

Conversion of a manganese–carbon-bonded complex to a manganese–oxygen-bonded complex, some reactions of manganese carbonato complexes

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Abstract

Stirring a solution of the manganese carboxylate, $(dppe)(CO)_3Mn-C(O)OCH_3$, **1**, in dichloromethane saturated with water converts it to the bridging carbonato complex, $(dppe)(CO)_3Mn-OC(O)O-Mn(CO)_3(dppe)$, **2**. This multi-step conversion involves the in-situ transformation of a Mn–C bonded complex to a Mn–O bonded one. When **2** is stirred with HCl, it is converted quantitatively to the covalent chloride $(dppe)(CO)_3Mn-Cl$, **11**, with evolution of carbon dioxide. Similar HCl treatment of the manganese carboxylate **1** gives three compounds: the same covalent chloride, **11**; the ionic chloride, $[(dppe)(CO)_3Mn]^+Cl^-$, **12**, and the hydride, $(dppe)(CO)_3Mn-H$, **5**. Reasonable schemes for these conversions are suggested. Heating the ionic chloride complex to its melting point converts it to the covalent chloride complex; the same transformation is accomplished by refluxing the ionic chloride in acetonitrile. © 1997 Elsevier Science S.A.

Keywords: Manganese phosphine complexes; Manganese–carbon metallocarboxylate complex; Manganese–oxygen bridging carbonato complex; Hydrolysis; Crystal structure

1. Introduction

Over the past few years, we [1–6] and others [7–9] have reported on the preparation and reactions of a variety of functional groups (Z) attached to a transition metal in the octahedral complexes of the general formula $(P-P)(CO)_3M-Z$ where (P–P)'s are bisphosphino compounds such as 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(diethylphosphino)ethane (depe); Z = H, OTs, OR, OC(O)OR, NCO, N₃, X, CHO, C(O)OR, CH₂OR, NHR, etc.; and M = Mn or Re. We now wish to report on the unusual reaction of $(dppe)(CO)_3Mn-C(O)OMe$, **1**, when it is dissolved in dichloromethane saturated with water.

It is known [2] that **1** ionizes in this solvent to give the cationic complex $[(dppe)(CO)_3Mn]^+$. The cation is readily recognized by its characteristic high-frequency

bond in the IR at 2094 cm^{-1} which appears almost immediately after dissolving the covalent compound. The product isolated after several hours of stirring at room temperature is the bridging carbonato complex $(dppe)(CO)_3Mn-OC(O)O-Mn(CO)_3(dppe)$, **2**. Although there are quite a number of cases where transition metal oxygen bonds are transformed to metal carbon bonds [1,10–15], the reaction reported here is unusual in that it occurs spontaneously and involves the conversion of Mn–C bonds to Mn–O bonds.

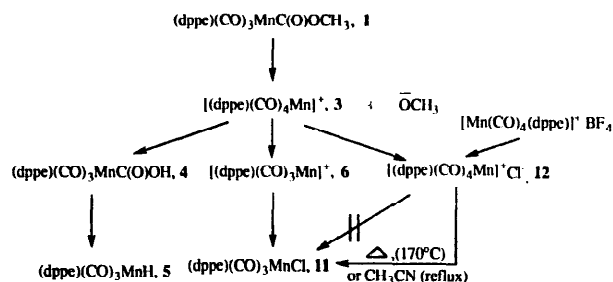
2. Results and discussion

2.1. Conversion of the manganese carboxylate $(dppe)(CO)_3Mn-C(O)OMe$, **1, to the bridging carbonato complex, $(dppe)(CO)_3Mn-OC(O)O-Mn(CO)_3(dppe)$, **2****

Treatment of the Mn ester, **1**, by stirring its solution in CH_2Cl_2 saturated with H_2O for about 4 h at room temperature gave the bridging carbonato complex, **2**.

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The sequence of reactions we suggest for this conversion is outlined in Scheme 1. None of the intermediates shown have been isolated directly from the multicomponent reaction mixture even when the reaction is interrupted before all the starting material is consumed. However, there is substantial evidence for each of the reactions shown. The dissociation equilibrium reaction (1) can be demonstrated by the appearance of the 2094 cm^{-1} band (characteristic of the ion, 3) in the IR spectrum of solutions of 1 even in *dry* dichloromethane. If such a solution is evaporated, the original covalent compound is recovered unchanged. Equilibrium reaction (2) follows from (1). Separate attempts to prepare the Mn carboxylic acid, 4, by the treatment of $[(\text{dppe})(\text{CO})_4\text{Mn}][\text{BF}_4]$ with sodium hydroxide were unsuccessful. The acid appears to be very unstable, immediately undergoing decarboxylation to the very robust hydride, 5, via reaction (3) analogous to the decarboxylation of the corresponding Re acid [16], which, contrary to the manganese acid is relatively stable. Although manganese carboxylic acids frequently have been postulated as intermediates, they have never been isolated. The hydride, 5, can be isolated by chromatography and is readily characterized by its 1995 cm^{-1} band in its IR spectrum [3]. Reaction (4) involves decarbonylation to the postulated tricarbonyl Mn ion, 6. Although no quantitative analysis for CO was performed it was identified (GLC) in the vapor over the reaction mixture; also its postulated intermediacy is made more credible by the reactions shown in Scheme 2 which will be discussed later. The Mn^+ tricarbonyl species, 6, may be trapped either by the OH^- ion, reaction (5), or by the CH_3O^- ion, reaction (6) to give the unknown MnOH , 8, and the previously characterized [1] alkoxide, 7, respectively. The alkoxide 7 is known [3] to react very rapidly with carbon dioxide, reaction (8), to give the methyl carbonate, 9. In situ hydrolysis of the methyl carbonate, 9, would lead to the bicarbonate, 10. In a separate experiment, this hydrolysis was shown (see below) to occur under the same

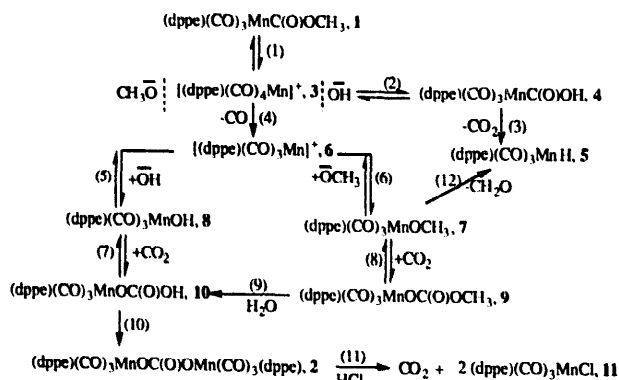


Scheme 2.

conditions as was used in Scheme 1. The final step to the isolated bridging bicarbonato product, reaction (10), is reasonable since the bicarbonate, 10, prepared in a separate set of experiments, on stirring with wet dichloromethane is also converted to 2. The conversion of the mononuclear bicarbonate, 10, to the bridging dinuclear carbonato, reaction (10), is rather difficult to substantiate. One possibility consists of the reaction between the Mn tricarbonyl cation, 6, [via equilibria reactions (7) and (5)], and the anion of the bicarbonate, 10, with the net loss of a mole of water; it is also possible that a reaction between the alkoxide, 7, and the bicarbonate, 10, with the net loss of a mole of methanol, a reaction that has been separately verified, can account for the formation of 2. The conversion of a Mn ester to a bridging carbonato complex is not unique for the dppe ligand; when its analog, dppp, (bis(diphenylphosphino)propane), is substituted for the dppe ligand in the methyl carboxylate, 1, and it is treated under the same conditions that were used to generate 2 from 1, the corresponding bridging carbonato complex, $(\text{dppp})(\text{CO})_4\text{Mn-OC(O)O-Mn}(\text{CO})_3(\text{dppp})$ is formed.

2.2. Reactions of the methyl carboxylate, $(\text{dppe})(\text{CO})_3\text{Mn-C(O)OMe}$, 1, with HCl in methanol

When a methanol solution of 1 is stirred with HCl at room temperature there is immediate gas evolution. On working up the reaction mixture after stirring for about an additional 2 h, three compounds were identified: the hydride, 5; the covalent chloride, 11, and the ionic chloride, 12, formed as shown in Scheme 2. This scheme involves the intermediacy of the same two cations, the tetracarbonyl, 3 and the tricarbonyl 6, of Scheme 1, with the former leading to the ionic chloride, 12 and the tricarbonyl, leading to the covalent chloride, 11. The ionic chloride is a new compound which we have fully characterized and which can be prepared independently from the corresponding well-known tetrafluorate salt by anionic chloride exchange. The ionic chloride is converted at its melting point (170°C) to the covalent chloride, a decarbonylation reaction that can also be



Scheme 1.

Table 1
Crystal data and structure refinement

Chemical formula	$C_{30}H_{24}ClMnO_4P_2$
Formula weight	572.81
$F(000)$	2352
Temperature	23(2)°C
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Phca</i>
Unit cell dimensions	$a = 16.223(3)$ Å, $\alpha = 90^\circ$ $b = 14.783(4)$ Å, $\beta = 90^\circ$ $c = 22.356(8)$ Å, $\gamma = 90^\circ$
Volume, z	$5361(2)$ Å ³ , 8
Goodness-of-fit on F^2	1.031
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0522$, $wR2 = 0.0974$
R indices (all data)	$R1 = 0.1099$, $wR2 = 0.1327$

Table 2
Selected bond distances (Å) and angles (°) for *fac*-(CO)₃(dppe)MnCl

Mn–C(1)	1.823(4)	Mn–Cl	2.376(1)
Mn–C(2)	1.841(5)	Mn–P(1)	2.328(1)
Mn–C(3)	1.827(4)	Mn–P(2)	2.335(1)
P(1)–C(4)	1.833(4)	P(2)–C(5)	1.835(4)
P(1)–C(6)	1.828(4)	P(2)–C(18)	1.832(4)
P(1)–C(12)	1.830(4)	P(2)–C(24)	1.825(3)
C(1)–O(1)	1.132(4)	C(2)–O(2)	1.033(4)
C(3)–O(3)	1.135(4)	C(4)–C(5)	1.537(5)
P(1)–Mn–P(2)	84.81(3)	C(1)–Mn–Cl	94.10(12)
Mn–C(1)–O(1)	175.7(3)	C(2)–Mn–Cl	175.31(11)
Mn–C(2)–O(2)	179.3(4)	C(3)–Mn–Cl	88.17(11)
Mn–C(3)–O(3)	177.0(3)	P(2)–Mn–Cl	88.25(4)
P(1)–Mn–Cl	83.57(4)	P(2)–Mn–C(1)	177.29(1)
P(1)–Mn–C(1)	94.11(12)	P(2)–Mn–C(2)	88.10(11)
P(1)–Mn–C(2)	93.17(11)	P(2)–Mn–C(3)	92.48(11)
P(1)–Mn–C(3)	171.37(11)		

achieved by refluxing a solution of the ionic chloride in acetonitrile. The covalent chloride is identical to the one formed in quantitative yield from the bridging carbonate, Scheme 1, reaction (11). An X-ray diffraction study was performed on a suitable crystal of **11**. The conformation and the atomic numbering scheme are shown in Fig. 1 and crystal data are given in Table 1. Selected bond distances and angles are given in Table 2. The tricarbonyl covalent chloride, (dppe)(CO)₃MnCl, **11**, has a monomeric pseudooctahedral structure, with the manganese atom coordinated to three terminal carbonyl groups, a chlorine atom and a chelating dppe ligand. The Mn–Cl distance is 2.376(1) Å. The average of Mn–P and Mn–CO distances are 2.332 Å and 1.830 Å, respectively. The P–Mn–P bite angle is 84.81(3)°. All of these structural features are comparable to those

previously observed in the related *fac*-(CO)₃(depe)MnCl complex [5].

2.3. Reactions of the methyl carbonate, (dppe)(CO)₃Mn-OC(O)OMe, **9**, in organic solvents containing water

Stirring the methyl carbonate complex, **9**, with either CH₂Cl₂/H₂O or THF/H₂O results in hydrolysis to the bicarbonate complex, **10**, but similar treatment with C₆H₆/H₂O left **9** unaffected. On the other hand the **depe** analog to **9** underwent hydrolysis under the same conditions (C₆H₆/H₂O) to give the **depe** bicarbonate. This difference in behavior as a function of the bisphosphine ligand is difficult to rationalize at present.

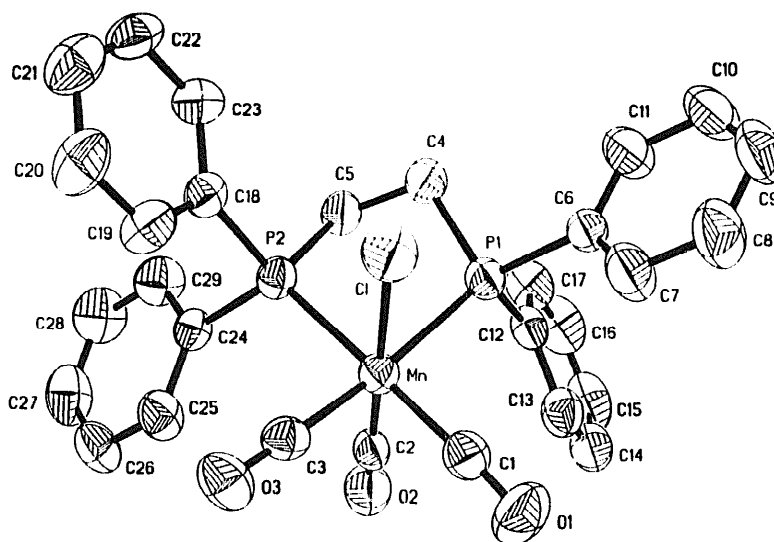


Fig. 1. Perspective drawing of molecule **11**, *fac*-(dppe)(CO)₃MnCl.

2.4. Reactions of the bicarbonato complex, $(dppe)(CO)_3Mn-OC(O)OH$, **10**

Stirring a CH_2Cl_2/H_2O solution of **10** for 4 days at room temperature gives the bridging carbonato complex, **2** (see above), as well as trace of recovered starting material, but no hydride, **5**, is observed. The conversion of mononuclear **10** to dinuclear **2** requires the net loss of one mole each of H_2O and CO_2 between 2 moles of **10** (reaction 10 in Scheme 1). Exactly how this occurs is not clear but one possibility is suggested by Scheme 1 as discussed above. In one interesting reaction, a CH_2Cl_2 solution containing the bicarbonate, **10**, and the methoxide, **7**, was stirred at room temperature for 1 day and then worked up. The main product of the reaction was the bridging carbonato, **2**, which can be accounted for by the loss of methanol (observed by GLC) between the two starting compounds. Some methyl carbonate, **9**, was also isolated. The methoxide is a notorious scavenger of adventitious carbon dioxide. Surprisingly, some of the hydride **5** was also observed (IR) in this reaction. In this instance, the source of the hydride is unlikely to be the carboxylic acid, **4**, since this would require the unlikely conversion of a Mn–O bond to an Mn–C bond in this system. The source of the hydride is more likely the result of a beta-hydride elimination from the starting methoxide, **7**, [reaction (12) in Scheme 1], a reaction which is reputed to account for the relative instability of transition metal alkoxides and which we have observed [1] in our prior work with such compounds. Finally, it was found that treatment of the bicarbonate **10** with CH_2Cl_2/HCl gives a good yield of the covalent chloride, **11**, a result that supports the possible formation of the Mn tricarbonyl intermediate cation, **6**, (postulated in both Schemes 1 and 2) followed by trapping **6** with the chloride ion.

3. Experimental details

3.1. General and instrumental

All reactions were carried out under a dry argon atmosphere on a double-manifold Schlenk vacuum line. Chromatographies were performed without any attempt to exclude air. Solvents were purified by standard methods. HCl (38% aqueous solution), CH_2Cl_2 , THF, C_6H_6 , hexane, CH_3CN and CH_3OH were purchased from Aldrich Chemical. 1,2-Bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and 1,2-bis(diethylphosphino)ethane (depe) were purchased from either Pressure Chemicals or Strem Chemical. $Mn_2(CO)_{10}$ and $fac-(P-P)(CO)_3Mn-Z$ ($P-P = dppe, dppp, depe$; $Z = C(O)OMe, OC(O)OMe$) were prepared according to literature methods [2,3]. IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR instru-

ment. 1H NMR spectra using a Bruker AC-250 spectrometer were obtained on $CDCl_3$ solutions with chemical shifts recorded relative to internal Me_4Si . Mass spectra were recorded on a Kratos MS-80 spectrometer. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories.

3.2. Preparation of $fac-(dppe)(CO)_3Mn-OC(O)OH$, **10**

A solution of 0.40 g (0.65 mmol) of the methyl carbonate, **9**, in 100 cm^3 of THF was stirred with 2 cm^3 of water at room temperature for 2 days. After the hydrolysis was complete, the THF was removed on a rotary evaporator. The residue was extracted with dichloromethane. The dichloromethane solution was concentrated and mixed with hexane, and the resultant mixture was cooled. The yellow crystals of the bicarbonate, **10**, were collected by filtration, washed with hexane ($3 \times 15\text{ cm}^3$), and dried in vacuo. mp $148-149^\circ C$. IR (cm^{-1} , CH_2Cl_2): $\nu(C\equiv O)$ 2022s, 1953s, 1897s, and $\nu(C=O)$ 1684m, 1668m. 1H NMR (δ , $CDCl_3$): 7.41 (m, 20H, C_6H_5), 5.29 (s, 1H, CH_2Cl_2), 2.82 (m, 4H, CH_2). Anal. Found: C, 57.40; H, 4.04. $C_{30}H_{25}MnO_6P_2 \cdot 0.5CH_2Cl_2$ Calc.: C, 57.16; H, 4.09%.

3.3. Preparation of $fac-(depe)(CO)_3Mn-OC(O)OH$

A 0.20 g (0.48 mmol) sample of $fac-(depe)(CO)_3Mn-OC(O)OMe$ was treated with 3 cm^3 of water in benzene (40 cm^3) in a manner similar to that described for the preparation of **10**. The reaction was complete in about 2 days. The product that precipitated was collected by filtration, washed with hexane, and dried in vacuo. The product was further purified by recrystallization from dichloromethane/hexane to give an analytically pure sample. mp $172-174^\circ C$. IR (cm^{-1} , CH_2Cl_2): $\nu(C\equiv O)$ 2023s, 1950s, 1894s, and $\nu(C=O)$ 1688m, 1672m. 1H NMR (δ , $CDCl_3$): 1.83 (m, 12H, CH_2), 1.20 (m, 12H, CH_3). Anal. Found: C, 41.27; H, 6.09. $C_{14}H_{25}MnO_6P_2$ Calc.: C, 41.39; H, 6.20%.

3.4. Reaction of $fac-(CO)_3(P-P)MnOC(O)OH$ ($P-P = depe, dppe$) with HCl

A solution of 0.2 g of $fac-(P-P)(CO)_3Mn-OC(O)OH$ ($P-P = depe, dppe$) in 30 cm^3 of dichloromethane was stirred with a tenfold molar excess of HCl (38%) at room temperature for 2 h. The excess acid was removed by extraction with water. The dichloromethane solution was dried over Na_2SO_4 and evaporated to dryness. The crude product was chromatographed on a column of silica gel with dichloromethane as eluent. The analytical samples of the two chlorides were obtained by recrystallization from dichloromethane/hexane (1:1) mixture. Both complexes have been characterized previously [5].

3.5. Preparation of $(dppe)(CO)_3Mn-OC(O)O-Mn(CO)_3(dppe)$, **2**

This complex was prepared *via* four independent methods and the isolated bridging carbonate complex, regardless of the method of preparation, showed identical properties (solubility, melting point, IR, 1H NMR).

3.5.1. Method 1: preparation from the reaction of **1** with CH_2Cl_2/H_2O

A 0.50 g sample of **1** was stirred with dichloromethane in the presence of water (2 cm³) under argon for 14 h. The solvent was removed on a rotary evaporator. The residue was chromatographed on a column of silica gel with dichloromethane as eluent. The fraction containing **2** (TLC) was evaporated and the residue was recrystallized from a dichloromethane–hexane mixture. mp 170–172°C. IR (cm⁻¹, CH_2Cl_2): $\nu(C=O)$ 2025s, 1955s, 1914s. Anal. Found: C, 59.44; H, 4.17; Mn, 9.60; P, 11.05. $C_{59}H_{48}Mn_2O_9P_4 \cdot 0.75CH_2Cl_2$ Calc.: C, 59.88; H, 4.16; Mn, 9.17; P, 10.34%. 1H NMR (d, $CDCl_3$): 7.52 (m, 40H, C_6H_5), 5.27 (s, 1.5H, CH_2Cl_2), 2.87 (m, 8H, CH_2). MS (m/z) observed: 1197.7, Calcd.: 1197.7. Attempts to obtain a complete X-ray structure of the bridging carbonate complex, **2**, have thus far been unsuccessful but the crystal structure of a related Re bridging carbonate complex has been reported [8].

3.5.2. Method 2: preparation from the reaction of **10** with CH_2Cl_2/Et_2O

Here, **10** (60 mg) and water (0.25 cm³) were mixed with dichloromethane (15 cm³) and stirred under an argon atmosphere for about 4 days. The solvent was removed on a rotary evaporator. The residue was chromatographed on a column of silica gel with dichloromethane as eluent and the product was recrystallized from a dichloromethane/hexane mixture. The resulting yellow crystals of **2** were filtered, washed with 2×5 cm³ portions of hexane and dried in vacuo.

3.5.3. Method 3: preparation from the reaction of **10** with **7**

A mixture of 100 mg of the bicarbonate, **10**, 95 mg of the methoxide, **7**, and 30 cm³ of dichloromethane was stirred under argon at room temperature for 1 day. The solvent was then evaporated to dryness to give a yellow product, which was purified by column chromatography on silica gel (230–400 mesh) with dichloromethane as eluent. Evaporation of the solvent gave pure **2** as yellow crystals.

3.5.4. Method 4: preparation from the reaction of **9** with CH_2Cl_2/H_2O

To 0.28 g of the methyl carbonate, **9** in dichloromethane (20 cm³) was added an excess of water

(5 cm³). After stirring for 7 days, water was separated out by centrifugation. The dichloromethane solution was dried over Na_2SO_4 and evaporated to dryness. The crude product was chromatographed on a column of silica gel with dichloromethane as eluent. The analytical sample was obtained by recrystallization from a dichloromethane/hexane (1:1) mixture.

3.6. Preparation of $(dppp)(CO)_3Mn-OC(O)O-Mn(CO)_3(dppp)$

A procedure similar to that as described for the preparation of **2** (Method 1), except for the use of the dppp complex, *fac*-(dppp)(CO)₃Mn-C(O)OMe (0.5 g) instead of the dppe complex, **1**, was employed. The product was a yellow microcrystalline material. mp 212–213°C dec. IR (cm⁻¹, CH_2Cl_2): $\nu(C=O)$ 2028s, 1959s, 1909s. 1H NMR (δ , $CDCl_3$): 7.44 (m, 40H, C_6H_5), 5.29 (s, 1H, CH_2Cl_2), 2.69 (m, 12H, CH_2). Anal. Found: C, 60.78; H, 4.36; Mn, 9.07; P, 10.07. $C_{61}H_{52}Mn_2O_9P_4 \cdot 0.5CH_2Cl_2$ Calc.: C, 61.19; H, 4.40; Mn, 9.12; P, 10.28%.

3.7. Reaction of **2** with HCl

A solution of 0.50 g of the bridging carbonate complex, **2** in dichloromethane (20 cm³) was treated with 5 cm³ of concentrated HCl. When carbon dioxide gas evolution ceased, the excess acid was removed by extraction with water. The dichloromethane solution was then concentrated and mixed with hexane, and the resultant mixture was cooled. The yellow crystals that separated were collected by filtration, washed with hexane (3×5 cm³), and dried under vacuum to give pure **11** in almost quantitative yield. The melting point, IR, 1H NMR, MS matched those previously reported for this compound [5]. A sample for X-ray diffraction study was crystallized from dichloromethane/hexane (1:1).

3.8. Preparation of $[Mn(CO)_4(dppe)]^+ Cl^-$, **12**

To a solution of $[Mn(CO)_4(dppe)]^+ BF_4^-$ (0.2 g) in dichloromethane (25 cm³) was added an excess of HCl. The reaction mixture was allowed to stir for 20 h. The acids were removed by extraction with water. The dichloromethane solution was concentrated and a small quantity of ether was added to precipitate the tetracarbonyl ionic chloride, **12**. Finally, vacuum drying afforded an almost-white product. The analytical sample was obtained after chromatography on a column of silica gel with methanol as eluent. mp 167–170°C. IR (cm⁻¹, CH_2Cl_2): $\nu(C=O)$ 2092s, 2018s, 2013s, 1997s. 1H NMR (δ , $CDCl_3$): 7.51 (m, 20H, C_6H_5), 3.63 (m, 4H, CH_2). MS (m/z): 565 ($[Mn(CO)_4(dppe)]^+$, 13.6), 537 ($[Mn(CO)_3(dppe)]^+$, 18.7), 454 ($[Mn(dppe) + H]^+$, 20.5), 398 ($[(dppe)]^+$, 64.5), 370 ($[P_2Ph_4]^+$, 33.1), 289

($[\text{Ph}_3\text{PCH}=\text{CH}_2]^+$, 83.7), 262 ($[\text{PPh}_3]^+$, 81.0), 185 ($[\text{PPh}_2]^+$, 100.0), 108 ($[\text{PPh}]^+$, 43.2). Anal. Found: C, 57.38; H, 4.37; Cl, 5.69. $\text{C}_{30}\text{H}_{24}\text{ClMnO}_4\text{P}_2 \cdot 2\text{CH}_3\text{OH}$ Calc.: C, 57.75; H, 4.81; Cl, 5.41%. ^1H NMR spectrum of the complex showed resonances owing to solvated CH_3OH which when integrated were consistent with the empirical formula shown.

3.9. Reaction of **1** with HCl

To a solution of 0.2 g of **1** in methanol (15 cm^3) was added about a tenfold excess of HCl and the solution was stirred for 2 h. The solvent was removed using a rotary evaporator and the solid residue was dissolved in dichloromethane (25 cm^3). Excess acid was removed by extracting with water. The solution was evaporated to dryness and the residue was chromatographed on a column of silica gel with dichloromethane and methanol as eluents. The three complexes, **5**, **11** and **12**, shown in Scheme 2 were obtained.

3.10. Conversion of $[\text{Mn}(\text{CO})_4(\text{dppe})]^+\text{Cl}^-$ to *fac*-(*dppe*)(*CO*)₃Mn–Cl

A solution of 0.52 g of the tetracarbonyl ionic complex, **12**, in 30 cm^3 of CH_3CN was refluxed under argon for 12 h. After cooling, the solvent was removed on a rotary evaporator and the residue was chromatographed on a column of silica gel with dichloromethane as eluent. The yellow solid product was recrystallized from 1:1 dichloromethane/hexane to give analytically pure yellow crystals of the tricarbonyl covalent complex, **11**.

3.11. Crystal structure determination of **11**

A suitable crystal measuring $0.70 \times 0.50 \times 0.35\text{ mm}$ was coated with a light film of epoxy resin and mounted on a glass fiber for X-ray examination and data collection. Intensity data were collected at 23°C on a Siemens P3 diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073\text{ \AA}$). Lattice parameters were obtained by least squares refinement of the angular settings from 25 reflections lying in a 2θ range of $15\text{--}30^\circ$. Intensity data were collected using $\theta\text{--}2\theta$ scans in the range $3.5 \leq 2\theta \leq 55^\circ$ ($+h$, $+k$, $+l$). A decay correction (minimum 0.9744 and maximum 1.0211) was applied to the 6163 unique reflections based on three standard reflections monitored every 300 reflections. The data

were also corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by a combination of direct methods using SHELXTL v5.03 [17] and the difference Fourier technique and refined by full-matrix least squares on F^2 . The non-hydrogen atoms were refined with anisotropic displacement parameters. Weights were assigned as $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $a = 0.0419$, $b = 3.6035$ and $P = 0.33333 F_o^2 + 0.66667 F_c^2$. All hydrogen atom positions were calculated based on geometric criterion and allowed to ride on their respective atoms ($\text{C--H} = 0.93\text{ \AA}$ for aromatic H and $0.97\text{ \AA}$ for methylene H). Hydrogen atom isotropic temperature factors were defined as $U(H) \times a = U(C)$ where $a = 1.2$. The refinement converged with crystallographic agreement factors of $R1 = 5.22\%$, $wR2 = 9.74\%$ and $S = 1.031$ for 3724 reflections with $I \geq 2\sigma(I)$ and 325 variable parameters. A final difference Fourier map showed maximum residual electron density of $0.375\text{ e\AA}^{-3}$.

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