Synthesis and Reactions of Heterobimetallic Manganese–Palladium Complexes. Crystal and Molecular Structure of [MnPdBr(CO)$_3$-(μ-Ph$_2$PCH$_2$PPh$_2$)$_2$] †

Bernard F. Hoskins and Robyn J. Steen
Department of Inorganic Chemistry, University of Melbourne, Parkville, 3052 Victoria, Australia
Terence W. Turney *
CSIRO Division of Materials Science, Catalysis and Surface Science Laboratory, Parkville, 3052 Victoria, Australia

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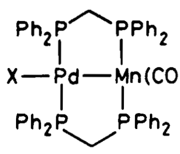
Reaction of [MnX(CO)$_5$] with [Pd(dba)$_2$] (dba = 1,5-diphenyl-1,4-pentadien-3-one) in hot toluene in the presence of Ph$_2$PCH$_2$PPh$_2$(dppm) affords [MnPdX(CO)$_3$(μ-dppm)$_2$] [X = Cl (1), Br (2), or I (3)] in varying yield dependent upon X. Metathesis of complex (2) with NaX gives (3; X = I), (4; X = N$_3$), (5; X = NCO), and (6; X = SCN), and a reversible insertion of SnCl$_2$ into the PdCl bond of (1) affords (7; X = SnCl$_3$). Protonation of complexes (1)—(7) or of [Pd$_2$Cl$_2$(μ-dppm)$_2$] with HBF$_4$·Et$_2$O or CF$_3$CO$_2$H affords unstable cationic hydride complexes. Infrared, ^{1}H, ^{31}P, and some ^{13}C n.m.r. data of (1)—(7) and their protonated forms are given and discussed. The structure of complex (2) was established by a single-crystal *X*-ray diffraction study: the crystals are monoclinic, space group *Cc*, with a = 18.317(2), b = 13.412(2), c = 21.013(4) Å, and β = 111.75(1)°; refined to R 0.057 for 7 286 reflections [$I \geqslant 3\sigma(I)$] collected by counter methods. The molecule consists of a near-planar Mn(CO)$_3$PdBr entity oriented perpendicular to the plane of the phosphorus atoms forming the (dppm)$_2$ framework. Including the Mn–Pd bond [2.810(2) Å], the palladium environment is square planar, but there is also evidence of an additional interaction involving a carbonyl. The manganese environment has an irregular six-co-ordinate geometry.

Bimetallic complexes with methylenebis(diphenylphosphine), dppm, bridges are attracting considerable attention. This ligand offers some degree of molecular flexibility in spanning a range of different metal–metal distances,[1] and has enabled the development of a rich co-ordination chemistry. In particular, some dppm complexes exhibit catalytic activity for the fixation of carbon dioxide and the water-gas shift reaction.[2] In order to modify the activity of such complexes, we have made heterobimetallic dppm systems with two strongly interacting metal centres, and report here details of the synthesis, structural characterization, and some chemistry of complexes with a MnPd(μ-dppm)$_2$ core.[3]



	X
(1)	Cl
(2)	Br
(3)	I
(4)	N$_3$
(5)	NCO
(6)	SCN
(7)	SnCl$_3$

Results and Discussion

Synthesis and Characterization of [MnPdX(CO)$_3$(μ-dppm)$_2$].—Reaction of a mixture of [MnX(CO)$_5$] (X = Cl, Br, or I), [Pd(dba)$_2$] [dba = dibenzylideneacetone (1,5-diphenyl-1,4-pentadien-3-one)], and dppm in hot toluene resulted in a rapid evolution of carbon monoxide and the formation of complexes analysing as [MnPdX(CO)$_3$(dppm)$_2$] [X = Cl (1), Br (2), or I (3)]. Yields starting from the less reactive [Pd-(PPh$_3$)$_4$] were poorer. In the preparations of complexes (1) and (2), traces of palladium metal were obtained in addition to an as yet uncharacterized, brown carbonyl-containing material.

The synthesis of complexes (1)—(3) in reaction (i) represents

$$[\mathrm{MnX(CO)_5}] + [\mathrm{Pd(dba)_2}] + 2\mathrm{dppm} \longrightarrow [\mathrm{MnPdX(CO)_3(dppm)_2}] + 2\mathrm{dba} + 2\mathrm{CO} \quad \text{(i)}$$

a formal oxidative addition of an Mn–X bond to Pd^0, affording a Pd$^{\mathrm{I}}$–Mn^0 unit. Such a reaction is analogous to the comproportionation of the palladium(II) complex [PdCl$_2$-(NCPh)$_2$] with [Pd$_2$(dba)$_3$] in the presence of dppm to afford the palladium(I) dimer, [Pd$_2$Cl$_2$(μ-dppm)$_2$], and the similar reaction of [PtCl$_2$(NCBu^t)$_2$] and [Pd(PPh$_3$)$_4$] giving the mixed platinum(I)–palladium(I) dimer, [ClPt(μ-dppm)$_2$PdCl].[4] It should be noted that complex (1) has recently been reported in low yield from the reaction of [Pd$_2$Cl$_2$(dppm)$_2$] with [Mn(CO)$_5$]$^-$ and from [Pd{Mn(CO)$_5$}$_2$(NCPh)$_2$] and dppm.[5]

Complexes (1)—(3) have been characterized by elemental analysis, ^{1}H and ^{31}P n.m.r. spectroscopy (Table 1), and i.r. spectroscopy (Table 2). In each case, the ^{31}P-{^{1}H} spectrum shows two doublets of doublets centred about +75 and +20 p.p.m. These are the main peaks in an AA′XX′ spin system, in which the minor peaks were not observed. The sharper high-field resonance is assigned to the phosphorus atoms co-ordinated to palladium, whereas the low-field resonance (phosphorus attached to manganese) was often broadened to an apparent triplet at room temperature. This sharpened somewhat on cooling to −70 °C, owing to an increase in the

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† Bis-μ-[bis(diphenylphosphino)methane-*PP′*]-1-bromo-2,2,2-tricarbonylpalladiummanganese (*Pd–Mn*).

Supplementary data available (No. SUP 23955, 19 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Proton and $^{31}P-\{^1H\}$ n.m.r. data for the complexes $[MnPdX(CO)_3(\mu\text{-dppm})_2]$

Complex	X	$\delta(PCH_2P)$ [a]	$\delta(MnP)$ [b]	$\delta(PdP)$ [b]	$^3J(PP)$ [c]
(1)	Cl	3.91	75.4	22.2	63.7, 56.2
(2)	Br	3.92	74.5	20.0	63.0, 55.5
(3)	I	4.04	74.1	16.6	61.0, 53.7
(4)	N_3	3.82	76.5(t, br)	22.1	63.9, 56.7
(5)	NCO	3.82	76.5(t, br)	22.7	65.3, 58.0
(6)	SCN	4.00	74.2(t, br)	23.1	61.0, 54.7
(7)	$SnCl_3$	4.00	69.5(t)	18.6(t)	54

[a] All ^1H n.m.r. spectra measured in $CDCl_3$. Each resonance was split into a symmetrical quintet with a separation of 4.6 ± 0.2 Hz. [b] All $^{31}P-\{^1H\}$ n.m.r. spectra measured in CH_2Cl_2, with chemical shifts reported in p.p.m. downfield from 85% H_3PO_4. Unless noted, each resonance was split into a resolved doublet of doublets. [c] Apparent values (in Hz) of $J(AX)$ and $J(AX')$ in an AA'XX' spectrum.

Table 2. Infrared data (cm^{-1}) for the complexes $[MnPdX(CO)_3(\mu\text{-dppm})_2]$

Complex	X	$\nu(CO)$ [a]	Other bands
(1)	Cl	1 932m, 1 860s	$\nu(Pd-Cl)$ 264 [b]
(2)	Br	1 933m, 1 860s	$\nu(Pd-Br)$ <200 [b]
(3)	I	1 932m, 1 860s	—
(4)	N_3	1 939m, 1 856s	$\nu_{asym}(N_3)$ 2 022s
(5)	NCO	1 929m, 1 853s	$\nu_{asym}(NCO)$ 2 194s, $\nu_{sym}(NCO)$ 1 337w [b]
(6)	SCN	1 937m, 1 860s	$\nu_{asym}(NCS)$ 2 095s
(7)	$SnCl_3$	1 948m, 1 872s	$\nu(Sn-Cl)$ 244 [b]

[a] Measured in CH_2Cl_2 unless otherwise stated. [b] Measured as a Nujol mull.

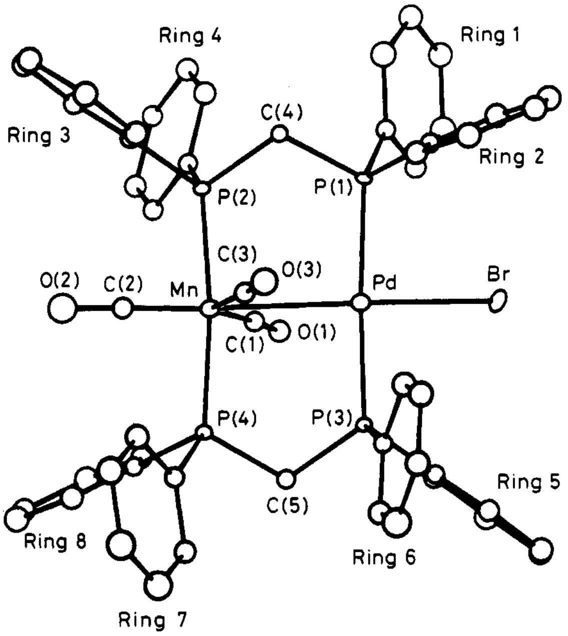

Figure 1. The molecular structure of $[MnPdBr(CO)_3(\mu\text{-dppm})_2]$ showing the atom numbering scheme

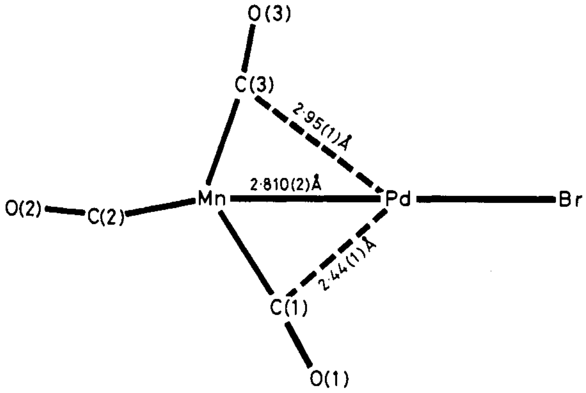

Figure 2. A view of the $Mn(CO)_3PdBr$ moiety

relaxation times of those phosphorus nuclei coupled to the quadrupolar manganese ($I = \frac{5}{2}$) at lower temperatures. In the $^1H-\{^{31}P\}$ n.m.r. spectra, the CH_2 resonances of the bridging dppm ligands are singlets intermediate in chemical shift between those of the symmetric $[Pd_2X_2(\mu\text{-dppm})_2]$ and $[Mn_2(CO)_6(\mu\text{-dppm})_2]$ dimers.[6] Coupling to both Mn–*P* and Pd–*P* affords a deceptively simple quintet in the ^1H n.m.r. spectra. The $^{13}C-\{^1H\}$ n.m.r. spectrum of a 60% CO-enriched sample of complex (2) shows two triplets of unequal intensity at 236.2 p.p.m. [$^2J(PC)$ = 18.8 Hz, intensity *ca.* 2] and at 228.0 p.p.m. [$^2J(PC)$ = 35 Hz, intensity *ca.* 1] both in the terminal-carbonyl region. These are assigned to the manganese-carbonyl ligands *cis* and *trans* respectively to the Mn–Pd bond. The spectrum is temperature invariant to −80 °C.

The i.r. spectra of complexes (1)—(3) exhibit two $\nu(CO)$ bands at *ca.* 1 930 and 1 860 cm^{-1} (Table 2). Although the latter band is quite low it is not inconsistent with a terminal-carbonyl stretching mode {*cf.* $[Mn_2(CO)_6(\mu\text{-dppm})_2]$ with $\nu(CO)$ at 1 987vw, 1 923(sh), 1 912s, and 1 866m cm^{-1}}.[6a] However, as will be seen from the *X*-ray crystal structure below, there is some interaction between the carbonyl ligands and the palladium centre.

Crystal and Molecular Structure of $[MnPdBr(CO)_3(\mu\text{-dppm})_2]$ (2).—The unit cell consists of four discrete molecules of complex (2) with the closest contact of 3.30(2) Å being that between the phenyl-carbon atom C(55) and C(44) from another molecule related by the operation $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$. The crystal is disordered such that the asymmetric unit is composed on average of two enantiomers in the ratio *ca.* 3 : 1. The molecular geometry is depicted in Figure 1, whilst important molecular dimensions are given in Table 3.

The molecule consists of an essentially planar $(CO)_3$-MnPdBr moiety which is approximately perpendicular to the plane containing the four phosphorus atoms of the two bridging dppm ligands. The manganese atom is six-co-ordinate, the geometry being conveniently described as an edge-capped trigonal bipyramid; the three bonded carbonyl groups form a trigonal plane which together with a phosphorus atom from each of the dppm ligands complete the trigonal bipyramid. The sixth bonded atom is the Pd which lies on a line passing somewhat asymmetrically through one of the trigonal edges formed by two of the CO groups, as shown in Figure 2; the Mn–Pd distance is 2.810(2) Å. The trigonal nature of the CO groups is comparable to similar geometries observed around one of the manganese atoms in each of the related compounds $[Mn_2(CO)_5(\mu\text{-dppm})_2]$ and $[Mn_2(CO)_4(CNC_6H_4Me\text{-}p)(\mu\text{-dppm})_2]$.[7] Gross variation in the Mn–C distances akin to those found for $[Mn_2(CO)_5(\mu\text{-dppm})_2]$ is observed in complex (2); 1.63(2), 1.78(1), and 1.96(1) Å. The marked non-linearity of the Mn–C(2)–O(2) system is probably an artifact of the constraints imposed in the structure analysis owing to the overlay of disordered Br atoms close to the O(2) site. The comparatively long Mn–C(1) distance

Table 3. Interatomic distances (Å) and angles (°) for [MnPdBr$(CO)_3$(μ-dppm)$_2$]

Pd–Mn	2.810(2)	Mn–P(2)	2.254(3)	P(1)–C(4)	1.86(1)	P(4)–C(5)	1.83(1)
Pd–P(1)	2.299(4)	Mn–P(4)	2.276(3)	P(2)–C(4)	1.84(1)	P(3)–C(51)	1.82(1)
Pd–P(3)	2.290(4)	Mn–C(1)	1.96(1)	P(1)–C(11)	1.82(1)	P(3)–C(61)	1.86(1)
Pd···C(1)	2.44(1)	Mn–C(2)	1.63(2)	P(1)–C(21)	1.82(1)	P(4)–C(71)	1.83(1)
Pd···O(1)	3.00(1)	Mn–C(3)	1.78(1)	P(2)–C(31)	1.84(1)	P(4)–C(81)	1.85(1)
Pd···C(3)	2.95(1)	C(1)–O(1)	1.17(2)	P(2)–C(41)	1.79(1)	P(1)···P(1)	3.006(5)
Pd–Br	2.547(2)	C(3)–O(3)	1.15(2)	P(3)–C(5)	1.85(1)	P(3)···P(4)	2.990(5)
C(2)–O(2)	1.17(2)						
Mn–C(1)–O(1)	173.7(10)	P(2)–Mn–C(2)	85.4(5)	Mn–Pd–P(3)	88.1(1)	Mn–P(2)–C(4)	116.8(4)
Mn–C(2)–O(2)	159.4(13)	P(4)–Mn–C(2)	86.7(5)	P(1)–Pd–P(3)	168.8(2)	Mn–P(4)–C(5)	113.7(4)
Mn–C(3)–O(3)	175.3(11)	P(2)–Mn–C(3)	90.9(4)	Pd–P(1)–C(4)	115.6(4)	Mn–P(2)–C(31)	118.6(4)
Pd–Mn–C(1)	58.3(3)	P(4)–Mn–C(3)	98.4(4)	Pd–P(3)–C(51)	116.3(4)	Mn–P(2)–C(41)	116.3(4)
Pd–Mn–C(2)	168.3(5)	Br–Pd–C(1)	137.5(3)	Pd–P(1)–C(11)	120.0(4)	Mn–P(4)–C(71)	118.8(4)
Pd–Mn–C(3)	76.4(4)	Pd–C(1)–Mn	78.7(4)	Pd–P(1)–C(21)	111.8(4)	Mn–P(4)–C(81)	111.5(4)
Pd–Mn–P(2)	90.6(1)	P(1)–Pd–C(1)	99.7(3)	Pd–P(3)–C(5)	115.3(4)	C(4)–P(2)–C(31)	98.2(6)
Pd–Mn–P(4)	95.9(1)	P(3)–Pd–C(1)	89.1(3)	Pd–P(3)–C(61)	110.0(4)	C(4)–P(2)–C(41)	103.0(5)
P(2)–Mn–P(4)	169.7(1)	Pd–C(1)–O(1)	107.6(9)	C(4)–P(1)–C(11)	103.2(6)	C(5)–P(4)–C(71)	106.7(5)
C(1)–Mn–C(2)	110.7(6)	Br–Pd–Mn	178.3(1)	C(4)–P(1)–C(21)	104.3(5)	C(5)–P(4)–C(81)	102.0(5)
C(1)–Mn–C(3)	134.6(5)	Br–Pd–P(1)	87.8(1)	C(5)–P(3)–C(51)	99.2(5)	C(31)–P(2)–C(41)	100.9(6)
C(2)–Mn–C(3)	114.6(7)	Br–Pd–P(3)	90.3(1)	C(5)–P(3)–C(61)	109.6(5)	C(71)–P(4)–C(81)	102.2(5)
P(2)–Mn–C(1)	90.4(4)	Mn–Pd–P(1)	93.6(1)	C(11)–P(1)–C(21)	99.7(5)	P(1)–C(4)–P(2)	108.9(6)
P(4)–Mn–C(1)	86.2(4)	Mn–Pd–C(1);	43.0(3)	C(51)–P(3)–C(61)	105.6(5)	P(3)–C(5)–P(4)	109.0(6)

Phenyl rings: C–C distances are in the range 1.28—1.50 Å, average estimated standard deviation (e.s.d.) *ca.* 0.03 Å, bond angles are in the range 116—125°, average e.s.d. *ca.* 1.0°.

suggests the presence of a bridging CO, but the absence of a close Pd···O(1) contact [3.00(1) Å], the linearity of the Mn(1)–C(1)–O(1) group [173.7(10)°], and the relatively long Pd···C(1) distance [2.44(1) Å] exclude the possibility of either a normal μ-CO bridge or the less common μ-η^2 type found in [$Mn_2(CO)_5$(μ-dppm)$_2$].[7a] However, these features together with the ν(CO) at 1 860 cm^{-1} suggest the presence of a semi-bridging carbonyl.[8] The Mn–P distances [2.254(3) and 2.276(3) Å] agree well with those found in comparable systems.[7]

The Pd atom, which is four-co-ordinate with essentially square-planar geometry, is bonded to a P atom from each of the dppm ligands, and the Br and Mn atoms. The Pd–Br distance of 2.547(2) Å is comparable with those found in [Pd_2Br_2(μ-dppm)$_2$] (average 2.535 Å).[9] The P···P bite distances of 3.006(5) and 2.990(5) Å are substantially longer than the Mn–Pd distance so that the P–M–P angles are significantly less than 180°.

It is of interest to compare the Mn–Pd distance of complex (2) with those found in the recently reported system [$Mn_2Pd_2(CO)_9$(dppm)$_2$] which has two distinct types of Mn–Pd interactions, one supported by a bridging dppm ligand [2.580(2) Å] whereas the other is unsupported [2.821(2) Å] and comparable to that found in (2).[5] It seems likely then that a direct Mn–Pd bond does exist in (2).

The gross distortion of the carbonyl geometry is probably the result of substantial steric pressures arising from the CO ligands themselves and the phenyl groups of the dppm ligands which force two of the CO groups into the cavity surrounding the Pd atom, and thereby accounting for the relatively close approach made by Pd with C(1) and C(3) of 2.44(1) and 2.95(1) Å respectively. The former is an example of a linear, semi-bridging carbonyl system, in which steric forces are insufficient to cause the bending of the carbonyl group which is normally associated with such interactions. There are numerous examples of heterobimetallic systems where the low co-ordination number of one metal permits extensive relaxation of the geometry of the other, resulting in the possibility of electronic interactions between the low-co-ordination-number centre and a linear carbonyl group.[10]

Reactions of [MnPdX$(CO)_3$(μ-dppm)$_2$].—Complexes (1)—(3) are quite stable once formed, showing no signs of disproportionation into the symmetric dimers even on prolonged heating in solution at 120 °C. Unlike the Pd_2, Pt_2, and PdPt dimers, (1)—(3) show no signs of forming simple 'A-frame' complexes upon treatment with non-oxidizing small molecules such as CO, H_2, CO_2, S_8, CS_2, CH_2N_2, or $C_2(CO_2Et)_2$ under a variety of conditions. Such lack of reactivity is a reflection of the co-ordinative saturation of the manganese centre. (However, 'A-frame' and related adducts are produced by oxidizing agents such as halogens and PhN_2BF_4.[11])

Metathesis and related reactions. The anionic ligand in complex (2) may readily be exchanged by the sodium salts of I^-, SCN^-, NCO^-, or N_3^- anions. Spectroscopic data for the new complexes, [MnPdX$(CO)_3$(μ-dppm)$_2$] [X = N_3 (4), NCO (5), or SCN (6)], are given in Tables 1 and 2. The cyanate complex (5) has i.r. absorptions indicative of an N-bound cyanate, whereas the thiocyanate appears to be S-bound.[4] Linkage isomers of (5) and (6) were not observed; both complexes show only a single species in the solid (from i.r. spectroscopy) and in solution between −80 and +60 °C (from ^{31}P n.m.r. spectroscopy), whereas both [$Pd_2(SCN)_2$(μ-dppm)$_2$] and [Pd_2(SCN)(NCS)(μ-dppm)$_2$] have been reported to co-exist.[4a,12]

Tin(II) chloride rapidly inserted into the Pd–Cl bond of (1) in dichloromethane, to afford a deep purple heterotrimetallic complex, [MnPd$(SnCl_3)(CO)_3$(μ-dppm)$_2$] (7). Both [Pd_2Cl_2(μ-dppm)$_2$] and its platinum analogue react similarly, producing bis- and tris-(trichlorostannate) complexes.[13] Unlike complexes [$M_2Cl(SnCl_3)$(μ-dppm)$_2$] (M = Pd or Pt), (7) readily dissociated to re-form (1) on dissolution in methanol, presumably reflecting an equilibrium shift caused by co-ordination of methanol to $SnCl_2$.

Protonation. Addition of a strong acid (*e.g.* $HBF_4 \cdot Et_2O$, CF_3CO_2H, or CF_3SO_3H) to a dichloromethane solution of complexes (1)—(7) resulted in a marked colour change to pink. Attempts to isolate pure samples from these solutions invariably resulted in partial decomposition back to the starting materials. However, from spectral studies in solution

Table 4. Effect of added acid on the ^1H, ^{31}P-{^1H}, and i.r. spectra (cm^{-1}) of [$MnPdX(CO)_3(\mu$-dppm$)_2$]

Complex	δ(PC*H*$_2$P) [a]	δ(Mn*H*Pd) [a]	δ(Mn*P*) [a]	δ(Pd*P*) [a]	'*J*(PP)' [b]	ν(CO) [c]
(1) X = Cl	3.9(m)	—	55.8(t)	17.0(t)	43.4	2 030m, 1 961vs, 1 950s(sh)
(2) X = Br	3.9(m)	—	56.4(t)	15.7(t)	42.8	2 020m, 1 959vs, 1 947s(sh)
(3) X = I	3.9(m)	−14.7(m)	57.3(t)	10.9(t)	41.5	2 015m, 1 956vs, 1 943s(sh)
[$Pd_2Cl_2H(\mu$-dppm$)_2$]$^+$	4.2(m)	−14.5(q) [d]	—	11.5(s)	—	—

[a] Proton n.m.r. spectra measured in $CDCl_3$, ^{31}P-{^1H} spectra in CH_2Cl_2; chemical shifts are in p.p.m. [b] 'J(PP)' = $\frac{1}{2}|J(AX) + J(AX')|$ in Hz. [c] In CH_2Cl_2. [d] δ(Pd*H*Pd), ^2J(PH) = 5.1 Hz.

we believe these to be cationic hydrides of the type [MnPdH(X)$(CO)_3(\mu$-dppm$)_2$]$^+$. The i.r. spectra of (1)—(3) in the presence of HBF_4 shifted to higher ν(CO) (Table 4), characteristic of a cationic complex {*cf.* ν(CO) for [$Mn_2(CO)_6(\mu$-dppm$)_2$] and [$Mn_2H(CO)_6(\mu$-dppm$)_2$]$^+$}.[6a,14] Detailed examination of the ^1H n.m.r. spectra of (3) in the presence of CF_3CO_2H revealed a rather broad resonance in the hydride region. On cooling to −60 °C this sharpened to reveal a complex multiplet, which upon broad-band ^{31}P decoupling collapsed to a singlet. The ^{31}P-{^1H} n.m.r. of complexes (1)—(3) and the ^{13}C-{^1H} n.m.r. of a 60%-enriched sample of (2) {δ(CO) in CD_2Cl_2 at −80 °C: 221.6 [t, ^2J(PC) = 18.0, intensity *ca.* 1] and 219.4 p.p.m. [t, ^2J(PC) = 15 Hz, intensity *ca.* 2]} indicate no marked alteration in structure upon protonation.

In a similar manner to complexes (1)—(3), we found that [$Pd_2Cl_2(\mu$-dppm$)_2$] could also be reversibly protonated in solution, presumably affording [$Pd_2Cl_2H(\mu$-dppm$)_2$]$^+$. In contrast, the known platinum analogue is thermally stable.[15] The magnitude of the hydride chemical shift found for the protonated form of (1) is almost that found for [$Pd_2Cl_2H(\mu$-dppm$)_2$]$^+$ rather than that for [$Mn_2(\mu$-H$)(CO)_6(\mu$-dppm$)_2$]$^+$.[14] Whether the hydride ligand is bridging the two metal atoms or co-ordinated to the palladium alone is not clear, particularly in light of a recent report concerning the fluxional nature of so-called 'bridging' hydride, A-frame systems, suggesting that any structural assignments, in the absence of variable-temperature n.m.r. data, are tenuous.[16]

Experimental

The starting materials, [$Pd(dba)_2$],[17] [$Pd(PPh_3)_4$],[18] [$Pd_2Cl_2(\mu$-dppm$)_2$],[4a] and [$MnX(CO)_5$][19] were prepared by known routes. Reaction of [$MnBr(CO)_5$] with gaseous ^{13}CO in $CHCl_3$ for 24 h at 50 °C afforded a 60% ^{13}CO-enriched sample (by mass spectrometry).[20] Reactions involving [$Pd(dba)_2$] and [$Pd(PPh_3)_4$] were performed under nitrogen in deoxygenated solvents. The products are air-stable in solution and after isolation may be handled in the atmosphere without further precautions.

N.m.r. spectra were recorded with a JEOL FX100 spectrometer. Infrared spectra were recorded for solutions in a cell with KBr windows or for Nujol mulls in either a Perkin-Elmer 577 or a Pye-Unicam SP3-300 i.r. spectrophotometer.

Syntheses.—[$MnPdBr(CO)_3(\mu$-dppm$)_2$] (2). An intimate solid mixture of [$MnBr(CO)_5$] (2.78 g, 10.1 mmol), [$Pd(dba)_2$] (5.88 g, 10.2 mmol), and dppm (8.09 g, 21.1 mmol) was added in small portions to rapidly stirred, hot (*ca.* 95 °C) toluene (150 cm^3) under nitrogen. Immediate and vigorous gas evolution occurred. After the addition was complete the resulting red-brown solution was refluxed for 30 min. Cooling to −10 °C for 16 h caused the product to precipitate as deep red crystals, which were filtered off in air and washed with diethyl ether (5 × 20 cm^3) until the washings were colourless. Dissolution in dichloromethane, filtration to remove a trace of palladium metal, and addition of diethyl ether afforded pure complex (2) on standing (9.42 g, 84%), m.p. 203 °C (decomp.) (Found: C, 58.5; H, 4.1; Br, 6.8; P, 11.5. $C_{53}H_{44}BrMnO_3P_4Pd$ requires C, 58.2; H, 4.1; Br, 7.2; P, 11.3%).

A sample of complex (2) 60% enriched in ^{13}CO was made similarly, from enriched [$MnBr(CO)_5$], [$Pd(dba)_2$], and dppm [ν(CO) in CH_2Cl_2: 1 920m and 1 851s, br cm^{-1}].

[$MnPdCl(CO)_3(\mu$-dppm$)_2$] (1). An intimate mixture of [$MnCl(CO)_5$] (1.54 g, 6.7 mmol), [$Pd(dba)_2$] (3.84 g, 6.7 mmol), and dppm (5.88 g, 15.3 mmol) was treated in toluene (50 cm^3) as above. The red crystals were filtered off from the cooled mixture and recrystallized from dichloromethane–diethyl ether to afford pure complex (1) (3.25 g, 46%), m.p. 197 °C (decomp.) (Found: C, 61.0; H, 4.2; Cl, 3.5; P, 11.8. $C_{53}H_{44}ClMnO_3P_4Pd$ requires C, 60.6; H, 4.2; Cl, 3.4; P, 11.8%). When diethyl ether was added to the toluene filtrate a brown solid was obtained. This was filtered off, washed with ether (2 × 20 cm^3), and dried under vacuum to afford a material (0.9 g) with ν(CO) in CH_2Cl_2 at 2 030s, 1 955m, 1 917s, and 1 833m cm^{-1} and a ^{31}P-{^1H} n.m.r. spectrum in CH_2Cl_2 with resonances (approximate relative intensities) at 23.3 (br, 0.5), 14.5 (br, 0.2), −3.9 (0.1), and −10.2 (1.0) p.p.m.

[$MnPdI(CO)_3(\mu$)-dppm$)_2$] (3). (*a*) *From* [$Pd(PPh_3)_4$]. A mixture of [$Pd(PPh_3)_4$] (1.15 g, 1.0 mmol) and dppm (0.77 g, 1.98 mmol) was dissolved in warm (60 °C) toluene (25 cm^3) to give a deep orange solution. Subsequent addition of [$MnI(CO)_5$] (0.32 g, 1.0 mmol) resulted in vigorous gas evolution and precipitation of red-brown crystals. The mixture was refluxed for 10 min to redissolve any solid product and then cooled (−10 °C) for 24 h. Pure complex (3) (0.78 g, 68%) was obtained by recrystallization of the crude product from dichloromethane–diethyl ether.

(*b*) *From* [$Pd(dba)_2$]. Using a method analogous to that for the preparation of (2) gave complex (3) in isolated yields in excess of 85%.

(*c*) *By metathesis from complex* (2). A solution of sodium iodide (5 g) in acetone (400 cm^3) was stirred with a solution of complex (2) (2.00 g) in dichloromethane (250 cm^3) for 2 h. The solid material, obtained by evaporating off all of the solvent, was extracted with dichloromethane (3 × 20 cm^3), filtered, and diethyl ether (150 cm^3) added. Cooling to −10 °C for 20 h resulted in the formation of red-brown crystals of complex (3) (1.90 g, 91%) (Found: C, 55.8; H, 3.8; I, 10.6; P, 10.4. $C_{53}H_{44}IMnO_3P_4Pd$ requires C, 55.8; H, 3.9; I, 11.1; P, 10.9%).

[$MnPdX(CO)_3(\mu$-dppm$)_2$] [X = N_3 (4), NCO (5), *or* SCN (6)]. These were each prepared as above, by metathesis of complex (2) in dichloromethane with an excess of NaX in acetone. Complex (4), yield 72% (Found: C, 60.0; H, 4.4; N, 3.9; P, 11.7. $C_{53}H_{44}MnN_3O_3P_4Pd$ requires C, 60.3; H, 4.2; N, 4.0; P, 11.7%); (5), yield 67% (Found: C, 61.5; H, 4.5; N, 1.3; P, 12.1. $C_{54}H_{44}MnNO_4P_4Pd$ requires C, 61.8; H, 4.2; N, 1.3; P, 11.8%); (6), yield 81% (Found: C, 59.9; H, 4.4

Table 5. Final fractional co-ordinates for [MnPdBr(CO)$_3$(dppm)$_2$]. Only the atomic co-ordinates for the major component of the disordered asymmetric unit are given; the relationship between these and those of the other component is given in the text

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mn	0.0	−0.079 8(1)	0.0
Pd	0.070 1(1)	0.094 0(1)	0.071 2(1)
Br	0.136 7(1)	0.248 4(1)	0.138 2(1)
P(1)	−0.047 4(2)	0.177 8(2)	0.041 3(2)
P(2)	−0.114 9(2)	0.001 5(2)	−0.049 9(2)
P(3)	0.183 8(2)	0.004 8(2)	0.120 7(2)
P(4)	0.113 0(2)	−0.170 2(2)	0.030 9(2)
C(1)	0.052 7(7)	0.016 4(9)	−0.038 4(6)
O(1)	0.082 3(5)	0.067 9(7)	−0.066 5(5)
C(2)	−0.040 6(9)	−0.168 3(11)	−0.055 0(8)
O(2)	−0.073 2(2)	−0.243 2(3)	−0.077 2(2)
C(3)	−0.016 2(7)	−0.088 8(9)	0.078 3(6)
O(3)	−0.031 2(6)	−0.098 6(8)	0.126 6(5)
C(4)	−0.137 1(7)	0.100 8(9)	0.000 3(6)
C(5)	0.202 0(7)	−0.095 3(8)	0.068 1(6)
C(11)	−0.065 8(7)	0.286 7(8)	−0.014 0(6)
C(12)	−0.139 2(8)	0.332 1(10)	−0.034 5(7)
C(13)	−0.150 1(9)	0.423 8(11)	−0.072 2(8)
C(14)	−0.082 0(12)	0.460 6(15)	−0.089 6(10)
C(15)	−0.016 6(11)	0.413 2(13)	−0.071 0(9)
C(16)	−0.002 4(8)	0.325 8(10)	−0.029 6(7)
C(21)	−0.060 6(7)	0.232 8(9)	0.115 4(6)
C(22)	−0.051 9(9)	0.330 7(10)	0.130 5(8)
C(23)	−0.053 6(8)	0.367 1(11)	0.194 2(8)
C(24)	−0.066 3(9)	0.302 8(11)	0.240 7(8)
C(25)	−0.072 2(9)	0.202 5(11)	0.227 5(8)
C(26)	−0.073 0(8)	0.164 7(10)	0.162 8(8)
C(31)	−0.207 0(7)	−0.069 2(9)	−0.072 2(7)
C(32)	−0.223 2(8)	−0.111 9(11)	−0.015 4(8)
C(33)	−0.291 6(10)	−0.163 2(11)	−0.026 2(9)
C(34)	−0.342 4(9)	−0.176 9(10)	−0.090 4(8)
C(35)	−0.329 8(8)	−0.140 2(10)	−0.145 1(7)
C(36)	−0.260 5(8)	−0.085 4(8)	−0.138 1(7)
C(41)	−0.129 5(6)	0.061 4(7)	−0.129 7(5)
C(42)	−0.183 8(8)	0.139 9(10)	−0.153 2(7)
C(43)	−0.200 9(7)	0.175 9(10)	−0.220 9(6)
C(44)	−0.163 4(8)	0.137 1(10)	−0.260 7(7)
C(45)	−0.108 3(8)	0.064 3(10)	−0.238 5(7)
C(46)	−0.089 7(7)	0.024 0(8)	−0.170 6(6)
C(51)	0.274 3(7)	0.075 7(8)	0.139 6(6)
C(52)	0.291 4(8)	0.115 7(11)	0.088 1(7)
C(53)	0.366 3(10)	0.168 4(12)	0.106 1(8)
C(54)	0.420 0(8)	0.177 1(10)	0.174 5(7)
C(55)	0.398 2(7)	0.135 1(9)	0.227 1(7)
C(56)	0.326 1(9)	0.084 3(10)	0.210 0(8)
C(61)	0.188 6(7)	−0.047 3(8)	0.204 2(6)
C(62)	0.246 2(7)	−0.119 5(9)	0.237 9(6)
C(63)	0.247 9(8)	−0.152 8(10)	0.305 9(7)
C(64)	0.195 4(9)	−0.113 2(11)	0.329 7(7)
C(65)	0.140 0(8)	−0.046 1(10)	0.295 4(7)
C(66)	0.136 9(7)	−0.010 1(9)	0.231 7(6)
C(71)	0.124 5(7)	−0.278 0(9)	0.086 8(6)
C(72)	0.200 2(8)	−0.322 6(10)	0.120 9(7)
C(73)	0.209 8(9)	−0.412 8(12)	0.159 6(8)
C(74)	0.149 0(13)	−0.461 0(16)	0.158 8(11)
C(75)	0.069 8(9)	−0.419 5(11)	0.125 3(8)
C(76)	0.059 8(9)	−0.327 1(11)	0.090 6(8)
C(81)	0.126 5(6)	−0.225 8(8)	−0.044 5(6)
C(82)	0.118 5(9)	−0.332 4(11)	−0.055 6(8)
C(83)	0.123 3(9)	−0.373 4(12)	−0.112 5(8)
C(84)	0.132 0(8)	−0.314 3(10)	−0.162 0(8)
C(85)	0.143 9(9)	−0.210 0(12)	−0.150 9(8)
C(86)	0.135 9(8)	−0.167 3(10)	−0.094 7(8)

N, 1.3; P, 11.7. $C_{54}H_{44}MnNO_3P_4PdS$ requires C, 60.8; H, 4.2; N, 1.3; P, 11.6%).

[MnPd(SnCl$_3$)(CO)$_3$(μ-dppm)$_2$] (7). Addition of finely ground tin(II) chloride (0.10 g, 0.53 mmol) to complex (1) (0.17 g, 0.16 mmol) in dichloromethane (10 cm^3) resulted in a rapid colour change from red to yellow-brown. After filtering off the excess of tin(II) chloride, diethyl ether (80 cm^3) was added and the solution allowed to stand for 3 d at −10 °C. The fine purple crystals were washed with diethyl ether (3 × 10 cm^3) and dried *in vacuo*, to afford complex (7) (0.11 g, 55%) (Found: C, 52.0; H, 3.7; Cl, 9.1; P, 10.2. $C_{53}H_{44}Cl_3MnO_3P_4PdSn$ requires C, 51.4; H, 3.6; Cl, 8.6; P, 10.0%). Addition of methanol to a dichloromethane solution of complex (7) afforded a red precipitate of (1) (from i.r. and electronic spectra).

Protonation of Complexes (1)—(7).—Addition of an excess of HBF$_4$·Et$_2$O (0.8 cm^3) to complex (2) (0.44 g) in CH$_2$Cl$_2$ (20 cm^3) resulted in an immediate colour change to cherry red. Addition of diethyl ether (75 cm^3) precipitated a dark red crystalline product (0.36 g). Attempted recrystallization of this material from dichloromethane–diethyl ether in the absence of added acid resulted in more than 80% reversion to (2) (from i.r. spectrum). Addition of an excess of acid to solutions of complexes (1)—(7) in dichloromethane resulted in changes in the i.r. (addition of HBF$_4$·Et$_2$O), ^{1}H and ^{31}P n.m.r. spectra (addition of CF$_3$CO$_2$H). Reactions of [Pd$_2$Cl$_2$(μ-dppm)$_2$] were performed similarly.

Molecular Structure Determination of [MnPdBr(CO)$_3$(μ-dppm)$_2$] (2).—*Crystal data.* $C_{53}H_{44}BrMnO_3P_4Pd$, M = 1 094.1 monoclinic, a = 18.317(2), b = 13.412(2), c = 21.013(4) Å, β = 111.75(1)°, U = 4 795 Å^3, D_m = 1.51 g cm^{-3}, Z = 4, D_c = 1.515 g cm^{-3}, $F(000)$ = 2 208, Mo-$K_{\bar{\alpha}}$ radiation (graphite monochromated) ($\lambda_{\bar{\alpha}}$ = 0.710 69 Å), μ(Mo-K_α) = 16.6 cm^{-1}, space group Cc; from oscillation and Weissenberg photographs obtained on an Enraf–Nonius CAD-4F diffractometer.

Intensity data were collected in the ω–2θ scan mode at 294 K for 11 291 reflections in the range 5.0 ⩽ 2θ ⩽ 55.0°; no decomposition of the crystal was evident during the data collection. Absorption corrections [21] were applied and the amalgamation of equivalent terms yielded 7 286 independent reflections (including Friedel pairs) with $I > 3\sigma(I)$; $R_{\text{amal.}}$ 0.021.

The structure was solved by normal Fourier methods and refined by the use of a full-matrix least-squares procedure, with unit weights used throughout the refinement.[22] Anisotropic thermal parameters were used for the Mn, Pd, Br, and P atoms, whereas for the remaining non-hydrogen atoms individual isotropic thermal parameters were employed; R 0.084. The (dppm)$_2$ framework, which has a pseudo-centre of symmetry coinciding almost exactly with the midpoint of the Mn–Pd vector, allows the centrosymmetrically related isomer to replace partially that which defines the asymmetric unit, without any apparent alteration to its packing. The superimposition of the two enantiomers leads to a coincidence of the Br of one isomer with the site of O(2) of the other and a similar coincidence of Mn and Pd atoms, thus accounting for the substantial residual electron density at those positions and around the Pd atom. The asymmetric unit is on average composed of both enantiomers in the ratio 0.76 : 0.24, which was determined from the subsequent refinement; R 0.060, shift/e.s.d. <0.2.

Residual electron density of *ca.* 1.0 e Å^{-3} was observed in the final difference map close to both the metal atom sites; there was no evidence of disorder of either dppm group. The inclusion of all the hydrogen atoms in their calculated positions yielded *R* 0.057; 36 out of the total of 44 hydrogen atoms had been observed. In order to accommodate the disorder in the refinement the following conditions were imposed: (*i*) the Pd and Mn′ atoms were constrained to the same position as were Mn and Pd′, Br and O(2′), and O(2) and Br′; (*ii*) the thermal parameter of atom A and its enantiomeric partner A′ were restricted to the same value and that of O(2) was constrained to 1.5 × U_{iso} [C(2)]; and (*iii*) the atoms of the alternative $(CO)_3$ array were fixed in their calculated positions which corresponded well with the sites of unassigned residual electron density about the Pd atom mentioned earlier.

Neutral atomic scattering curves and the corrections for anomalous dispersion, for the Mn and Pd atoms, were taken from ref. 21 while those collected by Sheldrick [22] were used for the remaining atoms. All calculations were performed using the SHELX 76 system.[22] The atomic fractional coordinates of the non-hydrogen atoms are listed in Table 5.

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