The Synthesis of a Dinuclear Anionic Carbonyl Derivative of Manganese, $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$, and its Reactions with Complexes of Group 1B and Group 8A Metals to give Mixed-metal Clusters: Comparative Study of the *X*-Ray Crystal Structures of $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$, $[Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8]$, and $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ †

Jonathan A. Iggo, Martin J. Mays,* and Paul R. Raithby
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Kim Henrick
School of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB

The first anionic dinuclear carbonyl derivative of manganese, $[Mn_2(\mu\text{-}PPh_2)(CO)_8]^-$, has been prepared by deprotonation of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1) and isolated as its bis(triphenylphosphine)-iminium salt, $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$ (2). Complex (2) reacts with complexes of Group 1B and Group 8A metals to give the mixed-metal complexes, $[Mn_2(\mu\text{-}ML)(\mu\text{-}PPh_2)(CO)_8]$ [M = Cu, L = PEt_3 (3a); M = Ag, L = PEt_3 (3b); M = Au, L = PMe_2Ph (3c); M = Au, L = PPh_3 (3d); M = Au, L = PEt_3 (3e)], and $[Mn_2\{\mu\text{-}M(PPh_3)L\}(\mu\text{-}PPh_2)(CO)_8]$ [M = Rh, L = PPh_3 (4a); M = Ir, L = CO (4b)]. Complex (3e) ionises in solution in the presence of excess PEt_3 to give $[Au(PEt_3)_2]^+$ and $[Mn_2(\mu\text{-}PPh_2)(CO)_8]^-$. The crystal structures of (2) and (3c) have been determined and are discussed in relation to that of (1), the structure of which has been redetermined in a different crystalline modification to that previously reported, and to a greater degree of accuracy than that originally achieved. Crystals of (1) are Triclinic, space group $C\bar{1}$, with a = 8.157(2), b = 19.246(3), c = 14.510(2) Å, α = 89.10(3), β = 106.31(3), γ = 90.07(3)°, Z = 4; 2 710 reflections with $I \geqslant 3\sigma(I)$ [$3 < \theta < 25°$], refined to R = 0.0493 and R' = 0.0506. Complex (2) crystallises in space group $P2_1/c$ with a = 10.172(2), b = 30.441(4), c = 17.076(3) Å, β = 100.88(3)°, Z = 4; 4 005 reflections [$I \geqslant 3\sigma(I)$, $3 < \theta < 25°$], refined to R = 0.067 and R' = 0.063. Crystals of (3c) are Monoclinic, space group $P2_1/c$, a = 13.360(2), b = 14.645(1), c = 17.336(3) Å, β = 115.20(1)°, Z = 4; 1 843 reflections [$I \geqslant 2\sigma(I)$, $3 < \theta < 22.5°$], refined to R = 0.079 and R' = 0.065.

Although mono-[1] and tri-nuclear[2] anionic carbonyl complexes of manganese and the heterodinuclear anions[3] $[(CO)_5MnM(CO)_5]^-$ (M = Cr or Mo), are known, there have been no reports of anionic homodinuclear carbonyl derivatives of this metal. Such anionic dinuclear derivatives are well established for other first-row transition metals such as chromium[4] and iron.[5] A corresponding manganese anion would be of interest as a synthetic reagent in the preparation of mixed-metal complexes containing two manganese atoms, since redox condensation reactions between anionic and cationic metal complexes represent a well known route to such mixed-metal clusters.

We have recently reported a new, high-yield synthesis of the phosphido-bridged complex $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1).[6] Complexes of this type, containing bridging ligands, are resistant to fragmentation into lower nuclearity species,[6] and it therefore seemed likely that proton abstraction from (1) to give the dinuclear anion $[Mn_2(\mu\text{-}PPh_2)(CO)_8]^-$ would be feasible. We have previously shown that the phosphorus-capped cluster $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_9]$ can be deprotonated with base to give the anion $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPh)(CO)_9]^-$ (ref.7) and, in this paper, we show that (1) reacts in a similar manner with base to give the corresponding manganese anion, which we have isolated in good yield as its bis(triphenylphosphine)-iminium salt, $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$ (2). The structure of (2) has been determined by *X*-ray analysis and the reaction of the dinuclear anion with complexes of Group 1B and Group 8A metals, to give mixed-metal complexes, are described. The structure of one of these, $[Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8]$, is also reported and is compared with that of (1), the structure of which has been redetermined in a new crystalline modification to that previously reported.[8]

A preliminary account of part of this work has appeared.[9]

Results and Discussion

Preparation of $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$.—$Na[Mn_2(\mu\text{-}PPh_2)(CO)_8]$ was prepared by reaction of (1) with excess $NaBH_4$ in refluxing MeCN solvent and isolated as its $[N(PPh_3)_2]^+$ salt. An alternative route to (2) is *via* the preparation of $K[Mn_2(\mu\text{-}PPh_2)(CO)_8]$ by deprotonation of (1) with methanolic KOH. Complex (2) is readily soluble in tetrahydrofuran (thf), acetone, and chlorinated solvents, moderately soluble in alcohols and toluene, but insoluble in water and hydrocarbon solvents. The salt (2) is remarkably stable to both air and moisture and the solid may be stored in air indefinitely and is unaffected by water. Solutions of (2) are also stable in air for several days. Protonation of (2) with, for example, trifluoroacetic acid, regenerates (1) quantitatively. Infrared (ν_{CO}), ^1H n.m.r., and microanalytical data for (2) are given in Table 1.

The influence of the phosphido-bridge in preventing fragmentation of (1), and hence in allowing deprotonation to give the dinuclear anion, can be seen from a comparison of this reaction with that leading to the preparation of $[Mn_3H_3$-

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† Bis(triphenylphosphine)iminium μ-diphenylphosphido-bis(tetracarbonylmanganate)(*Mn*—*Mn*), μ-dimethylphenylphosphineaurio-μ-diphenylphosphido-bis(tetracarbonylmanganese)(*Mn*—*Mn*), and μ-diphenylphosphido-μ-hydrido-bis(tetracarbonylmanganese)(*Mn*—*Mn*).

Supplementary data available (No. SUP 23811, 78 pp.): H-atom co-ordinates, observed and calculated structure factors, thermal parameters, complete bonds lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Infrared (ν_{CO}), ^{1}H n.m.r., mass spectroscopic, and microanalytical data for the complexes

Compound	ν_{CO}/cm^{-1}	^{1}H N.m.r. [a]	Mass spectra		Analysis (%)	
			H	Fragmentation	C	H
(2) $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$	2 037m, 1 974s, 1 941vs, 1 914w, 1 888m, 1 872m [b]	7.60 (m, 40 H, Ph)			63.4 (63.6)	3.7 (3.8)
(3a) $[Mn_2\{\mu\text{-}Cu(PEt_3)\}(\mu\text{-}PPh_2)(CO)_8]$	2 011s, 1 977s, 1 950s, 1 920s [c]	7.57 (m, 10 H, Ph), 1.76 (q, $J_{PH} = J_{HH} = 7.5$, 6 H, CH$_2$), 1.13 (dt, $J_{PH} = 14.7$, $J_{HH} = 7.5$, 9 H, CH$_3$)	700/702	$M - n$CO, (n = 3—8)	44.2 (44.6)	3.6 (3.6)
(3b) $[Mn_2\{\mu\text{-}Ag(PEt_3)\}(\mu\text{-}PPh_2)(CO)_8]$	2 011s, 1 977s, 1 947m, 1 918s [c]	7.57 (m, 10 H, Ph), 1.83 (q, $J_{PH} = J_{HH} = 7.5$, 6 H, CH$_2$), 1.22 (dt, $J_{PH} = 17.5$, $J_{HH} = 7.5$, 9 H, CH$_3$)	744	$M - n$CO, (n = 4—8)	41.8 (41.9)	3.3 (3.4)
(3c) $[Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8]$	2 023s, 1 982s, 1 955s, 1 927s [c]	7.60 (m, 15 H, Ph), 1.61 (d, $J_{PH} = 9.1$, 6 H, Me)	854	$M - n$CO, (n = 0—8)	38.9 (39.3)	2.5 (2.5)
(3d) $[Mn_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}PPh_2)(CO)_8]$	2 022s, 1 981s, 1 954s, 1 931s [c]	7.59 (m, 25 H, Ph)	978	$M - n$CO, (n = 3—8)	46.2 (46.6)	2.6 (2.6)
(3e) $[Mn_2\{\mu\text{-}Au(PEt_3)\}(\mu\text{-}PPh_2)(CO)_8]$	2 023s, 1 985vs, 1 955s, 1 927s [c]	7.59 (m, 10 H, Ph), 1.96 (m, 6 H, CH$_2$), 1.12 (m, 9 H, CH$_3$)	834	$M - n$CO, (n = 2—8)	37.6 (37.4)	3.0 (3.0)
(4a) $[Mn_2\{\mu\text{-}Rh(PPh_3)_2\}(\mu\text{-}PPh_2)(CO)_8]$	2 016s, 1 981vs, 1 953m, 1 926m [b]	7.61 (m, 40 H, Ph)	676 [d]		58.3 (58.6)	3.5 (3.5)
(4b) $[Mn_2\{\mu\text{-}Ir(PPh_3)(CO)\}(\mu\text{-}PPh_2)(CO)_8]$	2 010s, 1 981s, 1 967 (sh), 1 939w, 1 911m [b]	7.47 (m, 25 H, Ph)	676 [d]		44.7 (46.8)	2.9 (2.5)

[a] Couplings in Hz; d = doublet, t = triplet, q = quintet, m = multiplet. [b] In CH_2Cl_2 solution. [c] In C_6H_{12} solution. [d] See text.

$(CO)_{12}]$,[10] in which $[Mn_2(CO)_{10}]$ is treated with ethanolic KOH followed by acidification with HBF_4. In this reaction the breakdown of $[Mn_2(CO)_{10}]$ to give mononuclear fragments must be postulated in order to account for the trinuclear product which is obtained.

On the basis of the 18-electron rule a Mn–Mn single bond is required for (2) to be a diamagnetic, electron-precise complex. The crystal structure of (2) has been determined in order to obtain further evidence as to the likely presence of such a bond in the crystal.

Crystal Structure of (2).—Crystals of (2) suitable for an *X*-ray diffraction study were grown from dichloromethane–hexane (1 : 1) solution. The molecular structure of (2) is shown in Figure 1. Tables 2 and 3 list the final bond lengths and angles respectively. The Mn–Mn distance of 2.867(2) Å lies in the range expected for Mn–Mn single bonds,[11] and is slightly shorter than that found in (1) [2.951(1) Å, see below]. This shortening may be correlated with the absence of a bridging hydride ligand in (2), since such ligands are generally observed to lengthen metal-metal bonds.[12]

The most striking difference between the structures of (1) and (2) is in the orientation of the carbonyl ligands about the metal centres. This again can be correlated with the absence in (2) of the hydride ligand. In (1) the Mn atoms are approximately octahedrally co-ordinated by the hydride, the phosphorus of the phosphido-bridge, and four carbonyl groups (if the second Mn atom is ignored). In (2) the carbonyl ligands *trans* to the phosphido-bridge move to fill the vacant co-ordination site created by removal of the hydride ligand. The average Mn–Mn–C(carbonyl *trans* to PPh_2) angles in (1) and (2) are 117.5(3) and 88.5(3)° respectively. The remaining carbonyl ligands move in a similar sense, bringing the carbonyl ligands originally *trans* to the hydride atom in (1) into near axial positions in (2). The average Mn–Mn–C(axial carbonyl) angle in (2) is 162.0(3)° [*cf.* the corresponding angle in (1) of 146.0(2)°].

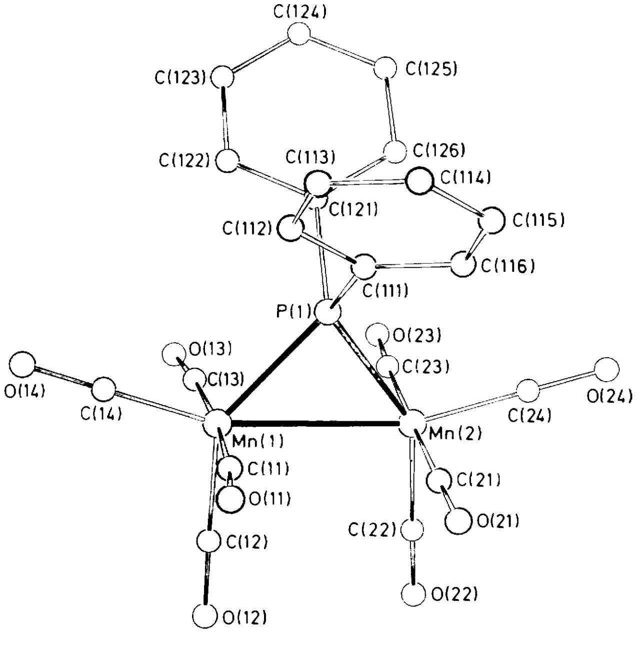

Figure 1. Molecular structure of $[Mn_2(\mu\text{-}PPh_2)(CO)_8]^-$ (2) including the atom numbering scheme

The Mn–CO distances in (2) vary according to the nature of the *trans* or pseudo-*trans* ligands. Thus the average Mn–C(carbonyl *trans* to CO) distance, 1.830(10) Å, is longer than both the Mn–C(carbonyl pseudo-*trans* to PPh_2), average

Table 2. Selected bond lengths (Å) for $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$ (2)

Mn(1)–Mn(2)	2.867(2)	C(22)–O(22)	1.153(11)	Mn(1)–C(11)	1.814(11)	C(23)–O(23)	1.126(12)
Mn(1)–C(12)	1.803(11)	C(21)–O(21)	1.152(13)	Mn(1)–C(13)	1.843(10)	C(24)–O(24)	1.158(15)
Mn(1)–C(14)	1.767(12)	P(1)–C(121)	1.852(8)	Mn(1)–P(1)	2.253(3)	P(1)–C(111)	1.861(8)
Mn(2)–C(23)	1.834(9)	P(2)–C(211)	1.804(5)	Mn(2)–C(22)	1.807(10)	P(2)–N	1.583(7)
Mn(2)–C(24)	1.776(12)	P(2)–C(231)	1.793(5)	Mn(2)–C(21)	1.828(10)	P(2)–C(221)	1.791(5)
Mn(2)–P(1)	2.268(3)	P(3)–C(311)	1.798(6)	C(11)–O(11)	1.154(13)	N–P(3)	1.576(7)
C(12)–O(12)	1.172(13)	P(3)–C(331)	1.774(5)	C(13)–O(13)	1.152(12)	P(3)–C(321)	1.780(6)
C(14)–O(14)	1.173(15)						

Table 3. Selected interbond angles (°) for $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$ (2)

C(11)–Mn(1)–Mn(2)	97.2(4)	C(12)–Mn(1)–Mn(2)	89.5(3)	C(21)–Mn(2)–C(23)	178.9(4)	C(21)–Mn(2)–C(22)	92.5(4)
C(12)–Mn(1)–C(11)	90.1(4)	C(13)–Mn(1)–Mn(2)	88.3(3)	C(21)–Mn(2)–C(24)	90.0(5)	P(1)–Mn(2)–Mn(1)	50.4(1)
C(13)–Mn(1)–C(11)	174.4(5)	C(13)–Mn(1)–C(12)	91.0(4)	P(1)–Mn(2)–C(23)	89.4(3)	P(1)–Mn(2)–C(22)	148.2(3)
C(14)–Mn(1)–Mn(2)	163.4(4)	C(14)–Mn(1)–C(11)	86.6(5)	P(1)–Mn(2)–C(24)	110.4(3)	P(1)–Mn(2)–C(21)	89.7(3)
C(14)–Mn(1)–C(12)	106.7(5)	C(14)–Mn(1)–C(13)	87.8(4)	O(11)–C(11)–Mn(1)	175.3(9)	O(12)–C(12)–Mn(1)	177.9(9)
P(1)–Mn(1)–Mn(2)	50.9(1)	P(1)–Mn(1)–C(11)	90.9(3)	O(13)–C(13)–Mn(1)	174.9(9)	O(14)–C(14)–Mn(1)	178.8(9)
P(1)–Mn(1)–C(12)	140.1(3)	P(1)–Mn(1)–C(13)	91.8(3)	O(23)–C(23)–Mn(2)	176.0(9)	O(22)–C(22)–Mn(2)	177.9(9)
P(1)–Mn(1)–C(14)	113.2(4)	C(23)–Mn(2)–Mn(1)	92.8(4)	O(24)–C(24)–Mn(2)	179.0(9)	O(21)–C(21)–Mn(2)	177.4(9)
C(22)–Mn(2)–Mn(1)	98.0(3)	C(22)–Mn(2)–C(23)	88.6(5)	Mn(2)–P(1)–Mn(1)	78.7(1)	C(111)–P(1)–Mn(1)	122.0(3)
C(24)–Mn(2)–Mn(1)	160.6(3)	C(24)–Mn(2)–C(23)	89.8(4)	C(111)–P(1)–Mn(2)	120.6(3)	C(121)–P(1)–Mn(1)	120.3(3)
C(24)–Mn(2)–C(22)	101.3(4)	C(21)–Mn(2)–Mn(1)	87.0(4)	C(121)–P(1)–Mn(2)	118.6(3)		

1.805(10) Å, and Mn–C(axial CO), average 1.772(10) Å, this last distance showing the expected shortening on replacement of a pseudo-*trans* phosphine ligand by a metal–metal bond. The average M–CO bond length, 1.809(10) Å, in (2) is less than that found in (1) [1.837(7) Å], due, perhaps to increased donation into the CO π* orbitals in (2) brought about by the overall negative charge on this complex. The average C≡O distance increases from 1.137(8) Å in (1) to 1.155(13) Å in (2), supporting this hypothesis.

The average Mn–P distance in (2) [2.260(3) Å] is less than that found in (1), 2.290(2) Å. This shortening may result from a combination of (*i*) donation of the negative charge of (2) into the ligand, (*ii*) the absence of a CO group *trans* to the phosphido-bridge, and/or (*iii*) the shorter Mn–Mn distance found in (2).

Redox Condensation Reactions of (2).—Redox condensation reactions involving the use of anionic transition metal complexes are currently being intensively studied since they can lead to the directed synthesis of mixed-metal clusters. For example, we have recently shown [7,13] that the cluster anion $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPh)(CO)_9]^-$ reacts with neutral or cationic complexes of other transition metals to yield a wide range of mixed-metal compounds in good yields. Mixed-metal clusters containing two directly bonded Mn atoms are, however, relatively unusual and we have therefore investigated some redox condensation reactions of (2). We find that such reactions lead to the formation, in high yield, of a wide variety of mixed-metal complexes containing two manganese atoms.

(*a*) *With Group* 1B *metal complexes*. Reaction of (2) at room temperature in CH_2Cl_2 solution with a small excess of the cationic complexes formed by abstraction of halide ion with $AgClO_4$ from $[\{MI(PEt_3)\}_4]$ (M = Cu or Ag) or [AuClL] {or reaction with a similar excess of $[Au(PMe_2Ph)_2][PF_6]$} gives the mixed-metal complexes $[Mn_2(\mu\text{-}ML)(\mu\text{-}PPh_2)(CO)_8]$, [M = Cu, L = PEt_3 (3a); M = Ag, L = PEt_3 (3b); M = Au, L = PMe_2Ph (3c); M = Au, L = PPh_3 (3d); M = Au,L = PEt_3 (3e)] in high yield. We have also prepared dimanganese–gold complexes from (1) using the general method of Stone and co-workers,[14] in which methane is eliminated from a phosphine–gold–methyl complex by reaction with a metal hydride.

Table 4. Phosphorus-31 n.m.r. data for selected complexes

Compound	^{31}P N.m.r. (δ) [a]
(2)	51.7 (s, $\mu\text{-}PPh_2$)
(3e)	80.6 (s, $\mu\text{-}PPh_2$), −75.7 (s, PEt_3)
$[Au(PEt_3)_2]^+$ [b]	−95.2 (s, PEt_3)
$[Au(PEt_3)_3]^+$ [b]	−100.2 (s, PEt_3)
(3e) + PEt_3 [c,d]	51.7 [s, (2)], −96.4 (s) [c]
(3e) + PEt_3 [c,e]	51.7 [s, (2)], −94.3 (s), −99.9 (s) [c]

[a] In p.p.m. relative to $P(OMe)_3$; ^1H noise decoupled. [b] Ref. 15; recorded at 175 K. [c] See text. [d] Recorded at 273 K. [e] Recorded at 203 K.

Infrared (ν_{CO}), ^1H n.m.r., mass spectroscopic, and microanalytical data for the complexes (3a)—(3e) are given in Table 1. The crystal structure of (3c) has been determined by *X*-ray analysis (see below) and the spectroscopic data suggest that the structures of all the other manganese–gold complexes listed in Table 1 are analogous.

It has previously been shown that gold(I) phosphine complexes such as $[AuCl(PEt_3)]$ take up additional PEt_3 ligands in solution to give, ultimately, in the presence of excess PEt_3, the cationic four-co-ordinate gold complex $[Au(PEt_3)_4]^+$ with ionisation of the chloride ligand (see below).[15]

$$[AuCl(PEt_3)] \xrightarrow{PEt_3} [Au(PEt_3)_2]^+ \xrightarrow{PEt_3} [Au(PEt_3)_3]^+ \xrightarrow{PEt_3} [Au(PEt_3)_4]^+$$

It seemed of interest to investigate whether (3) would similarly ionise in the presence of excess organophosphine. The reaction of (3e) with PEt_3 at −70 °C was therefore studied by ^{31}P n.m.r. spectroscopy. At this temperature the ^{31}P n.m.r. spectrum of (3e) in CD_2Cl_2 solution (Table 4) showed two singlet resonances at δ 80.6 and −75.7 [in p.p.m. from $P(OMe)_3$], assigned to the phosphorus atoms of the $\mu\text{-}PPh_2$ and Au–PEt_3 groups respectively. On addition of *ca.* 1.5 mol equiv. of PEt_3 at −70 °C, the ^{31}P n.m.r. spectrum (again run at −70 °C) showed three resonances at 51.7 ($\mu\text{-}PPh_2$), −94.3, and −99.9 p.p.m. On warming the solution to −10 °C the peaks at −94.3 and −99.9 p.p.m. first broaden and then collapse to a singlet at −96.4 p.p.m., these changes being reversed on cooling to −70 °C. The resonance associ-

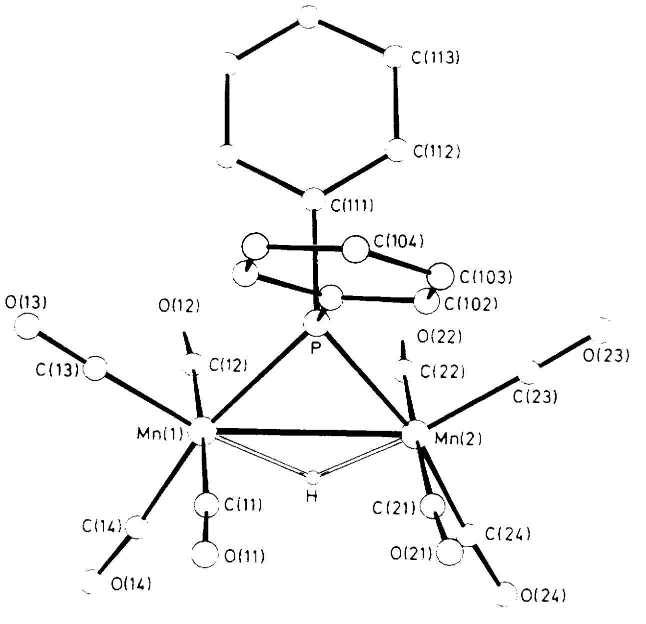

Figure 2. Molecular structure of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1) including the atom numbering scheme

ated with the phosphido-bridge, after addition of the PEt_3, occurs at the same chemical shift as that found in (2) and is essentially unaffected by changes in temperature. These observations are consistent with the initial ionisation of (3e) to give $[Mn_2(\mu\text{-}PPh_2)(CO)_8]^-$ and $[Au(PEt_3)_2]^+$, the latter species then reacting with free PEt_3 as previously described by Mays and Vergnano.[15]

(*b*) *With Group* 8A *metal complexes.* Reaction of (2) with cationic complexes of Rh or Ir (prepared by abstraction of Cl^- with $AgClO_4$ from an appropriate chloro-complex in acetone) afforded the new, mixed-metal complexes $[Mn_2\{\mu\text{-}M(PPh_3)L\}(\mu\text{-}PPh_2)(CO)_8]$ [M = Rh, L = PPh_3 (4a); M = Ir, L = CO (4b). I.r. (ν_{CO}) and ^1H n.m.r. data for these complexes are given in Table 1.

The close similarity in the i.r. (ν_{CO}) absorption patterns of (4a) and (4b) with that of (3c) suggests that these compounds have analogous structures to that determined crystallographically for (3c), in which the heterometal fragment bridges the Mn–Mn bond. These complexes were, however, found to be less stable with respect to loss of the heterometal than the complexes with Group 1B metals. Thus in the mass spectra of (4a) and (4b) the molecular ion peaks were not observed, the highest observed fragment in the spectra of both complexes, m/z = 676, being assigned to $[Mn_2(\mu\text{-}PPh_2)(PPh_2)(CO)_7]^+$. The complexes also decompose slowly in solution.

A Comparative Study of the Crystal Structures of (1), (2), *and* (3c).—Attention has recently been drawn [16,17] to the isolobal relationship that exists between a bridging hydride and a bridging $Au(PR_3)$ ligand. We have therefore determined the crystal structure of (3c) to compare the relative effects of μ-H and μ-$Au(PR_3)$ ligands in modifying the structure of (2). We have also redetermined the structure of (1) in a new crystalline modification which does not show the two-fold crystallographic symmetry found previously.[8]

Crystal structure of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1). Triclinic crystals of (1) were obtained from hexane solution. The crystalline modification of (1) studied by Ibers and co-workers [8] was monoclinic with the molecule showing crystallographic two-fold symmetry. For the crystals of (1) studied here the data were collected in the non-standard space group $C\bar{1}$, with two of the unit-cell angles almost equal to 90°. The hydride atom was located readily and was successfully refined. The structure of (1) is shown in Figure 2.

Table 5. Selected bond lengths (Å) for $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1)

Mn(1)–Mn(2)	2.951(1)	Mn(1)–P	2.290(2)
Mn(1)–C(11)	1.852(5)	Mn(1)–C(12)	1.848(6)
Mn(1)–C(13)	1.805(5)	Mn(1)–C(14)	1.832(6)
Mn(2)–P	2.289(1)	Mn(2)–C(21)	1.857(6)
Mn(2)–C(22)	1.858(6)	Mn(2)–C(23)	1.803(6)
Mn(2)–C(24)	1.837(5)	P–C(101)	1.831(5)
P–C(111)	1.839(4)	C(11)–O(11)	1.129(7)
C(12)–O(12)	1.140(7)	C(13)–O(13)	1.147(6)
C(14)–O(14)	1.133(8)	C(21)–O(21)	1.126(7)
C(22)–O(22)	1.132(7)	C(23)–O(23)	1.144(8)
C(24)–O(24)	1.144(6)		
C(101)–C(106)	1.381(7)	C(102)–C(103)	1.390(10)
C(103)–C(104)	1.345(10)	C(104)–C(105)	1.374(11)
C(105)–C(106)	1.408(9)	C(111)–C(112)	1.375(7)
C(111)–C(116)	1.360(8)	C(112)–C(113)	1.404(10)
C(113)–C(114)	1.330(12)	C(114)–C(115)	1.370(10)
C(115)–C(116)	1.410(9)		

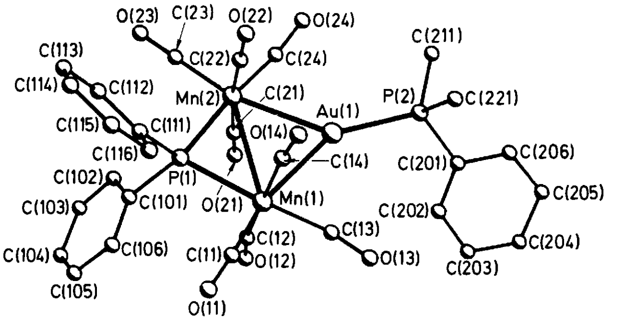

Figure 3. Molecular structure of $[Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8]$ (3c) including the atom numbering scheme

Tables 5 and 6 list the final bond lengths and interbond angles for (1). Although the two-fold crystallographic symmetry axis found in the structure of (1) [8] determined by Ibers is not present in this crystal modification, the molecule possesses approximate C_{2h} symmetry. The major deviations from C_{2h} symmetry in this crystal modification are associated with differences in the Mn–C(carbonyl) bond distances and not with differences in the orientation of the Mn–CO vectors. The Mn–Mn distance of 2.951(1) Å is slightly longer than that found previously [2.937(5) Å].[8] This necessarily requires a longer Mn–P distance and/or a more obtuse bite angle for the phosphido-bridge than that found in the structure of Ibers. Other important bond parameters were not, however, found to differ significantly: *e.g.* (values from ref. 8 in square brackets) Mn–P (average) 2.290(2) [2.284(6) Å]; Mn(1)–P–Mn(2) 80.3(1) [80.0(3)°]; Mn(1)–Mn(2)–P (average) 49.9(1) [50.0(3)°]; Mn–CO (average) 1.837(7) [1.814(18) Å]; C(13)–Mn(1)–C(14) 96.6(3) [96.5(8)°]; P–Mn(1)–C(13) 96.2(2) [96.6(6)°].

Crystal structure of $[Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8]$ (3c). Suitable crystals of (3c) were grown from hexane solution. The structure of (3c) is shown in Figure 3 and Tables 7 and 8 list the final bond lengths and interbond angles respectively. The co-ordination of the manganese atoms in (3c) is closely analogous to that found in (1). Thus the Mn centres of (3c) are approximately octahedrally co-ordinated by the

Table 6. Selected interbond angles (°) for $[\mathrm{Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8}]$ (1)

P–Mn(1)–Mn(2)	49.9(1)	C(11)–Mn(1)–Mn(2)	90.3(2)	C(23)–Mn(2)–C(22)	89.1(2)	C(24)–Mn(2)–Mn(1)	117.6(2)
C(11)–Mn(1)–P	91.2(2)	C(12)–Mn(1)–Mn(2)	91.8(2)	C(24)–Mn(2)–P	167.4(2)	C(24)–Mn(2)–C(21)	87.6(2)
C(12)–Mn(1)–P	91.2(2)	C(12)–Mn(1)–C(11)	177.4(3)	C(24)–Mn(2)–C(22)	90.0(2)	C(24)–Mn(2)–C(23)	96.3(2)
C(13)–Mn(1)–Mn(2)	146.0(2)	C(13)–Mn(1)–P	96.2(2)	Mn(2)–P–Mn(1)	80.3(1)	C(101)–P–Mn(1)	119.9(2)
C(13)–Mn(1)–C(11)	88.8(2)	C(13)–Mn(1)–C(12)	90.2(2)	C(101)–P–Mn(2)	118.9(1)	C(111)–P–Mn(1)	118.7(2)
C(14)–Mn(1)–Mn(2)	117.4(2)	C(14)–Mn(1)–P	167.2(2)	C(111)–P–Mn(2)	119.6(1)	C(111)–P–C(101)	100.6(2)
C(14)–Mn(1)–C(11)	89.9(3)	C(14)–Mn(1)–C(12)	87.9(3)	O(11)–C(11)–Mn(1)	176.3(6)	O(12)–C(12)–Mn(1)	175.9(5)
C(14)–Mn(1)–C(13)	96.6(3)	P–Mn(2)–Mn(1)	49.9(1)	O(13)–C(13)–Mn(1)	178.6(6)	O(14)–C(14)–Mn(1)	175.3(5)
C(21)–Mn(2)–Mn(1)	91.9(2)	C(21)–Mn(2)–P	91.3(1)	O(21)–C(21)–Mn(2)	175.9(5)	O(22)–C(22)–Mn(2)	175.8(5)
C(22)–Mn(2)–Mn(1)	90.2(2)	C(22)–Mn(2)–P	91.4(1)	O(23)–C(23)–Mn(2)	178.5(4)	O(24)–C(24)–Mn(2)	176.1(6)
C(22)–Mn(2)–C(21)	177.3(2)	C(23)–Mn(2)–Mn(1)	146.1(1)	C(102)–C(101)–P	121.8(4)	C(106)–C(101)–P	120.7(4)
C(23)–Mn(2)–P	96.2(2)	C(23)–Mn(2)–C(21)	90.1(2)				

Table 7. Selected bond lengths (Å) for $[\mathrm{Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8}]$ (3c)

Au(1)–Mn(1)	2.696(6)	Au(1)–Mn(2)	2.681(6)
Au(1)–P(2)	2.293(7)	Mn(1)–Mn(2)	3.066(8)
Mn(1)–P(1)	2.297(9)	Mn(1)–C(11)	1.765(35)
Mn(1)–C(12)	1.886(26)	Mn(1)–C(13)	1.832(29)
Mn(1)–C(14)	1.887(24)	Mn(2)–P(1)	2.279(9)
Mn(2)–C(21)	1.823(29)	Mn(2)–C(22)	1.761(26)
Mn(2)–C(23)	1.823(29)	Mn(2)–C(24)	1.721(31)
P(1)–C(101)	1.881(25)	P(1)–C(111)	1.845(25)
P(2)–C(201)	1.790(26)	P(2)–C(211)	1.837(33)
P(2)–C(221)	1.805(28)	C(11)–O(11)	1.129(41)
C(12)–O(12)	1.061(31)	C(13)–O(13)	1.120(38)
C(14)–O(14)	1.103(32)	C(21)–O(21)	1.122(34)
C(22)–O(22)	1.179(31)	C(23)–O(23)	1.140(38)
C(24)–O(24)	1.256(39)		

gold atom, the phosphorus of the phosphido-bridge, and four carbonyl ligands (if the second Mn centre is ignored). The Mn–P(1)–Mn–Au unit is nearly planar with the gold atom lying 0.06 Å above the Mn–P–Mn plane. The hydride in (1) is constrained by symmetry in the structure determined by Ibers [8] to lie in this plane but in the structure of (1) studied here it is 0.16 Å above the plane.

The Mn–Mn bond length [3.066(8) Å] is typical of Mn–Mn single bonds [11] and is longer than those found in both (1) [2.951(1) Å] and (2) [2.867(2) Å]. This lengthening of the metal–metal bond on introduction of a bridging hydride or bridging gold phosphine ligand is also found in other, similar systems (Table 9). The lengthening of the metal–metal bond in (3c) as compared to (1) may be due to the increased steric bulk of the gold phosphine ligand. This greater steric requirement is also seen in the movement of the *cis* carbonyl groups away from the bridging gold atom. The average Mn–Mn–C-(carbonyl *trans* to $\mathrm{PPh_2}$) angle increases from 117.5(2)° in (1) to 125.6(10)° in (3c). In the anion (2) this angle falls to 88.5(3)° due to the carbonyl groups moving to fill the (now vacant) site. The average Au–C(carbonyl *trans* to $\mathrm{PPh_2}$) distance of 2.682(34) Å approaches that required for incipient bridging of the gold–manganese bond. No evidence for such an interaction was seen in the i.r. (ν_{CO}) spectrum of (3c), however (Table 1). The average Mn–CO distances in (1) [1.837(7) Å] and in (3c) [1.812(28) Å] are not significantly different.

The average Mn–P(1) distances in (1) and (3c) of 2.290(2) and 2.288(9) Å are identical within experimental error. This requires a greater bite angle for the phosphido-ligand in (3c) 84.1(3)°, than in (1), 80.2(1)°. The average Mn–P(1) distance in (2) is 2.260(3) Å and the bite angle is 78.7(1)°.

A close structural analogy is thus seen to exist between a bridging hydride and a bridging gold phosphine ligand in this system. The principal structural differences between the complexes resulting from bridging the Mn–Mn bond in (2) with a gold phosphine as compared to a hydride are (*a*) an increase in the Mn–Mn bond length, (*b*) displacement of CO groups away from the bridging ligand, and (*c*) an increase in the phosphido-bridge bite angle. These may be rationalised in terms of the greater steric bulk of the gold phosphine moiety compared with that of a hydride ligand.

Experimental

All reactions were performed under a N_2 atmosphere in N_2-saturated solvents, pre-dried over 4 Å molecular sieves. I.r. spectra were recorded on a Perkin-Elmer 257 instrument in cyclohexane or dichloromethane solution using CO gas as calibrant. Hydrogen-1 and ^{31}P n.m.r. spectra were recorded in $CDCl_3$ solution on a Brucker WH250 spectrometer using the solvent resonances as reference. Mass spectra were recorded on an AEI MS12 instrument. Elemental analyses were performed at Cambridge.

Complex (1) was prepared as previously described by us,[6] and $[\mathrm{Au(PMe_2Ph)_2}][\mathrm{PF_6}]$,[18] $[\mathrm{AuMe(PR_3)}]$,[19] $[\mathrm{AuCl(PR_3)}]$,[20] $[\{\mathrm{AgI(PEt_3)}\}_4]$,[20] $[\{\mathrm{CuI(PEt_3)}\}_4]$,[21] and $[\mathrm{RhCl(PPh_3)_3}]$ [22] by literature methods. All other reagents were obtained from the usual commercial suppliers.

Preparation of $[\mathrm{N(PPh_3)_2}][\mathrm{Mn_2(\mu\text{-}PPh_2)(CO)_8}]$ (2).— $[\mathrm{Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8}]$ (1) (0.520 g, 1 mmol) and $\mathrm{NaBH_4}$ (0.076 g, 2 mmol) were refluxed in MeCN (125 cm^3) for 30 min, by which time the solution had turned golden orange. $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ (0.57 g, 1 mmol) was added, followed by distilled water (100 cm^3). The product was extracted into dichloromethane and the organic layer dried with anhydrous $\mathrm{Na_2SO_4}$. The solution was then taken to dryness and washed several times with hexane to remove unreacted (1). Recrystallisation of the residue from dichloromethane–hexane (1 : 1) to remove excess $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ afforded (2) as orange blocks; yield 0.725 g, 69%.

Alternatively, compound (1) (0.771 g, 1.48 mmol) in $\mathrm{CH_2Cl_2}$ (15 cm^3) was added to a solution of KOH (0.083 g, 1.48 mmol) and $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ (0.570 g, 1 mmol) in methanol (75 cm^3). The resulting solution was stirred for 3 h and then worked-up as described above to afford 0.490 g (64%) of (1) and 0.481 g (31%) of (2).

Prolonged reaction times or an excess of KOH resulted in appreciable decomposition and no increase in yield.

Reactions of (2).—(*a*) *With complexes of Group* 1B *metals.* In a typical experiment a small excess (*ca.* 10%) of the Group 1B reagent ($[\{\mathrm{CuI(PEt_3)}\}_4]$ for (3a); $[\{\mathrm{AgI(PEt_3)}\}_4]$ for (3b); * $[\mathrm{AuCl(PR_3)}]$ for (3c), $\mathrm{R_3} = \mathrm{Me_2Ph}$; for (3d), R = Ph; for

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* Complex (3b) is light sensitive and all operations in its preparation were performed in the dark.

Table 8. Selected interbond angles (°) for $[Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8]$ (3c)

Mn(1)–Au(1)–Mn(2)	69.5(1)	Mn(1)–Au(1)–P(2)	144.0(3)
Mn(2)–Au(1)–P(2)	145.0(3)	Au(1)–Mn(1)–Mn(2)	55.0(1)
Au(1)–Mn(1)–P(1)	102.7(3)	Mn(2)–Mn(1)–P(1)	47.7(2)
Au(1)–Mn(1)–C(11)	163.8(11)	Mn(2)–Mn(1)–C(11)	139.7(11)
P(1)–Mn(1)–C(11)	92.3(11)	Au(1)–Mn(1)–C(12)	93.9(9)
Mn(2)–Mn(1)–C(12)	89.0(11)	P(1)–Mn(1)–C(12)	86.4(10)
C(11)–Mn(1)–C(12)	93.3(13)	Au(1)–Mn(1)–C(13)	70.9(10)
Mn(2)–Mn(1)–C(13)	125.6(10)	P(1)–Mn(1)–C(13)	172.3(11)
C(11)–Mn(1)–C(13)	94.6(15)	C(12)–Mn(1)–C(13)	89.8(12)
Au(1)–Mn(1)–C(14)	81.7(9)	Mn(2)–Mn(1)–C(14)	87.8(11)
P(1)–Mn(1)–C(14)	93.7(9)	C(11)–Mn(1)–C(14)	91.2(13)
C(12)–Mn(1)–C(14)	175.5(13)	C(13)–Mn(1)–C(14)	89.6(11)
Au(1)–Mn(2)–Mn(1)	55.5(1)	Au(1)–Mn(2)–P(1)	103.6(3)
Mn(1)–Mn(2)–P(1)	48.2(2)	Au(1)–Mn(2)–C(21)	83.8(11)
Mn(1)–Mn(2)–C(21)	89.2(13)	P(1)–Mn(2)–C(21)	95.8(12)
Au(1)–Mn(2)–C(22)	88.5(10)	Mn(1)–Mn(2)–C(22)	87.5(12)
P(1)–Mn(2)–C(22)	87.2(10)	C(21)–Mn(2)–C(22)	172.2(14)
Au(1)–Mn(2)–C(23)	162.9(9)	Mn(1)–Mn(2)–C(23)	141.5(9)
P(1)–Mn(2)–C(23)	93.4(9)	C(21)–Mn(2)–C(23)	93.1(14)
C(22)–Mn(2)–C(23)	93.9(13)	Au(1)–Mn(2)–C(24)	70.0(11)
Mn(1)–Mn(2)–C(24)	125.5(12)	P(1)–Mn(2)–C(24)	173.5(12)
C(21)–Mn(2)–C(24)	84.9(14)	C(22)–Mn(2)–C(24)	91.3(13)
C(23)–Mn(2)–C(24)	93.0(14)	Mn(1)–P(1)–Mn(2)	84.1(3)
Mn(1)–P(1)–C(101)	116.2(10)	Mn(2)–P(1)–C(101)	119.7(11)
Mn(1)–P(1)–C(111)	117.9(10)	Mn(2)–P(1)–C(111)	115.8(9)
C(101)–P(1)–C(111)	103.4(11)	P(1)–C(101)–C(102)	120.5(23)
P(1)–C(101)–C(106)	114.9(24)		
P(1)–C(111)–C(116)	122.2(22)	P(1)–C(111)–C(112)	118.6(22)
Au(1)–P(2)–C(211)	116.4(10)	Au(1)–P(2)–C(201)	116.1(8)
Au(1)–P(2)–C(221)	109.0(9)	C(201)–P(2)–C(211)	106.1(13)
C(211)–P(2)–C(221)	103.3(14)	C(201)–P(2)–C(221)	104.5(14)
P(2)–C(201)–C(206)	117.5(19)	P(2)–C(201)–C(202)	124.6(20)
Mn(1)–C(12)–O(12)	170.3(27)	Mn(1)–C(11)–O(11)	175.8(28)
Mn(1)–C(14)–O(14)	174.0(28)	Mn(1)–C(13)–O(13)	168.9(29)
Mn(2)–C(22)–O(22)	179.2(31)	Mn(2)–C(21)–O(21)	178.5(28)
Mn(2)–C(24)–O(24)	172.2(25)	Mn(2)–C(23)–O(23)	179.4(23)

Table 9. Comparison of M–M distances in μ-L ($AuPR_3$ or H) complexes and in the corresponding anions

	$Au(PR_3)$	H	Anion
$[Mn_2(\mu\text{-}L)(\mu\text{-}PPh_2)(CO)_8]$	3.066(8)	2.951(1)	2.867(2)
$[Os_4(\mu\text{-}L)(\mu\text{-}H)(CO)_{13}]$	2.929(2) [a]		2.805(2) [b,c]
$[Os_4(\mu\text{-}L)(\mu\text{-}H)_3(CO)_{12}]$	2.960(1) [a]	2.964(2) [d,e]	2.798(2) [c,f]
$[Os_4(\mu\text{-}L)_2(\mu\text{-}H)_2(CO)_{12}]$	2.977(6) [g]	2.964(2) [d,e]	2.798(9) [c,h]

[a] B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 314. [b] P. A. Dawson, B. F. G. Johnson, J. Lewis, D. A. Kaner, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 961. [c] Average of long Os–Os bonds. [d] B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *Acta Crystallogr., Sect. B*, 1981, **37**, 1728. [e] Average of short Os–Os bonds. [f] B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *Acta Crystallogr., Sect. B*, 1978, **34**, 3765. [g] B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, and M. J. Taylor, *Polyhedron*, 1982, **1**, 105. [h] B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick, and G. Süss, *J. Organomet. Chem.*, 1978, **162**, 179.

(3e), R = Et was stirred in CH_2Cl_2 solution (5 cm^3) over a *ca.* two-fold excess of $AgClO_4$ for *ca.* 15 min. The solution was then filtered under N_2 onto compound (2) (0.027 g, 0.025 mmol) in CH_2Cl_2 (5 cm^3). An immediate reaction occurred and, after *ca.* 15 min, it had gone to completion [i.r. spectrum showed no ν_{CO} absorptions attributable to (2)]. For (3c)—(3e) the reaction was accompanied by a gradual darkening of the solution from yellow to deep brown. The reaction mixture was taken to dryness, the residue redissolved in the minimum of CH_2Cl_2 and separated either by (*i*) chromatography on Florisil (60—100 mesh) using hexane–dichloromethane (1 : 1) as eluant for (3a) and (3b) or (*ii*) preparative t.l.c. on silica using hexane–ethyl acetate (10 : 1) as eluant for (3c)—(3e). In all cases the desired complex was obtained as the only major product. Yields: (3a), 0.017g, 95%, orange-red solid; (3b), 0.017 g, 90%, yellow powder; (3c), 0.013 g, 60%, orange powder; (3d), 0.027 g, 88%, red crystalline solid; (3e) 0.019 g, 89%, orange crystalline solid. (3c) was also prepared by stirring a solution of (2) (0.053 g, 0.05 mmol) and $[Au(PMe_2Ph)_2][PF_6]$ (0.031 g, 0.05 mmol) in CH_2Cl_2 solution (5 cm^3) for 25 min. Separation as above gave (3c), 0.010 g, 23%.

(*b*) *With* $[MCl(PPh_3)_2L]$ *to give* (4a) (M = Rh, L = PPh_3) *and* (4b) (M = Ir, L = CO). $[MCl(PPh_3)_2L]$ [M = Rh, 0.051 g (0.05 mmol); M = Ir, 0.039 g (0.05 mmol)] was vigorously stirred in acetone (5 cm^3) with $AgClO_4$ (0.015 g, 1.5 times excess) for 90 min to yield a yellow solution which was then filtered under N_2 into a solution of (2) (0.053 g, 0.05 mmol) in acetone. An immediate colour change from yellow to orange occurred. The resulting solutions were stirred for 25 min and then treated as follows. For (4a), 10 cm^3 hexane were added to the solution and its volume reduced to precipitate [N-

Table 10. Fractional atomic co-ordinates for $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	0.194 61(8)	0.120 55(3)	0.355 91(5)	O(23)	0.206 3(5)	0.141 4(2)	−0.029 8(3)
Mn(2)	0.088 77(8)	0.129 43(3)	0.144 16(5)	C(24)	−0.141 3(7)	0.129 5(3)	0.082 9(4)
P	0.356 22(14)	0.124 98(6)	0.249 95(9)	O(24)	−0.282 2(5)	0.129 7(3)	0.039 9(4)
C(11)	0.186 6(6)	0.024 4(3)	0.351 1(4)	C(101)	0.497 0(5)	0.052 2(2)	0.244 1(3)
O(11)	0.179 9(5)	−0.034 1(2)	0.352 7(4)	C(102)	0.494 7(8)	0.021 9(3)	0.158 1(5)
C(12)	0.199 7(7)	0.216 2(3)	0.365 7(4)	C(103)	0.606 6(9)	−0.031 6(4)	0.154 2(6)
O(12)	0.202 9(6)	0.274 7(2)	0.377 4(3)	C(104)	0.718 4(8)	−0.056 7(3)	0.234 5(6)
C(13)	0.371 7(7)	0.113 3(3)	0.463 1(4)	C(105)	0.723 6(7)	−0.028 5(3)	0.321 7(5)
O(13)	0.486 5(5)	0.108 7(2)	0.530 1(3)	C(106)	0.609 2(7)	0.025 2(3)	0.326 5(4)
C(14)	0.025 5(7)	0.120 1(3)	0.416 5(4)	C(111)	0.502 8(5)	0.198 5(2)	0.255 5(3)
O(14)	−0.070 7(5)	0.120 5(3)	0.459 7(4)	C(112)	0.586 4(8)	0.227 5(3)	0.341 9(5)
C(21)	0.083 2(6)	0.033 3(3)	0.134 3(4)	C(113)	0.701 8(10)	0.282 1(4)	0.344 5(6)
O(21)	0.075 8(6)	−0.024 4(2)	0.122 6(3)	C(114)	0.733 9(7)	0.306 3(3)	0.264 9(6)
C(22)	0.085 2(6)	0.225 8(3)	0.149 3(4)	C(115)	0.651 9(7)	0.278 4(3)	0.177 9(5)
O(22)	0.076 9(5)	0.284 5(2)	0.146 7(4)	C(116)	0.533 3(7)	0.224 4(3)	0.174 2(4)
C(23)	0.158 5(6)	0.136 6(3)	0.037 0(4)				

Table 11. Fractional atomic co-ordinates for $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$ (2)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	−0.152 42(13)	0.384 67(4)	0.282 77(8)	C(212)	0.3241	0.0926	0.1852
Mn(2)	0.071 28(13)	0.369 63(4)	0.206 19(8)	C(213)	0.2360	0.0837	0.1140
C(11)	−0.062 5(10)	0.379 7(3)	0.384 7(7)	C(214)	0.2781	0.0885	0.0413
O(11)	−0.013 8(8)	0.376 3(3)	0.451 2(5)	C(215)	0.4084	0.1023	0.0399
C(12)	−0.185 5(9)	0.326 5(3)	0.279 9(6)	C(216)	0.4966	0.1113	0.1112
O(12)	−0.203 0(7)	0.288 4(2)	0.279 2(5)	C(221)	0.727 6(4)	0.126 9(2)	0.255 8(3)
C(13)	−0.257 7(9)	0.391 7(3)	0.183 2(6)	C(222)	0.7666	0.1697	0.2421
O(13)	−0.331 6(7)	0.395 6(3)	0.123 6(4)	C(223)	0.8880	0.1773	0.2176
C(14)	−0.281 7(11)	0.409 8(3)	0.322 9(6)	C(224)	0.9703	0.1420	0.2068
O(14)	−0.369 2(9)	0.426 1(3)	0.348 5(5)	C(225)	0.9313	0.0992	0.2206
C(23)	−0.025 5(9)	0.383 3(3)	0.107 4(6)	C(226)	0.8099	0.0916	0.2451
O(23)	−0.079 0(7)	0.390 8(2)	0.044 9(4)	C(231)	0.575 6(5)	0.066 6(1)	0.333 3(3)
C(22)	0.040 8(9)	0.312 2(3)	0.182 6(5)	C(232)	0.5453	0.0263	0.2952
O(22)	0.021 0(7)	0.275 9(2)	0.165 1(4)	C(233)	0.5605	−0.0125	0.3395
C(24)	0.222 0(11)	0.378 7(3)	0.170 5(7)	C(234)	0.6060	−0.0110	0.4218
O(24)	0.319 6(8)	0.384 2(3)	0.146 2(6)	C(235)	0.6363	0.0292	0.4598
C(21)	0.168 2(10)	0.357 0(3)	0.305 1(7)	C(236)	0.6211	0.0680	0.4156
O(21)	0.233 0(8)	0.348 5(2)	0.366 0(5)	C(311)	0.559 2(6)	0.238 6(2)	0.386 5(3)
P(1)	0.000 23(22)	0.432 89(7)	0.254 69(13)	C(312)	0.6688	0.2221	0.4400
C(111)	0.112 1(8)	0.464 2(3)	0.334 1(5)	C(313)	0.7504	0.2504	0.4922
C(112)	0.056 7(9)	0.490 0(3)	0.386 3(5)	C(314)	0.7223	0.2953	0.4909
C(113)	0.139 4(13)	0.516 4(3)	0.442 1(6)	C(315)	0.6127	0.3118	0.4375
C(114)	0.275 9(12)	0.516 3(3)	0.446 1(6)	C(316)	0.5312	0.2835	0.3853
C(115)	0.330 4(10)	0.490 5(3)	0.394 8(6)	C(321)	0.299 4(5)	0.200 0(2)	0.361 6(3)
C(116)	0.250 2(9)	0.464 5(3)	0.338 5(6)	C(322)	0.2070	0.2342	0.3449
C(121)	−0.051 9(8)	0.478 9(2)	0.184 7(5)	C(323)	0.0937	0.2346	0.3800
C(122)	−0.175 5(8)	0.498 8(3)	0.181 6(5)	C(324)	0.0728	0.2009	0.4316
C(123)	−0.211 5(10)	0.533 5(3)	0.130 3(5)	C(335)	0.1652	0.1668	0.4482
C(124)	−0.126 5(12)	0.549 1(3)	0.083 2(6)	C(336)	0.2785	0.1663	0.4132
C(125)	−0.002 7(11)	0.529 5(3)	0.085 9(6)	C(331)	0.410 5(6)	0.223 1(2)	0.225 4(3)
C(126)	0.035 4(9)	0.494 4(3)	0.137 5(5)	C(332)	0.3009	0.2054	0.1735
P(2)	0.564 94(20)	0.116 83(7)	0.277 76(12)	C(333)	0.2759	0.2173	0.0932
N	0.516 3(7)	0.154 2(2)	0.330 1(4)	C(334)	0.3605	0.2469	0.0647
P(3)	0.450 51(21)	0.201 26(7)	0.323 36(12)	C(335)	0.4701	0.2646	0.1166
C(211)	0.454 4(5)	0.106 4(2)	0.183 8(3)	C(336)	0.4951	0.2527	0.1970

$(PPh_3)_2]ClO_4$. The solution was then filtered under N_2 and taken to dryness. The solid residue was redissolved in the minimum of acetone and chromatographed on Florisil (60—100 mesh), using hexane–acetone (3 : 1) as eluant, to afford $[Mn_2\{\mu\text{-}Rh(PPh_3)_2\}(\mu\text{-}PPh_2)(CO)_8]$ (4a), 0.043 g (75%) as a yellow solid after removal of solvent. For (4b) the solution was taken to dryness, the residue redissolved in the minimum of acetone and applied to the top of a chromatography column (Florisil, 60—100 mesh). Elution with acetone–CH_2Cl_2 (3 : 1) afforded $[Mn_2\{\mu\text{-}Ir(PPh_3)(CO)\}(\mu\text{-}PPh_2)(CO)_8]$ (4b) 0.042 g (84%) as an olive coloured solid.

Reaction of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (1) *with* $[AuMe(PR_3)]$ *to give* (3d) (R = Ph) *and* (3e) (R = Et).—In a typical experiment (1) (0.053 g, 0.1 mmol) and a stoicheiometric amount of $[AuMe(PR_3)]$ were stirred in CH_2Cl_2 (5 cm^3) for 2 d. Separation as in (*a*) above gave the desired products, (3d), 0.025 g (60%) and (3e), 0.005 g (39%) [percentage yields based on (1) consumed].

Crystal Data.—For (1). $C_{20}H_{11}Mn_2O_8P$, $M = 520.2$, triclinic, space group $C\bar{1}$, $a = 8.157(2)$, $b = 19.246(3)$, $c = 14.510(2)$ Å, $\alpha = 89.10(3)$, $\beta = 106.31(3)$, $\gamma = 90.07)3)°$, $U =$

Table 12. Atomic co-ordinates (× 10^4) for $[Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8]$ (3c)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Au(1)	7 625(1)	4 783(1)	5 527(1)	C(205)	7 495(30)	8 662(24)	4 494(24)
Mn(1)	7 737(3)	3 356(3)	4 585(3)	C(206)	7 847(22)	7 993(18)	5 166(19)
Mn(2)	7 038(3)	3 235(3)	6 053(3)	C(211)	7 856(23)	6 772(18)	6 730(16)
P(1)	7 237(6)	2 146(5)	5 188(4)	C(221)	9 592(21)	6 392(19)	6 229(19)
C(101)	5 999(22)	1 471(18)	4 457(18)	C(11)	8 069(23)	2 631(19)	3 915(19)
C(102)	5 092(22)	1 422(17)	4 602(17)	O(11)	8 250(18)	2 125(14)	3 499(12)
C(103)	4 202(25)	932(20)	4 036(20)	C(12)	6 231(23)	3 427(18)	3 813(18)
C(104)	4 251(22)	498(17)	3 334(17)	O(12)	5 417(17)	3 580(15)	3 358(14)
C(105)	5 174(25)	541(20)	3 233(20)	C(13)	8 008(21)	4 412(17)	4 140(18)
C(106)	6 107(22)	1 066(18)	3 785(18)	O(13)	8 211(18)	4 967(13)	3 785(13)
C(111)	8 285(21)	1 260(17)	5 728(16)	C(14)	9 220(23)	3 349(18)	5 412(17)
C(112)	8 119(20)	667(17)	6 298(16)	O(14)	10 104(18)	3 396(16)	5 853(13)
C(113)	8 869(22)	−12(18)	6 718(17)	C(21)	5 643(27)	3 573(21)	5 317(21)
C(114)	9 750(25)	−101(22)	6 574(19)	O(21)	4 791(17)	3 781(15)	4 849(14)
C(115)	9 962(25)	443(21)	6 050(19)	C(22)	8 442(24)	3 056(18)	6 739(18)
C(116)	9 238(24)	1 166(20)	5 591(19)	O(22)	9 380(16)	2 940(12)	7 207(12)
P(2)	8 113(6)	6 283(5)	5 856(5)	C(23)	6 542(20)	2 421(16)	6 606(16)
C(201)	7 545(21)	7 075(16)	4 991(17)	O(23)	6 241(17)	1 909(14)	6 956(12)
C(202)	6 867(22)	6 841(19)	4 168(18)	C(24)	6 964(23)	4 139(18)	6 660(19)
C(203)	6 483(25)	7 439(22)	3 459(21)	O(24)	6 938(18)	4 721(13)	7 184(13)
C(204)	6 840(27)	8 346(24)	3 631(23)				

2 185.92 Å^3, $Z = 4$, $D_c = 1.579$ g cm^{-3}, $F(000) = 1\,040$, $\mu(\text{Mo-}K_\alpha) = 11.94$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

For (2). $C_{56}H_{40}Mn_2NO_8P_3$, $M = 1\,057.7$, monoclinic, space group $P2_1/c$, $a = 10.172(2)$, $b = 30.441(4)$, $c = 17.076(3)$ Å, $\beta = 100.88(3)^\circ$, $U = 5\,192.47$ Å^3, $Z = 4$, $D_c = 1.354$ g cm^{-3}, $F(000) = 2\,168$, $\mu(\text{Mo-}K_\alpha) = 5.78$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

For (3c). $C_{28}H_{21}AuMn_2O_8P_2$, $M = 854.27$, monoclinic, space group $P2_1/c$, $a = 13.360(2)$, $b = 14.645(1)$, $c = 17.336(3)$ Å, $\beta = 115.20(1)^\circ$, $U = 3\,069.1$ Å^3, $Z = 4$, $D_c = 1.78$ g cm^{-3}, $F(000) = 1\,504$, $\mu(\text{Mo-}K_\alpha) = 56.42$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

Intensity Measurements.—For (1) and (2) these were collected from crystals of dimensions *ca.* 0.23 × 0.20 × 0.18 mm and 0.36 × 0.29 × 0.12 mm respectively on a Philips PW1100 four-circle diffractometer with Mo-K_α radiation from a graphite monochromator. A θ—2θ scan mode was used with a constant scan speed of 0.5° s^{-1}, a scan width of 0.7°, and reflections with $3.0 \leqslant \theta \leqslant 25.0^\circ$ were examined using the technique previously described.[23] The variance of the intensity (I) was calculated as $\{[\sigma_c(I)]^2 + (0.04I)^2\}^{\frac{1}{2}}$, where $[\sigma_c(I)]$ is the variance due to counting statistics, and the term in I^2 was introduced to allow for other sources of error.

For (3c), a single crystal with dimensions *ca.* 0.247 × 0.114 × 0.057 mm was mounted on a glass fibre, and preliminary cell dimensions and space group determined photographically. The crystal was transferred to a Stoe A.E.D. four circle diffractometer and accurate cell dimensions derived from a least-squares fit of angular measurements of 57 strong reflections in the range $15 \leqslant 2\theta \leqslant 25^\circ$. 4 369 Intensities were recorded in the range $5 \leqslant 2\theta \leqslant 45^\circ$ using graphite-monochromated Mo-K_α radiation and a 24-step ω/θ scan technique. The step width was set at 0.05° and the time for each step varied between 0.75 and 3 s per step dependent on the intensity measured on a 0.75 s prescan; reflections with intensities less than 6 counts were not re-measured but the prescan intensity was retained. Throughout the course of data collection the reflections were subjected to an 'on-line' profile-fitting correction using the method of Clegg.[24] Three intensity check reflections were monitored at hourly intervals during the course of data collection but showed no significant variation in intensity. A semi-empirical absorption correction based on a pseudo-ellipsoid model and 300 azimuthal scan data from 10 independent reflections was applied. Transmission factors ranged from 0.460 to 0.637 for the full data set. Lorentz-polarisation corrections were applied and equivalent reflections averaged to give 1 843 unique observed data $[F > 4\sigma(F)]$.

Structure Solution and Refinement.—For (1), (2), and (3c) the metal and P atoms were located from respective Patterson syntheses, and in each case the remaining non-hydrogen atoms were found from subsequent difference maps. The hydride atom position in (1) was located from a difference map and included in the refinement without constraint. The remaining H atom positions in (1), (2), and (3c) were estimated geometrically (C−H 1.08 Å) and all the non-hydrogen atoms in (1); those excepting the $[N(PPh_3)_2]^+$ phenyl carbon atoms in (2) and the Au, Mn, P, O atoms in (3c) were assigned anisotropic thermal parameters in the final cycles of refinement. For (1) and (2) the reflections were weighted as $1/\sigma^2(F_o)$, and for (3c) a weighting scheme in the form $w = [\sigma^2(F_o) + 0.0002|F_c|^2]^{-1}$ was used.

The final R and R' values were: 0.0493 and 0.0506 for (1), 0.067 and 0.063 for (2), and 0.079 and 0.065 for (3c), where $R' = \Delta w^{\frac{1}{2}}/\Delta w^{\frac{1}{2}}|F_o|$. For (1) and (2) final difference maps calculated showed no regions of significant electron density, while for (3c) the map showed ripples of *ca.* 1e Å^{-3} close to the Au atom position but no other regions of significant electron density.

Complex neutral-atom scattering factors[25] were employed throughout the three structure solutions and refinements. Computations were performed using programs written by Professor G. M. Sheldrick. The molecular plots were drawn by ORTEP2, for (1) and (2), and PLUTO, for (3c) (both written by Dr. D. S. Motherwell).

The final atomic co-ordinates are given in Tables 9, 10, and 11 for compounds (1), (2), and (3c) respectively; bond lengths and angles are in Tables 2—7.

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