Synthesis and Characterization of Di- and Tricarbonylhydridomanganese(I) Complexes

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Abstract. Hydrido complexes $[MnH(CO)_3L^{1-3}]$ $[L^1 = 1,2$ -bis-(diphenylphosphanoxy)-ethane (1); $L^2 = 1,2$ -bis-(diisopropylphosphanoxy)ethane (2); $L^3 = 1,3$ -bis-(diphenylphosphanoxy)-propane (3)] were prepared by treating $[MnH(CO)_5]$ with the appropriate bidentate ligand by heating to reflux. Photoirradiation of a toluene solution of complexes 1 and 2 in the presence of PPh_n(OR)_{3-n} (n = 0, 1; R = Me, Et) leads to the replacement of a CO ligand by the corresponding monodentate

Introduction

Interest in the chemistry of hydrido transition metal complexes is increasing in inorganic, biochemical and organometallic research owing to their reactivity and applications in areas such as catalysis and materials science, amongst others [1]. The reactivity of these compounds is highly dependent on the metal atom and the co-ligands that complete the coordination sphere of the metal. Appropriate design of this environment allows tuning both the steric and electronic properties of the resulting compound. Phosphites are currently used as ancillary ligands because their high π -acceptor and low σ -donor character (more marked than in the case of phosphanes [2]) allows the design of highly Lewis acidic centers. One of our areas of interest in the field of hydrido transition metal chemistry is the study of the influence of mono- and bidentate mixed phosphite co-ligands $[PR_n(OR)_{3-n}; n = 0-3]$ on the properties of different hydrido carbonyl compounds [3] with the aim to evaluate the effects on structure, bonding and chemical properties of the hydrido and the corresponding η^2 -H₂ manganese complexes when an oxygen atom is introduced near the phosphorus atom belonging to an ancillary ligand.

We report here the synthesis and characterization of a set of a new manganese hydridotricarbonyl complexes, which bear different chelating diphosphinite ligands [1,2-bis(diphenylphosphanoxy)ethane (L^1), 1,2-bis(diisopropylphosphanoxy)ethane (L^2) and 1,3-bis(diphenylphosphanoxy)propane (L^3)], as well as their photo-substitution reactions involving the reformula $[MnH(CO)_2(L^{1-2})(L)] [L = P(OMe)_3 (1a-2a); P(OEt)_3 (1b-2b); PPh(OMe)_2 (1c-2c); PPh(OEt)_2 (1d-2d)]. All complexes were characterized by IR, ¹H, ¹³C and ³¹P NMR spectroscopy. In case of compounds 2 and 3, suitable crystals for X-ray diffraction studies were isolated.$

phosphite or phosphonite ligand to give new hydrido compounds of

placement of one carbonyl ligand by different monodentate phosphites [P(OR)₃; R = Me, Et] or phosphonites [PPh(OR)₂; R = Me, Et].

Results and Discussion

Synthesis and Spectroscopic Characterization of fac-[$MnH(CO)_3(L^1)$] (1), fac-[$MnH(CO)_3(L^2)$] (2) and mer-[$MnH(CO)_3(L^3)$] (3)

The complexes fac-[MnH(CO)₃(L¹)] (1), fac-[MnH(CO)₃-(L²)] (2) and *mer*-[MnH(CO)₃(L³)] (3) were prepared by thermal substitution of two carbonyl ligands in the hydrido pentacarbonyl complex [MnH(CO)₅] by the appropriate bidentate ligand L¹⁻³ (Scheme 1).



Scheme 1.

The new hydrido complexes are pale yellow and air-stable in both the solid state and in solution at room temperature. The



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IR spectra of tricarbonyl compounds **1** and **2** show three strong bands (1885–2003 cm⁻¹) in the \tilde{v} (CO) region, as expected for a *facial* disposition of the three CO ligands. In contrast, compound **3** presents one medium intensity band at $\tilde{v} = 2016 \text{ cm}^{-1}$ and two strong bands ($\tilde{v} = 1914$ and 1947 cm⁻¹), which is consistent with a *meridional* arrangement [4] of the carbonyl ligands.

The room temperature ³¹P{¹H} NMR spectra of complexes 1 and 2 show, in both cases, a single singlet resonance, which indicates the magnetic equivalence of the two phosphorus nuclei of the bidentate ligand. The ³¹P{¹H} NMR spectrum of compound 3 shows two broad unresolved signals (173.3 and 176.0 ppm), which indicates that the two phosphorus nuclei of the bidentate ligand L³ are not equivalent. On the other hand, the high field region of the ¹H NMR spectra display a sharp triplet at -6.89 ppm [J(H,P) = 48.7 Hz] for 1 and at -7.31 ppm $(J_{\rm H,P} = 50.3 \text{ Hz})$ for 2 at room temperature, both integrating to one proton and assignable to the hydrido ligand. In the case of compound 3 this signal appears as a doublet of doublets at 8.88 ppm, which is due to the coupling of the hydrogen nucleus of the hydrido ligand with one of the phosphorus nuclei of L³ in the trans position $[{}^{2}J_{H,P(trans)} = 77.0 \text{ Hz}]$ and with the other one in the cis position $[{}^{2}J_{\text{H,P}(cis)} = 14.0 \text{ Hz}]$, as depicted in Scheme 1. All of these spectroscopic features allow us to confirm the proposed fac stereochemistry for compounds 1 and 2 and the mer stereochemistry for compound 3, both in solid state and in solution. It is worth mentioning that the propensity of the L³ ligand to favor the mer arrangement in hydridotricarbonyl compounds has been observed previously for analogous rhenium(I) derivatives [3f]. Variable temperature ¹H and ³¹P{¹H} NMR experiments were performed for compounds 1-3 with the aim of detecting interconversion processes between conformers of the chelate rings that are similar to those observed for the analogous rhenium(I) complexes [3f]. A decrease in the temperature from 293 to 193 K only led to a slight broadening of the signals in both the ¹H and ³¹P{¹H} spectra, indicating a much lower energy barrier for the interconversion processes cited above in comparison with those for the rhenium compounds.

Determination of the minimum spin-lattice relaxation time $[T_{1(\min)}]$ for the hydrido nuclei of compounds 1–3, at 400 MHz by the standard inversion-recovery method, gave values in the range expected for this type of complex (Table 1) [4a] and significantly lower than those for the analogous rhenium(I) derivatives [3f].

Table 1. $T_{1(\min)}$ values for complexes 1–3.

Compound	$T_{1(\min)}$ /ms	T/K
$[MnH(CO)_3(L^1)]$ (1) $[MnH(CO)_2(L^2)]$ (2)	151 122	210 187
$[MnH(CO)_3(L^3)]$ (3)	131	222

Protonation of transition metal hydrido complexes with strong acids is a common method to obtain dihydrogen complexes. We therefore carried out protonation experiments on compounds 1-3 with HBF₄·Me₂O, the aim of which was to

obtain the corresponding dihydrogen complexes. With this goal in mind, a slight excess of acid (1.1 equiv.) was added to CD_2Cl_2 solutions of the complexes in an NMR tube at low temperature (193 K). Unfortunately, a mixture of unidentified compounds was obtained and signals corresponding to the dihydrogen derivatives were not observed, probably due to the high lability of the corresponding dihydrogen ligand and its immediate substitution by species present in solution (BF₄⁻, Me₂O or even water from adventitious sources) on the highly electrophilic resulting fragment [5].

Description of the Structures

Perspective views of the molecular structures of compounds 2 and 3 are shown in Figure 1 and Figure 2, respectively, along with the atom numbering scheme. Selected bond lengths and angles are listed in Table 2.



Figure 1. ORTEP diagram (20 % probability ellipsoids) for complex 2.



Figure 2. ORTEP diagram (20 % probability ellipsoids) for complex 3.

X-ray crystallography confirmed the structures proposed for complexes 2 and 3 on the basis of spectroscopic data. Complexes 2 and 3 consist of discrete molecules with no significant H-bonds between neighbors.

In both complexes, one hydrido ligand, three carbonyl ligands and two phosphorus atoms are octahedrally coordinated to a manganese(I) atom. In complex **2**, the three carbonyl li-

Table 2. Selected bond lengths /Å and angles /° for complexes 2 and 3.

Complex	2	3		
Bond lengths /Å				
Mn-H(1)	1.52(3)	1.50(2)		
Mn-P(1)	2.2917(10)	2.2473(14)		
Mn-P(2)	2.2870(9)	2.2407(14)		
Mn-C(1)	1.789(4)	1.810(5)		
Mn-C(2)	1.801(4)	1.821(5)		
Mn-C(3)	1.793(4)	1.779(5)		
O(1) - C(1)	1.153(3)	1.148(4)		
O(3)–C(3)	1.148(4)	1.172(5)		
O(2) - C(2)	1.144(4)	1.153(5)		
Bond angles /°				
H(1)-Mn-C(3)	86.0(11)	72.1(10)		
C(3)–Mn– $C(1)$	84.30(15)	90.8(2)		
C(3)–Mn– $C(2)$	94.72(17)	90.4(2)		
H(1)-Mn-P(2)	82.8(10)	80.8(10)		
C(1)– Mn – $P(2)$	166.33(11)	87.00(14)		
H(1)-Mn-P(1)	83.7(11)	164.9(10)		
C(1)– Mn – $P(1)$	86.70(11)	92.16(14)		
P(2)-Mn-P(1)	96.53(3)	111.49(5)		
H(1)-Mn-C(1)	84.3(10)	97.4(10)		
H(1)-Mn-C(2)	177.9(10)	82.8(9)		
C(1)–Mn– $C(2)$	97.72(14)	178.7(2)		
C(3)– Mn – $P(2)$	90.14(11)	152.21(16)		
C(2)–Mn–P(2)	95.17(10)	91.79(15)		
C(3)– Mn – $P(1)$	166.99(12)	96.27(16)		
C(2)-Mn-P(1)	95.79(11)	87.98(15)		

gands are disposed around the metal in a *facial* arrangement, and the seven-membered chelate ring adopts a boat conformation with a chelate angle of $96.53(3)^\circ$. In complex **3**, the 1,3-bis(diphenylphosphanoxy)propane bidentate ligand allows the formation of an eight-membered chelate ring and the three carbonyl ligands are situated around the metal in a *meridional* arrangement.

The Mn–H bond lengths are 1.52(3) Å and 1.50(2) Å for compounds **2** and **3**, respectively, and these are slightly shorter than those found in the literature [6–8], although in some cases [6, 7] the data were obtained by neutron diffraction studies which provide greater values than those obtained by X-ray diffraction.

The Mn–P and Mn–C distances are in the range found for similar complexes of manganese(I) [8–10]. The Mn–P distances in compound **2** [2.2894(9) Å in average] are slightly longer than in compound **3** [2.244(1) Å in average]. In compound **2**, both phosphorus atoms are *trans* to carbonyl ligands, but in compound **3** one phosphorus atom is *trans* to a carbonyl ligand and the other one is *trans* to a hydrido ligand. Despite the expected difference between the *trans*-influence of the hydrido and the CO ligands, the differences between the two Mn–P bond lengths in complex **3** are not remarkable. To the best of our knowledge, compound **3** is the first example of a manganese complex with a terminal hydrido ligand *trans* to a phosphorus atom that has been resolved by X-ray diffraction methods.

The Mn–C distances in complex **2** are not significantly different, with the Mn–C distance of the CO ligand *trans* to the hydrido ligand only 0.01 Å longer than those of CO ligands *trans* to phosphorus atoms. In compound **3**, the two mutually *trans* CO ligands present a longer Mn–C distance (about 0.02 Å) than the CO ligand, which is *trans* to a phosphorus atom, a situation that reflects their mutual competition for the electrons of the same metal d orbital. This effect is also reflected in the C–O distances, those of the mutually *trans* CO ligands are about 0.02 Å shorter than the one of the third CO ligand.

The main source of distortion from the ideal octahedral structure comes from the small steric requirements of the hydrido ligand. Thus, in the case of complex **3**, in which the hydrido ligand is located in the same plane as the bidentate ligand, the P(1)–Mn–P(2) angle is $111.49(5)^{\circ}$, i.e. far from the ideal value of 90°. This distortion is also present (albeit to a lesser extent) in compound **2**, in which the angles between the C(2) atom (from the CO group *trans* to the hydrido ligand) and its *cis* neighbors C(1), C(3), P(1) and P(3) are 5–7° wider than 90°.

Synthesis and Spectroscopic Characterization of cis,fac-[$MnH(CO)_2(L^{1-2})(L')$]; [$L' = P(OMe)_3$ (1a–2a), $P(OEt)_3$ (1b–2b), $PPh(OMe)_2$ (1c–2c), $PPh(OEt)_2$ (1d–2d)]

The neutral hydridodicarbonyl complexes $[MnH(CO)_2-(L^{1-2})(L')]$ (1a–d and 2a–d) were prepared as outlined in Scheme 2. UV irradiation of toluene solutions of compounds 1 or 2, which contained an excess of the appropriate monodentate phosphite or phosphonite ligands gave new hydrido compounds by substitution of one carbonyl ligand for the corresponding L' ligand. In the case of compound 3, the photoirradiation reaction produced a mixture of unidentified products.





The new hydrides were pale yellow solids and were air-stable at room temperature. The stability of these compounds is very similar to that of their rhenium analogues, although one would expect manganese compounds to be less stable than rhenium ones because of the smaller size of Mn^I relative to Re^I [5]. The IR spectra of compounds **1a–d** and **2a–d** show two strong bands in the region $\tilde{v} = 1930-1857$ cm⁻¹, which are assigned to \tilde{v} (CO) vibrations of the two CO ligands in a mutually *cis* position [11]. A medium intensity band at $\tilde{v} = 1831$ (**1c**) and 1830 (**1d**) cm⁻¹ could be assigned to the \tilde{v} (Mn–H) vibration. In the case of compounds **1a** and **1b**, this band appears as a shoulder on the much more intense \tilde{v} (CO) absorption at 1869 cm⁻¹. In the case of compounds **2a–d**, the \tilde{v} (Mn–H) band is probably totally obscured by the *v*(CO) absorptions.

The ${}^{31}P{}^{1}H$ spectra of compounds **1a–d** and **2a–d** display three signals, which indicate the inequivalence of the three phosphorus nuclei. These signals were broad unresolved mul-



Figure 3. ³¹P{¹H} NMR experimental (upwards) and simulated (downwards) spectra of compound 1c at 273 K.

tiplets in all cases except for compounds **1c** and **1d**, for which these multiplet signals appeared to be well resolved. A simulation study [12] carried out for compound **1c** at 273 K showed that the multiplet signals correspond to an ABM spin system (A and B nuclei corresponding to P_A and P_B from the bidentate ligand, and the M nucleus corresponding to P_C from the monodentate ligand) with J values of $J_{A,B} = 66.5$, $J_{A,M} = 59.7$ and $J_{B,M} = 40.7$ Hz (Figure 3).

At room temperature, the ¹H NMR spectra of the complexes show a signal corresponding to an ABMX spin system at high field, in which the hydrido nucleus (X) couples to the three magnetically different phosphorus nuclei (one located in a *trans* position and two located in *cis* positions with respect to the hydrido proton) with $J_{XA} \approx J_{XC} \approx 51$ Hz and $J_{XB} = 56$ Hz (Figure 4).



Figure 4. ¹H NMR spectrum of compound 1c in CD_2Cl_2 in the high-field region.

Different arrangements (I–IV) can be postulated for compounds **1a**–**d** and **2a**–**d** (Scheme 3). A *fac* structure of type II can be proposed for these compounds based on the spectroscopic features discussed above.



Scheme 3.

Variable-temperature ${}^{31}P{}^{1}H$ and ${}^{1}H$ NMR spectroscopic experiments were performed on compounds **1a–d** and **2a–d** in the temperature range between 293 and 183 K. The ${}^{31}P{}^{1}H$ NMR spectra of compounds **2a–d** did not show any significant modification in the signals and contained three broad signals, which is in agreement with three magnetically inequivalent phosphorus nuclei. In contrast, the spectra of complexes **1a–d** are temperature dependent; the two unresolved signals observed at 179.9 and 208.6 ppm at room temperature change as the temperature is lowered and are resolved into two multiplet signals at –40 °C (Figure 5).



Figure 5. $^{31}P\{^1H\}$ NMR spectra of compound 1c in CD_2Cl_2 at various temperatures.



Longitudinal relaxation times of the hydrido resonance were measured in CD₂Cl₂ solutions at 400 MHz by the inversionrecovery method at different temperatures. The $T_{1(\min)}$ values obtained for the compounds (Table 3) are similar to those reported for other hydridocarbonylmanganese compounds bearing these types of phosphorus ligands [4a]. The $T_{1(\min)}$ values observed for compounds 2a-d are lower than those of compounds 1a-d, which is probably due to the nature of the R groups attached to the bidentate L ligand. Thus, in the case of L^2 , seven hydrogen nuclei from each isopropyl group are located in the vicinity of the hydrido nucleus, thus producing a greater number of effective dipolar-dipolar interactions and, consequently, faster relaxation rates [13]. In the case of the phenyl groups of the L¹ ligand, only the two H_{ortho} nuclei from each phenyl group contribute to the relaxation of the hydrido ligand (Hmeta and Hpara are too far away from the hydrido nucleus to produce effective dipolar interactions). A similar, although less pronounced effect was also observed for the tricarbonyl derivatives 1 and 2 (See Table 1).

Table 3. T_{1(min)} values for complexes 1a-d and 2a-d.

Compound	$T_{1(\min)}$ /ms	T/K
$[MnH(CO)_2(L^1){P(OMe)_3}]$ (1a)	133	231
$[MnH(CO)_2(L^1) \{P(OEt)_3\}]$ (1b)	129	225
$[MnH(CO)_2(L^1){PPh(OMe)_2}] (1c)$	127	226
$[MnH(CO)_2(L^1){PPh(OEt)_2}] (1d)$	134	241
$[MnH(CO)_2(L^2){P(OMe)_3}]$ (2a)	66	209
$[MnH(CO)_2(L^2){P(OEt)_3}]$ (2b)	72	227
$[MnH(CO)_2(L^2){PPh(OMe)_2}] (2c)$	111	212
$[MnH(CO)_2(L^2){PPh(OEt)_2}] (2d)$	64	215

Protonation of complexes **1a-d** and **2a-d** with $HBF_4 \cdot Me_2O$ gave a mixture of unidentified compounds.

Experimental Section

General Experimental Techniques

Synthetic work was carried out in a dry argon atmosphere using standard Schlenk techniques. All solvents were purified by conventional procedures [14] and distilled prior to use. Monodentate phosphites and phosphonites (Aldrich) were used as received. The ligands $L^1 = 1,2$ bis(diphenylphosphanoxy)ethane, $L^2 = 1,2$ -bis(diisopropylphosphanoxy)ethane, $L^3 = 1,3$ -bis(diphenylphosphanoxy)propane and the hydrido precursor [MnH(CO)₅] were prepared by published methods [3f, 15]. Photoirradiation was carried out with a 150 W medium-pressure Hg lamp using a Pyrex Schlenk flask. ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were obtained with a Bruker ARX-400 spectrometer operating at frequencies of 400, 100 and 161 MHz, respectively; the spectra were recorded in CD₂Cl₂ solutions, using the solvent as the internal lock. ¹H and ¹³C{¹H} signals were referred to internal TMS and those of $^{31}P{^{1}H}$ to 85 % H₃PO₄; downfield shifts were considered positive. Variable-temperature spin-lattice relaxation times T_1 were determined in deuterated dichloromethane by the inversion-recovery method by using a standard $180^{\circ}-\tau-90^{\circ}$ pulse sequence and 16 different values of τ at each temperature. IR spectra (KBr disc) were recorded with a Bruker VECTOR IFS 28 FT apparatus. Microanalyses were carried out with a Fisons model EA 1108 elemental analyser and mass spectra were obtained with a Micromass Autospec M LISMS (FAB⁺) system.

Preparation of fac- $[MnH(CO)_3(L^1)]$ (1), fac- $[MnH(CO)_3(L^2)]$ (2) and mer- $[MnH(CO)_3(L^3)]$ (3)

An excess of the appropriate ligand L^{1-3} (5.0 mmol) was added to a solution of [MnH(CO)₅] (1.25 mmol, 0.25 g) in toluene (15 mL). The reaction mixture was held at a temperature of 90 °C for about 5 h. The solvent was removed under vacuum and the residual oil was treated with ethanol (2 mL) to give a pale yellow product, which was filtered off, washed with ethanol, dried under vacuum and recrystallized from a 2:10 (v/v) CH₂Cl₂/EtOH solution by slow evaporation of the solvent.

Compound 1: Yield ≥83 %. Anal. C₂₉H₂₅MnO₅P₂ (570.40); C 60.72 (calcd. 61.07); H 4.50 (calcd. 4.42)%. **MS** (referred to the most abundant isotopes): $m/z = 570 \text{ [M}^+\text{]}$, 569 [M⁺ – H], 543 [M⁺ – CO], 486 [M⁺ – 3CO], 485 [M⁺ – 3CO–H]. **IR** (KBr): $\tilde{v} = 2003$ (s), 1932 (s), 1908 (s) cm⁻¹. ¹**H NMR** (400 MHz, CD₂Cl₂): $\delta = -6.89$ (t, ²*J*_{P,H} = 49 Hz, 1 H, Mn*H*), 3.94–4.53 (m, 4 H, OC*H*₂C*H*₂O), 7.42–7.72 (m, 20 H, Ph). ³¹P{¹H} **NMR** (161 MHz, CD₂Cl₂): $\delta = 175.2$ (s). ¹³C{¹H} **NMR** (100 MHz, CD₂Cl₂): $\delta = 65.4$ (s, OCH₂CH₂O), 127.5–141.6 (Ph), 220.5 (br., CO), 222.0 (br., CO).

Compound 2: Yield ≥79 %. Anal. C₁₇H₃₃MnO₅P₂ (434.33); C 46.72 (calcd. 47.01); H 7.30 (calcd. 7.66)%. **MS** (referred to the most abundant isotopes): m/z = 434 [M⁺], 433 [M⁺ − H], 350 [M⁺ − 3CO], 377 [M⁺ − 2CO − H], 349 [M⁺ − 3CO–H]. **IR** (KBr): $\tilde{v} = 1987$ (s), 1910 (s), 1885 (s) cm⁻¹. ¹**H NMR** (400 MHz, CD₂Cl₂): $\delta = -7.31$ (t, ²*J*_{P,H} = 50 Hz, 1 H, Mn*H*), 1.30 [m, 24 H, CH(CH₃)₂], 2.25 [s, br, 2 H, CH(CH₃)₂], 2.40 [s, br, 2 H, CH(CH₃)₂], 4.11 (br. s, 4 H, OCH₂CH₂O). ³¹P{¹H} **NMR** (161 MHz, CD₂Cl₂): $\delta = 203.5$ (s). ¹³C{¹H} **NMR** (100 MHz, CD₂Cl₂): $\delta = 17.2-18.6$ [CH(CH₃)₂], 33.8 [s, br, CH(CH₃)₂], 66.5 (s, OCH₂CH₂O), 218.0 (br., CO), 223.7 (br., CO).

Compound 3. Yield ≥68 %. Anal. $C_{30}H_{27}MnO_5P_2$ (584.43); C 62.02 (calcd. 61.66); H 4.55 (calcd. 4.66)%. **MS** (referred to the most abundant isotopes): m/z = 584 [M⁺], 583 [M⁺ − H], 500 [M⁺ − 3CO], 527 [M⁺ − 2CO − H], 499 [M⁺ − 3CO−H]. **IR** (KBr): $\tilde{v} = 2016$ (m), 1947 (s), 1914 (s) cm^{-1.} ¹**H NMR** (400 MHz, CD₂Cl₂): $\delta = -8.88$ (dt, $^2J_{P,H} = 77.0, ^2J_{P,H} = 14.0$ Hz, 1 H, MnH), 2.04 (m, 2 H, OCH₂CH₂CH₂O), 3.99 (br. s, 4 H, OCH₂CH₂CH₂O), 7.07–7.99 (m, 20 H, Ph). ³¹P{¹H} **NMR** (100 MHz, CD₂Cl₂): $\delta = 173.3$ (br), 176.0 (br). ¹³C{¹H} **NMR** (100 MHz, CD₂Cl₂): $\delta = 32.7$ (br., OCH₂CH₂CH₂O), 59.8–61.5 (OCH₂CH₂CH₂O), 127.3–142.0 (Ph), 212.2 (br., CO), 221.0 (br., CO).

Preparation of cis,mer-[$MnH(CO)_2(L^1)(L')$]; [$L' = P(OMe)_3$ (1a), $P(OEt)_3$ (1b), $PPh(OMe)_2$ (1c), $PPh(OEt)_2$ (1d)]

An excess of the appropriate phosphite or phosphonite ligand was added to a solution of $[MnH(CO)_3(L^1)]$ (0.50 mmol) in toluene (15 mL) in a 1:3 molar ratio. The reaction mixture was irradiated with UV light for about 6 h. The solvent was removed under reduced pressure to give an oil, which was treated with methanol or ethanol (3 mL), depending on the *OR* group, to afford a colourless product. The solid was filtered off, washed with ethanol or methanol, dried under vacuum, and recrystallized from a 2:10 (v/v) CH₂Cl₂/MeOH (EtOH) solution by slow evaporation of the solvent.

Compound 1a: Yield \geq 49 %. Anal. C₃₁H₃₄MnO₇P₃ (666.47); C 55.31 (calcd. 55.87); H 5.22 (calcd. 5.14)%. **MS** (referred to the most abundant isotopes): $m/z = 666 [M^+]$, 486 $[M^+ - P(OMe)_3 - 2CO]$. **IR** (KBr): $\tilde{v} = 1930$ (s), 1869 (s) cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = -7.32$ (br. m, 1 H, MnH), 3.23 (d, ³*J*_{H,P} = 11.1 Hz, 9 H, OCH₃), 4.05 (m, 4 H, OCH₂CH₂O), 7.10–7.80 (m, 20 H, Ph). ³¹P{¹H} **NMR** (161 MHz, CD₂Cl₂) (See Scheme 2 for labelling): $\delta = 180.2$ (br. m, P_A, P_B), 195.5

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(br. s, P_C). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): $\delta = 51.3$ (s, OCH₃), 65.8 (s, OCH₂CH₂O), 127.2–148.0 (Ph), 225.6 (br. m, CO).

Compound 1b: Yield ≥47 %. Anal. $C_{34}H_{40}MnO_7P_3$ (708.55); C 57.27 (calcd. 57.64); H 5.70 (calcd. 5.69)%. **MS** (referred to the most abundant isotopes): $m/z = 708 [M^+]$, 486 $[M^+ - P(OEt)_3 - 2CO]$. **IR** (KBr): $\tilde{\nu} = 1931$ (s), 1869 (s) cm⁻¹. ¹**H NMR** (400 MHz, CD₂Cl₂): $\delta = -7.27$ (dt, ² $J_{P,H} = 58.5$, 49.9 Hz, 1 H, Mn*H*), 0.96 (t, ³ $J_{H,H} = 6.80$ Hz, 9 H, OCH₂CH₃), 3.62 (m, 6 H, OCH₂CH₃), 4.10 (m, 4 H, OCH₂CH₂O), 7.00–8.00 (m, 20 H, Ph). ³¹**P**{¹**H**} **NMR** (161 MHz, CD₂Cl₂) (See Scheme 2 for labelling): $\delta = 180.9$ (m, P_A, P_B), 189.8 (m, P_C). ¹³C{¹**H**} **NMR** (100 MHz, CD₂Cl₂): $\delta = -16.1$ (s, OCH₂CH₃), 60.2 (s, OCH₂CH₃), 65.7 (s, OCH₂CH₂O), 127.0–146.6 (Ph), 225.7 (m, CO).

Compound 1c: Yield ≥48 %. Anal. $C_{36}H_{36}MnO_6P_3$ (712.54); C 60.55 (calcd. 60.68); H 5.19 (calcd. 5.09)%. **MS** (referred to the most abundant isotopes): $m/z = 712 [M^+]$, 486 $[M^+ - PPh(OMe)_2 - 2CO]$. **IR** (KBr): $\tilde{v} = 1932$ (s), 1874 (s), 1831 (m) cm⁻¹. ¹**H NMR** (400 MHz, CD₂Cl₂): $\delta = -6.94$ (dt, ² $J_{P,H} = 50.8$, 56.2 Hz, 1 H, MnH), 3.04 (d, ³ $J_{H,P} = 10.9$ Hz, 3 H, OCH₃), 3.07 (d, ³ $J_{H,P} = 11.0$ Hz, 3 H, OCH₃), 3.50–4.40 (m, 4 H, OCH₂CH₂O), 7.10–7.93 (m, 25 H, Ph). ³¹**P**{¹**H**} **NMR** (161 MHz, CD₂Cl₂) (See Scheme 2 for labelling): $\delta = 179.9$ (m, P_A, P_B), 208.6 (m, P_C). ¹³C{¹**H**} **NMR** (100 MHz, CD₂Cl₂): $\delta = 51.4$ (s, OCH₃), 65.4 (s, OCH₂CH₂O), 126.9–132.3 (Ph), 141.3–146.2 (Ph), 225.2 (m, CO).

Compound 1d: Yield ≥45 %. Anal. $C_{38}H_{40}MnO_6P_3$ (740.59); C 61.58 (calcd. 61.63); H 5.38 (calcd. 5.44)%. **MS** (referred to the most abundant isotopes): $m/z = 740 [M^+]$, 486 $[M^+ - PPh(OEt)_2 - 2CO]$. **IR** (KBr): $\tilde{v} = 1932$ (s), 1872 (s), 1830 (m) cm⁻¹. ¹**H NMR** (400 MHz, CD₂Cl₂): $\delta = -6.90$ (dt, ² $J_{P,H} = 53.0$, 54.4 Hz, 1 H, MnH), 0.89–0.93 (m, 6 H, OCH₂CH₃), 3.00–4.35 (m, 4 H, OCH₂CH₃; 4 H, OCH₂CH₂O), 7.16–7.80 (m, 25 H, Ph). ³¹P{¹H} **NMR** (161 MHz, CD₂Cl₂) (See Scheme 2 for labelling): $\delta = 179.6-181.1$ (m, P_A, P_B), 202.4 (m, P_C). ¹³C{¹H} **NMR** (100 MHz, CD₂Cl₂): $\delta = 16.0$ (s, OCH₂CH₃), 16.1 (s, OCH₂CH₃), 61.2 (d, ² $J_{C,P} = 4.1$ Hz, OCH₂CH₃), 61.4 (d, ² $J_{C,P} = 8.3$ Hz, OCH₂CH₃), 65.7 (s, OCH₂CH₂O), 127.2–133.0 (Ph), 141.7–143.2 (Ph), 225.5 (m, CO).

Preparation of cis,mer-[$MnH(CO)_2(L^2)(L')$]; [$L' = P(OMe)_3$ (2a), $P(OEt)_3$ (2b), $PPh(OMe)_2$ (2c), $PPh(OEt)_2$ (2d)]

To a solution of $[MnH(CO)_3(L^2)]$ (0.15 g, 0.35 mmol) in toluene (15 mL) was added an excess of the appropriate phosphite or phosphonite ligand in a 1:3 molar ratio. The reaction mixture was irradiated with UV light at room temperature for about 10 h. The solvent was evaporated under reduced pressure and the resulting oil was purified by chromatography on a silica gel column (length 46 cm, diameter 1.5 cm) using a mixture of light petroleum (40–60 °C) and diethyl ether in a 10:5 (v/v) ratio as eluent. The first fraction eluted (35 mL) was evaporated to dryness. The resulting oil was treated with ethanol or methanol (3–5 mL) depending on the OR group. A yellow solid slowly separated from the resulting solution and this was filtered off, dried under vacuum, and recrystallized from a 2:10 (v/v) CH₂Cl₂/ MeOH (EtOH) solution by slow evaporation of the solvent.

Compound 2a: Yield \geq 56 %. Anal. C₁₉H₄₂MnO₇P₃ (530.40); C 42.89 (calcd. 43.03); H 7.56 (calcd. 7.98)%. **MS** (referred to the most abundant isotopes): $m/z = 530 \, [\text{M}^+]$, 350 [M⁺ – P(OMe)₃ – 2CO]. **IR** (KBr): $\tilde{v} = 1925$ (s), 1863 (s) cm⁻¹. ¹**H NMR** (400 MHz, CD₂Cl₂): $\delta = -7.31$ (dt, ²*J*_{P,H} = 59.0, 49.0 Hz, 1 H, Mn*H*), 0.98–1.70 [m, 24 H, CH(CH₃)₂], 2.01–2.60 [m, 4 H, C*H*(CH₃)₂], 3.61 (d, ³*J*_{H,P} = 10.9 Hz, 9 H, OC*H*₃), 3.82–4.51 (m, 4 H, OC*H*₂C*H*₂O). ³¹**P**{¹**H**} **NMR** (161 MHz, CD₂Cl₂)

(See Scheme 2 for labelling): $\delta = 198.1$ (br., P_C), 202.0 (br., P_B), 213.2 (br., P_A). ¹³C{¹H} **NMR** (100 MHz, CD₂Cl₂): $\delta = 15.0-20.0$ [CH(CH₃)₂], 30.1–38.1 [CH(CH₃)₂], 51.5 (d, ²*J*_{C,P} = 3.4 Hz, OCH₃), 65.6 (s, OCH₂CH₂O), 67.0 (s, OCH₂CH₂O), 227.0 (br., CO).

Compound 2b: Yield ≥50 %. Anal. C₂₂H₄₈MnO₇P₃ (572.48) C 45.89 (calcd. 46.16); H 8.03 (calcd. 8.45)%. **MS** (referred to the most abundant isotopes): m/z = 572, [M⁺], 486 [M⁺ − P(OEt)₃ − 2CO]. **IR** (KBr): $\tilde{v} = 1921$ (s), 1860 (s) cm⁻¹. ¹H **NMR** (400 MHz, CD₂Cl₂): $\delta = -7.53$ (br., 1 H, Mn*H*), 1.20 [br, 24 H, CH(CH₃)₂; 9 H, OCH₂CH₃], 2.20 [br, 4 H, CH(CH₃)₂], 4.00 (br, 4 H, OCH₂CH₂O; 6 H, OCH₂CH₃). ³¹P{¹H} **NMR** (161 MHz, CD₂Cl₂): $\delta = 192.0$ (br., P_C), 203.0 (br., P_A), 213.0 (br., P_B). ¹³C{¹H} **NMR** (100 MHz, CD₂Cl₂): $\delta = 15.2$ −20.0 [CH(CH₃)₂; OCH₂CH₃], 30.1−37.0 [CH(CH₃)₂], 60.2 (br. s, OCH₂CH₃), 65.6 (s, OCH₂CH₂O), 66.9 (s,OCH₂CH₂O), 227.1 (m, CO).

Compound 2c: Yield ≥44 %. Anal. C₂₄H₄₄MnO₆P₃ (576.47); C 49.74 (calcd. 50.01); H 8.02 (calcd. 7.69)%. **MS** (referred to the most abundant isotopes): m/z = 576 [M⁺], 486 [M⁺ – PPh(OMe)₂ – 2CO]. **IR** (KBr): $\tilde{v} = 1918$ (s), 1857 (s) cm⁻¹. ¹**H NMR** (400 MHz, CD₂Cl₂): $\delta = -7.31$ (br., 1 H, MnH), 0.98–1.70 [m, 24 H, CH(CH₃)₂], 2.01–2.60 [m, 4 H, CH(CH₃)₂], 3.61 (d, ³J_{H,P} = 10.9 Hz, 9 H, OCH₃), 3.82–4.51 (m, 4 H, OCH₂CH₂O), 6.8–8.0 (m, 5 H, Ph). ³¹P{¹H} **NMR** (161 MHz, CD₂Cl₂) (See Scheme 2 for labelling): $\delta = 203.5$ (br., P_A, P_B), 210.8 (br., P_C). ¹³C{¹H} **NMR** (100 MHz, CD₂Cl₂): $\delta = 14.8–19.8$ [CH(CH₃)₂], 30.4–36.9 [CH(CH₃)₂], 52.0 (br. s, OCH₃), 65.3 (s, OCH₂CH₂O), 67.2 (s, OCH₂CH₂O), 226.3 (m, CO).

Compound 2d: Yield ≥40 %. Anal. $C_{26}H_{48}MnO_6P_3$ (604.52); C 51.58 (calcd. 51.66); H 7.77 (calcd. 8.00)%. **MS** (referred to the most abundant isotopes): m/z = 604 [M⁺], 486 [M⁺ – PPh(OEt)₂ – 2CO]. **IR** (KBr): $\tilde{v} = 1917$ (s), 1859 (s) cm⁻¹. ¹**H NMR** (400 MHz, CD₂Cl₂): $\delta = -7.21$ (br., 1 H, Mn*H*), 0.87–1.39 [m, 24 H, CH(C*H*₃)₂; 6 H, OCH₂C*H*₃], 2.03–2.62 [m, 4 H, C*H*(CH₃)₂], 3.37–4.60 [m, 4 H, OC*H*₂C*H*₂O; 4 H, OC*H*₂C*H*₃], 7.18–7.69 (m, 5 H, Ph). ³¹P{¹H} **NMR** (161 MHz, CD₂Cl₂): (See Scheme 2 for labelling): $\delta = 204.9$ (m, P_A, P_B), 210.7 (m, P_C). ¹³C{¹H} **NMR** (100 MHz, CD₂Cl₂): $\delta = 16.1–20.0$ [CH(CH₃)₂; OCH₂CH₃], 30.1–36.0 [CH(CH₃)₂], 61.4 (br., OCH₂CH₃), 62.9 (br., OCH₂CH₃), 65.7 (br., OCH₂CH₂O), 127.6–132.6 (Ph), 227.2 (m, CO).

X-Ray Crystallographic Analysis

Compounds 2 and 3 were mounted on glass fibers and studied on a Bruker Smart 1000 CCD diffractometer using graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) with corrections for Lorentz and polarization effects. The software SMART [16] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters. SAINT [17] was used to integrate the intensity of reflections and scaling, and SADABS [18] was used for empirical absorption correction.

Both structures were solved and refined with the Oscail program [19] by direct methods and refined by full-matrix least-squares based on F^2 [20]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters – except for those bonded to the metal atom, which were located in the density map and refined isotropically. Details of crystal data and structural refinement are given in Table 4. ORTEP [21] drawings of the compounds, along with the numbering schemes adopted, are shown in Figure 1 and Figure 2.

Table 4.	Crystal	and	structure	refinement	data	for	comp	lexes	2	and	3.
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	2	3
Empirical formula	C ₁₇ H ₃₃ MnO ₅ P ₂	C ₃₀ H ₂₇ MnO ₅ P ₂
Formula weight	434.31	584.40
T/K	293(2)	293(2)
Wavelength /Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_{1}/n$
Unit cell dimensions /Å	a = 14.8564(12)	a = 11.9885(16)
	b = 9.5725(8)	b = 15.811(2)
	c = 16.3296(13)	c = 15.113(2)
	$\beta = 109.783(2)^{\circ}$	$\beta = 104.496(3)^{\circ}$
$V/Å^3$	2185.2(3)	2773.5(6)
Ζ	4	4
$D_{\rm calc}/{\rm g}\cdot{\rm cm}^{-3}$	1.320	1.400
Absorption coefficient /mm ⁻¹	0.772	0.629
F(000)	920	1208
Crystal size /mm	$0.24 \times 0.20 \times 0.18$	$0.38 \times 0.20 \times 0.05$
θ Range for data collection /°	1.6 to 25.0	1.9 to 24.0
Index ranges	$-17 \le h \le 17;$	$-10 \le h \le 13;$
	$-11 \le k \le 10;$	$-15 \le k \le 18;$
	$-19 \le l \le 18$	$-17 \le l \le 17$
Reflections collected	10263	11606
Independent reflections (R_{int})	3737 (0.0360)	4179 (0.0698)
Reflections observed (> 2σ)	2485	2156
Data Completeness /%	97.1	96.0
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	1.0000 and 0.8776	1.0000 and 0.839117
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3737/0/238	4179/0/347
Goodness-of-fit on F^2	0.900	0.799
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0396$	$R_1 = 0.0453$
	$wR_2 = 0.0890$	$wR_2 = 0.0671$
R indices (all data)	$R_1 = 0.0693$	$R_1 = 0.1208$
	$wR_2 = 0.0961$	$wR_2 = 0.0783$
Largest diff. peak and hole /e·Å ⁻³	0.463 and -0.323	0.380 and -0.247

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre as Supplementary Publication No. CCDC-735578 and -735579 for compounds **2** and **3**, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: +44-1223-3-36-0 33; E-Mail for inquiry: fileserv@ccdc. cam.ac.uk].

Conclusion

New hydrido complexes $[MnH(CO)_3L^{1-3}]$ $[L^1 = 1,2$ -bis(diphenylphosphanoxy)ethane (1); $L^2 = 1,2$ -bis(diisopropylphosphanoxy)ethane (2); $L^3 = 1,3$ -bis(diphenylphosphanoxy)propane (3)] were prepared by thermal substitution of two CO ligands of $[MnH(CO)_5]$ with the appropriate bidentate ligand. The spectroscopic features and X-ray analysis (in the case of compounds 2 and 3) indicate a *fac*-octahedral geometry for compounds 1 and 2 and a *mer*-octahedral geometry in the case of compound 3. UV irradiation of toluene solutions of complexes 1 and 2 in the presence of PPh_n(OR)_{3-n} (n = 0, 1; R = Me, Et) led to the replacement of a CO ligand by the corresponding monodentate phosphite or phosphonite ligand to give new hydrido compounds of formulae [MnH(CO)₂(L¹⁻²)(L)] [$L = P(OMe)_3$ (1a–2a); P(OEt)₃ (1b–2b); PPh(OMe)₂ (1c–2c);

PPh(OEt)₂ (1d-2d)]. All of these dicarbonyl compounds are air-stable and their spectroscopic characterization suggests an octahedral arrangement with the three phosphorus donor atoms in a *fac* disposition.

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