110. *Cationic Carbonyl Complexes of Manganese*(I).

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Complexes containing the cation $[Mn(CO)_2(Diphos)_2]^+$ (Diphos = 1,2-bis-diphenylphosphinoethane) have been prepared from the halogenocarbonyls. Their physical properties have been found to be consistent with a structure in which the carbonyl groups of the cation are in *trans*-positions.

BROMO- and IODO-PENTACARBONYLMANGANESE react at 120° with 1,2-bisdiphenylphosphinoethane (Diphos), to yield the compounds $Mn(CO)_3(Diphos)Br$ and $Mn(CO)_3(Diphos)I$.[1] Under the same conditions, however, chloropentacarbonylmanganese reacts to form the salt-like complex $[Mn(CO)_2(Diphos)_2]Cl$. From chloroform solution, two molecules of the solvent are retained by this and other salts, and only after prolonged pumping at 100° can the solvent be removed. Molecular weight, conductance, and magnetic measurements are consistent with the formulation. Infrared spectra in the C–O stretching region show only one band, which is suggestive of a *trans*-disposition of the carbonyl groups (D_{4h} point group; E_u species).

The tendency of the chlorocarbonyl to give a cationic complex rather than a simple substitution product, noted also by Joshi, Pauson, and Stubbs,[2] is presumably a consequence of the high electronegativity of chlorine compared with other halogens. The behaviour does suggest, however, that provided reactions could be carried out under conditions whereby expulsion of the anions Br^- or I^- from the other halogenocarbonyls was facilitated, a similar ionic product might be formed. We observe that in boiling methanol, (here solvation of the anion being presumbly important), the compound $[Mn(CO)_2(Diphos)_2]Br,2MeOH$ is formed readily. The chloroform solvate is made simply by recrystallisation from this solvent.

In order to demonstrate clearly the existence of the cation, the perchlorate has been prepared also, by anion exchange in methanol. Perhaps as a result of the presence of the larger anion, the complex is isolated unsolvated.

The compound $[Mn(CO)_2(Diphos)_2]Cl,2CHCl_3$ has been observed also as a product of a different reaction. While studying the reactions of $Mn_2(CO)_{10}$ with the diphosphine,[3] a product, probably containing bridging diphosphine groups, is found to be very reactive towards chloroform. The product is the same as that formed from the halogenocarbonyl.

The *trans*-structure of the carbonyl cation is of interest. Complexes of the type $[Mn(CO)_4L_2]AlCl_4$ [4] (L = monodentate tertiary phosphine) have been prepared by carbonylation of the complexes $Mn(CO)_3L_2Cl$ in the presence of aluminium chloride. Here again the two phosphine ligands are *trans*. In neutral carbonyls, however, substitution occurs predominently in *cis*-positions, the usual explanation being that in these positions, different $d\pi$ orbitals are involved. It might be suggested that in a carbonyl cation, where π-bonding effects are less, this factor is no longer of sufficient magnitude to direct *cis*-substitution, the more symmetric structure being preferred.

Properties of carbonyldi(tertiary phosphine)manganese(I) complexes.

Complex *	Conductances in $PhNO_2$ $\Lambda_M(\Lambda^{-1}$ cm.$^2)$	concn. ($\times 10^3$M)	C–O stretching freqns. (cm.$^{-1}$) in $CHCl_3$
$[Mn(CO)_2(Diphos)_2]Cl,2MeOH$	25·2	0·95	1897
$[Mn(CO)_2(Diphos)_2]Cl,2CHCl_3$	27·2	0·98	1897
$[Mn(CO)_2(Diphos)_2]Br,2MeOH$......	24·8	0·91	1898
$[Mn(CO)_2(Diphos)_2]Br,2CHCl_3$......	26·1	1·07	1897
$[Mn(CO)_2(Diphos)_2]ClO_4$	28·8	1·11	1897

* All are yellow and diamagnetic in the solid state at 20°.

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[1] Osborne and Stiddard, *J.*, 1962, 4715.

[2] Joshi, Pauson, and Stubbs, *J. Organometallic Chem.*, 1963, **1**, 51.

[3] Osborne and Stiddard, unpublished.

[4] Kruck and Noack, *Chem. Ber.*, 1963, **96**, 3028.

Attempts have been made to prepare similar derivatives containing other bidentate ligands, *e.g.*, 2,2′-bipyridyl. Only simple substitution has been observed. Also, the diphosphine has been treated with the compound $Re(CO)_5Cl$ in boiling methanol, but yielded $Re(CO)_3(Diphos)Cl$ only.

EXPERIMENTAL

Dicarbonylbis-(1,2-*bisdiphenylphosphinoethane*)*manganese*(I) *Chloride Dimethanol.*—Monochloropentacarbonylmanganese (0·3 g.) and the diphosphine (1·0 g.) were refluxed in methanol for 4 hr. After cooling, the solution was filtered, concentrated to 10 ml., and after addition of ether (10 ml.), set aside overnight at 0°. The product (0·3 g.) was crystallised from methanol and dried *in vacuo* (Found: C, 66·6; H, 5·6; Cl, 4·0; P, 11·9. $C_{56}H_{56}ClMnO_4P_4$ requires C, 66·5; H, 5·5; Cl, 3·5; P, 12·3%). The *compound*, together with those described hereafter, is stable to air and soluble in most polar and non-polar organic solvents except light petroleum and ether, in which it is insoluble.

Dicarbonylbis-(1,2-*bisdiphenylphosphinoethane*)*manganese*(I) *Chloride Dichloroform.*—(*a*) Monochloropentacarbonylmanganese (0·4 g.) and the diphosphine (1·6 g.) were heated under nitrogen at 150° until evolution of gas had ceased (30 min.). The red solid was dissolved in chloroform, the solution filtered, excess of light petroleum added, and the compound allowed to crystallise overnight at 0°. The yellow crystals (0·4 g.) were washed with light petroleum and dried *in vacuo* [Found: C, 57·5; H, 4·7; Cl (total), 22·5; Cl (ionic), 3·3; P, 10·1; Mn, 4·4%; *M* (cryoscopic in $PhNO_2$), 250. $C_{56}H_{50}Cl_7MnO_2P_4$ requires C, 57·0; H, 4·2; Cl (total), 21·1; Cl (ionic) 3·0; P, 10·5; Mn, 4·7%; *M* ($\frac{1}{4}$ of molecular wt.) = 296].

(*b*) Decacarbonyldimanganese (0·2 g.) and the diphosphine (0·4 g.) were heated at 150° for 2 hr. in an evacuated glass tube. After cooling, the solid was dissolved in a minimum of chloroform. After filtration, pentane was added, and the solution set aside at 0°. The product (0·4 g.) was recrystallised from chloroform–pentane and dried *in vacuo* (Found: C, 57·45; H, 4·2; P, 10·5; Mn, 4·7%).

Dicarbonylbis-(1,2-*bisdiphenylphosphinoethane*)*manganese*(I) *Perchlorate.*—The complex $[Mn(CO)_2(Diphos)_2]Cl,2CHCl_3$ (0·13 g.) in methanol (10 ml.) was added to a solution of lithium perchlorate (0·2 g.) in methanol (10 ml.). The mixture was shaken and kept at 0° overnight. Yellow crystals separated; these (0·05 g.) were crystallised from methanol and dried *in vacuo* [Found: C, 63·8; H, 4·7; Cl, 3·3; Mn, 5·0%; *M* (cryoscopic in $PhNO_2$), 505. $C_{54}H_{48}ClMnO_6P_2$ requires C, 64·4; H, 4·8; Cl, 3·5; Mn, 5·4%; *M* ($\frac{1}{2}$ of molecular wt.), 503].

Dicarbonylbis-(1,2-*bisdiphenylphosphinoethane*)*manganese*(I) *Bromide Dimethanol.*—Monobromopentacarbonylmanganese (0·2 g.) was refluxed in methanol with a large excess of the diphosphine (1 g.) for 3 hr. After cooling the solution was filtered and concentrated (5 ml.). Yellow crystals (0·3 g.), which were slowly formed at 0°, were washed with methanol, and dried *in vacuo* (Found: C, 63·9; H, 5·3; Br, 7·7; P, 11·2. $C_{56}H_{56}BrO_4P_4Mn$ requires C, 63·9; H, 5·3; Br, 7·6; P, 11·8%).

Dicarbonylbis-(1,2-*bisdiphenylphosphinoethane*)*manganese*(I) *Bromide Dichloroform.*—The complex $[Mn(CO)_2(Diphos)_2]Br,2MeOH$ was crystallised from chloroform–pentane and dried *in vacuo* (Found: C, 53·9; H, 4·4; P, 9·5. $C_{56}H_{50}BrCl_6MnO_2P_4$ requires C, 54·5; H, 4·1; P, 10·0%).

Dicarbonylbis-(1,2-*bisdiphenylphosphinoethane*)*manganese*(I) *Bromide.*—The complex $[Mn(CO)_2(Diphos)_2]Br,2CHCl_3$ was heated *in vacuo* (100°/0·1 mm.) for 4 hr. in an Abderhalden apparatus (Found: C, 65·2; H, 4·7; Br, 8·4; P, 12·5. $C_{54}H_{48}BrMnO_2P_4$ requires C, 65·7; H, 4·9; Br, 8·1; P, 12·6).

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