

CRYSTAL STRUCTURE OF THE DICARBONYL CATIONS *cis*- AND *trans*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2]^+$ AND THEIR REACTIONS WITH NUCLEOPHILES

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Summary

The crystal structures of the compounds *cis*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2]\text{Br} \cdot 1/3\text{H}_2\text{O}$ and *trans*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2][\text{ClO}_4] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ have been determined. The salt *cis*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2][\text{ClO}_4]$ was shown to react with KCN in the presence of the crown-ether 18-Crown-6 in refluxing acetone to give the neutral complex *cis,mer*- $[\text{Mn}(\text{CN})(\text{CO})_2(\text{dppm-PP}')(\text{dppm-P})]$. This compound, its thiocyanate analogue *cis,mer*- $[\text{Mn}(\text{NCS})(\text{CO})_2(\text{dppm-PP}')(\text{dppm-P})]$, and the unstable cationic dicarbonyl *cis,mer*- $[\text{Mn}(\text{NCMe})(\text{CO})_2(\text{dppm-PP}')(\text{dppm-P})][\text{ClO}_4]$ were prepared in good yield from *cis,mer*- $[\text{MnBr}(\text{CO})_2(\text{dppm-PP}')(\text{dppm-P})]$ and TIX (X = CN or NCS) or $\text{TiClO}_4/\text{MeCN}$, while the iodo derivative *cis,mer*- $[\text{MnI}(\text{CO})_2(\text{dppm-PP}')(\text{dppm-P})]$ was made from $\text{MnI}(\text{CO})_5$ and dppm in refluxing toluene. Both *cis*- and *trans*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2][\text{ClO}_4]$ reacted under UV irradiation at low temperature with KX (X = Cl, Br, I, CN, NCS) in the presence of 18-Crown-6 to give the neutral monocarbonyls *trans*- $[\text{MnX}(\text{CO})(\text{dppm-PP}')_2]$, and with NCMe to give *trans*- $[\text{Mn}(\text{NCMe})(\text{CO})(\text{dppm-PP}')_2][\text{ClO}_4]$. A qualitative study of the latter reactions showed that, in the case of the *cis*-dicarbonyl, the cation *trans*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2][\text{ClO}_4]$ and/or the neutral species *cis,mer*- $[\text{MnX}(\text{CO})_2(\text{dppm-PP}')(\text{dppm-P})]$, depending on X, were formed as intermediates.

Introduction

We previously described the preparation of several salts of the dicarbonyl cations *cis*- and *trans*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2]^+$ (dppm = bis(diphenylphosphinomethane))

and noted that the former reacted photochemically with Br^- to give *trans*- $[\text{MnBr}(\text{CO})(\text{dppm-PP}')_2]$ in low yield [1]. In order to explore further the chemistry of these two dicarbonyls we have determined their X-ray crystal structure and studied their reactions with several nucleophiles such as Cl^- , Br^- , I^- , CN^- , SCN^- or NCMe . This has led to the preparation in good yield of several complexes of the types *cis,mer*- $[\text{MnX}(\text{CO})_2(\text{dppm-PP}')(\text{dppm-P})]$ and *trans*- $[\text{MnX}(\text{CO})(\text{dppm-PP}')_2]$.

Results and discussion

The molecular structures of the cations *cis*- and *trans*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2]^+$ (I and II respectively), determined in the salts *cis*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2][\text{Br} \cdot 1/3\text{H}_2\text{O} \cdot]$ and *trans*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2]\text{ClO}_4 \cdot 1/2\text{CH}_2\text{Cl}_2$, are shown in Figs. 1 to 4. The relevant data are presented in Tables I to 6.

In both cations the Mn atom has a distorted octahedral coordination. In I (the *cis* complex) the P(4) atom is 0.333(6) Å from the mean plane of Mn, P(1), P(2), C(51), and P(2) is 0.304(6) Å from the mean plane of Mn, P(3), P(4), C(61); the

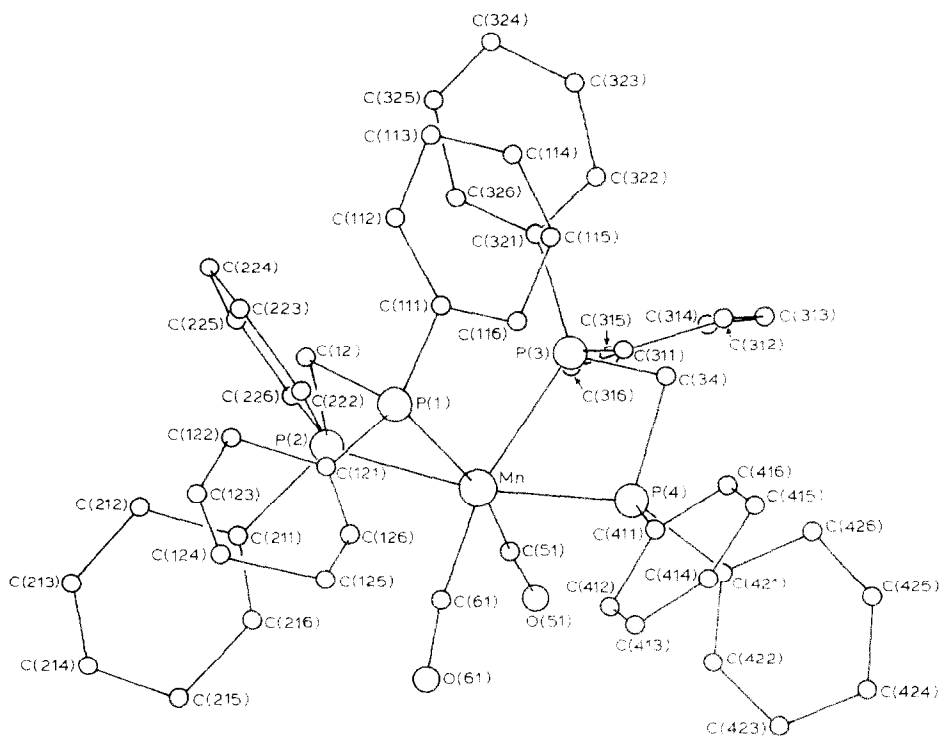


Fig. 1. Structure of *cis*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2]^+$ (I), with atomic numbering.

* The salt *cis*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2][\text{Br}]$, prepared as described in ref. 1, was crystallized from CH_2Cl_2 /hexane as the 1/3 hydrate. Obviously the water (0.6% by weight) came from incompletely dried solvents.

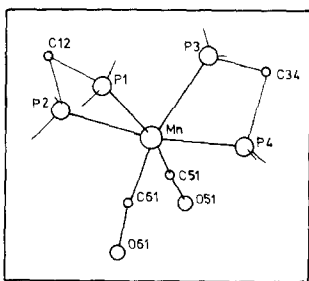


Fig. 2. A schematic view of I.

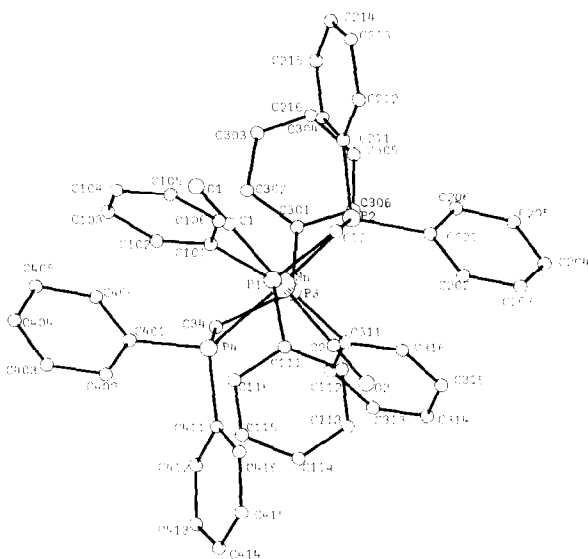


Fig. 3. Structure of *trans*-[Mn(CO)₂(dppm-PP')₂]⁺ (II), with atomic numbering.

dihedral angle between these two planes is $91.0(2)^\circ$. In II (the *trans* complex) the Mn and the four phosphorus atoms are almost coplanar with a deviation from the mean plane of $-0.010(4)$ (Mn), $0.036(4)$ (P(1)), $-0.031(4)$ (P(2)), $0.036(4)$ (P(3))

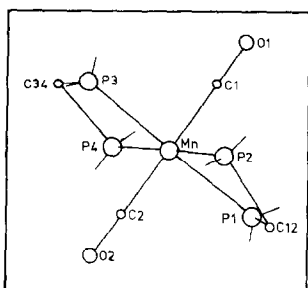


Fig. 4. A schematic view of II.

TABLE 1

FINAL ATOMIC COORDINATES ($\times 10^5$ FOR Mn; $\times 10^4$ FOR OTHER ATOMS) AND THERMAL PARAMETERS FOR *cis*-[Mn(CO)₂(dppm-PP')₂]Br·1/3H₂O

Atom	x	y	z	B_{eq}
Mn	21208(12)	1560(21)	9820(8)	4.40(15)
P(1)	1778(2)	83(4)	1571(1)	4.77(28)
C(111)	2288(10)	89(18)	2007(5)	6.05(126)
C(112)	2763(11)	-686(18)	2116(7)	7.17(138)
C(113)	3180(12)	-594(21)	2466(9)	8.37(171)
C(114)	3098(14)	207(27)	2708(6)	8.07(170)
C(115)	2589(15)	953(21)	2588(9)	8.55(194)
C(116)	2203(9)	897(20)	2254(6)	6.34(133)
C(121)	1162(9)	-903(18)	1641(5)	5.47(121)
C(122)	1294(12)	-1879(20)	1569(6)	6.56(137)
C(123)	3862(16)	-2606(19)	1650(7)	8.99(173)
C(124)	315(14)	-2343(26)	1826(8)	8.86(186)
C(125)	151(13)	-1371(24)	1887(9)	8.99(187)
C(126)	591(12)	652(20)	1827(7)	8.46(157)
C(12)	1321(10)	1311(15)	1517(6)	7.45(125)
P(2)	1295(3)	1342(4)	1014(2)	4.87(29)
C(211)	438(11)	1049(15)	813(7)	5.95(129)
C(212)	275(12)	1016(22)	465(8)	9.39(180)
C(213)	-382(15)	838(23)	272(8)	10.95(195)
C(214)	-923(12)	775(22)	475(10)	9.57(192)
C(215)	-770(15)	751(38)	834(10)	18.68(312)
C(216)	-98(16)	1116(21)	1025(8)	11.51(205)
C(221)	1361(9)	2665(16)	891(6)	5.38(121)
C(222)	1114(11)	3362(22)	1098(8)	9.23(173)
C(223)	1126(13)	4445(26)	1010(10)	10.23(213)
C(224)	1356(13)	4662(21)	690(12)	8.96(198)
C(225)	1605(19)	4045(30)	484(10)	14.50(277)
C(226)	1556(13)	2918(21)	562(7)	9.97(185)
P(3)	3108(2)	1074(4)	1223(2)	4.53(27)
C(311)	3598(11)	1703(17)	923(5)	4.44(113)
C(312)	3387(22)	2139(37)	674(11)	23.66(384)
C(313)	3649(29)	2950(35)	456(13)	19.93(393)
C(314)	4414(18)	2759(26)	479(8)	11.73(228)
C(315)	4612(22)	2261(35)	709(13)	24.41(409)
C(316)	4321(19)	1617(29)	969(11)	16.50(290)
C(321)	3218(12)	1881(15)	1620(6)	4.68(113)
C(322)	3696(12)	1631(17)	1940(7)	6.51(141)
C(323)	3783(12)	2273(23)	2262(7)	7.37(163)
C(324)	3346(21)	3112(28)	2228(9)	9.66(234)
C(325)	2946(18)	3439(20)	1926(10)	9.12(205)
C(326)	2833(11)	2757(20)	1593(8)	9.13(171)
C(34)	3596(8)	-65(13)	1366(5)	4.88(99)
P(4)	3044(3)	-907(4)	1062(2)	4.97(29)
C(411)	3438(11)	-1105(14)	659(5)	5.49(123)
C(412)	4186(11)	-1106(18)	696(8)	9.67(172)
C(413)	4447(13)	-1322(22)	364(8)	9.02(185)
C(414)	4074(17)	-1631(19)	60(8)	7.98(188)
C(415)	3360(14)	-1628(15)	3(6)	7.03(149)
C(416)	3071(11)	-1407(15)	355(6)	6.40(132)
C(421)	3085(10)	-2119(16)	1285(6)	6.23(122)
C(422)	3655(13)	-2333(15)	1559(7)	6.91(148)

TABLE 1 (continued)

Atom	x	y	z	B_{eq}
C(423)	3774(17)	-3244(26)	1729(9)	10.70(231)
C(424)	3257(21)	-4023(24)	1582(9)	9.82(221)
C(425)	2704(15)	-3883(20)	1309(9)	9.27(183)
C(426)	2627(10)	-2888(17)	1147(7)	7.28(137)
C(51)	2195(8)	466(15)	529(6)	4.59(101)
O(51)	2175(8)	660(11)	210(4)	7.67(97)
C(61)	1535(9)	-753(16)	793(6)	5.01(116)
O(61)	1177(7)	-1423(12)	672(4)	7.22(91)
Br	5266(3)	394(5)	6765(2)	10.26(41)
Br	407(3)	2466(5)	2132(2)	11.80(47)
O _w	0(0)	4994(34)	2500(0)	11.67(67)

and $-0.031(4)$ (P(4)) Å. The average P–Mn–P and P–C–P angles of the dpmm ligands for the *cis* isomer (70.5 and 94.4°) and for the *trans* isomer (73.2 , 94.7°) are well within the range encountered in complexes with other chelated dpmm [2–4], but, whereas in the *cis* isomer the two MnP₂C rings are not coplanar, with dihedral angles between the planes MnP₂ and CP₂ of ca. 15° (P(2)–Mn–P(1)–C(12) -13.9° , P(4)–Mn–P(3)–C(34) -16.3°), one of the rings in the *trans* has a very similar dihedral angle (P(4)–Mn–P(3)–C(34) -14.2°) and the other is closer to planar (P(2)–Mn–P(1)–C(12) 4.9°). It is likely that this effect is caused by packing forces.

The Mn–P distances in both isomers are similar to those observed in other manganese–phosphine complexes [5], but in I there are significant variations as a function of the ligand *trans* to the phosphorus atom. Thus, when the *trans* ligand is

TABLE 2

MAIN BOND LENGTHS (Å) FOR *cis*-[Mn(CO)₂(dpmm-PP')₂]Br·1/3H₂O

P(1)–Mn	2.387(6)
P(2)–Mn	2.306(6)
P(3)–Mn	2.370(5)
P(4)–Mn	2.308(6)
C(51)–Mn	1.750(21)
C(61)–Mn	1.749(19)
C(111)–P(1)	1.756(19)
C(121)–P(1)	1.849(22)
C(12)–P(1)	1.869(20)
P(2)–C(12)	1.845(22)
C(211)–P(2)	1.798(22)
C(221)–P(2)	1.831(22)
C(311)–P(3)	1.801(22)
C(321)–P(3)	1.801(21)
C(34)–P(3)	1.835(17)
P(4)–C(34)	1.824(17)
C(411)–P(4)	1.813(23)
C(421)–P(4)	1.807(22)
O(51)–C(51)	1.198(26)
O(61)–C(61)	1.185(26)

TABLE 3

MAIN BOND ANGLES ($^{\circ}$) FOR *cis*-[Mn(CO)₂(dppm-PP')₂][Br·1/3H₂O]

P(2)-Mn-P(1)	70.4(2)
P(3)-Mn-P(1)	91.5(2)
P(3)-Mn-P(2)	100.8(2)
P(4)-Mn-P(1)	101.7(2)
P(4)-Mn-P(2)	168.6(2)
P(4)-Mn-P(3)	70.6(2)
C(51)-Mn-P(1)	163.9(6)
C(51)-Mn-P(2)	93.5(6)
C(51)-Mn-P(3)	92.3(6)
C(51)-Mn-P(4)	94.3(6)
C(61)-Mn-P(1)	93.4(7)
C(61)-Mn-P(2)	93.2(7)
C(61)-Mn-P(3)	166.0(7)
C(61)-Mn-P(4)	95.5(7)
C(61)-Mn-C(51)	86.6(9)
C(12)-P(1)-Mn	94.3(7)
P(2)-C(12)-P(1)	93.5(10)
C(12)-P(2)-Mn	97.7(6)
C(34)-P(3)-Mn	93.0(5)
P(4)-C(34)-P(3)	95.3(8)
C(34)-P(4)-Mn	95.4(6)
O(51)-C(51)-Mn	173.3(15)
O(61)-C(61)-Mn	171.5(15)

CO, the Mn-P bond lengths average 2.378(8) Å, while the corresponding value for the Mn-P bond *trans* to a PPh₂ group is 2.307(1) Å (0.07 Å shorter). The latter distance is very close to the average Mn-P bond length in the *trans* isomer (II) (2.298(12) Å). Those effects are consistent with the observations made on complexes of the type *trans*-[Cr(CO)₄LL'] (L = PPh₃, P(OPh)₃, L' = CO, PR₃, P(OR)₃) [6] and it may thus be possible that there is significant π -bonding between the Mn^I and the dppm ligand in the dicarbonyl cations. In this case the shorter Mn-P bonds in I could be rationalized in terms of the change in the π -bonding ability of a PPh₂ group depending on whether the ligand *trans* to it is CO or another PPh₂, as was suggested to account for the short Cr-P(OPh)₃ bond in the complex *trans*-[Cr(CO)₄(P(OPh)₃)₂] [7].

On the other hand, the Mn-P bond distances may also be affected, directly or indirectly, by steric effects, as in the complexes *cis*-[Mo(CO)₄(PR₃)₂] [8]. This could be more significant for the *cis* isomer I, in which the angles P(1)-Mn-P(4) and P(2)-Mn-P(3) are ca. 101°, a value close to those in *cis*-[Mo(CO)₄(PR₃)₂], where they are thought to imply considerable steric interaction between the phosphine ligands which affects the M-P bonds [8]. In fact the distortions observed in the *cis* isomer (I) are in accord with those expected on the basis of Keppert's repulsion model for *cis*-[M(chelate)₂(monodentate)₂]²⁺ species [9] (Table 7), which predicts two longer Mn-P bonds (Mn-P(1) and Mn-P(2)). The distortions observed in the *trans* isomer (II) are also in good agreement with the prediction of the model (Table 7). All the observed Mn-C and C-O distances (Tables 2 and 5) are normal.

As noted previously [1], the cation II isomerizes on heating to the thermodynamically more stable isomer I (reaction i in Scheme 1). It is known that the relative

TABLE 4

FINAL ATOMIC COORDINATES ($\times 10^5$ FOR Mn; $\times 10^4$ FOR OTHER ATOMS) AND THERMAL PARAMETERS FOR *trans*-[Mn(CO)₂(dppm-PP')₂]ClO₄· $\frac{1}{2}$ CH₂Cl₂

Atom	x	y	z	B_{eq}
Mn	33296(8)	3670(0)	74198(17)	2.67(7)
P(1)	4069(2)	-354(2)	8024(3)	2.97(15)
P(2)	3720(2)	838(2)	9076(3)	3.09(14)
C(101)	3880(6)	-1249(8)	8391(13)	3.40(66)
C(102)	3955(7)	-1742(8)	7567(16)	4.75(78)
C(103)	3771(7)	-2416(8)	7751(15)	4.96(81)
C(104)	3503(8)	-2568(8)	8828(17)	5.39(92)
C(105)	3451(8)	-2090(9)	9677(16)	5.78(97)
C(106)	3602(8)	-1434(9)	9458(15)	5.05(87)
C(111)	4774(5)	-409(7)	7263(12)	3.43(62)
C(112)	5317(6)	-469(8)	7887(13)	4.13(71)
C(113)	5851(6)	-489(8)	7290(15)	4.59(77)
C(114)	5831(7)	-502(8)	6061(17)	5.59(90)
C(115)	5301(7)	-460(8)	5434(14)	4.54(77)
C(116)	4798(6)	-422(8)	6011(13)	4.23(73)
C(12)	4223(6)	126(7)	9389(12)	3.75(67)
C(201)	3228(5)	951(8)	10336(11)	3.32(61)
C(202)	3043(6)	389(10)	11014(11)	4.54(70)
C(203)	2595(10)	490(13)	11852(15)	6.88(116)
C(204)	2341(9)	1124(13)	11985(17)	6.88(113)
C(205)	2522(7)	1680(10)	11313(16)	5.79(92)
C(206)	2964(7)	1600(8)	10490(14)	4.84(80)
C(211)	4191(5)	1616(7)	9120(11)	3.18(59)
C(212)	4137(6)	2107(8)	8311(15)	3.89(75)
C(213)	4509(8)	2709(9)	8326(16)	5.32(92)
C(214)	4908(7)	2800(10)	9225(16)	5.13(89)
C(215)	4954(8)	2307(10)	10038(17)	5.64(95)
C(216)	4603(6)	1710(9)	10021(13)	4.76(81)
P(3)	2609(2)	1122(2)	6766(3)	2.87(14)
P(4)	2919(2)	-107(2)	5775(3)	2.99(15)
C(301)	1875(6)	1151(7)	7396(12)	3.37(61)
C(302)	1356(7)	1261(9)	6701(16)	5.04(86)
C(303)	817(7)	1359(10)	7213(18)	5.72(99)
C(304)	770(9)	1332(10)	8404(18)	6.04(106)
C(305)	1252(8)	1208(10)	9096(17)	5.47(93)
C(306)	1813(6)	1127(8)	8589(12)	3.73(67)
C(311)	2745(6)	2043(7)	6512(12)	3.04(60)
C(312)	2573(7)	2516(8)	7369(13)	4.36(73)
C(313)	2718(7)	3213(9)	7224(17)	5.76(94)
C(314)	8053(8)	3406(10)	8726(17)	5.62(98)
C(315)	8231(8)	2973(9)	9562(18)	5.69(96)
C(316)	3066(7)	2261(9)	5577(15)	4.94(85)
C(34)	2539(6)	723(7)	5307(12)	3.43(64)
C(401)	2324(6)	-753(7)	5875(13)	3.33(65)
C(402)	1874(6)	-753(8)	5064(13)	3.96(72)
C(403)	1440(8)	-1257(9)	5130(17)	5.81(98)
C(404)	1449(7)	-1742(8)	5973(17)	5.20(87)
C(405)	1913(7)	-1747(8)	6767(17)	4.92(83)
C(406)	2332(7)	-1274(8)	6717(13)	3.95(71)
C(411)	3359(7)	-430(9)	4550(12)	4.50(74)
C(412)	3441(8)	-1157(10)	4393(17)	6.08(103)

TABLE 4 (continued)

Atom	x	y	z	B_{eq}
C(413)	3860(12)	-1354(15)	3470(24)	12.42(192)
C(414)	5783(9)	4052(13)	7120(21)	8.02(126)
C(415)	5885(8)	4733(17)	7014(14)	8.60(123)
C(416)	3687(8)	48(12)	3878(15)	6.41(105)
C(1)	3867(6)	825(8)	6523(12)	3.16(61)
O(1)	4206(5)	1115(6)	5947(10)	5.04(56)
C(2)	2792(6)	-79(8)	8351(12)	3.40(66)
O(2)	2459(5)	-357(7)	8940(9)	4.78(55)
Cl	757(2)	322(3)	3115(4)	5.24(19)
O(3)	348(8)	-53(14)	3731(18)	14.60(163)
O(4)	1051(10)	-195(11)	2556(18)	13.20(143)
O(5)	1168(9)	607(9)	3856(17)	12.61(135)
O(6)	486(12)	740(12)	2329(22)	17.25(186)
Cl	9030(4)	1821(5)	2018(6)	3.86(34)
Cl	9846(5)	2584(5)	518(9)	6.29(53)
C	9768(14)	2031(26)	1367(32)	6.91(222)

stability of the *cis* and *trans* isomeric forms in carbonyl-phosphine complexes depends on electronic and steric factors [10] and various theoretical analyses have shown that for species $[M(CO)_2L_4]$ (L = lesser π -accepting ligand than CO) the electronic effects favour the *cis* form [11]. The discussion of the preference in terms of repulsion factors for the $[M(\text{chelate})_2(\text{monodentate})_2]^+$ species is more complex because normalized bites as well as the degree of asymmetry have to be considered [9].

TABLE 5

MAIN BOND LENGTHS (Å) FOR *trans*- $[Mn(CO)_2(\text{dppm-PP}')_2]ClO_4 \cdot \frac{1}{2}CH_2Cl_2$

P(1)-Mn	2.290(4)
P(2)-Mn	2.287(4)
P(3)-Mn	2.318(4)
P(4)-Mn	2.297(4)
C(1)-Mn	1.824(14)
C(2)-Mn	1.835(15)
C(101)-P(1)	1.844(15)
C(111)-P(1)	1.818(13)
C(12)-P(1)	1.857(14)
C(12)-P(2)	1.829(14)
C(201)-P(2)	1.835(13)
C(211)-P(2)	1.853(14)
C(301)-P(3)	1.808(14)
C(311)-P(3)	1.845(13)
C(34)-P(3)	1.853(14)
C(34)-P(4)	1.910(14)
C(401)-P(4)	1.844(14)
C(411)-P(4)	1.832(15)
O(1)-C(1)	1.158(18)
O(2)-C(2)	1.147(18)

TABLE 6

MAIN BOND ANGLES (°) FOR *trans*-[Mn(CO)₂(dppm-PP')₂][ClO₄·½CH₂Cl₂]

P(2)–Mn–P(1)	73.4(1)
P(3)–Mn–P(1)	177.7(1)
P(3)–Mn–P(2)	106.5(1)
P(4)–Mn–P(1)	107.2(1)
P(4)–Mn–P(2)	178.8(2)
P(4)–Mn–P(3)	73.0(1)
C(1)–Mn–P(1)	89.3(5)
C(1)–Mn–P(2)	90.9(4)
C(1)–Mn–P(3)	88.4(5)
C(1)–Mn–P(4)	90.1(4)
C(2)–Mn–P(1)	90.9(5)
C(2)–Mn–P(2)	87.8(5)
C(2)–Mn–P(3)	91.4(5)
C(2)–Mn–P(4)	91.2(5)
C(2)–Mn–C(1)	178.6(7)
C(12)–P(1)–Mn	94.7(4)
C(12)–P(2)–Mn	95.6(5)
P(2)–C(12)–P(1)	95.8(6)
C(34)–P(3)–Mn	94.9(5)
C(34)–P(4)–Mn	94.1(4)
P(4)–C(34)–P(3)	93.6(6)
O(1)–C(1)–Mn	179.6(10)
O(2)–C(2)–Mn	179.4(12)

The difference between the two types of Mn–P bonds in I suggested that under nucleophilic attack the PPh₂ groups of the dppm ligand with the longer Mn–P distance might be displaced. In keeping with this, the reaction of the salt *cis*-[Mn(CO)₂(dppm-PP')₂][ClO₄] with KCN in refluxing acetone, in the presence of the crown-ether 18-Crown-6 (see reaction iia in Scheme 1) gave a good yield of the neutral species *cis,mer*-[Mn(CN)(CO)₂(dppm-PP')(dppm-P)] (IIIa) in which one dppm is monodentate. The structure proposed for IIIa is consistent with the analytical and spectroscopic data (Tables 8 and 9). Further support came from its synthesis (also in good yield) from the previously known *cis,mer*-[MnBr(CO)₂(dppm-PP')(dppm-P)] [1] which has the structure shown in Scheme 1)

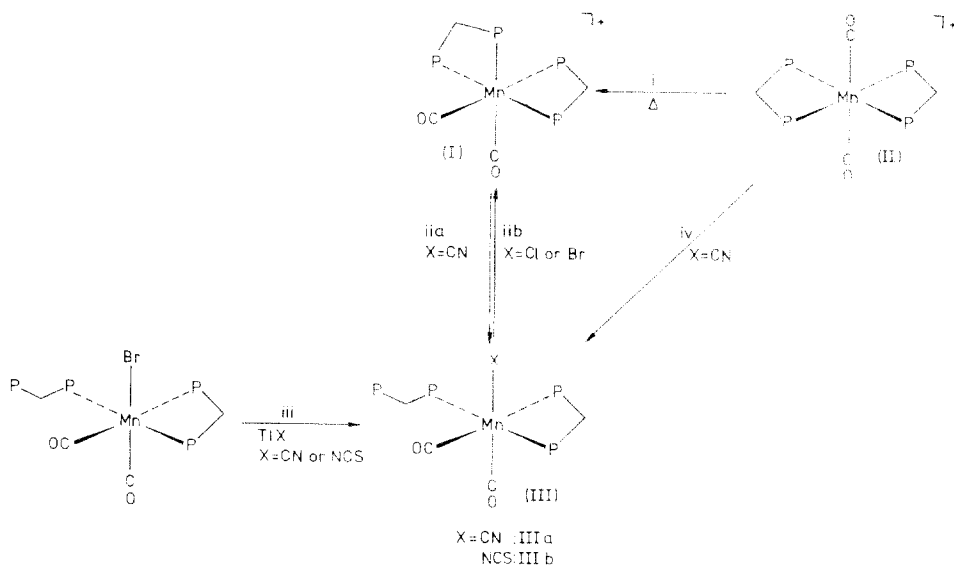
TABLE 7

STEREOCHEMICAL PARAMETERS FOR THE CATIONS *cis*- AND *trans*-[Mn(CO)₂(dppm-PP')₂]⁺

	φ _A	φ _B	φ _E	θ _A	θ _B
<i>cis</i> -Isomer (I)					
Exp.	99	134	45	5	–64
Calc. ^a	95	134	43	0	–67
<i>trans</i> -Isomer (II)					
Exp.	54	127	89		
Calc. ^b	54	127	91		

^a Calculated from the data in ref. 9, using the experimentally determined normalized bite, *b* 1.15 Å.

^b idem with *b* 1.19 Å.



SCHEME 1. (i) Refluxing toluene or acetone; (ii) with KCN and 18-Crown-6 in refluxing acetone; (iib) in refluxing toluene; (iii) with TiX in CH_2Cl_2 ; (iv) as in iii.

and TiCN in CH_2Cl_2 , a reaction that can be expected to occur with retention of the stereochemistry (iii in Scheme 1). The analogous complex *cis,mer*-[Mn(NCS)(CO)₂(dppm-PP')(dppm-P)] (IIIb) was similarly prepared in good yield from TiNCS*, while the iodo derivative *cis,mer*-[MnI(CO)₂(dppm-PP')(dppm-P)] (IIIc) was made refluxing in toluene [MnI(CO)₅] and dppm** in the way used for the bromo [1] and chloro [12] analogues. Similar to reaction iii (Scheme 1), *cis,mer*-[MnBr(CO)₂(dppm-PP')(dppm-P)] reacted with TiClO₄ and MeCN in CH_2Cl_2 to give the salt *cis,mer*-[Mn(NCMe)(CO)₂(dppm-PP')(dppm-P)][ClO₄] (IIIId), which in solution in the absence of MeCN gives *cis*-[Mn(CO)₂(dppm-PP')₂][ClO₄] by displacement of the coordinated MeCN by the free PPh₂ group of the monodentate dppm.

No reaction was observed between the perchlorate salt of I and KCN in the absence of the crown-ether, indicating that the higher concentration and/or exalted nucleophilicity of the CN⁻ in the reaction mixture may be important.

The *cis*-[Mn(CO)₂(dppm-PP')₂][ClO₄] did not react with the potassium salts KX for X = Cl, Br, I or NCS in refluxing acetone to give III even in the presence of the crown-ether. It has previously been reported that heating the neutral species III for X = Br (or Cl [12]) in refluxing toluene results in the formation of the corresponding

* Clearly the use of the thallos salts for the preparation of CN or NCS carbonyl complexes has advantages over the previous method employing XAg (X = CN or NCS) [4]. The yields reported for the preparation of *cis,cis*-[MnX(CO)₂(dppm-PP')P(OPh)₃] by use of AgX can, however, be improved by treating the reaction mixture with aqueous Na₂S₂O₃ to remove the excess of coordinated silver.

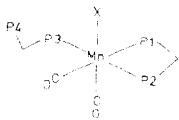
** The compound IIIc had to be separated from *fac*-[MnI(CO)₃(dppm-PP')] and *fac*-[MnH(CO)₃(dppm-PP')] formed in the reaction.

TABLE 8
MELTING POINTS, ANALYTICAL AND IR DATA FOR THE COMPLEXES

Compound	M.p. ^a (°C)	Analysis (Found (calc.) (%))			IR ^b (cm ⁻¹)	
		C	H	N	$\nu(\text{CN})$	$\nu(\text{CO})$
<i>cis,mer</i> -[Mn(CN)(CO) ₂ (dppm-PP')(dppm-P)]·CH ₂ Cl ₂ (IIIa)	176	65.2 (65.9)	4.65 (4.62)	1.48 (1.40)	2092	1946s, 1888s
<i>cis,mer</i> -[Mn(NCS)(CO) ₂ (dppm-PP')(dppm-P)] (IIIb)	179	68.1 (67.9)	4.79 (4.73)	1.53 (1.49)	2099	1946s, 1878s
<i>cis,mer</i> -[MnI(CO) ₂ (dppm-PP')(dppm-P)]· $\frac{1}{2}$ CH ₂ Cl ₂ (IIIc)	165	60.4 (60.1)	4.32 (4.32)			1937s, 1862s
<i>cis,mer</i> -[Mn(NCMe)(CO) ₂ (dppm-PP')(dppm-P)][ClO ₄] ^c (IIIId)	270 ^d	63.8 (63.6)	4.72 (4.64)	1.30 (1.37)		1959s, 1892 s
<i>trans</i> -[MnCl(CO)(dppm-PP') ₂] (IVa)	165	62.2 (62.6)	4.83 (4.53)			1850s
<i>trans</i> -[MnI(CO)(dppm-PP') ₂] (IVc)	155	67.3 (66.5)	4.89 (4.88)			1832s

^a With decomposition. ^b In CH₂Cl₂ solution. ^c It shows a sharp signal at 1.13 δ (s, 3H) in the ¹H NMR. ^d It transforms slowly into the *cis*-[Mn(CO)₂(dppm-PP')₂][ClO₄].

TABLE 9

³¹P NMR DATA ^a

Compound	X or L	$\delta(\text{P})$	$\delta(\text{P}(1))$	$\delta(\text{P}(2))$	$\delta(\text{P}(3))$	$\delta(\text{P}(4))$ ^c	J_{43}
<i>cis,mer</i> -[MnX(CO) ₂ (dppm-PP') (dppm-P)] ^b	Br ^d		-1.6	35.6	49.1	-30.2	19
	I		-0.2	34	41	-25.0	29
	CN		13	42	58	-25.9	29
	NCS		5	35	54	-28.0	32
<i>cis,mer</i> -[MnL(CO) ₂ (dppm-PP') (dppm-P)](ClO ₄)	NCMe		11	40	57	-25.4	49
	CO ^d		10	30	49	-27.0	57
<i>trans</i> -[MnX(CO)(dppm-PP') ₂]	Cl	36.2					
	Br ^e	34.4					
	I	31.6					

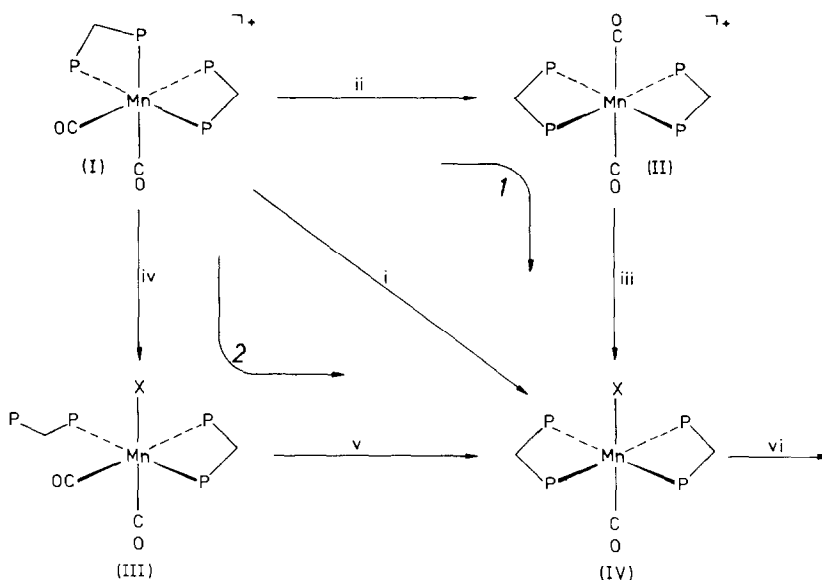
^a Proton decoupled. Measured in CDCl₃ solution at room temperature, with positive shifts to high field of external 85% H₃PO₄. δ in ppm. $J(\text{PP})$ in Hz. ^b The signals from the phosphorus atoms 1, 2 and 3 are broad unresolved multiplets and only the center is quoted. ^c Sharp doublet. ^d From ref. 1. ^e From ref. 4.

salt of I (iib in Scheme 1). In contrast, the thiocyanate derivative IIIb remained unchanged, and a complex decomposition took place for X = I.

The perchlorate of the *trans*-dicarbonyl cation (II) reacted in refluxing acetone with KX in the presence of 18-Crown-6, only for X = CN to give IIIa (iv in Scheme 1), but monitoring of the reaction by IR showed that the attack of the CN⁻ was, in fact, on the *cis* isomer I formed by isomerization of II, as indicated for the process i in the Scheme 1.

Under low temperature UV irradiation the *cis* dicarbonyl [Mn(CO)₂(dppm-PP')₂][ClO₄] reacted with KX for X = Cl, Br, I, CN or NCS in the presence of 18-Crown-6 in CH₂Cl₂ to give the neutral monocarbonyls *trans*-[MnX(CO)(dppm-PP')₂] (IV) in 40–50% yields (reaction i in Scheme 2). Similarly, the reaction with NCMe gave good yields of the previously reported [13] *trans*-[Mn(NCMe)(CO)(dppm-PP')₂][ClO₄]. The compounds IV with X = CN or NCS have been prepared previously [4], but in much poorer yield, starting from the long known *trans*-[MnBr(CO)(dppm-PP')₂] [14].

Monitoring of reaction i (Scheme 2) by IR revealed that in the case of X = CN, the dicarbonyls II and III are intermediates in the formation of IV, whereas only the cation II was clearly observed in the other cases. Other experiments showed that the irradiation (from the same UV source) of the perchlorate salt of II with KX and 18-Crown-6 in CH₂Cl₂ (iii in Scheme 2) and of the neutral species III (v in Scheme 2) also gave IV, which subsequently decomposed slowly on prolonged irradiation to as yet unidentified products (vi in Scheme 2). Although the experiments allowed no reliable comparison of the relative rates of the reactions of Scheme 2, it appeared that those of i and iii were very similar and slightly lower than those of ii and v, while variations as X was changed were insignificant in all cases. Thus, in the



SCHEME 2. (i) $h\nu$ with KX ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{NCS}$) + 18-Crown-6 in CH_2Cl_2 (-15°C); (ii) $h\nu$; (iii) As in (i); (iv) as in i; (v) $h\nu$; (vi) $h\nu$ to unknown products.

photochemical reactions, only for $\text{X} = \text{CN}^-$ is there clear evidence of attack on the cation I with formation of III as intermediate (reaction iv in Scheme 2) as observed in the thermal process. However, the data do not permit a firm conclusion concerning the relative contribution of the paths 1 (ii + iii) and 2 (iv + v) to reaction i (Scheme 2).

Experimental

All reactions were carried out under dry argon. The IR spectra were recorded with a Perkin-Elmer 298 spectrometer and calibrated with reference to the 1602 cm^{-1} band of polystyrene. The NMR spectra were recorded with a Varian FT-80A.

The compound $\text{cis-}[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2]\text{Br}$ was prepared as described elsewhere [1], and crystals suitable for X-ray diffraction were obtained by the liquid diffusion method [15] using $\text{CH}_2\text{Cl}_2/\text{hexane}$. The crystals of $\text{trans-}[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2][\text{ClO}_4]$ [1] were obtained similarly from $\text{Cl}_2\text{CH}_2/\text{hexane}$.

The compounds $[\text{MnI}(\text{CO})_5]$ [16], $\text{cis,mer-}[\text{MnBr}(\text{CO})_2(\text{dppm-PP}')(\text{dppm-P})]$ [1], TICN and TINCS [17] were made as previously described.

Preparation of $\text{cis,mer-}[\text{Mn}(\text{CN})(\text{CO})_2(\text{dppm-PP}')(\text{dppm-P})]$ (IIIa)

(a) A mixture of $\text{cis-}[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2][\text{ClO}_4]$ (0.153 g, 0.1596 mmol), KCN (0.026 g, 0.399 mmol) and 18-Crown-6 (0.2 g, 0.479 mmol), and acetone (30 ml) was refluxed for 6 h in the absence of light. The resulting solution was filtered (Celite), the volatiles were removed in vacuo, and the oily residue was washed with water ($2 \times 50\text{ ml}$). The solid formed was dissolved in toluene (30 ml), and the solution was filtered, dried over Na_2SO_4 , and evaporated to give IIIa as a yellow solid (0.11 g, 80%).

(b) The compounds *cis,mer*-[MnBr(CO)₂(dppm-PP')(dppm-P)] (0.7 g, 0.729 mmol) and TiCN (0.20 g, 0.868 mmol) were stirred with CH₂Cl₂ (50 ml) for 2 h at room temperature. The mixture was filtered and evaporated in vacuo, to leave a solid, which was washed twice with hexane (30 ml). Recrystallization from a concentrated CH₂Cl₂ solution at -10 °C gave crystalline IIIa as the CH₂Cl₂ solvate (0.59 g, 89%).

Preparation of cis,mer-[Mn(NCS)(CO)₂(dppm-PP')(dppm-P)] (IIIb)

A mixture of *cis,mer*-[MnBr(CO)₂(dppm-PP')(dppm-P)] (0.5 g, 0.52 mmol) TiNCS (0.164 g, 0.625 mmol) and CH₂Cl₂ (40 ml) was refluxed for 4 h then filtered. The filtrate was dried in vacuo and the residue was washed twice with hexane (30 ml) to give a yellow solid (0.43 g, 88%), which was recrystallized from CH₂Cl₂/hexane.

Preparation of cis,mer-[MnI(CO)₂(dppm-PP')(dppm-P)] (IIIc)

A mixture of [MnI(CO)₅] (0.5 g, 1.553 mmol) and dppm (0.675 g, 1.756 mmol), and toluene (50 ml) was refluxed for 1 h then cooled to room temperature. More dppm (0.675 g, 1.756 mmol) was added and refluxing was continued for another 8 h. The solution was then filtered, concentrated in vacuo to ca. 10 ml, and cooled to -10 °C. The precipitate formed was redissolved in 50 ml of refluxing toluene, and the solution was filtered, concentrated to 25 ml, and cooled to -10 °C to give a precipitate. This procedure was repeated once more, to give orange crystalline IIIc (0.5 g, 32%), which was recrystallized as the $\frac{1}{3}$ CH₂Cl₂ solvate from CH₂Cl₂/hexane.

Preparation of cis,mer-[Mn(NCMe)(CO)₂(dppm-PP')(dppm-P)][ClO₄] (III'd)

A mixture of the complex *cis,mer*-[MnBr(CO)₂(dppm-PP')(dppm-P)] (0.50 g, 0.521 mmol) TiClO₄ (0.2 g, 0.658 mmol), and NCMe (30 ml) was stirred for 2 h at room temperature and then filtered (*Care*: The TiClO₄ is soluble in MeCN). The filtrate was dried in vacuo and the residue was extracted with CH₂Cl₂ (50 ml). The extract was filtered then evaporated quickly in vacuo. The resulting yellow solid was washed twice with diethyl ether (30 ml) and dried in vacuo (0.49 g, 92%). The molar conductivity of a 5 × 10⁻⁴ M acetone solution was 119 Ω⁻¹ cm² mol⁻¹.

Preparation of trans-[MnX(CO)(dppm-PP')₂] (IV)

A mixture of *cis*-[Mn(CO)₂(dppm-PP')₂][ClO₄] (0.306 g, 0.312 mmol) and KX (2.5 × 0.312 mmol) and 18-Crown-6 (3 × 0.312 mmol) in CH₂Cl₂ (10 ml) at -15 °C was irradiated with UV light until the ν(CO) bands of the starting complex were no longer present in the IR spectrum of the mixture. The solvent was evaporated in vacuo, then the residue was washed with water (2 × 30 ml) and redissolved in CH₂Cl₂. The solution was dried over Na₂SO₄, concentrated, diluted with hexane, and concentrated until precipitation began. The first precipitate was filtered off and discarded, and the remaining solution was cooled to -10 °C to give a red crystalline solid, which was washed with hexane. The yield ranged from 40% (X = Br) to 51% (X = NCS).

Preparation of trans-[Mn(NCMe)(CO)(dppm-PP')₂][ClO₄]

The salt *cis*-[Mn(CO)₂(dppm-PP')₂][ClO₄] (0.306 g, 0.312 mmol) was irradiated with UV light in CH₃CN (10 ml) at -15 °C until the ν(CO) bands of the starting

complex were no longer present in the IR spectrum of the mixture. The solvent was evaporated in vacuo and the residue was dissolved in CH_2Cl_2 . The solution was filtered, diluted with hexane (10 ml), concentrated, and cooled to -10°C , to give a red crystalline solid (0.127 g, 41%).

Preparation of trans-[Mn(NCS)(CO)(dppm-PP')₂]

The complex *cis,mer*-[Mn(NCS)(CO)₂(dppm-PP')(dppm-P)] (0.15 g, 0.156 mmol) was irradiated with UV light in CH_2Cl_2 (5 ml) at -15°C until the IR spectrum of the solution no longer showed the $\nu(\text{CO})$ bands of the starting complex. The solution was then filtered and the filtrate evaporated in vacuo. The residue was washed with hexane (2×30 ml) to leave an orange solid (0.117 g, 82%). The other complexes III likewise gave IV, but in yields of ca. 30%.

Structure determination of cis-[Mn(CO)₂(dppm-PP')₂]Br · 1/3H₂O

Crystal data: $\text{C}_{52}\text{H}_{44}\text{O}_2\text{P}_4\text{Mn} \cdot \text{Br} \cdot 1/3\text{H}_2\text{O}$, $FW = 965.7$, monoclinic, a 20.027(3), b 13.326(2), c 36.876(4) Å, β 99.46(2) $^\circ$, V 9708(4) Å³, $C2/c$, D_x 1.321 g cm⁻³, $Z = 8$, $F(000) = 3962.7$, $\lambda(\text{Mo-K}_\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}_\alpha)$ 13.29 cm⁻¹. Room temperature.

A yellow tabular crystal (0.1 × 0.2 × 0.2 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. The unit cell parameters were determined from 25 reflections ($4 \leq \theta \leq 9^\circ$) and refined by least squares. Intensities were collected with graphite monochromated Mo- K_α radiation, using the ω -scan technique (scan width 1° , scan speed 0.03° s⁻¹). Three intensities were measured each 2 h in orientation and intensity checks, and no significant variations were observed. 1969 intensities were measured in the range $2 \leq \theta \leq 24.5^\circ$ and 1931 were taken as observed by application of the condition $I \geq 2.5\sigma(I)$. Lorentz-polarization, but no absorption corrections were made.

The structure was solved by direct methods, using the MULTAN system of computer programs [18]. An *E*-map computed from the set of phases with the highest combined figure of merit revealed the positions of the Mn and P atoms. The disordered Br atom, 22 C and the O atoms were located using the DIRDIF system [19] and the remaining atoms from successive difference synthesis. The structure was refined isotropically and anisotropically by full-matrix least-squares method, using the SHELX76 computer program [20]; f , f' and f'' were taken from International Tables of X-Ray Crystallography [21]. The function minimized was $w \parallel F_o - |F_c| \parallel^2$, where $w = (\sigma^2(F_o) + 0.098 |F_o|^2)^{-1}$. After three isotropic cycles of refinement a subsequent difference synthesis showed a peak which we assumed to be a water molecule with an occupancy factor of 0.5. After the anisotropic cycles we refined the occupancy factors for the disordered atoms, obtaining 0.50(1) for both Br sites and 0.38(3) for the water molecule. The final *R* value was 0.072 ($R_w = 0.076$) for all observed reflections.

Structure determination of trans-[Mn(CO)₂(dppm-PP')₂][ClO₄] · ½CH₂Cl₂

Crystal data: $\text{C}_{52}\text{H}_{44}\text{O}_2\text{P}_4\text{Mn} \cdot \text{ClO}_4 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$. $FW = 1021.7$, orthorhombic, a 22.567(4), b 19.500(3), c 11.473(3) Å, V 5049(3) Å³, $Pn2_1a$, D_x 1.344 g cm⁻³, $Z = 4$, $F(000) = 2108$, $\lambda(\text{Mo-K}_\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}_\alpha)$ 5.56 cm⁻¹, 288 K.

A prismatic crystal (0.1 × 0.1 × 0.15 mm) was selected and mounted on a Philips four-circle diffractometer. Unit-cell parameters were determined from 25 reflections

($4 \leq \theta \leq 12^\circ$) and refined by least-squares. Intensities were collected with graphite-monochromated Mo- K_α radiation, using the ω -scan technique: scan width 0.8° , scan speed $0.03^\circ \text{ s}^{-1}$. 3224 reflections were measured in the range $2 \leq \theta \leq 24.5^\circ$ and 3018 were taken as observed by application of the condition $I \geq 2.5\sigma(I)$. Three reflections were measured every 2 h in orientation and intensity checks, and no significant decay was observed. Lorentz-polarization, but no absorption corrections were made. The Mn atom was located from a Patterson synthesis and refined by full-matrix least-squares method using the SHELX76 computer program. The function minimized was $w \sum (|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(F_o)$. The positions of the H atoms were calculated and refined with an overall isotropic temperature factor and the remaining atoms were refined anisotropically. The final R factor was 0.065 ($R_w = 0.066$) for all observed reflections.

For both structures complete lists of bond lengths and angles and tables of thermal parameters and structure factors are available from the authors.

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