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Thermal reactions between $[Mn_2(CO)_8(PBu_3)_2]$ and alkyl halides; evidence for an outer-sphere electron transfer process

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Abstract

Thermal reactions between $[Mn_2(CO)_8(PBu_3)_2]$ and some alkyl halides (RX) yield both $[MnR(CO)_4PBu_3]$ and $[MnX(CO)_4PBu_3]$. Kinetic and other studies suggest that the reactions proceed by an outer-sphere electron transfer mechanism. Thus, these thermal reactions follow a different mechanistic pathway from that followed under photochemical conditions.

We have previously reported on the photochemical reactions of $[Mn_2(CO)_8L_2]$ (L = CO, PBu_3, PEt_3, $P(OPh)_3$, PPh_3) and alkyl halides (RX) which yield the alkyl and halo complexes, $[MnR(CO)_4L]$ and $[MnX(CO)_4L]$, in equimolar quantities. Kinetic and quantum yield studies of the reaction between $[Mn_2(CO)_8(PBu_3)_2]$ * and $PhCH_2Cl$ indicated that the reaction proceeds by a radical chain pathway involving CO dissociation from the dinuclear complex and metal–metal bond homolysis of the coordinatively unsaturated dinuclear intermediate (Scheme 1) [1].

$$Mn_2(CO)_8L_2 \rightleftharpoons Mn_2(CO)_7L_2 + CO$$

$$Mn_2(CO)_7L_2 \rightleftharpoons Mn(CO)_3L^{\cdot} + Mn(CO)_4L^{\cdot}$$

$$Mn(CO)_3L^{\cdot} + RX \longrightarrow MnX(CO)_3L + R^{\cdot}$$

$$R^{\cdot} + Mn_2(CO)_7L_2 \longrightarrow MnR(CO)_4L + Mn(CO)_3L^{\cdot}$$

$$MnX(CO)_3L + CO \longrightarrow MnX(CO)_4L$$

$$Mn(CO)_3L^{\cdot} + CO \longrightarrow Mn(CO)_4L^{\cdot}$$

Scheme 1

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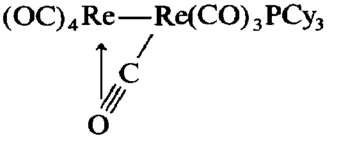
* Throughout this paper PBu_3 refers to tri-n-butylphosphine.

We now present a study of the reactions between $[Mn_2(CO)_8(PBu_3)_2]$ (I) and alkyl halides carried under thermal conditions.

Poë et al. [2] have previously studied the reactions of $[Mn_2(CO)_8(PPh_3)_2]$ with $C_2H_2Cl_4$ and $C_{16}H_{33}I$ and $[Re_2(CO)_8(PCy_3)_2]$ (Cy = cyclohexyl) with $C_{16}H_{33}I$. In the case of the manganese dimer, mechanisms involving rate determining homolysis of the metal–metal bond or ligand dissociation were excluded, and it was proposed that the reaction of the alkyl halide was with a reactive isomer of the dimer, possible $[Ph_3P(OC)_4Mn(\mu\text{-}CO)Mn(CO)_3PPh_3]$ [2]. The reaction of the dirhenium complex was reported to involve three pathways. The major one, accounting for 93% of the total rate, involves PCy_3 dissociation. One minor process (5% of the rate) involves CO dissociation and the details of the other could not be established. It was suggested that the intermediate involved in the major pathway could adopt either of the structures II or III [3].



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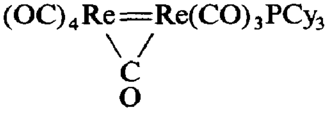


(III)

Results and discussion

All reactions were carried out in water-jacketed reactors, ensuring good temperature control. The reactors were wrapped in black tape to exclude light. The reaction between I and $PhCH_2Cl$ at 40 ° C was clean, yielding $[MnCH_2Ph(CO)_4PBu_3]$ (IV) and $[MnCl(CO)_4PBu_3]$ (V) in equimolar quantities. IV and V were characterised by spectroscopic means, as reported in our earlier paper [1]. Theses results parallel those observed for the corresponding photochemical reaction, the mechanism of which is shown in Scheme 1.

In attempting to establish the mechanism of the thermal reaction, we carried out a kinetic study in order to determine the reaction orders with respect to both I and $PhCH_2Cl$. The order with respect to I was determined by measuring the rate of change of the infrared absorption of I at 1975 cm^{-1} and applying the initial rate treatment to the data obtained. The plot of initial rate versus concentration of I is shown in Fig. 1 (correlation coefficient, 0.990). Similar plots of initial rate versus either $[I]^{1/2}$ or $[I]^2$ did not yield good straight lines. Thus, in contrast to the photochemical reaction, the present reaction is first order in metal dimer. Furthermore, unlike that of the photochemical reaction, the rate in the presence of CO was not reduced, but was found to be slightly higher than that under nitrogen. This rate enhancement was accompanied by formation of $[Mn_2(CO)_9(PBu_3)]$. These results indicate that neither metal–metal bond cleavage or CO dissociation is involved in the rate determining step.

Attempts to ascertain whether phosphine dissociation from I was occurring, by measuring the reaction rate in the presence of excess PBu_3, were unsuccessful. Poë et al. observed no inhibition of the reaction between $[Mn_2(CO)_8(PPh_3)_2]$ and alkyl halides in the presence of PPh_3 [2], but found that the reaction between $[Re_2(CO)_8(PCy_3)_2]$ and $C_{16}H_{33}I$ was retarded by PCy_3. However, they did not

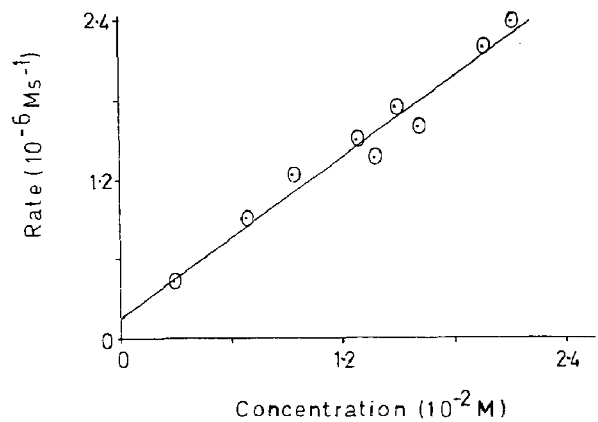


Fig. 1. Plot of initial reaction rate versus concentration of $[Mn_2(CO)_8(PBu_3)_2]$.

discuss the nature of the products from the reaction of the rhenium dimer in the presence of an excess of PCy_3. Infrared spectra of the reaction between I and $PhCH_2Cl$ in the presence of excess PBu_3, under either N_2 or CO, showed *mer*-$[MnCl(CO)_3(PBu_3)_2]$ to be the only halogeno-product (ν(CO), 2020 (w), 1942 (vs), 1897 (s) cm^{-1}), there being no evidence for V or *fac*-$[MnCl(CO)_3(PBu_3)_2]$. Both IV and *mer*-$[MnCH_2Ph(CO)_3(PBu_3)_2]$ (ν(CO), 2007 (w), 1919 (vs), 1895 (s) cm^{-1}) were also observed. in order to investigate whether *mer*-$[MnCl(CO)_3(PBu_3)_2]$ was formed from V, a further reaction was performed. Thus, I was allowed to react to completion with $PhCH_2Cl$, to yield a mixture of IV, V and the excess of $PhCH_2Cl$. PBu_3 was then added, and the mixture heated further. V reacted with the phosphine to yield *fac*-$[MnCl(CO)_3(PBu_3)_2]$ within 15 min. This then slowly isomerised to the *mer*-complex during 2 h. During that time, IV reacted slowly with PBu_3 to yield *mer*-$[MnCH_2Ph(CO)_3(PBu_3)_2]$. Comparison of the reaction of I with $PhCH_2Cl$ in the presence of excess PBu_3 with that between I and $PhCH_2Cl$ followed by the addition of PBu_3 shows that if V had been formed in the first reaction and then subsequently reacted with PBu_3, *fac*-$[MnCl(CO)_3(PBu_3)_2]$ should have been observed prior to the appearance of the *mer*-isomer.

Clearly, the presence of an excess of PBu_3 alters the course of the reaction, probably by substitution of I to yield either $[Mn_2(CO)_7(PBu_3)_3]$ or $[Mn_2(CO)_6(PBu_3)_4]$, which subsequently react with $PhCH_2Cl$. A separate reaction between I and PBu_3 proceeded slowly to give *mer*-$[MnH(CO)_3(PBu_3)_2]$. Such reactions have previously been reported to proceed via formation of tri- and tetra-substituted metal carbonyl dimers [4]. Furthermore, we also examined the reaction between *mer*-$[MnH(CO)_3(PBu_3)_2]$ and $PhCH_2Cl$ and observed formation of both *mer*-$[MnCl(CO)_3(PBu_3)_2]$ and low concentrations of *mer*-$[MnCH_2Ph(CO)_3(PBu_3)_2]$. In view of the above findings, we can draw no direct conclusions for reactions of I with $PhCH_2Cl$ in the presence of excess PBu_3 in respect of a step involving dissociation of the phosphine ligand.

The order with respect to $PhCH_2Cl$ was determined by monitoring the decrease in the concentration of the chloride by GLC involving use of electron capture detection (ECD). This method was employed since the sensitivity of ECD allows use of the isolation method, in which the concentration of I is very high relative to that of $PhCH_2Cl$. (This requires very low concentrations of $PhCH_2Cl$ because of the

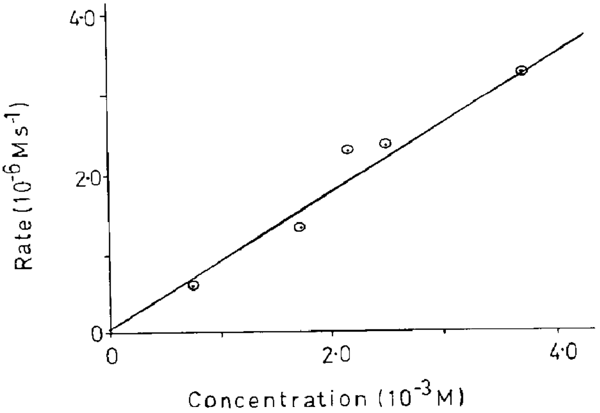


Fig. 2. Plot of initial reaction rate versus concentration of $PhCH_2Cl$.

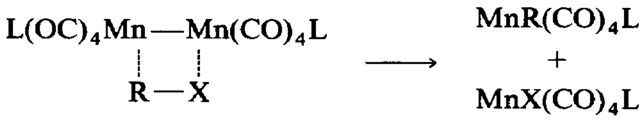
limited solubility of I.) The quality of the data was not as good as that obtained from the study of the variation of [I], but a first order dependence on [$PhCH_2Cl$] is indicated (Fig. 2, correlation coefficient, 0.981).

The observed rate equation is thus of the form shown in. 1. The mechanism of the thermal reaction is, therefore, different from that of the photochemical process (Scheme 1, rate expression: Eq. 2). The reaction kinetics also rule out all but one of the mechanisms considered for the photochemical reaction in our earlier paper [1]. Mechanisms in agreement with the observed kinetics are considered below.

$$\text{Rate} = k_{\text{obs}}[\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2][\text{PhCH}_2\text{Cl}] \tag{1}$$

$$\text{Rate} = \frac{k[\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2]^{1/2}[\text{PHCH}_2\text{Cl}]}{[\text{CO}]^{1/2}} \tag{2}$$

A concerted reaction proceeding by a four-membered transition state may be considered, and this is shown in Scheme 2. An atom abstraction or inner-sphere electron transfer mechanism is shown in Scheme 3, and an outer-sphere electron transfer sequence is shown in Scheme 4. Schemes 3 and 4 both involve the



$$\begin{array}{c}\text{L(OC)}_4\text{Mn—Mn(CO)}_4\text{L}\\ \vdots \quad \vdots\\ \text{R—X}\end{array} \longrightarrow \begin{array}{c}\text{MnR(CO)}_4\text{L}\\ +\\ \text{MnX(CO)}_4\text{L}\end{array}$$

Scheme 2

$$\text{Mn}_2(\text{CO})_8\text{L}_2 + \text{RX} \longrightarrow \text{MnCl(CO)}_4\text{L} + \text{Mn(CO)}_4\text{L}^{\cdot} + \text{R}^{\cdot}$$

$$\text{Mn(CO)}_4\text{L}^{\cdot} + \text{R}^{\cdot} \longrightarrow \text{MnR(CO)}_4\text{L}$$

$$2\text{R}^{\cdot} \longrightarrow \text{R}_2$$

$$2\text{Mn(CO)}_4\text{L}^{\cdot} \longrightarrow \text{Mn}_2(\text{CO})_8\text{L}_2$$

Scheme 3

$$Mn_2(CO)_8L_2 + RX \longrightarrow Mn_2(CO)_8L_2^{\cdot+} + RX^{\cdot-}$$

$$RX^{\cdot-} \longrightarrow R^{\cdot} + X^{-}$$

$$Mn_2(CO)_8L_2^{\cdot+} + X^{-} \longrightarrow MnX(CO)_4L + Mn(CO)_4L^{\cdot}$$

$$Mn(CO)_4L^{\cdot} + R^{\cdot} \longrightarrow MnR(CO)_4L$$

$$2R^{\cdot} \longrightarrow R_2$$

$$2Mn(CO)_4L^{\cdot} \longrightarrow Mn_2(CO)_8L_2$$

Scheme 4

production of alkyl radicals, whereas this is not the case for Scheme 1. In order to test for alkyl radical formation, the reaction between I and 6-bromohex-1-ene was investigated. Reactions of this halide have previously been used to indicate the intermediacy of alkyl radical formation, since the hexenyl radical is known to cyclise rapidly to the cyclopentylmethyl radical [5,6,7]. Thus, identification of the alkyl complex formed in this reaction should allow differentiation between radical and non-radical processes. The reaction between I and 6-bromohex-1-ene resulted in two products, [$MnBr(CO)_4PBu_3$] (ν(CO), 2080 (m), 2019 (ms), 2000 (s), 1949 (vs) cm^{-1}) and a complex whose infrared spectrum (ν(CO), 2045 (mw), 1973 (m), 1958 (s), 1932 (s) cm^{-1}) is very similar to that of [$MnCH_2Ph(CO)_4PBu_3$]. The latter was unstable in the presence of an excess of 6-bromohex-1-ene, a finding similar to that observed previously for [$MnCH_2Ph(CO)_4PBu_3$] in the presence of $PhCH_2Br$ [1]. However, reduction of the amount of 6-bromohex-1-ene used in the reaction allowed the complex sufficient lifetime for removal of the solvent and the reactant halide from the reaction mixture, and this was followed by chromatography and ^{13}C NMR studies of the product. The difficulty in handling and purifying the products of this reaction meant that the spectrum obtained (Fig. 3) was not of high quality. The intense high field peaks arise from PBu_3 ligands of [$MnBr(CO)_4PBu_3$] and the alkyl complex. However, other peaks were clearly visible in this region which can be assigned to a coordinated alkyl group. No peaks were observed in the alkenyl region

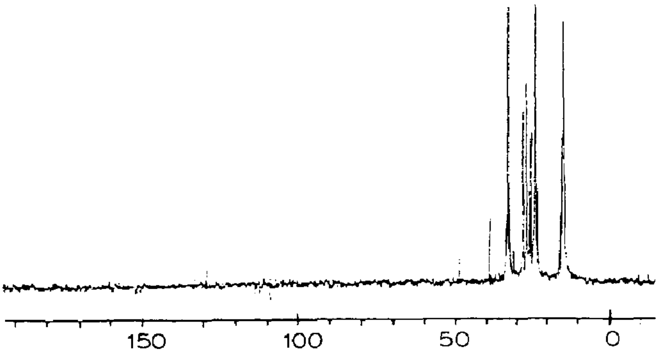


Fig. 3. ^{13}C NMR spectrum of the product of the reaction between [$Mn(CO)_8(PBu_3)_2$] and $CH_2{=}CH(CH_2)_4Cl$.

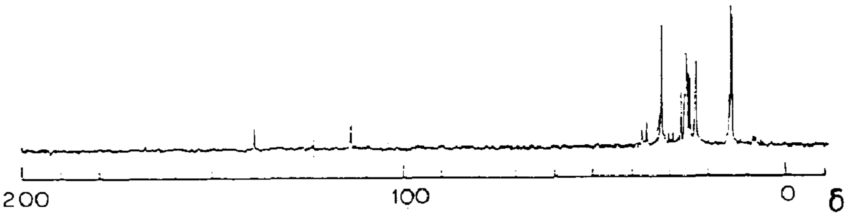


Fig. 4. ^{13}C NMR spectrum of $[Mn\{(CH_2)_4CH{=}CH_2\}(CO)_4PBu_3]$.

indicating that this ligand was not $CH_2{=}CH(CH_2)_4$. This was confirmed by comparing the spectrum with those of authentic samples of $[Mn\{(CH_2)_4CH{=}CH_2\}$-$(CO)_4PBu_3]$ and $[Mn\{CH_2(\overline{CHCH_2CH_2CH_2CH_2})\}(CO)_4PBu_3]$ (Figs. 4 and 5). Although the strong PBu_3 absorptions overlay some of the alkyl peaks in Fig. 3, signals at δ 25.5, 27.1, 28.3, 38.9 and 49.7 are identical to those from the cyclopentylmethyl complex. We also observed that the hexenyl complex was not converted into the cyclopentylmethyl complex when maintained at the temperature of the reaction between I and 6-bromohex-1-ene (40 °C). The initial rate of the reaction (2.5×10^{-6} *M* s^{-1}) between $[Mn_2(CO)_8(PBu_3)_2]$ and $CH_2{=}CH(CH_2)_4Cl$ was very similar to that observed for other alkyl halides (vide infra). Therefore, on the basis of the study of the 6-bromohex-1-ene reaction, we do not favour the non-radical, concerted process (Scheme 2).

In an attempt to differentiate between the inner-sphere atom abstraction and out-sphere electron transfer mechanisms, we studied the relative rates of reaction of I with the series of alkyl halides, $PhCH_2X$ (X = Cl, BrI), n-$C_6H_{13}X$ (X = Br, I) and *para*-$YC_6H_4CH_2Br$ (Y = NO_2, Br, CN, Me). This approach was used previously by Halpern and co-workers in studies of the reactions of a range of Co^{II} complexes with alkyl halides [8–10]. They found that outer-sphere electron transfer reactions have relative rate ratios, k_{RI}/k_{RBr} and k_{RBr}/k_{RCl} of less than 10. Inner-sphere atom transfer reactions have much larger rate ratios, typically of the order of 10^2–10^3.

The initial rates of reaction between I and the alkyl halides are given in Table 1. For the benzyl halides (BzX), the rate ratio k_{BzI}/k_{BzBr} is 1.8 and k_{BzBr}/k_{BzCl} is 2.2. For the n-hexyl halides (HxX), the ratio k_{HxI}/k_{HxBr} is 1.1. These results are in accord with a reaction proceeding by outer-sphere electron transfer. The relative rates observed for the *para*-substituted benzyl bromides indicate that the reaction is

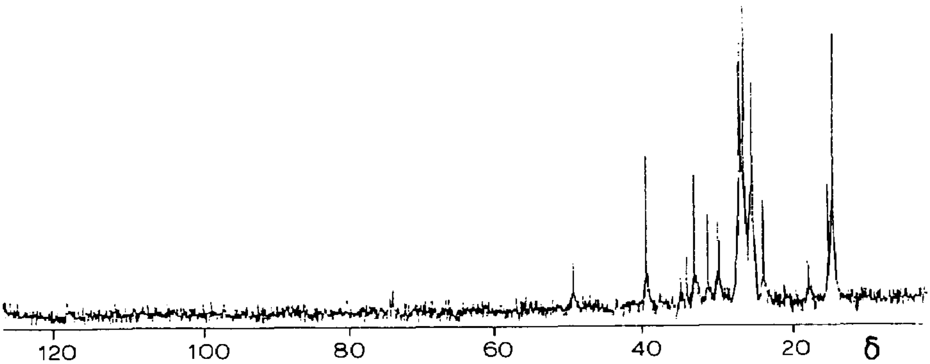


Fig. 5. ^{13}C NMR spectrum of $[Mn\{CH_2(CHCH_2CH_2CH_2CH_2)\}(CO)_4PBu_3]$.

Table 1

Rates of reactions between $[Mn_2(CO)_8(PBu_3)_2]$ and some alkyl halides

Alkyl halide	Rate (M s^{-1})	Alkyl halide	Rate (M s^{-1})
$PhCH_2Cl$	1.61×10^{-6}	p-$NO_2C_6H_4CH_2Br$	4.64×10^{-6}
$PhCH_2Br$	3.52×10^{-6}	p-$CNC_6H_4CH_2Br$	3.73×10^{-6}
$PhCH_2I$	6.31×10^{-6}	p-$BrC_6H_4CH_2Br$	3.35×10^{-6}
n-$C_6H_{13}Br$	2.8×10^{-6}	p-$MeC_6H_4CH_2Br$	2.99×10^{-6}
n-$C_6H_{13}I$	2.9×10^{-6}		

accelerated by electron-withdrawing substituents on the aromatic ring. This is also in accord with previous studies of electron transfer reactions [10].

We therefore favour an electron transfer mechanism (Scheme 4) for the thermal reaction of alkyl halides with $[Mn_2(CO)_8(PBu_3)_2]$, a mechanism which is in accordance with that proposed for similar thermal reactions of $[Mn_2(CO)_8(PPh)_2]$ [2] but contrasts with mechanisms observed for the photochemical reactions [1]. The latter are presumably initiated by photochemical cleavages of the Mn–CO and Mn–Mn bonds, processes not available in mild thermal reactions. Accordingly, the photochemical reactions are at least one hundred times faster than those reported here.

Experimental

All reactions were performed under dry deoxygenated nitrogen or, where appropriate, carbon monoxide, Solvents were purified by standard techniques and stored over sodium. Tri-n-butylphosphine was vacuum distilled immediately prior to use. Alkyl halides were distilled from $LiAlH_4$ and stored under vacuum.

Infrared spectra were recorded on a Perkin Elmer 782 spectrometer equipped with a 6300 data station. Nmr spectra were recorded on a Bruker WP80 FT spectrometer.

$[Mn_2(CO)_8(PBu_3)_2]$, $[MnX(CO)_4PBu_3]$ (X = Cl, Br, I) and $[MnCH_2Ph(CO)_4PBu_3]$ were prepared by the methods previously indicated [1]. Cyclopentyl bromomethane was prepared by the literature method [11]. The molar absorbtivities in hexane of $[MnX(CO)_4PBu_3]$ (X = Cl, Br, I) were: 995 (2087 cm^{-1} band), 983 (2080 cm^{-1} band), and 1630 M^{-1} cm^{-1} (2075 cm^{-1} band), respectively.

Reactions between $[Mn_2(CO)_8(PBu_3)_2]$ and alkyl halides

These were carried out in a water-jacketed reactor at 40 °C. The reactor was covered with black tape to exclude light. The same general method was used for all reactions. $[Mn_2(CO)_8(PBu_3)_2]$ was weighed and placed in the reactor, which was then degassed. Degassed hexane was added from a syringe and the solution allowed to equilibrate for 1 hour. The other reagent was then added from a syringe and the reaction commenced. The progress of the reaction was monitored by infrared spectroscopy, except in the case of the determination of the order with respect to benzyl chloride for which electron capture gas chromatography was employed. The sampling intervals were determined by the rate of the reaction in question.

Preparation of $cis[Mn\{CH_2(\overline{CHCH_2CH_2CH_2CH_2})\}(CO)_4PBu_3]$

$[Mn_2(CO)_8(PBu_3)_2]$ (0.601 g, 8.14×10^{-4} mol) was placed in a two necked round-bottomed flask fitted with a reflux condenser and a suba-seal. THF (30 ml) was added and the solution was degassed. $K[B(CHCH_3(C_2H_5))\}_3H]$ (2.5 ml of a 1.0 *M* solution in THF, 2.5×10^{-3} mol) was then added from a syringe. The resulting solution was refluxed for 11 h, after which infrared spectroscopy indicated that the dimer had been completely consumed. The solution, containing $K[Mn(CO)_4PBu_3]$, was allowed to cool and $BrCH_2\overline{CHCH_2CH_2CH_2CH_2}$ (0.39 g, 2.4×10^{-3} mol) in THF (8 ml) was added. (The use of excess halide allows for its consumption by reaction with any remaining potassium selectride.) The solution was then heated gently on a water bath until all peaks due to the carbonyl anion had disappeared from its infrared spectrum, and was then filtered through a long plug of basic alumina and the solvent removed under vacuum to leave an oil. This was then chromatographed under nitrogen on a column of dried degassed basic alumina using hexane, toluene, and THF as eluants. The product was a yellow oil.

Analysis: Found: C, 58.05; H, 8.81; P, 6.47. $MnC_{22}H_{38}PO_4$ calcd.: C, 58.41; H, 8.41; P, 6.85%. Infrared spectrum ν(CO), 2045 (m), 1973 (m-s), 1958 (vs), 1932 (s) cm^{-1} (hexane). Mass spectrum: m/z 452 (M^+). ^{13}C NMR spectrum: Fig. 5.

Preparation of $[Mn\{(CH_2)_4CH{=}CH_2\}(CO)_4PBu_3]$

$[Mn_2(CO)_8(PBu_3)_2]$ (0.58 g, 7.85×10^{-4} mol) in THF (15 ml) was stirred over sodium amalgam (Na (0.1 g) in Hg (1.2 ml)) for 1 h. The solution was left to stand for 15 min then carefully removed from the amalgam by canula and filtered through a Celite plug under nitrogen. 6-Bromohex-1-ene (0.21 ml, 1.57×10^{-3} mol) was added and the solution was stirred at room temperature for 20 h. The solution was then again filtered through Celite and the solvent removed under vacuum to leave an orange oil. This was purified by column chromatography on dried basic alumina. The product was somewhat unstable, and could not be completely freed from PBu_3.

Infrared spectrum: ν(CO), 2048 (m), 1975 (m-s), 1958 (vs), 1933 (s) cm^{-1} (hexane). ^{13}C NMR spectrum: Fig. 4.

The reaction of $[Mn(CO)_8(PBu_3)_2]$ *with 6-bromohex-1-ene*

The general method described above for this type of reaction was employed. The product mixture was subjected to column chromatography under nitrogen on dried degassed basic alumina. Hexane eluted a mixture of $[Mn_2(CO)_8(PBu_3)_2]$ and $[Mn(C_6H_{11})(CO)_4(PBu_3)]$. Hexane-THF eluted a mixture of $[Mn(C_6H_{11})(CO)_4PBu_3]$ and $[MnBr(CO)_4PBu_3]$, which could not be further separated. This second fraction was examined by ^{13}C NMR spectroscopy.

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References

1 M.A. Biddulph, R. Davis and F.I.C. Wilson, J. Organomet. Chem., 387 (1990) 357.
2 A.J. Poë and C.V. Sekhar, J. Am. Chem. Soc., 107 (1985) 4874.
3 A.J. Poë, C.N. Sampson and C.V. Sekhar, Inorg. Chem., 26 (1987) 1057.

4 D.J. Cox and R. Davis, J. Organomet. Chem., 186 (1980) 347 and refs. therein.
5 A. Bakac and J.H. Espenson, J. Am. Chem. Soc., 108 (1986) 713.
6 M.S. Ram, A. Bakac and J.H. Espenson, Inorg. Chem., 25 (1986) 3267.
7 D.J. Pasto, D.A. Timmers and N.Z. Huang, Inorg. Chem., 23 (1984) 4117.
8 L.G. Marzilli, P.A. Marzilli and J. Halpern, J. Am. Chem. Soc., 92 (1970) 5752.
9 L.G. Marzilli, P.A. Marzilli and J. Halpern, J. Am. Chem. Soc., 93 (1971) 1734.
10 J. Halpern and P.F. Phelan, J. Am. Chem. Soc., 94 (1972) 1881.
11 G.A. Wiley, R.L. Hershkowitz, B.M. Rein and B.C. Chung, J. Am. Chem. Soc., 86 (1964) 964.