

Tetranuclear and Dinuclear Phosphine- and Arsine-substituted Rhodium Carbonyls; Infrared Spectral Evidence for the Formation of Dirhodium Octacarbonyl

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The reactions of $\text{Rh}_4(\text{CO})_{12}$ with phosphine and arsine ligands have been investigated. Treatment of $\text{Rh}_4(\text{CO})_{12}$ with one or two moles of ligand under mild conditions yields the compounds $\text{Rh}_4(\text{CO})_{11}\text{L}$ and $\text{Rh}_4(\text{CO})_{10}\text{L}_2$ respectively, where $\text{L} = \text{PPh}_3$, $\text{P}(\rho\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(\rho\text{-FC}_6\text{H}_4)_3$, and AsPh_3 , $2\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, in which the basic structure of the parent cluster carbonyl is thought to be retained. Further reactions of the disubstituted derivatives with carbon monoxide under pressure, preferably in the presence of excess phosphine, yield the unstable dinuclear species $\text{Rh}_2(\text{CO})_8\text{L}_2$, where $\text{L} = \text{PPh}_3$, $\text{P}(\rho\text{-CH}_3\text{C}_6\text{H}_4)_3$, and $\text{P}(\rho\text{-FC}_6\text{H}_4)_3$, which readily revert to the tetranuclear compounds. The significance of this dimer-tetramer equilibrium is discussed in relation to the difficulty experienced in characterising $\text{Rh}_2(\text{CO})_8$. Infrared spectral evidence for the reversible formation of $\text{Rh}_2(\text{CO})_8$ from the reaction of $\text{Rh}_4(\text{CO})_{12}$ with high pressures of carbon monoxide at low temperatures is also described.

THERE is considerable current interest in the chemistry of metal carbonyl cluster compounds.¹ Recently, substitution reactions of phosphines and arsines with the polynuclear metal carbonyls of iron,² ruthenium,³ osmium,⁴ cobalt,⁵ and iridium⁶ have been described to yield products in which the basic structure of the parent cluster carbonyl is retained. Under more drastic reaction conditions, especially under pressures of carbon monoxide, breakdown of the cluster frequently occurs to give mononuclear or dinuclear substituted carbonyl compounds. Thus $\text{Ru}_3(\text{CO})_{12}$ reacts with triphenylphosphine in refluxing hexane to yield $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ ³ whereas $\text{Ru}(\text{CO})_4\text{PPh}_3$ is obtained at 150 °C and 75–100 atm carbon monoxide pressure.⁷ Also the reaction of $\text{Co}_4(\text{CO})_{12}$ with triphenylphosphine in light petroleum at room temperature yields $\text{Co}_4(\text{CO})_{11}\text{PPh}_3$ ⁵ whereas in *p*-xylene at 50 °C $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$ is the only product isolated.⁸

We have found that tetrarhodium dodecacarbonyl reacts with stoichiometric amounts of phosphines and arsines under mild conditions to yield analogous products to those described for cobalt and iridium.⁹ In addition, it has been shown that the disubstituted

products of the type $\text{Rh}_4(\text{CO})_{10}\text{L}_2$ may be reversibly cleaved by reaction with carbon monoxide, establishing a dimer-tetramer equilibrium which is of particular significance to the synthesis of $\text{Rh}_2(\text{CO})_8$ from $\text{Rh}_4(\text{CO})_{12}$. Full details of our work are described here together with i.r. spectral evidence for the reversible formation of $\text{Rh}_2(\text{CO})_8$ from the reaction of $\text{Rh}_4(\text{CO})_{12}$ with carbon monoxide at high pressures and low temperatures.¹⁰

RESULTS AND DISCUSSION

When hexane solutions of triphenylphosphine and tetrarhodium dodecacarbonyl are mixed in 1:1 mol ratio at room temperature the initially orange-red solution of $\text{Rh}_4(\text{CO})_{12}$ deepens to dark red and a compound analysing for $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$ slowly crystallises at 0 °C. Gas burette measurements indicate that one mole of carbon monoxide is evolved during the reaction and the similarity of the i.r. spectrum in the carbonyl-stretching region to that of $\text{Rh}_4(\text{CO})_{12}$ suggests that the tetranuclear cluster of rhodium atoms has been retained. The dark red complex is stable in air, slightly soluble in organic solvents, and a non-electrolyte in nitrobenzene. Additional monosubstituted derivatives

¹ P. Chini, *Inorg. Chim. Acta Rev.*, 1968, **2**, 31.

² R. J. Angelici and E. E. Siefert, *Inorg. Chem.*, 1966, **5**, 1457.

³ J. P. Candlin, K. K. Joshi, and D. T. Thompson, *Chem. and Ind.*, 1966, 1960.

⁴ C. W. Bradford and R. S. Nyholm, *Chem. Comm.*, 1967, 384.

⁵ G. Cetini, O. Gambino, R. Rossetti, and P. L. Stanghellini, *Inorg. Chem.*, 1968, **7**, 609.

⁶ L. Malatesta and G. Caglio, *Chem. Comm.*, 1967, 420.

⁷ K. K. Joshi and R. Whyman, unpublished results; F. Piacenti, M. Bianchi, E. Benedetti, and G. Braca, *Inorg. Chem.*, 1968, **7**, 1815.

⁸ W. Hieber and R. Breu, *Chem. Ber.*, 1957, **90**, 1259.

⁹ R. Whyman, *Chem. Comm.*, 1970, 230.

¹⁰ R. Whyman, *Chem. Comm.*, 1970, 1194.

of the type $\text{Rh}_4(\text{CO})_{11}\text{L}$, where $\text{L} = \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, and AsPh_3 , have been prepared by analogous methods and the compounds all display similar physical properties to those of $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$.

When the above reactants are mixed in a triphenylphosphine: $\text{Rh}_4(\text{CO})_{12}$ ratio of 2 : 1 very dark red crystals separate almost immediately from the hexane solution with the evolution of two moles of carbon monoxide. This dark red compound, whose analysis is consistent with the formula $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$, has physical properties similar to those of the monosubstituted derivative although it is less soluble in organic solvents. The compounds $\text{Rh}_4(\text{CO})_{10}\text{L}_2$, where $\text{L} = \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, and AsPh_3 , and $\text{Rh}_4(\text{CO})_{10}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ have also been isolated by this method.

polynuclear phosphine-substituted derivatives, *e.g.* $\text{Rh}_4(\text{CO})_{10}(\text{PEt}_3)_2$, but dark coloured intractable products rapidly precipitated and these were not studied further.

Infrared spectra of the complexes $\text{Rh}_4(\text{CO})_{11}\text{L}$ and $\text{Rh}_4(\text{CO})_{10}\text{L}_2$ in the carbonyl stretching region are summarised in Tables 1 and 2 respectively, for hexane and 1,2-dichloroethane solutions. Because of the insolubility of the disubstituted derivatives in paraffin hydrocarbon solvents, spectra in hexane were measured as supersaturated solutions withdrawn from the reaction mixtures used in their preparation. In 1,2-dichloroethane, spectra of $\text{Rh}_4(\text{CO})_{10}\text{L}_2$ were measured on freshly prepared solutions because additional peaks at *ca.* 2087 and 2058 cm^{-1} appeared and increased slowly in intensity with time. These peaks correspond

TABLE 1
Infrared spectra of the complexes $\text{Rh}_4(\text{CO})_{11}\text{L}$ in the $\nu(\text{CO})$ region (cm^{-1})

Hexane				1,2-Dichloroethane			
PPh_3	$\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$	$\text{P}(p\text{-FC}_6\text{H}_4)_3$	AsPh_3	PPh_3	$\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$	$\text{P}(p\text{-FC}_6\text{H}_4)_3$	AsPh_3
2087s	2086s	2089s	2089s	2087s	2086s	2089s	2089s
2057vs	2056vs	2059vs	2060vs	2057vs	2055vs	2058vs	2058vs
2053vs	2051vs	2055vs	2054vs				
2031s	2029s	2033s	2032s				
2020ms	2018ms	2021ms	2020ms	2024s,br	2023s,br	2027s,br	2028s,br
2009w	2007w	2010mw	2010w				
1902vw	1901vw	1902w	1901vw	1898w	1897w	1901w	1897w,sh
1871m	1870ms	1871ms	1873ms	1860ms	1858ms	1862ms	1861ms
1851m	1851m	1849m	1850m	1843ms,sh	1842ms	1842ms	1841ms

TABLE 2
Infrared spectra of the complexes $\text{Rh}_4(\text{CO})_{10}\text{L}_2$ in the $\nu(\text{CO})$ region (cm^{-1})

Hexane (supersaturated solution)					1,2-Dichloroethane				
PPh_3	$\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$	$\text{P}(p\text{-FC}_6\text{H}_4)_3$	AsPh_3	Diphos	PPh_3	$\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$	$\text{P}(p\text{-FC}_6\text{H}_4)_3$	AsPh_3	Diphos
2069s	2067s	2073	2071s	2071s	2067s	2064s	2070s	2070s	2068s
2044s	2040s	2046s	2046s	2041s	2041s	2038s	2044s	2044s	2039s
2018ms	2016ms	2023ms	2022ms	2021s					
2021m	2011m	2016m	2015m		2012s,br	2010s,br	2016s,br	2012s,br	2013s,br
2002m	2000m	2005ms	2004ms	1997w					1878w
1850mw	1851mw	1849m	1854mw	1854m	1840ms	1837ms	1841ms	1841ms	1840m
1815mw	1814mw	1813m	1816mw	1811m	1818m,sh	1818m,sh	1818m	1817m	1806m

Diphos = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$

Attempts at further substitution of $\text{Rh}_4(\text{CO})_{12}$ in hexane solution using higher mole ratios of triphenylphosphine gave complex mixtures of products as indicated by their i.r. spectra. Two components of these mixtures were the insoluble $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ and a yellow compound which probably resulted from breakdown of the tetrahodium cluster (see later). The use of different solvents, *e.g.* THF,¹¹ benzene, or dichloromethane,¹² in which the disubstituted product is soluble, has however enabled further substitution to be achieved by other workers with the isolation and characterisation of $\text{Rh}_4(\text{CO})_9(\text{PPh}_3)_3$ and $\text{Rh}_4(\text{CO})_8(\text{PPh}_3)_4$.

When similar substitution reactions were attempted with alkyl phosphines, *e.g.* triethylphosphine, i.r. spectra of samples withdrawn from the reaction solutions were consistent with the initial formation of

with bands observed in the spectra of $\text{Rh}_4(\text{CO})_{11}\text{L}$ and presumably result from slow rearrangement in solution to form some of the monosubstituted species. Such a rearrangement may well explain the discrepancy between the i.r. data for $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ reported in this work and that described by Booth *et al.*¹² The $\nu(\text{CO})$ frequencies in the latter paper (measured in dichloromethane) are all 10–15 cm^{-1} higher than those described here for $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ and $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$ (in 1,2-dichloroethane), and this suggests the additional possibility of a calibration error.

In hexane the spectra are considerably more complex than that of the parent $\text{Rh}_4(\text{CO})_{12}$, as would be expected because of the lowering of the molecular symmetry on replacement of one or two carbonyl groups by ligands. There is however a similarity, particularly between the spectra of the monosubstituted derivatives and $\text{Rh}_4(\text{CO})_{12}$ [$\nu(\text{CO})$ 2075vs, 2070vs, 2044s, and 1882s cm^{-1} in hexane]. Thus the very strong doublet at

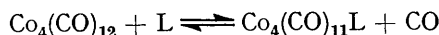
¹¹ P. Chini and S. Martinengo, *Chem. Comm.*, 1969, 1092.

¹² B. L. Booth, M. J. Else, R. Fields, and R. N. Haszeldine, *J. Organometallic Chem.*, 1971, 27, 119.

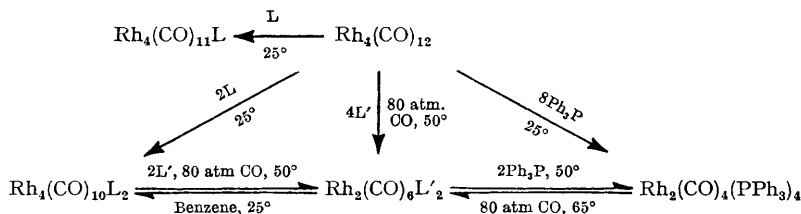
2075, 2070 shifts to *ca.* 2058, 2053 cm^{-1} in $\text{Rh}_4(\text{CO})_{11}\text{L}$ and the bridging carbonyl frequency at 1882 cm^{-1} is split and shifted to *ca.* 1871 and 1850 cm^{-1} . This is very similar to the behaviour observed with the analogous cobalt systems $[\text{Co}_4(\text{CO})_{11}\text{PPh}_3]$ exhibits $\nu(\text{CO})$ frequencies at 2084s, 2045vs, 2039vs, 2030s, 1854.5ms, and 1837.5m cm^{-1} in heptane^{5]} and it seems likely that a similar isomeric species is present.

The spectra of the disubstituted derivatives are very similar to that reported for $\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2$ [$\nu(\text{CO})$ 2060s, 2030s, 2000s, 1830s and 1790s cm^{-1}]. The crystal structure of this compound has been determined¹³ and shown to consist of a tetrahedron of iridium atoms joined by metal-metal bonds in which three basal iridium atoms are additionally supported by bridging carbonyl groups. The triphenylphosphine ligands are bonded to two of the basal iridium atoms and the remainder of the co-ordination sites are occupied by seven terminal carbonyl groups. In view of the close similarity between the i.r. spectra of the disubstituted rhodium and iridium derivatives it seems likely that the rhodium complexes have the same structures and this in turn suggests that initial substitution of $\text{Rh}_4(\text{CO})_{12}$ by a phosphine or arsine ligand occurs at one of the basal rhodium atoms rather than the apical one.

From the study of the reactions of tetracobalt dodecacarbonyl with ligands Cetini *et al.*⁵ demonstrated the presence of an equilibrium system:



For $\text{L} = \text{AsPh}_3$ and SbPh_3 the equilibrium was found to be readily displaced to the left by passage of carbon monoxide through the reaction solution. The corresponding rhodium systems have been investigated for similar behaviour but no evidence has been obtained for reversibility of the formation of either mono- or di-substituted derivatives by treatment with carbon monoxide under ambient conditions. However the reaction of $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$ with carbon monoxide at 80 atm pressure and 150 °C does yield $\text{Rh}_6(\text{CO})_{16}$.



SCHEME $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3, \text{P}(p\text{-FC}_6\text{H}_4)_3$, and $\frac{1}{2}\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. $\text{L}' = \text{PPh}_3, \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

Of greater significance, treatment of hexane suspensions of the disubstituted complexes $\text{Rh}_4(\text{CO})_{10}\text{L}_2$ with carbon monoxide at 80–100 atm pressure and 50 °C affords unstable yellow-brown compounds which have analyses consistent with the formula $[\text{Rh}(\text{CO})_3\text{L}]$, where

$\text{L} = \text{PPh}_3, \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, and $\text{P}(p\text{-FC}_6\text{H}_4)_3$. Highest yields of the products are obtained when the reaction is carried out in the presence of two equivalents of the ligand. The i.r. spectra of these complexes in the carbonyl stretching region (see Table 3) consist pre-

TABLE 3

Infrared spectra of the complexes $\text{Rh}_2(\text{CO})_6\text{L}_2$ in the $\nu(\text{CO})$ region (cm^{-1}) †

PPh_3	$\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$	$\text{P}(p\text{-FC}_6\text{H}_4)_3$
2065vw	2064vw	2052vw
2037w	2033vw	2037vw
2014vw	2013vw	2031vw
2001vw		
1980m,sh	1976m,sh	1987m,sh
1956vs	1953vs	1964vs
1912mw,sh	1910mw,sh	1920mw,sh
1807vw	1800vw	1775vw
1770vw		

† Liquid paraffin mull.

dominantly of one very strong band at *ca.* 1960 cm^{-1} together with shoulders at *ca.* 1980 and 1910 cm^{-1} , an absorption pattern which is very similar to that observed for the dimeric non-bridged phosphine-substituted complexes of dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8\text{L}_2$.¹⁴ The dimeric nature of the latter materials has been confirmed by X-ray analysis of $\text{Co}_2(\text{CO})_8[\text{P}(n\text{-Bu})_3]_2$.^{15,16} By analogy the rhodium complexes described here are formulated as dimeric species and further reactions with additional phosphine support this interpretation. Thus, treatment of hexane suspensions of $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ with two equivalents of triphenylphosphine at 50 °C results in the evolution of two moles of carbon monoxide, the colour of the suspension changes from dark yellow to light yellow, and the complex $\text{Rh}_2(\text{CO})_4(\text{PPh}_3)_4$ may be isolated [$\nu(\text{CO})$ 2018s, 1985vs, 1791s, and 1766vs cm^{-1} , liquid paraffin mull]. This compound has been obtained previously by Wilkinson and his co-workers^{17,18} from the reaction of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ with carbon monoxide and may also be prepared directly from $\text{Rh}_4(\text{CO})_{12}$ by reaction with eight equivalents of triphenylphosphine in paraffin

hydrocarbon solvents. The conversion of $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ into $\text{Rh}_2(\text{CO})_4(\text{PPh}_3)_4$ may be reversed by the reaction of hexane suspensions of the tetrasubstituted compound with carbon monoxide at 50–80 atm pressure and 65 °C.

¹³ V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Comm.*, 1967, 730.

¹⁴ O. Vohler, *Chem. Ber.*, 1958, **91**, 1235.

¹⁵ J. A. Ibers, *J. Organometallic Chem.*, 1968, **14**, 423.

¹⁶ R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316.

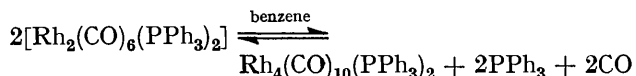
¹⁷ C. O'Connor, G. Yagupsky, D. Evans, and G. Wilkinson, *Chem. Comm.*, 1968, 420.

¹⁸ D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 2660.

These formally disubstituted derivatives of $\text{Rh}_2(\text{CO})_8$ are also present as one component of the mixture obtained when hexane solutions of $\text{Rh}_4(\text{CO})_{12}$ are treated with either three or four equivalents of the phosphine.

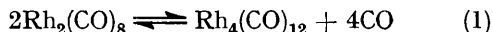
More recent work has shown that the complexes $\text{Rh}_2(\text{CO})_6\text{L}_2$, where $\text{L} = \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$, may also be obtained by the careful addition of hexane solutions of $\text{Rh}_4(\text{CO})_{12}$ to eight equivalents of the ligand in hexane under carbon monoxide at atmospheric pressure; the formation of the complexes $\text{Rh}_2(\text{CO})_4\text{L}_4$ is not observed under these conditions, in contrast to the case of $\text{L} = \text{PPh}_3$. If the same reaction is carried out in the presence of only four equivalents of phosphine the major product is $\text{Rh}_2(\text{CO})_6\text{L}_2$, where $\text{L} = \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$, but this is invariably contaminated with some of the tetranuclear species $\text{Rh}_4(\text{CO})_{10}\text{L}_2$. In contrast, for $\text{L} = \text{PPh}_3$, the reaction product from the addition of $\text{Rh}_4(\text{CO})_{12}$ to four equivalents of this ligand consists of a mixture of $\text{Rh}_4(\text{CO})_{10}\text{L}_2$, $\text{Rh}_2(\text{CO})_4\text{L}_4$, and a small amount of $\text{Rh}_2(\text{CO})_6\text{L}_2$. The factors governing the formation of different products with only small variations in the nature of the phosphine ligand are not clear at this time.

Molecular weight and n.m.r. studies on the complexes $\text{Rh}_2(\text{CO})_6\text{L}_2$ are unfortunately precluded since the compounds are either insoluble or react in the solvents examined. For example, when the yellow complex $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ is stirred in dry benzene or toluene under a carbon monoxide atmosphere it slowly dissolves yielding a red solution, the i.r. spectrum of which corresponds with that of $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$. Thus it seems likely that the reverse of the formation reaction occurs in these solvents, *i.e.*,



The corresponding tri-*p*-tolyl- and tri-*p*-fluorophenylphosphine complexes behave similarly.

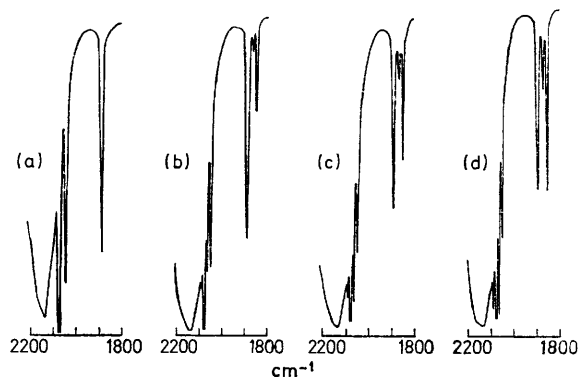
The normal function of phosphine ligands is to stabilise low or unstable oxidation states and thus the corresponding parent carbonyl $\text{Rh}_2(\text{CO})_8$ would be expected to be even less stable with respect to $\text{Rh}_4(\text{CO})_{12}$ and carbon monoxide, *i.e.* the equilibrium (1) should



lie on the right under ambient conditions. The existence of an equilibrium of this sort may well account for the difficulty experienced in characterising dirhodium octacarbonyl, a species which was first claimed in 1943 by Hieber and Lagally¹⁹ to be obtained from the reaction of carbon monoxide on freshly prepared rhodium metal at 460 atm pressure and 200 °C. There has been no subsequent confirmatory evidence to support the existence of this compound and several groups of

workers have unsuccessfully attempted to repeat the original preparation.²⁰ In view of this more recent work it appears that the original claim concerning the isolation of $\text{Rh}_2(\text{CO})_8$ must be seriously in doubt and that the compound is not stable under normal conditions of temperature and pressure. However, there remains the possibility that equilibrium (1) may be displaced to the left under high pressures of carbon monoxide. In order to investigate this possibility we have studied the reactions of paraffin hydrocarbon solutions of $\text{Rh}_4(\text{CO})_{12}$ under pressures of carbon monoxide by following i.r. spectral changes in a high pressure spectrophotometric cell.²¹

Initially the reaction was studied under the high pressures and high temperatures used in the reported preparation of dirhodium octacarbonyl. Under these conditions slow conversion of $\text{Rh}_4(\text{CO})_{12}$ to $\text{Rh}_6(\text{CO})_{16}$ occurred, behaviour which is consistent with the recent



Reaction of $\text{Rh}_4(\text{CO})_{12}$ with carbon monoxide in liquid paraffin-heptane: (a) 490 atm pressure and 20 °C, (b) 460 atm and 4 °C, (c) 445 atm and -7 °C, (d) 430 atm and -19 °C

work of Chini and Martinengo²⁰ on the reactions of $\text{Rh}_4(\text{CO})_{12}$ under pressures of carbon monoxide at elevated temperatures. The hexanuclear species $\text{Rh}_6(\text{CO})_{16}$ is formed in increasing amounts as the reaction temperature is raised above 50 °C.

However, on cooling a liquid paraffin-heptane (3 : 1) solution of $\text{Rh}_4(\text{CO})_{12}$ under 490 atm pressure of carbon monoxide below room temperature additional bands are observed in the spectra as illustrated in the Figure. At 20 °C the normal solution spectrum of $\text{Rh}_4(\text{CO})_{12}$ is observed with absorption maxima at 2076vs, 2071vs, 2045s, and 1883s cm^{-1} ; the strong broad band centred at *ca.* 2150 cm^{-1} is due to dissolved carbon monoxide. At 4 °C [spectrum (b)] additional bands are beginning to appear, increasing in intensity at -7 °C [spectrum (c)], and at -19 °C [spectrum (d)] the intensities of the new bands and those due to the starting $\text{Rh}_4(\text{CO})_{12}$ are approximately the same. This appears to be the limiting spectrum and little change is observed on further cooling. At -30 °C all the bands weaken considerably in intensity presumably due to the insolubility of the

¹⁹ W. Hieber and H. Lagally, *Z. anorg. Chem.*, 1943, **251**, 96.

²⁰ P. Chini and S. Martinengo, *Inorg. Chim. Acta*, 1969, **3**, 21; and references therein.

²¹ W. Rigby, R. Whyman, and K. Wilding, *J. Phys. Sci. Instr.*, 1970, **3**, 572.

compounds at low temperature. The system is completely reversible and warming to room temperature yields only the starting spectrum of $\text{Rh}_4(\text{CO})_{12}$.

The reaction has also been studied at initial carbon monoxide pressures of *ca.* 400, 300, and 200 atm over the same temperature range (20 to -30°). At the lower pressures the new frequencies still appear but are proportionally weaker in intensity; they also increase in relative intensity with decreasing temperature. The pressure dependence of the new bands suggests that the carbon monoxide to rhodium ratio of the species present in solution is increasing with increasing pressure. In addition, the reactions of $\text{Rh}_4(\text{CO})_{12}$ in the absence of carbon monoxide, *e.g.* under pressures of nitrogen, show no new absorptions and no band shifts from the starting $\text{Rh}_4(\text{CO})_{12}$.

Table 4 summarises the accurate band maxima for the new species together with spectra of the related compounds $\text{Co}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$, $\text{Co}_2(\text{CO})_8$, and $\text{HCo}(\text{CO})_4$.

TABLE 4

Metal carbonyl stretching frequencies (cm^{-1}) †					
$\text{Rh}_4(\text{CO})_{12}$	$\text{Co}_4(\text{CO})_{12}$	$\text{Rh}_2(\text{CO})_8$	$\text{Co}_2(\text{CO})_8$		$\text{HCo}(\text{CO})_4$
			Bridged isomer	Non-bridged isomer	
		2086s			2118vw
2076vs 2071vs			2071vs	2069vs	
	2063vs 2055vs	2061s			2052m
2045s			2044vs 2042vs		
	2038m 2028m			2031ms 2022vs	2029s
					1996vw
1883s	1867s	1860mw 1845s	1866sh 1857s		

† Paraffin hydrocarbon solvents.

for comparison. The frequencies and relative intensities of the new bands are very similar to the stronger bands which have been assigned to the spectrum of the bridged isomer of $\text{Co}_2(\text{CO})_8$.²² By analogy it thus seems likely that the high pressure-low temperature spectrum corresponds with the formation of the bridged isomer of dirhodium octacarbonyl.

In the case of the cobalt analogue, $\text{Co}_2(\text{CO})_8$, this species has been shown to exist in solution as a temperature and solvent dependent mixture of bridged and non-bridged isomeric forms.²² The mixture has been estimated to contain 43 and 84% of the bridged form at room temperature and -104°C respectively,²³ low temperatures stabilising the bridged isomer. By contrast, in the $\text{Rh}_2(\text{CO})_8$ case, no evidence has been obtained for the formation of a non-bridged isomer when the system is allowed to warm to room temperature, although the presence of the additional

spectrum of $\text{Rh}_4(\text{CO})_{12}$ is a complicating factor which could obscure small spectral changes. Even so, this result seems rather surprising in view of the general tendency favouring the formation of direct (*i.e.* non-bridged) metal-metal bonded isomers on progressing from the first to second and third row transition-metal carbonyls.²⁴

In addition, no evidence has been obtained for the formation of rhodium tetracarbonyl hydride, $\text{HRh}(\text{CO})_4$ (a compound which was also claimed by Hieber and Lagally¹⁹) when the pressure of the $\text{Rh}_4(\text{CO})_{12}$ - $\text{Rh}_2(\text{CO})_8$ system is increased with hydrogen at -19°C . However the peaks at 2071 and 2045 cm^{-1} due to $\text{Rh}_4(\text{CO})_{12}$ could overlap with the band positions expected for $\text{HRh}(\text{CO})_4$ [*ca.* 2068m, 2045s cm^{-1} , estimated by comparison with the terminal carbonyl stretching frequencies of $\text{Co}_2(\text{CO})_8$, $\text{Rh}_2(\text{CO})_8$, and $\text{HCo}(\text{CO})_4$] and hence the presence of small amounts of the hydrido-species would be obscured. If a pure spectrum of $\text{Rh}_2(\text{CO})_8$ uncontaminated by $\text{Rh}_4(\text{CO})_{12}$ could be obtained then spectral measurements of the reaction with hydrogen should be more conclusive.

Conclusion.—Dependent upon the reaction conditions, treatment of $\text{Rh}_4(\text{CO})_{12}$ with phosphines yields both tetranuclear and dinuclear phosphine-substituted derivatives. At low degrees of phosphine substitution the dinuclear species appear unstable with respect to the tetranuclear derivatives and loss of carbon monoxide. This behaviour is consistent with the difficulties previously experienced by various groups of workers in characterising the unsubstituted parent carbonyl, $\text{Rh}_2(\text{CO})_8$, and with our present i.r. spectral results demonstrating that this species may only be observed under high pressures of carbon monoxide and at low temperatures.

EXPERIMENTAL

All manipulations were performed under an atmosphere of dry nitrogen except where stated otherwise.

The ligands were normally recrystallised before use and solvents dried over sodium and presaturated with dry nitrogen.

Microanalyses for carbon, hydrogen, phosphorus, arsenic, and fluorine were performed by Mr. C. E. O'Brien.

Infrared spectra were recorded with a Perkin-Elmer model 257 spectrophotometer using $\times 10$ scale expansion and calibration with gaseous carbon monoxide. Details of the high pressure spectrophotometric cell have been described previously.²¹

Measurements of the amount of carbon monoxide evolved in the reactions were obtained in a gas burette of the usual type. The reaction was carried out by the addition of a hexane solution of the phosphine in a small tube to the $\text{Rh}_4(\text{CO})_{12}$ solution. The amount of $\text{Rh}_4(\text{CO})_{12}$ used was generally *ca.* 0.15 g giving an evolution of *ca.* 5 ml per mole of carbon monoxide.

Undecacarbonyl(triphenylphosphine)tetrarhodium.— Triphenylphosphine (0.13 g) in hexane (10 ml) was added

²² K. Noack, *Spectrochim. Acta*, 1963, **19**, 1925; G. Bor, *ibid.*, p. 2065.

²³ K. Noack, *Helv. Chim. Acta*, 1964, **47**, 1064.

²⁴ F. Calderazzo, R. Ercoli, and G. Natta, 'Organic Syntheses via Metal Carbonyls,' eds. I. Wender and P. Pino, Interscience-Wiley, 1968, vol. 1.

dropwise to a rapidly stirred solution of $\text{Rh}_4(\text{CO})_{12}$ (0.38 g) [*i.e.* $\text{Ph}_3\text{P}:\text{Rh}_4(\text{CO})_{12} = 1:1$] in hexane (100 ml). The colour of the solution deepened from orange-red to dark red during the addition and 1.1 mol of carbon monoxide were evolved per mol of $\text{Rh}_4(\text{CO})_{12}$. The volume of the solution was reduced to *ca.* 80 ml and the dark red compound $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$ (0.14 g) crystallised from the reaction mixture when set aside overnight at 0 °C; it was washed with hexane and dried *in vacuo* (Found: C, 35.4; H, 1.55; P, 3.5. $\text{C}_{29}\text{H}_{15}\text{O}_{11}\text{PRh}_4$ requires C, 35.45; H, 1.5; P, 3.2%). The mother liquor was further reduced in volume and a second crop of crystals (0.15 g) was isolated. An i.r. spectrum of this product suggested that it was predominantly $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$ contaminated with a small amount of the disubstituted derivative.

Undecacarbonyl(tri-p-tolylphosphine)tetrarhodium.—Tri-*p*-tolylphosphine (0.20 g) in hexane (80 ml) was added dropwise to $\text{Rh}_4(\text{CO})_{12}$ (0.45 g) in hexane (80 ml). Carbon monoxide (0.95 mol) was evolved and the dark red compound $\text{Rh}_4(\text{CO})_{11}\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$ (0.26 g) crystallised slowly at 0 °C; it was washed with hexane and dried *in vacuo* (Found: C, 37.4; H, 2.7; P, 3.2. $\text{C}_{32}\text{H}_{21}\text{O}_{11}\text{PRh}_4$ requires C, 37.5; H, 2.05; P, 3.0%).

Undecacarbonyl(tri-p-fluorophenylphosphine)tetrarhodium.—Tri-*p*-fluorophenylphosphine (0.16 g) in hexane (20 ml) was added dropwise to $\text{Rh}_4(\text{CO})_{12}$ (0.38 g) in hexane (100 ml) and the complex $\text{Rh}_4(\text{CO})_{11}\text{P}(p\text{-FC}_6\text{H}_4)_3$ (0.23 g) was isolated as above as dark red crystals (Found: C, 33.9; H, 1.1; F, 5.5; P, 3.3. $\text{C}_{29}\text{H}_{12}\text{F}_3\text{O}_{11}\text{PRh}_4$ requires C, 33.7; H, 1.2; F, 5.5; P, 3.0%).

Undecacarbonyl(triphenylarsine)tetrarhodium.—Triphenylarsine (0.15 g) in hexane (20 ml) was added dropwise to $\text{Rh}_4(\text{CO})_{12}$ (0.38 g) in hexane (100 ml) and the dark red product $\text{Rh}_4(\text{CO})_{11}\text{AsPh}_3$ (0.22 g) was isolated as above (Found: C, 33.8; H, 1.3; As, 7.2. $\text{C}_{29}\text{H}_{15}\text{AsO}_{11}\text{Rh}_4$ requires C, 33.9; H, 1.5; As, 7.3%).

Decacarbonylbis(triphenylphosphine)tetrarhodium.—Triphenylphosphine (0.18 g) in hexane (20 ml) was added dropwise to a rapidly stirred solution of $\text{Rh}_4(\text{CO})_{12}$ (0.26 g) [*i.e.* $\text{Ph}_3\text{P}:\text{Rh}_4(\text{CO})_{12} = 2:1$] in hexane (75 ml). The colour of the solution deepened to very dark red, 2.0 mol of carbon monoxide were evolved and the dark red compound $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ (0.30 g) crystallised almost immediately; it was washed with hexane and dried *in vacuo* (Found: C, 45.6; H, 2.4; P, 5.0. $\text{C}_{46}\text{H}_{30}\text{O}_{10}\text{P}_2\text{Rh}_4$ requires C, 45.4; H, 2.5; P, 5.1%).

Decacarbonylbis(tri-p-tolylphosphine)tetrarhodium.—Tri-*p*-tolylphosphine (0.31 g) in hexane (50 ml) was added dropwise to a rapidly stirred solution of $\text{Rh}_4(\text{CO})_{12}$ (0.38 g) in hexane (75 ml). The dark red complex $\text{Rh}_4(\text{CO})_{10}[\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3]_2$ (0.23 g) separated rapidly from solution; it was washed with hexane and dried *in vacuo* (Found: C, 48.5; H, 3.5; P, 5.1. $\text{C}_{52}\text{H}_{42}\text{O}_{10}\text{P}_2\text{Rh}_4$ requires C, 48.0; H, 3.2; P, 4.8%).

Decacarbonylbis(tri-p-fluorophenylphosphine)tetrarhodium.—Tri-*p*-fluorophenylphosphine (0.32 g) in hexane (25 ml) was added dropwise to $\text{Rh}_4(\text{CO})_{12}$ (0.38 g) in hexane (100 ml) and the dark red complex $\text{Rh}_4(\text{CO})_{10}[\text{P}(p\text{-FC}_6\text{H}_4)_3]_2$ (0.39 g) was isolated as above (Found: C, 41.9; H, 2.0; F, 8.5; P, 4.9. $\text{C}_{46}\text{H}_{24}\text{F}_6\text{O}_{10}\text{P}_2\text{Rh}_4$ requires C, 41.7; H, 1.8; F, 8.6; P, 4.7%).

Decacarbonylbis(triphenylarsine)tetrarhodium.—Triphenylarsine (0.31 g) in hexane (25 ml) was added dropwise to $\text{Rh}_4(\text{CO})_{12}$ (0.38 g) in hexane (100 ml) and the dark red product $\text{Rh}_4(\text{CO})_{10}(\text{AsPh}_3)_2$ (0.49 g) was isolated as above

(Found: C, 42.3; H, 2.3; As, 10.9. $\text{C}_{46}\text{H}_{30}\text{As}_2\text{O}_{10}\text{Rh}_4$ requires C, 42.4; H, 2.3; As, 11.5%).

Decacarbonyl(1,2-bisdiphenylphosphinoethane)tetrarhodium.—1,2-Bisdiphenylphosphinoethane (0.13 g) in hexane (40 ml) was added dropwise to a rapidly stirred solution of $\text{Rh}_4(\text{CO})_{12}$ (0.24 g) in hexane (90 ml). After filtration to remove a small amount of brown material the dark red compound $\text{Rh}_4(\text{CO})_{10}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (0.28 g) crystallised from the mixture when it was set aside at 0 °C overnight; it was washed with hexane and dried *in vacuo* (Found: C, 39.8; H, 2.2; P, 6.2. $\text{C}_{38}\text{H}_{24}\text{O}_{10}\text{P}_2\text{Rh}_4$ requires C, 39.6; H, 2.2; P, 5.7%).

Hexacarbonylbis(triphenylphosphine)dirrhodium.—(a) From $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$. A mixture of $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ (0.32 g), triphenylphosphine (0.14 g), and hexane (50 ml) in a glass liner was treated with carbon monoxide (80 atm) in a small autoclave at 50 °C for 7 h. After cooling and venting the excess pressure, the contents of the glass liner, a dark yellow solid in a pale orange solution, were transferred to a Schlenk tube under a carbon monoxide atmosphere, filtered, and the yellow compound $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ (0.40 g) washed with hexane and dried in a carbon monoxide stream (Found: C, 55.8; H, 3.3; P, 7.05. $\text{C}_{42}\text{H}_{30}\text{O}_6\text{P}_2\text{Rh}_2$ requires C, 56.1; H, 3.3; P, 6.9%).

(b) Directly from $\text{Rh}_4(\text{CO})_{12}$. Triphenylphosphine (0.70 g) in hexane (10 ml) was added to $\text{Rh}_4(\text{CO})_{12}$ (0.50 g) in carbon monoxide-saturated hexane (60 ml) in a glass liner. After treatment of the resulting brown mixture with carbon monoxide (80 atm) at 50 °C for 4 h the contents of the glass liner were transferred to a Schlenk tube and $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ (0.95 g) was isolated as above. Infrared spectra of the samples prepared by the two methods were identical.

Hexacarbonylbis(tri-p-tolylphosphine) dirrhodium.—Tri-*p*-tolylphosphine (0.82 g) in hexane (15 ml) was added to $\text{Rh}_4(\text{CO})_{12}$ (0.5 g) in hexane (60 ml) and the mixture was treated with carbon monoxide (80 atm) at 50 °C for 4 h. The dark yellow compound $\text{Rh}_2(\text{CO})_6[\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3]_2$ (1.06 g) was isolated in a Schlenk tube as above (Found: C, 58.3; H, 4.4; P, 6.3. $\text{C}_{48}\text{H}_{42}\text{O}_6\text{P}_2\text{Rh}_2$ requires C, 58.7; H, 4.3; P, 6.3%).

Hexacarbonylbis(tri-p-fluorophenylphosphine)dirrhodium.—Tri-*p*-fluorophenylphosphine (0.85 g) in hexane (15 ml) was added to $\text{Rh}_4(\text{CO})_{12}$ (0.5 g) in hexane (60 ml) and the brown mixture was treated with carbon monoxide (75 atm) at 50 °C for 5 h. The orange-yellow compound $\text{Rh}_2(\text{CO})_6[\text{P}(p\text{-FC}_6\text{H}_4)_3]_2$ (1.12 g) was isolated in a Schlenk tube as above (Found: C, 50.3; H, 2.4; P, 6.1. $\text{C}_{42}\text{H}_{24}\text{F}_6\text{O}_6\text{P}_2\text{Rh}_2$ requires C, 50.1; H, 2.4; P, 6.2%).

Tetracarbonyltetrakis(triphenylphosphine)dirrhodium.—(a) From $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$. Triphenylphosphine (0.13 g) in hexane (20 ml) was added to a suspension of $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ (0.23 g) in hexane (30 ml) in a Schlenk tube and the mixture was stirred for 3 h under a carbon monoxide atmosphere at 50 °C, during which time the suspension became a much lighter yellow in colour. After filtration the yellow complex $\text{Rh}_2(\text{CO})_4(\text{PPh}_3)_4$ (0.16 g) was washed with hexane and dried under a stream of carbon monoxide. An i.r. spectrum of this product [$\nu(\text{CO})$ 2018s, 1985vs, 1791s, 1766vs cm^{-1} , liquid paraffin mull] was identical with that reported for $\text{Rh}_2(\text{CO})_4(\text{PPh}_3)_4$.^{17,18}

(b) Directly from $\text{Rh}_4(\text{CO})_{12}$. $\text{Rh}_4(\text{CO})_{12}$ (0.37 g) in carbon monoxide-saturated hexane (50 ml) was added dropwise to a rapidly stirred solution of triphenylphosphine (1.05 g) in hexane (50 ml) in a Schlenk tube under a carbon

monoxide atmosphere. The light yellow complex $\text{Rh}_2(\text{CO})_4(\text{PPh}_3)_4$ (0.64 g) which precipitated was filtered, washed with hexane, dried under carbon monoxide, and identified by its i.r. spectrum.

Reaction of Tetracarbonyltetrahis(triphenylphosphine)dirhodium with Carbon Monoxide.—A suspension of $\text{Rh}_2(\text{CO})_4(\text{PPh}_3)_4$ (0.32 g) in hexane (70 ml) contained in a glass liner was treated with carbon monoxide (80 atm) at 65 °C for 12 h. After cooling and venting the excess of pressure the contents of the liner were transferred to a Schlenk tube and the dark yellow complex $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ (0.21 g) was filtered off, washed with hexane, and dried under a carbon monoxide atmosphere. An i.r. spectrum of this product was identical with that of a sample of $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ prepared by the previously described methods.

Reaction of Hexacarbonylbis(triphenylphosphine)dirhodium with Benzene.—A suspension of $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ (0.21 g) in benzene (20 ml) was stirred under a carbon monoxide atmosphere for 2 h. The solution turned red as the yellow solid dissolved. The clear red solution was reduced in volume to ca. 10 ml and hexane (20 ml) was slowly added when the dark red complex $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ (0.12 g) separated; it was filtered off, washed with hexane, and dried *in vacuo*. An i.r. spectrum of this product was identical with that of an authentic sample of $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$.

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