Reactions of Metal Carbonyls. Part V.[1] Reaction of A Series of Substituted Manganese Carbonyl Bromide Compounds with Nitrosonium Hexafluorophosphate

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The reactions of $NOPF_6$ with $[Mn(CO)_5Br]$ and *cis*-$[Mn(CO)_4(PMe_2Ph)Br]$ in acetonitrile solution have given the cations $[Mn(CO)_5(CH_3CN)]^+$ and *cis*-$[Mn(CO)_4(PMe_2Ph)(CH_3CN)]^+$. *Fac*- and *mer-trans*-$[Mn(CO)_3L_2Br]$-[L = $P(OMe)_3$, PMe_3, PMe_2Ph and dpm] are oxidised by $NOPF_6$ to give the salts *fac*-$[Mn(CO)_3L_2Br]PF_6$. Similar treatment of *mer-cis*-$[Mn(CO)_2L_3Br]$ [L = $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, PMe_3 and PMe_2Ph] with $NOPF_6$ gave *mer-cis*-$[Mn(CO)_2(PMe_3)_3Br]PF_6$ and *mer-trans*-$[Mn(CO)_2L_3Br]PF_6$ [L = $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$ and PMe_2Ph]. *Mer-trans*-$[Mn(CO)_2L_3Br]PF_6$ [L = $P(OMe)_3$, $P(OEt)_3$ and $P(OMe)_2Ph$] further react with L in refluxing chloroform to give the cations *cis*-$[Mn(CO)_2L_4]^+$. The reaction of *cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]PF_6$ with $NOPF_6$ gave the dipositive manganese(II) cation *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]^{2+}$ which is readily reduced by hydrazine to give *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]^+$. The reaction of the tetrasubstituted complex $[Mn(CO)\{P(OMe)_3\}_4Br]$ with $NOPF_6$ gave $[Mn(CO)(NO)\{P(OMe)_3\}_4](PF_6)_2$.

THE nitrosyl ion NO^+ has been widely used [2] as a nitrosylating agent for transition metal complexes. Few reactions have been reported, however, utilising this ion as a single electron oxidant and those cited, fall into two classes, *viz.* with or without solvent inclusion into the metal co-ordination sphere. Thus, treatment of nickel(II) amine complexes [3] and the decacarbonyls of manganese and rhenium [4] with NO^+ in acetonitrile solution has given oxidised products containing MeCN bonded to the metal atom, whereas oxidation of manganese(II) and molybdenum(III) cyanide salts [5] in non-aqueous media with NOCl has resulted in products with no solvent inclusion. We have recently briefly reported the generality of the latter type of reaction [6] in poorly co-ordinating solvents, *e.g.* single electron oxidations of $[Mn(CO)_3L_2Br]$, (L = PMe_2Ph, L_2 = dpm *), $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L]$, (L = CO or $P(OPh)_3$) and $[Mo(CO)_2(dpe\ ^*)_2]$ in dichloromethane solution using $NOPF_6$, and this work has since been extended by other workers [7] to include oxidations of $[(\pi\text{-}C_5H_5)_2Fe]$ and $[(\pi\text{-}C_5H_5)Fe(CO)(SMe)]_2$. As no systematic studies of the reactions of $NOPF_6$ with series of similar compounds have been undertaken, we have subjected the phosphine and phosphite substituted manganese carbonyl bromide derivatives $[Mn(CO)_{5-x}L_xBr]$, (x = 0—4), which we reported earlier,[8] to this type of oxidation reaction. The reactions have been carried out in various solvents and we have attempted to correlate the degree of carbonyl substitution with the stability and type of product formed. The salts formed are unusual in that previous oxidation reactions of compounds such as $[Mn(CO)_3(py)_2Br]$ and $[Mn(CO)_3(bipy)Br]$ have given [9] manganese(II) complexes only with complete expulsion of CO. In general, we have found that: (*i*) solvent dependence of the reactions decreases as the degree of carbonyl substitution of $[Mn(CO)_5Br]$ increases, and (*ii*) the ease of oxidation of the neutral compound and the stability towards reduction of the product formed, increases with the higher substituted complexes.

RESULTS AND DISCUSSION

No discernible reaction was observed when $[Mn(CO)_5Br]$ (I) was treated with an excess of $NOPF_6$ in dichloromethane solution. Similar reactions with *cis*-$[Mn(CO)_4LBr]$ (L = PMe_2Ph, $P(OMe)_2Ph$, and $PMePh_2$) (II), gave a slow (30 min) solution colour change to green. With nitromethane as solvent, complex (I) was converted to a deep red species and the reaction of complex (II) greatly accelerated, but the products were too readily reduced back to starting material in the absence of $NOPF_6$ to allow their identification. The increase in the rate of reaction of (I) and (II) in nitromethane is possibly related to the high solubility of $NOPF_6$ in this solvent and/or to the stabilisation of charged species in solvents with high dielectric constants. However, from our oxidation reactions with NO_2, we favour the latter reason as gaseous NO_2, which is an equally strong oxidant as NO^+, also gives no reaction in dichloromethane solution.

Treatment of complexes (I) or (II; L = PMe_2Ph) with $NOPF_6$ in the strong donor solvent acetonitrile gives an initial red colouration which reverts to yellow on warming the solution. From these yellow solutions $[Mn(CO)_5(CH_3CN)]PF_6$ (ref. 7) and *cis*-$[Mn(CO)_4(PMe_2Ph)(CH_3CN)]BPh_4$ (III) are isolated respectively, on addition of the appropriate anion. The structure of (III) was inferred from the carbonyl i.r. spectrum which is consistent with C_s symmetry (see Table 1). Surprisingly, the ^1H n.m.r. spectrum of the methyl resonance of the acetonitrile ligand in (III) consists of a doublet (Table 2),

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* dpm = $Ph_2PCH_2PPh_2$; dpe = $Ph_2PCH_2CH_2PPh_2$

[1] Part IV, R. H. Reimann and E. Singleton, *J. Organometallic Chem.*, in the press.

[2] G. R. Crooks and B. F. G. Johnson, *J. Chem. Soc.* (*A*), 1970, 1662.

[3] E. K. Barefield and D. H. Busch, *Chem. Comm.*, 1970, 522.

[4] N. G. Connelly and L. F. Dahl, *Chem. Comm.*, 1970, 880.

[5] J. R. Fowler and J. Kleinberg, *Inorg. Chem.*, 1970, **9**, 1005.

[6] R. H. Reimann and E. Singleton, *J. Organometallic Chem.*, 1971, **32**, C44.

[7] N. G. Connelly and J. D. Davies, *J. Organometallic Chem.*, 1972, **38**, 385.

[8] See Part III, R. H. Reimann and E. Singleton, *J.C.S. Dalton*, 1973, 841.

[9] M. R. Snow and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1966, 777.

presumably due to orbital interaction of the ^{31}P with the N≡C– moiety in the *cis*-position. The phosphine methyl groups in (III) are observed as a sharp doublet.

Dichloromethane solutions of the compounds $[Mn(CO)_3L_2Br]$, [L = PMe_3 and $P(OMe)_3$] react rapidly with $NOPF_6$ accompanied by evolution of NO gas, giving the deeply coloured salts *fac*-$[Mn(CO)_3L_2Br]PF_6$ (IV). These complexes are readily isolated in a crystalline form by the addition of ethanol at 0°. Addition of alcohols above this temperature or of $NaBPh_4$ to the reaction solutions results in rapid reduction back to the neutral precursors. For L = PMe_2Ph and L_2 = dpm, the oxidised species are too readily reduced to allow isolation by this method. However, treatment of benzene solutions of $[Mn(CO)_3L_2Br]$, (L = PMe_2Ph; L_2 = dpm) with $NOPF_6$ gave deeply coloured crystals of the required *fac*-$[Mn(CO)_3L_2Br]PF_6$ salts. These crystalline compounds (IV) were shown to be 1 : 1 electrolytes in acetone solution and to be paramagnetic by ^1H n.m.r. spectroscopy. They were sufficiently stable towards reduction to allow rapid handling in air. The carbonyl i.r. spectra of (IV) allowed unequivocal assignment as the *fac*-isomers (see Table 1) consistent with C_s symmetry. This isomer was exclusively formed from the oxidations of both *fac*- and *mer-trans*-$[Mn(CO)_3L_2Br]$ compounds, and is unusual since *fac*-$[Mn(CO)_3L_2Br]$ has been shown[10] to be the thermodynamically unstable isomer due to steric crowding. In fact, the reduction products of (IV) were always the *mer-trans* isomers of $[Mn(CO)_3L_2Br]$, except for L_2 = dpm which naturally gives the *fac* isomer. No solvent dependence was observed in these reactions of $[Mn(CO)_3L_2Br]$ with $NOPF_6$ and identical products were obtained from nitromethane and acetonitrile solutions at room temperature.

TABLE 1

Analytical data, melting points, conductivities, and carbonyl and nitrosyl i.r. absorption frequencies

	Compound	Colour	M.p. (t/°C)	Conductivity[a] Ω^{-1} cm^2 mol^{-1}	Calculated (%) C	H	Br	Found (%) C	H	Br	ν(CO) and ν(NO)/cm^{-1} [b]
(III)	*cis*-$[Mn(CO)_4(PMe_2Ph)(CH_3CN)]BPh_4$	Colourless	143	109	68·6	5·15	2·1 [c]	68·3	5·2	2·25 [c]	2105m, 2035sh, 2020s, 1997m
(IV)	*fac*-$[Mn(CO)_3(PMe_2Ph)_2Br]PF_6$	Olive green	88—90	110	35·65	3·45	12·5	35·35	3·6	12·4	2106m, 2068m, 2030s [d]
(IV)	*fac*-$[Mn(CO)_3(PMe_3)_2Br]PF_6$	Violet	74—77 [e]	142	20·95	3·5	15·5	20·9	3·55	15·45	2107m, 2064s, 2023vs
(IV)	*fac*-$[Mn(CO)_3\{P(OMe)_3\}_2Br]PF_6$	Violet	84 [e]	138	17·65	2·95	13·05	17·65	2·95	12·85	2116s, 2075s, 2047vs [d]
(IV)	*fac*-$[Mn(CO)_3(dpm)Br]PF_6$	Violet	108	127	44·9	2·95	10·7	44·9	2·95	10·45	2124s, 2085m, 2032vs [d]
(V)	$[Mn(CO)_2(PMe_3)_3Br]PF_6$	Bronze	138—141	134	23·4	4·8	14·2	23·15	4·7	14·4	2014s, 1944s [f]
(VI)	*mer-trans*-$[Mn(CO)_2(PMe_2Ph)_3Br]PF_6$	Red	80 [e]	163	41·6	4·45	10·65	41·35	4·55	10·4	2015w, 1947s
(VI)	*mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]PF_6$	Orange	106—109 [e]	142	18·65	3·8	11·3	18·5	3·95	11·3	2072w, 1994s
(VI)	*mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]PF_6$	Maroon	111—114 [e]	138	36·9	3·9	9·45	36·7	4·1	9·45	2065w, 1981s
(VII)	$[Mn(CO)(NO)\{P(OMe)_3\}_4](PF_6)_2$	Pink	168 [e]	296	17·35	4·0	1·55 [c]	17·6	4·0	1·6 [c]	2130m, 2092w, 1836s [f]
(VIII)	*cis*-$[Mn(CO)_2\{P(OMe)_3\}_4]BPh_4$	Colourless	153—156	110	49·25	6·05		49·4	6·1		2004s, 1947s
(VIII)	*cis*-$[Mn(CO)_2\{P(OEt)_3\}_4]BPh_4$	Colourless	183—187	102	54·9	7·4		54·75	7·3		1998s, 1940s
(VIII)	*cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]PF_6$	Colourless	203—205	181	43·55	4·7		43·85	4·65		1991s, 1937s
(IX)	*trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]PF_6$	Cream	223—226	187	43·55	4·7		43·75	4·7		2014w, 1933s
(X)	*trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4](PF_6)_2$	Dark blue	175 [e]	273	37·7	4·05		37·9	3·95		2054w, 1993s

[a] Measured in acetone solution. [b] In $CHCl_3$ solution unless otherwise indicated. [c] This entry refers to nitrogen. [d] In Nujol. [e] With decomposition. [f] In CH_2Cl_2 solution.

TABLE 2

N.m.r. data

	Compound	$-CH_3$-Resonances (τ)	$-OCH_3$-Resonances (τ)
(III) [a]	*cis*-$[Mn(CO)_4(PMe_2Ph)(CH_3CN)]BPh_4$	8·15 (d) J(PH) 9·5 Hz, 8·73 (d) J(PH) 1·8 Hz	
(VIII) [b]	*cis*-$[Mn(CO)_2\{P(OMe)_3\}_4]BPh_4$		6·37 (m)
(VIII) [b]	*cis*-$[Mn(CO)_2\{P(OEt)_3\}_4]BPh_4$	8·71 (t) J(HH) 7·0 Hz, 8·74 (t) J(HH) 6·5 Hz	5·97 (m) [c]
(VIII) [a]	*cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]PF_6$		6·47 (m)
(IX) [a]	*trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]PF_6$		6·52 (m) [d]

[a] Measured in CD_2Cl_2 solution. [b] Measured in $CDCl_3$ solution. [c] $-OCH_2-$ Resonance. [d] Characteristic symmetrical resonance (see ref. 12).

Dichloromethane solutions of *mer-cis*-$[Mn(CO)_2L_3Br]$, (L = PMe_2Ph, $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, and PMe_3) react rapidly with an excess of $NOPF_6$ to give varying products. For the small σ-donor phosphine, PMe_3, a single electron oxidation occurs to give the salt $[Mn(CO)_2(PMe_3)_3Br]PF_6$ (V), the i.r. spectrum of which is consistent with either a *mer-cis* or *fac-cis* configuration (see Table 1). For the larger phosphine, PMe_2Ph, the reaction proceeds with disproportionation in dichloromethane solution, yielding (IV; L = PMe_2Ph) as the sole isolable product. However, a solution of *mer-cis*-$[Mn(CO)_2(PMe_2Ph)_3Br]$ in ethanol is rapidly oxidised by $NOPF_6$ to give *mer-trans*-$[Mn(CO)_2L_3Br]PF_6$, (VI; L = PMe_2Ph), which precipitates from the reaction solution. Treatment of *mer-cis*-$[Mn(CO)_2L_3Br]$, (L = $P(OMe)_3$, $P(OEt)_3$, and $P(OMe)_2Ph$) with $NOPF_6$ in dichloromethane solution also yields the salts (VI). The carbonyl i.r. spectra of the complexes [VI; L = PMe_2Ph, $P(OMe)_3$, $P(OEt)_3$, and $P(OMe)_2Ph$] all contain the characteristic band pattern of one weak and one strong vibration, consistent with C_{2v} symmetry (see Table 1), indicating the *mer-trans* configuration for these compounds. The complexes (V) and (VI) are crystalline and air-stable, with the exception of [VI; L = $P(OEt)_3$]

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[10] R. J. Angelici, F. Basolo, and A. J. Poë, *J. Amer. Chem. Soc.*, 1963, **85**, 2215.

which was identified from the chloroform solution carbonyl i.r. spectrum only [ν(CO) = 2055w, 1982s]. In solution, reduction of the compounds (VI) occurs readily in the presence of warm alcohols and reducing agents such as $NaBH_4$, giving *mer-cis*-[$Mn(CO)_2L_3Br$] in all cases. Mild reduction of (VI; L = $P(OMe)_3$ and $P(OEt)_3$) however, with hydrazine in dichloromethane–light petroleum ether (b.p. 40—60°) mixtures at 0° gave the known [8] neutral isomers, *mer-trans*-[$Mn(CO)_2L_3Br$] [L = $P(OMe)_3$ and $P(OEt)_3$], in which the configuration of the manganese(II) salts is retained. These isomers are extremely unstable and readily revert to the more stable *mer-cis*-trisubstituted isomers above 10°. No additional products were obtained when *mer-cis*-[$Mn(CO)_2L_3Br$], [L = PMe_2Ph, $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, and PMe_3] were treated with $NOPF_6$ in nitromethane or acetonitrile solutions at room temperature, although total decomposition occurred with large excesses of $NOPF_6$ and long reaction times.

During one of our oxidation reactions of the known [8,11] compound [$Mn(CO)\{P(OMe)_3\}_4Br$] with $NOPF_6$ in dichloromethane solution, halogen displacement occurred to give a very low yield of the stable dicationic nitrosyl salt, [$Mn(CO)(NO)\{P(OMe)_3\}_4$]$(PF_6)_2$ (VII). The ν(NO) at 1836 cm^{-1} does not readily establish the identity of the co-ordinated nitrosyl ligand as NO^- or NO^+, as comparable dicationic nitrosyls are uncommon. However, the inert nature of the nitrosyl compound (VII) towards further reaction and reduction, suggests a d^6 electronic configuration with an NO^+ ligand. Similar reactive stability has been observed for the comparable cationic spin paired systems [$Mn(CO)_2L_4$]$^+$ (see below) and [$Mn(CO)_{5-x}L_x(CH_3CN)$]$^+$,* whereas the high spin systems [$Mn(CO)_2L_3Br$]$^+$ rapidly undergo further substitution and reduction. A structural assignment for (VII) from ^1H n.m.r. data was precluded by the low yield of the reaction. When [$Mn(CO)\{P(OMe)_3\}_4Br$] was oxidised with $NOPF_6$ in acetonitrile solution, only the disproportionation product, *mer-trans*-[$Mn(CO)_2\{P(OMe)_3\}_3Br$]PF_6 was isolated.

The compounds (VI; L = $P(OMe)_3$, $P(OEt)_3$, and $P(OMe)_2Ph$) further react with L in refluxing chloroform solution to give *cis*-[$Mn(CO)_2L_4$]X (X^- = PF_6^- or BPh_4^-) (VIII). Under similar conditions, only reduction of (V) and (VI; L = PMe_2Ph) occurs to give *mer-cis*-[$Mn(CO)_2L_3Br$], (L = PMe_3 and PMe_2Ph). The carbonyl i.r. spectra of the colourless, diamagnetic salts (VIII) indicate a *cis*-configuration of the CO groups (see Table 1). The methyl ^1H n.m.r. spectra of these compounds contain resonances characteristic of the phosphite ligands not being in a plane.[12] The salts are highly stable towards isomerisation as well as towards $NaBH_4$ reduction, bromine oxidation and substitution with CO or L in refluxing organic solvents. They were further oxidised with $NOPF_6$ in dichloromethane solution to give deep violet species which for L = $P(OEt)_3$ and $P(OMe)_3$ rapidly revert to *cis*-[$Mn(CO)_2L_4$]$^+$ in the absence of $NOPF_6$. For L = $P(OMe)_2Ph$ however, the product was isolated as the dicationic salt, *trans*-[$Mn(CO)_2\{P(OMe)_2Ph\}_4$]$(PF_6)_2$ (X). Although a similar dication has been previously prepared [9] (*viz.* [$Mn(CO)_2(DPE)_2$] $^{2+}$) by bromine oxidations, dipositive carbonyl cations of manganese are virtually unknown. Complex (X) is reduced in warm alcoholic solutions or by the action of $NaBH_4$ to [VIII; L = $P(OMe)_2Ph$] but hydrazine reduction in dichloromethane solution affords *trans*-[$Mn(CO)_2\{P(OMe)_2Ph\}_4$]PF_6 (IX), quantitatively. The configurations of (IX) and (X) were assigned from the characteristic $\nu_{(CO)}$ band pattern (see Table 1). The ^1H n.m.r. spectrum of the methyl groups in (IX) is also characteristic of compounds with four phosphite ligands in a plane.[12] (See Table 2.) As with the *cis*-isomer, (IX) is highly stable towards carbonylation reactions in organic solvents, and towards isomerisation. This is in contrast to the rapid carbonylation and isomerisation reactions undergone by the neutral, highly substituted complexes of manganese(I).[8]

The increasing ease of formation of [$Mn(CO)_{5-x}L_xBr$]PF_6 as x increases, reflects the expected ease of oxidation as the electron density on the central metal atom increases (and hence with decreasing $E_{\frac{1}{2}}$ values) [13] on replacing carbonyls with stronger σ-donor ligands. The increase in stability towards reduction of the oxidised product as x increases, is similarly explained. The general series of reactions of [$Mn(CO)_{5-x}L_xBr$] with $NOPF_6$ and the reactions of the salts [VI; L = $P(OMe)_3$, $P(OEt)_3$ and $P(OMe)_2Ph$] with ligands L, is summarised in the Scheme. The formation of substituted solvolysed species during treatment of [$Mn(CO)_5Br$] and *cis*-[$Mn(CO)_4(PMe_2Ph)Br$] with $NOPF_6$ in warm acetonitrile solution is postulated to occur *via* an oxidised product (A) in the Scheme, [*i.e.*, a kinetically labile high spin manganese(II) complex], corresponding to the red coloured species observed in nitromethane and acetonitrile solutions. No cationic salts were detected from corresponding reactions of [$Mn(CO)_5Br$] and *cis*-[$Mn(CO)_4(PMe_2Ph)Br$] in acetonitrile solution without NO^+. If the reaction of *mer-cis*-[$Mn(CO)_2\{P(OMe)_2Ph\}_3Br$] with NO^+ is performed in hot acetonitrile solution we obtain * a mixture of the cationic

$$\begin{tikzcd}
{[\mathrm{Mn(CO)}_{5-x}\mathrm{L}_x\mathrm{Br}]} \arrow[r, "(i)"] & {[\mathrm{Mn(CO)}_{5-x}\mathrm{L}_x\mathrm{Br}]^+ \quad (\mathrm{A})} \arrow[d, "(ii)"'] \\
{\underset{(\mathrm{C})}{[\mathrm{Mn(CO)}_{5-x}\mathrm{L}_x(\mathrm{L}')]^+}} & {\underset{(\mathrm{B})}{[\mathrm{Mn(CO)}_{5-x}\mathrm{L}_x(\mathrm{L}')]^{2+}} + \mathrm{Br}^-} \arrow[l, "(iii)"']
\end{tikzcd}$$

SCHEME (*i*) NO^+–solvent; (*ii*) L′, heat (L′ = CH_3CN or L); (*iii*) reduction

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* We have fully characterised a series of solvolysed cationic compounds of the types [$Mn(CO)_{5-x}L_x(CH_3CN)$]$^+$ and [$Mn(CO)_{4-x}L_x(CH_3CN)_2$]$^+$, including those members of the series mentioned here, which were more conveniently prepared by the action of $AgClO_4$ on the series [$Mn(CO)_{5-x}L_xBr$] in acetonitrile solution. These compounds form the basis of the next paper in this series, now in preparation.

[11] P. M. Treichel and J. J. Benedict, *J. Organometallic Chem.*, 1969, **17**, P37.

[12] L. M. Haines and E. Singleton, *J.C.S. Dalton*, 1972, 1891.

[13] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J.C.S. Dalton*, 1972, 1246.

salts $[Mn(CO)_2\{P(OMe)_2Ph\}_3(CH_3CN)]PF_6$ (80%) and $[Mn(CO)_2\{P(OMe)_2Ph\}_2(CH_3CN)_2]PF_6$ (20%), although the reaction does not proceed as readily as for $[Mn(CO)_5Br]$ and *cis*-$[Mn(CO)_4(PMe_2Ph)Br]$.

We have as yet been unable to isolate any of the dicationic solvolysed intermediates [(B) in the Scheme] from these reaction solutions. We have, however, succeeded in synthesising $[Mn(CO)_2\{P(OMe)_2Ph\}_3(CH_3CN)](PF_6)_2$ by $NOPF_6$ oxidation of $[Mn(CO)_2\{P(OMe)_2Ph\}_3(CH_3CN)]PF_6$ in dichloromethane solution. This dicationic salt was shown to readily reduce to the monocationic species in hot acetonitrile solution.

For the substitution reactions of the high spin manganese(II) systems [VI; $L = P(OMe)_3$, $P(OEt)_3$, and $P(OMe)_2Ph$] corresponding to (A) in the Scheme, with L to give the tetrasubstituted products (VIII), we propose a similar mechanism, in support of which we have isolated the easily reducible compound (X) = (B) and also [VIII; $L = P(OMe)_2Ph$] = (C) in the Scheme. We have discounted a reduction mechanism of (A) to give *mer-cis*-$[Mn(CO)_2L_3Br]$, followed by direct substitution to give (C; $x = 3$, $L' = L$), as further reaction of *mer-cis*-$[Mn(CO)_2L_3Br]$ with L has been shown[8] to give $[Mn(CO)L_4Br]$ for $L = P(OMe)_3$ and no higher substituted products for $L = P(OEt)_3$ and $P(OMe)_2Ph$.

Addition of silver nitrate to all the reactions involving bromide ligand exchange, gave characteristic AgBr precipitates. From this we assume that the bromide ligand is preferentially labilised in these high spin complexes as Br^- although we have no evidence to show why we found the bromide of the neutral $[Mn(CO)_{5-x}L_xBr]$ species to be more readily replaced for $x = 0$ and 1 than for $x = 3$.

EXPERIMENTAL

All parent compounds of the type $[Mn(CO)_{5-x}L_xBr]$, (L = phosphine or phosphite) were prepared as described previously.[8] $NOPF_6$ was obtained commercially and not further purified. M.ps. were obtained on a Kofler hot stage apparatus and conductivities on a Van Waters and Rogers model 31 conductivity bridge. I.r. spectra were recorded using a Perkin-Elmer 457 grating spectrophotometer and ^1H n.m.r. spectra with a Varian A60A instrument. Elemental analyses were performed in this laboratory. All physical data for the compounds prepared is presented in Tables 1 and 2.

Preparation of cis-$[Mn(CO)_4(PMe_2Ph)(CH_3CN)]BPh_4$.—An excess of $NOPF_6$ was added to a solution of *cis*-$[Mn(CO)_4(PMe_2Ph)Br]$ (0·5 g) in acetonitrile (10 ml). After initially darkening in colour, the solution lightened and NO gas was evolved. Precipitation was effected by the addition of an ethanolic solution of sodium tetraphenylborate (0·25 g) and recrystallisation from dichloromethane–ethanol gave the required product as plates. (Yield: 0·35 g.)

Preparation of fac-$[Mn(CO)_3(PMe_2Ph)_2Br]PF_6$.—An excess of $NOPF_6$ was added to a solution of *fac*- or *mer-trans*-$[Mn(CO)_3(PMe_2Ph)_2Br]$, (0·5 g) in benzene (8 ml). The solution rapidly darkened together with the evolution of NO gas and green crystals separated out. These were filtered off and recrystallised from chloroform–light petroleum (b.p. 60—80°) to give the product as plates. (Yield: 0·32 g.)

Similarly prepared was *fac*-$[Mn(CO)_3(dpm)Br]PF_6$ from *fac*-$[Mn(CO)_3(dpm)Br]$ and recrystallised from dichloromethane–ethanol as microcrystals.

Preparation of mer-trans-$[Mn(CO)_2(PMe_2Ph)_3Br]PF_6$.—An excess of $NOPF_6$ was added to a suspension of *mer-cis*-$[Mn(CO)_2(PMe_2Ph)_3Br]$, (0·5 g) in ethanol (8 ml) at 0°. Gas was liberated (NO) as the compound dissolved and blood-red crystals separated from the darkened solution. After 15 min the reaction was complete and the crystals were filtered off and recrystallised from dichloromethane–ethanol to give the product as needles. (Yield: 0·38 g.)

Preparation of fac-$[Mn(CO)_3\{P(OMe)_3\}_2Br]PF_6$.—A solution of *fac*- or *mer-trans*-$[Mn(CO)_3\{P(OMe)_3\}_2Br]$, (0·5 g) in dichloromethane (10 ml) was treated with an excess of $NOPF_6$, giving a deepening of colour and liberation of gas (NO). After 5 min the excess of $NOPF_6$ was filtered off and cold ethanol was added to the violet solution. Removal of the dichloromethane under reduced pressure then gave the required product as needles. (Yield: 0·31 g.)

Similarly prepared and recrystallised from dichloromethane–ethanol were: *fac*-$[Mn(CO)_3(PMe_3)_2Br]PF_6$ from *fac*- or *mer-trans*-$[Mn(CO)_3(PMe_3)_2Br]$ as microcrystals, *mer-cis*-$[Mn(CO)_2(PMe_3)_3Br]PF_6$ from *mer-cis*-$[Mn(CO)_2(PMe_3)_3Br]$ as needles, *mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]PF_6$ from *mer-cis*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$ as plates, *mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]PF_6$ from *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]$ as plates, *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4](PF_6)_2$ from *cis*- or *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]PF_6$ as plates and $[Mn(CO)(NO)\{P(OMe)_3\}_4](PF_6)_2$ from $[Mn(CO)\{P(OMe)_3\}_4Br]$ as microcrystals, with final crystallisation requiring addition of pentane. The complex *mer-trans*-$[Mn(CO)_2\{P(OEt)_3\}_3Br]PF_6$, prepared from *mer-cis*-$[Mn(CO)_2\{P(OEt)_3\}_3Br]$, was isolated only as a red oil.

Preparation of cis-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]PF_6$.—A solution of *mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]PF_6$, (1·0 g) and phenyldimethoxyphosphine (0·6 g) in chloroform (8 ml) was refluxed for 2 h, during which time the colour lightened from deep red to pale orange. On cooling, white crystals separated out which were recrystallised from dichloromethane–ethanol to give the required product as prisms. (Yield: 0·88 g.)

Preparation of cis-$[Mn(CO)_2\{P(OMe)_3\}_4]BPh_4$.—This compound was prepared from *mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]PF_6$ in a manner similar to that described above for the $P(OMe)_2Ph$ analogue. Crystals were only obtained from the reaction solution after addition of an ethanolic solution of sodium tetraphenylborate. These were recrystallised from dichloromethane–ethanol to give the required product as prisms. Similarly prepared and recrystallised from dichloromethane–methanol was *cis*-$[Mn(CO)_2\{P(OEt)_3\}_4]BPh_4$, from *mer-trans*-$[Mn(CO)_2\{P(OEt)_3\}_3Br]PF_6$, as plates.

Preparation of trans-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]PF_6$.—Treatment of a solution of *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4](PF_6)_2$ (0·8 g) in dichloromethane (10 ml) with anhydrous hydrazine (0·3 ml) at 0°, gave a white precipitate which was filtered off. Addition of ethanol to the concentrated, colourless solution gave the required product which was recrystallised from dichloromethane–ethanol as plates. (Yield: 0·69 g.)

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