

The Reaction of Hydridocarbonyltris(triphenylphosphine)rhodium with Carbon Monoxide, and of the Reaction Products, Hydridodicarbonylbis(triphenylphosphine)rhodium and Dimeric Species, with Hydrogen †

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A detailed study has been made, using infrared and nuclear magnetic resonance techniques, of the interaction of carbon monoxide and hydridocarbonyltris(triphenylphosphine)rhodium(I), $\text{RhH}(\text{CO})(\text{PPh}_3)_3$. The latter, which dissociates in solution to the square complex $\text{trans-RhH}(\text{CO})\text{PPh}_3_2$, initially forms the dicarbonyl complex $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$; in the presence of CO, this species loses hydrogen to give a yellow dimeric complex $(\text{Ph}_3\text{P})_2(\text{CO})\text{Rh}(\text{CO})_2\text{Rh}(\text{CO})(\text{PPh}_3)_2$. These reactions are reversed by hydrogen to re-form $\text{RhH}(\text{CO})(\text{PPh}_3)_2$. By sweeping with an inert gas, the yellow dimer loses carbon monoxide to form a red, solvated dimer, $(\text{Ph}_3\text{P})_2(\text{S})\text{Rh}(\text{CO})_2\text{Rh}(\text{S})(\text{PPh}_3)_2$, which reacts with carbon monoxide to re-form the yellow dimer.

HYDRIDOCARBONYLTRIS(TRIPHENYLPHOSPHINE)-RHODIUM(I) was first prepared¹ by the reaction of *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) and an excess of triphenylphosphine with hydrazine in ethanolic solution. It was stated to dissociate in benzene (Found: *M*, 407, conditions unspecified; required, 919), and to have bands in the infrared spectrum (in benzene) at 2004 (ν_{RhH}), 1926 (ν_{CO}), and 784 (δ_{RhH}) cm^{-1} ; the two stretches were later given as 2041 and 1923 cm^{-1} (mull) respectively.² The n.m.r. spectrum was stated¹ to be a broad band at τ 19.9.

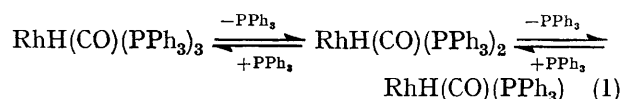
We have shown³⁻⁶ that $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ may act as a catalyst for hydrogen-atom exchange, isomerisation, hydrogenation, and hydroformylation reactions of olefins, resembling, though with significant differences, the behaviour of hydridotetracarbonylcobalt. In order to understand the mechanisms of these reactions, a detailed study of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and species formed from it by reaction with carbon monoxide, and of these species with hydrogen, has been necessary.

The infrared and n.m.r. data for species discussed herein are in the Table.

The Nature of Hydridocarbonyltris(triphenylphosphine)rhodium(I) in Solution.—The compound $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is moderately soluble in chloroform, dichloromethane, or benzene (ca. 40 mg. ml^{-1}), sparingly soluble in cyclohexane (ca. 1 mg. ml^{-1}), and insoluble in light petroleum.

We have confirmed that, in organic solvents, extensive dissociation of the complex occurs. The apparent molecular weights in benzene at 38°, measured in an inert atmosphere, are concentration-dependent. At ca. $1.3 \times 10^{-3}\text{M}$, the apparent molecular weight is close to 0.5 that of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, but at higher concentrations it increases to ca. 600 between 8.2×10^{-3} and $1.7 \times 10^{-2}\text{M}$. This suggests that considerable re-association is occurring. On dilution to the lowest concentrations that can be measured reproducibly by osmometric techniques (ca. $3 \times 10^{-4}\text{M}$), the apparent molecular weight drops to values ca. 400, suggesting that a

second dissociation step is occurring. It will be noted subsequently⁵ that, at the concentrations where this divergence occurs, there is also a change in behaviour in the catalytic hydrogenation of alk-1-enes. The molecular weight data in benzene suggests the equilibria:



The reality of the first dissociation and of the re-association can be shown in other ways.

(a) In a poorly co-ordinating solvent, cyclohexane, the apparent molecular weight of a saturated solution (10^{-3}M , osmometer) is 730.

(b) The cryoscopic molecular weight in benzene (m.p. 5.5°) at $5 \times 10^{-3}\text{M}$ is 900, and in *o*-xylene (m.p. -29°) it is 920, corresponding to $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, while at 38°, osmometrically in *o*-xylene, the value is 490.

(c) The n.m.r. spectrum at 25° consists of a broad line, as originally observed,¹ indicating that the dissociation process (1) is rapid on the n.m.r. timescale at this temperature. On cooling to -30°, the broad line is replaced by a 1 : 3 : 3 : 1 quartet of doublets (J_{PH} 14, $J_{\text{RRH}} \sim 1$ c./sec.), consistent with the undissociated form of the trigonal bipyramidal structure found in the solid by X-ray crystallography.⁷ This change has also been reported elsewhere.⁸ It is noteworthy that the chemical shift for the quartet attributed to $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is almost coincident with that of the broad line at 25° due to the dissociated species which is undergoing rapid exchange. This suggests that the chemical shifts of the multiplets for both species are very similar; this can be confirmed by observing that the broad line at 25° does not shift appreciably upon altering the relative concentrations of the two species by adding a large excess (>10 mol.) of triphenylphosphine.

(d) The infrared spectra of solutions of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$

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

⁵ C. O'Connor and G. Wilkinson, following paper.

⁶ D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, in the press.

⁷ S. J. La Placa and J. A. Ibers, *Acta Cryst.*, 1965, **18**, 511.

⁸ K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 1968, **7**, 546.

† No reprints available.

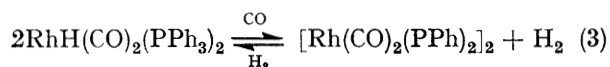
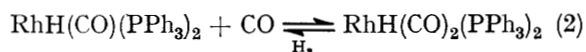
¹ S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

² L. Vaska, *J. Amer. Chem. Soc.*, 1966, **88**, 4100.

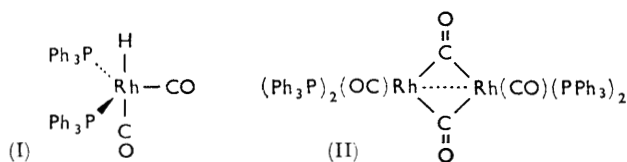
³ P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, *Chem. Comm.*, 1967, 305.

have two peaks, at 2000 (ν_{RhH}) and 1920 (ν_{CO}) cm^{-1} . The positions of these bands are similar in solvents such as benzene or dichloromethane, or in cyclohexane, where the degree of dissociation is known to be different. Further, on measuring the spectrum in chloroform at different temperatures in the range -45 to $+30^\circ$, no important change occurs; the band due to the CO stretch shows a small reversible shift of *ca.* 5 cm^{-1} on cooling. This indicates that both the species $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ have similar spectra in the RhH and CO stretching region. Hence, we can reasonably assume that, as in the tris-complex the H and CO groups are *trans* to each other in $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ and that it has a square geometry.

The Reaction of Hydridocarbonyltris(triphenylphosphine)rhodium(I) in Solution with Carbon Monoxide.—On treating solutions of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ in benzene or other solvents with carbon monoxide, complicated changes occur depending on the time of saturation and temperature. In order to facilitate the description of the spectral analyses, we anticipate the result by stating that the spectra can be interpreted in terms of three primary species: $\text{RhH}(\text{CO})(\text{PPh}_3)_2$; a dicarbonyl complex, $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ (I); and a dimeric species with both terminal and bridging carbonyl groups, $(\text{Ph}_3\text{P})_2(\text{CO})\text{Rh}(\text{CO})_2\text{Rh}(\text{CO})(\text{PPh}_3)_2$ (II). Since the changes produced by carbon monoxide at 1 atm. and 25° can be completely reversed to re-form $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ by hydrogen at 1 atm. at 25° , we have the following equilibria:



For reactions (1)—(3) there will be a set of equilibrium constants regulating the relative concentrations of the various species which may co-exist at a given temperature and for a combination of partial pressures of hydrogen and carbon monoxide. Reaction (3) is favoured since carbon monoxide sweeps hydrogen from the solution. Similarly, the reverse of reaction (2) is promoted by hydrogen because it removes carbon monoxide. At present we have not values for equilibrium constants; reaction (2) is very rapid and reaction (3) is slow. The equilibrium of reaction (1) is determining in that, if an excess of triphenylphosphine is added to the solution, the reactions with carbon monoxide proceed only slowly and are incomplete.



(a) *Reaction in benzene and dichloromethane.* The sequence of changes in the infrared spectra on treatment

with carbon monoxide are shown for $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ and for $\text{RhD}(\text{CO})(\text{PPh}_3)_2$ in Figure 1(a) and (b) respectively in the 1700—2100 cm^{-1} region. The precise sequence of appearance and disappearance of the various peaks due to the new species cannot be determined unambiguously in these solvents. This is due to the well known extensive solvent-broadening of the carbonyl bands plus the additional complication of strong benzene absorption at *ca.* 1950 and 1800 cm^{-1} . The reaction sequence can be distinguished, however, and spectra obtained in hexane and cyclohexane discussed below,

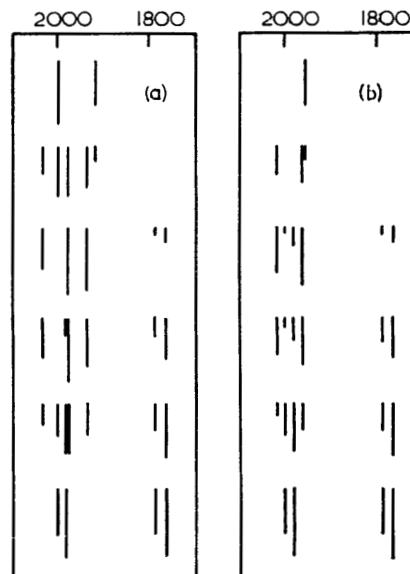


FIGURE 1 Infrared spectra (cm^{-1}) of dichloromethane solutions of (a) $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, and (b) $\text{RhD}(\text{CO})(\text{PPh}_3)_3$ (top) on treatment with increasing amounts of carbon monoxide to produce finally the dimer $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]_2$ (bottom)

though more satisfactory, serve mainly to confirm the conclusions.

Upon addition of CO the initial spectrum of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ [Figure 1(a)] disappears and the following features are observed. (i) The bands at 2038, 1980, and 1939 cm^{-1} [Figure 1(a)] appear rapidly, within a few seconds at 25° . (ii) These bands then weaken with appearance of the bands at 1765 and 1790 cm^{-1} (shoulder) and at 2005 and 1985 cm^{-1} which are almost superimposed on the bands in (i). When the three bands in (i) are very weak it is clear that the four bands in (ii) have increased in intensity simultaneously. No further change then occurs; this final stage is reached for concentrated solutions (*ca.* 40 mM) after bubbling carbon monoxide for about 30 min. The colour of the solution meanwhile changes from the yellow of $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ to the pale yellow of $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$, and finally to yellow-orange.

The bands at 2038, 1980, and 1939 cm^{-1} predominate in the first rapid stage, but inevitably different amounts of the initial and/or final species are present. Figure 2

shows the general appearance of the spectrum at the end of the first stage, *i.e.*, where the predominant species is $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$. The deuteride $\text{RhD}(\text{CO})(\text{PPh}_3)_3$ undergoes a similar series of spectral changes, but only

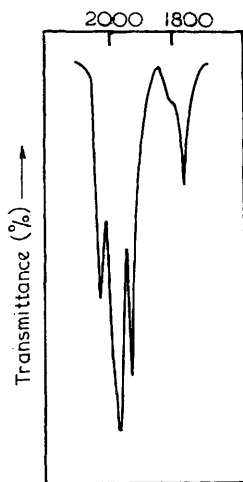


FIGURE 2 Infrared spectrum (cm^{-1}) of a dichloromethane solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ treated with $\text{CO} + \text{H}_2$ (1 : 1) and containing *ca.* 80% of $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ plus dimer

the spectra for the final stage is the same as with the hydride. The spectra of the $\text{RhD}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhD}(\text{CO})_2(\text{PPh}_3)_2$ differ from the analogous hydride spectra because of isotopic shifts and changes in the position and intensity of the carbonyl bands of the corresponding species owing to differing interactions of the carbonyl vibrations with Rh-H and Rh-D vibrations.²

We have shown by collection of the off-gases that, during the second slow step, molecular hydrogen is evolved according to the mass spectrum. At any stage it is possible to completely reverse the reaction sequence by introduction of molecular hydrogen. Indeed, by bubbling a 1 : 1 mixture of H_2 and CO , it is possible to maintain the species $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ as the predominant one (*ca.* 95%) at 20° and 1 atm., with only small amounts of the dimer present (*cf.* Figure 2).

The n.m.r. spectrum of benzene solutions of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, through which hydrogen and carbon monoxide have been bubbled to achieve *ca.* 95% conversion into $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$, shows that there is a shift to lower fields of *ca.* 0.17 p.p.m. compared to $\text{RhH}(\text{CO})(\text{PPh}_3)_2$. This shift is reversed on removal of the CO by hydrogen. In dichloromethane the shift is -0.06 p.p.m. For both cases the line is broad (10–15 c./sec.) owing to exchange processes, but the line for the dicarbonyl species is sharper. On cooling a toluene solution containing *ca.* 80% of $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ and *ca.* 20% of $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ to *ca.* -30°, the quartet lines due to the latter (re-associated) were clearly observed, whereas the band due to the former was still a broad line. On further cooling to -70° the band becomes unsymmetric, but at this point crystallisation of the small amount of yellow dimer begins to occur.

The spectra hence show that some rapid intramolecular process in $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ is occurring, doubtless similar to those to be described for the iridium analogue.⁹ It also may be noted that, on bubbling carbon monoxide through benzene solution at 25°, loss of hydrogen as noted above is shown by the slow disappearance of the high-field line. Introduction of hydrogen restores the original spectrum.

Finally, it may be noted that in mixtures of $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ it is possible, as will be discussed separately in due course, to distinguish between them readily, since only $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ reacts with ethylene, and the high-field line of this species disappears within 1–2 min. at 25°.

(b) *Reaction in hexane and cyclohexane.* The solvent-broadening of carbonyl bands is minimal in saturated hydrocarbons. However, $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is insoluble in hexane and only sparingly soluble in cyclohexane. Fortunately, the carbonylation products are appreciably soluble, so that on passing CO into a hexane or cyclohexane suspension of the complex a yellow solution is obtained. The infrared spectrum of the solution [Figure 3(A)] closely resembles that in dichloromethane (Figure 2) or benzene, except that the bands are now more clearly resolved; both $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ and the yellow dimer are present. Prolonged treatment of the

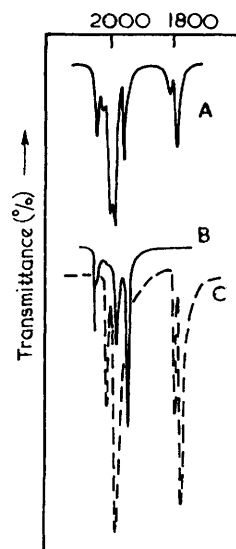


FIGURE 3 Infrared spectra (cm^{-1}) of (A) $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ treated with carbon monoxide in cyclohexane; (B) $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ treated with carbon monoxide in hexane and thereafter with hydrogen, giving essentially pure $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$; (C) the yellow dimer $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]_2$ as a Nujol mull

solution leads to precipitation of the dimer as a yellow solid. The solution spectra clearly show that the dimer is present even though the isolated solid dimer is virtually insoluble; a supersaturated solution must be produced

⁹ G. Yagupsky and G. Wilkinson, unpublished results.

in the formation reaction. The spectrum of the solid dimer is shown for comparison in Figure 3(C). Careful treatment of the hexane solution with hydrogen for a few minutes removes the dimer and gives the simple spectrum of Figure 3(B), which we consider to be that of pure $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$; on treatment with an excess of hydrogen, the insoluble $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is precipitated. The only difference between hexane and cyclohexane solutions is that the solubility of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is higher in the latter, so the additional absorption is also observed.

Again, using $\text{RhD}(\text{CO})(\text{PPh}_3)_3$ similar changes occur and the spectrum of pure $\text{RhD}(\text{CO})_2(\text{PPh}_3)_2$ can be obtained (Table).

Infrared (1700—2200 cm^{-1}) and n.m.r. spectral data for rhodium complexes

Compounds	I.r. (cm^{-1}) ^a		N.m.r.
	Solid ^e	Solution	(τ -values) ^b
$\text{RhH}(\text{CO})(\text{PPh}_3)_3$	2040s ($\nu_{\text{RH}}^{\text{H}}$), 1923m	2000s ($\nu_{\text{RH}}^{\text{H}}$), 1920m; ^d 2005s ($\nu_{\text{RH}}^{\text{H}}$), 1935m ^e	19.69(q, J_{RH} 14; J_{RH}^{H} 1 c./sec.) (-35°); ^a 19.27(br) ^f
$\text{RhD}(\text{CO})(\text{PPh}_3)_3$	1954s	1960s ^d	
$\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$	—	2038 ($\nu_{\text{RH}}^{\text{H}}$), 1980, 1939; ^g 2050m ($\nu_{\text{RH}}^{\text{H}}$), 1980m, 1942s ^g	19.1(br); ^f 19.63(br) ^d
$\text{RhD}(\text{CO})_2(\text{PPh}_3)_2$	—	2025m 1970s; ^g 2020m, 1965s ^d	
$[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]_2$	2017m, 1992s, 1800m, 1770s	2005sh, 1985s, 1790sh, 1765s ^{d, h}	
$[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2, \text{EtOH}]_2$	1718s		
$[\text{Rh}(\text{CO})(\text{PPh}_3)_2, \text{CH}_2\text{Cl}_2]_2$	1765w, 1739s	1980s, 1740s ^d	

^a All compounds showed typical bands due to PPh_3 or AsPh_3 .

^b Taken at 100 Mc./sec. and 35°, t = triplet, q = quartet.

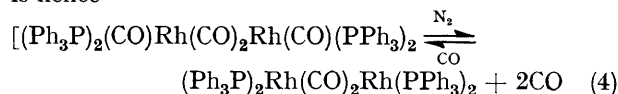
^c Nujol mulls. ^d Solution in CH_2Cl_2 . ^e Cyclohexane. ^f Benzene. ^g Hexane. ^h Super saturated solution.

(c) *Isolation of species.* The solutions containing $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ are exceedingly air-sensitive, and are stable only in an atmosphere of hydrogen plus carbon monoxide. Attempts to obtain a solid from such solutions have given only mixtures of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and the yellow dimer.

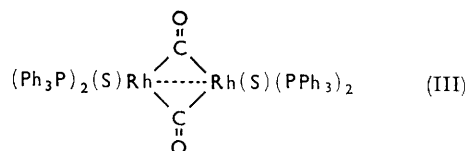
The final carbonylated solutions are also stable only in the presence of carbon monoxide, but they are not specially air-sensitive. The yellow crystalline solid which precipitates from hexane or cyclohexane solutions is unstable in air or in a vacuum; it can be handled only in CO, and even then only for short periods. The infrared spectrum [Table, Figure 3(C)] suggests the formulation (II). We can discount an ionic formulation of the type found in some related cobalt carbonyl phosphine complexes,¹⁰ e.g., $[(\text{R}_3\text{P})_2\text{Co}(\text{CO})_3][\text{Co}(\text{CO})_6]$, since the electrical conductivity of dichloromethane or benzene solutions, or of fresh acetone solutions of the solid, is negligible (Λ 26 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ at 10^{-3}M).

Finally, it is to be noted that the spectrum of the dimer is more complicated in the supersaturated solutions than might have been expected from structure (II). However, since this species is iso-electronic with octacarbonyldicobalt, this is not surprising, since tautomeric, bridged or non-bridged, and conformeric forms of (II) similar to those found with octacarbonyldicobalt¹¹ are possible, and are evidently the reason for the multiplicity of bands.

Decarbonylation of the Yellow Dimer.—When nitrogen or argon is bubbled through the yellow-orange solutions containing the dimeric species in benzene or dichloromethane, or, upon reduction of the pressure by evacuation, carbon monoxide is lost and the solution quickly becomes deep red. The infrared spectra show that the bands due to the yellow dimer are replaced by two broad bands in the bridging and terminal carbonyl region, at 1980 and 1740 cm^{-1} . The reaction is completely reversed by carbon monoxide in a few minutes at 25°, and gas-uptake studies show that 1 mole of carbon monoxide per mole of rhodium is absorbed. The reaction is hence



If the dichloromethane solutions are concentrated, or if benzene solutions are concentrated in the presence of small amounts of dichloromethane, a red crystalline solid $[\text{Rh}(\text{CO})(\text{PPh}_3)_2, \text{CH}_2\text{Cl}_2]_2$ can be isolated. If ethanol is present, an ethanol solvate is obtained. These complexes are stable in air for at least several days; once isolated they are isolable in dichloromethane but are soluble in benzene; n.m.r. measurement or g.l.c. study of these benzene solutions shows the presence of dichloromethane or ethanol. We have been unable to isolate any complex from the solution using only benzene as the reaction medium, and the benzene solutions tend to decompose on concentration. The infrared spectra of the two solids show only strong bridging carbonyl bands (Table), in agreement with structure (III), and



the lowering of the bands compared to the yellow dimer agrees with the substitution of CO by a solvent molecule. The reaction of the dichloromethane adduct with iodine gives the bridge-cleaved product *trans*- $\text{RhI}(\text{CO})(\text{PPh}_3)_2$ quantitatively.

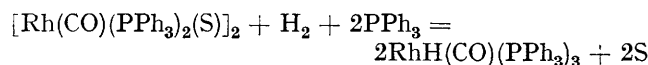
The difference between the spectra of the solutions as prepared, and of the crystalline solvates, is evidently due to the presence in solution of tautomeric species

¹⁰ W. Heiber and W. Freyer, *Chem. Ber.*, 1958, **91**, 1230.

¹¹ K. Noack, *Spectrochim. Acta*, 1963, **19**, 1925; G. Bor, *ibid.*, p. 2065.

which have terminal rather than bridging carbonyl groups.¹⁰ We expect the ratios of bridging and non-bridging bands to be both solvent- and temperature-dependent.

Finally, in the presence of an excess of triphenylphosphine, the red complex will absorb quantitatively and irreversibly 1 mole of hydrogen per mole of rhodium to re-form $\text{RhH}(\text{CO})(\text{PPh}_3)_3$. The reaction can be carried out with benzene solutions of the isolated crystals or in an *in situ* way; where S is CH_2Cl_2 or $\text{C}_2\text{H}_5\text{OH}$ we have:



EXPERIMENTAL

Direct CO determinations were done by treating the material with iodine in pyridine, and measuring the volume of gas evolved. Molecular weights at 37° were measured with a Hitachi Perkin-Elmer model 115 osmometer, under nitrogen or hydrogen. Cryoscopic determinations were measured with a conventional apparatus provided with a thermistor (we are indebted to Mr. R. Shadwick for these determinations).

N.m.r. spectra were obtained using a Varian 43100 spectrometer at 56.45 Mc./sec., and a Perkin-Elmer R-14 spectrometer at 100 Mc./sec., at 35°. Measurements at other temperatures were obtained on a Varian HA-100 spectrometer, at 100 Mc./sec. (by Mr. P. Jenkins and Miss L. M. Twan Moh, Imperial College).

Melting points were determined on a Kofler hot-stage microscope. Infrared spectra were taken on a Perkin-Elmer model 237 or a Perkin-Elmer model 21 (CaF₂ prism) spectrometer. I.r. spectra of solids were measured as Nujol mulls. Solution spectra were measured, with compensation, in 0.1, 0.5, or 1 mm. liquid cells.

Mass spectra were obtained using an AEI MS 9 spectrometer. G.l.c. measurements were made using a Perkin-Elmer model F-11 chromatograph with flame ionising detector.

Attempts to determine the Raman spectra of the solid rhodium dimers, using a Cary model 81 instrument equipped with a neon laser source, resulted in decomposition of the samples.

Materials.—Rhodium trichloride trihydrate was from Johnson Matthey Limited, and triphenylphosphine from Albright and Wilson Limited (recrystallised before use from benzene-ethanol). Carbon monoxide (Air Products Limited) was treated to remove pentacarbonyliron(0) impurity by passing the gas over asbestos wool at 500° and subsequently through a trap with activated charcoal at -100°. Hydrogen (British Oxygen Company) was passed through an Engelhard Deoxo catalyst tube. Deuterium was from Cambrian Chemicals Limited. All solvents were of reagent grade and were dried and degassed before use. Experiments were normally carried out under nitrogen or under the reacting gas (H_2 or CO).

Preparations.—*Hydridocarbonyltris(triphenylphosphine)rhodium(I)*. This is an improvement on the original procedure¹ which uses hydrazine as a hydride source. *trans*-Chlorocarbonyltris(triphenylphosphine)rhodium(I)¹² (1 g.,

0.0014 mole) and triphenylphosphine (1.5 g., 0.0057 mole) in ethanol (100 ml.) were stirred and heated under reflux. A solution of sodium borohydride (*ca.* 0.5 g.) in ethanol (*ca.* 60 ml.) was added slowly until a test portion of the suspended yellow solid showed that the carbonyl stretching frequency at 1960 cm^{-1} due to *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ had disappeared. The hot solution was filtered, and the collected complex washed with ethanol and dried in a vacuum (1.2 g., 90%) (Found: C, 72.6; H, 5.0; P, 10.2. Calc. for $\text{C}_{35}\text{H}_{46}\text{OP}_3\text{Rh}$: C, 72.7; H, 5.0; P, 10.1%).

The compound can also be prepared directly, starting with rhodium trichloride trihydrate to form *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, and reducing this compound *in situ* with sodium borohydride. In a typical preparation, a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (2 g., 7.6 mmoles) in ethanol (70 ml.) was added to a refluxing solution of triphenylphosphine (12 g., 46 mmoles) in ethanol (300 ml.). After 2 min., aqueous formaldehyde (10 ml.) was added dropwise, and the solution turned yellow with formation of yellow crystals of *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. Addition of sodium borohydride (*ca.* 2 g.) in ethanol to this hot mixture yielded the product, as described above (5 g., 72%).

Deuteriocarbonyltris(triphenylphosphine)rhodium(I). This was prepared by H-D exchange. A solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (*ca.* 30 mg.) in benzene (*ca.* 1 ml.) was exposed to *ca.* 100 ml. of deuterium with agitation. The exchange is rapid and 100% conversion is obtained in *ca.* 15 min. Deuterium can also be bubbled slowly through the solution and *ca.* 50% conversion is obtained in about 2 min. There is no evidence of appearance of C-D stretching frequencies in the infrared spectrum of the product, which would indicate exchange with the α -hydrogen atoms of the triphenylphosphine group [in contrast to the behaviour with $\text{RuClH}(\text{PPh}_3)_3$ ¹³ or $\text{CoH}(\text{N}_2)(\text{PPh}_3)_2$ ¹⁴] even after exposure to an excess of deuterium with rapid agitation for over 15 hr.

Dicarbonylbis(triphenylphosphine)rhodium(I) dimer. Carbon monoxide was bubbled through a suspension of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (50 mg.) in cyclohexane (20 ml.) for 5 min., and the resulting yellow solution filtered through a fritted disk into a flask purged with carbon monoxide. On bubbling more carbon monoxide through the solution, the *complex* was precipitated slowly as a yellow solid. After decanting and washing with carbon monoxide-saturated cyclohexane or light petroleum, the compound was dried under a stream of carbon monoxide (25 mg.) (Found: CO, 8.2, 8.1; P, 9.1. $\text{C}_{76}\text{H}_{60}\text{O}_4\text{P}_4\text{Rh}_2$ requires CO, 8.2; P, 9.1%).

The compound is unstable and can be handled only for short periods in an atmosphere of carbon monoxide. It can also be prepared on a larger scale by treating a saturated solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ in benzene with carbon monoxide for 30 min.; upon standing in an atmosphere of carbon monoxide at 10°, the yellow solid precipitates from the resulting orange solution.

Carbonylbis(triphenylphosphine)rhodium(I) ethanol dimer. A benzene solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (500 mg.) in benzene (10 ml.) was treated with carbon monoxide for 30 min. The resulting orange solution was concentrated slowly in a stream of nitrogen with addition, at intervals, of small portions (0.5 ml.) in ethanol. The deep red concentrated solution yielded, on standing, red crystals of the *complex*.

¹³ P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. (A)*, in the press.

¹⁴ G. W. Parshall, *J. Amer. Chem. Soc.*, 1968, **90**, 1669.

¹² D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Synth.*, 1968, **11**, 99.

These were collected, washed with ethanol, and dried in a vacuum (300 mg., 80%) (Found: C, 66.6; H, 4.8; O, 4.6; P, 8.2. $C_{78}H_{72}O_4P_4Rh_2$ requires C, 66.8; H, 5.2; O, 4.6; P, 8.8%).

Carbonylbis(triphenylphosphine)rhodium(I) dichloromethane dimer. As for the ethanol derivative above, but using dichloromethane instead of ethanol (80%) (Found: C, 60.5; H, 4.4; Cl, 10.6; P, 8.2. $C_{78}H_{64}Cl_2O_2P_4Rh_2$ requires C, 61.6; H, 4.4; Cl, 9.6; P, 8.4%).

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