
$[Rh_2(CN)_2(CO)_4(dpam)_2]$	1 994	2 100 [ν(RhCN)]
$[Rh_2(CN)_2(CO)_4(dpam)_2]\cdot 2(CH_3)_2CO$	1 987	2 096 [ν(RhCN)] 1 715 [$RhO{=}C(CH_3)_2$]
$[Rh_2(^{13}CN)_2(CO)_4(dpam)_2]$	1 994	2 056 [ν(RhCN)]
$[Rh_2(CN)_2(CO)_2(dpam)_2]$	1 977	2 110 [ν(RhCN)]
$[Rh_2(^{13}CN)_2(CO)_2(dpam)_2]$	1 975	2 062 [ν(RhCN)]
$[Rh_2Cl(N_3)(CO)_2(dppm)_2]$ [c]	2 080, 1 968	2 236 [ν(N_3)]

[a] Values in wavenumbers (cm^{-1}); spectra obtained from Nujol mulls. [b] Known complex, refs. 1—4. [c] Postulated complex for which characterisation is incomplete. [d] See footnote on previous page.

shown that the terminal carbonyl ligands are bent away from the bridging chloro-ligand because of steric interaction.[2,3] Increasing the size of the bridging ligand would increase this effect, Cl < Br < I. The intermediate in reaction (4) would be subject to an even greater steric interaction, thereby increasing the barrier to loss of CO from complex cation (3) with increasing size of halogen ion.

Table 2

N.m.r. spectral data

(*a*) ^{31}P N.m.r. spectra [a]

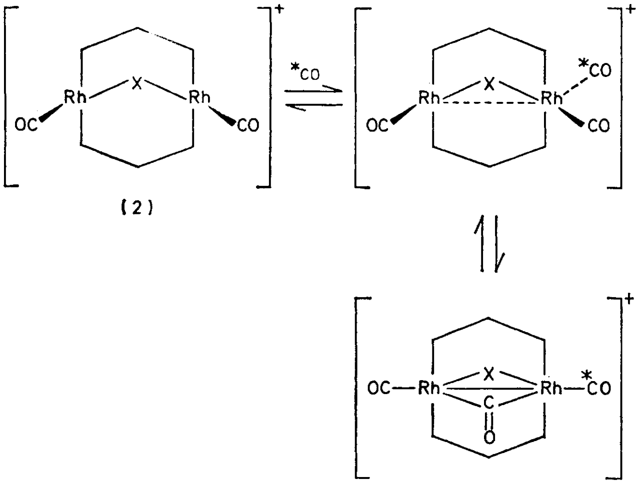
	δ(P)	^{1}J(RhP) + ^{x}J(RhP)
$[Rh_2(\mu\text{-}Cl)(CO)_2(dppm)_2]^+$	16.1	113.3
$[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dppm)_2]^+$	26.0	94.2
$[Rh_2(\mu\text{-}Br)(CO)_2(dppm)_2]^+$	18.0	110.4
$[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dppm)_2]^+$	28.1	93.4
$[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(dppm)_2]^+$	29.0	92.7
$[Rh_2(CN)_2(CO)_3(dppm)_2]$	31.0	109.9
$[Rh_2(CN)_2(CO)_4(dppm)_2]$ [b]	20.0	127.0
$[Rh_2Cl(N_3)(CO)_2(dppm)_2]$	18.1	127.7
	23.0	126.3

(*b*) ^{13}C N.m.r. spectra [c]

	δ(C)
$[Rh_2(^{13}CN)_2(CO)_3(dppm)_2]$	138 (br)
$[Rh_2(^{13}CN)_2(CO)_2(dpam)_2]$	114, 148 (br)

[a] Solutions are in [$^2H_2$]dichloromethane. Shifts are in p.p.m. downfield from external 85% H_3PO_4 and the separation of the major components of the second-order spectra are expressed in Hz. [b] Present in equilibrium with the tricarbonyl complex in the solution tested (see text). [c] ^{13}C Shifts are in p.p.m. downfield from $SiMe_4$.

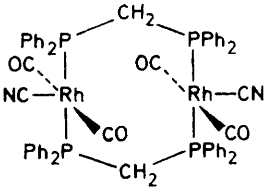
(b) *Pseudo-halogen Complexes.*—Pseudohalogen complexes of rhodium with diphosphine ligands have been described only infrequently.[8] Consequently, few assumptions can be made about the bonding modes in these complexes.



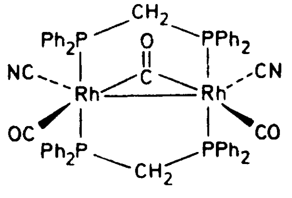
(2) (4) (3)

In solution in acetone–methanol and in the presence of either pseudohalogen ion (Z) SCN$^-$ or CN$^-$ complexes of formula $[Rh_2Z_2(CO)_4L_2]$ (L = dppm or dpam) were readily formed. In the presence of OCN$^-$ complexes of formula $[Rh(NCO)_2(CO)_2L_2]$ were formed instead. Incomplete replacement of chloride by azide occurred, even in the presence of an excess of azide ion, and the unsymmetrical complex $[Rh_2Cl(N_3)(CO)_2(dppm)_2]$ was isolated. In each case the i.r. spectrum of the product initially obtained did not exhibit a band assignable to a bridging CO or to unco-ordinated pseudohalide ligand (Table 1). The complexes were therefore not of types (2), (3), or (4).

The reaction of equivalent amounts of K[CN] and $[Rh_2Cl_2(cod)_2]$ in acetone–methanol under an atmosphere of CO rapidly gave a very dark solution. Subsequent addition of dppm or dpam caused the solution to become blood-red. Within hours a vermillion (dppm) or orange-red (dpam) precipitate developed which analysed as $[Rh_2(CN)_2(CO)_4L_2]$. The ^{13}CN (91% enriched) complexes were also synthesised. In each case the value of the i.r. band for the terminal carbonyl ligand (1 991—1 996 cm^{-1}) was of a higher value than that associated with complexes of types (1a) or (1b). The band assigned to the cyano-ligand (^{12}CN: 2 100 cm^{-1}; ^{13}CN: 2 056—2 058 cm^{-1}) was relatively weak, reflecting the low extent of metal–cyanide π bonding.[9,10] The values of the carbonyl and cyano-ligand bands, and the absence of i.r. bands associated with either free cyanide ion or bridging CO ligands (Table 1), mitigate against a structure such as (2)—(4). Solutions of these complexes in acetone are non-conducting. The tetracarbonyl dinuclear complexes are assigned structure (6) on the basis of the above data, elemental analyses, and the following evidence. The ^{31}P n.m.r. parameters are appropriate [2-5] for mutually *trans* phosphine ligands (Table 2). A *trans* trigonal-bipyramidal structure about each rhodium atom would cause considerable steric interaction. Therefore, the structure about each rhodium atom must be square pyramidal with mutually *trans* carbonyl ligands, thus giving rise to only one, relatively high, i.r.-active CO band. The cyano-ligand must compete with two carbonyl and two phosphine ligands for metal–ligand π bonding, and this results in the relatively low intensity of the Rh[CN] stretching band.[9,10] On dissociation of one mole of CO (see below) the intensity of this band increases.



(6)

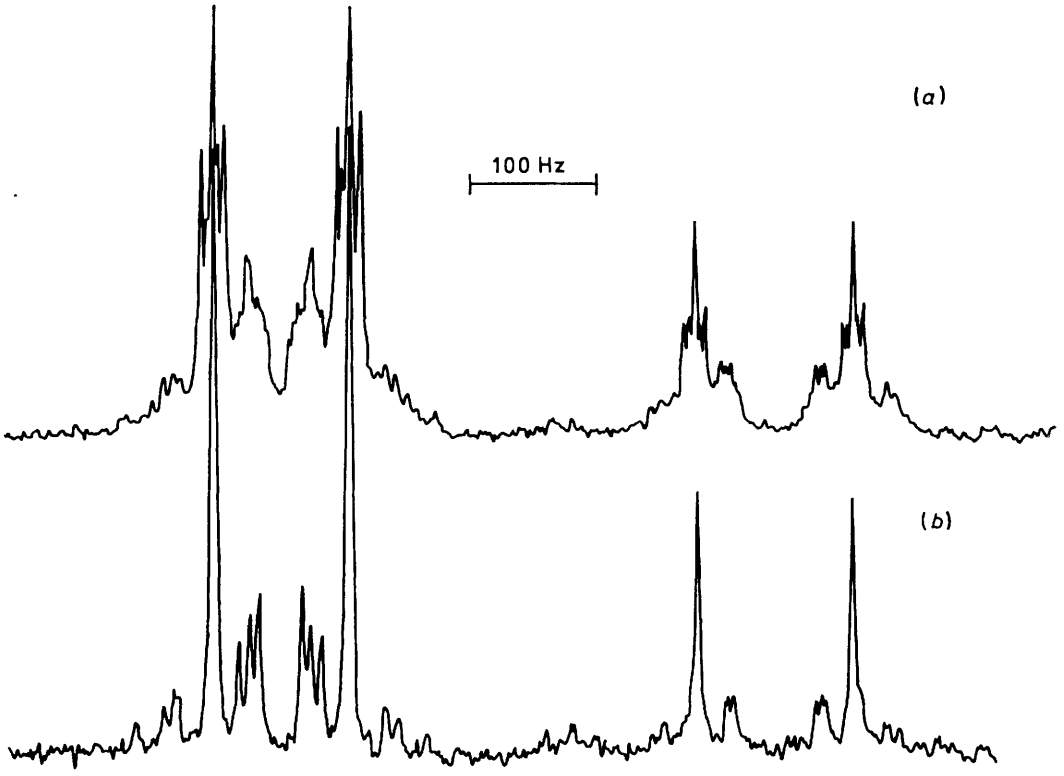


(7)

When a solution of the tetracarbonyl complex $[Rh_2(CN)_2(CO)_4(dppm)_2]$ in dichloromethane is slowly reduced in volume under a stream of dinitrogen the product is the tricarbonyl complex $[Rh_2(CN)_2(\mu\text{-}CO)(CO)_2(dppm)_2]$, (7). The i.r. spectrum of (7) exhibits bands appropriate for both terminal and bridging carbonyl ligands, and for terminal cyano-ligands (Table 1).[11] Treatment of (7) with CO regenerates (6) [equation (5)]. When a sample of complex (6) was dissolved in CD_2Cl_2 under an atmosphere of dinitrogen the major signal observed in the ^{31}P n.m.r. spectrum was that for (7), and (6) was observed

$$[Rh_2(CN)_2(CO)_4(dppm)_2] \rightleftharpoons [Rh_2(CN)_2(\mu\text{-}CO)(CO)_2(dppm)_2] + CO \quad (5)$$

only as a minor component (Figure), due to the lability of the fourth carbonyl ligand. For each ^{13}CN complex (91% enriched) coupling of each ^{31}P nucleus to two ^{13}C nuclei was observed at ambient temperature. Attempts to obtain low-temperature spectra were thwarted because the complexes precipitated from solution. It cannot be decided at this time whether the coupling of ^{31}P to two ^{13}C nuclei was due to real or accidental close equivalence of coupling constants, or due to rapid exchange of cyano-ligands, although the latter explanation is favoured. The parameters of the second-order spectrum of (6) (^{12}CN or ^{13}CN complex) indicate that the complex has a very low Rh–Rh interaction, further supporting the structure postulated. In contrast, the second-order spectrum of (7) (^{12}CN or ^{13}CN complex) showed that a strong Rh–Rh interaction exists,[2,3] as expected for the metal–metal bonded complex structure suggested.



Phosphorus-31 n.m.r. spectra of [$^2H_2$]dichloromethane solutions of (*a*) a mixture of [$Rh_2(^{13}CN)_2(CO)_3(Ph_2PCH_2PPh_2)_2$] and [$Rh_2(^{13}CN)_2(CO)_4(Ph_2PCH_2PPh_2)_2$], and (*b*) a mixture of the ^{12}CN analogues. The tricarbonyl complex is the major component in each spectrum (see text)

Dissolution of [$Rh_2(CN)_2(CO)_4(dpam)_2$] in dichloromethane under an atmosphere of dinitrogen gave a purple-red solution. Slow evaporation of solvent from this solution yielded [$Rh_2(CN)_2(CO)_2(dpam)_2$]. The i.r. spectrum of the dark purple-brown product showed bands for terminal cyano-(^{12}CN, 2 110; ^{13}CN, 2 062 cm^{-1}) and carbonyl ligands (1 975—1 977 cm^{-1}), but no band assignable to bridging CN or CO ligands. The values of these bands indicate that this product is of structure (1a) or (1b). It is noteworthy that loss of two moles of CO per mole of [$Rh_2(CN)_2(CO)_4L_2$] occurs for L = dpam, but that dissociation of only one mole of CO occurs readily when L = dppm. It has previously been observed that loss or exchange of CO ligands is more facile for [$Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dpam)_2$]$^+$ than for [$Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dppm)_2$]$^+$.[3] Under catalytic hydrogenation conditions each complex (6; L = dppm or dpam) slowly dissociates two moles of CO to form [$Rh_2(CN)_2(CO)_2L_2$].[7]

The ^{13}C n.m.r. spectra of the complexes [$Rh_2(CN)_2(\mu\text{-}CO)(CO)_2(dppm)_2$] and [$Rh_2(CN)_2(CO)_2(dpam)_2$], with either natural abundance of ^{13}C or ^{13}CN (91% enriched), were compared. For the dppm complexes a very broad and, unfortunately, weak signal was observed at 138 p.p.m. (*versus* $SiMe_4$) for the ^{13}CN-enriched complex only. The details of the signal were too indistinct to permit any deductions regarding the structure of the complex. However, this broad signal is between the values expected for Rh–CN and Rh–CN→Rh bonded complexes.[12] The spectrum of the diarsine complex, [$Rh_2(^{13}CN)_2(CO)_2(dpam)_2$] was potentially less complex due to the absence of ^{31}P–^{13}C couplings. Unfortunately, again only broad ^{13}C features (*ca.* 114, 148 p.p.m.) were resolved for the ^{13}CN complex only. From the available data it cannot be determined whether these broad features are linked, or due to independent causes, for example Rh–CN and Rh–CN→Rh respectively.[12]

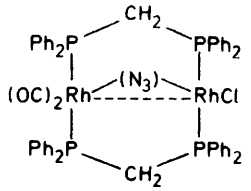
The thiocyanato-complexes with either dppm or dpam ligands are assigned tetracarbonyl structures similar to (6) on the basis of elemental analyses and the i.r. spectra. In each case the carbonyl band in the i.r. spectrum is of a similarly high value to that of (6). The values of the bands assigned to the thiocyanato-ligand (Table 1) are appropriate for SCN$^-$ ligands that are both terminal and are bonded to rhodium *via* the nitrogen atoms.[9,13] However, the possibilities of either N-bridging NCS, or intermolecular interactions involving Rh–NCS→Rh bridges,[9,14] cannot be totally excluded.

The value of the i.r. band for the NCO$^-$ ligands indicates that these ligands are also terminal and N-bonded in each cyanato-complex (Table 1).[15] In contrast to the above complexes the carbonyl bands were of values similar to those for dicarbonyl complex (1a) or (1b) (X = Cl). On the basis of these data and elemental analyses, the cyanato-complexes are tentatively assigned structure (1a) or (1b). Intermolecular Rh–NCO→Rh interactions may be the cause of the low solubility of the complexes in appropriate solvents.

In the presence of an excess of azide ion the product formed is the weakly ionisable complex $[Rh_2Cl(N_3)(CO)_2(dppm)_2]$. A solution of this material in acetone showed a low but significant molar conductivity ($\Lambda_M = 41$ S cm^2 mol^{-1}), suggesting that partial ionisation had occurred in acetone solution [equation (6)]. For comparison, the molar conductivity of $[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dppm)_2][BPh_4]$ is 108 S cm^2 mol^{-1}. Further evidence for the ionisation suggested was the observation of a band at 1 863 cm^{-1} in the i.r. spectrum of the solution only but the absence of any band assignable to unco-ordinated azide ion. Under an atmosphere of CO this

$$[Rh_2Cl(N_3)(CO)_2(dppm)_2] \underset{-CO}{\overset{CO}{\rightleftharpoons}} [Rh_2(\mu\text{-}N_3)(\mu\text{-}CO)(CO)_2(dppm)_2]Cl \quad (6)$$

material reacts with Na[BPh$_4$] and CO in a complex manner which has not yet been fully elucidated. The value for the i.r. band designated ν_3 for the azide ion is 2 030 cm^{-1}.[9] The value for the corresponding band for the above azido-complex is considerably higher. The ^{31}P n.m.r. spectrum of a dichloromethane solution of $[Rh_2Cl(N_3)(CO)_2(dppm)_2]$ demonstrates that there are two environments for ^{31}P, each giving rise to a second-order pattern. The fine structure of each component of the spectrum ($|^1J + {}^xJ|_{RhP}$ = 127.0 Hz and 126.3 Hz respectively) and lack of peaks close to the centre of each pattern indicate strongly that no metal–metal bond exists in this complex. The above data are consistent with an asymmetric structure. A structure similar to (1a) or (1b), but with inequivalent X (X_2 = Cl and N_3), is probable, but an azido-bridged complex is also possible (8). Confirmation of the structure of this complex must await a crystallographic analysis, the feasibility of which is at present being studied.[16]



(8)

Attempts to synthesise the acetate-bridge A-frame $[Rh_3(O_2CCH_3)(CO)_2L_2]^+$ by the reaction of $[\{RhCl(CO)_2\}_2]$ with, successively, sodium acetate, dppm (or dpam), and sodium tetraphenylborate were unsuccessful. However, recently the required complexes have been obtained by the treatment of $[Rh_2(\mu\text{-}Cl)(CO)_2L_2]^+$ with silver acetate.[17]

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