Bimetallic Systems. Part 13.[1] Platinum–Manganese Carbonyl Complexes containing Bridging $Ph_2PCH_2PPh_2$ (dppm) Ligands: Crystal Structure of $[(OC)_3Mn(\mu\text{-dppm})_2PtH(Br)]BF_4$†

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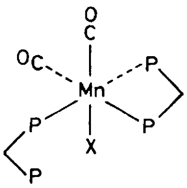
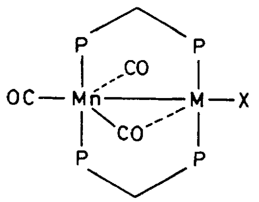
Treatment of $[MnCl(CO)_5]$ with $Ph_2PCH_2PPh_2$ (dppm) gives *cis,mer*-$[MnCl(CO)_2$(dppm-*PP'*)(dppm-*P*)] (**1b**). Treatment of complex (**1b**) with $[Pt(PPh_3)_4]$ under an atmosphere of CO gives $[(OC)_3Mn(\mu\text{-dppm})_2PtCl]$ (**2c**), with a manganese–platinum bond. The complex $[(OC)_3Mn(\mu\text{-dppm})_2PtBr]$ (**2d**) was made similarly. Complexes (**2c**) and (**2d**) are protonated reversibly with strong acids (HBF_4, toluene-*p*-sulphonic acid, or CF_3CO_2H), *e.g.* (**2d**) gives $[(OC)_3Mn(\mu\text{-dppm})_2PtH(Br)]BF_4$ whose crystal structure was determined (see below). Treatment of complex (**1b**) with *trans*-$[PtH(Cl)(PPh_3)_2]$ gave a deep red-purple complex, $[Cl(OC)_2Mn(\mu\text{-dppm})_2PtH(Cl)]$ (**4a**); the corresponding dibromide $[Br(OC)_2Mn(\mu\text{-dppm})_2PtH(Br)]$ (**4b**) was made similarly. When the chloro-complex (**1b**) was treated with *trans*-$[PtH(Br)(PPh_3)_2]$ or the corresponding bromo-complex (**1a**) with *trans*-$[PtH(Cl)(PPh_3)_2]$ the same mixture of $[Cl(OC)_2Mn(\mu\text{-dppm})_2PtH(Br)]$ and $[Br(OC)_2Mn(\mu\text{-dppm})_2PtH(Cl)]$ was produced in each case, showing that intramolecular halogen scrambling occurs. Treatment of the dichloro-complex (**4a**) with $TlBF_4$ under an atmosphere of CO caused rapid conversion into the orange salt, $[(OC)_3Mn(\mu\text{-dppm})_2PtH(Cl)]BF_4$ (**3a**). The corresponding bromide tetrafluoroborate (**3b**) was prepared similarly as were $[(OC)_3Mn(\mu\text{-dppm})_2PtH(X)]PF_6$ (X = Cl or Br), using $TlPF_6$–CO. The salt (**3a**) was deprotonated by sodium methoxide to give the metal–metal-bonded complex $[(OC)_3Mn(\mu\text{-dppm})_2PtCl]$ (**2c**). Many of the above-mentioned complexes showed broad $^{31}P\text{-}\{^1H\}$ n.m.r. patterns at 20 °C for the manganese-bonded P nuclei, due to quadrupole broadening by the Mn nucleus ($I = \frac{5}{2}$). At lower temperatures, *e.g.* −50 °C, the resonances were much sharper because of more rapid relaxation of the Mn nucleus. N.m.r. and i.r. spectroscopic data are given. Crystals of the title compound are monoclinic, space group $P2_1/n$ with a = 1 309.2(2), b = 2 657.2(4), c = 1 571.4(2) pm, and β = 97.37(1)°; final R factor 0.055 4 for 5 781 observed reflections. The structure shows the two metal centres are 287.1(4) pm apart and are bridged by the two dppm ligands giving an eight-membered ring in the boat conformation.

In previous papers in this series we have described systematic syntheses of heterobimetallic complexes with the metals bridged by two $Ph_2PCH_2PPh_2$ (dppm) ligands.[2] Also in a preliminary note[3] we described ring-opening reactions of Group 6 metal carbonyl derivatives of the type *fac*- or *mer*-$[M(CO)_3$(dppm-*PP'*)(dppm-*P*)] with rhodium or iridium carbonyls. Mixed Group 6 metal–platinum complexes of type $[(OC)_3M(\mu\text{-dppm})_2PtH(X)]$ (M = Cr, Mo, or W; X = Cl or Br) have also been prepared by treating *mer*-$[M(CO)_3$(dppm-*PP'*)(dppm-*P*)] with *trans*-$[PtH(X)(PPh_3)_2]$.[4] In the present paper we describe the preparation and reaction of some mixed manganese–platinum complexes, starting with the known manganese dppm complex *cis,mer*-$[MnBr(CO)_2$(dppm-*PP'*)(dppm-*P*)] (**1a**) and its chloride analogue (**1b**), which is new.



	X
(**1a**)	Br
(**1b**)	Cl



	M	X
(**2a**)	Pd	Cl
(**2b**)	Pd	Br
(**2c**)	Pt	Cl
(**2d**)	Pt	Br

Since Colton and Commons[5] prepared the first bis(dppm)-dimanganese complex $[(OC)_2Mn(\mu\text{-dppm})_2(\mu\text{-CO})Mn(CO)_2]$ with the very unusual σ,η-bridging CO there has been a lot of interest in dimanganese dppm chemistry.[6–9] In addition, some manganese–palladium complexes of the type $[(OC)_3Mn(\mu\text{-dppm})_2PdX]$ (X = Cl, Br, I, *etc.*) have been described. Treatment of $[MnX(CO)_5]$ with $[Pd(dba)_2]$ (dba = dibenzylideneacetone) in the presence of dppm gives $[(OC)_3Mn(\mu\text{-dppm})_2PdX]$, X = Cl (**2a**) or Br (**2b**).[10] A crystal structure determination of (**2b**) showed the presence of a semi-bridging CO group with a Pd ··· C distance of 2.44(1)Å and a correspondingly low ν(CO) frequency of 1 860 cm^{-1}.[10] The complex (**2a**) has also been synthesized by treating $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with $Na[Mn(CO)_5]$.[11]

It has been reported that $[MnBr(CO)_5]$ reacts with dppm to give *cis,mer*-$[MnBr(CO)_2$(dppm-*PP'*)(dppm-*P*)] (**1a**).[12] It seemed possible to us that this complex could be used for the systematic synthesis of heterobimetallic complexes of manganese and another metal and we now describe syntheses with platinum.

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† Bis[μ-bis(diphenylphosphino)methane]-1-bromo-2,2,2-tricarbonyl-1-hydridoplatinummanganese tetrafluoroborate.

Supplementary data available (No. SUP 56277, 8 pp.): thermal parameters, H-atom co-ordinates, full list of bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Infrared and analytical data

	Solid[a,b]		Solution[b,c]			Analyses (%)[d,e]		
Complex	$\tilde{\nu}$(C≡O)/cm^{-1}	$\tilde{\nu}$(Pt–H)/cm^{-1}	$\tilde{\nu}$(C≡O)/cm^{-1}	$\tilde{\nu}$(Pt–H)/cm^{-1}	$\tilde{\nu}$(M–Cl)[a]/cm^{-1}	C	H	X
(1a)	1 869s,1 938s		1 867s,1 939s			[f]	[f]	[f]
(1b)	1 864s,1 944s		1 866s,1 938s		n.o.	67.7(68.2)	5.0(4.8)	4.1(3.9)
(2c)·0.25C_6H_6	1 868s,1 939s		1 850s,1 931s		270	56.7(56.6)	3.9(4.0)	3.2(3.1)
(2d)·0.5C_6H_6	1 797s,1 847s,1 925s		1 851s,1 930s			54.5(54.5)	3.7(3.8)	6.7(6.8)
(3a)·CH_2Cl_2	1 925(sh),1 942s	2 025m	1 950s	2 040m	320	49.4(49.5)	3.5(3.6)	8.1(8.1)
(3b)·CH_2Cl_2	1 928(sh),1 941s	2 021m	1 850w,1 950s	2 031m		47.4(47.8)	3.5(3.5)	0.78(0.85)[g]
(3c)·Et_2O	1 850m,1 925(sh),1 945s	2 025m	1 850m,1 932(sh),1 952s	2 040m	319	55.6(55.5)	4.5(4.5)	2.8(2.5)
(3d)	1 842m,1 925(sh),1 941s	2 022m	1 852m,1 931(sh),1 954s	2 038m		52.9(53.2)	3.9(3.9)	5.8(5.9)
(3e)	1 860m,1 950s	2 028m	1 862w,1 958s	2 026m	322	49.2(49.6)	3.5(3.5)	3.0(2.8)
(3f)	1 950s	2 030m	1 860w,1 956s	2 036m		47.3(47.9)	3.4(3.4)	6.6(6.0)
(4a)·0.33C_6H_6	1 829s,1 917s	n.o.	n.d.	n.d.	260,302	55.4(55.6)	4.05(4.05)	6.05(6.10)
(4b)	1 831s,1 918s	n.o.	n.d.	n.d.		50.4(50.5)	3.6(3.7)	13.1(12.9)
(4c),**(4d)**[h]	1 840s,1 917s	n.o.	n.d.	n.d.	260,305	51.9(52.4)	3.6(3.8)	1.4(1.3)

[a] As Nujol mulls. [b] s = strong, m = medium, w = weak, sh = shoulder, n.d. = not determined, and n.o. = not observed. [c] Recorded in dichloromethane solution. [d] Calculated values in parentheses. [e] The presence of solvent of crystallization in some of the complexes was confirmed by ^{1}H n.m.r. spectroscopy. [f] Known compound. Characterized by its spectroscopic data. [g] Total halogen determination: titre of $Hg(NO_3)_2$ solution with calculated titre in parentheses. [h] Obtained as a mixture (see Results and Discussion and Experimental sections).

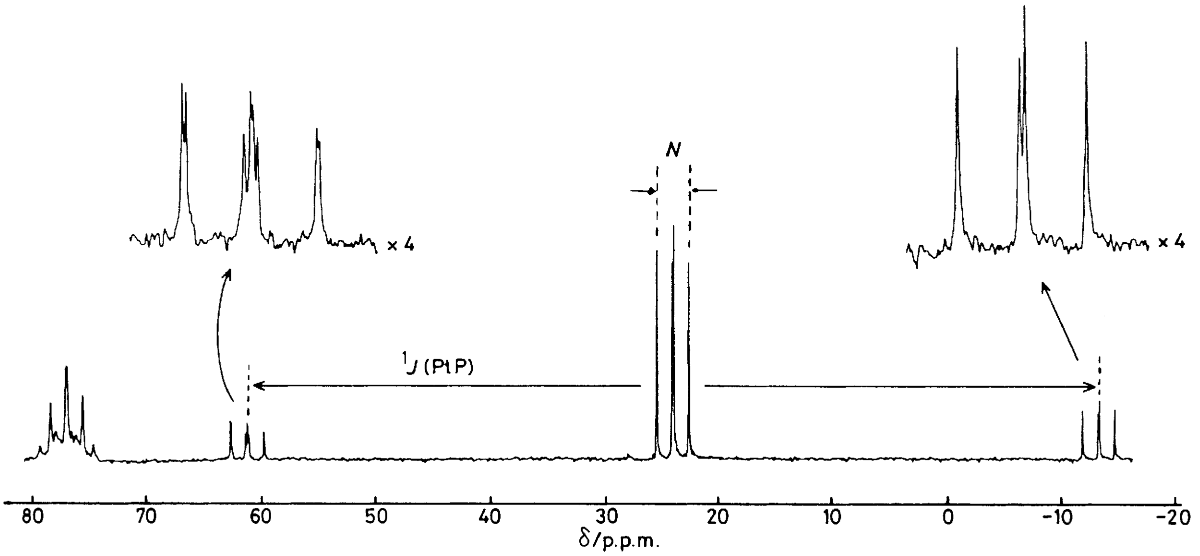


Figure 1. The ^{31}P-{^{1}H} n.m.r. spectrum (40.25 MHz) of [$(OC)_3Mn(\mu$-dppm$)_2PtCl$] **(2c)** in CD_2Cl_2 at 20 °C. The satellite due to ^{195}Pt coupling, at higher frequency, is more complex than the other satellite because of its proximity to the resonance of the manganese-bonded P nuclei

Results and Discussion

In the course of this work we made the new chloro-complex **(1b)** by treating [$MnCl(CO)_5$] with dppm. Preparative details and n.m.r. data are in the Experimental section, elemental analytical and i.r. data are in Table 1.

Treatment of *cis,mer*-[$MnCl(CO)_2$(dppm-*PP′*)(dppm-*P*)] **(1b)** with [$Pt(PPh_3)_4$] in benzene, under an atmosphere of carbon monoxide, gave the manganese(0)–platinum(I) complex [$(OC)_3Mn(\mu$-dppm$)_2PtCl$] **(2c)** in 56% yield by a combined ring-opening/redox process. This formulation, analogous to the mixed manganese(0)–palladium(I) complex **(2a)**,[10] is based on the elemental analysis (Table 1) and on the physical and chemical evidence. The ^{31}P-{^{1}H} n.m.r. spectrum (Figure 1) showed an AA′XX′ pattern with the resonance pattern of the phosphines bonded to managanese slightly broadened because of quadrupole broadening by the manganese nucleus ($I = \frac{5}{2}$) and with satellites due to ^{195}Pt coupling (see Table 2 for data). The ^{1}H-{^{31}P} n.m.r. spectrum showed a sharp PCH_2P resonance with coupling to ^{195}Pt, ^3J(PtCH_2) = 48.8 Hz, which was unaltered at −80 °C. The i.r. spectrum showed two strong bands due to ν(CO), at 1 931 and 1 850 cm^{-1} (in CH_2Cl_2 solution), and a strong band, at 270 cm^{-1} (Nujol mull), assigned to ν(Pt–Cl), and absent from the spectrum of the corresponding bromide **(2d)** which was made (86% yield) and characterized in an analogous fashion (see Experimental section and Tables 1 and 2).

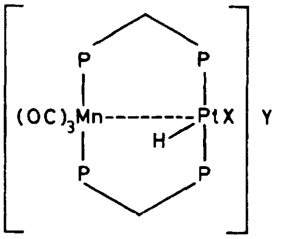
The two values for ν(C≡O) for each of our two manganese–platinum complexes **(2c)** and **(2d)** are very similar to those reported for the corresponding manganese–palladium complexes **(2a)** and **(2b)**.[10,11] We thus suggest a similar structure

Table 2. $^{31}P-\{^1H\}$[a,b] and $^1H-\{^{31}P\}$[b,c] n.m.r. data

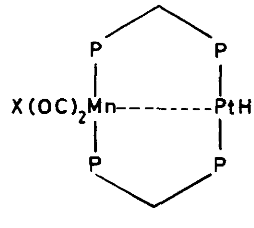
					Methylene		Hydride	
Complex	$\delta(P_A)$[d]	$\delta(P_B)$[e]	$^1J(PtP)$	N[e]	$\delta(CH_2)$	$^3J(PtH)$	$\delta(H)$	$^1J(PtH)$
(2c)	77.6	25.6	3 018	117.1	3.74	48.8		
(2d)	76.8	23.8	3 000	113.5	3.80	49.6		
(3a)	57.0	15.1	2 373	83.0	3.95	46.3	−19.9	933
(3b)	57.1	14.1	2 347	80.5	4.03	45.9	−18.5	975
(3c)	57.0	14.7	2 385	83.0	4.22	49.3	−19.7	951
(3d)	56.9	13.9	2 349	83.0	4.28	47.4	−18.3	996
(3e)	69.5	17.0	2 744	107.4	3.89	46.9	−20.0	928
(3f)	57.0	14.1	2 346	80.6	3.98	45.9	−17.1	743
(4a)[f]	55.0	11.1	2 600	83.0	4.12,3.70 $^2J(HH) = 12.0$	g	−18.4	1 073
(4b)[f]	53.0	9.7	2 552	83.7	4.17,3.95 $^2J(HH)$ *ca.* 10.0	g	−17.1	1 122
(4c)[f]	55.8	11.1	2 568	83.0	4.12,3.82 $^2J(HH) = 13.0$	g	−17.0	1 126
(4d)[f]	55.4	11.6	2 603	82.7	4.14,3.95 $^2J(HH) = 11.0$	g	−18.4	1 027

[a] Chemical shifts (δ) (in p.p.m.; ±0.1 p.p.m.) relative to 85% H_3PO_4 (positive shift to high frequency); coupling constants (J) in Hz (±2 Hz). Spectra were recorded at 25 °C, unless otherwise stated. [b] In CD_2Cl_2 solution. [c] Chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) relative to tetramethylsilane; coupling constants (J) in Hz (±0.3 Hz). Spectra recorded at 25 °C, unless otherwise stated. [d] P_A, P_B refer to the phosphorus atoms co-ordinated to manganese and platinum respectively. [e] $N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$. [f] $^{31}P-\{^1H\}$ data obtained at −30 °C and $^1H-\{^{31}P\}$ data at −50 °C. [g] The AB quartets were quite broad (down to −90 °C) and $^3J(^{195}PtH)$ was not measured.

with a semi-bridging carbonyl group for (**2c**) and (**2d**), as shown. These complexes (**2c**) and (**2d**) are quite stable and can be recovered unchanged after being boiled in hydrocarbon solvents, chlorinated solvents, or ethanol. It was reported that the managanese–palladium complex (**2a**) or (**2b**) reacted with strong acids (*e.g.* $HBF_4 \cdot Et_2O$ or CF_3CO_2H) to give cationic hydrides $[(OC)_3Mn(\mu\text{-dppm})_2PdH(X)]^+$ which were very unstable and were characterized only in solution.[10] We find that the orange manganese–platinum complex (**2c**) or (**2d**), when treated with an excess of $HBF_4 \cdot Et_2O$, immediately gives deep red solutions from which a deep red, nicely crystalline hydride $[(OC)_3Mn(\mu\text{-dppm})_2PtH(X)]BF_4$, X = Cl (**3a**) or Br (**3b**), is obtained in good yield (48 and 67% respectively). The crystal structure of (**3b**) has been determined (see below). The chloro-complex (**3a**) showed a well resolved $^{31}P-\{^1H\}$ n.m.r. pattern for the platinum-bonded P, characteristic of an AA′XX′ spin system with satellites due to ^{195}Pt coupling, but the manganese-bonded P gave a broad pattern attributed to quadrupole broadening by the Mn nucleus ($I = \frac{5}{2}$). When the solution was cooled to −50 °C the resonance pattern of the manganese-bonded P nuclei sharpened considerably and was of the AA′XX′ type (data in Table 2). The ^1H n.m.r. spectrum showed a hydride resonance at −19.9 p.p.m. with $^1J(PtH) = 933$ Hz. The hydride resonance was invariant in the presence of an excess of HBF_4 indicating that hydrogen exchange is slow on the n.m.r. time-scale. The CH_2 resonance in the $^1H-\{^{31}P\}$ resonance pattern was a sharp singlet with satellites due to ^{195}Pt coupling at ambient temperature. This pattern broadened at low temperature but even at −90 °C did not resolve into an AB pattern. We suggest that the hydride H in complex (**3a**) moves rapidly from one side of the P_4 plane to the other causing equivalence of the CH_2 hydrogens.



	X	Y
(3a)	Cl	BF_4
(3b)	Br	BF_4
(3c)	Cl	$SO_3C_6H_4Me-4$
(3d)	Br	$SO_3C_6H_4Me-4$
(3e)	Cl	PF_6
(3f)	Br	PF_6



(4a) X = X′ = Cl
(4b) X = X′ = Br
(4c) X = Cl, X′= Br
(4d) X = Br, X′= Cl

The i.r. spectrum of $[(OC)_3Mn(\mu\text{-dppm})_2PtH(Cl)]BF_4$ shows that a considerable shift of the CO stretches to a higher frequency (1 950 cm^{-1}) has occurred on protonation, indicating that the semi-bridging CO present in complexes of type (**2**) has become entirely terminal. The higher-frequency band at 2 040 cm^{-1} for (**3a**) is assigned to ν(Pt–H). The n.m.r. and i.r. data for the bromo-complex (**3b**) are similar to those for (**3a**). We found that the metal–metal-bonded complexes (**2c**) and (**2d**) were readily protonated by toluene-*p*-sulphonic acid and the corresponding hydrides (**3c**) and (**3d**) were isolated (details in the Experimental section and characterizing data in Tables 1 and 2). We also showed, by $^{31}P-\{^1H\}$ and $^1H-\{^{31}P\}$ n.m.r. spectroscopy, that trifluoroacetic acid or dry HCl would protonate (**2c**) and (**2d**) in dichloromethane solution to give $[(OC)_3Mn(\mu\text{-dppm})_2PtH(X)]^+$, X = Cl or Br, but the complexes obtained from the HCl treatment were not isolated pure and in the CF_3CO_2H experiments the unprotonated complexes (**2c**) or (**2d**) were recovered on attempted isolation, *i.e.* protonation is reversible. Treatment of (**2c**) or (**2d**) with acetic acid did not give a hydride.

We have also devised an alternative synthesis of manganese–platinum dppm complexes using *trans*-$[PtH(X)(PPh_3)_2]$ (X = Cl or Br). As mentioned above, we have shown that such platinum hydrides react smoothly with compounds of the type *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Cr, Mo, or W) to give highly coloured complexes of type $[(OC)_3M(\mu\text{-dppm})_2PtH(X)]$.[4] It seemed possible that the manganese complexes of type (**1**) would react similarly: this has been found to be the case. Treatment of the chloromanganese(I) complex (**1b**) with the equivalent amount of *trans*-$[PtH(Cl)(PPh_3)_2]$ gave a deep red-purple crystalline complex of the expected composition, *viz.* $[Cl(OC)_2Mn(\mu\text{-dppm})_2PtH(Cl)]$, in good (79%) yield. We assign structure (**4a**) to this compound on the basis of analytical and spectroscopic data (Tables 1 and 2) but do not know the detailed stereochemistry around each metal. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed a typical AA′XX′ pattern with platinum satellites and the proton $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum showed a hydride resonance at $\delta = -18.4$ p.p.m. with strong coupling to ^{195}Pt (1 073 Hz); the methylene PCH_2P resonance consisted of an AB pattern. The i.r. spectrum showed two strong bands, at 1 917 and 1 829 cm^{-1}, which we assign to $\nu(C\equiv O)$. Two bands at 302 and 260 cm^{-1} are assigned to metal–chlorine stretching vibrations and are absent from the spectrum of the corresponding dibromide (see below): we do not know which band is due to $\nu(Pt\text{–}Cl)$ and which to $\nu(Mn\text{–}Cl)$. We similarly made the corresponding dibromide (**4b**) from (**1a**) and *trans*-$[PtH(Br)(PPh_3)_2]$. The $^{31}P\text{-}\{^1H\}$ or $^1H\text{-}\{^{31}P\}$ n.m.r. spectra of (**4a**) and (**4b**) were well defined and indicated that only one structural isomer had been produced in each case, although three relative orientations of X and X′ are possible for (**4a**) or (**4b**). The intense colours of the manganese–platinum hydrides suggest a metal–metal interaction and we cannot exclude the presence of a bridging, or semi-bridging, ligand other than dppm, *viz.* H, CO, or halogen. When the bromomanganese complex (**1a**) was treated with *trans*-$[PtH(Cl)(PPh_3)_2]$ we obtained a mixture of two complexes which we formulate as mixed chloride–bromides (**4c**) and (**4d**). The same mixture was formed when the chloromanganese complex (**1b**) was treated with *trans*-$[PtH(Br)(PPh_3)_2]$. In neither case was any of the dichloro- (**4a**) or dibromo- (**4b**) complexes produced (n.m.r. evidence). This result suggests that intramolecular scrambling of halogens between manganese and platinum occurs but not intermolecular scrambling (data in Table 2): the scrambling is slow on the n.m.r. time-scale. The complexes (**4a**)—(**4d**) are insoluble in benzene and other hydrocarbon solvents, slightly soluble in acetone and, although they are soluble in chlorinated solvents such as dichloromethane, they react over a period of several hours to give a number of products including $[Pt(dppm\text{-}PP')_2]^{2+}$ and $[PtCl_2(dppm\text{-}PP')]$ ($^{31}P\text{-}\{^1H\}$ evidence).

We then attempted to convert the red-purple complexes of type (**4**) into the tricarbonyl salts of type (**3**) and thence to the metal–metal bonded species of type (**2**). Treatment of $[Cl(OC)_2Mn(\mu\text{-dppm})_2PtH(Cl)]$ (**4a**) with $TlBF_4$ under an atmosphere of carbon monoxide caused rapid conversion into the orange salt (**3a**) in 63% yield, identified by its $^{31}P\text{-}\{^1H\}$ and i.r. spectra. The corresponding bromide tetrafluoroborate salt (**3b**) was prepared similarly. Treatment of (**4a**) or (**4b**) with $TlPF_6$ and carbon monoxide similarly gave the new hexafluorophosphate salts (**3e**) and (**3f**) respectively; these were characterized by elemental analysis and by n.m.r. and i.r. spectroscopy, Tables 1 and 2.

Treatment of the tricarbonyl tetrafluoroborate salt (**3a**) with a slight excess of NaOMe caused deprotonation to give the metal–metal bonded chloro-complex (**2c**) in 74% yield. Similarly, treatment of the tricarbonyl bromide salt with NaOMe gave the metal–metal-bonded bromo-complex (**2d**) in 82% yield (details in the Experimental section).

Table 3. Selected interatomic distances (pm) and angles (°) for complex (**3b**) with estimated standard deviations (e.s.d.s) in parentheses

Mn ··· Pt	287.1(4)	Mn–C(1)	179.0(13)
Pt–Br	247.4(3)	Mn–C(2)	182.8(16)
Pt–P(1)	230.6(5)	Mn–C(3)	186.6(13)
Pt–P(3)	231.5(5)	C(1)–O(1)	116.7(15)
Mn–P(2)	230.2(5)	C(2)–O(2)	105.6(18)
Mn–P(4)	229.2(5)	C(3)–O(3)	115.3(14)
Pt ··· C(3)	267.9(14)		
Br–Pt–Mn	149.2(0.5)	O(2)–C(2)–Mn	175.8(11)
P(1)–Pt–Br	89.5(2)	O(3)–C(3)–Mn	174.6(10)
P(3)–Pt–Br	91.9(2)	P(3)–Pt–P(1)	168.6(1)
C(3)–Pt–Mn	39.1(2)	C(1)–Mn–P(4)	86.4(5)
P(4)–Mn–P(2)	174.1(1)	C(2)–Mn–P(2)	85.6(5)
C(1)–Mn–P(2)	88.3(5)	C(2)–Mn–C(1)	95.6(7)
C(2)–Mn–Pt	158.4(4)	C(3)–Mn–P(2)	93.1(5)
C(2)–Mn–P(4)	92.3(5)	C(3)–Mn–C(1)	170.5(6)
C(13)–P(2)–Mn	109.9(5)	C(13)–P(1)–Pt(1)	111.1(5)
C(33)–P(4)–Mn	110.2(5)	C(33)–P(3)–Pt(1)	109.8(5)
P(2)–C(13)–P(1)	111.8(7)	P(4)–C(33)–P(3)	113.7(6)
O(1)–C(1)–Mn	175.5(11)		

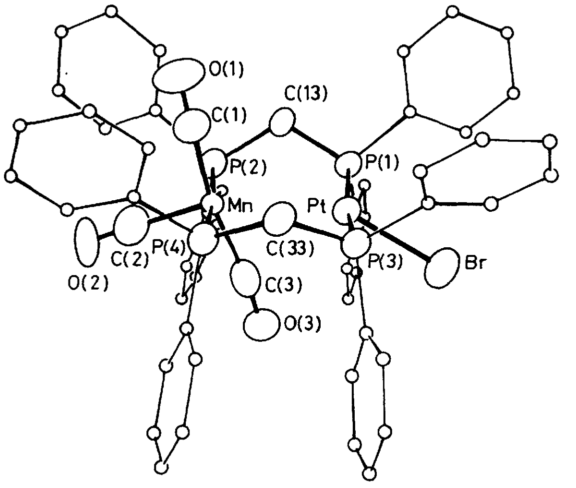


Figure 2. Molecular structure of $[(OC)_3Mn(\mu\text{-dppm})_2PtH(Br)]BF_4$ (**3b**) showing the principal atomic numbering

Crystal Structure of $[(OC)_3Mn(\mu\text{-dppm})_2PtH(Br)]BF_4$ (**3b**).—The complex (**3b**) crystallized from a dichloromethane–diethyl ether mixture. The structure is shown in Figure 2 and selected intramolecular distances and angles in Table 3. The Mn and Pt moieties are linked by two dppm bridges to give an eight-membered MnP_4C_2Pt ring in the 'boat' conformation; the Mn–Pt distance of 287.1(4) pm is slightly longer than the range 260—285 pm of Mn–Pt distances found in several (about 10) complexes[13–18] in which a Mn and Pt are directly bonded.

The hydride ligand in (**3b**) was not located but one presumes that it is approximately *trans* to Br and possibly therefore bridges the Pt and the Mn. The strong coupling to ^{195}Pt (975 Hz) (Table 2) indicates that the hydride ligand is strongly bonded to Pt and the interaction with Mn is probably less strong or non-existent. The Pt, Mn, and H may be interacting to form a three-centre bond. The carbon [C(3)] of one of the carbonyl ligands is 267.9(14) pm from the platinum. This is possibly indicative of some weak Pt ··· C interaction. In $[(OC)_3Mn(\mu\text{-dppm})_2PdBr]$ one of the carbonyl carbons is 244(1) pm from the palladium.[10]

Experimental

All reactions were carried out in an atmosphere of dry dinitrogen in degassed solvents. Dichloromethane was dried over molecular sieves (type 4A) and benzene over sodium wire. Infrared spectra were recorded as either Nujol mulls between KBr plates or as dichloromethane solutions on a Perkin-Elmer 257 grating spectrometer. Unless indicated otherwise, n.m.r. spectra were recorded on a JEOL FX100 instrument at 99.55 MHz (^{1}H) or 40.25 MHz (^{31}P) using solvent resonances as internal standards and referenced to $SiMe_4$ or 85% H_3PO_4 as appropriate.

trans-$[PtH(Br)(PPh_3)_2]$.—A solution of the complex *trans*-$[PtH(Cl)(PPh_3)_2]$ (0.5 g, 0.66 mmol) in dichloromethane (15 cm^3) and a solution of sodium bromide (0.67 g, 6.6 mmol) in water (3 cm^3), containing tetra-n-butylammonium bromide (0.042 g) as phase-transfer catalyst, was vigorously stirred at ambient temperature for 2 h. The product was isolated from the organic layer. It formed white prisms of a dichloromethane solvate from dichloromethane–light petroleum (b.p. 40—60 °C). Yield 0.46 g (82%) {Found: C, 50.8; H, 3.85%; halogen titration against 0.0057 mol dm^{-3} $Hg(NO_3)_2$ solution, 2.64 cm^3. $[PtH(Br)(PPh_3)_2]\cdot 0.75CH_2Cl_2$ requires C, 51.05; H, 3.8%; halogen titration, 2.54 cm^3}; ν(Pt–H) 2 218 cm^{-1} (Nujol). N.m.r. spectra ($CDCl_3$): ^{1}H, δ = −14.8 p.p.m. (hydride), ^1J(PtH) = 1 242 and ^2J(PH) = 12.7 Hz; ^{31}P, δ 29.1 p.p.m., ^1J(PtP) = 2 978 Hz.

cis,mer-$[MnCl(CO)_2$(dppm-*PP′*)(dppm-*P*)] (**1b**).—A solution of $[MnCl(CO)_5]$ (0.800 g, 3.5 mmol) and dppm (2.94 g, 7.6 mmol) in toluene (60 cm^3) was refluxed under dinitrogen. The reaction was monitored by i.r. spectroscopy, until the peak at 2 036 cm^{-1}, due to *fac*-$[MnCl(CO)_3$(dppm-*PP′*)], had disappeared (*ca.* 7 h). The mixture was then allowed to cool to room temperature and a yellow solid, identified as *cis*-$[Mn(CO)_2$(dppm-*PP′*)$_2$]Cl (0.83 g), filtered off. The filtrate was then cooled to −20 °C for 2 d, after which the required product had separated as a yellow microcrystalline solid which was filtered off and washed with n-hexane. Yield 0.85 g (27%). This product was sufficiently pure for most purposes but could be recrystallized from dichloromethane–n-hexane to give the pure compound. N.m.r. data (in CD_2Cl_2): ^{31}P-{^{1}H}, similar to literature values for compound (**1a**), δ −30.7 (P_A), 3.9 (P_B), 37.8 (P_C), 51.4 p.p.m. (P_D), $J(P_BP_C)$ = 35, $J(P_AP_C)$ = 6, $J(P_AP_D)$ = 17, $J(P_BP_D)$ = 48, and $J(P_CP_D)$ = 74 Hz; ^{1}H-{^{31}P}, two AB quartets, δ 3.6 and 2.0 p.p.m. [^2J(HH) = 16], 4.83 and 4.48 p.p.m. [^2J(HH) = 13.9 Hz].

$[(OC)_3Mn(\mu\text{-dppm})_2PtCl]$ (**2c**) *from* (**1b**).—The complex $[Pt(PPh_3)_4]$ (0.128 g, 0.011 mmol) was added with stirring to a solution of *cis,mer*-$[MnCl(CO)_2$(dppm-*PP′*)(dppm-*P*)] (**1b**) (0.100 g, 0.011 mmol) in benzene (15 cm^3) under an atmosphere of carbon monoxide. Upon dissolution of the platinum compound (*ca.* 5 min) the resultant solution was heated to 60 °C for 1.5 h under carbon monoxide. The resultant red solution was cooled, filtered, and evaporated to half-bulk under reduced pressure. Addition of light petroleum (b.p. 30—40 °C) then gave the required product as orange prisms. Upon washing with diethyl ether the product changed to an amorphous yellow solid. Yield 0.071 g (56%). The corresponding bromide complex (**2d**) was prepared analogously in 86% yield.

Protonation of Complex (**2c**) *to give* (**3a**).—An excess of $HBF_4\cdot Et_2O$ (50 μl) was added to a solution of $[(OC)_3Mn(\mu\text{-dppm})_2PtCl]$ (**2c**) (0.100 g, 0.087 mmol) in dichloromethane (10 cm^3). The solution changed from orange to deep red almost immediately. Diethyl ether (8 cm^3) was then added and the required product separated as deep red prisms over a period of 1 h. Yield 0.051 g (48%). The corresponding bromide complex (**3b**) was prepared analogously in 67% yield.

Action of Trifluoroacetic acid on Complex (**2c**).—Trifluoroacetic acid (1 cm^3) was added to a solution of $[(OC)_3Mn(\mu\text{-dppm})_2PtCl]$ (**2c**) (0.100 g, 0.087 mmol) in dichloromethane (10 cm^3): an immediate colour change to deep red was observed. The solution was evaporated under reduced pressure to give an oily residue. The protonated complex of type (**3**) was shown to be present in this residue by n.m.r. and i.r. spectroscopy (see Results and Discussion section). Attempted crystallization (dichloromethane–diethyl ether) gave back $[(OC)_3Mn(\mu\text{-dppm})_2PtCl]$. The corresponding bromide (**2a**) when treated with trifluoroacetic acid behaved similarly.

$[(OC)_3Mn(\mu\text{-dppm})_2PtH(Cl)][SO_3C_6H_4CH_3\text{-}4]$ (**3c**).—An excess of toluene-*p*-sulphonic acid (0.025 g) was added to a stirred solution of $[(OC)_3Mn(\mu\text{-dppm})_2PtCl]$ (0.100 g, 0.087 mmol) in dichloromethane (10 cm^3). The resultant solution was stirred for 0.5 h during which time it changed from orange to red. Diethyl ether was then added until the solution was just turbid, after which red crystals separated over a period of *ca.* 3 h. These were filtered off and washed with diethyl ether. Yield 0.075 g (64%). The corresponding bromide (**3d**) was prepared similarly, in 77% yield.

$[Cl(OC)_2Mn(\mu\text{-dppm})_2PtH(Cl)]$ (**4a**).—The complex *trans*-$[PtH(Cl)(PPh_3)_2]$ (0.041 g, 0.054 mmol) was added to a stirred solution of *cis,mer*-$[MnCl(CO)_2$(dppm-*PP′*)(dppm-*P*)] (0.050 g, 0.054 mmol) in benzene (5 cm^3) and the resultant mixture stirred until the platinum complex had dissolved (*ca.* 10 min). The solution was put aside for 2 h, after which the required complex (**4a**) had separated as a deep red-purple solid. This was collected and washed with benzene and ether. Yield 0.051 g (79%). The corresponding dibromide complex (**4b**) was prepared similarly except that the required product separated from the reaction mixture over 16 h. Yield 62%. A mixture of the chloride–bromide complex (**4c**) or (**4d**) was prepared analogously by treating *trans*-$[PtH(Cl)(PPh_3)_2]$ with *cis,mer*-$[MnBr(CO)_2$(dppm-*PP′*)(dppm-*P*)] for 16 h (yield 81%) or by treating *trans*-$[PtH(Br)(PPh_3)_2]$ with *cis,mer*-$[MnCl(CO)_2$(dppm-*PP′*)(dppm-*P*)] over 4 h (yield 66%). The same mixture was obtained by either method (see Results and Discussion section).

Conversion of Complex (**4a**) *into* (**3a**).—The complex $[Cl(OC)_2Mn(\mu\text{-dppm})_2PtH(Cl)]$ (0.240 g, 0.21 mmol) was added with vigorous stirring to a solution of $TlBF_4$ (0.061 g, 0.21 mmol) in acetone (20 cm^3) saturated with carbon monoxide. An orange solid formed almost immediately accompanied by decomposition of TlCl. The mixture was stirred for a further 0.5 h and then evaporated to dryness under reduced pressure. The required product (**3a**) was isolated with dichloromethane and formed orange prisms from dichloromethane–diethyl ether and shown to be identical with an authentic sample (above). Yield 0.162 g (63%). The corresponding bromide (**3b**) (yield 84%), chloride hexafluorophosphate (**3e**) (yield 56%), and bromide hexafluorophosphate (**3f**) (yield 77%) complexes were prepared analogously.

Conversion of Complex (**3a**) *into* (**2c**).—A methanol solution of sodium methoxide (7 μl, 0.152 mol dm^{-3}, 0.1 mmol) was added with stirring to a solution of $[(OC)_3Mn(\mu\text{-dppm})_2PtH(Cl)]BF_4$ (**3a**) (0.100 g, 0.088 mmol) in dichloromethane (10 cm^3). The resultant orange solution was stirred for a further 0.5 h, evaporated to dryness under reduced pressure, and the product (**2c**) isolated with benzene. It formed orange prisms from benzene–light petroleum (b.p. 30—40 °C), yield 0.070 g

Table 4. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	3 489.7(3)	5 083.9(2)	1 994.8(3)	C(311)	3 780(5)	3 746(2)	1 993(4)
Mn(1)	2 192(1)	5 121(1)	3 334(1)	C(312)	2 843(5)	3 733(2)	1 460(4)
Br(1)	3 717(1)	4 871(1)	498(1)	C(313)	2 441(5)	3 274(2)	1 140(4)
P(1)	3 059(2)	5 895(1)	1 567(2)	C(314)	2 977(5)	2 829(2)	1 354(4)
P(2)	1 606(2)	5 912(1)	2 921(2)	C(315)	3 915(5)	2 842(2)	1 887(4)
P(3)	4 245(2)	4 336(1)	2 501(2)	C(316)	4 316(5)	3 301(2)	2 206(4)
P(4)	2 804(2)	4 365(1)	3 887(2)	C(321)	5 634(4)	4 324(3)	2 472(4)
C(111)	2 094(4)	5 982(3)	643(3)	C(322)	6 006(4)	4 456(3)	1 709(4)
C(112)	1 467(4)	5 581(3)	331(3)	C(323)	7 061(4)	4 436(3)	1 655(4)
C(113)	664(4)	5 660(3)	−330(3)	C(324)	7 743(4)	4 285(3)	2 365(4)
C(114)	488(4)	6 140(3)	−678(3)	C(325)	7 371(4)	4 154(3)	3 128(4)
C(115)	1 115(4)	6 541(3)	−366(3)	C(326)	6 316(4)	4 173(3)	3 181(4)
C(116)	1 918(4)	6 452(3)	294(3)	C(33)	4 108(8)	4 260(4)	3 643(6)
C(121)	4 174(4)	6 237(2)	1 312(4)	C(411)	2 086(5)	3 788(3)	3 589(4)
C(122)	4 798(4)	6 508(2)	1 938(4)	C(412)	1 072(5)	3 812(3)	3 190(4)
C(123)	5 671(4)	6 755(2)	1 727(4)	C(413)	529(5)	3 371(3)	2 963(4)
C(124)	5 920(4)	6 731(2)	891(4)	C(414)	999(5)	2 904(3)	3 135(4)
C(125)	5 296(4)	6 460(2)	265(4)	C(415)	2 014(5)	2 879(3)	3 534(4)
C(126)	4 423(4)	6 213(2)	477(4)	C(416)	2 557(5)	3 321(3)	3 760(4)
C(13)	2 603(8)	6 253(4)	2 435(6)	C(421)	2 988(5)	4 344(3)	5 072(3)
C(211)	404(4)	5 988(3)	2 172(4)	C(422)	3 964(5)	4 345(3)	5 548(3)
C(212)	−283(4)	5 587(3)	2 027(4)	C(423)	4 062(5)	4 355(3)	6 442(3)
C(213)	−1 194(4)	5 645(3)	1 469(4)	C(424)	3 184(5)	4 364(3)	6 860(3)
C(214)	−1 418(4)	6 104(3)	1 056(4)	C(425)	2 209(5)	4 362(3)	6 384(3)
C(215)	−731(4)	6 505(3)	1 202(4)	C(426)	2 111(5)	4 352(3)	5 490(3)
C(216)	180(4)	6 448(3)	1 760(4)	C(1)	2 955(10)	5 404(4)	4 235(7)
C(221)	1 366(6)	6 306(2)	3 813(4)	O(1)	3 481(8)	5 558(4)	4 834(6)
C(222)	2 185(6)	6 529(2)	4 334(4)	C(2)	1 020(11)	5 070(5)	3 847(8)
C(223)	2 004(6)	6 799(2)	5 061(4)	O(2)	324(7)	5 020(4)	4 110(6)
C(224)	1 003(6)	6 845(2)	5 268(4)	C(3)	1 597(8)	4 826(5)	2 312(7)
C(225)	184(6)	6 623(2)	4 747(4)	O(3)	1 169(6)	4 630(3)	1 715(5)
C(226)	365(6)	6 353(2)	4 020(4)				

(74%), and was shown to be identical to an authentic sample (above) by n.m.r. and i.r. spectroscopy. Compound (**2d**) in 82% yield was prepared analogously from $[(OC)_3Mn(\mu\text{-dppm})_2\text{-}PtH(Br)]BF_4$.

Crystallographic Studies.—All crystallographic measurements were made on a Syntex $P2_1$ diffractometer operating in the ω—2θ scan mode using graphite monochromated Mo-K_α radiation ($\lambda = 71.069$ pm) following a standard procedure described in detail elsewhere.[19] The data set was corrected for absorption empirically.[20]

Crystal data. $C_{57}H_{55}BBrF_4MnO_4P_4Pt$, $M = 1\,216.83$, monoclinic, $a = 1\,309.2(2)$, $b = 2\,657.2(4)$, $c = 1\,571.4(2)$ pm, $\beta = 97.37(1)°$, $U = 5.421$ nm^3, space group $P2_1/n$ ($= P2_1/c$, no. 14), $Z = 4$, $D_c = 1.49$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 35.66$ cm^{-1}, $F(000) = 2\,596$, $T = 290$ K. 7 469 Data were collected, 5 781 being considered observed [$I > 2\sigma(I)$]. Scans from 0.8° below $K_{\alpha 1}$ to 0.8° above $K_{\alpha 2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0°$.

Structure determination and refinement. The structure was determined by standard heavy-atom procedures and refined by full-matrix least squares using the SHELX program system.[21] All non-hydrogen atoms of the cation were assigned anisotropic thermal parameters with the phenyl rings refined as rigid bodies with hexagonal symmetry (C–C 139.5 pm), while all hydrogen atoms [which were included in calculated positions (C–H 108 pm)] and the anion were assigned isotropic thermal parameters. Residual electron density on the Fourier difference map indicated the presence of a disordered ether solvent molecule. Peaks showing significant electron density were therefore also included in the refinement and assigned isotropic thermal parameters. A weighting scheme $w = 1/[\sigma^2(F_o) + 0.0003(F_o)^2]$ was used at the end of refinement to give a flat analysis of variance with increasing sin θ and $(F/F_{max.})^{\frac{1}{2}}$. Final R value 0.0554, and $R' = 0.0578$ (541 parameters). The final atomic co-ordinates and their standard deviations are listed in Table 4.

Acknowledgements

We thank Johnson Matthey PLC for the generous loan of platinum salts, and the S.E.R.C. for support.

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Received 31*st January* 1985; *Paper* 5/173