Some Addition Reactions of a New Rhodium(I) Ditertiary Phosphine Complex

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GREAT interest has been shown recently in catalytic hydrogenation[1,2a] and oxidative addition reactions[3] of d^8-transition-metal systems. $[RhCl(PPh_3)_3]$ is one of the most active and extensively studied of these. Here dissociation of one triphenylphosphine molecule is considered to be an essential prelude to oxidative addition in such reactions.[2] Thus, at first sight, it is not surprising that $[Rh(dppe)_2]Cl$ (dppe = $Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2$) is inactive,[4] because the chelate ligand should be less prone to dissociate from the complex. $[Rh(dppe)_2]Cl$ does not react with hydrogen or carbon monoxide under ambient conditions. It was of interest, therefore, to see whether its aliphatic analogue $[Rh(dmpe)_2]Cl$ would show oxidative addition and similar reactions. Again, dissociation would not be expected, but the less electronegative character of the ligand would increase electron density at the metal atom, thus encouraging oxidation. We have, therefore, prepared $Rh(dmpe)_2Cl$ (dmpe = $Me_2PCH_2{\cdot}CH_2{\cdot}PMe_2$) by the reaction of the aliphatic diphosphine on $[RhCl(PPh_3)_3]$ in benzene and find it to be thermally very stable but chemically reactive. In methanol solution it conducts as a 1 : 1 electrolyte and it activates hydrogen under ambient conditions in tetrahydrofuran (THF) dispersion to give a suspension of $[RhH_2(dmpe)_2]Cl$, which, from the infrared spectrum appears to have a *cis*-configuration. Upon reducing the pressure of hydrogen to a few mm. over the suspension, or over a solution of the dihydride complex, it reverts to the original chloride (1).

$$[Rh(dmpe)_2]Cl \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} [RhH_2(dmpe)_2]Cl \qquad (1)$$

Carbon monoxide reacts with a solution or suspension of the rhodium(I) complex in tetrahydrofuran very rapidly to give a five-co-ordinated Rh^I carbonyl complex. This complex is very much more stable than the hydrogen complex; however, on suspension in boiling toluene, decarbonylation occurs to give the original complex (2). Decarbonylation occurred only slowly in boiling benzene, if at all.

$$[Rh(dmpe)_2]Cl \underset{-CO}{\overset{CO}{\rightleftharpoons}} [Rh(CO)(dmpe)_2]Cl \qquad (2)$$

TABLE

Compound	Colour	Characteristic i.r. frequencies (cm.$^{-1}$)	
cis-$[RhH_2(dmpe)_2]Cl$	buff white	1900, 1870 (sh)	ν(M–H)
trans-$[Rh(H)Cl(dmpe)_2]Cl$	white	2050	ν(M–H)
trans-$[Rh(H)Br(dmpe)_2]Cl$	pale yellow	2030	ν(M–H)
$[Rh(CO)(dmpe)_2]Cl$	pale yellow	1920	ν(CO)
$[Rh(dmpe)_2]Cl$	yellow	710, 740	ν(P–Me)
trans-$[RhCl_2(dmpe)_2]Cl$†	pale yellow	720, 750	ν(P–Me)†
trans-$[RhBr_2(dmpe)_2]Cl$	bright yellow	720, 755	ν(P–Me)

† *cis*-$[RhCl_2(dmpe)_2]Cl$ has also been prepared. Four bands are in the P–Me region.

The carbonyl complex can also be prepared from $[Rh_2Cl_2(CO)_4]$ and the aliphatic ditertiary phosphine dmpe in benzene (3), in contrast to the corresponding reaction with dppe[5] (4).

$$[Rh_2Cl_2(CO)_4] + 4\ \mathrm{dmpe} \rightarrow 2[Rh(CO)(dmpe)_2]Cl + 2CO \qquad (3)$$

$$[Rh_2Cl_2(CO)_4] + 4\ \mathrm{dppe} \rightarrow 2[Rh(dppe)_2]Cl + 4CO \qquad (4)$$

It should be noted that $[Rh(CO)(dmpe)_2]Cl$ does not activate hydrogen under ambient conditions probably because the strong π-bonding nature of the carbonyl drains electron density from the metal so that the hydrogen is not reduced. This is consistent with the strong conditions needed to remove CO from the d^8-complex. On the other hand, CO is easily removed by an oxidative addition of elemental halogen or hydrogen halides to give the d^6-complexes of equations (5) and (6). These six-co-ordinated rhodium(III) complexes may also be prepared directly from $[Rh(dmpe)_2]Cl$ by the action of HX or X_2.

$$[Rh(CO)(dmpe)_2]Cl \xrightarrow[-CO]{HX}$$
$$trans\text{-}[Rh(H)X(dmpe)_2]Cl \xleftarrow{HX} [Rh(dmpe)_2]Cl \qquad (5)$$

$$[Rh(CO)(dmpe)_2]Cl \xrightarrow[-CO]{X_2}$$
$$trans\text{-}[RhX_2(dmpe)_2]Cl \xleftarrow{X_2} [Rh(dmpe)_2]Cl \qquad (6)$$

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