

## Bimetallic Systems. Part 15.<sup>1</sup> Some Reactions of Platinum–Manganese Carbonyl Complexes containing Bridging Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (dppm) Ligands

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Treatment of [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>PtCl] with either Li(C≡CPh) or with PhC≡CH–NEt<sub>3</sub> gives [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-CO)Pt(C≡CPh)] (**1c**), in which one of the CO ligands is probably weakly semi-bridging. A C≡CC<sub>6</sub>H<sub>4</sub>Me-*p* complex was made similarly. Treatment of compound (**1c**) with HBF<sub>4</sub>·Et<sub>2</sub>O gives [(OC)<sub>3</sub>Mn(μ-H)(μ-dppm)<sub>2</sub>Pt(C≡CPh)]BF<sub>4</sub>, reversibly. Treatment of [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>PtBr] with NaBH<sub>4</sub> or N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O gives the corresponding hydride [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-CO)PtH] which reacts reversibly with HBF<sub>4</sub>·Et<sub>2</sub>O to give [(OC)<sub>3</sub>Mn(μ-H)(μ-dppm)<sub>2</sub>PtH]BF<sub>4</sub>. Treatment of [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>PtBr] with TIPF<sub>6</sub>–CO gives [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>Pt(CO)]PF<sub>6</sub>, which is protonated by HBF<sub>4</sub>·Et<sub>2</sub>O to give [(OC)<sub>3</sub>Mn(μ-H)(μ-dppm)<sub>2</sub>Pt(CO)]BF<sub>4</sub>(PF<sub>6</sub>) and also reacts reversibly with OMe<sup>–</sup> to give [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-CO)Pt(CO<sub>2</sub>Me)]. The compound [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>PtBr] reacts with CNBu<sup>t</sup> to give [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-CO)Pt(CNBu<sup>t</sup>)]<sup>+</sup> which, in turn, could be protonated reversibly by HBF<sub>4</sub>·Et<sub>2</sub>O to give [(OC)<sub>3</sub>Mn(μ-H)(μ-dppm)<sub>2</sub>Pt(CNBu<sup>t</sup>)]<sup>2+</sup>, isolated as the mixed BF<sub>4</sub><sup>–</sup>PF<sub>6</sub><sup>–</sup> salt. Treatment of [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>PtBr] with NOBF<sub>4</sub> gives an NO<sup>+</sup> adduct possibly with a weakly bridging NO ligand, *viz.* [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>(μ-NO)PtBr]BF<sub>4</sub>. Hydrogen-1, <sup>31</sup>P-<sup>1</sup>H} n.m.r. and i.r. data are given.

The chemistry of manganese carbonyls and of related species such as manganese carbonyl cyanides and isonitrile complexes bridged by Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (dppm) is quite extensive. Most of it involves dimanganese derivatives bridged by two dppm ligands,<sup>2–10</sup> although *mer,cis*-[MnBr(CO)<sub>2</sub>(dppm-PP′)(dppm-P)]<sup>11</sup> has been described, as have mixed manganese–palladium complexes of the type [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>PdX] or [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-CO)PdX], X = Cl or Br,<sup>12,13</sup> with one CO strongly bonded to Mn, *i.e.* end-on but apparently weakly interacting with the Pd, a so-called semi-bridging CO. A tetranuclear dimanganese complex has also been described, *viz.* [Pd<sub>2</sub>Mn<sub>2</sub>(CO)<sub>9</sub>(dppm)<sub>2</sub>] with a triply bridging CO.<sup>13</sup>

We have shown in a previous paper<sup>14</sup> that treatment of *mer,cis*-[MnX(CO)<sub>2</sub>(dppm-PP′)(dppm-P)] (X = Cl or Br) with [Pt(PPh<sub>3</sub>)<sub>4</sub>] under an atmosphere of CO gives mixed manganese(0)–platinum(I) complexes, analogous to the manganese(0)–palladium(I) complexes mentioned above and of type [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>PtX] or [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-CO)PtX], X = Br or Cl, with a weakly semi-bridging CO ligand as depicted in (**1a**) or (**1b**). We now describe an extensive chemistry of such complexes which, for convenience, is summarized in the Scheme.

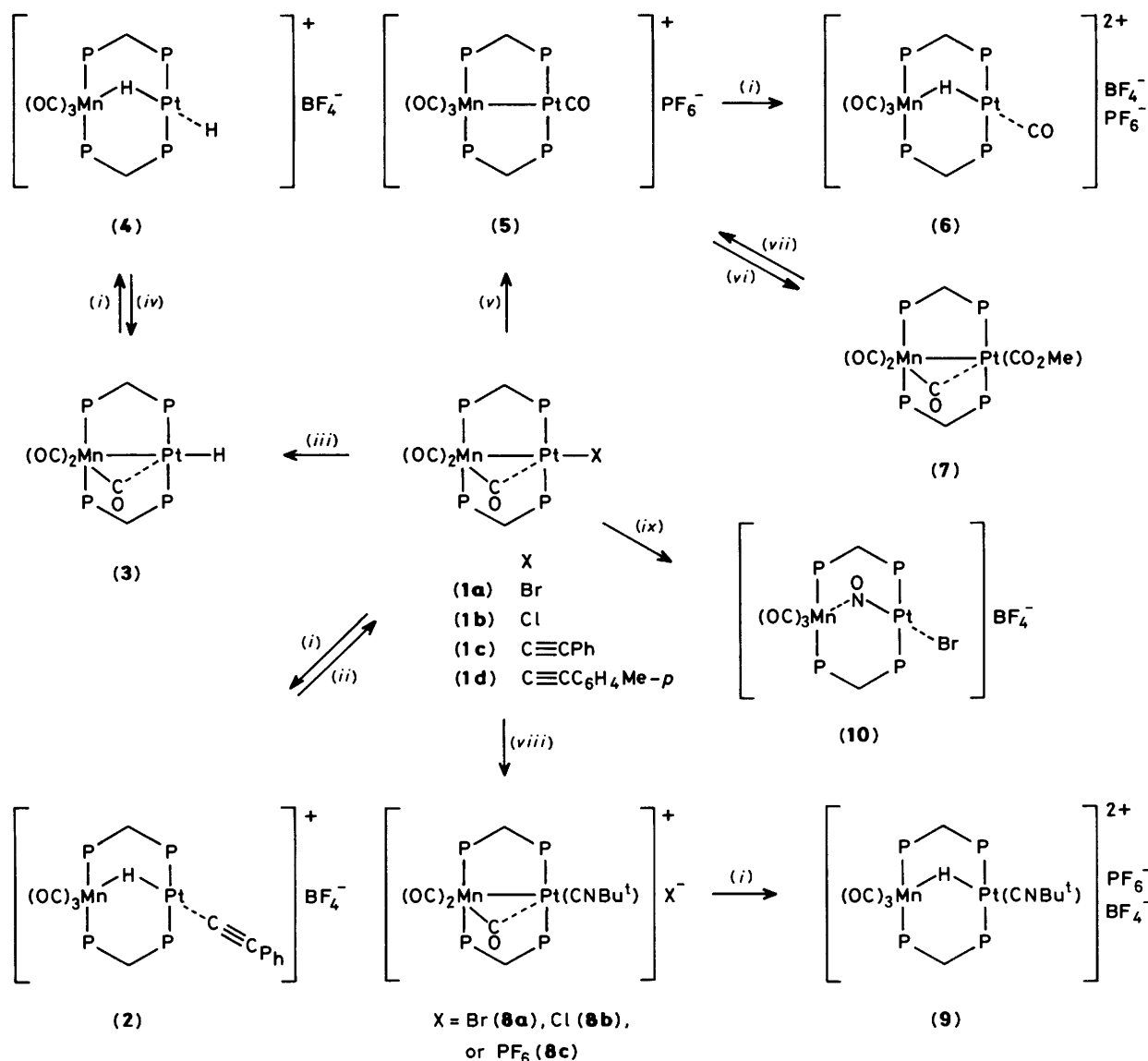
### Results and Discussion

Previously,<sup>14</sup> we showed that [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>PtBr] (**1a**) reacted reversibly with HBF<sub>4</sub> to give [(OC)<sub>3</sub>Mn(μ-H)(μ-dppm)<sub>2</sub>PtBr]BF<sub>4</sub>. We wished to establish whether a corresponding acetylide complex [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>Pt(C≡CR)], *e.g.* with R = Ph, could be made and whether it would protonate similarly to give a μ-hydride, *i.e.* [(OC)<sub>3</sub>Mn(μ-H)(μ-dppm)<sub>2</sub>Pt(C≡CR)]<sup>+</sup>, or whether the acetylide group would protonate to give a μ-alkylidene complex. We found that treatment of the chloro-complex (**1b**) with either Li(C≡CPh) or with PhC≡CH–NEt<sub>3</sub> gave the hoped for phenylacetylide complex (**1c**) in good yield. This complex was characterized by elemental analysis (Table 1) and the <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectrum showed the expected AA'XX' pattern together with satellites due to coupling to platinum-195 (data in Table 2). The pattern

of the P nuclei bonded to manganese is sharp, indicating that in this particular compound the quadrupolar manganese nucleus (<sup>55</sup>Mn, *I* = 5/2, 100% abundant) is relaxing rapidly, even at 20 °C. The PCH<sub>2</sub>P resonance in the <sup>1</sup>H n.m.r. spectrum consisted of a singlet with satellites (due to platinum-195 coupling). The i.r. spectrum in solution showed a band at 2120w cm<sup>–1</sup> due to ν(C≡C) and two bands due to ν(C≡O), 1836s and 1908m cm<sup>–1</sup>; the low-frequency band is probably associated with a semi-bridging CO as with complexes of the type [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-CO)MX], M = Pd or Pt, X = Cl or Br, mentioned above.<sup>12–14</sup> We similarly made the corresponding *p*-tolylacetylide complex (**1d**); details in the Experimental section, characterizing data in Tables 1 and 2.

The presence or absence of a semi-bridging CO in these and other compounds described in this paper is not clear cut. Semi-bridging CO ligands have been described in some detail<sup>15</sup> and the bridging interaction can be induced by electronic and/or steric effects. Sometimes the bridging interaction is weak and in such cases ν(CO) (semi-bridging) is quite high, *e.g.* for [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-CO)PdBr] ν(CO) is at 1860s cm<sup>–1</sup>. It is arguable whether in such a case the CO is bridging or not.<sup>12</sup> For [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-σ,η-CO)Mn(CO)<sub>2</sub>] ν(CO) is at 1645 cm<sup>–1</sup> and the unique CO is strongly bridging.<sup>2</sup>

Treatment of the phenylacetylide complex (**1c**) with an excess of HBF<sub>4</sub> rapidly gave the hydride adduct [(OC)<sub>3</sub>Mn(μ-H)(μ-dppm)<sub>2</sub>Pt(C≡CPh)]BF<sub>4</sub> (**2**). The protonation is reversible and on treatment with methanol the proton was removed, giving back the starting complex (**1c**). The protonated complex was characterized by elemental analysis (Table 1), <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectroscopy (Table 2), and particularly by <sup>1</sup>H-<sup>31</sup>P} n.m.r. spectroscopy; the hydride resonance occurred at –15.0 p.p.m. and the relatively small value of <sup>1</sup>J(PtH) (584 Hz) was in agreement with a bridging hydride. The methylene hydrogens PCH<sub>2</sub>P at ambient temperature showed a broad singlet with satellites (due to platinum-195) and when cooled to –90 °C a broad pattern (possibly of the AB type) was observed. There was no sign of a resonance which might be attributed to a bridging alkylidene group, *viz.* μ-C=CHPh. The i.r. spectrum as a Nujol mull showed three bands due to ν(C≡O) at 1868s,



**Scheme.** (i) HBF<sub>4</sub>; (ii) MeOH; (iii) NaBH<sub>4</sub> or N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O; (iv) water; (v) CO + TIPF<sub>6</sub>; (vi) NaOMe-MeOH; (vii) HPF<sub>6</sub>; (viii) CNBu<sup>+</sup>; (ix) NOBF<sub>4</sub>

1 884s, and 1 952s and a medium-intensity band at 2 060 cm<sup>-1</sup> due to ν(C≡C). A ν(Pt-H) was not observed but it may lie under the acetylide band as the ν(Pt-H) bands appear in the region 2 050–2 060 cm<sup>-1</sup> for related complexes (see below).

We also found that the halogen in [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>PtX] could be replaced by hydride: treatment of the bromide (**1a**) with either NaBH<sub>4</sub> or with hydrazine hydrate gave the corresponding hydride [(OC)<sub>2</sub>Mn(μ-dppm)<sub>2</sub>(μ-CO)PtH]. This was characterized by elemental analysis and by the <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectrum (Table 2). The <sup>1</sup>H-<sup>31</sup>P} n.m.r. spectrum showed a hydride resonance at δ = -3.1 p.p.m., with a large coupling to platinum-195 (1 145 Hz), indicative of a terminal hydride. The i.r. spectrum (in CH<sub>2</sub>Cl<sub>2</sub> solution) showed a band due to ν(Pt-H) at 2 004 cm<sup>-1</sup> and three bands due to ν(C≡O) at 1 794s, 1 822m, and 1 948m cm<sup>-1</sup>. The very low-frequency band clearly indicates a bridging (or semi-bridging) CO and we formulate the compound as (**3**) with such a CO.

Treatment of the yellow terminal hydride complex (**3**) with HBF<sub>4</sub>·Et<sub>2</sub>O immediately gave a bright red complex which we formulate as the dihydride [(OC)<sub>3</sub>Mn(μ-H)(μ-dppm)<sub>2</sub>PtH]-

BF<sub>4</sub>. The protonation was reversed on the addition of water. This proton-addition complex showed a characteristic AA'XX'<sup>31</sup>P-<sup>1</sup>H} n.m.r. pattern with satellites due to platinum-195 and in the <sup>1</sup>H-<sup>31</sup>P} n.m.r. pattern it showed a terminal hydride resonance at δ = -2.0 p.p.m., <sup>1</sup>J(PtH) = 1 272 Hz, and a bridging hydride resonance at -12.3 p.p.m., <sup>1</sup>J(PtH) = 561 Hz: the two hydrides were mutually coupled, <sup>2</sup>J(HH) = 5.8 Hz. We formulate this complex therefore as (**4**). The absence of an i.r. absorption band due to ν(CO) below 1 888 cm<sup>-1</sup> suggests that all the CO groups are terminal, as was found for [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>(μ-H)PtBr]<sup>+</sup>.<sup>14</sup>

We also investigated displacement of the halide ligand from complex (**1a**) or (**1b**) by neutral ligands such as CO or CNBu<sup>+</sup>. Treatment of the bromide (**1a**) with TIPF<sub>6</sub> in the presence of CO gave TlBr and the cationic platinum carbonyl complex [(OC)<sub>3</sub>Mn(μ-dppm)<sub>2</sub>Pt(CO)]PF<sub>6</sub> (**5**). Characterizing elemental analytical and i.r. and n.m.r. data are in the Tables. In particular, in the i.r. spectrum (in CH<sub>2</sub>Cl<sub>2</sub>) there was an absorption band at 2 067 cm<sup>-1</sup> due to ν(C≡O)(Pt-bonded). This complex, which contains a manganese-platinum bond, was

**Table 1.** Analytical and i.r. (cm<sup>-1</sup>) data

Complex	Analyses (%) <sup>a</sup>			I.r. data <sup>b</sup>		
				Carbonyl $\nu(\text{C}\equiv\text{O})$		Others
	C	H	Cl or Br	Solid	Solution	
(1c)-0.25C <sub>6</sub> H <sub>6</sub>	61.2 (61.3)	4.1 (4.1)		1 780s, 1 832s, 1 909m	1 836s, 1 908m	$\nu(\text{C}\equiv\text{C})$ 2 105w (solid) 2 120w (solution)
(1d)	61.4 (61.1)	4.0 (4.2)		1 786s, 1 842s, 1 910m	1 850s, 1 930m	$\nu(\text{C}\equiv\text{C})$ 2 105w (solid) 2 112w (solution)
(2)-1.5CH <sub>2</sub> Cl <sub>2</sub>	51.1 (51.5)	3.65 (3.65)	7.3 (7.3)	1 868s, 1 884s, 1 952s	1 865s, 1 885s, 1 985s	$\nu(\text{C}\equiv\text{C})$ 2 060m (solid) 2 054m (solution)
(3)-CH <sub>2</sub> Cl <sub>2</sub>	54.75 (54.6)	3.85 (4.0)	5.8 (5.9)	1 792s, 1 824s, 1 948s	1 794s, 1 822s, 1 948m	$\nu(\text{Pt-H})$ 2 000m (solid) 2 004m (solution)
(4)-CH <sub>2</sub> Cl <sub>2</sub>	50.4 (50.8)	3.6 (3.8)	5.5 (5.55)	1 888s, 1 940s	1 892s, 1 942s	$\nu(\text{Pt-H})$ 2 059m, 2 018m (solid) 2 061m, 2 015m (solution)
(5)	50.9 (50.8)	3.3 (3.3)		1 880s, 1 898s, 1 960m, 2 051m	1 881s, 1 890s, 1 958m, 2 067m	
(6)	47.4 (47.4)	3.4 (3.3)		1 942s, 1 982s, 2 036m <sup>c</sup>	1 936s, 1 990s, 2 045m	$\nu(\text{Pt-H})$ 2 050m <sup>c</sup> (solid)
(7)-1.5CH <sub>2</sub> Cl <sub>2</sub>	52.4 (52.6)	3.9 (3.9)	8.0 (8.2)	1 778s, 1 824s, 1 899s	1 825s, 1 904m	$\nu(\text{C}=\text{O})$ 1 637m, 1 626m (solid) 1 630m (solution)
(8a)-0.75C <sub>6</sub> H <sub>6</sub> <sup>d</sup>	56.8 (56.7)	8.3 (8.4)	6.4 (6.0)	1 840s, 1 852s, 1 926m	1 860s, 1 942s	$\nu(\text{C}\equiv\text{N})$ 2 185m (solid) 2 188m (solution)
(8b)-0.25C <sub>6</sub> H <sub>6</sub> <sup>e</sup>	57.7 (57.6)	4.5 (4.4)	2.5 (2.8)	1 845(sh), 1 855s, 1 930m	1 850(sh), 1 872s, 1 940m	$\nu(\text{C}\equiv\text{N})$ 2 192m (solid) 2 182m (solution)
(8c) <sup>f</sup>	52.1 (52.3)	3.9 (4.0)		1 850s, 1 868s, 1 933m	1 850(sh), 1 860s, 1 936m	$\nu(\text{C}\equiv\text{N})$ 2 180m (solid) 2 186m (solution)
(9)-CH <sub>2</sub> Cl <sub>2</sub> <sup>g</sup>	47.4 (47.1)	3.9 (3.7)	4.5 (4.7)	1 895w, 1 931s, 1 958s	1 944s, 1 968s, 1 986s	$\nu(\text{C}\equiv\text{N})$ 2 240m $\nu(\text{Pt-H})$ 2 051m } (solid) $\nu(\text{C}\equiv\text{N})$ 2 228w $\nu(\text{Pt-H})$ 2 056w } (solution)
(10) <sup>h</sup>	48.7 (49.0)	3.45 (3.4)	6.2 (6.1)	1 826(sh), 1 850s, 1 981s	1 828(sh), 1 850s, 1 979s	$\nu(\text{NO})$ 1 732vs (solid) $\nu(\text{NO})$ 1 729vs (solution)

<sup>a</sup> Calculated values in parentheses. The presence of solvent of crystallization in some of the complexes was confirmed by <sup>1</sup>H n.m.r. spectroscopy. <sup>b</sup> As Nujol mulls (solid) or in dichloromethane (solution).  $\nu$  = very, s = strong, m = medium, w = weak, and sh = shoulder. The assignments of  $\nu(\text{Pt-H})$  to a bridging hydride in compounds (4), (6), and (9) are very tentative. We suggest that the hydride in these cations is much more strongly bonded to Pt than to Mn, hence the high frequency. However, these bands could be due to  $\nu(\text{CO})$  (terminal) and the values of  $\nu(\text{CO})$  might be at a much lower frequency and obscured. <sup>c</sup> See text. <sup>d</sup> N 1.0 (1.0%). <sup>e</sup> N 0.8 (1.1%). <sup>f</sup> N 1.1 (1.1%). <sup>g</sup> N 0.9 (0.9%). <sup>h</sup> N 1.1 (1.1%).

**Table 2.** <sup>31</sup>P-{<sup>1</sup>H} and <sup>1</sup>H-{<sup>31</sup>P} n.m.r. data

Complex	<sup>31</sup> P <sup>a,b</sup>				<sup>1</sup> H <sup>a,c</sup>				
					Methylene		Hydride		Others
	$\delta\text{P}(\text{Mn})$	$\delta\text{P}(\text{Pt})$	<sup>1</sup> J(PtP)	N <sup>d</sup>	$\delta(\text{PCH}_2\text{P})$	<sup>3</sup> J(PtCH <sub>2</sub> )	$\delta\text{H}$	<sup>1</sup> J(PtH)	
(1c)	81.3	21.0	2 819	107	4.02	38.6			
(1d)	81.6	21.2	2 756	107	3.82	49.8			$\delta(\text{CH}_3)$ 2.06
(2)	53.6	14.1	1 967	78	4.15	36.2	-15.0	584	
(3)	84.7	26.3	2 941	110	3.97	35.6	-3.1	1 145	
(4)	53.7	14.1	2 309	71	4.06	30.8	-2.0	1 272	
							-12.3	561	
							<sup>2</sup> J(HH)	5.8	
(5)	69.5	17.0	2 744	110	4.50	53.7			
(6)	53.9	14.1	2 951	71	4.67	39.1	-17.2	931	
(7)	80.9	17.0	2 991	105	4.05	41.3			$\delta(\text{CH}_3)$ 2.26, <sup>4</sup> J(Pt-H) 5.6
(8a)	81.5	21.3	2 750	107	4.30	49.3			$\delta(\text{Bu}^t)$ 0.51
(8b)	74.5	19.6	2 734	110	4.29	49.3			$\delta(\text{Bu}^t)$ 0.50
(8c)	74.5	19.6	2 722	110	4.28	49.1			$\delta(\text{Bu}^t)$ 0.50
(9)	56.4	13.3	2 101	75	4.47	42.9	-17.1	745	$\delta(\text{Bu}^t)$ 0.52
(10)	57.7	19.5	2 488	112	3.62, 3.06 3.70, <sup>e</sup> 2.99 <sup>e</sup> <sup>2</sup> J(HH) 11.8	f			

<sup>a</sup> Recorded in CD<sub>2</sub>Cl<sub>2</sub> solution at 21 °C, unless stated otherwise. Coupling constants in Hz. <sup>b</sup> Positive shifts to high frequency of external 85% H<sub>3</sub>PO<sub>4</sub>. <sup>c</sup> Chemical shifts ( $\delta$ ) in p.p.m. ( $\pm$  0.01 p.p.m.) relative to SiMe<sub>4</sub>, coupling constants (J) in Hz ( $\pm$  0.3 Hz). <sup>d</sup> N = [<sup>2</sup>J(P<sub>Mn</sub>P<sub>Pt</sub>) + <sup>4</sup>J(P<sub>Mn</sub>P'P<sub>Pt</sub>)]. <sup>e</sup> Data at 0 °C. <sup>f</sup> Not observed.

protonated when treated with HBF<sub>4</sub>·Et<sub>2</sub>O to give the dication [(OC)<sub>3</sub>Mn(μ-H)(μ-dppm)<sub>2</sub>Pt(CO)]<sup>2+</sup> isolated as the mixed

BF<sub>4</sub><sup>-</sup>-PF<sub>6</sub><sup>-</sup> salt (6); characterizing analytical and spectroscopic data are in the Tables. In particular, in the <sup>1</sup>H-{<sup>31</sup>P} n.m.r.

spectrum, it showed a hydride resonance at  $-17.2$  p.p.m. with  $^1J(\text{PtH}) = 931$  Hz and in the i.r. spectrum it showed two bands above  $2000\text{ cm}^{-1}$ , viz. at  $2050$  and  $2036\text{ cm}^{-1}$ , one of which might be due to  $\nu(\text{Pt-H})$  although the dipositive charge (*i.e.* a  $2+$  cation) would make the wavenumbers for CO large. The high values for  $\nu(\text{CO})$  indicated the absence of a semi-bridging CO. We also found that the cationic carbonyl complex (5) reacted reversibly with methoxide ion. Thus, treatment with sodium methoxide in methanol-dichloromethane gave the neutral methoxycarbonyl complex (7). The characterizing data are in the Tables. In particular, in the  $^1\text{H}\{-^{31}\text{P}\}$  n.m.r. spectrum, the observation of coupling between platinum-195 and the  $\text{CH}_3$ ,  $^4J(\text{PtOCH}_3) = 5.6$  Hz shows that the methoxide attack has occurred on the platinum-bonded carbonyl. In the i.r. spectrum ( $\text{CH}_2\text{Cl}_2$  solution) the carbonyl absorption  $\nu(\text{C=O})$  for  $\text{CO}_2\text{Me}$  occurs at  $1630\text{ cm}^{-1}$ . The occurrence of a  $\nu(\text{C=O})$  band at  $1778\text{ cm}^{-1}$  suggests a semi-bridging  $\text{C=O}$  ligand as depicted. Treatment of complex (7) with the equivalent amount of acid gave back the cationic carbonyl complex (5) ( $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. evidence).

*t*-Butyl isocyanide reacted rapidly with the metal-metal bonded bromo complex  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtBr}]$  (1a) to give a cationic complex  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{Pt}(\text{CNBu}^+)\text{Br}]$  (8a); the chloride (8b) was prepared similarly. Treatment of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtBr}]$  with  $\text{TIPF}_6\text{-Bu}^+\text{NC}$  gave the corresponding  $\text{PF}_6$  salt (8c). All three complexes were characterized by elemental analysis and by i.r. and n.m.r. spectroscopy. A semi-bridging  $\text{C=O}$  ligand may be present. The  $\text{PF}_6$  salt was protonated when treated with an excess of  $\text{HBF}_4\cdot\text{Et}_2\text{O}$ . The resultant hydride dication was isolated as the mixed  $\text{PF}_6\text{-BF}_4$  salt (9). It gave a good elemental (C, H) analysis (Table 1); the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum showed a pattern typical of an AA'XX' system, with satellites due to platinum-195 and in the  $^1\text{H}\{-^{31}\text{P}\}$  n.m.r. spectrum the hydride resonance occurs at  $-17.1$  p.p.m.,  $^1J(\text{PtH}) = 745$  Hz. The wavenumbers for  $\nu(\text{C=O})$  suggest the absence of a semi-bridging  $\text{C=O}$  ligand.

We have also studied the action of  $\text{NO}^+$  on the manganese(0)-platinum(i) complex (1a), which when treated with  $\text{NOBF}_4$  in dichloromethane gave an adduct salt in 84% yield. We tentatively formulate this complex as  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2(\mu\text{-NO})\text{PtBr}]\text{BF}_4$  (10) on the basis of elemental analysis (Table 1), the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. data (Table 2), the occurrence of three carbonyl stretching bands in the i.r. spectrum (Table 1), and a very intense band at  $1729\text{ cm}^{-1}$  due to NO. At  $+21^\circ\text{C}$  the  $^1\text{H}$  n.m.r. spectrum shows two broad resonances for  $\text{PCH}_2\text{P}$  which at  $0^\circ\text{C}$  became an AB pattern  $\delta_1 = 3.70$ ,  $\delta_2 = 2.99$ ,  $^2J(\text{H}^1\text{H}^2) = 11.8$  Hz.

## Experimental

The general procedures and apparatus used were the same as in other recent publications from this laboratory.<sup>14</sup>

**Preparations.**— $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{Pt}(\text{C}\equiv\text{CPh})]$  (1c). (i) Using  $\text{HC}\equiv\text{CPh}$ . Phenylacetylene ( $2\text{ cm}^3$ ) and triethylamine ( $2\text{ cm}^3$ ) were added to a solution of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtCl}]$  ( $0.100\text{ g}$ ,  $0.087\text{ mmol}$ ) in dichloromethane ( $15\text{ cm}^3$ ). The resultant mixture was stirred at ambient temperature for 24 h, over which period a white precipitate formed. The mixture was then evaporated to dryness and the required product isolated with benzene. It formed yellow needles from benzene-light petroleum (b.p.  $30\text{--}40^\circ\text{C}$ ). Yield  $0.065\text{ g}$  (58%). The *p*-tolylacetylde complex (1d) was prepared analogously in 65% yield.

(ii) Using  $\text{Hg}(\text{C}\equiv\text{CPh})_2$ . A solution of  $\text{Hg}(\text{C}\equiv\text{CPh})_2$  ( $0.018\text{ g}$ ,  $0.044\text{ mmol}$ ) in benzene ( $3\text{ cm}^3$ ) was added to a stirred solution

of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtCl}]$  ( $0.100\text{ g}$ ,  $0.087\text{ mmol}$ ) in benzene ( $5\text{ cm}^3$ ). The mixture was then stirred for 1 h, filtered, and the filtrate evaporated to dryness under reduced pressure. The residue was triturated with diethyl ether, the product isolated and purified by three recrystallizations from benzene-*n*-hexane. Yield  $0.020\text{ g}$  (19%).

(iii) Using  $\text{Li}(\text{C}\equiv\text{CPh})$ . The compound  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtCl}]$  ( $0.10\text{ g}$ ,  $0.087\text{ mmol}$ ) was added to a stirred solution of  $\text{Li}(\text{C}\equiv\text{CPh})$ , prepared from  $\text{HC}\equiv\text{CPh}$  ( $0.013\text{ g}$ ,  $0.13\text{ mmol}$ ) and  $\text{LiBu}^n$  ( $0.087\text{ mmol}$ ) in tetrahydrofuran (thf) ( $10\text{ cm}^3$ ). The mixture was stirred for a further 2 h and then evaporated to dryness under reduced pressure. The required product was isolated with dichloromethane and purified as above. Yield  $0.059\text{ g}$  (52%).

$[(\text{OC})_3\text{Mn}(\mu\text{-H})(\mu\text{-dppm})_2\text{Pt}(\text{C}\equiv\text{CPh})]\text{BF}_4$  (2). An excess of  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  ( $20\text{ }\mu\text{l}$ ) was added to a solution of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{Pt}(\text{C}\equiv\text{CPh})]$  ( $0.050\text{ g}$ ,  $0.041\text{ mmol}$ ) in dichloromethane ( $3\text{ cm}^3$ ). The mixture was left to stand for 1 h. Diethyl ether was then added to the solution and the required product separated as deep yellow prisms. Yield  $0.031\text{ g}$  (56%).

$[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtH}]$  (3). (i) Using  $\text{NaBH}_4$ . Sodium tetrahydroborate ( $0.050\text{ g}$ ,  $1.3\text{ mmol}$ ) was added with vigorous stirring to a solution of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtBr}]$  ( $0.10\text{ g}$ ,  $0.084\text{ mmol}$ ) in dichloromethane ( $10\text{ cm}^3$ ). Methanol ( $3\text{ cm}^3$ ) was then added and after stirring for a further 20 min the reaction mixture was filtered and the filtrate evaporated to low volume under reduced pressure. The required product separated as yellow microcrystals and was collected. Yield  $0.061\text{ g}$  (61%).

(ii) Using  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ . A mixture of  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  ( $0.1\text{ cm}^3$ ) and  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtBr}]$  ( $0.10\text{ g}$ ,  $0.084\text{ mmol}$ ) was stirred for 16 h in dichloromethane ( $10\text{ cm}^3$ ). The dichloromethane layer was washed with water and then evaporated to dryness and the residue triturated with diethyl ether to give the required product. This formed yellow microcrystals from dichloromethane-diethyl ether. Yield  $0.085\text{ g}$  (85%).

$[(\text{OC})_3\text{Mn}(\mu\text{-H})(\mu\text{-dppm})_2\text{PtH}]\text{BF}_4$  (4). The adduct  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  ( $20\text{ }\mu\text{l}$ ) was added to a solution of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtH}]$  ( $0.10\text{ g}$ ,  $0.090\text{ mmol}$ ) in dichloromethane ( $4\text{ cm}^3$ ). The solution changed immediately to red and on addition of diethyl ether gave the required product as red prisms. Yield  $0.061\text{ g}$  (56%).

$[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{Pt}(\text{CO})]\text{PF}_6$  (5). The compound  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtBr}]$  ( $0.080\text{ g}$ ,  $0.067\text{ mmol}$ ) was added to a stirred solution of  $\text{TIPF}_6$  ( $0.022\text{ g}$ ,  $0.13\text{ mmol}$ ) in acetone ( $20\text{ cm}^3$ ) saturated with carbon monoxide;  $\text{TiBr}$  was precipitated and the solution became orange. The mixture was stirred for 1 h then evaporated to dryness under reduced pressure and the product isolated with dichloromethane. It formed orange prisms from dichloromethane-*n*-hexane. Yield  $0.058\text{ g}$  (61%).

$[(\text{OC})_3\text{Mn}(\mu\text{-H})(\mu\text{-dppm})_2\text{Pt}(\text{CO})]\text{BF}_4(\text{PF}_6)$  (6). An excess of  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  ( $100\text{ }\mu\text{l}$ ) was added to a solution of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{Pt}(\text{CO})]\text{PF}_6$  ( $0.050\text{ g}$ ,  $0.039\text{ mmol}$ ) in dichloromethane ( $3\text{ cm}^3$ ). Diethyl ether ( $3\text{ cm}^3$ ) was then added to the deep red solution and the required product gradually separated, as red prisms. Yield  $0.035\text{ g}$  (66%).

$[(\text{OC})_2\text{Mn}(\mu\text{-dppm})_2(\mu\text{-CO})\text{Pt}(\text{CO}_2\text{Me})]$  (7). A methanolic solution of sodium methoxide ( $0.26\text{ cm}^3$ ,  $0.152\text{ mol dm}^{-3}$ ,  $0.039\text{ mmol}$ ) was added to a solution of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{Pt}(\text{CO})]\text{PF}_6$  ( $0.050\text{ g}$ ,  $0.039\text{ mmol}$ ) in dichloromethane ( $1.5\text{ cm}^3$ ). The required product separated as yellow needles from the resultant solution. Yield  $0.034\text{ g}$  (68%).

$[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{Pt}(\text{CNBu}^+)\text{Cl}]$  (8b). *t*-Butyl isocyanide ( $15\text{ }\mu\text{l}$ ,  $0.18\text{ mmol}$ ) was added to a stirred solution of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PtCl}]$  ( $0.085\text{ g}$ ,  $0.074\text{ mmol}$ ) in benzene ( $10\text{ cm}^3$ ). The required product precipitated almost immediately as a yellow, microcrystalline solid. This was filtered off, washed with diethyl ether, and dried. Yield  $0.051\text{ g}$  (56%). The

analogous bromide complex (**8a**) was prepared similarly in 67% yield.

$[(OC)_3Mn(\mu-dppm)_2Pt(CNBu^t)]PF_6$  (**8c**). The compound  $[(OC)_3Mn(\mu-dppm)_2PtBr]$  (0.20 g, 0.17 mmol) was added with stirring to a solution of  $TlPF_6$  (0.042 g, 0.25 mmol) and  $Bu^tNC$  (21  $\mu$ l, 0.25 mmol) in benzene (20  $cm^3$ ). After 30 min the resultant mixture was evaporated to dryness under reduced pressure and the product was isolated with dichloromethane and washed with diethyl ether. Yield 0.161 g (72%).

$[(OC)_3Mn(\mu-H)(\mu-dppm)_2Pt(CNBu^t)]BF_4(PF_6)$  (**9**). A large excess of  $HBF_4 \cdot Et_2O$  (80  $\mu$ l) was added to a solution of  $[(OC)_3Mn(\mu-dppm)_2Pt(CNBu^t)]PF_6$  (0.050 g, 0.039 mmol) in dichloromethane (3  $cm^3$ ). Diethyl ether was then added until the solution was just turbid. The required product then gradually separated over a period of 1 h as deep red prisms. Yield 0.303 g (56%).

$[(OC)_3Mn(\mu-dppm)_2(\mu-NO)PtBr]BF_4$  (**10**). The salt  $NOBF_4$  (0.020 g, 0.17 mmol) was added to a solution of  $[(OC)_3Mn(\mu-dppm)_2PtBr]$  (0.20 g, 0.17 mmol) in dichloromethane (30  $cm^3$ ). The resultant mixture was then stirred for 3 h, filtered, and n-hexane added to the filtrate until it became just turbid. The solution was then cooled to  $-20^\circ C$  when it deposited the required product as deep red prisms. Yield 0.185 g (84%).

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