Redistribution Reactions of Organometallic Complexes: Carbonyl, Halogen, and Phosphine Ligand Exchange Between Co-ordinately Unsaturated Rhodium(I) and Iridium(I) Complexes

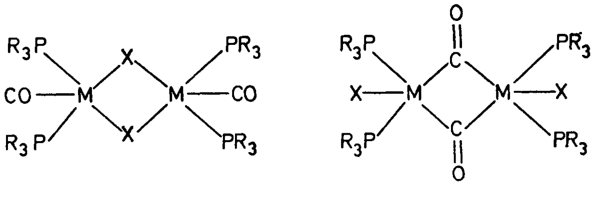
By PHILIP E. GARROU and GEORGE E. HARTWELL*
(*Department of Chemistry, Indiana University, Bloomington, Indiana* 47401)

Summary Intermolecular redistribution of carbonyl, halide, and phosphine ligands is found to occur in systems of the type $M(CO)X(PR_3)_2$ (M = Rh, Ir; X = Cl, Br); carbonyl and halogen exchange is proposed to occur through doubly five-co-ordinate bridged intermediates.

REDISTRIBUTION reactions of transition-metal complexes have not received the extensive study given to complexes of the main group elements.[1] We now report on carbonyl, halogen, and phosphine intermolecular redistribution in complexes of the type $M(CO)X(PR_3)_2$ (M = Rh, Ir; X = Cl, Br). An i.r. study of the redistribution of PR_3 in $Ir(CO)Cl(PR_3)_2$ complexes has been reported previously.[2]

Reaction of $Rh(^{13}CO)Cl(PPh_3)_2$ with $Rh(CO)Cl[(o\text{-}CH_3C_6H_4)_3Sb]_2$, $Rh(CO)(acac)(PPh_3)$, or $Ir(CO)Cl(PPh_3)_2$, (benzene; 25°) is complete within a few seconds. The i.r. spectra of the mixtures indicate that random redistribution of ^{13}CO has occurred. However $Rh(^{13}CO)Cl(PPh_3)_2$ with $Rh(CO)Cl_3(PPh_3)_2$ under similar conditions for a period of 4 h shows no sign of exchange, although the latter species does exchange rapidly with excess of carbon monoxide.[3] The ^1H n.m.r. spectra of complexes of the type $Rh(CO)Cl(PPh_3)(PR_3)$ have recently been explained by the equilibrium (1).[4]

$$2Rh(CO)Cl(PPh_3)(PR_3) \rightleftharpoons Rh(CO)Cl(PPh_3)_2 + Rh(CO)Cl(PR_3)_2 \qquad (1)$$



FIGURE

The ^{31}P spectra (benzene; 25°) of $Rh(CO)Cl(PPh_3)(L)$, (L = $AsPh_3$ or PPh_2Et) and the corresponding ^{31}P spectra of equimolar mixtures of $Rh(CO)Cl(PPh_3)_2$ and $Rh(CO)Cl(L)_2$ are identical. Analyses of these spectra verify the existence, in solution, of the three proposed species. Under these conditions phosphine also exchanges between $Rh(CO)Cl(PR_3)_2$ and $Ir(CO)Cl(PR_3)_2$. The ^{31}P spectrum of a benzene solution containing $Rh(CO)Cl(PR_3)_2$ and $Ir(CO)Br(PR_3)_2$ consists of two doublets and two singlets consistent with redistribution of the halogens.

Halogen exchange through an ionic mechanism is unlikely in benzene. Dissociation of CO would cause the precipitation of insoluble $[RhCl(PPh_3)_2]_2$ which was not observed. Thus it is suggested that the exchange of halogen and carbonyl occur through a doubly five-co-ordinate, bridged intermediate (Figure). The lack of exchange involving $Rh(CO)Cl_3(PPh_3)_2$ possibly indicates the necessity for co-ordinate unsaturation if redistribution of ^{13}CO is to occur.

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