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Electron-Donor Ability of the Unsaturated Dimanganese Hydrides $[Mn_2(\mu\text{-}X)(\mu\text{-}H)(CO)_6(\mu\text{-dppm})]$ (X = H, $AuPPh_3$; dppm = $Ph_2PCH_2PPh_2$). X-ray Crystal Structures of $[Mn_2\{\mu\text{-}Ag(ClO_4)PPh_3\}(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ and $[Mn_2(\mu\text{-}AuPPh_3)_2(\mu\text{-}H)(CO)_6(\mu\text{-dppm})][PF_6]\cdot C_7H_8$

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The electron-donor ability of the unsaturated dimanganese hydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ and $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)(CO)_6(\mu\text{-dppm})]$ (dppm = $Ph_2PCH_2PPh_2$) is shown by the reactions of the former with $[AuPPh_3]^+$ or $[Ag(ClO_4)PPh_3]$ and those of the Mn_2Au cluster with H^+ or $[AuPPh_3]^+$. All these reactions result in the coordination of the unsaturated dimanganese moiety to the acidic species, thus affording the new unsaturated heterometallic clusters $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]A$ (A^- = BF_4^-, PF_6^-), $[Mn_2\{\mu\text{-}Ag(ClO_4)PPh_3\}(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$, and $[Mn_2(\mu\text{-}AuPPh_3)_2(\mu\text{-}H)(CO)_6(\mu\text{-dppm})][PF_6]$. The last two compounds display dynamic behavior in solution, and their crystal structures have been solved by X-ray diffraction methods. The manganese–silver cluster crystallizes in the triclinic space group $P\bar{1}$ (a = 13.308 (2) Å, b = 14.660 (1) Å, c = 14.738 (1) Å, α = 113.90 (1)°, β = 91.19 (4)°, γ = 109.08 (1)°, V = 2445 (1) Å^3, Z = 2). The structure was refined to R = 0.031 (R_w = 0.037) for 3682 reflections with $I \geq 3\sigma(I)$. The triangular metal core is characterized by a short Mn–Mn distance (2.740 (1) Å) and long Mn–Ag ones (average 2.945 (1) Å), and it is triply bridged by one hydrido ligand; in addition, the Mn–Mn edge is bridged by a second hydrogen atom and the dppm ligand. The manganese–gold cluster (toluene solvate) crystallizes in the monoclinic space group $P2_1/a$ (a = 17.539 (9) Å, b = 25.532 (9) Å, c = 17.888 (3) Å, β = 118.02 (5)°, V = 7158 Å^3, Z = 4). The structure was refined to R = 0.051 (R_w = 0.057) for 2317 reflections with $I \geq 3\sigma(I)$. The cation contains an asymmetrical butterfly Mn_2Au_2 core with a somewhat short Mn–Mn distance (2.864 (5) Å). The hydrido ligand could not be located, but it is deduced that it must be triply bridging the $Mn_2Au(2)$ face by consideration of the bond angles involved and the significant differences between MnAu(2) (average 2.806 (4) Å) and MnAu(1) (average 2.684 (4) Å), this being in agreement with the variable-temperature NMR data in solution.

Introduction

Transition-metal carbonyls which contain the unsaturated moiety $M_2(\mu\text{-}H)_2$ (M=M) have received considerable attention because of their high reactivity toward a great variety of molecules under mild conditions, this being evidenced by the extensive chemistry developed around $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.[1,2] Bonding in these $M_2(\mu\text{-}H)_2$ moieties is still a matter of controversy, and although a formal double metal–metal bond is usually postulated so as to fulfill the EAN rule, there seems to be little support for this assumption. Rather, MO calculations on $[Os_3(\mu\text{-}H)_2(CO)_{10}]$[3] and $[M_2(\mu\text{-}H)_2(CO)_8]^{n-}$ (n = 2, M = Cr, Mo, W; n = 0, M = Mn, Re)[4] indicate small[3] or practically nonexistent[4] direct M–M bonding, this being mostly accomplished through the hydrogen bridges, as in diborane. Just as in the case for diborane, the above hydrido complexes exhibit a marked Lewis acid behavior, as expected for electron-deficient species, while there is no experimental evidence of neutral unsaturated $M_2(\mu\text{-}H)_2$ centers behaving as pure electron donors. Previous work in this area includes NMR studies on $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and related complexes in CF_3CO_2H solution, which suggested protonation at the unbridged Os–Os bonds,[5] although independent work on this reaction (in dichloromethane as solvent) has suggested that the process also involves coordination of the trifluoroacetate anion,[6] a circumstance which, in fact, leads to the electronic saturation of the cluster. However, we have reported recently,[7] that the unsaturated dihydride $[Mn_2(\mu\text{-}H)_2(\mu\text{-dppm})(CO)_6]$ (1;[8] dppm = $Ph_2PCH_2PPh_2$) reacts with borane, thus suggesting an incipient Lewis base character of compound 1. In this paper we describe the reactions of HBF_4 and some group 11 complex cations with compounds 1 and $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)(CO)_6(\mu\text{-dppm})]$ (2), a cluster related to 1 through the isolobal relationship H ↔ $AuPPh_3$.[9] These results provide the first experimental evidence of a pure Lewis base behavior of unsaturated $M_2(\mu\text{-}H)_2$ centers in neutral, low-valent complexes, and they are likely to provide some indirect information about the electron density distribution at these centers. An analogous behavior has

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Table I. Spectroscopic Data for New Compounds

compd	ν(CO)/cm^{-1}	^{1}H NMR/δ^a	^{31}P NMR/δ^a
$[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)(CO)_6(\mu\text{-}dppm)]$ (2)	2005 vs, 1970 vs, 1928 m, 1897 vs, br^b	7.5–7.0 (m, Ph), 3.8, 3.6 (2 × q, 10,^{c,d} CH$_2$), −21.06 (t, 25,^{d} μ-H)^e	64.7 (s, br, dppm), 70.0 (s, br, PPh$_3$)^e
$[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)_2(CO)_6(\mu\text{-}dppm)]^+$ (3) (BF_4^- salt)	2047 vs, 2024 vs, 1979 s, 1953 s^f	7.7–6.8 (m, Ph), 3.9 (q of d, 12.5,^{c,d} 3.5,^{c} CH$_2$), 3.5 (dt, 12.5,^{c} 10.5,^{d} CH$_2$), −14.1 (dt, 74, 16,^{d} μ_3-H), −18.6 (t, 16,^{d} μ_2-H)	61.6 (s, br, dppm), 57.5 (s, PPh$_3$)
$[Mn_2\{\mu\text{-}Ag(ClO_4)PPh_3\}(\mu\text{-}H)_2(CO)_6(\mu\text{-}dppm)]$ (4)	2037 vs, 2012 vs, 1958 s, sh, 1940 vs^b	7.9–6.9 (m, Ph), 3.6 (s, br, CH$_2$), −17.7 (t, br, 17,^{d} μ-H)^g 4.4 (s, br, CH$_2$), 2.9 (s, br, CH$_2$), −17.1 (br, μ_3-H), −18.4 (br, μ_2-H)^h	62.4 (s, br, dppm), 15.0 (br, PPh$_3$)^g 62.1 (s, dppm), 14.5 (dd, 666,^{i} 577,^{j} PPh$_3$)^h
$[Mn_2(\mu\text{-}AuPPh_3)_2(\mu\text{-}H)(CO)_6(\mu\text{-}dppm)]^+$ (5) (PF_6^- salt)	2015 s, 1986 vs, 1948 m, 1932 m, sh, 1925 s	7.8–6.7 (m, Ph), 4.06 (t, 11,^{d} CH$_2$), −18.07 (tt, 33, 22,^{d} μ-H) 4.2, 3.8 (2 × m, br, CH$_2$), −18.1 (br, μ_3-H)^k	63.6 (s, br, dppm), 62.7 (s, br, PPh$_3$) 67.8 (s, br, PPh$_3$), 63.6 (s, br, dppm), 54.0 (s, br,^{l} PPh$_3$)^k

[a] In units of ppm relative to internal TMS (^{1}H) or external 85% aqueous H_3PO_4 (^{31}P, proton decoupled), in CD_2Cl_2 at 295 K unless otherwise stated. Positive values correspond to frequencies higher than the reference. Coupling constants are in Hz and are given in parentheses. [b] Toluene solution. [c] J(HH). [d] J(PH). [e] In $CDCl_3$. [f] In dichloromethane. [g] In toluene-d_8, at 295 K. [h] In toluene-d_8, at 243 K. [i] $J(^{109}AgP)$. [j] $J(^{107}AgP)$. [k] In CD_2Cl_2, at 183 K. [l] J(PH) = 60 Hz (from a ^{1}H-coupled spectrum).

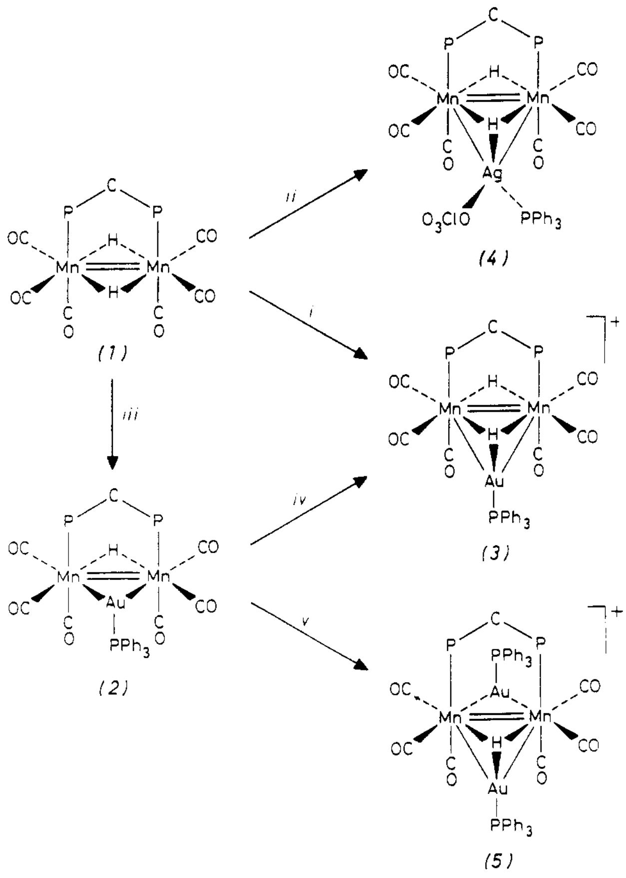
been found in the reactions of the dirhenium(IV) polyhydride $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]$ ($Re\equiv Re$) with H$^+$ and $[AuPPh_3]^+$,[10] but the presence here of both bridging and terminal hydrido ligands in the parent substrate makes it doubtful to conclude whether the active electron-donor center responsible for the acid–base reaction should be placed at the bridging or rather at the terminal hydrido positions. In fact, the electron-donor ability of terminal metal–hydrogen bonds is a well-known feature which has found wide synthetic applications.[11]

Results and Discussion

Preparation of $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)(CO)_6(\mu\text{-}dppm)]$ (2). Compound 2 can be prepared in high yield through the reaction of 1 with $MeAuPPh_3$ at room temperature. Spectroscopic data for 2 (Table I) indicate a close structural similarity with $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$,[12] for which an X-ray crystal structure study[13] has confirmed the proposed geometry. Compounds 1 and 2 are then isostructural as well as isolobal (recalling the relationship H ↔ AuPPh$_3$). However, electron densities at the respective unsaturated dimanganese centers are different, and their donor abilities must also differ. This difference would be essentially derived from the lower electronegativity of the gold fragment relative to that of a hydrogen atom, and it is reflected in a lower average ν(CO) frequency for 2 (1939 cm^{-1}) when compared with 1 (1967 cm^{-1}, both in toluene solution). Then, it is predicted that compound 2 should be a better electron donor than 1.

Reactions with $HBF_4{\cdot}OEt_2$. Compound 1 reacts with $HBF_4{\cdot}OEt_2$ in dichloromethane at room temperature, but the species initially formed has not been yet characterized, as it quickly evolves into a complicated mixture of products. In contrast, the analogous reaction of 2 and this acid at −10 °C gives the moderately stable violet cation $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)_2(CO)_6(\mu\text{-}dppm)]^+$ (3) (BF_4^- salt) in essentially quantitative yield. The structure proposed for this cation (Scheme I) is derived from that found in the X-ray study of 4 (discussed below; Figure 1) and is consistent with the corresponding spectroscopic data (Table I), which denote the presence of a mirror plane perpendicular to the Mn–Mn bond containing two distinct hydrido ligands as well as the Au–PPh$_3$ moiety. The −18.6 ppm resonance is assigned to a symmetrical $Mn_2(\mu_2\text{-}H)$ bridging H atom, on the basis of its chemical shift and absence of coupling with the PPh$_3$ phosphorus atom, whereas the lower field resonance (−14.1 ppm) is assigned to a μ_3-hydrogen atom bridging the Mn$_2$Au triangle, which is consistent with its relatively large coupling (74 Hz) with that phosphorus atom, somewhat lower than the usual values found in $M(\mu_2\text{-}H)Au$ systems (80–110 Hz).[14,15] In accord with the lack of symmetry relative to the pseudoplane defined by the manganese and phosphorus atoms

Scheme I[a]



[a] Legend: P–C–P = dppm; (i) $[AuPPh_3]^+$, dichloromethane; (ii) $[Ag(ClO_4)PPh_3]$, toluene; (iii) $MeAuPPh_3$, toluene; (iv) $HBF_4{\cdot}OEt_2$, dichloromethane; (v) $[AuPPh_3]^+$, dichloromethane.

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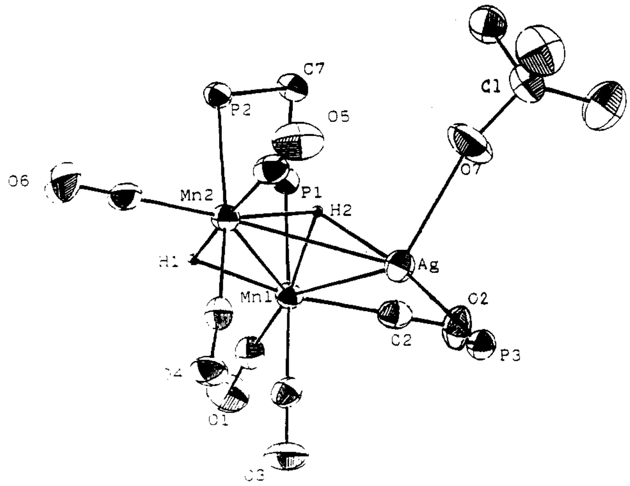

Figure 1. Molecular structure of **4**. Phenyl rings are omitted for clarity; C (CO) labels are the same as for the corresponding O atoms.

of the dppm ligand, the methylenic protons are nonequivalent, one of them displaying an observable long-range (five-bond) P–H coupling of 3.5 Hz, which can be compared with $^5J(PH)$ = 1.5 Hz for the cationic species *cis*-$[Fe(CNPh)_2\{C(NHPh)NMeC{=}NPh\}\{Ph_2P(CH_2)_2PPh_2\}]ClO_4$.[16]

The structure of **3** could suggest that proton attack on **2** occurs at the $Mn_2(\mu\text{-}Au)$ bridge. However, by consideration of the higher electronegativity of H relative to that of $AuPPh_3$, it is expected that electron density at the $Mn_2(\mu\text{-}H)$ bridging region in compound **2** should be higher than that at the $Mn_2(\mu\text{-}Au)$ one, leading to the prediction that the initial H^+ attack on **2** should be directed rather at the $Mn_2(\mu\text{-}H)$ bridge. In the latter case, the acid–base adduct initially formed would have to experience an hydrogen migration in order to yield cation **3**, a process which would not require much energy, given the well-known high mobility of hydrido ligands in cluster compounds.[17] Therefore, in light of the current data alone, we cannot exclude either of the possibilities stated above.

Reactions with Group 11 Metal Complexes. Having examined the reactions of compounds **1** and **2** toward H^+, we turned our attention to the related cationic fragments $[M(PPh_3)]^+$ (M = Cu, Ag, Au), which can be generated "in situ" from the corresponding chloro derivatives in the presence of $TlPF_6$ as halide abstractor.[17]

No stable mixed-metal compounds were identified in the reactions of the copper or silver complexes with **1**. In these cases, the only carbonyl-containing species present in the mixtures obtained after long reaction times was $[Mn_2(CO)_8(\mu\text{-dppm})]$.[18] Surprisingly, however, **1** reacts in toluene at room temperature with $[Ag(ClO_4)(PPh_3)]$ (presumably an alternative source of the silver–phosphine cation) to afford the violet neutral unsaturated cluster $[Mn_2\{\mu\text{-}Ag(ClO_4)PPh_3\}(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm}]$ (**4**) in high yield. The presence of coordinated perchlorate in **4** was suggested by the appearance of new bands in the solid-state IR spectrum (Nujol mull) at 1140 s, 1040 s, and 920 m cm^{-1}, possibly derived from unidentate coordination;[19] however, assignments here can only be tentative in the presence of coordinated dppm and PPh_3, which also absorb in this region of the spectrum. Moreover, NMR spectra for **4** were indicative of a dynamic behavior in solution (Table I). Therefore, in order to elucidate more precisely the structure of this cluster, an X-ray diffraction study was undertaken.

Table II. Experimental Data for the Crystallographic Analysis of the Compounds $[Mn_2\{\mu\text{-}Ag(ClO_4)PPh_3\}(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ (4) and $[Mn_2(\mu\text{-}AuPPh_3)_2(\mu\text{-}H)(CO)_6(\mu\text{-dppm})][PF_6]\bullet C_7H_8$ (5)

	4	5
formula	$C_{49}H_{39}AgClMn_2O_{10}P_3$	$C_{74}H_{61}Au_2F_6Mn_2O_6P_5$
M_r	1134	1810.9
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/a$
a, Å	13.308 (2)	17.539 (9)
b, Å	14.660 (1)	25.532 (9)
c, Å	14.738 (1)	17.888 (3)
α, deg	113.90 (1)	
β, deg	91.19 (4)	118.02 (5)
γ, deg	109.08 (1)	
V, Å^3	2445 (1)	7158 (4)
Z	2	4
d(calcd), g cm^{-3}	1.54	1.68
rflns for lattice params: no., range	25, 14–15	25, 10–12
$F(000)$	1144	3560
temp, °C	18	18
cryst size, mm	0.50 × 0.35 × 0.25	0.65 × 0.30 × 0.15
diffractometer	Philips PW1100	
monochromator	graphite	
radiation	Mo Kα	
scan type	ω–2θ	
scan width	$1.2 + 0.34 \tan\theta$	
θ range, deg	1–25	1–20
std rflns	two, measd every 2 h	
μ, cm^{-1}	10.9	45.8
no.of measd rflns	4421	3375
no. of rflns used with $I \geq 3\sigma(I)$	3682	2317
min, max final $\Delta\rho$, e Å^{-3}	–0.07, 0.09	–1.3, 1.3
no. of refined params	622	473
$R = [\sum\lvert\Delta F\rvert/\sum F_o]$	0.031	0.051
$R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$	0.037	0.057
w	1	1

The molecular structure of **4** is shown in Figure 1. The cluster consists of a Mn_2Ag metal triangle bridged by the hydrido ligand H(2), with the Mn_2 edge bridged by a second hydrogen atom, H(1), and the dppm ligand. As anticipated from IR data, each of the manganese atoms has three terminal carbonyl ligands. The silver atom is further bonded to an oxygen atom of the perchlorate ligand (O(7)) and the triphenylphosphine phosphorus (P(3)), the latter pointing away from the dppm ligand. Mn(1), Mn(2), O(7), and P(3) define a distorted-tetrahedral geometry around silver, Mn–Ag–Mn and O–Ag–P angles being 55.43 (3) and 115.8 (2)°, respectively. The intermetallic distances are worthy of comment. The Mn–Mn distance is short (2.740 (1) Å), only 0.04 Å longer than that found in **1** (2.699 (2) Å[9]), and therefore consistent with the formal unsaturation of the cluster, whereas the Mn–Ag distances (2.961 (1) and 2.929 (1) Å) must be considered long (for instance, Mn–Ag is 2.6464 (3) Å for $[Cp(CO)_2Mo(\mu\text{-}PPh_2)(\mu\text{-}AgPPh_3)Mn(CO)_4]$[20]). Therefore, it seems that the unsaturated $Mn_2(\mu\text{-}H)_2$ center in **1** experiences little perturbation upon coordination to the acidic bent $Ag(ClO_4)(PPh_3)$ fragment. As the latter should provide the dimanganese center with no electrons, thus resembling $[Au(PPh_3)]^+$ or bent $[Au(PPh_3)_2]^+$,[10] the above structural data point to a description of the bonding in **4** in terms

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Table III. Atomic Positional and Thermal Parameters for Compound 4[a]

atom	*x/a*	*y/b*	*z/c*	*U*(equiv), Å^2	atom	*x/a*	*y/b*	*z/c*	*U*(equiv), Å^2
Mn(1)	0.10748 (8)	0.12278 (8)	0.38246 (7)	0.0363	C(22)	0.0496 (6)	0.4458 (6)	0.3644 (6)	0.0587
Mn(2)	0.26766 (8)	0.06737 (8)	0.43906 (7)	0.0367	C(23)	0.1167 (7)	0.4775 (6)	0.3045 (6)	0.0636
Ag(1)	0.23054 (5)	0.03087 (4)	0.22847 (4)	0.0480	C(24)	0.2143 (7)	0.4651 (6)	0.3014 (6)	0.0643
P(1)	0.2039 (1)	0.3067 (1)	0.4766 (1)	0.0370	C(25)	0.2456 (6)	0.4180 (6)	0.3555 (5)	0.0491
P(2)	0.3791 (1)	0.2459 (1)	0.5357 (1)	0.0365	C(30)	0.5218 (5)	0.2677 (5)	0.5297 (5)	0.0384
P(3)	0.1923 (2)	−0.1208 (2)	0.0666 (1)	0.0448	C(31)	0.5753 (6)	0.2395 (6)	0.5903 (6)	0.0546
Cl(1)	0.4354 (2)	0.2683 (2)	0.2080 (2)	0.0689	C(32)	0.6778 (7)	0.2396 (7)	0.5772 (7)	0.0670
O(1)	−0.0909 (4)	0.1513 (5)	0.4483 (4)	0.0697	C(33)	0.7267 (6)	0.2687 (7)	0.5067 (7)	0.0689
O(2)	0.0545 (4)	0.1591 (4)	0.2068 (4)	0.0663	C(34)	0.6730 (6)	0.2956 (7)	0.4474 (7)	0.0678
O(3)	−0.0457 (4)	−0.1024 (4)	0.2730 (4)	0.0681	C(35)	0.5709 (6)	0.2960 (6)	0.4594 (6)	0.0535
O(4)	0.1280 (4)	−0.1629 (4)	0.3431 (4)	0.0542	C(40)	0.3793 (5)	0.3053 (5)	0.6710 (5)	0.0408
O(5)	0.4474 (4)	0.0113 (5)	0.3460 (5)	0.0724	C(41)	0.3062 (6)	0.2525 (6)	0.7154 (6)	0.0615
O(6)	0.3330 (5)	0.0172 (5)	0.6003 (4)	0.0768	C(42)	0.3079 (7)	0.3001 (8)	0.8178 (6)	0.0804
O(7)	0.3546 (9)	0.2101 (8)	0.2394 (7)	0.0906	C(43)	0.3802 (7)	0.4016 (8)	0.8767 (6)	0.0752
O(8)	0.477 (1)	0.3647 (8)	0.2990 (9)	0.0691	C(44)	0.4518 (7)	0.4552 (6)	0.8342 (6)	0.0621
O(9)	0.5180 (8)	0.2283 (9)	0.1821 (8)	0.1020	C(45)	0.4525 (6)	0.4088 (6)	0.7322 (5)	0.0525
O(10)	0.3977 (9)	0.285 (1)	0.127 (1)	0.1148	C(50)	0.2547 (6)	−0.2126 (5)	0.0710 (5)	0.0433
O(7)′	0.312 (2)	0.207 (2)	0.198 (2)	0.095 (7)*	C(51)	0.2251 (8)	−0.2609 (6)	0.1361 (6)	0.0685
O(8)′	0.489 (2)	0.383 (2)	0.283 (2)	0.045 (7)*	C(52)	0.277 (1)	−0.3245 (1)	0.1467 (7)	0.0810
O(9)′	0.459 (3)	0.176 (2)	0.216 (2)	0.115 (8)*	C(53)	0.3565 (9)	−0.3405 (8)	0.0948 (8)	0.0892
O(10)′	0.446 (3)	0.259 (3)	0.123 (2)	0.072 (8)*	C(54)	0.3861 (7)	−0.2955 (8)	0.0300 (7)	0.0838
C(1)	−0.0107 (6)	0.1423 (6)	0.4257 (5)	0.0487	C(55)	0.3353 (6)	−0.2305 (6)	0.0186 (6)	0.0602
C(2)	0.0765 (5)	0.1460 (5)	0.2754 (5)	0.0478	C(60)	0.2329 (6)	−0.0968 (6)	−0.0407 (5)	0.0514
C(3)	0.0187 (5)	−0.0188 (6)	0.3146 (5)	0.0453	C(61)	0.3248 (8)	−0.0102 (7)	−0.0240 (7)	0.0828
C(4)	0.1789 (5)	−0.0729 (6)	0.3765 (5)	0.0421	C(62)	0.362 (1)	0.0059 (9)	−0.1073 (9)	0.1137
C(5)	0.3793 (6)	0.0348 (6)	0.3814 (6)	0.0522	C(63)	0.306 (1)	−0.063 (1)	−0.2025 (8)	0.0997
C(6)	0.3062 (6)	0.0389 (6)	0.5393 (6)	0.0515	C(64)	0.2152 (8)	−0.1484 (9)	−0.2184 (6)	0.0844
C(7)	0.3504 (5)	0.3385 (5)	0.4927 (5)	0.0374	C(65)	0.1785 (6)	−0.1665 (7)	−0.1377 (6)	0.0656
C(10)	0.1806 (5)	0.3765 (5)	0.6032 (5)	0.0410	C(70)	0.0457 (6)	−0.1940 (7)	0.0287 (5)	0.0544
C(11)	0.2363 (6)	0.4868 (6)	0.6562 (5)	0.0539	C(71)	−0.0165 (7)	−0.1351 (9)	0.0308 (7)	0.0741
C(12)	0.2229 (7)	0.5429 (6)	0.7530 (6)	0.0633	C(72)	−0.1287 (9)	−0.187 (1)	−0.0005 (8)	0.1007
C(13)	0.1536 (7)	0.4899 (7)	0.7986 (6)	0.0694	C(73)	−0.1719 (9)	−0.294 (1)	−0.0290 (8)	0.0939
C(14)	0.0991 (7)	0.3806 (7)	0.7478 (6)	0.0701	C(74)	−0.1158 (8)	−0.353 (1)	−0.0299 (8)	0.1036
C(15)	0.1135 (6)	0.3246 (6)	0.6518 (5)	0.0547	C(75)	−0.0021 (7)	−0.3045 (8)	−0.0021 (7)	0.0868
C(20)	0.1778 (5)	0.3845 (5)	0.4147 (5)	0.0395	H(1)	0.156 (3)	0.114 (4)	0.494 (3)	0.08 (2)*
C(21)	0.0797 (6)	0.3990 (6)	0.4203 (6)	0.0526	H(2)	0.239 (4)	0.131 (4)	0.359 (3)	0.11 (3)*

[a] Values marked with an asterisk are isotropic *U*'s.

of a rather weak interaction between the $Mn_2(\mu\text{-}H)_2$ center (base) and the silver moiety (acid), which is reflected chemically in the fact that compound 4 easily dissociates in solution (for instance, in donor solvents such as diethyl ether or tetrahydrofuran) to regenerate the parent dihydride 1. This description is also substantiated by comparison of the average ν(CO) stretching frequencies (1967 cm^{-1} for 1 and 1977 cm^{-1} for 4, both in toluene solution), which is indicative of a modest electron density flow from the dimanganese center to the silver fragment, certainly lower than in the case of compound 3 (average ν(CO) 1991 cm^{-1} in dichloromethane).

As stated before, compound 4 displays a dynamic behavior in solution. In fact, the ^{1}H NMR spectrum at 295 K cannot be reconciled with the solid-state structure, as the spectrum shows a single resonance for both the methylenic protons (3.57 ppm) and the two hydrido ligands (−17.7 ppm). At 243 K, however, each of these signals has split into two (4.38 and 2.85 ppm, −17.1 and −18.4 ppm), in agreement with the solid-state structure. The −17.1 ppm signal is assigned to the μ_3-H ligand because of its higher chemical shift and its substantially higher half-width (130 Hz, compared with 65 Hz for the −18.4 ppm signal), which could be indicative of unresolved H-Ag coupling. The ^{31}P{^{1}H} NMR spectra of 4 (Table I) indicate that both phosphorus atoms of the dppm ligand remain equivalent in the temperature range studied, and a single environment for the PPh_3 ligand is also apparent from these data. The fact that no Ag–PPh_3 coupling is observed at 295 K is not unusual,[21] and it can be ascribed to a fast dissociative process of the PPh_3 ligand which, while being almost completely shifted to the complex side, decreases the lifetime of the bonded state enough so as to preclude the observation of Ag–P coupling.[21] On the whole, the ^{31}P NMR data suggest that the plane that is perpendicular to the Mn–Mn bond and contains the silver atom remains as an effective element of symmetry during the dynamic process experienced by 4 in solution. Figure 2a shows our

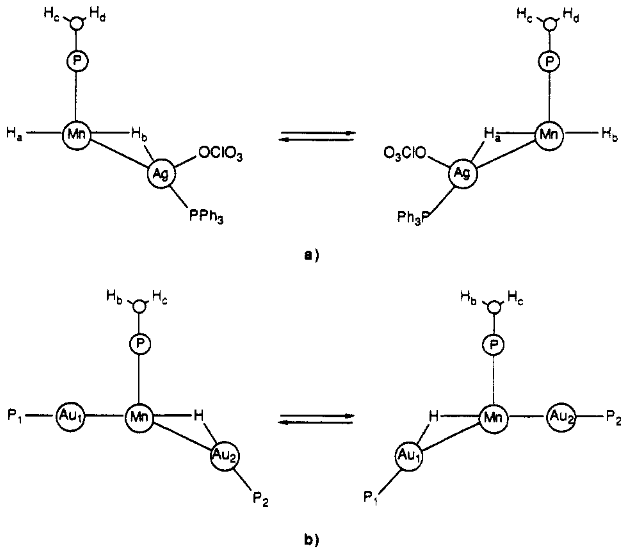

Figure 2. Proposed dynamic processes for compounds 4 (a) and 5 (b) in solution (see text). Drawings are simplified projections along the Mn–Mn vectors (carbonyl ligands and phenyl rings omitted), and the CH_2 (dppm) group is depicted at its averaged position in solution.

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(21) Socol, S. M.; Verkade, J. G. *Inorg. Chem.* 1984, *23*, 3487 and references therein.

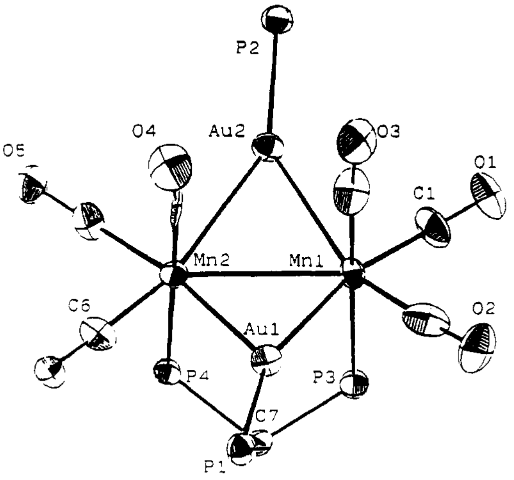

Figure 3. Molecular structure of the cation in **5**. Phenyl rings are omitted for clarity; C (CO) labels are the same as for the corresponding O atoms.

proposed mechanism to explain the above NMR data, which consists basically of a shift in the acidic $Ag(ClO_4)(PPh_3)$ fragment between the two donor centers, that is the $Mn_2(\mu\text{-}H_a)$ and $Mn_2(\mu\text{-}H_b)$ positions. This is likely to occur via complete dissociation of the silver fragment, given the weakness of the acid–base interaction which supports complex **4** (see above). Any process involving only the hydrido ligands in a static metal cluster geometry can be safely excluded, since it could make H_a and H_b equivalent, but not H_c and H_d (Figure 2).

As opposed to the apparent lack of stability of the copper and silver adducts of compounds **1** and **2**, the latter give reasonably stable gold derivatives by reaction with $[AuPPh_3]^+$. Thus, although no reaction was observed between **1** and this gold cation in tetrahydrofuran, removal of the solvent and addition of dichloromethane yielded cation **3** (PF_6^- salt) as the major product. Spectroscopic data for this salt were identical with those from the BF_4^- salt previously discussed, although yields and stability (even as a solid) were found to be lower.

In a similar way, compound **2** does not react with $[AuPPh_3]^+$ in tetrahydrofuran but gives with good yield the blue unsaturated cluster $[Mn_2(\mu\text{-}AuPPh_3)_2(\mu\text{-}H)(CO)_6(\mu\text{-}dppm)][PF_6]$ (**5**) in dichloromethane. The molecular structure of the cation in **5** is shown in Figure 3. The cluster displays as asymmetric "butterfly" Mn_2Au_2 core with a dppm ligand bridging the manganese atoms on the convex side of the metal framework. The Mn–Mn distance (2.864 (5) Å) is considerably longer than those for **1** or **4** (by ca. 0.16 and 0.12 Å, respectively) yet significantly shorter (by ca. 0.2 Å) than the distances found for related saturated Mn_2Au clusters (for example, 3.090 (3) Å in $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}Br)(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$[22] or 3.066 (8) Å in $[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)(CO)_8]$[23]), and this is consistent with the formal unsaturation proposed for **5** on the basis of the effective atomic number rule. The gold atoms are not equivalent in the structure, Au(1) being more tightly bound to the manganese atoms than Au(2) (averaged Mn–Au distances are 2.684 (4) Å for Au(1) and 2.806 (4) Å for Au(2)). In addition, it has to be noted that while the Mn–Au(1) distances are comparable with those found for the above-mentioned Mn_2Au clusters,[22,23] the Mn–Au(2) distances are significantly longer by ca. 0.1 Å. On the other hand, the $Mn_2Au(1)$ plane is almost perpendicular to the least-squares $Mn_2P(3)P(4)$ plane (angle 92.5°), whereas the latter plane and the $Mn_2Au(2)$ plane form an angle of 111.1°. All these data strongly suggest that the bridging hydrido atom (not located in this X-ray study) is bridging the $Mn_2Au(2)$ triangle in a μ_3 fashion, on the side closer to the dppm ligand (Figure 2b), a proposal also consistent with the NMR data (see below) and closely related with the structure found for compound **4**. Further evidence for the presence of the hydrido ligand can be found in the positions of the phosphorus atoms of the PPh_3 ligands, P(1) being almost in the $Mn_2Au(1)$ plane (deviation −0.030 Å) while P(2) is shifted 0.203 Å from the $Mn_2Au(2)$ plane, away from the dppm ligand. On the whole, this cluster can be viewed as an acid–base adduct between the unsaturated $Mn_2(\mu\text{-}H)(\mu\text{-}AuPPh_3)$ moiety in **2** (the base, interacting through its $Mn_2(\mu\text{-}H)$ edge) and a $[AuPPh_3]^+$ fragment (acid). The strength of this interaction seems to be higher than that in **4**, as indicated by the somewhat higher stability of **5** in solution and a larger shift of $\nu(CO)$ stretching bands (averaged frequencies are 1961 cm^{-1} for **5** and 1939 cm^{-1} for **2**), which reflects a greater electron density flow from **2** to the incoming gold atom.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Compound 4

Mn(1)–Mn(2)	2.740 (1)	Mn(1)–Ag(1)	2.961 (1)
Mn(1)–P(1)	2.340 (2)	Mn(1)–C(1)	1.775 (7)
Mn(1)–C(2)	1.810 (8)	Mn(1)–C(3)	1.836 (7)
Mn(1)–H(1)	1.83 (4)	Mn(1)–H(2)	1.76 (4)
Mn(2)–Ag(1)	2.929 (1)	Mn(2)–P(2)	2.330 (2)
Mn(2)–C(4)	1.817 (7)	Mn(2)–C(5)	1.829 (8)
Mn(2)–C(6)	1.797 (7)	Mn(2)–H(1)	1.90 (4)
Mn(2)–H(2)	1.87 (4)	Ag(1)–P(3)	2.409 (2)
Ag(1)–O(7)	2.542 (9)	Ag(1)–O(7)′	2.67 (3)
Ag(1)–H(2)	1.87 (4)	O(1)–C(1)	1.157 (7)
O(2)–C(2)	1.151 (8)	O(3)–C(3)	1.138 (7)
O(4)–C(4)	1.148 (7)	O(5)–C(5)	1.136 (8)
O(6)–C(6)	1.152 (8)		

Ag(1)–Mn(1)–Mn(2)	61.69 (3)	P(1)–Mn(1)–Mn(2)	93.34 (6)
P(1)–Mn(1)–Ag(1)	109.45 (5)	C(1)–Mn(1)–Mn(2)	137.0 (2)
C(1)–Mn(1)–Ag(1)	154.4 (2)	C(1)–Mn(1)–P(1)	89.0 (2)
C(2)–Mn(1)–Mn(2)	132.9 (2)	C(2)–Mn(1)Ag(1)	73.0 (2)
C(2)–Mn(1)–P(1)	89.9 (2)	C(2)–Mn(1)–C(1)	90.0 (3)
C(3)–Mn(1)–Mn(2)	91.1 (2)	C(3)–Mn(1)–Ag(1)	76.7 (2)
C(3)–Mn(1)–P(1)	173.6 (2)	C(3)–Mn(1)–C(1)	84.6 (3)
C(3)–Mn(1)–C(2)	90.4 (3)	H(1)–Mn(1)–Ag(1)	105 (1)
H(1)–Mn(1)–P(1)	84 (2)	H(1)–Mn(1)–C(1)	94 (1)
H(1)–Mn(1)–C(2)	172 (2)	H(1)–Mn(1)–C(3)	96 (2)
H(2)–Mn(1)–P(1)	79 (2)	H(2)–Mn(1)–C(1)	168 (2)
H(2)–Mn(1)–C(2)	93 (1)	H(2)–Mn(1)–C(3)	107 (2)
H(2)–Mn(1)–H(1)	82 (2)	Ag(1)–Mn(2)–Mn(1)	62.87 (3)
P(2)–Mn(2)–Mn(1)	92.58 (6)	P(2)–Mn(2)–Ag(1)	108.46 (6)
C(4)–Mn(2)–Mn(1)	89.5 (2)	C(4)–Mn(2)–Ag(1)	77.7 (2)
C(4)–Mn(2)–P(2)	173.8 (2)	C(5)–Mn(2)–Mn(1)	133.8 (2)
C(5)–Mn(2)–Ag(1)	72.1 (2)	C(5)–Mn(2)–P(2)	91.8 (2)
C(5)–Mn(2)–C(4)	90.9 (3)	C(6)–Mn(2)–Mn(1)	137.7 (3)
C(6)–Mn(2)–Ag(1)	154.5 (2)	C(6)–Mn(2)–P(2)	88.0 (2)
C(6)–Mn(2)–C(4)	86.6 (3)	C(6)–Mn(2)–C(5)	88.4 (3)
H(1)–Mn(2)–Ag(1)	104 (2)	H(1)–Mn(2)–P(2)	84 (2)
H(1)–Mn(2)–C(4)	93 (2)	H(1)–Mn(2)–C(5)	174 (1)
H(1)–Mn(2)–C(6)	96 (1)	H(2)–Mn(2)–P(2)	79 (2)
H(2)–Mn(2)–C(4)	106 (2)	H(2)–Mn(2)–C(5)	97 (1)
H(2)–Mn(2)–C(6)	166 (1)	H(2)–Mn(2)–H(1)	77 (2)
Mn(2)–Ag(1)–Mn(1)	55.43 (3)	P(3)–Ag(1)–Mn(1)	137.42 (5)
P(3)–Ag(1)–Mn(2)	135.39 (5)	O(7)–Ag(1)–Mn(1)	95.3 (3)
O(7)–Ag(1)–Mn(2)	101.1 (2)	O(7)–Ag(1)–P(3)	115.8 (2)
H(2)–Ag(1)–P(3)	169 (2)	H(2)–Ag(1)–O(7)	75 (2)
O(1)–C(1)–Mn(1)	176.1 (6)	O(2)–C(2)–Mn(1)	178.4 (6)
O(3)–C(3)–Mn(1)	172.1 (6)	O(4)–C(4)–Mn(2)	173.8 (6)
O(5)–C(5)–Mn(2)	177.5 (7)	O(6)–C(6)–Mn(2)	176.6 (7)
P(2)–C(7)–P(1)	108.0 (3)	Mn(2)–H(1)–Mn(1)	98 (2)
Mn(2)–H(2)–Mn(1)	98 (2)	Ag(1)–H(2)–Mn(1)	109 (2)
Ag(1)–H(2)–Mn(2)	103 (2)		

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[22] Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1551.

[23] Iggo, J. A.; Mays, M. J.; Raithby, P. R.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 633.

Table V. Atomic Positional and Thermal Parameters for Compound 5[a]

atom	x/a	y/b	z/c	U(equiv), Å^2	atom	x/a	y/b	z/c	U(equiv), Å^2
Au(1)	0.85407 (6)	0.21735 (5)	0.65072 (6)	0.0422	C(53)	0.571 (2)	0.080 (1)	0.075 (2)	0.08 (1)*
Au(2)	0.68766 (6)	0.21345 (5)	0.36114 (6)	0.0411	C(54)	0.651 (2)	0.096 (1)	0.126 (2)	0.067 (9)*
Mn(1)	0.8374 (2)	0.1848 (2)	0.5021 (2)	0.0359	C(55)	0.669 (2)	0.142 (1)	0.169 (2)	0.062 (9)*
Mn(2)	0.6926 (2)	0.2149 (2)	0.5224 (2)	0.0350	C(60)	0.522 (2)	0.268 (1)	0.185 (2)	0.044 (8)*
P(1)	0.9207 (4)	0.2387 (3)	0.7942 (4)	0.0400	C(61)	0.470 (2)	0.256 (1)	0.220 (2)	0.050 (8)*
P(2)	0.6219 (4)	0.2332 (3)	0.2196 (4)	0.0421	C(62)	0.394 (2)	0.286 (1)	0.196 (2)	0.067 (8)*
P(3)	0.8269 (4)	0.0987 (3)	0.5398 (4)	0.0391	C(63)	0.372 (2)	0.323 (1)	0.135 (2)	0.067 (9)*
P(4)	0.6642 (4)	0.1289 (2)	0.5416 (4)	0.0325	C(64)	0.420 (2)	0.335 (1)	0.100 (2)	0.08 (1)*
O(1)	0.879 (1)	0.1489 (8)	0.370 (1)	0.0729	C(65)	0.496 (2)	0.308 (1)	0.122 (2)	0.057 (8)*
O(2)	1.023 (1)	0.1833 (8)	0.617 (1)	0.0734	C(70)	0.592 (2)	0.089 (1)	0.450 (2)	0.047 (7)*
O(3)	0.866 (1)	0.2942 (8)	0.468 (1)	0.0666	C(71)	0.552 (2)	0.112 (1)	0.370 (2)	0.048 (7)*
O(4)	0.735 (1)	0.3270 (7)	0.524 (1)	0.0715	C(72)	0.496 (2)	0.085 (1)	0.295 (2)	0.070 (9)*
O(5)	0.511 (1)	0.2425 (8)	0.422 (1)	0.0670	C(73)	0.481 (2)	0.035 (1)	0.309 (2)	0.08 (1)*
O(6)	0.668 (1)	0.2411 (8)	0.668 (1)	0.0654	C(74)	0.517 (2)	0.011 (1)	0.389 (2)	0.08 (1)*
C(1)	0.860 (2)	0.161 (1)	0.420 (2)	0.0582	C(75)	0.576 (2)	0.039 (1)	0.461 (2)	0.055 (8)*
C(2)	0.950 (2)	0.185 (1)	0.574 (2)	0.0686	C(80)	0.615 (2)	0.120 (1)	0.611 (2)	0.043 (7)*
C(3)	0.852 (2)	0.252 (1)	0.480 (2)	0.0531	C(81)	0.532 (2)	0.139 (1)	0.581 (2)	0.060 (8)*
C(4)	0.721 (1)	0.282 (1)	0.520 (2)	0.328	C(82)	0.493 (2)	0.138 (1)	0.632 (2)	0.072 (9)*
C(5)	0.583 (2)	0.229 (1)	0.460 (2)	0.0506	C(83)	0.583 (2)	0.115 (1)	0.714 (2)	0.067 (9)*
C(6)	0.680 (2)	0.230 (1)	0.613 (2)	0.0507	C(84)	0.619 (2)	0.095 (1)	0.745 (2)	0.059 (8)*
C(7)	0.762 (2)	0.0882 (9)	0.594 (1)	0.0362	C(85)	0.658 (2)	0.097 (1)	0.691 (2)	0.055 (8)*
C(10)	0.859 (1)	0.284 (1)	0.826 (1)	0.040 (6)*	C(90)	0.784 (2)	0.049 (1)	0.457 (2)	0.045 (7)*
C(11)	0.815 (2)	0.320 (1)	0.768 (2)	0.061 (8)*	C(91)	0.734 (2)	0.061 (1)	0.376 (2)	0.055 (8)*
C(12)	0.770 (2)	0.359 (1)	0.794 (2)	0.09 (1)*	C(92)	0.692 (2)	0.022 (1)	0.312 (2)	0.072 (9)*
C(13)	0.775 (2)	0.352 (1)	0.870 (2)	0.09 (1)*	C(93)	0.701 (2)	−0.029 (1)	0.336 (2)	0.09 (1)*
C(14)	0.819 (2)	0.317 (1)	0.928 (2)	0.08 (1)*	C(94)	0.750 (2)	−0.042 (1)	0.419 (2)	0.069 (9)*
C(15)	0.867 (2)	0.281 (1)	0.907 (2)	0.054 (7)*	C(95)	0.793 (2)	−0.004 (1)	0.484 (2)	0.074 (9)*
C(20)	0.938 (2)	0.179 (1)	0.856 (1)	0.038 (7)*	C(100)	0.929 (2)	0.070 (1)	0.614 (2)	0.042 (7)*
C(21)	1.013 (2)	0.158 (1)	0.908 (2)	0.060 (8)*	C(101)	0.963 (2)	0.073 (1)	0.699 (2)	0.069 (9)*
C(22)	1.022 (2)	0.111 (1)	0.949 (2)	0.08 (1)*	C(102)	1.045 (2)	0.053 (1)	0.758 (2)	0.09 (1)*
C(23)	0.952 (2)	0.084 (1)	0.941 (2)	0.07 (1)*	C(103)	1.091 (2)	0.032 (1)	0.720 (2)	0.10 (1)*
C(24)	0.871 (2)	0.105 (1)	0.886 (2)	0.068 (9)*	C(104)	1.064 (2)	0.031 (1)	0.635 (2)	0.08 (1)*
C(25)	0.867 (2)	0.154 (1)	0.844 (2)	0.045 (7)*	C(105)	0.981 (2)	0.050 (1)	0.581 (2)	0.071 (9)*
C(30)	1.026 (1)	0.2691 (9)	0.838 (1)	0.033 (7)*	P(5)	0.2595 (7)	0.0029 (4)	0.0131 (7)	0.092 (3)*
C(31)	1.050 (2)	0.310 (1)	0.897 (2)	0.050 (8)*	F(1)	0.244 (2)	0.063 (1)	0.001 (2)	0.25 (2)*
C(32)	1.133 (2)	0.331 (1)	0.931 (2)	0.057 (8)*	F(2)	0.270 (2)	0.006 (1)	0.103 (2)	0.25 (2)*
C(33)	1.188 (2)	0.312 (1)	0.904 (2)	0.056 (8)*	F(3)	0.271 (2)	−0.059 (1)	0.024 (2)	0.26 (2)*
C(34)	1.163 (2)	0.273 (1)	0.843 (2)	0.053 (8)*	F(4)	0.250 (2)	−0.001 (1)	−0.078 (2)	0.28 (2)*
C(35)	1.082 (2)	0.252 (1)	0.812 (2)	0.049 (7)*	F(5)	0.354 (2)	0.008 (2)	0.048 (2)	0.34 (2)*
C(40)	0.686 (2)	0.2716 (9)	0.188 (1)	0.040 (7)*	F(6)	0.162 (2)	−0.004 (2)	−0.022 (2)	0.32 (2)*
C(41)	0.674 (2)	0.265 (1)	0.104 (2)	0.056 (8)*	C(200)	0.123 (1)	0.0828 (9)	0.309 (2)	0.16 (2)*
C(42)	0.719 (2)	0.300 (1)	0.076 (2)	0.070 (9)*	C(201)	0.096 (1)	0.057 (1)	0.232 (1)	0.17 (2)*
C(43)	0.773 (2)	0.336 (1)	0.129 (2)	0.08 (1)*	C(202)	0.155 (2)	0.033 (1)	0.212 (1)	0.15 (2)*
C(44)	0.786 (2)	0.340 (1)	0.213 (2)	0.074 (9)*	C(203)	0.241 (2)	0.036 (1)	0.269 (2)	0.12 (1)*
C(45)	0.745 (2)	0.309 (1)	0.244 (2)	0.063 (9)*	C(204)	0.269 (1)	0.062 (1)	0.346 (2)	0.13 (2)*
C(50)	0.600 (2)	0.172 (1)	0.160 (1)	0.039 (7)*	C(205)	0.210 (2)	0.0853 (9)	0.366 (1)	0.11 (1)*
C(51)	0.518 (2)	0.155 (1)	0.112 (2)	0.08 (1)*	C(206)	0.058 (2)	0.109 (1)	0.330 (3)	0.23 (3)*
C(52)	0.504 (2)	0.107 (1)	0.069 (2)	0.09 (1)*					

[a] Values marked with asterisks are isotropic *U*'s.

Compound 5 undergoes a fluxional process in solution that is best illustrated by its $^{31}P\{^1H\}$ NMR spectra (Table I). Thus, a single resonance each is observed for the dppm and the PPh_3 ligands at 295 K (δ 63.6 and 62.7 ppm, respectively), indicating an obviously time-averaged equivalence of both $AuPPh_3$ fragments. On lowering of the temperature, the PPh_3 resonance broadens, disappears at 223 K, and eventually splits into two signals (67.8 and 54.0 ppm at 183 K) roughly centered at the original chemical shift. The low-frequency signal becomes a doublet (J(PH) = 60 Hz) with partial ^1H coupling (hydrido region only) and is thus assigned to the phosphorus atom bonded to the gold one bearing the μ_3-hydrido ligand (Au(2)), in agreement with the X-ray structure. Unfortunately, the low-temperature ^1H NMR spectra showed only broad signals, and all that can be said is that the process averaging the gold environments has the same effect on the CH_2 resonances. Interestingly, the time-averaged hydrido resonance appears at 295 K as a triplet of triplets with $^2J(H{-}PPh_3)$ = 33 Hz, this value being almost half of the coupling constant measured in the 183 K ^{31}P spectrum. Since it is expected that coupling between H and P(1) in the static structure should be close to zero (for example, no such coupling is observed in 2), the value of the time-averaged J(PH) coupling suggests that the dynamic process probably involves an alternating binding of the hydrido ligand with either Au(1) or Au(2) (Figure 2b)), which would only require a minor rearrangement of the metallic Mn_2Au_2 core. Accordingly, a low activation energy ($\Delta G^{\ddagger}$ = 39 ± 1 kJ mol^{-1}) is estimated from the observed coalescence temperature.[24] Dynamic behavior involving group 11 metal atoms placed at inequivalent positions is not unusual for mixed-metal clusters containing two or more ML fragments (M = Cu, Ag, Au; L = two-electron-donor ligand).[17]

Conclusions

The results reported here show that the unsaturated hydrido compound 1 behaves as a pure electron donor toward the acidic entities $[Au(PPh_3)]^+$ and $[Ag(ClO_4)PPh_3]$, and this is also the case for compound 2 toward H^+

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(24) Value obtained with T_c = 223 K and the modified Eyring equation $\Delta G^{\ddagger} = 19.14T_c[9.97 + \log(T_c/\delta\nu)]$. See for example: Gunther, H. *NMR Spectroscopy*; Wiley: Chichester, U.K., 1980; p 243.

or $[Au(PPh_3)]^+$. This behavior is reflected in a shift to higher frequencies of the C–O stretching vibrations of the corresponding $Mn_2(CO)_6$ moieties upon reaction. Structural data indicate that in all these cases the interaction involves one "electron-deficient" $Mn_2(\mu\text{-}H)$ bridge and either Au or Ag atoms, this pointing to a description of the bonding in the acid–base adduct in terms of a four-center–two-electron interaction. This interaction is consistent with the theoretical descriptions of the bond in unsaturated $M_2(\mu\text{-}H)_2$ (M=M) moieties as being accomplished mainly through the hydrido bridges.

Experimental Section

General Procedures. All manipulations were carried out under a dry oxygen-free nitrogen atmosphere using Schlenk-tube techniques. Filtrations were routinely carried out through diatomaceous earth. Solvents were purified by standard procedures.[25] Petroleum ether refers to that fraction boiling at 60–65 °C. Infrared spectra were recorded on Perkin-Elmer 577 and FT1720-Y spectrophotometers, using CaF_2 cells for solution measurements and Nujol mulls or KBr pellets for solid-state measurements. ^1H (300.13 MHz) and ^{31}P (121.44 MHz) NMR spectra were recorded on a Bruker AC-300 instrument in CD_2Cl_2 solution at 295 K unless otherwise stated. Chemical shifts (ppm) are referenced against internal TMS (^1H) or external 85% aqueous H_3PO_4 (^{31}P) and taken to be positive at frequencies higher than the reference; coupling constants are given in Hz. Elemental analyses (C, H) were performed with a Perkin-Elmer 204B instrument. Compounds 1[8], $[AuMe(PPh_3)]$,[26] $[AuCl(PPh_3)]$,[27] and $[Ag(ClO_4)(PPh_3)]$[28] were prepared according to literature methods. Other reagents were obtained from commercial suppliers and used without further purification.

$[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)(CO)_6(\mu\text{-}dppm)]$ (2). Compound 1 (0.1 g, 0.15 mmol) and $[AuMe(PPh_3)]$ (0.076 g, 0.16 mmol) were stirred in toluene (15 mL) at room temperature for 8 h, affording a deep violet solution. Solvent was removed under vacuum and the residue extracted with dichloromethane–petroleum ether (1/9 v/v) and chromatographed on alumina (Aldrich, activity IV). A violet fraction was collected by elution with dichloromethane–petroleum ether (1/7), which yielded, after removal of solvents under vacuum, 0.154 g (91%) of compound 2 as a dark violet microcrystalline powder. Anal. Calcd for $C_{49}H_{38}AuMn_2O_6P_3$: C, 52.4; H, 3.4. Found: C, 52.1; H, 3.4.

$[Mn_2(\mu\text{-}AuPPh_3)(\mu\text{-}H)_2(CO)_6(\mu\text{-}dppm)]^+$ (3). Method A (BF_4^- Salt). A slight excess of $HBF_4{\cdot}OEt_2$ (0.04 mL, 0.053 mmol) was added to a solution of compound 2 (0.05 g, 0.045 mmol) in dichloromethane (10 mL) at -10 °C, and the mixture was stirred for 30 min. Removal of the solvent under vacuum gave an oily residue which yielded, after washing with diethyl ether (3 × 3 mL), 0.045 g (83%) of cation 3 (BF_4^- salt) as a dark violet microcrystalline solid. Anal. Calcd for $C_{49}H_{39}AuBMn_2F_4O_6P_3$: C, 48.6; H, 3.2. Found: C, 48.2; H, 3.1.

Method B (PF_6^- Salt). The complex $[AuCl(PPh_3)]$ (0.049 g, 0.1 mmol) and $TlPF_6$ (0.035 g, 0.1 mmol) were stirred in tetrahydrofuran (10 mL) for 30 min. The mixture was then filtered into a solution of compound 1 (0.066 g, 0.1 mmol) in tetrahydrofuran (5 mL). The solvent was then removed under vacuum, the residue dissolved in dichloromethane at 0 °C, and this solution filtered at the same temperature. Removing the solvent under vacuum from the filtrate and washing the residue thus obtained with toluene (3 × 3 mL) yielded 0.038 g (30%) of cation 3 (PF_6^- salt) as a dark violet, unstable microcrystalline solid. Spectroscopic data for this cation were found to be identical with those from the BF_4^- salt.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for Compound 5

Mn(1)–Mn(2)	2.864 (5)	Au(1)–Mn(2)	2.703 (3)
Au(1)–Mn(1)	2.665 (4)	Au(2)–P(2)	2.291 (7)
Au(1)–P(1)	2.331 (7)	Au(2)–Mn(2)	2.845 (3)
Au(2)–Mn(1)	2.768 (4)	Mn(2)–P(4)	2.316 (7)
Mn(1)–P(3)	2.332 (8)	Mn(2)–C(4)	1.79 (3)
Mn(1)–C(1)	1.80 (3)	Mn(2)–C(5)	1.77 (3)
Mn(1)–C(2)	1.80 (3)	Mn(2)–C(6)	1.79 (3)
Mn(1)–C(3)	1.81 (3)	O(4)–C(4)	1.17 (3)
O(1)–C(1)	1.15 (3)	O(5)–C(5)	1.18 (3)
O(2)–C(2)	1.16 (3)	O(6)–C(6)	1.13 (3)
O(3)–C(3)	1.14 (3)		
Mn(2)–Au(1)–Mn(1)	64.5 (1)	Mn(2)–Au(2)–Mn(1)	61.4 (1)
P(1)–Au(1)–Mn(1)	158.8 (2)	P(2)–Au(2)–Mn(1)	146.9 (2)
P(1)–Au(1)–Mn(2)	136.7 (2)	P(2)–Au(2)–Mn(2)	151.0 (2)
Au(2)–Mn(1)–Au(1)	115.8 (1)	Au(2)–Mn(2)–Au(1)	112.1 (1)
Mn(2)–Mn(1)–Au(1)	58.4 (1)	Mn(1)–Mn(2)–Au(1)	57.1 (1)
Mn(2)–Mn(1)–Au(2)	60.6 (1)	Mn(1)–Mn(2)–Au(2)	58.0 (1)
P(3)–Mn(1)–Au(1)	89.6 (2)	P(4)–Mn(2)–Au(1)	96.5 (2)
P(3)–Mn(1)–Au(2)	109.9 (2)	P(4)–Mn(2)–Au(2)	103.4 (2)
P(3)–Mn(1)–Mn(2)	91.1 (2)	P(4)–Mn(2)–Mn(1)	92.0 (2)
C(1)–Mn(1)–Au(1)	163.0 (10)	C(4)–Mn(2)–Au(1)	78.7 (8)
C(1)–Mn(1)–Au(2)	80.3 (10)	C(4)–Mn(2)–Au(2)	82.2 (8)
C(1)–Mn(1)–Mn(2)	138.6 (10)	C(4)–Mn(2)–Mn(1)	88.7 (7)
C(1)–Mn(1)–P(3)	89.8 (10)	C(4)–Mn(2)–P(4)	173.8 (8)
C(2)–Mn(1)–Au(1)	74.0 (9)	C(5)–Mn(2)–Au(1)	160.7 (8)
C(2)–Mn(1)–Au(2)	157.0 (9)	C(5)–Mn(2)–Au(2)	82.3 (8)
C(2)–Mn(1)–Mn(2)	132.4 (10)	C(5)–Mn(2)–Mn(1)	139.9 (8)
C(2)–Mn(1)–P(3)	90.2 (10)	C(5)–Mn(2)–P(4)	92.2 (9)
C(2)–Mn(1)–C(1)	89.0 (14)	C(5)–Mn(2)–C(4)	91.2 (11)
C(3)–Mn(1)–Au(1)	87.8 (9)	C(6)–Mn(2)–Au(1)	76.2 (8)
C(3)–Mn(1)–Au(2)	73.8 (9)	C(6)–Mn(2)–Au(2)	165.6 (9)
C(3)–Mn(1)–Mn(2)	89.9 (9)	C(6)–Mn(2)–Mn(1)	132.8 (9)
C(3)–Mn(1)–P(3)	176.2 (10)	C(6)–Mn(2)–P(4)	86.6 (8)
C(3)–Mn(1)–C(1)	91.9 (13)	C(6)–Mn(2)–C(4)	88.3 (11)
C(3)–Mn(1)–C(2)	86.4 (13)	C(6)–Mn(2)–C(5)	87.2 (11)
O(1)–C(1)–Mn(1)	174.6 (28)	O(4)–C(4)–Mn(2)	172.6 (21)
O(2)–C(2)–Mn(1)	176.4 (27)	O(5)–C(5)–Mn(2)	175.2 (24)
O(3)–C(3)–Mn(1)	175.4 (27)	O(6)–C(6)–Mn(2)	176.8 (25)

$[Mn_2\{\mu\text{-}Ag(ClO_4)PPh_3\}(\mu\text{-}H)_2(CO)_6(\mu\text{-}dppm)]$ (4). Compound 1 (0.050 g, 0.075 mmol) and $[Ag(ClO_4)(PPh_3)]$ (0.035 g, 0.075 mmol) were stirred in the dark in toluene (10 mL) for 10 min. The mixture was then filtered, affording a violet solution which yielded, after removal of the solvent under vacuum and washing of the residue with petroleum ether (2 × 5 mL) 0.060 g (70%) of compound 4 as a purple microcrystalline solid. The single crystals used for the X-ray study were grown by recrystallization from a dichloromethane–petroleum ether solution at -20 °C. Anal. Calcd for $C_{49}H_{39}AgClMn_2O_{10}P_3$: C, 49.2; H, 3.4. Found: C, 49.5; H, 3.4.

$[Mn_2(\mu\text{-}AuPPh_3)_2(\mu\text{-}H)(CO)_6(\mu\text{-}dppm)]PF_6$ (5). The complex $[AuCl(PPh_3)]$ (0.030 g, 0.06 mmol) and $TlPF_6$ (0.021 g, 0.06 mmol) were stirred in tetrahydrofuran (10 mL) for 30 min. The mixture was then filtered onto a solution of compound 2 (0.067 g, 0.06 mmol) in tetrahydrofuran (5 mL). The solvent was then removed under vacuum, affording a blue residue. The latter was dissolved in dichloromethane (15 mL) at 0 °C and filtered at the same temperature. Removing the solvent from the filtrate under vacuum and washing the residue first with toluene (2 × 5 mL) and then with petroleum ether (2 × 5 mL) yielded 0.070 g (68%) of compound 5 as a deep blue microcrystalline solid. The single crystals used for the X-ray study were grown from a dichloromethane–toluene solution of 5 at -20 °C. Anal. Calcd for $C_{67}H_{53}Au_2F_6Mn_2O_6P_5$: C, 46.6; H, 3.2. Found: C, 46.9; H, 3.3.

Crystal Structure Analysis of Compounds 4 and 5. The structures were solved by direct methods and subsequent Fourier maps. An absorption correction was applied with the program DIFABS[29] from CRYSTALS.[30] Scattering factors were corrected from anomalous dispersion. Further details of the data collection and refinements are given in Table II. Tables III and V contain atomic and thermal parameters for refined atoms in compounds 4 and 5, respectively, and the corresponding selected bond distances and angles are shown in Tables IV and VI.

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For compound 4, oxygen atoms of the perchlorate ligand were found disordered. Two positions were introduced, the multiplicity of which converged toward 0.8 and 0.2; oxygen atoms of multiplicity 0.2 were isotropically refined. Almost all hydrogen atoms were found on difference maps but were geometrically located, except the bridging ones. We tried to refine the latter, but their positions did not converge; thus, we refined them with restraints on the metal–hydrogen bond lengths. In this way the isotropic thermal parameters kept reasonable values; we therefore could think they had been correctly located. Other hydrogen atoms were given an overall isotropic thermal parameter.

For compound 5 (toluene solvate), on account of the small number of significant reflections measured, the phenyl groups were isotropically refined. The toluene molecule was introduced as a rigid group, and PF_6^- was restrained to chemically reasonable dimensions. The maximum residual electron density was in the vicinity of PF_6^-. Hydrogen atoms did not appear in difference maps, and their positions were computed except for the bridging one, which was not introduced.

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Registry No. 1, 116405-31-3; 2, 142237-62-5; $3{\cdot}BF_4^-$, 142237-66-9; $3{\cdot}PF_6^-$, 142292-98-6; 4, 142237-67-0; 5, 142237-64-7; $5{\cdot}C_7H_8$, 142292-99-7; $Ag(ClO_4)(PPh_3)$, 73165-02-3; $AuMe(PPh_3)$, 23108-72-7; $AuCl(PPh_3)$, 14243-64-2; Mn, 7439-96-5; Ag, 7440-22-4; Au, 7440-57-5.

Supplementary Material Available: Drawings of the molecular structures of compounds 4 and 5, showing all atoms, and tables of additional atomic coordinates and thermal parameters for compounds 4 and 5, and additional bond lengths and angles for compound 5 (11 pages). Ordering information is given on any current masthead page.

OM910385H

Notes

Ferrocene Derivatives. 27.[1] Ferrocenyldimethylphosphine

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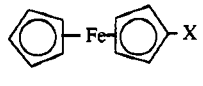
Summary: **An improved synthesis of ferrocenyldimethylphosphine, $FcPMe_2$, is limited only by the unreliable literature procedure for preparing precursor dichloroferrocenylphosphine, $FcPCl_2$. The latter compound yields a crystalline copper(I) iodide complex on reaction with lithium dimethylcuprate. Methanolysis of $FcPCl_2$ yields unstable dimethyl ferrocenylphosphonite, $FcP(OMe)_2$, which is converted to methyl ferrocenylphosphinite, FcPH(O)OMe, on heating or chromatography.**

The possibility of limitless variation in the identity of substituent groups has made trivalent phosphines and phosphites popular ligands in organometallic chemistry. Consequently, it has been possible to investigate both steric and electronic effects of these ligands and to influence the coordination number of the metal atom. Increasingly, interest is focusing on chiral phosphines and their complexes for use in asymmetric synthesis. Comprehensive reviews of different aspects of this chemistry have appeared.[2] Phosphorus derivatives of ferrocene were first investigated in 1962 by Sollott and co-workers[3] but most were poorly characterized or relatively inaccessible. Some synthetically useful intermediates have been reported,[4] but the most important derivatives are the chiral auxiliaries developed by Kumada and Hayashi.[5] The simple derivatives ferrocenyldimethylphosphine, $FcPMe_2$, and 1,1′-bis(dimethylphosphino)ferrocene, 1,1′-$Fc(PMe_2)_2$, have also been described,[6] but very surprisingly, the chemistry of these materials has not been developed, although each compound is expected to be a relatively strong σ-donor.[7] This paper describes a new synthesis of $FcPMe_2$, some aspects of its chemistry, and some related compounds.

Results and Discussion

We considered that dichloroferrocenylphosphine, $FcPCl_2$ (1), might be a convenient synthetic precursor. This compound was first prepared by a Friedel–Crafts method from ferrocene and phosphorus trichloride but was not isolated. An improved method using Me_2NPCl_2 was reported[3c] to give a cleaner product in higher (11%) yield. We have undertaken an extensive investigation of these literature[3c] processes and after 37 experiments find that the reactions are totally inconsistent and the yields are not reproducible. We have been unable to identify the reason



X = PCl_2 1, PH(O)OH 2, $PH(O)OPCl_2$ 3, $P(OMe)_2$ 4,

PH(O)OMe 5, PMe_2 6, $PMe_2.Fe(CO)_4$ 7, $P(O)Me_2$ 9.

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