Co-ordination Chemistry of Manganese. Part III.[1] The Reaction of Manganese(II) Halides with Tertiary Phosphine and Arsine Ligands to Produce Ligand Oxide Complexes

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Triphenyl-phosphine and -arsine react with manganese(II) halides to produce $Mn(OEPh_3)_2X_2$ (E = P, As; X = Cl, Br, I) complexes; this implies than an earlier report of $Mn(EPh_3)_2X_2$ complexes is mistaken. Similarly the bidentate ligands bisdiphenylphosphinomethane, *cis*-1,2-bisdiphenylphosphinoethylene, 1,2-bisdiphenylphosphinoethane, and 1,2-bisdiphenylarsinoethane react with MnX_2 to form Mn(ligand dioxide)X_2 complexes. Manganous chloride and bromide react with diphenylphosphine to form bis(diphenylphosphinite)manganese(II), a novel reaction involving both ligand deprotonation and oxidation. A possible mechanism of the oxidation of these ligands is discussed.

MANGANESE(II) HALIDES form stable complexes with a wide range of oxygen and nitrogen donor ligands.[2] In contrast, the number of complexes formed with phosphorus and arsenic donors is small. Nyholm and Sutton [3] found that *o*-phenylenebisdimethylarsine (das) reacts with anhydrous manganese(II) halides to form $Mn(das)_2X_2$ (X = Cl, Br, I); no reaction occurred in water, alcohols, or acetone. In acetone solution triphenylphosphine reacts with manganese(II) halides to form $[PPh_3H]_2MnX_4$.[4] Naldini [5] claimed that triphenylphosphine and triphenylarsine in tetrahydrofuran (THF) solution under anhydrous conditions converted manganese(II) halides into $Mn(EPh_3)_2X_2$ (E = P, As) whilst in the presence of an excess of ligand $[Mn(EPh_3)_4]^{2+}$ ions formed. However, Negoui [6] has subsequently reported that Naldini's $Mn(PPh_3)_2Br_2$ was identical with a genuine sample of $Mn(OPPh_3)_2Br_2$. In contrast to the scarcity of simple phosphine or arsine complexes manganese(II) readily combines with phosphine and arsine oxides: $OPPh_3$,[7,8] $OAsPh_3$,[9,10] $OPBu^t_3$,[11] $OPMe_3$, $OAsMe_3$,[12] $OPPh_2Me$,[13] $OAsPh_2Me$,[13,14] and $OAs(CH_2Ph)_3$.[15]

Here we report a reinvestigation of the reactions of manganese(II) halides with triphenyl-phosphine and -arsine and new reactions with triphenylstibine, diphenylphosphine, diphenylmethylphosphine, bisdiphenylphosphinomethane (dpm), 1,2-bisdiphenylphosphinoethane (dpe), 1,2-bisdiphenylarsinoethane (dae), and *cis*-1,2-bisdiphenylphosphinoethylene (vpp).

EXPERIMENTAL

Reagent grade tetrahydrofuran was refluxed over sodium wire for 3 days, and freshly distilled under nitrogen from sodium wire before use. 'Anhydrous' manganese(II) halides were obtained either by heating the hydrated compounds (B.D.H. Reagent Grade) *in vacuo* at 110—130° for 8—10 h, or by refluxing them in thionyl chloride for

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12 h. Triphenyl-phosphine and -arsine were obtained from B.D.H., and the dioxides of *cis*-1,2-bisdiphenylphosphinoethylene [16] and 1,2-bisdiphenylphosphinoethane [17] and all other ligands were prepared by literature methods.

No reaction occurred between manganese(II) halides which had been refluxed in thionyl chloride and the ligands. However, with manganese(II) halides which had been rendered 'anhydrous' by heating *in vacuo* we did obtain reactions after prolonged periods. The experimental procedure is illustrated by the reaction between $MnCl_2$ and PPh_3. Finely powdered 'anhydrous'* manganese(II) chloride (0·63 g, 5 mmol) and triphenylphosphine (2·6 g, 10 mmol) were dissolved in dry THF (50 ml), under nitrogen, and the magnetically stirred mixture was heated to 40 °C in sealed evacuated tubes for 3 days. The resulting yellow solution was filtered, dry diethyl ether (2 ml) was added to the filtrate, and the mixture set aside. After several days small pale yellow crystals separated, which were filtered off under nitrogen and dried *in vacuo* (yield *ca.* 0·7 g; yields were generally of the order of 5—15%).

The reactions with other ligands were similar, a 2 : 1 ligand : MnX_2 ratio being used for unidentate ligands, and a 1 : 1 ratio for bidentate ligands. For the bidentate cases the work-up of the reaction mixture was modified as follows. The solution was rotatory evaporated to dryness in an inert atmosphere, extracted with hot dichloromethane, filtered to remove manganese halide, and concentrated to small volume. The solids, which crystallised during 2—3 days were recrystallised from dichloromethane.

TABLE 1

Analytical results and infrared data of the $MnX_2 + EPh_3$ (E = P, As) reaction

Reaction [a]	M.p. (t/°C)	% Found C	% Found H	% Calc. for $Mn(Eph_3)_2X_2$ C	% Calc. for $Mn(Eph_3)_2X_2$ H	% Calc. for $Mn(OEPh_3)_3X_3$ C	% Calc. for $Mn(OEPh_3)_3X_3$ H	ν(E=O)/cm^{-1}	ν(Mn–X)/cm^{-1}	ν(E=O)/cm^{-1} reported for $Mn(OEPh_3)_2X_2$
$MnCl_2 + PPh_3$	234	63·7	4·5	66·5	4·6	63·4	4·4	1152	310, 290	1155
$MnCl_2 + PPh_3$ [b]	236	63·5	4·7							
$MnBr_2 + PPh_3$	265	56·2	3·8	58·5	4·1	56·0	3·9	1160sh, 1150	240, 225	1163sh, 1151
$MnI_2 + PPh_3$	227	49·7	3·5	51·8	3·6	50·0	3·4	1160, 1148		1161, 1148
$MnCl_2 + AsPh_3$	230	56·3	4·0	58·6	4·1	56·1	3·9	920, 900	295, 278	923, 892
$MnBr_2 + AsPh_3$	212	50·4	3·6	52·3	3·7	50·3	3·5	910, 882	225	911, 883
$MnI_2 + AsPh_3$	193	45·6	3·4	46·9	3·3	45·3	3·1	898, 884		

[a] All reactions carried out in dry THF under nitrogen except [b] Fused.

The reaction between manganese(II) chloride and fused triphenylphosphine was carried out as follows. An intimate mixture of 'anhydrous' manganese(II) chloride (2·5 g, 20 mmol) and triphenylphosphine (13·0 g, 50 mmol) was melted under nitrogen, and the temperature maintained just above the melting point for 1 h. The product was worked up in the usual way (yield 1·0 g).

The diphosphine dioxides, $vppO_2$ [16] and $dpeO_2$ [17] were treated with manganese(II) chloride in a 1 : 1 ratio in hot THF. After ½ h under reflux the solutions were cooled and the solid complexes precipitated. These were filtered off and recrystallised from dichloromethane (yields 60—70%).

Infrared spectra were recorded in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer; conductivities were measured in *ca.* 10^{-3}M-nitromethane solution on a Cambridge conductivity bridge (specific conductance of $MeNO_2 = 1 \times 10^{-5}\ \Omega^{-1}$).

RESULTS

It has been discovered that MnX_2, derived from hydrated salts by refluxing in thionyl chloride, do not react with the ligands used in this study. However, the reaction of 'anhydrous' MnX_2, derived from hydrated salts by heating at 110—130° *in vacuo*, with PPh_3 and $AsPh_3$ in dry THF produces low yields of manganese(II) complexes of Ph_3PO or Ph_3AsO. The reactions are slow, *ca.* 12—15% yields being obtained after 3—4 days under reflux. In Table 1 are compared the analytical results obtained with those expected for $Mn(EPh_3)_2X_2$ or $Mn(OEPh_3)_2X_2$ (E = P or As) complexes. In all cases analytical data indicate that the products of the reactions are $Mn(OEPh_3)_2X_2$ derivatives. Further evidence for this formulation is obtained from their i.r. spectra (Table 1), the ν(E=O) frequencies observed being almost identical with those reported by Goodgame and Cotton [9] for the products obtained by direct reaction of MnX_2 with $OEPh_3$. The reaction of $OAsPh_3$ is reported [9] to yield only $[Mn(OAsPh_3)_4]I_2$. Starting with $AsPh_3$ we isolated a complex of formula $Mn(OAsPh_3)_2I_2$ as yellow crystals. In freshly prepared nitromethane solution this complex has an almost negligible conductivity, but this increases with time until after *ca.* 2 h Λ_0 is *ca.* 40 Ω^{-1} cm^2 mol^{-1} [calculated as $Mn(OAsPh_3)_2I_2$]. It is possible that over a period of time the initial complex rearranges into $[Mn(OAsPh_3)_4][MnI_4]$. All the other complexes of $OPPh_3$ and $OAsPh_3$ are effectively non-conductors in nitromethane.

In the reaction between manganese(II) chloride and triphenylstibine a greyish white solid was isolated, along with much unchanged $MnCl_2$. An infrared spectrum of this solid did contain bands in the region 750—650 cm^{-1} which may be assignable to ν(SbO),[18] but the product undoubtedly contained a considerable amount of unchanged $MnCl_2$ and even after many preparations no pure complex could be isolated.

From the reaction between 'anhydrous' manganese(II) chloride and diphenylmethylphosphine a small amount of pale yellow crystals were obtained, the analysis of which indicated a formulation $Mn(OPPh_2Me)_2Cl_2,2H_2O$. The analogous reaction with MnI_2 yielded $Mn(OPPh_2Me)_4I_2,H_2O$. The i.r. spectra of these two complexes, unlike those of all the other complexes isolated in this study, show the presence of water.† The former complex is a nonconductor in nitromethane, but the iodo-derivative has Λ_0 = 46 Ω^{-1} cm^2 mol^{-1}, a significant conductance value but rather low for

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* From here onwards 'anhydrous' manganese halides means the products obtained by heating MnX_2,nH_2O *in vacuo*.

† Nyholm and his co-workers (ref. 13) have similarly found that manganese(II) complexes tend to pick up water during work-up.

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characterisation of this compound as a 1 : 1 electrolyte (1 : 1 electrolytes in $MeNO_2$ usually range from 70—95 Ω^{-1} cm^2 mol^{-1}). The ν(P=O) frequency in $OPPh_2Me$ occurs at 1171 cm^{-1},[13] and, as expected, the complexes reported here exhibit values of ν(P=O) *ca.* 20—30 cm^{-1} lower (Table 2).

When ' anhydrous ' $MnCl_2$ or $MnBr_2$ are allowed to react with diphenylphosphine for 3—4 days in THF a white solid may be isolated (Table 2). The products of these reactions contain only a trace of halogen (<1%), and had identical i.r. spectra which exhibit no ν(P–H) or ν(O–H) bands. The most satisfactory explanation of these facts is that in these reactions PPh_2H both loses a proton and undergoes oxidation to yield the $Mn(OPPh_2)_2$ complex. The production of bis(diphenylphosphinite)manganese(II) in this way is unique. There is one other report of a diphenyl phosphinite complex, $AgOPPh_2$, obtained by Hunt and Saunders [19] by slow reaction of $AgNO_3$ with $OPPh_2H$.

TABLE 2

Analytical and infrared data

Compound	M.p. (t/°C)	Found (%) C	Found (%) H	Found (%) X [a]	Calc. for phosphine complex (%) C	Calc. for phosphine complex (%) H	Calc. for phosphine complex (%) X	Calc. for Phosphine oxide complex (%) C	Calc. for Phosphine oxide complex (%) H	Calc. for Phosphine oxide complex (%) X	ν(P=O)/cm^{-1}	ν(M–X)/cm^{-1}
$Mn(OPPh_2)_2$ [b]	160—163	63·8	4·9	(<1)				63·2	4·6			
$Mn(OPPh_2)_2$ [c]	164	63·5	5·0									
$Mn(OPPh_2Me)_2Cl_2,2H_2O$	110	52·7	5·1	11·7	55·6	4·5	12·7	52·8	5·2	11·9	1151	273
$Mn(OPPh_2Me)_4I_2,H_2O$	160	51·8	4·2	22·4	55·4	4·8	22·6	52·5	4·6	22·2	1145	—
$Mn(dpmO_2)Cl_2$	302	56·0	4·5	13·0	58·9	4·3	13·9	55·6	4·1	13·1	1160	270
$Mn(dpmO_2)I_2$	220	41·8	3·5	34·9	43·4	3·2	36·7	41·4	3·0	35·1	1163, 1155sh	—
$Mn(dpmO_2)_2Br_2$	290	56·7	4·3	15·1	61·0	4·5	16·3	57·3	4·2	15·3	1165, 1158sh	—
$Mn(vppO_2)Cl_2$ [d]	252	57·0	4·5	12·6	59·9	4·2	13·6	56·4	4·0	12·8	1160	273
$Mn(vppO_2)Cl_2$ [e]	252	56·8	4·4	12·5							1158	273
$Mn(vppO_2)Br_2$	295	48·8	3·9	24·8	51·5	3·6	26·2	48·7	3·4	24·9	1155	225
$Mn(vppO_2)I_2$	230	42·5	3·7	34·2	44·4	3·1	36·1	42·3	3·0	34·5	1165	—
$Mn(dpeO_2)Cl_2$ [f]	280	56·3	5·0	12·7	59·8	4·6	13·5	56·2	4·4	12·8	1150 [h]	280
$Mn(dpeO_2)Cl_2$ [g]	280	56·4	4·8	12·7							1148	280
$Mn(dpeO_2)Br_2$	305	47·9	4·0	24·6	50·9	3·9	26·2	48·5	3·7	24·8	1150 [h]	222
$Mn(dpeO_2)I_2$	290	42·8	3·8	34·6	44·1	3·7	35·9	42·5	3·0	34·5	1155 [h]	—
$Mn(daeO_2)Cl_2$	225	49·0	4·2	11·2	51·0	4·4	11·6	48·7	3·8	11·0 [j]	886, 870 [j]	—

[a] X = halogen. [b] From $MnCl_2$. [c] From $MnBr_2$. [d] From vpp. [e] From $vppO_2$. [f] From dpe. [g] From $dpeO_2$. [h] A strong band at *ca.* 1175—1180 cm^{-1} is a C–H deformation mode (ref. 23). [j] Refer to arsine oxide, ν(As=O).

Bisdiphenylphosphinylmethane ($dpmO_2$) complexes, *i.e.* containing the ligand $Ph_2P(O)CH_2P(O)Ph_2$, are obtained from the reaction of dpm with ' anhydrous ' manganous halides. In nitromethane solution $Mn(dpmO_2)X_2$ (X = Cl, I) are nonconductors, but $Mn(dpmO_2)_2Br_2$ behaves as a 1 : 2 electrolyte (Λ_0 = 126 Ω^{-1} cm^2 mol^{-1}); this $[Mn(dpmO_2)_2]Br_2$ co-ordination presumably also exists in the solid state since an i.r. spectrum of the solid contains no bands assignable to ν(Mn–Br). The ν(P=O) vibration is readily observed in the spectrum of all the complexes, and this vibration occurs at *ca.* 25 cm^{-1} lower energy than in the free $dpmO_2$ ligand.[20]

The reaction between vpp and ' anhydrous ' MnX_2 salts yields $Mn(vppO_2)X_2$ (X = Cl, Br, I) complexes. The analytical data do not unequivocally distinguish between the presence of $Ph_2P(O)CHCHP(O)PPh_2$ ($vppO_2$) and the hitherto unknown $Ph_2P(O)CHCHPPh_2$ (vppO), but the m.p. and i.r. spectrum of the complex isolated from the reaction between $MnCl_2$ and vpp are identical to the product from the reaction between $MnCl_2$ and an authentic sample of $vppO_2$. That both P=O donors are co-ordinated in these complexes is implied by the shift to lower frequencies of the ν(P=O) absorption (1180 cm^{-1}) in parent $vppO_2$. All of the three complexes are effectively nonconductors in nitromethane.

White solids, $Mn(dpeO_2)X_2$ (X = Cl, Br, I), were obtained from reaction between dpe and ' anhydrous ' MnX_2 in THF. Like the $vppO_2$ derivatives these complexes were non-electrolytes in nitromethane, effectively ruling out a formulation such as $[Mn(dpeO_2)_2][MnX_4]$. Thus, these complexes with the diphosphine dioxide ligands may be either monomeric $[MnLX_2]$, or polymeric. Complexes containing a chelating 1,2-bisdiphenylphosphinylethane ligand, or its unsaturated analogue, would contain a strained seven-membered ring. Both chelating $dpeO_2$, *e.g.* in $[Sc(dpeO_2)_3](ClO_4)_3$ [17] and $[Co(dpeO_2)_2(H_2O)_2](ClO_4)_2$,[21] and bridging $dpeO_2$, *e.g.* in $Cu(dpeO_2)Cl_2$,[22] have been suggested, although only in the last of these complexes has the structure been determined by *X*-ray methods. Free $dpeO_2$ exhibits the ν(P=O) absorption at 1184 cm^{-1}.[23]

Manganous chloride and dae in THF solution yielded a white solid, $Mn(daeO_2)Cl_2$. The free ligand $daeO_2$ exhibits ν(As=O) at 885 and 865 cm^{-1} [17] and in the complex reported here ν(As=O) occur at 886 and 870 cm^{-1}. However, unlike the corresponding ν(P=O) in phosphine oxides, ν(As=O) in arsine oxide ligands does not appreciably alter upon complexation.[9]

DISCUSSION

The results described above show that all of the ligands used in this study, with one exception, react with manganese(II) halides under apparently ' anhydrous ' conditions to produce complexes of the corresponding oxidised ligand. The sole exception, triphenylstibine, while appearing to oxidise, did not yield a characterisable complex. This is not unexpected since Ph_3SbO, itself

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only poorly characterised, is not known to form any complexes.[18,24] No evidence of the existence of manganese(II) complexes of the phosphine and arsine ligands studied was obtained. Merely shaking the ligands with a solution of MnX_2 in dry THF, or heating such solutions for short periods (up to 1 h) did not result in any apparent reaction, the starting materials being recovered unchanged. When these solutions were heated for 3—4 days, small yields of phosphine- or arsine-oxide complexes were obtained (*ca.* 15%), whilst the excess of MnX_2 and unoxidised ligand could be isolated by working-up the reaction mixture. (Note, none of the uncomplexed materials recovered showed evidence of phosphine or arsine oxidation, indicating that complexation accompanied oxidation.) The different stoicheiometries of some of the products—$Mn(OPPh_2Me)_2Cl_2,2H_2O$ but $Mn(OPPh_2Me)_4I_2,H_2O$, and $Mn(dpmO_2)X_2$ ($X = Cl, I$) but $Mn(dpmO_2)_2Br_2$—are probably not significant in the sense that using appropriate ratios of authentic ligand (*i.e.* phosphine *oxide*) : MnX_2 would probably result in complexes of both types of stoicheiometries being isolated for each halide. In reactions of the type studied here, in which a ligand is oxidised by an unknown mechanism (see below), followed by complexation of the oxidised ligand, the stoicheiometry of the resulting complex may clearly depend upon other factors in addition to the relative stabilities of complexes with various ligand : metal ratios.

The main point we make is that the ligand undergoes oxidation in these reactions, and we made no attempt to isolate ' missing ' complexes in any particular MnL_nX_2 series. Indeed, for the reasons just outlined this would be very much a hit or miss process. The preparation of complexes by this method is unsatisfactory for two other reasons: (i) the low yields, and (ii) the difficulty of separating the complexes from the excess of unchanged ligand. The separation of the complex from excess of MnX_2 is relatively easy, but we found that as the ligands became more complex it became increasingly difficult to separate unchanged ligand (qualitatively, in the order PPh_3, $AsPh_3 < PPh_2Me <$ dpm $<$ dpe, vpp).

The mechanism of the ligand oxidation is unknown, but we suggest a tentative explanation from the following reasoning. Fusion of $MnCl_2$ with PPh_3 also produced $Mn(OPPh_3)_2Cl_2$, seemingly eliminating THF as a source of oxygen; and the same products were obtained by reaction in THF under N_2 or in evacuated sealed tubes, seemingly eliminating oxygen as a source of P=O. The most likely source is water in the ' anhydrous ' manganese salts. Removal of even traces of water from the manganese halides by refluxing in thionyl chloride * did, in fact, prohibit any reaction under otherwise identical conditions, and this would seem to verify that the oxygen for the ligand oxidation is derived from traces of water in incompletely dehydrated MnX_2 salts. Many metal halides (including those of manganese) are notoriously difficult to dry and the resulting ' anhydrous ' salts are exceedingly deliquescent. However, heating the hydrated salts *in vacuo* is usually a satisfactory route to the anhydrous salt, *e.g.* anhydrous MnX_2 prepared in this way react satisfactorily with das in THF to yield $Mn(das)_2X_2$.[25] Presumably if the tendency of a ligand to co-ordinate to Mn^{II} is strong enough, as in the case of das, then minute quantities of water have no effect, but with the ligands used in this study it may well be this residual water which is responsible for the conversion into the oxide. One important point is that if this (variable) quantity of water is responsible for the oxidation of the ligands the varying stoicheiometries of the products may merely reflect the ratio of ligand : water in the reaction mixture.

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