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Reactivity of the unsaturated manganese dihydrides $[Mn_2(\mu-H)_2(CO)_6(\mu-L_2)]$ $[L_2 = (EtO)_2POP(OEt)_2$, Ph₂PCH₂PPh₂, Me₂PCH₂PMe₂] toward silicon and tin hydrides

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ABSTRACT

The dimanganese hydride complexes $[Mn_2(\mu-H)_2(CO)_6(\mu-L_2)] [L_2 = (EtO)_2POP(OEt)_2 (tedip), Ph_2PCH_2PPh_2 (tedip), Ph_2P$ (dppm)] react with primary and secondary silanes H_2 SiPhR (R = Ph, Me, H) to give the corresponding derivatives $[Mn_2(\mu-H_2SiPhR)(CO)_6(\mu-L_2)]$ having a silane molecule displaying a relatively unusual $\mu-\kappa^2$: κ coordination mode (averaged values are ca. Mn-H = 1.59 Å, H-Si = 1.69 Å and Mn-Si = 2.381 Å, when R = Ph and $L_2 = tedip$). These complexes display in solution *cis* and/or *trans* arrangement of the bridging silane relative to the diphosphorus ligands (and facial and/or meridional arrangements of the corresponding carbonyl ligands), depending on the bridging groups. The novel unsaturated dihydride $[Mn_2(\mu-H)_2(CO)_6(\mu-dmpm)]$ (dmpm = Me₂PCH₂PMe₂) has been prepared through the reaction of $[Mn_2(\mu-Cl)_2(\mu-dmpm)(CO)_6]$ and 5 equiv of Li[BH₂Me₂] in tetrahydrofuran followed by addition of water. The dihydride complexes $[Mn_2(\mu-H)_2(CO)_6(\mu-L_2)]$ (L₂ = tedip, dppm, dmpm) react with HSnPh₃ to give different mixtures of products strongly dependent on the particular reaction conditions. We have thus been able to isolate and characterize five new types of dimanganese-tin derivatives: $[Mn_2(\mu-SnPh_2)_2(CO)_6(\mu-L_2)]$, $[Mn_2(\mu-H)(\mu-Ph_2SnO(H)SnPh_2)(CO)_6(\mu-L_2)]$ (average values are Mn-Sn = 2.54 Å, Sn-O = 2.11 Å, when $L_{2} = tedip), \ [Mn_{2}(\mu-H)(\mu-\kappa^{1}:\kappa^{2}-HSnPh_{2})(CO)_{6}(\mu-L_{2})], \ [Mn_{2}(\mu-H)(\mu-\kappa^{1}:\kappa^{1}-O(H)SnPh_{2})(CO)_{6}(\mu-L_{2})], \ and \ (\mu-\kappa^{1}:\kappa^{2}-HSnPh_{2})(CO)_{6}(\mu-L_{2})], \ (\mu-\kappa^{1}:\kappa^{2}-HSnPh_{2})(CO)_{6}(\mu-L_{2}))(CO)_{6}(\mu-L_{2})(L_{2$ $[Mn_2(\mu-H)(SnPh_3)(CO)_7(\mu-L_2)]$ $(Mn-Mn = 3.237(1) \text{ Å}, Mn-Sn = 2.642(1) \text{ Å}, when L_2 = dppm).$ © 2010 Elsevier B.V. All rights reserved.

1. Introduction

In the last decades the interest in the chemistry of metallic complexes containing bonds to semimetallic p-block elements (E) such as silicon and tin has grown remarkably, with many of the synthetic and catalytic reactions under study involving the cleavage of E–H bonds by transition metals. For instance, the oxidative addition of E–H bonds to a transition-metal center is not only a widespread synthetic method to obtain complexes containing metal–silicon bonds [1], but also a fundamental step involved in several transition-metal catalyzed processes of relevance such as hydrosilylation [2], dehydrocoupling of organotin and organosilicon hydrides [3], and redistribution reactions of silanes [4], among others. While the reactivity of mononuclear complexes with silicon and tin hydrides has been examined in detail, the number of studies involving binuclear complexes is more scarce, especially in the case of unsaturated complexes having multiple metal–metal

bonds. The latter species in principle should be able to react with these reagents under mild conditions, thus leading to products difficult or impossible to obtain from electron-precise binuclear precursors, because the latter usually require more forcing conditions (i.e. heating or photochemical induction) to react with these mild reagents.

Some time ago we reported a preliminary study revealing that the reactions of the unsaturated dihydride complexes $[Mn_2(\mu-H)_2(CO)_6(\mu-L_2)]$ ($L_2 = (EtO)_2POP(OEt)_2$, tedip (**1a**) [5], Ph_2PCH_2PPh_2, dppm (**1b**) [6], Chart 1) with H_2SiPh_2 and HSnPh_3 could take place readily under mild conditions and involved in all cases some kind of E–H bond activation by the dimanganese center [7]. Thus, **1b** reacted with diphenylsilane to give $[Mn_2(\mu-H_2SiPh_2)(CO)_6(\mu-dppm)]$, a complex with the silane molecule displaying a relatively unusual $\mu-\kappa^2:\kappa^2$ coordination mode. In contrast, the reactions with HSnPh_3 were more complex and gave stannylene (μ -SnPh_2) or hydrostannyl-bridged (μ -HSnPh_2) products, among other uncharacterized species at the time [7]. Again, the stannyl complexes displayed a relatively uncommon $\mu-\kappa^1:\kappa^2$ -bridging mode involving a tricentric Mn–H–Sn interaction. These results were in marked contrast with the reactions of the triosmium

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dihydride $[Os_3(\mu-H)_2(CO)_{10}]$ (a cluster having an unsaturated $Os_2(\mu-H)_2$ center comparable to those in compounds 1) with H₂SiPh₂ and HSnMe₃ to give products having only terminal silyl or stannyl groups [8], and this prompted us to further study the reactions of our dimanganese hydrides with organosilicon and tin hydrides. In this paper we give full details of the reactions reported in our preliminary studies, which we have further extended to other silanes and, in the case of the complex reactions with HSnPh₃, to the novel unsaturated hydride $[Mn_2(\mu-H)_2(CO)_6(\mu-dmpm)]$ (1c), the latter having a diphosphine ligand ($dmpm = Me_2PCH_2PMe_2$) with smaller steric demands and higher electron donor ability than the tedip and dppm ligands. Since our preliminary report, only a few related studies involving unsaturated hydride-bridged complexes and silicon or tin hydrides have appeared. Suzuki et al. studied the reactions of several secondary and tertiary silanes with the 28-electron complexes $[Fe_2Cp_2^*(\mu-H)_4]$ [9] and $[Ru_2Cp_2^*(\mu-H)_4]$ [10], to give different silylene- and silyl-bridged derivatives, with the μ - κ^2 : κ^2 coordination mode of a silane ligand being found only for the bulky H₂Si^{*i*}Pr₂ and H₂Si^{*t*}Bu₂ molecules [9b,10b]. More recently, we have reported the reaction of the 30-electron complex $[Mo_2Cp_2(\mu-H)(\mu-PCy_2)(CO)_2]$ with HSnPh₃ to give $[Mo_2Cp_2(\mu-PCy_2)$ $(\mu$ -SnPh₃)(CO)₂], a molecule displaying a triorganostannyl group unusually bridging two metal atoms exclusively through its tin atom, and [Mo₂Cp₂(µ-H)(HPCy₂)(SnPh₃)(CO)₂], a molecule following from an unexpected combination of Sn-H bond cleavage and P-H bond formation steps [11].

2. Results and discussion

2.1. Reactions of the dihydride complexes **1a**,**b** with organosilanes

Compounds **1a**,**b** do not react with tertiary silanes $HSiR_3$ (R = Ph, Et) under heating (refluxing toluene solutions) or under exposure to the visible-UV light. In contrast, these unsaturated hydrides react with primary and secondary silanes H_2 SiPhR (R = Ph, Me, H) at room temperature or under moderate heating to give the corresponding derivatives $[Mn_2(\mu-H_2SiPhR)(CO)_6(\mu-L_2)]$ having a silane molecule displaying a relatively unusual μ - κ^2 : κ^2 coordination mode, and two possible isomeric forms: mer-[Mn₂(µ- $H_2SiPhR(CO)_6(\mu-L_2)$ (2) and fac-[Mn₂(μ -H₂SiPhR(CO)₆(μ -L₂)] (3). These isomers differ in the relative positioning of the CO ligands around each manganese center (meridional or facial) and in the relative positioning of the bridging ligands (trans or cis) (Chart 2). The ratio of mer to fac isomers present in the corresponding reaction mixtures was found to be dependent on the steric requirements of the silane. Thus, for the bulkier diphenylsilane molecule, only the mer isomers 2a.1 and 2b.1 were observed in solution. On the other extreme, the fac isomers were the species dominant when using a silane with small steric requirements such as H₃SiPh. Thus, the dppm dihydride 1b gave exclusively the corresponding fac isomer **3b.3**, while the ratio mer to fac was found to be 1:6 for the tedip-bridged isomers 2a.3 and 3a.3. This influence can be understood by considering that the repulsive steric interactions between the bridging diphosphorus and silane ligands should be much higher in the fac isomer, hence the preferential formation of mer



isomers upon increasing bulkness of the bridging groups. Incidentally, we note that all the H_3 SiPh derivatives were quite unstable and would decompose in the absence of excess of silane to give the starting dihydrides **1a** and **1b**. Under the above interpretation, we could predict that the use of a silane with intermediate steric requirements should accordingly yield a mixture of isomers with intermediate *mer/fac* ratios. Indeed, the tedip-bridged hydride **1a** reacted with H₂SiPhMe to give a mixture of the corresponding *mer* (**2a.2**) and *fac* (**3a.2**) isomers in a 5:1 ratio. Surprisingly, no reaction was observed between **1b** and H₂SiPhMe, even in refluxing toluene and by using a large excess of silane.

We should note that, except for compounds **2a.1** and **2b.1**, all other silane derivatives of the hydrides **1a** and **1b** were obtained as oily species and could not be isolated as solids, nor the *mer* and *fac* isomers could be separated in each case. In addition, all these complexes were found to be rather unstable species in solution, especially in the absence of excess silane, and slowly would decompose to give back the corresponding starting dihydrides. Presumably, different polysilanes and polysiloxanes are formed in these processes, as revealed by ²⁹Si NMR inspection of some of these solutions after decomposition, although we did not investigate further this matter.

2.2. Characterization of the silane complexes 2 and 3

The structure of compound **2a.1** has been confirmed by an X-ray diffraction study and is shown in the Fig. 1, while the most relevant bond distances and angles are collected in the Table 1. The molecule is made up of two meridional (or T-shaped) Mn(CO)₃ fragments



Fig. 1. ORTEP diagram (30% probability) of compound **2a.1**, with Et and Ph groups (except the ipso C atoms in the latter) omitted for clarity.

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Selected bond lengths	(Å) and angles (°) for compound	2a.1.

		, ,	
Mn(1)-Mn(2)	2.9375(8)	Si(1)-Mn(1)-Mn(2)	51.75(3)
Mn(1)-Si(1)	2.388(1)	P(1)-Mn(1)-Mn(2)	88.45(3)
Mn(1)-P(1)	2.202(1)	P(1)-Mn(1)-Si(1)	139.06(5)
Mn(1)-C(1)	1.784(4)	C(1) - Mn(1) - Si(1)	124.4(1)
Mn(1)-C(2)	1.828(4)	C(1) - Mn(1) - P(1)	96.3(1)
Mn(1)-C(3)	1.832(4)	Mn(1)-Si(1)-Mn(2)	76.13(4)
Mn(1) - H(1)	1.59(1)	C(10)-Si(1)-C(20)	106.7(2)
Si(1)-H(1)	1.669(6)	Si(1)-Mn(2)-Mn(1)	52.13(3)
Mn(2)-Si(1)	2.376(1)	P(2)-Mn(2)-Mn(1)	85.63(3)
Mn(2)-P(2)	2.189(1)	P(2)-Mn(2)-Si(1)	136.68(5)
Mn(2)-C(4)	1.783(5)	C(4) - Mn(2) - P(2)	94.7(1)
Mn(2) - C(5)	1.828(4)	Mn(1)-H(1)-Si(1)	94.4(2)
Mn(2) - C(6)	1.837(4)	Mn(2)-H(2)-Si(1)	93.1(1)
Mn(2)-H(2)	1.59(1)	H(1)-Si(1)-H(2)	158.0(6)
Si(1)-H(2)	1.694(3)	H(1)-Mn(1)-P(1)	174.1(2)
		H(2)-Mn(2)-P(2)	177.9(1)

connected by a metal–metal bond and bridged by tedip and silane ligands arranged mutually in *trans*, with the latter displaying a μ - κ^2 : κ^2 coordination mode with two tricentric Mn–H–Si interactions. This is a relatively rare coordination mode of silanes that has been previously identified only in a reduced number of dinuclear complexes of Re [12], Ru [10,13], Fe [9b], and Pt [14].

Overall, the structure of **2a.1** can be related to that of the Mn₂Zn cluster $[Mn_2Zn(\mu-H)_2(CO)_6(Me_2NCH_2CH_2NMe_2)(\mu-tedip)]$ [15], the latter having the same electron count and displaying two hydride ligands bridging the Mn–Zn edges. Indeed the Mn–Mn distance in 2a.1, 2.9375(8) Å, is consistent with the single metal-metal bond expected for an electron-precise dimanganese complex, although somewhat shorter than the value of 3.039(5) Å found in the mentioned Mn₂Zn cluster, or the value of 2.9889(6) Å measured in the related tetrahydroborate-bridged complex $[Mn_2(\mu-H)(\mu-\kappa^2:\kappa^2 BH_4$)(CO)₆(μ -dppm)] [7,16], the differences being easily ascribed to the distinct bridging groups being present in each case. The bridging silicon atom in 2a.1 is found at ca. 2.38 Å from the manganese atoms, a distance within the range of values found in mononuclear compounds displaying tricentric Mn-H-Si interactions, typically 2.25–2.46 Å [1,17]. As for the Si–H distances, the values of 1.67(2) and 1.70(2) Å are substantially longer than those reported for the free organosilanes (ca. 1.48 Å [1]), suggesting a considerable strength for the tricentric interactions. The Mn-H distances [1.59(1) Å] are even shorter than the values of ca. 1.65 Å measured in the mentioned tetrahydroborate complex and therefore suggestive of a very strong interaction too. Indeed, these values are comparable to those of a Mn-H bond in a terminal hydride complex (eg. 1.601(16) Å in $[MnH(CO)_5]$ [18]). At the same time, the angles Mn–H–Si have rather low values [94(1)° and 93(1)°] and therefore we can classify the corresponding Si-H-Mn interactions in 2a.1 as of the side-on type, as opposed to the end-on type coordination of the B-H bonds described for the mentioned tetrahydroborate complex [7,16], the latter being characterized by more open E–H–Mn angles (120–130°).

Spectroscopic data in solution for compounds **2a.1** and **2b.1** are similar to each other and consistent with the solid-state structure just discussed for the tedip-bridged complex. In particular, both complexes display medium to weak symmetrical C–O stretching bands above 2000 cm⁻¹ (Table 2), this denoting the presence of T-shaped Mn(CO)₃ oscillators in these molecules [19], and both display a single resonance in the corresponding ³¹P{¹H} NMR spectra as expected (Table 3). The symmetrical coordination of the silane molecule involving agostic-type, tricentric Mn–H–Si interactions is denoted in each case by the presence of highly shielded false triplet resonances at -12.10 (**2a.1**) or -13.09 (**2b.1**) ppm, due to the chemically equivalent but magnetically inequivalent Mn-

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IR data i	tor	new	compound	s.
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Compound	$\nu(\text{CO})^{a}/\text{cm}^{-1}$
$[Mn_2(\mu-H)_2(CO)_6(\mu-dmpm)]$ (1c)	2032 (vs), 1988 (vs), 1944 (m), 1915 (vs)
mer- $[Mn_2(\mu-H_2SiPh_2)(CO)_6]$	2014 (m), 1974 (vs), 1943 (m)
(µ-tedip)] (2a.1)	
$mer-[Mn_2(\mu-H_2SiPh_2)(CO)_6]$	2037 (vw), 1995 (s), 1955 (vs), 1925 (s) ^b
(μ-dppm)] (2b.1)	
mer-[Mn ₂ (µ-H ₂ SiPhMe)(CO) ₆	2016 (m), 1976 (vs, br) ^c , 1947 (s) ^d
(µ-tedip)] (2a.2)	
fac-[Mn ₂ (µ-H ₂ SiPhMe)(CO) ₆	2048 (m), 2001 (s), 1976 (s, br) ^c ,
(µ-tedip)] (3a.2)	1957 (vs, sh), 1936 (m, sh) ^e
$mer-[Mn_2(\mu-H_2SiPhH)(CO)_6$	2020 (m), 1985 (vs, br) ^c , 1944 (s) ^c ,
(µ-tedip)] (2a.3)	1940 (s) ^c
$fac-[Mn_2(\mu-H_2SiPhH)(CO)_6$	2050 (vs), 2005 (vs), 1985 (vs, br) ^c ,
(µ-tedip)] (3a.3)	1956 (s, br), 1940 (s) ^c
fac-[Mn ₂ (µ-H ₂ SiPhH)(CO) ₆	2033 (vs), 1990 (vs), 1963 (m),
(μ-dppm)] (3b.3)	1942 (m, sh), 1934 (m), 1919 (w) ^e
$[Mn_2(\mu-SnPh_2)_2(CO)_6]$	2012 (s), 1981 (vs), 1940 (m, sh),
(µ-tedip)] (4a)	1928 (vs), 1913 (s, sh)
$[Mn_2(\mu-SnPh_2)_2(CO)_6]$	2010 (s), 1972 (s), 1925 (s, sh), 1915 (vs)
(μ-dppm)] (4b)	
$[Mn_2(\mu-H){\mu-Ph_2SnO(H)}$	2031 (vw), 2007 (w), 1957 (vs), 1930 (sh),
$SnPh_2$ (CO) ₆ (μ -tedip)] (5a)	1917 (m) ^{d,f}
$[Mn_2(\mu-H){\mu-Ph_2SnO(H)}$	2035 (vw), 1992 (w), 1942 (vs), 1914 (sh),
$SnPh_2$ (CO) ₆ (μ -dppm)] (5b)	1907 (s)
$[Mn_2(\mu-H){\mu-Ph_2SnO(H)}$	2015 (w), 1991 (w), 1936 (vs), 1902 (m)
$SnPh_2$ (CO) ₆ (μ -dmpm)] (5c)	
$[Mn_2(\mu-H)(\mu-HSnPh_2)(CO)_6$	2057 (vs), 2015 (vs), 1987 (vs),
(µ-tedip)] (6a)	1964 (s, sh), 1959 (s), 1930 (s, br) ^d
$[Mn_2(\mu-H)(\mu-HSnPh_2)(CO)_6$	2033 (vs), 1988 (vs), 1960 (m), 1942 (s),
(µ-dmpm)] (6c)	1910 (s)
$[Mn_2(\mu-H){\mu-O(H)SnPh_2}(CO)_6$	2032 (s), 1997 (s), 1953 (m), 1930 (m),
(μ-dppm)] (7b)	1920 (vs) ^d
$[Mn_2(\mu-H){\mu-O(H)SnPh_2}(CO)_6$	2028 (vs), 1990 (vs), 1944 (s), 1917 (s)
(µ-dmpm)] (7c)	
$[Mn_2(\mu-H)(\mu-OH)(CO)_6]$	2027 (s), 1995 (vs), 1934 (m), 1905 (vs)
(µ-dmpm)] (8c)	
$[Mn_2(\mu-H)(SnPh_3)(CO)_7$	2088 (m), 2021 (s), 2005 (vs), 1977 (s),
(μ-dppm)] (9b)	1907 (s), 1892 (s)
$[Mn_2(\mu-H)(SnPh_3)(CO)_7$	2079 (m), 2016 (m), 1993 (vs), 1977 (sh),
(µ-dmpm)] (9c)	1969 (sh), 1908 (m), 1890(m)

^a Recorded in CH₂Cl₂ solution unless otherwise stated.

^b Recorded in tetrahydrofuran.

^c Band due to both *fac* and *mer* isomers.

^d Recorded in petroleum ether.

e Recorded in toluene.

^f ν (O–H) 3340 (w) in Nujol mull.

bound hydrogen atoms in each case. Other resonances present in the ¹H spectra of these complexes are in agreement with the symmetrical structure found for **2a.1** in the crystal and need not to be discussed in detail.

The spectroscopic features of the fac isomer 3b.3 are significantly different from those of the mer isomers just discussed. In the first place, its IR spectrum (Table 2) displays five strong C-O stretching bands with a pattern comparable to that of related dimanganese compounds having facial Mn(CO)₃ groups, such as [Mn₂(µ-H)(µ-BH₄)(CO)₆(µ-dppm)] [16] and [Mn₂Au₂SnCl₂(CO)₆(µdppm){P(p-tol)₃}₂ [20]. The stretching band due to the Si-H terminal bond is not observed in this spectrum, most likely obscured by the C–O stretching bands of the complex [21]. That bond, however, is denoted by the presence of a resonance at 5.89 ppm in the ¹H NMR spectrum [22], with the latter also displaying a broad resonance at -10.22 ppm with intensity corresponding to 2H atoms, indicative of the presence of a symmetrically coordinated μ - κ^2 : κ^2 -H₂SiHPh molecule. Although there are two possible orientations of the silane molecule with respect to the diphosphine ligand, only a single conformer is present in the solutions of **3b.3**, presumably the one with the Ph substituent on the silane pointing away from the bridging diphosphine, more favored on steric grounds (Chart 2).

Table 3			
${}^{31}P{}^{1}H{}^{a}$ and ${}^{1}H{}^{1}$	NMR ^b data fo	r new com	oounds.

	δ [P]/ppm		δ [H]/ppm			J/Hz ^c			
	P ¹	P ²	Mn-H-Mn	Mn-H-E	O-H	J(PP)	<i>J</i> (HP)	J(H ¹ Sn)	J(H ² Sn)
1c	42.4 ^d		-18.02 ^e				20		
2a.1	179.5			-12.10 (ft)			15		
2b.1	63.3			-13.09 (ft)			12		
2a.2	179.9			-12.42 (ft)			14		
3a.2	171.6			-11.02 (br)					
2a.3	178.9 ^f			-12.96 (ft) ^g			12		
3a.3	175.2 ^f			–11.58 (ft) ^g			23		
3b.3	63.5			-10.22 (br) ^e					
4a	168.4 ^h								
4b	45.9 ^h								
5a	176.2 ^h		-24.40 (t) ^h		2.32		13	85	
5b	66.4 ^h		–25.90 (t) ^h		2.50		15	75	21
5c	36.8		-25.50 (t)		2.10		13	90	
6a	175.5 (d) ^{h,i}	165.3 (d) ^{h,i}	-18.40 (t) ^h	-9.49 (d)		88	28	124	97
6c	31.01 (AB) ^j	27.7 (AB) ^j	$-18.20 (t)^{k}$	–9.43 (d) ^k		68	23	142	93
7b	61.0 (d) ^{h,i}	43.8 (d) ^{h,i}	$-20.40 (dd)^{h}$		-2.08	54	22, 37		32
7c	33.5 (AB) ^j	30.1 (AB) ^j	-21.75 (t)		-2.95	65	26	120	26
8c	31.3 ^j		-11.86 (t) ^k		-2.49 (t)		5, 21		
9b	71.1 (d) ^{d,l}	50.0 (d) ^{d,l}	-24.84 (dd) ^{e,m}			70	14, 21	35	
9c ⁿ	38.2 (d) ^{d,l}	25.7 (d) ^{d,l}	$-24.85 (dd)^{e,l}$			60	7, 20	47	

a Recorded at room temperature in C₆D₆ solution at 121.50 MHz, unless otherwise stated; δ in ppm relative to external 85% aqueous H₃PO₄, with multiplicity indicated in brackets; labeling according to the figure shown below.

Recorded at room temperature in C₆D₆ solution at 300.13 MHz, unless otherwise stated; δ in ppm relative to internal TMS, with multiplicity indicated in brackets; ft stands for false triplet; in those cases, the values quoted as J(HP) are actually the absolute values of J(HP) + J(HP').

J (HSn) refers to the average coupling between H and the ¹¹⁹Sn and ¹¹⁷Sn isotopes.

d Recorded at 161.9 MHz.

Recorded at 400.13 MHz.

f Recorded in toluene-d₈ at 253 K.

Recorded in CD₂Cl₂.

Recorded in CDCl₃.

Recorded in CDCl3 at 243 K.

Recorded at 81.01 MHz.

k Recorded at 200.13 MHz.

Recorded in CD₂Cl₂ at 223 K.

^m Recorded in CD₂Cl₂ at 263 K.

ⁿ Data for the isomer *B*.



As stated above, the tedip-bridged complexes $[Mn_2(\mu-H_2SiPhH)]$ $(CO)_6(\mu$ -tedip)] and $[Mn_2(\mu$ -H₂SiPhMe)(CO)_6(\mu-tedip)] are obtained as mixtures of the corresponding mer and fac isomers, this being apparent from the complexity of the corresponding IR spectra and the appearance in each case of separated ³¹P and ¹H NMR resonances that are comparable to those of compounds 2a.1 (mer) or to those of **3b.3** (*fac*) (Tables 2 and 3). We notice that the Mn–H–Si resonance in the fac isomer 3a.3 displays a large overall coupling to phosphorus ($J_{PH} + J_{P'H} = 23$ Hz), comparable to the *cis* couplings observed in many dimanganese compounds of the type $[Mn_2(\mu-H)]$ $(\mu$ -X)(CO)₆(μ -L₂)] (20–30 Hz). These values are much higher than the overall values observed in the mer isomers (cf. $J_{PH} + J_{P'H} = 12$ Hz for **2b.3**), obviously as a result of the much different H–Mn–P angles involved (90° vs. 180°).

2.3. Synthesis of $[Mn_2(\mu-H)_2(CO)_6(\mu-dmpm)]$ (1c)

The dihydride complex 1c can be prepared by following a procedure analogous to that previously described for the tedip and dppm complexes 1a,b [5,6], except that a different reducing reagent gives the best results in this case. Thus, the chloridebridged complex $[Mn_2(\mu-Cl)_2(CO)_6(\mu-dmpm)]$ is first reacted with ca. 5 equiv of Li[BH₂Me₂] in tetrahydrofuran at room temperature to yield a red-greenish solution after 3 h stirring. The subsequent addition of degassed water to the latter mixture and removal of the solvents under vacuum gives a dark-red residue yielding ca. 70% of the purple dihydride complex 1c after chromatographic purification at 243 K. Compound **1c** can be also obtained analogously by using K[BH(CHMeEt)₃] as reducing agent, but the yield is significantly lower (ca. 45%), while the use of Li[HBEt₃] failed to give significant amounts of the desired complex.

Spectroscopic data for 1c are very similar to those of the dppmbridged analog 1b [6] and need not to be discussed in detail. We just note that 1c displays C–O stretching bands some 7 cm⁻¹ lower than those of **1b**, this illustrating the better donor properties of the dmpm ligand (compared to dppm), while the equivalent hydride ligands give a strongly shielded triplet resonance $(J_{PH} = 20 \text{ Hz})$ at -18.02 ppm, comparable to the one observed for the dppm complex **1b** ($\delta = -17.5$ ppm, $J_{PH} = 21$ Hz).

2.4. Reactions of the dihydride complexes 1a-c with HSnPh₃

The reactions of compounds 1a-c with HSnPh₃ are far less selective than the reactions with silanes just discussed, and they were found to be strongly dependent on the reaction conditions and the nature of the bridging phosphorus ligand. The Table 4 summarizes the distribution of products (based on yields of isolated species) obtained under different experimental conditions.

The reactions of the tedip-bridged complex **1a** with HSnPh₃ give three major species that can be separated through low temperature chromatography: the stannylene complex $[Mn_2(\mu-SnPh_2)_2(CO)_6(\mu$ tedip)] (**4a**), the stannylene-stannyl complex $[Mn_2(u-H)\{u-Ph_2SnO\}]$ (H)SnPh₂ $(CO)_6(\mu$ -tedip)] (5a), and the hydrostannyl complex $[Mn_2(\mu-H)(\mu-HSnPh_2)(CO)_6(\mu-tedip)]$ (6a) (Chart 3). All of these products follow from the loss of a Ph group from the organotin hydride, mostly eliminated as benzene, as shown by GC-MS analysis of the corresponding reaction mixtures. As expected, the formation of 6a is favored when using equimolar amounts of reagents and if carrying the reaction at 273 K, although significant amounts of this product are obtained even when using excess of reagent. With the appropriate stoichiometry for ditin derivatives (2:1), the major products are 4a and 5a if the reaction is carried out in toluene solution, while compound 5a becomes dominant if using THF as solvent. Since the formation of the latter complex requires an external source of oxygen atoms, it is very likely for such a source to be the traces of water present in the solvent, expected to be higher in the more hygroscopic THF solvent (compared with toluene). Under these conditions, another uncharacterized compound was present in significant amounts in the reaction mixture. The only significant spectroscopic feature associated to this compound was the presence in the ¹H spectrum of an AA'XX' multiplet at $-22.07 \text{ ppm} (|J_{HP} + J_{HP'}| = 18 \text{ Hz})$ due to hydride-like ligands. No resonances for this species could be clearly identified in the ${}^{31}P{}^{1}H$ spectrum of the reaction mixture, perhaps being obscured by the quite broad resonance of the major product 5a. Unfortunately, this product decomposed completely upon chromatographic workup of the reaction mixture and could not be characterized.

The reactions of **1b** with HSnPh₃ are analogous to those of **1a**, except that no hydrostannyl compound isostructural to **6a** was formed at all. Instead, the related hydroxylstannyl complex [Mn₂- $(\mu$ -H){ μ -O(H)SnPh₂}(μ -dppm)(CO)₆] (**7b**) was obtained under comparable circumstances (Chart 3). Thus, the reaction between stoichiometric amounts of **1b** and HSnPh₃ in toluene at 273 K gave **7b** as major product. Interestingly, a very small amount of a new type of product was detected under these conditions. Fortunately, the latter complex could be generated as the major product by carrying out the reaction under a CO atmosphere, and it could be identified as the stannyl heptacarbonyl complex [Mn₂(μ -H)(SnPh₃)(μ -dppm) (CO)₇] (**9b**). At this point we should note that in our preliminary study of the above reactions [7], the hydroxylstannyl complex **7b** was

Table	4
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Product distribution	in the	reactions of	compounds	1a-c with	HSnPh ₃ . ^a
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					-				-	
L ₂	Rr	T/K	solv	t/h	4	5	6	7	8	9
tedip	1	293	Tol	1	15	15	20			
tedip	1	273	Tol	1	ta	ta	70			
tedip	2	293	Tol	2	40	15	18			
tedip	2.5	293	THF	0.5	ta	50	20			
dppm	1	293	Tol	1	22	10		10		
dppm	1	273	Tol	1				70		ta
dppm	2	293	Tol	2	40	10		20		
dppm	1	293	Tol ^b	4				25		55
dmpm	2.5	293	THF	1		10	20	25	20	ta
dmpm	1	273	Tol	2.5		ta		82		
dmpm	1	293	THF ^b	2.5			ta	15		75

^a Given in % of products isolated after column chromatography of the corresponding reaction mixture; ta stands for trace amounts of product, Rr stands for the molar ratio of HSnPh₃ to compound **1** used in each experiment, and solv stands for solvent, either toluene (Tol) or tetrahydrofuran (THF).

^b Reaction performed under a CO atmosphere.



erroneously identified as an hydrostannyl analog of the tedip complex **6a**. Actually, we have now been unable to identify such a stannyl derivative of the dppm-bridged compound **1b** under any conditions, presumably due to the high reactivity to traces of water of the intermediate species involved (see later).

The reactions of the dihydride **1c** and HSnPh₃ were also of low selectivity (Table 4). The main differences with the reactions of **1a** and **1b** just discussed are as follows: (a) no stannylene complex of type **4** could be identified in significant amounts under any conditions, (b) both hydrostannyl-bridged and hydroxylstannyl-bridged complexes (**5c** and **6c**) can be isolated in these reactions, (c) the novel hydroxide-bridged complex [Mn₂(μ -H)(μ -OH)((μ -dmpm)(CO)₆] (**8c**) is formed in significant amounts if using THF as solvent, and (d) under a CO atmosphere, no product other than the heptacarbonyl complex **9c** is formed in significant amounts (Chart 3).

Compounds **5** to **7** are formally related to each other through some simple reactions, so we examined some possible conversions (Scheme 1). From these we concluded that none of these products are efficient precursors of any of the others, and therefore must be formed through independent reaction pathways, to be discussed later on. Thus, although the hydroxylstannyl compounds **7** are formally derived from the addition of an oxygen atom to the hydrostannyl compounds **6**, the dmpm-bridged complex **6c** did not react rapidly with oxygen at room temperature, and only a generalized decomposition was observed after several hours. As for the tedip compound **6a**, the reaction with oxygen also required several hours for completion and yielded a mixture of several uncharacterized products. One of the minor species present in the mixture



Scheme 1. Hypothetical reactions relating compounds 5 to 7 [$Mn_2 = Mn_2(CO)_6(\mu-L_2)$, with $L_2 =$ tedip, dppm, dmpm].

showed upfield ¹H NMR resonances [δ –2.9 (s, J_{HSn} = 30 Hz, 1H, OH) and δ –23.02 (t, J_{HP} = 31, $J_{\text{HSn}} \approx$ 91, 1H, Mn–H–Mn)] comparable to those of the hydroxylstannyl complex **7b** (Table 3) and therefore it is likely to be the corresponding hydroxylstannyl complex [Mn₂(μ -H){ μ - κ ¹: κ ¹-O(H)SnPh₂}(CO)₆(μ -tedip)] (**7a**), although we were not able to purify this minor product.

We also examined the possibility that the compounds of type **5** might be formed through the reaction of **6** with HOSnPh₃ (a possible hydrolysis product of HSnPh₃) or from the reaction of **7** with excess of HSnPh₃ (Scheme 1). We carried out these tests with the dmpm compounds **6c** and **7c**, but no reaction was observed at room temperature in either case. We also examined the reaction of the tedip-bridged complex **6a** with an excess HOSnPh₃, this now requiring several days for completion at room temperature and yielding a complex mixture containing compounds **5a**, **7a** and small amounts of **4a**. From all this we can conclude that neither **6** nor **7** are real precursors of the stannyl–stannylene complexes of type **5** that are formed rapidly in the reactions of the hydride complexes **1a–c** with HSnPh₃.

2.5. Solid-state and solution structure of compounds 4

The structure of the tedip-bridged complex **4a** was confirmed in our preliminary study by X-ray diffraction and it is depicted in the Fig. 2. The molecule displays a rhombic planar arrangement of the four metallic atoms similar to those found in the compounds [Re₂(μ -SnPh₂)₂(CO)₈] [23], and [Mn₂{ μ -Sn(Br)Mn(CO)₅}₂(CO)₈] [24]. The manganese atoms are also bridged by the tedip ligand, and the slightly distorted octahedral coordination environment around the manganese atoms is completed by three carbonyls in a local facial arrangement. The intermetallic distance in **4a** [3.1045(5) Å] is similar to those measured in the mentioned Mn₂Sn₂ cluster (3.086 Å, [24]) and in the Mn₂Au cluster [Mn₂(μ -AuPPh₃)(μ -Br)(CO)₆(μ tedip)](3.090(3) Å, [25]), in agreement with the single Mn–Mn bond to be formulated for this compound on the basis of the EAN rule. On the other hand, the average Mn–Sn distance (ca. 2.61 Å) is within the usual range found for single Mn–Sn bonds (2.55–2.75 Å, [26]).

Spectroscopic data in solution for compounds **4a** and **4b** are fully consistent with the highly symmetrical solid-state structure just discussed. In particular, both compounds exhibit five strong C–O stretching bands in the IR spectra (Table 2), as expected for these C_{2v} molecules [19] and display a single resonance in the corresponding ³¹P{¹H} NMR spectra (Table 3). The presence of effective symmetry elements relating both sides of the averaged Mn₂P₂ plane in each case is denoted in the ¹H NMR spectra by the appearance of a single methyl resonance for the tedip compound **4a**



Fig. 2. ORTEP diagram (30% probability) of compound **4a**, with H atoms omitted for clarity (taken from Ref. [7]). Selected bond lengths (Å) and angles (°): Mn(1)-Mn'(1) = 3.1045(5), Mn(1)-Sn(1) = 2.6053(5), Mn'(1)-Sn(1) = 2.6178(6), Mn(1)-P(1) = 2.2472(4); Mn(1)-Sn(1)-Mn'(1) = 72.94(2), Sn(1)-Mn(1)-Sn'(1) = 106.93(2), C(10)-Sn(1)-C(20) = 98.6(1), P(1)-Mn(1)-Sn(1) = 91.49(3).

and of a single methylenic resonance for the dppm compound **4b** (see the Experimental section).

2.6. Solid-state and solution structure of compounds 5

Crystals of medium quality for an X-ray diffraction study were obtained after many unsuccessful attempts for compound 5a. An ORTEP view of the molecule is shown in the Fig. 3, while the most relevant bond distances and angles are collected in the Table 5. The molecule in made up of two T-shaped Mn(CO)₃ fragments connected through a significantly elongated intermetallic bond (Mn-Mn = 3.179(4) Å) and bridged symmetrically by two ligands in a pseudotrans arrangement: a tedip ligand, and a Ph₂SnO(H) SnPh₂ bridge. Although the hydrogen atom on this hydroxyl group was not located in the X-ray study, its presence is denoted by the corresponding IR and ¹H NMR data, to be discussed below. In the same way, the spectroscopic data clearly indicate the presence in this molecule of a hydride ligand bridging the manganese atoms but this atom could not be located either, although its presence can be guessed from the elongation of the Mn–Mn separation noted above (cf. Mn–Mn: 2.9038(6) Å in $[M_2(CO)_{10}]$, [27]). Both metal fragments are significantly twisted (by some 27°) from each other, thus defining a conformation intermediate between the staggered and eclipsed conformations of M2L10 molecules, a feature not unusual in diphosphine-bridged dimanganese complexes (cf. 24° and in the dppm-bridged complex $[Mn_2(CO)_6(\mu-dppm)_2]$ [28]).

The molecule of **5a** was found to crystallize with one molecule of water for every two molecules of complex, they being interacting through hydrogen bonds. Indeed, the distance $O(7)\cdots O(H_2O)$ of



Fig. 3. ORTEP diagram (30% probability) of compound **5a**, with Et and Ph groups (except the ipso C atoms in the latter) omitted for clarity. Hydrogen atoms were not located in this study.

2.89(1) Å is indicative of a weak hydrogen bond (O···O separations in the range 2.70–2.90 Å for weak interactions, [29]). This seems to be a fundamental element in the stabilization of the crystal lattice, and justifies the unexpected water capture during the crystallization process in dichloromethane–petroleum ether mixtures.

The most remarkable structural feature in **5a** is the presence of the symmetrical ditin moiety Ph₂Sn-O(H)-SnPh₂ that can be described as a 3-electron donor ligand resulting from the O-Sn coupling between hydroxylstannyl and stannylene fragments. To our knowledge, this is a quite rare fragment of which we can quote only a couple of precedents. Actually we have found no examples of related hydroxyl-bridged groups bound to transition-metal centers, but can quote the anionic complex [Re₂{µ-Ph₂SnO(Me)SnPh₂} $(CO)_8$, containing a related methoxyl-bridged ditin moiety [30]. Interestingly, the Sn–O lengths in this anion (ca. 2.13 Å) are almost identical to those in **5a** (ca. 2.12 Å). We can also quote the hydride complex $[\text{Re}_2(\mu-H)\{\mu-Ph_2\text{GeO}(H)\text{GePh}_2\}(\text{CO})_8]$ [30], a molecule strictly comparable to compound **5a** after replacing Ge by Sn and two CO ligands by the tedip bridge. Interestingly, this complex is formed in the reaction of a dirhenium precursor with HGePh₃ in the presence of water, in agreement with our experimental data discussed above. An Ir₂ complex containing the same Ge₂ ligand has been recently reported as a low-yield product (4%) of the thermal decomposition of [Ir(H)(GePh₃)₂(CO)₃] [31]. It is worth of note that this complex was found to crystallize with a water molecule involved in hydrogen bonding with the Ph₂GeO(H)GePh₂ ligand.

The structure of compound **5a** can be also related to that of a complex formulated as $[Re_2(\mu-Bu_2SnOSnBu_2)(CO)_8]$ after an X-ray diffraction study [32]. Surprisingly, the Sn–O length in this complex (ca. 2.13 Å) is almost identical to the values measured for **5a** or for

Table 5				
Selected bond lengt	hs (Å) and	l angles (°) for com	pound 5a .

Mn(1)-Mn(2)	3.179(4)	P(1)-Mn(1)-Mn(2)	83.0(2)
Sn(1)-Mn(1)	2.549(3)	P(2)-Mn(2)-Mn(1)	83.2(2)
Sn(1)-O(7)	2.12(1)	Sn(1)-Mn(1)-Mn(2)	94.3(1)
Mn(1)-P(1)	2.180(5)	Sn(2)-Mn(2)-Mn(1)	95.5(1)
Mn(1)-C(1)	1.75(2)	P(1)-Mn(1)-Sn(1)	177.2(2)
Mn(1)-C(2)	1.80(2)	P(2)-Mn(2)-Sn(2)	178.1(2)
Mn(1)-C(3)	1.83(2)	C(1)-Mn(1)-Mn(2)	176.7(6)
Sn(2)-Mn(2)	2.539(3)	C(1)-Mn(1)-C(2)	89.5(8)
Sn(2)-O(7)	2.11(1)	C(4) - Mn(2) - Mn(1)	174.3(7)
Mn(2)-P(2)	2.171(6)	C(4) - Mn(2) - C(5)	93.5(9)
Mn(2)-C(4)	1.76(2)	Sn(2) - O(7) - Sn(1)	127.1(6)
Mn(2) - C(5)	1.78(2)	O(7) - Sn(1) - Mn(1)	108.0(3)
Mn(2)-C(6)	1.82(2)	O(7) - Sn(2) - Mn(2)	105.2(3)

the Re₂ anion mentioned above, and the same can be said about the Sn–O–Sn angles (133.9° in this Re₂ complex, and 127.1(6)° in **5a**). This similarity is not easy to explain, because the Sn–O lengths in a R₂Sn–O–SnR₂ group are expected to be significantly shorter than the corresponding distances in a R₂Sn–O(H)–SnR₂ chain, due to the loss of multiplicity in the Sn–O bonds in the second case [30]. For instance, the Sn–O lengths in Ph₃Sn–O–SnPh₃ are ca. 1.96 Å [33a], that is, more than 0.2 Å shorter than the values in [Ph₃Sn(μ -OH)]_n (2.197(5) and 2.255(5) Å, [33b]). Thus the possibility of a wrong formulation should not be excluded for this dirhenium complex even if the ¹H NMR spectrum did not show clear resonances for OH or hydride groups at the time [32].

Spectroscopic data for **5a** are consistent with its solid-state structure and provide support for the hydrogen atoms (hydroxyl and hydride) not located in the X-ray study. Thus, the presence of the OH group is revealed by the appearance of a characteristic O–H stretching band at 3340 cm⁻¹ in the IR spectrum of **5a** when recorded in a Nujol emulsion, and also by a ¹H NMR resonance at 2.32 ppm. The presence of a hydride ligand symmetrically bridging the manganese atoms is clearly denoted by the appearance of a highly shielded triplet resonance at -24.4 ppm ($J_{HP} = 13$ Hz) displaying satellites due to coupling with the ¹¹⁹Sn/¹¹⁷Sn nuclei (J_{HSn} ca. 85 Hz). Finally, we note that the IR spectrum of **5a** en dichloromethane solution shows five bands, with the C–O symmetrical stretches above ca. 2000 cm⁻¹ being of weak intensity (Table 2), in agreement with the retention of the T-shaped Mn(CO)₃ fragments in solution.

Spectroscopic data for compounds **5b** and **5c** are comparable to those of **5a**, indicating that all these compounds are isostructural (Tables 2, 3 and Experimental section). We just notice that the OH NMR resonance for **5b** displays tin satellites ($J_{HSn} = 23$ Hz), in agreement with its positioning between two Sn atoms. We finally should stress that the hydride ligands in all three compounds display a relatively low P-H coupling of 13-15 Hz, a value comparable to those measured in the silane complexes of type 2 (merisomers), and significantly lower than the usual values for cis P-H couplings in our dimanganese complexes (20–30 Hz). This suggests that the hydride ligand in compounds 5 might be placed in the average plane defined by the Mn, P, and Sn atoms. Interestingly, the hydride ligand in $[Re_2(\mu-H){\mu-Ph_2GeO(H)GePh_2}(CO)_8]$, a complex isoelectronic with compounds 5, was successfully located in that plane through an X-ray study, a position also consistent with the results of DFT calculations on that molecule [30].

2.7. Structural characterization of compounds 6-8

The IR spectra of compounds **6a,c** show the typical five to six strong C–O band pattern usually observed in many dimanganese compounds of the type $[Mn_2(\mu-H)(\mu-X)(CO)_6(\mu-L_2)]$ having two *fac*-M(CO)₃ oscillators, with lower frequencies for the dmpm-bridged complex **6c**, as expected. The inequivalence of both manganese centers is apparent from the corresponding ³¹P NMR spectra, showing two separated resonances corresponding to an AX (**6a**) or an AB spin system (**6c**). For complex **6a**, only the more deshielded resonance displays P–Sn satellites (J_{PSn} ca. 414 Hz) and is thus assigned to the P atom placed further away from the MnHSn edge (P¹ in Table 3), and the same is assumed for compound **6c**.

The most remarkable feature in the ¹H NMR spectra of compounds **6** is the presence of two hydride-like resonances in each case. One of them appears as a strongly shielded triplet resonance at ca. -18 ppm with a characteristic *cis* H–P coupling of ca. 25 Hz, and is therefore assigned to a hydride ligand bridging a Mn–Mn edge in an essentially symmetrical way. The second resonance is less shielded (ca. -9.5 ppm) and displays coupling to a single phosphorus atom, and is therefore assigned to a hydrogen

atom bridging a Sn–Mn edge, therefore implying the presence of a tricentric, agostic-like Sn–H–Mn interaction. An unusual feature of these resonances in compounds **6** is the unexpectedly low H–Sn couplings of ca. 95 Hz, actually lower than the two-bond couplings of ca. 130 Hz observed for the hydride resonances in the same compounds. These one-bond couplings are considerably lower than those measured in related complexes having tricentric Sn–H–M interactions, such as [CpMn(CO)₂(κ^2 -HSnPh₃)] (ca. 260 Hz, [34]) and [Os₃(μ -H)(μ - κ^1 : κ^2 -HSnR₂)(CO)₁₀] (ca. 280 Hz, R = CH(SiMe₃)₂, [35]). This might be indicative in our case of the presence of a Sn–H–Mn interaction in the limit of the full cleavage of the corresponding Sn–H bond, close to the point of yielding bridging stannylene and terminal hydride ligands. Unfortunately, all attempts to obtain X-ray quality crystals of compounds **6a,c** (to confirm this hypothesis) were unsuccessful.

The structure proposed for compounds 7 (Chart 3) is based on the corresponding spectroscopic data and also on an incomplete X-ray diffraction study of the dppm complex 7b. Although the diffraction data were of very low quality and did not allow for a satisfactory refinement of the structure, the gross structural features of the molecule were clearly defined: two facial Mn(CO)₃ fragments bridged by the dppm ligand with a SnPh₂ group asymmetrically bridging the Mn atoms (Mn-Mn = 3.26 Å, Sn-Mn = 2.44 Å and 3.27 Å). While the short distance is a bit shorter than expected for a Mn-Sn bond, the long one is clearly out of the usual range for Mn–Sn bonds (2.55–2.75 Å, [26]). No clear indication of the presence of an oxygen atom in the vicinity of these metal atoms was obtained with these low-quality data. We note. however, that the related Re₂Si complexes [Re₂(μ -H)(μ - κ^{1} : κ^{1} -O(Me) $Si(OMe)_2(CO)_7(L)$] (L = CO, PMe₂Ph) have been characterized structurally [36] and indeed display Re₂SiO rings very similar to the Mn_2SnO ring proposed to be present in compounds 7.

The IR spectra of compounds **7** are similar to those of compounds **6**, supporting the proposal of a similar arrangement of the CO and L_2 ligands, while the latter ligands give rise also to separate ³¹P NMR resonances in each case. As found for compounds **6**, a strongly shielded resonance at ca. –21 ppm with the usual *cis* P–H couplings is present in the ¹H NMR spectra of these compounds, corresponding to a hydride ligand bridging the Mn atoms. However, the second resonance in the hydride region of the spectra of compounds **7** appears as a much more deshielded resonance at ca. –2 ppm and exhibits no coupling to phosphorus. Therefore this resonance is assigned to the hydrogen atom of an hydroxyl group bridging the Sn and Mn atoms. In agreement with this proposal, we note that these resonances display a low P–Sn coupling of ca. 30 Hz, close to the value of 21 Hz measured for the SnO(H)Sn resonance in compound **5b**.

The proposed structure for **8c** is analogous to the numerous compounds of the type $[Mn_2(\mu-H)(\mu-ER)(CO)_6(\mu-L_2)]$ (E = O, S; $L_2 =$ tedip, dppm) previously synthesized from the reactions of the dihydrides 1a,b with different alcohols, thiols, aldehydes and ketones [37], as judged from the similarity in the corresponding spectroscopic data (Tables 2, 3 and Experimental section) and need not to be discussed in detail. We just note that, in addition to the ¹H NMR triplet resonance at -11.86 ppm ($J_{HP} = 21$ Hz) corresponding to the bridging hydride ligand, this complex gives rise to a second triplet resonance substantially more deshielded ($\delta = -2.49$ ppm) and displaying much lower coupling to phosphorus (5 Hz), which is therefore assigned to the H atom of the bridging hydroxide ligand. We note the similarity between these NMR parameters and those of the OH group in the hydroxylstannyl compounds 7 described above. Finally we should also stress that, although compound 8c might be viewed as the product resulting from the reaction of 1c with water, this reaction actually does not take place at a significant extent either in this case or for the related dihydrides **1a,b**.



2.8. Solid-state and solution structure of compounds 9

As discussed below, the compounds **9b.c** are present in solution as mixtures of three isomers that could not be separated from each other (A to C in Chart 4). Fortunately, one of these isomers is the dominant species in solution for the dppm-bridged complex 9b, and it could be crystallized and characterized through an X-ray diffraction study. The molecular structure of this isomer (Fig. 4 and Table 6, corresponding to isomer B in Chart 4) can be viewed as derived from that of $[Mn_2(CO)_{10}]$ after replacing two equatorial carbonyls with the dppm bridging ligand and one more equatorial carbonyl with a SnPh₃ group, trans to phosphorus, with the two metal fragments being twisted from each other by some 23°. As found for the Mn₂Sn₂ hydride compound 5a, the Mn–Mn separation in 9b is relatively large (3.2370(9) Å), but now the hydride ligand could be located, it being somewhat asymmetrically placed over that vector (Mn-H = 1.61(3), 1.70(3) Å), and positioned *cis* to the P atoms (H–Mn–P ca. 94°). The axial CO ligands are not colinear with the intermetallic vector, but rather the corresponding Mn–C vectors point to the center of the Mn₂H triangle, as usually found for tricentric $M_2(\mu-H)$ interactions of the closed type [38]. Finally, the SnPh₃ group displays no remarkable features, with the Mn-Sn bond length of 2.6415(7) Å being comparable to the values of 2.63-2.69 Å measured for several complexes of the type $[Mn(SnR_3)(CO)_5]$ [39].



Fig. 4. ORTEP diagram (30% probability) of compound **9b**, with H atoms (except the hydride ligand) and Ph groups (except the ipso C atoms) omitted for clarity.

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Selected bond lengths (Å) and angles (°) for compound **9b**.

	., .		
Mn(1)-Mn(2)	3.2370(9)	Sn(1)-Mn(1)-Mn(2)	98.99(2)
Mn(1)-Sn(1)	2.6415(7)	Sn(1)-Mn(1)-P(1)	172.4(1)
Mn(1)-P(1)	2.275(1)	Sn(1)-Mn(1)-C(1)	84.1(1)
Mn(1)-C(1)	1.784(4)	Sn(1)-Mn(1)-C(2)	84.6(1)
Mn(1)-C(2)	1.822(5)	C(1)-Mn(1)-Mn(2)	173.1(1)
Mn(1)-C(3)	1.819(5)	C(1)-Mn(1)-H(1)	173(2)
Mn(1) - H(1)	1.70(3)	C(4) - Mn(2) - Mn(1)	92.7(1)
Mn(2)-P(2)	2.307(1)	C(4) - Mn(2) - P(2)	90.6(1)
Mn(2)-C(4)	1.862(5)	C(5)-Mn(2)-P(2)	175.9(1)
Mn(2) - C(5)	1.841(5)	C(7) - Mn(2) - Mn(1)	175.1(1)
Mn(2) - C(6)	1.844(5)	C(7) - Mn(2) - H(1)	172(2)
Mn(2)-C(7)	1.810(5)	Mn(1)-H(1)-Mn(2)	155(3)
Mn(2)-H(1)	1.61(3)	H(1) - Mn(1) - Sn(1)	89(2)
P(1) - C(8)	1.837(4)	H(1)-Mn(1)-P(1)	93(2)
P(2)-C(8)	1.836(4)	H(1)-Mn(2)-P(2)	94(2)

The spectroscopic data in solution for **9b** (Tables 2 and 3, and Experimental section) are consistent with the structure found in the crystal, thus suggesting that the solid-state molecule is likely to be the major isomer in solution (*B* in Chart 4). Indeed the other two isomers (*A* and *C*) are expected to be significantly less stable for **9b** because of the steric repulsions derived from the close proximity of the bulky SnPh₃ and PPh₂ groups in these cases, and accordingly they are present only in very tiny amounts in solution, as judged from the appearance, in the ¹H NMR spectra of **9b**, of very weak hydride resonances at -19.2 and -22.2 ppm, in addition to the hydride resonance of the major isomer, with the latter appearing at -24.84 ppm and being coupled differently to the inequivalent P nuclei ($J_{PH} = 14$ and 21 Hz) as expected.

In contrast, isomers A and C are expected to be less disfavored in the presence of a sterically less demanding diphosphine as dmpm. Indeed, the hydride area of the ¹H NMR spectrum of **9c** reveals at room temperature the presence of three resonances with about the same relative intensity at ca. -19.3, -23.2 and -24.7 ppm. A detailed analysis of these spectra, either at room or low temperature, with the additional help of some selective ³¹P decoupling experiments and of a standard 2D-EXSY experiment, allowed the assignment of the different resonances (see the Experimental section). The latter experiment also revealed that isomers A and B convert one into each other but not with the most asymmetric isomer C (or not so rapidly), and that the hydride resonance of isomer B (but not that from A) displays a significant NOE with the ortho hydrogens of the phenyl rings, as expected from the close proximity of the bridging hydride and SnPh₃ groups in that isomer (Chart 4).

2.9. Reaction pathways in the formation of compounds 4-9

From the results discussed above it is clear that, unlike the reactions of the unsaturated hydrides **1** with silicon hydrides, those with HSnPh₃ are rather complex events involving several reaction pathways. Although we have detected no intermediate species in these reactions, we can make reasonable proposals to account for the formation of most of the observed products (Scheme 2).

In the first place it is reasonable to assume that, because of the electronic unsaturation of compounds **1** and their credited ligand–acceptor behavior, the first step in these reactions would be the addition of a HSnPh₃ molecule (by establishing an agostic-like Sn–H–Mn interaction) to one of the manganese atoms, with a concerted movement of one of the bridging hydride ligands into a terminal position, to give an electron-precise intermediate **A** (Scheme 2). This process would be comparable to the addition of "normal" two-electron donors such as phosphines to the unsaturated dirhenium hydrides [Re₂(μ -H)₂(CO)₆(μ -L₂)] [39]. Intermediate **A** could now evolve in two different ways, either through



Scheme 2. Reaction pathways proposed for the reactions of compounds 1a-c with HSnPh₃ [Mn₂ = Mn₂(CO)₆(µ-L₂), with L₂ = tedip, dppm, dmpm].

dehydrogenation, or through benzene elimination. In the first case, a 32 electron intermediate **B** (not detected) with bridging stannyl and hydride ligands would be formed, that would spontaneously react with CO (formed in small amounts through decomposition) to give the heptacarbonyl complexes of type **9**. Apparently, this is not a dominant pathway unless CO is deliberately added to the solution. Yet, we should remark that the sequence $\mathbf{1} \rightarrow \mathbf{B} \rightarrow \mathbf{9}$ is completely parallel to the recently reported reaction between the 30-electron dimolybdenum hydride $[Mo_2Cp_2(\mu-H)(\mu-PCy_2)(CO)_2]$ and HSnPh₃ to give the stannyl-bridged complex $[Mo_2Cp_2(\mu-SnPh_3)$ $(\mu-PCy_2)(CO)_2]$ (characterized through and X-ray study), an unsaturated molecule also reacting with CO to give an electron-precise derivative having a terminally-bound SnPh₃ group [11].

The prevalent evolution of the intermediate **A**, however, would be the elimination of a benzene molecule (as noted above, C₆H₆ has been actually detected in these reaction mixtures), to produce an unsaturated hydride **C**, similar to the intermediate **B** mentioned above. However, the presence of a Sn–H bond in **C** would now enable this molecule to reach electronic saturation by a simple intramolecular rearrangement involving the coordination of the H–Sn bond to a manganese atom, thus leading to the hydrostannylbridged compounds of type **6**. Yet, in the presence of an excess of HSnPh₃, the intermediate **C** would rather add a second molecule of reactant to give the species **D**, isoelectronic with **A**. This might be followed by new processes of elimination of benzene and hydrogen (proposing an exact sequence of events here would be exceedingly speculative) to finally yield the stannylene-bridged compounds of type **4**.

The formation of compounds **5**, **7** and **8** require the incorporation of an oxygen atom at some of the intermediate steps just described, possibly through reactions with traces of water present in the solvent, as noted above. As a result, an hydroxyl group is incorporated into the reaction products bridging either two tin atoms (**5**), two manganese atoms (**8**) or manganese and tin atoms (**7**). However, we have no experimental data to identify or make a sensible guess about the precise steps for the incorporation of this extra oxygen atom in each case.

3. Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures [40], and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 338-343 K. The hydride complexes $[Mn_2(\mu-H)_2(CO)_6(\mu-L_2)]$ (L₂ = (EtO)₂POP(OEt)₂, tedip (1a); $L_2 = Ph_2PCH_2PPh_2$, dppm (**1b**)) were prepared according to literature procedures [15,6b]. The complex $[Mn_2(\mu-Cl)_2(CO)_6(\mu-dmpm)]$ $(dmpm = Me_2PCH_2PMe_2)$ was prepared from $[Mn_2(CO)_8(\mu-dmpm)]$ [41], by following the procedure described previously for the related dppm-bridged complex [42]. All other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns, kept at the desired temperature with a cryostat. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR stretching frequencies of CO ligands were measured either in solution (using CaF₂ windows) or in Nujol mulls (using NaCl windows) and are referred to as ν (CO). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (¹H), 121.50 (³¹P $\{^{1}H\}$) and 75.47 MHz ($^{13}C\{^{1}H\}$) at 290 K in C₆D₆ solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (¹H and ¹³C), and external 85% aqueous H₃PO₄ solutions (³¹P). Coupling constants (*J*) are given in Hertz.

3.1. Preparation of $[Mn_2(\mu-H)_2(CO)_6(\mu-dmpm)]$ (1c)

A solution of Li[BH₂Me₂] (10 mL of a 0.5 M solution in petroleum ether, 5.0 mmol) was slowly added to a dry THF solution (15 mL) of [Mn₂(μ -Cl)₂(CO)₆(μ -dmpm)] (0.500 g, 1.03 mmol) at room temperature, and the mixture was stirred for 3 h to give a red-greenish solution. Degassed water (1 mL, excess) was then added to the solution, the mixture was stirred for 2 min and the solvent was then removed under vacuum. The red purple solid thus obtained was dissolved in the minimum amount of dichloromethane and chromatographed at 243 K on an alumina column (activity 2, 30 × 2.5 cm) prepared in petroleum ether. Elution with toluene–petroleum ether (1:1) gave a purple fraction yielding, after removal of solvents under vacuum, complex **1c** as a purple solid (0.302 g, 70%). Anal. Calcd. for C₁₁H₁₆Mn₂O₆P₂: C, 31.75; H, 3.88. Found: C, 31.81; H, 3.86. ¹H NMR (400.13 MHz): δ 0.95 [false t, |J_{HP} + J_{HP'}| = 7.5, 12 H, Me], 0.52 (t, J_{HP} = 11, 2H, CH₂), -18.02 (t, J_{HP} = 20, 2H, μ -H).

3.2. Preparation of mer- $[Mn_2(\mu-H_2SiPh_2)(CO)_6(\mu-tedip)]$ (2a.1)

Compound **1a** (0.050 g, 0.093 mmol) and H₂SiPh₂ (170 µL, 0.93 mmol) were stirred in toluene (5 mL) at room temperature for 8 h. The resulting yellow solution was filtered and the solvent was removed under vacuum. The residue was then washed with cold petroleum ether (253 K, 2 × 2 mL) and dried under vacuum to give compound **2a.1** as a yellow microcrystalline solid (0.057 g, 85%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex. Anal. Calcd. for C₂₆H₃₂Mn₂O₁₁P₂Si: C, 43.35; H, 4.48. Found: C, 43.42; H. 4.70. ¹H NMR: δ 7.79 (false d, *J*_{HH} = 7, 12H, Ph), 7.59–7.00 (m, 6H, Ph), 3.83 (m, 8H, OCH₂), 0.99 (t, *J*_{HH} = 7, 12H, Me), -12.10 [false t, |*J*_{HP} + *J*_{HP'}| = 15, 2H, Mn–H–Si].

3.3. Preparation of mer- $[Mn_2(\mu-H_2SiPh_2)(CO)_6(\mu-dppm)]$ (2b.1)

Compound **1b** (0.040 g, 0.06 mmol) and H_2SiPh_2 (110 μL , 0.60 mmol) were stirred in toluene (5 mL) at 328 K for 1.5 h. Workup

as described for **2a.1** yielded compound **2b.1** as a microcrystalline yellow solid (0.040 g, 79%). Anal. Calcd. for C₄₃H₃₄Mn₂O₆P₂Si: C, 61.00; H, 4.05. Found: C, 61.19; H, 4.35. ¹H NMR: δ 8.1–6.5 (m, 30H, Ph), 3.99 (t, *J*_{HP} = 10, 2H, CH₂), -13.09 [false t, *J*_{HP} + *J*_{HP'}] = 12, 2H, Mn–H–Si].

3.4. Reaction of compound **1a** with H₂SiPhMe

Compound **1a** (0.050 g, 0.093 mmol) and H₂SiPhMe (60 µL, 0.44 mmol) were stirred in petroleum ether (5 mL) at room temperature for 15 h. Workup as described for **2a.1** gave an oily yellow residue containing the isomers *mer*-[Mn₂(µ-H₂SiMePh)(CO)₆(µ-tedip)] (**2a.2**) and *fac*-[Mn₂(µ-H₂SiMePh)(CO)₆(µ-tedip)] (**3a.2**) in a ratio 5:1. Data for **2a.2**: ¹H NMR: δ 7.93 (m, 2H, Ph), 7.39–7.27 (m, 3H, Ph), 4.02 (m, 8H, OCH₂), 1.23, 1.16 (2t, *J*_{HH} = 7, 2 × 6H, Me), 1.08 (s, 3H, SiMe), -12.42 [false t, |*J*_{HP} + *J*_{HP}| = 14, 2H, Mn–H–Si]. Data for **3a.2**: ¹H NMR: δ -11.02 [br, Mn–H–Si]; other resonances for this isomer were obscured by those of the major isomer.

3.5. Reaction of compound 1a with H₃SiPh

Compound **1a** (0.050 g, 0.093 mmol) and H₃SiPh (116 µL, 0.93 mmol) were stirred in toluene (5 mL) at room temperature for 2 h. Workup as described for **2a.1** gave an oily yellow residue containing the isomers *mer*-[Mn₂(µ-H₂SiPhH)(CO)₆(µ-tedip)] (**2a.3**) and *fac*-[Mn₂(µ-H₂SiPhH)(CO)₆(µ-tedip)] (**3a.3**) in a ratio 1:6. Data for **3a.3**: ¹H NMR (CD₂Cl₂): δ 7.8–7.2 (m, 5H, Ph), 5.85 (t, *J*_{HP} = 12.5, 1H, Si–H), 3.99 (m, 8H, OCH₂), 1.32 (m, 12H, Me), -11.58 [false t, *J*_{HP} + *J*_{HP'}| = 23, 2H, Mn–H–Si]. Data for **2a.3**: ¹H NMR (CD₂Cl₂): δ –12.96 [false t, *J*_{HP} + *J*_{HP'}| = 12, 2H, Mn–H–Si]; other resonances for this isomer were obscured by those of the major isomer.

3.6. Preparation of compound fac- $[Mn_2(\mu-H_2SiPhH)(CO)_6(\mu-dppm)]$ (**3b.3**)

Compound **1b** (0.040 g, 0.060 mmol) and H₃SiPh (40 μ L, 0.32 mmol) were stirred in toluene (5 mL) at 323 K for 2 h. Workup as described for **2a.1** yielded complex **3b.3** as an oily yellow residue. ¹H NMR (400.13 MHz): δ 7.8–6.6 (m, 25H, Ph), 5.89 (t, *J*_{HP} = 12.5, 1H, Si–H), 3.39, 3.00 (2 × dt, *J*_{HH} = 15, *J*_{HP} = 11, 2H, CH₂), –10.22 [br, 2H, Mn–H–Si].

3.7. Preparation of $[Mn_2(\mu-SnPh_2)_2(CO)_6(\mu-tedip)]$ (4a)

Compound **1a** (0.100 g, 0.186 mmol) and HSnPh₃ (0.120 g, 0.372 mmol) were stirred in toluene (20 mL) for 2 h to give a yellow solution. Solvent was then removed from the solution under vacuum, and the oily residue was dissolved in petroleum ether and chromatographed on an alumina column (activity 4) at 243 K. Elution with the same solvent gave a yellow fraction yielding, after removal of the solvent under vacuum, compound **6a** as a yellow solid (0.027 g, 18%). Elution with dichloromethane—petroleum ether (1:8) gave another yellow fraction, yielding analogously 0.015 g (15%) of compound **5a**. Elution with a 1:4 solvent mixture gave finally a third yellow fraction, yielding, after removal of solvents, compound **4a** as a yellow solid (0.040 g, 40%). Data for **4a**: Anal. Calcd. for C₃₈H₄₀Mn₂O₁₁P₂Sn₂: C, 42.18; H, 3.73. Found: C, 42.03; H. 3.81. ¹H NMR (CDCl₃): δ 8.02 (m, 4H, Ph), 7.9 (m, 4H, Ph), 7.68–7.16 (m, 12H, Ph), 3.75 (m, 4H, OCH₂), 3.3 (m, 4H, OCH₂), 1.01 (t, J_{HH} = 7, 12H, Me).

3.8. Preparation of $[Mn_2(\mu-H){\mu-Ph_2SnO(H)SnPh_2}(CO)_6(\mu-tedip)]$ (5a)

Compound **1a** (0.100 g, 0.186 mmol) and $HSnPh_3$ (0.163 g, 0.465 mmol) were stirred in tetrahydrofuran (15 mL) for 25 min to give an orange solution that was filtered. The solvent was then

removed from the solution under vacuum and the oily reddish residue was dissolved in petroleum ether and chromatographed on an alumina column (activity 3) at 253 K. Elution with dichloromethane–petroleum ether (1:8) gave a yellow fraction yielding, after removal of solvents, 0.030 g (20%) of compound **6a**. Elution with a 1:1 solvent mixture gave another yellow fraction yielding, after removal of solvents, compound **5a** as a yellow solid (0.102 g, 50%). The crystals used in the X-ray diffraction study were grown by slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at 253 K. Anal. Calcd. for C₃₈H₄₂Mn₂O₁₂P₂Sn₂: C, 41.49; H, 3.85. Found: C, 41.80; H, 3.94. ¹H NMR (CDCl₃): δ 7.6–7.1 (m, 20H, Ph), 4.10 (m, 8H, OCH₂), 2.32 (s, OH), 1.38 (t, *J*_{HH} = 7, 12H, Me), –24.4 (t, *J*_{HP} = 13, *J*_{119SnH} \approx *J*_{117SnH} = 85, µ-H). ¹³C{¹H} NMR (CDCl₃): δ 220.3 (m, 2CO), 218.7 (m, 4CO), 149.0 [s, C¹(Ph)], 135.6 [s, C³(Ph)], 128.9 [s, C⁴(Ph)], 128.3 [s, C²(Ph)], 61.3 (s, OCH₂), 16.0 (s, Me).

3.9. Preparation of $[Mn_2(\mu-SnPh_2)_2(CO)_6(\mu-dppm)]$ (**4b**) and $[Mn_2(\mu-H)\{\mu-Ph_2SnO(H)SnPh_2\}(CO)_6(\mu-dppm)]$ (**5b**)

Compound 1b (0.100 g, 0.150 mmol) and HSnPh₃ (0.106 g, 0.300 mmol) were stirred in toluene (20 mL) at room temperature for 2 h to give an orange solution. The solvent was then removed under vacuum and the resulting oily residue was extracted with dichloromethane-petroleum ether (1:9), and the extracts were chromatographed on an alumina column (activity 4) at 243 K. Elution with petroleum ether gave a yellow-orange fraction yielding, after removal of solvents under vacuum, compound **7b** as an orange solid (0.028 g. 20%). Elution with dichloromethane-petroleum ether (1:6) gave a second orange fraction yielding analogously compound **5b** as an orange solid (0.018 g, 10%). Finally, elution with dichloromethane-petroleum ether (1:4) gave another orange fraction yielding compound **4b** as an orange solid (0.072 g, 40%). Data for 4a: Anal. Calcd. for C₅₅H₄₂Mn₂O₆P₂Sn₂: C, 54.68; H, 3.50. Found: C, 54.31; H. 3.35. ¹H NMR (CDCl₃): δ 7.60–6.97 (m, 40H, Ph), 3.07 (t, $J_{\rm HP} = 11, 2H, CH_2$). Data for **5b**: Anal. Calcd. for C₅₅H₄₄Mn₂O₇P₂Sn₂: C, 53.87; H, 3.62. Found: C, 54.19; H, 3.87. ¹H NMR (CDCl₃): δ 7.50–7.10 $(m, 40H, Ph), 3.9(t, J_{HP} = 10, 2H, CH_2), 2.5(s, J_{119SnH} \approx J_{117SnH} = 21, 1H,$ OH), -25.9 (t, $J_{HP} = 15$, $J_{119SnH} \approx J_{117SnH} = 75$, 1H, μ -H).

3.10. Preparation of $[Mn_2(\mu-H)(\mu-HSnPh_2)(CO)_6(\mu-tedip)]$ (**6a**)

Compound **1a** (0.100 g, 0.186 mmol) and HSnPh₃ (0.060 g, 0.186 mmol) were stirred in toluene (20 mL) at 273 K for 1 h to give a yellow solution. The solvent was then removed from the solution under vacuum, and the oily residue was dissolved in petroleum ether and chromatographed on an alumina column (activity 4) at 243 K. Elution with the same solvent gave a yellow fraction yielding, after removal of the solvent under vacuum, compound **6a** as a yellow solid (0.102 g, 68%). Anal. Calcd. for C₂₆H₃₂Mn₂O₁₁P₂Sn: C, 38.50; H, 3.98. Found: C, 38.85; H, 4.05. ¹H NMR (CDCl₃): δ 7.70–7.30 (m, Ph, 4H), 7.30–7.10 (m, 6H, Ph), 4.03, 3.70, 3.40, 3.20 (4m, 4 × 2H, OCH₂), 1.36, 1.34, 1.06, 0.97 (4t, *J*_{HH} = 7, 4 × 3H, Me), -9.49 (d, *J*_{HP} = 29, *J*_{119SnH} ≈ *J*_{117SnH} = 97, 1H, Mn–H–Sn), -18.40 (t, *J*_{PH} = 28, *J*_{119SnH} ≈ *J*_{117SnH} = 124, 1H, Mn–H–Mn). ³¹P{¹H} NMR (CDCl₃, 243 K): δ 175.5 (d, *J*_{PP} = 88, *J*_{119SnP} ≈ *J*_{117SnP} = 415, 1P, µ-tedip), 165.3 (d, *J*_{PP} = 88, 1P, µ-tedip).

3.11. Preparation of $[Mn_2(\mu-H)\{\mu-O(H)SnPh_2\}(CO)_6(\mu-dppm)]$ (**7b**)

The procedure is completely analogous to that described for **6a** but using **1b** as starting material. After similar workup, complex **7b** was obtained as a yellow-orange solid (0.098 g, 70%). Anal. Calcd. for C₄₃H₃₄Mn₂O₇P₂Sn: C, 54.18; H, 3.60. Found: C, 54.49; H, 3.87. ¹H NMR (CDCl₃): δ 8.0–6.6 (m, 30H, Ph), 3.42, 3.24 (AB mult, *J*_{HH} = 13,

 $J_{\text{HP}} = 12, 2\text{H}, \text{CH}_2$, -2.08 (s, $J_{119\text{SnH}} \approx J_{117\text{SnH}} = 32, 1\text{H}, \text{OH}$), -20.40 [dd, $J_{\text{HP}} = 22, 37, 1\text{H}, \mu$ -H].

3.12. Reaction of compound 1c with excess HSnPh₃

Compound 1c (0.080 g, 0.19 mmol) and HSnPh₃ (0.182 g, 0.52 mmol) were stirred in THF (15 mL) at room temperature for 1 h to give a reddish solution. Solvent was then removed from the solution under vacuum and the oily residue was then dissolved in petroleum ether and chromatographed on an alumina column (activity 2.5) at 253 K. Elution with dichloromethane-petroleum ether (3:7) gave a yellow fraction yielding, after removal of solvents, 0.025 g (20%) of compound 6c. Elution with dichloromethane-petroleum ether (2:3) gave an orange fraction yielding analogously compound **5c** as a orange solid (0.020 g, 10%). Elution with a 1:1 solvent mixture gave a yellow fraction yielding compound **7c** as a dark yellow solid (0.035 g, 25%). Then an orange fraction was eluted with a 3:1 solvent mixture, containing a trace amount of compound 9c that was discarded. Finally, elution with neat dichloromethane gave a yellow fraction yielding compound 8c as a yellow solid (0.015 g, 20%). Data for 5c: Anal. Calcd. for C₃₅H₃₆Mn₂O₇P₂Sn₂: C, 42.99; H, 3.71. Found: C, 42.63; H, 3.37. ¹H NMR (CD₂Cl₂): δ 7.60-7.20 (m, 20H, Ph), 2.70 (s, 1H, OH), 2.75 (t, $J_{\text{HP}} = 10$, 2H, CH₂), 1.77 (false t, $|J_{\text{HP}} + J_{\text{HP}'}| = 7$, 12H, Me), -25.8 $[t, J_{HP} = 14, 1H, \mu$ -H]. ¹H NMR: δ 7.50–7.30 (m, 20H, Ph), 2.10 (s, 1H, OH), 1.72 (t, $J_{HP} = 11$, 2H, CH₂), 1.10 (false t, $|J_{HP} + J_{HP'}| = 7$, 12H, Me), -25.5 [t, $J_{HP} = 13$, $J_{119SnH} \approx J_{117SnH} = 90$, μ -H]. ³¹P{¹H} NMR (CD₂Cl₂): δ 37.4 (s, μ -dmpm, 2P). Data for **6c**: Anal. Calcd. for C₂₃H₂₆Mn₂O₆P₂Sn: C, 40.10; H, 3.80. Found: C, 39.87; H, 3.85. ¹H NMR (200.13 MHz): δ 8.04–7.05 (m, 10H, Ph), 0.84 (d, J_{HP} = 7, 3H, Me), 0.81 (d, J_{HP} = 7, 6H, Me), 0.6 (d, $J_{HP} = 7$, 3H, Me), 0.70 (m, 1H, CH₂), 0.29 (td, $J_{HP} = 13$, $J_{\rm HH} =$ 12, 1H, CH₂), -9.43 (d, $J_{\rm HP} =$ 9.4, $J_{119SnH} \approx J_{117SnH} =$ 93, 1H, Sn-H-Mn), -18.2 [t, $J_{HP} = 23$, $J_{119SnH} \approx J_{117SnH} = 142$, Mn-H-Mn]. Data for **8c**: Anal. Calcd. for C₁₁H₁₆Mn₂O₇P₂: C, 30.58; H, 3.73. Found: C, 30.45; H, 3.66. 1 H NMR (200.13 MHz): δ 0.79 (false t, $|J_{HP} + J_{HP'}| = 6.4, 6H, Me$, 0.67 (false t, $|J_{HP} + J_{HP'}| = 7.2, 6H, Me$), 0.1 (q, $J_{\rm HH} = J_{\rm HP} = 13, 1H, CH_2$, $-0.26 (dt, J_{\rm HH} = 13, J_{\rm HP} = 11, 1H, CH_2$, -2.49 $(t, J_{HP} = 5, 1H, OH), -11.86 (t, J_{HP} = 21, 1H, \mu-H).$

3.13. Preparation of $[Mn_2(\mu-H)\{\mu-O(H)SnPh_2\}$ (CO)₆(μ -dmpm)] (**7c**)

Compound 1c (0.036 g, 0.085 mmol) and HSnPh₃ (0.030 g, 0.085 mmol) were stirred in toluene (15 mL) at 273 K for 2.5 h to give a yellow solution. Solvent was then removed from the solution under vacuum and the oily residue was dissolved in petroleum ether and chromatographed on an alumina column (activity 2.5) at 253 K. Elution with dichloromethane-petroleum ether (2:3) gave a yellow fraction containing very small amounts (<5%) of complex **5c**. Elution with a 1:1 solvent mixture gave another yellow fraction vielding, after removal of solvents under vacuum, compound **7c** as a yellow solid (0.050 g, 82%). Anal. Calcd. for C₂₃H₂₆Mn₂O₇P₂Sn: C, 39.19; H, 3.72. Found: C, 38.87; H, 4.04. ¹H NMR: δ 7.90–7.10 $(m, 10H, Ph), 1.68 (dt, J_{HH} = 13, J_{HP} = 9, 1H, CH_2), 0.98-0.84 (m, 13H, 10H)$ Me and CH₂), -2.95 (s, $J_{119SnH} \approx J_{117SnH} = 26$, 1H, OH), -21.75 (t, $J_{HP} = 26$, $J_{119SnH} \approx J_{117SnH} = 120$, 1H, μ -H). ¹H NMR (CD₂Cl₂): δ 7.60–7.30 (m, 10H, Ph), 2.30–2.10 (m, ABMX, 2H, CH_2), 1.70–1.30 (m, 12H, Me), -1.91 (s, 1H, OH), -21.80 (t, $J_{\rm HP} = 26$, 1H, μ -H).

3.14. Preparation of [Mn₂(μ-H)(SnPh₃)(CO)₇(μ-dppm)] (**9b**)

Carbon monoxide was bubbled through a solution of compound **1b** (0.057 g, 0.085 mmol) in toluene (20 mL) for 30 s, and then HSnPh₃ (0.030 g, 0.085 mmol) was added, and the mixture was stirred for 4 h. The solvent was then removed under vacuum, and the residue was then chromatographed on an alumina column (activity

3) at 253 K. Elution with dichloromethane–petroleum ether (1:5) gave a fraction yielding, after removal of solvents under vacuum, complex **9b** as a purple solid (0.050 g, 55%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a saturated dichloromethane solution of **9b** at 253 K. Elution with dichloromethane–petroleum ether (1:1) gave a fraction yielding analogously compound **7b** (0.020 g, 25%) as a yellow solid. Data for **9b**: Anal. Calcd. for C₅₀H₃₈Mn₂O₇P₂Sn: C, 57.67; H, 3.67. Found: C, 57.47; H. 3.61. ¹H NMR (400.13 MHz, CD₂Cl₂, 263 K): δ 7.60–7.10 (m, 35H, Ph), 3.70 (t, *J*_{HP} = 11, 2H, CH₂), –24.84 (dd, *J*_{HP} = 14, 21, *J*_{119SnH} ≈ *J*_{117SnH} = 35, µ-H). This spectrum exhibits very weak resonances at –19.2 and –22.2 ppm due to the isomers of type **C** and **A** respectively.

3.15. Preparation of $[Mn_2(\mu-H)(SnPh_3)(CO)_7(\mu-dmpm)]$ (9c)

Carbon monoxide was bubbled through a solution of compound 1c (0.036 g, 0.085 mmol) in tetrahydrofuran (15 mL) for 30 s, and then HSnPh₃ was added (0.030 g, 0.085 mmol), and the mixture was stirred for 2.5 h to give a red solution that was filtered using dry diatomaceous earth. The solvent was removed under vacuum from the filtrate, and the residue was then chromatographed on an alumina column (activity 2.5) at 253 K. Elution with dichloromethane-petroleum ether (3:7) gave a yellow fraction containing a tiny amount of compound 6c. Elution with a 7:13 solvent mixture gave another fraction, containing 3 isomers of compound 9c. Removal of solvents under vacuum from this fraction vielded compound 9c (0.050 g. 75%) as a red solid. A final elution with neat dichloromethane gave a deep-vellow fraction vielding analogously complex 7c as a minor product (0.010 g, 15%). Data for 9c: Anal. Calcd. for C₃₀H₃₀Mn₂O₇P₂Sn: C, 45.43; H, 3.81. Found: C, 45.21; H, 3.54. ¹H NMR (400.13 MHz, CD₂Cl₂): δ 7.67–7.32 (m, 45H, Ph, isomers A, B, C). Data for isomer A: 2.08 (t, J_{HP} = 11.2, 2H, CH₂), 1.62 (d, J_{HP} = 8.1, 6H, Me), 1.21 (d, $J_{HP} = 6.3, 6H, Me$), -23.2 (br, 1H, μ -H). Data for isomer B: $2.64 (t, J_{HP} = 10, 2H, CH_2), 1.72 (d, J_{HP} = 7.2, 6H, Me), 1.65 (d, J_{HP} = 8.9, 1.65 (d, J_{HP} = 8.9))$ 6H, Me), -24.65 (d, br, 1H, μ -H). Data for isomer C: 2.04 (t, $J_{HP} = 10.7$, 2H, CH₂), 1.59 (d, $J_{HP} = 6.7$, 3H, Me), 1.57 (d, $J_{HP} = 5.8$, 3H, Me), 1.39 (d, $J_{\rm HP} = 8.1, 3H, Me$, 1.35 (d, $J_{\rm HP} = 7.6, 3H, Me$), -19.3 (t, $J_{\rm HP} = 23.3, J_{\rm HP} = 23.3,$ $J_{119SnH} \approx J_{117SnH} = 79, 1H, \mu$ -H). ¹H NMR (400.13 MHz, CD₂Cl₂, 223 K): Hydride data for isomer A: $-23.09 (t, J_{HP} = 25, J_{119SnH} \approx J_{117SnH} = 65,$ 1H, μ -H). Hydride data for isomer *B*: -24.85 (dd, $J_{HP} = 7, 20,$ $J_{119SnH} \approx J_{117SnH} = 47, 1H, \mu$ -H). Hydride data for isomer C: -19.25 (dd, $J_{\text{HP}} = 20.5, 26, J_{119\text{S}\text{nH}} \approx J_{117\text{S}\text{nH}} = 78, 1\text{H}, \mu\text{-H}$). ³¹P{¹H} NMR (161.98 MHz, CD₂Cl₂, 223 K): Data for isomer A: δ 31.3 (br, μ-dmpm), 30.3 (AB mult, br, $J_{PP} = 47$, $J_{119SnP} \approx J_{117SnP} = 165$, μ -dmpm). Data for isomer *B*: δ 38.2 (d, $J_{PP} = 60, J_{119SnH} \approx J_{117SnH} = 266, \mu$ -dmpm), 25.7 (d, $J_{PP} = 60$, 1P, μ -dmpm). Data for isomer C: δ 37.5 (d, $J_{PP} = 61$, μ dmpm), 24.4 (d, $J_{PP} = 61$, μ -dmpm).

3.16. X-ray data collection, structure determination and refinements for compounds **2a.1**, **5a** and **9b**

Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well-centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table 7. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (Difabs) [43] were applied. For compound **9b**, and extinction correction was applied.

Computations were performed by using CRYSTALS [44] adapted on a Micro Vax II. Atomic form factors for neutral C, O, Mn, P, Sn, Si and H were taken from Ref. [45]. Anomalous dispersion was taken into account. The structures were solved by direct methods and subsequent Fourier maps. For compounds **2a.1** and **9b**, some

	2a.1	5a · 1/2H ₂ O	9b
Molecular formula	C26H32Mn11O3P2Si	C38H42Mn2O12.5P2Sn2	C ₅₀ H ₃₈ Mn ₂ O ₇ P ₂ Sn
Molecular weight	720.4	1107.9	1041.4
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2 ₁ /c	C 2/c	P 2 ₁ /a
Radiation (λ, Å)	0.71073	0.71073	0.71073
a (Å)	12.779(3)	14.131(7)	18.531(3)
b (Å)	11.179(4)	16.937(4)	14.749(3)
c (Å)	23.277(6)	37.945(9)	16.431(2)
α (°)	90	90	90
β (°)	93.87(2)	90.09(3)	91.87(1)
γ (°)	90	90	90
$V(Å^3)$	3318(2)	9082(5)	4488(1)
Ζ	4	8	4
Calculated density	1.44	1.62	1.54
(g cm ⁻³)			
Absorption	0.91	1.741	1.206
coefficient			
(mm^{-1})			
Diffractometer	Nonius CAD4	Nonius CAD4	Nonius CAD4
Temperature (K)	291	291	291
Scan type	$\omega - 2\theta$	$\omega/2\theta$	$\omega/2\theta$
θ range (°)	1-25	2-20	1-25
index ranges	-15, 15; 0, 13; 0,	-13, 13; 0, 14; 0, 36	-22, 22; 0, 17; 0,
(h, k, l)	27		19
Independent	5833	4513	7883
reflections			
Reflections with	3994	2555	5457
$[I > 3\sigma(I)]$			
$R \left[I > 3\sigma(I) \right]^{a}$	0.036	0.064	0.031
$R_w[I > 3\sigma(I)]^{\mathbf{b}}$	0.036	0.069	0.033
Restraints/	0/390	0/389	0/566
parameters			

^a $R = \Sigma |F_o - |F_c|| / \Sigma F_o$.

^b $R_w = [\Sigma w (F_o - |F_c|)^2 / \Sigma w F_o^2]^{1/2}.$

hydrogen atoms were found on difference maps and others were geometrically located. Their positions were not refined and they were given an isotropic overall thermal parameter, except for the bridging H in each case, this being refined isotropically with an individual isotropic thermal parameter. Non hydrogen atoms were anisotropically refined. Because of the small number of reflections available for compound **5a**, the hydrogen atoms were not located on difference maps in that compound, and the carbon atoms of the phenyl groups had to be isotropically refined. The crystal lattice also contains a water molecule located on a binary axis.

Least-squares refinements were carried out with approximation in three blocks to the normal matrix by minimizing the function $\sum w(|F_0| - |F_c|)^2$ where F_0 and F_c are the observed and calculated structure factors. Unit weight was used. Models reached convergence with $R = \sum (|F_0| - |F_c|)/\sum |F_0|$ and $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w$ $(|F_0|)^2]^{1/2}$ having values listed in Table 1. For **2a.1** and **9b**, in the last stages of refinement, each reflection was assigned a weight unity and for **5a** the weighting scheme was $w = w'[1-(|F_0| - |F_c|)/6\sigma$ $(F_0))^2]^2$, where $w' = 1/\sum_{r=1,3}A_rT_r(X)$ with $X = F_0/F_0$ max. Criteria for satisfactory complete analysis were the ratios of root-mean-square shifts to standard deviation being less than 0.1 and no significant features in the final difference maps.

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Appendix A. Supplementary material

CCDC 796136, 796137 and 796138 contain the supplementary crystallographic data for compounds **2a.1**, **5a** and **9b** respectively.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ cif.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.12.016.

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