Synthesis of Cationic Pentacarbonyl, *fac*- and *mer*-Tricarbonyl, and *cis*- and *trans*-Dicarbonyl Complexes of Manganese(I)

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The complexes $[Mn(CO)_5(OClO_3)]$ and *fac*-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$ obtained by the reaction of $[Mn(CO)_5Br]$ with $Ag[ClO_4]$ in dichloromethane or acetone solution are suitable precursors for the synthesis of cationic complexes of the type $[Mn(CO)_5L][ClO_4]$ and of the types *fac*-$[Mn(CO)_3L_3][ClO_4]$ and *cis*-$[Mn(CO)_2L_4][ClO_4]$ (L = a Group 5B ligand) which, when L is a strong π acceptor, isomerize under reflux to *mer*-$[Mn(CO)_3L_3][ClO_4]$ or, respectively, to *trans*-$[Mn(CO)_2L_4][ClO_4]$.

THE preparation of cationic manganese(I) carbonyl derivatives of the $[Mn(CO)_xL_y]^+$ type is hindered by the fact that $[Mn(CO)_6]^+$ is inert and that its CO groups cannot therefore be displaced by other ligands. Until 1970[1] the principal and almost unique route was to abstract (*e.g.* by using $AlCl_3$) the halogen of a carbonyl halide in the presence of a Lewis base[2,3] (frequently CO), a reaction which must be carried out at high temperature and pressure. More recently, new preparative methods have been described. Thus, Mews[4] prepared cationic pentacarbonyls by treating $[Mn(CO)_5Br]$ with $Ag[AsF_6]$ in liquid SO_2, Drew *et al.*[5] obtained penta- and tri-carbonyl derivatives $[Mn(CO)_3L_2(NCMe)]^+$ by starting from $[Mn(CO)_5(NCMe)][PF_6]$, whilst Reimann and Singleton[6,7] started from $[Mn(CO)_3(NCMe)_3][PF_6]$ and displaced generally 1 or 2 mol of MeCN by other ligands, a route which was subsequently used by other workers.[8]

Previously we have reported[9] the synthesis of cationic carbonyls of the $[Mn(CO)_3L(L')]^+$ type (L = chelate ligand). In the present paper we describe how this method has been generalized to the cationic pentacarbonyls $[Mn(CO)_5L][ClO_4]$, the tricarbonyls *fac*-$[Mn(CO)_3L_3][ClO_4]$, and the dicarbonyls *cis*-$[Mn(CO)_2L_4][ClO_4]$. These solvent-free complexes with a single type of ancillary ligand could be obtained by carefully adjusting the generally mild working conditions. We also describe the isomerizations *fac*- to *mer*-$[Mn(CO)_3L_3][ClO_4]$ and *cis*- to *trans*-$[Mn(CO)_2L_4][ClO_4]$, which before had been detected only for neutral manganese(I) carbonyl complexes.[7,10]

RESULTS AND DISCUSSION

Preparations.—(*a*) *Cationic pentacarbonyl complexes.* The reaction (1) of dichloromethane solutions of $[Mn(CO)_5Br]$ with $Ag[ClO_4]$ (mol ratio 1 : 1.5), subsequent

$$[Mn(CO)_5Br] + Ag[ClO_4] \xrightarrow[\text{room temperature}]{CH_2Cl_2} AgBr + [Mn(CO)_5(OClO_3)] \quad (1)$$

elimination of the precipitated AgBr, and vacuum concentration of the filtrate yields yellow crystals of $[Mn(CO)_5(OClO_3)]$ (1), which are stable under nitrogen but sensitive to light, moisture, and air.

The addition of stoicheiometric amounts of a ligand L to a yellow solution of (1) leads according to (2) [L = PEt_3, PBu_3, $PEtPh_2$, $PMePh_2$, PEt_2Ph, PPh_3, $AsPh_3$, $SbPh_3$, $PPh_2(OEt)$, $P(OMe)_3$, $P(OEt)_3$, *o*-$C_6H_4(NH_2)_2$, 4-methylpyridine (4Me-py), Me_2CO, or C_4H_8O] to the corresponding cationic carbonyls, which in a few cases precipitate spontaneously [L = *o*-$C_6H_4(NH_2)_2$ or 4Me-py] or can be crystallized by evaporating the solvent, except for L = PBu_3, Me_2CO, and C_4H_8O which afford non-crystallizable oils. The course of each reaction has been monitored by scanning the carbonyl-stretching region of the i.r. spectrum. The time for completion of reaction is dependent on the ligand L used, varying from 5 min to 80 h.

$$[Mn(CO)_5(OClO_3)] + L \xrightarrow{CH_2Cl_2} [Mn(CO)_5L][ClO_4] \quad (2)$$

(*b*) fac- *and* mer-*tricarbonyl complexes.* The addition of acetone or tetrahydrofuran (thf) to solutions of (1) or the use of these compounds as solvents, according to (3),

$$[Mn(CO)_5Br] + Ag[ClO_4] \xrightarrow{Me_2CO \text{ or } C_4H_8O} AgBr + [Mn(CO)_5L][ClO_4] \quad (3)$$

(L = Me_2CO or C_4H_8O) gives cationic pentacarbonyl derivatives. As may be seen from the ν(CO) stretching vibrations, the acetone solutions of $[Mn(CO)_5(OCMe_2)][ClO_4]$ are either slowly (45 h, room temperature) or quickly (1 h, reflux temperature) transformed into those of *fac*-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$ or, respectively, *fac*-$[Mn(CO)_3(C_4H_8O)_3][ClO_4]$, which on evaporation yield red non-crystallizable oils, as has already been reported for the complex $[Mn(CO)_3(OCMe_2)_3][PF_6]$.[5]

Solutions of *fac*-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$ are, nevertheless, useful precursors for the synthesis of cationic *fac*-tricarbonyl derivatives [equation (4); L = PEt_3, PBu_3, PEt_2Ph, $PMePh_2$, $PEtPh_2$, $PPh_2(OEt)$, or 4Me-py].

$$fac\text{-}[Mn(CO)_3(OCMe_2)_3][ClO_4] + 3L \xrightarrow{Me_2CO} fac\text{-}[Mn(CO)_3L_3][ClO_4] \quad (4)$$

Although the i.r. spectra seem to show conclusively that the substitution of the acetone groups by the new ligand L takes place stepwise, we were not able to isolate any of the intermediate products. We generally used stoicheiometric amounts of the ligand L. If the duration of reaction (4) is prolonged, either at room temperature [L = $PEtPh_2$ or $PPh_2(OEt)$] or at reflux in acetone (L = PEt_3, PBu_3, PEt_2Ph, or $PMePh_2$), the initially formed *fac*-$[Mn(CO)_3L_3]^+$ isomerizes to the corresponding *mer*-$[Mn(CO)_3L_3]^+$ derivative. When L = $PPh_2(OEt)$, the use of an excess (4 : 1) of the ligand accelerates process (4) and increases the proportion of the *fac* isomer in the resulting mixture. The *mer*-tricarbonyls are very soluble, even in hexane, and their tendency to form oils prevents crystallization. Actually, only *mer*-$[Mn(CO)_3(PEtPh_2)_3][ClO_4]$, *mer*-$[Mn(CO)_3\{PPh_2(OEt)\}_3][ClO_4]$, and *mer*-$[Mn(CO)_3(PMePh_2)_3][ClO_4]$ could be isolated. In all the other cases the presence of the *mer*-tricarbonyl can clearly be detected from the ν(CO) pattern of the solutions.

If the *fac* isomers are heated under reflux in chloroform solution the speed of the *fac*-to-*mer* isomerization increases in the sequence $PEt_3 < PBu_3 < PMePh_2 \ll PEtPh_2 \simeq PPh_2(OEt)$, *i.e.* with increasing π-acid character of the ligand L. Thus no isomerization could be observed when L = a *N*- or *O*-donor. Similarly, other workers [7] could not observe any isomerization of cationic manganese(I) carbonyls with one or more *N*-donor ligands.

In the above cases the isomerization also takes place in the solid state and its speed increases with increasing temperature. For the *fac*-to-*mer* isomerization of neutral manganese(I) carbonyls a mechanism involving a five-co-ordinate intermediate has been proposed.[11]

We obtained several cationic *fac*-tricarbonyls by treating $[Mn(CO)_5(OClO_3)]$ with an excess of the ligand L [equation (5); L = py or 4Me-py; $L_3 = C_7H_8$].

$$[Mn(CO)_5(OClO_3)] + L(excess) \xrightarrow{CH_2Cl_2} [Mn(CO)_3L_3][ClO_4] + 2CO \quad (5)$$

(*c*) cis- *and* trans-*dicarbonyl complexes*. The addition (4 : 1) of stronger π-acceptor ligands to acetone solutions of $[Mn(CO)_3(OCMe_2)_3][ClO_4]$ not only displaces the three acetone groups but also one of the CO groups [equation (6); L = $PPh(OMe)_2$, $PPh(OEt)_2$, $P(OMe)_3$, or $P(OEt)_3$].

$$fac\text{-}[Mn(CO)_3(OCMe_2)_3][ClO_4] + 4L \xrightarrow{Me_2CO} cis\text{-}[Mn(CO)_2L_4][ClO_4] + CO \quad (6)$$

The i.r. spectra of the solutions show conclusively that a mixture of the *fac*-tricarbonyl and the respective *cis*-dicarbonyl is formed at the beginning of the addition, even when the complex is present in excess (mol ratio 2 : 1). It is therefore not possible to obtain the *fac*-tricarbonyl free from the respective *cis*-dicarbonyl. Nevertheless, if the reaction is carried out with a mol ratio 4 : 1 it is possible to separate the *cis* isomer except for L = $P(OEt)_3$ where non-crystallizable oils are obtained.

It has been reported [12] that in the case of neutral manganese(I) carbonyls the formation of the *cis* isomers occurs according to the sequence *fac*-tricarbonyl ⟶ *mer*-tricarbonyl ⟶ *cis*-dicarbonyl. This is not so in our case since: (*a*) heating *fac*-$[Mn(CO)_3\{PPh(OEt)_2\}_3][ClO_4]$ under reflux for 3 h in acetone does not lead to the *mer* derivative; and (*b*) the conversion of a sample of *mer*-$[Mn(CO)_3\{PPh(OEt)_2\}_3][ClO_4]$ (in refluxing acetone and in the presence of an excess of the ligand) into the respective *cis* derivative takes place extremely slowly.

The *cis*- to *trans*-dicarbonyl isomerization cannot be accomplished in refluxing acetone, only in solvents having higher boiling points, such as ethanol or butanol [when L = $PPh(OEt)_2$, $PPh(OMe)_2$, or $P(OMe)_3$]. These processes generally lead to equilibrium mixtures of the isomers, although the *trans*-dicarbonyl can be isolated in each case. On the other hand, *trans*-$[Mn(CO)_2\{PPh_2(OEt)\}_4][ClO_4]$ is obtained on adding the ligand to *fac*-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$ in refluxing acetone.

The described processes are the first isomerizations which have been observed for cationic manganese(I) carbonyls and, to our knowledge, few isomerizations have been reported [13] for cationic carbonyls of other transition metals.

Table 1 shows the analytical data, conductivities in acetone (or in nitromethane), colours, and melting or decomposition points for all the isolated complexes. The conductivities (Λ 75—90 S cm^2 mol^{-1} in nitromethane, or 100—140 S cm^2 mol^{-1} in acetone) are within the range expected for 1 : 1 electrolytes.[14] Those complexes which could not be crystallized because of their tendency to form oils were identified by the ν(CO) patterns of their solutions. The ^1H n.m.r. spectra of some of the complexes were recorded. The locations as well as the intensities of the resonances are as expected for each complex, although no additional information could be obtained from these data.

Infrared Spectra.—Only complex (1) shows bands at 1 160s, 1 020s, 873m, and 605s,br cm^{-1} which are characteristic of a perchlorate group attached to a metal atom (C_{3v}). The other isolated complexes and the solutions of those which could not be crystallized exhibit two bands, one in the 1 080—1 100vs,br cm^{-1} and another in the 615—630m or s cm^{-1} region assignable to the $[ClO_4]^-$ anion (T_d). In some cases the assignment of the latter band is difficult, *i.e.* whenever the absorptions coincide either with those of the ligand L or with ν(Mn–C) stretching or δ(Mn–CO) bending modes. Tables 2—6 summarize the ν(CO) absorptions and the force constants (obtained by the Cotton–Kraihanzel method [15,16]) of the pentacarbonyls, *fac*- and *mer*-tricarbonyls, and *cis*-dicarbonyls. The notation is that given in refs. 15 and 16.

Pentacarbonyl complexes. The cations $[Mn(CO)_5L]^+$, as well as complex (1), belong to the structural type $M(CO)_5L$, and if no account is taken of the ligands L the local symmetry of the $Mn(CO)_5$ moiety is C_{4v}. As discussed by Cotton and Kraihanzel [15] three i.r.-active stretching fundamentals are to be expected in this case: the two A_1 modes and the E mode, the latter being lower in frequency than one of the A_1 fundamentals. Both A_1 fundamentals will be much weaker than the E fundamental. The presence of L removes all the symmetry elements (C_1) so that the fundamental B_1, which is not i.r. active for rigorous C_{4v} symmetries, becomes active.

In the light of these considerations we assign the

TABLE 1

Analytical data, colour, conductivities, and melting points

	Complex	Analysis(%)[a]		Colour	Λ[b]	M.p.[c]
		C	H		S cm² mol⁻¹	(θ_c/°C)
(1)	$[Mn(CO)_5(OClO_3)]$	20.25 (20.4)		Yellow	81.9	135—138
(2)	$[Mn(CO)_5(PEt_3)][ClO_4]$	32.1 (32.05)	3.80 (3.65)	White	117.5	169
(3)	$[Mn(CO)_5(PEt_2Ph)][ClO_4]$	39.2 (39.15)	3.30 (3.25)	White	129.2	110—112
(4)	$[Mn(CO)_5(PMePh_2)][ClO_4]$	44.65 (43.7)	2.80 (2.65)	White	132.4	165—166
(5)	$[Mn(CO)_5(PEtPh_2)][ClO_4]$	45.0 (44.9)	2.90 (2.95)	White	136.4	139
(6)	$[Mn(CO)_5(PPh_3)][ClO_4]$	49.45 (49.65)	2.85 (2.70)	White	138.5	168
(7)	$[Mn(CO)_5(AsPh_3)][ClO_4]$	46.5 (46.0)	2.60 (2.50)	Pale yellow	133.3	167—168
(8)	$[Mn(CO)_5(SbPh_3)][ClO_4]$	42.45 (42.65)	2.30 (2.30)	Pale yellow	112.4	170
(9)	$[Mn(CO)_5\{PPh_2(OEt)\}][ClO_4]$	42.8 (43.5)	2.90 (2.85)	White	120.9	126—128
(10)	$[Mn(CO)_5\{P(OMe)_3\}][ClO_4]$	22.95 (22.95)	2.20 (2.15)	White	139.8	156—157
(11)	$[Mn(CO)_5\{P(OEt)_3\}][ClO_4]$	28.9 (28.7)	3.45 (3.25)	White	137.4	120
(12)	$[Mn(CO)_5\{o\text{-}C_6H_4(NH_2)_2\}][ClO_4]$	31.7 (32.85)	2.10[d] (2.00)	Yellow	73.4[e]	105—108
(13)	$[Mn(CO)_5(4Me\text{-}py)][ClO_4]$	33.2 (34.1)	1.90[d] (1.80)	Pale yellow	90.1[e]	98—100
(14)	*fac*-$[Mn(CO)_3(PEt_3)_3][ClO_4]$	42.4 (42.55)	7.30 (7.60)	White	141.7	132—133
(15)	*fac*-$[Mn(CO)_3(PBu_3)_3][ClO_4]$	56.15 (55.45)	9.55 (9.60)	White	133.3	128
(16)	*fac*-$[Mn(CO)_3(PEt_2Ph)_3][ClO_4]$	52.25 (53.8)	5.55 (6.10)	Pale yellow	133.4	149—150
(17)	*fac*-$[Mn(CO)_3(PMePh_2)_3][ClO_4]$	60.2 (60.15)	4.55 (4.65)	Pale yellow	133.0	169—170
(18)	*fac*-$[Mn(CO)_3\{PPh_2(OEt)\}_3][ClO_4]$	57.65 (58.2)	4.70 (4.85)	White	132.8	142—145
(19)	*fac*-$[Mn(CO)_3(4Me\text{-}py)_3][ClO_4]$	48.65 (48.75)	4.45[d] (4.85)	Yellow	81.4[e]	155—160
(20)	*fac*-$[Mn(CO)_3(C_7H_8)][ClO_4]$	35.65 (36.35)	2.40 (2.40)	Yellow	85.7[e]	165—170
(21)	*cis*-$[Mn(CO)_2\{PPh(OMe)_2\}_4][ClO_4]$	45.95 (45.85)	5.10 (4.95)	White	139.4	205
(22)	*cis*-$[Mn(CO)_2\{PPh(OEt)_2\}_4][ClO_4]$	50.45 (50.30)	6.15 (6.00)	White	127.3	186—188
(23)	*cis*-$[Mn(CO)_2\{P(OMe)_3\}_4][ClO_4]$	23.65 (23.8)	5.40 (5.10)	White	140.9	206
(24)	*mer*-$[Mn(CO)_3(PEtPh_2)_3][ClO_4]$	60.25 (61.35)	5.25 (5.10)	Yellow	135.1	148—149
(25)	*mer*-$[Mn(CO)_3\{PPh_2(OEt)\}_3][ClO_4]$	58.3 (58.2)	4.80 (4.85)	Cream	132.0	193—195
(26)	*mer*-$[Mn(CO)_3(PMePh_2)_3][ClO_4]$	59.9 (60.15)	5.15 (4.65)	Yellow	101.0	138—140
(27)	*trans*-$[Mn(CO)_2\{PPh(OMe)_2\}_4][ClO_4]$	45.5 (45.85)	5.15 (4.95)	Pale yellow	134.8	208
(28)	*trans*-$[Mn(CO)_2\{PPh(OEt)_2\}_4][ClO_4]$	50.0 (50.3)	6.20 (6.00)	Cream	128.3	209—210
(29)	*trans*-$[Mn(CO)_2\{P(OMe)_3\}_4][ClO_4]$	23.1 (23.8)	5.00 (5.10)	White	137.5	216—217
(30)	*trans*-$[Mn(CO)_2\{PPh_2(OEt)\}_4][ClO_4]$	61.2 (61.6)	5.10 (5.30)	Yellow	131.6	149—150

[a] Calculated values are given in parentheses. [b] In acetone. [c] With decomposition. [d] N: (12), 6.45 (6.95); (13), 3.50 (3.60); (19), 7.60 (8.10%). [e] In nitromethane.

band of highest frequency to the $A_1^{(2)}$ mode (w), the following very weak one to B_1, and the subsequent strong band to E. The other band assignable to $A_1^{(1)}$ (m) is either situated next to or, in some cases, superimposed by E, and its location varies with the type of ligand. Thus, it appears either as an unresolved shoulder on the high-frequency side of E [Figure 1(*a*)] or as an independent band at a lower frequency than E [Figure 1(*b*)]. Figure 1 shows the ν(CO) pattern when (*a*) L = a phosphine or phosphite, and (*b*) L = an *N* or *O*-donor. The absorption attributed to the B_1 mode appears either as a well resolved band (in $CHCl_3$ or CH_2Cl_2 solution) or only as a shoulder on E (in MeCN or Me_2CO).

Considering the approximate method used and the difficulties arising from determining the accurate position of the absorption due to the $A_1^{(1)}$ mode, the force constants in Table 2 should not be taken too literally. For L = a phosphite we have observed, in accordance with the only example in the literature,[5] that $K_1 > K_2$. This requires us to accept a direct donation from these ligands to the π^* orbitals of the equatorial CO groups. In all other cases (L being an *N*- or *O*-donor, or a phosphine), as expected, $K_2 > K_1$, although both constants are very similar in magnitude. On the basis of this assignment and if MeCN or Me_2CO is used as solvent, the position of the B_1 mode can be calculated with reasonable accuracy. Moreover, the values of K_1 (corresponding mainly to the A_1 mode, *i.e.* to the CO *trans* to L) increase with increasing π-acid character of L.

mer-*Tricarbonyls*. For the local symmetry C_{2v} the i.r.-active CO stretching fundamentals $2A_1 + B_1$ are to be expected. The two types of spectra which were recorded are in Figure 2: for (*a*) L = a phosphine and for (*b*) L = $PEtPh_2$ or a phosphite. The highest-frequency band, in every case the weaker one, is assigned to the A_1 mode. If only one other band (intense and at

TABLE 2

Observed ν(CO) values and calculated CO stretching force constants for $[Mn(CO)_5L]^+$ and $[Mn(CO)_5(OClO_3)]$

Complex [a]	$\tilde{\nu}$(CO) [b]/cm^{-1}			Force constant/mdyn Å^{-1}		
	$A_1^{(2)}$	$A_1^{(1)}$	E	K_1	K_2	K_i
(1)	2 154w	2 020m	2 070s	16.57	17.75	0.22
$[Mn(CO)_5(thf)]^+$	2 135w	2 006m	2 049s	16.35	17.40	0.23
$[Mn(CO)_5(OCMe_2)]^+$	2 139w	2 012m	2 049s	16.45	17.42	0.23
(12)	2 137w	2 008m	2 050m	16.38	17.43	0.23
(13)	2 139w	2 018 (sh)	2 043s	16.57	17.35	0.25
$[Mn(CO)_5(PBu_3)]^+$	2 141m	2 059 (sh)	2 047s	17.30	17.39	0.23
(2) [c]	2 141m	2 058 (sh)	2 046s	17.29	17.38	0.24
(3)	2 142m	2 060 (sh)	2 049s	17.31	17.42	0.23
(5)	2 142m	2 053 [d]	2 053s	17.17	17.47	0.23
(4) [c]	2 143m	2 064 (sh)	2 053s	17.37	17.47	0.22
(6) [c]	2 142m	2 067 (sh)	2 054s	17 43	17.48	0.22
$[Mn(CO)_5(AsPh_3)]^+$	2 143m	2 068 (sh)	2 054s	17.45	17.48	0.22
(8)	2 138m	2 062 (sh)	2 051s	17.34	17.42	0.21
(9)	2 144m	2 076 (sh)	2 051s	17.62	17.44	0.23
(11)	2 150m	2 081 (sh)	2 060s	17.75	17.56	0.21
(10)	2 153m	2 084 (sh)	2 062s	17.74	17.62	0.22

1 dyn = 10^{-5} N.

[a] All the cations were isolated as the $[ClO_4]^-$ salts. [b] The i.r. spectra were recorded in CH_2Cl_2, except for those of $[Mn(CO)_5(OCMe_2)]^+$ and $[Mn(CO)_5(C_4H_8O)]^+$ in acetone or thf solution. [c] For L = PEt_3, $PMePh_2$, and PPh_3 the i.r. spectra were also recorded in acetonitrile and acetone. The results are [in the order $A_1^{(2)}$, B_1, $A_1^{(1)}$, E, K_1, K_2, K_i, B_1 (calc.)]: (2) in MeCN, 2 142m, 2 084 (sh), 2 062 (sh), 2 049s, 17.35, 17.42, 0.23, 2 077; in Me_2CO, 2 140m, 2 082 (sh), 2 041,[d] 2 041s, 17.09, 17.40, 0.23, 2 076; (4) in MeCN, 2 145m, 2 089 (sh), 2 064 (sh), 2 055s, 17.37, 17.51, 0.23, 2 082; in Me_2CO, 2 143m, 2 085 (sh), 2 053,[d] 2 053s, 17.17, 17.48, 0.23, 2 080; (6) in MeCN, 2 145m, 2 090 (sh), 2 068 (sh), 2 057s, 17.44, 17.53, 0.22, 2 083; in Me_2CO, 2 143m, 2 090 (sh), 2 064 (sh), 2 054s, 17.37, 17.48, 0.22, 2 081. [d] Obscured by the E mode.

TABLE 3

Observed ν(CO) values and calculated CO stretching force constants for *mer*-$[Mn(CO)_3L_3]^+$

Complex [a]	ν(CO) [b]/cm^{-1}			Force constant/mdyn Å^{-1}		
	$A_1^{(2)}$	$A_1^{(1)}$	B_1	K_1	K_2	K_i
mer-$[Mn(CO)_3(PBu_3)_3]^+$	2 020w	1 895m	1 940s	14.58	15.81	0.30
mer-$[Mn(CO)_3(PEt_3)_3]^+$	2 022w	1 894m	1 940s	14.58	15.81	0.30
mer-$[Mn(CO)_3(PEt_2Ph)_3]^+$ [c]	2 020w	1 897m	1 950s	14.60	15.88	0.26
(26)	2 036w	1 908m	1 952s	14.80	16.01	0.31
(24) [c]	2 033w	1 947s,br	1 947s,br	15.46	15.92	0.31
(25) [c]	2 050w	1 968s,br	1 968s,br	15.79	16.23	0.30
mer-$[Mn(CO)_3\{PPh(OEt)_2\}_3]^+$ [c]	2 056w	1 974s,br	1 974s,br	15.88	16.33	0.30
mer-$[Mn(CO)_3\{P(OMe)_3\}_3]^+$ [c]	2 063w	1 985s,br	1 985s,br	16.05	16.49	0.28

[a] All the cations were isolated as the $[ClO_4]^-$ salts. [b] All frequencies were determined in CH_2Cl_2 except for those where L = PEt_3, PBu_3, and PEt_2Ph which were determined in chloroform. [c] For L = $PEtPh_2$ or a phosphite the $A_1^{(1)}$ and B_1 vibrations practically overlap.

TABLE 4

Observed ν(CO) values and calculated CO stretching force constants for *fac*-$[Mn(CO)_3L_3]^+$

Complex [a]	$\tilde{\nu}$(CO) [b]/cm^{-1}		Force constant/mdyn Å^{-1}	
	A_1	E	K	K_i
(20)	2 002s	1 932vs,br	15.44	0.37
fac-$[Mn(CO)_3(C_4H_8O)_3]^+$	2 040s	1 920vs,br	15.51	0.64
fac-$[Mn(CO)_3(OCMe_2)_3]^+$	2 023s	1 935s,br	15.59	0.47
fac-$[Mn(CO)_3(py)_3]^+$	2 042s	1 950s,br	15.84	0.49
(19)	2 041s	1 944s,br	15.78	0.52
(15)	2 022s	1 943s,br	15.66	0.42
(14)	2 021s	1 943s,br	15.66	0.42
(16)	2 023s	1 946s,br	15.70	0.41
(17)	2 030s	1 956s,br	15.85	0.40
(18)	2 040s	1 972s,br	16.07	0.37

[a] All the cations were isolated as the $[ClO_4]^-$ salt. [b] All i.r. spectra were recorded in CH_2Cl_2 except for those of *fac*-$[Mn(CO)_3(OCMe_2)_3]^+$ and *fac*-$[Mn(CO)_3(thf)_3]^+$ which were determined in acetone or thf solution.

TABLE 5

Observed ν(CO) values and calculated CO stretching force constants for *cis*-$[Mn(CO)_2L_4]^+$

Complex [a]	$\tilde{\nu}$(CO) [b]/cm^{-1}		Force constant/mdyn Å^{-1}	
	A_1	B_1	K	K_i
(22)	1 988s	1 935s	15.54	0.42
(21)	1 992s	1 938s	15.59	0.43
(23)	2 000s	1 944s	15.70	0.45

[a] All complexes were isolated as the $[ClO_4]^-$ salts. [b] All frequencies were determined in CH_2Cl_2 solution.

TABLE 6

Observed ν(CO) values for *trans*-$[Mn(CO)_2L_4]^+$

Complex [a]	$\tilde{\nu}$(CO)[b]/cm^{-1}
	A_{2u}
(30)	1 909s
(28)	1 925s
(27)	1 930s
(29)	1 943s

[a] All complexes were isolated as the $[ClO_4]^-$ salts. [b] All the i.r. spectra were determined in CH_2Cl_2 solution.

lower frequency) is to be seen it has been considered as a superimposition of the A_1 and B_1 absorptions, whereas if two more bands are observed the higher-frequency one is attributed to the B_1 fundamental. The force constants collected in Table 3 are in accordance with these criteria. In every case $K_2 > K_1$, and the relative order of the ligands coincides with the variation of their π-acid character. With decreasing π-acid character of L the band corresponding to the $A_1^{(1)}$ mode (due to the CO *trans* to L) is shifted towards lower energies.

fac-*Tricarbonyls and* cis- *and* trans-*dicarbonyls*. For these complexes the fundamentals can be assigned unambiguously because of the requirement that $K_i > 0$. The recorded CO stretching vibrations and the calculated force constants are listed in Tables 4—6. They are consistent with expectations. Thus, (*a*) the values of K decrease with decreasing π-acid character of the ligand, and (*b*) within each type of carbonyl the values due to K_i increase with decreasing π-acid character of the ligand. The force constants also decrease with increasing number of CO groups substituted by L.

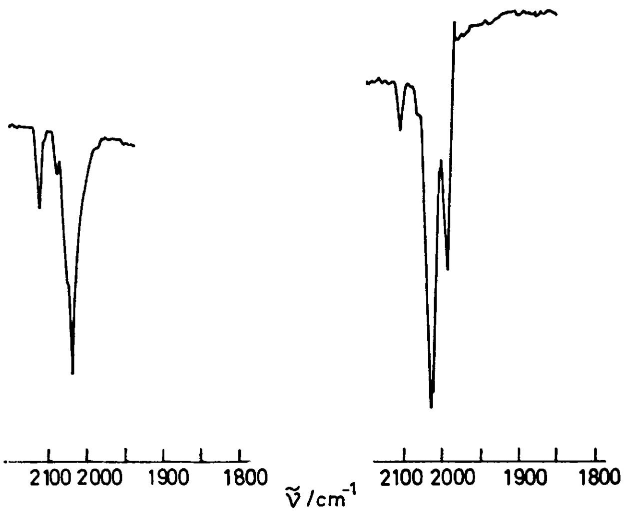

FIGURE 1 Infrared spectra in the ν(CO) region of $[Mn(CO)_5L][ClO_4]$ complexes: (*a*) L = phosphine or phosphite; (*b*) L = *N*- or *O*-donor

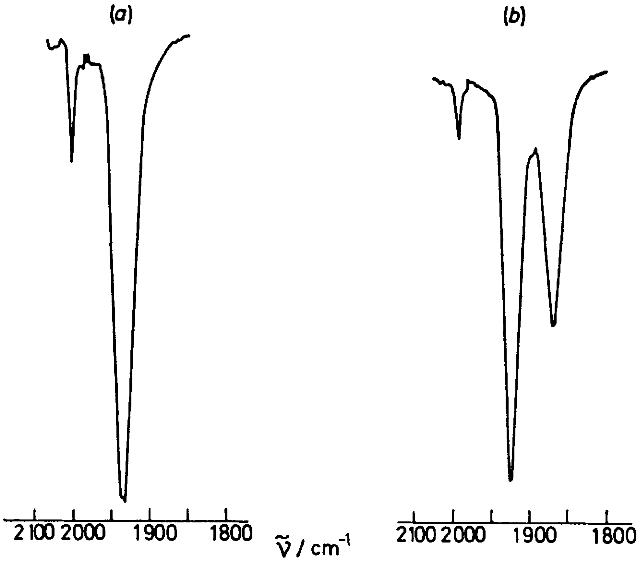

FIGURE 2 Infrared spectra in the ν(CO) region of *mer*-$[Mn(CO)_3L_3][ClO_4]$ complexes in CH_2Cl_2 solution: (*a*) L = phosphine, (*b*) L = $PEtPh_2$ or phosphite

EXPERIMENTAL

All the reactions were carried out under an atmosphere of nitrogen. Carbon, H, and N analyses were made with a Perkin-Elmer 240 microanalyser. Conductivities were measured in acetone or nitromethane solutions with a Philips PW 9501 instrument. The i.r. spectra in the ν(CO) stretching region were recorded on a Perkin-Elmer 577 for solutions in dichloromethane or acetone solutions between NaCl discs. The i.r. spectra of the solids were recorded on the same spectrophotometer using Nujol mulls between polyethylene sheets. The polystyrene absorption at 1 601.8 cm^{-1} was always used as a standard. The ^1H n.m.r. spectra were recorded on a Perkin-Elmer R-12B spectrometer, using $SiMe_4$ as an internal standard.

The complex $[Mn(CO)_5Br]$ was prepared according to the method of King.[17] The ligands were used as purchased from commercial sources, except for the amines which were freshly distilled from K[OH]. Triphenylarsine was prepared according to the method of Pope and Turner.[18] Ultraviolet irradiation from a 125-W medium-pressure mercury-arc lamp (Baird and Tatlock) was used.

Preparations.—Pentacarbonylperchloratomanganese(I), (1). A magnetically stirred solution of $[Mn(CO)_5Br]$ (0.274 g, 1 mmol) in dichloromethane (50 cm^3) was treated with $Ag[ClO_4]$ (0.310 g, 1.5 mmol) for 3 h at room temperature and with exclusion of light. The precipitated AgBr was filtered off together with the excess of $Ag[ClO_4]$ and the yellow filtrate was evaporated to dryness *in vacuo* yielding (1) as a yellow crystalline solid (0.26 g, 90%).

Solutions of $[Mn(CO)_5(OCMe_2)][ClO_4]$ *and of* $[Mn(CO)_5(C_4H_8O)][ClO_4]$. A magnetically stirred solution of $[Mn(CO)_5Br]$ (0.274 g, 1 mmol) in acetone (40 cm^3) was treated with $Ag[ClO_4]$ (0.207 g, 1 mmol) for 10 min at room temperature with exclusion of light, and the precipitated AgBr was filtered off. The i.r. spectrum of the orange filtrate showed a ν(CO) absorption which is characteristic of a pentacarbonyl derivative [*cf*. Figure 1(*b*)] together with bands due to ionic perchlorate. The complex $[Mn(CO)_5(C_4H_8O)][ClO_4]$ was similarly prepared in solution (5 min, room temperature).

$[Mn(CO)_5L][ClO_4]$. A magnetically stirred solution of (1) (1 mmol) in dichloromethane was treated with PEt_2Ph (0.166 g, 1 mmol) for 45 min at room temperature. After addition of ethanol (5 cm^3) the solvents were evaporated under reduced pressure until a crystalline solid was obtained. The resulting $[Mn(CO)_5(PEt_2Ph)][ClO_4]$ (3) was recrystallized from dichloromethane–ethanol and washed with diethyl ether, yield 0.38 g (83%). The other cationic pentacarbonyls $[Mn(CO)_5L][ClO_4]$ were prepared similarly. The specific conditions for each reaction {mol ratio [ligand : complex (1)], reaction time, yield, and observations} were as follows: (2), 1 : 1, 5 min, 66%; $[Mn(CO)_5(PBu_3)][ClO_4]$, 1 : 1, 5 min at −10 °C, non-crystallizable oils; (4), 1 : 1, 5 min, 81%; (5), 1 : 1, 1 h, 63%; (6), 3 : 1, 2 h, 79%; (7), 3 : 1, 3.5 h, 50%, low yield since complex was isolated from a solution which according to its i.r. spectrum contained more than one complex; (8), 3 : 1, 3 h, 30%, very low yield (when the reaction was carried out at 1 : 1 mol ratio it led to a solution, the i.r. spectrum of which indicated a complex mixture); (9), 1 : 1, 1 h, 86%; (10), 3 : 1, 5 h, 77%; (11), 3 : 1, 2.5 h, 61%; (12), 1.26 : 1, 2 h, 64%, complex precipitated during the reaction and was recrystallized from dichloromethane–hexane; (13), 1 : 1, 1.5 h, 58%, complex precipitated during the reaction, was recrystallized from dichloromethane, and washed with hexane.

Solutions of fac-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$ *and of fac*-$[Mn(CO)_3(C_4H_8O)_3][ClO_4]$. A solution of $[Mn(CO)_5(OCMe_2)][ClO_4]$ (1 mmol) in acetone (40 cm^3) was heated under reflux for 1 h (or allowed to react for 45 h at room temperature). The resulting yellow solution showed the ν(CO) stretching absorptions characteristic of a *fac*-tricarbonyl derivative. The complex could, however, not be isolated since orange non-crystallizable oils were always obtained.

Solutions of *fac*-$[Mn(CO)_3(C_4H_8O)_3][ClO_4]$ were obtained similarly by refluxing $[Mn(CO)_5(C_4H_8O)][ClO_4]$ for 45 min in thf. The process again led to non-crystallizable oils.

fac-$[Mn(CO)_3L_3][ClO_4]$ (L = P-*donors*). A solution of *fac*-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$ (1 mmol) in acetone (40 cm^3) (prepared as described above) was treated with PEt_3 (0.356 g, 3 mmol) for 20 min at reflux (or for 6 h at room temperature). Ethanol (5 cm^3) was added, and the solvents were evaporated under reduced pressure until a crystalline solid formed. The latter was recrystallized from dichloromethane–ethanol and washed with diethyl ether, yield of *fac*-$[Mn(CO)_3(PEt_3)_3][ClO_4]$ (14), 0.33 g (56%).

The following complexes were prepared similarly and the specific conditions of each reaction are given as mol ratio {ligand: *fac*-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$}, reaction time at reflux (or at room temperature), yield, observations: (15), 3 : 1, 40 min (15 h), 50%; (16), 3 : 1, 3 h (30 h), 36%; (17), 3 : 1, — (14 h), 52%, precipitated spontaneously [when the reaction was interrupted after 10 min stirring (room temperature) the ν(CO) stretching vibrations of the solution indicated the presence of a *fac*-tricarbonyl derivative containing acetone, although the addition of ethanol followed by evaporation under reduced pressure led to the isolation of (17)]; (18), 4 : 1, — (30 h), 28%, large excess of ligand used to slow down the *fac*-to-*mer* isomerization. [Although only the presence of the *fac* isomer could be detected in the i.r. spectrum of the solution, since the ν(CO) of the *mer* derivative is masked by those of the former, two different complexes could be isolated: a fraction containing *mer*-$[Mn(CO)_3\{PPh_2(OEt)\}_3][ClO_4]$, and one of the required complex (18).]

fac-$[Mn(CO)_3L_3][ClO_4]$ (L = N-*donor*; $L_3 = C_7H_8$). The complex *fac*-$[Mn(CO)_3(4Me\text{-}py)_3][ClO_4]$ (19) can be prepared by two different methods.

Method (*a*). A magnetically stirred acetone solution of *fac*-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$ (1 mmol) was treated with 4Me-py (0.279 g, 3 mmol) for 10 min at room temperature. A small amount of ethanol was added and the solvents were evaporated under reduced pressure to give an oil which was washed with hexane and diethyl ether. The solid (19) was obtained on addition of hexane (0.39 g, 72%).

Method (*b*). A solution of (1) (1 mmol) in dichloromethane (50 cm^3) was treated with 4Me-py (0.28 g, 3 mmol) for 10 h. A precipitated yellow solid {probably $[Mn(CO)_5(4Me\text{-}py)][ClO_4]$} dissolved during the reaction. The solution was centrifuged, ethanol was added to the clear liquid, and the solvents were finally evaporated under reduced pressure until the formation of crystalline solid (19) was observed.

If the reaction was carried out at room temperature for 15 h it led to a precipitate of $[Mn(CO)_5(4Me\text{-}py)][ClO_4]$ and a yellow solution from which *fac*-$[Mn(CO)_3(4Me\text{-}py)_3][ClO_4]$ could be isolated in low yield. Method (*b*) was also used to prepare *fac*-$[Mn(CO)_3(py)_3][ClO_4]$ by treating pyridine with (1) (5 : 1) for 60 h at room temperature. Slow addition of hexane to the magnetically stirred solution gave first a white precipitate with very complex ν(CO) stretching bands and then a white solid identified by its i.r. spectrum as *fac*-$[Mn(CO)_3(py)_3][ClO_4]$, in accordance with the data reported in the literature.[5]

The complex *fac*-$[Mn(CO)_3(C_7H_8)][ClO_4]$ (20) was prepared by method (*b*); C_7H_8 and (1) (5.66 : 1) were heated under reflux for 5 h. The resulting precipitate was recrystallized from dichloromethane–hexane (82% yield). Complex (20) could not be obtained by method (*a*).

cis-$[Mn(CO)_2L_4][ClO_4]$. A solution of *fac*-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$ (1 mmol) in acetone (40 cm^3) was treated with $PPh(OMe)_2$ (0.680 g, 4 mmol) for 8 h at reflux (or for 18 h at room temperature). The resulting precipitate was identified as *cis*-$[Mn(CO)_2\{PPh(OMe)_2\}_4][ClO_4]$ (21). From the solution, whose i.r. spectrum indicates the presence of a mixture of a *fac*-tricarbonyl together with the *cis*-dicarbonyl, a second fraction of (21) could be obtained by adding ethanol (5 cm^3) and evaporating the solvents. The solid was recrystallized from dichloromethane–ethanol and washed with diethyl ether [yield of (21), 0.453 g (51%)]. The mother liquids, which according to the i.r. spectra contain a mixture of the *cis*-dicarbonyl and the *fac*-tricarbonyl (a larger quantity of the latter), were evaporated almost to dryness to give an oil which was repeatedly washed with diethyl ether to eliminate the excess of the ligand. The small amount of white crystals obtained by treating the oil with ethanol–diethyl ether was characterized as *fac*-$[Mn(CO)_3\{PPh(OMe)_2\}_3][ClO_4]$, although trace amounts of the *cis*-dicarbonyl derivative could not be eliminated.

Other *cis*-dicarbonyls were prepared similarly with L = $PPh(OEt)_2$ and $P(OMe)_3$. The specific conditions for each reaction are given as mol ratio ligand: *fac*-$[Mn(CO)_3(OCMe_2)_3][ClO_4]$, reaction time at reflux (or at room temperature), yield, and observations: (22), 4 : 1, 9 h (24 h), 53%, the *cis*-dicarbonyl did not precipitate during the reaction; (23), 4 : 1, 3 h (10 h), 44%, the *cis*-dicarbonyl did not precipitate during the reaction and must be crystallized as for (21).

mer-[Mn(CO)$_3$(PEtPh$_2$)$_3$][ClO$_4$] (24) *and* *mer*-[Mn(CO)$_3${PPh$_2$(OEt)}$_3$][ClO$_4$] (25). A magnetically stirred solution of *fac*-[Mn(CO)$_3$(OCMe$_2$)$_3$][ClO$_4$] (1 mmol) in acetone (40 cm^3) was treated with PEtPh$_2$ (0.428 g, 2 mmol) for 17 h at room temperature. A new fraction of PEtPh$_2$ (0.214 g, 1 mmol) was added and the reaction was continued for another 8 h until the i.r. spectrum of the solution showed almost only the bands due to the *mer*-tricarbonyl. Ethanol (5 cm^3) was added and the solvents were evaporated under reduced pressure until a solid was formed. This was recrystallized from dichloromethane–ethanol and washed with diethyl ether (0.24 g, 30% yield). The reaction can also be carried out by adding a stoicheiometric amount of the ligand at the start, although in this case it takes much longer to go to completion.

Complex (25) was obtained similarly by adding 2 mmol of PPh$_2$(OEt) and then another 1 mmol of the ligand after 5 h. The reaction was continued at room temperature for another 22 h until the i.r. spectrum showed mainly the ν(CO) due to the *mer*-tricarbonyl [yield of (25), 0.23 g (25%)].

mer-[Mn(CO)$_3$L$_3$][ClO$_4$] (L = PEt$_3$, PBu$_3$, PEt$_2$Ph, *or* PMePh$_2$). A solution of *fac*-[Mn(CO)$_3$(PEt$_3$)$_3$][ClO$_4$] (0.30 g, 0.5 mmol) in chloroform (30 cm^3) was heated under reflux for 10 h until the ν(CO) bands were those of a *mer*-tricarbonyl. The complex *mer*-[Mn(CO)$_3$(PEt$_3$)$_3$][ClO$_4$] could not be isolated since treatment of the solution always led to non-crystallizable oils. Solutions of *mer*-[Mn(CO)$_3$(PBu$_3$)$_3$][ClO$_4$] and *mer*-[Mn(CO)$_3$(PEt$_2$Ph)$_3$][ClO$_4$] were prepared similarly (6 h or 8 h reflux).

The complex *mer*-[Mn(CO)$_3$(PMePh$_2$)$_3$][ClO$_4$] (26) was prepared in the same way (5 h, reflux) and could be isolated by addition of hexane (10 cm^3) and evaporation of the solvents under reduced pressure. This process was repeated several times to remove the chloroform. Finally, the solution was concentrated under reduced pressure and cooled to −78 °C. The resulting crystals were washed with hexane at −78 °C and dried first in a stream of dry nitrogen and subsequently *in vacuo*. The yields of (26) were very low since the complex is soluble even in cold hexane.

Solutions of *mer*-[Mn(CO)$_3${PPh(OEt)$_2$}$_3$][ClO$_4$] *and of* *mer*-[Mn(CO)$_3${P(OMe)$_3$}$_3$][ClO$_4$]. Carbon monoxide was bubbled for 2.5 h through a solution of *cis*-[Mn(CO)$_2${PPh(OEt)$_2$}$_4$][ClO$_4$] (22) (0.10 g, 0.10 mmol) in dichloromethane (50 cm^3) under u.v. irradiation. The complex *mer*-[Mn(CO)$_3${PPh(OEt)$_2$}$_3$][ClO$_4$] could not be isolated from the solution, whose i.r. spectrum in the ν(CO) stretching region was that of a *mer*-tricarbonyl. Non-crystallizable oils were obtained in each case. The solution of *mer*-[Mn(CO)$_3${P(OMe)$_3$}$_3$][ClO$_4$] was prepared similarly from *cis*-[Mn(CO)$_2${P(OMe)$_3$}$_4$][ClO$_4$] (0.15 g, 0.21 mmol) in dichloromethane (30 cm^3) (28 h, u.v. irradiation).

trans-[Mn(CO)$_2${PPh(OMe)$_2$}$_4$][ClO$_4$] (27). A solution of *cis*-[Mn(CO)$_2${PPh(OMe)$_2$}$_4$][ClO$_4$] (21) (0.30 g, 0.34 mmol) in n-butanol (30 cm^3) was heated under reflux for 3 h until the ν(CO) stretching vibrations were those of a *trans*-dicarbonyl. Complex (27) crystallized when the solution was allowed to cool; the resulting solid was washed with hexane (12% yield).

trans-[Mn(CO)$_2${PPh(OEt)$_2$}$_4$][ClO$_4$] (28). Heating a solution of *cis*-[Mn(CO)$_2${PPh(OEt)$_2$}$_4$][ClO$_4$] (22) (0.30 g, 0.30 mmol) in ethanol (30 cm^3) under reflux led to the partial precipitation of the *trans*-dicarbonyl (28). After 15 h the reaction was interrupted since longer reaction times increase the complexity of the reaction and lead to decomposition. Complex (28) (0.15 g, 50%) and a small portion of the starting *cis*-dicarbonyl were isolated from the suspension.

trans-[Mn(CO)$_2${P(OMe)$_3$}$_4$][ClO$_4$] (29). Heating a solution of *cis*-[Mn(CO)$_2${P(OMe)$_3$}$_4$][ClO$_4$] (23) (0.30 g, 0.42 mmol) in n-butanol (30 cm^3) under reflux for 38 h led to a mixture of dicarbonyls. As before the reaction was interrupted to avoid decomposition processes. The similar solubility of the two isomers made it difficult to isolate the *trans*-dicarbonyl. It was, however, possible to recrystallize a small amount of (29) from ethanol–carbon tetrachloride, and satisfactorily characterize the complex.

trans-[Mn(CO)$_2${PPh$_2$(OEt)}$_4$][ClO$_4$] (30). A solution of *fac*-[Mn(CO)$_3$(OCMe$_2$)$_3$][ClO$_4$] (1 mmol) in acetone (40 cm^3) was treated with PPh$_2$(OEt) (1.380 g, 6 mmol) for 15 h at reflux. The ν(CO) stretching pattern of the resulting solution was complex and indicated the presence of a mixture of *fac*- and *mer*-tricarbonyls together with *trans*-dicarbonyls. The proportion of these complexes could not be altered by more prolonged refluxing. Ethanol was added to the solution and the solvents were almost completely evaporated under reduced pressure. The addition of diethyl ether led to the precipitation of a solid which was recrystallized from dichloromethane–ethanol [yield of (30), 0.26 g (23%)].

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