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Manganese–Group 11 Element and –Zinc Mixed-Metal Clusters Derived from the Unsaturated Hydride $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})]$ [tedip = $(EtO)_2POP(OEt)_2$]. X-ray Structures of $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)(CO)_6(\mu\text{-tedip})]$ and $[Mn_2\{\mu\text{-}Zn(N,N'\text{-}Me_2NCH_2CH_2NMe_2)\}(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})]$

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The unsaturated hydride $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})]$ (1) [tedip = $(EtO)_2POP(OEt)_2$] is prepared by treatment of $[Mn_2(\mu\text{-}Br)_2(CO)_6(\mu\text{-tedip})]$ with 4 equiv of $Li[HBEt_3]$ or $K[HB(HCMeEt)_3]$ in tetrahydrofuran at room temperature. Compound 1 reacts with $[AuMe(PPh_3)]$ at room temperature to give the unsaturated cluster $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)(CO)_6(\mu\text{-tedip})]$ (6) which in turn gives the tetrametallic compound $[Mn_2(\mu\text{-}AuPPh_3)_2(CO)_6(\mu\text{-tedip})]$ upon reaction with $[AuMe(PPh_3)]$ under photochemical conditions. The structure of 6 has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/a$ with $Z = 4$ in a unit cell of dimensions $a = 18.015(8)$ Å, $b = 20.700(8)$ Å, $c = 10.230(6)$ Å, and $\beta = 94.90(2)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods, and refined by full matrix least squares on the basis of 3579 observed reflections to R and R_w values of 0.0562 and 0.0577, respectively. In the triangular cluster the Mn–Mn distance, 2.739(3) Å, is short and consistent with a formal electronic unsaturation, whereas the Mn–Au distances, 2.665(2) and 2.638(2) Å, are normal. This cluster reacts easily with CO at room temperature to give the fluxional compound $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)(CO)_7(\mu\text{-tedip})]$, where the H ligand bridges Au and Mn atoms. Compound 1 reacts with CuX (X = Cl, I) to give $[Mn_2(\mu\text{-}H)(\mu\text{-}X)(CO)_6(\mu\text{-tedip})]$ and the hexametallic cluster $[Mn_4Cu_2(\mu\text{-}H)_6(CO)_{12}(\mu\text{-tedip})_2]$, which exhibits dynamic behavior in solution. The related trimetal clusters $[Mn_2M(\mu\text{-}H)_3(CO)_6(PPh_3)(\mu\text{-tedip})]$ (M = Cu, Ag) can be prepared from 1 through one or several of the following routes: (a) reaction with $[HCu(PPh_3)]_6$; (b) reaction with $[M(BH_4)(PPh_3)_2]$; (c) reaction with $Na(BH_4)$ followed by addition of $[ClM(PPh_3)]_4$ and $TlPF_6$. The last route involves the anionic intermediate $Na[Mn_2H_3(CO)_6(\mu\text{-tedip})]$. Compound 1 reacts with Zn amalgam in tetrahydrofuran at room temperature to cleanly give the yellow solvate cluster $[Mn_2Zn(\mu\text{-}H)_2(OC_4H_8)_2(CO)_6(\mu\text{-tedip})]$, which upon removal of solvent under vacuum yields the blue cluster $[Mn_2Zn(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})]_2$. The latter reacts instantaneously with tetramethylethylenediamine (tmeda) to afford the yellow cluster $[Mn_2Zn(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})(tmeda)]$ (11). The structure of 11 has been determined by X-ray diffraction methods. Crystals are orthorhombic, space group $Pcab$ with $Z = 8$ in a unit cell of dimensions $a = 16.198(5)$ Å, $b = 14.494(4)$ Å, and $c = 26.894(9)$ Å. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full matrix least squares on the basis of 1464 observed reflections to R and R_w values of 0.0537 and 0.0598, respectively. Compound 11 is the first Mn_2Zn cluster characterized by X-ray diffraction methods, so the values of the Mn–Zn distances, 2.525(4) and 2.544(4) Å, should be the first ones reported for Mn–Zn metal–metal bonds. The Zn–Mn edges in 11 are symmetrically bridged by two hydrido ligands and the P atoms of the tedip ligand are *trans* to the latter. The coordination geometry can be considered octahedral around the Mn atoms and tetrahedral around zinc, which bears a chelated tmeda ligand. The structure of the new compounds and the presence of isomers in some of them are discussed on the basis of the IR and NMR (^1H, ^{31}P, ^{13}C) data.

Introduction

Heterometallic complexes have been extensively studied during the last years.[1] Those containing hydrido ligands[2] are of particular interest, partly due to their potential utility in catalytic reactions. Yet, more selective synthetic routes to heterometallic hydrido cluster compounds need to be developed. Unsaturated dimetal complexes are usually quite reactive toward a great variety of reagents

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under mild conditions and therefore should be useful building blocks for mild, selective reactions leading to heterometallic complexes. In this paper we report the use of the unsaturated dimanganese dihydride $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})]$ (1) (tedip = $(EtO)_2POP(OEt)_2$) as a selective precursor of several Cu–, Ag–, Au–, and Zn–dimanganese hydrido clusters. Compound 1 belongs to a family of reactive carbonyl complexes containing the unsaturated moiety $M_2(\mu\text{-}H)_2$ (M═M).[3] So far, however, only $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ has been used in the synthesis of heterometallic clusters to some extent,[4] although some reactions starting from $[Re_2(\mu\text{-}H)_2(CO)_8]$ (to give Re—Pt clusters),[5,6] $[Re_3(\mu\text{-}H)_4(CO)_{10}]^{2-}$ (Re—Au clusters),[7] and $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ (Mn—Au and Mn—Ag[8a] or Mn—W and Mn—Fe[8b] clusters) have also been reported. A preliminary account on part of this work has appeared.[9]

Results and Discussion

(a) Synthesis of Compound 1. Compound 1 can be conveniently prepared from $[Mn_2(\mu\text{-}Br)_2(CO)_6(\mu\text{-tedip})]$ and ca. 4 equiv of either $Li[HBEt_3]$ or $K[HB(CHMeEt)_3]$ in tetrahydrofuran at room temperature. This gives a highly air-sensitive dark green solution. Attempts to identify or isolate the species present in this solution have been unsuccessful. However, addition of water to this solution and removal of solvent under vacuum gives a deep red residue from which 1 can be extracted. This procedure is completely analogous to that followed for $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$, which we have analyzed with some detail[3] and therefore will not be further discussed. We only note here that similar yields of 1 were obtained when relative amounts of the boron reagents ranging from 4 to 3 equiv (but not less than 3 equiv) were used. The latter suggests a 1:3 stoichiometry for the reaction leading to complex 1, but this should be taken only as tentative, as the yield of the reaction is very sensitive to the experimental conditions, regardless of the stoichiometry.

(b) Copper and Silver Derivatives of Compound 1. Compound 1 reacts readily with CuX (X = Cl, I) in tetrahydrofuran at room temperature, giving a mixture of the hexametallic cluster $[Mn_4Cu_2(\mu\text{-}H)_6(CO)_{12}(\mu\text{-tedip})_2]$ (**2**) and the corresponding halogenohydrido complex $[Mn_2(\mu\text{-}H)(\mu\text{-}X)(CO)_6(\mu\text{-tedip})]$ (**3a,b**) (**a**, X = Cl; **b**, X = I), in an 1:1 ratio. Complex **3b** had been previously prepared by us through a more general route.[10] Spectroscopic data for **3a** indicate that it is isostructural with the former, and they will not be discussed.

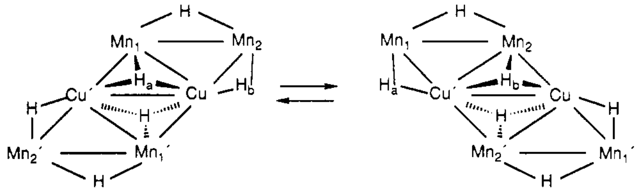

Figure 1. Schematic view of the fluxional rearrangement proposed for compound 2 in solution.

The structure of 2 was determined by an X-ray study,[9] which revealed the presence of a centrosymmetric planar Mn_4Cu_2 core (Figure 1, left). This uncommon arrangement is reminiscent of that found for the rhenium clusters $[Re_4Cu_2H_{16}(PMe_2Ph)_8]^{2+}$ [11] and $[Re_4Cu_2H_{14}(PMe_2Ph)_8]$.[12] In 2, the copper atoms are more naked in nature, as only four H ligands are involved in bonding with Cu atoms (bridging the Mn(2)–Cu vectors and the Mn(1)–Cu_2 faces). The other two H ligands were found bridging the manganese atoms. These metal atoms display a rather large intermetallic separation (3.282(3) Å), in the upper part of the range of distances attributed to single manganese–manganese bonds.[13] In contrast, the Cu–Cu′ distance (2.461(2) Å) is shorter (0.03–0.07 Å) than those found in the above mentioned Re_4Cu_2 clusters and significantly shorter (0.1–0.2 Å) than those found[14] for the raft, naked Cu–Fe clusters $[Cu_3Fe_3(CO)_{12}]^{3-}$ and $[Cu_5Fe_4(CO)_{16}]^{3-}$. As there are no apparent constraints imposed on the metal core of 2, the observed distance must be a consequence of a genuine bonding interaction between the copper atoms.

NMR data for 2 at room temperature (Table I and Experimental Section) cannot be conciliated with the structure found in the solid, as they imply a more symmetrical arrangement, having equivalent phosphorus and Mn(μ-H)Cu hydrido atoms. At 263 K, however, the spectra indicate two different environments for the phosphorus atoms (1:1 occupancy) and three different ones for the hydrido ligands (1:1:1 occupancy), in agreement with the solid state structure. The ^1H resonance at ca. −26 ppm, which corresponds to the H atoms bridging the Mn–Mn edges, is not involved in the fluxional process. In order to explain the above observations, we propose some rearrangement involving both the Mn(μ-H)Cu bridges and the metal core itself (Figure 1). We assume that a synchronized exchange of the Mn(μ-H)Cu hydrido ligands between the μ_2 and μ_3 bridging positions is taking place (H_a/H_b in Figure 1). At the same time, each of the copper atoms alternates with one of the Mn atoms to which it is bonded (for example, Cu with Mn_1 and $Mn_{2'}$) whereas it remains always bound to the other metal atoms (in this example, to Cu′, Mn_2, and $Mn_{1'}$). It should be noted that the proposal of a metal rearrangement is necessary, as any process involving the hydrido ligands only would not render equivalent magnetic environments for the phosphorus atoms of the molecule. In a topological sense, our proposal is similar to that postulated for several Au_2Ru_3 clusters,

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Table I. IR and ^{31}P NMR Data for New Compounds

compd	ν(CO)^{a}/cm^{-1}	^{31}P{^{1}H} NMR^{b}/δ
$Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})$ (**1**)	2053 (s), 2020 (vs), 1977 (m), 1959 (m), 1943 (vs)	171.9 (s, br)
$Mn_4Cu_2(\mu\text{-}H)_6(CO)_{12}(\mu\text{-tedip})_2$ (**2**)	2034 (vs), 2016 (s), 1965 (vs), 1940 (vs, br)^{c}	171.1 (d, 55^{d}), 165.9 (d, 55^{d})^{e}
$Mn_2(\mu\text{-}H)(\mu\text{-}Cl)(CO)_6(\mu\text{-tedip})$ (**3a**)	2064 (s), 2032 (s), 1983 (s), 1968 (s), 1947 (vs)	158.3 (s, br)^{f}
$Mn_2Cu(\mu\text{-}H)_3(CO)_6(PPh_3)(\mu\text{-tedip})$ (**4a**)	2038 (s), 2004 (s), 1961 (s), 1927 (s, br)^{c}	174.2 (s, MnP, 2P), −0.7 (s, CuP, 1P)^{g}
$Mn_2Ag(\mu\text{-}H)_3(CO)_6(PPh_3)(\mu\text{-tedip})$ (**4b**)	2032 (vs), 2003 (s), 1957 (vs), 1933 (sh), 1926 (s)^{h}	176.3 (s, MnP, 2P), 12.3 (2xd,^{i} AgP, 1P)^{g}
$Na[Mn_2H_3(CO)_6(\mu\text{-tedip})]$ (**5**)	1998 (s), 1936 (vs), 1915 (s), 1876 (s), 1855 (m)^{h}	188.5 (s, br)^{j}
$Mn_2Au(\mu\text{-}H)(CO)_6(PPh_3)(\mu\text{-tedip})$ (**6**)	2024 (s), 1986 (vs), 1951 (s), 1929 (s), 1917 (vs)	175.9 (br, MnP, 2P), 68.7 (t, 19,^{d} AuP, 1P)^{k}
$Mn_2Au(\mu\text{-}H)(CO)_7(PPh_3)(\mu\text{-tedip})$ (**7**)	2042 (s), 1975 (vs), 1970 (sh), 1956 (s), 1933 (m), 1889 (m)	182.3, 180.2 (AB, 85,^{d} MnP, 2P), 47.7 (s, AuP, 1P)^{l}
$Mn_2Au_2(CO)_6(PPh_3)_2(\mu\text{-tedip})$ (**8**)	1992 (s), 1951 (vs), 1921 (s), 1899 (sh), 1887 (vs)^{m}	190.4 (br, MnP, 2P), 64.1 (t, 20,^{d} AuP, 2P)
$Mn_2Zn(\mu\text{-}H)_2(CO)_6(thf)_2(\mu\text{-tedip})$ (**9**)	2007 (s), 1953 (vs), 1929 (vs), 1903 (sh), 1893 (s), 1883 (s)^{h}	190.4 (s, MnP, iso B), 186.7 (s, MnP, iso A)^{n}
$[Mn_2Zn(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})]_2$ (**10**)	2046 (s), 1975 (vs), 1952 (m), 1926 (m), 1897 (m)^{m}	173.5, 169.3 (AB, 76,^{d} MnP, 2P)^{o}
$Mn_2Zn(\mu\text{-}H)_2(CO)_6(tmeda)(\mu\text{-tedip})$ (**11**)	2008 (w), 1951 (s), 1922 (vs), 1887 (s)^{m}	190.1 (s, MnP, iso B), 186.4 (s, MnP, A)^{o,p}

[a] Recorded in petroleum ether solution, unless otherwise stated. [b] Recorded at room temperature in C_6D_6 solution, at 121.5 MHz, unless otherwise stated. [c] In dichloromethane. [d] J_{PP}. [e] In $CDCl_3$ at 233 K (169.0 (s, br) at 295 K). [f] In $CDCl_3$ at 32.20 MHz. [g] In CD_2Cl_2 at 218 K. [h] In tetrahydrofuran (thf). [i] $J_{P^{107}Ag}$ = 408 Hz, $J_{P^{109}Ag}$ = 470 Hz. [j] Tetrahydrofuran–C_6D_6. [k] In $CDCl_3$. [l] In CD_2Cl_2 at 183 K [181.0 (br) and 48.7 (s) at 295 K]. [m] In toluene. [n] In OC_4D_8 at 193 K; see text for discussion on isomers A and B. [o] In CD_2Cl_2 at 193 K. [p] 189.8 ppm in C_6D_6 at room temperature (isomer B), see text.

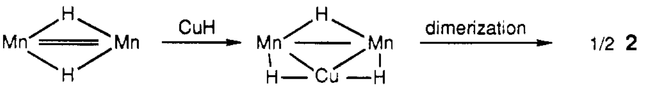
where alternated binding of the gold atoms with different ruthenium centers has been invoked.[15]

Attempts to synthesize Ag or Au analogues of compound **2** were unsuccessful. In the case of silver, no reaction was observed between **1** and AgX (X = I, Cl) in tetrahydrofuran at room temperature for several hours. On the other hand, [AuCl(tht)] (tht = tetrahydrothiophene) is reduced rapidly by **1** in petroleum ether, giving compound **3a** and metallic gold. Therefore, this reaction follows eq 1 whereas eq 2 can be written for the reaction with CuX. The main difference is the absence of group 11 metal reduction in the last case.

$$1 + AuCl(tht) \rightarrow \mathbf{3a} + Au + {}^{1}/{}_{2}H_2 + tht \qquad (1)$$

$$1 + {}^{1}/{}_{2}CuCl \rightarrow {}^{1}/{}_{4}\mathbf{2} + {}^{1}/{}_{2}\mathbf{3a} \qquad (2)$$

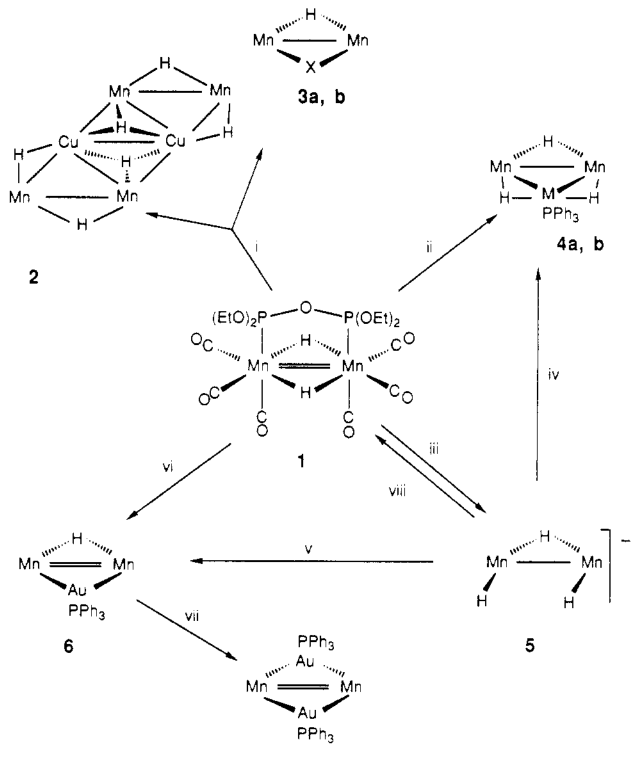
Formation of cluster **2** can be viewed as the insertion of a hypothetical molecule of CuH into a Mn(μ-H)Mn bridge in **1** and further dimerization of the intermediate A thus formed.



A

Thus, it was thought that **1** should react with [HCu(PPh$_3$)] to give a stable trimetallic cluster related to intermediate A. Indeed, this reaction takes place rapidly a room temperature, giving cleanly the orange and stable cluster [$Mn_2Cu(\mu\text{-}H)_3(CO)_6(PPh_3)(\mu\text{-tedip})$] (**4a**) (Scheme I). This behavior is reminiscent of that of [$Os_3(\mu\text{-}H)_2(CO)_{10}$] which under similar conditions gives an $Os_3Cu(\mu\text{-}H)_3$ cluster closely related to **4a**.[16]

Scheme I[a]



[a] Mn_2 refers to the moiety $(CO)_3Mn\{\mu\text{-}(EtO)_2POP(OEt)_2\}Mn(CO)_3$ except for compound **1**, for which a more complete structural drawing is shown. Key: (i) CuX (**a**, X = Cl; **b**, X = I); (ii) [$HCu(PPh_3)]_6$ or [$M(BH_4)(PPh_3)_2$] (**a**, M = Cu; **b**, M = Ag); (iii) $NaBH_4$; (iv) [$MCl(PPh_3)]_4$, $TlPF_6$ (M = Cu, Ag); (v) [$AuCl(PPh)_3$], $TlPF_6$; (vi) [$AuMe(PPh_3)$]; (vii) [$AuMe(PPh_3)$], $h\nu$; (viii) $AgClO_4$.

IR and NMR data for **4a** are fully consistent with a geometry derived from that of **1** after replacement of one μ-H bridge by a CuPPh$_3$ unit and addition of one bridging H atom to each of the Mn–Cu edges. Furthermore, NMR data indicate that the molecule is highly symmetric and rigid on the NMR time scale. No exchange was observed between the (μ-H)Mn$_2$ bridging hydride (δ = −25.98 ppm) and the Mn(μ-H)Cu ones (δ = −8.42 ppm). This situation contrasts with that found for the mentioned Os$_3$Cu cluster, where both types of hydrido ligands were found to exchange their positions.

As there are no Au or Ag analogues of [HCu(PPh$_3$)] available, we attempted to design alternative routes to compound **4a** which could also be extended to these metals. In the first place, we examined the reactions of **1** with the tetrahydroborate complexes [$M(BH_4)(PPh_3)_2$] (M = Cu, Ag). The reaction proceeds easily and selectively in tetrahydrofuran at room temperature, yielding the desired

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clusters **4a** or its silver analogue **4b** as main products, along with $BH_3 \cdot PPh_3$ (eq 3).

$$1 + [M(BH_4)(PPh_3)_2] \rightarrow 4 + H_3B \cdot PPh_3 \qquad (3)$$

The formation of the phosphine–borane adduct (confirmed by NMR monitoring of the reaction mixtures) is probably an important driving force of the process. The tetrahydroborate complex, then, can be considered as a source of the corresponding (unsaturated) hydrido complex "$MH(PPh_3)$".

In contrast with the relatively high stability of the copper cluster **4a**, its silver analogue **4b** was found to be thermally unstable. Solutions of **4b** decompose slowly at −20 °C and more rapidly at room temperature, and all attempts to isolate it as a solid yielded impure materials. In spite of this, IR and low temperature NMR spectra of **4b** clearly indicate that this cluster is isostructural with **4a**. Thus, two different hydrido resonances are present in the ^1H NMR spectrum, at −7.30 (Mn–H–Ag) and −23.6 ppm (Mn–H–Mn), with relative intensities 2:1. Both resonances show couplings with silver and with the phosphorus atoms of the tedip ligand. The one-bond H–Ag coupling for the first resonance (72 Hz) is within the range observed for other heterometallic hydrido complexes.[17] As expected for a coupling through two bonds, J_{HAg} for the second resonance is lower (24 Hz). Unfortunately, we have not found examples in the literature to be used for comparative purposes. In many instances, two-bond (through metal) J_{HAg} coupling is not observed. This is the case, for example, of the clusters $[Os_3(\mu\text{-}H)(\mu\text{-}AgPPh_3)(CO)_{10}]$[18a] or $[Ru_3(\mu\text{-}AgPEt_3)(\mu\text{-}H)(\mu\text{-}S)L(CO)_8]$ (L = CO, PPh_3).[18b] Finally, there is no apparent coupling of the $Mn(\mu\text{-}H)Ag$ hydrido ligands with the phosphorus atom of triphenylphosphine in complex **4b**, a situation also found in **4a**. This is perhaps indicative of a low value (<10 Hz) of the corresponding coupling constant, which would be then obscured by the intrinsic broadness of the resonance (due to the quadrupolar ^{55}Mn nuclei).

The second alternative route for the synthesis of **4a** and the related Ag and Au analogues uses the intermediate action of a hydrido source followed by addition of the appropriate precursor of the corresponding $[M(PPh_3)]^+$ cation. Thus, **1** reacts quickly with $Na[BH_4]$ in tetrahydrofuran at room temperature to give a yellow solution shown (by IR and NMR data) to contain a single species, formulated as $Na[Mn_2H_3(CO)_6(\mu\text{-tedip})]$ (**5**) (Scheme I). Complex **5** gives back **1** and metallic silver upon reaction with $AgClO_4$ in tetrahydrofuran. Li^+, K^+, or $[PPN]^+$ (PPN = Ph_3PNPPh_3) salts of this anion can be prepared by use of the corresponding borohydride salt, but they were found to be thermally unstable. The ^{31}P NMR spectrum of **5** shows a single resonance at 188.5 ppm, which does not change on cooling the solution to −80 °C. On the other hand, its ^1H NMR spectrum exhibits a single and quite broad resonance around −16 ppm at temperatures ranging from +25 to −80 °C ($w_{1/2}$ ca. 55 Hz at −80 °C), with an integrated area corresponding to three H atoms. However, the methyl groups of the tedip ligand give rise to two different resonances, an indication of distinct magnetic environments at each side of the Mn_2POP pseudoplane. All these data, and the IR spectrum of **5**, can be reasonably conciliated with a structure derived from **1** after replacement of one bridging hydride by two terminal hydrides (Scheme I) and allowing complete and fast (on the NMR time scale) exchange between bridging and terminal positions of these ligands. In this way, **5** would be strongly related to the neutral $[Re_2(\mu\text{-}H)H(CO)_6\{P(OMe)_3\}(\mu\text{-tedip})]$, obtained from $[Re_2(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})]$ and found also to experience exchange between bridging and terminal hydride positions.[19]

Compound **5** reacts almost instantaneously with either $[CuCl(PPh_3)]_4$, $[AgCl(PPh)_3]_4$, or $[AuClPPh_3]$ in the presence of $TlPF_6$ as halide abstractor. This reaction, however, is of little use for the preparation of complexes **4**. In the case of copper, the reaction gives compound **4a** as expected, but the yield is lower than those obtained by any of the methods previously described. This is due to the formation of uncharacterized side products (metallic copper seems also to be formed at some extent). The case of silver is even worse, as compound **4b** is found to be only a minor product in the reaction mixture, which also contains metallic silver. As in the previous case, the undesired products, which have not been characterized, contain neither hydrido ligands nor group 11 metal. Finally, reaction of **1** with $[AuCl(PPh_3)]$ gives unexpectedly the unsaturated cluster $[Mn_2Au(\mu\text{-}H)(CO)_6(PPh_3)(\mu\text{-tedip})]$ (**6**) in moderate yield. IR monitoring of this reaction reveals the presence of some intermediates as well as uncharacterized side products. Some metallic gold is also formed. The above observations can be interpreted by assuming that the initial product in the reaction could be the gold analogue of **4a** and **4b** which, being thermally unstable, would decompose either by evolving H_2 (to give **6**) or through a redox process (giving metallic gold and other products). Attempts to isolate the initial intermediate product were unsuccessful.

(c) Gold Derivatives of Compound 1. Compound **1** reacts slowly in toluene at room temperature with $[AuMe(PPh)_3]$ to give the blue-violet cluster **6** in almost quantitative yield. Compounds **6** and **1** can be considered as isolobal analogues by recalling the relationship H ↔ $AuPPh_3$,[20] as is also the case for $[Mn_2Au(\mu\text{-}H)(CO)_6(PPh_3)(\mu\text{-dppm})]$.[8a] Although the spectroscopic data for **6** clearly supported the proposed geometry (Scheme I), it was of interest for us to obtain accurate structural data for the cluster, and therefore we decided to perform an X-ray diffraction study.

The structure of **6** is depicted in Figure 2, together with the atom-numbering scheme and is fully consistent with the spectroscopic data in solution. A summary of the important bond distances and angles is given in Table II. The cluster consists of a Mn_2Au triangle in which the Mn–Mn side is bridged by a hydrido ligand H(1) and the tedip ligand through the P atoms. The tedip bridge is nearly orthogonal to the Mn_2Au plane. The structure of **6** can be compared to that of the strictly related compound $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$[21] from which **6** can be derived

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[17] (a) $Ir(\mu\text{-}H)Ag$ complexes: Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 6874. (b) $Rh(\mu\text{-}H)Ag$ complexes: Ott, J.; Venanzi, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1760. (c) $Pt(\mu\text{-}H)Ag$ complexes: Albinati, A.; Demartin, F.; Venanzi, L. M.; Wolfer, M. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 563.

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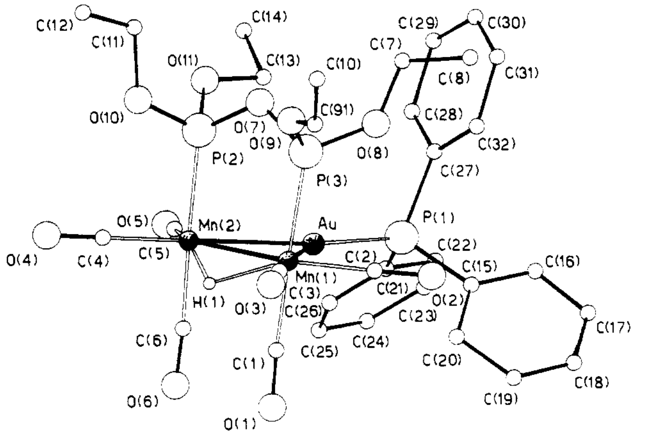

Figure 2. Molecular structure of [$Mn_2(\mu$-$AuPPh_3)(\mu$-$H)(CO)_6(\mu$-tedip)] (**6**) with the atom-numbering scheme.

Table II. Important Interatomic Distances (Å) and Angles (deg) for Compound 6

Mn(1)-Mn(2)	2.739(3)	P(1)-C(27)	1.81(1)
Mn(1)-Au	2.665(2)	P(2)-O(7)	1.59(1)
Mn(2)-Au	2.638(2)	P(3)-O(7)	1.61(1)
Au-P(1)	2.318(3)	P(2)-O(10)	1.56(1)
Mn(1)-P(3)	2.210(5)	P(2)-O(11)	1.58(1)
Mn(2)-P(2)	2.213(5)	P(3)-O(8)	1.54(2)
Mn(1)-C(1)	1.79(2)	P(3)-O(9)	1.56(2)
Mn(1)-C(2)	1.78(2)	C(1)-O(1)	1.15(2)
Mn(1)-C(3)	1.76(2)	C(2)-O(2)	1.16(2)
Mn(2)-C(4)	1.78(2)	C(3)-O(3)	1.14(2)
Mn(2)-C(5)	1.74(2)	C(4)-O(4)	1.15(2)
Mn(2)-C(6)	1.78(2)	C(5)-O(5)	1.19(2)
P(1)-C(15)	1.80(1)	C(6)-O(6)	1.16(2)
P(1)-C(21)	1.83(1)		
Mn(1)-Au-Mn(2)	62.2(1)	C(4)-Mn(2)-C(6)	91.2(8)
Mn(1)-Au-P(1)	140.7(1)	C(5)-Mn(2)-C(6)	87.8(8)
Mn(2)-Au-P(1)	157.1(1)	Mn(2)-P(2)-O(7)	118.1(4)
Au-Mn(1)-Mn(2)	58.4(1)	Mn(2)-P(2)-O(10)	112.6(5)
Au-Mn(1)-P(3)	87.4(1)	Mn(2)-P(2)-O(11)	121.1(5)
Au-Mn(1)-C(1)	91.3(6)	O(7)-P(2)-O(10)	102.5(6)
Au-Mn(1)-C(2)	84.1(6)	O(7)-P(2)-O(11)	100.2(6)
P(3)-Mn(1)-C(2)	88.9(6)	O(10)-P(2)-O(11)	99.2(6)
P(3)-Mn(1)-C(3)	91.4(6)	Mn(1)-P(3)-O(7)	117.5(4)
P(3)-Mn(1)-Mn(2)	91.0(2)	Mn(1)-P(3)-O(8)	115.2(6)
C(1)-Mn(1)-C(2)	89.5(8)	Mn(1)-P(3)-O(9)	116.6(8)
C(1)-Mn(1)-C(3)	89.7(8)	O(7)-P(3)-O(8)	102.0(8)
C(2)-Mn(1)-C(3)	90.5(8)	O(7)-P(3)-O(9)	96.8(7)
Au-Mn(2)-Mn(1)	59.4(1)	O(8)-P(3)-O(9)	106.1(9)
Au-Mn(2)-P(2)	90.3(1)	P(2)-O(7)-P(3)	122.2(7)
Au-Mn(2)-C(5)	82.4(5)	Mn(1)-C(1)-O(1)	169.7(16)
Au-Mn(2)-C(6)	87.8(5)	Mn(1)-C(2)-O(2)	178.3(17)
P(2)-Mn(2)-C(4)	90.5(6)	Mn(1)-C(3)-O(3)	173.2(17)
P(2)-Mn(2)-C(5)	90.4(6)	Mn(2)-C(4)-O(4)	176.8(16)
P(2)-Mn(2)-Mn(1)	90.6(1)	Mn(2)-C(5)-O(5)	176.8(16)
C(4)-Mn(2)-C(5)	92.6(8)	Mn(2)-C(6)-O(6)	174.8(14)

by substituting a hydride with the isolobal $AuPPh_3$ group and the dppm ligand with the tedip ligand.

The Mn-Mn distance in **6**, 2.739(3) Å, is only slightly longer than that in [$Mn_2(\mu$-$H)_2(CO)_6(\mu$-dppm)], 2.699(2) Å,[21] and is consistent with the formal electronic unsaturation of the cluster. Thus, substitution of a bridging H atom by the isolobal group $AuPPh_3$ brings about no substantial elongation of the Mn-Mn separation. This has also been observed for the short Os-Os distances in [$Os_3(\mu$-$AuPPh_3)(\mu$-$H)(CO)_{10}$], 2.699(1) Å,[22] and in [$Os_3(\mu$-$AuPPh_3)_2(CO)_{10}$], 2.684(1) Å,[23] very close to that found in [$Os_3(\mu$-$H)_2(CO)_{10}$], 2.681(1) Å.[24] As expected, the Mn-Mn distance in **6** is much shorter than that in the related cluster [$Mn_2(\mu$-$AuPPh_3)(\mu$-$Br)(CO)_6(\mu$-tedip)], which is electron precise (Mn-Mn = 3.090(3) Å[10]). By contrast, the electronic unsaturation in **6** does not influence the Mn-Au distances, 2.665(2) and 2.638(2) Å, which are very close to those found in the latter (2.679(3) and 2.640(3) Å[10]).

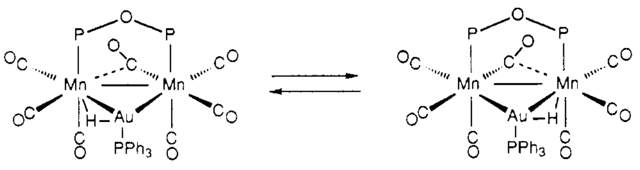

Figure 3. Fluxional rearrangement proposed for compound **7** in solution.

The electron deficiency of compound **6** influences its chemical behavior. For example, **6** reacts rapidly with simple Lewis bases such as CO or phosphites. We have examined the reaction with CO. That takes place easily at room temperature, giving the yellow, electron precise cluster [$Mn_2(\mu$-$AuPPh_3)(\mu$-$H)(CO)_7(\mu$-tedip)] (**7**) almost quantitatively. Spectroscopic data for **7** indicate that considerable structural reorganization of the cluster has occurred upon CO uptake. Thus, the hydride resonance appears at a relatively high chemical shift (-6.60 ppm) and shows a large coupling (90 Hz) with the PPh_3 phosphorus atom, as is usual for $M(\mu_2$-$H)Au$ systems (80-110 Hz).[25,26] However, the hydrido ligand is equally coupled (J_{HP} = 23 Hz) with the phosphorus atoms of the tedip ligand, which in turn give rise to a single resonance in the ^{31}P NMR spectrum. On a symmetry basis alone, these data are not consistent with a $Mn(\mu_2$-$H)Au$ formulation. Besides, the IR spectrum of **7** gives no indication of the presence of a bridging CO, but rather that of a semibridging one, denoted by the band at 1889 cm^{-1}. Again, this is not consistent with a plane of symmetry relating the phosphorus atoms, as apparently indicated by the room temperature NMR spectra. As suspected, **7** is fluxional, and the ^{31}P NMR spectrum at 183 K shows two different sites for the phosphorus atoms of the tedip ligand. In agreement with this, the hydrido ligand then exhibits different couplings with these atoms (20 and 26 Hz), the average of which is exactly the value measured at room temperature. In order to explain the above data, we propose the dynamic process depicted in Figure 3. That consists basically of the alternated binding of the semibridging CO and hydrido ligands to each of the manganese atoms, synchronized so as to keep constant the electronic balance at the dimanganese center. We have not been able to confirm further this mechanism through ^{13}C NMR spectroscopy. In principle, the averaged structure should contain four different carbonyl sites (2:2:2:1 occupancy), whereas seven are to be expected for the static structure. In fact, the ^{13}C NMR spectrum of **7** at 183 K exhibited only three broad resonances (2:4:1 relative intensities) and adds therefore no new information, except to confirm the absence of a symmetrically bridging CO (which would exhibit a considerably higher chemical shift), in agreement with the IR data.

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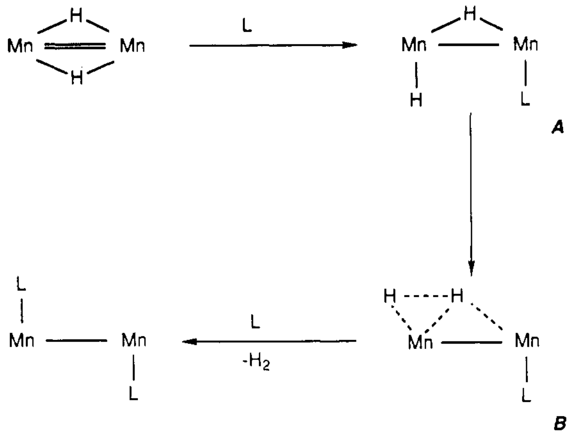
(24) Churchill, M. R.; Hollander, F. J.; Hutchinson, P. *Inorg. Chem.* **1977**, *16*, 2697.

(25) $W(\mu$-$H)Au$ complexes: Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2497.

(26) $Ir(\mu$-$H)Au$ complexes: Albinati, A.; Auklin, C.; Janser, P.; Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chem.* **1989**, *28*, 1105.

Scheme II. Hypothetical Mechanism for the Reactions of 1 with Two-Electron Donor Molecules (L) Which Lead to Dihydrogen Elimination



Taking into account the isolobal analogy H/AuPPh$_3$, the structure of 7 can be considered as a new model for the intermediates involved in the reactions of 1 (or its dppm analogue) with simple two electron donor ligands (L), when they result in H$_2$ elimination. Previous work on [Re$_2$(μ-H)$_2$(CO)$_6$(μ-tedip)]^{19} and [Os$_3$(μ-H)$_2$(CO)$_{10}$]^4 has shown that the reactions of these species with L does not result in loss of H$_2$ but causes the opening of one Mn(μ-H)M bridge much in the same way as proposed for the anion 5 (Scheme I). The structure of 7 would then model a further step toward the elimination of hydrogen in these reactions (intermediate B in Scheme II). It would be interesting to know whether a reasonably stable dihydrogen complex similar to B will ever be prepared.

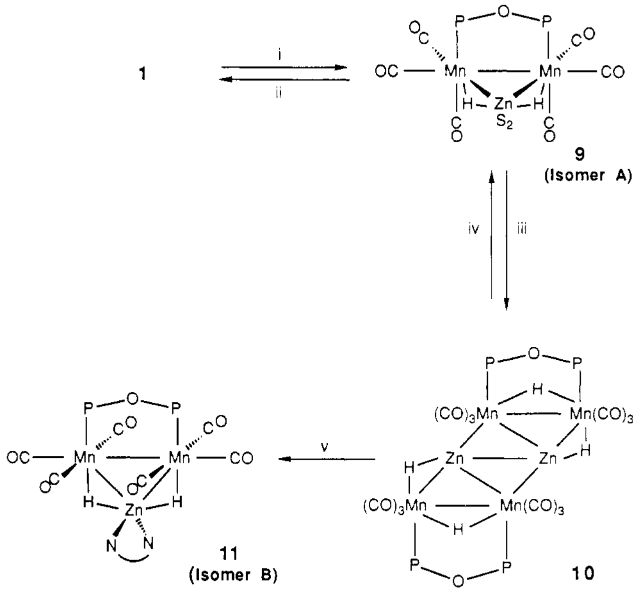
When the preparation of cluster 6 is performed on a relatively large scale (0.5 mmol), a small amount (1%) of the blue tetranuclear cluster [Mn$_2$Au$_2$(CO)$_6$(PPh$_3$)$_2$(μ-tedip)] (8) can be isolated. Surprisingly, compound 8 could not be prepared efficiently from 6 and [AuMe(PPh$_3$)] at room temperature, and the use of higher temperatures led only to decomposition. However, UV irradiation of a toluene solution of 6 and a slight excess of [AuMe(PPh$_3$)] gives 8 as the major product. The yield is moderate (ca. 40%), because substantial decomposition occurs in this slow reaction.

The structure proposed for this unsaturated cluster (derived from 1, after replacement of the hydrido ligands by the isolobal AuPPh$_3$ fragments) is fully consistent with its IR and NMR spectra. The pattern of the ν(CO) stretching bands is analogous to that of 6, but bands are shifted toward a lower frequency, as expected from the lower electronegativity of the Au(PPh$_3$) group when compared with the H atom. Moreover, the decrease in the averaged frequency (27 cm^{-1}, in toluene solution) is similar to that which occurred from 1 to 6 (29 cm^{-1}, in toluene solution). The NMR spectra give further support to the C_{2v} structure proposed for 8, as they reveal in each case a single environment for the phosphorus atoms of the ligands (tedip or PPh$_3$) and the methyl groups.

We must note that, in our early work,^{9} cluster 8 was erroneously thought to be the red product obtained after treatment of 1 with sodium amalgam followed by addition of 2 equiv of [AuCl(PPh$_3$)] in the presence of TlPF$_6$. Now we know that this red product is in fact an electron precise isomer of 8.^{27}

(d) Zinc Derivatives of Compound 1. As stated before, the formation of cluster 2 can be thought to be the result of the insertion of a molecule of "CuH" into a Mn–H–Mn bridge in 1, followed by dimerization. Then, the possibility was considered that the group 12 elements, which have the same number of valence electrons as "CuH", could react in a similar way with the dihydride 1.

Scheme III[a]



[a] P—O—P = (EtO)$_2$POP(OEt)$_2$. Key: (i) Zn(Hg), tetrahydrofuran (=S); (ii) H$_3$PO$_4$; (iii) vacuum; (iv) tetrahydrofuran (=S); (v) Me$_2$NCH$_2$CH$_2$NMe$_2$ (=N—N).

No reaction was observed between 1 and either cadmium amalgam or mercury in tetrahydrofuran at room temperature. However, zinc amalgam (1%) reacts with 1 easily under the same conditions, giving a yellow complex which we formulate as [Mn$_2$Zn(μ-H)$_2$(OC$_4$H$_8$)$_2$(CO)$_6$(μ-tedip)] (9) (Scheme III). Clearly, this compound contains coordinated tetrahydrofuran, because removal of the solvent from these solutions under vacuum causes the transformation of 9 into the blue cluster 10 (see below), which contains no tetrahydrofuran at all. Solid 10, in turn, reverts to 9 only by addition of tetrahydrofuran. We have not been able to isolate this solvate complex as a solid, and therefore the number of coordinated tetrahydrofuran molecules is somewhat uncertain. Nevertheless, the proposal of two molecules of tetrahydrofuran bonded to the zinc atom in cluster 9 seems the most reasonable, after consideration of the well-known preference of Zn for tetrahedral coordination and the strong similarities in the NMR spectra of 9 and 11 (see below). On the other hand, compound 9 exists in solution as a mixture of two isomers, as is the case of 11, and therefore the structural analysis of 9 will be deferred until the crystal structure of 11 has been discussed.

As mentioned previously, removal of solvent under vacuum from tetrahydrofuran solutions of 9 gives quantitatively a blue compound which we formulate as [Mn$_2$Zn(μ-H)$_2$(CO)$_6$(μ-tedip)]$_2$ (10) (Scheme III). This compound can be dissolved in benzene, toluene, or dichloromethane, but decomposition to uncharacterized species occurs slowly under nitrogen at room temperature. The same thermal instability is observed in the solid state, although the rate of decomposition is slower. Spectro-

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(27) [Mn$_2$(μ-AuPPh$_3$)$_2${μ-P(OEt)$_2$}{μ-OP(OEt)$_2$}(CO)$_6$]: Liu, X. Y.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. Results to be published.

scopic data for **10** give full support to the proposed composition, but evidence about the nuclearity of the cluster is weaker. Unfortunately, we have not been able to carry out an X-ray diffraction study on this compound.

The IR spectrum of **10** in the ν(CO) region indicates that its $M(CO)_3$ units have a local arrangement of the *facial* type, as is the case of all compounds described above. On the other hand, no significant changes were observed in the ^1H or ^{31}P NMR solution spectra of **10** from +25 to -80 °C. The ^{31}P NMR spectrum of **10** shows that each tedip ligand occupies two chemically different positions in the molecule. In agreement with this, at least three different chemical environments can be recognized for the methyl groups of this ligand (the unresolved multiplet at 1.20 ppm is obviously the superimposition of two somewhat broad triplets). The hydrido ligands give rise to resonances at -8.03 (pseudodoublet) and -23.23 ppm (triplet), each corresponding to 1H (relative to tedip). The most shielded resonance has a chemical shift and phosphorus coupling comparable to that found in the unsaturated cluster **6** and is therefore assigned to a hydrido ligand bridging two manganese atoms. The chemical shift of the other resonance is indicative of the presence of a hydrido ligand bridging Mn and Zn atoms (ca. -9 ppm for Mu(μ-H)Cu in compound **2** or ca. -7 ppm for Mn(μ-H)Au in **7**). The shape of this resonance is similar to those found for the Mn(μ-H)Cu resonances in **2** or **4a** (now closer to a first order doublet). This is attributed to the presence of an AA′XX′ spin system (A = H; X = P) and therefore is not compatible with a trinuclear Mn_2Zn formulation for **10**.

We propose that **10** is the result of dimerization of the unsaturated trinuclear moiety generated when the thf molecules are removed from the coordination sphere of Zn in compound **9**. This would then be similar to the process supposed to be responsible for the formation of the Mn_4Cu_2 cluster **2**. Under this hypothesis, **2** and **10** would be isoelectronic, and accordingly, we have formulated for **10** a structure related to that found for **2**, although this should be taken only as tentative. It has to be noted, however, than **10** is blue whereas **2** is orange, and therefore a significant difference in the electronic distribution in these clusters must be suspected.

Compound **10** reacts rapidly with simple donor molecules, thus relieving the coordinative unsaturation of the Zn atoms in the molecule. As noted before, addition of tetrahydrofuran causes the immediate transformation of **10** into **9**. In a similar way, tetramethylethylenediamine (tmeda) reacts instantaneously with **10** in toluene at room temperature to give quantitatively the yellow-orange cluster $[Mn_2Zn(\mu\text{-}H)_2(CO)_6(tmeda)(\mu\text{-tedip})]$ (**11**) (Scheme III).

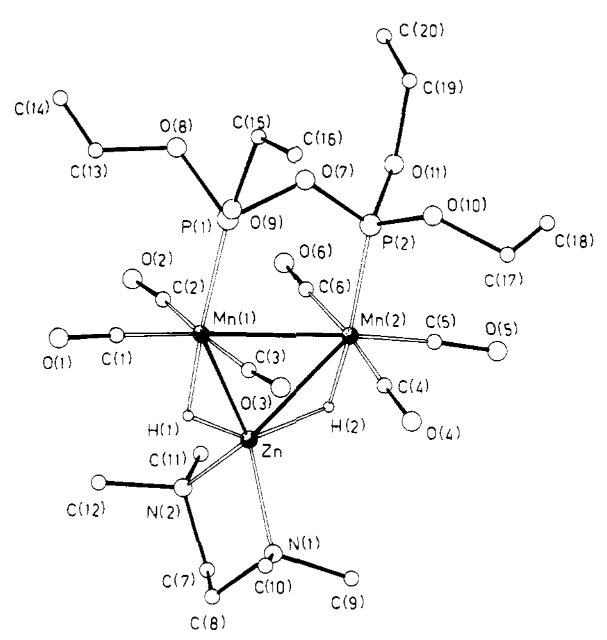

Figure 4. Molecular structure of $[Mn_2Zn(\mu\text{-}H)_2(CO)_6(Me_2NCH_2CH_2NMe_2)(\mu\text{-tedip})]$ (**11**) with the atom-numbering scheme.

Table III. Important Interatomic Distances (Å) and Angles (deg) for Compound 11

Mn(1)–Mn(2)	3.039(5)	P(2)–O(7)	1.61(2)
Mn(1)–Zn	2.525(4)	P(1)–O(8)	1.61(2)
Mn(2)–Zn	2.544(4)	P(1)–O(9)	1.60(2)
Mn(1)–P(1)	2.171(7)	P(2)–O(10)	1.60(2)
Mn(2)–P(2)	2.172(8)	P(2)–O(11)	1.56(2)
Zn–N(1)	2.13(2)	N(1)–C(8)	1.48(3)
Zn–N(2)	2.13(2)	N(2)–C(7)	1.49(3)
Mn(1)–C(1)	1.74(2)	C(7)–C(8)	1.54(3)
Mn(1)–C(2)	1.79(2)	C(1)–O(1)	1.16(3)
Mn(1)–C(3)	1.83(3)	C(2)–O(2)	1.16(3)
Mn(2)–C(4)	1.84(2)	C(3)–O(3)	1.15(3)
Mn(2)–C(5)	1.74(2)	C(4)–O(4)	1.13(3)
Mn(2)–C(6)	1.82(2)	C(5)–O(5)	1.18(3)
P(1)–O(7)	1.59(2)	C(6)–O(6)	1.14(3)
Mn(1)–Zn–Mn(2)	73.7(1)	C(5)–Mn(2)–C(6)	93.7(11)
Mn(1)–Zn–N(1)	128.3(5)	Mn(1)–P(1)–O(7)	120.2(6)
Mn(1)–Zn–N(2)	123.1(5)	Mn(1)–P(1)–O(8)	121.9(7)
Mn(2)–Zn–N(1)	123.6(5)	Mn(1)–P(1)–O(9)	112.0(6)
Mn(2)–Zn–N(2)	130.0(5)	O(7)–P(1)–O(8)	93.5(9)
N(1)–Zn–N(2)	84.8(7)	O(7)–P(1)–O(9)	101.4(9)
Zn–Mn(1)–Mn(2)	53.4(1)	O(8)–P(1)–O(10)	104.5(5)
Zn–Mn(1)–C(2)	83.0(7)	Mn(2)–P(2)–O(7)	120.8(7)
Zn–Mn(1)–C(3)	91.9(8)	Mn(2)–P(2)–O(10)	120.1(9)
P(1)–Mn(1)–Mn(2)	87.7(2)	Mn(2)–P(2)–O(11)	113.3(8)
P(1)–Mn(1)–C(1)	94.9(8)	O(7)–P(2)–O(10)	93.8(12)
P(1)–Mn(1)–C(2)	90.7(8)	O(7)–P(2)–O(11)	100.2(9)
P(1)–Mn(1)–C(3)	89.7(8)	O(10)–P(2)–O(11)	105.2(12)
C(1)–Mn(1)–C(2)	94.5(11)	P(1)–O(7)–P(2)	123.6(10)
C(1)–Mn(1)–C(3)	92.9(11)	Mn(1)–C(1)–O(1)	178(2)
Zn–Mn(2)–Mn(1)	52.9(1)	Mn(1)–C(2)–O(2)	177(2)
Zn–Mn(2)–C(4)	82.2(7)	Mn(1)–C(3)–O(3)	174(2)
Zn–Mn(2)–C(6)	92.8(8)	Mn(2)–C(4)–O(4)	174(2)
P(2)–Mn(2)–Mn(1)	86.3(2)	Mn(2)–C(5)–O(5)	177(2)
P(2)–Mn(2)–C(4)	94.4(8)	Mn(2)–C(6)–O(6)	174(2)
P(2)–Mn(2)–C(5)	94.4(8)	Zn–N(1)–C(8)	103(1)
P(2)–Mn(2)–C(6)	89.0(8)	Zn–N(2)–C(7)	105(1)
C(4)–Mn(2)–C(5)	89.8(11)		

The structure of **11**, fully elucidated by an X-ray diffraction study, is depicted in Figure 4, together with the atom-numbering system. A summary of the important bond distances and angles is given in Table III. Compound **11** displays a triangular Mn_2Zn core geometry which is, to our knowledge, the first one characterized by X-ray diffraction methods. Thus, the values of the Mn–Zn distances, 2.525(4) and 2.544(4) Å, should be the first ones reported for Mn–Zn metal-metal bonds. In the complex $[MnZn_2(crotonate)_6(quinoline)_2]$, the only other Zn–Mn complex structurally characterized so far, three crotonate ligands bridge each Zn–Mn unit of the linear Zn–Mn–Zn metal arrangement.[28] There, the Mn–Zn separations of *ca.* 3.3 Å do not indicate any significant interaction between metal atoms but rather reflect the geometrical constraints imposed by the bridging ligands. The Mn–Mn bond distance in cluster **11**, 3.039(5) Å, is only slightly shorter than those found in the saturated Mn_2Au clusters

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[28] Clegg, W.; Little, I. R.; Straughan, B. P. *Inorg. Chem.* **1988**, *27*, 1916.

$[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}Br)(CO)_6(\mu\text{-}tedip)]$, 3.090(3) Å,[10] or $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)(CO)_8]$, 3.066(8) Å.[29] The manganese atoms are bridged by the tedip ligand, with its P atoms *trans* to the hydrido ligands. The latter in turn bridge symmetrically the two Mn–Zn edges of the cluster. This $Mn_2(\mu\text{-}H)_2Zn$ moiety is quite novel for hydridic M_2Zn compounds (M = transition metal); the only related structure is that of $[Zn(\mu\text{-}H)_2V(PMePh_2)_2(BH_4)]_2$, which exhibits a squashed butterfly V_2Zn_2 core made up of two similar $V_2(\mu\text{-}H)_2Zn$ moieties sharing a common V–V edge [V–Zn distances, 2.633(2) and 2.656(1) Å; V–V distance, 2.400(2) Å].[30] If the Mn–Zn bonds are ignored, the coordination geometry can be considered octahedral around the Mn atoms and tetrahedral around the zinc atom, which bears a tmeda molecule acting as a chelating ligand through the N atoms [values of the Zn–N bonds, 2.13(2) Å].

Spectroscopic data for **11** are fully consistent with its solid state structure. The weak intensity of the ν(CO) band at highest frequency (2008 cm^{-1}) denotes a *meridional* disposition of the CO ligands in the $Mn(CO)_3$ fragments of the molecule.[31] In agreement with the overall C_{2v} symmetry, the NMR spectra in C_6D_6 evidence single chemical environments for the phosphorus atoms or each the N–CH_2, N–Me and Me(tedip) hydrogen atoms of the molecule. The two equivalent hydrido ligands give rise to a somewhat broad singlet ($w_{1/2}$ = 12 Hz) at −12.74 ppm. The fact that no P–H coupling is observed in this signal is quite unexpected, given the approximately *trans* disposition of the atoms involved. $^2J_{HP}$ (through metal) coupling constants are commonly higher for *trans* than for *cis* relative arrangements of P and H atoms in octahedral complexes. However, the hydrido and P atoms in **11** constitute an AA′XX′ spin system, where $^2J_{HP}$ and $^3J_{HP}$ are the main contributions to P–H coupling. Two- and three-bond P–H coupling constants are frequently opposite in sign, and this could result in partial cancellation, causing the multiplet to collapse into a somewhat broad singlet.[32]

When the NMR spectrum of **11** is recorded in CD_2Cl_2, two isomers are detected in a ratio of ca. 1:7. No significant change in this ratio was observed in the range +25 to −80 °C. The major isomer corresponds to the species detected in C_6D_6 solution (and in the crystal). On the other hand, the minor isomer is characterized by a more shielded ^{31}P resonance, two different environments for the Me groups of the tedip ligand, and a broad hydrido resonance (−11.30 ppm, 2H) exhibiting P–H coupling. The latter resonance can be also interpreted as arising from an AA′XX′ spin system, but the shape is now analogous to those observed for the complexes **2** and **4** (angles between the trimetal planes and Mn_2POP pseudoplanes around 90°). At this point we should recall that the tetrahydrofuran complex **9** also exhibits two isomers in solution. Comparison of the NMR data for **9** and **11** (Table I and Experimental Section) reveals very strong similarities, and it is concluded that the same type of isomers are involved in both cases. We have called them isomers A and B. Isomer A is the major species for **9** and the minor one for **11**. It should then dominate the IR spectrum of **9**, which in fact exhibits six strong ν(CO) bands, itself consistent with the overall C_s symmetry of the molecule but also indicative of a facial disposition of the CO ligands in the $Mn(CO)_3$ fragments of the molecule.[31] We have chosen this isomer to represent the geometry of **9** in Scheme III. Finally, the more symmetrical isomer (B), corresponds to the structure found in the crystal for **11**, also the most abundant in its solutions, and the minor isomer in **9**.

The fact that the ratio of isomers for either **9** or **11** does not change significantly with the temperature can be interpreted as a consequence of their similar thermodynamic stabilities.[33] However, we cannot exclude the possibility that a kinetic barrier, perhaps only effective below room temperature, could be responsible for these observations. In any case, consideration of the geometries involved suggests that isomer A should be the isomer formed initially when **10** reacts with tetrahydrofuran or tmeda, as this represents a smaller reorganization at the dimanganese center.

The high reactivity exhibited by the blue cluster **10** should make it a valuable precursor for the synthesis of novel manganese–zinc mixed-metal clusters, and further studies in that direction are currently in progress in our laboratory.

Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified according to standard literature procedures[34] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 60–65 °C. The compounds $[Mn_2(\mu\text{-}Br)_2(CO)_6(\mu\text{-}tedip)]$,[35] $[HCu(PPh_3)]_6$,[36] $[Cu(BH_4)(PPh_3)_2]$,[37] $[Ag(BH_4)(PPh_3)_2]$,[38] $[CuCl(PPh_3)]_4$,[37] $[AuCl(PPh_3)]$,[39] and $[AuMe(PPh_3)]$,[40] were prepared according to literature procedures.

All other reagents were purchased from the usual commercial suppliers and used as received. Alumina for column chromatography was deactivated by appropriate addition of water under nitrogen to the commercial material (Aldrich, neutral, activity I). Filtrations were carried out using diatomaceous earth. Photochemical reactions were performed by irradiation with an Applied Photophysics 400-W mercury lamp using jacketed Pyrex vessels refrigerated by a closed 2-propanol circuit kept at the desired temperature with a Haake-3 cryostat. Infrared spectra were recorded on Perkin-Elmer 298 or 1720-X (FT) instruments. Proton, carbon, and phosphorus NMR spectra were measured with Varian FT-80-A or Bruker AC-300 instruments, at room temperature unless otherwise stated. Chemical shifts are given in ppm, relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 aqueous solution, with positive values for frequencies higher than that of the reference. Coupling constants are given in hertz. Elemental C, H, and N analyses were obtained with a Perkin-Elmer 240B microanalyzer.

Preparation of $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}tedip)]$ (1). (a) Using $Li[HBEt_3]$. A solution of $[Mn_2(\mu\text{-}Br)_2(CO)_6(\mu\text{-}tedip)]$ (1.000 g, 1.437 mmol) in tetrahydrofuran (30 mL) was treated with

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[32] The spacing between the most intense couple of lines in the A (or X) part of the spectrum arising from an AA′XX′ spin system is given by $|J_{AX} + J_{AX'}|$. In the case of compound **11** this is mainly the result of $^2J_{HP}$ + $^3J_{HP}$.

[33] If $\Delta H° \approx 0$ for the equilibrium A $\rightleftarrows$ B, then $\ln K_{eq} \approx -\Delta S°/R$, a value approximately temperature independent.

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Li[HBEt$_3$] (6.0 mL of an 1 M tetrahydrofuran solution, 6.0 mmol) for 1.5 h at room temperature. Degassed water (1 mL) was then added to the resulting dark green solution (gas evolution occurs), and solvents were removed in vacuum. The deep reed resulting residue was extracted with petroleum ether (5 × 10 mL), and the extractions were chromatographed on an alumina column (activity IV, 20 × 2.5 cm). Elution with petroleum ether gave a red-purple band which yielded, after removal of solvents in vacuum, compound **1** as a dark red microcrystalline solid. Usually, about 0.5 g of **1** are obtained (64%). This yield, however, is strongly dependent on the quality of the boron hydride (Superhydride, Aldrich) and solvent used, and yields in the range 0–83% have been obtained by us.

(b) Using K[HB(s-Bu)$_3$]. The procedure is completely analogous to the one previously described. The extraction step with petroleum ether is somewhat more facile (the deep red residue is less oily and sticky). Typical yields are around 60%, this also being strongly dependent on the quality of reagent (K-Selectride 1.0 M in tetrahydrofuran, Aldrich) and solvents used. Anal. Calcd for $C_{14}H_{22}Mn_2O_{11}P_2$: C, 31.25; H, 4.12. Found: C, 31.09; H, 4.25. ^{1}H NMR (79.54 MHz, CDCl$_3$): δ 4.13 (m, OCH$_2$, 8H), 1.38 (t, J_{HH} = 8, Me, 12H), −19.4 (t, J_{PH} = 30, μ-H, 2H).

Reaction of Compound 1 with CuX (X = Cl, I). (a) With CuI. Compound **1** (0.054 g, 0.1 mmol) and CuI (0.019 g, 0.1 mmol) were stirred in tetrahydrofuran (10 mL) for 2 h at room temperature, affording an orange solution. Solvent was then removed under vacuum to give an oil which was washed with cold petroleum ether to remove compound **3b** from the mixture (2 × 3 mL at −20 °C). The residue was dissolved in toluene and the solution filtered and concentrated under vacuum. Crystallization at −20 °C yielded [Mn$_4$Cu$_2$(μ-H)$_6$(CO)$_{12}$(μ-tedip)$_2$] (**2**) as well formed orange prisms (0.018 g, 30%). Anal. Calcd for $C_{28}H_{46}Cu_2Mn_4O_{22}P_4$: C, 27.91; H, 3.85. Found: C, 28.16; H, 3.78. ^{1}H NMR (300.13 MHz, CDCl$_3$, 22 °C): δ 4.1–3.9 (m, OCH$_2$, 16H), 1.38, 1.25 (2 × t, J_{HH} = 6.5, Me, 2 × 12H), −8.91 (AA′XX′ system, $J_{HP} + J_{HP'}$ = 39, Mn(μ-H)Cu, 4H), −25.98 (t, J_{HP} = 23, Mn$_2$(μ-H), 2H). ^{1}H NMR (300.13 MHz, CDCl$_3$, −45 °C): δ −8.42 (d, J_{HP} = 41, Mn(μ-H)Cu, 2H), −9.28 (d, J_{HP} = 38, Mn(μ-H)Cu, 2H), −26.56 (br, Mn$_2$(μ-H), 2H).

(b) With CuCl. The procedure is completely analogous to that described above, using CuCl (0.010 g, 0.1 mmol) instead of CuI. The orange oil was extracted with cold petroleum ether (2 × 5 mL, −20 °C), and the extractions were filtered and concentrated under vacuum. Crystallization of this solution at −20 °C yielded [Mn$_2$(μ-H)(μ-Cl)(CO)$_6$(μ-tedip)] (**3a**) as orange crystalline aggregates (0.015 g, 26%). Anal. Calcd for $C_{14}H_{11}ClMn_2O_{11}P_2$: C, 29.37; H, 3.70. Found: C, 29.42; H, 3.69. ^{1}H NMR (79.54 MHz, CDCl$_3$): δ 4.04 (m, OCH$_2$, 8H), 1.37, 1.31 (2 × t, J_{HH} = 7, 2 × 6H), −14.6 (t, J_{HP} = 29, Mn$_2$(μ-H), 1H). The residue obtained after extraction with petroleum ether was treated as described in the previous reaction and yielded 0.022 g (36%) of compound **2**.

Preparation of [Mn$_2$Cu(μ-H)$_3$(CO)$_6$(PPh$_3$)(μ-tedip)] (4a). Method A. Compound **1** (0.060 g, 0.11 mmol) and [HCu(PPh$_3$)]$_6$ (0.040 g, 0.12 mequiv) were stirred in toluene (10 mL) at room temperature for 20 min, yielding an orange solution. The solvent was removed under vacuum, the residue was extracted with petroleum ether (6 × 10 mL) and the extractions were filtered. Removal of solvent under vacuum gave a solid which was recrystallized from toluene–petroleum ether at −20 °C, yielding orange plates of compound **4a** (0.062g, 65%). Anal. Calcd for $C_{32}H_{38}CuMn_2O_{11}P_3$: C, 44.43; H, 4.43. Found: C, 44.83; H, 4.58. ^{1}H NMR (79.54 MHz, CDCl$_3$): δ 7.80–7.25 (m, Ph, 15H), 4.02, 3.69 (2 × m, OCH$_2$, 2 × 4H), 1.33, 1.01 (2 × t, J_{HH} = 7, Me, 2 × 6H), −9.0 (broad AA′XX′ system, $J_{HP} + J_{HP'}$ = 45, Mn(μ-H)Cu, 2H), −23.2 (t, J_{HP} = 29, Mn$_2$(μ-H), 1H).

Method B. Compound **1** (0.054 g, 0.1 mmol) and [Cu(BH$_4$)(PPh$_3$)$_2$] (0.060g, 0.1 mmol) were stirred in tetrahydrofuran (10 mL) for 20 min, yielding an orange solution. Workup as in the previous method yielded 0.052 g (60%) of compound **4a**.

Preparation of [Mn$_2$Ag(μ-H)$_3$(CO)$_6$(PPh$_3$)(μ-tedip)] (4b). Compound **1** (27 mg, 0.05 mmol) and [Ag(BH$_4$)(PPh$_3$)$_2$] (0.033 g, 0.05 mmol) were stirred in toluene (10 mL) at −20 °C for 10 min, affording an orange solution. IR and NMR spectra of this solution showed the presence of a species isostructural with the copper complex **4a** as the main product. This silver cluster, however, was thermally unstable even at −20 °C, and all attempts to isolate it as a solid resulted in progressive decomposition of the complex. ^{1}H NMR spectra for **4b** were obtained by carrying out the preparative reaction using toluene-d_8 as solvent and filtering the resulting solution with a cannula into an NMR tube kept at the same temperature. ^{1}H NMR (300.13 MHz, toluene-d_8, −45 °C): δ 4.0, 3.8 (2 × m, OCH$_2$, 2 × 4H), 1.05, 0.81 (2 × t, J_{HH} = 7, Me, 2 × 6H), −7.30 (broad AA′XX′M system, $J_{H-^{109}Ag} \approx J_{H-^{107}Ag}$ = 72, $J_{H-P} + J_{H-P'}$ = 42, Mn(μ-H)Ag, 2H), −23.61 (broad q, $J_{HP} \approx J_{H-^{109}Ag} \approx J_{H-^{107}Ag}$ = 24, Mn$_2$(μ-H), 1H).

Preparation of Tetrahydrofuran Solutions of Na[Mn$_2$H$_3$(CO)$_6$(μ-tedip)] (5). In a typical experiment, compound **1** (0.027 g, 0.05 mmol) and NaBH$_4$ (0.004 g, 0.1 mmol) were stirred in tetrahydrofuran at room temperature for 0.5 h, affording a yellow solution of pure compound **5**. Residual NaBH$_4$ is removed by filtration using a cannula. Lithium and potassium analogues of **5** can be prepared in a similar way, using LiBH$_4$ or KBH$_4$, respectively. These were found to be less stable than the sodium salt. The [PPN]$^+$ salt can be prepared analogously using [PPN]BH$_4$. All attempts to isolate the above salts as solid materials were unsuccessful and resulted in decomposition of the anion. ^{1}H NMR (300.13 MHz, tetrahydrofuran–C$_6$D$_6$): δ 4.0 (br, OCH$_2$, 8H), 1.23, 1.20 (2 × t, J_{HH} = 6, Me, 2 × 6H), −15.8 (br, Mn–H, 3H).

Preparation of [Mn$_2$Au(μ-H)(CO)$_6$(PPh$_3$)(μ-tedip)] (6). Compound **1** (0.280 g, 0.52 mmol) and [AuMe(PPh$_3$)] (0.270 g, 0.57 mmol) were stirred in toluene (25 mL) for 1 day at room temperature. The black-blue resulting solution was concentrated to ca. 5 mL under vacuum, mixed with 25 mL of petroleum ether, and chromatographed through an alumina column (activity V, 35 × 2.5 cm, 12 °C). Elution with toluene–petroleum ether (1:4) gave first a yellow fraction containing trace amounts of uncharacterized species and then a blue-violet fraction. Removal of solvents under vacuum from the latter yielded compound **6** as a blue-violet microcrystalline solid (0.495 g, 95%). The crystals used in the X-ray study were grown from a toluene–petroleum ether solution of **6** at −20 °C. Anal. Calcd for $C_{32}H_{36}AuMn_2O_{11}P_3$: C, 38.5; H, 3.64. Found: C, 38.92; H, 3.72. ^{1}H NMR (79.54 MHz, CDCl$_3$): 7.4 (m, Ph, 15H), 4.2 (m, OCH$_2$, 8H), 1.40, 1.14 (2 × t, J_{HH} = 7, Me, 2 × 6H), and −23.1 (t, J_{HP} = 33, Mn$_2$(μ-H), 1H).

Elution with toluene–petroleum ether (1:2) gave a minor blue fraction containing compound **8** (0.008 g, 1%).

Preparation of [Mn$_2$Au(μ-H)(CO)$_7$(PPh$_3$)(μ-tedip)] (7). Carbon monoxide was gently bubbled through a stirred toluene solution (10 mL) of compound **6** (0.070 g, 0.07 mmol) at room temperature for 0.5 h. Removal of solvent under vacuum gave a yellow oil which was recrystallized from dichloromethane–petroleum ether at −20 °C, to yield compound **7** as a yellow microcrystalline solid. This solid was separated from the solution, washed with petroleum ether at −20 °C (5 mL), and dried under vacuum (0.060 g, 85%). Anal. Calcd for $C_{33}H_{36}AuMn_2O_{12}P_3$: C, 38.69; H, 3.46. Found: C, 39.19; H, 3.60. ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$, 22 °C): δ 7.50–7.30 (m, Ph, 15H), 3.94 (m, OCH$_2$, 8H), 1.23, 1.06 (2 × t, J_{HH} = 7, Me, 2 × 6H), −6.50 (dt, J_{HP} = 90, 23, Mn(μ-H)Au, 1H). ^{1}H NMR (−90 °C): δ 7.50–7.30 (br, Ph), 3.91 (br, OCH$_2$), 1.19, 1.03 (2 × s, br, Me, 2 × 6H), −6.60 (ddd, J_{HP} = 90, 26, 20, Mn(μ-H)Au, 1H). ^{13}C{^{1}H} NMR (−90 °C): δ 227.7 (br, 2CO), 226.0 (br, 4CO), 220.4 (br, 1CO).

Preparation of [Mn$_2$Au$_2$(CO)$_6$(PPh$_3$)$_2$(μ-tedip)] (8). Compound **6** (0.025 g, 0.025 mmol) and [AuMe(PPh$_3$)] (0.015 g, 0.032 mmol) in toluene (8 mL) were stirred and irradiated with visible–UV light at 15 °C for 6 h, affording a dark green solution. Solvent was removed under vacuum and the residue extracted with toluene–petroleum ether (1:2) and chromatographed on an alumina column (activity V, 15 × 2.5 cm, 12 °C). Elution with the same solvent mixture gave first a minor yellow fraction, which was discarded, and then a blue fraction. Removal of solvents

Table IV. Experimental Data for the X-ray Diffraction Studies

	compd **6**	compd **11**
mol formula	$C_{32}H_{36}AuMn_2O_{11}P_3$	$C_{20}H_{38}Mn_2N_2O_{11}P_2Zn$
mol wt	996.39	719.73
cryst syst	monoclinic	orthorhombic
space group	$P2_1/a$	$Pcab$
radiatn	Nb-filtered Mo Kα (λ = 0.710 73 Å)	
a, Å	18.015(8)	16.198(5)
b, Å	20.700(8)	14.494(4)
c, Å	10.230(6)	26.894(9)
β, deg	94.90(2)	
V, Å^3	3801(3)	6314(3)
Z	4	8
D_{calcd}, g cm^{-3}	1.741	1.514
F(000)	1960	2960
cryst dimens, mm	0.30 × 0.36 × 0.42	0.15 × 0.20 × 0.24
μ(Mo Kα), cm^{-1}	46.49	16.79
2θ range, deg	6–50	6–48
reflectns measd	$\pm h,k,l$	h,k,l
no. of unique total data	6722	5525
no. of unique obsd data	3579 [$I > 2\sigma(I)$]	1464 [$I > 2\sigma(I)$]
R	0.0562	0.0537
R_w	0.0577	0.0598

under vacuum from the latter yielded compound 8 as a blue microcrystalline solid (0.015 g, 41%). Anal. Calcd for $C_{50}H_{50}Au_2Mn_2O_{11}P_4$: C, 41.29; H, 3.46. Found: C, 41.63; H, 3.40. ^1H NMR (300.13 MHz, C_6D_6): δ 7.40–6.91 (m, Ph, 30H), 4.66, 4.51 (2 × m, OCH_2, 2 × 4H), 1.24 (t, J_{HH} = 7, Me, 12H).

Preparation of Tetrahydrofuran Solutions of [$Mn_2Zn(\mu$-H)$_2(OC_4H_8)_2(CO)_6(\mu$-tedip)] (9). In a typical experiment, compound 1 (0.027 g, 0.05 mmol) and 1% zinc amalgam (ca. 10 g, 1.5 mmol of Zn) were stirred in tetrahydrofuran (10 mL) for 40 min, affording a yellow solution. The latter was filtered using a cannula and was then ready for further use. Removal of solvent under vacuum from these solutions causes the transformation of **9** into **10**. This process is reversed instantaneously by addition of tetrahydrofuran to the blue residue thus obtained. ^1H NMR (200.13 MHz, tetrahydrofuran-d_8): δ 4.30–3.80 (complex, OCH_2, isomers A and B); (isomer A) δ 1.36, 1.28 (2 × t, Me, 2 × 6H), −10.9 (broad AA′XX′ system, $J_{HP} + J_{HP'}$ = 34, Mn(μ-H)Zn, 2H); (isomer B) δ 1.35 (t, J_{HP} = 7, Me, 12H), −12.52 (s, $w_{1/2}$ = 15, Mn(μ-H)Zn, 2H). Ratio A:B = 2:1.

Preparation of [$Mn_2Zn(\mu$-H)$_2(CO)_6(\mu$-tedip)]$_2$ (10). To a solution of compound **9**, prepared as described above, was added 10 mL of toluene at 0 °C, and the solvents were removed under vacuum giving a blue residue. This residue was recrystallized from toluene–petroleum ether at −20 °C, giving compound **10** as an air-sensitive microcrystalline solid (0.024 g, 80%). Crystalline samples of **10** decompose slowly at room temperature under nitrogen and more rapidly (several hours) in toluene, benzene, or dichloromethane solution. Anal. Calcd for $C_{28}H_{44}Mn_4O_{22}P_4Zn_2$: C, 27.86; H, 3.67. Found: C, 28.38; H, 3.55. ^1H NMR (300.13 MHz, C_6D_6): δ 4.15–3.70 (m, OCH_2, 16H), 1.10 (unresolved m, Me, 12H), 1.00 (t, J_{HH} = 6, Me, 12H), −8.03 (AA′XX′ system, $J_{HP} + J_{HP'}$ = 34, Mn(μ-H)Zn, 2H), −23.23 (t, J_{HP} = 25, $Mn_2(\mu$-H), 2H).

Preparation of [$Mn_2Zn(\mu$-H)$_2(CO)_6(Me_2NCH_2CH_2NMe_2)(\mu$-tedip)] (11). Tetramethylethylenediamine (30 μL, ca. 0.2 mmol) was added to a stirred solution of compound **10** (0.060 g, 0.051 mmol) in toluene (10 mL) at 0 °C, which then turned yellow almost instantaneously. Solvent was removed under vacuum after 3 min, and the residue was washed with petroleum ether (2 × 5 mL), yielding compound **11** as a yellow microcrystalline solid (0.065 g, 90%). The crystals used in the X-ray study were grown by slow diffusion of a dichloromethane solution of 11 into a layer of petroleum ether, at room temperature. Anal. Calcd for $C_{20}H_{38}Mn_2N_2O_{11}P_2Zn$: C, 33.38; H, 5.32; N, 3.89. Found: C, 33.17; H, 5.22; N. 4.30. ^1H NMR (300.13 MHz, C_6D_6): δ 4.15 (m, OCH_2, 8H), 1.94 (s, NMe, 12H), 1.49 (s, NCH_2, 4H), 1.22 (t, J_{HH} = 7, Me, 12H), −12.74 (s, $w_{1/2}$ = 12 Hz, Mn(μ-H)Zn, 2H). ^1H NMR (CD_2Cl_2): (isomer B) δ 3.95 (m, OCH_2), 2.64 (s, NCH_2), 2.46 (s, NMe), 1.23 (t, J_{HH} = 7, Me), −13.03 (s, $w_{1/2}$ = 18 Hz, Mn(μ-H)Zn); relative integrals as in the C_6D_6 spectrum; (isomer A) δ 3.70 (br, OCH_2, other resonances obscured by those of the main isomer), 2.70 (s, NCH_2, 4H), 2.50 (s, NMe, 12H), 1.26 (t, obscured by isomer B, Me), 1.13 (t, J_{HH} = 7, Me, 6H), −11.30 (broad pseudodoublet, J_{HP} = 30, Mn(μ-H)Zn, 2H). Ratio A:B = 1:7.

Table V. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of Complex 6

	x/a	y/b	z/c	U
Au	2373(1)	1083(1)	3278(1)	518(2)^a
Mn(1)	1596(1)	186(1)	1885(2)	580(8)^a
Mn(2)	3076(1)	21(1)	2670(2)	541(7)^a
P(1)	2234(2)	2103(2)	4163(4)	458(11)^a
P(2)	3388(2)	477(2)	839(4)	628(15)^a
P(3)	1876(2)	705(2)	105(4)	724(17)^a
O(1)	1110(8)	−488(7)	4180(14)	1195(65)^a
O(2)	352(7)	1090(7)	2066(15)	1198(65)^a
O(3)	637(8)	−740(8)	442(14)	1195(71)^a
O(4)	4000(9)	−1105(7)	2159(15)	1250(74)^a
O(5)	4316(7)	648(7)	4213(14)	1066(59)^a
O(6)	2728(7)	−530(6)	5197(12)	1001(62)^a
O(7)	2746(5)	796(5)	−111(10)	723(40)^a
O(8)	1584(9)	1403(8)	−22(15)	1489(75)^a
O(9)	1646(10)	372(11)	−1238(15)	1691(110)^a
O(10)	3748(7)	−12(5)	−86(11)	899(46)^a
O(11)	3993(5)	1028(5)	871(11)	784(44)^a
C(1)	1359(9)	−210(8)	3352(19)	777(69)^a
C(2)	837(10)	726(9)	2004(17)	821(72)^a
C(3)	1013(10)	−353(9)	944(18)	865(76)^a
C(4)	3619(10)	−673(8)	2357(17)	815(62)^a
C(5)	3822(11)	399(8)	3554(17)	763(61)^a
C(6)	2831(9)	−314(7)	4177(17)	668(71)^a
C(7)	1701(14)	1878(12)	−884(27)	1497(85)
C(8)	991(12)	2223(10)	−1267(24)	1297(72)
C(91)	1062(45)	250(37)	−1772(93)	1578(296)
C(92)	1685(36)	331(28)	−2581(67)	1393(200)
C(10)	923(19)	227(15)	−3093(38)	1762(122)
C(11)	3991(17)	155(13)	−1397(26)	1711(96)
C(12)	4231(18)	−304(14)	−2093(32)	2341(135)
C(13)	3872(9)	1671(7)	1382(18)	772(45)
C(14)	4609(10)	2011(9)	1436(22)	1119(61)
C(15)	1298(7)	2264(6)	4568(14)	570(35)
C(16)	1032(10)	2888(9)	4718(18)	907(52)
C(17)	301(11)	2980(11)	5076(19)	1052(60)
C(18)	−106(13)	2469(9)	5311(20)	1116(64)
C(19)	114(12)	1866(11)	5171(21)	1115(67)
C(20)	870(9)	1736(8)	4801(15)	748(44)
C(21)	2798(7)	2289(6)	5687(13)	523(35)
C(22)	2799(10)	2892(9)	6226(19)	856(51)
C(23)	3190(10)	3042(9)	7407(19)	880(53)
C(24)	3581(10)	2565(8)	8051(20)	890(52)
C(25)	3574(10)	1956(9)	7550(18)	892(53)
C(26)	3171(9)	1828(8)	6345(16)	762(45)
C(27)	2433(7)	2732(6)	3009(13)	516(36)
C(28)	3123(11)	2998(8)	3021(20)	943(55)
C(29)	3292(13)	3445(9)	1998(20)	1036(63)
C(30)	2762(11)	3601(10)	1092(21)	997(56)
C(31)	2081(14)	3354(10)	1116(24)	1223(71)
C(32)	1907(11)	2900(8)	2074(18)	893(52)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray Data Collection, Structure Determination, and Refinement for Compounds 6 and 11. All crystals of compound 11 were of small size, so only a limited number of observed reflections could be obtained from the data collection. The crystallographic data for both compounds are summarized in Table IV. Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the niobium-filtered Mo Kα radiation and the $\theta/2\theta$ scan type. The reflections for both 6 and 11 were collected with a variable scan speed of 3–12° min^{-1} and a scan width from $(\theta - 0.60)°$ to $(\theta + 0.60 + 0.346 \tan \theta)°$. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following Lehmann and Larsen.[41] Intensities were corrected for Lorentz and po-

Table VI. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of Complex 11

	x/a	*y/b*	*z/c*	*U*
Zn	826(2)	498(2)	1454(1)	433(8)[a]
Mn(1)	865(2)	1581(2)	719(1)	431(11)[a]
Mn(2)	−66(2)	1876(2)	1687(1)	450(11)[a]
P(1)	460(4)	2946(4)	494(2)	543(24)[a]
P(2)	−503(4)	3156(5)	1360(3)	611(27)[a]
O(1)	1768(12)	1223(12)	−194(7)	852(80)[a]
O(2)	2301(10)	2376(12)	1240(7)	759(72)[a]
O(3)	−657(11)	810(12)	261(6)	810(77)[a]
O(4)	−1397(12)	708(13)	1268(7)	861(91)[a]
O(5)	−1085(12)	2015(13)	2583(7)	928(95)[a]
O(6)	1318(12)	2885(14)	2156(7)	965(87)[a]
O(7)	−106(10)	3546(10)	854(6)	665(69)[a]
O(8)	1102(10)	3773(11)	399(6)	701(71)[a]
O(9)	−91(12)	2915(10)	2(6)	793(73)[a]
O(10)	−1428(15)	3232(16)	1161(10)	1360(119)[a]
O(11)	−384(14)	4010(12)	1706(7)	1181(93)[a]
N(1)	404(11)	−892(12)	1479(6)	555(68)[a]
N(2)	1912(11)	−32(13)	1802(7)	554(80)[a]
C(1)	1422(16)	1367(15)	177(9)	560(100)[a]
C(2)	1723(15)	2067(15)	1047(8)	507(90)[a]
C(3)	−82(17)	1090(16)	463(8)	533(84)[a]
C(4)	−878(16)	1166(16)	1403(9)	552(89)[a]
C(5)	−666(14)	1983(15)	2223(10)	567(100)[a]
C(6)	805(16)	2505(18)	1952(9)	604(102)[a]
C(7)	1679(16)	−975(17)	1976(9)	652(105)[a]
C(8)	1181(14)	−1417(15)	1551(9)	542(103)[a]
C(9)	−195(14)	−1060(16)	1901(8)	614(70)
C(10)	14(14)	−1176(16)	997(8)	641(65)
C(11)	2180(16)	501(18)	2243(10)	837(78)
C(12)	2603(16)	−68(19)	1442(10)	747(79)
C(13)	1771(25)	3598(28)	50(15)	1280(140)
C(14)	1993(24)	4292(29)	−247(15)	2348(134)
C(15)	−497(21)	3748(23)	−180(12)	1176(111)
C(16)	−1225(25)	3492(26)	−458(16)	1441(145)
C(17)	−2194(42)	3235(46)	1422(23)	1945(293)
C(18)	−2773(20)	2413(24)	1399(11)	2394(107)
C(19)	−656(26)	4997(32)	1517(15)	1593(150)
C(20)	−89(27)	5576(29)	1741(15)	1564(147)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

larization effects. A correction for absorption was applied only to **6** (maximum and minimum values for the transmission factors were 1.311 and 0.653).[42] Only the observed reflections were used in the structure solution and refinements.

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, first with isotropic thermal parameters and then with anisotropic thermal parameters for the non-hydrogen atoms, except the carbons of the phenyl and ethyl groups for **6** and the carbons of the methyl and ethyl groups for **11**. An ethyl group of **6** was found disordered with the C(9) atom distributed in two positions of equal occupancy factors. The hydride atoms of both **6** and **11** were clearly localized from a ΔF map and refined isotropically. The hydrogen atoms (except those of the disordered ethyl group of **6** and all those of the ethyl groups of **11**) were placed at their geometrically calculated positions and refined "riding" on the corresponding carbon atom, with isotropic thermal parameters. The final cycles of refinement were carried out on the basis of 350 (**6**) and 307 (**11**) variables; after the last cycles, no parameters shifted by more than 0.79 (**6**) and 0.32 (**11**) e/Å^3. In the final cycles of refinement a weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K and g values were 0.795 and 0.0033 (**6**) and 0.578 and 0.0349 (**11**), respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 43. All calculations were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and the GOULD POWERNODE 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[44] The final atomic coordinates for the non-hydrogen atoms are given in Tables V (**6**) and VI (**11**). The atomic coordinates of the hydrogen atoms are given in Tables SI (**6**) and SII (**11**), and the thermal parameters, in Tables SIII (**6**) and SIV (**11**).

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Supplementary Material Available: Tables of hydrogen atom coordinates (Tables SI and SII), thermal parameters for the non-hydrogen atoms (Tables SIII and SIV), and complete bond distances and angles (Tables SV and SVI) (10 pages). Ordering information is given on any current masthead page.

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