The synthesis and reactions of Mn and Re formyl complexes, *fac*-(P–P)M(CO)$_3$CHO. The X-ray structure of *fac*-(dppp)Mn(CO)$_3$CH$_2$OCH$_3$

Santosh K. Mandal, Jeanette A. Krause and Milton Orchin

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 (USA)

(Received January 6, 1993; in revised form June 25, 1993)

Abstract

Treatment of the salts *fac*-[(P–P)M(CO)$_4$][BF$_4$] (M = Mn, Re; P–P = dppe, dppp) with NaBH$_4$ gives the corresponding formyl complexes, *fac*-(P–P)M(CO)$_3$CHO in excellent yield. Solutions of these formyls undergo spontaneous loss of CO to give the corresponding hydrides, *fac*-(P–P)M(CO)$_3$H. On treatment with methyl triflate or protic acids the formyls undergo expected disproportionation reactions; the X-ray crystal structure determination of one of the products, *fac*-(dppp)Mn(CO)$_3$CH$_2$OCH$_3$, is reported.

Key words: Manganese; Rhenium; Formyl; Crystal structure

1. Introduction

Transition metal formyls are postulated intermediates in the transition metal carbonyl-catalyzed homogeneous hydrogenation of carbon monoxide [1] as well as in the important heterogenous Fischer–Tropsch reaction where surface formyls may play an important role [2]. Our earlier work [3], on the reaction of various nucleophiles with the cationic salts [(P–P)M(CO)$_4$][BF$_4$] has now been extended to the reaction of them with sodium borohydride leading to the efficient preparation of the Mn and Re formyls *fac*-(P–P)M(CO)$_3$CHO. These formyls undergo disproportionation reactions in the presence of protic acids. In benzene solution they undergo spontaneous decarbonylation to the corresponding hydrides. The X-ray structure of the methoxymethyl complexes, *fac*-(dppp)Mn4-(CO)$_3$ CH$_2$OCH$_3$, derived from the corresponding formyl in a one step reaction is reported.

2. Results and discussion

2.1. Preparation and characterization of manganese and rhenium formyls

Solutions of the cationic salts **1** in CH$_3$CN/CH$_3$OH/H$_2$O react with NaBH$_4$ to give the formyls **2** in high yield, eqn. (1):

$$\underset{\mathbf{1}}{[(\text{P–P})\text{M(CO)}_4][\text{BF}_4]} + \text{NaBH}_4 \longrightarrow \underset{\mathbf{2}}{fac\text{-(P–P)M(CO)}_3\text{CHO}} + \text{NaBF}_4 + \text{BH}_3 \quad (1)$$

a, P–P = dppe; M = Mn
b, P–P = dppp; M = Mn
c, P–P = dppe; M = Re
d, P–P = dppp; M = Re

The IR spectra of all the complexes **2a–d** show, as expected [4], one medium intensity band for the carbonyl of the formyl group in the region 1595–1573 cm^{-1} and the three strong terminal carbonyl stretching bands consistent with *fac*-geometry. Also all of them show a triplet for the formyl proton in the ^{1}H NMR spectra in

---

Correspondence to: Professor M. Orchin.

0022-328X/94/$7.00
SSDI 0022-328X(93)24007-R

the range δ 16.63–14.35. This triplet is a consequence of coupling with the two equivalent phosphorus atoms which are both *cis* to the formyl group in the *fac*-configuration. However, in each of the spectra of the manganese complexes **2a** and **2b** there is, in addition, a low intensity downfield doublet of doublets. These additional resonances are consistent with the presence of a small quantity (about 4–5%) of the isomeric *mer* isomer in which the formyl group is *cis* to one phosphorus but *trans* to the other. Unfortunately we were unable either to purify our sample or to isolate the suspected isomer owing to handling difficulties which are characteristic of most formyl complexes. The formyl carbon resonances in the ^{13}C NMR spectra of all the complexes were observed in the δ 263.5–286.6 range, highly deshielded as expected [4a,b].

TABLE 1. Crystallographic data for *fac*-(dppp)Mn(CO)$_3$CH$_2$OCH$_3$ [a]

$C_{32}H_{29}MnO_4P_2$	FW = 594.4
Crystal system: orthorhombic	Crystal size: 0.40 × 0.40 × 0.55 mm^3
space group: *Pbca*	Reflections collected = 7530
$a = 17.994(4)$ (Å)	Reflections merged (R_m) = 6860
$b = 16.483(2)$ (Å)	Reflections observed = 2367
$c = 20.021(3)$ (Å)	$F(000) = 2464$
$V = 5938(2)$ (Å^3)	$F \geq 4\sigma(F)$
$Z = 8$	No. of variables = 352
$d_{calcd} = 1.330$ mg m^{-3}	$R = 0.0723$
μ (Mo Kα) = 0.565 mm^{-1}	$R_w = 0.0747$
	Goodness of fit = 1.36

[a] Details of measurement: radiation: Mo Kα ($\lambda = 0.71073$ Å), monochromator; highly oriented graphite crystal, temperature: 296 K, scan type: $2\theta-\theta$, 2θ range: 3.5–55°, scan speed: 2.00–14.65° min^{-1} in ω, scan range (ω): 0.60 plus Kα separation, R: $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, R_w: $[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ where $w = [\sigma^2(F)+|g|F^2]^{-1}$ and $g = 0.0006$.

2.2. *Decarbonylation of the formyl complexes*

All the formyl complexes slowly lose carbon monoxide in solution to give the corresponding hydrides, *fac*-(P–P)M(CO)$_3$H. The times for half decomposition for the Mn formyls **2a** and **2b** were about 15 and 16 h and for the Re formyls **2c** and **2d** about 8 and 24 h, respectively. In an attempt to secure evidence for a radical mechanism, 10% of the radical initiator AIBN was added. However, it produced no change in the rate, contrary to what has been observed in an related example [5]. A second mechanism for the decarbonylation of transition metal formyls involves prior dechelation of one of the phosphorus atoms [6]. Careful monitoring of the decarbonylation reaction by ^1H NMR of our formyls failed to give evidence for this well-documented proposal. We are inclined to favor a third suggested mechanism for the decarbonylation which postulates a unimolecular reaction and a three-centered transition state involving the metal, and the carbon and hydrogen atoms of the formyl group [7]. The mechanism for the decarbonylations remains controversial and we have not pursued the subject.

2.3. *Reactions for formyl complexes with electrophiles*

The reaction of CH_2Cl_2 solutions of the formyl complexes **2a** and **2b** with HBF_4, HOTf, HOTs, or

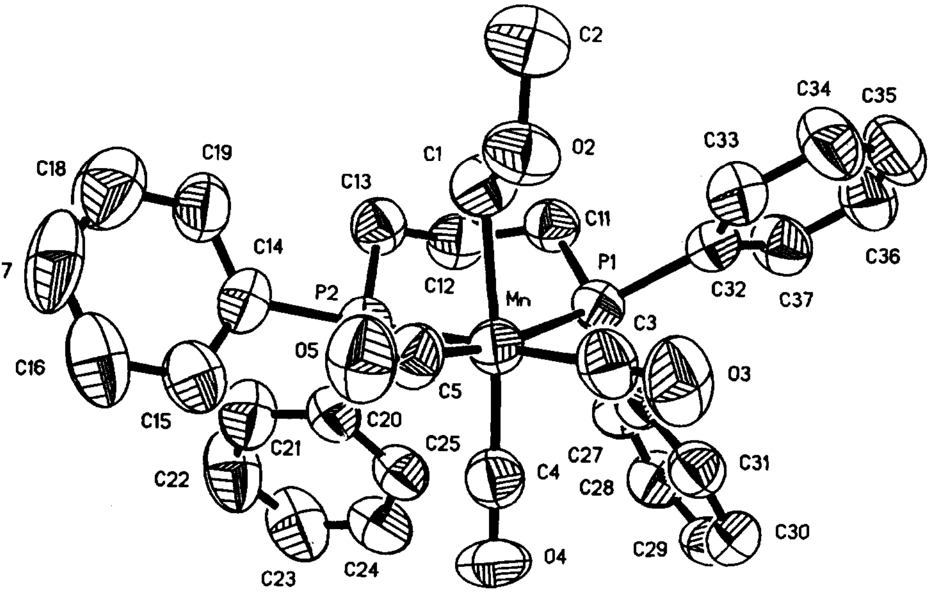

Fig. 1. Perspective drawing of molecule **4b**, *fac*-(dppp)Mn(CO)$_3$CH$_2$OCH$_3$.

CF_3CO_2H yields the corresponding methyl complexes **3a** (P–P) = dppe, and **3b** (P–P) = (dppp), corresponding to eqn. (2):

$$fac\text{-}(P\text{–}P)Mn(CO)_3CHO + H^+ \longrightarrow$$

$$fac\text{-}(P\text{–}P)Mn(CO)_3CH_3 + [(P\text{–}P)Mn(CO)_4]^+ \quad (2)$$

3

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *fac*-(dppp)Mn(CO)$_3$CH$_2$-OCH$_3$ (**4b**)

Atom	x	y	z	U_{eq} [a]
Mn	1098(1)	3215(1)	1980(1)	57(1)
P(1)	1964(2)	3427(2)	2826(1)	58(1)
P(2)	1937(2)	3684(2)	1191(1)	58(1)
O(2)	39(4)	4559(5)	2292(4)	81(3)
O(3)	−5(5)	2605(6)	2950(4)	103(4)
O(4)	1397(5)	1493(4)	1681(4)	94(4)
O(5)	−151(4)	3255(5)	1038(4)	92(3)
C(1)	813(5)	4488(6)	2098(5)	71(4)
C(2)	−122(6)	3561(7)	2461(7)	92(5)
C(3)	441(7)	2864(7)	2594(6)	73(4)
C(4)	1316(6)	2172(7)	1803(5)	71(4)
C(5)	352(6)	3228(7)	1388(5)	65(4)
C(11)	2635(6)	4263(6)	2711(5)	66(4)
C(12)	3025(6)	4338(6)	2032(5)	72(4)
C(13)	2518(6)	4550(6)	1459(5)	69(4)
C(14)	1493(6)	4031(7)	417(5)	67(4)
C(15)	1161(6)	3477(8)	−4(5)	79(4)
C(16)	791(6)	3733(10)	−570(6)	94(6)
C(17)	746(7)	4553(12)	−711(7)	113(7)
C(18)	1065(8)	5090(10)	−296(8)	113(7)
C(19)	1429(7)	4850(8)	263(6)	85(5)
C(20)	2676(5)	3022(6)	875(5)	64(4)
C(21)	3028(6)	3187(8)	274(6)	88(5)
C(22)	3628(7)	2741(10)	69(7)	110(7)
C(23)	3897(8)	2133(9)	463(7)	105(6)
C(24)	3578(6)	1965(7)	1063(6)	84(5)
C(25)	2960(6)	2399(6)	1269(5)	70(4)
C(26)	2531(6)	2550(6)	3054(5)	61(3)
C(27)	3299(6)	2517(7)	3016(6)	73(4)
C(28)	3675(6)	1830(8)	3224(5)	80(4)
C(29)	3305(7)	1182(7)	3464(6)	78(5)
C(30)	2547(7)	1202(7)	3512(5)	76(4)
C(31)	2160(6)	1877(7)	3295(5)	69(4)
C(32)	1610(6)	3701(6)	3657(5)	63(4)
C(33)	899(7)	4015(7)	3760(6)	78(5)
C(34)	651(8)	4231(8)	4392(6)	94(5)
C(35)	1109(9)	4127(8)	4937(6)	97(6)
C(36)	1804(9)	3845(8)	4854(5)	96(6)
C(37)	2061(7)	3630(6)	4227(5)	77(4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Selected bond lengths (Å) and angles (°) for *fac*-(dppp)Mn(CO)$_3$CH$_2$OCH$_3$ (**4b**)

Mn–P(1)	2.328(3)	Mn–P(2)	2.137(3)
Mn–C(1)	2.173(10)	Mn–C(3)	1.802(12)
Mn–C(4)	1.797(12)	Mn–C(5)	1.791(10)
P(1)–C(11)	1.846(10)	P(1)–C(26)	1.828(10)
P(1)–C(32)	1.839(10)	P(2)–C(13)	1.849(11)
P(2)–C(14)	1.835(11)	P(2)–C(20)	1.831(10)
O(2)–C(1)	1.451(12)	O(2)–C(2)	1.395(14)
O(3)–C(3)	1.154(14)	O(4)–C(4)	1.156(14)
O(5)–C(5)	1.145(13)	C(11)–C(12)	1.535(14)
C(12)–C(13)	1.508(14)		
P(1)–Mn–P(2)	90.5(1)	P(1)–Mn–C(1)	86.2(3)
P(2)–Mn–C(1)	84.6(3)	P(1)–Mn–C(3)	89.5(4)
P(2)–Mn–C(3)	179.2(4)	C(1)–Mn–C(3)	94.6(4)
P(1)–Mn–C(4)	98.1(3)	P(2)–Mn–C(4)	92.5(3)
C(1)–Mn–C(4)	174.8(4)	C(3)–Mn–C(4)	88.3(5)
P(1)–Mn–C(5)	168.9(4)	P(2)–Mn–C(5)	92.0(3)
C(1)–Mn–C(5)	83.3(4)	C(3)–Mn–C(5)	87.9(5)
C(4)–Mn–C(5)	92.5(5)	Mn–P(1)–C(11)	117.4(3)
Mn–P(1)–C(26)	115.9(3)	C(11)–P(1)–C(26)	104.8(5)
Mn–P(1)–C(32)	117.6(4)	C(11)–P(1)–C(32)	98.9(5)
C(26)–P(1)–C(32)	99.3(5)	Mn–P(2)–C(13)	115.4(3)
Mn–P(2)–C(14)	113.3(4)	C(13)–P(2)–C(14)	104.4(5)
Mn–P(2)–C(20)	120.6(3)	C(13)–P(2)–C(20)	98.7(5)
C(14)–P(2)–C(20)	102.2(5)	C(1)–O(2)–C(2)	110.0(8)
Mn–C(1)–O(2)	109.6(6)	Mn–C(3)–O(3)	174.8(10)
Mn–C(4)–O(4)	174.6(10)	Mn–C(5)–O(5)	176.0(9)
P(1)–C(11)–C(12)	118.0(7)	C(11)–C(12)–C(13)	114.6(8)
P(2)–C(13)–C(12)	112.5(7)	P(2)–C(14)–C(15)	119.9(9)
P(2)–C(14)–C(19)	121.8(8)	P(2)–C(20)–C(21)	120.9(8)
P(2)–C(20)–C(25)	120.7(8)	P(1)–C(26)–C(27)	125.1(8)
P(1)–C(26)–C(31)	116.9(8)	P(1)–C(32)–C(33)	122.9(8)
P(1)–C(32)–C(37)	121.0(8)		

Treatment of the formyl complexes with *p*-toluenesulfonic acid (HOTs) in methanol solution gives methoxymethyl complexes, **4** (eqn. (3)):

$$fac\text{-}(P\text{–}P)M(CO)_3CHO + HOTs + CH_3OH \longrightarrow$$

$$fac\text{-}(P\text{–}P)M(CO)_3CH_2OCH_3$$

4

$$+ [(P\text{–}P)M(CO)_4][OTs] \quad (3)$$

(**4a**, M = Mn, P–P = dppe; **4b**, M = Mn, P–P = dppp; **4c**, M = Re; P–P = dppe; **4d**, M = Re, P–P = dppp)

Treatment of the formyl complexes with the methylating agent, methyl triflate, also gave the same methoxymethyl complexes. These conversions are now well understood [8].

2.4. *X-ray structure of the methoxymethyl complex, 4b*

Although methoxymethyl complexes are not uncommon only crystal structures of three of them have been determined [9] and none of these involve a Mn atom.

Figure 1 shows the molecular structure of **4b**. The crystal data were obtained under the conditions summarized in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are given in Table 2 and selected bond lengths and angles are compiled in Table 3. The molecule consists of a Mn atom octahedrally coordinated to three terminal carbonyl groups, a methoxymethyl ligand, and a chelating dppp ligand. The methoxymethyl ligand is trans to a carbonyl while the remaining two carbonyls and the dppp ligand occupy *cis* positions. The Mn–CH_2 bond length of 2.173(10) Å is within the range for a Mn–C single bond and close to the average Mn–CH_2 bond length of 2.152(4) Å in $(PPh_3)(CO)_4Mn–CH_2–O–Mn–CH_2–Mn(CO)_4(PPh_3)$ [10] considered by us to be the closest model whose structure has been determined. The H_2C–O bond length of 1.451(12) Å or our **4b** is similar to a conventional sigma C–O bond length of 1.43 Å and the average (1.436 Å) of the two H_2C–O bonds of the above di-Mn complex. The angles involving the terminal CO's are all in the range 174.6–176.0°. The Mn–C–O angle of 109.6(6)° is almost identical to the average (109.8(3)°) of the two similar angles in the above di-Mn model compound.

3. Experimental details

All manipulations and reactions were carried out in an argon atmosphere and with solvents dried prior to use. Reagent grade chemicals were used without further purification as were the compounds $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) purchased from either Pressure Chemicals or Strem Chemical. *p*-Toluenesulfonic acid monohydrate, $NaBH_4$, $HBF_4 \cdot Et_2O$, HOTf, HOTFA, and CH_3OTf were purchased from Aldrich Chemical. Literature procedures were used to prepare the salts, $[(P–P)M(CO)_4][BF_4]$ [3] and the hydrides, *fac*-$(P–P)M(CO)_3H$ [11]. The IR spectra were determined on a Perkin-Elmer 1600 series FT-IR instrument. NMR spectra were obtained on a Bruker AC-250 spectrometer (250.133 MHz ^1H; 101.256 MHz ^{31}P; 62.896 MHz ^{13}C). Melting points were obtained with a Mel-Temp apparatus and are uncorrected. Microanalysis were carried out by Galbraith Laboratories.

3.1. General procedure for the preparation of fac-(P–P)M(CO)$_3$CHO (2a–d)

A solution of 1–3 mmol $[(P–P)M(CO)_4][BF_4]$ in 120 ml of acetonitrile/methanol/water (1 : 20 : 1) was cooled to 0°C and a slight excess of one mol $NaBH_4$ per mol of complex was added with stirring. After about 5 min the solid which separated was filtered and vacuum dried giving **2a–d** in very high yield. This procedure is based on similar syntheses reported earlier [12]. Data for **2a**: yield, 94%; pale yellow powder, m.p. 132–134°C with decomposition, with the color changing to brown and then deep red and the evolution of gas. Satisfactory analysis could not be obtained since in the time required for sample handling and mailing, the compound slowly decomposed at room temperature. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2001s, 1921s, br, and $\nu(C=O)$ 1598 m. ^1H NMR (δ, C_6D_6, 5°C): 15.72 (dd, *J* 11 Hz, 1 Hz, CHO, *mer*, *cis*), 14.39 (t, *J*, 1 Hz, CHO, *fac*), [integration ratio of the formyl protons, *mer* : *fac* = 1 : 25], 7.51 (m, 20 H, C_6H_5), 2.05 (m, 4 H, CH_2). ^{13}C NMR (δ, C_6D_6, 5°C): 278.2 (t, *J* 20 Hz, C=O), 223.1 (s, br, 2 C≡O), 217.6 (t, *J* 15 Hz, *C*≡O), 137.5–128.6 (m, C_6H_5), 27.0 (t, *J* 21 Hz, CH_2). ^{31}P (δ, C_6D_6): 82.7 (s). Data for **2b**: yield, 96%; pale yellow powder, m.p. 137–140°C with decomposition, color changes and behavior similar to **2a**. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2004s, 1934s, 1915s, and $\nu(C=O)$ 1588 m. ^1H NMR (δ, C_6D_6, 5°C): 15.40 (t, *J* 3 Hz, CHO, *fac*), 14.65 (dd, *J* 10 Hz, 1 Hz, CHO, *mer, cis*), [integration ratio of the formyl protons, *mer* : *fac* = 1 : 25], 7.40 (m, 20 H, C_6H_5), 2.35 (m, 6 H, CH_2). ^{13}C NMR (δ, C_6D_6, 5°C): 286.6 (t, *J* 19 Hz, C=O), 221.1 (t, *J* 7 Hz 2 C≡O), 218.1 (t, *J* 14 Hz, C≡O), 137.8–127.6 (m, C_6H_5), 24.9 (t, *J* 12 Hz, CH_2), 19.5 (s, CH_2). ^{31}P (δ, C_6D_6): 40.0 (s). Data for **2c**: yield, 92%; pale yellow powder, m.p. 139–143°C with decomposition and lightening of color. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2013s, 1928s, br, and $\nu(C=O)$ 1582 m. ^1H NMR (δ, C_6D_6, 5°C): 15.75 (t, *J* 1 Hz, CHO), 7.52 (m, 20 H, C_6H_5), 2.35 (m, 4 H CH_2). ^{13}C NMR (δ, C_6D_6, 5°C): 263.5 (t, *J* 12 Hz, C=O), 196.4 (dd, *J* 49 Hz, 10 Hz, 2 C≡O), 188.8 (s, br, C≡O), 139.4–128.5 (m, C_6H_5), 27.2 (m, CH_2). ^{31}P (δ, C_6D_6): 38.1(s). Anal. Found: C, 51.1; H, 3.6. $C_{30}H_{25}O_4P_2Re$ calcd: C, 51.6; H, 3.6. Data for **2d**: yield; 96%; pale yellow powder, m.p. 170–174°C with decomposition and lightening of color. ^1H NMR (δ, C_6D_6, 5°C): 16.63 (t, *J* 1 Hz, CHO), 7.47 (m, 20 H, C_6H_5), 2.85 (m, 6H CH_2). ^{13}C NMR (δ, C_6D_6, 5°C): 270.6 (t, *J* 11 Hz, C=O), 196.6 (dd, *J* 52 Hz, 6 Hz, 2 C≡O), 193.8 (t, *J* 18 Hz, C≡O) 136.9–127.6 (m, C_6H_5), 24.3 (t, *J* 15 Hz, CH_2), 19.5 (s, CH_2), ^{31}P NMR (δ, C_6D_6): −6.3(s). Anal: Found: C, 52.8; H, 4.0. $C_{31}H_{27}O_4P_2Re$ calcd: C, 52.3; H, 3.8.

3.2. Decarbonylation of the formyl complexes 2a–d

Solution of formyls **2a–d** (approximately 0.02 g, 0.03 mmol) in 0.40 ml of C_6D_6 were placed in an NMR tube and the progress of the decarbonylations was monitored by periodic observations of the ^1H NMR spectra. In the early stages of the decarbonylations of the Mn formyls **2a** and **2b** (10 min) traces of *mer*, *cis*-unconverted formyl remained but after two days only the hydrides were present [11], *fac*-(dppe)Mn(CO)$_3$H: δ −7.82 (t) and *fac*-(dppp)Mn(CO)$_3$H: δ −6.50 (t). The solid hydrides **2a** and **2b** were recovered from their solutions after work-up in 67% and 78% yield, respectively. The times for half decomposition of **2a** and **2b** were 15 and 16 h, respectively. The times for half decomposition of the Re formyls **2c** and **2d** were 8 and 24 h, respectively. The corresponding known [11] hydrides [*fac*-(dppe)Re(CO)$_3$H: δ −5.13 (t) and *fac*-(dppp)Re(CO)$_3$H: δ −4.07 (t)] were recovered from the NMR tubes in 61 and 68% yield, respectively.

3.2.1. Effect of AIBN (azobis(isobutyronitrile) on rate of decarbonylation

Samples of C_6D_6 solutions of the formyls **2a–d** were treated with 10 mol percent of AIBN but no change in the rate of decarbonylation was observed in any case by monoriting with ^{1}H NMR. The same was true for samples dissolved in THF.

3.3. Reaction of the Mn formyls 2a and 2b with protic acids

To a solution of approximately 1.5 mmol of either **2a** or **2b** in 75 ml of CH_2Cl_2 at −78°C was added an equivalent amount of $HBF_4 \cdot Et_2O$. The mixture was allowed to warm to room temperature over a period of 1.5 h. The solvent was then removed at the rotary evaporator. The residue was extracted with 50 ml of benzene and filtered from the insoluble impure [(P–P)M(CO)$_4$][BF$_4$] which was then recrystallized from CH_2Cl_2 to give pure material. The benzene-soluble filtrate was evaporated to dryness and the residue recrystallized from benzene/hexane to give the methyl complexes, *fac*-(P–P)Mn(CO)$_3$CH$_3$ (**3a**, **3b**) in about 75% yield. The methyl complexes **3a**, **3b** have been reported previously [4c,d] and the spectral properties of our compounds closely match those in the literature. The reaction with the other protic acids, toluenesulfonic acid, triflic acid and trifluoroacetic acid gave similar results.

3.4. Reaction of the formyl complexes 2a–d with HOTs in CH$_3$OH

To 1.5–3.5 mmol of **2a–d** dissolved in about 100 ml CH_3OH at 0°C was added an equivalent amount of HOTs $\cdot$ H$_2$O in 5–10 ml of CH_3OH and the solutions stirred for 15 min. The almost white solid precipitates were filtered, washed with CH_3OH and vacuum dried. Recrystallization from CH_2Cl_2/benzene/hexane gave high yields of **4a–d** as white powders. The filtrates were evaporated to dryness and the residues were recrystallized from CH_2Cl_2/Et_2O to give pure [(P–P)M(CO)$_4$][OTs]. Data for **4a**: yield, 91%; m.p. 195–197°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 1999s, 1941s, 1899s. ^{1}H NMR (δ, C_6D_6): 7.65 (m, 20 H, C_6H_5), 3.05 (t, 2H, CH_2O), 2.85 (m, 4 H, CH_2), 2.44 (s, 3 H, CH_3). ^{13}C NMR (δ, CD_2Cl_2): 226.0 (s, br, 2 $C\equiv O$), 218.2 (t, *J* 16 Hz, $C\equiv O$), 138.8–128.5 (m, C_6H_5), 71.5 (t, *J* 21 Hz, CH_2) Anal. Found: C, 64.3; H, 5.1. $C_{31}H_{29}MnO_4P_2$ calcd: C, 64.0, H 5.0. Data for **4b**: yield, 92%; m.p. 179–181°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 1997s, 1895s. ^{1}H NMR (δ, C_6D_6): 7.55 (m, 20 H, C_6H_5), 3.25 (s, 3 H, CH_3), 2.12 (t, 2H, CH_2–O), 295 (m, 6 H, CH_2). ^{13}C NMR (δ, CD_2Cl_2): 223.2 (s, br, 2 $C\equiv O$), 219.6 (s, br, $C\equiv O$), 138.2–128.3 (m, C_6H_5), 73.2 (t, *J* 17 Hz, CH_2O), 64.5 (s, CH_3), 25.7 (t, *J* 11 Hz, CH_2), 19.5 (s, CH_2). Anal. Found: C, 64.0; H, 5.2. $C_{32}H_{31}MnO_4P_2$ calcd: C, 64.4, H 5.2. Data for **4c**: yield, 89%; m.p. 209–211°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2005s, 1921s, 1900s. ^{1}H NMR (δ, C_6D_6): 7.75 (m, 20 H, C_6H_5), 3.15 (t, 2H, CH_2), 2.85 (m, 4 H, CH_2), 2.35 (s, 3 H, CH_3). ^{13}C NMR (δ, CD_2Cl_2): 197.6 (dd *J* 53 Hz, 12 Hz, 2 $C\equiv O$), 193.2 (t, *J* 6 Hz, $C\equiv O$), 137.1–128.5 (m, C_6H_5), 64.2 (s, CH_3), 57.0 (t, *J* 9 Hz, CH_2O), 28.0 (m, CH_2). Anal. Found: C, 51.9; H, 4.1. $C_{31}H_{29}O_4P_2Re$ calcd: C, 52.1, H 4.1. Data for **4d**: yield, 84%; m.p. 198–200°C. IR (cm^{-1}, C_6H_6): $\nu(C\equiv O)$ 2010s, 1929s, 1898s. ^{1}H NMR (δ, $CDCl_3$): 7.35 (m, 20 H, C_6H_5), 3.80 (t, 2H, CH_2O), 2.10 (m, 6 H, CH_2). ^{13}C NMR (δ, CD_2Cl_2): 194.5 (dd *J* 64 Hz, 24 Hz, 2 $C\equiv O$), 194.6 (t, *J* 7 Hz, $C\equiv O$), 137.1–1.28.5 (m, C_6H_5), 64.8 (s, CH_3), 58.2 (t, *J* 9 Hz, CH_2O), 25.4 (t, *J* 13 Hz, CH_2), 19.9 (s, CH_2). Anal. Found: C, 53.2; H, 4.4. $C_{32}H_{31}O_4P_2Re$ calcd: C, 52.9; H, 4.3.

3.5. Reaction of the formyl complexes 2a–d with methyl triflate

To 1.5 mmol of **2a–d** dissolved in 100 ml CH_2Cl_2 at −78°C was added 0.75 mmol of methyl triflate and the solutions stirred for 15 min. After coming to room temperature the solvent was removed and the residue extracted with 50 ml benzene and filtered. Evaporation of the filtrate and recrystallization of the residues from CH_2Cl_2/benzene/hexane gave the methoxymethyl complexes **4a–d** in about 90% yield. The benzene insolubles were recrystallized from CH_2Cl_2/Et_2O to give pure [(P–P)M(CO)$_4$][OTf] in about 95% yield.

3.6. X-ray crystal structure of fac-(dppp)Mn(CO)$_3$-CH$_2$OCH$_3$ (4b)

Suitable single crystals of **4b** were grown by crystallization from CH_2Cl_2/benzene/hexane at 0°C. Data were collected on a Siemens R3m/V four-circle diffractometer and are reported in Table 1. Of the 7530 reflections collected in the range $3.5 \leq 2\theta \leq 55°$, 2367 with $F \leq 4\sigma\ (F)$ were used in the final refinement. The structure was solved by a combination of direct methods using SHELXTL PLUS [13] and the difference Fourier technique and refined by full-matrix least squares. The non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were allowed to ride on their respective atoms at a distance of 1.00 Å. A final R index of 0.0723 with $R_W = 0.0747$ was obtained.

Details of structure factors and anisotropic temperature parameters are available from the authors.

References and notes

1 (a) B.D. Dombek, *J. Chem. Educ., 63* (1986) 210; (b) J.C. Selover, G.D. Vaughn, C.E. Strouse and J.A. Gladysz, *J. Am. Chem. Soc., 108* (1986) 1455; (c) S.-I. Yoshida, Mori, H. Kinoshita and Y. Watanbe, *J. Mol. Catal., 42* (1987) 215.

2 (a) G. Henrici-Olivé and S. Olivé, *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*, Springer-Verlag, New York 1984; (b) J. Saussey, J.-C. Lavalley, J. Lamotte and T. Rais, *J. Chem. Soc., Chem. Commun.*, (1982) 278; (c) A. Deluzarche, J.P. Hindermann and R. Kieffer, *Tetrahedron Lett., 31* (1978) 2787.

3 S.K. Mandal, D.M. Ho and M. Orchin, *Polyhedron, 11* (1992) 2055.

4 (a) J.A. Gladysz, *Adv. Organomet. Chem., 20* (1982) 1; (b) P.C. Ford and A. Rokicki, *Adv. Organomet. Chem., 28* (1988) 139; (c) C.S. Kraihanzel and P.K. Maples, *J. Organomet. Chem., 20* (1969) 269; (d) C.S. Kraihanzel and P.K. Maples, *J. Organomet. Chem., 117* (1976) 159.

5 B.A. Narayan, C. Amatore, C.P. Casey and J.K. Kochi, *J. Am. Chem., Soc., 105* (1983) 6352.

6 (a) S.G. Davies, J. Hibberd and S.J. Simpson, *J. Chem. Soc., Chem. Commun.*, (1982) 1404 and references cited therein; (b) G. Smith and D.J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, (1984) 1203; (c) D.S. Barratt and D.J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, (1987) 2683.

7 See ref. 6c.

8 (a) G.R. Steinmetz and G.L. Geoffroy, *J. Am. Chem. Soc., 103* (1981) 1278; (b) W. Tam, G.-Y. Lin, W.-K. Wong, W.A. Kiel, V.K. Wong and J.A. Gladysz, *J. Am. Chem. Soc., 104* (1982) 141; (c) D.H. Gibson, S.K. Mandal, K. Owens, and J.F. Richardson, *Organometallics, 6* (1987) 2624; (d) D.H. Gibson, K. Owens, S.K. Mandal, W.E. Sattich and J.O. Franco, *Organometallics, 10* (1991) 1203.

9 (a) J.C. Calabrese, D.C. Roe, D.L. Thorn and T.H. Tulip, *Organometallics, 3* (1984) 1223; (b) L.G. Marzilli, F. Bayo, M.F. Summers, L.B. Thomas, E. Zangrando, N. Bresciani-Pahor, M. Mari and L. Randaccio, *J. Am. Chem. Soc., 109* (1987) 6045; (c) G. Erker, R. Schlund and C. Kruger, *J. Organomet. Chem., 338* (1988) C4.

10 S.K. Mandal, D.M. Ho, and M. Orchin, *J. Organomet. Chem., 397* (1990) 313.

11 For the preparation of: *fac*-(dppe)Mn(CO)$_3$H see B.D. Dombek, *Ann. N.Y. Acad. Sci., 415* (1983); *fac*-(dppp)Mn(CO)$_3$H see S.K. Mandal, D.M. Ho, and M. Orchin, *Organometallics, 12* (1993) 1714; *fac*-(dppe)Re(CO)$_3$H see S.K. Mandal, D.M. Ho and M. Orchin, *Inorg. Chem., 30* (1991) 2244; *fac*-(dppp)Re(CO)$_3$H see S.K. Mandal, D.M. Ho and M. Orchin, *J. Organomet. Chem., 439* (1992) 53.

12 (a) J.R. Sweet and W.A.G. Graham, *J. Am. Chem. Soc., 104* (1982) 2811; (b) D.H. Gibson, K. Owens, S.K. Mandal, W.E. Sattich and J.A. Franco, *Organometallics, 8* (1989) 498; (c) P. Leoni, A. Landi and M. Pasquali, *J. Organomet. Chem., 321* (1987) 365.

13 SHELXTL PLUS version 4.11 for R3/V and R3m/V crystallographic systems, G.M. Sheldrick, University of Göttingen, Germany, and Siemens/Nicolet Analytical X-Ray Instruments, Inc., Madison, WI, USA, 1989.