Reactions between Dinuclear Metal Carbonyl Complexes and Alkyl Halides: Formal Oxidative Addition across a Metal–Metal Single Bond

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Photochemical reactions between $[Mn_2(CO)_8(PR_3]_2]$ (R = Et, Bu^n, OEt) and alkyl halides (R′X) proceed to completion in 2 to 4 h yielding equimolar quantities of $[MnR'(CO)_4PR_3]$ and $[MnX(CO)_4PR_3]$, by a route involving reaction of R′X with mononuclear intermediates.

There has been considerable interest in the photochemical reactions of metal–metal bonded dimers of the type $[L_m(OC)_nM\text{-}M(CO)_nL_m]$. Until recently most of these processes were believed to proceed by M–M bond homolysis [equation (1)], the reactions, thus, being those of the 'metal-centred free radicals', $[M(CO)_nL_m]^{\bullet}$.[1b] Of particular interest have been the reactions of such radicals which are believed to involve oxidative addition processes. Thus, complexes such as $[Co(CO)_3(PBu^n_3)]_2$ react with $SnHBu^n_3$ to yield $[Co(SnBu^n_3)(CO)_3(PBu^n_3)]$ and H_2 by a complex mechanism in which the two critical steps are equations (2) and (3).[2] It has also been suggested that the photochemical reaction of $[Mn_2(CO)_8(PR_3)_2]$ (R = Bu, OEt) with HCl yielding $[Mn(H)(CO)_4PR_3]$ and $[MnCl(CO)_4PR_3]$, a reaction which is a *formal* oxidative addition across a metal–metal bond, involves oxidative addition of HCl to the intermediate, $[Mn(CO)_3PR_3]$, giving $[Mn(H)Cl(CO)_4PR_3]$, as the crucial step.[3]

$$[L_m(CO)_nM\text{-}M(CO)_nL_m] \rightleftharpoons 2[M(CO)_nL_m] \qquad (1)$$

$$[M(CO)_nL_m] \rightleftharpoons [M(CO)_{n-1}L_m] + CO \qquad (2)$$

$$M[M(CO)_{n-1}L_m] + SnHBu_3 \rightarrow [M(H)(SnBu_3)(CO)_{n-1}L_m] \qquad (3)$$

$$[L_m(CO)_nM\text{-}M(CO)_nL_m] \rightleftharpoons [L_m(CO)_nM\text{-}M(CO)_{n-1}L_m] + CO \qquad (4)$$

We have been interested in the reactions of dinuclear metal complexes with halogenoalkanes[4] and wished to examine such reactions under photochemical conditions, with the aim of employing the oxidative addition to produce halogeno and alkyl metal complexes. Since commencement of this work, others have reported that there is no evidence for CO dissociation from $[Mn(CO)_5]$, $[Mn(CO)_4PR_3]$, and $[Mn(CO)_3(PR_3)_2]$,[1a,5,6] and furthermore, there is now sound evidence that CO dissociation from metal carbonyl dimers [equation (4)] is a primary photoprocess which is able to compete effectively with metal–metal bond homolysis.[5,6] It is also noteworthy that in the case of $[Mn_2(CO)_{10}]$, the rate constant for the recombination reaction of equation (1) is approximately 10^3 times that of the recombination reaction of equation (4).[6]

We have now examined photochemical reactions between $Ph(CH_2)_nCl$ (n = 1,2) and $[Mn_2(CO)_8(PR_3)_2]$ (R = Et, Bu^n, OEt; 150 W mercury discharge lamp; hexane solution) and have observed the formation of equimolar amounts of $[MnCl(CO)_4PR_3]$ and $[Mn\{(CH_2)_nPh\}(CO)_4PR_3]$ as the only products† in reactions that proceed cleanly to completion in 2.5 h (R = Et) to 4.0 h (R = Bu^n). Similar reactions with $[Mn_2(CO)_8(PPh_3)_2]$ also yield products of this type, but are much slower, not having reached completion in 35 h. The reactions were monitored by following changes in i.r. spectra in the metal carbonyl region, the halogeno and alkyl metal complexes being produced at equal rates. When comparable reactions were performed under an atmosphere of CO, both products were again formed at identical, but reduced rates.

These findings contrast with the recently reported flash photogeneration of $[Mn(CO)_4PR_3]$ in the presence of halogeno- and polyhalogeno-alkenes which led to the observation of $[MnX(CO)_4PR_3]$ only.[7] However, we have found that observation of both halogeno and alkyl metal complexes is very dependent on the reaction system. Thus, while both products are observed in reactions involving $[Mn_2(CO)_8(PR_3)_2]$ and $Ph(CH_2)_nCl$ (n = 1, 2), reactions with $PhCH_2Br$ yield only $[MnBr(CO)_4PR_3]$. However, in separate experiments we have found that $[Mn(CH_2Ph)(CO)_4PBu^n_3]$ undergoes a rapid photochemical reaction with $PhCH_2Br$ leading to $[MnBr(CO)_4PBu^n_3]$, whereas no reaction is observed with $PhCH_2Cl$. We have also confirmed the findings of Brown and co-workers,[7] who observed that reactions of CCl_4 with $[Mn_2(CO)_8L_2]$ (L = CO, PBu^n_3) lead only to $[MnCl(CO)_4L]$, however, we have found both of these reactions to be inhibited by CO. Furthermore, we have observed that reactions between $[Mo_2(CO)_6(\eta\text{-}cp)_2]$, $[Fe_2(CO)_4(\eta\text{-}cp)_2]$, and $[Co_2(CO)_6(PBu^n_3)_2]$ and $PhCH_2X$ (X = Cl, Br) give only halogeno complexes together with dibenzyl (cp = cyclopentadienyl).

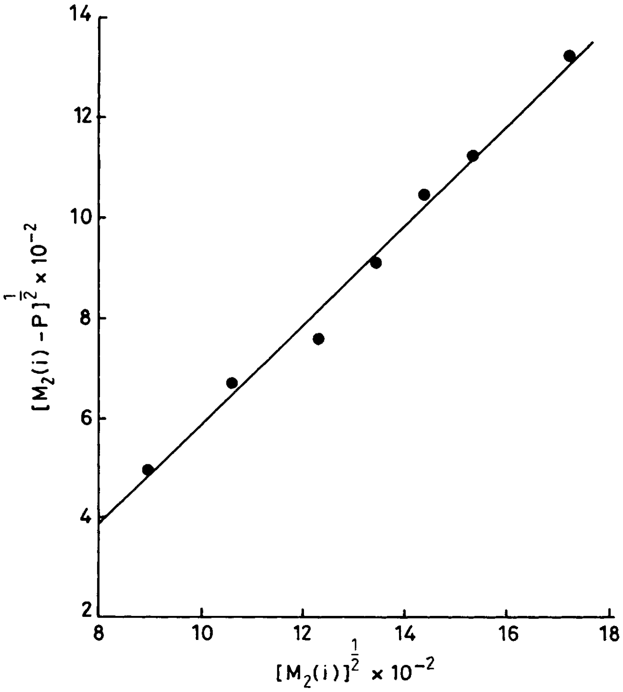

Figure 1. Plot of $[M_2(i)]^{\frac{1}{2}}$ *vs.* $[M_2(i) - P]^{\frac{1}{2}}$.

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† Prolonged irradiation leads to the further production of small quantities of *mer*-$[MnCl(CO)_3(PR_3)_2]$.

$$[Mn_2(CO)_8(PR_3)_2] \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} 2[Mn(CO)_4(PR_3)]$$

$$[Mn(CO)_4PR_3] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Mn(CO)_3PR_3] + CO$$

$$[Mn(CO)_3PR_3] + R'X \xrightarrow{k_3} [Mn(R')X(CO)_3PR_3]$$

$$[Mn(R')X(CO)_3PR_3] + [Mn(CO)_4PR_3] \xrightarrow{k_4} [MnR'(CO)_3PR_3] + [MnX(CO)_4PR_3]$$

$$[MnR'(CO)_3PR_3] + CO \xrightarrow{k_5} [MnR'(CO)_4PR_3]$$

Scheme 1

$$[Mn_2(CO)_8(PR_3)_2] \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} 2[Mn(CO)_4PR_3]$$

$$[Mn(CO)_4PR_3] + R'X \xrightarrow{k_2} [Mn(CO)_4PR_3]^+ + R'X^{\bullet -}$$

$$R'X^{\bullet -} \xrightarrow{k_3} R'^{\bullet} + X^-$$

$$[Mn(CO)_4PR_3]^+ + X^- \xrightarrow{k_4} [MnX(CO)_4PR_3]$$

$$[Mn(CO)_4PR_3] + R'^{\bullet} \xrightarrow{k_5} [MnR'(CO)_4PR_3]$$

Scheme 2

In order to probe the mechanism of these reactions in more detail, we have carried out a kinetic study of the reaction between $[Mn_2(CO)_8(PBu^n_3)_2]$ and $PhCH_2Cl$, employing a thermostated merry-go-round photoreactor.‡ Figure 1 shows the reaction rate to be proportional to $\{[Mn_2(CO)_8(PBu^n_3)_2]\}^{\frac{1}{2}}$,§ a finding that suggests metal–metal bond scission is an important feature of the reaction. It has not been possible to measure the reaction order with respect to $PhCH_2Cl$, as the balance between solubility limitations and measurable reaction rates makes it impossible to obtain pseudo-first order conditions $\{[Mn_2(CO)_8(PBu^n_3)_2] \geqslant 10[PhCH_2Cl]\}$.

Mechanisms consistent with the experimental findings are shown in Schemes 1—3. In view of the facts that $[Mn(CO)_4PR_3]$ has been found not to undergo CO dissociation[1a] but that all the reactions of $[Mn_2(CO)_8L_2]$ (L = CO, PR_3) with halogenoalkanes reported here are inhibited by CO, we do not favour the mechanism shown in Scheme 1. The mechanism shown in Scheme 2 does not require a CO dissociation step and thus should not strictly be subject to inhibition by added CO. However, the 16-electron intermediate, $[Mn(CO)_4PR_3]^+$ would probably be susceptible to capture by CO leading to the known stable cation, $[Mn(CO)_5PR_3]^+$, thereby inhibiting the reaction. If this were the case, it might be expected that i.r. absorptions arising from the 18-electron cation[8a] would be observed and that the rate of production of the halogeno complex would be retarded, while that of the alkyl complex is unaffected. Neither of these phenomena is observed.

$$[Mn_2(CO)_8(PR_3)_2] \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} [Mn_2(CO)_7(PR_3)_2] + CO$$

$$[Mn_2(CO)_7(PR_3)_2] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Mn(CO)_3PR_3] + [Mn(CO)_4PR_3]$$

$$[Mn(CO)_3PR_3] + R'X \xrightarrow{k_3} [Mn(R')X(CO)_3PR_3]$$

$$[Mn(R')X(CO)_3PR_3] + [Mn(CO)_4PR_3] \xrightarrow{k_4} [MnR'(CO)_3PR_3] + [MnX(CO)_4PR_3]$$

$$[MnR'(CO)_3PR_3] + CO \xrightarrow{k_5} [MnR'(CO)_4PR_3]$$

Scheme 3

We, therefore, favour the mechanism shown in Scheme 3. This is in accord with the experimental findings and the relative recombination rates of equations (1) and (4). As yet, we have no direct evidence for the third step, the oxidative addition of R'X to $[Mn(CO)_3PR_3]$, but believe it is a reasonable postulate in view of the fact that such a species would almost certainly have three unpaired electrons, thereby displaying an electronic configuration analogous to $[V(\eta\text{-}cp)_2]$. Vanadocene has been shown to react with alkyl halides to produce $[VR(\eta\text{-}cp)_2]$ and $[VX(\eta\text{-}cp)_2]$ by a mechanism involving formation of $[V(R)X(\eta\text{-}cp)_2]$.[8b]

Thus, although the reaction discussed above could be viewed as a *formal* oxidation addition across a metal–metal single bond, the reaction proceeds by interaction between the alkyl halide and mononuclear intermediates.

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‡ The reaction rate was measured by monitoring the production of $[MnCl(CO)_4(PBu^n_3)]$ by means of i.r. spectroscopy. The results obtained in this way display greater accuracy since the enhanced stability of this compound, compared to the benzyl analogue, allows its isolation in a higher state of purity. This, together with its higher stability leads to more accurate measurement of molar absorptivities of the CO stretching frequencies. However, monitoring the rate of production of $[Mn(CH_2Ph)(CO)_4(PBu^n_3)]$ gives essentially the same results.

§ The merry-go-round reactor enables product concentrations to be measured in a series of solutions containing different concentrations of starting material, but all irradiated for the same period of time. The rate expression is thus integrated to give an expression relating initial reactant concentration to product concentration. In this case this leads to the expression $[M_2(i)]^{\frac{1}{2}} - kt = [M_2(i) - P]^{\frac{1}{2}}$ where $M_2(i)$ is the initial concentration of metal dimer and P is the concentration of product at time, *t*. It is this relationship which is plotted in Figure 1.

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