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CARBONYL COMPLEXES OF MANGANESE(I) WITH CHELATING PHOSPHINO-ALKYL OR -ACYL LIGANDS. CRYSTAL AND MOLECULAR STRUCTURE OF $[Ph_2PCH_2CH_2(O)CMn(CO)_2(dppm)]$

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Summary

The phosphine $Ph_2PCH_2CH_2Cl$ reacts with *fac*-$[XMn(CO)_3(dppm)]$ (X = Cl or Br) in refluxing toluene to give the complexes *cis,cis*-$[XMn(CO)_2(dppm)(Ph_2PCH_2CH_2Cl)]$ (I). Treatment of those species with Na amalgam in THF leads to the alkyl complex $[Ph_2PCH_2CH_2Mn(CO)_2(dppm)]$ (II), which does not react with CO under normal conditions but can be converted into *cis,cis*-$[ClMn(CO)_2(dppm)(PPh_2Et)]$ by reacting with HCl (g) in ether. If the reduction of I with Na/Hg is carried out in the presence of CO the compound *cis*-$[Ph_2PCH_2CH_2(O)CMn(CO)_2(dppm)]$ (III) is obtained. The latter has also been prepared directly from *fac*-$[BrMn(CO)_3(dppm)]$, $Ph_2PCH_2CH_2Cl$, and Na/Hg in THF, and characterized by X-ray crystallography. The crystals are monoclinic, space group $P2_1/n$; refinement gave $R = 0.053$ for 2593 reflections with $I \geqslant 2.5\sigma(I)$. The reaction of the complex *fac*-$[O_3ClOMn(CO)_3(dppm)]$ with $Ph_2PCH_2CH_2Cl$ in Cl_2CH_2 gives the salt *fac*-$[Mn(CO)_3(dppm)(Ph_2PCH_2CH_2Cl)]ClO_4$ which isomerizes to *mer*-$[Mn(CO)_3(dppm)(Ph_2PCH_2CH_2Cl)]ClO_4$ in boiling butanol. Both cationic carbonyl complexes give the acyl species III upon reduction with Na amalgam.

Introduction

The tertiary phosphine $Ph_2PCH_2CH_2Cl$ [1] is an interesting ligand because of its potential bifunctional character. Recently, Lindner et al. have studied the use of the

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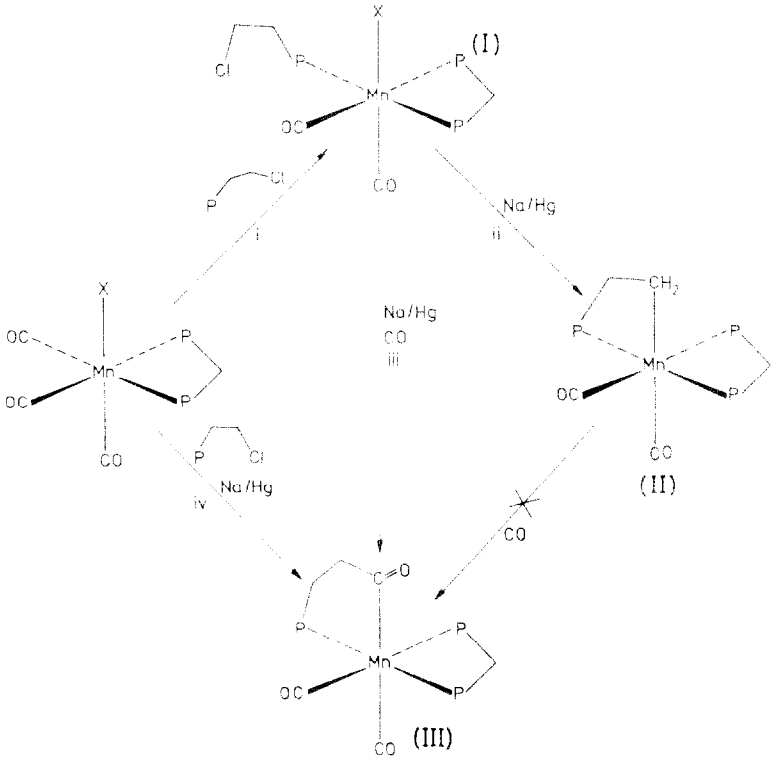
reactions of $BrMn(CO)_5$ with this and other chloroalkyl-diphenylphosphines for the synthesis of carbonyl complexes of Mn^I with chelating phosphino-alkyl or -acyl ligands (phospha-mangana-cycloalkanes or cycloketones) [2–5]. In an attempt to explore further the stereochemical implications of the presence of other ligands in the starting halo-carbonyl complexes in this type of reaction we have examined the reactions of the ligand $Ph_2PCH_2CH_2Cl$ with *fac*-$[XMn(CO)_3(dppm)]$ (X = Cl or Br) under various conditions. This has given, inter alia, the dicarbonyl complex $[Ph_2PCH_2CH_2(O)CMn(CO)_2(dppm)]$, the stereochemistry of which has been established by an X-ray study.

Results and discussion

Refluxing a mixture of *fac*-$[XMn(CO)_3(dppm)]$ (X = Cl or Br) and $Ph_2PCH_2CH_2Cl$ in toluene afforded the orange crystalline compounds Ia and Ib (reaction i in Scheme 1). Because of concomitant decomposition, with formation of some *cis*-$[Mn(CO)_2(dppm)_2]Br$ [6], the yield is poor in the case of X = Br, but owing to the more *cis*-labilizing effect of the chloride ligand [7,8] the reaction is faster for the *fac*-chloro-tricarbonyl and the yield is better (ca. 54%). The assignments of the stereochemistries of the products were based on the results reported for related reactions [6]. The IR spectra in CH_2Cl_2 solution of Ia and Ib showed two



SCHEME 1

TABLE 1

MELTING POINTS, CONDUCTIVITY AND ANALYTICAL DATA AND ν(CO) FREQUENCIES FOR THE COMPOUNDS I–V

Compound	M.p. (°C)	Λ_M [a]	Analyses (Found (calcd.)(%))		IR ν(CO) [b] (cm^{-1})
			C	H	
$[BrMn(CO)_2(dppm)(Ph_2PCH_2CH_2Cl)]$ (Ia)	182	5	60.8 (59.8)	4.41 (4.41)	1936,1866
$[ClMn(CO)_2(dppm)(Ph_2PCH_2CH_2Cl)]$ (Ib)	182	5	62.8 (63.2)	4.59 (4.66)	1936,1866
$[Ph_2\overline{PCH_2CH_2}\overline{Mn(CO)_2(dppm)}]$ (II)	145	14	68.5 (69.5)	5.15 (5.13)	1910,1842
$[Ph_2\overline{PCH_2CH_2(O)C}\overline{Mn(CO)_2(dppm)}]$ (III)	194	0	68.2 (68.5)	4.99 (4.94)	1918,1958,1567
fac-$[Mn(CO)_3(dppm)(Ph_2PCH_2CH_2Cl)]ClO_4$ (IV)	146	128	57.8 (57.9)	4.23 (4.17)	2030s,1968s,1952s
mer-$[Mn(CO)_3(dppm)(Ph_2PCH_2CH_2Cl)]ClO_4$ (V)	145	118	58.2 (57.9)	4.35 (4.17)	2040w,1960s

[a] Measured in acetone, 5×10^{-4} *M* (in ohm $^{-1}$ mol $^{-1}$ cm^2). [b] In CH_2Cl_2 unless otherwise stated. In toluene.

TABLE 2

^{31}P NMR [a] DATA FOR THE COMPOUNDS [b]

Compound	δ(P(a))	δ(P(b))	δ(P(c))	J(ab)	J(cb)	J(ac)
Ib	1.5	38.3	51.9	[d]		
II [c]	13.7	26.3	44.7	47.6	52.5	35.5
III	18.4	37.9	93.4	61.0	39.0	44.0
V [e]	12.1	31.0	48.0	[d]		

[a] Measured in $CDCl_3$ (unless otherwise indicated). δ(P) in ppm. to high frequency of external 85% H_3PO_4; J(PP) in Hz. [b] Assignments explained in Fig. 2. [c] In C_6D_6. [d] Unresolved multiplet. [e] For the *fac*-isomer IV, δ(dppm) 10.5, δ($Ph_2PCH_2CH_2Cl$) 34 ppm.

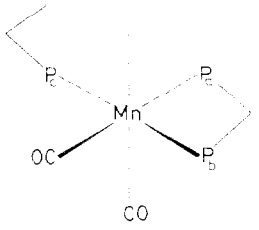


Fig. 1. Assignment of the phosphorus atoms corresponding to Table 2.

absorptions of nearly the same intensity (Table 1) which were slightly split both in toluene and in the solid state IR. The $^{31}P\{^1H\}$ NMR of Ib taken in $CDCl_3$ at room temperature showed three very broad unresolved absortions centered at 1.5, 38.3 and 51.9 ppm, which are very near to the chemical shifts observed for the three phosphorus atoms attached to the Mn atom in the related compound *cis,cis*-[$BrMn(CO)_2(dppm)_2$] [6].

Treatment of Ia or Ib with Na amalgam in THF gave the yellow compound *cis*-[$Ph_2PCH_2CH_2Mn(CO)_2(dppm)$] (II) (reaction ii in Scheme 1), data for which are given in Tables 1 and 2 *. The ^1H NMR spectrum of a C_6D_6 solution showed broad unresolved absorptions in the region of 1.1–1.7 and 3.5 ppm, attributable to CH_2CH_2Mn protons [2], and there was no sign of hydride ligands. The $^{31}P\{^1H\}$ NMR spectrum showed three sets of signals (AMX pattern), consistent with the arrangement of the phosphorus atoms shown in Fig. 1. The assignment of the chemical shifts (Table 2) was based on earlier results [6,9], taking into account that in going from I to II the ring contribution (ΔR) [10] of the four-membered ring formed might produce a shielding of the P(c) atom of ca. −15 ppm, as found for the related species *mer*-[$Mn(CO)_3(dppm)_2$]$^+$ [6]: in the case of compound II however this ΔR contribution is, in fact, only −7 ppm.

Further support for the structure of II came from its reaction with HCl(g) in ether, which gave the chlorodicarbonyl complex *cis,cis*-[$ClMn(CO)_2(dppm)$-(Ph_2PEt)]; this was characterized from its IR spectrum, which exhibits two bands of similar intensity at 1934 and 1860 cm^{-1}, as expected for this type of dicarbonyl, and

* The $^{31}P\{^1H\}$ NMR spectrum of the crude product showed that small amounts of other complexes are also formed in the reaction, some of them possibly binuclear and with monodentate dppm.

its ^1H NMR spectrum which shows two signals centered at 0.73 ppm (dt, 3H, CH_3, $J(^1H-^{31}P)$ 14, $J(^1H-^1H)$ 7 Hz) and 2.26 ppm (dq, 2H, CH_2, $J(^1H-^{31}P)$ 38 $J(^1H-^1H)$ 7 Hz) indicating the presence of the ethyl group. Moreover, when this compound was treated with $TlPF_6$ and CO in Cl_2CH_2 it gave the salt *mer*-$[Mn(CO)_3(dppm)(PEtPh_2)]PF_6$, the IR spectrum of which in the $\nu(CO)$ region (bands at 2041w and 1961s cm^{-1}) is very close to that reported for the analogous *mer*-tricarbonyl cations [11].

It is clear that reaction ii is analogous to the reductive cycloelimination reaction of *cis*-$[BrMn(CO)_4(Ph_2CH_2CH_2Cl)]$ with Na/Hg [2]. However, in contrast with the formation of an acyl complex in the reaction of *cis*-$[Ph_2PCH_2CH_2Mn(CO)_4]$ and CO (g) at 50°C in hexane [3], compound II did not react with CO at atmospheric pressure in THF at room or reflux temperature or under UV irradiation.

It was, however, found that treatment of the complexes Ia or Ib with Na amalgam in THF under CO(g) (1 atm.) at room temperature gave the yellow crystalline compound $[Ph_2\overline{PCH_2CH_2(O)CMn(CO)_2(dppm)}]$ (III) (reaction iii in Scheme 1) data for which are given in Tables 1 and 2. The presence of the acyl group was indicated by an absorption at 1567 cm^{-1} in the IR spectrum and this was confirmed by the $^{13}C\{^1H\}$ NMR spectrum, which showed an unresolved signal at 299 ppm assignable to the acyl carbon [12]. Other peaks in the ^{13}C NMR were 230 (m, br, CO), 128–133 (C_6H_5), 57.2 (d, CH_2CO, $J(^{13}C-^{31}P)$ 15.4 Hz), 41.8 (m, $CH_2(PPh_2)_2$) and 23.4 ppm (d, CH_2PPh_2, $J(^{13}C-^{31}P)$ 19.8 Hz). The $^{31}P\{^1H\}$ NMR spectrum of III, taken at room temperature in $CDCl_3$, showed three groups of sharp signals corresponding approximately to an AMX system. The assignments shown in Table 2 are based on the structure indicated in Scheme 1 for III taking account of the fact that the ring current in the five-membered ring should result in deshielding of the P(c) atom (Fig. 1) by about +30–40 ppm [10] as compared with, e.g., compound I.

In order to establish the stereochemistry of compound III unambiguously, it was structurally characterized by X-ray diffraction study. The results are summarized in Tables 3–5 and the structure is shown in Fig. 2 along with the atomic numbering scheme.

The Mn atom displays distorted octahedral coordination, with Mn, P(1), P(2), P(3) and C(4) in the best plane (the largest deviation from the mean plane is −0.112(2) Å in Mn atom). The carbon atom of the acyl group (C(33)) is *cis* to all the phosphorus atoms and *trans* to one CO, and the Ph_2P group of the phospha-

(*Continued on p. 200*)

TABLE 3

MAIN BOND LENGTHS (Å) FOR COMPOUND III

P(1)–Mn	2.352(2)	C(211)–P(2)	1.830(8)
P(2)–Mn	2.267(2)	C(221)–P(2)	1.812(8)
P(3)–Mn	2.260(2)	C(311)–P(3)	1.831(6)
C(33)–Mn	2.207(6)	C(321)–P(3)	1.819(7)
C(4)–Mn	1.759(6)	C(31)–P(3)	1.869(10)
C(5)–Mn	1.767(9)	C(32)–C(31)	1.468(15)
C(12)–P(1)	1.813(7)	C(33)–C(32)	1.338(13)
C(111)–P(1)	1.831(7)	O(34)–C(33)	1.272(8)
C(121)–P(1)	1.845(8)	O(4)–C(4)	1.152(8)
P(2)–C(12)	1.852(6)	O(5)–C(5)	1.175(11)

TABLE 4

MAIN BOND ANGLES (°) FOR COMPOUND III

P(2)–Mn–P(1)	71.8(1)	C(221)–P(2)–C(12)	107.4(3)
P(3)–Mn–P(1)	97.8(1)	C(221)–P(2)–C(211)	101.1(3)
P(3)–Mn–P(2)	166.9(1)	C(112)–C(111)–P(1)	119.4(6)
C(33)–Mn–P(1)	90.1(1)	C(116)–C(111)–P(1)	122.6(5)
C(33)–Mn–P(2)	91.3(2)	C(122)–C(121)–P(1)	122.1(6)
C(33)–Mn–P(3)	80.5(2)	C(126)–C(121)–P(1)	117.5(7)
C(4)–Mn–P(1)	163.8(3)	C(212)–C(211)–P(2)	121.7(6)
C(4)–Mn–P(2)	92.9(2)	C(216)–C(211)–P(2)	119.4(6)
C(4)–Mn–P(3)	96.5(2)	C(222)–C(221)–P(2)	120.0(8)
C(4)–Mn–C(33)	84.8(3)	C(226)–C(221)–P(2)	123.3(6)
C(5)–Mn–P(1)	98.3(2)	C(311)–P(3)–Mn	120.2(3)
C(5)–Mn–P(2)	95.4(3)	C(321)–P(3)–Mn	119.1(2)
C(5)–Mn–P(3)	94.0(3)	C(321)–P(3)–C(311)	102.4(3)
C(5)–Mn–C(33)	170.6(2)	C(31)–P(3)–Mn	104.2(3)
C(5)–Mn–C(4)	88.2(3)	C(31)–P(3)–C(311)	104.8(4)
C(12)–P(1)–Mn	93.5(2)	C(31)–P(3)–C(321)	104.4(4)
C(111)–P(1)–Mn	125.4(2)	C(312)–C(311)–P(3)	124.7(6)
C(111)–P(1)–C(12)	101.3(3)	C(316)–C(311)–P(3)	119.6(6)
C(121)–P(1)–Mn	125.0(2)	C(322)–C(321)–P(3)	122.8(6)
C(121)–P(1)–C(12)	102.5(3)	C(326)–C(321)–P(3)	119.8(6)
C(121)–P(1)–C(111)	100.6(3)	C(32)–C(31)–P(3)	108.1(8)
P(2)–C(12)–P(1)	95.3(3)	C(33)–C(32)–C(31)	118.6(8)
C(12)–P(2)–Mn	95.3(2)	C(32)–C(33)–Mn	119.3(6)
C(211)–P(2)–Mn	117.7(3)	O(34)–C(33)–Mn	116.7(4)
C(211)–P(2)–C(12)	107.6(3)	O(34)–C(33)–C(32)	121.8(7)
C(221)–P(2)–Mn	126.2(2)	O(4)–C(4)–Mn	174.4(7)
		O(5)–C(5)–Mn	174.0(6)

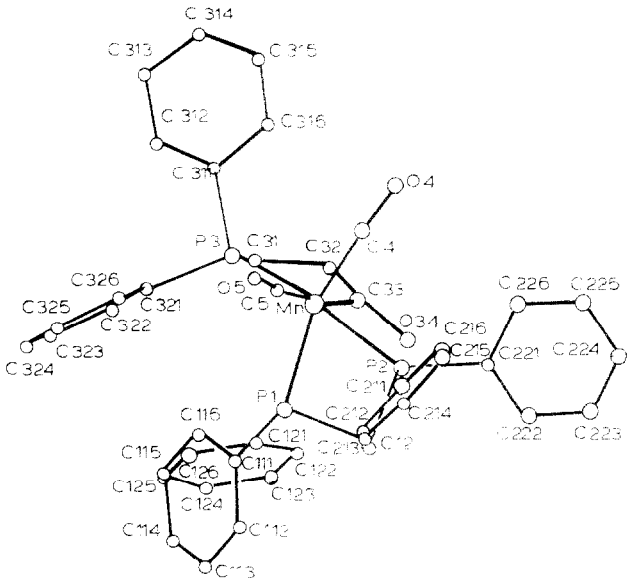


Fig. 2. A view of the molecule $[Ph_3\overline{PCH_2CH_2(O)CMn(CO)_2(dppm)}]$ (III) showing the atomic numbering scheme.

TABLE 5

FINAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS FOR COMPOUND III

Atom	x	y	z	B_{eq}
Mn	9700(1)	1593(0)	5888(1)	3.06(5)
P(1)	7738(1)	1597(1)	4740(1)	3.34(9)
C(12)	8032(5)	2162(3)	3962(5)	3.61(34)
P(2)	9682(1)	2105(1)	4463(1)	3.36(9)
C(111)	7106(6)	1079(3)	3728(5)	3.44(39)
C(112)	6136(6)	1213(4)	2898(5)	4.81(40)
C(113)	5673(8)	850(5)	2072(6)	6.57(57)
C(114)	6215(10)	336(6)	2109(7)	7.02(63)
C(115)	7177(9)	170(4)	2926(8)	7.32(61)
C(116)	7612(8)	563(4)	3731(7)	5.76(52)
C(121)	6390(6)	1779(4)	5113(5)	3.64(38)
C(122)	6143(6)	2308(4)	5318(6)	4.68(46)
C(123)	5142(8)	2423(4)	5649(7)	7.04(56)
C(124)	4396(8)	1986(7)	5736(7)	7.94(70)
C(125)	4657(8)	1467(6)	5546(8)	7.66(65)
C(125)	5663(6)	1354(4)	5230(6)	5.62(46)
C(211)	10195(6)	1775(3)	3443(5)	3.95(38)
C(212)	9449(6)	1432(4)	2686(6)	5.72(45)
C(213)	9893(8)	1165(4)	1991(7)	7.30(55)
C(214)	11049(10)	1219(5)	2002(8)	7.42(67)
C(215)	11784(9)	1557(4)	2719(11)	8.37(75)
C(216)	11337(7)	1839(4)	3451(7)	6.13(49)
C(221)	10290(5)	2794(3)	4475(5)	3.93(37)
C(222)	9766(7)	3158(4)	3674(7)	6.04(52)
C(223)	10209(9)	3680(5)	3649(9)	7.21(63)
C(224)	11143(9)	3854(4)	4430(9)	6.28(62)
C(225)	11669(9)	3508(5)	5218(7)	7.61(61)
C(226)	11251(8)	2983(4)	5250(6)	6.67(53)
P(3)	9309(1)	1174(1)	7261(1)	3.62(9)
C(311)	10533(6)	891(4)	8333(5)	4.02(40)
C(312)	10559(8)	371(5)	8720(8)	7.55(57)
C(313)	11468(10)	177(4)	9595(8)	9.05(67)
C(314)	12428(8)	528(5)	10006(7)	6.84(56)
C(315)	12441(7)	1040(5)	9659(6)	6.67(53)
C(316)	11517(8)	1224(4)	8825(6)	6.42(47)
C(321)	8205(5)	622(3)	7013(5)	3.53(35)
C(322)	7237(6)	633(4)	7382(6)	5.79(46)
C(323)	6383(7)	220(4)	7127(7)	6.57(56)
C(324)	6513(7)	−206(4)	6524(7)	6.01(52)
C(325)	7482(8)	−242(4)	6173(7)	6.59(54)
C(326)	8317(7)	180(4)	6417(6)	5.43(47)
C(31)	8652(8)	1734(4)	7881(7)	6.32(54)
C(32)	9105(13)	2266(4)	7632(7)	11.31(75)
C(33)	9289(4)	2326(2)	6697(4)	1.34(27)
O(34)	8953(5)	2757(3)	6142(4)	6.24(34)
C(4)	11202(6)	1756(3)	6541(5)	4.48(37)
O(4)	12206(4)	1853(3)	6894(4)	8.80(37)
C(5)	10207(6)	980(4)	5439(5)	4.28(39)
O(5)	10646(5)	589(3)	5186(4)	6.65(37)

mangana-cyclopentanone ring (P(3)) is *trans* to one of the phosphorus of the dppm ligand (P(2)). This corresponds to the structure indicated for III in Scheme 1. The angle P(1)–Mn–P(2) (71.82°) is within the range expected for a chelating dppm, as is the torsion angle P(2)–Mn–P(1)–C(12) (−14.03°) [13]. Also as expected, the angles about the acyl carbon (C(33)) are close to 120° and the C(33)–O(34) bond distance of 1.272 Å is within the usual range for a C=O double bond of an acyl group. The Mn–C(33) distance is long (2.207 Å), however, compared with the values observed in the few acyl complexes of manganese so far studied by X-ray crystallography, which range around 2.05–2.09 Å [14]. It is possible that steric factors may be partially responsible for this.

The torsion angle P(3)–C(31)–C(32)–C(33) (34.8(8)°), and the short C(33)–C(32) and C(32)–C(31) bond distances in the five-membered ring are affected by the disorder of the C(32) atom, which shows the highest thermal coefficient.

The Mn–CO distances of the carbonyl ligand are also very similar (mean value 1.763(4) Å), but the Mn–P bond lengths appears to be more sensitive to the ligands *trans* to them: thus Mn–P(3) and Mn–P(2) bonds are ca. 0.09 Å shorter than Mn–P(1) bond, which has a CO *trans* to it.

Compound III was prepared more rapidly in one-pot reaction by treatment of a mixture of *fac*-[$BrMn(CO)_3$(dppm)] and $Ph_2PCH_2CH_2Cl$ in THF with Na amalgam at room temperature (iv in Scheme 3).

It is likely that this reaction involves the initial formation of the anion [$Mn(CO)_3$(dppm)]$^-$, which subsequently displaces the Cl atom in the $Ph_2PCH_2CH_2Cl$ to give an intermediate alkyl [$Ph_2PCH_2CH_2Mn(CO)_3$(dppm)], which would give III by an internal insertion reaction. The validity of the assumed first step was confirmed by reducing *fac*-[$BrMn(CO)_3$(dppm)] with Na/Hg, followed by addition of $Ph_2PCH_2CH_2Cl$ to the resulting [$Mn(CO)_3$(dppm)]$^-$, which gave identical results. The presence of some *fac*-[$HMn(CO)_3$(dppm)] [15] in the products of reaction iv is also consistent with the assumed first step.

There are not enough data to show whether alkyl migration is always easier or more difficult in more substituted species [16], and it is not clear why the assumed β-diphenylphosphinoalkyl-tricarbonyl intermediate should so readily undergo the rearrangement leading to the acyl complex III. It is possible that the presence of an uncoordinated Ph_2P group in this phosphino-alkyl intermediate favours the rapid formation of the acyl species because of its high "local concentration" near the manganese atom.

On the other hand the stereochemistries of the final products of the reactions of alkyl-carbonyl complexes with various ligands can be very dependent on steric factors [17,18]. Thus, if we assume that the final step in reaction iv is the migration of the alkyl group, whatever the nature of the pentacoordinate intermediate [16] the Ph_2P group would coordinate to the manganese *trans* to one of the phosphorus atoms of the dppm rather than at the more sterically crowded site *cis* to both phosphorus atom. This assumption, which is consistent with the *fac*- to *mer*-isomerization of the species [$M(CO)_3$(diphos)L]^n (M = Mo, $n = 0$ [19], M = Mn, $n = 1$ [20]), could account for the stereochemistry found for compound III.

The result of reaction iv also helps us to understand why the acyl complex III, is formed in reaction iii whereas compound II does not react with CO to give III at room temperature. A possible explanation is that the reduction of compound I with Na amalgam initially gives the anion [$Mn(CO)_2$(dppm)($Ph_2PCH_2CH_2Cl$)]$^-$, which

then reacts with CO to give the tricarbonyl anion $[Mn(CO)_3(dppm)]^-$ and free $Ph_2PCH_2CH_2Cl$; the interaction of these two products, would then give III, as in path iv. We confirmed the plausibility of the first step, i.e., replacement of the phosphine by the CO in the dicarbonyl anion, by treating *cis,cis*-[Cl-$Mn(CO)_2(dppm)(PPh_2Et)$] with Na/Hg in the presence of CO, and obtaining, after hydrolysis, the known complex *fac*-$[HMn(CO)_3(dppm)]$ [15]. Several attempts to decarbonylate the acyl complex III led mostly to decomposition, but when the reaction was carried out with UV irradiation in THF at $-10°C$ some of the alkyl complex II was found in the final residue, as evidenced by its two $\nu(CO)$ bands in the IR spectrum.

As expected, the ligand $Ph_2PCH_2CH_2Cl$ replaced the coordinated O_3ClO ligand in the *fac*-$[O_3ClOMn(CO)_3(dppm)]$ [20] to give the salt *fac*-$[Mn(CO)_3(dppm)$-$(Ph_2PCH_2CH_2Cl)]ClO_4$ (IV). The IR spectrum in the $\nu(CO)$ region (Table 1) and the $^{31}P\{^1H\}$ NMR spectrum (two broad signals in a 1/2 ratio centered at 34 and 10.5 ppm) were consistent with the formulation indicated. Again as expected [20], compound IV isomerized in boiling butanol to the *mer*-$[Mn(CO)_3(dppm)$-$(Ph_2PCH_2CH_2Cl)]ClO_4$ isomer (V). The IR and $^{31}P\{^1H\}$ NMR spectra (Tables 1 and 2) were consistent with those observed for the closely related species *mer*-$[Mn(CO)_3(dppm)_2]ClO_4$ [6].

Interestingly, both of the cationic carbonyl complexes IV and V gave the acyl complex III when reduced with Na/Hg in THF. Apparently in those cases also the reaction is between the anion $[Mn(CO)_3(dppm)]^-$ and the free ligand $Ph_2PCH_2CH_2Cl$, formed in situ in the reduction of the carbonyl cations. This explanation was supported by the observation that reduction of the salt *mer*-$[Mn(CO)_3(dppm)(Ph_2PEt)]ClO_4$ with Na/Hg in THF, followed by hydrolysis, gave the known hydride *fac*-$[HMn(CO)_3(dppm)]$ [15].

Experimental

All reactions were carried out under dry argon. The ligand $Ph_2PCH_2CH_2Cl$ [1] and the complexes *fac*-$[BrMn(CO)_3(dppm)]$ and *fac*-$[O_3ClOMn(CO)_3(dppm)]$ [20], were prepared by published methods. IR spectra were recorded using a Perkin–Elmer 298 spectrophotometer and calibrated against the 1601.4 cm^{-1} polystyrene absorption. NMR spectra were recorded on a JEOL FX 90Q instrument.

Structure determination of compound $[Ph_2\overline{PCH_2CH_2(O)CMn(CO)_2(dppm)}]$

Crystal data. $C_{42}H_{36}O_3P_3Mn$, Fw. 736.6, monoclinic, a 11.715(3), b 24.212(6), c 13.366(2) Å, β 107.40(2)°, V 3618(2) Å^3, $P2_1/n$, $D_x = 1.35$ g cm^{-3}, $Z = 4$, $F(000) = 1528$, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 5.56 cm^{-1}. Room temperature.

A yellow prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters were determined from 23 reflections ($3 \leqslant \theta \leqslant 18°$). Intensities were collected with graphite monochromatized Mo-K_α radiation, using the $\omega/2\theta$ scan technique. Three reflections were measured each 2 h as orientation and intensity control, significant variations were not observed. 4631 intensities were collected in the range $2 \leqslant \theta \leqslant 25°$, and 2593 of these were treated as observed using the criterion $I \geqslant 2.5\sigma(I)$. Lorentz-polarization effects were taken into account but no absorption corrections were made.

The structure was solved by direct methods using the MULTAN system computer programs [21], and refined isotropically and anisotropically by full-matrix least-squares, using the SHELX76 computer program [22]. The function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma^2(F_o) + 0.0039|F_o|^2)^{-1}$; f, f' and f'' were taken from International Tables of X-Ray Crystallography [23]. 33 (of 36) hydrogen atoms were determined from a ΔF-synthesis and refined with an overall isotropic temperature factor. The final R value was 0.053 ($R_w = 0.057$).

cis-[XMn(CO)$_3$(dppm)(Ph$_2$PCH$_2$CH$_2$Cl)] (Ia, Ib)

A mixture of *fac*-[ClMn(CO)$_3$(dppm)] (1 g, 1.79 mmol) and Ph$_2$PCH$_2$CH$_2$Cl (0.50 g, 2 mmol) in toluene (30 ml) was refluxed for 7 h. The volatiles were evaporated off in vacuo and the resulting yellow oil was washed with a mixture of 10% diethyl ether in hexane (3 × 30 ml) to give a yellow solid. This was dissolved in toluene (100 ml) and the solution was filtered, to give ca. 0.1 g of solid *cis*-[Mn(CO)$_2$(dppm)$_2$]Cl. The toluene solution was evaporated almost to dryness and treated with hexane to give Ib (0.76 g, 54%).

Ia was similary prepared in 30% yield from *fac*-[BrMn(CO)$_3$(dppm)] with 15 h reflux.

cis-[Ph$_2$PCH$_2$CH$_2$Mn(CO)$_3$(dppm)] (II)

A solution of Ib (0.8 g, 1.03 mmol) in THF (20 ml) was stirred with 20 g of 0.5% Na amalgam for 2 h at room temperature. The liquid was removed with a syringe and evaporated to dryness under vacuum, and the residue extracted with toluene (5 × 20 ml). The extracts were evaporated and the remaining solid was washed with hexane to give the yellow compound II (0.36 g, 50%). The product can be crystallized from toluene/hexane.

cis-[Ph$_2$PCH$_2$CH$_2$(O)CMn(dppm)] (III)

(a) From Ib. A solution of Ib (0.4 g, 0.5 mmol) in thf (30 ml) was saturated with CO and then 20 g of 0.5% Na amalgam was added. The mixture was stirred for 1 h with CO bubbling through. After removal of the excess amalgam the liquid was evaporated in vacuo and the residue was extracted with toluene (4 × 20 ml). The extracts were concentrated nearly to dryness and then washed several times with hexane to remove the *fac*-[HMn(CO)$_3$(dppm)], leaving crude III, which was crystallized from toluene/hexane (0.245 g, 45%).

(b) From fac-[BrMn(CO)$_3$(dppm)]. To a solution of *fac*-[BrMn(CO)$_3$(dppm)] (1 g, 1.66 mmol) and Ph$_2$PCH$_2$CH$_2$Cl (0.55 g, 2.2 mmol) in THF (35 ml) was added 35 g of 0.5% of Na amalgam. The mixture was stirred for 2 h at room temperature then the liquid was removed with a syringe and evaporated. The resulting yellow oil was washed with hexane to give a solid which was treated as in the preceding experiment to give III (0.91 g, 75%).

(c) From fac- or mer-[Mn(CO)$_3$(dppm)(Ph$_2$PCH$_2$CH$_2$Cl)]ClO$_4$. Treatment of IV or V (0.2 g, 0.23 mmol) with 0.5% Na amalgam (10 g) in 10 ml of THF for 1 h, followed by work-up similar to that in (a) and (b) above, gave III in 45% yield.

fac-[Mn(CO)$_3$(dppm)(Ph$_2$PCH$_2$CH$_2$Cl)]ClO$_4$ (IV)

A solution of *fac*-[O$_3$ClOMn(CO)$_3$(dppm)] (1 g, 1.6 mmol) and Ph$_2$PCH$_2$CH$_2$Cl (0.6 g, 2.4 mmol) in CH$_2$Cl$_2$ (40 ml) was refluxed until the IR spectrum of the

solution no longer showed the ν(CO) bands due to the starting material. The volatiles were removed in vacuo and the residue was washed several times with diethyl ether to give yellow IV (1.1 g, 84%).

mer-[Mn(CO)$_3$(dppm)(Ph$_2$PCH$_2$CH$_2$Cl)]ClO$_4$ (V)

The salt IV (0.4 g, 0.46 mmol) was heated in refluxing n-butanol (25 ml) for 7 h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (50 ml) and the solution filtered. The filtrate was concentrated to 0.5 ml and sufficient diethyl ether was added to precipitate the yellow compound V (0.35 g, 88%).

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