Mixed Ligand Carbonyl Complexes of Rhodium(I) and Rhodium(III)[1]

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Evidence is presented which suggests that the compounds *trans*-[$RhX(CO)_2PPh_3$] (Ia) (X = Cl, Br, I), made from [$RhCl(CO)_2]_2$ and triphenylphosphine (1 : 2 molar ratio), should be reformulated as the dimeric complexes *trans*-[$RhXCOPPh_3]_2$ (Ib). Similar compounds with X = SCN,OCOMe are also described. Detailed i.r. solution studies of the preparative reaction for X = Cl are interpreted in terms of the initial formation of a labile intermediate *cis*-[$RhCl(CO)_2PPh_3]_n$ (III) (*n* probably 2), followed by partial decarbonylation and isolation of (Ib) and a small amount of *cis*-[$RhCl(CO)PPh_3]_2$ (Ic). The compounds (Ib) undergo bridge cleavage reactions with various Lewis bases, giving [$RhX(CO)(PPh_3)L$] (L = PPh_3, $PMePh_2$, $P(C_6H_{11})_3$, $AsPh_3$, $SbPh_3$, C_5H_5N, Me_2S, *etc.*). With $SbPh_3$, the five-co-ordinate complex [$RhCl(CO)PPh_3(SbPh_3)_2$] is also formed. The ^1H n.m.r. of [$RhCl(CO)$-$(PPh_3)(PMePh_2)$] shows only a singlet for the methyl resonance, indicative of easy phosphine exchange in a strongly coupled PP′ complex. As expected, [$RhCl(CO)(PPh_3)(AsPh_3)$] readily undergoes oxidative addition reactions, giving [$RhClYZCO(PPh_3)(AsPh_3)$] (YZ = Cl_2, I_2, CH_3I). The latter product is in equilibrium with its acyl isomer [$RhClI(COCH_3)(PPh_3)(AsPh_3)]0{\cdot}5CH_3I$. However, pure [$RhClI(CH_3)(CO)(PPh_3)(AsPh_3)$] can be synthesised by reaction of the acyl–alkyl mixture [$RhClI(CH_3)(CO)PPh_3]_2$ (IV) and [$RhClI(COCH_3)PPh_3]_2$ (V) (previously formulated as the single compound [$RhClI(CO)(COCH_3)PPh_3$]) with $AsPh_3$. Similarly, [$RhClI(CH_3)$-$(CO)PPh_3L$] (L = PPh_3 or $SbPh_3$) can be obtained. These compounds readily undergo isomerisation to the more stable acyl isomer. Finally, [$RhCl_3(CO)PPh_3(AsPh_3)$] can also be prepared by reaction of *trans*-[$RhCl_3(CO)$-$PPh_3]_2$ (originally formulated as *trans*-[$RhCl_3(CO)_2PPh_3$]) with $AsPh_3$.

RECENTLY the reaction of [$RhCl(CO)_2]_2$ with triphenylphosphine (1 : 2 molar ratio) was reported to give the complex *trans*-[$RhCl(CO)_2PPh_3$] (Ia; X = Cl).[2] Further papers by the same authors discussed oxidative addition reactions of complex (Ia),[3,4] reaction with electronegative olefins [2,5] and with various bidentate ligands.[2,5]

Our initial interest in this novel starting material was based on the observation [2] that reaction of (Ia, X = Cl) with more PPh_3 gave the well-known [6] *trans*-[$RhCl(CO)$-$(PPh_3)_2$]. Thus, by reacting other ligands L (L = $AsPh_3$, $SbPh_3$, $PMePh_2$, C_5H_5N, *etc.*) with (Ia), we hoped to synthesise the mixed ligand complexes [$RhXCO(PPh_3)L$] (II), which may be useful catalytic precursors for olefin hydroformylation, *etc.* (*cf.* *trans*-[$RhClCO(PPh_3)_2$] [7]). Although some mixed ligand complexes containing tertiary phosphines have been recently reported, *e.g.* [$HRh(PPh_3)_3(AsPh_3)]0{\cdot}5C_6H_6$ [8] and [$RhCl_3(PBu^n_3)_2$-$(P\{OMe\}_3)$],[9] the only reported complex of type II is [$RhICO(PPh_3)(P\{C_6H_{11}\}_3)$], made by reacting *trans*-[$RhICO(PPh_3)_2$] with $P(C_6H_{11})_3$ (ten-fold excess) in toluene at 25° for 24 h.[10] In this instance, 100% conversion to the mixed ligand complex is observed. However, in all other systems investigated by this method,[10] the result has been either mixtures of [$RhXCOL_2$], [$RhXCOLL'$], and [$RhXCOL'_2$] or completely exchanged products (i.r. evidence).

RESULTS AND DISCUSSION

(*a*) *Reaction of I with Arsenic-, Nitrogen-, and Sulphur-containing Ligands.*—Reaction of '*trans*-[$RhCl(CO)_2$-PPh_3]' with excess of L (L = $AsPh_3$, C_5H_5N, *p*-$CH_3C_6H_4NH_2$, Me_2S) in benzene solution at room temperature, followed by concentration *in vacuo* and precipitation with pentane or ether, gives good yields of the mixed ligand complexes [$RhClCO(PPh_3)L$] (II). These compounds have been fully characterised by elemental analyses, molecular weights (Table), and detailed i.r. spectra (4000—200 cm^{-1}), which confirm the presence of PPh_3, L, and CO. The compounds are non-electrolytes and diamagnetic. T.l.c. of (II; L = $AsPh_3$) clearly shows that the observed *single* spot has an R_F value intermediate between that of the bis-phosphine and -arsine compounds, proving that the compound is not an equimolar mixture of *trans*-[$RhClCO(PPh_3)_2$] and *trans*-[$RhClCO(AsPh_3)_2$]. In fact this compound can be recrystallised from dichloromethane–acetone and appears indefinitely stable both in solid and solution state. In contrast, (II; L = C_5H_5N) decomposes slowly in solution and (II; L = Me_2S) gradually loses Me_2S on prolonged air-exposure of the solid. A *trans*-configuration for (II) (*i.e.*, L *trans* to PPh_3) is assigned on the basis of the similarity of the positions of both ν(CO) (*ca.* 1960 cm^{-1}) and ν(RhCl) (*ca.* 310 cm^{-1}) to those found for *trans*-[$RhClCO(PPh_3)_2$].[11,12]

As expected, [$RhClCO(PPh_3)(AsPh_3)$] readily undergoes oxidative addition reactions, giving [$RhClYZCO$-$(PPh_3)(AsPh_3)$] (YZ = Cl_2, I_2, CH_3I, *etc.*). For YZ = Cl_2, I_2, analytical and mass spectral data indicate the presence of some CCl_4 solvate (*ca.* 0·25 mol/rhodium). Refluxing for short periods (*ca.* 30 min) with methyl iodide gives a brown solid with i.r. bands 2060s, 1980w, 1712m cm^{-1} and, in addition, the absorptions expected

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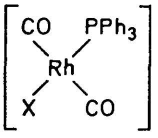
Analytical data for some rhodium(I) and rhodium(III) complexes

Complex	Colour	M.p. (°C)	Found (%)				Required (%)			
			C	H	Others	*M* [a]	C	H	Others	*M*
$[RhCl(CO)(PPh_3)(AsPh_3)]$	Pale yellow	230 (d)	60·4	4·1	As, 9·7; O, 2·2	737	60·5	4·1	As, 10·2; O, 2·2	734
$[RhCl(CO)(PPh_3)(C_5H_5N)]$	Buff-yellow	180 (d)	56·8	3·9	N, 3·1; O, 4·7	570	56·8	3·9	N, 2·8; O, 3·2	507
$[RhCl(CO)(PPh_3)(MeC_6H_4NH_2)]$	Yellow	128—130 (d)	56·5	4·4	N, 2·7		56·0	5·0	N, 2·6	
$[RhCl(CO)(PPh_3)(Me_2S)]$	Yellow-brown	105	50·9	4·1			51·4	4·3		
$[RhCl(CO)(PPh_3)(PMePh_2)]$	Lemon-yellow	150—153	61·2	4·5			61·1	4·5		
$[RhCl(CO)(PPh_3)(P\{C_6H_{11}\}_3)]$	Pale yellow	190 (d)	62·6	6·5			62·7	6·8		
$[RhCl(CO)(PPh_3)(SbPh_3)]$	Yellow	220 (d)	57·1	3·9	P, 4·4; Sb, 16·2	804	56·9	3·8	P, 4·0; Sb, 15·6	781
$[RhCl(CO)(PPh_3)(SbPh_3)_2]$ [b]	Red-brown	230 (d)	57·7	3·9	P, 2·9; Sb, 20·7		58·2	4·0	P, 2·7; Sb, 21·5	
$[RhCl_3(CO)(PPh_3)(AsPh_3)]0{\cdot}25CCl_4$ [c]	Yellow	210 (d)	52·1	3·6	Cl, 13·7		52·0	3·6	Cl, 16·7	
$[RhClI_2CO(PPh_3)(AsPh_3)]0{\cdot}25CCl_4$ [c]	Brown	235 (d)	41·6	2·8	Cl, 7·2; I, 25·5	1022	43·5	2·9	Cl, 6·9; I, 24·7	1027
$[RhClI(COCH_3)(PPh_3)(AsPh_3)]$-$0{\cdot}5CH_3I$ [c,d]	Dark brown	125—129	48·7	3·6	I, 21·9		48·7	3·7	I, 20·2	
$[RhCl_3(CO)(PPh_3)(SbPh_3)]$ [e]	Yellow	126—129	50·4	3·5			52·1	3·5		
$[RhClI(COCH_3)PPh_3]_2$ [f]	Dark brown	131	43·4	3·4	I, 22·3, Cl, 4·7		42·1	3·2	I, 22·3; Cl, 6·2	
$[RhClI(CH_3)(CO)(PPh_3)AsPh_3]$ [g]	Orange-yellow	168—170 (d)	51·1 (52·0) [h]	3·7 (3·8) [h]	Cl, 4·2; I, 14·3		52·1	3·8	Cl, 4·1; I, 14·5	
$[RhClI(CH_3)(CO)(PPh_3)_2]$ [g]	Orange-yellow	160—162	55·2 (55·1) [h]	4·1 (4·1) [h]	Cl, 5·2; I, 12·8		54·8	4·0	Cl, 4·3; I, 15·3	
$[RhClI(CH_3)(CO)(PPh_3)SbPh_3]$ [g]	Orange-yellow	165—167	49·6 (49·6) [h]	3·6 (3·7) [h]	Cl, 4·1; I, 14·0		49·4	3·6	Cl, 3·85; I, 13·8	
$[RhBr(CO)PPh_3]_2$	Orange-brown	153—156 (d)	48·2	3·2		935	48·3	3·2		944
$[RhBr(CO)(PPh_3)(AsPh_3)]$	Orange-brown	200—205	56·6	3·8		740	57·0	3·9		778
$[RhBr(CO)(PPh_3)(C_5H_5N)]$	Buff-brown	165 (d)	52·6	3·7	N, 2·9		52·3	3·6	N, 2·5	
$[RhSCN(CO)PPh_3]_2$	Pale yellow	150 (d)	50·8	3·3	N, 3·6; O, 3·4	[i]	53·2	3·3	N, 3·1; O, 3·3	
$[RhNCS(CO)(PPh_3)(AsPh_3)]$	Yellow	205 (d)	60·2	4·0	N, 2·0	685	60·3	4·0	N, 1·9	757
$[Rh(OCOMe)(CO)PPh_3]_2$	Red-orange	127 (d)	55·5	4·1			55·9	4·0		
$[Rh(OCOMe)(CO)(PPh_3)(AsPh_3)]$	Golden-yellow	150—153 (d)	62·1	4·1			61·7	4·3		
$[RhI(CO)(PPh_3)AsPh_3)]$ [j]	Brown	164—166	52·0	3·4		816	53·8	3·6		826

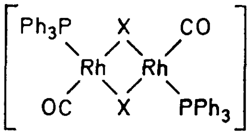
[a] Osmometrically in $CHCl_3$ (37°). [b] From $[RhCl(CO)PPh_3]_2$ and an excess of $SbPh_3$. [c] From $[RhCl(CO)(PPh_3)(AsPh)_3]$. [d] In equilibrium with a small amount of $[RhClI(CH_3)(CO)PPh_3AsPh_3]$. [e] From $[RhCl_3(CO)PPh_3]_2$ and $SbPh_3$. [f] In equilibrium with a small amount of $[RhClI(CH_3)(CO)PPh_3]_2$. [g] From $[RhClI(COCH_3)PPh_3]_2$ (plus alkyl isomer). [h] Analytical figures for aged samples (14 days) in parentheses. [i] Too insoluble for molecular weight determination. [j] Contains some $[RhI_2(CO)$-$PPh_3(AsPh_3)]$.

for PPh_3 and $AsPh_3$. After 4 h under reflux, a deeper brown solid is isolated with very weak bands at 2060, 1980cm^{-1} and a strong, broad band at 1712 cm^{-1}. This dark brown solid analyses closely for $[RhClI(COCH_3)PPh_3AsPh_3]0{\cdot}5CH_3I$ (Table). The presence of methyl iodide solvate is confirmed by mass spectroscopy. These results are consistent with those reported in detail by Douek and Wilkinson [13] for the reaction of *trans*-$[RhXCO(PR_3)_2]$ with CH_3I, *viz.* rapid oxidative addition of CH_3I giving initially $[RhXI(CH_3)(CO)(PR_3)_2]$, followed by a slower isomerisation to the acetyl complex $[RhXI(COCH_3)(PR_3)_2]$. Neither in this work nor in that reported by Wilkinson *et al.*[13] has it been possible to separate the two isomers when prepared by this method (but see section *f*).

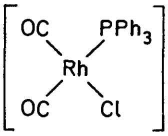
(*b*) *Reformulation of* ' trans-$[RhCl(CO)_2PPh_3]$.'—Rather surprisingly, the reactions of ' *trans*-$[RhCl(CO)_2PPh_3]$ ' with L show very little evidence of carbon monoxide evolution (visual and subsequently mass spectral evidence), an observation which casts grave doubt on the 'dicarbonyl' formulation. An osmometric molecular weight determination on complex (Ia) in chloroform indicates a dimeric structure and, together with a direct oxygen analysis, suggests that '*trans*-$[RhCl(CO)_2PPh_3]$' should be reformulated as the binuclear complex *trans*-$[RhCl(CO)PPh_3]_2$ (Ib, X = Cl). Uguagliati *et al.*[2] support their formulation of the compound as (Ia) on the observed position of ν(RhCl) (295 cm^{-1}), which is in agreement with that expected for a chloride atom *trans* to a tertiary arylphosphine in a rhodium(I) complex.[12] However, since ν(RhCl) is assigned at 284, 274, and 303 cm^{-1} in the bridged chloro-compounds, $[RhCl(CO)_2]_2$ and $[RhCl(PPh_3)_2]_2$ respectively,[12] it is reasonable to expect that ν(RhCl) will occur for the mixed dimer $[RhCl(CO)PPh_3]_2$ in the region 285—295 cm^{-1}. In fact, reaction of equimolar amounts of $[RhCl(CO)_2]_2$ and $[RhCl(PPh_3)_2]_2$ in benzene does give a small amount of complex (Ib). The extreme insolubility of the phosphine dimer is probably the reason why this reaction was not more successful (*cf.* the preparation of $[RhCl(CO)C_2H_4]_2$),[14] although the possibility that $[RhCl(PPh_3)_2]_2$ simply acts as a source of free PPh_3 cannot be discounted. It is very easy to formulate this compound wrongly, since the expected C, H, P, and Cl percentages for (Ia) and (Ib) are very similar: only the oxygen percentage [(Ia), 7·0%; (Ib), 3·7%; Found, O, 3·6%], molecular weight [(Ia), 457; (Ib), 857; Found, 865] and certain chemical reactions enable a distinction to be made. In an independent



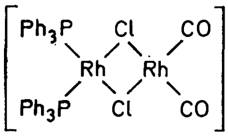
Ia



Ib



IIIa



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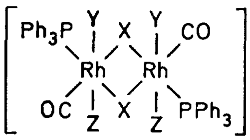

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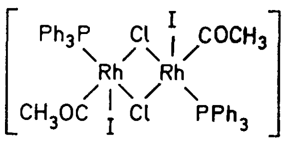

V

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[14] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 211.

investigation, Poilblanc and Gallay[15] reached the same conclusions as those given in this work on the basis of gas evolution and molecular weight measurements. In addition, they synthesised the complex *trans*-$[\mathrm{RhCl(CO)(PMe_3)}]_2$, where the analytical and molecular weight data unequivocably support the dimeric formulation. (Ib) (X = Cl) has also been recently prepared by reaction of $[\mathrm{C_5H_5Rh(CO)PPh_3}]$ with HCl.[16]

The complexes '*trans*-$[\mathrm{RhX(CO)_2PPh_3}]$' made by metathetical reactions on (Ia)[3] can also be reformulated as the dimers (Ib) (X = Br,[3] I,[3] SCN, OCOMe) (see Table). Examination of the i.r. spectrum of the thiocyanato-complex shows ν_{CN} 2135 $\mathrm{cm^{-1}}$, close to that expected for a bridging SCN group [*cf.* 2153—2162 $\mathrm{cm^{-1}}$ in similar palladium(II) compounds].[17] The acetate complex has i.r. bands at 1572 and 1439 $\mathrm{cm^{-1}}$, attributed to asymmetric (ν_{as}) and symmetric (ν_{s}) carboxylate stretching frequencies respectively (*cf.* $[\mathrm{Rh(CO)_2(OCOMe)}]_2$ 1560 and 1439 $\mathrm{cm^{-1}}$).[18] The separation (Δ) of 133 $\mathrm{cm^{-1}}$ between these frequencies is indicative of *symmetrical* co-ordination of the acetate ligand.[19a] These complexes also readily undergo bridge cleavage with $\mathrm{AsPh_3}$, *etc.*, giving monomeric mixed ligand complexes $[\mathrm{RhXCO(PPh_3)L}]$ (Table). Examination of the i.r. spectrum of $[\mathrm{Rh(NCS)(CO)(PPh_3)(AsPh_3)}]$ (ν_{CN} 2064, ν_{CS} 840 $\mathrm{cm^{-1}}$) indicates that the thiocyanate ligand is bound through the nitrogen atom. This is a feature common to all known rhodium(I) compounds containing a terminal SCN group.[17,20] The acetato-complex $[\mathrm{Rh(OCOMe)CO(PPh_3)(AsPh_3)}]$ has ν_{as} 1606, ν_{s} 1323, Δ 283 $\mathrm{cm^{-1}}$, indicative of unidentate co-ordination[19a] (*cf.* $[\mathrm{Rh(OCOMe)CO(PPh_3)_2}]$ made from $[\mathrm{Rh(CO)_2(OCOMe)}]_2$ and excess $\mathrm{PPh_3}$ with ν_{as} 1610, ν_{s} 1325, Δ 285 $\mathrm{cm^{-1}}$).*

The compounds $[\mathrm{RhXCO(PPh_3)(AsPh_3)}]$ can also be synthesised directly from $[\mathrm{RhCl(CO)(PPh_3)(AsPh_3)}]$ and LiX. Pure products are obtained with LiBr and LiSCN provided that short reaction times (5—20 min) are employed. Longer reaction times lead to contamination by rhodium(III) species ($\nu_{\mathrm{CO}} > 2000$ $\mathrm{cm^{-1}}$).[11] With LiI, even short reaction times give a small amount of rhodium(III).

The i.r. spectrum of the orange-yellow product (Ib, X = Cl), isolated by the method given in ref. 2, shows two very weak bands at 2091 and 2023 $\mathrm{cm^{-1}}$ (Nujol); 2090 and 2023 $\mathrm{cm^{-1}}$ (benzene) in addition to the strong, broad absorption at 1980 $\mathrm{cm^{-1}}$. The compound giving rise to these weak absorptions can be removed by refluxing compound (Ib) in benzene for *ca.* 30 min, after which pure *trans*-$[\mathrm{RhCl(CO)PPh_3}]_2$ (ν_{CO} 1980 $\mathrm{cm^{-1}}$) is recovered (Uguagliati *et al.*[2] note that their product 'Ia' readily disproportionates to *trans*-$[\mathrm{RhCl(CO)(PPh_3)_2}]$ (ν_{CO} 1960 $\mathrm{cm^{-1}}$ in warm benzene solution!). Carbonylation of (Ib) with or without the extra i.r. bands) in benzene, toluene, or chloroform gives a lemon-yellow solution, whose i.r. spectrum contains two sharp, intense bands at 2090 and 2008 $\mathrm{cm^{-1}}$ (benzene); 2094 and 2013 $\mathrm{cm^{-1}}$ (chloroform); 2090 and 2007 $\mathrm{cm^{-1}}$ (toluene). If nitrogen is bubbled through the yellow benzene solution, it rapidly turns orange and the i.r. spectrum shows several interesting changes: the band at 2090 $\mathrm{cm^{-1}}$ decreases considerably in intensity, the 2008 $\mathrm{cm^{-1}}$ band disappears and is replaced by a weaker one at 2023 $\mathrm{cm^{-1}}$, and a very strong band appears at 1980 $\mathrm{cm^{-1}}$. Removal of solvent regenerates (Ib), together with the complex with weak i.r. bands at 2090 and 2023 $\mathrm{cm^{-1}}$. Deganello *et al.*[3] have reported the isolation of a red labile intermediate with very similar i.r. absorptions [2082 and 2019 $\mathrm{cm^{-1}}$ (Nujol)]. This readily converts to 'Ia' at room temperature and has been assigned the structure '*cis*-$[\mathrm{RhCl(CO)_2PPh_3}]$' (IIIa).[3] Poilblanc and Gallay[15] observed similar behaviour, on carbonylation of (Ib) in toluene, to that reported here (*i.e.* two ν_{CO} 2088 and 2002 $\mathrm{cm^{-1}}$) and showed that the CO uptake was one CO per rhodium. Furthermore, they observed that a compound with the same i.r. spectrum was formed in solution when $[\mathrm{RhCl(CO)_2}]_2$ and $\mathrm{PPh_3}$ (1 : 2 molar ratio) were mixed. Attempts to isolate this species resulted in CO evolution (one CO/Rh) and formation of *trans*-$[\mathrm{RhCl(CO)(PPh_3)}]_2$. We have also followed the i.r. changes of this reaction in benzene and confirm that the first step is the loss of $[\mathrm{RhCl(CO)_2}]_2$ carbonyl bands and the growth of two strong bands at 2090 and 2008 $\mathrm{cm^{-1}}$. Then, concentration of the solution results (as just described) in the appearance of two weak absorptions at 2090 and 2023 $\mathrm{cm^{-1}}$ and the strong band at 1980 $\mathrm{cm^{-1}}$.

Poilblanc *et al.*[15] interpreted their observations in terms of equation (1) with the same postulated intermediate as Deganello *et al.*,[3] *cis*-$[\mathrm{RhCl(CO)_2PPh_3}]$ (IIIa).

$$\begin{aligned}[\mathrm{Rh_2Cl_2(CO)_4}] + 2\mathrm{PPh_3} &\longrightarrow 2\ cis\text{-}[\mathrm{RhCl(CO)_2PPh_3}] \\ &\rightleftharpoons trans\text{-}[\mathrm{RhCl(CO)(PPh_3)}]_2 + 2\mathrm{CO} \quad (1)\end{aligned}$$

However, this infers that $\mathrm{PPh_3}$ initially reacts with $[\mathrm{RhCl(CO)_2}]_2$ with halide bridge cleavage and formation of complex (IIIa). On attempted isolation, one CO group is lost from each molecule of (IIIa) and the co-ordinatively unsaturated fragments recombine to give the halide bridged species (Ib). Finally, with more $\mathrm{PPh_3}$, (Ib) is cleaved giving *trans*-$[\mathrm{RhCl(CO)(PPh_3)_2}]$. We suggest that a more plausible interpretation is that the yellow labile intermediate [ν_{CO} 2090 and 2008 $\mathrm{cm^{-1}}$ (benzene)] is the dimeric *cis*-$[\mathrm{RhCl(CO)_2PPh_3}]_2$ (IIIb), probably with *trans*-addition of $\mathrm{PPh_3}$ to minimise steric

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* This compound has also been recently reported by Csontos *et al.*[19b] who formulate it as a five-co-ordinate complex with a bidentate acetato-group ν_{as} 1610, ν_{s} 1470, Δ 140 $\mathrm{cm^{-1}}$. Unfortunately, the quoted 'ν_{s}' occurs in the same region as a strong triphenylphosphine absorption which tends to negate their conclusion.

[15] R. Poilblanc and J. Gallay, *J. Organometallic Chem.*, 1971, **27**, C53.

[16] F. Faraone, C. Ferrara, and E. Rotondo, *J. Organometallic Chem.*, 1971, **33**, 221.

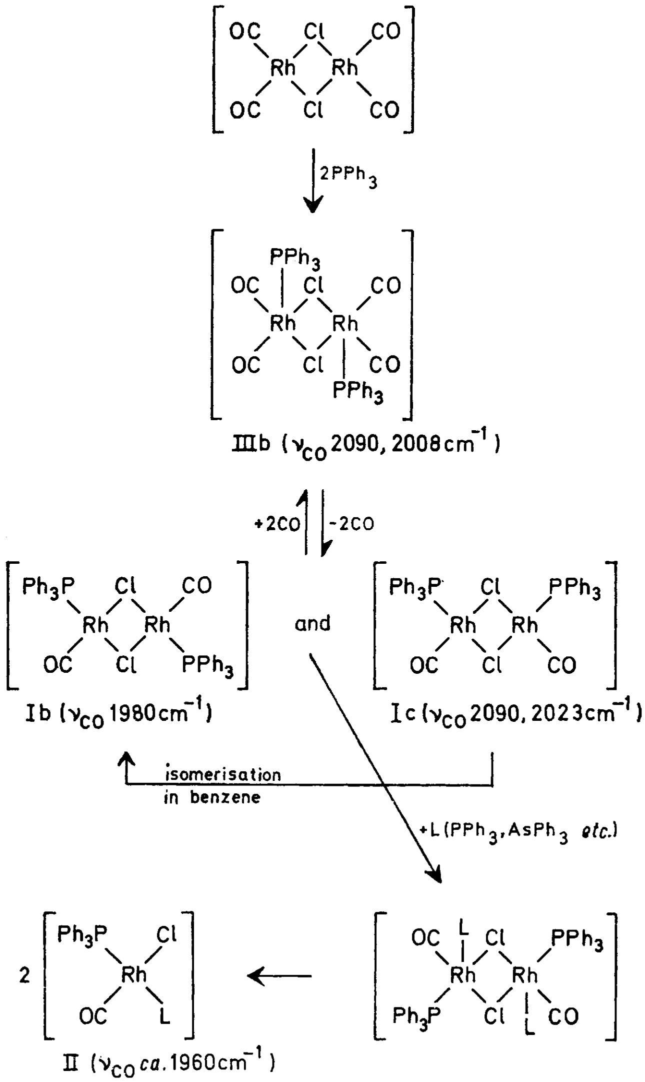
[17] For detailed references, see M. A. Jennings and A. Wojcicki, *Inorg. Chem.*, 1967, **6**, 1854.

[18] D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1965, 1900.

[19] (*a*) For detailed discussion, see T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632; (*b*) G. Csontos, B. Heil, and L. Marko, *J. Organometallic Chem.*, 1972, **37**, 183.

[20] N. J. De Stefano and J. L. Burmeister, *Inorg. Chem.*, 1971, **10**, 998.

repulsions. This intermediate readily loses CO to give mainly (Ib). In this way, bridge cleavage and subsequent recombination need not be invoked to explain the observations. Because of the low stability of this compound it has proved impossible to directly verify whether the compound is of formula (IIIa) or (IIIb). However, carbonylation of *trans*-[Rh(OCOMe)CO(PPh$_3$)]$_2$ gives an orange solution with ν_{CO} 2094 and 2009; ν_{as} 1570, ν_s 1435, Δ 135 cm^{-1}, indicative of symmetrical acetate co-ordination, as expected for (IIIb) and not unidentate co-ordination as expected for (IIIa).



SCHEME Proposed mechanism for reaction of [RhCl(CO)$_2$]$_2$ with PPh$_3$

A similar intermediate [RhCl(CO)(PPh$_3$)L]$_2$ could be postulated for the reaction of (Ib) with L (PPh$_3$, AsPh$_3$, *etc.*) followed by halide bridge cleavage and formation of [RhCl(CO)PPh$_3$L]. However, an i.r. study of the reaction of (Ib, X = Cl) with AsPh$_3$ shows that the immediate yellow solution has ν_{CO} 1976, ν(RhCl) 310 cm^{-1} identical with that found for [RhCl(CO)(PPh$_3$)(AsPh$_3$)] in benzene solution. This could indicate either that ν_{CO} and ν(RhCl) are the same for [RhCl(CO)(PPh$_3$)(AsPh$_3$)]$_n$ (n = 1 and 2), that the dimeric intermediate is very labile or that it never forms!

We suggest that the other complex isolated with (Ib) is *cis*-[RhCl(CO)PPh$_3$]$_2$ (Ic; ν_{CO} 2091 and 2023 cm^{-1}), formed simultaneously with (Ib) by CO displacement from (IIIb) and readily isomerised to (Ib) by warming in benzene. Although the i.r. spectrum is also consistent with the other *cis*-dicarbonyl isomer (Id) [and would possibly be more compatible with the observed ν(CO) values than (Ic)] * the observation that recarbonylation of a mixture of (Ib) and another dicarbonyl compound gives *only* the single product (IIIb) suggests that we can discount the formulation (Id). Reaction of [RhCl(CO)$_2$]$_2$ and PPh$_3$ at a lower temperature gave the same products but an attempted chromatographic separation was unsuccessful. Only a single 'streaky' band was obtained (t.l.c.) suggesting similar R_F values for the isomers. For clarity, our suggestions are summarised in the Scheme shown opposite.

(*c*) *Reaction with Triphenylstibine.*—Reaction of [RhCl(CO)PPh$_3$]$_2$ with triphenylstibine (1 : 2 molar ratio) in benzene gives an orange solution which, on concentration and pentane addition, gives the yellow solid [RhCl(CO)(PPh$_3$)(SbPh$_3$)]. In addition, the filtrate contains another rhodium complex; the red-brown five-co-ordinate [RhCl(CO)PPh$_3$(SbPh$_3$)$_2$]. A better method of making this compound is to react benzene solutions of [RhCl(CO)PPh$_3$]$_2$, [RhCl(CO)(PPh$_3$)(AsPh$_3$)], or [RhCl(CO)(PPh$_3$)(C$_5$H$_5$N)] with a four-fold excess of SbPh$_3$. However, if the reaction of (Ib) (X = Cl) and excess SbPh$_3$ is carried out in CH$_2$Cl$_2$, concentration of the deep red solution gives a yellow precipitate of *trans*-[RhCl(CO)(PPh$_3$)$_2$] and the filtrate contains [RhCl(CO)(SbPh$_3$)$_3$] and some free PPh$_3$. Furthermore, in the absence of excess SbPh$_3$, [RhCl(CO)PPh$_3$(SbPh$_3$)$_2$] in benzene readily dissociates to [RhCl(CO)(PPh$_3$)(SbPh$_3$)] and SbPh$_3$ (*cf.* the behaviour of [RhCl(CO)(SbPh$_3$)$_3$]).[21] This suggests that in solution the following complexes are present in equilibria (equation (2)):

$$\begin{gathered}3[\mathrm{RhCl(CO)(PPh_3)(SbPh_3)}] + 3\mathrm{SbPh_3}\\ \Big\updownarrow\\ 3[\mathrm{RhCl(CO)(PPh_3)(SbPh_3)_2}] \rightleftharpoons\\ [\mathrm{RhCl(CO)(PPh_3)_2}] + 2[\mathrm{RhCl(CO)(SbPh_3)_3}] + \mathrm{PPh_3}\end{gathered} \qquad (2)$$

[RhCl(CO)(SbPh$_3$)$_3$]C$_6$H$_6$ can be prepared directly from [RhCl(CO)$_2$]$_2$ and excess SbPh$_3$ [21,22] in benzene and also from *trans*-[RhCl(CO)(AsPh$_3$)$_2$] and excess SbPh$_3$. The most interesting features of this compound are the low position of ν(RhCl) (270 cm^{-1}) (confirmed by preparing the corresponding bromo-compound) and the presence of a

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* We thank a referee for this suggestion.

[21] R. Ugo, F. Bonati, and S. Cenini, *Inorg. Chim. Acta*, 1969, **3**, 220.

[22] W. Hieber and V. Frey, *Chem. Ber.*, 1966, **99**, 2614.

strongly clathrated benzene molecule.[21] The latter might provide an explanation for the stability of [RhCl(CO)-$PPh_3(SbPh_3)_2$] in benzene compared to dichloromethane, although a more likely explanation is the low solubility of *trans*-[RhCl(CO)$(PPh_3)_2$] in CH_2Cl_2 (as compared to C_6H_6) which results in a shift of the equilibrium to the right hand side of equation (2).

Reaction of [RhCl(CO)$(SbPh_3)_3$]C_6H_6 with excess $AsPh_3$ regenerates *trans*-[RhCl(CO)$(AsPh_3)_2$]; similarly, [RhCl(CO)$PPh_3(SbPh_3)_2$] gives [RhCl(CO)$(PPh_3)(AsPh_3)$]. Thus, [RhCl(CO)$(SbPh_3)_3$] and [RhCl(CO)(PPh_3)-$(SbPh_3)_2$] are two members of a series containing five-co-ordinate rhodium(I) and triphenylstibine. A third is the cation $[Rh(CO)_2(SbPh_3)_3]^+$ recently prepared by Hieber *et al.*[22] Reaction of *trans*-[RhCl(CO)$(PPh_3)_2$] and excess triphenylstibine gives an orange-yellow solution, probably containing the unknown [RhCl(CO)-$(PPh_3)_2SbPh_3$] complex but removal of solvent gives only *trans*-[RhCl(CO)$(PPh_3)_2$]. This and earlier work[22] clearly indicates that, as $SbPh_3$ groups are replaced by PPh_3 (and $AsPh_3$), the stability of the five-co-ordinate rhodium(I) complexes decrease. Similarly, Westland[23] concluded that 'for palladium(II) and platinum(II), the tendency of ligand donor atoms to confer upon the metal atom the ability to engage in five-co-ordination increases in the sequence $N < P < As < Sb$.' However, the reasons why antimony donor ligands promote five-co-ordination in low-spin d^8 complexes is not at present obvious although, doubtless, both steric and electronic factors play an important role, *e.g.*, the longer rhodium–antimony bond distances allow more $SbPh_3$ molecules to be packed around the rhodium atom.

All these results suggest that the only remaining six-co-ordinate rhodium(I) complex containing triphenylstibine [Rh$(C_5H_7O_2)$CO$(SbPh_3)_3$] ($C_5H_7O_2^- =$ acetylacetonate ion)[24] is probably the five-co-ordinate [Rh$(C_5H_7O_2)$CO$(SbPh_3)_2$]. The quoted analytical figures C, 54·5, H, 4·2, O, 3·7% are intermediate between those required for [Rh$(C_5H_7O_2)$CO$(SbPh_3)_3$] (C, 55·9, H, 4·0; O, 3·2, Sb 28·4%) and [Rh$(C_5H_7O_2)$CO$(SbPh_3)_2$] (C, 53·8, H, 4·0; O, 5·1, Sb 26·0%). An antimony analysis is required to distinguish between these possibilities but the rarity of six-co-ordinate rhodium(I) complexes and the close similarity of the compound to [RhCl(CO)-$(SbPh_3)_3$] and [RhCl(CO)$(PPh_3)(SbPh_3)_2$] strongly favours the five-co-ordinate bis-stibine formulation.

(*d*) *Reaction of Complex* (Ib) *with Tertiary Phosphines.*—Treatment of [RhCl(CO)$PPh_3]_2$ with methyldiphenylphosphine or tricyclohexylphosphine (1 : 2 molar ratio) in acetone, followed by solvent removal and addition of ether give the products [RhCl(CO)PPh_3L], characterised by analysis, m.p. (Table), and i.r. spectra. The ^1H n.m.r. spectra (methyl region) of [RhCl(CO)(PPh_3)-$(PMePh_2)$] in deuteriochloroform shows only a single resonance (τ 7·86). Similarly, examination of the n.m.r. spectrum of an equimolar mixture of *trans*-[RhClCO$(PMePh_2)_2$] and *trans*-[RhClCO$(PPh_3)_2$] (in $CDCl_3$) shows a single methyl peak (τ 7·82). In contrast, *trans*-[RhCl(CO)$(PMePh_2)_2$] in $CDCl_3$ shows the expected doublet of triplets[25] (J_{RhH} 1·0 Hz) centred at τ 7·84. Addition of *trans*-[RhCl(CO)$(PPh_3)_2$] to this solution gives a single resonance (τ 7·82) at a minimum ratio ($PMePh_2$ to PPh_3 complex) of *ca.* 10 : 1. The same effect is observed when the n.m.r. spectrum of *trans*-[RhCl(CO)$(PMePh_2)_2$] is run in CS_2.

The only explanation which appears applicable in this instance to explain the loss of P–H coupling is that given by Fackler *et al.*[26] to explain the ^1H n.m.r. spectra of compounds such as *cis*-[$PdCl_2(PMePh_2)_2$] and *trans*-[RhCl(CO)$(PMe_2Ph)_2$],[27] namely that P–H decoupling occurs in strongly coupled PP′ systems because of easy phosphine exchange. The singlet observed in this mixed ligand complex corresponds to the calculated n.m.r. spectra given in Figure 2, ref. 26 (*i.e.* that expected at intermediate exchange rates). Cooling a $CDCl_3$ solution of [RhCl(CO)$(PPh_3)(PMePh_2)$] to −60° produces the line broadening expected for a slower exchange rate but not the triplet predicted in the slow exchange limit. Similarly, heating in chlorobenzene to 80° does not give the doublet expected in the fast exchange limit. Presumably, the small amount of free phosphine required to cause P–H decoupling in *trans*-[RhCl(CO)$(PMePh_2)_2$] comes from either partial dissociation of the added [RhCl(CO)$(PPh_3)_2$] and/or some displacement of $PMePh_2$ by PPh_3 and consequent scrambling of phosphine groups in these labile, square-planar d^8 compounds. The singlet found for *trans*-[RhCl(CO)$(PMePh_2)_2$] in CS_2, could be the result of enhanced dissociation in this solvent compared to $CDCl_3$ due to the ready formation of 1 : 1 adducts between tertiary phosphines and CS_2.[28] For [RhCl(CO)(PPh_3)-$(PMePh_2)$] in solution, the existence of an equilibrium of the type given by equation 3 would account for easy

$$2[RhCl(CO)PPh_3L] \rightleftharpoons [RhCl(CO)(PPh_3)_2] + [RhCl(CO)L_2] \quad (3)$$

phosphine exchange processes and consequent P–H decoupling. There is more convincing evidence for the existence of this equilibrium for compounds [RhCl(CO)-PPh_3L]. Reaction of [RhCl(CO)$PPh_3]_2$ with tertiary phosphines (L = PMe_2Ph or PEt_2Ph) gives oils on solvent removal which on trituration with ethers or pentane gives a precipitate of *trans*-[RhCl(CO)$(PPh_3)_2$] and evidence in solution for [RhCl(CO)L_2]. Similar results are found when using excess $AsEt_3$ and Me_2SO. However, we suggest that for all the [RhCl(CO)PPh_3L] compounds reported (and attempted) in this paper, the equilibrium in solution lies predominantly to the left-hand side of equation (3). Thus, precipitation from solution with

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[23] A. D. Westland, *J. Chem. Soc.*, 1965, 3060.

[24] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 3156.

[25] K. C. Dewhurst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 1968, **7**, 546.

[26] J. P. Fackler, jun., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, 1969, **91**, 1941.

[27] J. P. Facker, jun., *Inorg. Chem.*, 1970, **9**, 2625.

[28] See L. Maier in 'Progress in Inorganic Chemistry,' ed. F. A. Cotton, vol. 5, Interscience, 1963, p. 129.

pentane, *etc.*, gives pure samples of [$RhCl(CO)PPh_3L$] ($L = AsPh_3$ (t.l.c.), $PMePh_2$ (t.l.c.), $SbPh_3$, *etc.*) since these compounds are expected to be of similar low solubility in these solvents to that of *trans*-[$RhCl(CO)(PPh_3)_2$], postulated to be present in only low concentration. However, when L is a more alkylated phosphine, arsine, or an alkyl sulphoxide, the mixed compounds (and [$RhCl(CO)L_2$]) will be of higher solubility in pentane, *etc.*, than *trans*-[$RhCl(CO)(PPh_3)_2$]. Thus, preferential precipitation of the latter will occur and the equilibrium will be pushed to the right-hand side of equation 3.

An excellent confirmation of this hypothesis is provided by the low pressure carbonylation of [$RhCl(CO)PPh_3$]$_2$ in various solvents. As discussed in detail earlier, benzene, toluene and chloroform (in which [$RhCl(CO)(PPh_3)_2$] is soluble) contain a complex with two $\nu_{CO} > 2000$ cm^{-1}, believed to be *cis*-[$RhCl(CO)_2PPh_3$]$_n$ (III) (with *n* probably 2). However, carbonylation of a methanol suspension (or concentrated dichloromethane solution) of (Ib) gives a precipitate of *trans*-[$RhCl(CO)(PPh_3)_2$] and [$RhCl(CO)_2$]$_2$ can be isolated from the solution, *i.e.*, *trans*-[$RhCl(CO)(PPh_3)_2$] is of much lower solubility in these solvents than *cis*-[$RhCl(CO)_2PPh_3$]$_n$. Note that equation (3) predicts that the other product should be [$RhCl(CO)_3$] but it is not inconceivable that this compound (at present unknown) might readily lose carbon monoxide and then dimerise (*cf.* $2RhCl(PPh_3)_3 \rightleftharpoons [RhCl(PPh_3)_2]_2 + 2PPh_3$).[29]

(*e*) *Oxidative Addition Reactions of Complex* (Ib).—The reformulation of '*trans*-[$RhX(CO)_2PPh_3$]' as *trans*-[$RhX(CO)PPh_3$]$_2$ also implies that the reported oxidative addition products [$RhXYZ(CO)_2PPh_3$][3] ($YZ = Cl_2$, PhI, $ClCO_2Et$, *etc.*) are incorrect. This is readily verified by an oxygen analysis on '[$RhCl_3(CO)_2PPh_3$]' (required 6·1; found 3·3%), which suggests that the compound should be reformulated as *trans*-[$RhXYZ(CO)PPh_3$]$_2$ (IV, X = Cl, $YZ = Cl_2$; required O, 3·2%). The position of ν(RhCl) 354 and 340 cm^{-1} suggests *trans*-addition of the halogen.[30] This compound is too insoluble for a molecular weight determination but it reacts with excess triphenylarsine (without CO evolution) giving [$RhCl_3(CO)(PPh_3)(AsPh_3)$]: with $SbPh_3$ a product close in analysis to [$RhCl_3(CO)(PPh_3)(SbPh_3)$] is formed but partial reduction to [$RhCl(CO)(PPh_3)(SbPh_3)$] also occurs. Triphenylphosphine gives mainly *trans*-[$RhCl(CO)(PPh_3)_2$]. Rather surprisingly, extended reaction with pyridine gives a sample of 1,2,6-[$RhCl_3(C_5H_5N)_3$] (the isomeric form was confirmed by comparison with the i.r. spectrum of an authentic sample).[31]

It is therefore suggested that with the exception of the methyl iodide reaction, the other oxidative addition products reported in ref. 3 should be reformulated as the dimeric compound (IV) (or isomers of this compound).

(*f*) *Reaction of Complex* (Ib) *with Methyl Iodide*.—Deganello *et al.*[3] report that the reaction of methyl iodide with '[$RhCl(CO)_2PPh_3$]' gives [$RhClI(CO)(COMe)(PPh_3)$], probably *via* a labile intermediate [$RhClI(CH_3)(CO)_2PPh_3$]. The final product has an i.r. spectrum exhibiting both terminal metal carbonyl (2065 cm^{-1}) and acyl carbonyl (1710 cm^{-1}) stretching frequencies. We have undertaken a detailed re-examination of this reaction and find that on prolonged reaction between methyl iodide and complex (Ib, X = Cl) (followed by i.r. spectroscopy) the terminal carbonyl band decreases and the acyl carbonyl band increases in intensity as the reaction proceeds. Unfortunately, the compound is not sufficiently stable in solution for molecular weight measurements and a mass spectrum shows only the fragmentation pattern of triphenylphosphine. However, by analogy with the other oxidative addition reactions of complex (Ib) and earlier work by Wilkinson *et al.*,[13] we suggest that the terminal carbonyl stretch arises from compound (IV) ($YZ = CH_3I$, X = Cl), which is in equilibrium with an acetylrhodium(III) dimer (V) and that, on extended reaction, most of the product is present as the acetyl dimer. This explanation is consistent with the results of a kinetic study carried out by Uguagliati *et al.*,[4] where rapid formation of an intermediate followed by a second slower rate determining step was observed.

The reaction of this mixture of isomers with an excess of L ($L = AsPh_3$, PPh_3, $SbPh_3$) in chloroform or dichloromethane gives, on immediate precipitation with pentane or ether, orange-yellow crystalline compounds, which analyse for [$RhClICH_3(CO)PPh_3L$] (Table).

The i.r. spectra of these compounds shows a strong terminal rhodium(III) carbonyl band, a very weak rhodium(I) carbonyl band but no acyl band [*e.g.*, $L = AsPh_3$, 2065s, 2056m, and 1980w cm^{-1} (Nujol); 2070s and 1980m cm^{-1} ($CHCl_3$)]. These compounds also precipitate out when the reaction is carried out in concentrated dichloromethane or methyl iodide solution.

There are few reports of the isolation of pure rhodium(III) methyl carbonyl compounds because of the ready isomerisation to the acyl form. Heck[32] reports the preparation of [$RhClI(CH_3)(CO)(PBu^n_3)_2$] which absorbs CO at 1 atm and 25° to give the acyl compound [$RhClI(COCH_3)CO(PBu^n_3)_2$] and Wilkinson *et al.*[33] by reaction of acetyl chloride with $RhCl(PPh_3)_3$ at 0°, have isolated the compound [$RhCl_2(CH_3)(CO)(PPh_3)_2$]. In solution, this rapidly isomerises to [$RhCl_2(COCH_3)(PPh_3)_2$]. Graham *et al.*[34] also report the preparation of [$(C_5H_5)Rh(CH_3)(CO)(PMe_2Ph)$]$BPh_4$ by treatment of the acyl complex [$(C_5H_5)RhBr(Ac)(PMe_2Ph)$] with $NaBPh_4$. The chloroiodo-compounds reported here are reasonably

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

[30] P. R. Brookes and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 1079.

[31] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 1224.

[32] R. F. Heck, *J. Amer. Chem. Soc.*, 1964, **86**, 2796.

[33] M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 1347.

[34] A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 2658.

stable if stored under nitrogen in the absence of light. However, on light exposure, they slowly turn darker brown and the i.r. spectrum shows the growth of an acyl band (1712 cm^{-1}) but the analytical figures (carbon and hydrogen) remain virtually unchanged (Table). Similarly, if the compounds are dissolved in $CHCl_3$–CH_3I, the solution rapidly darkens in colour and is accompanied by the growth of an acyl carbonyl band and a decrease in the terminal carbonyl band intensity. In $CHCl_3$ alone, the acyl band also increases in intensity but this is followed by the rapid growth of a band at 1980 cm^{-1}, *i.e.*, reductive elimination of methyl iodide is probably occurring (*cf.* refs. 13 and 33) giving $[RhClCO(PPh_3)(AsPh_3)]$.

Thus, it appears that cleavage of the mixture of dimers (IV) and (V) by Lewis bases provides a convenient preparation of pure rhodium methyl carbonyl compounds. The reason for the formation of the pure alkyl form from a solution predominantly containing the acetyl complex (V) lies probably in the greater lability of the alkyl dimer (IV) [compared to (V)] towards bridge cleavage by Lewis bases and also to the low solubility of the resultant monomeric alkyl compound in various solvents. Hence, the equilibrium in solution is shifted towards the formation of more alkyl dimer. A well established precedent is the isolation of the more insoluble *cis*-$[PdCl_2(SbPh_3)_2]$ from solutions containing predominantly the *trans*-isomer.[35]

CONCLUSION

The reaction of $[RhCl(CO)_2]_2$ with PPh_3, originally reported by Vallarino,[6] to give *trans*-$[RhCl(CO)(PPh_3)_2]$ reveals, on closer examination, a number of isolatable intermediates which exhibit some interesting chemical properties. It is likely that similar detailed studies on other rhodium(I) dimers will be equally valuable both in providing an insight into the reaction pathways of these complicated reactions and synthesising new rhodium(I) and (III) compounds.

EXPERIMENTAL

Microanalyses were by the N.P.L., Teddington, A. Bernhardt, West Germany and the University of Edinburgh, Chemistry Department. Analytical data for many of the new compounds are given in the Table. Molecular weights were determined on a Mechrolab Osmometer at 37° in ethanol-free chloroform. I.r. spectra were recorded in the region 4000—200 cm^{-1} on a Perkin-Elmer 225 grating spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Useful i.r. data is given below for each compound (measured as mull unless otherwise stated). ^1H N.m.r. spectra were obtained on a Perkin-Elmer model RS10 60 MHz spectrometer and a Varian Associates HA-100 spectrometer. Mass spectra were measured on an A.E.I. MS 9 mass spectrometer and conductivity measurements on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected.

Materials.—Rhodium trichloride trihydrate (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine, iodomethane, dimethylsulphide (B.D.H.); triphenylarsine (Ralph Emanuel); triphenylstibine (Koch–Light); and carbon monoxide (Air Products Ltd.). The other tertiary phosphines were prepared by standard literature methods.

Rhodium(I) *Compounds*

trans-*Di-μ-chloro-dicarbonylbis*(*triphenylphosphine*)*dirhodium*(I).—Triphenylphosphine (0·52 g, 2·0 mmol) in benzene (20 ml) was added, dropwise with stirring to a solution of di-μ-chlorotetracarbonyldirhodium(I) [11] (0·39 g, 1·0 mmol) in dry benzene (20 ml). The mixture was stirred for 15 min, the solution concentrated *in vacuo*, and pentane added to precipitate the *product* as a golden yellow powder (0·8 g, 93%) [ν_{CO} 2091w, 2023w, 1980vs cm^{-1}; $\nu(RhCl)$ 295 cm^{-1}]. Recrystallisation from hot benzene gives the pure *trans*-isomer (ν_{CO} 1980 cm^{-1}).

trans-*Di-μ-bromo-dicarbonylbis*(*triphenylphosphine*)*dirhodium*(I).—$[RhCl(CO)PPh_3]_2$ (0·43 g, 0·50 mmol) Was suspended in acetone (25 ml) and an excess of lithium bromide (*ca.* 3·0 g) was added. The suspension dissolved and after shaking for 10 min, acetone was removed *in vacuo* and the *product* precipitated with distilled water. The orange-brown powder was filtered, washed well with methanol, ether and dried *in vacuo* at 40° (0·43 g, 91%) [ν_{CO} 1982 cm^{-1}; $\nu(RhBr)$ 230 cm^{-1}]. trans-*Di-μ-iodo-dicarbonylbis*(*triphenylphosphine*)*dirhodium*(I) (ν_{CO} 1980 cm^{-1}) and trans-*di-μ-thiocyanato-dicarbonylbis*(*triphenylphosphine*)*dirhodium*(I) (ν_{CO} 2001; ν_{CN} 2135; ν_{CS} 781 cm^{-1}) were prepared by analogous metathetical reactions with the appropriate lithium salts.

trans-*Di-μ-acetato-dicarbonylbis*(*triphenylphosphine*)*dirhodium*(I).—$[RhCl(CO)PPh_3]_2$ Was treated with an excess of silver acetate in dry benzene for 1 h giving a dark orange-red solution. After filtering off the excess of silver acetate and precipitated silver chloride, the solution was concentrated *in vacuo* and the orange crystalline *product* was precipitated with dry pentane and dried in the usual way [ν_{CO} 1974; ν_{as} 1572; ν_s 1439 ($CHCl_3$); Δ 133 cm^{-1}].

Chlorocarbonyl(*triphenylphosphine*)(*triphenylarsine*)*rhodium*(I).—$[RhCl(CO)PPh_3]_2$ (0·39 g, 0·45 mmol) Was suspended in benzene (25 ml) and triphenylarsine (0·61 g, 2·0 mmol) in benzene (10 ml) was added. The suspension immediately dissolved giving a pale yellow solution. Removal of solvent and addition of pentane gave the *product*, recrystallised from dichloromethane–acetone as pale yellow needles (0·61 g, 91%) (ν_{CO} 1961; ν_{RhCl} 311 cm^{-1}). *Bromocarbonyl*(*triphenylphosphine*)(*triphenylarsine*)*rhodium*(I) (ν_{CO} 1959 cm^{-1}), *isothiocyanatocarbonyl*(*triphenylphosphine*)(*triphenylarsine*)*rhodium*(I) (ν_{CO} 1981; ν_{CN} 2064; ν_{CS} 840 cm^{-1}) and *acetatocarbonyl*(*triphenylphosphine*)(*triphenylarsine*)*rhodium*(I) (ν_{CO} 1969; ν_{as} 1606; ν_s 1323; Δ 283 cm^{-1}) were also synthesised from the respective dimers and excess $AsPh_3$. The bromo- and thiocyanato-compounds can also be prepared by reaction of $[RhCl(CO)PPh_3AsPh_3]$ with the appropriate lithium salts (short reaction times). For LiI, even short reaction times gave a mixture of $[RhI(CO)PPh_3AsPh_3]$ (ν_{CO} 1982s cm^{-1}) and $[RhI_3(CO)PPh_3AsPh_3]$ (ν_{CO} 2080w cm^{-1}) [*cf.* analytical figures in the Table].

Chlorocarbonyl(*triphenylphosphine*)(*pyridine*)*rhodium*(I).—$[RhCl(CO)PPh_3]_2$ (0·20 g, 0·23 mmol) Was suspended in benzene (20 ml) and dry redistilled pyridine (1·6 ml, 2·0 mmol) was added slowly with stirring. The suspension

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[35] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1953, 70.

dissolved giving a pale yellow solution. Removal of solvent *in vacuo* gave a red-brown oil which on trituration with light petroleum (b.p. 60—80°) gave the buff-yellow *powder* (0·20 g, 85%) (ν_{CO} 1962; ν_{RhCl} 304 cm^{-1}). Attempts to recrystallise or prolonged standing in chloroform led to extensive decomposition. *Bromocarbonyl(triphenylphosphine)(pyridine)rhodium*(I) (ν_{CO} 1966 cm^{-1}) was similarly prepared from the bromo-dimer. *Chlorocarbonyl(triphenylphosphine)*(p-*toluidine*)*rhodium*(I) (ν_{CO} 1960; ν_{RhCl} 301 cm^{-1}) and *chlorocarbonyl(triphenylphosphine)(dimethyl sulphide)rhodium*(I) (ν_{CO} 1965; ν(RhCl) 310 cm^{-1}) were prepared in analogous manner to $[RhCl(CO)(PPh_3)(C_5H_5N)]$ using $[RhCl(CO)PPh_3]_2$ and excess *p*-toluidine or dimethyl sulphide respectively. The latter compound slowly loses dimethyl sulphide on exposure to air.

Chlorocarbonyl(triphenylphosphine)(triphenylstibine)rhodium(I).—$[RhCl(CO)PPh_3]_2$ (0·30 g, 0·35 mmol) Was dissolved in benzene (20 ml) and treated dropwise with a benzene (10 ml) solution of triphenylstibine (0·25 g, 0·70 mmol). The orange solution rapidly gave a pale orange-yellow solution. Removal of some solvent *in vacuo* and addition of pentane precipitated the yellow *product* which was washed with ether and dried *in vacuo* (0·80 g, 80%) (ν_{CO} 1959; ν(RhCl) 311 cm^{-1}). The orange-yellow filtrate on evaporation of solvent gave the reddish-brown crystalline *solid chlorocarbonyl(triphenylphosphine)bis(triphenylstibine)rhodium*(I) (ν_{CO} 1960; ν(RhCl) 317 cm^{-1}). The same compound can be made in high yield by reaction of benzene solutions of either $[RhCl(CO)PPh_3]_2$, $[RhCl(CO)(PPh_3)AsPh_3)]$ or $[RhCl(CO)PPh_3(C_5H_5N)]$ with a four-fold excess of $SbPh_3$. Removal of solvent and addition of ether gave the same red-brown crystalline *product*. However, in dichloromethane, the initial dark red solution from $[RhCl(CO)PPh_3]_2$ and an excess of $SbPh_3$ gave, on concentration, the pale yellow solid *trans*-$[RhCl(CO)(PPh_3)_2]$ (characterised by i.r. spectrum and m.p.). The remaining orange-red solution on solvent removal and addition of diethyl ether–pentane gave a dark red precipitate of *chlorocarbonyltris(triphenylstibine)rhodium*(I) (ν_{CO} 1960; ν(RhCl) 270 cm^{-1}). The ethereal filtrate contained triphenylphosphine. An authentic sample of $[RhCl(CO)(SbPh_3)_3]C_6H_6$ was prepared by the method of Ugo *et al.*[21] ($[RhCl(CO)_2]_2$ and an excess of $SbPh_3$). The same compound can also be prepared from the reaction of *trans*-$[RhCl(CO)(AsPh_3)_2]$ and excess $SbPh_3$ in benzene (Found: C, 54·8; H, 3·7; Cl, 2·2; O, 1·1; Sb, 31·2. Calc. for $C_{61}H_{51}ClOSb_3Rh$: C, 56·2; H, 3·8; Cl, 2·7; O, 1·1; Sb, 28·2%).

Chlorocarbonyl(triphenylphosphine)(methyldiphenylphosphine)rhodium(I).—$[RhCl(CO)PPh_3]_2$ (0·10 g, 0·11 mmol) was suspended in dry acetone (15 ml) and methyldiphenylphosphine (0·04 g, 0·22 mmol) in acetone (5 ml) was added slowly with stirring. The suspension dissolved giving a pale yellow solution. Removal of solvent and addition of ether to the resultant oily solid gave the *product* as a lemon-yellow powder (ν_{CO} 1963; ν(RhCl) 308 cm^{-1}). T.l.c. showed a single spot with a R_F value slightly larger than *trans*-$[RhCl(CO)(PPh_3)_2]$. Similarly, *chlorocarbonyl(triphenylphosphine)(tricyclohexylphosphine)rhodium*(I) (ν_{CO} 1950; ν(RhCl) 310 cm^{-1}) was made in chloroform solution, precipitating the *product* with light petroleum (b.p. 40—60°).

Attempts to prepare $[RhCl(CO)PPh_3L]$ (L = PMe_2Ph, PEt_2Ph) by the same method gave only a precipitate of *trans*-$[RhCl(CO)(PPh_3)_2]$ and yellow ethereal solutions containing $[RhClCOL_2]$ (confirmed by comparison with authentic samples made by literature methods).[11] Similarly, only *trans*-$[RhCl(CO)(PPh_3)_2]$ was isolated from the reaction of $[RhCl(CO)PPh_3]_2$ with excess $AsEt_3$ or Me_2SO.

Carbonylation of $[RhCl(CO)PPh_3]_2$.—(a) *In benzene, toluene, or chloroform.* Reaction of the orange benzene solution with CO at room temperature gives an immediate lemon-yellow solution (ν_{CO} 2090 and 2008 cm^{-1}) which on removal of solvent *in vacuo* or purging with nitrogen reverts to $[RhCl(CO)PPh_3]_2$ (ν_{CO} 1980vs, 2090w cm^{-1}, 2023w cm^{-1}).

(b) *In methanol suspension.* $[RhCl(CO)PPh_3]_2$ was suspended in methanol and CO passed for 1 h giving a pale yellow precipitate and an orange solution. The yellow precipitate was *trans*-$[RhCl(CO)(PPh_3)_2]$ (i.r. spectrum and analysis) (Found: C, 64·7; H, 4·4. Calc. for $C_{37}H_{30}ClOP_2Rh$: C, 64·3; H, 4·3%). Removal of solvent from the methanolic orange solution gave a black solid. Extraction with light petroleum (b.p. 60—80°) and concentration of the resultant orange solution gave orange-red needles of $[RhCl(CO)_2]_2$. The same behaviour was observed in concentrated dichloromethane solution.

Rhodium(III) *Compounds*

trans-*Di-μ-chloro-tetrachlorodicarbonylbis(triphenylphosphine)dirhodium*(III).—Dry chlorine was bubbled through a suspension of *trans*-$[RhCl(CO)PPh_3]_2$ in dichloromethane for *ca.* 5 min. The solid dissolved completely giving an orange-yellow solution which on concentration *in vacuo* and addition of pentane gave the *product* as an orange-yellow powder (ν_{CO} 2110, ν(RhCl) 354, 340 cm^{-1}).

Di-μ-chloro-di-iododiacetylbis(triphenylphosphine)dirhodium(III) *and di-μ-chloro-di-iododimethyldicarbonylbis(triphenylphosphine)dirhodium*(III) *mixture.*—$[RhCl(CO)PPh_3]_2$ Was treated with methyl iodide for 3 h giving a red-brown solution. Removal of solvent and addition of pentane gave the *product* as a dark brown powder (ν_{CO} 2065; ν($COCH_3$) 1710 cm^{-1}). If the reaction was carried out for 18 h the same products were formed but the amount of methyl isomer had substantially decreased and that of acyl increased (i.r. evidence).

Trichlorocarbonyl(triphenylphosphine)(triphenylarsine)rhodium(III).—$[RhCl_3(CO)PPh_3]_2$ Was shaken in chloroform with excess $AsPh_3$ for *ca.* 30 min. Removal of solvent and addition of pentane gave the *product* as a deep yellow crystalline powder (ν_{CO} 2102 cm^{-1}). A small amount of $[RhCl(CO)(PPh_3)(AsPh_3)]$ was also formed. Similarly, *trichlorocarbonyl(triphenylphosphine)(triphenylstibine)rhodium*(III) (ν_{CO} 2098, ν(RhCl) 345 cm^{-1}) was prepared from $[RhCl_3(CO)PPh_3]_2$ and excess $SbPh_3$. Again some $[RhCl(CO)PPh_3SbPh_3]$ was also formed. With $[RhCl_3(CO)PPh_3]_2$ and PPh_3 (1 : 2 molar ratio) the main product was *trans*-$[RhCl(CO)(PPh_3)_2]$. $[RhCl_3(CO)PPh_3AsPh_3]$ Was also prepared by chlorination of $[RhCl(CO)PPh_3AsPh_3]$ in CCl_4 (the compound contained *ca.* 0·25 mol CCl_4 solute per rhodium). Similarly, treatment of $[RhCl(CO)PPh_3AsPh_3]$ with iodine in CCl_4 gave *chlorodi-iodocarbonyl(triphenylphosphine)(triphenylarsine)rhodium*(III) 0·25 *carbon tetrachloride* (ν_{CO} 2080 cm^{-1}).

Reaction of $[RhCl(CO)PPh_3AsPh_3]$ with methyl iodide heated under reflux for 30 min followed by concentration and addition of pentane gave a dark brown powder which is a mixture of predominantly *chloroiodoacetyl(triphenylphosphine)(triphenylarsine)rhodium*(III) 0·50 *methyl iodide* (ν_{COCH_3} 1712 cm^{-1}) and *chloroiodomethylcarbonyl(triphenylphosphine)-triphenylarsine rhodium*(III) (ν_{CO} 2060 cm^{-1}). After 4 h heating under reflux, almost all the product was in the acetyl form. A small amount of rhodium(I) complex (ν_{CO} 1980 cm^{-1}) is also present.

Reaction of the isomeric mixture $[RhClI(CH_3)(CO)PPh_3]_2$ and $[RhClI(COCH_3)PPh_3]_2$ with excess $AsPh_3$ in chloroform or dichloromethane followed by immediate precipitation with pentane gave the pure orange-yellow *product* $[RhClI(CH_3)(CO)(PPh_3)(AsPh_3)]$ (ν_{CO} 2065 cm^{-1}). Similarly, reaction with L (L = PPh_3 or $SbPh_3$) gave $[RhClI(CH_3)(CO)PPh_3L]$. In solution, these rapidly isomerise to the corresponding acyl isomer.

Trichlorotris(pyridine)rhodium(III).— $[RhCl_3(CO)PPh_3]_2$ Was treated with an excess of pyridine in benzene for 24 h giving a yellow solution. Removal of solvent and addition of light petroleum (b.p. 60—80°) gave an oil which after prolonged treatment with ether (24 h) gave a yellow powder, washed with methanol and dried *in vacuo* (Found: C, 40·2; H, 3·3, N, 8·6. Calc. for $C_{15}H_{15}Cl_3N_3Rh$: C, 40·3; H, 3·4; N, 9·4%). Comparison with the i.r. spectra of authentic samples of 1,2,3- and 1,2,6-$[RhCl_3(C_5H_5N)]_3$ [31] indicates the latter has been formed.

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