Reactions of the Dirhodium Cation Rh_2^{4+}, with Triphenylphosphine and Alkali Metal Carboxylates, Dithiocarbamates and Other Anions †

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Rhodium(I) carboxylates of stoicheiometry $Rh(OCOR)(PPh_3)_3$, (where R = alkyl, aryl, or substituted alkyl), have been obtained by the interaction of the dirhodium(II) cation, Rh_2^{4+}, with a stoicheiometric amount of triphenylphosphine and an excess of the lithium salt of the appropriate carboxylic acid. The chemical properties of these carboxylates are described, and include reactions with hydrogen, oxygen, carbon monoxide and aldehydes. In benzene solution the Rh^I carboxylates catalyse the homogeneous hydrogenation of alkenes and alkynes; the rates are compared with those using chlorotris(triphenylphosphine)rhodium(I). The interaction of Rh_2^{4+} with triphenylphosphine in presence of sodium diethyldithiocarbamate, mercaptobenzthiazole, pyridine-2-thiol, toluene-3-thiol, diphenylphosphorodithioic acid, diethoxyphosphorodithioic acid and lithium thiocyanate have been studied, and also the interaction of chlorotris(triphenylphosphine)rhodium(I) with tin(II) chloride.

THE tris(triphenylphosphine)rhodium(I) tetrafluoroborate $Rh(PPh_3)_3{}^+BF_4{}^-$, obtained [1] by the action of triphenylphosphine on the green dirhodium(II) ion, Rh_2^{4+}, gives, on treatment with lithium chloride, chlorotris(triphenylphosphine)rhodium(I).

This reaction can be readily extended using other lithium salts to give analogues of $RhCl(PPh_3)_3$ [2] which are not otherwise readily synthesised. It is not necessary to isolate the fluoroborate, and solutions of Rh_2^{4+} containing PPh_3 may be used. The carboxylates are of interest in order to compare their properties with $RhCl(PPh_3)_3$ as hydrogenation catalysts.

Carboxylatotris(triphenylphosphine)rhodium(I) *Complexes*. When a solution of Rh_2^{4+} in methanol (prepared from rhodium(II) acetate by protonation with fluoroboric acid [1]) containing triphenylphosphine (Rh : PPh_3, 1 : 4) and an excess of lithium acetate is heated, red crystals of the acetate, $Rh(OCOCH_3)(PPh_3)_3$, are obtained. Since the yield is over 80%, disproportionation of Rh_2^{4+} to Rh^I and Rh^{III} can be excluded, and since triphenylphosphine oxide is formed in the reaction, reduction by triphenylphosphine is clearly involved as it is in the preparation of $RhCl(PPh_3)_3$.[2] Other carboxylates, either homologous or α-halogen-substituted, can be obtained similarly in high yields, although the butyrate and caproate are more soluble and only *ca.* 50% yields are obtained by crystallisation from methanol at 25°. There is increasing solubility in non-polar solvents with increasing chain length as expected; the benzoate is quite soluble in diethyl ether.

The carboxylates show characteristic asymmetric carboxylate stretches around 1600 cm^{-1} and symmetric stretches at lower frequencies with the value of $\Delta\nu$ ($\nu_{as}COO - \nu_sCOO$) being consistent with a unidentate carboxylate grouping.[3] For halogen-substituted carboxylates the energies of ν_{as} and ν_s are higher than for the unsubstituted compounds. The chemical properties of $Rh(OCOR)(PPh_3)_3$ are generally similar to those of $RhCl(PPh_3)_3$ and the compounds will undergo oxidative-addition reactions, interaction with CO or aldehydes to give *trans*-$Rh(OCOR)CO(PPh_3)_2$ complexes, and will act as homogeneous hydrogenation catalysts for alkenes and alkynes.

Osmometric molecular weight determinations, *e.g.* for the acetate, in benzene under nitrogen suggested that dissociation is extensive. Since the values in dichloromethane were normal, *i.e.* in the range 950—1050, this suggested that even using the best precautions to exclude oxygen, the use of benzene as solvent, in which oxygen is quite readily soluble, is to be regarded with suspicion. During our studies, two other groups,[4] stimulated by the apparent discrepancy between ^{31}P n.m.r. spectra, which suggested no dissociation of $RhCl(PPh_3)_3$, and osmometric data which did, have made cryoscopic studies under rigorous oxygen free conditions and confirm that there is indeed no dissociation.

We have checked the molecular weights of the chloride and some of the carboxylates in benzene by the cryoscopic method using an apparatus similar to that described by Shriver [5] which allows total exclusion of air. The solid was weighed out into a side limb of the apparatus which could be rotated and the solid tipped into the cell. Benzene was thoroughly degassed under vacuum, cooled, melted, and condensed into the cryoscopy cell attached to a high vacuum line. Determinations made on freshly prepared orange solutions of $RhCl(PPh_3)_3$ in benzene ranging from $2{\cdot}35 \times 10^{-3}$ to $2{\cdot}80 \times 10^{-3}$M under nitrogen gave molecular weights of 950 ± 10 (calculated 925). The solutions were stable for several hours but the slow formation of the halide bridged dimer [2] $Rh_2Cl_2(PPh_3)_4$ with loss of phosphine overnight led to values *ca.* 440—480.

On evacuating a freshly prepared and measured solution and filling the cell with hydrogen, the solution immediately turned pale yellow, due to formation of the

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† No reprints available.

[1] P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 3322.

[2] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[3] (*a*) C. A. Agambar and K. G. Orrell, *J. Chem. Soc.* (*A*), 1969, 897; (*b*) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffner, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1965, 3632.

[4] (*a*) C. A. Tolman, Central Research Laboratories, E.I. du Pont de Nemours, Wilmington, Del. personal communication; (*b*) D. D. Lehman, D. F. Shriver, and I. Wharf, *Chem. Comm.*, 1970, 1487.

[5] D. F. Shriver, 'The Manipulation of Air Sensitive Compounds,' McGraw-Hill, New York, 1969, p. 161—163; J. A. Dilts and D. F. Shriver, *J. Amer. Chem. Soc.*, 1968, **90**, 5796.

dihydrido-species[2] and the apparent molecular weight fell to 460 ± 10. Removal of hydrogen by evacuation reformed an orange solution but this now had also molecular weight values 460 ± 10.

Similar experiments using oxygen were in agreement with previous findings[4b] and gave values *ca.* 450. Molecular weights in benzene for the acetate, propionate and halogen-substituted acetates under air-free conditions are normal but also show dissociation promoted by hydrogen or oxygen. We conclude therefore that all molecular weights of air-sensitive substances such as $RhCl(PPh_3)_3$ determined by osmometers of the Mechrolab type must be considered as suspect. The Hitachi–Perkin-Elmer osmometer is easier to sweep out, but even so, solutions have to be made up externally and injected. It would be possible to do all of the operations in an inert-atmosphere bag or box but even then, rigorously purified nitrogen should be used. Hence it follows that oxidative addition of molecular oxygen, and indeed of other molecules such as H_2, HCl, CH_3I *etc.* promotes the dissociation. That is the resulting octahedral tris(triphenylphosphine)rhodium(III) species are evidently unstable, readily losing triphenylphosphine to give five-co-ordinate complexes. This fact has already been confirmed for the addition of CH_3I, which gives a five-co-ordinate complex whose structure has been determined.[6] If the added molecule can be readily removed, like hydrogen, then at least in dilute solution, reassociation of triphenylphosphine does not occur, and formally three-co-ordinate solvated bisphosphine species are presumably formed. Hence where X = Cl, OCOR *etc*, we have:

$$Rh^{I}X(PPh_3)_3 \xrightarrow{+H_2} Rh^{III}XH_2(PPh_3)_3 \xrightarrow{-PPh_3}$$

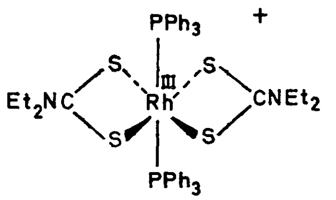
$$Rh^{III}XH_2(PPh_3)_2 \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} Rh^{I}X(PPh_3)_2$$

It was clearly shown[7] that for the most effective hydrogenation, the ratio $PPh_3 : Rh$ is 2 : 1 and that at high PPh_3 concentrations the reaction is inhibited, evidently due to reassociation. The fact that $RhX(PPh_3)_3$ compounds are not dissociated in solution as originally thought[2] does not alter the kinetic and mechanistic treatment other than to require that dissociation is a property of the rhodium(III) species formed after oxidative addition of hydrogen has taken place.

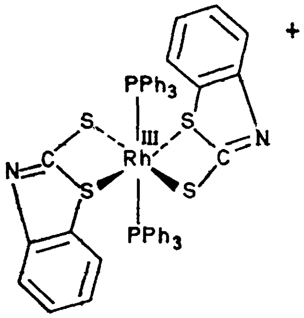
Alkene Hydrogenations.—The carboxylates have been studied using the same procedure as before.[2,7] However, in view of the known sensitivity to oxygen, some of the original experiments using $RhCl(PPh_3)_3$ were repeated with even more stringent precautions to remove traces of oxygen than those originally used, including for example, distillation of benzene into the reaction flask *in vacuo*. No differences between current and previous runs were observed.

At 25° with 1 mmol l^{-1} catalyst concentration, 1 mol l^{-1} alkene concentration, the rate of H_2 uptake, measured at 40 cmHg pressure and 25 °C for hex-1-ene and cyclohexene were 9·45 and 4·13 ml min^{-1} at s.t.p. compared to the values of 9·47 and 4·20 ml min^{-1} obtained previously.[2]

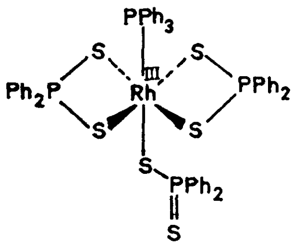
It may be noted that both here and in previous studies,[2] the catalyst solutions were stirred under hydrogen for several minutes before addition of alkene and that rates were measured after a short period of rapid stirring under steadily state conditions. Under such conditions, complete oxidative dissociation has occurred as shown by cryoscopy, so that it is unlikely that oxygen affects the maximum rate for a given set of conditions as has been claimed.[8]



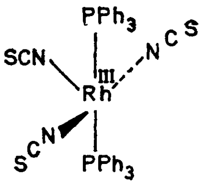
(I)



(II)



(III)



(IV)

It is perhaps worth noting that numerous studies extending our original work[2] have been made but the precautions taken by other workers to purify the hydrogen or nitrogen used, and to remove oxygen or peroxides from solvents or substrates have not always been as stringent as ours, nor have the reaction systems been high vacuum ones. Some of the results should therefore be regarded as provisional until repeated under rigorous conditions. For example, one experimental description[8b]

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[6] P. G. H. Troughton and A. C. Skapski, *Chem. Comm.*, 1968, 575.

[7] S. Montelatichi, A. Van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 1054.

[8] (*a*) R. L. Augustine and J. F. Van Peppen, *Chem. Comm.*, 1970, 497; (*b*) R. L. Augustine and J. F. Van Peppen, *J. Amer. Oil Chemists' Soc.*, 1971, **47**, 478.

indicates that a vacuum line technique was not employed and the solutions were exposed to and hence presumably saturated with water vapour; no statement about necessary purification of commercial gases was made; heptene was distilled before use, but our own experience has shown that alkenes must be distilled over sodium into the reaction flask under nitrogen. In another case,[9] alkenes were used as received, but we have found that alkenes from this particular source almost invariably contain peroxides.

The carboxylate system resembles that of the chloride in that the hydrogenated solutions are yellow and that if stirring in of H_2 is stopped in solutions containing large concentrations of alkene, the colour rapidly becomes red. The kinetics are similar in both cases; in dilute solution, the rate of hydrogenation is approximately first order dependent on both rhodium and olefin concentrations.

TABLE 1

Infrared spectra of carboxylato-complexes $Rh(OCOR)(PPh_3)_3$ and $Rh(OCOR)(CO)(PPh_3)_2$ [a]

Compound	ν_{as}(COO)	ν_s(COO)	$\nu_{as} - \nu_s$	ν_{CO}
$Rh(OCOCH_3)(PPh_3)_3$	1601	1370	231	
$Rh(OCOC_2H_5)(PPh_3)_3$	1599	1379	220	
$Rh(OCOC_3H_7)(PPh_3)_3$	*b*	1383		
$Rh(OCOC_5H_{11})(PPh_3)_3$	*b*	1389		
$Rh(OCOPh)(PPh_3)_3$	1590	1355	235	
$Rh(OCOCH_2Cl)(PPh_3)_3$	1644	1405	239	
$Rh(OCOCClF_2)(PPh_3)_3$	1673	*b*		
$Rh(OCOCF_3)(PPh_3)_3$	1673	1418	255	
$Rh(OCOC_2F_5)(PPh_3)_3$	1685	*b*		
$Rh(OCOCH_3)(CO)(PPh_3)_2$	1608	1377	231	1976
$Rh(OCOC_2H_5)(CO)(PPh_3)_2$	1607	1382	225	1980
$Rh(OCOC_3H_7)(CO)(PPh_3)_2$	*b*	*b*		1981
$Rh(OCOCH_2Cl)(CO)(PPh_3)_2$	1600	1410	190	1979
$Rh(OCOCClF_2)(CO)(PPh_3)_2$	*b*	*b*		1980
$Rh(OCOCF_3)(CO)(PPh_3)_2$	1692	1410		1982
$Rh(OCOC_2F_5)(CO)PPh_3)_2$				1981
$Rh(OCOCF_3)(O_2)(CO)(PPh_3)_2$				1982

[a] Nujol or hexachlorobutadiene mulls, cm^{-1}. [b] Bands obscured.

TABLE 2

Comparative rates of hydrogenation of substrates using acetato- and chloro-tris(triphenylphosphine)rhodium(I) [a]

	Uptake of H_2 in ml min^{-1} at s.t.p.	
Substrate	$Rh(OCOCH_3)(PPh_3)_3$	$Rh(Cl)(PPh_3)_3$
Hex-1-ene	45·0	212·0
Pent-1-ene	31·8	204·8
Hex-1-yne	95·5	211·8
Cyclohexene	$<0·1$	92·6
Cyclo-octene	$<0·1$	
Cyclopentene	20·6	
Cyclo-octa-1,3-diene	30·9	
Cyclo-octa-1,5-diene	$<0·1$	$<0·1$

[a] Catalyst concentration 1mM; substrate 1M in benzene. 25 °C. Rate at 40 cmHg pressure.

Table 2 gives some representative data comparing the acetate and chloro-compounds, while Table 3 gives relative rates for hex-1-ene for different carboxylates.

The acetate is less than 0·25 as effective as the chloride for hex-1-ene and hex-1-yne, but is less than 0·025 as active toward cyclohexene, so that evidently the steric or other factors involved allow some potentially useful selective reductions. The nature of the carboxylate group has evidently no profound effect on the rate of hex-1-ene hydrogenation, but the rates for the more electron withdrawing carboxylate groups are lower at 25°. However, at 25° (relative to the chloride) they are relatively faster than at 40°, possibly because of a lower tendency to form dimers with carboxylate bridges, which are known to be formed in concentrated solutions on warming, *e.g.* the butyrate rapidly precipitates the dimer from benzene.

TABLE 3

Relative rates of hydrogenation of hex-1-ene at 25 and 40° using tris(triphenylphosphine)rhodium(I) complexes [a]

	Rate of H_2 uptake in ml min^{-1} at s.t.p.	
Compound	25°	40°
$Rh(Cl)(PPh_3)_3$	212·0	>1000
$Rh(OCOCH_3)(PPh_3)_3$	45·0	168·5
$Rh(OCOC_2H_5)(PPh_3)_3$	36·5	112·5
$Rh(OCOCH_2Cl)(PPh_3)_3$	$<0·1$	116·1
$Rh(OCOCClF_2)(PPh_3)_3$	$<0·1$	115·5
$Rh(OCOCF_3)(PPh_3)_3$	$<0·1$	116·9
$Rh(OCOC_2F_5)(PPh_3)_3$	$<0·1$	121·0
$Rh(OCOPh)(PPh_3)_3$	$<0·1$	$<0·1$

[a] Catalyst concentration 1mM; hex-1-ene concentration 1M; solvent benzene.

TABLE 4

Infrared spectra for rhodium(III) complexes [a]

	ν_{Rh-S}			ν_{P-S}	
Compound	ν_s	ν_{as}	ν_{CN}	ν_s	ν_{as}
$[Rh(S_2CNEt_2)_2(PPh_3)_2]BF_4$	345	413	1518		
$[Rh(mbt)_2(PPh_3)_2]BF_4$	319	408			
$[Rh(pyS)_2(PPh_3)_2]BF_4$	344				
$[Rh(tt)_2(PPh_3)_2]BF_4$	350				
$Rh(S_2PPh_2)_3(PPh_3)$	310	350		568	574, 642 [b]
$Rh[S_2P(EtO)_2](PPh_3)_3$	290	413			638 [b]
$Rh(SCN)_3(PPh)_2$			2085		

[a] Nujol or Vaseline mulls, cm^{-1}, mbt = 2-merceptobenzthiazole, pyS = 2-mercaptopyridine, tt = toluene-3-thiol. [b] Band due to P=S vibration.

Although negligible amounts of isomerised alkene were detected in early studies,[2] the reaction times involved were only a few minutes and less than 1% of the alkene was hydrogenated. Although some isomerisation has been shown to occur in ethanol–benzene solutions [10] we now confirm that even in pure benzene, some isomerisation takes place. For 1mM catalyst, 1M-hexene at 25° and *ca.* 1 atm hydrogen, the hydrocarbon composition after 1 h was: hex-1-ene 52·9%, n-hexane, 41·5%, *cis* + *trans*-hex-2-ene, 5—6%. Similarly, after 24 h using the acetate, the composition was hex-1-ene 23·5%, n-hexane 38·2%, *trans*-hex-2-ene, 22·6%, *cis*-hex-2-ene, 15·7%. The trifluoroacetate under similar conditions but after only ½ h gave a similar mixture but with an additional 1—2% of hex-3-ene. The rates of hydrogenation and isomerisation are thus comparable

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[9] G. C. Bond and R. A. Hillyard, *Discuss. Faraday Soc.*, 1968, **46**, 20.

[10] J. F. Bielmann and M. J. Jung, *J. Amer. Chem. Soc.*, 1968, **90**, 1073; A. S. Hussey and Y. Takeguchi, *J. Amer. Chem. Soc.*, 1969, **91**, 672.

for the carboxylates. Hence a two step transfer of hydrogen involving an alkyl intermediate evidently proceeds in pure benzene solutions as suggested for the benzene–ethanol solutions by Bielmann and Jung.[10]

Reaction with Carbon Monoxide.—On bubbling carbon monoxide through a suspension of the acetate in benzene, the solid rapidly dissolves and a yellow solution is obtained from which yellow crystals of the complex *trans*-$\mathrm{Rh(OCOCH_3)(CO)(PPh_3)_2}$ are obtained quantitatively:

$$\mathrm{Rh(OCOCH_3)(PPh_3)_3 + CO \longrightarrow \textit{trans}\text{-}Rh(OCOCH_3)(CO)(PPh_3)_2 + PPh_3}$$

The i.r. spectrum shows the carbonyl band ν_{CO} at 1976 $\mathrm{cm^{-1}}$ (Table 1), and the assymmetric and symmetric carboxylate frequencies occur at higher energy than in the parent acetate, consistent with a monodentate carboxylate grouping *trans* to CO. The other carboxylates behave similarly giving stable yellow crystalline solids of stoicheiometry $\mathrm{Rh(OCOR)(CO)(PPh_3)_2}$. The reaction is irreversible even in an excess of molten triphenylphosphine. The carboxylates also abstract CO from aldehydes. Thus, the acetate in benzene reacts quantitatively with n-heptaldehyde or valeraldehyde in the cold, or extremely rapidly on warming to give the *trans*-carbonyl derivatives. This CO abstraction from aldehydes presumably follows the same reaction path as with $\mathrm{RhCl(PPh_3)_3}$.[11] Although the carbonyl acetate and other carboxylates are unreactive towards oxygen at atmospheric pressure and room temperature, the fluorocarboxylates are quite reactive and unless very thoroughly degassed benzene solutions are used, an oxygen adduct is formed reversibly.

$$\mathrm{Rh(OCOCF_3)(PPh_3)_3 \xrightarrow[-PPh_3]{+CO} \underset{\text{yellow}}{\textit{trans}\text{-}Rh^{I}(OCOCF_3)(CO)(PPh_3)_2} \underset{-O_2}{\overset{+O_2}{\rightleftharpoons}} \underset{\text{orange-red}}{Rh^{III}(OCOCF_3)(CO)(O_2)(PPh_3)_2}}$$

The orange-red adduct has a band at 833 $\mathrm{cm^{-1}}$ in the i.r. assignable as $\nu_{\mathrm{O-O}}$ but there is no appreciable difference in the values of ν_{CO} of the yellow and red complexes. The weakness of the binding of $\mathrm{O_2}$ is also shown by the fact that on evacuation or sweeping with CO, the oxygen is removed, and also by the fact that the oxygen complex cannot be formed when more strongly solvating solvents such as alcohols or ketones are used instead of benzene.

Rhodium(III) *Complexes with Sulphur Containing Ligands*

By treatment of a methanolic solution of $\mathrm{Rh_2^{4+}}$ with a slight excess of triphenylphosphine, followed by a stoicheiometric amount of the ligand in methanol, triphenylphosphine rhodium complex salts of the type $\mathrm{[Rh^{III}(L)_2(PPh_3)_2]BF_4}$, where L is a bidentate anionic ligand ($\mathrm{L^-}$) (*e.g.* diethyldithiocarbamate) or a monodentate ligand (*e.g.*, $\mathrm{SCN^-}$ or *p*-$\mathrm{CH_3C_6H_4S^-}$), have been obtained. In the absence of triphenylphosphine (*i.e.*, direct interaction of the ligand with $\mathrm{Rh_2^{4+}}$ in methanol), brown insoluble and presumably polymeric solids are immediately precipitated from solution. The addition of an excess of triphenylphosphine produces a clear red solution from which salts of the above stoicheiometry can be obtained. These complexes doubtless arise by initial reduction of $\mathrm{Rh^{II}}$ to $\mathrm{Rh^{I}}$ by triphenylphosphine. Since the reactions are accompanied by the formation of $\mathrm{Ph_3PO}$, an extra 2 moles of $\mathrm{PPh_3}$ per $\mathrm{Rh_2^{4+}}$ are required to complete the reduction; the oxygen presumably arises from the methanolic solvent, followed by oxidation to $\mathrm{Rh^{III}}$ in the presence of the anionic ligands.

Dithiocarbamato and other Salts of Stoicheiometry $\mathrm{[Rh(L)_2(PPh_3)_2]BF_4}$.—On treatment of a green methanolic solution of $\mathrm{Rh_2^{4+}}$ with an excess of triphenylphosphine and a stoicheiometric quantity of sodium diethyldithiocarbamate in methanol, a yellow crystalline solid is deposited from solution. The i.r. spectrum of this substance shows in addition to triphenylphosphine and tetrafluoroborate absorptions, a stretching vibration (ν_{CN}) at 1518 $\mathrm{cm^{-1}}$ characteristic of a bidentate dithiocarbamate[12] (Table 4). The conductivity in nitromethane corresponds to that for a 1 : 1 electrolyte[13] ($\Lambda_0 - \Lambda_e$ *vs.* $\sqrt{c}$ gave a slope of 178). The salt thus appears to be $\mathrm{[Rh(S_2CNEt_2)_2(PPh_3)_2]BF_4}$, (I). It is stable in air indefinitely, and is slightly soluble in the more polar solvents such as nitromethane, methanol and to a limited extent in acetone, but insoluble in non-polar solvents such as benzene or toluene. By contrast, treatment of the four-co-ordinate cationic complex,[1] $\mathrm{[Rh^{I}(CO)(PPh_3)_3]BF_4}$, in methanol with sodium diethyldithiocarbamate yields orange crystals identical with an authentic sample of $\mathrm{Rh(S_2CNEt_2)_3(PPh_3)}$[12] in which two of the dithiocarbamate groups are chelated, and the other unidentate at room temperature but are undergoing rapid interconversions at higher temperatures.[14] Other complexes of stoicheiometry $\mathrm{[Rh(L)_2(PPh_3)_2]^+BF_4^-}$ (where L = 2-mercaptopyridine, pyS; toluene-3-thiol, tt; or 2-mercaptobenzthiazole, mbt) have been obtained similarly (see Experimental section). For the bis(mercaptobenzthiazole) complex cation $\mathrm{[Rh(mbt)_2(PPh_3)_2]^+}$, the absence of a Rh–N stretching vibration, and the presence of the symmetric and asymmetric Rh–S vibrations suggests sulphur bonding of the ligand, and an octahedral ion as in (II). The complex is air stable, and slightly soluble in alcohols and ketones, but virtually insoluble in benzene or toluene. Both pyridine-2-thiol and toluene-3-thiol give complexes of stoicheiometry similar to the above and also show Rh–S stretching frequencies. The toluene-3-thiol complex clearly

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[11] M. C. Baird, C. J. Nyman and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 348.

[12] C. O'Connor, J. D. Gilbert, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 84.

[13] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.* (*A*), 1964, 4587.

[14] R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc.* (*A*), 1971, 1994.

cannot have a chelate ligand, although the pyridine-2-thiolate could be chelated as in the ruthenium complex $Ru(pyS)_2(PPh_3)_2$ where the ligand is bidentate.[11] Since the two complexes are very similar and square rhodium(III) complexes are so far unknown, it is conceivable that the reason why the thiolato-ligands act as unidentate groups binding only through sulphur atoms is that there is additional co-ordination of the BF_4^- ion. This has been proposed [1] in the case of $Rh(PPh_3)_3BF_4$, and as for this compound, conductivities of the thiolates in nitromethane or nitrobenzene (10^{-2} to 10^{-4}M) suggest that both species are weak electrolytes. This implies ion-pair formation or some degree of co-ordination of BF_4^-.

Complexes of Other Stoicheiometry.—Neutral Rh^{III} complexes of stoicheiometry $Rh(L)_3(PPh_3)_n$ (where $n = 1$, 2 or 3) have been obtained from Rh_2^{4+}, triphenylphosphine and an excess of the ligand L in methanol. When diphenylphosphorodithioic acid (Ph_2PS_2H) is used, $n = 1$, and the octahedral complex $Rh(S_2PPh_2)_3(PPh_3)$, (III) is obtained as red crystals. Unless the normal octahedral co-ordination of Rh^{III} is not to be exceeded, at least one of the ligands must bond through only one sulphur atom [*cf.* $Rh(S_2CNMe)_3(PPh_3)$]. Both the symmetric and asymmetric P–S stretching vibrations appear in the i.r. spectrum (Table 5), and in addition, the P=S stretch of the unidentate group occurs at 642 cm^{-1}.

The complex was obtained in almost quantitative yield by treatment of the salt $Rh(CO)(PPh_3)_3{}^+BF_4{}^-$ [1] with excess of the free acid (Ph_2PS_2H), the crystalline red product separating from solution after several hours. The complex is insoluble in alcohols, and is only appreciably soluble in benzene, toluene and chlorinated solvents such as chloroform or dichloromethane. By contrast, presumably for steric and electronic reasons, diethoxyphosphorodithioic acid [$(EtO)_2PS_2H$] (or the sodium salt), produces the octahedral complex of stoicheiometry $Rh[(EtO)_2PS_2]_3(PPh_3)_3$ indicating that all the three anionic ligands are unidentate ($\nu_{P=S}$ 638 cm^{-1}). The interaction of methanolic Rh_2^{4+} with triphenylphosphine and excess methanolic lithium thiocyanate gives an orange microcrystalline solid of stoicheiometry $Rh(SCN)_3(PPh_3)_2$, (VI). The SCN group appears to be *N*-bonded from the i.r. spectrum, and since the compound is monomeric in solution, it provides another example of five-co-ordinate Rh^{III}, with two PPh_3 groups, which by analogy with $Rh(CH_3)(I)_2(PPh_3)_2$ [6] are probably *trans*. The complex is air stable, and very soluble in both polar and non-polar solvents to give stable yellow solutions.

EXPERIMENTAL

Spectrometers.—N.m.r.: Perkin-Elmer R14 and Varian HA100 at 100 MHz. I.r.: Perkin-Elmer 257 and 457. U.v.–visible: Perkin-Elmer 137. G.l.c.: Perkin-Elmer F11, with flame ionisation detector and Kent Chromalog integrator.

Materials.—Johnson–Matthey Limited rhodium trichloride trihydrate and Albright and Wilson Limited triphenylphosphine. Reagent grade solvents were used throughout, and were thoroughly deoxygenated prior to use. All reactions and other operations were carried out under nitrogen unless otherwise stated.

Preparations.—Solutions of Rh_2^{4+} were prepared [1] by treating a suspension of the methanol adduct of rhodium(II) acetate, $Rh_2(OCOMe)_4,2MeOH$, (1·0 g) in methanol (100 ml) with fluoroboric acid (3 ml of 40% aq. solution) at 60° for *ca.* 20 h. Analytical data is collected in Tables 5 and 6.

Carboxylatotris(triphenylphosphine)rhodium(I).— Complexes of the type $Rh(OCOR)(PPh_3)_3$ were prepared by the following procedure. To the green methanolic solution of Rh_2^{4+} (20 ml) was added a solution of triphenylphosphine (1·0 g) in methanol, followed by an excess of a methanolic solution of the lithium carboxylate. In all cases, except for the butyrate, caproate and benzoate, the red mixture was refluxed for 20 min, filtered hot and the crystalline product washed with methanol and vacuum dried. The butyrate, caproate and benzoate complexes were precipitated from the red mixture at 25° after standing for several hours.

Carboxylato(carbonyl)bis(triphenylphosphine)rhodium(I).—Complexes of the type $Rh(OCOR)(CO)(PPh_3)_2$ were prepared as follows. Carbon monoxide was passed through a suspension of the carboxylate $Rh(OCOR)(PPh_3)_3$, (0·5 g) in benzene (10 ml) to give a bright yellow solution which was then concentrated to *ca.* 1 ml. Addition of diethyl ether gave the product. The *oxygen adduct* of the trifluoroacetate, $Rh(OCOCF_3)(CO)(O_2)(PPh_3)_2$, was obtained quantitatively by bubbling oxygen into the carbon monoxide-saturated yellow solution above. The solution was evaporated to small volume under oxygen, and crystallised from ether. $\lambda_{max.}$(ε 10^{-3}) in benzene for $Rh(OCOCF_3)(CO)(PPh_3)_2$: 389 nm (13·5); for $Rh(OCOCF_3)(CO)(O_2)(PPh_3)_2$ 389, (12·9), 424 (7·7).

Interaction of $Rh(OCOCH_3)(PPh_3)_3$ *with Aldehydes*.—A solution of the acetate complex (0·5 g) in deoxygenated benzene was heated to 40° under nitrogen, and n-heptaldehyde (*ca.* 2 ml) was added dropwise. After 10 min a bright yellow solution was obtained. Vacuum evaporation and crystallisation of the product from methanol–ether gave yellow crystals identical with an authentic sample of $Rh(OCOCH_3)(CO)(PPh_3)_2$. Similar results were obtained using the propionate or the substituted carboxylates, or using valeraldehyde as the CO source.

Interaction of Methanolic Rh_2^{4+} *with Triphenylarsine and Lithium Acetate*.—A methanolic solution of Rh_2^{4+} (15 ml) was refluxed for 20 min with triphenylarsine (1·2 g) in methanol (*ca.* 20 ml), and an excess of lithium acetate to give maroon crystals. The spectroscopic data and elemental analysis indicates a triphenylarsine adduct of rhodium acetate $Rh_2(OCOMe)_4,2AsPh_3$, analogous to the triphenylphosphine adduct described previously.[1]

The adduct was also obtained quantitatively by treating rhodium(II) acetate (or the methanol adduct) (0·5 g) in boiling methanol (100 ml) with excess methanolic triphenylarsine. The crystals were precipitated almost immediately and had melting point and analytical data identical with an authentic sample above. The propionato-, chloroacetato- and trifluoroacetato-complexes were obtained similarly. All the complexes were diamagnetic by the Gouy method, and since the molecular weights in solution were consistent with a dimeric species, it seems reasonable to propose that the complexes are metal–metal bonded, which is further evidence for the metal–metal interaction in Rh_2^{4+}.

The weakness of the binding of the triphenylarsine groups is shown by the fact that the acetate $Rh_2(OCOMe)_4,2AsPh_3$

dissolves in good donor solvents such as alcohols and ketones when warmed to give bluish green solutions, the electronic absorption spectra being similar to that of $Rh_2(OCOMe)_4,2L$ (where L = solvent), whereas in benzene, the adduct dissolves giving purple coloured solutions.

Trichlorostannatobis(*triphenylphosphine*)*rhodium*(I).—To a solution of tin(II) chloride (0·23 g) in methanol (20 ml) was added a solution of $RhCl(PPh_3)_3$ (0·96 g) in methylene chloride (20 ml) and the mixture was refluxed for 5 min and then cooled to −10°. The resulting precipitate was washed with diethyl ether to give maroon crystals of the *complex*.

The compound is fairly soluble in methylene chloride and nitromethane in which it is a poor conductor.

Bis(*tetramethylammonium*)*tris*(*trichlorostannato*)*triphenylphosphinerhodium*(I).—A solution of $RhCl(PPh_3)_3$ (0·96 g) in chloroform (20 ml) was added to a solution of tin(II) chloride (0·7 g) in acetone–methanol (20 ml of a 1 : 1 mixture). The mixture was heated to boiling and a solution of tetramethylammonium chloride in methanol was added. Cooling the solution to −10° precipitated the *complex* as a red powder. $\Lambda_e(10^{-3}\text{M}) = 83·3\ \text{ohm}^{-1}\ \text{cm}^{-1}$ in nitromethane.

Rhodium(III) *Complexes*

Bis(NN-*diethyldithiocarbamato*)*bis*(*triphenylphosphine*)*rhodium*(III) *tetrafluoroborate*.—To a methanolic solution of Rh_2^{4+} (20 ml) was added a saturated methanolic solution of triphenylphosphine (15 ml). To this red solution was added a solution of sodium diethyldithiocarbamate (0·8 g) in methanol (10 ml). The *complex* which was precipitated on standing at 25° was filtered off, washed with methanol and dried *in vacuo*.

TABLE 5

Analytical and other data for rhodium(I) complexes

Compound	Yield (%)	Colour	M.p. (°C)	Analyses: found (calc.) (%) C	H
$Rh(OCOCH_3)(PPh_3)_3$	80	Orange	134—136	71·0 (70·9)	5·1 (5·1)
$Rh(OCOC_2H_5)(PPh_3)_3$	75	Orange	134—135	71·1 (71·2)	5·4 (5·2)
$Rh(OCOC_3H_7)(PPh_3)_3$	55	Orange	130—132	71·4 (71·3)	5·6 (5·3)
$Rh(OCOCH_2Cl)(PPh_3)_3$	75	Orange	135—137	68·1 (68·4)	5·6 (4·8)
$Rh(OCOCClF_2)(PPh_3)_3$	72	Orange	136—138	65·7 (66·0)	4·4 (4·4)
$Rh(OCOCF_3)(PPh_3)_3$	70	Orange	138—139	67·2 (67·1)	4·6 (4·5)
$Rh(OCOC_2F_5)(PPh_3)_3$	70	Orange	136—138	65·0 (65·2)	4·1 (4·3)
$Rh(OCOCH_3)(CO)(PPh_3)_2$	95	Yellow	171—173	65·8 (65·6)	4·8 (4·6)
$Rh(OCOC_2H_5)(CO)(PPh_3)_2$	90	Yellow	147—148	65·8 (65·9)	5·2 (4·8)
$Rh(OCOCH_2Cl)(CO)(PPh_3)_2$	95	Yellow	172—174	62·3 (62·6)	4·6 (4·3)
$Rh(OCOCF_3)(CO)(PPh_3)_2$	95	Yellow	175—177	61·0 (60·9)	4·0 (3·9)
$Rh(OCOCF_3)(CO)(O_2)(PPh_3)_2$	95	Yellow	176—178	59·0 (58·5)	4·0 (3·8)
$Rh_2(OCOCH_3)_4(AsPh_3)_2$	30	Maroon	267—268	49·8 (50·0)	4·1 (4·0)
$Rh_2(OCOC_2H_5)_4(AsPh_3)_2$	30	Maroon	228—229	52·4 (52·0)	4·4 (4·5)
$Rh(SnCl_3)(PPh_3)_3$	95	Maroon	128—129	58·4 (58·2)	3·9 (4·0) [a]
$(Me_4N)_2[Rh(SnCl_3)_3(PPh_3)]$	95	Red		26·3 (26·6)	2·8 (3·3) [b]

[a] Sn, 10·5 (10·6) %. [b] Cl, 27·3 (27·2); N, 2·4 (2·5); Sn, 30·7 (30·3) $\Lambda_e = 83·3\ \text{ohm}^{-1}\ \text{cm}^2$ (10^{-3}M nitromethane).

TABLE 6

Analytical and other data for rhodium(III) complexes

Compound	Yield (%)	Colour	M.p. (°C)	Analysis: found (calc.) (%)
$[Rh(S_2CNEt_2)_2(PPh_3)_2]BF_4$	45	Yellow	252—253	C, 54·3 (54·5); H, 5·3 (5·0); N, 2·4 (2·7); P, 6·1 (6·1)
$[Rh(mbt)_2(PPh_3)_2]BF_4$	35—40	Orange	220—222	C, 58·8 (58·2); H, 3·6 (3·8); N, 2·6 (2·7); P, 5·0 (5·9)
$[Rh(pyS)_2(PPh_3)_2]BF_4$	*ca.* 40	Yellow	>260	C, 57·9 (58·9); H, 4·1 (4·3); N, 2·8 (3·0)
$[Rh(tt)_2(PPh_3)_2]BF_4$ [a]	*ca.* 30	Orange-brown	125—127	C, 62·7 (62·6); H, 5·0 (4·6)
$Rh(S_2PPh_2)_3(PPh_3)$ [b]	40	Maroon	112—114	C, 58·7 (58·3); H, 4·2 (4·1); P, 10·5 (11·1); S, 18·2 (17·3)
$Rh[S_2P(EtO)_2]_3(PPh_3)_3$	40	Red		C, 55·2 (54·9); H, 5·1 (5·2)
$Rh(SCN)_3(PPh_3)_2$ [c]	45	Yellow-orange	159—160	C, 58·4 (58·5); H, 4·9 (3·8); N, 4·7 (5·2)

[a] *M* (in MeOH by osmometer) 465 (required 962). [b] *M* (in benzene by osmometer) 1140 (required 1120). [c] *M* (benzene by osmometer) 845 (required 801).

Conductivity measurements were made in nitromethane solutions varying in concentration from 10^{-2} to 10^{-4}M. A straight line plot of Λ_e *vs.* $\sqrt{c}$ was extrapolated to give Λ_0, and a further plot of $\Lambda_0 - \Lambda_e$ *vs.* $\sqrt{c}$ gave a straight line passing through the origin. A slope of 178 for nitromethane as solvent is consistent with a 1 : 1 electrolyte.[13]

Bis(2-*mercaptobenzthiazolato*)*bis*(*triphenylphosphine*)*rhodium*(III) *Tetrafluoroborate*.—Similarly, using 2-mercaptobenzthiazole (0·4 g). The crystals were collected and dried *in vacuo*.

Bis(2-*mercaptopyridinato*)*bis*(*triphenylphosphine*)*rhodium*(III) *Tetrafluoroborate*.—Similarly, using 2-mercaptopyridine (0·2 g) in methanol, to give after *ca.* 24 h the *complex*, which was washed with light petroleum and vacuum dried.

Bis(*toluene*-3-*thiolato*)*bis*(*triphenylphosphine*)*rhodium*(III) *Tetrafluoroborate*.—Similarly, using toluene-3-thiol (0·4 g) in the minimum of methanol to give after standing for some time, orange crystals of the *complex*, which was washed in a little methanol and dried in a stream of nitrogen.

Tris(*diphenylphosphorodithioato*)*triphenylphosphinerhodium*(III).—Similarly, using diphenyldithiophosphoric acid (0·8 g) in methanol. The red solution slowly deposited the *complex* which was recrystallised from benzene–methanol.

This complex can also be obtained by action of excess diphenylphosphoroditlinoic acid in methanol on $[Rh(CO)(PPh_3)_3]BF_4$ in methanol. An improved procedure for the preparation of this carbonyl complex [1] is to treat $Rh(CO)_2(acac)$ in methanol with a stoicheiometric amount of 40% aqueous HBF_4 in the presence of a stoicheiometric amount of PPh_3. The solution is refluxed for 30 min and on cooling the complex is obtained quantitatively.

Tris(diethoxyphosphorodithioato)tris(triphenylphosphine)-rhodium(III).—Similarly, using the sodium salt of the free acid [$(EtO)_2PS_2H$] (0·75 g) in methanol, to give after several hours, orange crystals of the *complex*, which was washed with methanol and vacuum dried.

Tris(thiocyanato)bis(triphenylphosphine)rhodium(III).—Similarly, using excess lithium thiocyanate. The crystals were washed with a few ml of light petroleum and vacuum dried.

Catalytic Studies.—The apparatus and general procedure was that described previously.[2,7] A chromous solution was used for removal of oxygen from both N_2 and H_2 (followed by drying train of conc. sulphuric acid bubblers and silica gel) but no difference in results was found. Substrates were purified as before and freshly distilled under pure N_2 prior to use, and benzene (as solvent) was distilled from trap to trap, frozen, pumped and melted and finally distilled into the hydrogenation flask before use. Further purification was achieved by evacuating and sweeping with hydrogen several times before the catalyst was added. On addition of the catalyst, stirring under H_2 was continued until all solid had dissolved, and when a clear homogeneous solution was obtained, substrate was added and rate measurements recorded while the mixture was vigorously stirred after steady state conditions had been achieved.

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