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Reactions of the unsaturated dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ ($L_2 = (EtO)_2POP(OEt)_2$, $Ph_2PCH_2PPh_2$) with phosphines containing P–H bonds

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Abstract

The unsaturated dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ ($L_2 = (EtO)_2POP(OEt)_2$ (tedip), $Ph_2PCH_2PPh_2$ (dppm)) react readily at room temperature with PH_3, PH_2Cy or $PHPh_2$ to give, after elimination of dihydrogen the corresponding saturated μ-hydrido μ-phosphido complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}X)(CO)_6(\mu\text{-}L_2)]$ ($X = PH_2$, PHCy, PPh_2) in high yield. Reactions with the dppm bridged dihydride are slower than those with the tedip bridged complex. A general reaction pathway is proposed. The structures of the new complexes are discussed on the basis of infrared and NMR (^1H, ^{31}P) data, which in the case of $[Mn_2(\mu\text{-}H)(\mu\text{-}PHCy)(CO)_6(\mu\text{-}tedip)]$, reveal the presence of two isomers derived from the two possible orientations of the P–H hydrogen atom relative to the pyrophosphite ligand.

Introduction

In the course of a general study of the reactions of the unsaturated dimanganese hydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ (**1a, b**), (**1a**: $(EtO)_2POP(OEt)_2$ (tedip) [1]; **1b**: $Ph_2PCH_2PPh_2$ (dppm) [2]) we found that they react readily with several species containing E–H bonds (E = B, Si, Sn) [3], some kind of E–H bond activation always being involved. In this context it was of interest to examine the reactions of compounds **1a, b** towards phosphines containing one or more P–H bonds. Compounds **1a, b** are electron-deficient species, and so could be expected to react with phosphines under very mild conditions, as previously observed for the related unsaturated dihydrides $[Re_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ (L_2 = dppm, tedip [4]), $[Mn_2(\mu\text{-}H)_2(CO)_4(\mu\text{-dppm})_2]$ [5], $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ [6] or $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ [7]. Our main interest, however, was to find out whether these reactions would also involve activation of the P–H bonds. Cleavages of P–H bonds are known most commonly as the result of thermal reactions, usually under forcing conditions, of primary or secondary phosphines with transition metal carbonyl species, to give phosphido complexes [8]. Moreover, phosphido bridged di- and poly-nuclear complexes are attracting increasing attention because of the reactivity associated with the phosphido bridge itself [9–11], and in this context the reactions of compounds **1a, b** with

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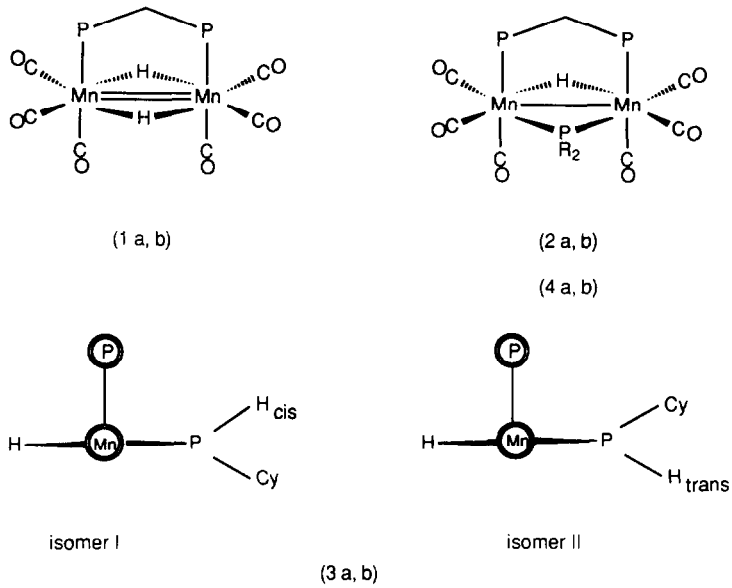


Fig. 1. Proposed structure and isomers for the new phosphido complexes ($\widehat{PP}$ = tedip or dppm). Possible isomers for compounds **3a,b** are depicted as their projections along the Mn–Mn vector (CO ligands omitted) showing the different orientations (*cis* and *trans*) of H atoms relative to the bidentated bridging ligand.

phosphines containing P–H bonds might provide an alternative, mild route for the synthesis of new phosphido species. We present below the results of our study of the reactions of complexes **1a** and **1b** with PH_3, PH_2Cy and $PHPh_2$, which in all cases lead to μ-hydrido μ-phosphido dimanganese species, generally in high yield.

Results and discussion

(a) Reactions with PH_3

When a current of PH_3 is gently bubbled through a petroleum ether solution of compound **1a** at room temperature an inmediate colour change, from red-purple to yellow, is observed. This corresponds to the formation of $[Mn_2(\mu\text{-H})(\mu\text{-}PH_2)(CO)_6(\mu\text{-tedip})]$ (**2a**), the only species detected in the reaction mixture. The structure proposed for this compound (Fig. 1) is firmly supported by the spectroscopic data. The solution IR spectrum (Table 1) contains five strong bands in the CO stretching region rather than the six expected for this C_s geometry, suggesting that there is an accidental degeneracy that seems to be typical of $[Mn_2(\mu\text{-H})(\mu\text{-X})(CO)_6(\mu\text{-}L_2)]$ species (X = halogen) [12]. The presence of the μ-PH_2 ligand is denoted by a broad (reflecting the effect of the quadrupolar ^{55}Mn nucleus) resonance at -21.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum of **2a**, which becomes a broad triplet with ^1H coupling (average J(PH) ca. 340 Hz). The asymmetry of the molecule relative to the pseudoplanes Mn_2POP and Mn_2HP is reflected in the observation of two chemical shifts for each the Me protons of the tedip ligand and the P–H protons, respectively, the latter appearing at 2.66 and 3.25 ppm with typical ^1J(PH) couplings of 335 and 354 Hz, and ^3J(PH) couplings of 12.7 and 11.5 Hz, respec-

Table 1

Infrared and other data for new compounds

Compound	IR (cm^{-1})		Yield (%)	Analysis (Found (calcd.) (%))	
	ν(CO) [a]	ν(PH) [b]		C	H
2a	2046vs, 2014vs, 1977vs, 1957m, 1942vs	2347w,br	76	30.5 (29.7)	4.2 (4.1)
2b	2032vs, 2004vs, 1962s, 1940m,sh, 1926vs	2336w,br	74	54.5 (53.5)	3.9 (3.6)
3a	2039s, 2010vs, 1970s, 1966s,sh, 1951m, 1947m,sh 1940vs, 1933s,sh	2332w	74	36.6 (36.9)	4.6 (5.0)
3b	2029vs, 1995vs, 1947vs, 1912vs,br [c]	2329w	68	56.5 (57.1)	4.5 (4.3)
4a	2045vs, 2015vs, 1965s, 1945m,sh, 1930vs [d]		78	42.7 (43.3)	4.1 (4.3)
4b	2022vs, 1993vs, 1946m, 1925m,sh, 1913vs [d]		5	60.3 (60.9)	3.8 (3.9)

[a] In petroleum ether, unless otherwise stated. [b] Nujol mull. [c] In toluene. [d] In dichloromethane.

tively. ^3J(PH) coupling constants usually show a Karplus-type dependence on the dihedral angle (ϕ) defined by the bonds involved, with a minimum value for $\phi = 90°$ and relative maxima at 0 and 180°, the latter being higher than that at 0° [13]. As the dihedral angles for the two P–H protons in **2a** are expected to be complementary (ca. 30 and 150°), it follows that ^3J(PH) for the proton having $\phi = 150°$, that is the one directed away from the phosphite ligand (H_{trans}), should be higher than that for the one pointing towards it (H_{cis}, Fig. 1). This allows the assignment of the signal at δ 2.66 to H_{trans} and that at δ 3.25 ppm to H_{cis}.

Reaction between PH_3 and **1b** at room temperature proceeds in the same way as the previous one, to give [$Mn_2(\mu$-H)(μ-PH_2)$(CO)_6(\mu$-dppm)] (**2b**) in high yield. The time required for completion of the reaction is, however, substantially longer (ca. 30 min), probably mainly because of the greater steric hindrance of the dppm ligand (compared with tedip) which would hinder the approach of the incoming PH_3 molecule in the first stage of the reaction (see later). Spectroscopic data for **2b** are very similar to those for **2a**, especially in the case of the IR spectrum and the chemical shifts and coupling constants of the μ-H and μ-PH_2 atoms, suggesting that **2a** and **2b** are isostructural (Fig. 1). The assignment of NMR resonances for the PH protons is again based on the above-mentioned relationship between ^3J(PH) and geometry, which gives $\delta(H_{trans}) = 3.64$ [J(PH) 10] and $\delta(H_{cis}) = 2.82$ [J(PH) 9]; in this case H_{cis} (closer to the dppm ligand) resonates at lower field than H_{trans} (opposite to the case of **2a**), and this can be interpreted as a shielding effect of the dppm phenyl rings.

(b) Reactions with PH_2Cy

The reaction between equimolecular amounts of PH_2Cy and the dihydride **1a** in petroleum ether at room temperature gives almost immediately the yellow complex [$Mn_2(\mu$-H)(μ-PHCy)$(CO)_6(\mu$-tedip)] (**3a**) in high yield. Unexpectedly, although the CO stretching frequencies are similar to those for **2a**, the IR spectrum of **3a** in

petroleum ether contains eight bands, which implies that more than one isomer is present in solution. This is confirmed by both the ^{1}H and ^{31}P NMR data, which indicate that the two isomers are present in a ca. 3 : 1 ratio; we have not been able to separate these isomers, which are always present in the same proportions for a given solvent, suggesting that they undergo rapid interconversion, so that the equilibrium distribution is quickly reached. These isomers have different chemical shifts for the P atoms and PH protons, but show the same μ-H resonance. ^{3}J(PH) coupling for the PH proton is 10 Hz for the major isomer, and 12 Hz for the minor one. Consideration of the previously mentioned relationship between PH couplings and geometry indicates that the major isomer has the PH hydrogen in a cis position (isomer I) and the minor one in a trans position (isomer II, figure 1), both relative to the pyrophosphite ligand. It is evident that isomer II has the bulky cyclohexyl group close to the tedip ligand, and it is expected to be somewhat less stable than isomer I, in which there is much less steric interaction, therefore isomer II would be expected to be the minor one, in agreement with the NMR assignments.

The reaction of complex **1b** with stoichiometric amounts of PH_2Cy in toluene at room temperature proceeds at a lower rate than that discussed above. IR monitoring of the reaction mixture shows the presence of an intermediate species after 7 min, characterized by ν(CO) bands at 2029vs, 1985vs, 1952s, 1922sh, 1912vs and 1902sh which is quickly transformed into the final product, [Mn_2(μ-H)(μ-PHCy)(CO)$_6$(μ-dppm)] (**3b**), obtained in high yield. We have not fully characterized this short-lived intermediate, but make a reasonable proposal about its identity later.

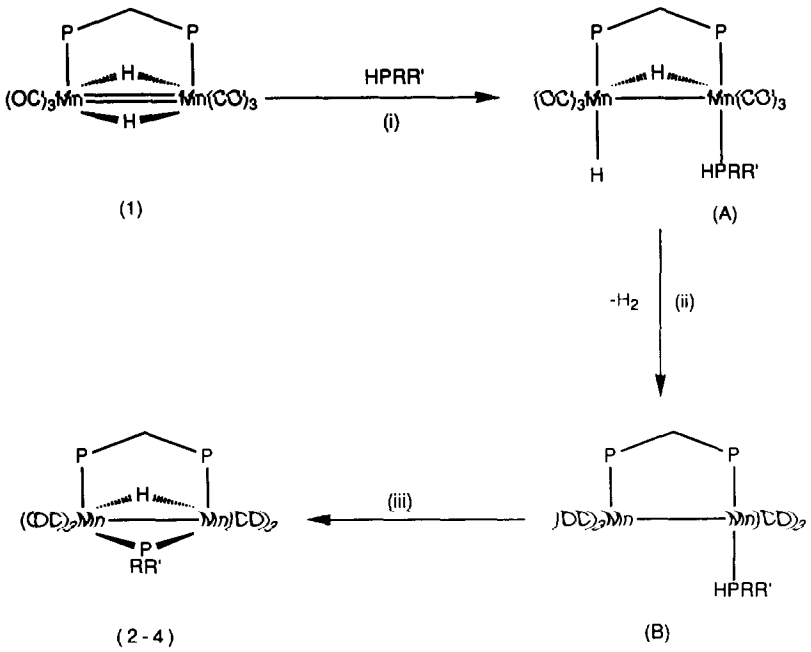
Spectroscopic data for **3b** indicate that it is structurally related to **3a**. However, the IR spectrum contains just four ν(CO) bands in toluene, at 2029s, 1995s, 1947s and 1912vs, br cm^{-1}, which suggests the presence of just one type of species in the solution. This is further confirmed by the NMR data; the signal from the PH proton is obscured by those from the cyclohexyl group, but the $^{31}P\{^{1}H\}$ spectrum shows a single resonance for the phosphido group at 111.8 ppm, which becomes a broad doublet (^{1}J(PH) 305 Hz) with proton coupling.

The presence of just one isomer for **3b** is not surprising in view of the much greater steric requirements of the dppm ligand than of tedip; this would make isomer II (fig. 1) exceedingly crowded, owing to dppm-Cy repulsions, leaving isomer I, which contains the Cy group pointing away from the dppm ligand, as the only reasonable possibility.

(c) Reactions with $PHPh_2$

Reaction of equimolecular amounts of **1a** and $PHPh_2$ in petroleum ether at room temperature leads almost immediately to formation of the yellow complex [Mn_2(μ-H)(μ-PPh_2)(CO)$_6$(μ-tedip)] (**4a**), which can be isolated in 80% yield. When the reaction is carried out with an excess of phosphine, yields of **4a** are slightly lower (ca. 70%) owing to the formation of other unidentified products probably resulting from CO substitution in **4a**.

Complex **4a** was previously prepared in low yield (16%) by thermal reaction of [Mn_2(μ-H)(μ-PPh_2)(CO)$_8$] with tedip [8a]; the reported spectroscopic data (no ^{31}P data available) are in acceptable agreement with our own data. The μ-PPh_2 group gives rise to a ^{31}P resonance at 152.6 ppm, a value indicative of the presence of a bonding metal–metal interaction [14]. This also the case for all the other phosphido



Scheme 1. Proposed pathway for the reactions between the dihydrides **1a,b** and phosphines PHRR' (see text).

complexes described in this paper, and is consistent with the formal metal–metal bonding postulated in order to fulfil the E.A.N. rule.

In marked contrast with the reactions discussed above, which have been shown to be highly selective, reaction of $HPPh_2$ and **1b** in toluene at room temperature gives a complicated mixture of rather insoluble products irrespective of the molar ratio used. This is probably a reflection of the steric repulsions involved in the mutual approach of two relatively bulky moieties, dppm and diphenylphosphine. The only product we have characterized in the reaction mixture is $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\mu\text{-dppm})]$ (**4b**), which can be isolated in low yield (5%). Spectroscopic data for **4b** indicate that has close structural similarity to **4a** (Fig. 1).

(d) Proposed pathway for the formation of complexes 2–4

Except for of the reaction between **1b** and $PHPh_2$, we have shown that reactions of the unsaturated dihydrido complexes **1a** and **1b** with phosphines containing one or more PH bonds proceed quickly at room temperature to give μ-hydrido μ-phosphido species in high yield, and so there must be H_2 elimination at some stage in the reaction. It is reasonable to assume that the first step is the coordination of the incoming phosphine, so as to relieve the electronic unsaturation of the dihydrides **1a**, **b**, thus leaving a saturated dihydride (**A** in Scheme 1); this would be the intermediate species detected in the reaction of PH_2Cy with **1b**, and its stereochemistry would be similar to that proposed for the rhenium complexes $\{Re_2H_2(CO)_6(\mu\text{-}L_2)\{P(OMe)_3\}\}$, ($L_2$ = dppm, tedip), obtained as stable products form the reactions of the unsaturated dihydrides $[Re_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ with $P(OMe)_3$ [4]. Intermediate A would subsequently lose H_2 (ii in Scheme 1), and since other donor

molecules such as CO, ^{t}BuNC, and MeCN can induce H_2 elimination [2] we suggest that both of the H atoms of the H_2 came from two hydrido ligands rather than from MnH and PH hydrogen atoms. This step would generate a 16e Mn centre (**B** in Scheme 1), which would then quickly induce oxidative addition of a P–H bond of the coordinated phosphine (iii in Scheme 1) finally yielding the stable complexes **2–4**. Interestingly, step iii closely resembles the oxidative addition of PH bonds observed in the reactions between $[M(HPR'R)L_n]$ complexes and $[Pt(C_2H_4)(PPh_3)_2]$ (the latter acting as source of the highly unsaturated (14e) species $Pt(PPh_3)_2$) which lead at room temperature to the formation of heterodimetallic hydrido phosphido species [15]. It is also noteworthy that the transformation resulting from steps ii and iii has been observed for the osmium complexes $[Os_3H(\mu\text{-}H)(PHR'R)(CO)_{10}]$ (R, R' = H, Me) [16], which upon controlled heating yield the corresponding $[Os_3(\mu\text{-}H)(\mu\text{-}PRR')(CO)_{10}]$ species. The fact that this type of transformation occurs at lower temperatures for our dimanganese complexes is probably a result of the lower strength (relative to Os) of the Mn–H bonds [17].

Experimental section

All manipulations were carried out under dry oxygen-free nitrogen by Schlenk-tube techniques. Solvents were purified by standard procedures [18]. Petroleum ether refers to that fraction boiling at 60–65 °C. Infrared spectra were recorded on Perkin–Elmer 577 or FT1720-X spectrophotometers, using CaF_2 cells for solution measurements and Nujol mulls or KBr pellets for solid state measurements. ^{1}H (300.13 MHz) and ^{31}P (121.44 MHz) NMR spectra were recorded on a Bruker AC-300 instrument in $CDCl_3$ solution at 298 K unless otherwise stated. Chemical shifts (ppm) are referenced against internal TMS (^{1}H) or external 85% aqueous H_3PO_4 (^{31}P), and positive values indicate at frequencies higher than that of the reference; coupling constants are given in Hz, and $w_{1/2}$ refers to the width (in Hz) at half the height of a peak. Elemental analysis (C, H) was performed with a Perkin–Elmer 240B instrument. Compounds **1a** [1], **1b** [2] and PH_3 [19] were prepared by published methods. $PCyH_2$ and PPh_2H were obtained from commercial suppliers and used without further purification.

*(a) Preparation of $[Mn_2(\mu\text{-}H)(\mu\text{-}PH_2)(CO)_6(\mu\text{-tedip})]$ (**2a**)*

Gaseous PH_3 was bubbled gently through a petroleum ether solution (10 ml) of compound **1a** (0.050 g, 0.093 mmol), the solution immediately turning yellow. After 10 min the solution was filtered through celite, reduced in volume under vacuum to ca. 2 ml, and kept at −20 °C for 24 h. The yellow crystals formed were separated from the solution and washed with cold petroleum ether, yielding 0.040 g (76%) of pure **2a**. ^{1}H NMR: δ 3.75, 3.55 (2 × m, OCH_2, 2 × 4H); 3.25 [dtd, ^1J(PH) 354, ^3J(PH) 11.5, ^2J(HH) 4, PH_{cis}, 1H]; 2.66 (dtd, ^1J(PH) 335, ^3J(PH) 12.7, ^2J(HH) 4, PH_{trans}, 1H]; 0.97, 0.88 [2 × t, J(HH) 7, Me, 2 × 6H] and −17.7 [td, ^2J(PH) 32, 25, μ-H, 1H]. ^{31}P{^{1}H} NMR: δ 172.9 (s, br, μ-tedip, 2P) and −21.1 (s, br, $\mu\text{-}PH_2$, 1P). ^{31}P NMR: δ −21.0 [t, br, ^1J(PH) ≃ 340, $\mu\text{-}PH_2$].

*(b) Preparation of $[Mn_2(\mu\text{-}H)(\mu\text{-}PH_2)(CO)_6(\mu\text{-dppm})]$ (**2b**)*

Gaseous PH_3 was bubbled gently through a toluene solution (10 ml) of **1b** (0.05 g, 0.075 mmol) for 30 min at room temperature resulting on a gradual colour change

from red purple to yellow. The solution was stirred for a further 10 min, then filtered through Celite and evaporated to dryness under vacuum. The residue was washed with cold petroleum ether to give 0.04 g (74%) of compound **2b** as a yellow microcrystalline powder. ^{1}H NMR: δ 7.64–7.40 (m, Ph, 20H0; 3.64 [dtd, ^1J(PH) 340, ^3J(PH) 10, ^2J(HH) 3.3, PH_{trans}, 1H); 2.82 [dtd, ^1J(PH) 320, ^3J(PH) 9, ^2J(HH) 3.3, PH_{cis}, 1H]; 2.89, 2.64 [2 × q, ^2J(PH) ≃ ^2J(HH) 12, CH_2, 2 × 1H] and −17.1 [dt, ^2J(PH) 37, 19, μ-H, 1H]. ^{31}P{^{1}H} NMR: δ 59.8 [d, ^2J(PP) 35, μ-dppm, 2P] and −13.6 (br, $w_{1/2}$ 90, μ-PH_2, 1P). ^{31}P NMR: δ −13.5 [t, br, ^1J(PH) ≃ 335, μ-PH_2].

*(c) Preparation of [Mn_2(μ-H)(μ-PHCy)$(CO)_6$(μ-tedip)] (**3a**)*

PH_2Cy (0.012 ml, 0.093 mmol) was added to a solution of **1a** (0.050 g, 0.093 mmol) in petroleum ether (10 ml), and the mixture was stirred at room temperature for 10 min give a yellow solution. The solution was filtered and the solvent removed in vacuum. The oily residue was converted into a yellow solid during 24 h under vacuum. This solid was washed with cold petroleum ether to yield 0.045 g (74%) of compound **3a** as a yellow microcrystalline powder. ^{1}H NMR: δ 3.97 [dtd, ^1J(PH) 335, ^3J(PH) ≃ ^3J(HH) 12, PH, isomer II]; 3.9 (m, OCH_2, 8H); ≃ 3.4 (part of multiplet obscured by the OCH_2 signals [dtd, ^1J(PH) ≃ 320 (from ^{31}P), ^3J(PH) ≃ ^3J(HH) 10, PH, isomer I]; 2.42 (m, Cy, 2H); 1.85 (m, Cy, 2H); 1.75 (m, Cy, 1H); 1.3–1.2 (m, Cy and Me, 18H) and −17.65 [q, ^2J(PH) 28, μ-H, 1H]. ^{31}P{^{1}H} NMR (223 K): δ 174.1 [d, J(PP) 53, μ-tedip, isomer II]; 171.9 [d, J(PP) 52, μ-tedip, isomer I]; 107.7 [t, J(PP) 52, μ-PHCy, isomer I] and 102.5 [t, J(PP) 53, μ-PHCy, isomer II]. ^{31}P NMR: δ 104.9 [d, br, $w_{1/2}$ 145, ^1J(PH) 320, μ-PHCy, isomer I]; 102.1 [d, br, $w_{1/2}$ 145 ^1J(PH) 335, μ-PHCy, isomer II].

*(d) Preparation of [Mn_2(μ-H)(μ-PHCy)$(CO)_6$(μ-dppm)] (**3b**)*

PH_2Cy (0.010 ml, 0.075 mmol) was added to a solution of **1b** (0.050 g, 0.075 mmol) in toluene (10 ml), and the mixture was stirred at room temperature for 15 min to give a yellow solution. After work-up as for **2b**, 0.040 g (68%) of **3b** were obtained as a yellow microcrystalline powder. ^{1}H NMR: δ 7.5–6.7 (m, Ph, 20H); 4.4, 3.3 [2 × q, ^2J(PH) ≃ ^2J(HH) 10, CH_2, 2 × 1H]; 3.06–2.97 (m, Cy, 2H); 2.5–1.8 (m, Cy and PH, 10H) and −16.4 [dt, ^2J(PH) 34, 19, μ-H, 1H]. ^{31}P{^{1}H} NMR: δ 111.8 [t, J(PP) 38, μ-PHCy, 1P] and 60.2 [d., J(PP) 38, μ-dppm, 2P]. ^{31}P NMR: δ 111.8 [d, br, $w_{1/2}$ 110, ^1J(PH) 305].

*(e) Preparation of [Mn_2(μ-H)(μ-PPh_2)$(CO)_6$(μ-tedip)] (**4a**)*

$PHPh_2$ (0.016 ml, 0.093 mmol) was added to a solution of **1a** (0.050 g, 0.093 mmol) in petroleum ether (10 ml), and the mixture was stirred at room temperature for 15 min to give a yellow solution. After work-up as for **2b** 0.035 g (70%) of **4a** were obtained as a yellow microcrystalline powder. ^{1}H NMR: δ 7.9–7.3 (m, Ph, 10H); 4.1 (m, OCH_2, 4H); 3.54, 3.14 (2 × m, OCH_2, 2 × 4H); 1.36, 1.05 [2 × t J(HH) 7, Me, 2 × 6H] and −17.12 [q, J(PH) 30, μ-H, 1H]. ^{31}P{^{1}H} NMR: δ 169.6 (s, br, $w_{1/2}$ 205, μ-tedip, 2P) and 152.6 (s, br, $w_{1/2}$ 135, μ-PPh_2, 1P).

*(f) Reaction of **1b** with $PHPh_2$*

$PHPh_2$ (0.018 ml, 0.105 mmol) was added to a solution of **1b** (0.070 g, 0.105 mmol) in toluene (10 ml) and the mixture was stirred at room temperature for 15 min to give a yellow solution along with a yellow solid. (The yellow solid was

insoluble in all common solvents.) The solution was filtered through Celite and the solvent removed in vacuum to yield 0.005 g (5%) of **4b** as a yellow powder. ^{1}H NMR (CD_2Cl_2): δ 7.4–6.8 (m, Ph, 30H), 2.40 [dtd, ^2J(PH) $\simeq$ ^2J(HH) 14, ^4J(PH) 6, CH_2, 1H]; 1.75 [dt, ^2J(HH) 14, ^2J(PH) 11, CH_2, 1H] and −16.2 [dt, ^2J(PH) 32, 22, μ-H, 1H]. ^{31}P{^{1}H} NMR: δ 148.7 (s, br, μ-PPh_2, 1P0 and 50.8 (s, br, μ-dppm, 2P).

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