Reactions of Metal Carbonyls. Part 7.[1] Substitution Reactions of Decacarbonyldimanganese with Tertiary Phosphorus and Arsenic Ligands

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Thermal or photochemical reactions of $[Mn_2(CO)_{10}]$ with L produce $[Mn_2(CO)_9L]$ for L = PMe_2Ph, $AsMe_2Ph$, and $PMePh_2$, diaxially substituted $[Mn_2(CO)_8L_2]$ for L = PMe_2Ph, $PMePh_2$, $PPh(OMe)_2$, and $PPh_2(OMe)$ and diequatorially substituted $[Mn_2(CO)_8L_2]$ for L = $AsMe_2Ph$, $AsEt_3$, and $AsMe_3$. The diequatorial product $[Mn_2(AsMe_2Ph)_2(CO)_8]$ undergoes ligand exchange with $PPh(OMe)_2$ and $P(OMe)_3$ to give diaxial $[Mn_2(CO)_8L_2]$ [L = $PPh(OMe)_2$ and $P(OMe)_3$]. Thermal reactions of $[Mn_2(CO)_{10}]$ with an excess of L [L = $PMePh_2$, $PEtPh_2$, PMe_2Ph, $PPh(OMe)_2$, and $P(OMe)_3$] in high boiling solvents give the hydrido-complexes *mer-trans*-$[Mn(CO)_3HL_2]$ which are more conveniently prepared using $Na[BH_4]$ in refluxing ethanol. Treatment of the hydrides with HPF_6 in acetonitrile gives the salts $[Mn(CO)_3(NCMe)L_2][PF_6]$. Other cationic complexes of formula $[Mn(CO)_5L][PF_6]$ [L = CO, $P(OMe)_3$, $PPh(OMe)_2$, or $PPh_2(OMe)$] are produced from reactions of $[Mn_2(CO)_8L_2]$ with $NOPF_6$ in dichloromethane. Bromination of $[Mn_2(CO)_8L_2]$ [L = $PPh(OMe)_2$ or $PPh_2(OMe)$] produces *trans*-$[MnBr(CO)_4L]$ which isomerise to *cis*-$[MnBr(CO)_4L]$ in refluxing chloroform. Infrared and ^1H n.m.r. data for all the complexes prepared are discussed.

DECACARBONYLDIMANGANESE undergoes substitution reactions with large unidentate tertiary phosphorus or arsenic ligands with preservation of the metal–metal bond to give mono- and di-substituted derivatives [2-8] in which axial replacement (*i.e. trans* to the metal–metal bond) of carbonyl groups has occurred. The stereochemistry of these complexes was initially inferred from i.r. spectra [5,9] and later confirmed by the *X*-ray structural determination of $[Mn_2(CO)_8(PEt_3)_2]$.[10] Under

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more extreme conditions, substitution is usually accompanied by metal–metal bond fission forming initially paramagnetic intermediates [2,8] and then hydrides of the type $[Mn(CO)_3HL_2]$.[11] Recent studies [12,13] on the reactivity of $[Re_2(CO)_{10}]$ towards the strong σ-donor ligands PMe_2Ph, $PMePh_2$, and $AsMe_2Ph$ have shown, however, that as well as forming mono- and di-substituted products, trisubstituted complexes are also obtained. Furthermore, at least one ligand in the di- and trisubstituted species is *cis* to the metal–metal bond. The formation of these equatorially substituted complexes, together with our current interest [14–16] in the steric and stereochemical factors governing octahedral metal-carbonyl substitutions, has prompted us to investigate the reactions of $[Mn_2(CO)_{10}]$ with a series of ligands of variable size and electronic properties. The results of this investigation are now presented.

TABLE 1

Analytical (%) and infrared spectroscopic data (cm⁻¹) for new substituted manganese carbonyl complexes

Complex	Analysis [a]			C–O Stretching frequencies
	C	H	Other	
$[Mn_2(CO)_9(PMe_2Ph)]$	40.7 (40.8)	2.1 (2.2)		2 094w, 2 016s, 1 993vs, 1 969 (sh), 1 938m [c]
$[Mn_2(AsMe_2Ph)(CO)_9]$	37.4 (37.5)	2.1 (2.0)		2 092m, 2 020s, 1 991vs, 1 968 (sh), 1 936m [c]
$[Mn_2(CO)_9(PMePh_2)]$	47.3 (47.0)	2.4 (2.3)		2 092m, 2 014s, 1 992vs, 1 953w, 1 936m [c]
$[Mn_2(CO)_8(PMe_2Ph)_2]$	47.3 (47.2)	3.6 (3.6)		1 982w, 1 950vs [c]
$[Mn_2(AsMe_2Ph)_2(CO)_8]$	41.5 (41.3)	3.1 (3.2)		2 056w, 1 989s, 1 956s, 1 914m [c]
$[Mn_2(CO)_8(PMePh_2)_2]$	55.4 (55.6)	3.7 (3.5)		1 983w, 1 954vs [c]
$[Mn_2(AsEt_3)_2(CO)_8]$	36.5 (36.5)	4.6 (4.6)		2 055w, 1 980s, 1 952s, 1 927w, 1 915m [d]
$[Mn_2(AsMe_3)_2(CO)_8]$	29.3 (29.3)	3.1 (3.2)		2 055m, 1 986s, 1 959s, 1 918s [d]
$[Mn_2(CO)_8\{PPh(OMe)_2\}_2]$	42.3 (42.6)	3.7 (3.6)		1 987w, 1 968s [d]
$[Mn_2(CO)_8\{PPh_2(OMe)\}_2]$	53.3 (53.0)	3.8 (3.9)		1 984 (sh), 1 960s [b]
$[Mn(CO)_3H(PMePh_2)_2]$	64.7 (64.6)	5.2 (4.9)		2 000w, 1 915vs, br [c]
$[Mn(CO)_3H(PEtPh_2)_2]$	65.3 (65.6)	5.6 (5.3)		2 002w, 1 908s, br [c]
$[Mn(CO)_3H(PMe_2Ph)_2]$	n.m.	n.m.		1 998w, 1 950 (sh), 1 911vs, 1 904 (sh) [d]
$[Mn(CO)_3H\{PPh(OMe)_2\}_2]$	n.m.	n.m.		2 023w, 1 944s, 1 927m [d]
$[Mn(CO)_3H\{P(OMe)_3\}_2]$	n.m.	n.m.		2 028w, 1 952s, 1 930m, 1 895w [d]
$[Mn(CO)_3(NCMe)(PMePh_2)_2][ClO_4]$	54.4 (54.7)	4.4 (4.3)	N 1.9 (2.1)	2 065w, 1 977s, 1 942m [e]
$[Mn(CO)_3(NCMe)(PEtPh_2)_2][PF_6]$	52.2 (52.3)	4.6 (4.9)	N 1.8 (1.8)	2 064w, 1 975s, 1 942m [e]
$[Mn(CO)_5\{P(OMe)_3\}][PF_6]$	20.7 (20.7)	1.9 (2.0)		2 161m, 2 110 (sh), 2 064s [e]
$[Mn(CO)_5\{PPh(OMe)_2\}][PF_6]$	30.9 (30.6)	2.2 (2.2)		2 155m, 2 098 (sh), 2 058s [e]
$[Mn(CO)_5\{PPh_2(OMe)\}][PF_6]$	38.9 (38.9)	2.4 (2.4)		2 154m, 2 104 (sh), 2 056s [e]
trans-$[MnBr(CO)_4\{PPh_2(OMe)\}]$	44.4 (44.1)	2.85 (2.85)		2 098w, 1 995vs [f]
trans-$[MnBr(CO)_4\{PPh(OMe)_2\}]$	34.6 (34.6)	2.6 (2.7)	Br 19.1 (19.2)	2 100w, 2 013vs [e]

[a] Calculated values are given in parentheses; n.m. = not measured. [b] In acetone. [c] In benzene. [d] In cyclohexane. [e] In dichloromethane. [f] In chloroform.

RESULTS AND DISCUSSION

Ultraviolet irradiation of a solution of $[Mn_2(CO)_{10}]$ and one molar equivalent per molecule of L (L = PMe_2Ph, $AsMe_2Ph$, or $PMePh_2$) in benzene gave a mixture of starting material, $[Mn_2(CO)_9L]$, and $[Mn_2(CO)_8L_2]$. Thermal reactions in benzene produced the same products only more slowly. The very low yields obtained of the monosubstituted dimer can be explained in terms of the competing photolysis (1) which has recently been shown,[17]

$$[Mn_2(CO)_9L] \xrightarrow{h\nu} [Mn_2(CO)_{10}] + [Mn_2(CO)_8L_2] \quad (1)$$

for L = PPh_3, to produce the decacarbonyl and the disubstituted dimer in an almost 1 : 1 ratio in high yield. Pure samples of $[Mn_2(CO)_9L]$ were separated on an alumina column using dichloromethane–light petroleum (b.p. 30—40 °C) mixtures, the complexes being eluted in the order $[Mn_2(CO)_{10}]$, $[Mn_2(CO)_9L]$, and $[Mn_2(CO)_8L_2]$. The carbonyl i.r. spectra of $[Mn_2(CO)_9L]$ contained five bands indicative of C_{4v} symmetry and axial substitution [9] (Table 1), and the ^1H n.m.r. methyl resonances appeared as doublets for L = PMe_2Ph and $PMePh_2$ and a singlet for L = $AsMe_2Ph$ (Table 2). The *X*-ray analysis [18] of $[Mn_2(CO)_9(PMe_2Ph)]$ confirmed that the ligand was bonded *trans* to the metal–metal bond.

Reaction of $[Mn_2(CO)_{10}]$ with 2 moles of L [L = PMe_2Ph, $AsMe_2Ph$, $PMePh_2$, $AsMe_3$, $AsEt_3$, $PPh(OMe)_2$, and $PPh_2(OMe)$] in benzene solution under u.v. irradiation gave the disubstituted complexes $[Mn_2(CO)_8L_2]$ in high yield. For L = PMe_2Ph, $PMePh_2$, $PPh(OMe)_2$, and $PPh_2(OMe)$, the solution i.r. carbonyl spectra exhibited one weak and one very strong band, indicative of D_{4d} symmetry and a diaxially substituted species. This spectral pattern is well established, having been observed previously for all the known phosphine-substituted $[Mn_2(CO)_8L_2]$ species (with the exception of L = PF_3 [7]), and the validity of the stereochemical assignment has been shown by the *X*-ray crystal structures of diaxial $[Mn_2(CO)_8(PEt_3)_2]$ [10] and $[Mn_2(CO)_8(PMePh_2)_2]$.[19] A different stereochemistry is predicted from the four

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TABLE 2

Melting points, molecular weights, and ^{1}H n.m.r. spectroscopic data for new substituted manganese carbonyl complexes

Complex	Melting point (θ_c/°C)	M [a]	^{1}H N.m.r. data (τ) [b]		
			CH$_2$	CH$_3$ and OCH$_3$	Other resonances
$[Mn_2(CO)_9(PMe_2Ph)]$	105—108	485 (500)		7.99 (d) [J(P–H) 4.3]	
$[Mn_2(AsMe_2Ph)(CO)_9]$	67—69	565 (544)		8.26 (s) [c]	
$[Mn_2(CO)_9(PMePh_2)]$	136—138	559 (562)		7.80 (d) [J(P–H) 8.1] [c]	
$[Mn_2(CO)_8(PMe_2Ph)_2]$	147 [d]	593 (610)		8.10 (d) [J(P–H) 4.3]	
$[Mn_2(AsMe_2Ph)_2(CO)_8]$	109	720 (698)		8.25 (s) [c]	
$[Mn_2(CO)_8(PMePh_2)_2]$	126—132	728 (734)		7.89 (d) [J(P–H) 7.0] [c]	
$[Mn_2(AsEt_3)_2(CO)_8]$	58—62	673 (658)	7.98 (dq) [J(H–H) 7.8]	8.73 (dt) [J(H–H) 7.8)	
$[Mn_2(AsMe_3)_2(CO)_8]$	83	565 (573)		8.43 (s)	
$[Mn_2(CO)_8\{PPh(OMe)_2\}_2]$	164 [d]	628 (676)		6.20 (d) [J(P–H) 11.9]	
$[Mn_2(CO)_8\{PPh_2(OMe)\}_2]$	143—146 [d]	748 (770)		6.50 (d) [J(P–H) 12.4]	
$[Mn(CO)_3H(PMePh_2)_2]$	131—134	527 (539)		7.92 (d) [J(P–H) 7.2] [e]	Hydride: 17.38 (t) [J(P–H) 33] [e]
$[Mn(CO)_3H(PEtPh_2)_2]$	119	524 (567)	7.56 (q) [J(H–H) 7.4], 7.64 (q) [J(H–H) 7.4] [e]	8.91 (t) [J(H–H) 7.4], 9.08 (t) [J(H–H) 7.4] [e]	Hydride: 17.97 (t) [J(P–H) 32] [e]
$[Mn(CO)_3H\{P(OMe)_3\}_2]$	Oil	n.m.		n.m.	Hydride: 23.6 (t) [J(P–H) 44]
$[Mn(CO)_3(NCMe)(PMePh_2)_2][ClO_4]$	142—148	n.m.		7.76 (i) [J^* 7.6] [e]	Nitrile: 8.31 (t) [J(P–H) 1.9] [e]
$[Mn(CO)_3(NCMe)(PEtPh_2)_2][PF_6]$	134—138	n.m.	7.24 (q) [J(H–H) 7.1], 7.36 (q) [J(H–H) 7.1] [e]	8.80 (t) [J(H–H) 7.1], 9.08 (t) [J(H–H) 7.1] [e]	Nitrile: 8.52 (t) [J(P–H) 1.8] [e]
$[Mn(CO)_5\{P(OMe)_3\}][PF_6]$	174 [d]	n.m.		5.80 (d) [J(P–H) 11.8]	
$[Mn(CO)_5\{PPh(OMe)_2\}][PF_6]$	114	n.m.		5.88 (d) [J(P–H) 12.0]	
$[Mn(CO)_5\{PPh_2(OMe)\}][PF_6]$	176—178 [d]	n.m.		6.36 (d) [J(P–H) 12.8]	
trans-$[MnBr(CO)_4\{PPh_2(OMe)\}]$	88—95	n.m.		6.63 (d) [J(P–H) 12.5]	
trans-$[MnBr(CO)_4\{PPh(OMe)_2\}]$	93—95	n.m.		6.34 (d) [J(P–H) 11.8]	

[a] Measured in benzene solution; calculated values are given in parentheses. n.m. = Not measured. [b] Recorded in [$^2H_6$]acetone solution. s = Singlet, d = doublet, t = triplet, dt = distorted triplet, q = quartet, dq = distorted quartet, i = intermediate coupling pattern. J Values (Hz) are given in square brackets; J^* = the separation of the outer peaks of the observed resonance and represents $|^2J(P\text{–}H) + {}^4J(P\text{–}H)|$ (R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275. [c] Recorded in $CDCl_3$ solution. [d] With decomposition. [e] Recorded in CD_2Cl_2 solution.

carbonyl-stretching frequencies observed in the i.r. spectra of the arsine complexes $[Mn_2L_2(CO)_8]$ (L = $AsMe_2Ph$, $AsMe_3$, or $AsEt_3$) (Figure 1), and the *X*-ray structural analysis [19] of $[Mn_2(AsMe_2Ph)_2(CO)_8]$ has confirmed the anticipated C_{2h} symmetry for diequatorial substitution. The $[Mn_2(AsMe_2Ph)_2(CO)_8]$ molecule possesses severe steric crowding with distortion of the axial carbonyl groups away from the Mn–Mn axis. The di-equatorial substitution is also seen to impose an almost eclipsed conformation on the equatorial carbonyl groups in contrast with the more usual lower-energy staggered configuration.[10,20] It thus appears that there is a distinct steric resistance to substitution in the equatorial positions and this may hence explain the different isomers obtained for the tertiary phosphorus and arsenic ligands. Substitution in the equatorial position is statistically and kinetically favoured, and in fact in manganese carbonyl bromide systems *trans*-carbonyl groups are a prerequisite for the substitution reaction to take place.[15,21] For the reaction *cis*-$[MnBr(CO)_4L]$ + L $\longrightarrow$ $[MnBr(CO)_3L_2]$ the mechanistic path has been shown [15,21,22] to consist of a kinetically controlled initial step producing the *fac* isomer followed by a sterically controlled isomerisation giving *mer-trans*-$[MnBr(CO)_3L_2]$. For L = $AsMe_2Ph$, however, an equilibrium exists between *fac*- and *mer-trans*-$[Mn(AsMe_2Ph)_2Br(CO)_3]$, and the pure *mer-trans* isomer slowly converted into an isomeric mixture in refluxing benzene, presumably because now electronic factors overrule steric factors. A comparison of the Mn–As and As–C bond lengths with those of Mn–P and P–C in the two structures of $[Mn_2(CO)_8L_2]$ (L = $PMePh_2$

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or $AsMe_2Ph$)[19] shows that the Mn–As and Mn–C bonds in the arsine complex are longer than their phosphine counterparts, effectively reducing the contact between the substituent groups on the arsine ligands with the adjacent carbonyls. It is interesting that although we obtained diequatorial $[Mn_2L_2(CO)_8]$ (L = $AsMe_2Ph$, $AsMe_3$, and $AsEt_3$), the larger arsine ligand, $AsPh_3$, has been reported to give diaxial substitution.[5] We also find that the reaction of diequatorial $[Mn_2(AsMe_2Ph)_2(CO)_8]$ with two equivalents of $PPh(OMe)_2$ and $P(OMe)_3$ in benzene solution, using either u.v. or thermal excitation, gives diaxial $[Mn_2(CO)_8L_2]$ [L = $PPh(OMe)_2$ and $P(OMe)_3$] respectively. Similar reactions with the phosphine ligands PMe_2Ph and $PMePh_2$, however, failed to displace the arsine.

The ^1H n.m.r. methyl resonances of $[Mn_2(CO)_8L_2]$ [L = PMe_2Ph, $PMePh_2$, $PPh(OMe)_2$, and $PPh_2(OMe)$] all appeared as doublets with no mutual ^{31}P–^{31}P couplings transmitted through the Mn–Mn bond. For L = $AsMe_3$ and $AsMe_2Ph$ singlet methyl resonances were observed for the magnetically equivalent arsine ligands and a distorted quartet and triplet for the ethyl resonances in $AsEt_3$.

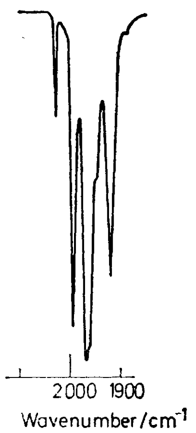

FIGURE 1 Solution i.r. carbonyl spectrum of diequatorial $[Mn_2(AsMe_2Ph)_2(CO)_8]$

No trisubstituted products of the type $[Mn_2(CO)_7L_3]$ could be prepared in this work, and in fact trisubstitution of $[Mn_2(CO)_{10}]$ with tertiary phosphorus or arsine ligands has only been reported previously for PF_3.[7] This may be due to the small steric size of PF_3, as with the spacially larger $[Re_2(CO)_{10}]$ molecule the trisubstituted derivatives $[Re_2(CO)_7L_3]$ have been characterised for the ligands L = PMe_2Ph, $AsMe_2Ph$, and $PMePh_2$.[12,13] However, the reason why trisubstitution could not be obtained with $P(OMe)_3$ can hardly be steric as the ligand is known[15] to give unusually highly substituted derivatives with $[MnBr(CO)_5]$. It is possibly attributable to the weakness of the Mn–Mn bond compared with the Re–Re bond,[23] because, under similar forcing conditions as used in the $[Re_2(CO)_7L_3]$ preparations, monomeric disubstituted products of the type $[Mn(CO)_3HL_2]$ are eventually formed. Thus with a large excess of ligand in a high-boiling solvent such as light petroleum (b.p. 100—120 °C) or propanol, $[Mn_2(CO)_{10}]$ or $[Mn_2(CO)_8L_2]$ reacted further under reflux conditions with concomitant cleavage of the metal–metal bond to give the hydrides, $[Mn(CO)_3HL_2]$ [L = $PMePh_2$, $PEtPh_2$, PMe_2Ph, or $PPh(OMe)_2$]. In the case of $PMePh_2$ evidence for the formation of a paramagnetic species during some of the substitution reactions in light petroleum came from the almost total loss of resolution in the ^1H n.m.r. spectrum of the initial product isolated from the reaction mixture. Recrystallisation in the presence of ethanol or addition of ethanol to this reaction mixture effected total conversion into the hydride. The paramagnetic species may be the radical $[Mn(CO)_3(PMePh_2)_2]$ and the formation of the corresponding $[Mn(CO)_3H(PMePh_2)_2]$ from this radical in light petroleum may occur *via* hydride abstraction from the aromatic rings on the $PMePh_2$ ligand. The complexes $[Mn(CO)_3HL_2]$ [L = $PMePh_2$, $PEtPh_2$, PMe_2Ph, $PPh(OMe)_2$, and $P(OMe)_3$] were more readily formed however by treating a boiling ethanolic solution of $[Mn_2(CO)_{10}]$ or $[Mn_2(CO)_8L_2]$ and L with sodium tetrahydridoborate. Most of these complexes were difficult to crystallise and only for the ligands $PMePh_2$ and $PEtPh_2$ were they fully characterised. For the remainder, the tetrahydridoborate–ethanol reagents were used simply to demonstrate the generality of this type of reaction, and the formation of the complexes was inferred from i.r. and ^1H n.m.r. spectra and/or their reactions with HX (X = PF_6 or ClO_4) in acetonitrile solution.

The i.r. solution spectra of $[Mn(CO)_3HL_2]$ (Table 1) were very similar to that previously reported[11] for $[Mn(CO)_3H(PPh_3)_2]$, with a single very strong band in the region of 1 910 cm^{-1}, typical of a *mer-trans*-substituted molecule, but with an additional weaker band at higher frequency. We cannot comment on the validity of the additional i.r. absorptions observed for L = PMe_2Ph and $P(OMe)_3$ because of difficulties in purifying these complexes. The ^1H n.m.r. hydride resonances (Table 2) for $[Mn(CO)_3HL_2]$ [L = $PMePh_2$, $PEtPh_2$, or $P(OMe)_3$] appeared as symmetrical 1 : 2 : 1 triplets arising from the equal ^{31}P couplings of the two phosphorus ligands *cis* to the hydride. The ligand methyl resonance for $[Mn(CO)_3H(PMePh_2)_2]$ was, however, a sharp doublet [Figure 2 (*a*)], suggestive of *cis*-phosphine groups and not what is anticipated from the i.r. data [Figure 2(*b*)]. To resolve the stereochemistry an *X*-ray structural determination[24] was completed and this confirmed the *mer-trans* configuration. Although the $Mn(CO)_3(PMePh_2)_2$ skeleton is distorted towards a trigonal bipyramid caused by bending of the bulky phosphine ligands towards the hydride group, the phosphines are still definitely *trans* so we cannot explain why negligible or very small ^{31}P–^{31}P couplings are apparently observed, when in all the other manganese carbonyl systems containing methyl phosphines or phosphites strong virtual couplings have been

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[24] M. Laing, E. Singleton, and G. Kruger, *J. Organometallic Chem.*, 1973, **54**, C30.

recorded for both *cis*- and *trans*-phosphorus groups.[15] The formation of all the complexes $[Mn(CO)_3HL_2]$ [L = $PMePh_2$, $PEtPh_2$, PMe_2Ph, $PPh(OMe)_2$, or $P(OMe)_3$] was however inferred from their characteristic reactions with HX (X = ClO_4 or PF_6) in acetonitrile producing the cations $[Mn(CO)_3(NCMe)L_2]^+$ isolated as either the $[PF_6]^-$ or $[ClO_4]^-$ salts. Of these salts, only those containing the ligands $PMePh_2$ and $PEtPh_2$ were new and were fully characterised. The rest were inferred by comparing their spectra with those of authentic samples prepared from *mer-trans*-$[MnBr(CO)_3L_2]$ [L = PMe_2Ph, $PPh(OMe)_2$, or $P(OMe)_3$] and AgX (X = ClO_4 or PF_6) in acetonitrile.[1] Once again the i.r. carbonyl spectra of one weak and two strong bands for these cations did not distinguish between the *mer-trans* isomers of C_{2v} symmetry and the *mer-cis* isomers of C_s symmetry. Furthermore, intermediate coupling patterns observed for ligand methyl groups in the ^1H n.m.r. spectra could not be used to distinguish between *cis*- and *trans*-bonded phosphines, so that no accurate structural assignment was possible The nitrile methyl resonances in all these complexes appeared as symmetrical triplets due to ^{31}P couplings.

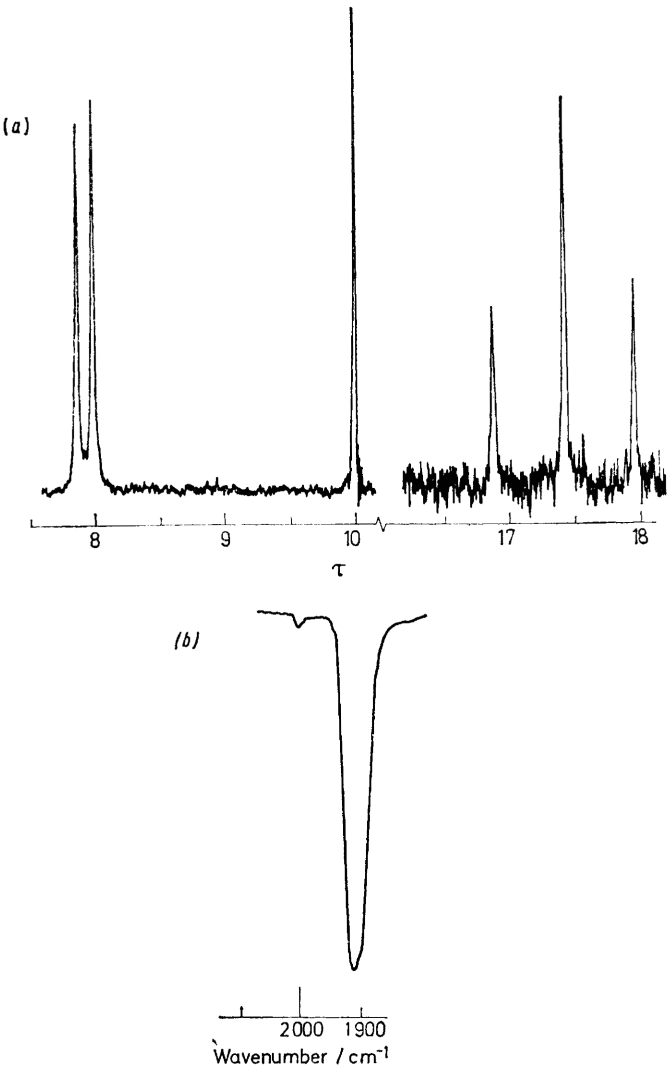

FIGURE 2 Spectral characteristics of $[Mn(CO)_3H(PMePh_2)_2]$: (*a*) ^1H n.m.r. methyl and hydride resonances in CD_2Cl_2 solution; (*b*) i.r. carbonyl bands in benzene solution

Treatment of $[Mn_2(CO)_{10}]$ with $NOPF_6$ in acetonitrile has been shown[25] to give the salt $[Mn(CO)_5(NCMe)][PF_6]$, presumably by an oxidative fission mechanism. We have studied the reactions of the disubstituted dimers with $NOPF_6$ in poorly co-ordinating solvents at room temperature and find that oxidative metal–metal bond cleavage is accompanied, not by solvent inclusion, but by a disproportionation reaction. Thus $[Mn_2(CO)_{10}]$ and $NOPF_6$ in dichloromethane gave low yields of the hexacarbonyl cation $[Mn(CO)_6]^+$ which was characterised from i.r. evidence alone.[26] When the complexes $[Mn_2(CO)_8L_2]$ [L = $P(OMe)_3$, $PPh(OMe)_2$, or $PPh_2(OMe)$] were treated with $NOPF_6$ in CH_2Cl_2 the oxidation proceeded rapidly producing $[Mn(CO)_5L]^+$ in moderate yields. These cations were isolated and characterised as the $[PF_6]^-$ salts and although they are similar to the known complexes $[Mn(CO)_5L]^+$ [L = PPh_3 or $P(C_6H_{11})_3$] this procedure represents a much more convenient preparative route to these cationic salts than that previously reported.[26] The i.r. spectra of the carbonyl groups in $[Mn(CO)_5L]^+$ consisted of two medium and one strong band and are characteristic of C_{4v} symmetry. The ^1H n.m.r. methyl resonances were observed as doublets.

Jolly and Stone[27] earlier reported that the reaction of $[Mn_2(CO)_8(PPh_3)_2]$ with bromine in chloroform solution at 0 °C produces a mixture of *cis*- and *trans*-$[MnBr(CO)_4(PPh_3)]$ which is converted entirely into the *cis* isomer on warming the reaction solution to room temperature. The isomerisation is said to be thermodynamically controlled, which implies that in the series of complexes $[MnBr(CO)_4L]$ the stability of the *trans* isomer will increase as the electronic characteristics of the ligand L change from strong σ donor to strong π acceptor. In our series of disubstituted dimers, $[Mn_2(CO)_8L_2]$ bromination in CCl_4 at 0 °C produced only *cis*-$[MnBr(CO)_4L]$ for L = PMe_2Ph and $PMePh_2$, whereas the corresponding reactions for the ligands L = $PPh_2(OMe)$ and $PPh(OMe)_2$ effected a complete conversion into the *trans* isomer. Both *trans* isomers could be recrystallised readily at room temperature without undergoing isomerisation, although *trans*-$[MnBr(CO)_4\{PPh_2(OMe)\}]$ was slowly converted into the *cis* isomer in chloroform over a period of time. The *trans* isomers were identified from the single strong carbonyl-stretching frequency observed in their i.r. spectra which is characteristic of the D_{4h} point group. Thus in the series *trans*-$[MnBr(CO)_4L]$ the stability of the *trans* isomer decreases in the order of L of $PPh(OMe)_2 > PPh_2(OMe) > PPh_3 > PMePh_2 \sim PMe_2Ph$, which parallels the decrease in ligand π acidity. This is in keeping with a thermodynamically controlled

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[25] N. G. Connelly and L. F. Dahl, *Chem. Comm.*, 1970, 880.
[26] T. Kruck and M. Noack, *Chem. Ber.*, 1963, **96**, 3028.
[27] P. W. Jolly and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5259.

equilibrium as the bonding-energy advantage [28] in forming the ' all-*cis* ' carbonyl species is less pronounced for the more ' carbonyl-like ' phosphine ligands.

EXPERIMENTAL

The complex $[Mn_2(CO)_{10}]$, $NOPF_6$, and all the phosphine, phosphite, and arsine ligands were obtained commercially and were not further purified. Melting points were determined on a Kofler hot-stage apparatus and conductivities were measured in acetone solution on a Van Waters and Rogers model 31 conductivity bridge. Molecular weights were recorded in benzene solution using a Mechrolab vapour-pressure osmometer at 37 °C. Infrared spectra were recorded on a Perkin-Elmer model 457 grating spectrophotometer and ^1H n.m.r. spectra with Varian A-60A and HA-100 instruments. Elemental analyses were carried out in this laboratory. All physical data for the complexes prepared are presented in Tables 1 and 2. The majority of dimeric complexes described here were light-sensitive, requiring darkness for extended storage.

Preparations.— *Nonacarbonyl(dimethylphenylphosphine)-dimanganese.* A solution of $[Mn_2(CO)_{10}]$ (4.0 g, 10.26 mmol) and dimethylphenylphosphine (1.56 g, 11.29 mmol) in benzene–light petroleum (b.p. 60—80 °C) (100 cm^3) was saturated with nitrogen and irradiated with a Hanovia 125 W u.v. lamp for 6 h. The crimson solution was evaporated to a red oil and the crude material chromatographed on an alumina column, using dichloromethane–light petroleum (b.p. 30—40 °C) mixtures. Twenty-five fractions were collected. Fractions 1—4 contained unchanged $[Mn_2(CO)_{10}]$ and PMe_2Ph, 6—10 yielded crystals on evaporation which were crystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to give the desired product as yellow plates (0.75 g, 15%), and the remainder contained $[Mn_2(CO)_8(PMe_2Ph)_2]$.

Similarly prepared were $[Mn_2(AsMe_2Ph)(CO)_9]$ as pale yellow microcrystals in 28% yield and $[Mn_2(CO)_9(PMePh_2)]$ as orange needles in 65% yield.

Octacarbonylbis(dimethylphenylphosphine)dimanganese. A solution of $[Mn_2(CO)_{10}]$ (4.0 g, 10.26 mmol) and PMe_2Ph (3.12 g, 22.57 mmol) in benzene (80 cm^3) was saturated with nitrogen and irradiated with a Hanovia 125 W u.v. lamp for 10 h. The resulting solution was evaporated to a red oil which was crystallised from hot ethanol. Recrystallisation from acetone–ethanol afforded the product as yellow plates (3.1 g, 51%).

Similarly prepared were: $[Mn_2(AsMe_2Ph)_2(CO)_8]$ as golden plates in 67% yield; $[Mn_2(CO)_8(PMePh_2)_2]$ by recrystallistion from diethyl ether–ethanol as orange needles in 85% yield; $[Mn_2(AsEt_3)_2(CO)_8]$ by crystallisation from hot light petroleum (b.p. 60—80 °C) and recrystallisation from acetone–light petroleum (b.p. 60—80°C) as orange prisms in 80% yield; $[Mn_2(AsMe_3)_2(CO)_8]$ by recrystallisation from benzene–ethanol as orange plates in 55% yield; $[Mn_2(CO)_8\{PPh(OMe)_2\}_2]$ as yellow needles in 75% yield; and $[Mn_2(CO)_8\{PPh_2(OMe)\}_2]$ as golden-yellow needles in 80% yield.

mer-trans-*Tricarbonylhydridobis(methyldiphenylphosphine)manganese.* A solution of $[Mn_2(CO)_{10}]$ (2.0 g, 5.13 mmol) and methyldiphenylphosphine (5.1 g, 25.50 mmol) in propanol (15 cm^3) was heated under reflux for 15 h. The solution turned dark brown and deposited a dark solid on cooling. This was recrystallised from diethyl ether–ethanol to give the required product as yellow prisms (2.1 g, 76%). Alternately the reagents could be refluxed in similar quantities in ethanol (15 cm^3) together with $Na[BH_4]$ (0.19 g) for 10 h. Evaporation of the solvent under reduced pressure gave a solid residue which was washed with water (10 cm^3). Recrystallisation from acetone–ethanol gave the desired product in a similar yield.

Similarly prepared, using either of the above methods, were $[Mn(CO)_3H(PEtPh_2)_2]$ as colourless prisms in 65% yield and $[Mn(CO)_3HL_2]$ [L = $P(OMe)_3$, $PPh(OMe)_2$, and PMe_2Ph] in *ca.* 80% yield which could not be obtained in a crystalline form and were characterised from their i.r. carbonyl spectra and metal–hydride ^1H n.m.r. resonances.

Acetonitriletricarbonylbis(methyldiphenylphosphine)manganese perchlorate. To a solution of $[Mn(CO)_3H(PMePh_2)_2]$ (0.35 g, 0.65 mmol) in acetonitrile (10 cm^3) at room temperature was added dropwise $HClO_4$ (0.07 g, 0.70 mmol). The colour lightened immediately accompanied by some effervescence. Ethanol (5 cm^3) was added and the solution concentrated under reduced pressure to give the product which could be recrystallised from dichloromethane–ethanol as lemon-yellow plates (0.39 g, 88%). Conductivity in acetone solution: 132 S cm^2 mol^{-1}.

Similarly prepared was *mer*-$[Mn(CO)_3(NCMe)(PEtPh_2)_2][PF_6]$ by reaction of $[Mn(CO)_3H(PEtPh_2)_2]$ and HPF_6 in acetonitrile, followed by recrystallisation from methanol–pentane to give yellow plates in 65% yield. Conductivity in acetone solution: 120 S cm^2 mol^{-1}.

Pentacarbonyl(trimethyl phosphite)manganese hexafluorophosphate. An excess of $NOPF_6$ was added to a solution of the known [5] complex $[Mn_2(CO)_8\{P(OMe)_3\}_2]$ (0.6 g, 1.03 mmol) in dichloromethane (10 cm^3). The colour darkened initially and lightened again after 5 min. The solution was then filtered and concentrated under reduced pressure. Crystallisation was effected by the addition of ethanol (5 cm^3) and recrystallisation from the same solvent mixture gave the required product as colourless plates (0.41 g, 43%). Conductivity in acetone solution: 150 S cm^2 mol^{-1}.

Similarly prepared were $[Mn(CO)_5\{PPh(OMe)_2\}][PF_6]$ from $[Mn_2(CO)_8\{PPh(OMe)_2\}_2]$ as colourless plates in 33% yield (conductivity 151 S cm^2 mol^{-1}) and $[Mn(CO)_5\{PPh_2(OMe)\}][PF_6]$ from $[Mn_2(CO)_8\{PPh_2(OMe)\}_2]$ as pale yellow needles in 22% yield (conductivity 147 S cm^2 mol^{-1}).

trans-*Bromotetracarbonyl(dimethoxyphenylphosphine)-manganese.* To a solution of $[Mn_2(CO)_8\{PPh(OMe)_2\}_2]$ (0.2 g, 0.30 mmol) in carbon tetrachloride (30 cm) at 0 °C was added dropwise a solution of bromine (0.05 g, 0.31 mmol) in carbon tetrachloride (3 cm^3). After stirring for 30 min, the reaction solution was concentrated to *ca.* 4 cm^3 under reduced pressure, keeping the temperature at 0 °C throughout the operation. Cold pentane (10 cm^3) was added dropwise and the solid obtained was recrystallised from the same solvent mixture to give the product as orange needles (0.07 g, 56%).

Similarly prepared was *trans*-$[MnBr(CO)_4\{PPh_2(OMe)\}]$ from $[Mn_2(CO)_8\{PPh_2(OMe)\}_2]$ as orange prisms in 65% yield.

[6/199 *Received*, 30*th January*, 1976]

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[28] J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 1970, **92**, 5852.