J.C.S. Снем. Сомм., 1981

## Associative Substitution Reactions of 'Re(CO)<sub>5</sub>

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Summary Studies of competition between substitution and chlorine abstraction reactions of photochemically generated  $\cdot \text{Re}(\text{CO})_5$  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 metalcentred radicals such as  $\cdot Mn(CO)_5$  and  $\cdot Re(CO)_5$  is due to rapid CO dissocation.<sup>1</sup> 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.<sup>3-5</sup> 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  $\cdot \operatorname{Re}(\operatorname{CO})_{5}$ . Similar studies (involving competition between chlorine atom abstraction and other oxidation reactions) have been reported recently by Hepp and Wrighton<sup>6</sup> and such studies clearly provide a powerful method of characterizing reaction mechanisms and reactivities of metal-centred organometallic radicals of this kind.

The •Re(CO)<sub>5</sub> radicals were generated <sup>1,6,7</sup> in deoxygenated cyclohexane by photolysing Re<sub>2</sub>(CO)<sub>10</sub> at room temperature with a 500 W Hanovia mercury lamp without a filter. In the presence of mixtures of CCl<sub>4</sub> and triphenylphosphine or tri-n-butylphosphine the only reaction products discernible by i.r. spectroscopy were ClRe(CO)<sub>5</sub> and ClRe(CO)<sub>4</sub>L.<sup>†</sup> The mechanism proposed for the formation of these products is shown in equations (1)--(6). The ratio  $[CIRe(CO)_5]/$  $[ClRe(CO)_4L] = [U]/[S] = (A_u/\epsilon_u)/(A_s/\epsilon_s)$  was found to

$$\operatorname{Re}_{2}(\operatorname{CO})_{10} \stackrel{h\nu}{\rightleftharpoons} 2 \cdot \operatorname{Re}(\operatorname{CO})_{5}$$
(1)

$$\cdot \operatorname{Re}(\operatorname{CO})_{5} \xrightarrow{\operatorname{CCl}_{4}} \operatorname{ClRe}(\operatorname{CO})_{5} \tag{2}$$

$$\cdot \operatorname{Re}(\operatorname{CO})_5 \quad \rightleftharpoons \quad \cdot \operatorname{Re}(\operatorname{CO})_4 + \operatorname{CO} \tag{3}$$

$$\cdot \operatorname{Re}(\operatorname{CO})_4 + L \rightarrow \cdot \operatorname{Re}(\operatorname{CO})_4 L \tag{4}$$

$$\operatorname{Re}(\operatorname{CO})_{\mathbf{5}} + L \rightarrow \operatorname{Re}(\operatorname{CO})_{\mathbf{4}}L + \operatorname{CO}$$
 (5)

$$\cdot \operatorname{Re}(\operatorname{CO})_{4} \operatorname{L} \xrightarrow{\operatorname{CU}_{4}} \operatorname{ClRe}(\operatorname{CO})_{4} \operatorname{L}$$
(6)

be independent of irradiation time over the range 5-25 min and 20–60% reaction ( $A_{\rm u}$  and  $A_{\rm s}$ , and  $\epsilon_{\rm u}$  and  $\epsilon_{\rm s}$ , are appropriate absorbances and molar absorption coefficients of the unsubstituted and substituted products). It was also closely proportional to [CCl<sub>4</sub>] at constant [PPh<sub>3</sub>], confirming the expected second-order nature of reaction (2). Further substitution into .Re(CO)<sub>4</sub>L must be relatively slow since no disubstituted products were observed.

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

$$[S]/[U] = (A_8/A_u)(\epsilon_u/\epsilon_8) = \{k_3 + k_5[L]\}/k_2[CCl_4]$$
(7)

of [S]/[U] on  $[PPh_a]/[CCl_a]$  is linear, the straight line having a negligible intercept at  $[PPh_3] = 0$ . 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 [PPh<sub>3</sub>] and associative in nature. The gradients lead to the values  $k_5/k_2 = 16.9$  and 19.2 when the yields of the products were monitored at  $2\,106$  and  $1\,945$  cm<sup>-1</sup>,



FIGURE. Dependence of the ratio of substituted to unsubstituted rhenium carbonyl chloride product on  $[PPh_3]/[CCl_4]$ . S = ClRe(CO)<sub>4</sub>(PPh<sub>3</sub>), U = ClRe(CO)<sub>5</sub>,  $x = \epsilon(2\ 106\ \text{cm}^{-1})/\epsilon(2\ 045\ \text{cm}^{-1}) = 0.0826$  for  $\bigcirc$ , reactions under atmospheres of Ar, and  $\blacksquare$ , reactions under atmospheres of CO;  $x = \epsilon (1 \ 945 \text{ cm}^{-1})$  $\epsilon(2.045 \text{ cm}^{-1}) = 0.187$  for  $\bigcirc$ , reactions under Ar, and  $\square$ , reactions under CO.

respectively, and when  $\epsilon_{
m s}/\epsilon_{
m u}=x$  was taken as 0.0826 and 0.187, respectively. Analysis of other data over a wide range of both [PPh3] and [CCl4] leads to a mean value  $k_5/k_2 = 22.1$  with a maximum uncertainty of ca.  $\pm 15\%$ . Similar behaviour was found when  $L = PBu_3^n$  and  $k_5/k_2 = 34$ when  $[ClRe(CO)_4(PBu_3^n)]$  was monitored at 1 935 cm<sup>-1</sup>, the maximum uncertainty being ca. 15%.

Although both substitutions are associative in nature the dependence of  $k_5$  on the nucleophilicity of the entering ligand is small.<sup>8</sup> This low selectivity shown by  $\cdot \text{Re(CO)}_5$  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  $\cdot$ Mn(CO)<sub>5</sub>(PPh)<sub>3</sub> inferred for associative replacement of the PPh3.4

We thank the University of Toronto and the Natural Science and Engineering Research Council, Ottawa, for support.

(Received, 7th July 1981; Com. 786.)

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 $<sup>\</sup>uparrow$  ClRe(CO)<sub>6</sub> has an i.r. band at 2 045 cm<sup>-1</sup> that is easily resolved from the bands due to Re<sub>2</sub>(CO)<sub>10</sub> at 2 070 and 2 015 cm<sup>-1</sup>. ClRe- $(CO)_4(PPh_3)$  has bands at 2 106 and 1 954 cm<sup>-1</sup> and  $CIRe(CO)_4(PBu_3^n)$  has one at 1 935 cm<sup>-1</sup> that are all also clearly resolvable.