Associative Substitution Reactions of $\cdot Re(CO)_5$

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Summary Studies of competition between substitution and chlorine abstraction reactions of photochemically generated $\cdot Re(CO)_5$ radicals show that substitution proceeds *via* a second-order associative path and not *via* CO dissociation.

IT has been strongly argued that the pronounced lability towards substitution of 17-electron 5-co-ordinate metal-centred radicals such as $\cdot Mn(CO)_5$ and $\cdot Re(CO)_5$ is due to rapid CO dissocation.[1] There is, however, substantial indirect evidence in the literature that CO dissociation is relatively slow[2,3] and that rapid substitution proceeds *via* an associative mechanism.[3–5] We have supplemented this indirect evidence by more direct studies that involve competition between chlorine atom abstraction from carbon tetrachloride and ligand substitution reactions of $\cdot\mathrm{Re(CO)_5}$. Similar studies (involving competition between chlorine atom abstraction and other oxidation reactions) have been reported recently by Hepp and Wrighton[6] and such studies clearly provide a powerful method of characterizing reaction mechanisms and reactivities of metal-centred organometallic radicals of this kind.

The $\cdot\mathrm{Re(CO)_5}$ radicals were generated [1,6,7] in deoxygenated cyclohexane by photolysing $\mathrm{Re_2(CO)_{10}}$ at room temperature with a 500 W Hanovia mercury lamp without a filter. In the presence of mixtures of $\mathrm{CCl_4}$ and triphenylphosphine or tri-n-butylphosphine the only reaction products discernible by i.r. spectroscopy were $\mathrm{ClRe(CO)_5}$ and $\mathrm{ClRe(CO)_4L}$.† The mechanism proposed for the formation of these products is shown in equations (1)—(6). The ratio $[\mathrm{ClRe(CO)_5}]/[\mathrm{ClRe(CO)_4L}] = [\mathrm{U}]/[\mathrm{S}] = (A_\mathrm{U}/\epsilon_\mathrm{U})/(A_\mathrm{S}/\epsilon_\mathrm{S})$ was found to

$$\mathrm{Re_2(CO)_{10}} \overset{h\nu}{\rightleftharpoons} 2\,\cdot\mathrm{Re(CO)_5} \qquad (1)$$

$$\cdot\mathrm{Re(CO)_5} \xrightarrow{\mathrm{CCl_4}} \mathrm{ClRe(CO)_5} \qquad (2)$$

$$\cdot\mathrm{Re(CO)_5} \rightleftharpoons \cdot\mathrm{Re(CO)_4} + \mathrm{CO} \qquad (3)$$

$$\cdot\mathrm{Re(CO)_4} + \mathrm{L} \rightarrow \cdot\mathrm{Re(CO)_4L} \qquad (4)$$

$$\cdot\mathrm{Re(CO)_5} + \mathrm{L} \rightarrow \cdot\mathrm{Re(CO)_4L} + \mathrm{CO} \qquad (5)$$

$$\cdot\mathrm{Re(CO)_4L} \xrightarrow{\mathrm{CCl_4}} \mathrm{ClRe(CO)_4L} \qquad (6)$$

be independent of irradiation time over the range 5—25 min and 20—60% reaction (A_U and A_S, and ϵ_U and ϵ_S, are appropriate absorbances and molar absorption coefficients of the unsubstituted and substituted products). It was also closely proportional to $[\mathrm{CCl_4}]$ at constant $[\mathrm{PPh_3}]$, confirming the expected second-order nature of reaction (2). Further substitution into $\cdot\mathrm{Re(CO)_4L}$ must be relatively slow since no disubstituted products were observed.

The ratio [S]/[U] must, therefore, be given by equation (7). The Figure shows that when $\mathrm{L} = \mathrm{PPh_3}$ the dependence

$$[\mathrm{S}]/[\mathrm{U}] = (A_\mathrm{S}/A_\mathrm{U})(\epsilon_\mathrm{U}/\epsilon_\mathrm{S}) = \{k_3 + k_5[\mathrm{L}]\}/k_2[\mathrm{CCl_4}] \qquad (7)$$

of [S]/[U] on $[\mathrm{PPh_3}]/[\mathrm{CCl_4}]$ is linear, the straight line having a negligible intercept at $[\mathrm{PPh_3}] = 0$. No effect due to the presence or absence of CO was observed. These results show unambiguously that k_3, the rate constant for CO dissociation, is negligible and that substitution is exclusively first order in $[\mathrm{PPh_3}]$ and associative in nature. The gradients lead to the values $k_5/k_2 = 16{\cdot}9$ and $19{\cdot}2$ when the yields of the products were monitored at 2 106 and 1 945 $\mathrm{cm^{-1}}$, respectively, and when $\epsilon_\mathrm{S}/\epsilon_\mathrm{U} = x$ was taken as 0·0826 and 0·187, respectively. Analysis of other data over a wide range of both $[\mathrm{PPh_3}]$ and $[\mathrm{CCl_4}]$ leads to a mean value $k_5/k_2 = 22{\cdot}1$ with a maximum uncertainty of *ca.* ±15%. Similar behaviour was found when $\mathrm{L} = \mathrm{PBu^n_3}$ and $k_5/k_2 = 34$ when $[\mathrm{ClRe(CO)_4(PBu^n_3)}]$ was monitored at 1 935 $\mathrm{cm^{-1}}$, the maximum uncertainty being *ca.* 15%.

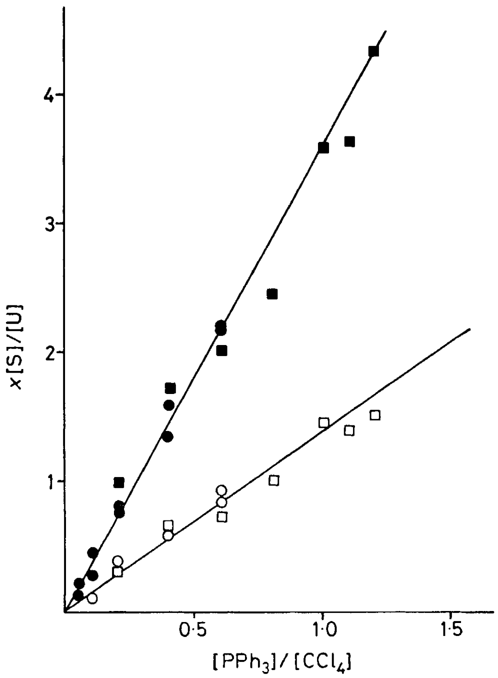

FIGURE. Dependence of the ratio of substituted to unsubstituted rhenium carbonyl chloride product on $[\mathrm{PPh_3}]/[\mathrm{CCl_4}]$. $\mathrm{S} = \mathrm{ClRe(CO)_4(PPh_3)}$, $\mathrm{U} = \mathrm{ClRe(CO)_5}$, $x = \epsilon(2\,106\ \mathrm{cm^{-1}})/\epsilon(2\,045\ \mathrm{cm^{-1}}) = 0{\cdot}0826$ for ●, reactions under atmospheres of Ar, and ■, reactions under atmospheres of CO; $x = \epsilon(1\,945\ \mathrm{cm^{-1}})/\epsilon(2\,045\ \mathrm{cm^{-1}}) = 0{\cdot}187$ for ○, reactions under Ar, and □, reactions under CO.

Although both substitutions are associative in nature the dependence of k_5 on the nucleophilicity of the entering ligand is small.[8] This low selectivity shown by $\cdot\mathrm{Re(CO)_5}$ can be associated with a high susceptibility to nucleophilic attack that must arise from the half-empty orbital available for L–Re bond making. A similar explanation has been offered for the low selectivity of $\cdot\mathrm{Mn(CO)_5(PPh)_3}$ inferred for associative replacement of the $\mathrm{PPh_3}$.[4]

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† $\mathrm{ClRe(CO)_5}$ has an i.r. band at 2 045 $\mathrm{cm^{-1}}$ that is easily resolved from the bands due to $\mathrm{Re_2(CO)_{10}}$ at 2 070 and 2 015 $\mathrm{cm^{-1}}$. $\mathrm{ClRe(CO)_4(PPh_3)}$ has bands at 2 106 and 1 954 $\mathrm{cm^{-1}}$ and $\mathrm{ClRe(CO)_4(PBu_3{}^n)}$ has one at 1 935 $\mathrm{cm^{-1}}$ that are all also clearly resolvable.

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