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NEUTRAL AND CATIONIC DICARBONYL COMPLEXES OF MANGANESE(I) WITH DIPHOSPHINES

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Summary

The reaction of $BrMn(CO)_5$ with dppm in refluxing toluene gives the neutral compound *cis-cis*-$BrMn(CO)_2(dppm)_2$ which has been shown by ^{31}P NMR spectroscopy to have one dppm monodentate and the other bidentate. This complex reacts with $TlPF_6$ in dichloromethane solution to give the salt *cis*-$[Mn(CO)_2(dppm)_2]PF_6$ or, if the reaction is carried out in the presence of CO, the salt *mer*-$[Mn(CO)_3(dppm)_2]PF_6$, which also has one monodentate dppm (by ^{31}P NMR). The cationic complex *cis*-$[Mn(CO)_2(dppm)_2]^+$ isomerizes to the *trans*-isomer when irradiated with UV light, while heating of the latter gives back the *cis*-isomer. The perchlorate salts of the cation *cis*-$[Mn(CO)_2(dppm)_2]^+$ can be prepared by reacting *fac*-$O_3ClOMn(CO)_3(dppm)$ with dppm in refluxing toluene, and *trans*-$[Mn(CO)_2(diphos)(diphos)']^+$, diphos or diphos' being dppm or dppe, by treating the *fac*-$O_3ClMn(CO)_3(diphos)$ with dppm or dppe under UV irradiation.

Introduction

The reaction between $BrMn(CO)_5$ and the potentially bidentate diphosphine dppm * has been previously studied [1,2], but, as far as we know, only the species *cis*-$BrMn(CO)_4(dppm)$ [2], *fac*-$BrMn(CO)_3(dppm)$ [1,2] and *trans*-$BrMn(CO)(dppm)_2$ [1] have been reported. It has been shown, however, that the tricarbonyls *fac*-$BrMn(CO)_3(diphos)$ (diphos = dppm or dppe) undergo facile CO substitution by phosphorus donor ligands L to give the dicarbonyls *cis-cis*-$BrMn(CO)_2(diphos)L$ [3,4], which are similar to other bromocarbonyls containing polydentate phosphines [3,5,6,7], e.g. $BrMn(CO)_2(triphos)$ (triphos = PhP-

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* Throughout this paper the diphosphines $(Ph_2P)_2(CH_2)_n$ are referred as dppm (n = 1) or dppe (n = 2).

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$(CH_2CH_2PPh_2)_2$) [3]. These results, and the observation that the dppm can be monodentate [8], suggested that the *fac*-$BrMn(CO)_3$(dppm) might react with dppm to give *cis-cis*-$BrMn(CO)_2(dppm)_2$. On the other hand, this neutral dicarbonyl could be an intermediate in the formation of *trans*-$BrMn(CO)(dppm)_2$ from $BrMn(CO)_5$ and an excess of dppm [1].

Accordingly, we have found that, when a mixture of $BrMn(CO)_5$ and dppm is refluxed in toluene, the complex *cis-cis*-$BrMn(CO)_2(dppm)_2$(I) is formed. Moreover, irradiation of I with UV light gave *trans*-$BrMn(CO)(dppm)_2$. The structure of I, with one dppm monodentate in *cis* with the Br atom, suggested that this complex should be able to react with halide abstractors to give the hitherto unknown *cis*-$[Mn(CO)_2(dppm)_2]^+$ cation, and this has been also confirmed by experiment.

In this paper we also discuss the reactions between the neutral $O_3ClOMn(CO)_3$(diphos) and the diphosphine (diphos = dppm or dppe) under various conditions, and also the *cis* → *trans* and *trans* → *cis* isomerizations in the cation $[Mn(CO)_2(dppm)_2]^+$.

Results and discussion

On refluxing a mixture of $BrMn(CO)_5$ and dppm (1/2 molar ratio) in toluene for several hours, the initially formed *fac*-$BrMn(CO)_3$(dppm) reacts further with the dppm to give the yellow compound *cis-cis*-$BrMn(CO)_2(dppm)_2$(I) (reaction i in Scheme 1) which can be crystallized as several solvates *. The analytical results (Table 1) and the osmometric molar mass, determined in benzene (calc. 959, obs. 1000) agreed with the monomeric formulation of I. The molar conductivity in 5×10^{-4} *M* acetone solution (Table 1) clearly indicated that it was a non-electrolyte. The IR spectrum showed two bands of nearly the same intensity in the $\nu(CO)$ region at 1938 and 1867 cm^{-1} (Cl_2CH_2 solution) which are very close to those reported for similar compounds [3,5,6,7], and so the two CO's are mutually *cis*. The proton-decoupled ^{31}P NMR spectrum of I taken in Cl_2CH_2 at room temperature showed a sharp doublet centered at 27.6 ppm ** and three broad multiplets centered at circa −0.8, −36 and −51 ppm. Nevertheless, on cooling to −60° C, all these signals are resolved as three double doublets and a doublet of doublet of doublets, respectively. This pattern, and the fact that only the three signals at lower fields are broad (the ones of the phosphorus directly bonded to the ^{55}Mn atom which has $I = 5/2$), are consistent with the structure proposed for I (Fig. 1(a)). The resulting ^{31}P chemical shifts (δP, ppm), coordination chemical shifts (Δ) [11], and phosphorus—phosphorus coupling constants ($^xJ(P—P)$, cps), namely: δPa 30.2 (Δa 6.6), δPb −49.1 (Δb −72.6), δPc −1.6 (Δc −25.2), δPd −35.6 (Δd −49.1), $^2J(Pa—Pb)$ 19, $^2J(Pb—Pc)$ 46, $^2J(Pb—Pd)$ 67, $^2J(Pc—Pd)$ 33 and $^4J(Pa—Pd)$ ca. 4.5 (the signs of the $J(P—P)$ were not determined), are reasonable on the basis of other work [12—20]. The

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[*] Small amounts of the known $HMn(CO)_3$(dppm) [9] and $Mn_2(CO)_5(dppm)_2$ [10] were also detected (by their $\nu(CO)$ bands) among the products.

[**] Throughout this paper resonances downfield from external 85% H_3PO_4 are assigned negative shifts. For the free dppm $\delta P = 23.6$.

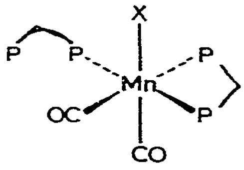
TABLE 1

ANALYTICAL RESULTS OF THE COMPOUNDS I—VI

	Compound	M.p. [a] (°C)	Λ [b] (S cm^2 mol^{-1})	Analysis (Found (calcd.) (%))		ν(CO) [c] frequencies (cm^{-1})	
				C	H		
I	*cis-cis*-BrMn$(CO)_2(dppm)_2$	187	0.9	65.0(65.1)	4.78(4.59)	1938s	1867s
Ia	*cis-cis*-BrMn$(CO)_2(dppm)_2 \cdot C_6H_5CH_3$	187	0.9	67.4(67.4)	5.34(4.94)	1938s	1867s
II	*mer*-$[Mn(CO)_3(dppm)_2]PF_6$	152	120	59.1(60.5)	4.51(4.21)	2041w	1963s(br)
IIIa	*cis*-$[Mn(CO)_2(dppm)_2]Br \cdot Cl_3CH$	237	81	59.7(59.0)	4.68(4.20)	1960s	1906s [d]
IIIb	*cis*-$[Mn(CO)_2(dppm)_2]PF_6$	297	138	60.8(60.9)	4.23(4.29)	1961s	1908s [e]
IIIc	*cis*-$[Mn(CO)_2(dppm)_2]ClO_4$	278	123	63.8(63.8)	4.84(4.52)	1961s	1908s [e]
IV	*trans*-$[Mn(CO)_2(dppm)_2]ClO_4$	277 [f]	132	63.4(63.8)	4.52(4.52)	1916s	
V	*trans*-$[Mn(CO)_2(dppm)(dppe)]ClO_4$	239	128	64.3(64.1)	4.80(4.63)	1909s	
VI	*trans*-$[Mn(CO)_2(dppe)_2)ClO_4$	237	132	63.2(64.4)	4.81(4.99)	1899s	

[a] All with decomposition. [b] In 5×10^{-4} acetone solution near 25°C. [c] In Cl_2CH_2 solution. [d] In the solid state the bands are at 1942 and 1890 cm^{-1}. [e] In the solid state at 1938 and 1878 cm^{-1}. [f] At circa 200°C the colour changed from orange to yellow.

value of $^{2}J(\mathrm{P}a{-}\mathrm{P}b)$ is, however, low as compared with the reported 64.4 for the analogous complex *mer*-$\mathrm{Mo(CO)_3(dppm)_2}$ [12], and with other coupling constants between the coordinated phosphorus and the uncoordinated one in other monodentate polyphosphine complexes [12,14,15,16,21]. The ^{1}H NMR spectrum of I showed the resonances of the Ph-groups as two broads multiplets centered at 7.1 and 6.9 (δ) and the signals of the $\mathrm{CH_2}$-groups as two broad complex multiplets between 3.5—3.9 and 4.6—4.9 (δ), which are close to those reported for the analogous complex $[\mathrm{Mo(CO)_2(dppm)_2X}]^+$, in which one dppm is monodentate and the other bidentate [22].

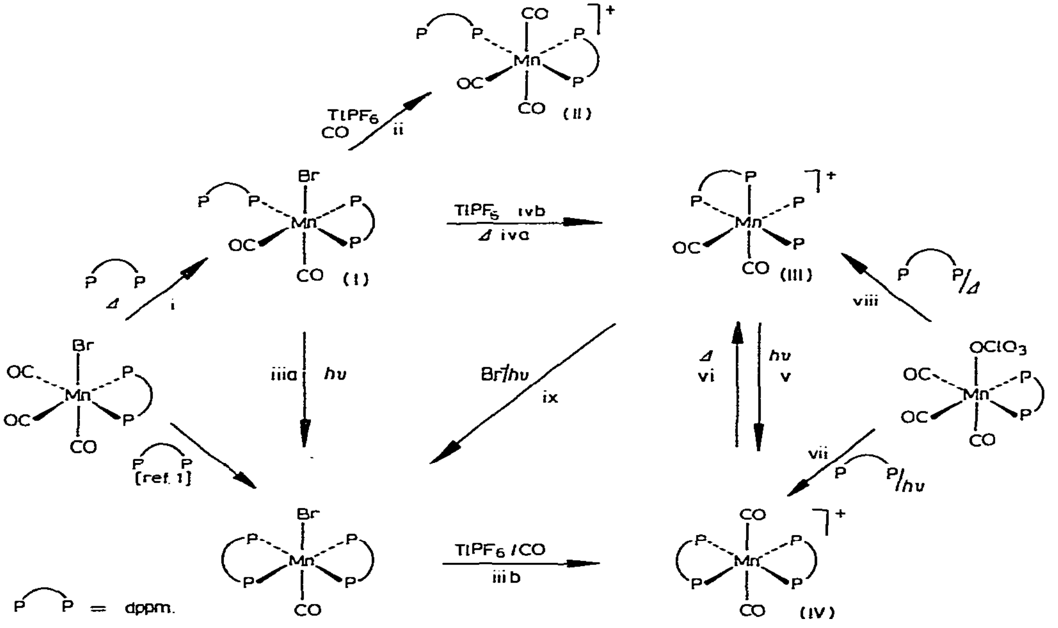


(a) X = Br,(b) X = CO

Fig. 1.

The reaction between I and CO (1 atm) in the presence of $\mathrm{TlPF_6}$ in $\mathrm{Cl_2CH_2}$ at room temperature (ii in Scheme 1) gave mainly (see below) the yellow salt *mer*-$[\mathrm{Mn(CO)_3(dppm)_2]PF_6}$ (II), analogous to the neutral Mo complex mentioned above [12]. The analytical and conductivity data for II (Table 1) were in accord with this formulation. The ν(CO) IR spectrum in $\mathrm{Cl_2CH_2}$ solution

SCHEME 1



showed a weak band at 2041 and a strong broad band at 1963 cm^{-1}, which is the pattern observed for other analogous cationic *mer*-tricarbonyls [4,23]. Thus, the fact that II is not a *fac*-tricarbonyl provides further support for the structure proposed for I. One sharp doublet centered at +27.0 ppm (separation of 58 cps) in the $^{31}P\{^1H\}$ spectrum of II in Cl_2CH_2 at room temperature, clearly evidenced the presence of one monodentate dppm in this complex. The spectrum also showed three partially resolved multiplets centered at circa —10, —30 and —49.5 ppm, which is also consistent with the structure shown in Fig. 1(b) ($^2J(ab) \simeq 58$). Other five sharp peaks centered at +144 ppm and separated by an average of 708 cps were assigned to the heptet of the PF_6^- anion ($^1J(P—F)$ 708).

It has been found that the reaction of $BrMn(CO)_5$ with dppm under UV irradiation in benzene gives *fac*-$BrMn(CO)_3$(dppm) or *trans*-BrMn(CO)(dppm)$_2$ [1]. However, the reactions between $BrMn(CO)_5$ and the phosphorus-donor ligands are believed to proceed stepwise [3], and the unstable *cis*-$BrMn(CO)_4$(dppm) has been shown to be an intermediate in the formation of *fac*-$BrMn(CO)_3$(dppm) [2]. Thus, it seemed likely that the *cis-cis*-$BrMn(CO)_2$(dppm)$_2$(I) could be an intermediate in the formation of the highly substituted monocarbonyl. In accord with this we observed that the irradiation of I with UV light (iiia in Scheme 1) results in substitution of the CO *cis* to the Br atom by the free Ph_2P group of the monodentate dppm. The structure of the resulting *trans*-BrMn(CO)(dppm)$_2$ (identical to the reported on [1]) was confirmed by reacting it with CO (1 atm) and $TlPF_6$ in Cl_2CH_2, a reaction which led to the orange salt *trans*-[Mn(CO)$_2$(dppm)$_2$]PF$_6$. (iiib in Scheme 1). This latter compound has been prepared by several methods in the present study and will be considered later.

A yellow precipitate was also formed in reaction (i) along with compound I. The same yellow product was obtained when a solution of I in toluene was refluxed for several hours (iva in Scheme 1). The compound was recrystallized from Cl_3CH/hexane and characterized tentatively as the salt *cis*-[Mn(CO)$_2$(dppm)$_2$]Br · Cl_3CH (IIIa), analogous to the known *cis*-[Re(CO)$_2$(dppe)$_2$]Br [24]. The analytical data, conductivity and ν(CO) region IR spectrum (two strong bands at 1960 and 1906 cm^{-1} in Cl_2CH_2) were in accord with its formation. Moreover, stirring a Cl_2CH_2 solution of IIIa with $TlPF_6$ gave the yellow salt *cis*-[Mn(CO)$_2$(dppm)$_2$]PF$_6$ (IIIb). This latter was also prepared by reacting I with $TlPF_6$ as shown in reaction ivb of Scheme 1. The compound IIIb is also formed together with the *mer*-[Mn(CO)$_3$(dppm)$_2$]PF$_6$ in the reaction between I and $TlPF_6$ in the presence of CO (see above), in which there is competition between the uncoordinated -PPh_2 and the CO to occupy the vacant coordination site left by the Br$^-$. The IR spectrum of IIIb in Nujol showed two strong ν(CO) frequencies at 1938 and 1878 cm^{-1} (very low as compared with the values of 1961 and 1908 cm^{-1} observed in Cl_2CH_2 solution), and the strong band at 834 cm^{-1} due to the octahedral PF_6^- anion. The ^{31}P-$\{^1H\}$ NMR spectrum of IIIb in Cl_2CH_2 at —60° C, showed two partially resolved complex multiplets (AA′BB′ pattern) centered at —25.7 and —8.2 ppm, consistent with the *cis* structure proposed for it. The other signals centered at +144 ppm separated 708 cps, were those of the PF_6^- anion.

The UV irradiation of a Cl_2CH_2 solution of IIIb (v in Scheme 1) gave the orange *trans*-[Mn(CO)$_2$(dppm)$_2$]PF$_6$, as evidenced by IR spectroscopy. The complex isolated from this reaction had only one ν(CO) absorption in the IR at

1916 cm^{-1} as expected for a *trans*- dicarbonyl, and the full range IR spectrum of the solid (KBr disk) also showed the presence of the anion PF_6^- (834 cm^{-1}). Although the salts *cis*[$Mn(CO)_2(dppm)_2$] A (A = PF_6^- or ClO_4^-) isomerized to the *trans* isomer under UV irradiation, heating of the latter in refluxing toluene resulted in the re-formation of the original *cis*-isomer (vi in Scheme 1), and so the *cis* isomer is evidently more thermally stable than the *trans*. This is in accord with the greater thermodynamic stability of the *cis*-$Mo(CO)_2(dppm)_2$ [25] and *cis*-[$Re(CO)_2(dppm)_2$]$^+$ [24] compared with their *trans*-isomers.

Previously we have reported [23] that the neutral perchlorate complex *fac*-$O_3ClOMn(CO)_3(dppm)$ reacts with phosphites (L) under different conditions to give *fac*-[$Mn(CO)_3(dppm)L$]ClO_4 (room temperature), *mer*-[$Mn(CO)_3$-(dppm)L]ClO_4 (120°C) or *trans*-[$Mn(CO)_2(dppm)L_2$]ClO_4 (UV irradiation), but this could not be achieved with ligands with lower π-acceptor ability. Similarly the reaction between *fac*-$O_3ClOMn(CO)_3(dppm)$ and dppm under UV irradiation gave *trans*-[$Mn(CO)_2(dppm)_2$]ClO_4 (IV) (vii in Scheme 1). The analogous salts *trans*-[$Mn(CO)_2$(diphos)(diphos)$'$]ClO_4 (V) and (VI) (Table 1), were prepared in the same manner by reacting *fac*-$O_3ClOMn(CO)_3(dppe)$ with dppm or dppe *. Thus in those cases, the diphosphines resemble the phosphites in their ability to displace CO groups, as noted previously [1,26]. Monitoring by IR spectroscopy showed that the reactions proceeded stepwise, and that the cations *fac*-[$Mn(CO)_3$(diphos)$_2$]$^+$ (ν(CO) in the region of 1935s, 1960s cm^{-1}) and possibly *mer*-[$Mn(CO)_3$(diphos)$_2$]$^+$ (ν(CO) at about 2040w, 1960s cm^{-1}), presumably with one diphosphine monodentate, were intermediates in the formation of the *trans*-dicarbonyls. No clear evidence of the presence of *cis*-[Mn-$(CO)_2$(diphos)$_2$]$^+$ as an intermediate was observed. Attempts to prepare *fac*- and *mer*-[$Mn(CO)_3$(diphos)$_2$]ClO_4 by reacting *fac*-$O_3ClOMn(CO)_3$(diphos) with the diphosphine at room temperature or in boiling ethanol, respectively, for diphos = dppm or dppe, gave yellow solids with the correct IR spectra and which could be converted into the *trans*-[$Mn(CO)_2$(diphos)$_2$]ClO_4 by UV irradiation. Nevertheless we did not obtain satisfactory analytical results, probably due to the formation of bridged species. It was also observed that the heating of *fac*-$O_3ClOMn(CO)_3(dppe)$ in boiling ethanol gave *trans*-[$Mn(CO)_2(dppe)_2$]-ClO_4 directly. The IR spectra of the solids *trans*-[$Mn(CO)_2$(diphos)$_2$]ClO_4 showed the broad strong absorption at 1090 cm^{-1} of the ClO_4^- anion and only one strong band in the ν(CO) region. The frequency of this band (A2*u* in approximate *D4h* symmetry) in Cl_2CH_2 solution is higher in the dppm complexes (see Table 1), in accord with the trend observed in other complexes with diphosphines [23]. The ^{31}P-{^1H} NMR spectrum of the salt *trans*-[$Mn(CO)_2$-$(dppm)_2$]ClO_4 in Cl_2CH_2 at room temperature showed only one singlet at −33 ppm, which is consistent with the equivalency of the four phosphorus atoms. By comparing this chemical shift at −33 ppm (Δ = −56.6) with the value of −49 ppm (Δ = −72.6) for the coordinated phosphorus of the monodentate dppm in I or II, the shielding ring contribution (+Δ_R) [19,28] of the formation of the dppm four membered chelate ring can be estimated as +16 ppm. Com-

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* The compound *trans*-[$Mn(CO)_2(dppe)_2$]ClO_4 was already known [27].

parable values have been reported [29] for the complexes *cis*-$M(CO)_4(dppm)$ e.g. $\Delta_R = +12$ (M = Cr) or 19.3 (M = Mo).

On the other hand, when the reaction between *fac*-$O_3ClOMn(CO)_3(dppm)$ and dppm was carried out in refluxing toluene (viii in Scheme 1), the salt *cis*-$[Mn(CO)_2(dppm)_2]ClO_4$ (IIIc) was obtained instead of the *trans*-isomer. This result is in accord with the greater thermal stability of the *cis*-isomer as discussed above. Some $[Mn(CO)_4(dppm)]ClO_4$ [23] was also formed in the reaction viii, probably due to the decomposition of some *fac*-$O_3ClOMn(CO)_3(dppm)$.

Finally, UV irradiation of a mixture of *cis*-$[Mn(CO)_2(dppm)_2]PF_6$ and $BrNEt_4$ in Cl_2CH_2 (ix in Scheme 1) gave the same *trans*-$BrMn(CO)(dppm)_2$ as was obtained by irradiation of *cis-cis*-$BrMn(CO)_2(dppm)_2$ (I). The latter compound was not found as an intermediate in the reaction ix (by monitoring by IR). Thus, unless the formation of the monocarbonyl from I (see iiia in Scheme 1) is very fast compared with the formation of I by nucleophilic attack of the Br^- on the *cis*-$[Mn(CO)_2(dppm)_2]^+$, it is possible that the Br^- initially displaces one CO in the latter cation and this is followed by the isomerization of the resulting *cis*-$BrMn(CO)(dppm)_2$ to the obtained *trans*-monocarbonyl. The same *trans*-$BrMn(CO)(dppm)_2$ was formed when the salt *cis*-$[Mn(CO)_2(dppm)_2]Br$ was irradiated with UV light, resembling the formation of $BrRe(CO)(dppe)_2$ upon heating of *cis*-$[Re(CO)_2(dppe)_2]Br$ at 270°C [24]. In contrast, the irradiation of *trans*-$[Mn(CO)_2(dppm)_2]PF_6$ in the presence of Br^- anion resulted only in decomposition.

Experimental

The reactions were carried out under N_2. The IR spectra were recorded with a Perkin—Elmer 599 Spectrometer and calibrated against the polystyrene absorption at 1602 cm^{-1}. The ^{31}P NMR were obtained with JEOL FX90Q instrument using external 85% PO_4H_3 as reference. The complexes *fac*-$O_3ClOMn(CO)_3$(diphos) were prepared as described elsewhere [23].

Reaction of $BrMn(CO)_5$ *and dppm*

A mixture of $BrMn(CO)_5$ (0.2 g, 0.73 mmol) and dppm (0.62 g, 1.61 mmol) was refluxed in toluene (15 ml) for 5 h. The yellow precipitate of impure *cis*-$[Mn(CO)_2(dppm)_2]Br$ (0.1 g) was filtered off and the resulting orange solution was kept overnight at —10°C to give yellow crystals of *cis-cis*-$BrMn(CO)_2(dppm)_2 \cdot C_6H_5CH_3$ (0.24 g, 31%). Recrystallization from toluene or Cl_2CH_2/hexane followed by prolonged drying in vacuo gave pure I (the reaction time and the yield depend upon the amount of dppm used, the scale, and the volume of toluene employed).

Preparation of cis-$[Mn(CO)_2(dppm)_2]A$ *(A =* PF_6^- *or* ClO_4^-*)*

(a) from *cis-cis*-$BrMn(CO)_2(dppm)_2$ (I). The complex I (0.23 g, 0.24 mmol) and $TlPF_6$ (0.4 g, 1.1 mmol) were stirred overnight in Cl_2CH_2. The mixture was filtered and the solution was evaporated to dryness. The residue was washed with diethyl ether to give 0.11 g (50%) of *cis*-$[Mn(CO)_2(dppm)_2]PF_6$. Recrystallization was from Cl_2CH_2/hexane.

(b) from *fac*-$O_3ClOMn(CO)_3(dppm)$. A suspension of *fac*-$O_3ClOMn(CO)_3$-

(dppm) (0.44 g, 0.7 mmol) and dppm (0.36 g, 0.93 mmol) in toluene (15 ml) was refluxed for 45 min. The resulting yellow precipitate was washed with hot toluene and diethyl ether and recrystallized from Cl_2CH_2/hexane to give 0.5 g (72%) of *cis*-[Mn(CO)$_2$(dppm)$_2$]ClO$_4$. Recrystallization was from Cl_2CH_2/ethanol.

(c) from *trans*-[Mn(CO)$_2$(dppm)$_2$]ClO$_4$. A suspension of the salt *trans*-[Mn(CO)$_2$(dppm)$_2$]ClO$_4$ (0.095 g, 0.097 mmol) in 10 ml of toluene was refluxed for 3 h. The yellow precipitate of *cis*[Mn(CO)$_2$(dppm)$_2$]ClO$_4$ (0.089 g, 94%) was recrystallized from Cl_2CH_2/ethanol.

Preparation of mer-[Mn(CO)$_3$(dppm)$_2$]PF$_6$

CO gas (1 atm) was bubbled for 3 h through a stirred mixture of *cis-cis*-BrMn(CO)$_2$(dppm)$_2$ (0.2 g, 0.21 mmol) and TlPF$_6$ (0.09 g, 0.25 mmol) in 20 ml Cl_2CH_2. Filtration and evaporation of the solvent gave ca. 0.13 g of a mixture of *mer*-[Mn(CO)$_3$(dppm)$_2$]PF$_6$ and *cis*-[Mn(CO)$_2$(dppm)$_2$]PF$_6$. The *mer*-tricarbonyl was extracted with toluene and the extracts were evaporated to half volume. Addition of hexane led to precipitation of *mer*-[Mn(CO)$_3$(dppm)$_2$]PF$_6$, which was recrystallized from Cl_2CH_2/hexane. The yield depends upon the amount of the *cis*-dicarbonyl formed, which varies with the scale of the reaction, the concentration and the stirring conditions.

Preparation of trans-[Mn(CO)$_2$(diphos)$_2$]ClO$_4$

A magnetically stirred solution of *fac*-O$_3$ClOMn(CO)$_3$(dppm) (0.25 g, 0.4 mmol) and dppm (0.18 g, 0.48 mmol) in 20 ml of Cl_2CH_2 was irradiated with UV light for 2 h. After filtration, ethanol (10 ml) was added and the solution concentrated at reduced pressure. Addition of diethyl ether completed the precipitation of *trans*-[Mn(CO)$_2$(dppm)$_2$]ClO$_4$ (0.15 g, 38%), which was recrystallized several times from Cl_2CH_2/ethanol.

Following the same procedure, the complex *fac*-O$_3$ClOMn(CO)$_3$(dppe) was reacted with dppm to give *trans*-[Mn(CO)$_2$(dppe)(dppm)]ClO$_4$ (6 h, 42% yield) and with dppe to give the known [27] *trans*-[Mn(CO)$_2$(dppe)$_2$]ClO$_4$ (4 h, 89% yield).

The *trans*-[Mn(CO)$_2$(dppm)$_2$]ClO$_4$ was also prepared in 56% yield by UV irradiation of a Cl_2CH_2 solution of *cis*-[Mn(CO)$_2$(dppm)$_2$]ClO$_4$.

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