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Patterns of Nucleophilic Attack on Tricarbonyl π-Arene Complexes of Manganese(I)

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Nucleophiles are shown to react with the cationic complex $[(C_6H_6)Mn(CO)_3]^+$ in four different ways: (a) by addition to the arene ligand, (b) by attack at the metal with displacement of a carbonyl ligand, (c) by attack at the metal with liberation of arene, and (d) by addition to the carbon atom of a carbonyl group. New complexes resulting from each of these four modes of attack are reported. Some related reactions of complexes of other arenes, $[(C_5H_{6-n}Me_n)Mn(CO)_3]^+$, are also described.

Introduction

In a recent paper,[1] we reported the preparation of a range of cyanocyclohexadienyl compounds of manganese(I) by the reaction of cyanide ion with cationic arene complexes $[(C_6H_{6-n}Me_n)Mn(CO)_3]^+$, this being the first example of the addition of any nucleophile other than hydride, alkyl or aryl to a coordinated arene. In this paper, we describe the various ways in which these cationic arene complexes react with other weaker nucleophiles.

Experimental Section

All the work described in the paper was carried out under an atmosphere of dry nitrogen, using oxygen-free solvents. The arene complexes $[(C_6H_{6-n}Me_n)Mn(CO)_3]Y$ required as starting materials were prepared by the method of Winkhaus *et al.*[2]

Preparation of new complexes. Tricarbonyl{di(ethoxycarbonyl)methyl}cyclohexadienylmanganese (1). A solution of diethylsodiomalonate (0.27 g) in ethanol (3 ml) was added to a stirred suspension of $[(C_6H_6)Mn(CO)_3]BF_4$ (0.3 g) in ethanol (3 ml). After a few minutes, the solvent was removed under reduced pressure and the residue treated with *n*-pentane (6 × × 10 ml). Concentration of the extracts yielded yellow crystals. (Found: C, 51.16; H, 4.58. $C_{15}H_{17}MnO_7$ requires C, 51.08; H, 4.55).

Tricarbonyl{diacetylmethyl}cyclohexadienylmanganese(I). A solution of sodium acetylacetonate (0.12 g) in ethanol (4 ml) was added to a stirred suspension of $[(C_6H_6)Mn(CO)_3]BF_4$ (0.3 g) in tetrahydrofuran (30 ml). After 1 hr, petroleum ether (100 – 120°C, 60 ml) was added, the solution was filtered and the filtrate reduced in volume by evaporation under reduced pressure. A very small quantity of yellow crystals was obtained: these were washed with *iso*-pentane and dried *in vacuo.*

Tricarbonylazidocyclohexadienylmanganese(I). Sodium azide (0.1 g) and $[(C_6H_6)Mn(CO)_3]BF_4$ (0.3g) were stirred in acetone for 7 hr. Addition of petroleum ether (60 – 80°C, 50 ml), followed by filtration of the solution and removal of the solvent from the filtrate under reduced pressure left a yellow oil which could not be induced to crystallize, whose i.r. spectrum in *n*-pentane solution was compatible with the formula $(C_5H_6N_3)Mn(CO)_3$.

Tricarbonylmethoxycyclohexadienylmanganese(I). The i.r. spectrum of the solution obtained by stirring a suspension of sodium methoxide (0.15 g) and $[(C_6H_6)Mn(CO)_3]BF_4$ (0.36 g) in ether (50 ml) exhibited three bands in the terminal C–O stretching region at 2026, 1957 and 1949 cm^{-1}. The close similarity of this spectrum to that of the fully characterized complex $\{C_6H_6CH(CO_2Et)_2\}Mn(CO)_3$ indicated that the solution contained $(C_5H_5OMe)Mn(CO)_3$. Removal of the solvent, sowever, was accompanied by wich decomposition, and extraction from the residue much *n*-pentane yielded only trace amounts of the products.

Tricarbonyldiphenylphosphinocyclohexadienylmanganese(I). A solution of $LiPPh_2$ (1.5 g) in ether (30 ml) and tetrahydrofuran (30 ml) was added to a stirred suspension of $[(C_6H_6)Mn(CO)_3]BF_4$ (0.3 g) in tetrahydrofuran (20 ml). After 2 hr, the solvent was removed under reduced pressure and the residue partitioned between water and ether. The ether layer was dried over magnesium chloride, the solvent removed under reduced pressure and the residue purified by column chromatography on deactivated alumina. After elution with petroleum ether, the desired product was obtained on elution with ether. Concentration of the ether solution yielded a very small amount of the crystalline complex.

Tricarbonylthiocyanatocyclohexadienylmanganese(I)

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(1) P.J.C. Walker and R.J. Mawby, *J. Chem. Soc., Dalton*, 622 (1973).

(2) G. Winkhaus, L. Pratt and G. Wilkinson, *J. Chem. Soc.* 3807 (1961).

Solutions of potassium thiocyanate (2 g) in water (10 ml) and $[(C_6H_6)Mn(CO)_3][AlCl_3Br]$ (6 g) in water (50 ml) were mixed. The yellow precipitate which was formed was removed by filtration and washed with water, dissolved in acetone and partitioned between water and ether. The ether layer was dried over sodium sulphate and evaporated to dryness under reduced pressure. Recrystallization of the residue from *n*-pentane gave a very small yield of orange crystals.

Dicarbonyltri-n-butylphosphine-π-benzenemanganese(I) hexafluorophosphate. A solution of $[(C_6H_5)Mn(CO)_3]PF_6$ (3.6 g) and tri-*n*-butylphosphine (3.0 g) in acetone (20 ml) was stirred for 1 hr. After filtration, the filtrate was treated with ether. The precipitate formed was removed by filtration, washed with petroleum ether (40 – 60°C) and recrystallized from acetone/ether. (Found: C, 45.00; H, 6.07. $C_{20}H_{33}F_6MnO_2P_2$ requires C, 44.79; H, 6.20).

Dicarbonyldimethylphenylphosphine-π-benzenemanganese(I) hexafluorophosphate. This was prepared in the same way as the complex above. (Found: C, 40.85; H, 3.70. $C_{16}H_{17}F_5MnO_2P_2$ requires C, 40.70; H, 3.63).

Dicarbonyltriphenylphosphine-π-benzenemanganese(I) hexafluorophosphate. This was prepared in the same way as the tri-*n*-butylphosphine complex, except that the reaction time was 2 days. (Found: C, 58.46; H, 3.63. $C_{25}H_{21}BF_4MnO_2P$ requires C, 58.03; H, 3.93).

Dicarbonyltri-n-butylphosphine-π-mesitylenemanganese(I) hexafluorophosphate. This was prepared in the same way as its benzene analogue. (Found: C, 47.45; H, 7.35. $C_{23}H_{39}F_5MnO_2P_2$ requires C, 48.28; H, 7.52).

Dicarbonyltriphenylphosphinecyanocyclohexadienylmanganese(I). Solutions of sodium cyanide (0.015 g) in water (10 ml) and $[(C_6H_5)Mn(CO)_2PPh_3]PF_6$ (0.1 g) in acetone (5 ml) were mixed and shaken for 3 hr. The solution was shaken with 10 ml portions of ether until the ether extracts were no longer coloured. The combined extracts were washed with water (6 × 10 ml), dried over magnesium chloride and evaporated to dryness under reduced pressure. Recrystallization of the residue from acetone/ether gave yellow crystals (Found: C, 67.56; H, 4.51; N, 2.72. $C_{27}H_{21}MnNO_2P$ requires C, 67.93; H, 4.43; N, 2.93).

Tricarbonyltrisacetonitrilemanganese(I) tetraphenylborate. 0.5 dichloromethane. The complex $[(C_6H_6)Mn(CO)_3]BPh_4$ (0.23 g) was heated under reflux in acetonitrile (5 ml) for 6 hr. After removal of the solvent under reduced pressure the residue was washed with ether and recrystallized from dichloromethane. (Found: C, 64.35; H, 4.89; N, 6.42. $C_{33.5}H_{30}BClMnN_3O_3$ requires C, 64.49; H, 4.85; N, 6.73).

Dicarbonylcarbomethoxy-π-benzenemanganese(I). Sodium methoxide (0.07 g) $[(C_5H_5)Mn(CO)_3]BF_4$ (0.3 g) were stirred in methanol (5 ml) for 10 min. Concentration of the solution under reduced pressure yielded a yellow crystalline solid which decomposed fairly quickly at room temperature. The complex was characterized by i.r. and n.m.r. spectroscopy.

The analogous mesitylene and hexamethylbenzene complexes were prepared in a similar manner.

I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer, and n.m.r. spectra on Perkin-Elmer R10 (60 MHz) and J.E.O.L. (100 MHz) spectrometers. For the kinetic studies on the reaction of the arene complexes with acetonitrile, solutions were contained in sealed n m.r. tubes.

Results

(*a*) *Nucleophilic addition to the arene.* The benzene complex $[(C_6H_5)Mn(CO)_3]BF_4$ was found to react rapidly with the anion $(EtO_2C)_2CH^-$ in ethanol at room temperature. Removal of the solvent followed by recrystallization from pentane yielded a low-melting crystalline solid for which analysis indicated the formulation $\{C_6H_5CH(CO_2Et)_2\}Mn(CO)_3$. The complexity of the n.m.r. spectrum (Table I) and the similarity of the chemical shifts for the ring protons to those observed[1] for the cyanocyclohexadienyl complex $(C_6H_6CN)Mn(CO)_3$ confirm that the reaction involves nucleophilic addition to the benzene ligand. The i.r. spectrum (Table II) exhibits the expected three bands in the terminal C–O stretching region, together with bands due to C–O stretching modes of the $CH(CO_2Et)_2$ group at 1740 and 1758 cm^{-1}. The absence of a C–H stretching band in the region 2750 – 2800 cm^{-1} (characteristic of cyclohexadienyl complexes containing a hydrogen atom in the *exo*-position on the sp^3-hybridized carbon atom[3]) indicates that the $CH(CO_2Et)_2$ substituent is in the *exo*-position.

A similar reaction occurred between $[(C_6H_6)Mn(CO_3]BF_4$ and the acetylacetonate anion. Although the yield of crystalline product after purification was too small to allow complete characterization, the similarity of the i.r. spectrum in the terminal C–O stretching region (Table II) to that of $\{C_6H_5CH(CO_2Et)_2\}Mn(CO)_3$ indicated that the product was $\{C_5H_5CH(COMe)_2\}Mn(CO)_3$. A further band observed at 1603 cm^{-1} was attributed to a C–O stretching mode of the acetylacetonato-group. The cation $[(C_6H_5)Mn(CO)_3]^+$ was also found to react with the anions $Y^- = N_3^-$, OMe^-, PPh_2^- and NCS^- at room temperature in suitable solvents to give products whose i.r. spectra suggested that they also were cyclohexadienyl complexes $(C_6H_5Y)Mn(CO)_3$. The compound $(C_6H_6N_3)Mn(CO)_3$ also exhibited a weak band at 2118 cm^{-1}, presumably due to a stretching mode of the azido group. Complete characterization of the complexes was rendered impossible by the small yields from the reactions and the decomposition which occurred during attempted purification.

(*b*) *Nucleophilic attack on the metal, with loss of a carbonyl ligand.* In contrast to its reaction with the diphenylphosphide anion, the cation $[(C_6H_5)Mn(CO_3]^+$ was found to react with triphenylphosphine in acetone with evolution of carbon monoxide

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[3] I.U. Khand, P.L. Pauson and W.E. Watts, *J. Chem. Soc.* (*C*), 2024 (1969).

Table I. N.m.r. spectra[a] of new complexes formed by reactions of nucleophiles with cationic arene complexes of manganese(1).

Complex	Solvent	Chemical Shift	Assignment
$\mathrm{[C_6H_6CH(CO_2Et)_2]Mn(CO)_3}$	$\mathrm{CDCl_3}$	1.21 (t,6, J=7Hz)	$\mathrm{CH(CO_2CH_2C\mathit{H}_3)_2}$
		2.56 (d,1, J=10Hz)	$\mathrm{C\mathit{H}(CO_2Et)_2}$
		3.0-3.4 (c,3)	$\mathrm{H^1,H^2,H^6}$[b]
		4·14 (q,4, J=7Hz)	$\mathrm{CH(CO_2C\mathit{H}_2Me)_2}$
		4.89 (dd,2)[c,d]	$\mathrm{H^3,H^5}$[b]
		5.82 (t,1, J=5.5Hz)[d]	$\mathrm{H^4}$[b]
$\mathrm{[(C_6H_6)Mn(CO)_2PPh_3]BF_4}$	$\mathrm{CD_3COCD_3}$	6.28 (d,6, J=1Hz)[e]	$\mathrm{C_6\mathit{H}_6}$
		7.50 (c,15)	$\mathrm{P(C_6\mathit{H}_5)_3}$
$\mathrm{[(C_6H_6)Mn(CO)_2PMe_2Ph]PF_6}$	$\mathrm{CD_3COCD_3}$	2.03 (d,6, J=10Hz)[e]	$\mathrm{P(C\mathit{H}_3)_2Ph}$
		6.26 (d,6, J=1Hz)[e]	$\mathrm{C_6\mathit{H}_6}$
		7.62 (c,5)	$\mathrm{PMe_2C_6\mathit{H}_5}$
$\mathrm{[(C_6H_5)Mn(CO)_2PBu_3{}^n]PF_6}$	$\mathrm{CD_3COCD_3}$	1.00 (t,9, J=5.5Hz)	$\mathrm{P[(CH_2)_3C\mathit{H}_3]_3}$
		1.60 (c,18)	$\mathrm{P[(C\mathit{H}_2)_3Me]_3}$
		6.44 (d,6, J=1.5Hz)[e]	$\mathrm{C_6\mathit{H}_6}$
$\mathrm{[(C_6H_3Me_3)Mn(CO)_2PBu_3{}^n]PF_6}$	$\mathrm{CD_3COCD_3}$	0.95 (t,9, J=5.5Hz)	$\mathrm{P[(CH_2)_3C\mathit{H}_3]_3}$
		1.60 (c,18)	$\mathrm{P[(C\mathit{H}_2)_3Me]_3}$
		2.32 (s,9)	$\mathrm{C_6H_3(C\mathit{H}_3)_3}$
		5.98 (s,3)[f]	$\mathrm{C_6\mathit{H}_3Me_3}$
$\mathrm{(C_6H_6CN)Mn(CO)_2PPh_3}$	$\mathrm{CDCl_3}$	2.30 (dd,2)[d,f,g]	$\mathrm{H^2,H^6}$[b]
		3.44 (t,1, J=6Hz)[d,f]	$\mathrm{H^1}$[b]
		4.43 (dd,2)[d,f,g]	$\mathrm{H^3,H^5}$[b]
		5.64 (t,1, J=6Hz)[d,f]	$\mathrm{H^4}$[b]
		7.32 (c,15)	$\mathrm{P(C_6\mathit{H}_5)_3}$
$\mathrm{[Mn(CO)_3(NCMe)_3]BPh_4}$	$\mathrm{CD_3CN}$	2.20 (s,9)	$\mathrm{(NCC\mathit{H}_3)_3}$
		6.8-7.5 (c,20)	$\mathrm{B(C_6\mathit{H}_5)_4}$
$\mathrm{(C_6H_6)Mn(CO)_2CO_2Me}$	$\mathrm{CD_3COCD_3}$	3.33 (s,3)	$\mathrm{CO_2C\mathit{H}_3}$
		5.84 (s,6)	$\mathrm{C_6\mathit{H}_6}$
$\mathrm{(C_6H_3Me_3)Mn(CO)_2CO_2Me}$	$\mathrm{CD_3COCD_3}$	2.20 (s,9)	$\mathrm{C_6H_3(C\mathit{H}_3)_3}$
		3.32 (s,3)	$\mathrm{CO_2C\mathit{H}_3}$
		5.37 (s,3)	$\mathrm{C_6\mathit{H}_3Me_3}$
$\mathrm{(C_6Me_6)Mn(CO)_2CO_2Me}$	$\mathrm{CD_3COCD_3}$	2.21 (s,18)	$\mathrm{C_6(C\mathit{H}_3)_6}$
		3.32 (s,3)	$\mathrm{CO_2C\mathit{H}_3}$

[a] Chemical shifts are on the δ scale, measured relative to TMS which was used as an internal standard. Multiplicities, relative peak areas and coupling constants (to other hydrogen nuclei except where otherwise stated) are given in parentheses: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, c = complex. [b] Ring protons are numbered starting from the proton ($\mathrm{H^1}$) on the carbon atom to which the added nucleophile is attached. [c] Coupling constants to both adjacent protons *ca* 5.5 Hz. [d] With slight additional splitting due to coupling to more distant protons. [e] Couplet to ^{31}P. [f] Broadened by slight coupling to ^{31}P. [g] Coupling constants to both adjacent protons *ca* 6 Hz.

Table II. I.r. Spectra[a] of new complexes formed by reactions of nucleophiles with cationic arene complexes of manganese(I).

Complex	Solvent	νC-O cm^{-1}
$\mathrm{[C_6H_6CH(CO_2Et)_2]Mn(CO)_3}$	*n*-pentane	2030, 1960, 1948
$\mathrm{[C_6H_6CH(COMe)_2]Mn(CO)_3}$	*n*-pentane	2028, 1958, 1946
	tetrahydrofuran	2021, 1935
$\mathrm{(C_6H_6N_3)Mn(CO)_3}$	*n*-pentane	2027, 1956, 1946
$\mathrm{(C_6H_6OMe)Mn(CO)_3}$	*n*-pentane	2023, 1952, 1941
$\mathrm{(C_6H_6PPh_2)Mn(CO)_3}$	tetrahydrofuran	2020, 1940
$\mathrm{(C_6H_6NCS)Mn(CO)_3}$	*n*-pentane	2031, 1958, 1948
$\mathrm{[(C_6H_6)Mn(CO)_2PPh_3]BF_4}$	acetone	2007, 1960
$\mathrm{[(C_6H_6)Mn(CO)_2PPhMe_2]PF_6}$	acetone	2002, 1958
$\mathrm{[(C_6H_6)Mn(CO)_2PBu_3{}^n]PF_6}$	acetone	1997, 1950
$\mathrm{[(C_6H_3Me_3)Mn(CO)_2PBu_3{}^n]PF_6}$	acetone	1986, 1938
$\mathrm{(C_6H_6CN)Mn(CO)_2PPh_3}$	*n*-pentane	1954, 1900
$\mathrm{[Mn(CO)_3(NCMe)_3]BPh_4}$	dichloromethane	2068, 1972
$\mathrm{(C_6H_6)Mn(CO)_2CO_2Me}$	*n*-pentane	1990, 1944
$\mathrm{(C_6H_3Me_3)Mn(CO)_2CO_2Me}$	*n*-pentane	1974, 1929
$\mathrm{(C_6Me_6)Mn(CO)_2CO_2Me}$	*n*-pentane	1971, 1927

[a] In the terminal C-O stretching region. Other bands are mentioned, where relevant, in the text.

and formation of the monsubstituted complex $\mathrm{[(C_6H_6)Mn(CO)_2PPh_3]^+}$, which was isolated and characterized as its fluoroborate salt. The n.m.r. spectrum of the complex (Table I) showed that all the protons in the benzene ring were still equivalent, and coupled to the ^{31}P nucleus. Similar complexes were obtained from the reactions of the benzene complex with dimethylphenylphosphine and tri-*n*-butylphosphine, and from that of the mesitylene complex $\mathrm{[(C_6H_3Me_3)Mn(CO)_3]^+}$ with tri-*n*-butylphosphine. All the products exhibited the expected two bands in the terminal C–O stretching region of their i.r. spectra (Table II).

That the susceptibility of the arene to nucleophilic attack was not removed by the replacement of a carbonyl group by a phosphorus(III) ligand was shown by the isolation and characterization of the cyanocyclohexadienyl complex $(C_6H_6CN)Mn(CO)_2PPh_3$ from the reaction of $[C_6H_6)Mn(CO)_2PPh_3]PF_6$ with cyanide ion at room temperature. The retention of the positive charge on the complex is clearly important in this respect, since the related uncharged compound $(C_6H_6)Mn(CO)_2CN$[4] does not react with cyanide ion to form a cyanocyclohexadienyl complex.

(*c*) *Nucleophilic attack on the metal, with loss of the arene.* When the complex $[(C_6H_6)Mn(CO)_3]BPh_4$ was heated under reflux in acetonitrile, a crystalline product $[Mn(CO)_3(NCMe)_3]BPh_4$ was obtained. Recrystallization from dichloromethane yielded the solvated species $[Mn(CO)_3(NCMe)_3]BPh_4 \cdot \frac{1}{2}CH_2Cl_2$, which was fully characterized. The observation of a single resonance for the three sets of methyl protons in the n.m.r. spectrum of the complex indicates that it has the *fac*-configuration, and this is compatible with the observation of two bands in the C–O stretching region of the i.r. spectrum. A much weaker band at 2323 cm^{-1} was assigned to a C–N stretching mode of the acetonitrile ligands.

The reaction could conveniently be followed by n.m.r. spectroscopy in acetonitrile solution. The resonance due to complexed benzene at δ 6.45 was replaced by a new peak, due to free benzene, at δ 7.28. Rate constants were obtained in this way for the reaction: $[(C_6H_6)Mn(CO)_3]^+ + 3MeCN \rightarrow [Mn(CO)_3(NCMe)_3]^+ + C_6H_6$ and for the corresponding reactions of the analogous toluene, *p*-xylene and mesitylene complexes, which were all found to be first order in arene complex. The results (see Table III) reveal that the rate of arene displacement decreases with increasing substitution on the arene, a trend which could be caused either by increasingly strong bonding between arene and metal, or by increasing hindrance to attack by the incoming acetonitrile. It is also noticeable that the rate of reaction of the cation $[(C_6H_6)Mn(CO)_3]^+$ increases with increasing size of the anion present. This suggests that there may be ion pairing in the acetonitrile, the increase in rate with increasing anion size reflecting the decrease in the extent of ion pairing.

Table III. Observed rate constants for the reactions of complexes $[(arene)Mn(CO)_3]Y$ with acetonitrile.[a]

Temperature °C	Arene	Y	10^4 k_{obs} sec^{-1}
90	benzene	BF_4	0.90±0.09 [b]
95	benzene	BF_4	1.60±0.07 [b]
	benzene	PF_6	1.70±0.06
	benzene	BPh_4	2.23±0.07
100	benzene	BF_4	2.68±0.14 [b]
	toluene	BF_4	2.17±0.08
	p-xylene	BF_4	0.97±0.12
	mesitylene	BF_4	0.85±0.05
105	benzene	BF_4	4.11±0.21 [b]

[a] In acetonitrile solution: initial concentration of complex was in all cases 0.4*M*. [b] From these fiigures, $\Delta H^{*} = 29 \pm 3$ kcal mol^{-1}.

The addition of iodide ion to a solution of $[(C_6H_6) \cdot Mn(CO)_3]^+$ in acetonitrile resulted in a much more rapid reaction, during which benzene was again liberated. Apart from a little $[Mn(CO)_3(NCMe)_3]^+$, the main product (characterized by i.r. bands in the C–O stretching region at 2042, 1956 and 1941 cm^{-1}) was $Mn(CO)_3(NCMe)_2I$. identical with a sample prepared from $Mn(CO)_5I$ and acetonitrile: the i.r. spectrum is closely related to those of $Mn(CO)_3(NCMe)_2X$ (X = Cl, Br)[5].

Although the complexes $[(C_6H_{6-n}Me_n)Mn(CO)_3]^+$ did not react with acetone, addition of iodide ion to acetone solutions of the complexes caused loss of arene and ultimate formation of the known compound $Mn_2(CO)_8I_2$.[6] An i.r. study of the reaction of the benzene complex indicated that it took place in two steps: first the C–O stretching bands of the starting material were replaced by bands at 2016 and 1935 cm^{-1}, and then these were more slowly replaced by those of $Mn_2(CO)_8I_2$, which in this solvent appear at 2068, 1998, 1974 and 1929 cm^{-1}. (The conversion of the mesitylene complex $[(C_6H_3Me_3)Mn(CO)_3]^+$ to $Mn_2(CO)_8I_2$ by iodide ion in acetone solution has also been reported by Davison and Reger,[7] but they failed to observe the formation of the intermediate complex.)

An n.m.r. study of the reaction in acetone-d^6 revealed that the benzene was liberated in the first step of the reaction. It seems clear that the intermediate is either $Mn(CO)_3(OCMe_2)_2I$ or $[Mn(CO)_3(OCMe_2)I]_2$, and this is consistent with the fact that addition of acetonitrile to the solution immediately converted the intermediate to $Mn(CO)_3(NCMe)_2I$. Unlike $Mn(CO)_3(NCMe)_2I$, the intermediate evidently decomposes in solution, liberating carbon monoxide which converts the remainder of the intermediate to $Mn_2(CO)_8I_2$. (In the presence of free carbon monoxide, the i.r. spectrum of $[(C_6H_6)Mn(CO)_3]^+$ was replaced by that of $Mn_2(CO_8I_2$ without the observation of any intermediate species).

(*d*) *Nucleophilic addition to the carbon atom of a carbonyl group.* Whereas the reaction of the cation $[(C_6H_5)Mn(CO)_3]^+$ with methoxide ion in ether yielded the methoxycyclohexadienyl complex $(C_6H_6OMe)Mn(CO)_3$, the reaction in methanol followed a different course. The solution changed colour immediately, and the i.r. spectrum in the terminal C–O stretching region exhibited new bands at 1988 and 1939 cm^{-1}. Removal of the solvent was accompanied by considerable decomposition, but it was possible to isolate some of the product formed as a yellow solid, which decomposed fairly rapidly at room temperature even under a nitrogen atmosphere.

The i.r. spectrum of the product in *n*-pentane solution contained, in addition to the two bands in the terminal C–O stretching region, a band at 1623 cm^{-1}, which is in the region characteristic of the $> C = O$

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[4] P.J.C. Walker and R.J. Mawby, *J. Chem. Soc.* (*A*), 3006 (1971).

[5] M.F. Farona and K.F. Kraus, *Inorg. Chem.*, *9*, 1700 (1970).

[6] E.W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

[7] A. Davison and D.L. Reger, *J. Organometal. Chem.*, *23*, 491 (1970).

grouping. The n.m.r. spectrum in acetone-d_6 consisted of singlet resonances assignable to the methoxy-protons and the protons of the coordinated benzene. Although the rapid decomposition of the complex prevented its complete characterization, the obvious formula for it is $(C_6H_6)Mn(CO)_2CO_2Me$. Similar compounds, also of very limited stability, were obtained by addition of methoxide ion to a carbonyl ligand in the mesitylene and hexamethylbenzene complexes, $[(C_6H_3Me_3)Mn(CO)_3]^+$ and $[(C_6Me_6)Mn(CO)_3]^+$, and characterized by i.r. and n.m.r. spectroscopy.

The existence of relacted compounds $(C_6H_{6-n}Me_n)Mn(CO)_2CONHR$, formed by attack on $[(C_6H_{6-n}Me_n)Mn(CO)_3]^+$ by amines, has very recently been reported by Angelici and Blacik.[8]

Discussion

The reactions described above illustrate clearly how delicate the balance is between attack at different sites within the cations $[(C_6H_{6-n}Me_n)Mn(CO)_3]^+$ Thus, triphenylphosphine and the diphenylphosphide anion react in different ways. while a change in solvent is sufficient to alter the site of attack by methoxide ion from the arene to a carbonyl group. Uncharged phosphorus ligands attack the metal with displacement of carbon monoxide, yet the nitrogen-donor ligand acetonitrile displaces the arene.

The apparent failure of any of the uncharged ligands to add to the arene may be the result of the unfavourable localization of positive charge which must ensue:

$$[(C_6H_6)Mn(CO)_3]^+ + L \longrightarrow (C_6H_6\overset{+}{L})Mn(CO)_3$$

but it is interesting to note that the cyclopentadienyl ligand (at first sight an even less attractive prospect for nucleophilic attack than an arene) in the molybdenum(II) complex $(\pi\text{–}C_5H_5)Mo(CO)_3Cl$ *is* attacked by tri-*n*-butylphosphine.[9] The difference in behaviour may be related to the fact that in this case the adduct can react further, with transfer of two electrons from ligand to metal, to yield the cation $[C_5H_5PBu^n{}_3]^+$ and a molybdenum(0) complex, whereas formation of the adduct with the arene complex cannot be followed by any further reaction.

The loss of a carbonyl group in the reactions of the complexes $[(C_6H_{6-n}Me_n)Mn(CO_3]^+$ with phosphorus(III) ligands is in marked contrast to the corresponding reactions of complexes $(C_6H_{6-n}Me_n)Mo(CO)_3$, where arene is lost to yield products $Mo(CO)_3(PR_3)_3$.[10] It may be that the higher oxidation state of the manganese is responsible for the difference in behaviour, since this should strengthen the bonding of the arene to the metal by virtue of greater donation of electron density from ring to metal, but weaken the bonding to the π–accepting carbonyl groups.

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