Chemistry of the Metal Carbonyls. Part LXIX.[1] Synthesis and Reactions of Complexes of Manganese Containing the Substituted and Unsubstituted 2,5-Dioxacyclopentylidene Ligand

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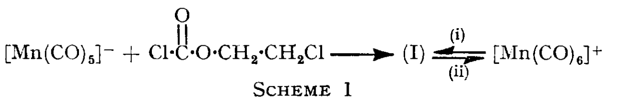
Addition of 2-chloroethyl chloroformate to $[Mn(CO)_5]^-$ affords $[Mn\{C(O)\cdot O\cdot CH_2\cdot CH_2Cl\}(CO)_5]$, which can also be obtained by treating $[Mn(CO)_6]^+$ with 2-chloroethanol. Reaction of this acyl complex with $AgPF_6$ or $AgBF_4$ results in an intramolecular cyclisation reaction to give the 2,5-dioxacyclopentylidene complex $[MnC\cdot O\cdot CH_2\cdot CH_2O(CO)_5]^+$. This cationic complex reacts with halide anions (X = Cl, Br, I) in methanol to give the neutral carbene species $[MnX(C\cdot O\cdot CH_2\cdot CH_2O)(CO)_4]$, but in acetone or acetonitrile as solvent, a competitive ring-opening reaction becomes important. Reaction of the cyclic alcohol, *trans*-2-chlorocyclopentanol, with $[Mn(CO)_6]^+$ affords the acyl complex $[Mn\{C(O)\cdot O\cdot CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot C(H)Cl\}(CO)_5]$, which cyclises with $AgBF_4$ to give the carbene complex $[Mn\{C\cdot O\cdot CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH\cdot O\}(CO)_5]^+$. Treatment of the latter with halide anions affords neutral complexes without any competitive ring-opening. These neutral, halogeno-carbene(carbonyl)manganese complexes react with phosphines, phosphites, and arsines to give stereospecifically the *fac*-substituted isomers; there is no evidence for displacement of the carbene ligand. An unusual deuterium exchange reaction of the substituted halogeno-complexes is discussed.

We have recently described [1] the synthesis of manganese, iron, and ruthenium complexes containing the coordinated 2-oxacyclopentylidene ligand. There is currently considerable interest in such species, which may be depicted either as metal stabilised carbenes or as carbonium ion complexes.[2]

In this paper we report the synthesis of manganese complexes containing the 2,5-dioxacyclopentylidene ligand, and also describe some of their reactions. The new compounds prepared have been characterised by elemental analysis, i.r. and n.m.r. spectroscopy.

Slow addition of a tetrahydrofuran solution of sodium pentacarbonylmanganese to an excess of 2-chloroethyl chloroformate leads to a selective nucleophilic attack giving the acyl complex (I) in good yield (72%). An alternative, although somewhat less satisfactory method of preparation of this compound, is the reaction of hexacarbonylmanganese tetrafluoroborate with 2-chloroethanol in the presence of triethylamine; a reaction which is reversed on addition of HBF_4 (Scheme 1). Similar reactions are well known with unsubstituted alcohols.[3,4]

Treatment of (I) with the silver salts $AgPF_6$ or $AgBF_4$ in acetone solution caused the rapid precipitation of silver chloride and formation of the cationic 2,5-dioxacyclopentylidene complexes (II) and (III) as air-stable, white, crystalline solids, which in contrast to the hexacarbonyl cation $[Mn(CO)_6]^+$, are not sensitive to moisture. The i.r. spectra, in the terminal carbonyl region for (II) and (III), exhibit one strong and two weak bands consistent with C_{4v} symmetry, and are shifted by 35 cm^{-1} to higher frequency than in the neutral acyl precursor (I), in agreement with the complexes being cationic. No bands were observed in the region (1600 cm^{-1}) expected for an acyl complex. In agreement with the proposed structure, the ^1H n.m.r. spectra showed a single sharp singlet, and conductivity measurements demonstrated that (II) and (III) behaved as electrolytes in nitrobenzene solution.



$$[Mn(CO)_5]^- + Cl\cdot\overset{O}{\overset{\|}{C}}\cdot O\cdot CH_2\cdot CH_2Cl \longrightarrow (I) \underset{(ii)}{\overset{(i)}{\rightleftharpoons}} [Mn(CO)_6]^+$$

Scheme 1

(i) $Cl\cdot CH_2\cdot CH_2\cdot OH$–$Et_3N$ (ii) HBF_4

The formation of these complexes clearly involves an intramolecular nucleophilic attack by the acyl oxygen atom on the carbon atom carrying the chlorine leaving group; carbon–chlorine heterolysis is facilitated by the silver cation (Scheme 2). It is interesting that it was not possible [1] to effect a similar silver promoted cyclisation of $[(OC)_5MnC(O)\cdot CH_2\cdot CH_2\cdot CH_2Cl]$, and it is possible that there is some assistance from the non-bonding electrons on the alkoxy-oxygen of (I).

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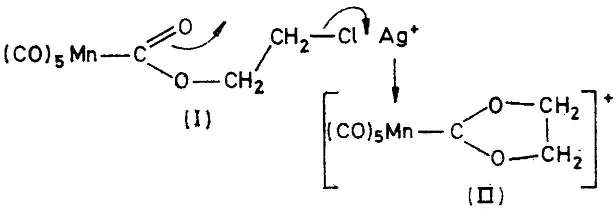
[1] Part LXVIII, C. H. Game, M. Green, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, **351**.

[2] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487; D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, 99, and references cited therein.

[3] E. W. Abel and S. P. Tyfield, *Adv. Organometallic Chem.*, 1970, **8**, 117.

[4] A. M. Brodie, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1970, **24**, 201.

In the cation (II) there are two possible points of attack for the nucleophilic reagents LiX (X = Cl, Br, or I). There is a reaction at the methylene carbon atom with resultant ring-opening to form an acyl complex (I), (IV), or (V) a reaction path which tends to emphasise the carbonium ion character of the complex. Secondly, there is the possibility of nucleophilic attack at the manganese atom with displacement of either carbon monoxide or the 2,5-dioxacyclopentylidene ligand, and the formation of a neutral species. It was found that the actual reaction path followed was very dependent on the nature of the solvent.



SCHEME 2

In acetone solution, lithium iodide reacted with (II) to give only the ring-opened complex (V), which showed a band at 1659 cm^{-1} in its i.r. spectrum, and the expected two triplet resonances in its ^{1}H n.m.r. spectrum. The corresponding reaction of (II) with LiX (X = Cl or Br) in acetone led to extensive decomposition, however, in acetonitrile a smooth ring-opening reaction occurred to give the acyl complexes (I) and (IV). In contrast, if the reactions of the lithium salts are carried out in methanol, nucleophilic attack also occurs at the manganese atom giving a series of neutral 2,5-dioxacyclopentylidene complexes (VI)—(VIII). The acyl complexes (I), (IV), and (V) are also formed in this reaction, but undergo a *trans*-esterification reaction with the solvent to afford methoxycarbonylpentacarbonylmanganese. In a separate experiment it was shown that (I) was converted to [$Mn(CO_2Me)(CO)_5$] in methanol solution.

The neutral complexes (VI)—(VIII) are air-stable, yellow to orange, crystalline solids, and are assigned the illustrated structures on the basis of their i.r. and ^{1}H n.m.r. spectra; the halogen and 2,5-dioxacyclopentylidene ligands have a relative *cis*-configuration. Examination of the i.r. spectrum of the reaction mixture, during the formation of these complexes, provided no evidence for the formation of an isomeric complex, suggesting that (VI)—(VIII) are formed under kinetic control. This might suggest that the 2,5-dioxacyclopentylidene ligand has a weaker *trans*-influence than carbon monoxide, however, an *X*-ray crystallographic study[5] of (VIII), besides confirming the structural identity of the complex, showed, from a comparison of the Mn–C(O) bond lengths, that the *trans*-influence of the 2,5-dioxacyclopentylidene ligand is almost identical with that of carbon monoxide.

The yields of the complexes (VI)—(VIII) are relatively poor, and therefore these compounds do not provide a really satisfactory starting point for further synthetic work. In order to reduce the possibility of the competitive ring-opening reaction, it was decided to examine the synthesis of the complex (IX), in the belief that in the derived cationic species (X), S_N2 attack by halide anion on carbon, *i.e.* ring-opening, would be made sterically difficult. In addition, the electronic influence of the additional ring system would reduce the rate of ring-opening.

Reaction of *trans*-2-chlorocyclopentanol with hexacarbonylmanganese tetrafluoroborate at 0° in the presence of triethylamine afforded the acyl complex (IX). The choice of the *trans*-stereochemistry of the reacting alcohol was dictated by the view that the intramolecular cyclisation reaction, required to form (X), involved S_N2 attack by the acyl-oxygen atom on the carbon atom carrying the chlorine substituent. The compound (IX) showed the expected spectroscopic properties, and on treatment with silver tetrafluoroborate in acetone solution formed the cationic complex (X) as air-stable white crystals (60%).

The i.r. spectrum of (X) was very similar to those of compounds (II) and (III), there being no evidence for an acyl band. The ^{1}H n.m.r. spectrum showed a singlet at τ 4·3 which is assigned to the protons attached to the carbon adjacent to the oxygen of the 2,5-dioxacyclopentylidene ligand. In addition, a complex multiplet was observed at higher field which is attributed to the CH_2 groups of the cyclopentane ring.

Reaction of (X) with LiX (X = I, Br, or Cl) in methanol proceeded smoothly to give good yields of the neutral complexes (XI)—(XIII). There was no evidence for the presence of products arising from ring-opening reactions. The halogeno-complexes (XI)—(XIII) are yellow-orange solids, stable to moisture, air, and light, and have reasonable stability to heat. In contrast, the action of heat (130 °C) on the iodo-complex (VI) resulted in the displacement of the 2,5-dioxacyclopentylidene ligand, and the formation of the known complexes [$MnI(CO)_5$] and [$Mn_2I_2(CO)_8$].

The colour intensity for (XI)—(XIII) increased in the order Cl < Br < I. The i.r. spectra showed three terminal carbonyl bands appropriate to a *cis*-configuration, and the ^{1}H n.m.r. spectra confirmed the presence of the carbene ligand.

Reaction of (VIII) with triphenylphosphine in benzene solution at room temperature gave the substituted complex (XIV). The i.r. spectrum showed three strong bands indicating that the complex has the illustrated *fac*-configuration. The ^{1}H n.m.r. spectrum indicated that the 2,5-dioxacyclopentylidene ligand remains intact during the course of this substitution reaction.

Analogous substitution reactions occurred between (XIII) and the ligands PPh_3, PMe_2Ph, $PMePh_2$, $AsMe_2Ph$, and $P(OCH_2)_3CMe$ to give the crystalline complexes (XV)—(XIX) respectively. The appearance in the i.r. spectra of three strong terminal carbonyl bands confirmed the illustrated *fac*-stereochemistry.

When the ^{1}H n.m.r. spectra of the complexes (XIV)—(XVIII) were recorded in either $CDCl_3$ or $(CD_3)_2CO$ it

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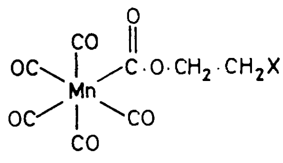
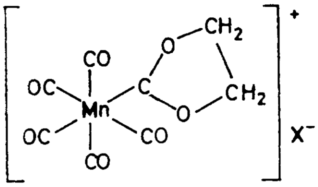
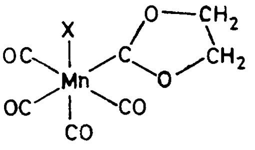
[5] M. Green, J. R. Moss, I. W. Nowell, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1339.



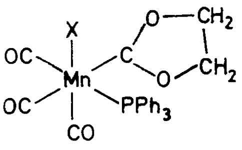
(I; X = Cl)
(IV; X = Br)
(V; X = I)



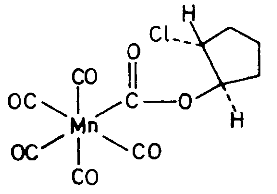
(II; X = PF$_6$)
(III; X = BF$_4$)



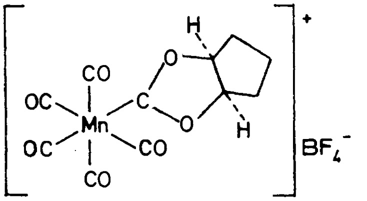
(VI; X = I)
(VII; X = Br)
(VIII; X = Cl)



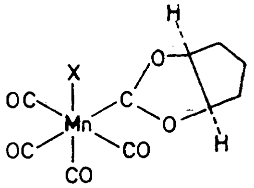
(XIV; X = Cl)



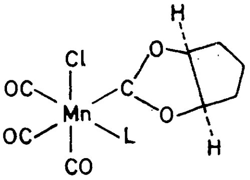
(IX)



(X)



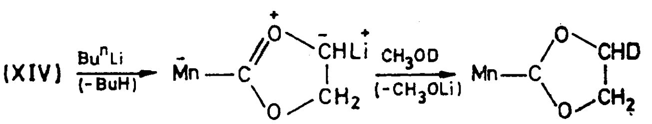
(XI; X = I)
(XII; X = Br)
(XIII; X = Cl)



(XV; L = PPh$_3$)
(XVI; L = PMe$_2$Ph)
(XVII; L = PMePh$_2$)
(XVIII; L = AsMe$_2$Ph)
(XIX; L = P[OCH$_2$]$_3$CMe)

was observed that considerable broadening and a reduction in the relative intensity of the signals attributed to the protons Mn–C–O–C*H* had occurred. In certain cases, for example, (XV), the signal for these protons could not be observed at all, and in the other cases the signal diminished on standing in these deuteriated solvents. However, in C_6H_6 or C_6D_6 solution the expected signal was clearly observable for all the complexes. These observations suggest that deuterium exchange was readily occurring. However, with (VIII), (XIII), and (XIX) no exchange was observed under the same conditions in $CDCl_3$ or $(CD_3)_2CO$.

Some insight into the nature of this process was obtained from the observation that treatment of (XIII) with n-butyl-lithium (one equivalent) in tetrahydrofuran (−78°) led to a change in colour from yellow to red. When the reaction mixture was warmed to −40 °C and quenched with CH_3OD, the complex (XIII) was recovered (25%), and, from examination of the ^1H n.m.r. and mass spectra, was shown to contain deuterium (30% incorporation) in the Mn–C–O–C*H* environment.



SCHEME 3

Although a base promoted exchange has been observed with α-alkoxyethylidene[6] and 2-oxacyclopentylidene[7] metal complexes, and has formed the basis of alkylation and acylation reactions,[8] no such processes have been previously observed with 2,5-dioxacyclopentylidene or related complexes. A possible explanation for these observations is that removal of a proton from (XIII) or (XIV), for example, leads to a species which may be considered to be a carbonyl ylide (Scheme 3). Carbonyl ylides, $(\gt C{=}\overset{+}{O}{-}\overset{-}{C}\lt)$, have been previously implicated[9] in a number of reactions, particularly ring-opening reactions of oxiranes. However, this must remain a tentative suggestion since it is not clear why replacement of CO in (VIII) by triphenylphosphine or other ligands should lead to an enhanced rate of exchange. In the exchange reactions there was no evidence for deuterium incorporation into the phosphorus or arsenic ligands.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on Varian Associates T 60 and HA 100 spectrometers; chemical shifts are relative to tetramethylsilane (τ 10·00). I.r. spectra were recorded using a Perkin-Elmer 257 spectrophotometer. Mass spectra were measured on an A.E.I. MS 902 double focussing mass spectrometer at 70 V ionising potential. Light petroleum refers to the fraction b.p. 60—80°. All reactions were carried out in an atmosphere of dry oxygen-free nitrogen in deoxygenated dry solvents. Conductivity measurements

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[6] C. G. Kreiter, *Angew. Chem. Internat. Edn.*, 1968, **7**, 390.

[7] C. P. Casey, *Chem. Comm.*, 1970, 1220.

[8] C. P. Casey, R. A. Boggs, and R. L. Anderson, *J. Amer. Chem. Soc.*, 1972, **94**, 8947.

[9] J. H. Hall and R. Huisgen, *Chem. Comm.*, 1971, 1187; J. H. Hall, R. R. Huisgen, C. H. Ross, and W. Scheer, *ibid.*, p. 1188.

were made using a Cambridge Instruments conductance bridge.

Reaction of 2-Chloroethyl Chloroformate with Sodium Pentacarbonylmanganese.—A solution of sodium pentacarbonylmanganese (61·6 mmol) in tetrahydrofuran (150 ml) was added dropwise, with stirring, to 2-chloroethyl chloroformate (13·9 g, 98·0 mmol) over a period of 40 min and the resulting mixture stirred at room temperature for 1·25 h. Solvent and unreacted chloroformate were removed *in vacuo*, and the residue extracted with methylene chloride (3 × 50 ml) and centrifuged. Removal of solvent from the clear solution gave a residue, which was crystallised from light petroleum to give pale yellow *needles* of (I) (13·5 g, 72%), m.p. 71—73° [Found: C, 32·1; H, 1·2; Cl, 11·8; Mn, 18·4; O, 37·0%; *M*, 311 (in benzene). $C_8H_4ClMnO_7$ requires C, 31·8; H, 1·3; Cl, 11·7; Mn, 18·2; O, 37·0%; *M*, 303], ν(CO) (cyclohexane) 2129w, 2036vs, 2015s, and 1659m cm^{-1}; ^1H n.m.r. resonances (C_6D_6) at τ 6·02 [(t) 2H, CH_2, *J* (HH) 6·0 Hz] and 6·92 [(t) 2H, CH_2, *J* (HH) 6·0 Hz].

Reaction of Hexacarbonylmanganese Tetrafluoroborate with 2-Chloroethanol.—A suspension of $[Mn(CO)_6]^+BF_4^-$ (0·21 g, 0·68 mmol) in methylene chloride (25 ml) containing 2-chloroethanol (1·2 g, 15·0 mmol) was treated dropwise with triethylamine (0·7 mmol) until all the manganese cation had dissolved. Solvent was removed *in vacuo*, and the residue extracted with light petroleum. The solution was filtered and solvent removed to give (I) (0·14 g, 52%), which was purified by sublimation (50°, 0·1 mmHg) and identified (see above) by its i.r. and ^1H n.m.r. spectrum.

Reaction of Complex (I) *with Silver Hexafluorophosphate.*—A solution of (I) (0·31 g, 1·02 mmol) in acetone (8 ml) was treated with a solution of silver hexafluorophosphate (0·26 g, 1·02 mmol) in acetone (4 ml). A white precipitate of silver chloride rapidly formed. After 1 h at room temperature, the reaction mixture was filtered and the solvent removed *in vacuo*. The residue was dissolved in methanol and treated with powdered charcoal (0·2 g) to remove traces of silver. The solution was filtered, the volume of solvent reduced, and diethyl ether added to give white *needles* of (II) (0·21 g, 50%), m.p. 163—166° (Found: C, 23·2; H, 0·9; F, 27·7; Mn, 13·5. $C_8H_4F_6MnO_7P$ requires C, 23·3; H, 1·0; F, 27·7; Mn, 13·3%), ν(CO) (CH_2Cl_2) 2156w, 2106w, 2069vs cm^{-1}; $\nu_{max.}$ (Nujol) 1430sh, 1300w, 1265s, 1215s, 913m, 880m, 837vs (PF), 722w, 693s, 655sh, and 638s cm^{-1}; ^1H n.m.r. resonance $[(CD_3)_2CO]$ at τ 4·90 [(s) 4H, OCH_2]; the equivalent conductance for a *ca.* 10^{-3}M-solution in nitrobenzene was Λ_e 29·8 Ω^{-1} cm^2 mol^{-1}.

A similar reaction with silver tetrafluoroborate gave white *needles* of (III) (49%), m.p. 150—152° (Found: C, 27·3; H, 1·0; F, 21·3. $C_8H_4BF_4MnO_7$ requires C, 27·5; H, 1·2; F, 21·7%), ν(CO) (CH_2Cl_2) 2157w, 2106w, 2069vs cm^{-1}; ^1H n.m.r. resonance $[(CD_3)_2CO]$ at τ 4·94 [(s) 4H, OCH_2]; the equivalent conductance for a *ca.* 10^{-3}M-solution in nitrobenzene was Λ_e 32·5 Ω^{-1} cm^2 mol^{-1}.

Reaction of Complex (I) *with Methanol.*—A solution of (I) (0·53 g, 1·75 mmol) in methanol (10 ml) was allowed to stand at room temperature for 1 h. The solvent was removed *in vacuo* and the residue recrystallised from light petroleum to give colourless plates of *methoxycarbonylpentacarbonylmanganese* (0·33 g, 75%), m.p. 95—97° dec. (Found: C, 33·4; H, 1·2. $C_7H_3MnO_7$ requires C, 33·1; H, 1·2%), ν(CO) (cyclohexane), 2127w, 2034vs, 2012s, and 1658m cm^{-1}; ^1H n.m.r. resonance (C_6D_6) at τ 6·60 [(s) 3H, OCH_3].

Reaction of Complex (II) *with Lithium Iodide in* (*a*) *Acetone.*—A solution of (II) (0·30 g, 0·73 mmol) in acetone (15 ml) was treated with anhydrous lithium iodide (1·96 g, 14·7 mmol) and the mixture stirred for 1 h at room temperature. Solvent was removed *in vacuo* and the residue extracted with light petroleum (3 × 30 ml). The extracts were filtered, and the volume of solvent reduced (10 ml) *in vacuo*; cooling (−20°) gave colourless *needles* of (V) (0·16 g, 56%), m.p. 99—100° (Found: C, 24·6; H, 1·1; I, 32·5; O, 28·2. $C_8H_4IMnO_7$ requires C, 24·4; H, 1·0; I, 32·2; O, 28·4%), ν(CO) (cyclohexane) 2129w, 2034vs, 2014s, and 1659m cm^{-1}; ^1H n.m.r. resonances (C_6D_6) at τ 6·00 [(t), 2H, CH_2, *J*(HH) 6·5 Hz] and 7·24 [(t) 2H, CH_2, *J*(HH) 6·5 Hz].

(*b*) *Methanol.* A solution of (II) (0·36 g, 0·87 mmol) in methanol (10 ml) was treated with a solution of lithium iodide (1·90 g, 14·2 mmol) in ethanol (10 ml). After 1 h at room temperature, solvent was removed *in vacuo* and the residue extracted with light petroleum (3 × 25 ml), filtered, and the solvent removed. The resulting pale yellow solid (0·052 g) was shown to be a mixture of methoxycarbonylpentacarbonylmanganese and complex (V) by its i.r. and ^1H n.m.r. spectrum. Addition of water to the light petroleum insoluble material gave an orange solid, which was collected and recrystallised from methylene chloride–light petroleum to give orange needles of (VI) (0·14 g, 44%), m.p. 141—143° [Found: C, 23·4; H, 0·8; I, 35·0%; *M*, 366 (mass spectrum). $C_7H_4IMnO_6$ requires C, 23·0; H, 1·1; I, 34·7%; *M*, 366], ν(CO) (CH_2Cl_2) 2097m, 2016vs, 1971s; $\nu_{max.}$ (Nujol) 1407m, 1296w, 1232s, 1194sh, 1183s, 908m, 880m, 724w, 695s, 652s, and 634s cm^{-1}; ^1H n.m.r. resonance $[(CD_3)_2CO]$ at τ 5·00 [(s) 4H, OCH_2]. The mass spectrum showed peaks at *m/e* 366 (*P*, 32%), 322 $[MnI(CO)_5$, 3%], 310 (*P* − 2CO, 9%), 282 (*P* − 3CO, 21%), 266 $[MnI(CO)_3$, 2%], 254 (*P* − 4CO, 30%), 238 $[MnI(CO)_2$, 5%], 210 [MnI(CO), 14%], 182 (MnI, 100%), 127 (I, 24%), and 55 (Mn, 77%).

Reaction of Complex (II) *with Lithium Bromide in* (*a*) *Acetonitrile.*—A solution of (II) (0·24 g, 0·58 mmol) in acetonitrile (10 ml) was treated with lithium bromide (1·02 g, 11·7 mmol). After stirring at room temperature for 1·5 h, solvent was removed *in vacuo*, and the residue extracted with light petroleum (3 × 25 ml). The solution was filtered and the solvent removed to give a crystalline solid (0·19 g, 94%), which was recrystallised from light petroleum to give white needles of (IV), m.p. 72—74° (Found: C, 28·0; H, 1·2; Br, 22·8. $C_8H_4BrMnO_7$ requires C, 27·7; H, 1·2; Br, 23·0), ν(CO) (cyclohexane) 2130w, 2035vs, 2015s, and 1659 cm^{-1}; ^1H n.m.r. resonances (C_6D_6) at τ 5·99 [(t) 2H, CH_2, *J*(HH) 6·0 Hz] and 7·07 [(t) 2H, CH_2, *J*(HH) 6·0 Hz].

(*b*) *Methanol.* A solution of (II) (1·02 g, 2·47 mmol) and LiBr (4·30 g, 49·4 mmol) in methanol (30 ml) was stirred at room temperature for 1·5 h. Solvent was removed *in vacuo*, and the residue extracted with light petroleum (3 × 30 ml). This solution contained a mixture of methoxycarbonylpentacarbonylmanganese and complex (IV). The light petroleum insoluble material was washed with water and recrystallised from methylene chloride–light petroleum to give orange *needles* of (VII) (0·19 g, 23%), m.p. 126—130° (Found: C, 26·5; H, 1·5; Br, 25·7. $C_7H_4BrMnO_6$ requires C, 26·4; H, 1·3; Br, 25·1%), ν(CO) (CH_2Cl_2) 2104m, 2023vs, and 1969s cm^{-1}; $\nu_{max.}$ (Nujol) 1413m, 1252sh, 1288w, 1246s, 1203s, 912m, 890m, 725w, 688s, 662s, and 634s cm^{-1}; ^1H n.m.r. resonance $[(CD_3)_2CO]$ at τ 5·00 [(s) 4H, OCH_2].

Reaction of Complex (II) *with Lithium Chloride in* (*a*) *Acetonitrile.*—In a similar manner, reaction of (II) with

LiCl gave only (I) as white needles (95%), having identical i.r. and ^{1}H n.m.r. with an authentic sample.

(*b*) *Methanol.* Similarly, reaction of (II) (0·74 g, 1·79 mmol) with LiCl (1·47 g, 35·0 mmol) in methanol (20 ml) gave a mixture of $[Mn(CO_2Me)(CO)_5]$ and (I), together with a yellow solid, which was recrystallised from methylene chloride–light petroleum to give yellow *needles* of (VIII) (0·19 g, 39%), m.p. 120—125° dec. [Found: C, 30·6; H, 0·9; Cl, 13·1; Mn, 20·2; O, 34·9%; *M*, 287 (in CH_2Cl_2). $C_7H_4ClMnO_6$ requires C, 30·6; H, 1·5; Cl, 12·9; Mn, 20·0; O, 35·0%; *M*, 275], ν(CO) (CH_2Cl_2) 2107m, 2025vs, and 1967s cm^{-1}; ^{1}H n.m.r. resonance [$(CD_3)_2CO$] at τ 5·02 (s 4H).

Reaction of Hexacarbonylmanganese Tetrafluoroborate with trans-2-*Chlorocyclopentanol.*—Triethylamine (2·4 ml) was added dropwise with stirring, over 1 h at 0° to a suspension of hexacarbonylmanganese tetrafluoroborate (2·0 g, 6·45 mmol) and *trans*-2-chlorocyclopentanol (6·39 g, 53·2 mmol) in methylene chloride (50 ml). After 1·5 h, solvent was removed *in vacuo*, and the resultant sticky solid washed (2 × 20 ml) with ice-cold light petroleum. Sublimation (70—80°, 0·1 mmHg) onto an ice cooled probe, followed by recrystallisation from light petroleum, gave white feathery *crystals* of (IX) (1·31 g, 59%), m.p. 132—135° dec. (Found: C, 39·0; H, 2·4; Cl, 10·3. $C_{11}H_8ClMnO_7$ requires C, 38·5; H, 2·4; Cl, 10·3%), ν(CO) (cyclohexane) 2129w, 2034s, 2004m, and 1663w, br cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 4·74 (m, 1H), 5·81 (m, 1H), and 7·5—8·5 [br (m) 6H]. The mass spectrum showed peaks at *m*/*e* 342 (*P*), 314 (*P* − CO), 286 (*P* − 2CO), 258 (*P* − 3CO), 230 (*P* − 4CO), 223, 90 (MnCl), 67 (C_5H_7), and 55 (Mn).

Reaction of Complex (IX) *with Silver Tetrafluoroborate.*—To a solution of (IX) (1·02 g, 2·98 mmol) in acetone (35 ml) was added silver tetrafluoroborate (0·58 g, 2·95 mmol). After stirring at room temperature for 0·75 h, the precipitated silver chloride was filtered off, and the solvent removed *in vacuo*. The residue was dissolved in methanol (20 ml) and treated with decolourising charcoal (1·2 g). Diethyl ether was added to the filtered solution, and the resultant precipitate collected. Recrystallisation from methanol–diethyl ether gave white *needles* of (X) (0·7 g, 61%), m.p. 142—145° dec. (Found: C, 33·7; H, 2·1; F, 19·0; Mn, 13·9. $C_{11}H_8BF_4MnO_7$ requires C, 33·5; H, 2·1; F, 19·3; Mn, 14·0%), ν(CO) (CH_2Cl_2) 2156w, 2105w, 2068s cm^{-1}, $\nu_{max.}$ (Nujol) 1416s, 1343m, 1258s, 1220s, 1110m, 1060s, br (BF), 1024m, 947m, 874m, 798w, 709s, 662s, 647s, 630m, 605w, and 533w cm^{-1}; ^{1}H n.m.r. resonances (CD_3OD) at τ 4·3 [(s) 2H, OCH] and 7·55—8·3 [br (m) 6H].

Reaction of Complex (X) *with Lithium Iodide in Methanol.*—A solution of (X) (0·10 g, 0·25 mmol) and anhydrous lithium iodide (0·35 g, 2·5 mmol) in methanol (10 ml) was stirred at room temperature for 2·5 days. The solvent was removed *in vacuo*, and the residue washed with water (2 × 3 ml). After drying *in vacuo*, the residue was recrystallised (−20°) from methylene chloride–light petroleum to give amber *prisms* of (XI) (0·078 g, 68%), m.p. 99—100° (Found: C, 29·6; H, 2·0; I, 31·0. $C_{10}H_8IMnO_6$ requires C, 29·6; H, 2·0; I, 31·2%), ν(CO) (cyclohexane) 2096m, 2016s, and 1967, $\nu_{max.}$ (Nujol) 1334s, 1227s, 1214m, 1195s, 1095w, 1012m, 937s, 917w, 861s, 796w, 702s, 655s, 634s, and 619s cm^{-1}.

Reaction of Complex (X) *with Lithium Bromide in Methanol.*—Similarly, reaction of (X) (0·095 g, 0·24 mmol) with LiBr (0·26 g, 3·0 mmol) in methanol (10 ml) gave, on recrystallisation (−20°) from methylene chloride–light petroleum, yellow *crystals* of (XII) (0·062 g, 76%), m.p. 84·5—86·5 (Found: C, 33·5; H, 2·3; Br, 22·6. $C_{10}H_8BrMnO_6$ requires C, 33·5; H, 2·2; Br, 22·3%), ν(CO) (CH_2Cl_2) 2102m, 2021s, and 1965m cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 4·40 [(s) 2H, OCH] and 7·5—8·5 [br (m) 6H].

Reaction of Complex (X) *with Lithium Chloride in Methanol.*—In a similar way, reaction of (X) (0·094 g, 0·24 mmol) with LiCl (0·10 g, 2·4 mmol) in methanol (10 ml) gave, from methylene chloride–light petroleum, pale yellow *needles* of (XIII) (0·055 g, 74%), m.p. 87—89° (Found: C, 37·9; H, 2·5; Cl, 11·0. $C_{10}H_6ClMnO_6$ requires C, 38·1; H, 2·5; Cl, 11·3%), ν(CO) (CH_2Cl_2) 2107m, 2025s, and 1965m cm^{-1}; ^{1}H n.m.r. resonances (C_6D_6) at τ 5·70 [br (s) 2H, OCH] and 8·2—9·5 [br (m) 6H]. The mass spectrum showed peaks at *m*/*e* 558 $[Mn_2(CO)_8(carbene)_2]$, 474 $[Mn_2(CO)_9(carbene)]$, 362 $[Mn_2(CO)_9]$, and 67 (C_5H_7).

Reaction of Complex (VIII) *with Triphenylphosphine.*—A solution of (VIII) (0·10 g, 0·37 mmol) in benzene (20 ml) was treated with triphenylphosphine (0·14 g, 0·53 mmol) and the solution allowed to stand at room temperature for 24 h. Solvent was removed *in vacuo*, and the residue washed with light petroleum. Recrystallisation of the residue from methylene chloride–light petroleum gave yellow *needles* of (XIV) (0·17 g, 66%), m.p. 143—145° dec. (Found: C, 56·0; H, 4·0; Cl, 7·4. $C_{24}H_{19}ClMnO_5P$ requires C, 56·7; H, 3·8; Cl, 7·0%), ν(CO) (CH_2Cl_2) 2036s, 1967s, and 1923s cm^{-1}, $\nu_{max.}$ (Nujol) 1312w, 1212m, 1192sh, 1171m, 1092m, 1030w, 1002w, 970w, 909m, 882w, 747m, 724m, and 698s cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 2·50 [(m) 15H, C_6H_5] and 5·74 [br (s) 4H, OCH_2].

Reaction of Complex (XIII) *with* (*a*) *Triphenylphosphine.*—A solution of (XIII) (0·05 g, 0·16 mmol) and triphenylphosphine (0·10 g, 0·38 mmol) in methylene chloride (10 ml) was stirred at room temperature. After 18 h the solution was filtered, the solvent removed *in vacuo*, the residue washed with light petroleum, and then recrystallised from methylene chloride–light petroleum to give yellow *needles* of (XV) (0·08 g, 91%), m.p. 136—139° dec. (Found: C, 58·1; H, 4·1; Cl, 6·6; P, 5·4; Mn, 10·5. $C_{27}H_{23}ClMnO_5P$ requires C, 59·1; H, 4·2; Cl, 6·5; P, 5·6; Mn, 10·0%), ν(CO) ($CHCl_3$) 2038s, 1970s, and 1922mcm^{-1}; $\nu_{max.}$ (Nujol) 1320w, 1268w, 1222m, 1204m, 1179m, 1090w, 1014w, 932w, 857w, 790w, 743m, 721w, 696s, and 661w cm^{-1}; ^{1}H n.m.r. resonances (C_6D_6) at τ 2·8 [(d) 15H, C_6H_5], 5·65 [(s) 2H, OCH], and 8·2—9·4 [br (m) 6H, CH_2].

(*b*) *Dimethylphenylphosphine.* A similar reaction gave yellow *crystals* of (XVI) (89%), m.p. 103—105° (Found: C, 47·7; H, 4·7. $C_{17}H_{19}ClMnO_5P$ requires C, 48·1; H, 4·5%), ν(CO) (CH_2Cl_2) 2032s, 1960s, and 1912m; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 2·45 [(m) 5H, C_6H_5], 5·15 [br(s) OCH], 7·6—8·8 [br (m) 6H, CH_2], and 8·35 [(d) 6H, CH_3P, *J*(HP) 8·0 Hz].

(*c*) *Methyldiphenylphosphine.* In a similar way there were obtained yellow *crystals* of (XVII) (85%), m.p. 45—48° dec. (Found: C, 54·8; H, 4·7. $C_{22}H_{21}ClMnO_5P$ requires C, 54·4; H, 4·3%), ν(CO) (CH_2Cl_2) 2031s, 1960s, and 1912m cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 2·5 [br (m) 10H, C_6H_5], 5·15 [br (s) OCH], 7·6—8·6 [br (m) 6H, CH_2], and 8·35 [(d) 3H, CH_3P, *J*(HP) 8·0 Hz].

(*d*) *Dimethylphenylarsine.* A similar reaction gave pale yellow *crystals* of (XVIII) (74%), m.p. 85—87° (Found: C, 43·2; H, 4·3. $C_{17}H_{19}AsClMnO_5$ requires C, 43·5; H, 4·1%), ν(CO) (CH_2Cl_2) 2032s, 1958s, and 1912m cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 2·5 [br (m) 5H, C_6H_5], 4·9 [br (s) OCH], 7·6—8·6 [br (m) 6H, CH_2], and 8·33 [(s) 6H, CH_3As].

(*e*) 1-*Methyl*-3,5,8-*trioxa*-4-*phosphabicyclo*[2.2.2]*octane*. A similar reaction gave yellow *crystals* of (XIX) (73%), m.p. 147—150° dec. (Found: C, 38·8; H, 4·0. $C_{14}H_{17}Cl$-MnO_8P requires C, 38·7; H, 3·9%), ν(CO) (CH_2Cl_2) 2048s, 1986s, and 1932m cm^{-1}; ^1H n.m.r. resonances ($CDCl_3$) at τ 4·62 (s, 2H, OCH), 5·8 [(d) 6H, $POCH_2$, *J*(HP) 4·0 Hz], 7·6—8·6 [br (m) 6H, CH_2], and 9·2 [(s) 3H, CH_3].

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