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Reaction Mechanisms of Metal–Metal Bonded Carbonyls; Substitution *via* Homolytic Fission

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Summary Evidence is presented that the substitution by triphenyl phosphite, in decalin or cyclohexane of one triphenylphosphine in the complex $[Mn(CO)_4PPh_3]_2$ occurs *via* initial reversible homolytic fission of the Mn–Mn bond followed by an associative interchange reaction of triphenyl phosphite with the $Mn(CO)_4PPh_3$ radical.

PATHWAYS for substitution reactions of metal–metal bonded carbonyls include simple dissociative and associative paths[1] that are well established for mononuclear carbonyls and their derivatives.[2] However, some reactions of dimetal carbonyls, other than substitution, appear to proceed *via* slow, reversible homolytic fission of the metal–metal bond as the initial step.[3] We report here the first example of a simple substitution that also proceeds by initial homolytic fission.

Reactions of the complex $[\{Mn(CO)_4PPh_3\}_2]$ with triphenyl phosphite in xylene,[4] cyclohexane,[5] or decalin proceed cleanly to form $[Mn_2(CO)_8(PPh_3)P(OPh)_3]$ at 30—50 °C and the rate rises towards a limiting value as $[P(OPh)_3]$ is increased. The limiting rate is identical with the comparable rate of reaction with carbon monoxide over the whole temperature range. The dependence of the initial rate on the initial concentration of complex is shown in Figure 1 for two values of $[P(OPh)_3]$: a higher one that leads to rates very close to the limiting value, and a lower one giving substantially lower rates. The reaction is first order in $[Mn_2(CO)_8(PPh_3)_2]$ at higher $[P(OPh)_3]$ and substantially less than first order at low $[P(OPh)_3]$. This suggests that reversible homolytic fission is important and the following mechanism is in full agreement with all the data. Under all our conditions the reaction goes to completion, and no $[Mn(CO)_4P(OPh)_3]_2$ is formed. In the absence of added

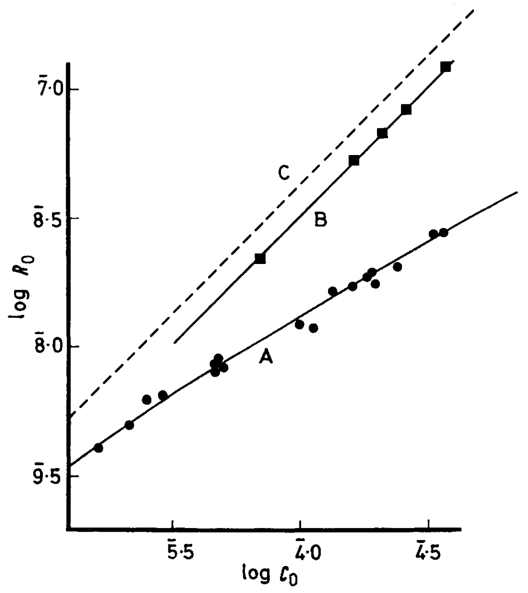

FIGURE 1. Dependence of initial rates on initial concentrations of $[Mn(CO)_4PPh_3]_2$. (A) $[P(OPh)_3] = 0{\cdot}010$M; 39·9 °C. (B) $[P(OPh)_3] = 0{\cdot}19$M; 38·0 °C. (C) Calculated limiting rate at 39·9°C.

$$[Mn_2(CO)_8(PPh_3)_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2[Mn(CO)_4PPh_3] \quad (1)$$

$$[Mn(CO)_4PPh_3] + P(OPh)_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Mn(CO)_4P(OPh)_3] + PPh_3 \quad (2)$$

$$[Mn(CO)_4PPh_3] + [Mn(CO)_4P(OPh)_3] \xrightarrow{k_3} [Mn_2(CO)_8(PPh_3)P(OPh)_3] \qquad (3)$$

triphenylphosphine the reverse of reaction (2) can be neglected and rate equation (4) can easily be derived. R_1 and R_0 are the limiting and observed initial rates,

$$(R_1 - R_0)^{\frac{1}{2}}/R_0 = k_{-1}^{\frac{1}{2}}/k_2[P(OPh)_3] \qquad (4)$$

respectively. Rearrangement to equation (5) leads to a form suitable for graphically deriving k_1 and k_{-1}/k_2^2

$$R_0/C_0 = k_1 - (k_{-1}/k_2^2)(R_0/C_0^{\frac{1}{2}}[P(OPh)_3])^2 \qquad (5)$$

(Figure 2), C_0 being the initial concentration of complex. The intercept of $17{\cdot}6 \times 10^{-4}$ s^{-1} compares with the limiting value $17{\cdot}8 \times 10^{-4}$ s^{-1} of the rate constant at 49·9 °C for reaction with carbon monoxide, and $k_{-1}/k_2^2 = 3{\cdot}47 \times 10^3$ mol l^{-1} s.

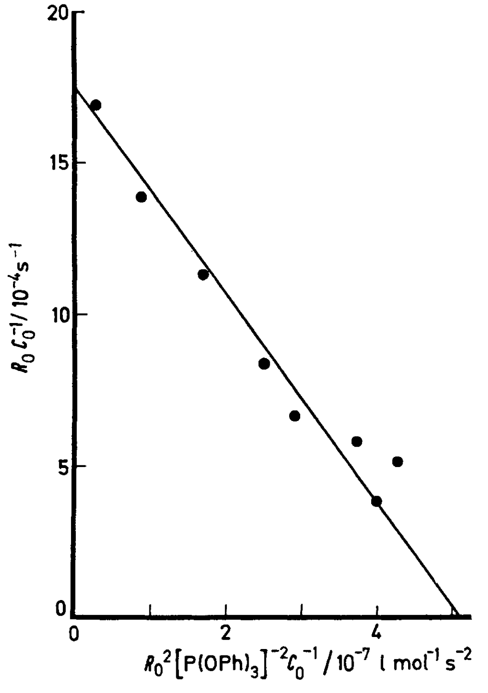

FIGURE 2. Dependence of initial rates at 49·9 °C on $[P(OPh)_3]$. $C_0 = ca.\ 3 \times 10^{-4}$ mol l^{-1}; $[PPh_3]_0 = 0$.

The continuous curve (A) in Figure 1 was calculated using $k_1 = 42{\cdot}4 \times 10^{-5}$ s^{-1} and $k_{-1}/k_2^2 = 1{\cdot}7 \times 10^4$ mol l^{-1} s, appropriate to 39·9 °C.

In the presence of added triphenylphosphine, rate equation (6) applies, where R is the observed initial rate and R_0 is the corresponding initial rate that would obtain in the absence of triphenylphosphine.

$$(R_1 - R)\{1/R - (R_1 - R_0)^{\frac{1}{2}}/(R_1 - R)^{\frac{1}{2}}R_0\} = (k_{-1}k_{-2}/k_2k_3)[PPh_3]/[P(OPh)_3] \qquad (6)$$

This can be estimated from equation (5) by using the values of k_1 and k_{-1}/k_2^2 quoted above. Data obtained at various values of $[PPh_3]$ and $[P(OPh)_3]$ are plotted in Figure 3 according to equation (6). Considering the complexity of the left-hand side of this equation the data agree very well with the predicted linear trend with zero intercept. As well as being correct in their general form the data are therefore in excellent quantitative agreement with the proposed mechanism.

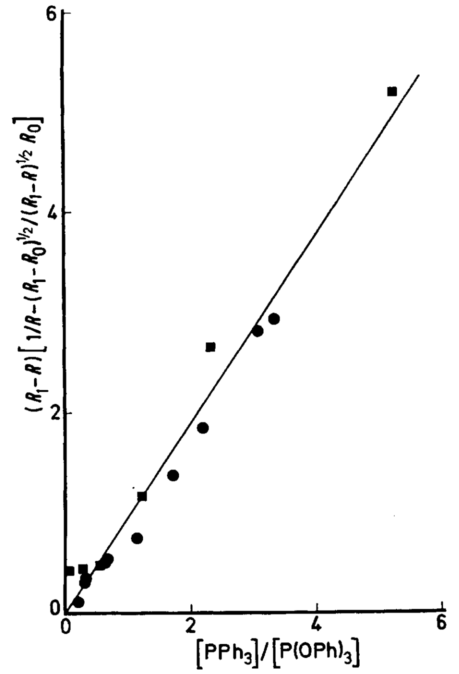

FIGURE 3. Dependence of initial rates at 49·9 °C on $[PPh_3]$ and $[P(OPh)_3]$. ●: $[PPh_3] = 0{\cdot}0312$M and $[P(OPh)_3] = (9{\cdot}24$—$156) \times 10^{-3}$M; ■: $[P(OPh)_3] = 0{\cdot}0180$M and $[PPh_3] = (1{\cdot}28$—$95{\cdot}5) \times 10^{-3}$M. $C_0 = ca.\ 3 \times 10^{-4}$ mol l^{-1}.

It is implicit in the mechanism that the proposed intermediate $[Mn(CO)_4PPh_3]$ must undergo an associative interchange reaction with triphenyl phosphite and, presumably, carbon monoxide. This is not unreasonable since it should be easier to make a 'half-bond' to form a 19-electron transition state rather than to break a complete bond to form the 15-electron intermediate that would be required by a dissociative process. The latter would not be in accord with the data since the rate should always attain the limiting value, independent of $[P(OPh)_3]$, in the absence of free triphenylphosphine. If substitution *via* homolytic fission is at all general it makes more understandable the frequently very close agreement between activation parameters for substitution and for reaction with oxygen.[6]

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