

Reactivity of the unsaturated manganese dihydrides $[\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-L}_2)]$ ($\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ or $(\text{EtO})_2\text{POP}(\text{OEt})_2$) towards small molecules

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Abstract

The unsaturated dihydrides $[\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-L}_2)]$ ($\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, dppm, **1** or $(\text{EtO})_2\text{POP}(\text{OEt})_2$, tedip, **2**) react with carbon dioxide or formic acid to yield a mixture containing the hydridoformate isomers $[\text{Mn}_2(\mu\text{-H})(\mu\text{-}\eta^1\text{-O}_2\text{CH})(\text{CO})_6(\mu\text{-L}_2)]$ ($\text{L}_2 = \text{dppm}$, **3a**; tedip, **3b**) and $[\text{Mn}_2(\mu\text{-H})(\mu\text{-}\eta^1\text{-OC(O)H})(\text{CO})_6(\mu\text{-L}_2)]$ ($\text{L}_2 = \text{dppm}$, **4a**; tedip, **4b**) in equilibrium. Our previous characterization of the second complex as $[\text{Mn}_2(\mu\text{-H})(\mu\text{-OH})(\text{CO})_6(\mu\text{-L}_2)]$ was erroneous. In contrast, reaction of **1** with CH_3COOH yields the acetate complex $[\text{Mn}_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-O}_2\text{CCH}_3)(\text{CO})_6(\mu\text{-dppm})]$ (**3c**) as the sole product. Dihydride **1** also reacts with organic Brønsted acids such as 4-nitrophenol, *tert*-butylmercaptan and 4-toluenethiol yielding the corresponding hydridoalkoxide $[\text{Mn}_2(\mu\text{-H})(\mu\text{-O-4-C}_6\text{H}_4\text{-NO}_2)(\text{CO})_6(\mu\text{-dppm})]$ (**5a**), or hydridothiols $[\text{Mn}_2(\mu\text{-H})(\mu\text{-SR})(\text{CO})_6(\mu\text{-dppm})]$ ($\text{R} = \text{C}(\text{CH}_3)_3$, **6a**; $4\text{-C}_6\text{H}_4\text{-CH}_3$, **6b**) respectively. Related hydridoalkoxides, $[\text{Mn}_2(\mu\text{-H})(\mu\text{-OR})(\text{CO})_6(\mu\text{-L}_2)]$ ($\text{L}_2 = \text{dppm}$; $\text{R} = \text{CH}_2\text{CH}_3$, **5c**; $\text{CH}_2\text{-4-C}_6\text{H}_4\text{-CH}_3$, **5d**; $\text{CH}(\text{CH}_3)_2$, **5f**, $\text{L}_2 = \text{tedip}$, $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$, **5e**; $\text{CH}(\text{CH}_3)_2$, **5g**; $\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$, **5h**), can be obtained in good yield by treatment of **1** or **2** with the appropriate aldehydes or ketones at room temperature.

Keywords: Manganese; Dihydrides; X-ray structure

1. Introduction

The interaction of small molecules with metal clusters is of permanent interest, mainly because the presence of several close metal atoms can promote a wide variety of transformations in the substrates and because clusters may be appropriate models for transition metal surfaces [1]. Among clusters, those containing the unsaturated moiety $\text{M}_2(\mu\text{-H})_2$ ($\text{M}=\text{M}$) are particularly interesting, as evidenced by the fascinating reactivity which the unsaturated dihydrido cluster $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ displays towards small molecules [2]. Similarly, we have found that the unsaturated binuclear dihydrides $[\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})]$ (**1**) [3], and $[\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-tedip})]$ (**2**) [4], react easily with a wide

range of small molecules such as 1-alkynes [5a], boron hydrides [5b], organosilicon or tin hydrides [5c], secondary phosphines [5d], and nitriles or isonitriles [5e]. As a part of our studies in this area, we report the reactions of the above dimanganese dihydrides **1** and **2** with several organic compounds such as alcohols, thiols, aldehydes, ketones and carboxylic acids as well as with CO_2 . Insertion of the last into metal–hydrogen bonds to give formate derivatives is a well established reaction [6], and it appears to be an important step in carbon dioxide reduction [6a]. However, no reactions of unsaturated dihydridometal complexes with carbon dioxide have been reported, even when unsaturated hydrido complexes seem to be involved in the metal-catalyzed hydrogenation of carbon dioxide [7]. A preliminary account, including the reaction of dihydrides **1** and **2** with CO_2 , has been published [8], but the results were misinterpreted at the time.

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2. Results and discussion

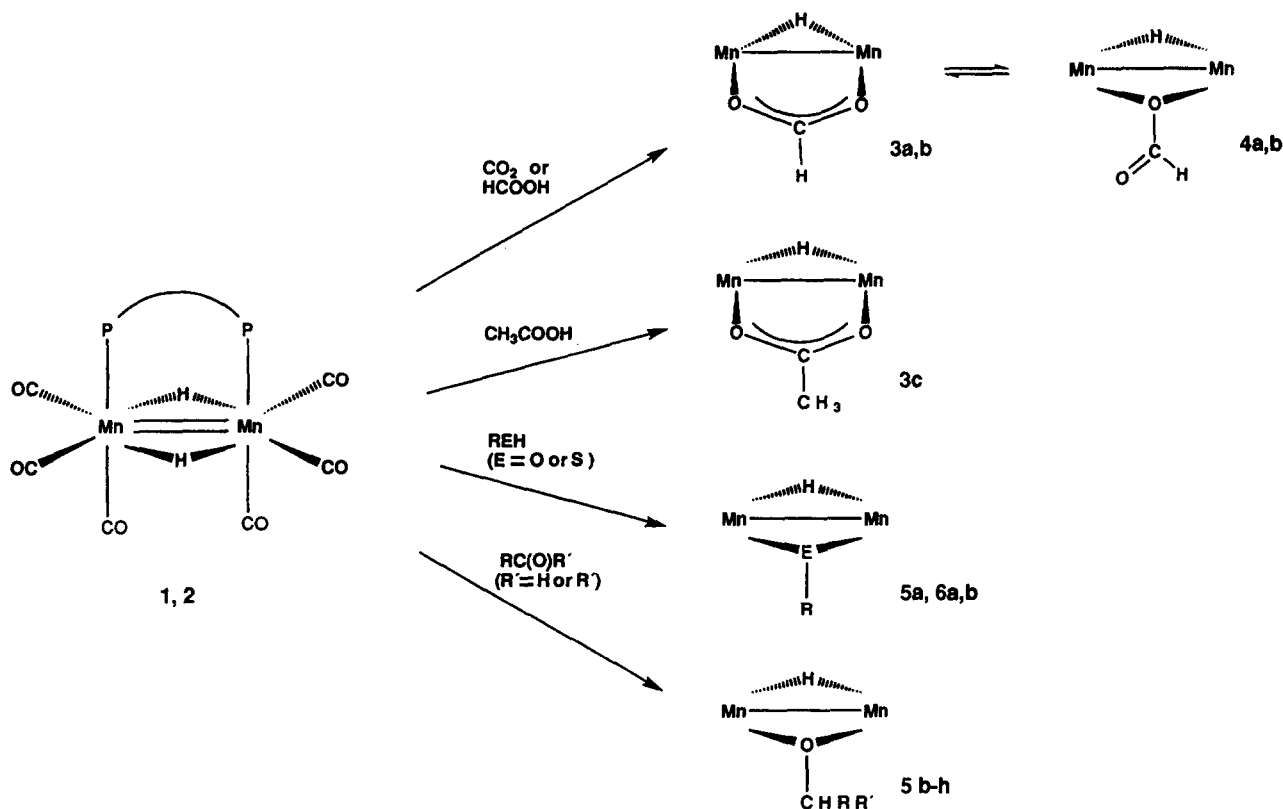
2.1. Reactions of 1 and 2 with carbon dioxide and carboxylic acids

The unsaturated dihydridocomplexes $[\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-L-L})]$ ($\text{L-L} = \text{dppm}$, **1** or **tedip**, **2**) do not react with carbon dioxide at 1 atm and 20°C but do so slowly under pressure (50 atm, 20°C) to yield a mixture of two isomeric hydridoformates $[\text{Mn}_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-O}_2\text{CH})(\text{CO})_6(\mu\text{-L}_2)]$ ($\text{L}_2 = \text{dppm}$, **3a** or **tedip**, **3b**) and $[\text{Mn}_2(\mu\text{-H})(\mu\text{-}\eta^1\text{-OC(O)H})(\text{CO})_6(\mu\text{-L}_2)]$ ($\text{L}_2 = \text{dppm}$, **4a** or **tedip**, **4b**), (see Scheme 1). In solution, isomers **3** and **4** are in equilibrium, as shown by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, and their relative proportions are solvent- and temperature-dependent. Moreover, the same mixture of products is obtained by treating **1** and **2** with formic acid at room temperature, (see Scheme 1). In contrast, the reaction of complex **1** with acetic acid yields the hydridoacetate derivative $[\text{Mn}_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-O}_2\text{CCH}_3)(\text{CO})_6(\mu\text{-dppm})]$ (**3c**) as a single isomer.

The structure of **3c** has been fully elucidated through an X-ray diffraction study (Fig. 1 and Tables 1 and 2). The molecule contains a dimanganese core bridged by the diphosphine, a hydrogen atom and the acetate group, which are symmetrically bonded to each metal through an oxygen atom ($\text{Mn(1)-O(7)} = 2.037(6)$ Å, Mn(2)-

$\text{O(8)} = 2.031(6)$ Å). The hydrido and acetate ligands lie in a plane roughly perpendicular to the approximate plane defined by the phosphorus and metal atoms. The coordination environment around the manganese atoms is completed by three carbonyls and can be viewed as a distorted octahedral (ignoring the intermetal vector) as a result of the different steric requirements of the bridging hydrido and acetate groups. The hydrido ligand, although located with not very high accuracy, appears to be quite close to the intermetallic vector ($\text{Mn-H-Mn} = 142.4(8)^\circ$). The latter, added to the relatively large intermetallic distance ($3.140(2)$ Å) suggests that the three-centre, two-electron interaction describing the bonding in the $\text{Mn}_2(\mu\text{-H})$ moiety can be classified as intermediate between the 'open' and 'closed' types [9].

The spectroscopic data for **3c**, both in solution and in the solid state, are fully consistent with the structure found in the crystal. For example, the IR spectrum of **3c** in a KBr pellet exhibits bands at 1565 (s) and about 1430 (m, sh) cm^{-1} corresponding to the asymmetric and symmetric C–O stretches within the acetate group, with a frequency difference (125 cm^{-1}) characteristic of bridging carboxylates coordinated through both oxygen atoms [10]. (For example, these bands appear at 1546 and 1447 cm^{-1} in $[\text{Os}_3(\mu\text{-H})(\mu\text{-O}_2\text{CMe})(\text{CO})_{10}]$ [11].) In solution, compound **3c** displays a similar IR spectrum, and shows characteristic NMR resonances at



Scheme 1. Reactions of **1** and **2** with several small molecules.

56.5 ppm (^{31}P) and -16.3 ppm (^1H , bridging hydrido). All these data allow the identification of the isomers present in the formate derivatives.

As stated above, the formate derivatives of dihydrides **1** and **2** reveal two isomers in solution. In the case of the dpmm-bridged complexes, we found that the major isomer (**3a**) exhibits spectroscopic features (IR, ^{31}P and ^1H NMR) almost identical to those of **3c** (see Table 3), and is thus safely identified as the isomer containing the formate bonded through both oxygen atoms ($\mu\text{-}\eta^2\text{-O}_2\text{CH}$). In contrast, the minor isomer (**4a**) exhibits a more shielded ^{31}P resonance (47.2 ppm) and a more deshielded hydrido resonance (-11.9 ppm), these chemical shifts being very close to those measured for alkoxo complexes **5a–d** (see Table 3). Thus it is reasonable to assume that the minor isomer **4a** contains the formate bonded to both metals through a single oxygen atom ($\mu\text{-}\eta^1\text{-O}_2\text{CH}$). The tedip-bridged formate compounds **3b** and **4b** can be characterized in the same way, so that the ($\mu\text{-}\eta^2\text{-O}_2\text{CH}$) isomer (**3b**) is also the major species in solution. The formate in these complexes gives rise to ^{13}C and ^1H resonances which are not greatly influenced by its particular coordination mode (see Table 3). We note that the ^{13}C resonance for **4a** is similar to that for free HCO_2H ($\delta = 166.7$ ppm) [12] and to those for mononuclear formate complexes such as $[\text{Re}(\eta^2\text{-O}_2\text{CH})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ ($\delta = 171.9$ ppm) [13] and $[\text{Re}(\eta^1\text{-O}_2\text{CH})(\text{NO})(\text{PPh}_3)\text{Cp}]$ ($\delta = 171.4$ ppm) [14], whereas isomers **3** display a more deshielded resonance (about 179 ppm).

The relative amounts of isomers **3** and **4** in solution

are solvent-dependent. The ratio **4a**:**3a** for the dpmm complexes seems to increase with the polarity of the solvent (about 1:5 in benzene, 1:3 in chloroform, 1:2 in tetrahydrofuran and 1:1 in acetone, all determined by ^{31}P and ^1H NMR spectroscopies). This is reasonable, as the $\mu\text{-}\eta^1\text{-O}_2\text{CH}$ isomer **4a** is expected to be somewhat more polar owing to the presence of the non-coordinated oxygen atom. However, for the tedip bridged compounds the influence of solvent is modest, as the ratio **4b**:**3b** remains around 1:10 in the above solvents, with the exception of benzene (about 1:20). This may be due to additional molecule–solvent interactions arising from the oxygen atoms of the tedip, which could counterbalance those arising from the formate group. This difference in the behaviour of the dpmm and tedip bridged compounds is also reflected in the effect of temperature. Thus, on lowering the temperature, the ratio **4**:**3** increases slightly for the dpmm species (about 1:1.3 in tetrahydrofuran at 213 K) but decreases for the tedip species (about 1:20 under the same conditions).

The changes measured by NMR spectroscopy are consistent with the modifications observed in the solution IR spectra of these complexes. Thus, although the C–O stretching bands of the carbonyls seem to be insensitive to the coordination mode of the formate, two bands at about 1680 cm^{-1} (weak to medium) and about 1575 cm^{-1} (medium to strong) are present in the solution spectra of the complexes under discussion. The relative intensities of these two bands change with the solvent in a way that parallels the changes observed in the NMR spectra. Thus, the band at about 1680 cm^{-1} ,

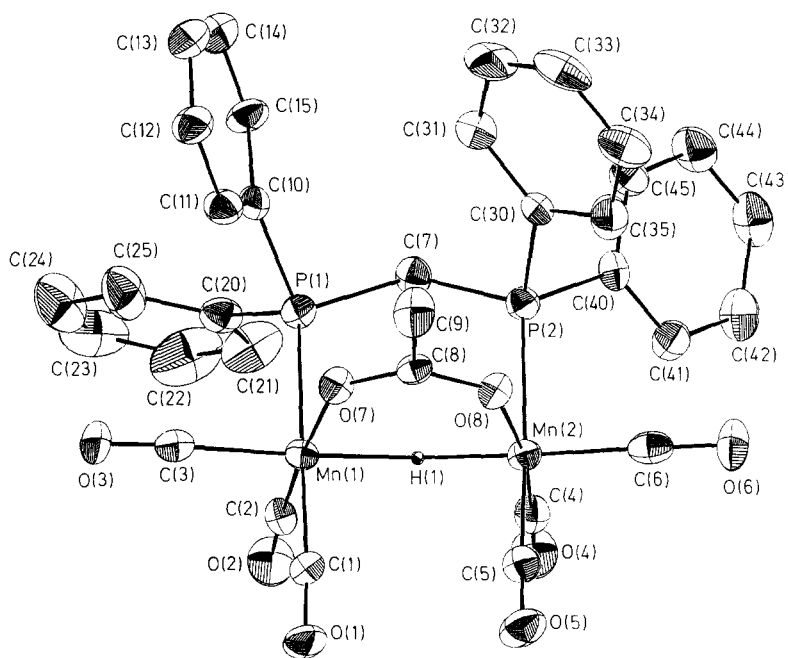


Fig. 1. Molecular structure of complex **3c**.

which is always weak in solvents such as petroleum ether or toluene, increases in intensity relative to the band at about 1575 cm^{-1} as the dielectric constant of the solvent increases. Therefore, the latter band is assigned to the asymmetric C–O stretch [10] of the η^2 -bridging formate (isomers 3), and it is in fact very similar to that observed for the acetato complex 3c discussed above. The weaker band at about 1680 cm^{-1} must therefore correspond to the high-frequency C–O stretch of the η^1 -bridging formate (isomers 4), close in frequency to those absorptions found for unidentate carboxylate groups. For comparison, we note the values of 1632 and 1570 cm^{-1} for the corresponding C–O stretches in the η^1 and μ - η^2 formates in the cluster $[\text{Os}_3(\text{CO})_9(\mu\text{-H})_2(\mu\text{-}\eta^2\text{-O}_2\text{CH})(\eta^1\text{-O}_2\text{CH})]$ [11]. Additionally, a formate ligand is expected to give rise to a second C–O stretch in the $1300\text{--}1450\text{ cm}^{-1}$ region [11]. In fact, several bands are present in that region in

the solution spectra of our complexes, and unambiguous assignment is not possible there. We note finally that the 1575 cm^{-1} band of the dppm complex exhibits a small splitting of about $5\text{--}10\text{ cm}^{-1}$ (depending on the solvent) for which we can give no satisfactory explanation. However, we cannot exclude the possibility that the latter could be an effect of the mixing of the C–O stretch with other vibrations of similar frequency but usually of weak intensity, such as those due to Mn–H–Mn.

Having established the nature of the formate derivatives of dihydrides 1 and 2 in solution, the question of their structure in the solid state remains. No answer can be given for the tedip-bridged derivative, as all attempts to isolate it as a solid gave an oily material. For the dppm derivative, we have found that the solid samples obtained by fast precipitation from its solutions (upon addition of petroleum ether) display in the IR spectrum

Table 1
Crystal structure determination details

<i>Crystallographic data</i>	
Formula	$\text{C}_{33}\text{H}_{26}\text{Mn}_2\text{O}_8\text{P}_2$
Formula weight	722.4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Cell dimensions a (Å)	19.941(8)
b (Å)	13.393(1)
c (Å)	12.245(4)
Cell volume (Å ³)	3270(3)
Z	4
D_{calc} (g cm ⁻³)	1.47
$F(000)$	1472
Monochromated Mo K α radiation	
μ (cm ⁻¹)	8.8
Crystal size (mm)	$0.65 \times 0.45 \times 0.30$
Diffractometer	Philips PW1100
Number of reflections for calculating unit cell	25
θ_{min} (deg), θ_{max} (deg)	14, 15
Scan mode for data collection	ω - 2θ
Scan width	$0.9 + 0.34 \tan \theta$
θ range, (deg)	1–25
Number of total reflections measured	2934
Number of reflections used $I > 2.5\sigma(I)$	2259
Absorption correction was applied using	DIFABS ^a
<i>Structure solution and refinement</i>	
Method for location of non-H atoms	CRYSTALS ^b
Refinement method	Least squares methods in four blocks
Hydrogen atoms	All hydrogen atoms located on difference maps, except five. Isotropic parameters given. Bridging hydride refined.
$R = [\sum(\Delta F)/\sum F_o]$	0.047
$R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$ ($w = 1$)	0.049
Number of variables	411
$(\Delta/\sigma)_{\text{max}}$	0.02
$(\Delta\rho)_{\text{max}}$ (e Å ⁻³), $(\Delta\rho)_{\text{min}}$ (e Å ⁻³)	$-0.31, -0.38$

^a N. Walker and D. Stuart, *Acta Crystallogr. A* 33 (1983) 158.

^b J.R. Carruthers and D.W. Watkin, CRYSTALS, an advanced crystallographic computer program, 1985, (Chemical Crystallographic Laboratory, Oxford University).

(Nujol mull) ν_{COO} bands attributable to both **3a** (major) and **4a** (minor) isomers. However, crystalline samples obtained by slow crystallization show only the formate band at 1570 cm^{-1} (Table 3). Therefore, we conclude that the $\mu\text{-}\eta^2\text{-O}_2\text{CH}$ isomer **3a** is the only species present in the solid phase if enough time to reach thermodynamic equilibrium is given.

In our preliminary study on the reactions of **1** and **2** with CO_2 and HCOOH , the isomers **4** were erroneously identified as the corresponding hydroxo complexes $[\text{Mn}_2(\mu\text{-H})(\mu\text{-OH})(\text{CO})_6(\mu\text{-L}_2)]$ [8]. This was encouraged by their nearly identical ^{31}P and hydrido resonances, and the fact that the authentic hydroxo complexes were actually obtained after column chromatography on alumina of the reaction mixture. We now conclude that the formate in isomers **3** and **4** was replaced by an hydroxo group on alumina. Water itself cannot promote this substitution. In fact, neither the formate complexes **3** and **4** nor even the dihydrides **1** and **2** react with water at room temperature.

Although many saturated hydrido complexes react with CO_2 to give formates [6], no reactions of unsaturated dihydrides with carbon dioxide seem to have been reported. It should also be noted that the hydridoformates $[\text{Os}_3(\text{CO})_9(\mu\text{-H})_2(\mu\text{-}\eta^2\text{-O}_2\text{CH})(\eta^1\text{-O}_2\text{CH})]$ [11] or $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-O}_2\text{CH})(\text{CO})_{10}]$ [15], which are strongly related to complexes **3**, have not been prepared from the unsaturated dihydride $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ but by other routes. The reaction of the last with trifluoroacetic acid does not lead to a bridging trifluoroacetate but to complexes containing unidentate trifluoroacetate and three hydrido ligands [16]. This difference can be

attributed to the higher lability of the hydrido ligands in compounds **1** and **2**, as observed previously in other reactions of our dimanganese hydrides [5c,d], this being possibly related to the relative weakness of the manganese–hydrogen bond.

2.2. Reactions of **1** with alcohols and thiols

Other organic molecules having acid protons such as 4-nitrophenol, or thiols (*tert*-butylmercaptan and 4-toluenethiol) react under mild conditions with **1** to yield the corresponding hydridoalkoxo and hydridothiolato complexes $[\text{Mn}_2(\mu\text{-H})(\mu\text{-O-4-C}_6\text{H}_4\text{-NO}_2)(\text{CO})_6(\mu\text{-dppm})]$ **5a**, and $[\text{Mn}_2(\mu\text{-H})(\mu\text{-SR})(\text{CO})_6(\mu\text{-dppm})]$ [R = $\text{C}(\text{CH}_3)_3$, **6a**, $4\text{-C}_6\text{H}_4\text{-CH}_3$, **6b**] respectively, (see Scheme 1). The spectroscopic data of complexes **5a** and **6a,b**, collected in Table 3, support the proposed structures. In particular, the presence of a mirror plane perpendicular to the Mn–Mn axis is reflected in the pattern of their IR carbonyl stretching bands, and in the single peak in their $^{31}\text{P}\{\text{H}\}$ NMR spectra.

The above reactions, as well as those of **1** and **2** with formic acid probably follow a similar mechanism. They would be initiated by the coordination of the acid, alcohol or thiol to one of the manganese atoms to yield an intermediate **A** $[\text{Mn}_2(\mu\text{-H})(\text{H})(\text{EHR})(\text{CO})_6(\mu\text{-dppm})]$ (E = $\text{OC}(\text{O})\text{H}$, $\text{O-C}_6\text{H}_4\text{-NO}_2$, $\text{SC}(\text{CH}_3)_3$, and $4\text{-S-C}_6\text{H}_4\text{-CH}_3$). Then, a hydrogen molecule would be lost, to yield the observed products **4**, **5a**, **6a,b**. In the case of formic acid, either isomer **3** or **4** can be formed initially, which in any case would rapidly reach the corresponding equilibrium distribution.

Table 2
Selected bond lengths (Å) and angles (deg) in the complex **3c**

Mn(1)–Mn(2)	3.140(2)	Mn(1)–P(1)	2.344(3)
Mn(2)–P(2)	2.326(3)	Mn(1)–O(7)	2.037(6)
Mn(2)–O(8)	2.031(6)	Mn(1)–C(1)	1.825(9)
Mn(2)–C(5)	1.826(9)	Mn(1)–C(2)	1.77(1)
Mn(2)–C(4)	1.79(1)	Mn(1)–C(3)	1.83(1)
Mn(2)–C(6)	1.80(1)	Mn(1)–H(1)	1.7(1)
Mn(2)–H(1)	1.6(1)	P(1)–C(7)	1.837(9)
P(2)–C(7)	1.86(1)	O(7)–C(8)	1.25(1)
O(8)–C(8)	1.26(1)	C(8)–C(9)	1.50(1)
O(7)–Mn(1)–P(1)	90.5(2)	O(8)–Mn(2)–P(2)	85.7(2)
C(1)–Mn(1)–P(1)	177.9(3)	C(5)–Mn(2)–P(2)	170.6(3)
C(1)–Mn(1)–O(7)	91.0(3)	C(5)–Mn(2)–O(8)	85.0(3)
C(2)–Mn(1)–P(1)	90.1(3)	C(4)–Mn(2)–P(2)	95.2(3)
C(2)–Mn(1)–O(7)	175.9(4)	C(4)–Mn(2)–O(8)	171.8(4)
C(3)–Mn(1)–P(1)	91.3(3)	C(6)–Mn(2)–P(2)	89.9(3)
C(3)–Mn(1)–O(7)	91.3(3)	C(6)–Mn(2)–O(8)	94.7(4)
H(1)–Mn(1)–P(1)	81.2(40)	H(1)–Mn(2)–P(2)	81.2(42)
H(1)–Mn(1)–O(7)	91.8(41)	H(1)–Mn(2)–O(8)	94.9(42)
C(7)–P(1)–Mn(1)	114.0(3)	C(7)–P(2)–Mn(2)	113.6(3)
C(8)–O(7)–Mn(1)	130.9(6)	C(8)–O(8)–Mn(2)	128.2(6)
P(2)–C(7)–P(1)	118.3(5)	O(8)–C(8)–O(7)	126.3(8)
C(9)–C(8)–O(7)	116.5(8)	C(9)–C(8)–O(8)	117.0(8)
Mn(2)–H(1)–Mn(1)	142.4(8)		

Table 3
Spectroscopic data for the new compounds

Compound	ν (CO) ^a	¹ H NMR ^b	³¹ P{ ¹ H} NMR ^b
[Mn ₂ (μ -H)(μ - η^2 -O ₂ CH)(CO) ₆ (μ -dppm)] (3a) ^c	2041 s 2015 s 1959 m 1944 m 1923 vs	7.7 (1H, s, μ - η^2 -O ₂ CH) 7.6–7.1 (20 H, m, Ph) 3.1 (2 H, br, CH ₂) –16.3 (1 H, t, J_{PH} = 27, μ -H)	55.3 (2 P, s, dppm)
[Mn ₂ (μ -H)(μ - η^2 -O ₂ CH)(CO) ₆ (μ -tedip)] (3b) ^d	2058 vs 2030 m 1980 s 1965 vs 1942 vs	7.9 (1H, s, μ - η^2 -O ₂ CH) 4.2 (4 H, m, CH ₂) 4.1 (4 H, m, CH ₂) 1.4 (6 H, t, J_{HH} = 6.9, CH ₃) 1.3 (6 H, t, J_{HH} = 6.9, CH ₃) –18.5 (1 H, t, J_{PH} = 33, μ -H)	163.9 (2 P, s, tedip)
[Mn ₂ (μ -H)(μ - η^2 -O ₂ CCH ₃)(CO) ₆ (μ -dppm)] (3c)	2040 vs ^e 2013 s 1957 m 1943 m 1923 vs	7.4–7.1 (20 H, m, Ph) 3.3 (2 H, m, CH ₂) 1.2 (3 H, s, CH ₃) –16.3 (1 H, t, J_{PH} = 27, μ -H)	56.5 (2 P, s, dppm)
[Mn ₂ (μ -H)(μ - η^1 -OC(O)H)(CO) ₆ (μ -dppm)] (4a) ^f	2041 s 2015 s 1959 m 1944 m 1923 vs	8.4 (1H, s, μ - η^1 -OC(O)H) 3.4 (2 H, br, CH ₂) –11.9 (1 H, m, μ -H) ^g	47.2 (2 P, s, dppm)
[Mn ₂ (μ -H)(μ - η^1 -OC(O)H)(CO) ₆ (μ -tedip)] (4b) ^h	2058 vs 2030 m 1980 s 1965 vs 1942 vs	8.0 (1H, s, μ - η^1 -OC(O)H) –13.4 (1 H, t, J_{PH} = 30, μ -H) ^g	160.4 (2 P, s, tedip)
[Mn ₂ (μ -H)(μ -O-4-C ₆ H ₄ -NO ₂)(CO) ₆ (μ -dppm)] (5a)	2040 s 2015 s 1958 m 1940 sh 1924 vs	8.2–6.9 (24 H, m, Ph) 2.7 (1 H, m), 2.4 (1 H, m) (CH ₂) –11.1 (1 H, t, J_{PH} = 21, μ -H)	49.6 (2 P, s, dppm)
[Mn ₂ (μ -H)(μ -OCH ₃)(CO) ₆ (μ -dppm)] (5b)	2040 s 2010 s 1935 m 1908 br, vs	7.4–7.0 (20 H, m, Ph) 4.1 (3 H, s, CH ₃) 2.8 (2 H, m, CH ₂) –11.2 (1 H, t, J_{PH} = 22, μ -H)	47.6 (2 P, s, dppm)
[Mn ₂ (μ -H)(μ -OCH ₂ CH ₃)(CO) ₆ (μ -dppm)] (5c)	2035 s 2010 s 1940 m 1910 br, vs	7.4–7.1 (20 H, m, Ph) 4.2 (2 H, q, J_{HH} = 6, CH ₂ CH ₃) 2.5 (2 H, m, PCH ₂) 1.5 (3 H, t, J_{HH} = 6, CH ₂ CH ₃) –11.2 (1 H, t, J_{PH} = 22, μ -H)	47.4 (2 P, s, dppm)
[Mn ₂ (μ -H)(μ -OCH ₂ -4-C ₆ H ₄ -CH ₃)(CO) ₆ (μ -dppm)] (5d)	2020 s 2005 s 1940 m 1915 br, vs	7.7–7.1 (24 H, m, Ph) 4.9 (2 H, m, CH ₂ C ₆ H ₄) 2.7 (1 H, m), 2.5 (1 H, m) (PCH ₂) 2.4 (3 H, s, C ₆ H ₄ CH ₃) –11.4 (1 H, t, J_{PH} = 22, μ -H)	47.7 (2 P, s, dppm)
[Mn ₂ (μ -H)(μ -OCH ₂ -C ₆ H ₅)(CO) ₆ (μ -tedip)] (5e)	2042 s 2015 s 1952 m 1920 br, vs	7.3–7.2 (5 H, m, Ph) 4.6 (2 H, s, CH ₂ Ph) 4.1 (4 H, m, CH ₂ CH ₃) 3.9 (4 H, m, CH ₂ CH ₃) 1.4 (6 H, t, J_{HH} = 6, CH ₂ CH ₃) 1.3 (6 H, t, J_{HH} = 7, CH ₂ CH ₃) –12.6 (1H, t, J_{PH} = 31, μ -H)	160.2 (2 P, s, tedip)
[Mn ₂ (μ -H)(μ -OCH(CH ₃) ₂)(CO) ₆ (μ -dppm)] (5f)	2027 vs 1999 s 1942 m 1923 sh 1912 vs	7.8–7.2 (20 H, m, Ph) 3.8 (1 H, m, OCH) 2.7 (1 H, m), 2.3 (1 H, m) (CH ₂) 1.2 (6 H, br, CH ₃) –11.8 (1 H, t, J_{PH} = 23, μ -H)	48.6 (2 P, s, dppm)
[Mn ₂ (μ -H)(μ -OCH(CH ₃) ₂)(CO) ₆ (μ -tedip)] (5g)	2041 vs 2010 vs 1957 m 1939 sh 1924 vs	4.1 (4 H, m, CH ₂ CH ₃) 4.0 (4 H, m, CH ₂ CH ₃) 3.6 (1 H, br, OCH(CH ₃) ₂) 1.4–1.1 (18 H, m; CH ₃) –12.6 (1 H, t, J_{PH} = 30; μ -H)	159.5 (2 P, s, tedip)

Table 3 (continued)

Compound	ν (CO) ^a	¹ H NMR ^b	³¹ P{ ¹ H} NMR ^b
[Mn ₂ (μ -H)(μ -OCH(CH ₃)CH ₂ CH ₃)(CO) ₆ (μ -tedip)] (5h)	2041 vs 2009 vs 1957 m 1939 sh 1924 vs	4.1 (4 H, m, OCH ₂ CH ₃) 4.0 (4 H, m, OCH ₂ CH ₃) 3.3 [1 H, m, OCH(CH ₃)CH ₂ CH ₃] 1.33–1.31 [14 H, m, OCH ₂ CH ₃ and OCH(CH ₃)CH ₂ CH ₃] 1.1 [3 H, d, J_{HH} = 6.6, OCH(CH ₃)] 0.8 (3 H, t, J_{HH} = 6.6; CHCH ₂ CH ₃) –12.7 (1 H, t, J_{PH} = 31, μ -H)	159.4 (2 P, s, tedip)
[Mn ₂ (μ -H)(μ -SC(CH ₃) ₃)(CO) ₆ (μ -dppm)] (6a)	2025 s 1997 s 1945 m 1916 br, vs	7.5–6.9 (20 H, m, Ph) ⁱ 2.4 (2 H, m, CH ₂) 1.5 (9 H, s, C(CH ₃) ₃) –15.0 (1 H, t, J_{PH} = 22, μ -H)	48.6 ^g (2 P, s, dppm)
[Mn ₂ (μ -H)(μ -S-4-C ₆ H ₄ -CH ₃)(CO) ₆ (μ -dppm)] (6b)	2040 s 2010 s 1955 s 1940 m 1920 vs	8.2–6.9 (24 H, m, Ph) ⁱ 2.6 (1 H, m), 2.3 (1 H, m) (CH ₂) 2.0 (3 H, s, CH ₃) –14.5 (1 H, t, J_{PH} = 21, μ -H)	50.5 ^g (2 P, s, dppm)

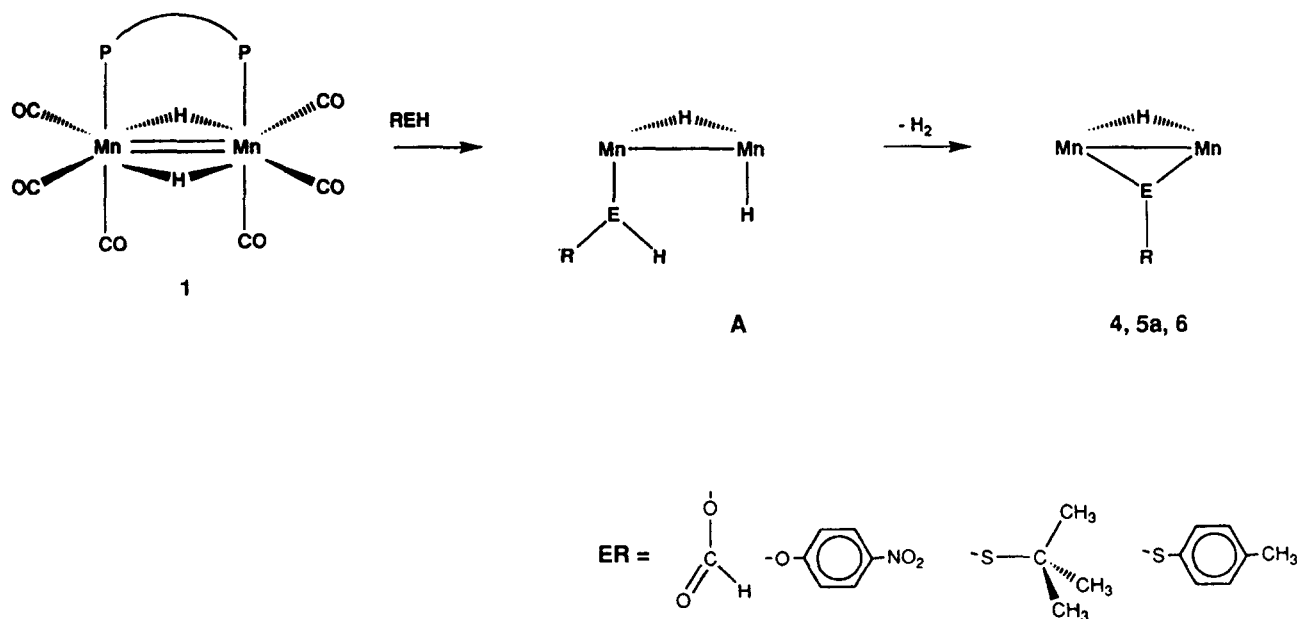
^a In toluene unless otherwise stated. ^b In CDCl₃, δ in ppm, J in Hz. ^c δ_C (CDCl₃) 178.3 ppm [1C, d, J_{HC} = 210 Hz, μ -O₂CH]; ν_{COO} (KBr): 1570 (s), 1420 (m, sh) cm⁻¹; ν_{COO} (CH₂Cl₂): 1578, 1571 cm⁻¹. ^d δ_C (CDCl₃) 178.8 ppm [1C, d, J_{HC} = 210 Hz, μ - η^2 -O₂CH]; ν_{COO} (CH₂Cl₂): 1578 cm⁻¹. ^e Hexane. ^f δ_C (CDCl₃): 170.9 ppm [1C, μ - η^1 -OC(O)H]; ν_{COO} (CH₂Cl₂): 1674 cm⁻¹. ^g Other resonances obscured by those from the major isomer. ^h ν_{COO} (CH₂Cl₂): 1680 cm⁻¹. ⁱ C₆D₆.

The above mechanism is the same as the one thought to be operative in the reactions of dihydrides **1** or **2** with primary and secondary phosphines [5d]. Although hydridoalkoxo or thiolato complexes comparable with **5a** or **6a,b**, such as [Os₃(μ -H)(μ -OR)(CO)₁₀] and [Re₂(μ -H)(μ -OR)(CO)₆(μ -dppm)] and [Os₃(μ -H)(μ -SR)(CO)₁₀] are known, they have not been obtained from the corresponding unsaturated dihydrides [Os₃(μ -

H)₂(CO)₁₀] and [Re₂(μ -H)₂(CO)₆(μ -dppm)] but by other routes [17–19].

2.3. Reactions of **1** and **2** with aldehydes and ketones

Dihydrides **1** and **2** react with aldehydes or ketones at room temperature to give hydridoalkoxo complexes comparable with **5a**. In this way, the complexes [Mn₂(μ -H)(μ -OCHRR')(CO)₆(μ -L₂)] (L₂ = dppm; R'

Scheme 2. Proposed mechanism for the formation of **4**, **5a**, and **6**.

= R or H, **5b**; R' = H; R = CH₃, **5c**; R' = H; R = 4-C₆H₄-CH₃, **5d**; R = R' = CH₃, **5f**.) (L₂ = tedip; R' = H; R = C₆H₅, **5e**; R' = R = CH₃, **5g**; R' = CH₃; R = CH₂CH₃, **5h**) can be prepared in good yield (see Scheme 1). Their spectroscopic data (Table 3) are very similar to those of **5a**, and therefore they are assumed to be isostructural. An hydridoalkoxo complex related to **5b–e**, [Mn₂(μ-H)(μ-OCH₂Me)(CO)₄(μ-dppm)₂], has been synthesized previously through the reaction of the unsaturated dihydride [Mn₂(μ-H)₂(CO)₄(μ-dppm)₂] with acetaldehyde [20], but the reactivity of the latter complex towards ketones has not been reported.

The reaction of aldehydes and ketones with **1** and **2** probably proceeds through the formation of a simple addition product [Mn₂(μ-H)(H)(OC(R')R)(CO)₆], **B**, similar to intermediate **A** proposed above. Complex **B** would then rearrange via an H-shift from the metal to the carboxylic carbon atom to yield the final alkoxo species (Scheme 3). A similar mechanism would account for the formation of the μ-η¹-hydridoformate complexes **4** from **1** or **2** and CO₂. Methyl ethyl ketone does not react with **1**, but it does react with **2**. The tedip in **2** makes the molecule more acidic and somewhat less sterically demanding, when compared with the dppm-bridged **1**, favouring the formation of the initial acid-base adduct **B**.

3. Experimental section

All reactions were carried out under dinitrogen using standard techniques. Solvents were purified according to standard literature procedures [21]. Petroleum ether refers to that fraction distilling in the range 60–65°C. The reagents were purchased from Aldrich and used as-received. The reactions with CO₂ were carried out in a Berghof BAR 845 autoclave. IR spectra were recorded on a Perkin Elmer 1720-X Infrared Fourier-Transform Spectrometer. ¹H, ¹³C and ³¹P NMR spectra were measured in Bruker AC-300 and AMX-400 instruments; chemical shifts are referred to internal TMS (¹H, ¹³C)

or external 85% H₃PO₄ aqueous solution (³¹P). ¹³C NMR assignments were routinely supported on standard DEPT experiments [22]. Elemental C, H, N analysis were obtained with a Perkin Elmer 240 B microanalyser. Compounds **1** [**5a**] and **2** [**23**] were prepared according to literature procedures.

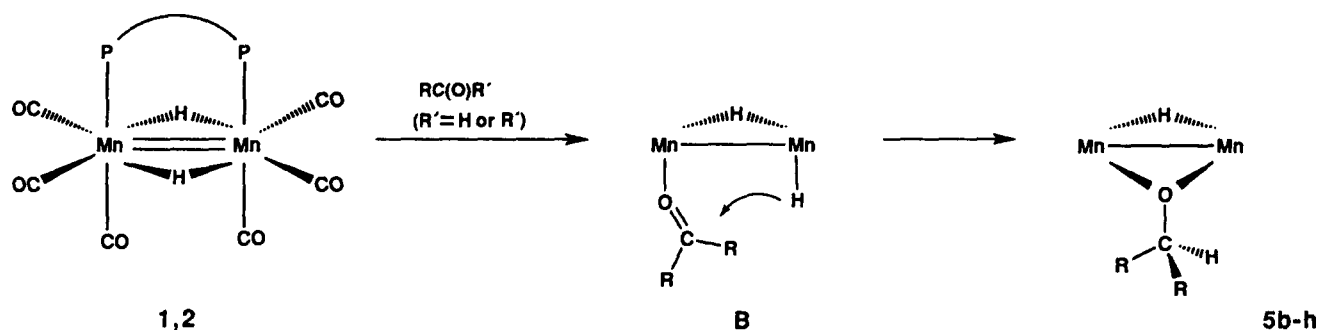
3.1. Reaction of compounds **1** and **2** with CO₂

The autoclave was charged under dinitrogen with a solution of **1** · toluene or **2** (0.133 mmol) in 25 ml of toluene. The autoclave was then closed, connected to a source of carbon dioxide and, after flushing twice with CO₂, pressurized with 50 atm of the gas. The mixture was stirred at room temperature for 4 days, after which the gas was released. The autoclave was then opened, and the resulting orange solution filtered. Evaporation of solvent under vacuum and washing of the residue with petroleum ether yielded a mixture of hydridoformate derivatives **3** and **4**. This was a yellow powder for the dppm derivatives (0.047 g, 50%) [Mn₂(μ-H)(μ-η²-O₂CH)(CO)₆(μ-dppm)], **3a**, and [Mn₂(μ-H)(μ-η¹-OC(O)H)(CO)₆(μ-dppm)], **4a**. Anal. Found: C, 54.30; H, 3.38. C₃₂H₂₄Mn₂O₈P₂. Calc. C, 54.26; H, 3.41%.

However, the tedip derivatives [Mn₂(μ-H)(μ-η²-O₂CH)(CO)₆(μ-tedip)], **3b**, and [Mn₂(μ-H)(μ-η¹-OC(O)H)(CO)₆(μ-tedip)], **4b**, were always obtained as oily residues.

3.2. Reactions of compounds **1** and **2** with formic acid

To a solution of **1** · toluene or **2** (0.133 mmol) in 25 ml of toluene, formic acid (0.010 cm³, 96%, 0.254 mmol) was added. The solution turned yellow instantaneously or after 2 h respectively. Afterwards, the mixture was washed with deoxygenated water (3 × 3 ml) to remove the excess of acid and then dried with MgSO₄. After filtration, the solvent was removed under vacuum and the residue was washed with light petroleum ether to afford a mixture of the corresponding complexes **3** and **4** having identical characteristics to the products



Scheme 3. Proposed pathway for the reactions of **1** and **2** with aldehydes and ketones.

obtained from the CO₂ reactions. (Yield for the mixture of **3a** and **4a** 80%).

3.3. Preparation of [Mn₂(μ-H)(μ-O₂CCH₃)(CO)₆(μ-dppm)] (**3c**)

A mixture of **1**·toluene (0.05 g, 0.066 mmol) and acetic acid (glacial, 0.008 ml, 0.183 mmol) in 15 cm³ of toluene was stirred for 48 h in the dark, after which the solution became yellow. The excess of acid was removed by washing the mixture with deoxygenated water (3 × 3 ml). The solution was then dried with MgSO₄. After filtration, the solvent was evaporated under reduced pressure to give a solid, which was recrystallized from methylene chloride–petroleum ether affording yellow-orange crystals of **3c**, suitable for X-ray. (0.033 g, 70%). Anal. Found: C, 54.69; H, 3.64. C₃₃H₂₆Mn₂O₈P₂. Calc.: C, 54.87; H, 3.63%.

3.4. Preparation of [Mn₂(μ-H)(μ-O-4-C₆H₄-NO₂)(CO)₆(μ-dppm)] (**5a**)

The preparation of this complex is similar to that described for the synthesis of **3c**. However, in the recrystallization a toluene–petroleum ether mixture was used instead of dichloromethane–petroleum ether. Yield: 0.021 g, 65%. Anal. Found: C, 55.23; H, 3.42; N, 1.78. C₃₇H₂₇Mn₂NO₉P₂. Calc.: C, 55.45; H, 3.40; N, 1.75%.

3.5. Preparation of [Mn₂(μ-H)(μ-SR)(CO)₆(μ-dppm)] (R = C(CH₃)₃ (**6a**); 4-C₆H₄-CH₃ (**6b**))

A mixture of the unsaturated dihydride **1**·toluene (0.1 g, 0.133 mmol) and the corresponding thiol (0.153 mmol) in 25 ml of toluene was stirred at room temperature until the solution became yellow (50 or 2 h respectively). After filtration, the solvent was removed under vacuum and the residue was washed with petroleum ether (3 × 3 ml, to remove the excess of ligand), affording **6a** (0.067 g, 67%) or **6b** (0.086 g, 83%) as yellow solids.

Anal. (**6a**): Found: C, 55.64; H, 4.43. C₃₅H₃₂Mn₂O₆-P₂S. Calc.: C, 55.85; H, 4.25%. Anal. (**6b**) Found: C, 57.80; H, 3.80. C₃₈H₃₀Mn₂O₆P₂S. Calc.: C, 58.00; H, 3.80%.

3.6. Preparation of [Mn₂(μ-H)(μ-OCH₃)(CO)₆(μ-dppm)] (**5b**)

Formaldehyde, generated by heating paraformaldehyde, was gently bubbled through a solution of compound **1**·toluene (0.060 g, 0.08 mmol) in toluene (15 ml) for 1 h until the solution turned yellow. After filtration, the solvent was removed under vacuum and the resulting residue was recrystallized from toluene–petroleum ether at –20°C to yield yellow crystals of **5b**

(0.037 g, 66%). Anal. Found: C, 55.39; H, 3.72. C₃₂H₂₆Mn₂O₇P₂. Calc.: C, 55.35; H, 3.77%.

3.7. Preparation of the complexes [Mn₂(μ-H)(μ-OR)(CO)₆(μ-L₂)] (L₂ = dppm, R = CH₂CH₃ (**5c**); CH₂-4-C₆H₄-CH₃ (**5d**); CH(CH₃)₂ (**5f**). L₂ = tedip, R = CH₂C₆H₅ (**5e**); CH(CH₃)₂ (**5g**); CH(CH₃)CH₂CH₃ (**5h**))

These compounds were obtained as yellow crystals (**5c**, **d**) or yellow solids following a procedure completely similar to that described for the preparation of **5b** but adding the corresponding aldehyde or using the appropriate ketone as solvent instead of bubbling H₂CO. Yields are in the interval 60–65%

Anal. (**5c**): Found: C, 55.74; H, 3.85. C₃₃H₂₈Mn₂O₇-P₂. Calc.: C, 55.95; H, 3.98%. Anal. (**5d**): Found: C, 59.91; H, 4.18. C₃₉H₃₂Mn₂O₇P₂. Calc.: C, 59.71; H, 4.11%. Anal. (**5e**): Found: C, 39.08; H, 4.58. C₂₁H₂₈Mn₂O₁₂P₂. Calc.: C, 39.15; H, 4.38%. Anal. (**5f**): Found: C, 56.70; H, 4.33. C₃₄H₃₀Mn₂O₇P₂. Calc.: C, 56.53; H, 4.18%. Anal. (**5g**): Found: C, 34.09; H, 4.69. C₁₇H₂₈Mn₂O₁₂P₂. Calc.: C, 34.25; H, 4.73%. Anal. (**5h**): Found: C, 35.52; H, 5.02. C₁₈H₃₀Mn₂O₁₂P₂. Calc.: C, 35.43; H, 4.96%

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