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SOME STUDIES OF THE REACTION OF μ-DICHLOROTETRACARBONYLDIRHODIUM WITH DIMETHYLPHENYLPHOSPHINE

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Summary

The addition of PMe_2Ph to solutions of $Rh_2Cl_2(CO)_4$ has been studied by infrared and ^1H NMR spectroscopy, by measurement of conductance and of the carbon monoxide evolved. Under an atmosphere of CO the dominant course of the reaction is chloride bridge cleavage followed by CO substitution, whereas in refluxing cyclohexane substitution occurs initially. The formation of $RhCl(CO)(PMe_2Ph)_2$ on addition of PMe_2Ph (2 mol/mol Rh) is independent of solvent whereas addition of more tertiary phosphine leads to very different behaviour, depending upon the solvent and whether the solution is under CO or N_2. ^1H NMR studies show that all species with no more than one PMe_2Ph coordinated to a rhodium atom are in rapid equilibrium leading to averaged NMR signals.

Introduction

Several studies have been reported on substitution and bridge splitting reactions of μ-dichlorotetracarbonyldirhodium $Rh_2Cl_2(CO)_4$ with tertiary phosphines and the subject has recently been reviewed [1]. Addition of tertiary phosphine L to the carbonyl dimer in the ratio L/Rh = 2 gives $RhCl(CO)L_2$, while several intermediates have been isolated or characterised spectroscopically in solutions with lower L/Rh ratios; namely $Rh_2Cl_2(CO)_3L$, $Rh_2Cl_2(CO)_2L_2$, $Rh_2Cl_2(CO)L_3$ and $RhCl(CO)_2L$. Authors have discussed whether substitution to give dimers or bridge cleavage to give monomers is dominant and now it appears that either, or more commonly both, occur depending on the ligand L and the concentration in solution of free CO. In this paper we describe an extension to the work of Gallay, De Montauzon and Poilblanc [2] on the $Rh_2Cl_2(CO)_4$/

PMe_2Ph system involving infrared, ^1H NMR, conductometric and gasometric studies.

Results and discussion

1. Infrared studies

We have recorded spectra around 2000 cm^{-1} after successive additions of PMe_2Ph to $Rh_2Cl_2(CO)_4$ in cyclohexane solution and almost entirely different spectra were obtained depending upon whether the solution is saturated with CO (Fig. 1a) or whether nitrogen is bubbled through the solution for 10 min after each addition to remove dissolved CO before recording the spectra (Fig. 1b). With a few exceptions our results are very similar to those reported earlier for n-octane solutions [2]. Figure 1b shows that substitution derivatives $Rh_2Cl_2(CO)_3(PMe_2Ph)$ [ν(CO) 2089s, 2022s and 2000s cm^{-1}] and $Rh_2Cl_2(CO)_2(PMe_2Ph)_2$ [ν(CO) 1985s cm^{-1}] are the most abundant intermediates if CO is

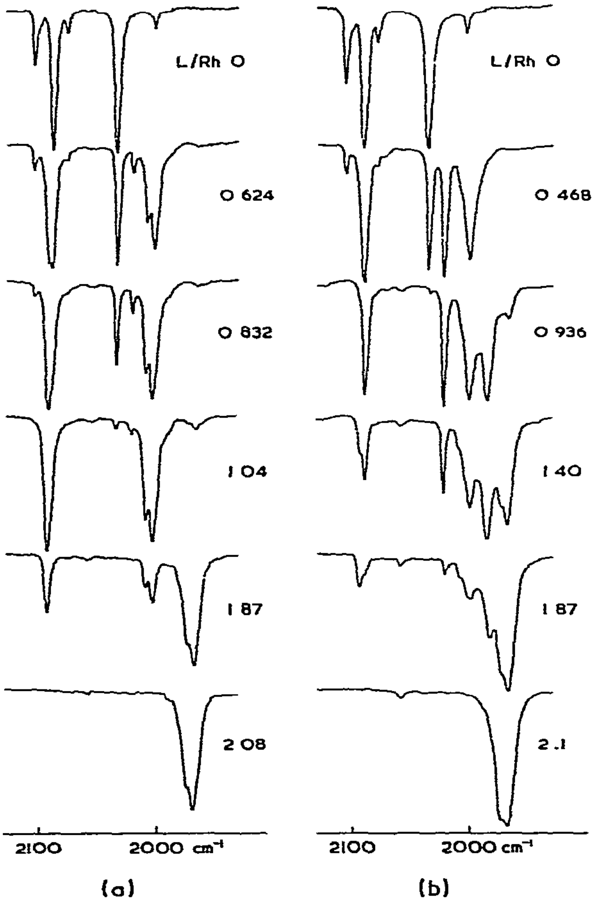

Fig. 1. Infrared spectra of $Rh_2Cl_2(CO)_4$ in cyclohexane on addition of PMe_2Ph(L) either (a) saturated with CO or (b) with N_2 bubbled through the solution for 10 min after each addition of PMe_2Ph.

displaced from solution. Under these conditions $RhCl(CO)_2(PMe_2Ph)$ [ν(CO) 2094vs, 2009s, and 2003vs cm^{-1}] is present in no more than low concentrations at any stage, but is the dominant intermediate on addition of ligand to $Rh_2Cl_2(CO)_4$ if the solution is saturated with CO. In this case $Rh_2Cl_2(CO)_3(PMe_2Ph)$ occurs only in low concentrations and $Rh_2Cl_2(CO)_2(PMe_2Ph)_2$ not at all. When L/Rh = 2, the product $RhCl(CO)(PMe_2Ph)_2$ is the only species in solution in each case. Hence with substituted CO displaced from solution:

$$Rh_2Cl_2(CO)_4 \xrightarrow[-CO]{+L} Rh_2Cl_2(CO)_3L \xrightarrow[-CO]{+L} Rh_2Cl_2(CO)_2L_2 \xrightarrow{+2L} 2\ RhCl(CO)L_2$$

In solutions saturated with CO:

$$Rh_2Cl_2(CO)_4 \xrightarrow{+2L} 2\ RhCl(CO)_2L \xrightarrow[-2CO]{+2L} 2\ RhCl(CO)L_2$$

All carbonyl absorptions in the infrared are as those given previously for n-octane solutions [2] except that only two strong absorptions at 2092 and 2003 cm^{-1} were reported for $RhCl(CO)_2(PMe_2Ph)$. We have found absorptions in cyclohexane at 2094vs, 2009s and 2003vs cm^{-1} corresponding to this species. The relative intensities of these absorptions (Fig. 1a) remain constant as this species increases and decreases in concentration as more PMe_2Ph is added. The presence of three absorptions could be due to isomers at equilibrium, possibly the *cis*-isomer [2094 and 2003 cm^{-1}] and the *trans*-isomer [2009 cm^{-1}]. Another possibility is that this species exists as the dimer $[RhCl(CO)_2(PMe_2Ph)]_2$ containing 5-coordinate rhodium, which could account for the presence of more than two ν(CO) absorptions. This has previously been proposed for similar species [1]. In an attempted isolation of the complex, PMe_2Ph (L/Rh = 1) was added to a hexane solution of $Rh_2Cl_2(CO)_4$ saturated with CO. After some precipitated $RhCl(CO)(PMe_2Ph)_2$ was removed the yellow-orange solution deposited an oil at −20°C which eventually gave well-formed yellow crystals. These were, however, only stable at −20°C under CO and rapidly darkened under vacuum. An infrared spectrum of a solution of these crystals in CO-saturated cyclohexane gave bands, 2094vs, 2009s and 2003vs cm^{-1}, already assigned to $RhCl(CO)_2(PMe_2Ph)$ or its dimer. We were unfortunately unable to obtain any far infrared or molecular weight data to differentiate these possibilities.

Addition of an excess of PMe_2Ph to $IrCl(CO)(PMe_2Ph)_2$ in chlorobenzene etc. gives the neutral 5-coordinate species $IrCl(CO)(PMe_2Ph)_3$ [3], but we have not attempted to identify or to isolate the rhodium analogue which is most likely formed when $L/Rh > 2$ in non-polar solvents.

2. *Gas evolution studies*

We have measured the evolution of gas on addition of PMe_2Ph to cyclohexane solutions of $Rh_2Cl_2(CO)_4$ in closed glass systems either under N_2 or CO at 1 atm and results are illustrated in Fig. 2. Under an atmosphere of CO for $L/Rh \leqslant 1$, addition of phosphine leads to bridge cleavage while in the range $1 \leqslant L/Rh \leqslant 2$ substitution occurs. More precisely, at complex concentrations we used (ca. 1.3×10^{-2} mol dm^{-3}) the first molecule of ligand added per rhodium atom (L/Rh = 1) gives 7% substitution and 93% bridge cleavage. The

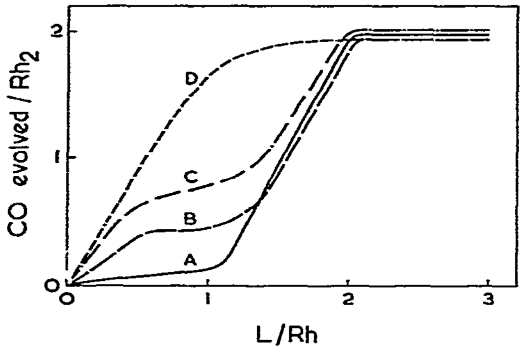

Fig. 2. Carbon monoxide evolution on addition of $PMe_2Ph(L)$ to $Rh_2Cl_2(CO)_4$ in cyclohexane solution. A. Under CO (1 atm) at 20°C. B. Under N_2 (1 atm) (25 ml) at 20°C. C. Under N_2 (1 atm) (75 ml) at 20°C D. Under N_2 (1 atm) (75 ml) in refluxing solution (81°C).

proportion of substitution increases under an atmosphere of N_2 but, since we employed closed systems, complete substitution did not occur. For example, with ca. 25 ml nitrogen gas in the vessel there was 23% substitution (L/Rh = 1), but with ca. 75 ml nitrogen gas the proportion of substitution had increased to 39%. In refluxing cyclohexane substitution becomes dominant (83% for L/Rh = 1) and this may be due to the removal of CO from solution rather than to the temperature dependence of the equilibrium. The results agree with the idea that a high or low degree of substitution may occur depending upon conditions of CO concentration and temperature. More than one molecule of CO per rhodium atom was not evolved and hence in this system the species $Rh_2Cl_2(CO)L_3$ is not formed as with L = PPh_3 [2].

We have also studied CO evolution under an atmosphere of CO for the same reaction in different solvents (Fig. 3). Approximately the same behaviour is observed in each solvent up to L/Rh = 2 and hence the degree of bridge-splitting versus substitution in the presence of CO is not markedly solvent dependent. Only on the addition of PMe_2Ph above L/Rh = 2 are major differences between

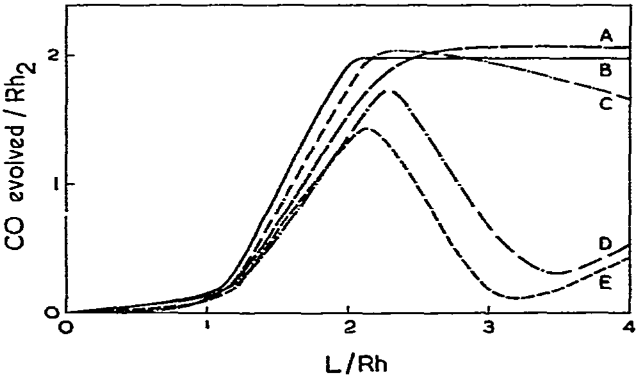

Fig. 3. Carbon monoxide evolution on addition of $PMe_2Ph(L)$ to $Rh_2Cl_2(CO)_4$ in different solvents under an atmosphere of carbon monoxide (20°C). A, toluene; B, cyclohexane; C, methylethylketone (butan-2-one); D, propan-2-ol; E, ethanol.

solvents observed. In ethanol or propan-2-ol a re-adsorption of CO follows the formation of $RhCl(CO)(PMe_2Ph)_2$. By analogy with the behaviour on addition of tertiary phosphines L or CO to $IrCl(CO)L_2$ in mixed benzene/ethanol solutions [4], we propose that 5-coordinate cationic complexes are produced so that the addition of an L molecule requires an equivalent uptake of CO:

$$RhCl(CO)L_2 + L + CO \rightarrow [Rh(CO)_2L_3]Cl$$

Figure 3 shows that less than two molecules of CO are evolved when $L/Rh = 2$ so that chloride substitution has occurred to some extent even when $RhCl(CO)_2L$ is still present. There is then indication that the following step occurs an addition of more L:

$$[Rh(CO)_2L_3]Cl + L \rightarrow [Rh(CO)L_4]Cl + CO$$

This last step is far from complete even when $L/Rh \gg 4$. In butan-2-one there is some re-adsorption of CO with electrolyte formation when $L/Rh > 2$ but this is far less extensive than in alcohols and no such uptake of CO is observed in cyclohexane or toluene. The uptake of CO thus reflects the ability of the solvent to assist electrolyte formation.

3. *Conductance studies*

The formation of electrolytes on addition of PMe_2Ph to $Rh_2Cl(CO)_4$ in ethanol for $L/Rh > 2$ is confirmed by conductance measurements (Fig. 4). Under CO an essentially quantitative conversion of $RhCl(CO)(PMe_2Ph)_2$ to $[Rh(CO)_2(PMe_2PH)_3]Cl$ is observed on going from $L/Rh = 2$ to $L/Rh = 3$, although there is some chloride substitution for $L/Rh < 2$ (about 8% when $L/Rh = 2$). If the same study is made with N_2 bubbling though the solution no electrolyte is formed when $L/Rh < 2$ and chloride substitution is not complete when $L/Rh = 4$. Presumably the species formed is $[Rh(CO)(PMe_2Ph)_4]Cl$ or $[Rh(PMe_2Ph)_4]Cl$. The lack of linearity for this curve shows that the conversion is not quantitative and essentially complete conversion to an electrolyte requires $L/Rh > 5$.

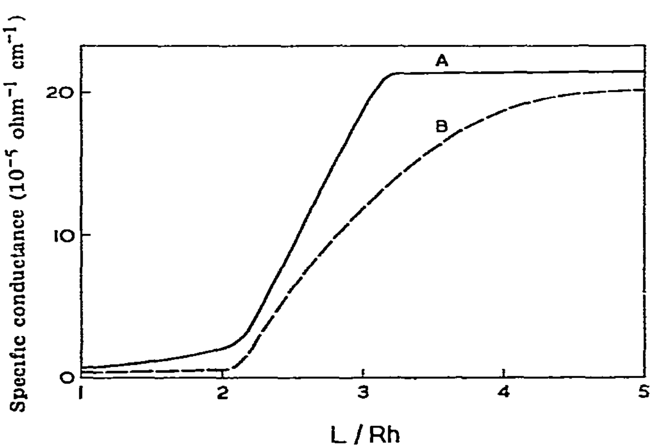

Fig. 4. Specific conductance of a solution of $Rh_2Cl_2(CO)_4$ (2×10^{-3} mol dm^{-3}) in ethanol on addition of $PMe_2Ph(L)$ with either CO (A) or N_2 (B) bubbled through the solution (20° C).

4. ^{1}H NMR studies

The ^{1}H NMR (methyl) spectrum was recorded after incremental additions of PMe_2Ph to cyclo-C_6D_{12} or benzene solutions of $Rh_2Cl_2(CO)_4$. Only two methyl signals were observed whether the reaction was carried out under N_2 or CO. As L/Rh was increased a well-resolved doublet of doublets (τ 8.2-8.3 in C_6D_{12}; τ 8.5-8.7 ppm in C_6H_6) increased in intensity and finally decreased as a triplet of doublets (τ 8.18 in C_6D_{12}; τ 8.40 ppm in C_6H_6) due to $RhCl(CO)(PMe_2Ph)_2$ was formed. No signal due to free PMe_2Ph was observed. It is known that addition of free PMe_2Ph to $RhCl(CO)(PMe_2Ph)_2$ ($L/Rh > 2$) in benzene leads to rapid exchange between free and coordinated PMe_2Ph and considerable line-shape changes [5,6]. Therefore we know that for $L/Rh \leqslant 2$ there is no more than a very low concentration of free PMe_2Ph.

The other signal (doublet of doublets) is due to all species with no more than one PMe_2Ph ligand per Rh atom [$Rh_2Cl_2(CO)_3L$, $Rh_2Cl_2(CO)_2L_2$, $RhCl(CO)_2L$ and probably $Rh_2Cl_2(CO)_4$] and these must be in rapid equilibrium not involving PMe_2Ph transfer between Rh atoms (^{103}Rh coupling observed even at the fast exchange limit). The chemical shift and coupling constants, J(P—H) and J(Rh—H), for this signal are not independent of L/Rh or whether the solutions are saturated with N_2 or CO (see Fig. 5) as found for the signal due to $RhCl(CO)(PMe_2Ph)_2$. Lower values of τ, J(P—H) and J(Rh—H) occur when the solutions are saturated with CO and must be associated with $RhCl(CO)_2(PMe_2Ph)$ (or its dimer). As nitrogen is bubbled through a solution initially saturated with CO, τ, J(P—H) and J(Rh—H) all steadily rise to higher values associated with $Rh_2Cl_2(CO)_3L$ and/or $Rh_2Cl_2(CO)_2L_2$. The differences are too small, however, to be used to analyse the composition of the mixture.

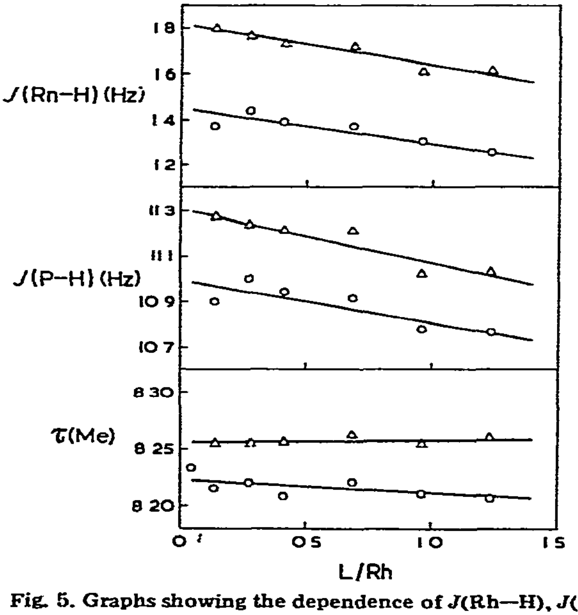

Fig. 5. Graphs showing the dependence of J(Rh—H), J(P—H) and τ-value for the PMe_2Ph ^{1}H NMR signal (sharply resolved double doublet) on addition of PMe_2Ph to $Rh_2Cl_2(CO)_4$ in cyclo-C_6D_{12}, saturated with N_2 (Δ) or CO (○).

As previously observed [2], broad spectra were obtained on lowering the temperature (ca. —120°C in Me_2O) which were not interpreted but must be due to the slowing down of the exchanges.

Experimental

μ-Dichlorotetracarbonyldirhodium was prepared by bubbling CO through a refluxing solution of rhodium trichloride trihydrate (4 g) in ethanol (absolute, 70 ml) for 4 h. Evaporation to dryness of the yellow solution obtained and sublimation of the residue gave dark red crystals of the product (yield 70-90%). Dimethylphenylphosphine was purchased from Maybridge Chemical Co. Ltd., distilled under N_2 and sealed in glass tubes till required. All solutions studied were kept under nitrogen or carbon monoxide. A Perkin—Elmer 257 infrared spectrometer, a Varian T60 and a HA100 ^{1}H NMR spectrometer were used in this work.

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