# Reactions of Metal Carbonyls. Part VI.[1] Formation of Cationic Carbonyl Salts of Manganese-(I) and -(II)

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The salt *fac*-$[Mn(CO)_3(MeCN)_3]PF_6$ has been prepared by heating under reflux $[Mn(CO)_5Br]$ in acetonitrile. It rapidly undergoes substitution of the acetonitrile groups with phosphines and phosphites (L) to give the species *fac*-$[Mn(CO)_3L(MeCN)_2]^+$, *fac*-$[Mn(CO)_3L_2(MeCN)]^+$, *cis*-$[Mn(CO)_2L_2(MeCN)_2]^+$, and *mer-cis*-$[Mn(CO)_2L_3(MeCN)]^+$ under varying reaction conditions. These cations are also formed on treating the complexes $[Mn(CO)_{5-x}L_xBr]$ ($x$ = 1—3) with $AgPF_6$ in acetonitrile. The dicarbonyl cations *cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_2(MeCN)_2]^+$ and *mer-cis*-$[Mn(CO)_2L_3(MeCN)]^+$ are oxidised by $NOPF_6$ to give *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_2(MeCN)_2]^{2+}$ and *mer-trans*-$[Mn(CO)_2L_3(MeCN)]^{2+}$ [L = $P(OMe)_2Ph$ and $P(OMe)_3$]. Hydrazine reduction of the cation *mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)]^{2+}$ gives *mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)]^+$ which reacts further with $P(OMe)_3$ to give *trans*-$[Mn(CO)_2\{P(OMe)_3\}_4]^+$. $^1H$ N.m.r. resonances of the nitrile methyl groups exhibit some unusual features which are discussed, together with steric factors governing the reactions.

THOUGH the binary cationic manganese(I) carbonyl $[Mn(CO)_6]^+$ is known,[2] the apparent low kinetic lability of its carbonyl groups [3] has discouraged its use as a route to substituted manganese carbonyl cations. Hence the absence of a suitable precursor for these species has resulted in many being prepared indirectly.[4] The most common route which has been used is halogen abstraction from a manganese carbonyl halide complex using aluminium trichloride in the presence of a neutral ligand, which requires stringent anhydrous conditions. Our current interest [1,5,6] in the formation and reactivity of transition-metal cations has prompted us to seek a simpler way to substituted cationic carbonyl salts of manganese *via* the co-ordinated acetonitrile group, the ease of substitution of this group being well established [7,8] for other transition-metal complexes. We have briefly communicated [9] that the trinitrile species $[Mn(CO)_3(MeCN)_3]PF_6$, (I), is readily formed by heating under reflux $[Mn(CO)_5Br]$ in acetonitrile and is an ideal precursor for further reactions, and thus we have now investigated the reactions of (I) with a representative series of phosphines and phosphites. The mixed-ligand complexes that result from these substitution reactions may also be prepared by treatment of acetonitrile solutions of the series $[Mn(CO)_{5-x}L_xBr]$ (L = phosphine or phosphite) [10] with $AgPF_6$, which is a much more convenient halogen abstractor than aluminium trichloride. $^1H$ N.m.r. and i.r. data for all these complexes are listed in Tables 1 and 2.

## RESULTS AND DISCUSSION

The salt $[Mn(CO)_3(MeCN)_3]PF_6$, (I), was prepared by heating under reflux $[Mn(CO)_5Br]$ in acetonitrile for 1 h and isolated in almost quantitative yield from an ethanolic solution, containing $NH_4PF_6$, on addition of water. The *fac*-configuration of salt (I) was assigned from two strong ν(CO) bands in the i.r. spectrum, indicative of $C_{3v}$ symmetry.

Treatment of salt (I) with dimethylphenylphosphine in refluxing chloroform gave *fac*-$[Mn(CO)_3L(MeCN)_2]^+$ (II; L = $PMe_2Ph$) with a 1 : 1 ratio of ligand to metal and *fac*-$[Mn(CO)_3L_2(MeCN)]^+$ (III; L = $PMe_2Ph$) with an excess of ligand. Similar reaction of salt (I) with an excess of trimethyl phosphite gave only [II; L = $P(OMe)_3$]. The three ν(CO) bands observed for cations (II) and (III) imply [11] either that the degeneracy of the *E* mode has been lifted in the *fac*-isomer because of lowering of symmetry from $C_{3v}$ to $C_s$ by the different ligands, or that the complexes exist as *mer*-isomers. However, these bands closely resemble the pattern observed [10] for the series *fac*-$[Mn(CO)_3L_2Br]$, implying that the carbonyl configuration of (I) is retained. $^1H$ N.m.r. spectra of cations (II) contained 1 : 1 methyl doublets, as expected for the phosphine and phosphite groups, but for (III) an intermediate coupling pattern was observed which may be indicative of either *cis*- or *trans*-phosphine ligands. We have previously observed [10] strong $^{31}P$–$^{31}P$ coupling in the complex *fac*-$[Mn(CO)_3(PMe_2Ph)_2Br]$, which we attributed to distortion within the molecule from ideal octahedral symmetry due probably to steric repulsion of the *cis*-phosphine ligands.

The reaction of (I) with 2 moles of ligand L [$P(OMe)_2Ph$, $P(OMe)_3$, and $PMe_2Ph$] per mole of salt in refluxing acetonitrile gave the cations *cis*-$[Mn(CO)_2L_2(MeCN)_2]^+$, (IV). The two strong ν(CO) bands in the i.r. spectra of cations (IV) indicate that the carbonyl groups are mutually *cis*-bonded. The configuration of the other ligands is unknown as intermediate $^{31}P$–$^{31}P$ coupling was again observed for the phosphine and phosphite methyl groups in the $^1H$ n.m.r. spectra.

With an excess of ligand L [$P(OMe)_2Ph$ and $P(OMe)_3$] in refluxing acetonitrile, salt (I) is rapidly converted to the cation *mer-cis*-$[Mn(CO)_2L_3(MeCN)]^+$, (V), but for

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L = $PMe_2Ph$ the reaction does not proceed beyond (IV; L = $PMe_2Ph$). Because of the ease with which $PMe_2Ph$ replaces MeCN in the reactions forming the cations (II; L = $PMe_2Ph$) and (III; L = $PMe_2Ph$) we attribute our inability to obtain (V; L = $PMe_2Ph$) to steric rather than electronic factors. The configuration of the cations (V) was unequivocally assigned from two strong ν(CO) bands in the i.r. spectra and an $^1H$ n.m.r. methyl resonance for [V; L = $P(OMe)_2Ph$] which is characteristic of three meridional phosphines.[10] For cation [V; L = $P(OMe)_3$] the $^1H$ n.m.r. methyl resonance was not unequivocal but a similar configuration is assumed by analogy.

TABLE 1

M.p.s, conductivities, and i.r. spectroscopic data ($cm^{-1}$)

| Complex | M.p. ($t$/°C) | Conductivity/ $\Omega^{-1}$ $cm^2$ $mol^{-1}$ | ν(CO) [a] | ν(CN) [b] |
|---|---|---|---|---|
| *fac*-$[Mn(CO)_3(MeCN)_3]PF_6$ (I) | 131—133 [c] | 128 | 2 060s, 1 982s,br | 2 328, 2 300 |
| *cis*-$[Mn(CO)_4(PMe_2Ph)(MeCN)]BPh_4$ (VI) | 143 | 109 | 2 105m, 2 035sh, 2 020s, 1 997m | 2 325, 2 296 |
| *fac*-$[Mn(CO)_3\{P(OMe)_3\}(MeCN)_2]PF_6$ (II) | 117—119 | 155 | 2 064s, 1 997s, 1 965s | 2 332, 2 304 |
| *fac*-$[Mn(CO)_3(PMe_2Ph)(MeCN)_2]BPh_4$ (II) | 148—153 [c] | 105 | 2 059s, 1 982s, 1 954s [d] | 2 326, 2 297 |
| *fac*-$[Mn(CO)_3(PMe_2Ph)_2(MeCN)]PF_6$ (III) | 132—135 | 138 | 2 034s, 1 972m, 1 945s | 2 323, 2 293 |
| $[Mn(CO)_3\{P(OMe)_2Ph\}_2(MeCN)]BPh_4$ (VII) | 96 | 90 | 2 070w, 1 991s, 1 967m | 2 330, 2 298 |
| $[Mn(CO)_3\{P(OMe)_3\}_2(MeCN)]PF_6$ (VII) | 141 | 151 | 2 083w, 2 001s, 1 975m | 2 320, 2 292 |
| $[Mn(CO)_3(PMe_2Ph)_2(MeCN)]ClO_4$ (VII) | 108—112 | 131 | 2 067w, 1 974s, 1 940m | 2 329, 2 297 |
| *cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_2(MeCN)_2]ClO_4$ (IV) | 121—122 | 130 | 1 974s, 1 908s [d] | 2 332, 2 301 |
| *cis*-$[Mn(CO)_2\{P(OMe)_2\}_2(MeCN)_2]PF_6$ (IV) | 81—83 [c] | 163 | 1 988s, 1 919s | 2 314, 2 288 |
| *cis*-$[Mn(CO)_2(PMe_2Ph)_2(MeCN)_2]PF_6$ (IV) | 126—129 [c] | 149 | 1 951s, 1 882s | Very weak |
| *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(MeCN)]PF_6$ (V) | 160—162 | 154 | 1 986s, 1 916s | Very weak |
| *mer-cis*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)]PF_6$ (V) | 126—129 | 136 | 1 996s, 1 927s | 2 330, 2296 |
| *mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(MeCN)]PF_6$ (X) | 132—138 | 148 | 2 035w, 1 937s | Very weak |
| *mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)]PF_6$ (X) | 120—125 | 155 | 2 047w, 1 946s | Very weak |
| *trans*-$[Mn(CO)_2\{P(OMe)_3\}_4]PF_6$ (XI) | 240—243 | 160 | 2 033w, 1 942s | |
| *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_2(MeCN)_2](PF_6)_2$ (VIII) | 67 [c] | 214 | 2 105w, 2 029s [d] | 2 323, 2 295 |
| *mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(MeCN)](PF_6)_2$ (IX) | 117—121 [c] | 254 | 2 093w, 2 014s [d] | 2 336, 2 303 |
| *mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)](PF_6)_2$ (IX) | 124—128 [c] | 212 | 2 104w, 2 034s [d] | 2 329, 2 296 |
| *trans*-$[Mn(CO)_2\{P(OMe)_3\}_4](PF_6)_2$ (XII) | 185—195 [c] | 235 | 2 076w, 2 008s [d] | |

[a] In $CHCl_3$ unless otherwise stated. [b] Nujol mull spectra. These bands were proportionately very much weaker than the ν(CO) bands. [c] With decomposition. [d] In $CH_2Cl_2$.

TABLE 2

Microanalytical and $^1H$ n.m.r. data

| | Found (Calc.) (%) | | | |
|---|---|---|---|---|
| Complex | C | H | N | $^1H$ N.m.r. data (τ) ($J$/Hz) [a] |
| *fac*-$[Mn(CO)_3(MeCN)_3]PF_6$ (I) | 26·3 (26·55) | 2·15 (2·25) | 10·15 (10·35) | 7·60 (s) |
| *cis*-$[Mn(CO)_4(PMe_2Ph)(MeCN)]BPh_4$ (VI) | 68·3 (68·6) | 5·20 (5·15) | 2·25 (2·10) | 8·15 (d) [$J_{(P-H)}$ 9·5],<br>8·73 (d) [$J_{(P-H)}$ 1·8] |
| *fac*-$[Mn(CO)_3\{P(OMe)_3\}(MeCN)_2]PF_6$ (II) | 24·7 (24·5) | 3·05 (3·10) | 6·05 (5·70) | 6·10 (d) [$J_{(P-H)}$ 10·9],<br>7·59 (d) [$J_{(P-H)}$ 1·9] |
| *fac*-$[Mn(CO)_3(PMe_2Ph)(MeCN)_2]BPh_4$ (II) | 68·75 (69·05) | 5·75 (5·50) | 4·35 (4·15) | 8·18 (d) [$J_{(P-H)}$ 8·6],<br>8·56 (d) [$J_{(P-H)}$ 1·7] [b] |
| *fac*-$[Mn(CO)_3(PMe_2Ph)_2(MeCN)]PF_6$ (III) | 42·05 (41·95) | 4·05 (4·20) | 2·30 (2·35) | 8·30 (i) ($J^*$ 8·8),<br>7·78 (t) [$J_{(P-H)}$ 2·2] |
| $[Mn(CO)_3\{P(OMe)_2Ph\}_2(MeCN)]BPh_4$ (VII) | 64·35 (64·4) | 5·40 (5·40) | 1·85 (1·70) | 6·27 (i) ($J^*$ 12·0), 9·15 (t) [$J_{(P-H)}$ 1·9] |
| $[Mn(CO)_3\{P(OMe)_3\}_2(MeCN)]PF_6$ (VII) | 22·9 (23·05) | 3·50 (3·70) | 2·45 (2·45) | 6·12 (i) ($J^*$ 11·0), 7·64 (t) [$J_{(P-H)}$ 1·9] |
| $[Mn(CO)_3(PMe_2Ph)_2(MeCN)]ClO_4$ (VII) | 45·15 (45·4) | 4·70 (4·55) | 2·65 (2·50) | 8·07 (m) [b] |
| *cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_2(MeCN)_2]ClO_4$ (IV) | 41·8 (41·8) | 4·50 (4·45) | 4·20 (4·45) | 6·23 (i) ($J^*$ 11·4), 8·18 (dt) [b] |
| *cis*-$[Mn(CO)_2\{P(OMe)_3\}_2(MeCN)_2]PF_6$ (IV) | 24·75 (24·6) | 4·30 (4·15) | 4·55 (4·80) | 6·19 (i) ($J^*$ 10·8), 7·64 (t) [$J_{(P-H)}$ 2·0] |
| *cis*-$[Mn(CO)_2(PMe_2Ph)_2(MeCN)_2]PF_6$ (IV) | 43·3 (43·0) | 4·60 (4·60) | 4·45 (4·55) | 8·18 (m) [b] |
| *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(MeCN)]PF_6$ (V) | 41·85 (41·65) | 4·45 (4·50) | 2·05 (1·75) | 6·27 (i) ($J^*$ 11·0), 6·30 (d) [$J_{(P-H)}$ 10·7],<br>8·78 (q) [$J_{(P-H)}$ 2·2] |
| *mer-cis*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)]PF_6$ (V) | 23·55 (23·35) | 4·60 (4·50) | 1·95 (2·10) | 6·20 (dt) ($J^*$ 10·2),<br>7·72 (q) [$J_{(P-H)}$ 2·2] |
| *mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(MeCN)]PF_6$ (X) | 41·5 (41·65) | 4·20 (4·50) | 1·75 (1·75) | 6·34 (i) ($J^*$ 11·0),<br>6·44 (d) [$J_{(P-H)}$ 10·8], 8·58 (m) [b] |
| *mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)]PF_6$ (X) | 23·6 (23·35) | 4·65 (4·50) | 1·95 (2·10) | 6·23 (i) ($J^*$ 11·0),<br>6·37 (d) [$J_{(P-H)}$ 10·8], 7·77 (dt) [b] |
| *trans*-$[Mn(CO)_2\{P(OMe)_3\}_4]PF_6$(XI) | 22·6 (22·35) | 4·80 (4·80) | | 6·21 (m) [c] |
| *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_2(MeCN)_2](PF_6)_2$ (VIII) | 30·35 (32·1) | 3·30 (3·45) | 3·00 (3·40) | Paramagnetic |
| *mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(MeCN)](PF_6)_2$ (IX) | 35·6 (35·3) | 3·90 (3·80) | 1·45 (1·45) | Paramagnetic |
| *mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)](PF_6)_2$ (IX) | 19·3 (19·2) | 3·80 (3·70) | 1·60 (1·70) | Paramagnetic |
| *trans*-$[Mn(CO)_2\{P(OMe)_3\}_4](PF_6)_2$ (XII) | 19·0 (18·75) | 4·00 (4·05) | | Paramagnetic |

[a] Recorded in $CD_2Cl_2$ solution using a Varian A-60A instrument; s = singlet, d = doublet, t = triplet, dt = distorted triplet, q = quartet i = intermediate coupling pattern, for which $J^*$ = the separation of the outer peaks of the observed resonance and represents $|^2J_{(P-H)} + {}^4J_{(P-H)}|$ (R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275). [b] Recorded using a Varian HA-100 instrument. [c] Characteristic symmetrical resonance (see ref. 5).

In contrast to the parent carbonyl, the phosphine and phosphite substituted derivatives of the complex [$Mn(CO)_5Br$], namely [$Mn(CO)_{5-x}L_xBr$] ($x = 1$—3), seemed to reach an equilibrium in refluxing acetonitrile, resulting in much lower yields of the solvolysed salts. However, when the reaction solutions were treated with $AgPF_6$, the yields improved. This trend in decreasing ease of halogen replacement as carbonyl substitution of the complex [$Mn(CO)_5Br$] increases has been noted previously.[4] Thus the complex *cis*-[$Mn(CO)_4(PMe_2Ph)Br$] [12] reacted rapidly with $AgPF_6$ in hot acetonitrile to give only (II; L = $PMe_2Ph$), in which replacement of one of the mutually *trans* carbonyl groups has occurred. To obtain the tetracarbonyl derivative it was necessary to utilise a method related to preparation of the cation [$Mn(CO)_5(MeCN)$]$^+$ from [$Mn_2(CO)_{10}$],[13] *i.e.* treatment of [$Mn(CO)_4(PMe_2Ph)$]$_2$ with $NOPF_6$ in acetonitrile. This gave *cis*-[$Mn(CO)_4L(MeCN)$]$^+$, (VI; L = $PMe_2Ph$), in moderate yield. The i.r. spectrum of cation (VI) exhibited ν(CO) bands typical of the *cis*-isomer of $C_s$ symmetry and the $^1H$ n.m.r. spectrum contained a 1 : 1 methyl doublet for the phosphine group.

Treatment of the complexes *mer-trans*-[$Mn(CO)_3L_2Br$] [L = $P(OMe)_2Ph$, $P(OMe)_3$, and $PMe_2Ph$] with $AgPF_6$ in warm acetonitrile gave [$Mn(CO)_3L_2(MeCN)$]$^+$, (VII), a second isomer of (III), in high yield. I.r. spectra of these cations exhibited one weak and two strong carbonyl bands and did not distinguish between the *mer-trans*-isomers of $C_{2v}$ symmetry and the *mer-cis*-isomers of $C_s$ symmetry. Furthermore, intermediate coupling patterns observed for ligand methyl groups in the $^1H$ n.m.r. spectra could not be used to distinguish between *cis*- and *trans*-bonded phosphines, so that no accurate structural assignment was possible. When the above halogen-abstraction reactions of the complexes *mer-trans*-[$Mn(CO)_3L_2Br$] with $AgPF_6$ were carried out in refluxing acetonitrile, decarbonylation occurred to give mixtures of the tricarbonyl (VII) and the disolvolysed dicarbonyl (IV) after 15 min for each of the three ligands used. The cations (IV) were more conveniently obtained as the sole products of the reactions of the complexes *mer-cis*-[$Mn(CO)_2L_3Br$] [L = $P(OMe)_2Ph$, $P(OMe)_3$, and $PMe_2Ph$] with $AgPF_6$ in warm acetonitrile.

This ready loss of the neutral ligand, L, from the complexes *mer-cis*-[$Mn(CO)_2L_3Br$] to give cations (IV) parallels our previous observations [10] on carbonylation reactions of *mer-cis*-[$M(CO)_2L_3Br$] (M = Mn and Re), which we ascribed to steric effects within the molecule. Surprisingly, when the reaction of the complexes *mer-cis*-[$Mn(CO)_2L_3Br$] [L = $P(OMe)_2Ph$ and $P(OMe)_3$] with $AgPF_6$ was carried out in refluxing acetonitrile, a mixture of [IV; L = $P(OMe)_2Ph$ and $P(OMe)_3$] and [V; L = $P(OMe)_2Ph$ and $P(OMe)_3$] was obtained. The relative ratios of cations (IV) and (V) obtained from different runs of this reaction were found to vary, although highly concentrated solutions appeared to favour (V), implying that this species was formed due to ligand attack on (IV) by the displaced phosphite. The failure to prepare cation (V; L = $PMe_2Ph$) by this method can again be attributed to steric factors.

Only the dicarbonyl species (IV) and (V) were readily oxidised by $NOPF_6$ in dichloromethane to give deeply coloured solutions containing $Mn^{II}$ cations. By contrast, the tri- and tetra-carbonyl species did not undergo similar oxidation reactions. We have observed previously [1] that only substituted derivatives of the complex [$Mn(CO)_5Br$] containing three phosphine or phosphite ligands gave stable $Mn^{II}$ oxidised products. Reaction of cation [IV; L = $P(OMe)_2Ph$] with $NOPF_6$ in dichloromethane gave *trans*-[$Mn(CO)_2L_2(MeCN)_2$]$(PF_6)_2$ (VIII), as an air-sensitive solid. Corresponding reactions of cations [IV; L = $P(OMe)_3$ and $PMe_2Ph$] gave only air-sensitive oils which were too readily reduced in the absence of $NOPF_6$ to allow characterisation. The *trans*-configuration of the carbonyl groups in cations (VIII) was confirmed by the single strong ν(CO) band in the i.r. spectrum, but the configuration of the other ligands could not be established from $^1H$ n.m.r. spectra of this paramagnetic complex. Attempts to prepare a *trans*-isomer of the cation [IV; L = $P(OMe)_2Ph$] by hydrazine reduction of (VIII) failed, although we have successfully utilised this method [1] to prepare *trans*-[$Mn(CO)_2\{P(OMe)_2Ph\}_4$]$PF_6$ from *trans*-[$Mn(CO)_2\{P(OMe)_2Ph\}_4$]$(PF_6)_2$ previously. Hydrazine reduction of cations (VIII) resulted in some disproportionation and i.r. solution spectra indicated that only mixtures of the products [IV; L = $P(OMe)_2Ph$] and [V; L = $P(OMe)_2Ph$] had formed in low yield.

Reaction of cations [V; L = $P(OMe)_2Ph$ and $P(OMe)_3$] with $NOPF_6$ in dichloromethane gave the stable dicationic salts *mer-trans*-[$Mn(CO)_2L_3(MeCN)$]$(PF_6)_2$, (IX). The configurations were unequivocally assigned from the single strong ν(CO) band in the i.r. spectra ($C_{2v}$ symmetry) and the paramagnetic nature of the salts was confirmed by $^1H$ n.m.r. spectroscopy. These carbonyl dications are of interest as very few are known for manganese.[1,14,15] The salts (IX) were successfully reduced with hydrazine in dichloromethane to give *mer-trans*-[$Mn(CO)_2L_3(MeCN)$]$^+$ [X; L = $P(OMe)_2Ph$ and $P(OMe)_3$] and their configurations were confirmed by i.r. and $^1H$ n.m.r. spectroscopy [10] (see Table 2).

The cation [X; L = $P(OMe)_3$] reacts further with an excess of trimethyl phosphite in refluxing chloroform to give the salt *trans*-[$Mn(CO)_2\{P(OMe)_3\}_4$]$PF_6$, (XI). A similar reaction of the cation [X; L = $P(OMe)_2Ph$] with an excess of $P(OMe)_2Ph$ gave *trans*-[$Mn(CO)_2\{P(OMe)_2Ph\}_4$]$PF_6$ which we have characterised previously.[1] The salt (XI) was characterised from the single strong ν(CO) band in the i.r. spectrum ($D_{4h}$ symmetry) and an $^1H$ n.m.r. methyl resonance indicative of four ligands in a plane.[5] We have previously isolated the *cis*-isomer of (XI) as the $BPh_4^-$ salt [1] and found that this could not be oxidised to the dicationic species with $NOPF_6$. We

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[12] R. H. Reimann, M.Sc. Thesis, University of South Africa, 1971.

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

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

[15] P. M. Treichel, G. E. Dirreen, and H. J. Mueh, *J. Organometallic Chem.*, 1972, **44**, 339.

now find that reaction of salt (XI) with $NOPF_6$ in dichloromethane gives quantitative formation of *trans*-$[Mn(CO)_2\{P(OMe)_3\}_4](PF_6)_2$, (XII), and conclude that the previous failure to obtain (XII) was due to the presence of $BPh_4^-$ which is a reducing agent towards these species.

I.r. spectra of all these complexes contain two $\nu$(CN) bands at a higher frequency than those observed for unco-ordinated acetonitrile and are indicative of an *N*-bonded ligand. The band observed at higher frequency in the range 2 314—2 336 cm$^{-1}$ is a combination band[16] of the symmetric Me deformation ($\nu_3$) and symmetric C–C stretch ($\nu_4$). The lower band is due to the symmetric C–N stretch ($\nu_2$) and occurs between 2 288 and 2 304 cm$^{-1}$. The increase on co-ordination over the values observed for free acetonitrile has been explained in terms of increased $\sigma$-bonding between C and N which increases the C≡N force constant.[17] Values obtained for $\nu$(CN) tend to be insensitive to the oxidation state of the metal and the presence of other co-ordinated ligands, and hence the changes in $\nu$(CN) found here were too small to be of use in assigning structures to the complexes.

$^1$H N.m.r. spectra however, showed large variations in the position of the nitrile proton resonances. The methyl resonance of co-ordinated acetonitrile normally appears downfield from the unco-ordinated position ($\tau$ 8·05 in $CD_2Cl_2$ solution). We find that a downfield shift occurs only for salt (I) and trimethyl phosphite-substituted derivatives of (I), the average value of the shift being $\tau$ 0·39. All complexes containing $P(OMe)_2Ph$ or $PMe_2Ph$, with the exception of cation (III; L = $PMe_2Ph$), showed either a near zero or an upfield shift and there appears to be no relation between the nitrile methyl-resonance position and the combined $\sigma$-donor properties of the other ligands. We conclude that the shifts are probably due to the 'neighbour-anisotropy effect'[18] of the phenyl rings. Similar effects have been noted previously for methyl groups attached to bonded phosphine[5] and acetate[19] ligands. Furthermore the largest upfield shifts are observed for those cations isolated as $BPh_4^-$ salts. To obtain comparable results we prepared the tetraphenylborate analogues of some of the hexafluorophosphate salts described here and find, for example, that $[Mn(CO)_3(MeCN)_3]BPh_4$ exhibits a methyl resonance at $\tau$ 8·11, an upfield shift of $\tau$ 0·51 over the $PF_6$ salt, (I). Similarly the acetonitrile methyl resonance of the salt *cis*-$[Mn(CO)_2\{P(OMe)_3\}_2(MeCN)_2]BPh_4$ exhibited an upfield shift of $\tau$ 0·45 over the $PF_6$ salt, [IV; L = $P(OMe)_3$]. No effect on the phosphite methyl resonance was observed. Previous workers have noted anomalous upfield shifts for both co-ordinated[20] and unco-ordinated[21,22] acetonitrile when measured in benzene solution.

Although a singlet resonance is predicted for the methyl protons of acetonitrile in the $^1$H n.m.r. spectra, we obtained a variety of well resolved multiplets for the present series of complexes. The presence of more than one $^1$H n.m.r. resonance for nitrile methyl protons has been previously explained as being due to acetonitrile ligands in non-identical magnetic environments[23] and coupling of the methyl protons with the nuclear quadrupole of the metal nucleus.[24] Comparison of the results in Table 2, however, shows that in the present series there is a direct correlation between the multiplicity of the nitrile methyl resonance and the number of bonded phosphine or phosphite groups in the complex. Thus the resonances vary from a singlet in salt (I), through regular 1 : 1 doublets and 1 : 2 : 1 triplets, to quartets for cations (V) which contain three phosphite groups. This $J_{(P-H)}$ coupling appears to differ in strength for phosphorus ligands in *cis*- and *trans*-position to acetonitrile, as the multiplets were observed to be irregular in cations (X) which contain both *cis*- and *trans*-phosphite ligands. For cations (VII; L = $PMe_2Ph$) and (IV; L = $PMe_2Ph$) the methyl resonances of bonded acetonitrile and dimethylphenylphosphine were overlapping and could not be distinguished. Reports of comparable complexes containing both acetonitrile and phosphine groups are not common[25-28] and $J_{(P-H)}$ coupling is rarely observed.[29] The methyl resonance of methyl isocyanide has also been observed to be a doublet when bonded *trans* to a phosphine in platinum complexes.[8]

Although the reaction of the complexes $[M(CO)_6]$ (M = Cr, Mo, and W) with acetonitrile to give $[M(CO)_3(MeCN)_3]$ has been shown[30] to proceed by accelerating stepwise replacement of the three carbonyl groups, the reaction of $[Mn(CO)_5Br]$ with acetonitrile to give salt (I) occurred too rapidly to enable us to identify intermediate solvolysed species. I.r. solution spectra of samples withdrawn during the course of the reaction did not indicate formation of the known complexes *fac*-$[Mn(CO)_3(MeCN)_2Br]$[31] or *fac*-$[Mn(CO)_5(MeCN)]^+$ (ref. 13) which might have established at which stage bromide replacement occurred. However, the low reactivity of

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carbonyl groups noted previously[3] in manganese carbonyl cations suggests that bromide replacement is the last step in the reaction.

The solvolysis reactions of the series of neutral complexes, $[Mn(CO)_{5-x}L_xBr]$ ($x = 0$—$3$) once again demonstrate the increased reactivity of mutually *trans*-bonded CO groups which we have reported previously in these systems.[10] The solvolysis products of this series may be summarised by noting that in each case the bromide ligand and all CO groups *trans* to a similar group are replaced with MeCN.

Apart from isomerisation associated with changes in oxidation state, no other isomerisations have been observed for the solvolysed cations. Interconversion of isomers did not occur even after prolonged heating under reflux in organic solvents and once again demonstrates the more inert nature of the cationic carbonyl groups compared with the neutral counterparts.

## EXPERIMENTAL

All parent complexes of the type $[Mn(CO)_{5-x}L_xBr]$ (L = phosphine or phosphite) were prepared as described previously.[10] $NOPF_6$, $AgPF_6$, and phosphine ligands were obtained commercially and not further purified. M.p.s were obtained on a Kofler hot-stage apparatus and conductivities were measured in acetone solution on a Van Waters and Rogers model 31 conductivity bridge. I.r. spectra were recorded using a Perkin-Elmer model 457 grating spectrophotometer and $^1H$ n.m.r. spectra with Varian A-60A and HA-100 instruments. Elemental analyses were carried out in this laboratory. All physical data for the complexes prepared are presented in Tables 1 and 2.

*Preparations*.—fac-$[Mn(CO)_3(MeCN)_3]PF_6$. A solution of the complex $[Mn(CO)_5Br]$ (5·0 g, 18·18 mmol) in acetonitrile (15 cm$^3$) was heated under reflux for 1 h. The dark red solution was filtered and concentrated to 4 cm$^3$ under reduced pressure. A hot solution of $NH_4PF_6$ (3·0 g, 18·40 mmol) in an equimolar mixture of water and ethanol (15 cm$^3$) was then added to give the required product. This was recrystallised from dichloromethane–ethanol as pale yellow *plates* (6·29 g). Yield 85%.

cis-$[Mn(CO)_4(PMe_2Ph)(MeCN)]BPh_4$. An excess of $NOPF_6$ was added to a solution of the complex $[Mn_2(CO)_8(PMe_2Ph)_2]$ (1·0 g, 1·64 mmol) in acetonitrile (10 cm$^3$). After an initial darkening of colour, the solution lightened again, accompanied by evolution of NO gas. After 10 min an ethanolic solution of sodium tetraphenylborate (0·60 g, 1·75 mmol) was added. Concentration of the solution under reduced pressure gave the required product which was recrystallised from dichloromethane–ethanol as colourless *plates* (0·49 g). Yield 45%.

fac-$[Mn(CO)_3(PMe_2Ph)_2(MeCN)]PF_6$. A solution of the salt *fac*-$[Mn(CO)_3(MeCN)_3]PF_6$ (1·0 g, 2·46 mmol) and dimethylphenylphosphine (0·71 g, 5·14 mmol) in chloroform (10 cm$^3$) was heated under reflux for 15 min. Cold ethanol (10 cm$^3$) was then added and removal of the chloroform under reduced pressure gave the required product which was recrystallised from dichloromethane–ethanol as pale yellow *prisms* (1·1 g). Yield 72%. Similarly prepared was *fac*-$[Mn(CO)_3\{P(OMe)_3\}(MeCN)_2]PF_6$ in 80% yield as pale yellow *plates*.

fac-$[Mn(CO)_3(PMe_2Ph)(MeCN)_2]BPh_4$. A hot solution of the complex *cis*-$[Mn(CO)_4(PMe_2Ph)Br]$ (0·6 g, 1·56 mmol) in acetonitrile was treated with $AgPF_6$ (0·59 g, 2·34 mmol). Precipitation of AgBr was observed almost immediately and i.r. solution spectra showed the conversion to be complete after 30 min. The solution was filtered while hot and an ethanolic solution (10 cm$^3$) of sodium tetraphenylborate (0·57 g, 1·67 mmol) was added. Concentration under reduced pressure gave the required product which was recrystallised from dichloromethane–ethanol as pale yellow needles (0·66 g). Yield 62%. Alternatively this complex may be prepared by the method described for preparation of *fac*-$[Mn(CO)_3(PMe_2Ph)_2(MeCN)]PF_6$, using 1·1 mol of $PMe_2Ph$ per mol of manganese.

$[Mn(CO)_3\{P(OMe)_3\}_2(MeCN)]PF_6$, (VII). Treatment of a warm solution of the complex *mer-trans*-$[Mn(CO)_3\{P(OMe)_3\}_2Br]$ (0·7 g, 1·34 mmol) in acetonitrile (8 cm$^3$) with $AgPF_6$ (0·36 g, 1·43 mmol) resulted in rapid precipitation of AgBr which was filtered off after 15 min. Addition of ethanol (10 cm$^3$) and concentration under reduced pressure gave the required product which was recrystallised from dichloromethane–ethanol as colourless *needles* (0·58 g). Yield 76%. Similarly prepared were: *mer-trans*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2(MeCN)]BPh_4$ from *mer-trans*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$ (with the addition of an ethanolic solution of sodium tetraphenylborate) in 68% yield as colourless *plates*; *mer-trans*-$[Mn(CO)_3(PMe_2Ph)_2(MeCN)]ClO_4$ from *mer-trans*-$[Mn(CO)_3(PMe_2Ph)_2Br]$ and $AgClO_4$ in 65% yield as pale yellow *plates*; and *cis*-$[Mn(CO)_2(PMe_2Ph)_2(MeCN)_2]PF_6$ from *mer-cis*-$[Mn(CO)_2(PMe_2Ph)_3Br]$ in 76% yield as lemon-yellow *plates*. The following complexes were also similarly prepared but the extent of reaction was monitored by i.r. solution spectra as the *mer-cis*-$[Mn(CO)_2L_3(MeCN)]^+$ species was formed as a by-product (maximum yields of the required products were obtained by using a minimum of heat and dilute solutions): *cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_2(MeCN)_2]ClO_4$ from *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]$ and $AgClO_4$ in 55% yield as lemon-yellow *prisms*; and *cis*-$[Mn(CO)_2\{P(OMe)_3\}_2(MeCN)_2]PF_6$ from *mer-cis*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$ in 51% yield as pale yellow *needles*.

mer-cis-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(MeCN)]PF_6$. A solution of the salt *fac*-$[Mn(CO)_3(MeCN)_3]PF_6$ (1·0 g, 2·46 mmol) and dimethoxyphenylphosphine (1·31 g, 7·71 mmol) in acetonitrile (15 cm$^3$) was heated under reflux for 2 h. Cold ethanol (15 cm$^3$) was then added and the solution concentrated under reduced pressure to give the required product which was recrystallised from dichloromethane–ethanol as cream coloured *prisms* (1·45 g). Yield 75%. Similarly prepared was *mer-cis*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)]PF_6$ in 70% yield as colourless *plates*.

trans-$[Mn(CO)_2\{P(OMe)_2Ph\}_2(MeCN)_2](PF_6)_2$. A solution of the salt *cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_2(MeCN)_2]PF_6$ (0·5 g, 0·74 mmol) in dichloromethane (10 cm$^3$) was treated with an excess of $NOPF_6$, resulting in a deepening of colour and liberation of NO gas. After 5 min the remaining $NOPF_6$ was filtered off and the solution concentrated under reduced pressure. Addition of cold ether (8 cm$^3$) gave the product as blood-red *plates* (0·29 g). Yield 48%. These readily underwent reduction both in solution and in the crystalline state and were not recrystallised. Similarly prepared were: *mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(MeCN)](PF_6)_2$ from *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(MeCN)]PF_6$ in 68% yield as violet *prisms* after recrystallisation from dichloromethane–ethanol; *mer-trans*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)](PF_6)_2$ from *mer-cis*-$[Mn(CO)_2\{P(OMe)_3\}_3(MeCN)]PF_6$ in 64% yield as golden-yellow *needles* after recrystallisation from dichloromethane–ether; and *trans*-[Mn(CO)$_2${P(OMe)$_3$}$_4$](PF$_6$)$_2$ from *cis*-[Mn(CO)$_2${P(OMe)$_3$}$_4$]PF$_6$ in 89% yield as orange *plates* after recrystallisation from dichloromethane–ethanol.

mer-trans-[Mn(CO)$_2${P(OMe)$_2$Ph}$_3$(MeCN)]PF$_6$. Treatment of a solution of the salt *mer-trans*-[Mn(CO)$_2${P(OMe)$_2$-Ph}$_3$(MeCN)](PF$_6$)$_2$ (0·4 g, 0·42 mmol) in dichloromethane (15 cm$^3$) with anhydrous hydrazine (0·2 cm$^3$) at 0 °C gave a white precipitate which was filtered off. Addition of ethanol (10 cm$^3$) to the concentrated solution gave the product which was recrystallised from dichloromethane–ethanol as lemon-yellow *needles* (0·20 g). Yield 58%.

(MeCN)]PF$_6$ from *mer-trans*-[Mn(CO)$_2${P(OMe)$_3$}$_3$(MeCN)]-(PF$_6$)$_2$ in 62% yield as pale yellow *plates*.

trans-[Mn(CO)$_2${P(OMe)$_3$}$_4$]PF$_6$. A solution of the salt *mer-trans*-[Mn(CO)$_2${P(OMe)$_3$}$_3$(MeCN)]PF$_6$ (0·4 g, 0·60 mmol) and trimethyl phosphite (0·11 g, 0·89 mmol) in chloroform (8 cm$^3$) was heated under reflux for 12 h. The solution was filtered while hot and cold ethanol (10 cm$^3$) was added. Removal of the chloroform under reduced pressure gave the product which was recrystallised from dichloromethane–ethanol as colourless *plates* (0·36 g). Yield 81%.