Reactions of Metal Carbonyls. Part III.† Steric and Stereochemical Limitations of Higher Substitution of Manganese Carbonyl Bromide

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The reaction of $[Mn(CO)_5Br]$ with the ligands, L [L = $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, PMe_3, PMe_2Ph, and $AsMe_2Ph$] have given *fac*- and *trans*-$[Mn(CO)_3L_2Br]$ and terminated with *mer*-$[Mn(CO)_2L_3Br]$. The complex *trans*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$, prepared by hydrazine reduction of *trans*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]PF_6$, further reacts with $P(OMe)_3$ to give the tetra substituted compound *trans*-$[Mn(CO)\{P(OMe)_3\}_4Br]$. Factors influencing the substitution reactions of $[Mn(CO)_5Br]$ with monodentate tertiary phosphorus and arsenic ligands are discussed in terms of incoming ligand size and the stereochemistry of the manganese carbonyl complexes. The i.r. and ^1H n.m.r. spectra of these complexes are discussed.

EXTENSIVE studies on the substitution reactions of halogenomanganese pentacarbonyl compounds with a variety of monodentate tertiary phosphine, phosphite, and arsine ligands have been reported [1] and the results of these reactions may be represented by the general scheme:

$$[Mn(CO)_5X] \xrightarrow{L} \underset{(I)}{[Mn(CO)_4LX]} \xrightarrow{L} \underset{(II)}{[Mn(CO)_3L_2X]}$$

$$(X = \text{halogen})$$

Only the *cis*-isomer of the monosubstituted complex (I) has been isolated by this method, whilst both *fac*- and *trans*-isomers of the disubstituted product (IIa and IIb) have been characterised. Attempts at further carbonyl substitutions with these ligands have been successful only for $P(OMe)_3$ and then extended reaction times, in boiling benzene under u.v. irradiation, were required.[2] Thus, just as the formation of *mer*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$ and $[Mn(CO)\{P(OMe)_3\}_4Br]$ were attributed to the 'carbonyl-like' π-character of $P(OMe)_3$,[3] the previous failures to induce further substitutions of the $[Mn(CO)_3L_2Br]$ species with monodentate tertiary phosphorus or arsenic ligands were ascribed to the unfavourable electronic properties of L with respect to CO.[4] That higher substitutions of octahedral metal carbonyls required ligands with strong π-acceptor properties seemed to gain support from force constant calculations relating decreases in $\nu(CO)$ in substituted products to increases in metal–carbon bond strength,[5] and formations of highly substituted products with RNC [4] and PF_3 [6] ligands. It has recently been shown, however, that the trisubstituted rhenium complexes *mer*-$[Re(CO)_2L_3Cl]$ (L = PMe_2Ph and $PMePh_2$) can be formed,[7,8] in spite of the unfavourable electronic properties of the ligands, L, and our reactions of $[Mn(CO)_5Br]$ with nucleophilic diphosphines [9] have readily given $[Mn(CO)(L_2)_2Br]$ (L_2 = dpe and dpm) under relatively mild conditions. This work, together with the recent demonstration that substitution of the tetrahedral carbonyl $[Ni(CO)_4]$ with phosphines and phosphites were dependent only upon the size of the incoming ligand [10] has prompted us to investigate the reaction of $[Mn(CO)_5Br]$ with a series of sterically favourable ligands of variable electronic properties and this paper presents our results.

Preparation of the Complexes $[Mn(CO)_{5-x}L_xBr]$ (x = 2—4).—$[Mn(CO)_5Br]$ reacts rapidly with two molar equivalents of L [L = $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, PMe_3, PMe_2Ph, and $AsMe_2Ph$] in refluxing benzene to give initially *fac*-$[Mn(CO)_3L_2Br]$ (IIa), followed by isomerisation to the *trans*-isomer (IIb), with the exception of $AsMe_2Ph$ which forms an equilibrium mixture favouring the *fac*-isomer. Typical complete isomerisation times ranged from 5 min for PMe_2Ph to 2 h for PMe_3 and were hence too rapid for most of the ligands to allow an easy separation of pure (IIa) from benzene solutions. This isomer was readily prepared, however, from $[Mn(CO)_5Br]$ and L using lower boiling acetone as solvent. When $[Mn(CO)_5Br]$ was treated with an excess of L [L = $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, PMe_3, and PMe_2Ph] in refluxing benzene, the trisubstituted complex *mer*-$[Mn(CO)_2L_3Br]$ (IIIa) was formed within 4 h, with the exception of PMe_3 which required 15 h. For $AsMe_2Ph$, trisubstitution was only effected by reacting (IIb; L = $AsMe_2Ph$) with an excess of ligand in refluxing n-hexane. Attempts to induce further direct substitutions of $[Mn(CO)_5Br]$ or *mer*-$[Mn(CO)_2L_3Br]$ with L in a variety of high boiling solvents failed. However, when *mer*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$ was reacted with neat boiling $P(OMe)_3$ the cation *cis*-$[Mn(CO)_2\{P(OMe)_3\}_4]^+$ was formed as characterised by an i.r. spectrum of the reaction solution.‡ Similar halide

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† Part I, E. Singleton, J. T. Moelwyn-Hughes, and A. W. B. Garner, *J. Organometallic Chem.*, 1970, **21**, 449. Part II, R. H. Reimann and E. Singleton, *J. Organometallic Chem.*, 1972, **38**, 113.

‡ We have fully characterised this cation as the product of the reaction of *trans*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]^+$ and an excess of $P(OMe)_3$ in refluxing chloroform. These compounds are fully discussed in a forthcoming publication.

[1] T. A. Manuel, *Adv. Organometallic Chem.*, 1965, **3**, 181.

[2] P. M. Treichel and J. J. Benedict, *J. Organometallic Chem.*, 1969, **17**, 37.

[3] W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.

[4] K. K. Joshi, P. L. Pauson, and W. H. Stubbs, *J. Organometallic Chem.*, 1963, **1**, 51.

[5] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

[6] R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, 1965, **4**, 1771.

[7] E. Singleton, J. T. Moelwyn-Hughes, and A. W. B. Garner, *J. Organometallic Chem.*, 1970, **21**, 449.

[8] J. T. Moelwyn-Hughes, A. W. B. Garner, and N. Gordon, *J. Organometallic Chem.*, 1971, **26**, 373.

[9] R. H. Reimann and E. Singleton, *J. Organometallic Chem.*, 1972, **38**, 113.

[10] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

labilisations in manganese carbonyl complexes have previously been observed[11] with strongly basic amines. Although (IIIa) is the only isomer obtained by the direct reaction of $[Mn(CO)_5Br]$ with L, we have been able to characterise *trans*-$[Mn(CO)_2L_3Br]$ (IIIb) indirectly for $L = P(OMe)_3$ and $P(OEt)_3$. Thus when [IIIa; $L = P(OMe)_3$ and $P(OEt)_3$] are treated with $NOPF_6$ in dichloromethane solution, rapid single-electron oxidation occurs to give the salt *trans*-$[Mn(CO)_2L_3Br]PF_6$ (IV) in high yield. (For details of technique see ref. 12.) Hydrazine reduction of (IV) in dichloromethane–light petroleum (b.p. 40—60°) mixtures at 0° gave (IIIb), which rapidly converted to (IIIa) in polar solvents or at temperatures above 20° in the absence of free L. For $L = P(OMe)_3$, the rapid removal of the dichloromethane at 0° under reduced pressure afforded orange crystals of (IIIb) which were fully characterised. However, for $L = P(OEt)_3$, isomer (IIIb) could be obtained only as a mixture with [IIIa; $L = P(OEt)_3$], and was identified by a strong i.r. carbonyl band similar to that observed for [IIIb; $L = P(OMe)_3$]. Although it was not possible to induce further carbonyl substitutions of (IIIa) with any of the ligands, L, used in this work, a 50% conversion of [IIIb; $L = P(OMe)_3$] to *trans*-$[Mn(CO)\{P(OMe)_3\}_4Br]$ (V) occurred within 10 min when a highly concentrated solution of this isomer in refluxing light petroleum (b.p. 80—100°) was treated with a large excess of $P(OMe)_3$. With longer reaction times isomerisation of (IIIb) to [IIIa; $L = P(OMe)_3$] occurs which terminates the reaction. Similar attempts at reacting [IIIb; $L = P(OEt)_3$] with either $P(OEt)_3$ or $P(OMe)_3$ gave only the isomerised product [IIIa; $L = P(OEt)_3$].

I.r. and ^1H n.m.r. data [a] for complexes of the type $[Mn(CO)_{5-x}L_xBr]$ (x = 2—4)

			Carbonyl stretching frequencies (cm^{-1})	$-CH_3$ or $-OCH_3$	$-OCH_2-$(τ)
(IIa)	*fac*-$[Mn(CO)_3L_2Br]$	PMe_2Ph	2020vs, 1954s, 1903s	8·29dt, J 7·0 Hz *	
		$AsMe_2Ph$	2024vs, 1951s, 1910s	8·44s; 8·49s	
		$P(OMe)_2Ph$	2045s, 1975s, 1927s	6·19m	
		$P(OEt)_3$	2046s, 1970s, 1932s	8·68t, J(H–H) = 7·3 Hz	5·77m
		PMe_3	2024s, 1952s, 1901s	8·39dt, J 8·4 Hz †	
(IIb)	*trans*-$[Mn(CO)_3L_2Br]$	PMe_2Ph	2030w, 1947vs, 1909m	8·09dt, J 8·3 Hz ‡	
		$AsMe_2Ph$	2033w, 1946vs, 1908s	8·26s	
		$P(OMe)_2Ph$	2052w, 1972vs, 1929m	6·17dt, J 11·4 Hz ‡	
		$P(OEt)_3$	2053w, 1967s, 1942m	8·67t, J(H–H) = 8·7 Hz	5·78m
		PMe_3	2033w, 1944s, 1900m	8·35dt, J 8·4 Hz ‡	
(IIIa)	*mer*-$[Mn(CO)_2L_3Br]$	PMe_2Ph [b]	1929s, 1851s	8·25m; 8·66d, J(P–H) = 7·2 Hz	
		$AsMe_2Ph$	1931s, 1852s	8·46s; 8·52s; 8·78s	
		$P(OMe)_2Ph$	1977s, 1885s	6·29m	
		$P(OEt)_3$ [c]	1973s, 1888s	8·70t, J(H–H) = 7·5) Hz	5·71m
		PMe_3	1929s, 1846s	8·43m [d]	
(IIIb)	*trans*-$[Mn(CO)_2L_3Br]$	$P(OMe)_3$	2010vw, 1916vs [e]		
		$P(OEt)_3$	2010vw, 1920vs [e]		
(V)	*trans*-$[Mn(CO)\{P(OMe)_3\}_4Br]$		1867s		

Complexes may be analysed as a limiting case of an $[AM_3X_3]_2$,* $[AM_3X_3Y_3]_2$,† or $[AX_3]_2$ ‡ system (ref. 15) with 'J' the separation of the outer peaks of the observed resonance.

s = Singlet. m = Multiplet. t = Triplet. dt = Distorted triplet.

[a] I.r. spectra measured for benzene solutions, ^1H n.m.r. spectra measured in $CDCl_3$ solution unless otherwise stated. [b] J. T. Moelwyn Hughes, A. W. B. Garner, and A. S. Howard, *J. Chem. Soc.* (*A*), 1971, 2370. [c] I. S. Butler, N. J. Coville, and H. K. Spendjian, *J. Organometallic Chem.*, 1972, **43**, 185. [d] Measured in $[^2H_6]$acetone solution. [e] In dichloromethane.

Infrared and ^1H *N.M.R. Spectra.*—I.r. and n.m.r. data for all the complexes described here, except [IIa, IIb, and IIIa; $L = P(OMe)_3$] which have been described previously,[2] are given in the Table. The disubstituted complexes, designated *fac*-$[Mn(CO)_3L_2Br]$ (IIa), exhibit three strong carbonyl stretching frequencies consistent with the proposed stereochemistry of $C_S(2A' + A'')$. For the other isomer of $[Mn(CO)_3L_2Br]$ prepared, the one weak and two strong ν(CO) bands observed could arise from either of the remaining conformers (IIb) (C_{2v}; $2A_1 + B_1$) or (IIc) (C_S; $2A' + A''$). However, we have assigned the *trans*-configuration (IIb) to our complexes by analogy to previously reported examples of these type of complexes prepared by the same reaction sequence.[13] The trisubstituted complexes all contain two strong ν(CO) bands of equal intensity, and of the three possible structures, (IIIa), (IIIb), and (IIIc), only (IIIb) can be eliminated as it is predicted to show one strong band in the ν(CO) region. Thus on i.r. evidence alone it was not possible unambiguously to assign the conformation of these isomers as (IIIa) (C_S; $2A'$) or (IIIc) (C_S; $A' + A''$). The compounds have been assigned as the *mer*-isomer (IIIa), however, on supplementary ^1H n.m.r. evidence and on empirical observations in this and other work,[14a] together with theoretical calculations,[14b] of the instability

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[11] R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, 1962, **84**, 2495.

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

[13] R. J. Angelici, F. Basolo, and A. J. Poë, *J. Amer. Chem. Soc.*, 1963, **85**, 2115.

[14] (*a*) P. W. Jolly and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5259; (*b*) D. A. Brown and W. J. Chambers, *J. Chem. Soc.* (*A*), 1971, 2083; R. F. Fenske and R. L. De Kock, *Inorg. Chem.*, 1970, **9**, 1053.

of manganese carbonyl complexes with L trans to bromine. The i.r. carbonyl spectra of *trans*-$[\mathrm{Mn(CO)_2L_3Br}]\mathrm{PF_6}$ and *trans*-$[\mathrm{Mn(CO)_2L_3Br}]$ $[\mathrm{L = P(OMe)_3}$ and $\mathrm{P(OEt)_3}]$ both contain one weak and one strong ν(CO) stretching vibration with the carbonyl of the salt absorbing at higher energy, in keeping with the C_{2v} symmetry ($A_1 + B_1$) of isomers (IV) and (IIIb). The conformation of the known compound $[\mathrm{Mn(CO)\{P(OMe)_3\}_4Br}]$ has been reported[2] as the *trans*-isomer (V) on the basis of carbonyl substitution precedents and ^{1}H n.m.r. evidence.

The ^{1}H n.m.r. methyl resonance patterns of the *fac*- and *trans*-disubstituted complexes, (IIa) and (IIb) ($\mathrm{L = PMe_3}$, $\mathrm{P(OMe)_2Ph}$, and $\mathrm{PMe_2Ph}$) respectively, were of no use in assigning conformations to the two sets of isomers as they were all of a type corresponding to 'virtually coupled' systems.[15] Thus in (IIa) for the non-equivalent methyl groups on the chemically identical ligands, ^2J(P–P) is sufficiently large for the observed resonances to appear as distorted triplets for $\mathrm{L = PMe_2Ph}$ and $\mathrm{PMe_3}$, and a five-line multiplet in the ratio of 1 : 4 : 6 : 4 : 1 for $\mathrm{L = P(OMe)_2Ph}$, in keeping with limiting cases of $[\mathrm{AM_3X_3}]_2$ and $[\mathrm{AM_3X_3Y_3}]_2$ type spectra.[15] These spectra were not observed to be solvent or temperature dependent. We have hence discounted the possibility of one or all of these resonances as arising from the presence of conformers in solution, due to restricted rotation about the metal–phosphorus bond, similar to those observed[16] in certain palladium and platinum tertiary butylphosphine complexes. The ^{1}H n.m.r. spectrum of (IIa; $\mathrm{L = AsMe_2Ph}$) consists of a doublet resonance corresponding to two non-identical methyl groups on the chemically equivalent arsine ligands, there being no plane of symmetry along the metal arsine bonds. The magnetically equivalent methyls bonded to the ligands in [IIb; $\mathrm{L = PMe_3}$, $\mathrm{PMe_2Ph}$, and $\mathrm{P(OMe)_2Ph}$] also give rise to distorted triplets typical of $[\mathrm{AX_3}]_2$ patterns for intermediate ^2J(P–P) couplings. Complex (IIb; $\mathrm{L = AsMe_2Ph}$) contains a broad single methyl resonance in its n.m.r. spectrum. For the trisubstituted complex $[\mathrm{Mn(CO)_2(PMe_2Ph)_3Br}]$, the n.m.r. spectrum consists of a broad, ill defined quartet arising from the two non-identical methyl groups on the 'virtually-coupled' *trans*-phosphine ligands, and a sharp doublet arising from the magnetically equivalent methyl groups on the third phosphine ligand. No *cis*-coupling was observed in this complex. The methyl resonances in the compound $[\mathrm{Mn(CO)_2(AsMe_2Ph)_3Br}]$ occur as a doublet and singlet in the ratio of 2 : 1 corresponding to the two *trans*-arsines and the chemically non-equivalent third arsine, respectively. Thus from this n.m.r. evidence we have assigned the *mer*-configuration (IIIa; $\mathrm{L = PMe_2Ph}$ and $\mathrm{AsMe_2Ph}$) to these compounds and the same conformation to the other trisubstituted complexes by analogy. The methyl spectra of [IIIa; $\mathrm{L = P(OMe)_2Ph}$ and $\mathrm{PMe_3}$] were observed as a four- and five-line multiplet, respectively and were not further analysed. No ^{1}H n.m.r. data for [IIIb; $\mathrm{L = P(OMe)_3}$ and $\mathrm{P(OEt)_3}$] were recorded due to rapid isomerisations occurring in solution.

DISCUSSION

Trisubstituted manganese carbonyl bromide complexes have been prepared in this study with surprising ease for both strong σ-donor and strong π-acceptor ligands with small steric requirements. With the bulkier ligands $\mathrm{PMePh_2}$ and $\mathrm{P(OMe)Ph_2}$ only disubstituted products were obtained. For $\mathrm{P(OPh)_3}$ an intermediate case was observed in which an approximately equimolar mixture of the di- and tri-substituted species was obtained in the reaction solution as characterised by i.r. spectroscopy. Attempts to isolate $[\mathrm{Mn(CO)_2\{P(OPh)_3\}_3Br}]$ gave only *trans*-$[\mathrm{Mn(CO)_3\{P(OPh)_3\}_2Br}]$ with the i.r. spectrum of the mother liquor still showing an approximate 1 : 1 ratio of these two compounds. In fact, initial kinetic results obtained by perturbation experiments involving variations in the free ligand concentrations have shown the existence of the equilibrium (*i*) for the larger ligands used in this study.

$$(\mathrm{IIb}) + \mathrm{L} \rightleftharpoons (\mathrm{IIIa}) + \mathrm{CO} \qquad (i)$$

As the steric crowding in the molecule increases, the effective competence by CO in the reverse reaction of equation (*i*), is demonstrated by the rapid carbonylations of (IIIa) in acetone solutions to give (IIb) within 10 min at ambient temperatures for $\mathrm{L = PMe_2Ph}$, $\mathrm{AsMe_2Ph}$, and $\mathrm{PMe_3}$, and under reflux for $\mathrm{L = P(OMe)_3}$, $\mathrm{P(OEt)_3}$, and $\mathrm{P(OMe)_2Ph}$, even in the presence of free L. No reaction of (IIb) with CO at atmospheric pressure was observed in cold or refluxing benzene for all the ligands used in these experiments. That the carbonylation reaction depicted in equation (*i*) is probably a steric assisted dissociative process is better demonstrated by corresponding reactions[17] of *mer*-$[\mathrm{Re(CO)_2L_3Br}]$ in refluxing benzene, which have given the rhenium analogues of (IIb) at rates corresponding to $\mathrm{P(OPh)_3 \sim P(OEt)Ph_2 \sim PEt_2Ph \sim PMePh_2 \gg PMe_2Ph > PMe_3 > P(OMe)_2Ph}$. It can also be seen from this series that the larger rhenium atom facilitates the formation of very stable trisubstituted carbonyl compounds with much bulkier ligands, than the manganese. We have noted, as has been found previously in substituted metal carbonyl complexes, that on successive replacement of carbonyl groups, the carbonyl stretching frequencies decrease in energy (see Table), with the greatest decrease noted for the phosphine ligands. However, qualitative investigations of the times required for successive substitutions of $[\mathrm{Mn(CO)_5Br}]$ with all the ligands L have revealed only slight differences in reaction times. These observations must hence cast doubt on the effective use of wholly empirical

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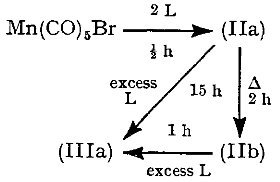
[15] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[16] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 1826.

[17] R. H. Reimann and E. Singleton, unpublished results.

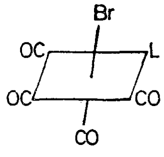
correlations of force constants, calculated from ν(CO) frequencies, with bond strength and/or carbonyl lability as explanations for low substitutions in metal carbonyls. It is pertinent to note that the reported[18] decreases in the rates of reactions of $[Mn(CO)_5X]$ as X varies from chlorine to the more polarisable iodine, and attributed to stronger metal carbon bonding inferred from decreases in ν(CO), can also be explained on simple size effects as only large tertiary phosphorus ligands were used in the study.

In addition to the reaction dependence on ligand size, we have also observed stereochemical limitations to the substitution reaction. A qualitative investigation of the reaction sequence obtained by treating $[Mn(CO)_5Br]$ with successive molar equivalents of PMe_3 in refluxing benzene is depicted in the Scheme, and has indicated that carbonyl substitution in this system is favoured only by isomers containing mutually *trans*-CO groups. The slow reaction of (IIa) to give (IIIa) can be related to earlier kinetic studies[13] which have shown the isomerisation rates of (IIa) to (IIb) to be suppressed by free ligand in solution. The inertness to substitution of isomers containing *cis*-carbonyl groups is also demonstrated by: (*a*) the failure to induce further reactions in all the compounds (IIIa) prepared here and (*b*) the failure to form (IIIa) with pyridine which can be related to the inability to effect isomerisation of *fac*-$[Mn(CO)_3(py)_2Br]$. On the other hand [IIIb; L = $P(OMe)_3$] with *trans*-CO groups readily reacts with $P(OMe)_3$ to give the tetrasubstituted complex (V), which was previously prepared[2] by treating $[Mn(CO)_5Br]$ with an excess of $P(OMe)_3$ in refluxing benzene under u.v. irradiation for 6 days. We have reinvestigated this reaction and find that (V) can be prepared by irradiating either (IIIa) or (IIIb) with u.v. in cold dichloromethane solution in the presence of $P(OMe)_3$. When (IIIa) was irradiated in cold dichloromethane solution, in the absence of $P(OMe)_3$, an i.r. spectrum of the solution showed the strong ν(CO) band characteristic of (IIIb), indicating that the substitution pathway of (IIIa) to (V) induced by u.v. also occurs *via* the formation of the thermally unstable isomer (IIIb).

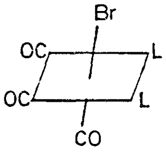


SCHEME Treatment of $[Mn(CO)_5Br]$ with PMe_3 in refluxing benzene solution

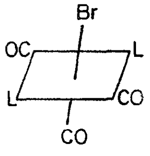
This may hence explain why long reaction times were required in the previous preparation of (V) as opposing reaction conditions were used. This type of 'kinetic *trans*-effect' is well established in square planar systems and has precedents in substitution reactions of octahedral[19] complexes. Studies[20a] on Pt^{II} complexes have shown that CO has a stronger *trans*-labilising influence than phosphines, and in our study the inability to replace either phosphines or phosphites with CO in (IIb) in refluxing benzene must further emphasise the much stronger labilising effect of the carbonyl group in these systems than phosphines or phosphites. It has been suggested[20b] from earlier studies that because isomer [IIa; L = PPh_3 and $P(OPh)_3$] is formed first, the preferential pathway to the disubstituted manganese carbonyl halide complexes may occur *via* the *fac*-isomer (IIa), because of greater reductions in the metal–carbon bond strength when two CO's are mutually *trans* rather than *trans* to L. However, our reactions have only demonstrated a *trans*-labilising effect and whether this is related to bond weakening has yet to be shown in these systems. It may be interesting to observe whether substitutions[21] of $[Mn(CO)_5H]$ with PF_3 to give the products $[Mn(CO)_{5-x}(PF_3)_xH]$ (x = 1—5) occurs more readily than the corresponding phosphines and phosphites because of the strong labilising effect of both the hydride and the PF_3 ligand coupled with the small size of the latter, and whether all five carbonyl groups can be replaced in $[Mn(CO)_5Br]$ with PF_3.



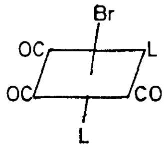
(I)



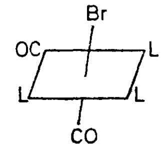
(IIa)



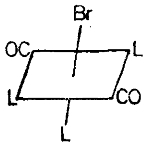
(IIb)



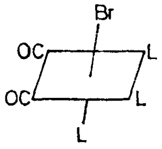
(IIc)



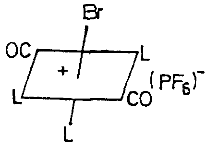
(IIIa)



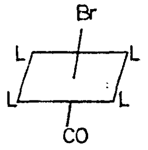
(IIIb)



(IIIc)



(IV)



(V)

We are currently investigating the substitution pathway of the dimer $[Mn_2(CO)_{10}]$ with phosphine and phosphite ligands to give the disubstituted dimeric species $[Mn_2(CO)_8L_2]$. *X*-Ray diffraction studies on the

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[18] R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, 1962, **84**, 2495; *Inorg. Chem.*, 1963, **2**, 728.

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complexes $[Mn_2(CO)_8L_2]$ (L = PEt_3 [22] and $PMePh_2$ [23]) have shown them to be diaxially substituted, whilst for the smaller ligand $AsMe_2Ph$ [23] i.r. and *X*-ray data, respectively have shown that diequatorial substitution has occurred. Initial *X*-ray data on the monosubstituted complex $[Mn_2(CO)_9L]$ (L = $PMePh_2$) has also indicated equatorial substitution, and thus it seems likely that the formation of the diaxial products with bulky ligands may occur *via* a thermodynamically controlled isomerisation from a diequatorial isomer.

EXPERIMENTAL

$[Mn(CO)_5Br]$ was prepared by the method of Abel and Wilkinson.[24] All ligands were obtained commercially and were not further purified. M.p.s were recorded on a Kofler hot-stage apparatus, i.r. spectra on a Perkin-Elmer 457 grating spectrophotometer, and n.m.r. spectra with Varian A-60A and HA 100 instruments. Elemental analyses were performed by Mr. G. J. Roberts of this laboratory.

trans-$[Mn(CO)_3(PMe_2Ph)_2Br]$.— Dimethylphenylphosphine (0·765 g, 5·54 mmol) was added to a suspension of $[Mn(CO)_5Br]$ (0·74 g, 2·71 mmol) in benzene (30 ml) and the mixture refluxed for 4 h. The orange solution was filtered while hot and the solvent removed under reduced pressure. The resultant oil was crystallised from hot light petroleum (b.p. 60—80°) to give the required product as yellow needles (1·21 g, 90%), m.p. 115—117° (Found: C, 46·25; H, 4·2; Br, 16·1. $C_{19}H_{22}O_3P_2BrMn$ requires: C, 46·1; H, 4·5; Br, 16·15%).

The following compounds were prepared in a similar way.

trans-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$ as orange needles (90% yield), m.p. 128—131° (Found: C, 41·05; H, 4·1; Br, 14·25. $C_{19}H_{22}O_7P_2BrMn$ requires: C, 40·8; H, 3·95; Br, 14·3%).

trans-$[Mn(CO)_3\{P(OEt)_3\}_2Br]$ as orange prisms (50% yield), m.p. 99° (Found: C, 32·50; H, 5·5; Br, 14·65. $C_{15}H_{30}O_9P_2BrMn$ requires: C, 32·65; H, 5·45; Br, 14·5%).

trans-$[Mn(CO)_3(PMe_3)_2Br]$, after refluxing for 15 h, as brown needles (50% yield), m.p. 129° (Found: C, 29·2; H, 4·95; Br, 21·75. $C_9H_{18}O_3P_2BrMn$ requires: C, 29·1; H, 4·85; Br, 21·55%).

fac- and *trans*-$[Mn(CO)_3(AsMe_2Ph)_2Br]$, isolated only as a crystalline mixture, which on separating mechanically, gave the *fac*-isomer as orange prisms (60% yield), m.p. 114° (Found: C, 39·25; H, 3·8; Br, 13·5. $C_{19}H_{22}O_3As_2BrMn$ requires: C, 39·1; H, 3·8; Br, 13·7%), and the *trans*-isomer as yellow needles (25% yield), m.p. 107° (Found: C, 39·3; H, 3·85; Br, 13·8%).

fac-$[Mn(CO)_3(PMe_3)_2Br]$ as yellow needles (75% yield), m.p. 63° (Found: C, 29·0; H, 4·95; Br, 21·75. $C_9H_{18}O_3P_2BrMn$ requires: C, 29·1; H, 4·85; Br, 21·55%).

mer-$[Mn(CO)_2(PMe_2Ph)_3Br]$ as brown prisms (82% yield), m.p. 131—133° (decomp.) (Found: C, 51·45; H, 5·65; Br, 13·4. $C_{26}H_{33}O_2P_3BrMn$ requires: C, 51·6; H, 5·5; Br, 13·2%).

mer-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]$, recrystallised from hot ethanol as orange needles (80% yield) m.p. 132° (Found: C, 44·45; H, 4·75; Br, 11·25. $C_{26}H_{33}O_8P_3BrMn$ requires: C, 44·5; H, 4·7; Br, 11·4%).

mer-$[Mn(CO)_2\{P(OEt)_3\}_3Br]$, crystallised by freezing out of ethanol solution to give orange plates (50% yield) m.p. 75° (Found: C, 34·9; H, 6·6; Br, 11·55. $C_{20}H_{45}O_{11}P_3BrMn$ requires: C, 34·85; H, 6·55; Br, 11·6%).

mer-$[Mn(CO)_2(PMe_3)_3Br]$, after refluxing for 15 h, as orange plates (50% yield), m.p. 120—128° (decomp.) (Found: C, 31·65; H, 6·55; Br, 19·3. $C_{11}H_{27}O_2P_3BrMn$ requires: C, 31·5; H, 6·45; Br, 19·1%).

mer-$[Mn(CO)_2(AsMe_2Ph)_3Br]$.—A suspension of *trans*-$[Mn(CO)_3(AsMe_2Ph)_2Br]$, (1·0 g, 1·72 mmol) and dimethylphenylarsine (0·83 g, 4·56 mmol) in hexane (30 ml), was refluxed for 18 h. The solution was filtered while hot and allowed to cool slowly, depositing large crystals of both *fac*- and *trans*-$[Mn(CO)_3(AsMe_2Ph)_2Br]$, together with the required product. Mechanical separation gave the required product as dark brown prisms (0·5 g, 40%) m.p. 103—106° (Found: C, 42·4; H, 4·5; Br, 11·15. $C_{26}H_{33}O_2As_3BrMn$ requires: C, 42·35; H, 4·5; Br, 10·85%).

fac-$[Mn(CO)_3(PMe_2Ph)_2Br]$.—A refluxing solution of $[Mn(CO)_5Br]$ (0·74 g, 2·71 mmol) and dimethylphenylphosphine (0·765 g, 5·54 mmol) in acetone (20 ml) was monitored by i.r. spectroscopy until total conversion to the required product was observed (*ca.* 1 h). The solvent was then removed under reduced pressure and the resultant red oil crystallised under hexane. Recrystallisation of the crude material from dichloromethane–light petroleum (b.p. 40—60°) gave the product as orange plates (0·69 g, 52%), m.p. 120° (Found: C, 46·0; H, 4·5; Br, 16·2. $C_{19}H_{22}O_3P_2BrMn$ requires: C, 46·1; H, 4·5; Br, 16·15%).

The following compounds were prepared in a similar way.

fac-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$, recrystallised from dichloromethane–methanol as orange plates (70% yield), m.p. 108—110° (decomp.) (Found: C, 40·7; H, 3·95; Br, 14·5. $C_{19}H_{22}O_7P_2BrMn$ requires: C, 14·8; H, 3·95; Br, 14·3%).

fac-$[Mn(CO)_3\{P(OEt)_3\}_2Br]$, crystallised by freezing out of methanol as yellow microcrystals (30% yield) (Found: C, 32·75; H, 5·6; Br, 14·7. $C_{15}H_{30}O_9P_2BrMn$ requires: C, 32·65; H, 5·45; Br, 14·5%).

trans-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$.—A solution of *mer*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$ [2] (0·5 g, 0·89 mmol) in dichloromethane (5 ml) was treated with an excess of $NOPF_6$ at room temperature, giving a deep red solution containing the cation *trans*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]^+$ after 2 min, accompanied by the evolution of NO gas. Light petroleum (b.p. 60—80°) was then added to the filtered solution and the mixture was cooled to 0°. After the addition of anhydrous hydrazine (0·1 ml), the dichloromethane was rapidly removed under reduced pressure to give the product as orange needles (0·38 g, 76%), m.p. 125° (decomp.) (Found: C, 23·45; H, 4·7; Br, 14·2. $C_{11}H_{27}O_{11}P_3BrMn$ requires: C, 23·45; H, 4·8; Br, 14·2%).

trans-$[Mn(CO)_2\{P(OEt)_3\}_3Br]$ was similarly prepared from *mer*-$[Mn(CO)_2\{P(OEt)_3\}_3Br]$ and characterised on i.r. evidence only (see Table).

$[Mn(CO)\{P(OMe)_3\}_4Br]$.—(a) A suspension of *trans*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$ (0·5 g, 0·89 mmol) in light petroleum (b.p. 80—100°, 5 ml) was refluxed with trimethyl phosphite (2·21 g, 17·8 mmol). After 10 min an i.r. spectrum of the reaction solution indicated the presence of an equimolar mixture of *mer*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$ and

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$[Mn(CO)\{P(OMe)_3\}_4Br]$. These compounds were identified by comparisons with solution spectra of the pure samples.

(*b*) A solution of *trans*-$[Mn(CO)_2\{P(OMe)_3\}_3Br]$ (0·5 g, 0·89 mmol) and trimethyl phosphite (0·17 g, 1·37 mmol) in dichloromethane (10 ml)–light petroleum (b.p. 60—80°, 200 ml) was irradiated with a Hanovia 125 W u.v. lamp for 10 min. After filtration the solvent was removed under reduced pressure. The resultant oil was washed with n-pentane and recrystallised from dichloromethane–light petroleum (b.p. 40—60°) to give the required product as yellow plates (0·19 g, 32%), m.p. 136° (decomp.) (Found: C, 23·7; H, 5·45; Br, 12·1. $C_{13}H_{36}O_{13}P_4BrMn$ requires C, 23·65; H, 5·45; Br, 12·15%).

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