Syntheses of Cationic Tri- and Di-carbonyl Complexes of Manganese(I) with Diphosphines from the Appropriate Neutral Bromocarbonyls

By **Francisco Bombin, Gabino A. Carriedo, Jesus A. Miguel, and Victor Riera,*** Department of Inorganic Chemistry, University of Valladolid, Spain

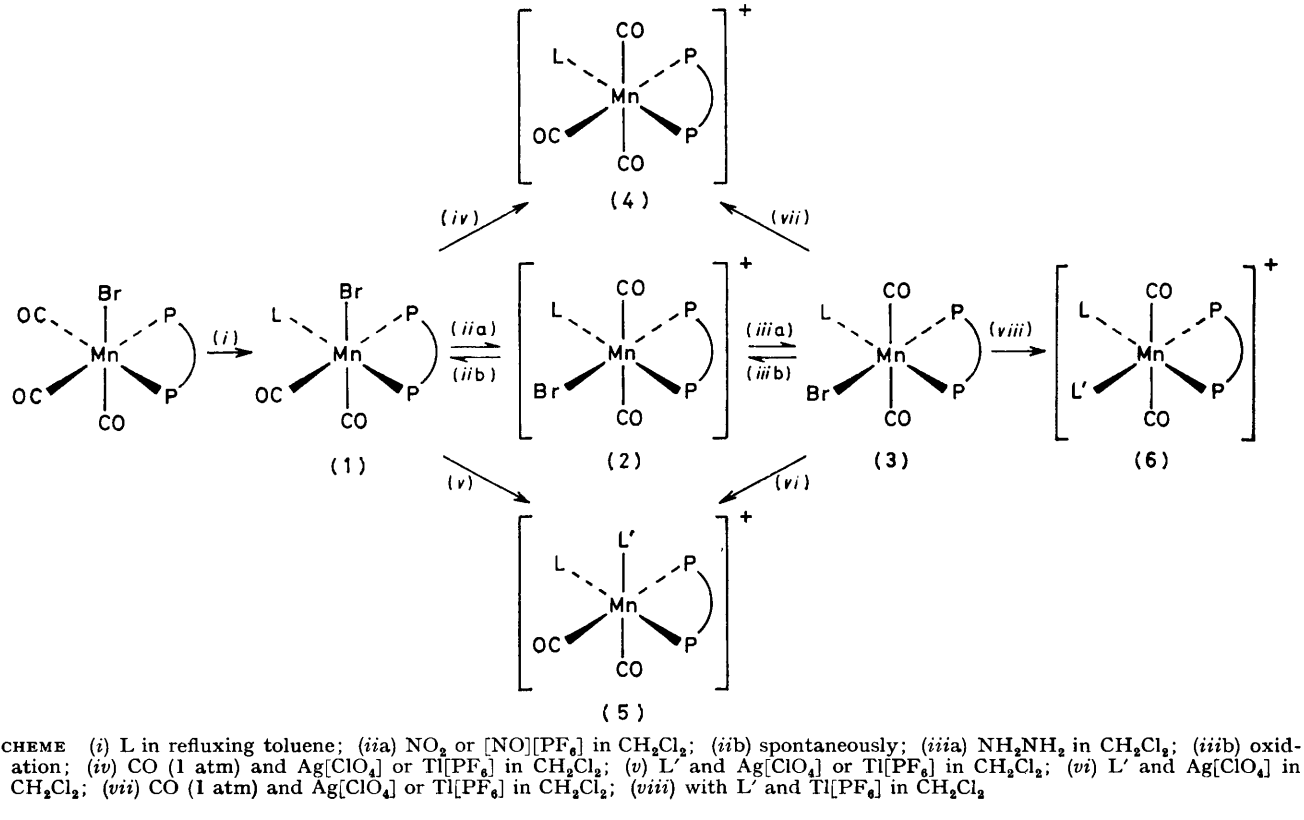
Reaction of the complexes *fac*-$[MnBr(CO)_3(L-L)]$ [L–L = $Ph_2P(CH_2)_nPPh_2$, *n* = 1 (dppm) or 2 (dppe)] with phosphorus-donor ligands, L, leads to the complexes *cis,cis*-$[MnBr(CO)_2(L-L)L]$. These neutral dicarbonyls are oxidized by NO_2 or $[NO][PF_6]$ to the unstable cationic species *trans*-$[MnBr(CO)_2(L-L)L]^+$ which may be isolated as hexafluorophosphate salts and which lead to the neutral *trans*-$[MnBr(CO)_2(L-L)L]$ when reduced by hydrazine. Replacement of the bromo-ligand in either *cis,cis*- or *trans*-$[MnBr(CO)_2(L-L)L]$, using $Tl[PF_6]$ in the presence of another ligand L′ (N or P donor), results in the formation of *cis,cis*- or *trans*-$[Mn(CO)_2(L-L)LL'][PF_6]$ respectively, or of *mer*-$[Mn(CO)_3(L-L)L][PF_6]$ if L′ = CO. However, using $Ag[ClO_4]$ as the halogen abstracter, the perchlorate salts of the *cis,cis*-cationic dicarbonyls (or the *mer* tricarbonyls) are obtained regardless of the neutral bromocarbonyl isomer used.

RECENTLY, we reported the syntheses of *fac*- and *mer*-$[Mn(CO)_3(L-L)L][ClO_4]$ and *trans*-$[Mn(CO)_2(L-L)L_2][ClO_4]$ [L–L,$Ph_2P(CH_2)_nPPh_2$ = dppm ($n = 1$), dppe ($n = 2$), dppp ($n = 3$), or dppb ($n = 4$) and L = N-, O-, P-, or S-donor ligands in the *fac* tricarbonyls; L–L = dppm and L = phosphites or PPh_3 in the *mer* tricarbonyls; and L–L = dppm and L = phosphites in the *trans* dicarbonyls].[1] Isomerization processes in the cationic carbonyls of Mn^I, $[Mn(CO)_{6-n}L_n]^+$, are now well established[2] but, as noted previously, only *mer*-$[Mn(CO)_3(dppm)L][ClO_4]$ [L = $P(OR)_3$ or PPh_3] can be prepared from its *fac* isomers by heating since this treatment results in decomposition in all other cases.[1] Furthermore, only the *trans*-$[Mn(CO)_2(dppm)L_2][ClO_4]$ [L = $P(OR)_3$] complexes were obtained by treating the corresponding *mer* tricarbonyl {or, directly, *fac*-$[Mn(OClO_3)(CO)_3(L-L)]$} with L under u.v. irradiation.[1]

In this paper we describe a more general procedure for synthesizing the species *mer*-$[Mn(CO)_3(L-L)L]^+$, *trans*-$[Mn(CO)_2(L-L)LL']^+$, and also the *cis,cis* isomers of the latter complexes, using the new neutral dicarbonyls *trans*- or *cis,cis*-$[MnBr(CO)_2(L-L)L]$ under mild conditions. We also report the differences found between $Ag[ClO_4]$ and $Tl[PF_6]$ as halogen abstracters, our results being in agreement with recently reported studies on silver(I) salts as reagents in organometallic chemistry.[3]

RESULTS AND DISCUSSION

The compounds *fac*-$[MnBr(CO)_3(L-L)]$[1] (L–L = dppm or dppe) reacted with phosphorus-donor ligands, L, in



SCHEME (*i*) L in refluxing toluene; (*ii*a) NO_2 or $[NO][PF_6]$ in CH_2Cl_2; (*ii*b) spontaneously; (*iii*a) NH_2NH_2 in CH_2Cl_2; (*iii*b) oxidation; (*iv*) CO (1 atm) and $Ag[ClO_4]$ or $Tl[PF_6]$ in CH_2Cl_2; (*v*) L′ and $Ag[ClO_4]$ or $Tl[PF_6]$ in CH_2Cl_2; (*vi*) L′ and $Ag[ClO_4]$ in CH_2Cl_2; (*vii*) CO (1 atm) and $Ag[ClO_4]$ or $Tl[PF_6]$ in CH_2Cl_2; (*viii*) with L′ and $Tl[PF_6]$ in CH_2Cl_2

refluxing toluene to give *cis,cis*-[MnBr(CO)$_2$(L–L)L] (1) [see (*i*) in the Scheme], the reaction being analogous to that reported by Reimann and Singleton [4] between L and *fac*- and *mer,trans*-[MnBr(CO)$_3$L$_2$]. The two strong bands of nearly the same intensity in the ν(CO) region of the i.r. spectra of the resulting complexes (1) (Table) clearly showed that the two CO groups are *cis* to each other. Moreover, (1) reacted with CO in the presence of either Tl[PF$_6$] or Ag[ClO$_4$] to give *mer*-[Mn(CO)$_3$(L–L)L]$^+$ (see later). Therefore, assuming that in these latter reactions the CO enters at the position of the departing bromide, as found in other cases,[5] we have adopted the *cis,cis* structure for (1) shown in the Scheme. This structure is also consistent with the greater *cis*-labilization effect of bromine towards CO substitution than that of the phosphorus atoms of the diphosphines [see reaction (*i*)] as stated by Angelici's rule [6] and by Atwood and Brown's 'site preference model' [7] (see also ref. 8). Reaction (*i*) took place readily (0.5—2 h) in refluxing toluene, being faster for dppm than for dppe, although the change in rate, as well as the changes arising from the nature of the entering ligand L, were small under these conditions.

Analytical, conductivity, and i.r. data

Complex	M.p.[a] (θ$_c$/°C)	Λ[b] S cm^2 mol^{-1}	Analysis (%)[c] C	H	N	Colour	$\tilde{\nu}$(CO)[d]/ cm^{-1}
cis,cis-[MnBr(CO)$_2$(dppm){P(OPh)$_3$}]	184	4	60.7 (61.0)	4.15 (4.20)		Orange	1 962s, 1 889s
cis,cis-[MnBr(CO)$_2$(dppe){P(OPh)$_3$}]	169	11	61.2 (61.4)	4.55 (4.35)		Orange	1 962s, 1 887s
cis,cis-[MnBr(CO)$_2$(dppe){P(OMe)$_3$}]	173	2	52.8 (52.1)	4.90 (4.40)		Orange	1 951s, 1 877s
cis,cis-[MnBr(CO)$_2$(dppe){P(OEt)$_3$}]	155	10	54.8 (54.1)	5.50 (5.20)		Orange	1 950s, 1 875s
cis,cis-[MnBr(CO)$_2$(dppe){PPh(OMe)$_2$}]	197	4	57.4 (56.9)	4.85 (4.65)		Orange	1 952s, 1 876s
cis,cis-[MnBr(CO)$_2$(dppe)(PEt$_3$)]	152	1	58.3 (57.7)	5.70 (5.55)		Orange	1 932s, 1 854s
trans-[MnBr(CO)$_2$(dppm){P(OPh)$_3$}]	145	2	61.5 (61.0)	4.15 (4.15)		Red	2 005vw, 1 924s [e]
trans-[MnBr(CO)$_2$(dppe){P(OPh)$_3$}]	165	7	61.7 (61.4)	4.65 (4.35)		Red	2 008vw, 1 918s [e]
trans-[MnBr(CO)$_2$(dppe){P(OEt)$_3$}]	145	6	54.8 (54.0)	5.45 (5.10)		Red	2 002vw, 1 898s [e]
trans-[MnBr(CO)$_2$(dppe){P(OPr^i)$_3$}]	194	16	53.6 (55.7)	5.70 (5.65)		Red	1 895s [e]
trans-[MnBr(CO)$_2$(dppe){PPh(OMe)$_2$}]	182	17	57.6 (57.0)	5.00 (5.40)		Red	1 897s [e]
mer-[Mn(CO)$_3$(dppm){P(OPh)$_3$}][ClO$_4$]	209	140	59.1 (59.2)	3.95 (4.00)		White	2 065w, 1 985s,br
mer-[Mn(CO)$_3$(dppe){P(OPh)$_3$}][ClO$_4$]	175	123	59.4 (59.5)	4.20 (4.10)		White	2 060w, 1 984s,br
mer-[Mn(CO)$_3$(dppe){P(OEt)$_3$}][ClO$_4$]	170	141	52.2 (52.3)	5.25 (4.85)		White	2 057w, 1 978s
mer-[Mn(CO)$_3$(dppe){P(OMe)$_3$}][ClO$_4$]	213	143	50.0 (50.5)	4.35 (4.35)		White	2 059w, 1 979s,br
mer-[Mn(CO)$_3$(dppe){PPh(OMe)$_2$}][ClO$_4$]	218	150	54.0 (55.1)	4.30 (4.35)		White	2 055w, 1 975s
mer-[Mn(CO)$_3$(dppe)(PEt$_3$)][ClO$_4$]	170	120	56.5 (55.7)	4.70 (5.15)		White	2 040w, 1 960s
cis,cis-[Mn(CO)$_2$(dppm){P(OPh)$_3$}$_2$][ClO$_4$]	182	140	62.2 (62.3)	4.25 (4.30)		White	1 993s, 1 940s
cis,cis-[Mn(CO)$_2$(dppe){P(OPh)$_3$}$_2$][ClO$_4$]	153	120	62.7 (62.5)	4.45 (4.45)		White	1 995s, 1 940s
cis,cis-[Mn(CO)$_2$(dppe){P(OPh)$_3$}{P(OEt)$_3$}][ClO$_4$]	125	140	56.5 (57.5)	4.90 (5.00)		Pale yellow	1 983s, 1 928s
cis,cis-[Mn(CO)$_2$(dppe){P(OEt)$_3$}$_2$][ClO$_4$]	153	122	51.7 (51.1)	6.30 (5.80)		Yellow	1 975s, 1 917s
cis,cis-[Mn(CO)$_2$(dppe){P(OPh)$_3$}(NCMe)][PF$_6$]	197	146	57.0 (57.3)	4.25 (4.70)	1.20 (1.40)	Yellow	1 980s, 1 919s
trans-[Mn(CO)$_2$(dppm){P(OPh)$_3$}$_2$][PF$_6$]	196	122	59.9 (59.9)	4.40 (4.35)		Yellow	2 020vw, 1 947s
trans-[Mn(CO)$_2$(dppm){P(OPh)$_3$}{P(OEt)$_3$}][PF$_6$]	190	138	54.7 (54.8)	4.80 (4.65)		Yellow	2 020vw, 1 938s
trans-[Mn(CO)$_2$(dppm){P(OPh)$_3$}(PPh$_3$)][PF$_6$]	157	124	62.7 (62.3)	4.30 (4.30)		Yellow	2 000vw, 1 922s
trans-[Mn(CO)$_2$(dppm){P(OPh)$_3$}(py)][PF$_6$]	163	137	58.3 (58.3)	3.80 (4.10)	1.45 (1.35)	Yellow	2 006vw, 1 922s
trans-[Mn(CO)$_2$(dppe){P(OPh)$_3$}(NCMe)][PF$_6$]	153	143	57.4 (57.3)	4.30 (4.70)	1.40 (1.40)	Yellow	2 025vw, 1 935s
trans-[Mn(CO)$_2$(dppe){P(OEt)$_3$}$_2$][PF$_6$]	123	135	48.5 (48.7)	5.70 (5.45)		Yellow	2 019vw, 1 925s

[a] All melted with decomposition. [b] In acetone. [c] Calculated values are given in parentheses. [d] I.r. spectra were recorded in dichloromethane. [e] $\tilde{\nu}$(CO) Values for the species *trans*-[MnBr(CO)$_2$(L–L)L]$^+$ are 1 992, 1 987, 1 978, 1 970, and 1 975 cm^{-1} for L–L = dppm, L = P(OPh)$_3$; dppe, P(OPh)$_3$; dppe, P(OEt)$_3$; dppe, P(OPr^i)$_3$; and dppe, PPh(OMe)$_2$ respectively.

As might be expected,[9-11] treatment of *cis,cis*-[MnBr(CO)$_2$(L–L)L] (orange) with NO$_2$ or [NO][PF$_6$] in dichloromethane [process (*ii*a) in the Scheme] afforded deep red *trans*-[MnBr(CO)$_2$(L–L)L]$^+$ (2), which could be isolated as rather unstable (solid and solution) hexafluorophosphate salts. In the decomposition process of these cationic manganese(II) bromocarbonyls [(*ii*b) in the Scheme], the neutral starting compounds (1) appeared as major products. The i.r. spectra of compounds (2) exhibited a strong ν(CO) absorption near 1 970—1 990 cm^{-1} (Table) and, in some cases, a very weak one at higher frequency could be observed. This pattern is characteristic of an octahedral *trans* dicarbonyl, whilst the high frequency of the bands is in accord with the formation of manganese(II) cationic species.[9-11] A band in the i.r. at 830 cm^{-1} showed the presence of the anion PF$_6^-$, and the conductivity data were also consistent with a 1 : 1 electrolyte.[12] Thus, oxidation in reaction (*ii*a) was accompanied by a *cis* to *trans* dicarbonyl rearrangement process. In fact, many reactions of octahedral metal carbonyls involving changes in the formal oxidation state of the metal also imply changes in the geometrical arrangement of the CO ligands.[3,9-11,13-16] Interestingly, most of the chemical [9-11,14-16] and electrochemical [13-16] oxidations of manganese(I) to manganese(II) carbonyl derivatives are accompanied by *cis* to *trans* rearrangement of CO groups. Therefore, on the basis of previous experimental [13,15,16] and theoretical [17] work it appears that the 17-electron species *cis,cis*-[MnBr(CO)$_2$(L–L)L]$^+$ initially formed in (*ii*a) easily isomerizes * (probably through an intramolecular twist mechanism) to the observed *trans* dicarbonyls, which might be favoured thermodynamically.

The manganese(II) species *trans*-[MnBr(CO)$_2$(L–L)L]$^+$ [L = P(OR)$_3$ or PPh(OMe)$_2$] reacted rapidly with NH$_2$NH$_2$ [(*iii*a) in the Scheme] to yield *trans*-[MnBr(CO)$_2$(L–L)L] (3), in accord with results of other reactions of this kind.[9-11] The i.r. spectra of (3) showed the characteristic pattern of a *trans* dicarbonyl, with the strong band at frequencies 70—80 cm^{-1} lower than the corresponding band of compounds (2) and the conductivity data suggestive of a non-electrolyte. Accordingly, reduction of (2) by hydrazine took place with complete retention of configuration. Conversely, the reduction of *trans*-[MnBr(CO)$_2$(L–L)L]$^+$ (L = PEt$_3$ or PMePh$_2$) resulted in the formation of *cis,cis*-[MnBr(CO)$_2$(L–L)L], due to the isomerization of the initially formed neutral *trans* isomer, as clearly seen by monitoring the reaction by i.r. in the ν(CO) region. No isomerization was observed in the case of complexes (3) even over a period of several days under similar conditions, but when *trans*-[MnBr(CO)$_2$(dppe){P(OPh)$_3$}] was heated in toluene, a rapid reaction took place and its isomer *cis,cis*-[MnBr(CO)$_2$(dppe){P(OPh)$_3$}], together with *trans*-[Mn(CO)$_2$(dppe)$_2$]Br and *fac*-[MnBr(CO)$_3$(dppe)] were found among the products [on the basis of their ν(CO) bands only]. Thus, it is apparent that for the manganese(I) species, the *cis* dicarbonyl derivatives are favoured when the ligands are poorer π acceptors.

Lately, the neutral halogeno-carbonyls have been widely used for synthesizing cationic species.[18] This suggested that (1) or (3) could be useful precursors to a variety of cationic *cis,cis* and *trans*-[Mn(CO)$_2$(L–L)LL′]$^+$ complexes, and prompted us to investigate the reactions discussed below.

A mixture of *cis,cis*-[MnBr(CO)$_2$(L–L)L] and Ag[ClO$_4$] in dichloromethane reacted with CO at normal pressure in the absence of light to give *mer*-[Mn(CO)$_3$(L–L)L][ClO$_4$] (4) in good yield [process (*iv*) in the Scheme]. The i.r. spectra of the compounds obtained showed one weak band and another strong one at lower frequency in the ν(CO) region; this pattern is consistent with a *mer* tricarbonyl stereochemistry [1] and thus, we have adopted for (4) the structure depicted in the Scheme. The dppm-containing *mer* tricarbonyls were identical to those obtained from their *fac* isomers.[1] The bands at 1 080s, br and 630m cm^{-1} in the i.r. (characteristic of the anion ClO$_4^-$) and the conductivity data also supported the formulation proposed for (4). Analogous results were obtained using Tl[PF$_6$] as bromide abstracter.

The addition of Ag[ClO$_4$] to a dichloromethane solution of pure (1) in the absence of light also resulted in the rapid formation of (4), presumably through a decomposition process in which the cation Ag$^+$ plays a part, as suggested by the dark precipitate formed. We have observed similar results in the formation of [Mn(CO)$_4$(L–L)][ClO$_4$] by treating *fac*-[MnBr(CO)$_3$(L–L)] with Ag[ClO$_4$] in dichloromethane.[1] Nevertheless, treatment of a mixture of (1) and the ligand L′ = P(OPh)$_3$, P(OEt)$_3$, pyridine (py), or MeCN (in excess of the stoicheiometric amount) with Ag[ClO$_4$] in dichloromethane, in the absence of light gave the salts *cis,cis*-[Mn(CO)$_2$(L–L)LL′][ClO$_4$] (5) in high yield [reaction (*v*) in the Scheme]. The two characteristic strong bands of nearly the same intensity in the ν(CO) region at higher frequencies than those of the starting neutral dicarbonyls (Table), the conductivity data, and the assumption that the ligand L′ entered at the position of the departing bromide, allowed us to propose the *cis,cis* structure of the Scheme for the compounds (5). If L′ = PEt$_3$ or PBu$^n_3$, reaction (*v*) led to slower and more complex processes, probably due to the formation of silver–phosphine complexes.[19] On the other hand, the reaction of *cis,cis*-[MnBr(CO)$_2$(dppe){P(OPh)$_3$}] with Ag[ClO$_4$] and P(OEt)$_3$ resulted, rather surprisingly, in the formation of a mixture of *cis,cis*-[Mn(CO)$_2$(dppe){P(OEt)$_3$}$_2$][ClO$_4$] and the expected *cis,cis*-[Mn(CO)$_2$(dppe){P(OPh)$_3$}{P(OEt)$_3$}][ClO$_4$]. This suggested substitution of P(OPh)$_3$ by P(OEt)$_3$ in the neutral starting dicarbonyl, as was demonstrated by treating *cis,cis*-[MnBr(CO)$_2$(dppe){P(OPh)$_3$}] and P(OEt)$_3$ in dichloromethane at room temperature. The ligand PBu$^n_3$ also replaced P(OPh)$_3$ from the bromocarbonyl derivative while py and MeCN failed to produce the same effect. Using Tl[PF$_6$] as bromide abstracter in reaction (*v*) (L–L = dppe), the *cis,cis* cationic dicarbonyls

---

* It is apparent [15-17] that the barrier to intramolecular interconversion of the possible isomers is lower in the 17-electron carbonyl complexes than in the 18-electron complexes.

were obtained for all ligands used, except for L′ = PPh$_3$ which seemed to lead to *mer*-[Mn(CO)$_3$(dppe)(PPh$_3$)]-[PF$_6$], according to the i.r. spectrum of the reaction mixture.

Reactions between complexes (**3**) and Ag[ClO$_4$] in the presence of ligand L′ were found to be more complex than the corresponding ones of the *cis,cis* isomers. Furthermore, complete retention of configuration was not observed. Instead, mixtures of *cis,cis* and *trans* cationic species were formed. For example, treatment of *trans*-[MnBr(CO)$_2$(dppe){P(OEt)$_3$}] with L′ = P(OEt)$_3$ or P(OPh)$_3$ and an excess of Ag[ClO$_4$] in dichloromethane led mainly to *cis,cis*-[Mn(CO)$_2$(dppe){P(OEt)$_3$}L′][ClO$_4$] rather than to the expected *trans* isomer [reaction (*vi*) in the Scheme]. Using L′ = CO (1 atm *) under similar conditions the compound *mer*-[Mn(CO)$_3$(dppe){P(OEt)$_3$}]-[ClO$_4$] was formed [(*vii*) in the Scheme]. In both cases, examination of the reaction mixture by i.r. revealed initial formation of *trans*-[MnBr(CO)$_2$(dppe){P(OEt)$_3$}]$^+$, according to the strong band at 1 978 cm^{-1}. Therefore, we are tempted to conclude that in reaction (*vi*) the starting complex was oxidized,† probably by the cation Ag$^+$ [(*iii*b) in the Scheme] which has been found to be a one-electron oxidant for organometallic species.[3,20] The resulting complex, *trans*-[MnBr(CO)$_2$(dppe){P(OEt)$_3$}]$^+$, could be the source of *cis,cis*-[MnBr(CO)$_2$(dppe){P(OEt)$_3$}] (see below) and thus, this latter complex reacted with Ag[ClO$_4$] to give the observed *cis,cis* cationic carbonyl derivative. Several other reactions were carried out to investigate this result further. Thus, it was found that Ag[ClO$_4$] oxidized the complex *trans*-[MnBr(CO)$_2$(dppe)-{P(OPh)$_3$}] to the 17-electron manganese(II) *trans* dicarbonyl. Treatment of *trans*-[MnBr(CO)$_2$(dppm)-{P(OPh)$_3$}][PF$_6$] with P(OEt)$_3$ in dichloromethane resulted in *cis,cis*-[MnBr(CO)$_2$(dppm){P(OPh)$_3$}] [no substitution of P(OPh)$_3$ for P(OEt)$_3$ was observed during the time required for the reduction]. This result, which seems to be analogous to the reduction of *mer,trans*-[MnBr(CO)$_2$L$_3$]$^+$ by L to *mer,cis*-[MnBi(CO)$_2$L$_3$] (L = PMe$_2$Ph),[9] may account for the formation of *cis,cis*-[MnBr(CO)$_2$(dppe){P(OEt)$_3$}] from *trans*-[MnBr(CO)$_2$-(dppe){P(OEt)$_3$}]$^+$ and P(OEt)$_3$ as commented above. Finally, the reaction of *trans*-[MnBr(CO)$_2$(dppe){P-(OEt)$_3$}][PF$_6$] and P(OEt)$_3$ with the non-oxidizing Tl[PF$_6$] resulted in the formation of *cis,cis*-[Mn(CO)$_2$-(dppe){P(OEt)$_3$}$_2$][PF$_6$]. The i.r. examination of this reaction revealed the initial formation of *cis,cis*-[MnBr-(CO)$_2$(dppe){P(OEt)$_3$}].

The failure to produce the cationic *trans* dicarbonyls using Ag[ClO$_4$] led us to investigate the effect of utilizing the non-oxidizing Tl[PF$_6$]. In this way, the complexes *trans*-[Mn(CO)$_2$(L–L)LL′][PF$_6$] (**6**) [L = P(OPh)$_3$ or P-(OEt)$_3$; L′ = P(OPh)$_3$, P(OEt)$_3$, PPh$_3$, MeCN, or py] were synthesised from (**3**), L′, and Tl[PF$_6$] in dichloromethane [reaction (*viii*) in the Scheme]. The i.r. of the complexes obtained showed only one strong band in the ν(CO) region at higher frequency than the ones corresponding to the neutral complex (**3**), and a band at 830 cm^{-1} characteristic of the anion PF$_6^-$. Moreover, as in the other classes of compounds hitherto discussed, the trends observed for the ν(CO) frequency values clearly reflected the expected changes in the π-acceptor abilities of the ligands (Table). In some cases, however, the complexes *trans*-[Mn(CO)$_2$(L–L)LL′][PF$_6$] were formed together with smaller amounts of the *cis,cis* isomer; this was observed for example, in reaction (*viii*) for L = L′ = P(OPh)$_3$ or P(OEt)$_3$. No bands in the i.r. indicating oxidation to manganese(II) species were observed, therefore the effects discussed above using Ag[ClO$_4$] do not operate here. In these cases an accurate explanation would require a more detailed examination of the problem.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer, and were calibrated against the polystyrene absorption at 1 602 cm^{-1}. Analyses were performed with a Perkin-Elmer 240 microanalyzer. All reactions were carried out under N$_2$. The compounds *fac*-[MnBr-(CO)$_3$(L–L)] were prepared as described in ref. 1.

Melting points, conductivity, analytical, and spectroscopic data for new compounds are given in the Table.

Syntheses.—cis,cis-[MnBr(CO)$_2$(L–L)L], (**1**). The following preparation is representative of that for all complexes (**1**).

The complex *fac*-[MnBr(CO)$_3$(dppm)] (0.40 g, 0.66 mmol) and P(OPh)$_3$ (1.03 g, 3.32 mmol) were heated under reflux (0.5 h) in toluene (10 cm^3). The solvent was removed under reduced pressure and hexane was added to give the yellow solid *cis,cis*-[MnBr(CO)$_2$(dppm){P(OPh)$_3$}] (0.46 g, 78%). The product was recrystallized from dichloromethane–ethanol (4 : 1) to give orange crystals.

trans-[MnBr(CO)$_2$(L–L)L][PF$_6$], (**2**). The following preparation is representative of that for all compounds (**2**).

The complex *cis,cis*-[MnBr(CO)$_2$(dppe){P(OPh)$_3$}] (0.30 g, 0.33 mmol) and [NO][PF$_6$] (0.07 g, 0.40 mmol) were stirred in dichloromethane (10 cm^3) for 30 min. The resulting deep red solution was filtered and the solvent removed *in vacuo* to give a red residue which was stirred with diethyl ether until a solid was formed (0.25 g, 75%). Attempts to recrystallize resulted in decomposition to the *cis,cis*-[MnBr-(CO)$_2$(dppe){P(OPh)$_3$}].

Alternatively NO$_2$(g) may be used to prepare dichloromethane solutions of (**2**).

trans-[MnBr(CO)$_2$(L–L)L], (**3**). The following preparation is representative of that for all complexes (**3**).

Dried NO$_2$ was bubbled through a solution of the complex *cis,cis*-[MnBr(CO)$_2$(dppm){P(OPh)$_3$}] (1.1 g, 1.24 mmol) in dichloromethane (30 cm^3) until the i.r. spectrum of the solution showed only one strong band at 1 992 cm^{-1}. Excess of NO$_2$ was removed from the solution by bubbling through N$_2$ and addition of a commercial solution of 80% hydrazine monohydrate (0.50 cm^3). The resulting solution was filtered over Kieselguhr and evaporated to dryness to give a red powder. The latter was washed with hexane and recrystallized (dichloromethane–hexane) affording crystals of *trans*-[MnBr(CO)$_2$(dppm){P(OPh)$_3$}] (0.75 g, 68%).

The compound [NO][PF$_6$] can be used instead of NO$_2$ with the same result.

---

* Throughout this paper: 1 atm = 101 325 Pa.

† It appears that oxidation of the *trans* species is easier than that of the corresponding *cis* ones.

mer-$[Mn(CO)_3(L{-}L)L][ClO_4]$, (4). Carbon monoxide (1 atm) was bubbled through a magnetically stirred solution of *cis,cis*-$[MnBr(CO)_2(dppe)\{P(OEt)_3\}]$ (0.30 g, 0.38 mmol) and $Ag[ClO_4]$ (0.123 g, 0.60 mmol) in dichloromethane (20 cm^3) for 30 min. The mixture was filtered, the solvent removed under reduced pressure, and the residue washed with diethyl ether to give *mer*-$[Mn(CO)_3(dppe)\{P(OEt)_3\}][ClO_4]$ (0.26 g, 81%). Recrystallization was from dichloromethane–ethanol.

The other complexes (4) were similarly prepared.

cis,cis-$[Mn(CO)_2(L{-}L)LL'][ClO_4]$, (5). The complex *cis,cis*-$[MnBr(CO)_2(dppm)\{P(OPh)_3\}]$ (0.30 g, 0.34 mmol) and $P(OPh)_3$ (0.54 g, 1.75 mmol) were stirred at room temperature in the absence of light with $Ag[ClO_4]$ (0.11 g, 0.53 mmol) in dichloromethane (20 cm^3) for 3.5 h. The mixture was filtered, the solvent evaporated under reduced pressure, and the resulting oil was washed several times with diethyl ether to give the white solid *cis,cis*-$[Mn(CO)_2(dppm)\{P(OPh)_3\}_2][ClO_4]$ (0.29 g, 71%). The compound was recrystallized by slow evaporation of an ethanolic solution.

The other complexes (5) were similarly prepared but the reaction time varies from 0.5 h [$L{-}L$ = dppe, $L = P(OEt)_3$, $L' = P(OPh)_3$] to 50 h [$L{-}L$ = dppe, $L = L' = P(OEt)_3$].

Using $Tl[PF_6]$ instead of $Ag[ClO_4]$ led to analogous results.

trans-$[Mn(CO)_2(L{-}L)LL'][PF_6]$, (6).—The complex *trans*-$[MnBr(CO)_2(dppm)\{P(OPh)_3\}]$ (0.20 g, 0.23 mmol), $P(OEt)_3$ (0.19 g, 1.13 mmol), and $Tl[PF_6]$ (0.16 g, 0.45 mmol) were stirred at room temperature for 4 h in dichloromethane (10 cm^3). The mixture was filtered and the solvent removed *in vacuo*. The resulting oil was washed with diethyl ether to give the white solid *trans*-$[Mn(CO)_2(dppm)\{P(OPh)_3\}\{P(OEt)_3\}][PF_6]$ (0.18 g, 64%). Recrystallization was from dichloromethane–ethanol.

The other complexes (6) were similarly prepared in times varying from 2 h [$L{-}L$ = dppm, $L = P(OPh)_3$, L' = MeCN] to 3 d [$L{-}L$ = dppm, $L = P(OPh)_3$, $L' = PPh_3$].

[1/309 *Received, 23rd February*, 1981]

REFERENCES

[1] G. A. Carriedo and V. Riera, *J. Organomet. Chem.*, 1981, **205**, 371.

[2] R. Uson, V. Riera, J. Jimeno, M. Laguna, and M. P. Gamasa, *J. Chem. Soc., Dalton Trans.*, 1979, 996.

[3] J. A. Connor and P. I. Riley, *J. Chem. Soc., Dalton Trans.*, 1979, 1231.

[4] R. H. Reimann and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1973, 841.

[5] P. M. Treichel and D. W. Firsich, *J. Organomet. Chem.*, 1979, **172**, 223.

[6] R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, 1965, **87**, 5586.

[7] J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, 1976, **98**, 3169.

[8] G. R. Dobson, *Inorg. Chem.*, 1980, **19**, 1413.

[9] R. H. Reimann and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1973, 2658.

[10] R. H. Reimann and E. Singleton, *J. Organomet. Chem.*, 1973, **57**, C75.

[11] R. H. Reimann and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1974, 808.

[12] W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

[13] F. L. Wimmer, M. R. Snow, and A. M. Bond, *Inorg. Chem.*, 1974, **13**, 1617.

[14] A. M. Bond, R. Colton, and M. J. McCormick, *Inorg. Chem.*, 1977, **16**, 155.

[15] A. M. Bond, B. S. Grabaric, and Z. Grabaric, *Inorg. Chem.*, 1978, **17**, 1013.

[16] A. M. Bond, R. Colton, and M. E. McDonald, *Inorg. Chem.*, 1978, **17**, 2842.

[17] D. M. P. Mingos, *J. Organomet. Chem.*, 1979, **179**, C29.

[18] See ref. in ref. 1.

[19] T. G. M. H. Dikhoff and R. G. Goel, *Inorg. Chim. Acta*, 1980, **44**, L72.

[20] P. K. Baker, K. Broadley, N. G. Connelly, B. A. Kelly, M. D. Kitchen, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 1710.