Nucleophilic addition to η^6-arenetricarbonylmanganese cations—the role of intermediates in the reactions with phosphines *

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Abstract

The structures of adducts of phosphines (e.g. PEt₃) with the η^6-arenetricarbonylmanganese cations $[(\eta^6\text{-}XYC_6H_4)Mn(CO)_3]^+$ (Ia, X = Y = H; Ib, X = Me, Y = H; Ic, X = Cl, Y = H; Id, X = Cl, Y = p-Me) in acetone have been determined by low-temperature ^{1}H and ^{13}C NMR spectroscopy. In all cases regiospecific *exo* addition occurs at the arene ring with formation of η^5-cyclohexadienylphosphoniumtricarbonylmanganese cations $[(\eta^5\text{-}XYC_6H_4PEt_3)Mn(CO)_3]^+$ with Ib giving *meta* addition only (IIb) and Ic and Id forming both *meta* and *ortho* adducts (IIc, IIIc and IId, IIId, respectively). Increase in temperature reverses the equilibria for IIa and IIb with formation of $[(\text{arene})Mn(CO)_2(PEt_3)]^+$ whereas IIc, IIIc and IId, IIId form *fac*-Mn(CO)₃(PEt₃)₂Cl involving direct attack by the PEt₃ at the chlorine-bearing ring carbon atom rather than through a metal-hydride intermediate.

Introduction

The reactions between nucleophiles and metal carbonyl complexes of π-acids have been the subject of extensive research over nearly three decades, including important contributions from Pauson and coworkers [1]. A number of reaction pathways and products have been clearly identified, including (a) addition of the nucleophile to the carbon atom of one of the carbonyl groups [2], (b) ring addition [3], (c) carbonyl substitution [2] and (d) breaking of the metal ring bond and formation of nucleophile substituted metal carbonyls [2]. However, despite extensive research, it is still difficult to make reliable predictions of either the reaction pathway or final products; indeed these may be quite different since frequently kinetic products are observed under one set of conditions (e.g. low temperatures) and thermodynamic products under other conditions (e.g. higher temperatures). Theoretical attempts to predict the regiochemistry of such reactions have been based on Hückel theory [4] and on reactivity indices such as P_{LUMO} calculations [5] (the density of the positive hole of the LUMO at a particular site). One of the main

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* Dedicated to Professor Peter Pauson on the occasion of his retirement.

problems is that simple interaction between the HOMO of the nucleophile and the LUMO of the complex appropriate to many organic reactions is frequently inappropriate in metal carbonyl complexes since there is often a band of LUMOs lying quite close in energy and the interaction of the HOMO of the nucleophile with all of these must be considered. In an attempt to overcome this problem, we developed the interaction determinant method (IDM) [6] to calculate the interaction energy between an incoming nucleophile and substrate LUMOs for a particular reaction pathway and then compared interaction energies for various sites within the substrate molecule. The problem of allowing for interaction between the HOMO of a nucleophile and a range of LUMOs as against "the LUMO" is well illustrated by the reaction between methoxide ion and the $[(\eta^7\text{-tropyllium})Mo(CO)_3]^+$ cation [7,8]. Calculation of P_{LUMO} values indicated initial attack at a ring carbon atom whereas calculations based on either ΣP_{LUMO} (summed over the band of LUMOs) or interaction energies (calculated by the IDM method) [6] predicted initial attack at the $Mo(CO)_3$ moiety [7] as confirmed by low-temperature spectroscopic studies [8].

In the present paper, we re-examine the reactions between phosphines and phosphites and the $[(\text{arene})Mn(CO)_3]^+$ cation series using low-temperature IR and NMR spectroscopy to determine the structures of intermediates (where formed) and the subsequent higher temperature reactions with formation of thermodynamically stable products.

Experimental

All solvents were freshly dried by standard methods prior to use. The η^6-arenetricarbonylmanganese cations were prepared from published methods [9,10].

Reagent-grade chemicals were used without further purification. Infrared spectra were recorded on a Perkin–Elmer 1720FT spectrometer linked to a Perkin–Elmer 3700 data station, using 0.1 mm CaF_2 cells. ^1H, ^{13}C, and ^{31}P spectra were recorded on a JEOL GX270 spectrometer. A typical low-temperature spectroscopic experiment is described below.

Low-temperature spectroscopic studies of the reaction of $[(\text{arene})Mn(CO)_3]PF_6$ with trialkylphosphines

To a stirred solution of the arenetricarbonylmanganesehexafluorophosphate (0.30 g, 0.76 mmol) in acetone (30 ml) at $-30°C$, triethylphosphine (0.18 g, 1.52 mmol) was added. The solution was stirred for 60 s and a sample removed immediately for IR analysis in the spectral region 2200–1775 cm^{-1}. For the ^1H and ^{13}C NMR experiments, the reaction was carried out on a small scale (40 mg cation in 0.8 ml of acetone-d_6) in the NMR tube which had been degassed with argon. Spectra were referenced to the solvent peak (no TMS was added). All reactions were monitored over a period of up to 2 h.

Preparation of fac and mer-$Mn(CO)_3(PR_3)_2Cl$ from $[(\eta^6\text{-}p\text{-}MeClC_6H_4)Mn(CO)_3]PF_6$

To a well-stirred solution of η^6-p-chlorotoluenetricarbonylmanganese hexafluorophosphate (0.50 g, 12.5 mmol) in acetone (50 ml), triethylphosphine (0.35 g, 2.52 mmol) was added at room temperature under a stream of nitrogen. Ring addition occurred in the first 60 s, but after 2 min the presence of *fac*-$Mn(CO)_3(PEt_3)_2Cl$ was indicated by three IR bands at 2015 vs, 1938 s, 1897 s

cm^{-1}. The reaction was followed by IR spectroscopy until complete conversion to the *fac*-isomer occurred. Addition of ether precipitated the phosphonium salt [p-MeC$_6$H$_4$PEt$_3$][PF$_6$] as a white solid identified by its ^{1}H NMR spectrum (Table 2). The filtrate was evaporated to dryness to give a yellow oily compound which on recrystallization from n-pentane at $-78\degree$C gave yellow needles of *fac*-Mn(CO)$_3$(PEt$_3$)$_2$Cl. Refluxing of the *fac*-isomer in acetone for 3 h gave the *mer*-isomer obtained as orange plates on recrystallization from n-pentane. Other compounds in this series were prepared similarly (phosphine = PMe$_2$Ph) (see supplementary material).

Preparation of [(arene)Mn(CO)$_2$PR$_3$]PF$_6$ (where R = Me, Et, ^{n}Bu, OMe, OEt, O^{n}Bu; R$_3$ = Me$_2$Ph, MePh$_2$)

All preparations were carried out under oxygen-free nitrogen. For a typical reaction of this series: Triethylphosphite (0.44 g, 1.17 mmol) was added to a stirred solution of η^6-benzenetricarbonylmanganesehexafluorophosphate (0.5 g, 1.38 mmol) in acetone (80 ml) at room temperature and the reaction mixture was stirred for 2.5 h. Reduction in solvent volume and addition of ether gave light yellow crystals of [(C$_6$H$_6$)Mn(CO)$_2$P(OEt)$_3$]PF$_6$ (0.20 g, 88% yield). The other compounds were prepared similarly. (For spectroscopic data see supplementary material.) All these compounds are stable for several months at 0$\degree$C under nitrogen.

Results and discussion

Solutions of the η^6-arenetricarbonylmanganese cations (Ia–Id), [(η^6-XYC$_6$H$_4$)Mn(CO)$_3$]$^+$, (Ia, X = Y = H), (Ib, X = Me; Y = H), (Ic, X = Cl; Y = H), (Id, X = Cl; Y = p-Me) in acetone and dichloromethane were reacted with solutions of phosphines, PR$_3$ (1:2 molar ratio) R = Me, Et, ^{n}Bu; R$_3$ = Me$_2$Ph, MePh$_2$, and phosphites P(OR)$_3$, R = Me, Et, ^{n}Bu, initially at low temperatures (-60 to $-20\degree$C) with subsequent increase of temperature to $+20\degree$C and, in some cases, to reflux temperatures (see Table 1). The course of reaction for the series of cations Ia–Id

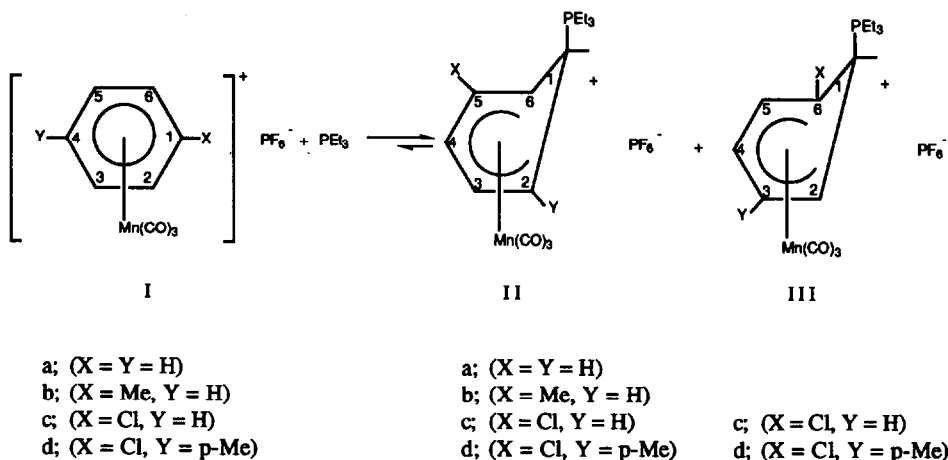| I	II	III
a; (X = Y = H)	a; (X = Y = H)	
b; (X = Me, Y = H)	b; (X = Me, Y = H)	
c; (X = Cl, Y = H)	c; (X = Cl, Y = H)	c; (X = Cl, Y = H)
d; (X = Cl, Y = p-Me)	d; (X = Cl, Y = p-Me)	d; (X = Cl, Y = p-Me)

Table 1

IR spectra of intermediate adducts and reaction products [a]

$[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn(CO)}_3]\text{PF}_6$	Nucleophile L	$[(\eta^5\text{-XYC}_6\text{H}_4\text{L})\text{Mn(CO)}_3]\text{PF}_6$	$[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn(CO)}_2\text{L}]\text{PF}_6$	$fac\text{-Mn(CO)}_3\text{L}_2\text{Cl}$ $mer\text{-Mn(CO)}_3\text{L}_2\text{Cl}$	T (°C)
Ia (X = Y = H)	PEt$_3$	2027, 1951	—	—	−20
Ia (X = Y = H)	PEt$_3$	—	1996, 1950	—	+20
Ia (X = Y = H)	PMe$_2$Ph	2027, 1951	—	—	−20
Ia (X = Y = H)	PMe$_2$Ph	—	2001, 1954	—	+20
Ib (X = Me, Y = H)	PEt$_3$	2024, 1950	—	—	−20
Ib (X = Me, Y = H)	PEt$_3$	—	1991, 1945	—	+20
Ib (X = Me, Y = H)	PMe$_2$Ph	2024, 1947	—	—	−20
Ib (X = Me, Y = H)	PMe$_2$Ph	—	1996, 1950	—	+20
Ic (X = Cl, Y = H)	PEt$_3$	2034, 1961	—	—	−20
Ic (X = Cl, Y = H)	PEt$_3$	—	—	2015 vs, 1938 s, 1987 s [b]	R.T.
Ic (X = Cl, Y = H)	PEt$_3$	—	—	2027 w, 1939 s, 1892 m [b]	reflux
Ic (X = Cl, Y = H)	PMe$_2$Ph	2034, 1961	—	—	−20
Ic (X = Cl, Y = H)	PMe$_2$Ph	—	—	2022 s, 1949 s, 1904 s [b]	R.T.
Ic (X = Cl, Y = H)	PMe$_2$Ph	—	—	2036 w, 1947 s, 1906 m [b]	reflux
Id (X = Cl, Y = p-Me)	PEt$_3$	2031, 1958	—	—	−55
Id (X = Cl, Y = p-Me)	PEt$_3$	—	—	2015 s, 1938 s, 1897 s [b]	R.T.
Id (X = Cl, Y = p-Me)	PEt$_3$	—	—	2027 w, 1939 s, 1892 m [b]	reflux

[a] In acetone solution.i [b] vs; very strong, s; strong, m; medium, w; weak

Table 2

Low-temperature ^{13}C and ^{1}H NMR data of intermediate adducts formed by reaction of triethylphosphine with η^6-arenetricarbonylmanganese cations [a]

Complex	C¹ (H¹)	C² (H²)	C³ (H³)	C⁴ (H⁴)	C⁵ (H⁵)	C⁶ (H⁶)	Me	-CH₂(P)	-CH₃(P)	J(P–C¹)ᶜ	J(-CH₂)ᶜ	J(-CH₃)ᶜ
Ia	102.5 (6.9, s)	102.5 (6.9, s)	102.5 (6.9, s)	102.5 (6.9, s)	102.5 (6.9, s)	102.5 (6.9, s)	–	–	–	–	–	–
Ib	121.88 (–)	103.85 (6.72, d)	101.11 (7.00, t)	98.39 (6.68, t)	101.11 (7.00, t)	103.85 (6.72, d)	20.49 (2.66, s)	–	–	–	–	–
Ic	121.80 (–)	104.16 (7.13, d)	100.13 (7.24, t)	97.75 (6.74, t)	100.13 (7.24, t)	104.16 (7.13, d)	(–)	–	–	–	–	–
Id	117.78 (–)	102.82 (7.20, d)	101.82 (6.99, d)	117.78 (–)	101.82 (6.99, d)	102.85 (7.20, d)	19.69 (2.61, s)	–	–	–	–	–
IIa	32.85, 32.47 (4.4, q)ᵇ	46.10 (3.4, t)ᵇ	83.14 (5.5, t)ᵇ	100.73 (6.4, t)ᵇ	83.14 (5.5, t)ᵇ	46.10 (3.4, t)ᵇ	– (–)	NR	NR	25.0	NR	NR
IIb	33.80, 33.16 (4.5, q)	46.09? (3.4, m)ᵈ	84.26 (5.5, t)	99.64 (6.3, d)	116.36 (–)	46.09? (3.4, m)ᵈ	22.95 (1.89, s)	10.11(d) (–)	6.23(d) (–)	25.8	43.0	5.4
IIc	34.52, 34.12 (4.68, q)	47.30? (3.52, t)	83.41 (5.63, t)	98.25 (6.72, d)	118.40 (–)	48.12? (3.82, d)ᵈ	–	10.22(d) (–)	6.16(d) (–)	26.8	43.0	5.3
IId	NR (5.94, d)	NR (–)	NR (6.59, d)	NR (6.61, d)	NR (–)	NR (4.69, d)	NR (NR)	–	–	–	–	–
IIIc	41.00, 40.64 (5.00, dt)	48.87 (3.80, td)ᵈ	80.79 (5.50, t)	100.24 (6.30, td)	99.37 (6.05, d)	67.80 (–)	– (–)	11.13(d) (–)	6.28(d) (–)	24.7	42.0	5.4
IIId	42.00, 41.65 (5.05, dt)	49.40 (3.75, dd)	115.03 (–)	98.94 (6.22, dd)	81.66 (6.05, d)	67.81 (–)	21.78 (1.87, s)	11.13(d) (–)	6.29(d) (–)	23.6	42.0	6.5
[p-CH₃C₆H₄·PEt₃]PF₆	– (–)	– (7.92, t)	– (7.62, d)	– (–)	– (7.62, d)	– (7.92, t)	– (2.50, s)	– (2.76, m)	– (1.27, m)	–	–	–

[a] NR: not recorded; ?: uncertain assignments. (CD₃)₂CO solvent. [b] Ref. 3. [c] ^{13}C data only; J in Hz. [d] Obscured by other peak.

was monitored in all cases by infra-red spectroscopy and by ^{1}H and ^{13}C NMR spectroscopy for reaction with PEt$_3$ (Table 2). Reaction with phosphites gave only mono-carbonyl substitution products [(arene)Mn(CO)$_2$(P(OR)$_3$)]$^+$ as first reported by Mawby and coworkers [2] with no spectroscopic evidence for formation of intermediates. A number of new compounds were thus prepared [(arene)Mn (CO)$_2$L]$^+$ (L = P(OR)$_3$; R = Me, Et, ^{n}Bu) and their infrared, ^{1}H, ^{13}C and ^{31}P NMR spectra listed as supplementary material. However, with the alkyl phosphines PR$_3$ (R = Et, ^{n}Bu), low-temperature IR spectroscopy showed clearly the formation of ring addition intermediates, i.e. (η^5-cyclohexadienylphosphonium)tricarbonylmanganese cations, e.g. [(η^5-C$_6$H$_6$PR$_3$)Mn(CO)$_3$]$^+$ as reported previously for R = ^{n}Bu by Kane-Maguire and coworkers [3] with ν(CO) frequencies in the range 2024–2034 and 1959–1961 cm^{-1} (see Table 1). Phosphines containing more than one phenyl group, e.g. PMePh$_2$ and PPh$_3$ did not form ring adducts at low temperatures but only gave carbonyl substitution products at higher temperatures (see supplementary material for spectroscopic data).

Low-temperature ^{1}H and ^{13}C NMR spectroscopy of ring adducts

The structures of the above ring adducts in solution (acetone-d_6) were determined by ^{1}H and ^{13}C NMR spectroscopy (Table 2). In the case of the reaction of the [(C$_6$H$_6$)Mn(CO)$_3$]$^+$ cation Ia with PEt$_3$ (or P^{n}Bu$_3$), the ^{1}H NMR spectrum was very similar to that reported previously by Kane-Maguire and coworkers [3] and the newly-acquired ^{13}C NMR spectrum supports fully the identification of the intermediate as the cyclohexadienylphosphoniumtricarbonylmanganese cation [(η^5-C$_6$H$_6$PEt$_3$)Mn(CO)$_3$]$^+$ (Table 2).

The ^{1}H and ^{13}C NMR data for IIa, IIb, IIc, IIIc, IId and IIId summarized in Table 2, are consistent only with a regiospecific *exo* addition of the alkylphosphine to the *meta* position in Ib (X = Me, Y = H) and to the *ortho* and *meta* positions in Ic (X = Cl, Y = H; $o:m = 2:1$) and Id (X = Cl, Y = p-Me; $o:m = 19:1$). These results are similar to those reported by Pauson and Segal [11] for the analogous stable 6-*exo*-phenylcyclohexadienyltricarbonylmanganese complexes obtained by reaction of PhLi with Ia, Ic and Id. Consider in more detail, for example, addition of PEt$_3$ at −20°C to Ic with formation of IIc and IIIc. The ^{1}H NMR spectrum shows a mixture of two adducts with a clear separation of their signals, thereby facilitating determination of the *ortho*: *meta* ratio while the NMR pattern was assigned with the aid of a series of single irradiation experiments. For the *ortho* adduct, the ^{1}H NMR spectrum consists of a triplet of doublets at δ 6.30 ppm assigned to H(4) (Table 2), a doublet at δ 6.05 ppm assigned to H(5), a triplet at δ 5.50 ppm to H(3), a triplet of doublets at δ 3.80 ppm to H(2) and a doublet of triplets at δ 5.0 ppm to H(1). Irradiation experiments confirmed that H(4) at δ 6.30 ppm couples with H(3) and H(5) giving a triplet (t, $J(4-6) = J(4-3) = 5.86$ Hz) which in turn is split by H(2) (d, $J(4-2) = 1.65$ Hz) giving rise to 6 lines as a triplet of doublets. H(2) at δ 3.80 ppm (slightly overlapped by H(6) of the *meta* adduct) is unsymmetrically split by H(3) and H(1) giving a triplet (t, $J(2-3) = 6.41$, $J(2-1) = 6.60$ Hz) which in turn is split by H(4) (d, $J(2-4) = 1.65$ Hz) again giving rise to 6 lines as a triplet of doublets. H(1) at δ 5.00 ppm is split by H(2) giving a doublet (d, $J(1-2) = 6.60$ Hz) which in turn is split unsymmetrically by H(3) and ^{31}P (t, $J(1-P) = 2.01$ and $J(1-3) < 0.6$ Hz) giving rise to 6 lines as a doublet of triplets. The value of $J(1-2) = 6.60$ Hz is typical of *exo* addition products as first clearly delineated by

Pauson and coworkers [12] and is strong evidence for *exo* addition in all the low-temperature intermediates reported here. Normally a large coupling constant would be expected between the phosphorus and ^1H; the small coupling constant observed here may be due to charge transfer between the chlorine and phosphorus atoms. H(5) at δ 6.05 ppm is split by H(4), (d, J(5–4) = 5.86 Hz) and H(3) at δ 5.50 ppm is split unsymmetrically by H(4) and H(2) giving a triplet (t, J(3–4) = 5.86, J(3–2) = 6.41 Hz) which in turn is split by H(1) (J value very small < 0.6 Hz).

The ^{13}C NMR spectra (analysed with the aid of the DEPT pulse sequence) support the above conclusion of *ortho* addition of PEt$_3$ to the $[(C_6H_5Cl)Mn(CO)_3]^+$ cation (Ic) where the most deshielded carbon atoms C(4), C(5) and C(3) are observed at δ 100.24, δ 99.37 and δ 80.79 ppm, respectively. The quaternary carbon atom C(6), which is one of the outer carbon atoms of the cyclohexadienyl system and retains some aromatic character, is observed at δ 67.80 ppm with slight splitting by phosphorus (J(C(Cl)–P) = 2.01 Hz) whilst the other outer carbon atom C(2) is at δ 48.87 ppm. Finally, the carbon atom C(1) to which the phosphorus is directly bonded is expected to be the most shielded of the ring carbon atoms and to suffer the maximum interaction with ^{31}P and so is assigned to a doublet at δ 41.00, δ 40.64 ppm with J(C–P) = 24.7 Hz. The most shielded carbon atoms are the CH$_2$ and CH$_3$ of the phosphine ligand, both being split by ^{31}P and observed as doublets at δ 11.13 ppm (J(C$_{CH_2}$–P) = 42.0 Hz) and δ 6.28 ppm (J(C$_{CH_3}$–P) = 5.4 Hz). Having assigned the major product peaks to the *ortho* adduct, those of the minor product can be assigned to the *meta* adduct as follows: the ^1H NMR spectrum shows a doublet at δ 6.72 ppm assigned to H(4) split by H(3) (d, J(4–3) = 5.86 Hz), a triplet at δ 5.63 ppm assigned to H(3) split by H(4) and H(2) (t, J(3–4) = 5.86, J(3–2) = 6.23 Hz), a quartet at δ 4.68 ppm assigned to H(1) symmetrically split by H(2), H(6) and ^{31}P (q, J(1–2) = J(1–6) = J(P–H^1) $\approx$ 5.5 Hz), a triplet at δ 3.52 ppm assigned to H(2) split by H(1) and H(3) (J(2–3) = 6.23, J(2–1) $\approx$ 5.5 Hz), and finally, a doublet at δ 3.82 ppm for H(6) (overlapped by H(2) of the *ortho* isomer) and split by H(1). For the ^{13}C NMR spectrum, the quaternary C(5) at δ 118.40 ppm is barely shifted from its value in the uncomplexed arene. Again the inner carbon atoms C(4) and C(3) of the cyclohexadienyl system are the next most shielded at δ 98.25 ppm and δ 83.41 ppm, respectively, with the outer carbon atoms C(6) and C(2) lying at δ 48.12 ppm and δ 47.30 ppm, respectively, although this assignment is not definite and could be reversed. The carbon atom C(1), to which the phosphine is attached, is again the most shielded of the ring carbon atoms and suffers the greatest coupling with ^{31}P and observed as a doublet [C(1) δ 34.52, 34.12 ppm, J(C–P) = 26.8 Hz]. Finally, the CH$_2$ and CH$_3$ carbon atoms of the phosphine ligand are the most shielded of all the carbon atoms and occur as doublets at δ 10.22 ppm and δ 6.16 ppm split by phosphorus with J(C–P) = 43.0 Hz and J(C–P) = 5.3 Hz, respectively.

The assignments of the ^1H and ^{13}C NMR spectra of IIb, IId and IIId given in Table 2 were made in a similar way as discussed in detail above for IIc and IIIc.

The above results show clearly that alkylphosphines undergo ring addition with a range of $[(arene)Mn(CO)_3]^+$ to form $[(\eta^5\text{-cyclohexadienylphosphonium})Mn(CO)_3]^+$ cations giving only the *meta* isomer with the toluene complex and a mixture of *ortho* and *meta* isomers with both the chloro and *p*-chlorotoluene complexes. In contrast, both phosphites and phenyl-substituted phosphines give only carbonyl substitution products, presumably because of the weaker nucleophilicity of the former group and the unfavourable cone angles of the latter group [13].

The formation of adducts by reaction of nucleophiles with the $[(arene)Mn(CO)_3]^+$ cations is consistent with calculations of interaction energies for these systems [14] based on the IDM [6], although in the case of harder anionic nucleophiles, e.g. OMe^-, initial attack is predicted at the $Mn(CO)_3$ moiety. Low-temperature IR studies confirm this prediction, although the course of reaction is extremely solvent dependent [15], indicating a delicate balance between charge control and orbital control [6].

Effect of raising the temperature

In the above spectroscopic studies, low temperatures were essential, otherwise further reactions occurred, the nature of which varied quite dramatically between the benzene and toluene complexes on the one hand and the chlorobenzene and p-chlorotoluene complexes on the other. In the former case, raising the temperature of the reaction mixture from -20 to $+20°C$ resulted in complete decomposition of the $[(\eta^5$-cyclohexadienylphosphonium)Mn(CO)_3]^+$ and formation of the corresponding carbonyl substituted $[(arene)Mn(CO)_2PR_3]^+$ cation. (See supplementary material for spectroscopic data.) In contrast, the chlorosubstituted adducts, e.g. $[(\eta^5$-ClC_6H_5PEt_3)Mn(CO)_3]^+$ form the phosphine-substituted metal carbonyl complex, fac-$Mn(CO)_3(PR_3)_2Cl$ [16] (together with $[PhPR_3]^+$) at $+20°C$; on prolonged refluxing, mer-$Mn(CO)_3(PR_3)_2Cl$ [17] is formed. In the case of $[(\eta^6$-p-MeClC_6H_4)Mn(CO)_3]^+$, the above fac and mer isomers are also formed together with $[p$-MeC_6H_4PR_3]^+$ as confirmed by ^1H NMR spectroscopy (see Table 2).

(C)
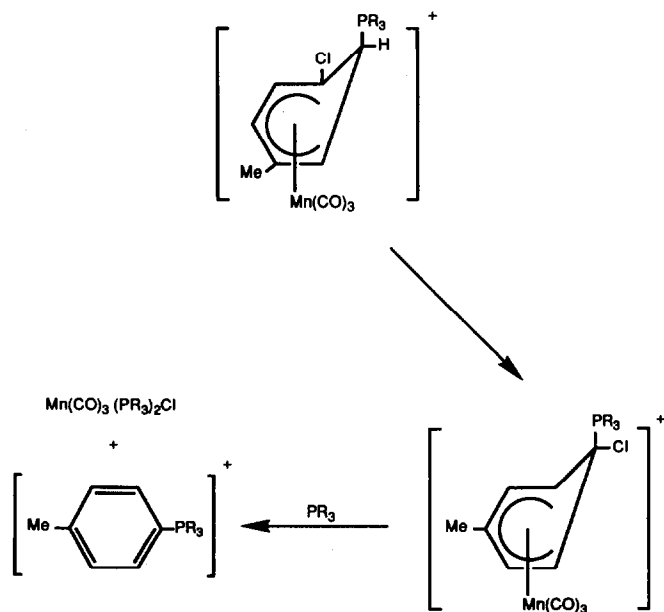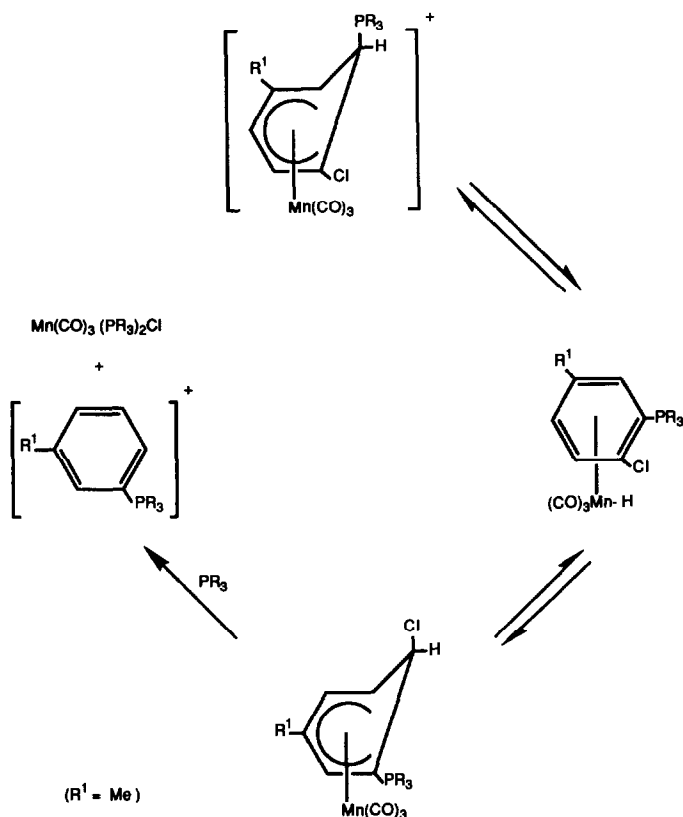
Scheme 1

Scheme 2

The higher temperature reaction pathways which lead to the formation of thermodynamically stable products, e.g. [(arene)Mn(CO)$_2$L]$^+$ are quite distinct from the low-temperature, kinetically controlled, initial-attack pathways. In the case of the benzene and toluene complexes, the equilibrium is "dead-end" and reversal leads to carbonyl substitution at higher temperatures as first observed by Mawby [2]. However, this reaction pathway is not followed by the chlorosubstituted ring adducts which, on increase in temperature, undergo breaking of the C–Cl bond and migration of the chlorine to the metal together with breaking of the metal–ring bond. It has been suggested [18] that nucleophilic displacement of a group such as chlorine from a π-complexed ring may proceed either by direct attack of the nucleophile at the carbon atom bearing the group giving the *ipso* product (C) as either an intermediate or transition station (Scheme 1) or via a metal-hydride intermediate (Scheme 2). With the latter scheme, we would expect formation of a *meta*-substituted phosphonium salt [*m*-CH$_3$C$_6$H$_4$P(C$_2$H$_5$)$_3$][PF$_6$] rather than the observed [*p*-CH$_3$C$_6$H$_4$P(C$_2$H$_5$)$_3$][PF$_6$] (Scheme 1). This result shows clearly that metal-hydride intermediates are not involved in this particular nucleophilic displacement of chlorine by alkylphosphines.

Although the course of reaction occurring on raising the temperature was monitored carefully by both IR and NMR spectroscopy, no evidence was obtained for the *ipso* structure (C, Scheme 1), presumably because it lies too high in energy

due to repulsion between the chlorine and phosphine; interestingly, gradual increase in temperature did result in disappearance of the minor *meta*-adduct before that of the major *ortho* isomer.

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