Homolytic Fission and Scrambling Reactions of $Mn_2(CO)_8(PCy_3)_2$ (Cy = cyclohexyl) and $Mn_2(CO)_8(PPh_3)_2$

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The complexes $Mn_2(CO)_8L_2$ (L = PCy_3 and PPh_3) (Cy = cyclohexyl) both react with 1,1,2,2-tetrachloroethane to form $ClMn(CO)_4L$ at rates which conform with initial homolytic fission of the Mn–Mn bond and this mechanistic assignment is confirmed by the occurrence of reaction between the two complexes to form $Mn_2(CO)_8(PCy_3)(PPh_3)$.

The non-occurrence of reaction (1) at 130—140 °C in decalin has recently shown clearly[1] that at least two of the decacarbonyls involved do not undergo reversible homolytic fission as

$$Mn_2(CO)_{10} + Re_2(CO)_{10} \rightleftharpoons 2MnRe(CO)_{10} \qquad (1)$$

expected.[2,3] Scrambling of isotopically labelled $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ at 150 °C only occurs in the absence of CO which confirms that $Re_2(CO)_{10}$ in particular does not undergo reversible homolytic fission under these conditions.[4] Evidence for homolytic fission rested mainly on the decomposition kinetics in the presence of O_2 and it is possible that homolytic fission of these complexes was induced in some way by the reactant, O_2, that was used to scavenge the radicals formed. Excellent evidence for initial homolytic fission in reaction (2) has been reported,[5] the dependence of the rates on [complex], [PPh_3], and [$P(OPh)_3$] being in close agreement with the quite complicated rate equation expected. We now report similar evidence for reaction (3) [L = $P(OEt)_3$] and additional evidence from studies of reactions (4) and (5), all in decalin at 40.0 °C.†

The rate of reaction (3) in the absence of free PCy_3 increases with [$P(OEt)_3$] to a limiting rate and the data fit very well (Figure 1) to equation (6) which is appropriate[5] to the scheme shown in equations (7)—(9) {L = $P(OEt)_3$, C = [$Mn_2(CO)_8(PCy_3)_2$]}. The rate of reaction (4) also follows equation (6),

$$Mn_2(CO)_8(PPh_3)_2 + P(OPh)_3 \rightarrow Mn_2(CO)_8(PPh_3)P(OPh)_3 + PPh_3 \qquad (2)$$

$$Mn_2(CO)_8(PCy_3)_2 + L \rightarrow Mn_2(CO)_8(PCy_3)L + PCy_3 \qquad (3)$$

$$Mn_2(CO)_8(PCy_3)_2 \xrightarrow{C_2H_2Cl_4} 2ClMn(CO)_4(PCy_3) \qquad (4)$$

$$Mn_2(CO)_8(PCy_3)_2 + Mn_2(CO)_8(PPh_3)_2 \rightleftharpoons 2Mn_2(CO)_8(PCy_3)(PPh_3) \qquad (5)$$

Cy = cyclohexyl

with [L] replaced by [$C_2H_2Cl_4$], over a very wide range of C and [$C_2H_2Cl_4$] (Figure 1) in accordance with the scheme shown by equations (7) and (10). Of particular importance is the fact that reactions proceeding at rates much less than the limiting value are not further retarded by free CO or PCy_3. The less-than-limiting rates cannot, therefore, be accounted for by reversal of dissociative loss of CO or PCy_3 from $Mn_2(CO)_8(PCy_3)_2$. The virtual identity of the limiting rate constants of reaction with $P(OEt)_3$ and $C_2H_2Cl_4$ (10^4k = 34.4 and 35.6 s^{-1}, respectively) is in accord with both rates being determined by the same, homolytic fission, process. Reactions with O_2[6] and $C_{16}H_{33}I$‡ also proceed at this limiting rate (10^4k = 34.1 and 33.6 s^{-1}, respectively).

Exactly the same type of kinetic behaviour is shown by the reactions of $Mn_2(CO)_8(PPh_3)_2$ with $C_{16}H_{33}I$‡ and $C_2H_2Cl_4$ at 49.9 °C. The limiting rates of these reactions are identical with those of $Mn_2(CO)_8(PPh_3)_2$ with PBu^n_3, $P(OEt)_3$, and O_2,[6] the average value being 29.1 × 10^4 s^{-1} with a mean deviation of

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† Reactions were carried out using Schlenk-tube techniques and monitored by i.r. spectroscopy. Values of the apparent pseudo-first-order rate constants, k_{obs}, were obtained from initial gradients of plots of $\ln(A_t - A_\infty)$ *vs.* t, A_t and A_∞ being the absorbances of a reactant band at time t and at the end of the reaction, respectively.

‡ Reaction with $C_{16}H_{33}I$ leads to $IMn(CO)_4L$ in a way analogous to equation (4).

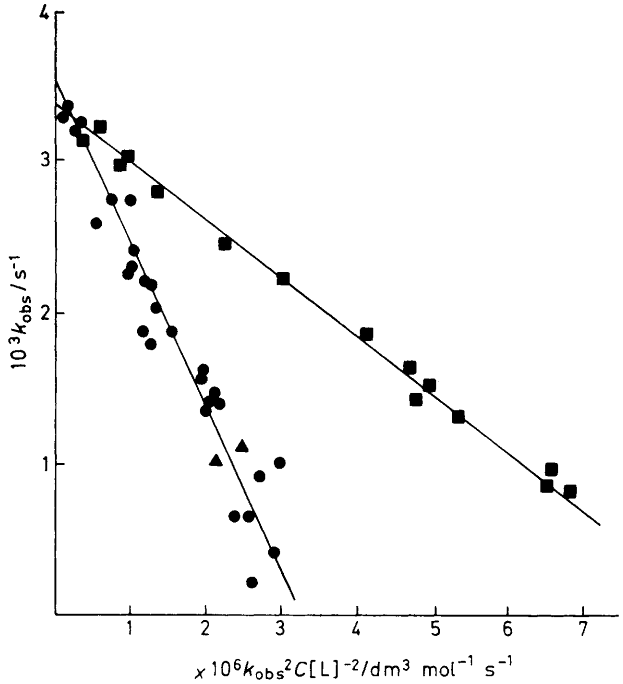

Figure 1. Dependence of k_{obs} on $xk_{obs}^2C/[L]^2$. ●: L = $C_2H_2Cl_4$, $x = 1$, $\sigma(k_{obs}) = 4.4\%$; ▲: L = $C_2H_2Cl_4$, reactions under 1 atm CO in the presence of 0.05 M PCy_3; ■: L = $P(OEt)_3$, $x = 80/3$, $\sigma(k_{obs}) = 2.2\%$. Values of $\sigma(k_{obs})$ were estimated from $100\{\Sigma[(k_{obs} - k_{calc})/k_{calc}]^2/(N-2)]\}^{\frac{1}{2}}$ where N is the number of measurements of k_{obs} and k_{calc} was calculated from equation (6) by using values of the intercepts (k_1) and gradients ($-4k_{-1}/k_2^2$) of the plots.

4%. There is, therefore, extensive kinetic evidence that reactions of both $Mn_2(CO)_8(PCy_3)_2$ and $Mn_2(CO)_8(PPh_3)_2$ with a wide variety of reactants all proceed by initial, reversible, homolytic fission of the Mn–Mn bond.

$$k_{obs} = k_1 - 4(k_{-1}/k_2^2)k_{obs}^2C/[L]^2 \qquad (6)$$

$$Mn_2(CO)_8(PCy_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Mn(CO)_4(PCy_3) \qquad (7)$$

$$Mn(CO)_4(PCy_3) + L \xrightarrow{k_2} Mn(CO)_4L + PCy_3 \qquad (8)$$

$$Mn(CO)_4(PCy_3) + Mn(CO)_4L \xrightarrow{\text{fast}} Mn_2(CO)_8(PCy_3)L \qquad (9)$$

$$Mn(CO)_4PCy_3 \xrightarrow{C_2H_2Cl_4} ClMn(CO)_4(PCy_3) \qquad (10)$$

The occurrence of homolytic fission, even in the absence of such reactants, is confirmed by the fact that reaction (5) proceeds smoothly to give an equilibrium mixture at rates comparable with those of the other reactions.§ Neither the rates nor the products of the scrambling reaction are affected by the presence of 0.01 M PCy_3 or PPh_3. This shows conclusively that scrambling could not have occurred *via* reactions (11)—(14). If such a scheme were operative PCy_3 and PPh_3 would have been present only at very low, steady-state, concentrations. Addition of 0.01 M PPh_3, for instance, would have so increased the concentration of PPh_3 that the only reaction that would have been observed under these conditions would have been (3) (L = PPh_3). This reaction has been studied independently and is very much slower than the scrambling reaction.

$$Mn_2(CO)_8(PCy_3)_2 \rightarrow Mn_2(CO)_8(PCy_3) + PCy_3 \qquad (11)$$

$$Mn_2(CO)_8(PPh_3)_2 \rightarrow Mn_2(CO)_8(PPh_3) + PPh_3 \qquad (12)$$

$$Mn_2(CO)_8(PCy_3) + PPh_3 \rightarrow Mn_2(CO)_8(PCy_3)(PPh_3) \qquad (13)$$

$$Mn_2(CO)_8(PPh_3) + PCy_3 \rightarrow Mn_2(CO)_8(PCy_3)(PPh_3) \qquad (14)$$

There can therefore be little doubt that homolytic fission of both $Mn_2(CO)_8(PCy_3)_2$ and $Mn_2(CO)_8(PPh_3)_2$ occurs even in the absence of reactants such as O_2, alkyl halides, or other P-donor ligands, and that the activation parameters obtained from the limiting rates in their presence must be a good measure of the strengths of the Mn–Mn bonds in the complexes. What does remain a possibility is that the increase in the Mn–Mn bond strength in $Mn_2(CO)_8L_2$ (L = P-donor or CO) as the cone angle of L decreases[7] may result in a change of mechanism for $Mn_2(CO)_{10}$ if the Mn–Mn bond strength then exceeds that of the Mn–CO bond.

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§ I.r. bands due to $Mn_2(CO)_8(PCy_3)_2$ (1 946 cm^{-1}) and $Mn_2(CO)_8(PPh_3)_2$ (1 960 cm^{-1}) decreased steadily in intensity and a band at 1 953 cm^{-1} grew. The last is the main band observed to grow in the reaction of $Mn_2(CO)_8(PPh_3)_2$ with PCy_3 and of $Mn_2(CO)_8(PCy_3)_2$ with PPh_3.