The Addition of Protic Acids to $[Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2]$ to give Bridging Hydrido-compounds

Helen C. Aspinall and Antony J. Deeming*
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ

Addition of protic acids with weakly co-ordinating anions (HBF_4 or HSO_3F) to dichloromethane solutions of $[Mn_2(CO)_5(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$)containing a μ-σ,η^2-CO ligand leads to the cationic complexes $[Mn_2H(CO)_6(dppm)_2][Y]$ (Y = BF_4 or $SO_3F{\cdot}nH_2O$). The extra CO must have come from destruction of a manganese carbonyl intermediate compound, but under an atmosphere of CO one molecule of CO is absorbed and better yields are obtained. Addition of HCl to $[Mn_2(CO)_5(dppm)_2]$ gives the neutral adduct $[Mn_2H(Cl)(CO)_5(dppm)_2]$. Trifluoroacetic acid shows both types of behaviour normally giving $[Mn_2H(CO)_6(dppm)_2][(CF_3CO_2)_2H]$, but if the reaction solution is flushed with N_2 or is kept under reduced pressure then an analogue of the chloro-compound, $[Mn_2H(CF_3CO_2)(CO)_5(dppm)_2]$, with monodentate trifluoroacetate is obtained. All protonated compounds give ^1H n.m.r. quintets at high field consistent with bridging hydride ligands. The products were further characterised by their ^{31}P-{^1H} n.m.r. spectra.

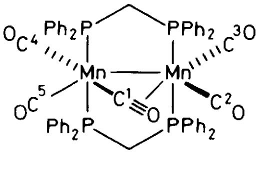
Treatment of $[Mn_2(CO)_{10}]$ with one equivalent of the diphosphine $Ph_2PCH_2PPh_2$ (dppm) readily gives $[Mn_2(CO)_8(dppm)]$ but the incorporation of a second dppm ligand at higher temperatures (refluxing *m*-xylene or decane) gives the orange-red compound $[Mn_2(CO)_5(dppm)_2]$ (**1**), which was first reported in 1975.[1,2] The most interesting feature of (**1**) is a μ-σ,η^2-CO ligand which was characterised by a ν(CO) absorption at 1 645 cm^{-1} and by a 'side-on' contact with one Mn atom (*X*-ray structure). On the basis of the 18-electron rule, the bridging CO is a four-electron donor and the η^2-co-ordination (with apparent donation from a filled π CO orbital) would seem to bear this out. Other compounds have since been shown to have similarly bridging CO such as $[(C_5H_5)_2Zr(\mu\text{-}MeCO)(\mu\text{-}\sigma,\eta^2\text{-}CO)Mo(CO)(C_5H_5)]$[3] and $[MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}\sigma,\eta^2\text{-}CO)_2(CO)_4(C_5H_5)_2]$,[4] but in these complexes the CO ligands bridge different metal elements whereas in compound (**1**) it is only the unsymmetrical bridge that makes the Mn atoms non-equivalent. Compound (**1**) is dynamic.[5,6] Although the non-equivalent Mn atoms do not exchange, there is an exchange of C^1O with C^4O and a simultaneous exchange of C^2O with C^3O. The reactivity of (**1**) has been little explored in spite of the current interest in the reactivity of CO ligands, especially of those in rather unusual environments. For example, it would be particularly valuable to know whether reduction of CO is in any way favoured for oxygen-bound CO ligands such as in (**1**).[7] In clusters such as $[Fe_4H(CO)_{13}]^-$ it would seem that CO reduction is favoured by side-on CO bonding,[8] although in this case reduction occurs by an initial electrophilic addition of H^+ or Me^+ at the bridging CO.

So far established for (**1**) is the reversible uptake of small two-electron-donor molecules such as CO[5] or RNC.[9,10] However, when R = 4-tolyl, CO rather than the isocyanide is lost from the adduct to give $[Mn_2(CO)_4(NCC_6H_4Me\text{-}4)(dppm)_2]$, containing a four-electron-donor bridging isocyanide.[9,10] Halogenation of (**1**) gives simple halogenomanganese(I) compounds.

We initially set out to examine the reactivity of (**1**) towards nucleophiles but, finding a singular lack of reactivity except with the most powerful nucleophiles, we turned our attention to reactions with electrophiles, in particular protic acids. We have already communicated some of our results on dimanganese compounds.[11,12]

Results and Discussion

Reactions of $[Mn_2(CO)_5(dppm)_2]$ (**1**) *with Nucleophiles.*—A tetrahydrofuran (thf) solution of $[Mn_2(CO)_5(dppm)_2]$ did not react with $LiBHEt_3$ (10 equivalents) after 3 days at room temperature. Similarly there was no reaction with LiMe (~10 equivalents) in thf solution after 2 days at room temperature. However, we did find reaction with a very large (60 fold) excess of $LiAlH_4$. A suspension of $[Mn_2(CO)_5(dppm)_2]$ and $LiAlH_4$ in thf was stirred at room temperature and after 15 min the i.r. spectrum of the solution showed complete reaction to give a new species [ν(CO)/cm^{-1} = 1 912vw, 1 868w, 1 829m, 1 774m, and 1 692s]. This new species was never isolated; on exposure to damp air it decomposed rapidly in thf solution to regenerate $[Mn_2(CO)_5(dppm)_2]$. As no uniquely low-frequency ν(CO) was observed in the i.r. spectrum, it seems unlikely that a formyl complex had formed and this reaction was not studied further. Turney[13] described the formation of $[Mn_2H(CO)_5(dppm)_2]^-$ in a similar reaction.



(1)

Complex (**1**) is clearly not very reactive towards nucleophiles. In particular, the four-electron-donor bridging mode for CO does not seem to activate it towards reduction. This is entirely compatible with recent theoretical results on compound (**1**) which show that the main component of the η^2 interaction is donation from Mn to a π^* CO orbital rather than donation from the filled CO π orbital.[14] The latter component was shown to be negligible so that the idea of this CO as a four-electron donor can only apply in a formal sense if at all. This is not unique; other ligands such as tetrafluoroethene lead to electron withdrawal from metal atoms even though they are formally two-electron donors and can even be regarded as two-electron oxidising agents undergoing oxidative addition at the metal.

Since it is rather unreactive as an electrophile, we studied the reactions of $[Mn_2(CO)_5(dppm)_2]$ (**1**) as a nucleophile.

Reactions of $[Mn_2(CO)_5(dppm)_2]$ (**1**) *with Protic Acids.*—Addition of an excess of trifluoroacetic, tetrafluoroboric, or fluorosulphonic acids to a CH_2Cl_2 solution of $[Mn_2(CO)_5(dppm)_2]$ at room temperature resulted in complete reaction to

Table 1. Selected infrared data for the bridging hydrido-compounds

Compound	ν(CO)/cm^{-1} (in CH_2Cl_2)	ν(CO)/cm^{-1} (Nujol mull)	Other absorptions/cm^{-1} (Nujol mull)
$[Mn_2H(CO)_6(dppm)_2][(CF_3CO_2)_2H]$	2 034w, 1 978vs, 1 956m(sh), 1 948m(sh)	2 032(sh), 2 026m, 1 970s, 1 956vs, 1 947(sh), 1 913w	$\nu_{asym}(CO_2)$ 1 780m* $\nu_{sym}(CO_2)$ 1 378w*
$[Mn_2H(CO)_6(dppm)_2][BF_4]$	2 035w, 1 976vs, 1 955m(sh), 1 946m(sh)	2 046w, 2 028m, 1 958vs, 1 936s(sh), 1 926vs	ν(BF) 1 070s
$[Mn_2H(CO)_6(dppm)_2][BPh_4]$	2 033w, 1 978vs, 1 956m(sh), 1 948m(sh)	2 045w, 2 024m, 1 963vs, 1 955s, 1 942vs, 1 933s	
$[Mn_2H(CO)_6(dppm)_2][SO_3F]\cdot nH_2O$	2 034w, 1 976vs, 1 958m(sh), 1 945m(sh)	2 027w, 1 956vs, 1 926s, 1 851vw	ν(OH) 3 400s ν(SO) 1 270vw, 1 229w, 1 160w
$[Mn_2H(CF_3CO_2)(CO)_5(dppm)_2]$	2 036w, 1 956s, 1 943m(sh), 1 928m(sh), 1 857m	2 033w, 1 950s, 1 947m(sh), 1 917m(sh), 1 848m	$\nu_{asym}(CO_2)$ 1 685m* $\nu_{sym}(CO_2)$ 1 402w*
$[Mn_2H(Cl)(CO)_5(dppm)_2]$	2 034w, 1 956s, 1 925s, 1 854m	2 043w, 1 963vs, 1 941s, 1 909s(sh), 1 859m, 1 829m	

* Hexachlorobuta-1,3-diene mull.

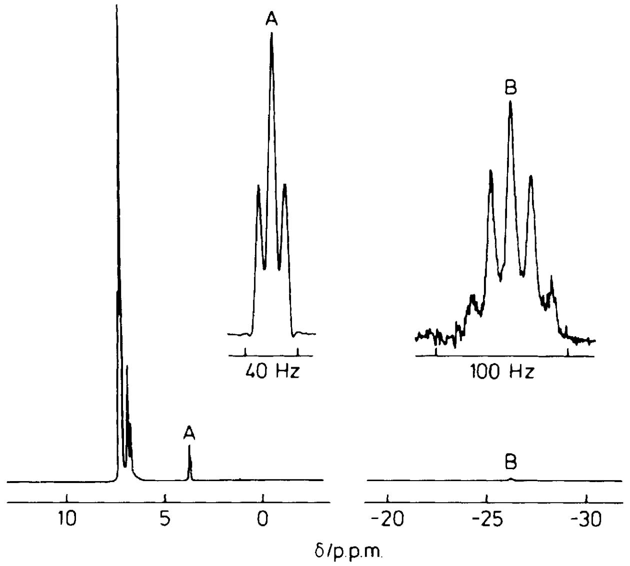
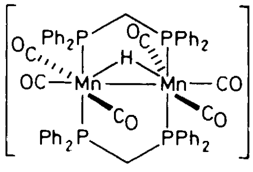
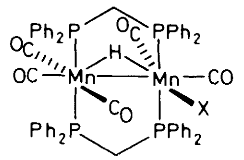


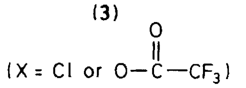
Figure. 200-MHz ^1H n.m.r. spectrum of $[Mn_2H(CO)_6(dppm)_2]^+$ (**2**), as the $[BPh_4]^-$ salt, in $CDCl_3$ at 22 °C



(**2**)



(**3**)



(X = Cl or $O-C(=O)-CF_3$)

give $[Mn_2H(CO)_6(dppm)_2]^+$ and, to judge from the ν(CO) spectrum of the final reaction solution, this was the only metal carbonyl product. For HBF_4 or HSO_3F, reaction was complete after *ca.* 30 min, but with CF_3CO_2H, complete reaction took several hours. In each case the product was obtained pure in *ca.* 30% yield, crystallising as $[Mn_2H(CO)_6(dppm)_2][Y]$ [Y = $(CF_3CO_2)_2H$, BF_4, or $SO_3F\cdot nH_2O$] on addition of Et_2O. These reactions were faster in the presence of an atmosphere of CO and from gas volume measurements one molecule of CO per Mn_2 was absorbed on adding CF_3CO_2H to $[Mn_2(CO)_5(dppm)_2]$ under these conditions.

Considering that this reaction may have proceeded *via* an air-sensitive intermediate which might be observed in the absence of air or free CO at room temperature, a suspension of $[Mn_2(CO)_5(dppm)_2]$ in $CHCl_3$ was degassed by a series of freeze-pump-thaw cycles. A six-fold excess of CF_3CO_2H was added and the reaction mixture was maintained at a reduced pressure of *ca.* 170 mmHg (22.6 × 10^3 Pa) (the saturated vapour pressure of $CHCl_3$ at 20 °C). After 14 h at room temperature, the $[Mn_2(CO)_5(dppm)_2]$ had reacted to give an orange-red solution which did not contain $[Mn_2H(CO)_6(dppm)_2]^+$ but a new product (i.r. evidence). This was isolated and characterised as $[Mn_2H(CF_3CO_2)(CO)_5(dppm)_2]$ and better prepared by passing H_2 or N_2 through a solution of $[Mn_2(CO)_5(dppm)_2]$ on adding CF_3CO_2H. Bubbling N_2 through a solution of $[Mn_2H(CO)_6(dppm)_2][(CF_3CO_2)_2H]$ for 12 h did not lead to the neutral compound $[Mn_2H(CF_3CO_2)(CO)_5(dppm)_2]$, while bubbling N_2 through a solution of $[Mn_2(CO)_5(dppm)_2]$ and $HBF_4\cdot Et_2O$ gave only $[Mn_2H(CO)_6(dppm)_2]^+$. Addition of HCl gas to a CH_2Cl_2 solution of $[Mn_2(CO)_5(dppm)_2]$ gave $[Mn_2H(Cl)(CO)_5(dppm)_2]$ rather than the cationic hexacarbonyl.

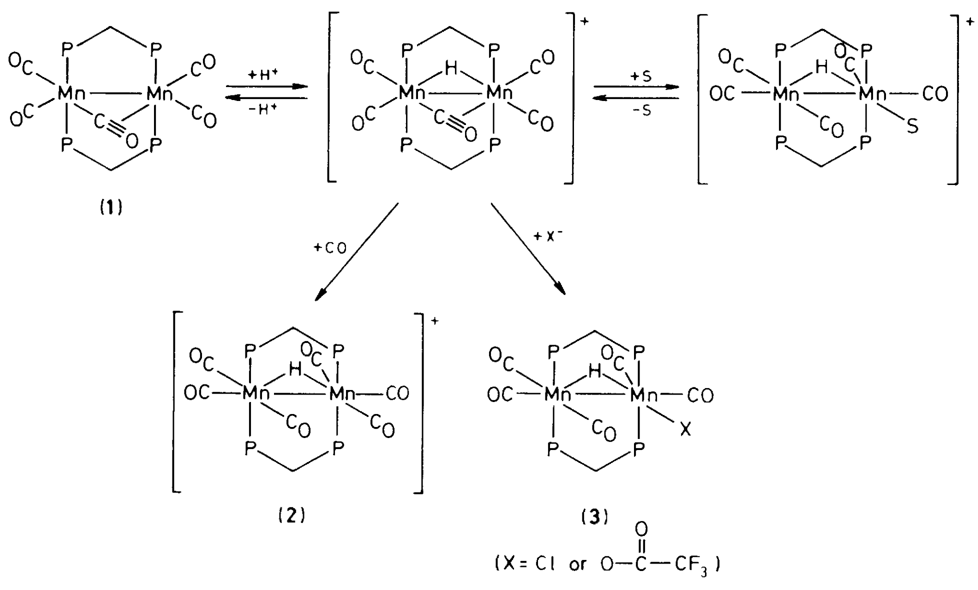
Spectroscopic Characterisation of the Dinuclear Manganese Hydrides.—Selected i.r. data are given in Table 1 and ^1H and ^{31}P n.m.r. data in Table 2. The Figure shows the ^1H n.m.r. spectrum of $[Mn_2H(CO)_6(dppm)_2]^+$. This and the ^{31}P spectrum are consistent with structure (**2**). The high-field ^1H n.m.r. quintets for the hydride ligands confirm that these are bridging. The single ^1H n.m.r. signal for the CH_2 groups confirms that there is a static or time-averaged plane of symmetry through the four P and two Mn atoms. Since the five-membered Mn_2P_2C rings are expected to adopt an envelope configuration with the C atom out of the plane, facile 'flipping' of the methylene groups (ring inversion) must be occurring to make the protons equivalent. In $[Pd_2Cl_2(dppm)_2]$, 'flipping' is not facile, due to a rigid Pd_2P_4 framework, and the methylene protons appear as a quartet of triplets in the ^1H n.m.r. spectrum.[15] The sharp singlet in the ^{31}P n.m.r. spectrum of $[Mn_2H(CO)_6(dppm)_2]^+$ indicates equivalence of the four P atoms.

For the compounds $[Mn_2H(X)(CO)_5(dppm)_2]$ (X = Cl or CF_3CO_2) the CH_2 groups give separate multiplets and when X = CF_3CO_2 there is an AA'BB' $^{31}P-\{^1H\}$ n.m.r. spectrum. The

Table 2. N.m.r. data for the bridging hydrido-compounds

	^{1}H N.m.r.[a]			
	C_6H_5	CH_2	MnHMn	^{31}P-{^{1}H} N.m.r.
$[Mn_2H(CO)_6(dppm)_2][(CF_3CO_2)_2H]$	7.0—7.8(m)	3.79 (t, J_{PH} 9.7)	−26.18 (quintet,[b] J_{PH} 15.2)	58.9(s)[c] 58.9(s)[d]
$[Mn_2H(CF_3CO_2)(CO)_5(dppm)_2]$	7.1—7.7(m)	4.44(m), 3.81(m)	−20.91 (quintet, J_{PH} 18.3)	57.2(m) 53.8(m) } AA′BB′[e]
$[Mn_2H(Cl)(CO)_5(dppm)_2]$	7.0—7.8(m)	4.06(m), 3.88(m)	−20.32 (quintet, J_{PH} 18.2)	59.7(s)[e]

[a] Recorded at 200 MHz and 25 °C in $CDCl_3$; J values in Hz. [b] The compounds $[Mn_2H(CO)_6(dppm)_2][Y]$ (Y = BF_4, BPh_4, or SO_3F) also give a quintet at about this shift. [c] At 25 °C in $CDCl_3$. [d] At −40 °C in $CDCl_3$. [e] Recorded at 32 MHz and −40 °C in $CDCl_3$.



Scheme. S = solvent

Mn atoms are different and there is no plane of symmetry through the Mn_2P_2C rings. Infrared absorptions [$\nu_{asym}(CO_2)$ 1 685 and $\nu_{sym}(CO_2)$ 1 402 cm^{-1}] for the trifluoroacetate ligand show monodentate co-ordination.[16] These combined data are only consistent with the structure (**3**), shown with terminal X *cis* rather than *trans* to the bridging hydride. We believe that $[Mn_2H(Cl)(CO)_5(dppm)_2]$ has a directly related structure. The occurrence of a ^{31}P-{^{1}H} n.m.r. singlet in this case must be due to accidental coincidence.

Complexes (**2**) and (**3**) are isoelectronically and isostructurally related to the anions $[M_2H(CO)_{10}]^-$ (M = Cr, Mo, or W) which have been well studied structurally.[17] By analogy with these Group 6 compounds one would expect a bent M–H–M arrangement but with rapid side-to-side jumping of the hydride ligand. In illustrating compounds (**2**) and (**3**) we have guessed at the hydride positions. In the cation (**2**), for example, n.m.r. spectra indicate a plane of symmetry through the Mn_2P_4 set of atoms resulting from time-averaging. The cation $[Mn_2H(CO)_{10}]^+$ appears to be unknown and if formed on acid treatment of $[Mn_2(CO)_{10}]$ presumably breaks down into mononuclear species.

Route from $[Mn_2(CO)_5(dppm)_2]$ (**1**) *to Protonated Compounds*.—The Scheme shows the route we favour for the formation of $[Mn_2H(CO)_6(dppm)_2]^+$ (**2**) and $[Mn_2H(X)(CO)_5(dppm)_2]$ (**3**) from $[Mn_2(CO)_5(dppm)_2]$ (**1**). The attack of free CO at an intermediate is suggested by the formation of one or other of these hydrido-compounds (X = CF_3CO_2) on addition of CF_3CO_2H, depending upon whether or not any free CO is flushed from the reaction mixture. $[Mn_2H(CF_3CO_2)(CO)_5(dppm)_2]$ reacts only very slowly with CO and therefore cannot be an intermediate in the formation of $[Mn_2H(CO)_6(dppm)_2]^+$. Likewise, once this hexacarbonyl cation has been formed, bubbling N_2 through the reaction solution does not lead to $[Mn_2H(CF_3CO_2)(CO)_5(dppm)_2]$. Therefore under the reaction conditions the additions of X$^-$ or CO to the intermediate are irreversible (see Scheme). Furthermore the hexacarbonyl cation cannot be formed in these reactions by an initial CO addition to $[Mn_2(CO)_5(dppm)_2]$ since we have shown that this CO addition as well as the protonation of $[Mn_2(CO)_6(dppm)_2]$ are both too slow to be steps in the formation of $[Mn_2H(CO)_6(dppm)_2]^+$. In the absence of added CO we presume that the required CO ligand comes from CO liberation on decomposition of some intermediate; the starting material and products do not decompose to give free CO.

The nature of the unobserved intermediate is, however, speculative. We believe that the intermediate is $[Mn_2H(CO)_5(dppm)_2]^+$ (or possibly its solvent adduct). The solvent-free intermediate would be isoelectronic with the neutral compound $[Mn_2H(CN)(CO)_4(dppm)_2]$ which we have isolated[18] and which we believe contains a μ-σ,η^2-CN ligand like that in $[Mo_2(CN)(CO)_4(C_5H_5)_2]^-$.[19] Likewise we have isolated compounds related to the solvent adduct but with rather more strongly co-ordinating molecules such as acetonitrile;[18] the acetonitrile compound decomposes thermally to give $[Mn_2H(CO)_6(dppm)_2]^+$ consistent with our proposal for a solvent adduct intermediate.

Experimental

$[Mn_2(CO)_{10}]$,[20] $Ph_2PCH_2PPh_2$ (dppm),[21] and $[Mn_2(CO)_5(dppm)_2]$ [22] were prepared as reported earlier. Difficulties were found in obtaining entirely satisfactory elemental analyses for the dppm manganese compounds partly because of difficulties in completely combusting the samples [10] and partly because of variable solvent content in the crystals.

Reaction of $[Mn_2(CO)_5(dppm)_2]$ *with Trifluoroacetic acid.*—Trifluoroacetic acid (0.130 cm^3, 1.68 mmol) was added to a solution of $[Mn_2(CO)_5(dppm)_2]$ (0.220 g, 0.24 mmol) in dichloromethane (15 cm^3) and the solution allowed to stand at room temperature for 16 h. The solvent and excess of acid were removed *in vacuo* to give an orange oil, which was extracted into $CHCl_3$. Filtration gave a clear orange solution, which was evaporated to *ca.* 2 cm^3. The product was crystallised as orange needles of $[Mn_2H(CO)_6(dppm)_2][(CF_3CO_2)_2H]$ by careful addition of Et_2O, and cooling to −20 °C. The crystals (0.099 g, 33%) broke down to a powder on drying *in vacuo* (Found: C, 56.35; H, 3.6; Cl, 0; P, 9.95. $C_{60}H_{46}F_6Mn_2O_{10}P_4$ requires C, 56.55; H, 3.65; Cl, 0; P, 9.7%). In a similar experiment addition of trifluoroacetic acid (0.300 cm^3, 3.9 mmol) to $[Mn_2(CO)_5(dppm)_2]$ (0.311 g, 0.30 mmol) in CH_2Cl_2 (15 cm^3) under CO (1 atm) gave complete reaction in less than 2 h and a similar work-up gave the same product in rather better yield (0.195 g, 51%). Carrying out the addition of trifluoroacetic acid (0.100 cm^3) to a solution of $[Mn_2(CO)_5(dppm)_2]$ (0.1596 g, 0.157 mmol) in 1,2-dichloroethane (30 cm^3) under CO in a closed vessel connected to a gas burette, carbon monoxide was absorbed (3.70 cm^3 at standard temperature and pressure, 0.160 mmol) and the i.r. spectrum of the solution showed complete conversion to $[Mn_2H(CO)_6(dppm)_2]^+$.

Preparation of $[Mn_2H(CF_3CO_2)(CO)_5(dppm)_2]$.—Trifluoroacetic acid (0.100 cm^3, 1.30 mmol) was added to a solution of $[Mn_2(CO)_5(dppm)_2]$ (0.233 g, 0.22 mmol) in dichloromethane (15 cm^3) at room temperature through which nitrogen was being bubbled. The nitrogen flow was continued for 2 h and then the solvent and excess of CF_3CO_2H were removed from the clear orange-red solution *in vacuo*. The residue was extracted into chloroform (20 cm^3), filtered, and the filtrate evaporated to *ca.* 1 cm^3. Addition of diethyl ether (~3 cm^3) and cooling to −20 °C gave the product as red needles (0.190 g, 77%) (Found: C, 59.7; H, 4.15; Cl, 0; P, 11.2. $C_{57}H_{45}F_3Mn_2O_7P_4$ requires C, 60.4; H, 4.0; Cl, 0; P, 10.95%).

Reaction of $[Mn_2(CO)_5(dppm)_2]$ *with Fluorosulphonic Acid.*—Fluorosulphonic acid (0.050 cm^3, 0.86 mmol) was added to a solution of $[Mn_2(CO)_5(dppm)_2]$ (0.166 g, 0.16 mmol) in dichloromethane (12 cm^3) and the mixture stirred at room temperature for 30 min. Solvent and excess of acid were removed *in vacuo* to give an orange oil, which was extracted into $CHCl_3$ (25 cm^3) and the solution filtered through Celite. The clear orange filtrate was evaporated to *ca.* 1 cm^3 and $[Mn_2H(CO)_6(dppm)_2][SO_3F]$ was precipitated as orange prisms (0.058 g, 32%) by careful addition of Et_2O and cooling to −20 °C. Drying *in vacuo* caused the crystals to break down to a powder (Found: C, 57.45; H, 4.05; Cl, 2.55, P, 10.65; S, 2.95. $C_{56}H_{45}FMn_2O_9P_4S$ requires C, 58.65; H, 3.95; Cl, 0; P, 10.80; S, 2.80%). An absorption at 3 400 cm^{-1} (Nujol mull) indicates that some water is present and the chloride content may be due to some $CHCl_3$ of crystallisation.

Reaction of $[Mn_2(CO)_5(dppm)_2]$ *with Tetrafluoroboric Acid.*—Tetrafluoroboric acid (as $HBF_4{\cdot}Et_2O$) (0.100 cm^3) was added to a solution of $[Mn_2(CO)_5(dppm)_2]$ (0.0914 g, 0.090 mmol) in dichloromethane (10 cm^3) which became orange-red but after 30 min the solution had lightened to orange with a slight whitish precipitate. Excess of acid was neutralised by stirring for 5 min with $NaHCO_3$. The reaction mixture was then filtered through Celite, and the clear orange filtrate evaporated to *ca.* 1 cm^3. $[Mn_2H(CO)_6(dppm)_2][BF_4]$ was precipitated as orange prisms (0.033 g, 32%) by careful addition of diethyl ether and cooling to −20 °C. This compound gave poor irreproducible elemental analyses but was characterised by its infrared and ^1H n.m.r. data which are closely similar to those of the other hexacarbonyl cations reported here. A similar preparation under an atmosphere of CO gave a better yield (71%) of the same product.

Preparation of $[Mn_2H(CO)_6(dppm)_2][BPh_4]$.—Sodium tetraphenylborate was added to a solution of $[Mn_2H(CO)_6(dppm)_2][(CF_3CO_2)_2H]$ (0.130 g, 0.10 mmol) in methanol (10 cm^3) until precipitation was complete. The salt was obtained as a pale orange microcrystalline powder (0.109 g, 80%) (Found: C, 68.55; H, 4.6; P, 8.85. $C_{80}H_{65}BMn_2O_6P_4$ requires C, 70.3; H, 4.8; P, 9.05%).

Preparation of $[Mn_2H(Cl)(CO)_5(dppm)_2]$.—HCl gas was bubbled gently through a suspension of $[Mn_2(CO)_5(dppm)_2]$ (0.094 g, 0.092 mmol) in dichloromethane (10 cm^3) for 5 min to give an orange solution with a little colourless precipitate. The solvent was removed *in vacuo* to give a red oil which was extracted into dichloromethane (10 cm^3). Filtration through Celite gave a clear orange solution which was evaporated to 4 cm^3. Methanol (~5 cm^3) was added and the solution left in an open flask in the dark. After several hours the product precipitated as red prisms which were washed with ether and dried in air (0.0528 g, 54%). Drying *in vacuo* caused the crystals to break down into a powder (Found: C, 61.25; H, 4.6; Cl, 3.55; P, 11.15. $C_{55}H_{45}ClMn_2O_5P_4$ requires C, 62.6; H, 4.3; Cl, 3.35; P, 11.75%).

Acknowledgements

We would like to thank the S.E.R.C. for a studentship (to H. C. A.) and ICI (Petrochemicals Division) for support through the S.E.R.C. CASE scheme.

References

1 C. J. Commons and B. J. Hoskins, *Aust. J. Chem.*, 1975, **28**, 1663.
2 R. Colton and C. F. Commons, *Aust. J. Chem.*, 1975, **28**, 1673.
3 J. A. Marsella, J. C. Huffman, K. G. Caulton, B. Longato, and J. R. Norton, *J. Am. Chem. Soc.*, 1982, **104**, 6360.
4 G. A. Carriedo, J. A. K. Howard, K. Marsden, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 1589.
5 K. G. Caulton and P. Adair, *J. Organomet. Chem.*, 1976, **114**, C11.
6 J. A. Marsella and K. G. Caulton, *Organometallics*, 1982, **1**, 274.
7 C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 61.
8 M. A. Drezdzon, K. H. Whitmire, A. A. Bhattacharyya, W-L. Hsu, C. C. Nagel, S. G. Shore, and D. F. Shriver, *J. Am. Chem. Soc.*, 1982, **104**, 5630 and refs. therein.
9 A. L. Balch and L. S. Benner, *J. Organomet. Chem.*, 1977, **135**, 339.
10 A. L. Balch, L. S. Benner, and M. M. Olmstead, *J. Organomet. Chem.*, 1978, **159**, 289.
11 H. C. Aspinall and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1981, 724.
12 H. C. Aspinall and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1983, 838.
13 T. W. Turney, *Inorg. Chim. Acta*, 1982, **64**, L141.
14 M. Bénard, A. Dedieu, and S. Nakamura, *Nouv. J. Chim.*, 1984, **8**, 149.

15 R. Colton, M. J. McCormick, and C. D. Pannan, *Aust. J. Chem.*, 1978, **31**, 1425.

16 F. A. Cotton, D. J. Darensbourg, and B. W. S. Kolthammer, *J. Am. Chem. Soc.*, 1981, **103**, 389.

17 R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 1; L. F. Handy, R. K. Ruff, and L. F. Dahl, *J. Am. Chem. Soc.*, 1970, **92**, 7312; J. Roziere, J. M. Williams, R. P. Steward, jun., J. L. Petersen, and L. F. Dahl, *ibid.*, 1977, **99**, 4497; J. Roziere, P. Teulon, and M. D. Grillone, *Inorg. Chem.*, 1983, **22**, 557.

18 H. C. Aspinall, A. J. Deeming, and S. Donovan-Mtunzi, *J. Chem. Soc., Dalton Trans.*, 1983, 2669.

19 M. D. Curtis, K. R. Han, and W. M. Butler, *Inorg. Chem.*, 1980, **19**, 2096.

20 R. B. King, J. C. Stokes, and T. F. Korenowski, *J. Organomet. Chem.*, 1968, **11**, 641.

21 A. M. Aguiar, J. Beisler, and A. Miller, *J. Org. Chem.*, 1964, **29**, 1660.

22 A. L. Balch, L. S. Benner, and M. M. Olmstead, *Inorg. Chem.*, 1979, **18**, 2996.

Received 19th April 1984; *Paper* 4/648