Synthesis and Reactivity of a Novel Unsaturated Dimanganese Hydride Complex, $[Mn_2H_2(CO)_6\{(OEt)_2POP(OEt)_2\}]$. *X*-Ray Structure of $[Mn_4Cu_2H_6(CO)_{12}\{(OEt)_2POP(OEt)_2\}_2]$

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The synthesis of $[Mn_2H_2(CO)_6\{(OEt)_2POP(OEt)_2\}]$ and its reactions with tetrahydrothiophene, methyltriphenylphosphinegold(I), sodium amalgam followed by triphenylphosphine–group 1b metal cations, and with copper(I) halides are described; the structure of $[Mn_4Cu_2H_6(CO)_{12}\{(OEt)_2POP(OEt)_2\}_2]$ has been established by *X*-ray diffraction.

Polynuclear metal carbonyl complexes containing the formally unsaturated $(\mu\text{-H})_2M{=}M$ unit are of current interest. As exemplified by the extensive chemistry of the most representative complex $Os_3H_2(CO)_{10}$,[1] they can react under mild conditions with a variety of small molecules to give complexes which are not accessible by other routes. $Os_3H_2(CO)_{10}$ has recently proved to be valuable in the designed synthesis of mixed-metal clusters.[2] Other complexes of this type: $[Re_2H_2(CO)_8]$,[3] $[Re_3H_{4-n}(CO)_{10}]^{(1+n)-}$ (n = 1 or 0),[4,5] $[M_2H_2(CO)_8]^{2-}$ (M = Cr, Mo, or W),[6] $[Re_2H_2(CO)_6(LL)]$ (**1**) [LL = $Ph_2PCH_2PPh_2$ (dppm) or $(OEt)_2POP(OEt)_2$ (tedip)],[7] and $[Mn_2H_2(CO)_4(dppm)_2]$[8] (**2**) have not been investigated so extensively.

$[Re_2H_2(CO)_6(LL)]$
(**1**)
LL = dppm or tedip
$[Mn_2H_2(CO)_4(dppm)_2]$
(**2**)

We now report the synthesis of a new unsaturated dimanganese compound, $[Mn_2H_2(CO)_6(tedip)]$ (**3**), which is closely related to compounds (**1**) and (**2**). Compound (**3**) appears to be even more reactive than (**1**), reacting at room temperature with the bulky PPh_3 and with $PhC{\equiv}CH$, where (**1**) fails to react;[7] furthermore, it has synthetic advantages over (**2**), mainly because it has only one bridging bis-phosphorus ligand with less severe steric requirements than dppm. We also report initial results on its reactivity, with particular respect to mixed-metal cluster synthesis, and the *X*-ray crystal structure of one of its derivatives, $[Mn_4Cu_2H_6(CO)_{12}(tedip)_2]$ (**9**), which has an unusual metal framework.

Compound (**3**) was obtained by reduction of $[Mn_2Br_2(CO)_6(tedip)]$ (**4**)[9] with $Li(HBEt_3)$ in tetrahydrofuran (thf) at room temperature (see Scheme 1), and isolated as a dark red–purple microcrystalline solid; analytical and spectroscopic data† are fully consistent with the proposed

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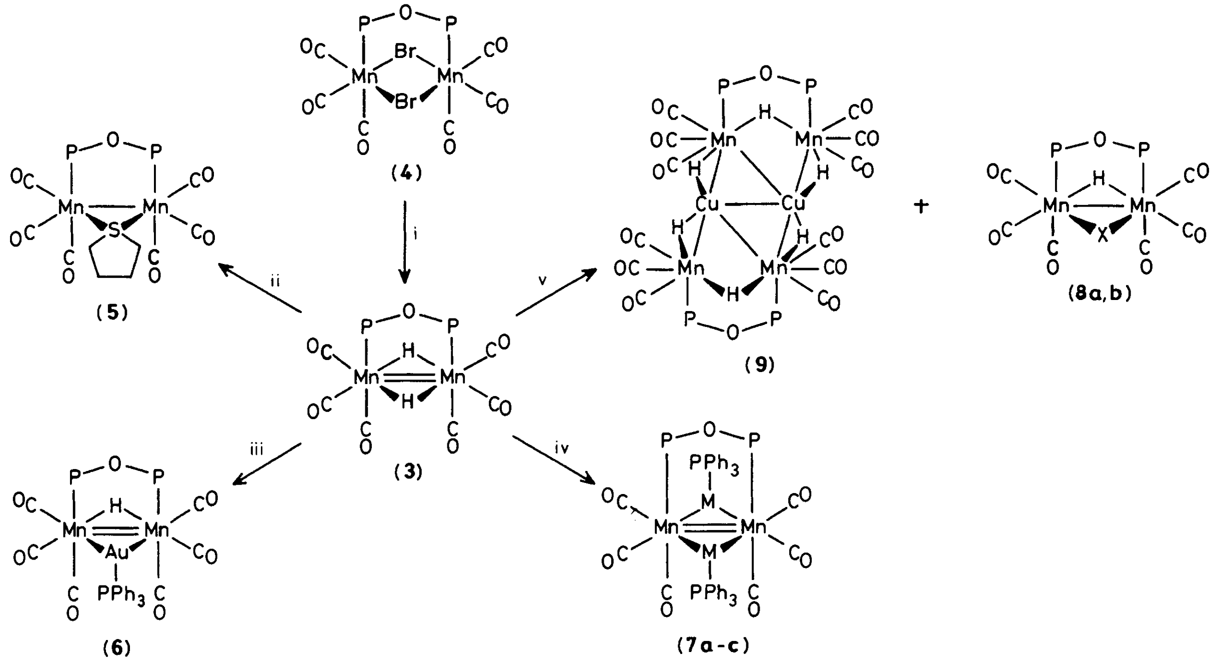
† Selected spectroscopic data [^{31}P chemical shifts are in p.p.m. to high frequency of 85% H_3PO_4 (external) for $^{31}P\{^1H\}$; coupling constants in Hz]. Compound (**3**), ν(CO) (petrol) 2057s, 2024s, 1978s, 1960s, and 1943vs cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ 4.1 (m, OCH_2, 8H), 1.4 (t, $^3J_{HH}$ 8, Me, 12H), and −19.4 (t, $^2J_{PH}$ 30, Mn–H–Mn, 2H); $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$), δ 168.9. Compound (**5**), ν(CO)(thf) 2016s, 1956vs, 1938vs, 1906m, and 1885m cm^{-1}; ^1H n.m.r. (C_6D_6), δ 3.9 and 3.5 (2 × m, OCH_2, 8H), 2.5 (m, SCH_2, 4H), 1.3 (m, SCH_2CH_2, 4H), and 0.9 and 0.8 (2 × t, $^3J_{HH}$ 6, 12H); $^{31}P\{^1H\}$ (C_6D_6), δ 178.5. Compound (**6**), ν(CO) (petrol) 2024s, 1986vs, 1951s, 1929s, and 1917vs cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ 7.4 (m, Ph, 15H), 4.2 (m, OCH_2, 8H), 1.4 and 1.1 (2 × t, $^3J_{HH}$ 7, Me, 12H), and −23.1 (t, $^2J_{PH}$ 33, 1H); $^{31}P\{^1H\}$($CDCl_3$), δ 173.9 (br, tedip) and 67.8 (t, $^3J_{PP}$ 19, $AuPPh_3$). Compound (**7a**), (thf) ν(CO) 1975m, 1936vs, 1891s, 1867s, and 1857m,sh cm^{-1}; (**7b**) and (**7c**) similar. Compound (**8a**), ν(CO) (petrol) 2064s, 2032s, 1983s, 1968s, and 1947vs cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ 4.0 (m, OCH_2, 8H), 1.4 and 1.3 (2 × t, $^3J_{HH}$ 7, Me, 12H), and −14.6 (t, $^2J_{PH}$ 29, Mn–H–Mn, 1H); $^{31}P\{^1H\}$($CDCl_3$), δ 158.3; (**8b**) similar. Compound (**9**), ν(CO) (CH_2Cl_2) 2034s, 2014m, 1963s, and 1938s, br cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ 4.0 (m, OCH_2, 8H), 1.4 and 1.2 (2 × t, $^3J_{HH}$ 7, Me, 12H), −9.0 (m, $J_{PH} + J_{P'H}$ 43, 2H), and −26.0 (t, $^2J_{PH}$ 25, Mn–H–Mn, 1H); $^{31}P\{^1H\}$($CDCl_3$), δ 167.6.



Scheme 1. *Reagents:* i, Li(BHEt$_3$) (4.1 equiv.), thf, room temp., 1.5 h; ii, excess of SC$_4$H$_8$, thf, room temp., 6 h; iii, MeAuPPh$_3$ 1.2 equiv.), toluene, room temp., 2 h; iv, Na–Hg, thf, room temp., 0.5 h, then ClMPPh$_3$, TlPF$_6$, thf, −15 °C, 10 min (**a**: M = Cu; **b**: M = Ag; **c**: M = Au); v, CuX, thf, room temp., 2 h (**a**: X = Cl; **b**: X = I). Ethoxy groups on phosphorus omitted for clarity.

structure, with the manganese–manganese double bond being required in order to fulfil the effective atomic number rule; so far we have been unable to obtain suitable crystals for an *X*-ray determination.

The reactivity of compound (**3**) is illustrated by Scheme 1. It reacts with tetrahydrothiophene in thf solution with displacement of both hydrides to afford [Mn(SC$_4$H$_8$)(CO)$_6$(tedip)] (**5**). Both hydrides are also displaced in the reaction of (**3**) with PPh$_3$; this result contrasts with the reactions of the analogous rhenium compounds (**1**) with two-electron donors, where no hydride displacement is observed;[7] however, we have not yet fully characterized the components of the resulting mixture.

One hydride can be replaced by the isolobal fragment AuPPh$_3$[10] in the reaction of (**3**) with MeAuPPh$_3$, to afford the trimetallic unsaturated cluster [Mn$_2$AuH(CO)$_6$(tedip)(PPh$_3$)] (**6**), which strongly resembles the osmium-gold cluster [Os$_3$AuH(CO)$_{10}$(PPh$_3$)];[11,12] the bridging tedip in (**6**) may be important in avoiding possible fragmentation of the cluster. The synthetic method for (**6**) has been described[11,13] by Stone and co-workers for the preparation of mixed-metal clusters containing the AuPPh$_3$ moiety.

Although further reaction of (**6**) with excess of MeAuPPh$_3$ under more forcing conditions led to decomposition, the tetranuclear cluster compounds (**7a**—**c**) can be obtained in a two-step process (see Scheme 1), probably involving the dianionic unsaturated intermediate [Mn$_2$(CO)$_6$(tedip)$_2$]$^{2-}$; however, the low stability of complexes (**7**) has precluded their complete characterization.†

The reaction of (**3**) with CuX (X = Cl or I) gives two compounds (Scheme 1): [Mn$_2$(μ-H)(μ-X)(CO)$_6$(μ-tedip)] (**8a,b**),† analogous to the bromo compound previously described by us,[9] and the manganese–copper cluster (**9**); in contrast, reaction of (**3**) with [(SC$_4$H$_8$)AuCl] gives (**8a**) as the only product. Spectroscopic† and analytical data for (**9**) were consistent with the stoicheiometry Mn$_2$CuH$_3$(CO)$_6$(tedip); its ^{1}H n.m.r. spectrum showed the presence of two types of hydride ligand in a ratio of 2 : 1, the more intense signal being compatible with either terminal hydrides bonded to manganese or hydrides bridging between manganese and copper atoms, and the less intense signal being assignable to a hydride bridging two manganese atoms. In order to characterize this compound completely, an *X*-ray structure determination was undertaken.‡

The structure of (**9**) (Figure 1) consists of a centrosymmetric dimer (with the crystallographic centre of symmetry lying on the midpoint of the Cu–Cu bond) showing an uncommon six-atom planar metal array. This can be described as an Mn$_2$Cu$_2$ lozenge with two further Mn atoms 'spiked', in the plane, to the Cu atoms. The difference Fourier map suggested that one hydride bridged the spike, Cu–Mn(2), the second triply bridged the triangle Cu,Cu′,Mn(1), and the third bridged the two Mn atoms which are too far apart for a metal–metal interaction [Mn(1) · · · Mn(2) 3.282(3) Å]. This metal array in (**9**) is comparable with that found in the

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‡ *Crystal data for* (**9**): C$_{28}$H$_{46}$Cu$_2$Mn$_4$O$_{22}$P$_4$, *M* = 1205.40, triclinic, space group $P\bar{1}$, a = 10.877(7), b = 13.849(8), c = 9.229(7) Å, α = 102.09(3), β = 102.99(3), γ = 109.02(2)°, U = 1219(1) Å^3, Z = 1, D_c = 1.642 g cm^{-3}, $F(000)$ = 608, λ = 0.710 69 Å, μ(Mo-K_α) = 20.23 cm^{-1}. The intensities of 4794 independent reflections were collected on a Philips PW 1100 diffractometer, (with θ in the range 3—26°) using the θ—2θ scan technique and graphite-monochromated Mo-K_α radiation. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares on the basis of 3008 observed reflections [$I \geqslant 3\sigma(I)$] with anisotropic thermal parameters for all the non-hydrogen atoms except those of the ethyl groups. One of the carbon atoms of the ethyl groups, C(12), was disordered and was placed in two positions with equal occupancy factors. Only three peaks were found in the final ΔF map in positions acceptable for hydridic hydrogen atoms and they were attributed to hydrides and introduced, but not refined, in the last structure factor calculations. Final R and R_w values 0.059 and 0.072.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

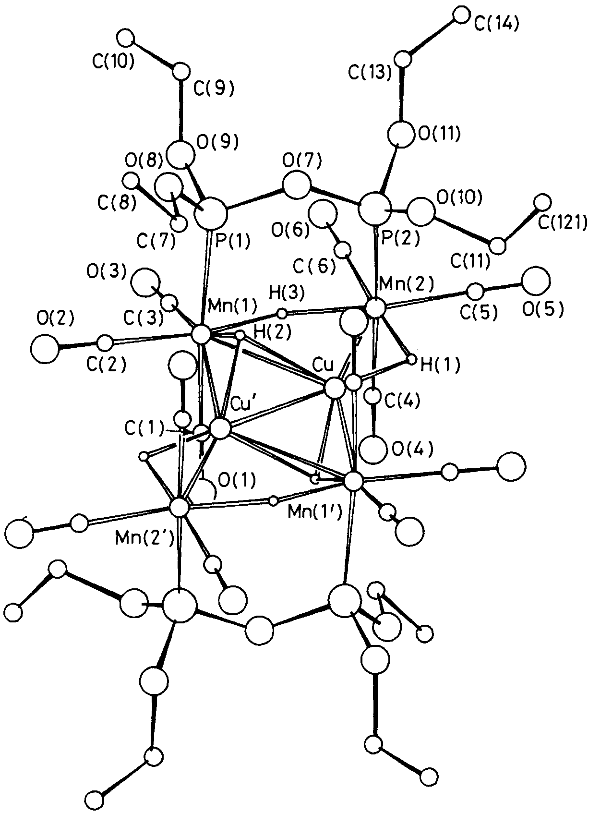

Figure 1. Structure of complex (**9**). Only the hydridic hydrogen atoms, found in acceptable positions, are indicated, for clarity. Only one position of the disordered ethyl group is shown. Selected bond distances (Å) and angles (°): Cu–Cu' 2.461(2), Cu–Mn(1) 2.735(2), Cu–Mn(1') 2.787(2), Cu–Mn(2) 2.565(2), Mn(1)–P(1) 2.231(3), Mn(2)–P(2) 2.212(3); Mn(1)–Cu–Mn(2) 76.4(1), Mn(1)–Cu–Mn(1') 127.1(1), Mn(2)–Cu–Mn(1') 156.5(1), Mn(1)–Cu–Cu' 64.6(1), Mn(2)–Cu–Cu' 141.1(1), Mn(1')–Cu–Cu' 62.5(1), Cu–Mn(1)–Cu' 52.9(1). The primed atoms are related to the unprimed ones by a crystallographic centre of symmetry.

structure of the cation $[Re_4Cu_2H_{16}(PMe_2Ph)_8]^{2+}$, in which, however, the Re–Re distance was very short and consistent with a metal–metal bond.[14]

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