Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

METAL CARBONYL CHEMISTRY
XIV*. REACTIONS OF RHODIUM CARBONYLS WITH LIGANDS

B. L. BOOTH, M. J. ELSE, R. FIELDS AND R. N. HASZELDINE

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD (Great Britain)

(Received September 11th, 1970)

SUMMARY

Dodecacarbonyltetrarhodium [$Rh_4(CO)_{12}$] reacts with phosphine and phosphite ligands under an atmosphere of nitrogen to give the compounds $Rh_4(CO)_{10}L_2$, $Rh_4(CO)_9L_3$ and $Rh_4(CO)_8L_4$ [where L = Ph_3P or $P(OCH_2)_3CEt$ (ETPO)**] in which the metal atom cluster is retained. Under similar conditions hexadecacarbonylhexarhodium [$Rh_6(CO)_{16}$] reacts with Ph_3P, $P(OCH_2)_3CEt$ or $P(OMe)_3$ to give complexes of the type $Rh_6(CO)_{10}L_6$. When the reaction of either $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$ with the ligands Ph_3P or Ph_3As is carried out in the presence of carbon monoxide, breakdown of the metal clusters occurs to give the bridged compounds $L_2(CO)Rh(CO)_2Rh(CO)L_2$ (where L = Ph_3P or Ph_3As) in high yields; reaction of $Rh_4(CO)_{12}$ with n-Bu_3P under similar conditions gives the compound [(n-$Bu_3P)_3$-$(CO)Rh]_2$. Dodecacarbonyltetrarhodium has also been shown to react with PhC_2Ph or $CF_3C_2CF_3$ to give the compounds $Rh_4(CO)_{10}(RC_2R)$ (R = CF_3 or Ph).

Some of these ligand-substituted rhodium carbonyls have been shown to be extremely active hydroformylation catalysts for 1-alkenes.

INTRODUCTION

Phosphorus- and arsenic-containing ligands have recently been reported to react with the polynuclear metal carbonyls $Co_4(CO)_{12}$[2], $Fe_3(CO)_{12}$[3], $Ru_3(CO)_{12}$[4], $Os_3(CO)_{12}$[5] and $Ir_4(CO)_{12}$[6] to give substitution products in which the basic structure of the parent cluster carbonyl is retained. With carbon monoxide, however, the carbonyls $Co_4(CO)_{12}$[7], $Co_6(CO)_{16}$[8], $Ru_3(CO)_{12}$[9], and phosphine-substituted ruthenium or osmium dodecacarbonyls[9] form simpler mononuclear or dinuclear carbonyls by breakdown of the metal atom cluster. We report here some substitution reactions of dodecacarbonyltetrarhodium and hexadecacarbonylhexarhodium with phosphine and phosphite ligands and with alkynes in which the metal atom cluster is either retained or broken down depending on the reaction conditions.

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* For Part XIII see ref. 1.

** ETPO = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

RESULTS AND DISCUSSION

Reaction of dodecacarbonyltetrarhodium with triphenylphosphine (molar ratio 1/4) in benzene at room temperature either in a sealed tube or in a closed system connected to a gas burette gave, as the major products, a mixture of the di- and tri-substituted tetrarhodium compounds and an unidentified yellow solid; it is noteworthy that during this reaction carbon monoxide was rapidly evolved during the initial stages of the reaction but was re-absorbed as reaction progressed. Although the yellow solid could not be obtained in a pure state, micro-analysis and the IR spectrum of a solution in CH_2Cl_2 [single ν(CO) band at 1970 cm^{-1}] suggest that it may be $[Rh(CO)_3PPh_3]_2$, which has recently been reported[10] as a yellow solid [ν(CO) (KBr disc) 1954 vs, 1979 s(sh) cm^{-1}].

In order to prevent the apparent reaction of the phosphine-substituted cluster compounds with the carbon monoxide displaced during the reaction, dodecacarbonyltetrarhodium was treated with triphenylphosphine under a stream of nitrogen, and in this way the di-, tri-, and tetra-substituted tetrarhodium compounds were obtained, depending on the conditions. Reaction in hexane using $Rh_4(CO)_{12}$ and PPh_3 in a 1/2 molar ratio at room temperature gave a 91% yield of pure disubstituted compound, $Rh_4(CO)_{10}(PPh_3)_2$, which has been reported, although without experimental detail, in a recent communication[10]. The di-substituted derivative is insoluble in hexane and further reaction is thus avoided. The tri-substituted tetrarhodium compound, $Rh_4(CO)_9(PPh_3)_3$, was obtained in almost quantitative yield by the reaction of $Rh_4(CO)_{10}(PPh_3)_2$ with triphenylphosphine in dichloromethane at room temperature. Further substitution did not occur readily at room temperature, but the reaction of dodecacarbonyltetrarhodium with triphenylphosphine (molar ratio 1/4) in benzene at 70–80° gave a low yield of the tetra-substituted complex.

When the reaction of $Rh_4(CO)_{12}$ with an excess of PPh_3 was carried out at room temperature in a stream of carbon monoxide breakdown of the metal atom cluster occurred to give an almost quantitative yield of tetrakis(triphenylphosphine)-dicarbonyl-μ-dicarbonyldirhodium, $(Ph_3P)_2(CO)Rh(CO)_2Rh(CO)(PPh_3)_2$, which has been independently prepared[11,12] from $HRh(CO)(PPh_3)_3$ and carbon monoxide. This bridged compound is unstable in the solid state under nitrogen or *in vacuo* giving an air-stable yellow solid [ν(CO) 1970 s cm^{-1}], from which $[Rh(CO)_2(PPh_3)_2]_2$ may be regenerated by passage of carbon monoxide through a solution in acetone or benzene. This compound is obviously quite different from the deep red compound ($\bar{\nu}$ 1980 s, 1740 s in CH_2Cl_2, 1765 w, 1739 s in solid state) reported[12] to be formed when $[Rh(CO)_2(PPh_3)_2]_2$ decomposes in solution. When a stream of hydrogen was passed through a benzene slurry of the yellow $[(Ph_3P)_2(CO)_2Rh]_2$, a deep red solution which showed a single ^1H NMR absorption characteristic of a Rh–H bond (τ 19.34) was formed, and the yellow crystals of the dimer were regenerated on passage of carbon monoxide through the solution. These observations are in accord with the existence in solution of equilibria between the carbonyl-bridged dimer and rhodium hydride species, as Wilkinson has suggested previously[12], but the colour change on passage of hydrogen through the slurry of the dimer in benzene is markedly different from that reported by Wilkinson for hexane solutions.

The reaction of dodecacarbonyltetrarhodium with triphenylarsine in the presence of an excess of carbon monoxide similarly gave tetrakis(triphenylarsine)dicarbonyl-μ-dicarbonyldirhodium, $(Ph_3As)_2(CO)Rh(CO)_2Rh(CO)(AsPh_3)_2$. When hydrogen was bubbled through a benzene solution of this compound a colour change from yellow to deep red was observed as with the analogous phosphine compound, and the yellow dimer was regenerated when carbon monoxide was bubbled through the red solution. Reaction of $Rh_4(CO)_{12}$ with tri-n-butylphosphine and carbon monoxide gave a yellow oil, having a similar IR spectrum to those of the phosphine and arsine dimers, but it could not be purified and further displacement of carbon monoxide during work-up *in vacuo* gave hexakis(tri-n-butylphosphine)dicarbonyldirhodium, $[(n\text{-}Bu_3P)_3CORh]_2$ identified by micro-analysis, and showing no bridging, and only a single terminal carbonyl stretching frequency.

Reaction of dodecacarbonyltetrarhodium with 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane gave only the di-, tri- and tetra-substituted tetrarhodium carbonyl compounds, depending upon the conditions employed. No breakdown of the metal cluster was observed even when these reactions were carried out in the presence of carbon monoxide, suggesting that breakdown of the metal atom cluster occurs only when strong σ-donor ligands are used in the presence of carbon monoxide.

The reaction of hexadecacarbonylhexarhodium with triphenylphosphine at 70° in benzene in a sealed tube gave a small amount of a compound thought to be $Rh_6(CO)_{10}(PPh_3)_6$, but a pure sample could not be obtained. When this reaction was carried out at a lower temperature in the presence of an excess of carbon monoxide, a 91% yield of the carbonyl-bridged dimer, $[Rh(CO)_2(PPh_3)_2]_2$, was obtained; triphenylarsine similarly gave a good yield of the corresponding arsine compound under comparable conditions. When the reaction with triphenylphosphine was carried

TABLE 1

CARBONYL STRETCHING FREQUENCIES FOR RHODIUM COMPLEXES[a]

Compound	ν(CO) terminal (cm^{-1})	ν(CO) bridging (cm^{-1})
$Rh_4(CO)_{12}$[b]	2089 s(sh), 2079 s, 2056 s(sh), 2043 (sh), 2035 s, 1919 m	1875 s
$Rh_4(CO)_{10}(PPh_3)_2$	2096 m, 2078 s, 2065 s(sh), 2052 s, 2024 s	1854 s, 1830 s
$Rh_4(CO)_9(PPh_3)_3$	2076 vs, 2049 vs, 2020 vs, 1992 vs	1851 s, 1827 s
$Rh_4(CO)_8(PPh_3)_4$[c]	2010 m, 1995 vs, 1990 vs, 1971 s, 1965 (sh)	1793 s, 1790 s
$Rh_4(CO)_{10}(ETPO)_2$[d,e]	2083 w, 2070 w, 2053 s, 2028 s	1898 w, 1866 s, 1835 s
$Rh_4(CO)_9(ETPO)_3$[d]	2085 m, 2060 s, 2040 s, 2024 s	1848 s
$Rh_4(CO)_8(ETPO)_4$[d]	2040 (sh), 2012 s, 1998 s	1825 s
$[Rh(CO)_2(PPh_3)_2]_2$[c]	2018 s, 1988 vs	1798 s, 1774 vs
$[Rh(CO)_2(AsPh_3)_2]_2$[c]	2024 s, 2012 w(sh), 1992 vs	1799 s, 1789 w(sh), 1775 vs
$Rh_6(CO)_{16}$[b]	2073 vs, 2026 s	1800 vs
$Rh_6(CO)_{10}(PPh_3)_6$	1984 s, 1965 s, 1938 m	1779 s
$Rh_6(CO)_{10}(ETPO)_6$[d]	2062 s, 2057 s, 2027 vs	1763 vs
$Rh_6(CO)_{10}[P(OMe)_3]_6$	2081 s, 2053 s, 2026 s	1765 s
$Rh_4(CO)_{10}(PhC_2Ph)$[f]	2087 s, 2068 vs, 2056 vs, 2043 vs, 2016 vs	1845 s, 1825 s
$Rh_4(CO)_{10}(CF_3C_2CF_3)$	2090 vs, 2085 vs, 2070 s, 2047 s	1910 s

[a] In CH_2Cl_2 solution. [b] See ref. 18. [c] Nujol mull. [d] ETPO = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane. [e] Contains also $Rh_4(CO)_{12}$ and/or $Rh_4(CO)_{11}$ETPO. [f] In hexane solution.

out in chloroform a high yield of chlorocarbonylbis(triphenylphosphine)rhodium was obtained. Under these conditions hexadecacarbonylhexarhodium is inert to chloroform, and even to bromine in chloroform solution, indicating that breakdown of the cluster must take place by the intermediate formation of a phosphine-substituted compound $Rh_6(CO)_{16-n}(PPh_3)_n$ which is then oxidised by the chloroform.

The phosphites, $P(OCH_2)_3CEt$ and $P(OMe)_3$, react far more readily with $Rh_6(CO)_{16}$ than the ligands described above to give hexasubstituted complexes in high yields; the compound from $(MeO)_3P$ could not be obtained analytically pure and was identified by IR spectroscopy only. The IR spectra of these compounds show only three terminal and one bridging carbonyl bands (Table 1), suggesting that the three compounds have similar symmetrical structures in which one terminal carbonyl group on each rhodium atom of the cluster has been replaced.

The reactions of dodecacarbonyltetrarhodium with alkynes were in general more complicated, and isolation of pure compounds was more difficult than in those with the phosphorus compounds. Analytically pure samples were obtained only for the compounds $Rh_4(CO)_{10}L$ ($L = PhC_2Ph$ or $CF_3C_2CF_3$); other alkynes investigated (EtC_2Et, $MeO_2CC_2CO_2Me$ and PhC_2H) all displaced carbon monoxide readily at room temperature but the products could not be separated. It is interesting that the reaction with diphenylacetylene gave, in addition to the monosubstituted tetrarhodium carbonyl, low yields of $Rh_6(CO)_{16}$, and a product believed to be either $Rh_6(CO)_{15}PhC_2Ph$ or $Rh_6(CO)_{14}PhC_2Ph$.

Hydroformylation reactions

Hydroformylation reactions with rhodium carbonyl catalysts have been shown to take place more readily than with cobalt catalysts, but the straight/branched chain aldehyde product ratios are usually disappointingly low[13]. There have been several recent claims[14] that the use of soluble rhodium catalysts formed by interaction of rhodium metal or a rhodium salt with donor ligands such as phosphines or phosphites under hydroformylation conditions improves the straight/branched chain aldehyde ratio, although in the majority of these reactions the nature of the catalyst is uncertain.

We have investigated the hydroformylation of a number of alkenes using $Rh_4(CO)_{12}$ (Table 2) or $Rh_6(CO)_{16}$ (Table 3) as catalysts, and have compared the results from these reactions with reactions in which these catalysts have been used in the presence of phosphine or phosphite ligands under conditions where significant amounts of the compounds $Rh_4(CO)_{10}L_2$ or $Rh_6(CO)_{10}L_6$ would be formed initially (Tables 2 and 3). Under the conditions employed in this work no marked improvement of the straight/branched chain aldehyde ratio was observed upon carrying out the hydroformylation reactions in the presence of donor ligands. The rates of hydroformylation appeared to be similar, based on yields, for $Rh_4(CO)_{12}$ alone and in the presence of the ligands, but the presence of the ligand with $Rh_6(CO)_{16}$ increased the rate almost twofold. Similarly, the hydroformylation of propene catalysed either by the yellow compound, believed to be $Rh_2(CO)_6(PPh_3)_2$ (see above) or the well-defined compound $Rh_4(CO)_8(ETPO)_4$ gave no significant improvement of the product ratio over that obtained using $Rh_4(CO)_{12}$ (Table 2).

The ready loss and uptake of carbon monoxide by the carbonyl-bridged dimer $[(Ph_3P)_2Rh(CO)_2]_2$ and its transformation by passage of hydrogen into a hydride species suggested that it might form a useful hydroformylation catalyst under very

TABLE 2

HYDROFORMYLATION OF ALKENES WITH $Rh_4(CO)_{12}$ ALONE[a] AND IN THE PRESENCE OF PHOSPHORUS-CONTAINING LIGANDS[b]

Catalyst	Ligand	Alkene	Aldehyde yield (%)[c]	Aldehyde product ratio[d]	Alkane yield (%)[c]
$Rh_4(CO)_{12}$		Ethylene	89		
	ETPO[e]		97		
	PPh_3[e]		97		
	$P(n\text{-}Bu)_3$		96		
$Rh_4(CO)_{12}$		Propene	92	1.04	7.3
	ETPO[f]		89	1.07	
	PPh_3		98	1.04	
	$P(n\text{-}Bu)_3$		93	1.09	
$Rh_2(CO)_6(PPh_3)_2$[g,h]			93	1.10	
$Rh_4(CO)_8(ETPO)_4$[h]			90	1.10	
$Rh_4(CO)_{12}$		1-Butene	92	1.59	1.6
	ETPO		90	1.36	1.5
	PPh_3		97	2.1	2.1
$Rh_4(CO)_{12}$		*cis*-2-Butene	93	0.003	1.4
	ETPO		89	0.006	
	PPh_3		95	0.011	
$Rh_4(CO)_{12}$		*trans*-2-Butene	92	0.007	1.0
	ETPO		95	0.006	
	PPh_3		95	0.010	

[a] $Rh_4(CO)_{12}$ (0.0013 mmole), pentane (30 ml), olefin (0.20 mmole), CO/H_2 (120 atm, 1/1) at 70° for 3 h. [b] $Rh_4(CO)_{12}$ (0.0013 mmole), ligand (0.0053 mmole), pentane (30 ml), olefin (0.20 mmole), CO/H_2 (120 atm, 1/1) at 70° for 3 h. [c] Based on olefin taken. [d] Straight/branched aldehyde ratio. [e] 1.0% of alcohol also formed. [f] 3.3% of alcohol also formed. [g] This compound has not been obtained analytically pure. [h] With benzene (30 ml) solvent.

TABLE 3

HYDROFORMYLATION OF ALKENES WITH $Rh_6(CO)_{16}$ ALONE[a] AND IN THE PRESENCE OF PHOSPHORUS-CONTAINING LIGANDS[b]

Catalyst	Ligand	Alkene	Yield[c] (%)	Aldehyde product ratio[d]
$Rh_6(CO)_{16}$		Ethylene	50	
	ETPO		91	
	PPh_3		93	
	$P(n\text{-}Bu)_3$		91	
$Rh_6(CO)_{16}$		Propene	51	1.02
	ETPO		93	1.18
	PPh_3		96	1.17
	$P(n\text{-}Bu)_3$		92	1.07
$Rh_6(CO)_{16}$		1-Butene	49	1.53
		cis-2-Butene	46	0.002
		trans-2-Butene	42	0.004

[a] $Rh_5(CO)_{16}$ (0.0009 mmole), benzene (30 ml), olefin (0.20 mmole), CO/H_2 (120 atm, 1/1) at 70° for 3 h. [b] $Rh_6(CO)_{16}$ (0.0009 mmole), benzene (30 ml), ligand (0.0054 mmole), olefin (0.20 mmole), CO/H_2 (120 atm, 1/1) at 70° for 3 h. [c] Based on olefin taken. [d] Straight/branched aldehyde ratio.

mild conditions. While this work was in progress, Wilkinson[15] reported his independent work on this reaction, in which the compounds $RhH(CO)(PPh_3)_3$ or $RhCl(CO)(PPh_3)_2$ were used as a source of the hydride, $RhH(CO)(PPh_3)_2$, which is itself converted to the carbonyl-bridged dimer by carbon monoxide. The compound $RhH(CO)(PPh_3)_3$ and an excess of olefin were treated in a static system at 25° and 1 atm with carbon monoxide and hydrogen to give essentially quantitative yields of aldehydes (based on rhodium complex) with a high preference for the straight-chain isomer. Our results using 1-hexene and $[(Ph_3P)_2(CO)_2Rh]_2$ are broadly similar (Table 4). We have used this compound directly in a low ratio to olefin in a system where it functions as a true catalyst, being regenerated *in situ* by either alternate or simultaneous passage of carbon monoxide and hydrogen through the olefin solution. Under these conditions, the yields of aldehyde based on olefin are high, with a high preference for the straight-chain isomer, and exceeded 16 moles per mole of catalyst, although no attempts have been made to find the optimum yield on this basis. With

TABLE 4

HYDROFORMYLATION WITH TETRAKIS(TRIPHENYLPHOSPHINE)DICARBONYL-μ-DICARBONYLDIRHODIUM[a]

Time (h)	Method A[b]		Method B[c]	
	Yield[d] (%)	Product ratio[e]	Yield[d] (%)	Product ratio[e]
1	21	16.4	22	10.5
2	40	15.8	27	9.9
3	57	15.4	40	10.2
4	71	15.2	50	9.9
5	82	15.1	58	9.7
6	92	15.1	65	9.7
8.5			73	9.9

[a] At 20°, 1 atm. [b] CO (7 ml·min^{-1}) and H_2 (7 ml·min^{-1}) passed alternately through the solution. [c] CO and H_2 (7 ml·min^{-1} each) passed simultaneously through the solution. [d] Based on initial 1-hexene. [e] Straight/branched chain aldehyde.

TABLE 5

HYDROFORMYLATION WITH TETRAKIS(TRIPHENYLARSINE)DICARBONYL-μ-DICARBONYLDIRHODIUM[a]

Time (h)	Method A[b]		Method B[c]	
	Yield (%)[d]	Product ratio[e]	Yield (%)[d]	Product ratio[e]
2	18	24.6	38	20.2
3	26	22.7	53	20.1
4	34	23.5	60	20.3
5	46	24.5	70	19.5
5.5	51	24.6	72	19.7

[a] At 20°, 1 atm. [b] CO (7 ml·min^{-1}) and H_2 (7 ml·min^{-1}) passed alternately through the solution. [c] CO and H_2 (7 ml·min^{-1} each) passed simultaneously through the solution. [d] On initial 1-hexene. [e] Straight/branched chain aldehyde.

the triphenylarsine complex, $[(Ph_3As)_2(CO)_2Rh]_2$, the preference for the formation of the straight-chain isomer is even more marked (Table 5), but since the dimer is more soluble than the corresponding one from triphenylphosphine it does not function so readily as an indicator for the carbon monoxide/hydrogen cycle. No reaction occurred with either $Rh_4(CO)_8(PPh_3)_4$ or $Rh_4(CO)_8(ETPO)_4$ and 1-hexene under similar conditions.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer model 21 or model 257 spectrophotometer, and ^1H NMR spectra were recorded on a Varian HA 100 spectrometer at 100 MHz. GLC separations were carried out using a Griffin and George D6 gas density detector with a Silicone column. Molecular weights were determined using a "Mechrolab" osmometer. Dodecacarbonyltetrarhodium and hexadecacarbonylhexarhodium were prepared by previously reported methods[16]. Except where stated all reactions were carried out in an atmosphere of dry nitrogen.

Reaction of dodecacarbonyltetrarhodium with phosphorus ligands

(*a*). *Triphenylphosphine*

(*i*). *Preparation of bis(triphenylphosphine)decacarbonyltetrarhodium.* Triphenylphosphine (0.52 g, 2.0 mmole) in hexane was added slowly (3 h) to a stirred solution of dodecacarbonyltetrarhodium (0.75 g, 1.0 mmole) in hexane (50 ml), and the mixture was kept overnight at room temperature. The solid product was washed (hexane) and recrystallised from a dichloromethane/hexane mixture to give bis(triphenylphosphine)decacarbonyltetrarhodium (1.10 g, 91%) as a red crystalline solid. (Found: C, 45.6; H, 2.7. $C_{46}H_{30}O_{10}P_2Rh_4$ calcd.: C, 45.4; H, 2.5%.)

Under the same conditions, and also at −78°, dodecacarbonyltetrarhodium (0.75 g) and triphenylphosphine (0.26 g, 1.0 mmole) in hexane gave only bis(triphenylphosphine)decacarbonyltetrarhodium (0.52 g, 43%) and dodecacarbonyltetrarhodium (0.39 g, 52%).

(*ii*). *Preparation of tetrakis(triphenylphosphine)octacarbonyltetrarhodium.* Dodecacarbonyltetrarhodium (0.98 g, 1.18 mmole) and benzene (50 ml) were kept at 70° and triphenylphosphine (1.23 g, 4.7 mmole) was added slowly. After 3 h the solid was filtered off and washed successively with benzene (2 × 20 ml), methanol (2 × 20 ml) and diethyl ether (2 × 20 ml) to give tetrakis(triphenylphosphine)octacarbonyltetrarhodium (0.57 g, 20%) as a red solid. (Found: C, 57.3; H, 3.8; P, 7.2. $C_{80}H_{60}O_8P_4Rh_4$ calcd.: C, 57.0; H, 3.6; P, 7.4%.) Evaporation of the solvent from the filtrate gave a black, intractable tar (1.83 g).

This reaction was repeated using dodecacarbonyltetrarhodium (0.88 g, 1.17 mmole), triphenylphosphine (1.23 g, 4.70 mmole) and benzene (100 ml) in a tube sealed *in vacuo*, and shaken at room temperature for 15 h; no carbon monoxide was present at the end of the reaction. The contents of the tube were filtered to give an unidentified yellow solid (0.28 g) [ν(CO) (in CH_2Cl_2 solution) 1970 s cm^{-1}], which was washed with benzene (3 × 20 ml) and recrystallised from a mixture of dichloromethane and light petroleum (b.p. 40–60°). (Found: C, 55.0; H, 4.0; P, 7.7. $C_{42}H_{30}O_6P_2Rh_2$ calcd.; C, 56.2; H, 3.3; P, 6.9%.) Light petroleum (b.p. 100–120°; 20 ml) was added to the filtrate, which was then concentrated *in vacuo* to give a red solid mixture (0.17 g) of $Rh_4(CO)_{10}(PPh_3)_2$ and $Rh_4(CO)_9(PPh_3)_3$, identified by IR spectroscopy.

When this reaction was repeated using dodecacarbonyltetrarhodium (1.1 g, 1.47 mmole), triphenylphosphine (1.57 g, 6.0 mmole) and benzene (60 ml) magnetically-stirred at room temperature (15 h) in a flask connected to a gas burette, a rapid, initial evolution of carbon monoxide (80 ml) was observed during the first few minutes, and this was gradually re-absorbed over the next 10 min. The products were found to be the yellow solid (0.17 g), a mixture (1.87 g) of $Rh_4(CO)_{10}(PPh_3)_2$ and $Rh_4(CO)_9(PPh_3)_3$, and an unidentified brown solid (0.09 g).

(*iii*). *Preparation of tetrakis(triphenylphosphine)dicarbonyl-μ-dicarbonyldirhodium.* Triphenylphosphine (2.20 g, 8.0 mmole) in dry acetone (10 ml) was added dropwise to dodecacarbonyltetrarhodium (0.75 g, 1.00 mmole) in dry acetone (70 ml) with a slow stream of carbon monoxide passing through. After about 1 h, the yellow solid was removed in a carbon monoxide atmosphere and dried to give tetrakis(triphenylphosphine)dicarbonyl-μ-dicarbonyldirhodium (2.49 g, 91%). (Found: C, 66.5; H, 4.2. $C_{76}H_{60}O_4P_4Rh_2$ calcd.: C, 66.8; H, 3.4%.) On standing *in vacuo* or under nitrogen the solid rapidly decomposed to give an unidentified yellow solid [ν(CO) 1970 cm^{-1}] (Found: C, 63.0; H, 4.7.); the bridging-carbonyl dimer was rapidly regenerated when carbon monoxide was passed through a solution of the unidentified solid in acetone or benzene.

When hydrogen was bubbled through a suspension of tetrakis(triphenylphosphine)dicarbonyl-μ-dicarbonyldirhodium (1.37 g, 1.55 mmole) in benzene (40 ml) for 15 min, the solution turned deep red and after ca. 5 min no yellow dimer could be seen. The IR spectrum of the red benzene solution showed bands at 2058 m (Rh–H), 2020 sh, 1996 s, 1972 sh, and 1949 sh [ν(CO)] cm^{-1}, and its ^1H NMR spectrum showed a single band 16.35 ppm to high field of benzene. Attempts to isolate the rhodium-hydride complex were unsuccessful. When carbon monoxide was subsequently bubbled through the same solution the yellow solid dimer separated out after ca. 10 min.

(*b*). *4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (ETPO)*

(*i*). *Preparation of bis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)decacarbonyltetrarhodium.* Propylidynetrimethanol phosphite (0.37 g, 2.32 mmole) in hexane (15 ml) was added slowly (3 h) to dodecacarbonyltetrarhodium (0.87 g, 1.16 mmole) in hexane (60 ml) and stirred at room temperature (15 h). Evaporation of the solvent and chromatography on florisil gave an unidentified orange solid (0.27 g) (Found: C, 24.1; H, 1.6%) eluted with light petroleum (b.p. 30–40°) and a red solid (0.48 g) which was rechromatographed [florisil eluted with light petroleum (b.p. 40–60°) and diethyl ether (ca. 2/1)] to give bis(ETPO)decacarbonyltetrarhodium (0.11 g) (Found: C, 25.4; H, 2.3. $C_{22}H_{22}O_{16}P_2Rh_4$ calcd.: C, 26.0; H, 2.2%.) contaminated (IR) with either dodecacarbonyltetrarhodium or ETPO undecacarbonyltetrarhodium.

(*ii*). *Preparation of tris(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)nonacarbonyltetrarhodium.* ETPO (0.36 g, 2.2 mmole) in a mixture of hexane and ether (15 ml) was added dropwise to dodecacarbonyltetrarhodium (0.55 g, 0.74 mmole) in hexane (30 ml) and ether (30 ml) and stirred overnight. Evaporation of the solvent and chromatography on florisil gave an unidentified orange solid (Found: C, 27.1; H, 3.0%.) and tris(ETPO)nonacarbonyltetrarhodium (0.67 g, 77%) [Found: C, 28.4; H, 2.8; mol.wt. in benzene, 1080. $C_{27}H_{33}O_{18}P_3Rh_4$ calcd.: C, 28.2; H, 2.9%; mol.wt., 1150.] as an orange solid.

(*iii*). *Preparation of tetrakis*(*4-ethyl-2,6,7-trioxa-1-phosphabicyclo*[*2.2.2*]*octane*)*octacarbonyltetrarhodium.* $Rh_4(CO)_8(ETPO)_4$ (0.84 g, 5.20 mmole) in benzene (10 ml) was slowly added to a solution of dodecacarbonyltetrarhodium (0.49 g, 0.65 mmole) in benzene (50 ml) through which carbon monoxide was passed (15 h). Evaporation of the solvent and chromatography (florisil column, 1/1 dichloromethane/ether) gave tetrakis(ETPO)octacarbonyltetrarhodium (0.56 g, 66%) [Found: C, 30.0; H, 3.5; mol.wt. in benzene, 1250. $C_{32}H_{44}O_{20}P_4Rh_4$ calcd.: C, 29.8; H, 3.55%; mol.wt., 1248.) as an orange solid.

Tetrakis(ETPO)octacarbonyltetrarhodium (0.42 g, 69%) was also obtained when a solution of ETPO (0.08 g, 0.48 mmole) in ether (15 ml) was added slowly (3 h) to tris(ETPO)nonacarbonyltetrarhodium (0.56 g, 0.48 mmole) in ether (60 ml) and the mixture stirred at room temperature (15 h). The product was purified by chromatography (elution with a dichloromethane/ether mixture) and recrystallisation from a mixture of dichloromethane and hexane.

(*c*). *Preparation of hexakis*(*tri-n-butylphosphine*)*dicarbonyldirhodium*

A solution of tri-n-butylphosphine (0.84 g, 4.16 mmole) in benzene (10 ml) was slowly added to a solution of dodecacarbonyltetrarhodium (0.39 g, 0.52 mmole) in benzene (30 ml) and carbon monoxide was passed through the solution for 15 h, during which the solution changed from red to yellow. No solid was precipitated by the addition of light petroleum to the residue after removal of most of the benzene, and so the solvent was again evaporated to give a yellow oil whose IR spectrum showed bands at 1950 vs, 1748 m–s, 1728 m–s cm^{-1}. The oil was extracted with hexane, filtered, and the solvent was evaporated under reduced pressure to give a white solid which was dried to give hexakis(tri-n-butylphosphine)dicarbonyldirhodium (0.31 g, 23%) [Found: C, 59.9; H, 10.6. $C_{74}H_{162}O_2P_6Rh_2$ calcd.: C, 60.2; H, 11.0%.], having a single carbonyl band at 1959 s cm^{-1} (hexane solution).

(*d*). *Preparation of tetrakis*(*triphenylarsine*)*dicarbonyl-μ-dicarbonyldirhodium*

Triphenylarsine (2.45 g, 8.0 mmole) in benzene (10 ml) was added dropwise* (15 min) to a solution of dodecacarbonyltetrarhodium (0.75 g, 1.0 mmole) in benzene (40 ml) through which carbon monoxide was passed. After 3 h the pale red solution was concentrated in a rapid stream of carbon monoxide, light petroleum (b.p. 40–60°, 20 ml) was added, and the yellow solid was washed with light petroleum (b.p. 40–60°, 3 × 15 ml) and dried in a stream of carbon monoxide to give tetrakis(triphenylarsine)-dicarbonyl-μ-dicarbonyldirhodium (2.34 g, 76%). (Found: C, 58.2; H, 3.9. $C_{76}H_{60}As_4O_4Rh_2$ calcd.: C, 59.1; H, 3.9%.)

When hydrogen was bubbled through a solution of tetrakis(triphenylarsine)-dicarbonyl-μ-dicarbonyldirhodium (0.58 g, 0.38 mmole) in benzene (20 ml) at room temperature, the solution turned deep red. The IR spectrum of the solution showed bands at 2041 w and 1970 s(br) cm^{-1}; no band in the 12–25 ppm region to high field of benzene could be detected in the ^1H NMR spectrum, possibly because of the low concentration. When carbon monoxide was subsequently bubbled through the same solution the dimer $[(AsPh_3)_2(CO)_2Rh]_2$ was recovered.

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* Rapid addition leads to deposition of rhodium metal.

Preparation of tris(triphenylphosphine)nonacarbonyltetrarhodium

Triphenylphosphine (0.39 g, 1.50 mmole) in dichloromethane (10 ml) was added slowly to a stirred solution of bis(triphenylphosphine)decacarbonyltetrarhodium (0.90 g, 0.75 mmole) in dichloromethane (50 ml) and the mixture was stirred (15 h) at room temperature. The solution was filtered, and hexane (15 ml) was added to the filtrate, which was then concentrated by evaporation of the solvent *in vacuo* to give a red solid. This was washed with diethyl ether (3 x 15 ml) to give tris(triphenylphosphine)nonacarbonyltetrarhodium (0.82 g, 96%) (Found: C, 51.8; H, 3.3; P, 6.9; mol.wt. in benzene, 1539. $C_{63}H_{45}O_9P_3Rh_4$ calcd.: C, 52.1; H, 3.1; P, 6.4%; mol.wt., 1450.) as a red solid.

Reactions of hexadecacarbonylhexarhodium with phosphorus ligands

(*a*). *Propylidynetrimethanol phosphite*

Hexadecacarbonylhexarhodium (0.53 g, 0.50 mmole), ETPO (0.49 g, 3.0 mmole), and benzene (80 ml) were shaken *in vacuo* at 70° (15 h), to give carbon monoxide (2.7 mmole), hexadecacarbonylhexarhodium (0.11 g, 20%), and hexakis(ETPO)-decacarbonylhexarhodium (0.65 g, 71%). (Found: C, 28.8; H, 3.3; P, 9.4; mol.wt. in benzene, 2010. $C_{46}H_{66}O_{12}P_6Rh_6$ calcd.: C, 28.6; H, 3.3; P, 9.2%; mol.wt., 1870.)

(*b*). *Trimethyl phosphite*

Trimethyl phosphite (0.18 g, 1.5 mmole) in benzene (15 ml) was added (2 h) to hexadecacarbonylhexarhodium (0.27 g, 0.25 mmole) in benzene (80 ml) and kept at 50° (15 h) to give hexadecacarbonylhexarhodium (0.04 g, 16%), and, after recrystallisation from a mixture of dichloromethane and light petroleum (b.p. 40–60°), red-brown crystals (0.29 g) tentatively identified as impure hexakis(trimethyl phosphite)-decacarbonylhexarhodium (Found: C, 19.0; H, 4.8. $C_{28}H_{54}O_{28}P_6Rh_6$ calcd.: C, 20.5; H, 3.3%.) with IR bands at 2081 s, 2053 s, 2026 s and 1765 s cm^{-1}.

(*c*). *Triphenylphosphine*

(*i*). *In benzene.* Hexadecacarbonylhexarhodium (0.63 g, 0.59 mmole), triphenylphosphine (0.94 g, 3.54 mmole), and benzene (80 ml) were shaken *in vacuo* at 70° (15 h), to give carbon monoxide (2.4 mmole), unchanged hexadecacarbonylhexarhodium (0.17 g, 27%), and dark red crystals (0.09 g), which were recrystallised from a mixture of dichloromethane and hexane (9/1) to give impure hexakis(triphenylphosphine)decacarbonylhexarhodium (Found: C, 54.0; H, 3.6; P, 5.9. $C_{118}H_{90}O_{10}P_6Rh_6$ calcd.: C, 57.2; H, 3.6; P, 7.5%.), which showed metal carbonyl bands at 1984 s, 1965 s, 1938 m, and 1779 s cm^{-1} in its IR spectrum.

(*ii*). *In chloroform.* Hexadecacarbonylhexarhodium (0.23 g, 0.22 mmole), triphenylphosphine (0.34 g, 1.30 mmole) and chloroform (80 ml) were shaken *in vacuo* at 65° (15 h) to give carbon monoxide (1.5 mmole), hexadecacarbonylhexarhodium (0.02 g, 12%), and chlorocarbonylbis(triphenylphosphine)rhodium (0.18 g, 20%) (Found: C, 64.5; H, 4.6. $C_{37}H_{30}ClOP_2Rh$ calcd.: C, 64.3; H, 4.4%.), identified by comparison with an authentic sample[17]. When the reaction was repeated at 90° with the ratio carbonyl/triphenylphosphine 1/14, the yield of the chlorocarbonyl compound was 72%.

Hexadecacarbonylhexarhodium (0.15 g, 0.14 mmole) was recovered quantitatively after being shaken at 90° (15 h) with chloroform (80 ml). The carbonyl (0.27 g, 0.25 mmole) was also recovered quantitatively after being shaken at 65° (15 h) with chloroform (80 ml) and bromine (2.5 g).

(iii). In an excess of carbon monoxide. Hexadecacarbonylhexarhodium (0.23 g, 0.22 mmole), triphenylphosphine (0.70 g, 2.65 mmole), and benzene (20 ml) were stirred at 45°, while a stream of carbon monoxide was passed through the solution. After 2 h the yellow solid was dried in a stream of carbon monoxide to give tetrakis(triphenylphosphine)dicarbonyl-μ-dicarbonylrhodium (0.83 g, 91%).

Reaction of hexadecacarbonylhexarhodium with triphenylarsine in an excess of carbon monoxide

Hexadecacarbonylhexarhodium (0.34 g, 0.32 mmole) and triphenylarsine (1.17 g, 3.84 mmole) in benzene (20 ml), stirred for 8 h at 45° while a stream of carbon monoxide was passed through the solution, gave tetrakis(triphenylarsine)dicarbonyl-μ-dicarbonylrhodium (1.26 g, 85%).

Reactions of dodecacarbonyltetrarhodium with alkynes

(a). With diphenylacetylene

Dodecacarbonyltetrarhodium (1.00 g, 1.34 mmole), diphenylacetylene (0.24 g, 1.34 mmole) and light petroleum (b.p. 40–60°, 50 ml) were shaken *in vacuo* at 45° (15 h), to give carbon monoxide (2.46 mmole), black crystals (0.47 g) tentatively identified as $Rh_6(CO)_{15}(Ph_2C_2)$ or $Rh_6(CO)_{14}(Ph_2C_2)$ (Found: C, 28.3; H, 0.6. $C_{29}H_{10}O_{15}Rh_6$ calcd.: C, 28.6; H, 0.9. $C_{28}H_{10}O_{14}Rh_6$ calcd.: C, 28.3; H, 0.8%.) and decacarbonyl(diphenylacetylene)tetrarhodium (0.16 g, 15%) (Found: C, 33.4; H, 1.4. $C_{24}H_{10}O_{10}Rh_4$ calcd.: C, 33.1; H, 1.2%.), together with three unidentified fractions all of which showed carbonyl stretching absorptions. A small amount (0.016 g) of hexadecacarbonylhexarhodium was also isolated from this reaction.

(b). With hexafluoro-2-butyne

Dodecacarbonyltetrarhodium (0.79 g, 1.06 mmole), light petroleum (b.p. 30–40°, 80 ml), and hexafluoro-2-butyne (0.18 g, 1.1 mmole) were shaken *in vacuo* at 65° (15 h) to give carbon monoxide (2.0 mmole). After removal of solvent *in vacuo*, chromatography on florisil and elution with light petroleum (b.p. 30–40°) gave decacarbonyl(hexafluoro-2-butyne)tetrarhodium (0.46 g, 51%). (Found: C, 20.0; H, 0.3; F, 13.2. $C_{14}F_6O_{10}Rh_4$ calcd.: C, 19.7; H, 0.0; F, 13.3%.) Further elution with light petroleum gave an unidentified yellow solid (0.007 g).

Hydroformylation of alkenes

(a). Using $Rh_4(CO)_{12}$ as a catalyst

A standard solution of dodecacarbonyltetrarhodium (10.0 mg, 0.013 mmole) in dry pentane (100 ml) was made up, and a 10 ml aliquot of this solution was pipetted into a 200 ml stainless-steel autoclave containing pentane (20 ml). The olefin (0.02 mmole) was condensed into the autoclave, which was then pressurised with carbon monoxide (60 atm) and hydrogen (60 atm), and heated with rocking at 70° for 3 h. The autoclave was then rapidly cooled and the products were analysed by GLC; the results are given in Table 2. The autoclave was thoroughly cleaned with concentrated HCl and blank runs were carried out before each experiment.

(b). Using $Rh_4(CO)_{12}$ and phosphorus-containing ligands as catalysts

Dodecacarbonyltetrarhodium (1.0 mg, 0.0013 mmole), the ligand (0.0053 mmole), pentane (30 ml) and the olefin (0.20 mmole) were kept together in a 200 ml stainless-steel autoclave. Carbon monoxide (60 atm) and hydrogen (60 atm) were introduced, and the mixture was heated at 70° for 3 h; the results are given in Table 2.

(c). Using $Rh_6(CO)_{16}$ as a catalyst

Identical conditions to those described above were used with the exception that hexadecacarbonylhexarhodium (1.0 mg, 0.0009 mmole) in benzene (30 ml) was employed as the catalyst; the results are given in Table 3.

(d). Using $Rh_6(CO)_{16}$ and phosphorus-containing ligands as catalysts

The conditions were as described above with the exception that hexadecacarbonylhexarhodium (1.0 mg, 0.0009 mmole) and the ligand (0.0054 mmole) in benzene (30 ml) were used; the results are given in Table 3.

(e). Using tetrakis(triphenylphosphine)dicarbonyl-μ-dicarbonyldirhodium as a catalyst

(*i*). 1-Hexene (2.02 g, 24.1 mmole) was added to a solution of tetrakis(triphenylphosphine)dicarbonyl-μ-dicarbonyldirhodium (1.80 g, 1.32 mmole) in benzene (60 ml), hydrogen was passed through [7(±2) ml·min^{-1}] until the yellow dimer had disappeared (10 min), and a sample was withdrawn and analysed. The hydrogen flow was stopped, and carbon monoxide was passed through the solution (10 ml·min^{-1}, 20 min) to regenerate the dimer. The cycle was then repeated, samples being withdrawn at half-hour intervals. The yields of n-heptaldehyde and 2-methylhexaldehyde, based on the initial 1-hexene, are summarised in Table 4 (Method A).

(*ii*). 1-Hexene (2.02 g, 24.1 mmole) was added to a solution of the catalyst (1.71 g, 1.26 mmole) in benzene (60 ml), hydrogen was bubbled through the solution until about half of the dimer had been consumed, and then both carbon monoxide and hydrogen were passed through (ca. 7 ml·min^{-1} each). Samples were withdrawn at half-hour intervals, and the results are summarised in Table 4 (Method B).

(f). Using tetrakis(triphenylarsine)dicarbonyl-μ-dicarbonyldirhodium.

Alternate passage of carbon monoxide and hydrogen as in (e) (*i*) above, through a solution of the catalyst (2.00 g, 1.30 mmole) and 1-hexene (2.02 g, 24.1 mmole) in benzene (60 ml) gave the results in Table 5 (Method A). Passage of both gases simultaneously gave the results in Table 5 (Method B). Samples were withdrawn at half-hour intervals; only representative values are given.

ACKNOWLEDGEMENT

Thanks are due to the Science Research Council for a studentship grant to one of us (M.J.E.).

REFERENCES

1 B. L. BOOTH, R. N. HASZELDINE AND N. P. WOFFENDEN, *J. Chem. Soc. A*, (1970) 1979.

2 G. CETINI, O. GAMBINO, R. ROSSETTI AND P. L. STANGHELLINI, *Inorg. Chem.*, 7 (1968) 609.

3 R. J. ANGELICI AND E. SIEFERT, *Inorg. Chem.*, 5 (1966) 1457; P. J. POLLICK AND A. WOJCICKI, *J. Organometal. Chem.*, 14 (1968) 469.

4 P. PIACENTI, M. BIANCHI AND E. BENEDETTI, *Chem. Commun.*, (1967) 775.

5 M. I. BRUCE AND F. G. A. STONE, *Angew. Chem. Int. Ed. Engl.*, 7 (1968) 429 and references therein.

6 P. CHINI, *Inorg. Chim. Acta Rev.*, 1 (1968) 31 and references therein.

7 R. ERCOLI AND F. BARBIERI-HERMITTE, *Rend. Accad. Lincei. Cl. Sci. Fis. Natur.*, 16 (1954) 249, cited in ref. 6.

8 P. CHINI, *Chem. Commun.*, (1967) 29, 440; P. CHINI AND V. ALBANO, *J. Organometal. Chem.*, 15 (1968) 433.

9 P. Piacenti, M. Bianchi, E. Benedetti and G. Braca, *Inorg. Chem.*, 7 (1968) 1815.
10 R. Whyman, *J. Chem. Soc. D*, (1970) 230.
11 C. O'Connor, G. Yagupsky, D. Evans and G. Wilkinson, *Chem. Commun.*, (1968) 420.
12 D. Evans, G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, (1968) 2660.
13 N. S. Imianitov and D. M. Rudkovskii, *Neftekhimiya*, 3 (1963) 198; *idem*, *Zh. Prikl. Khim.*, 15 (1967) 2020; Ya. T. Eidus and A. L. Lapidus, *Neftekhimiya*, 7 (1967) 51; H. Wakamatsu, *J. Chem. Soc. Japan*, 85 (1964) 227; Y. Takegami, Y. Watanabe and H. Masada, *Bull. Chem. Soc. Jap.*, 40 (1967) 1456, 1459; J. Falbe, H. Schulze–Steinen and F. Korte, *Chem. Ber.*, 98 (1965) 886; B. Heil and L. Marko, *Chem. Ber.*, 101 (1968) 2209; *idem*, *Magy. Kem. Lapja*, 23 (1968) 669.
14 *U.S. Pat.* 3,239,566 (1966); J. Falbe and N. Huppes, *Brennst.-Chem.*, 47 (1966) 314; *idem*, 48 (1967) 46; R. L. Pruett and J. A. Smith, *J. Org. Chem.*, 34 (1969) 327.
15 D. Evans, J. A. Osborn and G. Wilkinson, *J. Chem. Soc. A*, (1968) 3133; C. K. Brown and G. Wilkinson, *Tetrahedron Lett.*, (1969) 1725.
16 B. L. Booth, M. J. Else, R. Fields and R. N. Haszeldine, *J. Organometal. Chem.*, 14 (1968) 417.
17 J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, 8 (1966) 214.
18 W. Beck and K. Lottes, *Chem. Ber.*, 94 (1961) 2578.