Preparation and Reactivity of Halide-bridged Binuclear Carbonyl Manganese and Rhenium Anions, $[M_2(\mu\text{-}X)(CO)_{8-2n}\{(EtO)_2POP(OEt)_2\}_n]^-$ (X = halide; M = Mn, *n* = 1 or 2; M = Re, *n* = 1). *X*-Ray Crystal Structure of $[Mn_2Au(\mu\text{-}Br)(CO)_6(\mu\text{-}tedip)(PPh_3)]$†

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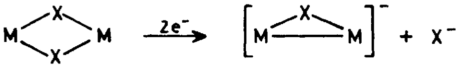
Reactions of bis halide-bridged carbonyl compounds of the type $[Mn_2(\mu\text{-}X)_2(CO)_{8-2n}(\mu\text{-}L\text{–}L)_n]$ [*n* = 1 or 2, M = Mn, L–L = $(EtO)_2POP(OEt)_2$ (tedip), X = Br or I; *n* = 1, M = Re, L–L = tedip, X = Br; *n* = 1, M = Mn, L–L = $Ph_2PCH_2PPh_2$, X = Cl] with excess of sodium amalgam afforded the corresponding binuclear carbonyl metalates of general formula $[M_2(\mu\text{-}X)(CO)_{8-2\pi}(\mu\text{-}L\text{–}L)_n]^-$ as Na^+ salts. Protonation of these anionic species gave the corresponding μ-hydrido complexes $[M_2(\mu\text{-}X)(\mu\text{-}H)(CO)_{8-2n}(\mu\text{-}L\text{–}L)_n]$ and reaction with $[\{M'Cl(PPh_3)\}_n]$ (*n* = 4, M′ = Cu or Ag; *n* = 1, M′ = Au) afforded the triangular mixed-metal clusters $[M_2M'(\mu\text{-}Br)(CO)_{8-2n}(\mu\text{-}tedip)_n(PPh_3)]$ (M = Mn, *n* = 1 or 2; M = Re, *n* = 1). The compounds were characterized by i.r., ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy, and the crystal structure of $[Mn_2Au(\mu\text{-}Br)(CO)_6(\mu\text{-}tedip)(PPh_3)]$ was determined by *X*-ray diffraction methods. Crystals are monoclinic, space group $P2_1/a$ with $Z = 4$ in a unit cell of dimensions $a = 18.581(8)$, $b = 17.652(6)$, $c = 12.326(6)$ Å, and $\beta = 104.42(3)$°. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to $R = 0.058$ for 3 812 observed reflections. The structure shows two Mn atoms at a distance of 3.090(3) Å, bridged by a gold atom from the $Au(PPh_3)$ group [Mn–Au 2.640(3) and 2.679(3) Å], a bromine atom [Mn–Br 2.458(3) and 2.477(3) Å], and by a tedip ligand through the two P atoms. The slightly distorted octahedral co-ordination around each Mn atom is completed by three carbon atoms.

Halogen-bridged binuclear carbonyl complexes of Group 7 metals containing bidentate two-electron donor ligands (L–L), of the type $[M_2(\mu\text{-}X)_2(CO)_{8-2n}(\mu\text{-}L\text{–}L)_n]$, are well known (L–L = E_2Ph_4 or E'_2Ph_2; E = P, As, or Sb; E′ = S, Se, or Te; *n* = 1; M = Mn[1] or Re[2]; L–L = $Ph_2AsCH_2AsPh_2$; *n* = 1 or 2; M = Mn[3] or Re[4]). However, the chemistry of these species has been little explored.

We have recently described[5] similar manganese complexes using the ligand $(EtO)_2POP(OEt)_2$ (tedip = tetraethyl diphosphite), and in this paper we show that chemical reduction of these bis halide-bridged compounds provides a general method of forming anionic binuclear carbonyl derivatives of Group 7 metals [see equation (1)]. These anionic species are



(1)

good precursors in the synthesis of new μ-hydrido derivatives and heterometallic clusters having a triangular core, M_2M' (M = Mn or Re; M′ = Cu, Ag, or Au), by protonation or by reaction with sources of the $[M'(PPh_3)]^+$ cations, respectively. A preliminary account of part of this work has appeared.[5]

Results and Discussion

Preparation of Anionic Dimetallic Carbonyl Complexes.—Chemical reduction of $[Mn_2(\mu\text{-}X)_2(CO)_6(\mu\text{-}tedip)]$ [X = Br, (**1a**), or I, (**1b**)], $[Mn_2(\mu\text{-}X)_2(CO)_4(\mu\text{-}tedip)_2]$ [X = Br, (**2a**), or I, (**2b**)], $[Mn_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}dppm)]$ (**3**) (dppm = $Ph_2PCH_2PPh_2$), or $[Re_2(\mu\text{-}Br)_2(CO)_6(\mu\text{-}tedip)]$ (**4**) in tetrahydrofuran (thf) at room temperature (r.t.) with an excess of sodium amalgam resulted in the displacement of one halide ligand [equation (1)] to form the Na^+ salts of the corresponding anions $[Mn_2(\mu\text{-}X)(CO)_6(\mu\text{-}tedip)]^-$ [(**5a**) and (**5b**)], $[Mn_2(\mu\text{-}X)(CO)_4(\mu\text{-}tedip)_2]^-$ [(**6a**) and (**6b**)], $[Mn_2(\mu\text{-}Cl)(CO)_6(\mu\text{-}dppm)]^-$ (**7**), and $[Re_2(\mu\text{-}Br)(CO)_6(\mu\text{-}tedip)]^-$ (**8**) (Figure 1). These species are highly air-sensitive and no efforts were made to isolate them; nevertheless, they have been characterized from their derivatives (see later) and by spectroscopic data (Table 1). The i.r. spectra for the anions (**5**)—(**8**) show a decrease in the $\tilde{\nu}$(CO) bands relative to their position in the neutral precursors (**1**)—(**4**) and an increase in the number of active vibrational modes in accord with the lowering of the symmetry from C_{2v} to C_s for the hexacarbonyls, and from D_{2h} to C_{2v} for the tetracarbonyl species. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**5a**) and (**8**) are also in agreement with the proposed structures.

In these complexes a single metal–metal bond is required by the effective atomic number (e.a.n.) rule and this is consistent with the results of a crystallographic determination of the structure of a related complex $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$.[6] Furthermore, in these molecules the metal–metal bond should be a reactive site because the corresponding molecular orbital (m.o.) is the highest occupied molecular orbital (h.o.m.o.), as demonstrated[7] by a m.o. analysis on the related anion $[Mo_2(\mu\text{-}Cl)(CO)_4(\eta\text{-}C_5H_5)_2]^-$. Therefore, we have studied the reactions of the anionic carbonyl complexes (**5**)—(**8**) with some electrophiles, resulting in addition of the electrophile to the electron-rich metal–metal bond.

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† μ-Bromo-μ-tetraethyl diphosphite-μ-triphenylphosphineaurio-bis-(tricarbonylmanganese).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

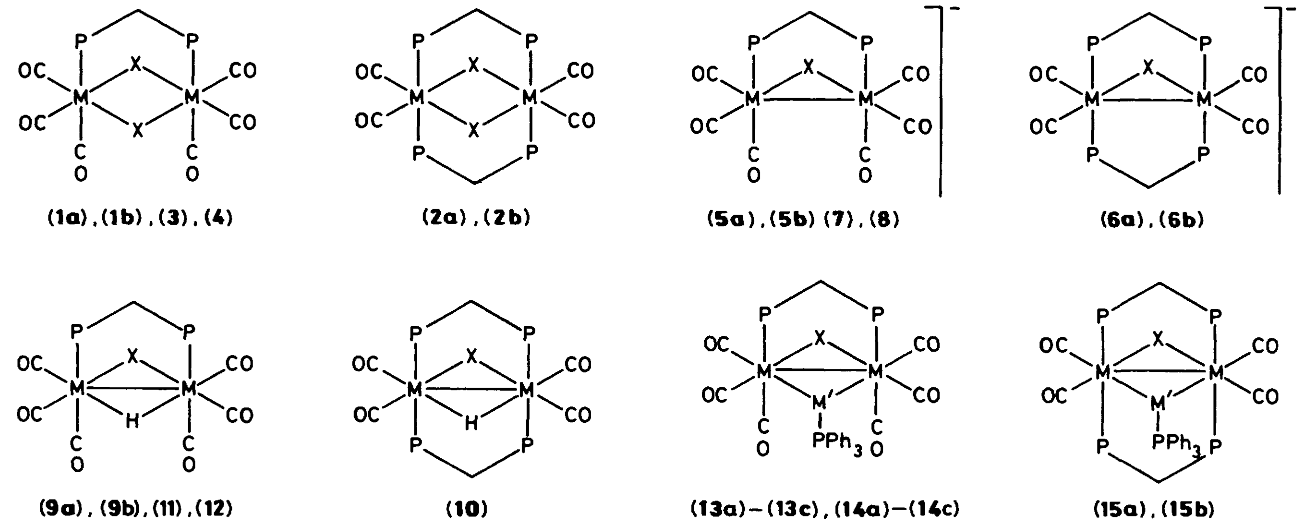
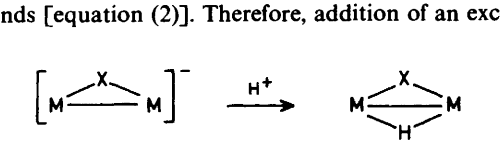

(1a), (1b), (3), (4) (2a), (2b) (5a), (5b) (7), (8) (6a), (6b)
(9a), (9b), (11), (12) (10) (13a)–(13c), (14a)–(14c) (15a), (15b)

Figure 1. Structures of complexes formed. P⌒P = tedip or dppm; X = Cl, Br, or I; M = Mn or Re (see text)

Protonation of the Anionic Dimetallic Carbonyl Complexes (**5**)—(**8**).—Protonation of metal–carbonyl anions is a classical route to hydridocarbonyl compounds,[8,9] and for species (**5**)—(**8**) the reaction must afford the corresponding μ-hydrido compounds [equation (2)]. Therefore, addition of an excess of degassed H_3PO_4 (aqueous 85%) to a thf solution of species (**5**)—(**8**) affords, cleanly, the corresponding hydrides [Mn_2(μ-X)(μ-H)$(CO)_6$(μ-tedip)] [X = Br, (**9a**), or I, (**9b**)], [Mn_2(μ-Br)(μ-H)$(CO)_4$(μ-tedip)$_2$] (**10**), [Mn_2(μ-Cl)(μ-H)$(CO)_6$(μ-dppm)] (**11**), and [Re_2(μ-Br)(μ-H)$(CO)_6$(μ-tedip)] (**12**) (Figure 1). Spectroscopic data (Table 1) support the structures proposed for these compounds. The ^1H n.m.r. spectra are especially informative, all showing a high-field signal whose pattern is indicative of a symmetrical μ-hydrido ligand between the two metal atoms [triplet for compounds (**9**), (**11**), and (**12**), and quintet for (**10**), due to *cis* ^2J(P–H) coupling]. Furthermore, the triplets assignable to the Me groups of the tedip ligand appear at two distinct chemical shifts [not well resolved in (**10**) and (**12**)] thus indicating non-equivalent magnetic environments at both sides of the M_2P_2 or M_2P_4 plane in the molecule; for comparison, the ^1H n.m.r. spectra of the more symmetrical precursors (**1**), (**2**), and (**4**) showed only one well resolved triplet for the Me groups of the ligand.



(2)

Again, a single metal–metal bond is required by the e.a.n. rule for compounds (**9**)—(**12**), although a more precise description should be made in terms of a delocalized two-electron three-centre bond;[9] accordingly, the crystal structure of (**10**) has been resolved by *X*-ray diffraction[5] and a Mn–Mn distance of 2.936(3) Å was found, revealing a substantial metal–metal interaction.

Reaction of Anionic Dimetallic Carbonyl Complexes with [M′(PPh_3)]$^+$ (M′ = Cu, Ag, *or* Au).—Reaction of polynuclear carbonyl anions with appropriate sources of the [M′(PPh_3)]$^+$ cations (M′ = Cu, Ag, or Au) is a well known route to the synthesis of heterometallic clusters containing a Group 1B metal.[10] Theoretical studies on the bonding properties of the Au(PH_3) and Cu(PH_3) groups indicate[11] that they are not isolobal and this has been invoked to explain structural differences found in several Au(PPh_3) containing compounds and its copper or silver analogues.[11,12] Our binuclear carbonyl anions would be a simple system where the results of electronic differences could be observed. We have therefore studied reactions of anions (**5a**), (**6a**), and (**8**) with sources of the cations [M′(PPh_3)]$^+$ (M′ = Cu, Ag, or Au).

When [{CuCl(PPh_3)}$_4$], [{AgCl(PPh_3)}$_4$], or [AuCl(PPh_3)] were treated with one equivalent (thf solution) of the anions (**5a**), (**8**), and (**6a**) (in the presence of $TlPF_6$, to remove halide ions in the reactions with manganese anions) a rapid reaction occurred, affording the heterometallic clusters [Mn_2M′(μ-Br)$(CO)_6$(μ-tedip)(PPh_3)] (**13a**)—(**13c**), [Re_2M′(μ-Br)$(CO)_6$(μ-tedip)(PPh_3)] (**14a**)—(**14c**), and [Mn_2M′(μ-Br)$(CO)_4$(μ-tedip)$_2$$(PPh_3)$] (**15a**) and (**15b**), respectively (M′ = Cu, Ag, or Au for each cluster respectively). The reactions of the manganese anions were more selective than those involving rhenium, which also gave minor amounts of uncharacterized products. The spectroscopic data (Table 1) completely support the proposed structures for these compounds (Figure 1). In particular, the ^1H n.m.r. spectra showed that there are two types of tedip methyl groups in very different magnetic environments, probably due to the strong magnetic influence of the phenyl rings of the PPh_3 ligand on one side of the M_2P_2 or M_2P_4 plane.*

In accord with the proposed structures for these compounds, two resonance signals are expected to appear in their ^{31}P-{^1H} n.m.r. spectra, a doublet for the tedip phosphorus and a triplet or quintet for the phosphine phosphorus atom, as a result of ^3J(PP) coupling. Because of the quadrupolar broadening effects of Re, Au, and especially, Mn and Cu nuclei, this ^3J(PP) coupling could only be observed in most cases from the spectra measured at −50 °C; even at this temperature the spectra of the Mn–Cu complexes (**13a**) and (**15a**) remained broad. When comparisons between low and room temperature could be made, no significant alterations in the spectra (chemical shifts and coupling constants) were observed.

In addition, the structure of a significant member of this group of compounds, (**13c**), was confirmed by an *X*-ray study.

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* Care must be taken in the choice of solvent; the data discussed here were taken in $CDCl_3$ solution. We have observed that the ^1H n.m.r. spectrum of compound (**13a**) in C_6D_6 solution shows only one well resolved triplet for the Me groups of the tedip ligand. Therefore, apparently, the benzene solvent 'magnetically equalizes' both sides of the Mn_2P_2 plane.

Table 1. Infrared and ^1H n.m.r. spectroscopic data for the complexes (coupling constants in Hz)

	Compound	$\tilde{\nu}(CO)/cm^{-1}$	^1H N.m.r.[a]/p.p.m.	$^{31}P\text{-}\{^1H\}$ N.m.r.[b]/p.p.m.
(1a)	$[Mn_2(\mu\text{-Br})_2(CO)_6(\mu\text{-tedip})]$	2 059s, 2 042s, 1 978vs (sh), 1 972vs, 1 936vs[c]	4.4 (m, OCH_2, 2 H), 1.5 (t, 7, Me, 3 H)	145.9
(2a)	$[Mn_2(\mu\text{-Br})_2(CO)_4(\mu\text{-tedip})_2]$	1 957s, 1 888s[c]	4.36 (m, OCH_2, 2 H), 1.42 (t, 7, Me, 3 H)	162.2
(5a)	$Na[Mn_2(\mu\text{-Br})(CO)_6(\mu\text{-tedip})]$	1 992s, 1 927vs, 1 904s, 1 872m, 1 863m, 1 843m[d]		176.1[e]
(6a)	$Na[Mn_2(\mu\text{-Br})(CO)_4(\mu\text{-tedip})_2]$	1 903m, 1 854vs, 1 819s[d]		
(7)	$Na[Mn_2(\mu\text{-Cl})(CO)_6(\mu\text{-dppm})]$	1 972s, 1 907vs, 1 870s br, 1 850s, 1 840s (sh), 1 825m (sh)[d]		
(8)	$Na[Re_2(\mu\text{-Br})(CO)_6(\mu\text{-tedip})]$	2 004s, 1 949vs, 1 907s, 1 890s, 1 866s[d]		121.7[e]
(9a)	$[Mn_2(\mu\text{-Br})(\mu\text{-H})(CO)_6(\mu\text{-tedip})]$	2 064s, 2 032s, 1 985s, 1 969s, 1 948s[f]	4.06 (m, OCH_2, 8 H), 1.37 and 1.31 (2 × t, 7, Me, 12 H), −15.3 [t, ^2J(P–H) 28.4, μ-H, 1 H]	158.3
(9b)	$[Mn_2(\mu\text{-I})(\mu\text{-H})(CO)_6(\mu\text{-tedip})]$	2 056s, 2 029s, 1 983s, 1 968s, 1 946s[f]	4.02 (m, OCH_2, 8 H), 1.36 and 1.29 (2 × t, 7, Me, 12 H), −16.4 [t, ^2J(P–H) 29, μ-H, 1 H]	158.6
(10)	$[Mn_2(\mu\text{-Br})(\mu\text{-H})(CO)_4(\mu\text{-tedip})_2]$	1 976m, 1 954s, 1 894s[c]	3.98 (m, OCH_2, 16 H), 1.26 (m, Me, 24 H), −15.2 [qnt, ^2J(P–H) 24, μ-H, 1 H]	168.7
(11)	$[Mn_2(\mu\text{-Cl})(\mu\text{-H})(CO)_6(\mu\text{-dppm})]$	2 049s, 2 022s, 1 967s, 1 950s, 1 931vs[f]	7.5—7.1 (m, Ph, 20 H), 2.8 [t, ^2J(P–H) 12, CH_2, 2 H], −13.3 [t, ^2J(P–H) 21, μ-H, 1 H]	47.5
(12)	$[Re_2(\mu\text{-Br})(\mu\text{-H})(CO)_6(\mu\text{-tedip})]$	2 070s, 2 044s, 1 982vs, 1 966vs, 1 942vs[f]	4.04 (m, OCH_2, 8 H), 1.34 (m, Me, 12 H), −12.8 [t, ^2J(P–H) 12.5, μ-H, 1 H]	104.9
(13a)	$[Mn_2Cu(\mu\text{-Br})(CO)_6(\mu\text{-tedip})(PPh_3)]$	2 019s, 1 978vs, 1 939s, 1 927s (sh), 1 887vs[g]	7.45—7.35 (m, Ph, 15 H), 3.96 (m, OCH_2, 8 H), 1.27 and 1.20 (2 × t, 7, Me, 12 H)	162.6 (s, br, Mn–tedip), −5.4 (s, br, Cu–PPh_3)[h]
(13b)	$[Mn_2Ag(\mu\text{-Br})(CO)_6(\mu\text{-tedip})(PPh_3)]$	2 022s, 1 975vs, 1 943s, 1 925s, 1 896vs[e]	7.6—7.5 (m, Ph, 15 H), 3.95 (m, OCH_2, 8 H), 1.29 and 1.15 (2 × t, 7, Me, 12 H)	161.3 (br, Mn–tedip), 8.3 [2 × dt, $^1J(^{109}Ag\text{–}P)$ 380.4, $^1J(^{107}Ag\text{–}P)$ 329.4, ^3J-(tedip–P) 9.8, Ag–PPh_3]
(13c)	$[Mn_2Au(\mu\text{-Br})(CO)_6(\mu\text{-tedip})(PPh_3)]$	2 026s, 1 986vs, 1 947s, 1 931s, 1 905s[e]	7.5—7.4 (m, Ph, 15 H), 3.9 (m, OCH_2, 8 H), 1.25 and 1.1 (2 × t, 7, Me, 12 H)	157.5 (br, Mn–tedip), 66.3 [t, ^3J(tedip–P) 19, Au–PPh_3][i]
(14a)	$[Re_2Cu(\mu\text{-Br})(CO)_6(\mu\text{-tedip})(PPh_3)]$	2 036s, 1 996vs, 1 950s, 1 930s, 1 898vs[c]	7.6—7.3 (m, Ph, 15 H), 3.94 (m, OCH_2, 8 H), 1.28 and 1.19 (2 × t, 7, Me, 12 H)	108.5 [d, ^3J(tedip–PPh_3) 5, Re–tedip], 2.9 (br, Cu–PPh_3)[h]
(14b)	$[Re_2Ag(\mu\text{-Br})(CO)_6(\mu\text{-tedip})(PPh_3)]$	2 034s, 1 997vs, 1 946s, 1 926s, 1 896s[c]	7.5—7.3 (m, Ph, 15 H), 3.96 (m, OCH_2, 8 H), 1.28 and 1.13 (2 × t, 7, Me, 12 H)	108.7 [dd, ^2J(tedip–Ag) 14.7, ^3J(tedip–PPh_3) 4.9, Re–tedip], 15.3 [2 × dt, $^1J(^{109}Ag\text{–}P)$ 393.1, $^1J(^{107}Ag\text{–}P)$ 339.3, Ag–PPh_3][h]
(14c)	$[Re_2Au(\mu\text{-Br})(CO)_6(\mu\text{-tedip})(PPh_3)]$	2 039s, 2 010vs, 1 952s, 1 933vs, 1 907vs[c]	7.6—7.4 (m, Ph, 15 H), 3.96 (m, OCH_2, 8 H), 1.27 and 1.1 (2 × t, 7, Me, 12 H)	106.3 [d, ^3J(tedip–PPh_3) 9.5, Re–tedip], 73.3 (t, 9.5, Au–PPh_3)
(15a)	$[Mn_2Cu(\mu\text{-Br})(CO)_4(\mu\text{-tedip})_2(PPh_3)]$	1 938w, 1 912vs, 1 856m, 1 842m (sh)[d]	7.6—7.4 (m, Ph, 15 H), 3.94 (m, OCH_2, 16 H), 1.25 and 1.1 (2 × t, 7, Me, 24 H)	171.5 (br, Mn–tedip), −8.5 (br, Cu–PPh_3)
(15b)	$[Mn_2Ag(\mu\text{-Br})(CO)_4(\mu\text{-tedip})_2(PPh_3)]$	1 934w, (sh), 1 911vs, 1 853s[c]	7.6—7.4 (m, Ph, 15 H), 3.96 (m, OCH_2, 16 H), 1.26 and 1.03 (2 × t, 7, Me, 24 H)	169.9 (br, Mn–tedip), 4.7 [2 × dq, $^1J(^{109}Ag\text{–}P)$ 342.6, $^1J(^{107}Ag\text{–}P)$ 296.8, ^3J-(tedip–P) 10, Ag–PPh_3]

[a] In $CDCl_3$ solution, relative to $SiMe_4$. [b] Relative to external H_3PO_4(85%), $CDCl_3$ solution at r.t. unless otherwise stated. [c] In CH_2Cl_2 solution. [d] In thf solution. [e] In thf solution, external D_2O lock. [f] In light petroleum solution. [g] In toluene solution. [h] In CD_2Cl_2 solution at −50 °C. [i] In $[^2H_8]$toluene solution at −50 °C.

Crystal Structure of $[Mn_2Au(\mu\text{-Br})(CO)_6(\mu\text{-tedip})(PPh_3)]$ **(13c)**.—The structure of **(13c)** is presented in Figure 2 together with the atomic labelling system. Selected bond distances and angles are given in Table 2.

The two manganese atoms, which are separated by a distance of 3.090(3) Å, are symmetrically bridged by a gold atom from the $Au(PPh_3)$ group [Mn(1)–Au 2.679(3) and Mn(2)–Au 2.640(3) Å] and by a bromine atom [Mn(1)–Br 2.458(3) and Mn(2)–Br 2.477(3) Å]. All four atoms are perfectly planar. The two Mn atoms are also bridged by a tedip ligand, through the two P atoms [Mn(1)–P(1) 2.218(4) and Mn(2)–P(2) 2.226(4) Å]. The tedip bridge is nearly orthogonal to the other two

Table 2. Selected bond distances (Å) and angles (°) for complex (**13c**)

Mn(1)–Au	2.679(3)	Mn(1)–C(1)	1.83(2)	P(1)–O(7)	1.61(1)	C(1)–O(1)	1.15(2)
Mn(2)–Au	2.640(3)	Mn(1)–C(2)	1.80(2)	P(2)–O(7)	1.63(1)	C(2)–O(2)	1.12(2)
Mn(1)–Br	2.458(3)	Mn(1)–C(3)	1.74(1)	P(1)–O(8)	1.58(1)	C(3)–O(3)	1.19(2)
Mn(2)–Br	2.477(3)	Mn(2)–C(4)	1.81(2)	P(1)–O(9)	1.58(1)	C(4)–O(4)	1.14(2)
Mn(1)–P(1)	2.218(4)	Mn(2)–C(5)	1.79(1)	P(2)–O(10)	1.60(1)	C(5)–O(5)	1.16(2)
Mn(2)–P(2)	2.226(4)	Mn(2)–C(6)	1.78(2)	P(2)–O(11)	1.58(1)	C(6)–O(6)	1.15(2)
Au–P(3)	2.320(4)						
Mn(1)–Au–Mn(2)	71.0(1)	Br–Mn(1)–C(2)	175.9(5)	C(2)–Mn(1)–C(3)	90.6(7)	P(2)–Mn(2)–C(4)	170.5(6)
Mn(1)–Au–P(3)	135.9(1)	Br–Mn(1)–C(3)	91.6(5)	Au–Mn(2)–C(4)	84.3(6)	P(2)–Mn(2)–C(5)	88.2(5)
Mn(2)–Au–P(3)	151.9(2)	P(1)–Mn(1)–Br	88.7(1)	Au–Mn(2)–C(5)	74.4(5)	P(2)–Mn(2)–C(6)	97.7(6)
Mn(1)–Br–Mn(2)	77.5(1)	P(1)–Mn(1)–Au	88.3(1)	Au–Mn(2)–C(6)	164.1(6)	C(4)–Mn(2)–C(5)	88.2(8)
Au–Mn(1)–Br	105.4(1)	P(1)–Mn(1)–C(1)	174.1(5)	Br–Mn(2)–C(4)	93.9(6)	C(4)–Mn(2)–C(6)	91.1(8)
Au–Mn(2)–Br	106.0(1)	P(1)–Mn(1)–C(2)	87.8(5)	Br–Mn(2)–C(5)	177.9(5)	C(5)–Mn(2)–C(6)	90.2(8)
Au–Mn(1)–C(1)	85.9(5)	P(1)–Mn(1)–C(3)	92.8(5)	Br–Mn(2)–C(6)	89.5(6)	Mn(1)–P(1)–O(7)	118.0(4)
Au–Mn(1)–C(2)	72.5(4)	C(1)–Mn(1)–C(2)	90.5(7)	P(2)–Mn(2)–Br	89.8(1)	Mn(2)–P(2)–O(7)	117.7(4)
Au–Mn(1)–C(3)	163.0(5)	C(1)–Mn(1)–C(3)	92.8(8)	P(2)–Mn(2)–Au	86.2(1)	P(1)–O(7)–P(2)	124.1(6)
Br–Mn(1)–C(1)	92.8(6)						

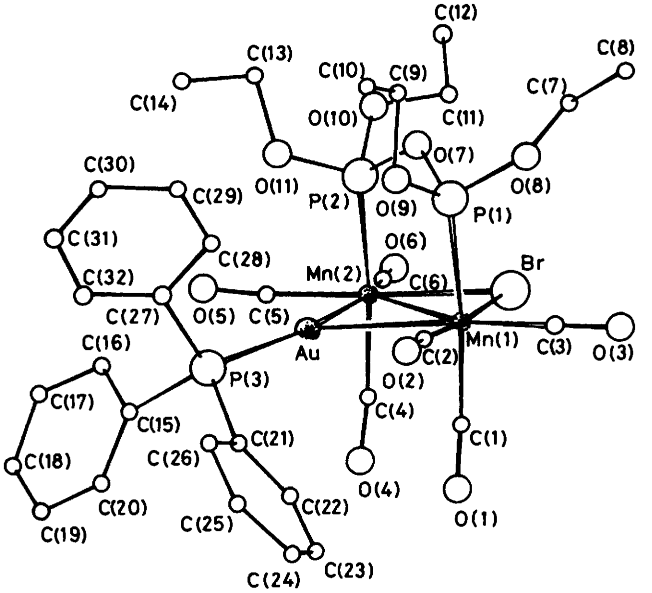

Figure 2. View of the molecular structure of the complex [$Mn_2Au(\mu$-$Br)(CO)_6(\mu$-tedip$)(PPh_3)$] with the atomic labelling system

bridging species, the dihedral angle between the Mn_2AuBr plane and the mean plane passing through Mn(1), Mn(2), P(1), and P(2) being 88.5(1)°.

Each Mn atom is in a distorted octahedral arrangement, involving the Au and Br atoms, the phosphorus of tedip, and three carbon atoms from carbonyl groups (if the second Mn centre is neglected). All carbonyl groups are terminal, the Mn–C–O angles ranging from 173(1) to 179(1)°. The Mn–Mn separation is longer than that found in the binuclear hydride- and bromide-bridged complex [$Mn_2(\mu$-$H)(\mu$-$Br)(CO)_4$(tedip$)_2$] [2.936(3) Å [5]].

The structure of (**13c**) is comparable with that of [$Mn_2Au(\mu$-$PPh_2)(CO)_8(PPh_3)$] [6] in which the bromine bridge is replaced by a phosphido bridge, the Au–Mn distances are only a little longer [2.681(6) and 2.696(6) Å], and the Mn–Mn distance is a little shorter [3.066(8) Å]. This Mn–Mn separation was considered as a typical Mn–Mn single bond and the elongation with respect to that found in the μ-hydrido precursor [2.951(1) Å] was suggested to arise from steric effects. In our opinion electronic factors can also be of great influence. Therefore, if we compare the mean ṽ(CO) bands of (**5a**) (anion), (**13c**) (gold bridge), or (**9a**) (hydride bridge), 1 900, 1 959, and 1 989 cm^{-1} respectively, we note that the $Au(PPh_3)$ group introduces substantially more electron density at the Mn centres than does the H atom. Following a m.o. calculation by Mason and Mingos [13] in related systems, this increase of electronic density would be reflected in an increased population in molecular orbitals that are antibonding with respect to the Mn–Mn bond, giving a rationale for the relatively long Mn–Mn distance observed.

Experimental

All reactions were performed under an argon atmosphere. Solvents were purified according to standard procedures [14] and distilled prior to use. I.r. spectra were recorded on a Perkin-Elmer 298 spectrometer using polystyrene as a reference. Hydrogen-1 and ^{31}P-{^1H} n.m.r. spectra were recorded on a Varian FT-80A spectrometer. Mass spectra were obtained on an AEI MS902 instrument. Elemental analyses were performed on a Perkin-Elmer 240 microanalyser. Complexes (**1**) and (**2**) were prepared as previously described,[5] and (**3**) and (**4**) by similar procedures. The compounds [$\{CuCl(PPh_3)\}_4$],[15] [$\{AgCl(PPh_3)\}_4$],[16] and [$AuCl(PPh_3)$] [17] were prepared by literature methods. All other reagents were obtained from the usual commercial suppliers. Light petroleum refers to that fraction of b.p. 60—65 °C. Spectroscopic data for compounds are given in Table 1.

Preparation of thf Solutions of the Anionic Carbonyl Complexes (**5**)—(**8**).—All preparations were very similar. Typically, 10 cm^3 of a 10^{-2} mol dm^{-3} thf solution of the neutral precursor (**1**)—(**4**) were stirred at r.t. over 20—40 min with sodium amalgam (15 g, 0.7%); deep red solutions were obtained for all manganese compounds, and a yellow solution for the rhenium anion. These solutions were filtered prior to use and contained equimolar amounts of sodium halide and sodium carbonylmetalate; however, no interference from the halide ions was observed in our subsequent reactions.

Preparation of Hydrido Complexes (**9**)—(**12**).—All preparations were very similar. In a typical experiment, an excess of degassed H_3PO_4 (aqueous 85%, 0.1 cm^3) was added to a thf solution of the corresponding carbonylanion (10 cm^3, see above). Reaction occurred immediately, producing orange solutions for manganese compounds, and a colourless solution for the rhenium compound. The solvent was removed under vacuum and the residual oil was extracted with light petroleum (3 × 8 cm^3) and filtered. Crystallization at −20 °C afforded orange, or colourless, crystals which were separated from the mother-liquors, washed with cold light petroleum (3 cm^3), and dried under vacuum. All these compounds are air-stable solids, soluble in all common organic solvents. [Mn$_2$(μ-Br)(μ-H)(CO)$_6$(μ-tedip)] (**9a**): orange-yellow crystals (yield 79%) (Found: C, 27.8; H, 3.60. Calc. for C$_{14}$H$_{21}$BrMn$_2$O$_{11}$P$_2$: C, 27.25; H, 3.45%). [Mn$_2$(μ-I)(μ-H)(CO)$_6$(μ-tedip)] (**9b**): orange crystals (yield 30%); mass spectrum [*m*/*z* (calc.)] M^+ 664.1 (663.87) (Found: C, 25.75; H, 3.4. Calc. for C$_{14}$H$_{21}$IMn$_2$O$_{11}$P$_2$: C, 25.35; H, 3.20%). [Mn$_2$(μ-Br)(μ-H)(CO)$_4$(μ-tedip)$_2$] (**10**): orange crystals (yield 64%); mass spectrum [*m*/*z* (calc.)] M^+ 819.9 (820.02, ^{81}Br) and 817.9 (818.02, ^{79}Br) (Found: C, 29.5; H, 6.00. Calc. for C$_{20}$H$_{41}$BrMn$_2$O$_{14}$P$_4$: C, 29.3; H, 5.05%). [Mn$_2$(μ-Cl)(μ-H)(CO)$_6$(μ-dppm)] (**11**): orange crystals (yield 65%) (Found: C, 53.95; H, 3.80. Calc. for C$_{31}$H$_{23}$ClMn$_2$O$_6$P$_2$: C, 53.25; H, 3.30%). [Re$_2$(μ-Br)(μ-H)(CO)$_6$(μ-tedip)]·$\frac{1}{6}$C$_6$H$_{14}$ (**12**): colourless crystals (yield 61%) (Found: C, 19.85; H, 2.45. Calc. for C$_{14}$H$_{21}$BrO$_{11}$P$_2$Re$_2$·$\frac{1}{6}$C$_6$H$_{14}$: C, 20.15; H, 2.35%); the presence of solvent in the crystals was verified by ^{1}H n.m.r. spectroscopy.

Preparation of Cluster Compounds (**13**)—(**15**).—Reaction conditions were all very similar. Typically, 1 equivalent of [{Cu(PPh$_3$)Cl}$_4$], [{Ag(PPh$_3$)Cl}$_4$], or [Au(PPh$_3$)Cl] was added to a thf solution (10 cm^3) containing the appropriate carbonyl anion (in the presence of 1 equivalent of TlPF$_6$ for manganese compounds). Reaction took place quickly and after stirring (10 min) the solvent was evaporated under vacuum. The isolation of the complexes differs slightly and so is described separately.

[Mn$_2$Cu(μ-Br)(CO)$_6$(μ-tedip)(PPh$_3$)] (**13a**). The residue was extracted with Et$_2$O (3 × 8 cm^3) and filtered. Light petroleum (15 cm^3) was added to the resulting red solution and the solvents were evaporated under vacuum to afford a red solid which was washed with cold light petroleum (3 cm^3) and dried under vacuum (yield 70%). The compound can be crystallized by slow diffusion (thf–light petroleum) at −20 °C to afford red plates (Found: C, 41.7; H, 4.00. Calc. for C$_{32}$H$_{35}$BrCuMn$_2$O$_{11}$P$_3$: C, 40.8; H, 3.75%).

[Mn$_2$Ag(μ-Br)(CO)$_6$(μ-tedip)(PPh$_3$)] (**13b**). The residue was extracted with light petroleum–diethyl ether (3:1, 3 × 8 cm^3) and filtered. Removal of the solvent under vacuum gave a red solid which was washed with cold light petroleum (3 cm^3) and dried under vacuum (yield 56%) (Found: C, 38.05; H, 3.70. Calc. for C$_{32}$H$_{35}$AgBrMn$_2$O$_{11}$P$_3$: C, 38.9; H, 3.6%).

[Mn$_2$Au(μ-Br)(CO)$_6$(μ-tedip)(PPh$_3$)] (**13c**). The residue was extracted with light petroleum–diethyl ether (3:1, 3 × 8 cm^3) and filtered to give a red solution. Solvent was removed under vacuum to yield a red solid which was washed with cold light petroleum (3 cm^3) and dried under vacuum (yield 60%). The red plates used in the *X*-ray study were grown by slow diffusion of light petroleum into a concentrated thf solution of the compound (Found: C, 36.55; H, 3.35. Calc. for C$_{32}$H$_{35}$AuBrMn$_2$O$_{11}$P$_3$: C, 35.7; H, 3.3%).

[Re$_2$Cu(μ-Br)(CO)$_6$(μ-tedip)(PPh$_3$)] (**14a**). The residue was extracted with light petroleum–toluene (3:1, 3 × 8 cm^3). The resulting yellow solution was filtered and dried under vacuum. Addition of light petroleum (5 cm^3) to the oily residue and stirring afforded a yellow powder (yield 40%). Recrystallization from diethyl ether–light petroleum at −20 °C yielded yellow needles which were shown to contain *ca.* $\frac{1}{8}$ C$_6$H$_{12}$ by ^{1}H n.m.r. spectroscopy (Found: C, 32.7; H, 3.00. Calc. for C$_{32}$H$_{35}$BrCuO$_{11}$P$_3$Re$_2$·$\frac{1}{8}$C$_6$H$_{12}$: C, 32.4; H, 3.05%).

[Re$_2$Ag(μ-Br)(CO)$_6$(μ-tedip)(PPh$_3$)] (**14b**). The residue was extracted with light petroleum–toluene (3:1, 3 × 8 cm^3) and filtered. The resulting yellow solution was concentrated under vacuum to *ca.* 3 cm^3 and then light petroleum (7 cm^3) was added. Cooling the mixture at −20 °C yielded yellow needles which were washed with cold light petroleum (3 cm^3) and dried under vacuum (yield 45%) (Found: C, 30.8; H, 2.85. Calc. for C$_{32}$H$_{35}$AgBrO$_{11}$P$_3$Re$_2$: C, 31.1; H, 2.90%).

[Re$_2$Au(μ-Br)(CO)$_6$(μ-tedip)(PPh$_3$)] (**14c**). The residue was extracted with diethyl ether–light petroleum (1:1, 3 × 8 cm^3) and filtered. The solution was concentrated under vacuum and

Table 3. Fractional atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses, for the non-hydrogen atoms of complex (**13c**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Au	2 434(1)	1 247(1)	7 527(1)	C(9)	3 853(27)	−887(30)	9 762(41)
Mn(1)	3 250(1)	1 698(1)	9 533(2)	C(10)	4 286(21)	−1 214(22)	9 233(30)
Mn(2)	1 544(1)	1 500(1)	8 857(2)	C(91)	4 376(45)	−673(49)	9 534(69)
Br	2 356(1)	1 911(1)	10 674(1)	C(101)	3 698(40)	−1 195(40)	9 221(62)
P(1)	3 325(2)	495(2)	10 069(4)	C(11)	1 324(10)	121(10)	11 266(15)
P(2)	1 745(2)	296(2)	9 383(3)	C(12)	754(10)	−291(11)	11 702(16)
P(3)	2 644(2)	1 044(2)	5 772(3)	C(13)	1 646(10)	−1 098(10)	8 472(15)
O(1)	3 068(8)	3 245(6)	8 536(12)	C(14)	1 697(9)	−1 416(10)	7 353(15)
O(2)	4 323(7)	1 376(8)	8 225(12)	C(15)	1 850(8)	1 287(8)	4 607(12)
O(3)	4 471(7)	2 157(8)	11 416(13)	C(16)	1 169(9)	933(10)	4 679(14)
O(4)	1 371(8)	3 008(7)	7 807(13)	C(17)	523(11)	1 069(11)	3 793(17)
O(5)	525(6)	924(7)	6 797(10)	C(18)	604(12)	1 564(12)	2 968(19)
O(6)	252(7)	1 759(8)	9 764(13)	C(19)	1 251(11)	1 924(11)	2 924(16)
O(7)	2 570(5)	71(5)	10 142(8)	C(20)	1 893(9)	1 775(9)	3 774(15)
O(8)	3 842(6)	324(9)	11 268(11)	C(21)	3 388(7)	1 657(8)	5 557(12)
O(9)	3 659(7)	−55(6)	9 304(12)	C(22)	3 442(9)	2 368(9)	5 970(14)
O(10)	1 263(6)	−112(6)	10 126(8)	C(23)	4 013(10)	2 835(11)	5 850(16)
O(11)	1 604(5)	−263(5)	8 352(8)	C(24)	4 527(11)	2 585(12)	5 345(17)
C(1)	3 131(9)	2 657(10)	8 952(13)	C(25)	4 473(13)	1 875(14)	4 862(21)
C(2)	3 880(9)	1 474(9)	8 685(11)	C(26)	3 875(11)	1 362(11)	4 979(17)
C(3)	3 991(8)	1 965(10)	10 634(12)	C(27)	2 891(7)	86(7)	5 451(10)
C(4)	1 466(10)	2 440(10)	8 260(16)	C(28)	3 397(8)	−297(9)	6 331(14)
C(5)	954(9)	1 168(9)	7 562(13)	C(29)	3 631(10)	−1 024(10)	6 096(16)
C(6)	753(10)	1 657(9)	9 395(14)	C(30)	3 336(9)	−1 348(9)	5 018(15)
C(7)	3 686(11)	106(11)	12 235(17)	C(31)	2 858(9)	−964(9)	4 238(15)
C(8)	4 431(11)	−137(11)	13 037(16)	C(32)	2 614(8)	−227(8)	4 398(12)

cooled to −20 °C affording a yellow microcrystalline solid which was washed with cold light petroleum (3 cm^3) and dried under vacuum (yield 35%). This solid was found (by ^{1}H n.m.r.) to retain *ca.* $\frac{1}{2}$ C_6H_{12} (Found: C, 30.05; H, 2.90. Calc. for $C_{32}H_{35}AuBrO_{11}P_3Re_2\cdot\frac{1}{2}C_6H_{12}$: C, 30.45; H, 3.0%).

$[Mn_2Cu(\mu\text{-}Br)(CO)_4(\mu\text{-tedip})_2(PPh_3)]$ (**15a**). The residue was extracted with Et_2O (3 × 8 cm^3) and filtered to give a red solution. Addition of light petroleum (15 cm^3) and removal of the solvents under vacuum yielded a red solid which was washed with cold light petroleum (3 cm^3) and dried under vacuum (yield 62%). This solid decomposes slowly in air (Found: C, 39.5; H, 4.85. Calc. for $C_{38}H_{55}BrCuMn_2O_{14}P_5$: C, 39.5; H, 4.85%).

$[Mn_2Ag(\mu\text{-}Br)(CO)_4(\mu\text{-tedip})_2(PPh_3)]$ (**15b**). As for (**15a**), an orange solid was obtained (yield 55%) (Found: C, 39.2; H, 4.75. Calc. for $C_{38}H_{55}AgBrMn_2O_{14}P_5$: C, 38.4; H, 4.6%).

Crystal-structure Determination of the Complex (**13c**).—*Crystal data.* $C_{32}H_{35}AuBrMn_2O_{11}P_3$, $M = 1\,075.29$, monoclinic, $a = 18.581(8)$, $b = 17.652(6)$, $c = 12.326(6)$ Å, $\beta = 104.42(3)°$, $U = 3\,915(3)$ Å^3 (by least-squares refinement from the θ values of 28 reflections accurately measured), $\lambda = 0.710\,69$ Å, space group $P2_1/a$, $Z = 4$, $D_c = 1.824$ g cm^{-3}, $F(000) = 2\,096$. A flattened crystal of approximate dimensions 0.10 × 0.44 × 0.64 mm was used for the structural analysis, $\mu(\text{Mo-}K_\alpha) = 55.25$ cm^{-1}. A correction for the absorption[18] was applied (maximum and minimum transmission factors 1.6681 and 0.8168) using the program ABSORB written by F. Ugozzoli, University of Parma.

Data collection and processing. Siemens AED diffractometer, θ—2θ mode, using niobium-filtered Mo-K_α radiation; all reflections in the range 3—25° were measured. Of 7 258 independent reflections, 3 812 having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis.

Structure analysis and refinement. Direct and Fourier methods, full-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for Au, Mn, Br, P, O atoms, and carbon atoms of the carbonyl groups. An ethyl group was found to be disordered and distributed in two positions of non-equal occupancy factors [C(9) and C(10), 0.6; C(91) and C(101), 0.4]. No attempts were made to locate the hydrogen atoms. The weighting scheme used in the last cycles was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.9359$ and $g = 0.005$. Final R and R' values were 0.058 and 0.076 respectively. The SHELX system of computer programs was used.[19] Atomic scattering factors, corrected for anomalous dispersion of Au, Mn, Br, and P are given in ref. 20. All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 3.

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