The Mechanism of the Reaction of Low-valent Metal Complexes with Electrophilic Olefins

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THE isoelectronic compounds, tetrafluoroethylene,[1,2] tetracyanoethylene,[3,4] hexafluoroacetone,[5] and carbon disulphide[6] have been shown to form complexes with low-valent transition-metal complexes. If a valence-bond description is adopted, the bonding in these complexes may be depicted as involving the metal atom in a three-membered σ-bonded ring framework. Recently, the stereochemistry[4,6,7] of these complexes has received attention, but little is known about the related topic of the mechanism of formation of these complexes.

The ruthenium(0) complex *trans*-$\{EtC[CH_2O]_3P\}_2Ru(CO)_3$ reacts very rapidly at room temperature with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene to form (I). The i.r. spectrum of (I) showed a single terminal carbonyl band at 2061 vs cm.$^{-1}$ (CH_2Cl_2) and the ^1H n.m.r. spectrum showed the ($POCH_2$) protons as a doublet (J_{HP} 4·5 c./sec.) centred at τ 5·70, which establishes the illustrated stereochemistry. The ^{19}F n.m.r. spectrum† containing a doublet (J_{PF} 5·8 c./sec.) at 54·4 p.p.m. confirming the structural assignment. The crystalline solid (I) isomerises in solution [$t_{\frac{1}{2}}$ 6 min. (MeCN), $t_{\frac{1}{2}}$ 30 min. (C_6H_6)] to form (II) with i.r. bands 2041 vs and 1938 vs cm.$^{-1}$ (CH_2Cl_2); the ^1H and ^{19}F n.m.r. spectra had bands at 5·63 (d, $POCH_2$, J_{HP} 4·5 c./sec.) and 5·70 τ (d, $POCH_2$, J_{HP} 4·5 c./sec.); and a doublet (J_{PF} 5·8 c./sec.) centred at 54·4 p.p.m., respectively.

Tetrafluoroethylene reacts with *trans*-$[(C_2H_5O)_3P]_2Ru(CO)_3$ to afford (III) m.p. 59°. ν_{CO} 2019 vs cm.$^{-1}$ (hexane) with ^1H n.m.r. bands at τ 6·30 (quint., $POCH_2CH_3$, J_{HP} 7·0 c./sec., J_{HH} 7·0 c./sec.), 8·72 (t, $POCH_2CH_3$, J_{HH} 7·0 c./sec.), and a ^{19}F n.m.r. band at 114·2 p.p.m. (typical X-resonance of an $X_2AA'X_2'$ system).[1]

The isolation of (I), (II), and (III) is of general interest in that these are the first examples of ruthenium fluoro-olefin complexes, moreover, the n.m.r. data provides support for the rigid σ-bonded structures illustrated *i.e.* the compounds are formally Ru^{II} complexes. However, the stereochemistry of (I), (II) and (III) is in striking

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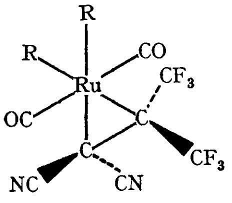
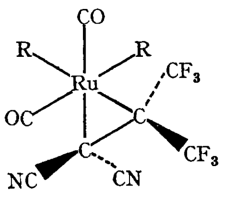
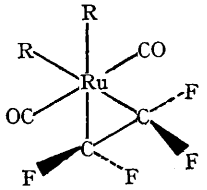
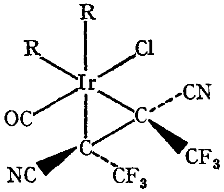
† The solvent used for the ^{19}F n.m.r. spectral work was $CFCl_3$.

contrast with that observed in the formally related‡ reaction of *trans*-$(Ph_3P)_2Ru(CO)_3$[8] or *trans*-$(Ph_2PMe)_2Ru(CO)_3$[8,9] with iodine, when *cis*-addition of iodine occurs and the phosphines retain their relative *trans*-configuration.


(I; R=EtC[CH$_2$O]$_3$P)

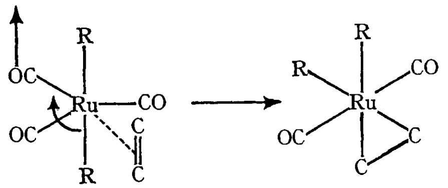

(II; R=EtC[CH$_2$O]$_3$P)

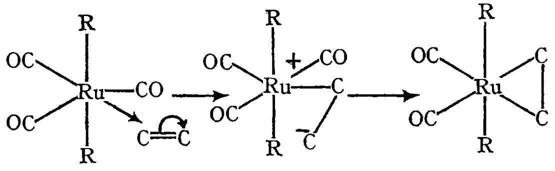

[III; R=(EtO)$_3$P]


[IV; R=(EtO)$_3$P]

In order to accommodate this difference in stereochemistry it is suggested, that in the reaction of $(CF_3)_2C{=}C(CN)_2$, C_2F_4 and other electrophilic olefins with ruthenium(0) complexes, the olefin approaches the metal broadside-on as depicted (mechanism A), rather than end-on (mechanism B) where reaction involves nucleophilic attack by the metal on the electrophilic olefin.

Further evidence for the reaction proceeding *via* direct co-ordination of the olefin to the metal was provided by studying the reaction of *trans*-$(Ph_3P)_2IrCO{\cdot}Cl$ with *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene.[10] The reaction is stereospecific leading to the formation of (IV) m.p. 267—268°, ν_{CO} 2041 vs cm.$^{-1}$ (Nujol). The ^{19}F n.m.r. spectrum showed two bands at 53·8 p.p.m. (d, J_{PF} 11·7) and 58·0 p.p.m. (d, J_{PF} 9·3 c./sec.). Since vicinal inequivalent CF_3 groups only show[10] F–F coupling when in a relative *cis*-configuration, no change in configuration of the olefin occurs on complexing to iridium. The stereospecificity of this reaction implies that ionic intermediates of the kind depicted in mechanism B are not involved. A study of the rate of reaction of *trans*-(Ph_3P)-$IrCO{\cdot}Cl$ with *trans*-$CF_3(CN){\cdot}C{=}C(CN){\cdot}CF_3$ in different solvents confirms this point. The reaction in nitromethane proceeds at a rate only twice as fast as in methylene chloride. If an ionic intermediate was involved a large rate difference would be expected.[10]


Mechanism A


Mechanism B

These experiments clearly suggest that in the reaction of low-valent metal species with electrophilic olefins, weak σ-donor interaction occurs followed by developing overlap between the metal *d*-orbitals and the olefinic π-antibonding orbitals.

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‡ The reaction of electrophilic olefins with $P_2Ru(CO)_3$ systems may be thought of as an oxidative–elimination reaction.

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