DALTON
FULL PAPER

Phosphine, arsine and stibine complexes of manganese(I) carbonyl halides: synthesis, multinuclear NMR spectroscopic studies, redox properties and crystal structures

Simon J. A. Pope and Gillian Reid *

Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ

Received 2nd February 1999, Accepted 7th April 1999

Reaction of [Mn(CO)$_5$X] (X = Cl or Br) with L–L {L–L = dppm (Ph$_2$PCH$_2$PPh$_2$), dppe (Ph$_2$PCH$_2$CH$_2$PPh$_2$), dppp (Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$), C$_6$H$_4$(PPh$_2$)$_2$-*o*, C$_6$H$_4$(PH$_2$)$_2$-*o*, dpae (Ph$_2$AsCH$_2$CH$_2$AsPh$_2$), diars [C$_6$H$_4$(AsMe$_2$)$_2$-*o*], dpsp (Ph$_2$SbCH$_2$CH$_2$CH$_2$SbPh$_2$) or dmsp (Me$_2$SbCH$_2$CH$_2$CH$_2$SbMe$_2$)} or with two molar equivalents of L (= PPh$_2$H, PCy$_2$H or PPhH$_2$) in refluxing CHCl$_3$ yielded the neutral manganese(I) complexes [MnX(CO)$_3$(L–L)] and [MnX(CO)$_3$L$_2$] as yellow or orange solids. Infrared spectroscopic studies confirmed the *fac*-tricarbonyl arrangement and ^{1}H, ^{13}C-{^{1}H}, ^{31}P-{^{1}H} and ^{55}Mn NMR spectroscopy have been used to probe the solution behaviour. For a given halide ^{55}Mn NMR spectroscopic studies showed some dependence of $\delta(^{55}$Mn) on halide, chelate ring size, substituent and donor atom. X-Ray crystallographic analyses on [MnCl(CO)$_3${C$_6$H$_4$(PPh$_2$)$_2$-*o*}], [MnBr(CO)$_3$(dppe)] and the diprimary phosphine complex [MnCl(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}]·CH$_2$Cl$_2$ confirmed a *fac*-tricarbonyl arrangement, with the ditertiary or diprimary phosphine chelating. The structure of [MnBr(CO)$_3$(PPhH$_2$)$_2$] also shows a *fac*-tricarbonyl arrangement with the primary phosphine ligands mutually *cis*.

Introduction

Recently we have been investigating manganese(I) carbonyl complexes incorporating Group 15 and 16 donor ligands, with particular interest in establishing trends in the carbonyl stretching frequencies (IR) and the ^{55}Mn chemical shift ranges which might convey information about the relative binding properties of these soft donor types to Mn^I.[1] Manganese-55 [100%, $I = 5/2$ ($\Xi = 24.84$ MHz)], possesses a moderately high quadrupole moment (0.55×10^{-28} m^2), thus for complexes with less than O_h or T_d symmetry a considerable electric field gradient is expected to result in substantial broadening of the resonances.[2] We have recently shown that ^{55}Mn NMR spectroscopy is a sensitive probe of the nature of the manganese–ligand bonding for *fac*-[Mn(CO)$_3$X(E–E)] (E–E = dithio-, diseleno- or ditelluro-ether ligand), with $\delta(^{55}$Mn) shifting to low frequency from S to Se to Te, indicative of increased σ bonding down the group.[1] In most cases the resonances for the individual invertomers were readily detected.

In this paper we are concerned with Group 15 donor ligands involving P, As and Sb donor atoms and we now describe the preparation and spectroscopic characterisation, including IR, ^{1}H, ^{13}C-{^{1}H}, ^{55}Mn and ^{31}P-{^{1}H} NMR spectroscopy, of the manganese(I) complexes [MnX(CO)$_3$(L–L)] and [MnX(CO)$_3$L$_2$] [X = Cl or Br; L–L = dppm, dppe, Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$ (dppp), C$_6$H$_4$(PPh$_2$)$_2$-*o*, C$_6$H$_4$(PH$_2$)$_2$-*o*, Ph$_2$AsCH$_2$CH$_2$AsPh$_2$ (dpae), C$_6$H$_4$(AsMe$_2$)$_2$-*o* (diars), Ph$_2$SbCH$_2$CH$_2$CH$_2$SbPh$_2$ (dpsp) or Me$_2$SbCH$_2$CH$_2$CH$_2$SbMe$_2$ (dmsp); L = PPh$_2$H, PCy$_2$H or PPhH$_2$]. The crystal structures of [MnCl(CO)$_3${C$_6$H$_4$(PPh$_2$)$_2$-*o*}], [MnBr(CO)$_3$(dppe)] and the primary phosphine complexes [MnCl(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}] and [MnBr(CO)$_3$(PPhH$_2$)$_2$] are also described. The redox properties of selected examples are also reported. Some of the compounds, notably [MnX(CO)$_3$(dppm)], [MnX(CO)$_3$(dppe)] and [MnX(CO)$_3$(dpae)], were reported a number of years ago and have been the focus of considerable interest due to the unusual electrochemical responses which they display.[3–6] However we have resynthesized these compounds to compare their NMR properties with those of the other phosphine, arsine and stibine derivatives. The compounds [MnBr(CO)$_4$(PPh$_2$H)], [MnBr(CO)$_3$(PPh$_2$H)$_2$], [MnBr(CO)$_4$(PPhH$_2$)], [MnBr(CO)$_3$(PPhH$_2$)$_2$][7] and a series of cationic manganese(I) complexes involving PPh$_2$H, [Mn(CO)$_x$(PPh$_2$H)$_{6-x}$]$^+$ (x = 2–5), have also been described previously,[8] although multinuclear NMR spectroscopic data for these are very limited. The chemistry of RSbCH$_2$SbR (R = Ph or Me) with metal carbonyls including Mn^I) has been reported, and the ligand binds either in an η^1 mode or μ-bridging mode.[9,10]

Results and discussion

Syntheses

Treatment of [MnX(CO)$_5$] (X = Cl or Br) with one molar equivalent of L–L [= dppm, dppe, dppp, C$_6$H$_4$(PPh$_2$)$_2$-*o*, C$_6$H$_4$(PH$_2$)$_2$-*o*, dpae, diars, dpsp or dmsp] or two molar equivalents of L (= PPh$_2$H, PCy$_2$H or PPhH$_2$) in gently refluxing CHCl$_3$ under an inert atmosphere affords the neutral species [MnX(CO)$_3$(L-L)] or [MnX(CO)$_3$L$_2$] as yellow or orange solids. The reaction progress was monitored by solution IR spectroscopy, and considered to be complete when ν(CO) associated with [MnX(CO)$_5$] had disappeared. In all cases the reaction flasks were wrapped with foil to protect the manganese species from bright light. Typically the isolated compounds are very soluble in chlorocarbons, and some are also quite soluble in hydrocarbons. The solids are stable, and solutions of the compounds also appear to be quite stable unless exposed to oxygen. The dmsp derivatives were rather more difficult to isolate than the other compounds.

The FAB or electrospray mass spectra for these compounds generally show peaks with the correct isotopic distributions consistent with [Mn(CO)$_3$(L–L)]$^+$ or [Mn(CO)$_3$L$_2$]$^+$ and [Mn(L–L)]$^+$ or [MnL$_2$]$^+$, although the parent molecule and/or fragmentation products containing Cl or Br are also seen in some cases.

Three isomeric forms are possible for [MnX(CO)$_3$L$_2$], *fac*, *mer-trans* and *mer-cis*, and, since they all have approximate C_s symmetry, group theory predicts three ν(CO) absorptions for

Table 1 The ^{55}Mn and ^{31}P-{^{1}H} NMR[a] and IR spectroscopic data[b] (CO region only)

Complex	$\delta(^{31}P\text{-}\{^1H\})$[c]	$\delta(^{55}Mn)$ ($w_{1/2}$/Hz)[d]	$\tilde{\nu}$(CO)/cm^{-1}
$[MnCl(CO)_3(dppm)]$	+12.9	−775 (7100)	2028, 1959, 1917
$[MnCl(CO)_3(dppe)]$	+70.0	−1141 (9600)	2027, 1960, 1916
$[MnCl(CO)_3(dppp)]$	+30.9	−916 (8500)	2031, 1965, 1910
$[MnCl(CO)_3\{C_6H_4(PPh_2)_2\text{-}o\}]$	+70.9	−1042 (10800)	2030, 1964, 1920
$[MnCl(CO)_3(dpae)]$	—	−932 (4000)	2028, 1957, 1918
$[MnCl(CO)_3(diars)]$	—	−1130 (3700)	2027, 1956, 1912
$[MnCl(CO)_3(dpsp)]$	—	−880 (3000)	2024, 1957, 1914
$[MnCl(CO)_3(dmsp)]$	—	−1004 (2550)	2017, 1945, 1907
$[MnBr(CO)_3(dppm)]$	+10.6	−890 (7900)	2024, 1954, 1917
$[MnBr(CO)_3(dppe)]$	+67.9	−1254 (9400)	2023, 1955, 1917
$[MnBr(CO)_3(dppp)]$	+25.7	−1005 (9800)	2027, 1959, 1915
$[MnBr(CO)_3\{C_6H_4(PPh_2)_2\text{-}o\}]$	+72.1	−1146 (10500)	2929, 1964, 1922
$[MnBr(CO)_3(dpae)]$	—	−1046 (4500)	2025, 1957, 1919
$[MnBr(CO)_3(diars)]$[e]	—	−1212 (4500)	2025, 1955, 1912
$[MnBr(CO)_3(dpsp)]$	—	−1006 (5000)	2021, 1954, 1914
$[MnBr(CO)_3(dmsp)]$	—	−1140 (4000)	2013, 1944, 1906
$[MnCl(CO)_3(PPh_2H)_2]$	+40.4	−976 (5600)	2035, 1968, 1917
$[MnCl(CO)_3(PCy_2H)_2]$	+51.6	−1052 (9350)	2021, 1950, 1901
$[MnCl(CO)_3(PPhH_2)_2]$	−14.7	−1051 (3350)	2040, 1975, 1928
$[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$	−0.8	−1261 (3200)	2041, 1972, 1930
$[MnBr(CO)_3(PPh_2H)_2]$	+38.9	−1098 (6450)	2031, 1968, 1918
$[MnBr(CO)_3(PCy_2H)_2]$	+47.6	−1158 (13300)	2022, 1949, 1904
$[MnBr(CO)_3(PPhH_2)_2]$	−17.3	−1173 (3850)	2039, 1976, 1931
$[MnBr(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$	−2.0	−1380 (4700)	2032, 1976, 1936

[a] Spectra recorded in CH_2Cl_2–$CDCl_3$ solution at 300 K. [b] Solutions in $CHCl_3$, all bands were strong. [c] At 145.8 MHz and referenced to external 85% H_3PO_4. [d] At 89.27 MHz and referenced to external aqueous $KMnO_4$. [e] Second species at δ −2070.

each. Thus, it is not possible to distinguish these on the basis of the number of bands observed. Many of the original assignments of isomers of $[MnX(CO)_3L_2]$ were however made on the basis of IR spectroscopic studies and this has led to some discrepancies in the literature. Owing to the limited solubilities of most of the compounds in non-polar solvents, and to provide a directly comparable set of data, the IR spectra were recorded in $CHCl_3$ (Table 1). The polarity of this solvent does broaden the bands and thus the data are less sensitive to small changes in ν. The values of ν(CO) obtained for the compounds reprepared in this work are in good agreement with the literature.[3,6,7] The solution IR spectroscopic studies show three strong CO stretching vibrations (Table 1), and the frequencies and relative intensities of the three bands do not differ greatly between compounds. In all cases the stretching frequencies are comparable with ν(CO) reported for *fac*-$[MnCl(CO)_3(SbPh_3)_2]$ (2024, 1955, 1912 cm^{-1}) but distinctly different from the values for *mer-trans*-$[MnCl(CO)_3(SbPh_3)_2]$ (1950, 1909 cm^{-1}).[9] Hence we assign all of the compounds in this work as *fac* isomers. In an early paper Abel and Wilkinson[11] assigned $[MnX(CO)_3L_2]$ (X = Cl, Br or I; L = PPh_3 or $AsPh_3$) as *fac* isomers. This assignment was subsequently questioned,[12] however our data for complexes involving PPh_2H, $PPhH_2$ and PCy_2H are in accord with the conclusions of Abel and Wilkinson and are supported by a single crystal structure determination on $[MnBr(CO)_3(PPhH_2)_2]$ (see below). As expected, the highest frequency ν(CO) band (CO *trans* to X) shifts to low frequency according to the series X = Cl > Br. Since, ν(CO) for these manganese compounds appears to be dependent on the terminal substituent on the donor atom and the interdonor linkage, and since the shifts are small, there is no obvious trend in ν(CO) with donor type.

Similar reactions were undertaken with $[MnX(CO)_5]$ (X = Cl or Br) and diars. For X = Cl the data are consistent with the formation of $[MnCl(CO)_3(diars)]$, however for X = Br there is evidence for a second species in addition to $[MnBr(CO)_3(diars)]$ (electrospray mass spectrometry: found *m*/*z* = 711, $[Mn(CO)_3(diars)_2]^+$; $\delta(^{55}Mn)$ −1702).

The ^{1}H, ^{13}C-{^{1}H}, ^{31}P-{^{1}H} and ^{55}Mn NMR spectroscopic data were also recorded for the compounds in this study. The combination of observable NMR nuclei provides a very convenient way in which to monitor the species present in solution and for a series of related compounds variations in chemical shift values may also reflect subtle differences in the bonding.

The ^{1}H NMR spectra were recorded for the new ditertiary ligand complexes and for all of the primary and secondary phosphine complexes. The spectra show broad resonances associated with the ligand, and for those with Me terminal substituents two distinct Me resonances are observed: one due to the Me groups adjacent to a CO ligand and the other due to the Me groups adjacent to Cl or Br. For the secondary phosphine complexes the PH protons appear as a widely separated multiplet, while for the primary phosphine derivatives the two distinct environments for the P-bonded protons are clearly identified.

^{13}C-{^{1}H} NMR spectroscopy provides evidence for the co-ordinated L–L or L in each case, and, for the ligands with Me substituents, two Me environments are seen. The CO resonances are broad (spanning a few ppm) due to the effect of the directly bonded ^{55}Mn quadrupole, however typically we do observe two resonances in a 1:2 ratio: the one to high frequency attributed to the CO *trans* to X and the lower frequency resonance due to the two CO ligands *trans* to L–L or L.

The ^{31}P-{^{1}H} and ^{55}Mn NMR data are presented in Table 1. For all of the monodentate and bidentate phosphine complexes ^{31}P-{^{1}H} NMR studies show a single resonance consistent with only one species (*fac*) in solution. Again, the directly bonded ^{55}Mn quadrupolar nucleus results in the ^{31}P-{^{1}H} NMR resonances being broadened, although coupling to ^{55}Mn is not resolved. The data are in accord with other phosphine complexes, exhibiting the same trends in co-ordination shift ($\delta_{complex} - \delta_{free\ phosphine}$) and chelate ring-size effects.[13] Thus, the $[MnX(CO)_3(L\text{–}L)]$ complexes involving dppe, $C_6H_4(PPh_2)_2$-*o* and $C_6H_4(PH_2)_2$-*o* each show a large, high frequency co-ordination shift consistent with the presence of a 5-membered chelate ring. For those compounds involving primary or secondary phosphines the ^{31}P NMR spectra show coupling to the directly bonded proton (*ca*. 300 Hz) with further splittings due to other nearby protonss, giving a second order pattern. These results clearly indicate that the primary and secondary phosphine ligands act as neutral two-electron donors to Mn^{I}, without deprotonation or decomposition such as occur for *e.g.* compounds of Pd^{II}, Pt^{II} and Rh^{III} of these ligands.[14–16] Generally, substituting Cl for Br also results in a small low frequency shift.

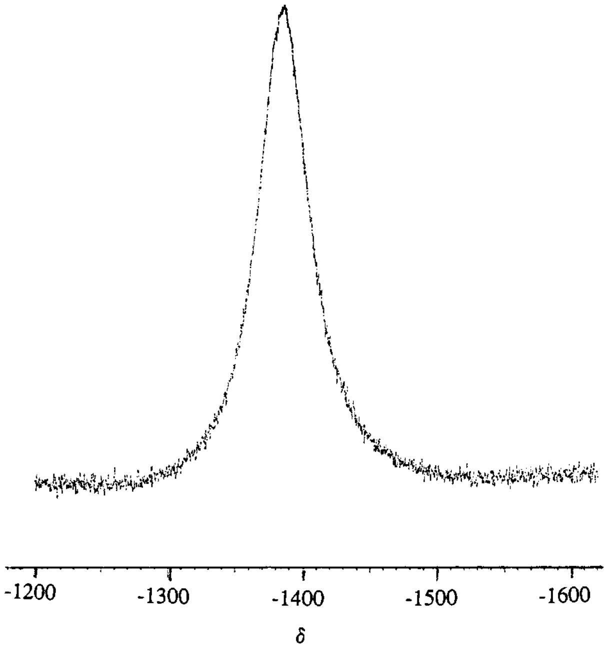

Fig. 1 The ^{55}Mn (89.27 MHz, $CDCl_3$) NMR spectrum of $[MnBr(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$.

The ^{55}Mn NMR spectra each show a single, broad resonance (Fig. 1). The linewidths vary widely between *ca.* 3000 and *ca.* 13300 Hz, and are typically much larger than those observed for *fac*-$[MnX(CO)_3(E\text{–}E)]$ (E–E = dithio-, diseleno- or ditelluroether) which are approximately 3000 Hz or less for each invertomer.[1] Coupling to ^{31}P is not resolved. The compounds $[MnX(CO)_3L_2]$ show $w_{1/2}$ increasing from L = $PPhH_2$ to PPh_2H to PCy_2H, due to the change in steric (increase in Tolman cone angle) and/or electronic effects (increase in σ donation) along the series. Both of these factors are expected to affect the electric field gradient at Mn. Similarly, for the complexes involving diphosphine, diarsine and distibine ligands bearing phenyl substituents there is a decrease in $w_{1/2}$ from P to As to Sb.

For the monodentate phosphine compounds $\delta(^{55}Mn)$ lies in the range -976 to -1173, with δ for the bromo derivatives occurring at lower frequency than for the chloro species. This is consistent with the trend observed for the parent $[MnX(CO)_5]$.[17] Unfortunately, since the ligands $R_2Sb(CH_2)_2SbR_2$ are not known it is not possible to study a complete set of directly analogous diphosphine, diarsine and distibine systems, however three trends are apparent: (i) for the compounds involving bidentate phosphines there also appears to be a trend in $\delta(^{55}Mn)$ with chelate ring size, with a shift to low frequency according to the series dppm (4-membered chelate ring) $\longrightarrow$ dppp (6-membered chelate ring) $\longrightarrow$ dppe, $C_6H_4(PH_2)_2\text{-}o$, $C_6H_4(PPh_2)_2\text{-}o$ (5-membered chelate ring); (ii) for the *o*-phenylene linked diphosphine complexes we find that $\delta(^{55}Mn)$ for the diphenyl-substituted species are to high frequency of the diprimary phosphine analogues, and the Ph-substituted stibine compounds are to high frequency of the Me-substituted analogues; (iii) there is a shift to high frequency according to the series P $\longrightarrow$ As $\longrightarrow$ Sb. The complex *fac*-$[MnCl(CO)_3(SbPh_3)_2]$ shows $\delta(^{55}Mn) = -730$ ($w_{1/2} = 1000$ Hz),[9] to high frequency of the distibine complexes in this work. The ^{55}Mn shifts for the group 15 complexes in this work are all to low frequency of those of *fac*-$[MnX(CO)_3(E\text{-}E)]$ (E-E = dithio-, diseleno- or ditelluro-ether ligand)[1] consistent with the general perception that the former are generally better σ donors than the Group 16 ligands, and also that π-back bonding is generally more important for the former.

X-Ray crystallography

In order to confirm the stereochemistries at the manganese(I) centre and to establish trends in the bond lengths and angles, single crystal structure analyses were undertaken on $[MnCl(CO)_3\{C_6H_4(PPh_2)_2\text{-}o\}]$, $[MnBr(CO)_3(dppe)]$ and the primary phosphine derivatives $[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$ and $[MnBr(CO)_3(PPhH_2)_2]$. Crystals of the complexes were obtained from vapour diffusion of light petroleum into a solution of the appropriate complex in $CHCl_3$. The crystal structures of $[MnCl(CO)_3\{C_6H_4(PPh_2)_2\text{-}o\}]$ (Fig. 2, Table 2), $[MnBr(CO)_3(dppe)]$ (Fig. 3, Table 3) and $[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$ (Fig. 4, Table 2) each show the *fac*-octahedral arrangement predicted from the spectroscopic studies, with the diphosphine chelating. Noticeably, the Mn–P distances for $[MnCl(CO)_3\{C_6H_4(PPh_2)_2\text{-}o\}]$ are significantly longer than those for the diprimary phosphine analogue, $[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$, probably reflecting the greater steric demands of the former. The P–Mn–P angles involved in the chelate rings are 81.97(6)° for $[MnCl(CO)_3\{C_6H_4(PPh_2)_2\text{-}o\}]$, 84.14(10) and 84.11(9)° for $[MnBr(CO)_3(dppe)]$ and 83.06(6)° for $[Mn(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$, *i.e.*

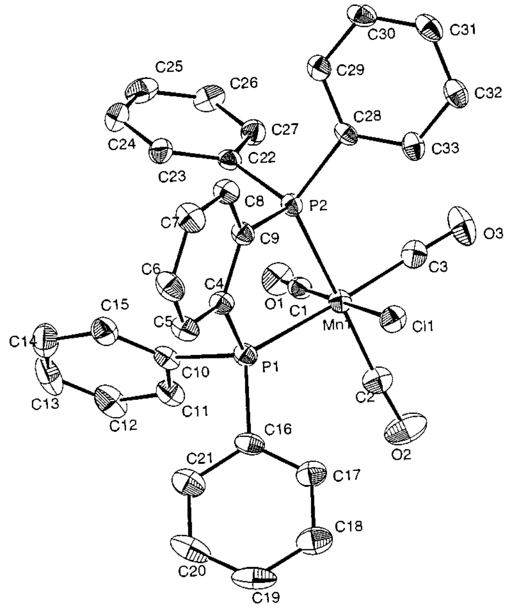

Fig. 2 View of the structure of $[MnCl(CO)_3\{C_6H_4(PPh_2)_2\text{-}o\}]$ with the numbering scheme adopted. Hydrogen atoms are omitted for clarity and ellipsoids are drawn at 40% probability.

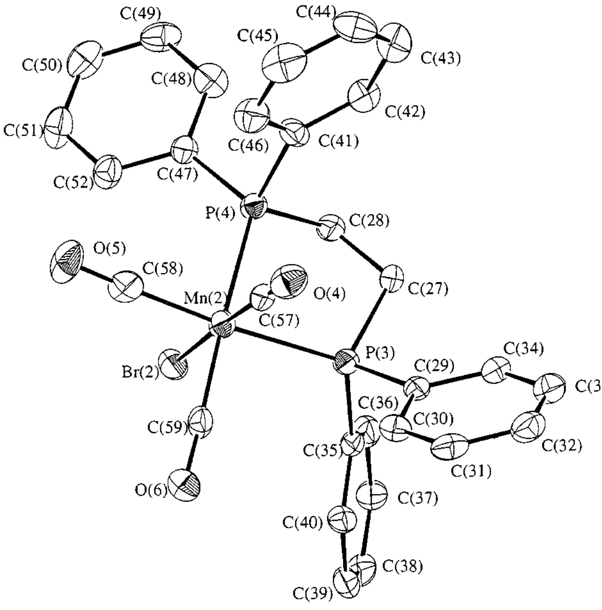

Fig. 3 View of the structure of one of the crystallographically independent $[MnBr(CO)_3(dppe)]$ molecules (the other molecule is essentially indistinguishable). Other details as in Fig. 2.

Table 2 Selected bond lengths (Å) and angles (°) for [$MnCl(CO)_3\{C_6H_4(PPh_2)_2$-*o*}], [$MnCl(CO)_3\{C_6H_4(PH_2)_2$-*o*}] and [$MnBr(CO)_3(PPhH_2)_2$]

	[$MnCl(CO)_3\{C_6H_4(PPh_2)_2$-*o*}]	[$MnCl(CO)_3\{C_6H_4(PH_2)_2$-*o*}]	[$MnBr(CO)_3(PPhH_2)_2$]
Mn–P(1)	2.325(2)	2.280(2)	2.305(1)
Mn–P(2)	2.320(2)	2.281(2)	2.322(1)
Mn–X(1)	2.386(2)	2.393(2)	2.5273(7)
Mn–C(1)	1.791(6)	1.786(6)	1.784(4)
Mn–C(2)	1.800(6)	1.814(6)	1.823(4)
Mn–C(3)	1.798(6)	1.830(6)	1.814(4)
P(1)–Mn–P(2)	81.97(6)	83.06(6)	89.17(4)
X(1)–Mn–P(1)	84.82(6)	83.26(5)	85.44(3)
X(1)–Mn–P(2)	85.59(6)	82.63(6)	84.63(3)
P(1)–Mn–C(1)	95.0(2)	93.8(2)	91.4(1)
P(1)–Mn–C(2)	94.2(2)	171.7(2)	174.9(1)
P(1)–Mn–C(3)	173.6(2)	91.3(2)	89.4(1)
P(2)–Mn–C(1)	94.3(2)	94.4(2)	92.6(1)
P(2)–Mn–C(2)	174.3(2)	91.4(2)	89.4(1)
P(2)–Mn–C(3)	93.2(2)	171.1(20	174.7(1)
X(1)–Mn–C(1)	179.8(2)	176.0(2)	175.8(1)
X(1)–Mn–C(2)	89.5(2)	89.9(2)	89.5(1)
X(1)–Mn–C(3)	90.7(2)	89.9(2)	90.2(1)
C(1)–Mn–C(2)	90.6(2)	92.9(2)	93.6(2)
C(1)–Mn–C(3)	89.5(2)	92.8(3)	92.5(2)
C(2)–Mn–C(3)	89.8(3)	93.4(3)	91.6(2)

Table 3 Selected bond lengths (Å) and angles (°) for [$MnBr(CO)_3$(dppe)]

Br(1)–Mn(1)	2.517(2)	Br(2)–Mn(2)	2.504(2)
Mn(1)–P(1)	2.317(3)	Mn(1)–P(2)	2.314(3)
Mn(1)–C(54)	1.84(1)	Mn(1)–C(55)	1.82(1)
Mn(1)–C(56)	1.77(1)	Mn(2)–P(3)	2.327(3)
Mn(2)–P(4)	2.334(3)	Mn(2)–C(57)	1.78(1)
Mn(2)–C(58)	1.83(1)	Mn(2)–C(59)	1.81(1)
Br(1)–Mn(1)–P(1)	88.82(9)	Br(1)–Mn(1)–P(2)	87.36(10)
Br(1)–Mn(1)–C(54)	91.1(3)	Br(1)–Mn(1)–C(55)	86.7(4)
Br(1)–Mn(1)–C(56)	178.0(3)	P(1)–Mn(1)–P(2)	84.14(10)
P(1)–Mn(1)–C(54)	91.9(3)	P(1)–Mn(1)–C(55)	173.4(3)
P(1)–Mn(1)–C(56)	89.7(3)	P(2)–Mn(1)–C(54)	175.8(3)
P(2)–Mn(1)–C(55)	90.8(3)	P(2)–Mn(1)–C(56)	91.2(3)
C(54)–Mn(1)–C(55)	93.0(4)	C(54)–Mn(1)–C(56)	90.2(4)
C(55)–Mn(1)–C(56)	94.6(5)	Br(2)–Mn(2)–P(3)	87.23(9)
Br(2)–Mn(2)–P(4)	85.01(8)	Br(2)–Mn(2)–C(57)	176.9(3)
Br(2)–Mn(2)–C(58)	91.3(3)	Br(2)–Mn(2)–C(59)	87.9(3)
P(3)–Mn(2)–P(4)	84.11(9)	P(3)–Mn(2)–C(57)	89.7(3)
P(3)–Mn(2)–C(58)	174.5(3)	P(3)–Mn(2)–C(59)	91.4(3)
P(4)–Mn(2)–C(57)	94.8(3)	P(4)–Mn(2)–C(58)	90.5(3)
P(4)–Mn(2)–C(59)	171.8(3)	C(57)–Mn(2)–C(58)	91.8(4)
C(57)–Mn(2)–C(59)	92.1(4)	C(58)–Mn(2)–C(59)	93.8(4)

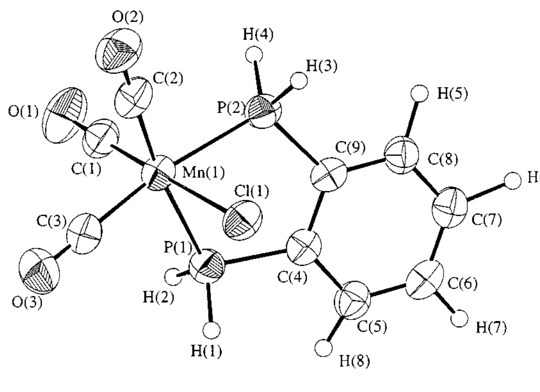

Fig. 4 View of the structure of [$MnCl(CO)_3\{C_6H_4(PH_2)_2$-*o*}] with the numbering scheme adopted. Ellipsoids are drawn at 40% probability.

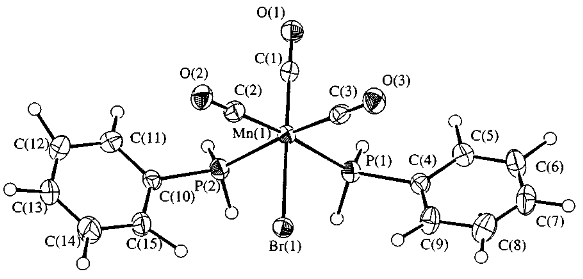

Fig. 5 View of the structure of [$MnBr(CO)_3(PPhH_2)_2$] with the numbering scheme adopted. Ellipsoids are drawn at 40% probability.

smaller than the 90° expected for a regular octahedron. The crystal structure of [$MnBr(CO)_3(PPhH_2)_2$] (Fig. 5, Table 2) is similar, once again showing three *fac* CO ligands and the $PPhH_2$ ligands mutually *cis*. The Mn–C bond length *trans* to Br is significantly shorter than Mn–C *trans* to P and the Mn-P distances are comparable with those for the bidentate ligand complexes above. The angles around Mn involving mutually *cis* donor atoms lie in the range 84.63(3)–95.5(2)°. These are the first structurally characterised manganese species involving primary phosphine ligands, and the structural analyses confirm the integrity of the co-ordinated PH_2 units and the same stereochemistry in the solution and solid states. The crystal structure of the dinuclear species [$Mn_2(CO)_9(PPh_2H)$] has been reported.[18] The related manganese(I) species involving monodentate phosphines, [$MnBr(CO)_3L_2$] [L = PPh_3, $P(C_6H_4Me$-*o*$)_3$ or $P(C_6H_4Me$-*m*$)_3$] have been described previously and assigned as *mer* on the basis of spectroscopic studies, although structural data were not presented,[12] while Levason and co-workers[9] have described both *fac*- and *mer*-*trans*-[$MnBr(CO)_3(SbPh_3)_2$], including X-ray crystallographic data. The Mn–P and Mn–CO bond lengths in the compounds reported here are similar to those reported for related species such as *fac*-[$MnCl(CO)_3(Et_2PCH_2CH_2PEt_2)$] [Mn–P 2.309(1), Mn–CO 1.770(5), 1.808(4) Å].[19]

Electrochemistry

Bond *et al.*[5] have studied the electrochemistry of [$MnX(CO)_3$(dppm)] in some detail and have shown that at room temperature this species undergoes an irreversible one-electron oxidation which is associated with a redox-induced *fac* ⟶ *mer* isomerisation. Electrochemical studies were subsequently undertaken on the dppe, dppp and dpae compounds. We have conducted cyclic voltammetry experiments (CH_2Cl_2 solution, 0.1 mol dm^{-3} $^nBu_4NBF_4$, platinum working electrodes) on a selection of the other new compounds. At scan rates of 50, 100 and 200 mV s^{-1} [$MnCl(CO)_3\{C_6H_4(PPh_2)_2$-*o*}] and [$MnCl(CO)_3$(diars)] both show a chemically reversible oxidation ($E_{1/2}$ = 0.74 and 0.82 V *vs.* Fc–Fc$^+$ respectively), attributed to a $Mn^{I/II}$ redox couple. These oxidation potentials are comparable with those reported by Bond *et al.* The compounds [MnX(CO)$_3${Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$}] each show an irreversible oxidation at 0.89 (X = Cl) and 0.98 V (X = Br) *vs.* Fc–Fc$^+$ respectively, while [MnX(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}] showed irreversible oxidations at 0.98 (X = Cl) and 1.04 V (X = Br).

Experimental

Infrared spectra were measured in solution using NaCl plates on a Perkin-Elmer 1600 FTIR spectrometer, mass spectra by fast-atom bombardment (FAB) using 3-nitrobenzyl alcohol as matrix on a VG Analytical 70–250-SE Normal Geometry Double Focusing Mass Spectrometer or by positive electrospray in MeCN solution using a VG Biotech platform. The ^{1}H NMR spectra were recorded in CDCl$_3$ using a Bruker AM300 spectrometer, ^{13}C-{^{1}H}, ^{55}Mn and ^{31}P-{^{1}H} NMR spectra in CH$_2$Cl$_2$–CDCl$_3$ (*ca.* 7 : 1) using a Bruker AM360 spectrometer operating at 90.1, 89.27 or 145.8 MHz respectively and referenced to Me$_4$Si, external saturated, aqueous K[MnO$_4$] and external 85% H$_3$PO$_4$ respectively (δ 0); [Cr(acac)$_3$] was added to the NMR solutions prior to recording ^{13}C-{^{1}H} NMR spectra and a pulse delay of 2 s was employed to take account of the long relaxation times. Cyclic voltammetry measurements were conducted using an EG&G Princeton Applied Research Model 362 scanning potentiostat using double platinum working and auxiliary electrodes and a SCE reference electrode. All potentials are quoted against the ferrocene–ferrocenium (Fc–Fc$^+$) couple ($E_{1/2}$ = 0 V). The compounds [MnX(CO)$_5$] (X = Cl, Br or I) were prepared according to literature procedures.[20,21]

Preparations

All of the compounds were synthesized by the same general procedures, hence only one example is described in detail below.

[MnCl(CO)$_3$(dppm)]. The compound [MnCl(CO)$_5$] (0.15 g, 6.5 × 10^{-4} mol) was dissolved in stirred, degassed CHCl$_3$ in the absence of light, dppm (0.250 g, 6.5 × 10^{-4} mol) added and the reaction stirred under a dinitrogen atmosphere for approximately 5 h, until solution IR studies showed the absence of bands associated with the starting material. The solvent volume was reduced to about 5 cm^3 and then added to stirred, ice cold, degassed hexane, yielding a yellow-orange powder which was filtered off, washed with hexane and dried *in vacuo*. Yield = 0.258 g, 71% (Required for C$_{28}$H$_{22}$ClMnO$_3$P$_2$: C, 60.2; H, 3.9. Found: C, 65.5; H, 4.1%). Electrospray mass spectrum: found *m/z* = 523 and 439; calculated for [Mn(CO)$_3$(dppm)]$^+$ *m/z* = 523, [Mn(dppm)]$^+$ *m/z* = 439. ^{13}C-{^{1}H} NMR: δ 220.9, 219.1 (br, CO), 133.5 (t, Ph), 133 −129 (Ph) and 39.4 (t, CH$_2$).

[MnCl(CO)$_3$(dppe)]. Yield = 68% (Required for C$_{29}$H$_{24}$ClMnO$_3$P$_2$: C, 60.8; H, 4.2. Found: C, 60.4; H, 4.3%). Electrospray mass spectrum: found *m/z* = 537 and 494; calculated for [Mn(CO)$_3$(dppe)]$^+$ *m/z* = 537, [Mn(dppe)(MeCN)]$^+$ *m/z* = 492. ^{13}C-{^{1}H} NMR: δ 219.6 (br, CO), 134.7 (m, Ph), 135.3–127.9 (Ph) and 26.1 (m, CH$_2$).

[MnCl(CO)$_3$(dppp)]. Yield = 80% (Required for C$_{30}$H$_{28}$ClMnO$_3$P$_2$: C, 61.4; H, 4.4. Found: C, 61.0; H, 4.6%). Electrospray mass spectrum: found *m/z* = 552 and 508; calculated for [Mn(CO)$_3$(dppp)]$^+$ *m/z* = 552, [Mn(dppp)(MeCN)]$^+$ *m/z* = 508. ^{13}C-{^{1}H} NMR: δ 222.2, 217.3 (br, CO), 147.8 (m, Ph), 134.0–128.6 (Ph), 24.1 (PCH$_2$) and 19.2 (PCH$_2$*C*H$_2$CH$_2$P).

[MnCl(CO)$_3${C$_6$H$_4$(PPh$_2$)$_2$-*o*}]. Yield = 74% (Required for C$_{33}$H$_{24}$ClMnO$_3$P$_2$: C, 63.8; H, 3.9. Found C, 64.8; H, 4.2%). Electrospray mass spectrum: found *m/z* = 585 and 542; calc. for [Mn(CO)$_3${C$_6$H$_4$(PPh$_2$)$_2$-*o*}]$^+$ *m/z* = 585; [Mn{C$_6$H$_4$(PPh$_2$)$_2$-*o*}(MeCN)]$^+$ *m/z* = 542. ^{1}H NMR: δ 7.0–8.1 (m, aromatic H). ^{13}C-{^{1}H} NMR: δ 220.2, 219.0 (br, CO), 141.8 (m, Ph) and 134.9–128.5 (Ph).

[MnCl(CO)$_3$(dpae)]. Yield = 72% (Required for C$_{29}$H$_{24}$As$_2$ClMnO$_3$: C, 52.7; H, 3.6. Found: C, 52.6; H, 3.7%). FAB mass spectrum: found *m/z* = 576 and 541; calculated for [Mn^{35}Cl(CO)$_3$(dpae)]$^+$ *m/z* = 576, [Mn(CO)$_3$(dpae)]$^+$ *m/z* = 541. ^{13}C-{^{1}H} NMR: δ 221–218 (br, CO), 140.0, 127.0 (Ph) and 24.4 (CH$_2$).

[MnCl(CO)$_3$(diars)]. Yield = 69% (Required for C$_{11}$H$_{16}$As$_2$ClMnO$_3$: C, 33.9; H, 3.5. Found C, 33.7; H, 3.5%). FAB mass spectrum: found *m/z* = 376 and 341; calculated for [Mn^{35}Cl{C$_6$H$_4$(AsMe$_2$)$_2$-*o*}]$^+$ *m/z* = 376, [Mn{C$_6$H$_4$(AsMe$_2$)$_2$-*o*}]$^+$ *m/z* = 341. ^{1}H NMR: δ 7.5–7.8 (br m, C$_6$H$_4$, 4H), 1.8 (s, Me, 6H) and 1.6 (s, Me, 6H). ^{13}C-{^{1}H} NMR: δ 217.0–212.0 (br, CO), 140.6–135.7 (Ph), 130.5 (Ph), 13.7, 8.8 (Me).

[MnCl(CO)$_3$(dpsp)]. Yield = 71% (Required for C$_{30}$H$_{26}$ClMnO$_3$Sb$_2$: C, 46.9; H, 3.4. Found: C, 47.2; H, 3.6%). FAB mass spectrum: found *m/z* = 733, 684 and 649; calculated for [Mn(CO)$_3$(dpsp)]$^+$ *m/z* = 733, [Mn^{35}Cl(dpsp)]$^+$ *m/z* = 684, [Mn(dpsp)]$^+$ *m/z* = 649. ^{1}H NMR: δ 7.1–8.0 (br m, Ph, 20 H), 2.3–2.7 (m, SbCH$_2$, 4H) and 1.9 (m, CH$_2$C*H*$_2$CH$_2$, 2H). ^{13}C-{^{1}H} NMR: δ 220.5, 218.7 (br, CO), 135.2, 131.9–128.8 (Ph), 23.8 (SbCH$_2$) and 17.2 (SbCH$_2$*C*H$_2$CH$_2$Sb).

[MnCl(CO)$_3$(dmsp)]. Required for C$_{10}$H$_{18}$ClMnO$_3$Sb$_2$: C, 23.1; H, 3.5. Found C, 23.5; H, 3.6%. ^{1}H NMR: δ 0.7–2.0 (br, m). ^{13}C-{^{1}H} NMR: δ 224–217 (br, CO), 24.2, 14.8 (CH$_2$), −3.9, −4.1 (Me).

[MnBr(CO)$_3$(dppm)]. Yield = 54% (Required for C$_{28}$H$_{22}$BrMnO$_3$P$_2$: C, 55.7; H, 3.6. Found: C, 55.2; H, 3.5%). Electrospray mass spectrum: found *m/z* = 523; calculated for [Mn(CO)$_3$(dppm)]$^+$ *m/z* = 523. ^{13}C-{^{1}H} NMR: δ 222.5, 219.4 (br, CO), 134.1 (m, Ph), 132.6–129.3 (Ph) and 40.1 (t, CH$_2$).

[MnBr(CO)$_3$(dppe)]. Yield = 66% (Required for C$_{29}$H$_{24}$BrMnO$_3$P$_2$: C, 56.4; H, 3.9. Found: C, 56.1; H, 3.8%). Electrospray mass spectrum: found *m/z* = 537; calculated for [Mn(CO)$_3$(dppe)]$^+$ *m/z* = 537. ^{13}C-{^{1}H} NMR: δ 221.0, 219.0 (br, CO), 134.5 (m, Ph), 132.7–127.9 (Ph) and 25.6 (CH$_2$).

[MnBr(CO)$_3$(dppp)]. Yield = 84%. Electrospray mass spectrum: found *m/z* = 551; calculated for [Mn(CO)$_3$(dppp)]$^+$ *m/z* = 551. ^{13}C-{^{1}H} NMR: δ 222.8, 216.7 (br, CO), 136.9 (m, Ph), 133.3–128.2 (Ph), 24.2 (PCH$_2$) and 18.5 (CH$_2$*C*H$_2$CH$_2$).

[MnBr(CO)$_3${C$_6$H$_4$(PPh$_2$)$_2$-*o*}]. Yield = 77% (Required for C$_{33}$H$_{24}$BrMnO$_3$P$_2$: C, 59.5; H, 3.6. Found: C, 60.0; H, 3.3%). Electrospray mass spectrum: found *m/z* = 585, calculated for [Mn(CO)$_3${C$_6$H$_4$(PPh$_2$)$_2$-*o*}]$^+$ *m/z* = 585. ^{1}H NMR: δ 7.1–8.0 (m, aromatic H). ^{13}C-{^{1}H} NMR: δ 221.2, 218.4 (br, CO), 141.8 (m, Ph) and 134.5–128.1 (Ph).

[MnBr(CO)$_3$(dpae)]. Yield = 70% (Required for C$_{29}$H$_{24}$As$_2$BrMnO$_3$: C, 49.4; H, 3.4. Found: C, 49.1; H, 3.5%). FAB mass spectrum: found *m/z* = 620 and 541; calculated for [Mn^{79}Br(CO)$_3$(dpae)]$^+$ *m/z* = 620, [^{55}Mn(CO)$_3$(dpae)]$^+$ *m/z* = 541. ^{13}C-{^{1}H} NMR: δ 220.7 (br, CO), 135.5–128.5 (Ph) and 24.7 (CH$_2$).

[MnBr(CO)$_3$(dpsp)]. Yield = 65% (Required for C$_{30}$H$_{26}$BrMnO$_3$Sb$_2$: C, 44.3; H, 3.2. Found: C, 44.4; H, 3.3%). FAB mass spectrum: found *m/z* = 728 and 649; calculated for [Mn^{79}Br(dpsp)]$^+$ *m/z* = 728, [Mn(dpsp)]$^+$ *m/z* = 649. ^{1}H NMR: δ 7.0–8.1 (br m, Ph, 20H), 2.3–2.7 (br m, SbCH$_2$, 4H) and 1.9 (br m, CH$_2$C*H*$_2$CH$_2$, 2H). ^{13}C-{^{1}H} NMR: δ 221.0, 216.0 (br, CO), 135.2, 130.3–129.1 (Ph), 23.0 (SbCH$_2$) and 16.9 (CH$_2$*C*H$_2$CH$_2$).

[MnBr(CO)$_3$(dmsp)]. (Required for C$_{10}$H$_{18}$BrMnO$_3$Sb$_2$: C, 21.3; H, 3.2. Found: C, 21.5; H, 3.0%). FAB mass spectrum:

Table 4 Crystallographic data collection and refinement parameters[a]

	$[MnCl(CO)_3\{C_6H_4(PPh_2)_2\text{-}o\}]$	$[MnBr(CO)_3(dppe)]\cdot 0.5CHCl_3$	$[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]\cdot CH_2Cl_2$	$[MnBr(CO)_3(PPhH_2)_2]$
Formula	$C_{33}H_{24}ClMnO_3P_2$	$C_{29.5}H_{24.5}Cl_{1.5}BrMnO_3P_2$	$C_{10}H_{10}Cl_3MnO_3P_2$	$C_{15}H_{14}BrMnO_3P_2$
M	620.89	676.99	401.43	439.06
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$C2/c$
a/Å	16.858(2)	17.926(10)	10.296(1)	28.781(5)
b/Å	10.915(4)	14.174(9)	10.188(1)	5.962(6)
c/Å	17.615(4)	23.76(1)	15.5896(7)	24.249(4)
β/°	116.72(1)	108.25(4)	91.936(5)	121.99(1)
V/Å^3	2895(1)	5734(5)	1634.4(2)	3528(3)
Z	4	8	4	8
D_c/g cm^{-3}	1.424	1.568	1.631	1.653
μ(Mo-Kα)/cm^{-1}	6.71	21.40	14.90	31.47
Maximum, minimum transmission factors	1.000, 0.905	1.000, 0.814	—	1.000, 0.786
Unique observed reflections	5385	9505	3076	3415
Observed reflections with $[I_o > 2\sigma(I_o)]$	2708	5198	1727	2366
No. parameters	361	685	172	199
R	0.043	0.055	0.039	0.029
R'	0.040	0.063	0.041	0.032

[a] All monoclinic.

found *m*/*z* 480 and 401; calculated for [MnBr(dmsp)]$^+$ *m*/*z* 480, [Mn(dmsp)]$^+$ *m*/*z* 401. ^{1}H NMR: δ 1.1–2.2 (br). ^{13}C-{^{1}H} NMR: δ 224.0–211.0 (br, CO), 24.2, 14.3 (CH$_2$), −3.8, −4.1 (Me).

[MnCl(CO)$_3$(PPh$_2$H)$_2$]. Yield = 83% (Required for C$_{27}$H$_{22}$ClMnO$_3$P$_2$: C, 59.3; H, 4.0. Found: C, 59.4; H, 4.1%). FAB mass spectrum: found *m*/*z* = 511, 462 and 427; calculated for [Mn(CO)$_3$(PPh$_2$H)$_2$]$^+$ *m*/*z* = 511, [Mn^{35}Cl(PPh$_2$H)$_2$] *m*/*z* = 462, [Mn(PPh$_2$H)$_2$]$^+$ *m*/*z* = 427. ^{1}H NMR: δ 7.1–7.8 (br m, Ph, 20 H) and 5.5 (m, PH 2H). ^{13}C-{^{1}H} NMR: δ 221.1, 217.3 (br, CO) and 135.9–126.9 (Ph).

[MnCl(CO)$_3$(PCy$_2$H)$_2$]. Yield = 79% (Required for C$_{27}$H$_{46}$ClMnO$_3$P$_2$: C, 56.8; H, 8.1. Found: C, 56.3; H, 7.7%). FAB mass spectrum: found *m*/*z* = 486 and 451; calculated for [Mn^{35}Cl(PCy$_2$H)$_2$]$^+$ *m*/*z* = 486, [Mn(PCy$_2$H)$_2$]$^+$ *m*/*z* = 451. ^{1}H NMR: δ 4.05 (m, PH, 2H), 1.2–2.6 (br m, CH$_2$, 40H) and 0.9 (m, CH, 2H). ^{13}C-{^{1}H} NMR: δ 222.0, 219.0 (br, CO), 34.8–31.9 (Cy) and 31.5–26.1 (Cy), 23.0 (Cy).

[MnCl(CO)$_3$(PPhH$_2$)$_2$]. Yield = 61% (Required for C$_{15}$H$_{14}$ClMnO$_3$P$_2$: C, 45.7; H, 3.6. Found: C, 45.4; H, 3.7%). Electrospray mass spectrum: found *m*/*z* = 350; calculated for [Mn^{35}Cl(PPhH$_2$)$_2$·MeCN]$^+$ *m*/*z* = 350. ^{1}H NMR: δ 7.3–7.7 (m, Ph, 10H), 5.6 (m, PH, 2H) and 5.3 (m, PH, 2H). ^{13}C-{^{1}H} NMR: δ 219.7, 216.7 (br, CO) and 133.0–125.0 (Ph).

[MnCl(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}]. Yield = 64% (Required for C$_9$H$_8$ClMnO$_3$P$_2$: C, 34.1; H, 2.5. Found: C, 34.6; H, 2.8%). FAB mass spectrum: found *m*/*z* = 289; calculated for [Mn^{35}Cl(CO)$_2${C$_6$H$_4$(PH$_2$)$_2$-*o*}]$^+$ *m*/*z* = 288. ^{1}H NMR: δ 7.6–8.0 (m, C$_6$H$_4$, 4H), 6.1 (m, PH, 2H) and 5.6 (m, Ph, 2H). ^{13}C-{^{1}H} NMR: δ 219.1, 217.9 (br, CO) and 137.8–128.0 (C$_6$H$_4$).

[MnBr(CO)$_3$(PPh$_2$H)$_2$]. Yield = 88% (Required for C$_{27}$H$_{22}$BrMnO$_3$P$_2$: C, 54.8; H, 3.7. Found: C, 55.0; H, 3.9%). FAB mass spectrum: found *m*/*z* = 592, 508, 427 and 320; calculated for [Mn^{79}Br(CO)$_3$(PPh$_2$H)$_2$]$^+$ *m*/*z* = 591, [Mn^{79}Br(PPh$_2$H)$_2$]$^+$ *m*/*z* = 506, [Mn(PPh$_2$H)$_2$]$^+$ *m*/*z* = 427, [Mn^{79}Br(PPh$_2$H)]$^+$ *m*/*z* = 320. ^{1}H NMR: δ 7.0–7.8 (m, Ph, 20H) and 5.45 (m, PH, 2 H). ^{13}C-{^{1}H} NMR: δ 222.2, 216.5 (br, CO) and 133.0–128.0 (Ph).

[MnBr(CO)$_3$(PCy$_2$H)$_2$]. Yield = 84% (Required for C$_{27}$H$_{46}$BrMnO$_3$P$_2$: C, 52.7; H, 7.5. Found: C, 53.0; H, 7.0%). FAB mass spectrum: found *m*/*z* = 530, 451 and 332; calculated for [Mn^{79}Br(PCy$_2$H)$_2$]$^+$ *m*/*z* = 530, [Mn(PCy$_2$H)$_2$]$^+$ *m*/*z* = 451, [Mn^{79}Br(PCy$_2$H)]$^+$ *m*/*z* = 332. ^{1}H NMR: δ 4.05 (m, PH, 2H), 1.2–2.7 (br, m, CH$_2$, 40H) and 0.85 (m, CH, 2H). ^{13}C-{^{1}H} NMR: δ 223.3, 219.4 (br, CO) and 34.9–26.0 (Cy).

[MnBr(CO)$_3$(PPhH$_2$)$_2$]. Yield = 66% (Required for C$_{15}$H$_{14}$BrMnO$_3$P$_2$: C, 41.0; H, 3.2. Found: C, 41.3; H, 3.3%). ^{1}H NMR: δ 7.35–7.55 (br m, Ph, 10H), 5.6 (m, PH 2H) and 5.3 (m, PH, 2H). ^{13}C-{^{1}H} NMR: δ 221.0, 216.9 (br, CO) and 132.8–125.5 (Ph).

[MnBr(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}]. Yield = 63% (Required for C$_9$H$_8$BrMnO$_3$P$_2$·CH$_2$Cl$_2$: C, 27.0; H, 2.3. Found: C, 27.5; H, 2.5%). Electrospray mass spectrum: found *m*/*z* 322; calculated for [Mn(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}·MeCN]$^+$ *m*/*z* = 322. ^{1}H NMR: δ 7.6–8.0 (m, C$_6$H$_4$, 4H), 6.2, (m, PH, 2H) and 5.9 (m, PH, 2H). ^{13}C-{^{1}H} NMR: 220.3, 217.3 (br, CO) and 137.6–129.3 (C$_6$H$_4$).

Crystal structures of [MnCl(CO)$_3${C$_6$H$_4$(PPh$_2$)$_2$-*o*}], [MnBr(CO)$_3$(dppe)]·0.5CHCl$_3$, [MnCl(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}]·CH$_2$Cl$_2$ and [MnBr(CO)$_3$(PPhH$_2$)$_2$]

Details of the crystallographic data collection and refinement parameters are given in Table 4. The crystals were grown by vapour diffusion of light petroleum into solutions of the complexes in CHCl$_3$, or CH$_2$Cl$_2$ for [MnCl(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}]. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems open-flow cryostat operating at 150 K and graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å). In the case of [MnBr(CO)$_3$(dppe)] considerable icing occurred during data collection in the final shell (2θ = 45–50°). This resulted in inaccurate intensities and hence the data set was truncated. Correspondingly, the quality of the structure determination was poorer. The structures were solved by heavy atom methods[22] and developed by iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses.[23] For [MnBr(CO)$_3$(dppe)] two crystallographically independent molecules were identified in the asymmetric unit as well as a CHCl$_3$ solvent molecule. All non-H atoms were refined anisotropically while H atoms were placed in fixed, calculated positions with *d*(C–H) = 0.96 Å, except for [MnCl(CO)$_3${C$_6$H$_4$(PH$_2$)$_2$-*o*}]·CH$_2$Cl$_2$ and [MnBr(CO)$_3$(PPhH$_2$)$_2$] where the H atoms associated with the phosphine ligand were located from the difference map and included but not refined.

CCDC reference number 186/1415.

See http://www.rsc.org/suppdata/dt/1999/1615/ for crystallographic files in .cif format.

Acknowledgements

We thank the EPSRC for a studentship (to S. J. A. P.) and Dr. W. Levason and Mr. N. Holmes (University of Southampton) for providing samples of R$_2$SbCH$_2$CH$_2$CH$_2$SbR$_2$ (R = Me or Ph).

References

1 J. Connolly, G. W. Goodban, G. Reid and A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.*, 1998, 2225; J. Connolly, M. K. Davies and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1998, 3833; W. Levason, S. D. Orchard and G. Reid, *Organometallics*, 1999, **18**, 1275.
2 D. Rehder, *Multinuclear NMR*, ed. J. Mason, Plenum, New York, 1987, ch. 19.
3 R. Colton and J. McCormick, *Aust. J. Chem.*, 1976, **29**, 1657; *Inorg. Chem.*, 1977, **16**, 155.
4 A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 634.
5 A. M. Bond, B. S. Grabaric and Z. Grabaric, *Inorg. Chem.*, 1978, **17**, 1013.
6 R. H. Reiman and E. Singleton, *J. Organomet. Chem.*, 1972, **38**, 113.
7 P. M. Treichel, W. K. Dean and W. M. Douglas, *J. Organomet. Chem.*, 1972, **42**, 145.
8 G. A. Carriedo, V. Riera, M. L. Rodriguez and J. J. Sainz-Velicia, *Polyhedron*, 1987, **6**, 1879.
9 N. J. Holmes, W. Levason and M. Webster, *J. Organomet. Chem.*, 1998, **568**, 213.
10 A. M. Hill, W. Levason, M. Webster and I. Albers, *Organometallics*, 1997, **16**, 5641.
11 E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.
12 A. M. Bond, R. Colton and M. E. McDonald, *Inorg. Chem.*, 1978, **17**, 2842.
13 P. Garrou, *Chem. Rev.*, 1981, **8**, 229.
14 W. Levason, C. A. McAuliffe and B. Riley, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 1201.
15 J. B. Brandon and K. R. Dixon, *Can. J. Chem.*, 1981, **59**, 1188.
16 B. Patel, S. J. A. Pope and G. Reid, *Polyhedron*, 1998, **17**, 2345.
17 F. Calderazzo, E. A. C. Lucken and D. F. Williams, *J. Chem. Soc. A*, 1967, 154.
18 R. Giordano, E. Sappa, A. Tiripicchio, M. T. Camellini, M. J. Mays and M. P. Brown, *Polyhedron*, 1989, **8**, 1855.
19 G. Q. Li, J. Feldman, J. A. Krause and M. Orchin, *Polyhedron*, 1997, **16**, 2041.
20 K. J. Reimer and A. Shaver, *Inorg. Synth.*, 1979, **19**, 159.
21 M. H. Quick and R. J. Angelici, *Inorg. Synth.*, 1979, **19**, 156.
22 PATTY, The DIRDIF Program System, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
23 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1995.

Paper 9/00875F