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Reactions of $[(CO)_3(P\text{-}P)Mn]_2$ with primary alcohols, where, P-P is dppe $\{Ph_2P(CH_2)_2PPh_2\}$, dppp $\{Ph_2P(CH_2)_3PPh_2\}$, dppb $\{Ph_2P(CH_2)_4PPh_2\}$, dpppe $\{Ph_2P(CH_2)_5PPh_2\}$, dtpe $\{(p\text{-tol})_2P(CH_2)_2P(p\text{-tol})_2\}$, or dcpe $\{(^c hex)_2P(CH_2)_2P(^c hex)_2\}$. Synthesis of *fac*-$(CO)_3$(P-P)MnH and the X-ray structure of *fac*-$(CO)_3$(dtpe)MnH

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Abstract

Treatment of the manganese(tricarbonyl)diphosphine dimers $[(CO)_3(P\text{-}P)Mn]_2$ (where, P-P is dppe $\{Ph_2P(CH_2)_2PPh_2\}$, dppp $\{Ph_2P(CH_2)_3PPh_2\}$, dppb $\{Ph_2P(CH_2)_4PPh_2\}$, dpppe $\{Ph_2P(CH_2)_5PPh_2\}$, dtpe $\{(p\text{-tol})_2P(CH_2)_2P(p\text{-tol})_2\}$, and dcpe $\{(^c hex)_2P(CH_2)_2P(^c hex)_2\}$), with 1-propanol, 1-butanol, 1-pentanol, or 1-hexanol yielded *fac*-$(CO)_3$(dppe)MnH (**1**), *fac*-$(CO)_3$(dppp)MnH (**2**), *fac*-$(CO)_3$(dppb)MnH (**3**), *fac*-$(CO)_3$(dpppe)MnH (**4**), *fac*-$(CO)_3$(dtpe)MnH (**5**), and *fac*-$(CO)_3$(dcpe)MnH (**6**), respectively, and the corresponding aldehydes. Also treatment of $Mn_2(CO)_{10}$ with P-P in 1-propanol, 1-butanol, 1-pentanol, or 1-hexanol yielded the corresponding manganese(I) hydrides (**1**–**6**) and aldehydes. Structural characterization of **5** demonstrates a manganese–hydrogen (Mn–H(1)) bond length of 1.57(3) Å which is in close agreement with the manganese–hydrogen bond length of 1.60(2) Å observed in $(CO)_5MnH$ by neutron diffraction analysis. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Manganese; Diphosphines; Dimers; Hydrides; X-ray

1. Introduction

Reactions of $Mn_2(CO)_{10}$ with dppe $\{Ph_2P(CH_2)_2PPh_2\}$ and dppp $\{Ph_2P(CH_2)_3PPh_2\}$ in 1-propanol [1,2] or 1-pentanol [3] and dppfe {1,1′-bis(diphenylphosphino)ferrocene} in 1-propanol [4] have been reported to yield the corresponding tricarbonyl(diphosphine)-manganese hydrides, *fac*-$(CO)_3$(P-P)MnH in 2–11 h. It has been reported that $[(CO)_3(dppe)Mn]_2$ and $[(CO)_3(dppp)Mn]_2$ are the intermediates in the reactions of $Mn_2(CO)_{10}$ with dppe and $Mn_2(CO)_{10}$ with dppp respectively in 1-pentanol and pentanal is the oxidation product of the alcohol [3]. However, no detailed studies of the reactions of isolated manganese(tricarbonyl)-diphosphine dimers, $[(CO)_3(P\text{-}P)Mn]_2$ with alcohols have been reported. Also it is not known whether the reactions of $[(CO)_3(P\text{-}P)Mn]_2$ with alcohols produce the corresponding aldehydes. In this paper we present results of the reactions of $[(CO)_3(P\text{-}P)Mn]_2$ (where P-P is dppe, dppp, dppb $\{Ph_2P(CH_2)_4PPh_2\}$, dpppe $\{Ph_2P(CH_2)_5PPh_2\}$, dtpe $\{(p\text{-tol})_2P(CH_2)_2P(p\text{-tol})_2\}$, and dcpe $\{(^c hex)_2P(CH_2)_2P(^c hex)_2\}$), with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol. Also presented are the direct and convenient syntheses of the manganese(I) hydrides, *fac*-$(CO)_3$(dppe)MnH (**1**), *fac*-$(CO)_3$(dppp)MnH (**2**), *fac*-$(CO)_3$(dppb)MnH (**3**), *fac*-$(CO)_3$(dpppe)MnH (**4**), *fac*-$(CO)_3$(dtpe)MnH (**5**), and

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fac-$(CO)_3$(dcpe)MnH (**6**), from the reactions of $Mn_2(CO)_{10}$ with the corresponding diphosphines (P-P) in 1-propanol, 1-butanol, 1- pentanol, and 1-hexanol and the X-ray crystal structure of **5**.

2. Results and discussion

2.1. Synthesis and characterizations of the manganese diphosphine dimers $[(CO)_3(P\text{-}P)Mn]_2$

The diphosphine dimers $[(CO)_3(dppm)Mn]_2$ and $[(CO)_3(dppe)Mn]_2$, where dppm = bis(diphenylphosphino)methane, were synthesized previously from the reaction of $Mn_2(CO)_{10}$ with the corresponding diphosphines in boiling benzene [5] according to Eq. (1).

$$Mn_2(CO)_{10} + P\text{-}P \rightarrow [(CO)_3(P\text{-}P)Mn]_2 + 4CO \qquad (1)$$

The diphosphine dimers $[(CO)_3(dppp)Mn]_2$, $[(CO)_3(dppb)Mn]_2$, $[(CO)_3(dpppe)Mn]_2$, $[(CO)_3(dtpe)Mn]_2$, and $[(CO)_3(dcpe)Mn]_2$ were synthesized using the procedure noted above [5]. The yields of the dimers range from 34–41%. Attempts to synthesize the diphosphine dimer, $[(CO)_3(dpph)Mn]_2$, where dpph is 1,6-bis(diphenylphosphino)hexane, were unsuccessful. The diphosphine dimers are extremely air sensitve as reported previously [5]. We have observed that the diphosphine dimers spontaneously decarbonylate to unidentified compounds at room temperature. Therefore, these compounds were stored in sample tubes filled with CO at −25°C. Our attempts to replace benzene with toluene did not yield any diphosphine dimers. Instead, the corresponding hydrides, *fac*-$(CO)_3$(P-P)MnH were obtained. Toluene, xylene and tetrahydrofuran have been used as the solvents as well as the hydrogen source for the preparation of many hydrides [6–8]. For example, the hydride $(CO)_3[\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]MnH$ was synthesized from the reaction of $Mn_2(CO)_{10}$ with two equivalents of $[\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]$ in boiling toluene [6].

The dimers $[(CO)_3(P\text{-}P)Mn]_2$ were characterized by IR spectroscopy only. The IR spectrum of each diphosphine dimer exhibits two $\nu(C{=}O)$ in the region 1900–1850 cm^{-1} which was previously observed in the IR spectrum of $[(CO)_3(dppm)Mn]_2$ and $[(CO)_3(dppe)Mn]_2$ [5]. The intensity of the high frequency band is about two times higher than the intensity of the low frequency band. The ^1H-NMR spectra are not helpful because no functional groups are present in the dimers. We knew that ^{13}C-NMR spectra would be helpful. Unfortunately, the diphosphine dimers did not survive in CH_2Cl_2 over a period of 1–2 h at ambient temperature. Low temperature studies were not performed because ^{13}C-NMR spectra of many manganese carbonyl complexes exhibited a very low intensity broad signal due to carbonyl carbon resonances [2]. Symmetrical dimeric structures $(P\text{-}P)(CO)_3Mn{-}Mn(CO)_3(P\text{-}P)$, with one diphosphine ligand bonded to each metal atom, were proposed for the dimers $[(CO)_3(dppm)Mn]_2$ and $[(CO)_3(dppe)Mn]_2$ [5]. We believe that the dppp, dpppe, dcpe and dtpe dimers have similar symmetrical structures.

2.2. Reactions of $[(CO)_3(P\text{-}P)Mn]_2$, with 1-propanol, 1-butanol, 1-pentanol or 1-hexanol and spectral studies of the hydrides **1–6**

Treatment of $[(CO)_3(P\text{-}P)Mn]_2$ with 1-propanol, 1-butanol, 1-pentanol or 1-hexanol yielded the corresponding hydrides *fac*-$(CO)_3$(P-P)MnH (**1**–**6**) and aldehydes. For example, *fac*-$(CO)_3$(dppb)MnH (**3**) was prepared by allowing $[(CO)_3(dppb)Mn]_2$ to react with boiling 1-propanol, Eq. (2):

$$[(CO)_3(dppb)Mn]_2 + CH_3CH_2CH_2OH$$

$$\rightarrow 2fac\text{-}(CO)_3(dppb)MnH,\ \mathbf{3} + CH_3CH_2CHO \qquad (2)$$

Almost quantitative yields of **1**–**6** were obtained in 0.5–3 h. The times required for the complete conversion of the diphosphine dimers to the corresponding hydrides were less in higher boiling alcohols. For example, all diphosphine dimers were converted completely to the corresponding hydrides in 0.5–0.75 h in 1-hexanol. The hydrides were separated by filtration. A small amount of the corresponding aldehydes was extracted in CH_2Cl_2 by solvent extraction of the filtrate with 1:2 CH_2Cl_2–water.

The hydrides **1** and **2** were characterized previously [1,2]. The IR spectral data for the complexes **3**–**6** are given in Section 3. The IR spectrum of each of the compounds **3**–**6** shows three strong $\nu(C{\equiv}O)$ expected for facial geometry of the terminal carbonyls. The ^1H and ^{13}C-NMR spectral data are given in Section 3. As expected, the ^1H-NMR spectral data of each of compounds **3**–**6** exhibit one triplet for the hydride proton coupled to phosphorus. Similar triplets for the hydride protons were also observed in the ^1H spectra of **1** [9], **2** [2], *fac*-$(CO)_3$(dppe)ReH [10], and *fac*-$(CO)_3$(dppp)ReH [11]. The ^{13}C-NMR spectrum of each of compounds **3**–**6** exhibits two triplets for the two sets of terminal carbonyls as was observed in the corresponding formyl and methoxymethyl complexes [12].

We did not study the mechanism of the reactions of the diphosphine dimers with alcohols. However, we recently observed that the reaction of one equivalent of $Re_2(CO)_{10}$ with two equivalents of dppp in the presence of CO_2 in boiling pentanol/propanol yielded one equivalent of *fac*-$(CO)_3$(dppp)ReH and one equivalent of propyl carbonato complex, *fac*-$(CO)_3$(dppp)ReOC(O)-$OCH_2CH_2CH_3$ [13]. The carbonato complex is formed presumably from the reaction of CO_2 with the intermediate alkoxide, $(CO)_3(dppp)ReOCH_2CH_2CH_3$. The above reaction did not yield any carbonato complex in the absence of CO_2; only two equivalents of the hydride, *fac*-$(CO)_3$(dppp)ReH were obtained. However, the reaction of the manganese diphosphine dimers in the presence of CO_2 in boiling alcohols yielded only the corresponding hydrides; carbonato complexes were not obtained. We believe that the diphosphine dimers, $[(CO)_3(P\text{-}P)Mn]_2$ react with alcohols to yield one equivalent of the corresponding hydrides, *fac*-$(CO)_3$(P-P)MnH and one equivalent of the intermediate alkoxides, *fac*-$(CO)_3$(P-P)$MnOCH_2R$ which β-eliminate the corresponding hydrides, *fac*-$(CO)_3$(P-P)MnH and aldehydes, RCHO, as shown in Eq. (3).

$$\begin{gathered}Mn_2(CO)_{10} + P\text{-}P \rightarrow (P\text{-}P)(CO)_3Mn\text{–}Mn(CO)_3(P\text{-}P)\\ (P\text{-}P)(CO)_3Mn\text{–}Mn(CO)_3(P\text{-}P) + RCH_2OH\\ \rightarrow (P\text{-}P)(CO)_3MnH + RCH_2OMn(CO)_3(P\text{-}P)\\ (P\text{-}P)(CO)_3MnOCH_2R \rightarrow (P\text{-}P)(CO)_3MnH + RCHO\end{gathered} \quad (3)$$

2.3. Direct synthesis of the hydrides *fac*-$(CO)_3$(P-P)MnH (**1**–**6**)

Syntheses of the hydrides **1** and **2** in 1-propanol and 1-pentanol have been reported previously [1–3]. The hydrides **1** and **2** have been prepared by us also in 1-butanol and 1-hexanol. The hydrides **3**–**6** have been synthesized in 1-propanol, 1-butanol, 1-pentanol and 1-hexanol using the same procedures. For example, the hydride *fac*-$(CO)_3$(dppb)MnH (**3**) was prepared from the reaction of dppb with $Mn_2(CO)_{10}$ in boiling 1-propanol, Eq. (4):

$$\begin{gathered}Mn_2(CO)_{10} + 2dppb + CH_3CH_2CH_2OH\\ \rightarrow 2fac\text{-}(CO)_3(dppb)MnH,\ \mathbf{1} + CH_3CH_2CHO\end{gathered} \quad (4)$$

When the reactions were complete, as indicated by the IR spectra of the reaction mixtures, the corresponding hydrides were separated from the mother liquors. The yields of the hydrides **1**–**6** were 60–90% in various alcohols. The aldehydes were separated according to the methods described in Section 2.2. Attempts to synthesize the hydride *fac*-$(CO)_3$(dpph)MnH were unsuccessful.

2.4. X-ray structure of **5**

The conformation and atomic numbering scheme for **5** are shown in Fig. 1. Crystal data for **5** were obtained under the conditions summarized in Table 1. The selected bond lengths and angles for **5** are compiled in Table 2. The Mn atom in **5** is octahedrally coordinated to three carbonyls, dtpe $\{(p\text{-tol})_2P(CH_2)_2P(p\text{-tol})_2\}$, and the hydride. The observed Mn–H(1) bond length of 1.57(3) Å is in excellent agreement with the $(CO)_5$Mn–H bond length of 1.60(2) Å determined by neutron diffraction [14]. The P(1)–Mn–P(2) angle of 85.08(2)° is lower than the corresponding P(1)–Mn–P(2) angle of 95.83(5)° observed in *fac*-$(CO)_3$(dppfe)MnH [4] and similar to the corresponding P(1)–Mn–P(2) angles of 84.81(3)° in *fac*-$(CO)_3$(depe)MnCl [15], 84.4(1)° in *fac*-$(CO)_3$(dppe)MnNCO [16], and 84.6(1)° in *fac*-$(CO)_3$(dppe)$MnOC(O)OCH_3$ [2]. The average Mn–P bond length of 2.263(7) Å is almost equal to the corresponding Mn–P bond lengths of 2.267(2) Å in *mer*, *trans*-$(CO)_3\{P(C_6H_5)_3\}_2$MnH [17] and 2.255(2) Å in *mer*, *trans*-$(CO)_3\{P(CH_3)(C_6H_5)_2\}_2$MnH [18].

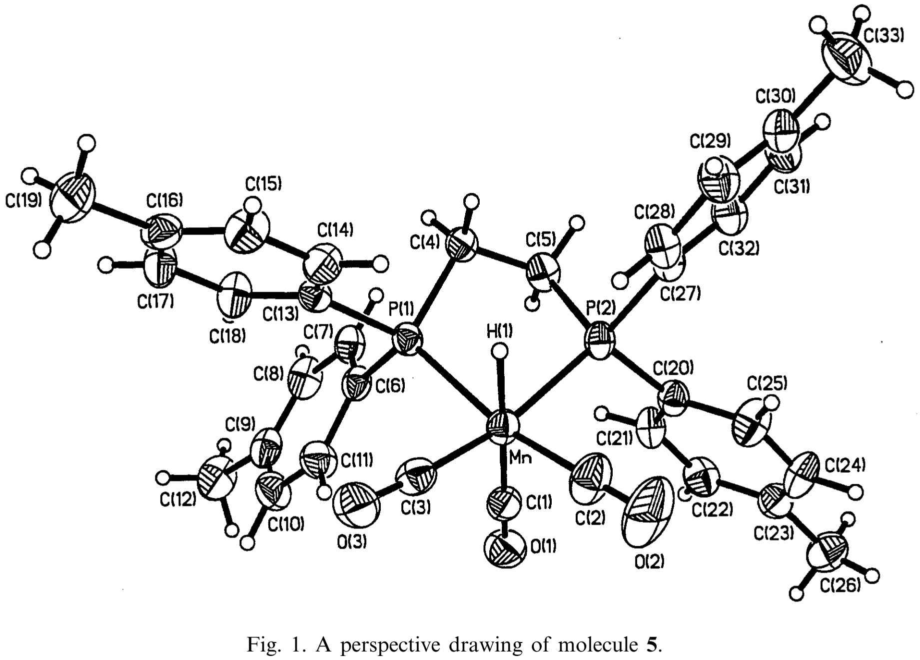

Fig. 1. A perspective drawing of molecule **5**.

Table 1
Summary of crystal data for *fac*-$(CO)_3(dtpe)MnH$ (**5**)

Color and habit	Pale yellow plate	Scan mode	ω, 1° × 530
Crystal size (mm)	$0.12 \times 0.24 \times 0.25$	Limiting indices	$0 \leq h \leq 19$, $0 \leq k \leq 15$, $-27 \leq l \leq 25$
Unit cell parameters		Chemical formula	$C_{33}H_{33}MnO_3P_2$
a (Å)	14.0352(4)	Absorption correction	Gaussian
b (Å)	10.8625(3)	Reflections collected	33411
c (Å)	19.6268(6)	Reflections/R_{int}	8123 (0.0636)
V (Å^3)	2992.2(2)	Reflections observed	6088
Wavelength (Å)	0.71073	No. of variables	360
Crystal system	Orthorhombic	R/wR_2 $[I > 2\sigma(I)]$ [a]	0.0392/0.0790
Space group	*Pna*2(1) (no. 33)	Goodness-of-fit	1.014
Z	4	Refinement method	Full-matrix least-squares on F^2
Diffractometer	Nonius Kappa CCD		
μ(Mo–K$_\alpha$) (mm^{-1})	0.580		
θ range (°)	2.08–30.02		

[a] Definitions of R and wR_2: $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma w_i(|F_o|^2 - |F_c|^2)^2/\Sigma w_i|F_o^2|^2]^{1/2}$.

3. Experimental

All manipulations were carried out under an argon atmosphere and the solvents were dried prior to use. Reagent grade chemicals were used without further purification. $Mn_2(CO)_{10}$, dppe, dppp, dpppe, dtpe, and dcpe were obtained from commercial sources.

IR spectra were recorded on a Perkin–Elmer 1600 series FT-IR instrument. NMR spectra were recorded on a Bruker AC 250 (250.133 MHz, ^1H; 62.896 MHz, ^{13}C) spectrometer. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Microanalyses were conducted by Quantitative Technologies Inc.

3.1. Synthesis and characterization of the manganese diphosphine dimers $[(CO)_3(P\text{-}P)Mn]_2$

To 25 ml of benzene were added 2.56 mmol of $Mn_2(CO)_{10}$ and 5.12 mmol of diphosphines (dppp, dppb, dpppe, dtpe or dcpe). The benzene solutions were refluxed under argon and the reactions were monitored with IR. The reflux times required for complete conversion of $Mn_2(CO)_{10}$ to the dimers, $[(CO)_3(P\text{-}P)Mn]_2$ were 4–6 h. The resultant solutions were allowed to cool to room temperature. Air-sensitive, yellow crystalline dimers were collected by filtration. The crystals were washed with hexane and stored at −35°C in glass tubes filled with CO. The yields of the dimers were 34–41%. Data for $[(CO)_3(dppp)Mn]_2$: m.p. 202–205°C with decomposition. IR (cm^{-1}, CH_2Cl_2): $\nu(C{\equiv}O)$ 1897s and 1859m. Data for $[(CO)_3(dppb)Mn]_2$: m.p. 167–170°C with decomposition. IR (cm^{-1}, CH_2Cl_2): $\nu(C{\equiv}O)$ 1896s and 1857m. Data for $[(CO)_3(dpppe)Mn]_2$: m.p. 180–185°C with decomposition. IR (cm^{-1}, CH_2Cl_2): $\nu(C{\equiv}O)$ 1897s and 1859m. Data for $[(CO)_3(dtpe)Mn]_2$: m.p. 150–155°C with decomposition. IR (cm^{-1}, CH_2Cl_2): $\nu(C{\equiv}O)$ 1900s and 1862m. Data for $[(CO)_3(dcpe)Mn]_2$: m.p. 138–143°C with decomposition. IR (cm^{-1}, CH_2Cl_2): $\nu(C{\equiv}O)$ 1890s and 1850. Elemental analyses were not performed because the dimers were not stable at room temperature.

3.2. Reactions of $[(CO)_3(P\text{-}P)Mn]_2$, with 1-propanol, 1-butanol, 1-pentanol or 1-hexanol and spectral studies of the hydrides **1**–**6**

To 25 ml of primary alcohol (1-propanol, 1-butanol, 1-pentanol or 1-hexanol) was added 0.84–0.93 mmol of the dimers $[(CO)_3(P\text{-}P)Mn]_2$. The slurries were heated at the boiling point of the alcohols. The reactions were

Table 2
Selected bond lengths (Å) and angles (°) for *fac*-$Mn(CO)_3(dtpe)H$ (**5**)

Mn–C(3)	1.801(2)	C(3)–O(3)	1.150(3)
Mn–C(2)	1.803(3)	P(1)–C(6)	1.822(2)
Mn–C(1)	1.812(3)	P(1)–C(13)	1.834(2)
Mn–P(1)	2.2612(7)	P(1)–C(4)	1.835(2)
Mn–P(2)	2.2645(7)	C(4)–C(5)	1.532(3)
Mn–H(1)	1.57(3)	P(2)–C(5)	1.852(2)
C(1)–O(1)	1.144(3)	P(2)–C(20)	1.827(2)
C(2)–O(2)	1.140(3)	P(2)–C(27)	1.828(2)
C(3)–Mn–C(2)	93.17(12)	C(6)–P(1)–C(4)	106.50(11)
C(3)–Mn–C(1)	98.56(11)	C(13)–P(1)–C(4)	104.77(10)
C(2)–Mn–C(1)	96.54(13)	C(6)–P(1)–Mn	116.80(7)
C(3)–Mn–P(1)	88.89(8)	C(13)–P(1)–Mn	118.83(7)
C(2)–Mn–P(1)	167.61(11)	C(4)–P(1)–Mn	108.19(8)
C(1)–Mn–P(1)	95.23(8)	C(5)–C(4)–P(1)	108.7(2)
C(3)–Mn–P(2)	167.61(8)	C(4)–C(5)–P(2)	107.67(14)
C(2)–Mn–P(2)	90.49(9)	C(20)–P(2)–C(27)	102.57(11)
C(1)–Mn–P(2)	92.76(7)	C(20)–P(2)–C(5)	106.08(10)
P(1)–Mn–P(2)	85.08(2)	C(27)–P(2)–C(5)	103.05(12)
C(3)–Mn–H(1)	83.1(12)	C(20)–P(2)–Mn	114.62(8)
C(2)–Mn–H(1)	86.7(12)	C(27)–P(2)–Mn	120.08(8)
C(1)–Mn–H(1)	176.3(12)	C(5)–P(2)–Mn	109.06(8)
P(1)–Mn–H(1)	81.5(12)	C(7)–C(6)–P(1)	125.3(2)
P(2)–Mn–H(1)	85.3(12)	C(11)–C(6)–P(1)	116.0(2)
O(1)–C(1)–Mn	179.4(2)	C(25)–C(20)–P(2)	119.6(2)
O(2)–C(2)–Mn	178.3(3)	C(21)–C(20)–P(2)	121.8(2)
O(3)–C(3)–Mn	176.3(2)	C(28)–C(27)–P(2)	121.5(2)
C(6)–P(1)–C(13)	100.53(10)	C(32)–C(27)–P(2)	120.9(2)

monitored with IR. The reflux times required for complete conversion of the dimers to the hydrides **1**–**6** in 1-propanol were 2.0, 1.5, 2.0, 3.0, 3.0, and 2.5 h respectively. The reflux times required for complete conversion were less in higher boiling alcohols. For example, the dimers were completely converted to the corresponding hydrides in 0.5–0.75 h using 1-hexanol. When the reactions were complete, the mixtures were cooled to 0°C. The hydrides were separated by filtration and the filtrates, which contain the corresponding alcohols, oxidized products of the alcohols, and small amounts of hydrides, were kept aside for further work. The solid hydrides were washed with the corresponding alcohols (2 × 5 ml) and hexane (2 × 5 ml). The yields of the hydrides were 95–98%. The hydrides **1** and **2** were characterized previously. Data for **3**: m.p. 202–205°C. IR (cm^{-1}, CH_2Cl_2): ν(C≡O) 1995vs, 1916s, and 1900s. ^{1}H-NMR (δ, C_6D_6): 7.35 (m, 20H, C_6H_5), 2.50 (m, 8H, $CH_2CH_2CH_2CH_2$), -6.50 (t, J(PH) = 45 Hz, H). ^{13}C-NMR (δ, C_6D_6): 223.4 (t, J(PC) = 7 Hz, 2C≡O), 221.8 (s, br, C≡O), 140.0–127.6 (m, C_6H_5), 33.0 (t, J(PC) = 11 Hz, PCH_2), 23.5 (s, $CH_2\mathit{C}H_2\mathit{C}H_2CH_2$). Anal. Found: C, 65.2; H, 5.2. Calc. for $C_{31}H_{29}MnO_3P_2$: C, 65.7; H, 5.2%. Data for **4**: m.p. 208–210°C with decomposition. IR (cm^{-1}, CH_2Cl_2): ν(C≡O) 1995vs, 1915s, and 1900s. ^{1}H-NMR (δ, C_6D_6): 7.38 (m, 20H, C_6H_5), 2.14–1.33 (m, 10H, $CH_2CH_2CH_2CH_2CH_2$), -6.51 (t, J(PH) = 47 Hz, H). ^{13}C-NMR (δ, C_6D_6): 223.5 (t, J(PC) = 8 Hz, 2C≡O), 221.8 (t, J(PC) = 14 Hz, C≡O), 140.3–129.5 (m, C_6H_5), 33.0 (t, J(PC) = 11 Hz, PCH_2), 23.6 (s, $CH_2\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2CH_2$). Anal. Found: C, 65.6; H, 5.2. Calc. for $C_{32}H_{31}MnO_3P_2$: C, 66.2; H, 5.3%. Data for **5**: m.p.188–190°C. IR (cm^{-1}, CH_2Cl_2): ν(C≡O) 1993vs and 1906vs, br. ^{1}H-NMR (δ, C_6D_6): 7.84–6.89 (m, 16H, $-C_6H_4-$), 2.50 (m, 8H, $CH_2CH_2CH_2CH_2$), 1.98 (s, 12H, CH_3), -7.59 (t, J(PH) = 47 Hz, H). ^{13}C-NMR (δ, C_6D_6): 225.5 (t, J(PC) = 6 Hz, 2C≡O), 221.8 (t, J(PC) = 12 Hz, C≡O), 140.1/139.9 (s, *p*, C_6H_5), 134.9–134.08 (m, *ipso*, C_6H_5), 133.2/131.6 (t, J(PC) = 5/5 Hz, *o*, C_6H_5), 129.6/129 (t, J(PC) = 5/5 Hz, *m*, C_6H_5), 29.9 (t, J(PC) = 22 Hz, PCH_2), 21.1 (s, CH_3). Anal. Found: C, 66.4; H, 5.7. Calc. for $C_{33}H_{33}MnO_3P_2$: C, 66.7; H, 5.6%. Data for **6**: m.p. 161–163°C. IR (cm^{-1}, toluene): ν(C≡O) 1985vs, 1907s, and 1888s. ^{1}H-NMR (δ, C_6D_6): 2.36 (s, br, 4 H, $-PCH_2CH_2P-$), 1.87–0.97 (m, 44 H, $-\underline{CHCH_2CH_2CH_2CH_2CH_2}$), -8.87 (t, J(PH) = 48 Hz, H). ^{13}C-NMR (δ, C_6D_6): 226.1 (t, J(PC) = 5 Hz, 2C≡O), 223.9 (s, br, C≡O), 40.0–26.3 (m, $-C_6H_{11}$), 23.8 (t, J(PC) = 19 Hz, PCH_2). Anal. Found: C, 60.9; H, 8.8. Calc. for $C_{29}H_{49}MnO_3P_2$: C, 61.8; H, 8.8%.

About 0.5 ml of the filtrates, which contain the corresponding alcohols, oxidized products of the alcohols, and small amount of hydrides, were transferred into small test tubes and the solvents were removed by passing a stream of argon through the solutions. The oily residues in the test tubes were dissolved in CH_2Cl_2. The IR spectra of the CH_2Cl_2 solutions of the oily residues confirmed the presence of the corresponding aldehydes and manganese hydrides in the filtrates; the ν(C=O) of the aldehydes formed from the oxidation of the corresponding alcohols match with the ν(C=O) of the commercially available aldehydes. For example, the IR spectra of the CH_2Cl_2 solutions of propanal, 1-butanal, 1-pentanal, and 1-hexanal obtained from both sources exhibit ν(C=O) at 1732, 1724, 1726, and 1723 cm^{-1} respectively. Now the rest of the filtrates were concentrated to about 2–3 ml and then cooled to 0°C. At this time some solids were separated from the concentrated, cooled filtrates. A small amount of the corresponding aldehydes were extracted in CH_2Cl_2 by solvent extractions of the filtrates with 15 ml of 1:2 CH_2Cl_2–water.

3.3. Direct synthesis of the hydrides *fac*-$(CO)_3$(P-P)MnH (**1**–**6**)

Mixtures of 2.564 mmol of $Mn_2(CO)_{10}$, 5.128 mmol of diphosphines (dppb, dpppe, dtpe, or dcpe), and 25 ml of alcohols (1-propanol, 1-butanol, 1-pentanol, or 1-hexanol) and mixtures of 2.564 mmol of $Mn_2(CO)_{10}$, 5.128 mmol of diphosphines (dppe or dppp) and 25 ml of alcohols (1-butanol or 1-hexanol) were heated to reflux and the reactions were monitored with IR periodically. The reflux times required for complete conversion of $Mn_2(CO)_{10}$ to the corresponding hydrides **3**–**6** in 1-propanol were 2.0, 3.0, 3.0, and 2.5 h respectively. The reflux times required for complete conversion were less in higher boiling alcohols. For example, the diphosphine dimers were completely converted to the corresponding hydrides in 0.5–1.0 h using 1-hexanol. The reflux times required for complete conversion of $Mn_2(CO)_{10}$ to the hydrides **1** and **2** were 2.5–3.0 h in 1-butanol and 0.5–0.75 h in 1-hexanol. When the reactions were complete, the mixtures were cooled to 0°C. The hydrides were separated by filtration and the filtrates, which contain the corresponding alcohols, oxidized products of the alcohols, and small amount of hydrides, were kept aside for further work. The solid hydrides were washed with the corresponding alcohols (2 × 5 ml) and hexane (2 × 5 ml). The yields of the hydrides were 60–90%. The characterizations of the hydrides have been reported in Section 3.2. Also the procedure for the detection of the aldehydes in the filtrates have been discussed in Section 3.2 above.

3.4. X-ray crystal structure of *fac*-$(CO)_3$(dtpe)MnH (**5**)

Crystals of **5** were grown from CH_2Cl_2–hexane at -5°C. Data were collected on a Nonius KappaCCD diffractometer and corrected for Lorentz-polarization and absorption effects. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL (version 5). The non-hydrogen atoms were refined anisotropically and the hydrogens were assigned isotropic displacement coefficients $U(\mathrm{H}) = 1.2U(\mathrm{C})$ or $1.5U(\mathrm{C}_{methyl})$ and allowed to ride on their respective carbons. The hydride atom H(1) was located in a difference-Fourier map, and its coordinates and isotropic displacement coefficient were free to vary. Convergence gave $R = 0.0392$ for 6088 reflections with $F \geq 4\sigma(F)$. Additional crystallographic data and results are summarized in Tables 1 and 2.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 138490 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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