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THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO ISOMERS OF DICARBONYLTETRA(DIMETHOXYPHENYLPHOSPHINE)-MANGANESE(I) HEXAFLUOROPHOSPHATE

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Summary

The crystal and molecular structures of the *cis*- and *trans*-isomers of dicarbonyltetra(dimethoxyphenylphosphine)manganese(I) hexafluorophosphate, $[Mn(CO)_2\{P(OMe)_2Ph\}_4][PF_6]$, have been determined using X-ray diffraction data recorded on an automatic diffractometer. The *cis*-isomer is monoclinic, space group $P2/c$, a 14.51(1), b 9.42(1), c 18.60(2) Å, β 124.5(2)°, $Z = 2$. The *trans*-isomer is monoclinic, space group $P2_1/n$, a 22.99(3), b 14.38(2), c 14.21(2) Å, β 107.0(2)°, $Z = 4$. Both structures were refined anisotropically by full-matrix least-squares methods to give R-values of 0.067 and 0.076 respectively for the *cis*- and *trans*-isomers. Both structures contain discrete $[Mn(CO)_2\{P(OMe)_2Ph\}_4]^+$ cations and $[PF_6]^-$ anions.

Introduction

During our investigation of the relationship between structure and reactivity in manganese(I) carbonyl systems, a series of comparable neutral and cationic manganese carbonyl complexes was characterized [1—3]. Though a kinetic labilizing effect for mutually *trans*-carbonyl groups was shown [4] to control the substitution reactions, our recent structural investigations of *fac*- and *mer*, *trans*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$ failed to draw a parallel with a structural *trans*-effect [5]. It is well established that cationic manganese(I) carbonyl salts are much more inert in substitution reactions than their neutral counterparts. The structural analysis of the two cationic complexes *cis*- and *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4][PF_6]$ has therefore been undertaken to see if (*i*) any variations in M—C

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bond lengths for the *cis*- and *trans*-carbonyl groups are apparent in these compounds and (*ii*) the more inert nature of the cationic carbonyl groups is paralleled by a reduction in metal—carbon bond lengths.

Experimental

Cell dimensions were determined and intensity data collected to a maximum 2θ of 40° on a Philips PW1100 single-crystal diffractometer fitted with a graphite monochromator and using Mo-K_α radiation.

cis-$[Mn(CO)_2\{P(OMe)_2Ph\}_4][PF_6]$

The complex crystallized as colourless needles from a mixture of dichloromethane and ethanol. A crystal cut to cubical shape (0.1 mm edges) was used for data collection.

Crystal data. $MnP_5C_{34}O_{10}H_{68}F_6$, $M = 822.5$. Monoclinic, a 14.51(1), b 9.42(1), c 18.60(2) Å, β 124.5(2)°, $D_m = 1.29(2)$, $Z = 2$, $D_c = 1.303$, $F(000) = 856$. Space group $P2/c$, ($h0l$, $l = 2n$). λ 0.7107 Å, μ(Mo-K_α) 5.2 cm^{-1}.

An ω-scan was used in data collection, with a scan width of 0.9° and a scan speed of 0.02° s^{-1}. Background was counted for half the total scanning time on each side of a reflection. Of the 1947 independent reflections, 397 were considered unobserved with $I < 1.65\ \sigma$. No absorption corrections were applied.

Structure solution and refinement. The structure was determined by Patterson and Fourier methods and refined by full-matrix least-squares calculations. Corrections were applied for anomalous dispersion. The value of the conventional R-index was 0.067 at convergence. No differential weighting was applied. A final difference map showed the positions of only a few hydrogen atoms and therefore none was included.

Scattering factors were taken from Cromer and Mann [6] and the anomalous dispersion corrections from Cromer and Liberman [7]. Computations were carried out with the X-RAY system of crystallographic programs [8] and drawings made with the plot program of Johnson [9]. Final atomic coordinates and thermal parameters are given in Table 1 and a selection of bond lengths and angles is given in Table 3.

trans-$[Mn(CO)_2\{P(OMe)_2Ph\}_4][PF_6]$

The complex crystallized as colourless plates from a mixture of dichloromethane and ethanol. A crystal with dimensions 0.12 × 0.12 × 0.08 mm was used for data collection.

Crystal data. $MnP_5C_{34}O_{10}H_{68}F_6 \cdot C_2H_5OH$, $M = 868.6$. Monoclinic, a 22.99(3), b 14.38(2), c 14.21(2) Å, β 107.0(2)°, $D_m = 1.29(2)$, $Z = 4$, $D_c = 1.284$, $F(000) = 1816$. Space group $P2_1/n$, ($h0l$, $h + l = 2n$; $0k0$, $k = 2n$). λ 0.7107 Å; μ(Mo-K_α) 4.9 cm^{-1}.

An ω-scan was used in data collection, with a scan width of 1.2° and scan speed of 0.02° s^{-1}. Of the 4254 independent reflections measured, 1944 were considered unobserved with $I < 2\sigma$. No absorption corrections were applied.

Structure solution and refinement. The structure was determined by Patterson and Fourier methods. The crystals were found to contain 1 molecule of ethanol per asymmetric unit as solvent of crystallization. Anisotropic refinement was by

(*continued on p. 230*)

TABLE 1

POSITIONAL ($\times 10^4$) AND THERMAL ($Å^2 \times 10^3$) PARAMETERS WITH e.s.d.'s FOR THE *cis*-ISOMER

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	5000	483(2)	2500	26(1)	40(1)	29(1)	0	10(1)	0
C(1)	4861(8)	−847(12)	3112(6)	37(6)	59(7)	43(6)	−3(5)	11(5)	10(6)
O(1)	4799(7)	−1751(9)	3502(6)	82(6)	89(7)	79(6)	−14(5)	31(5)	34(5)
P(1)	3138(2)	398(3)	1466(1)	30(1)	47(2)	32(1)	−3(1)	11(1)	−2(1)
P(2)	4721(2)	2142(3)	3252(2)	32(1)	56(2)	31(1)	6(1)	9(1)	−6(1)
O(11)	2920(5)	9(8)	546(4)	42(4)	84(5)	40(4)	−11(4)	18(3)	−14(4)
C(17)	1826(8)	−104(17)	−290(6)	36(6)	191(15)	33(6)	−20(8)	−3(5)	−43(8)
O(12)	2488(5)	1814(7)	1341(4)	45(4)	52(4)	47(4)	2(3)	13(3)	−2(3)
C(18)	1300(8)	2166(14)	738(7)	28(6)	103(10)	69(8)	31(7)	−8(6)	9(7)
O(21)	3891(5)	1449(9)	3459(4)	40(4)	120(7)	56(4)	−16(4)	29(4)	−25(5)
C(27)	3421(11)	2092(20)	3896(9)	69(10)	219(18)	118(11)	7(11)	71(9)	−51(12)
O(22)	4175(6)	3563(8)	2721(4)	76(5)	67(5)	45(4)	23(4)	11(4)	−9(4)
C(28)	3863(13)	4798(15)	3003(9)	161(14)	83(11)	100(11)	74(10)	38(10)	−19(9)
C(11)	2296(7)	−946(13)	1540(6)	20(5)	82(9)	47(6)	−4(5)	6(5)	22(6)
C(12)	2245(10)	−2290(14)	1219(9)	73(9)	50(8)	123(12)	−16(7)	30(8)	6(8)
C(13)	1532(14)	−3318(17)	1242(12)	88(13)	78(11)	149(16)	−27(11)	17(12)	35(11)
C(14)	957(14)	−2954(27)	1605(13)	53(10)	178(23)	95(15)	−23(14)	2(9)	86(16)
C(15)	1009(12)	−1621(26)	1916(10)	49(9)	203(20)	59(9)	−26(12)	3(7)	57(12)
C(16)	1711(8)	−563(15)	1904(7)	32(6)	145(12)	49(7)	−14(7)	10(5)	38(8)
C(21)	4141(7)	2813(12)	683(6)	31(5)	66(7)	38(6)	−4(6)	13(5)	14(6)
C(22)	3933(9)	2156(13)	−76(7)	46(7)	100(9)	38(7)	−3(7)	16(6)	9(7)
C(23)	3044(10)	2678(16)	−902(7)	59(8)	122(12)	43(8)	−2(8)	19(7)	15(7)
C(24)	2422(10)	3805(16)	−942(8)	59(8)	115(12)	58(9)	5(8)	27(7)	27(9)
C(25)	2612(11)	4459(14)	−196(8)	91(10)	87(10)	78(9)	31(8)	45(8)	34(8)
C(26)	3507(9)	3951(13)	642(7)	62(7)	79(9)	53(7)	21(7)	22(6)	24(7)
P(5)	0	3001(5)	2500	45(3)	60(3)	75(3)	0	22(3)	0
F(1)	0	1479(14)	2500	440(36)	47(9)	204(20)	0	−36(21)	0
F(2)	920(7)	3008(10)	3499(5)	112(6)	143(8)	73(5)	−3(6)	6(5)	18(5)
F(3)	882(9)	3121(23)	2356(8)	122(9)	548(31)	160(10)	78(14)	96(8)	4(15)
F(5)	0	4614(14)	2500	169(13)	99(11)	132(11)	0	−1(10)	0

TABLE 2

POSITIONAL ($\times 10^4$) AND THERMAL ($Å^2 \times 10^3$) PARAMETERS WITH e.s.d.'s FOR THE *trans*-ISOMER

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	2447(1)	4864(1)	−4(2)	71(2)	20(1)	38(1)	3(1)	29(1)	−1(1)
C(1)	2430(8)	3964(11)	−930(12)	100(15)	37(10)	47(11)	3(10)	53(11)	18(9)
0(1)	2421(7)	3425(8)	−1515(9)	196(15)	47(8)	78(9)	−28(9)	95(10)	−36(7)
C(2)	2434(7)	5755(10)	919(11)	70(12)	28(9)	41(10)	8(9)	19(9)	8(9)
O(2)	2413(6)	6309(7)	1471(8)	140(12)	32(7)	66(8)	18(7)	51(8)	−23(6)
P(1)	1703(2)	4139(3)	472(3)	78(3)	35(3)	45(3)	0(2)	31(3)	−3(2)
P(2)	3195(2)	4035(3)	1064(3)	72(3)	28(2)	48(3)	1(2)	33(3)	1(2)
P(3)	3195(2)	5700(3)	−373(3)	79(3)	25(2)	45(3)	2(2)	35(2)	−2(2)
P(4)	1708(2)	5583(3)	−1192(3)	84(3)	35(3)	46(3)	3(2)	31(3)	1(2)
O(11)	1930(5)	3794(7)	1582(6)	70(8)	53(7)	31(6)	−7(6)	23(6)	4(5)
C(17)	1610(9)	3120(12)	2037(11)	124(16)	66(13)	43(11)	−26(12)	46(11)	15(10)
O(12)	1112(5)	4760(7)	439(8)	94(9)	51(7)	78(8)	23(7)	42(7)	3(7)
C(18)	1013(11)	5314(16)	1213(14)	169(21)	119(19)	68(14)	81(17)	49(14)	−12(13)
O(21)	2973(5)	3025(6)	1320(7)	85(8)	26(6)	52(7)	−13(6)	21(6)	0(5)
C(27)	3336(9)	2433(11)	2118(12)	106(16)	34(10)	54(12)	7(10)	−3(11)	32(9)
O(22)	3768(5)	3701(7)	674(7)	84(9)	54(7)	57(7)	4(6)	38(7)	−5(6)
C(28)	3798(11)	2981(14)	89(18)	193(25)	57(13)	167(23)	25(15)	131(21)	−36(15)
O(31)	2960(5)	6700(7)	−842(8)	98(9)	36(6)	62(7)	3(6)	38(7)	−3(6)
C(37)	3331(9)	7308(12)	−1281(15)	122(17)	52(12)	111(17)	−30(11)	80(15)	28(11)
O(32)	3790(4)	5946(7)	516(7)	72(8)	39(6)	54(7)	−8(6)	24(6)	−10(5)
C(38)	3788(8)	6716(11)	1200(12)	118(16)	32(10)	63(12)	−8(10)	34(11)	−33(9)
O(41)	1935(5)	5921(7)	−2104(7)	86(8)	50(7)	44(7)	5(6)	32(6)	2(6)
C(47)	1646(10)	6620(13)	−2828(13)	152(20)	65(13)	58(12)	30(13)	39(13)	48(11)
O(42)	1128(5)	4949(8)	−1703(8)	103(9)	54(7)	54(7)	−4(7)	25(7)	−9(6)
C(48)	1013(13)	4448(19)	−2601(15)	220(30)	168(26)	63(15)	−127(23)	38(17)	−37(17)
C(11)	1323(7)	3138(11)	−247(11)	76(13)	50(11)	56(10)	−18(10)	35(9)	1(9)
C(12)	1693(7)	2362(10)	−317(11)	72(12)	30(10)	49(10)	−2(9)	29(9)	13(8)
C(13)	1429(10)	1605(13)	−955(13)	83(15)	56(14)	66(13)	−30(12)	38(11)	−8(11)

C(14)	822(13)	1646(13)	−1442(16)	140(23)	45(13)	96(17)	−6(15)	68(17)	0(12)
C(15)	433(9)	2409(16)	−1385(14)	85(15)	89(17)	66(14)	−18(14)	23(12)	17(13)
C(16)	713(8)	3175(13)	−754(13)	73(13)	79(14)	62(13)	−27(11)	20(10)	5(11)
C(21)	3591(7)	4557(9)	2255(10)	44(11)	29(9)	41(10)	−1(8)	4(8)	7(7)
C(22)	3239(7)	4806(10)	2854(11)	77(12)	30(9)	33(9)	12(9)	25(9)	6(8)
C(23)	3534(9)	5274(11)	3750(12)	66(13)	44(11)	53(12)	−2(10)	23(10)	5(9)
C(24)	4147(10)	5457(11)	4005(12)	100(17)	37(11)	53(11)	−7(10)	34(12)	5(9)
C(25)	4500(8)	5174(12)	3403(14)	87(13)	39(11)	78(13)	−2(10)	31(12)	15(11)
C(26)	4223(8)	4693(12)	2507(13)	68(14)	44(11)	67(13)	−8(10)	17(10)	10(10)
C(31)	3570(7)	5177(11)	−1226(11)	54(11)	41(10)	56(11)	1(9)	19(9)	10(9)
C(32)	4196(9)	4972(12)	−889(11)	96(15)	51(11)	49(10)	0(11)	35(11)	0(9)
C(33)	4472(8)	4490(13)	−1525(15)	80(14)	74(14)	98(15)	3(11)	65(13)	−14(12)
C(34)	4101(8)	4212(12)	−2452(13)	108(14)	53(12)	47(12)	−17(11)	42(11)	−12(10)
C(35)	3493(7)	4433(10)	−2782(11)	85(12)	33(10)	57(11)	5(9)	50(10)	6(9)
C(36)	3215(7)	4921(10)	−2149(10)	89(12)	41(10)	30(9)	−8(9)	28(9)	10(8)
C(41)	1308(7)	6602(12)	−850(10)	84(13)	65(12)	31(9)	24(10)	27(9)	20(9)
C(42)	696(8)	6558(12)	−996(13)	93(14)	53(12)	71(13)	18(11)	33(11)	12(10)
C(43)	421(10)	7318(15)	−647(16)	102(18)	71(15)	100(16)	36(14)	67(15)	24(13)
C(44)	762(11)	8059(13)	−176(14)	95(19)	47(13)	81(16)	26(12)	39(14)	14(11)
C(45)	1400(10)	8108(11)	−58(12)	101(17)	36(11)	58(12)	22(11)	37(11)	14(9)
C(46)	1689(8)	7372(10)	−425(11)	123(15)	11(9)	50(11)	−8(9)	27(11)	2(8)
P(5)	1791(3)	4896(4)	4631(4)	128(5)	50(3)	83(4)	7(3)	44(4)	1(3)
F(1)	1424(14)	4087(14)	4188(17)	453(39)	173(19)	260(24)	−178(23)	196(27)	−140(18)
F(2)	2326(12)	4327(23)	4891(23)	233(25)	317(35)	372(36)	162(26)	92(24)	133(30)
F(3)	1670(14)	4701(13)	5548(14)	660(47)	141(16)	208(19)	−9(23)	321(27)	16(14)
F(4)	1288(9)	5500(16)	4305(24)	142(17)	189(21)	520(45)	56(16)	89(23)	115(26)
F(5)	2146(13)	5739(16)	5007(16)	373(32)	197(22)	240(22)	−158(22)	118(21)	−101(18)
F(6)	1954(11)	5068(13)	3687(12)	362(27)	178(17)	144(14)	9(19)	149(16)	12(13)
O(5)	−61(9)	3178(20)	3734(22)	83(15)	288(31)	344(35)	63(17)	−11(18)	−105(28)
C(51)	−30(21)	3803(31)	4938(37)	207(39)	218(44)	266(48)	−58(36)	−102(34)	−15(40)
C(52)	173(13)	2899(30)	5736(36)	65(23)	235(43)	354(58)	45(24)	−64(27)	−105(41)

TABLE 3

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s

	cis	*trans*		*cis*	*trans*
Mn—C(1)	1.780(13)	1.839(17)	C(25)—C(26)	1.433(15)	1.425(24)
Mn—C(2)		1.839(17)	C(26)—C(21)	1.386(18)	1.403(25)
Mn—P(1)	2.262(3)	2.269(7)	C(31)—C(32)		1.407(25)
Mn—P(2)	2.281(4)	2.269(6)	C(32)—C(33)		1.428(29)
Mn—P(3)		2.281(7)	C(33)—C(34)		1.402(24)
Mn—P(4)		2.265(6)	C(34)—C(35)		1.374(24)
C(1)—O(1)	1.154(16)	1.132(21)	C(35)—C(36)		1.430(24)
C(2)—O(2)		1.130(20)	C(36)—C(31)		1.377(19)
P(1)—O(11)	1.597(8)	1.589(11)	C(41)—C(42)		1.360(25)
P(1)—O(12)	1.573(7)	1.615(13)	C(42)—C(43)		1.423(30)
P(1)—C(11)	1.819(13)	1.831(16)	C(43)—C(44)		1.376(28)
O(11)—C(17)	1.468(9)	1.476(22)	C(44)—C(45)		1.425(36)
O(12)—C(18)	1.466(11)	1.429(26)	C(45)—C(46)		1.429(26)
P(2)—O(21)	1.597(10)	1.614(11)	C(46)—C(41)		1.430(22)
P(2)—O(22)	1.584(8)	1.611(14)	P(5)—F(1)	1.434(14)	1.466(23)
P(2)—C(21)	1.829(8)	1.832(14)	P(5)—F(2)	1.558(7)	1.431(29)
O(21)—C(27)	1.457(22)	1.467(18)	P(5)—F(3)	1.453(17)	1.439(26)
O(22)—C(28)	1.450(20)	1.444(25)	P(5)—F(4)		1.411(22)
P(3)—O(31)		1.611(11)	P(5)—F(5)	1.520(14)	1.470(25)
P(3)—O(32)		1.605(10)	P(5)—F(6)		1.514(22)
P(3)—C(31)		1.840(19)	C(51)—Cl(5)		1.914(61)
O(31)—C(37)		1.480(25)	C(51)—C(52)		1.697(65)
O(32)—C(38)		1.475(20)			
P(4)—O(41)		1.608(13)	C(1)—Mn—C(2)	90.5(6)	177.9(8)
P(4)—O(42)		1.603(12)	C(1)—Mn—P(1)	90.3(3)	91.7(6)
P(4)—C(41)		1.868(18)	C(1)—Mn—P(2)	88.1(4)	87.8(5)
O(41)—C(47)		1.451(20)	C(1)—Mn—P(3)[P(1)']	86.8(3)	93.7(6)
O(42)—C(48)		1.421(26)	C(1)—Mn—P(4)[P(2)']	176.7(5)	86.2(5)
C(11)—C(12)	1.384(18)	1.423(23)	C(2)—Mn—P(1)		86.4(6)
C(12)—C(13)	1.436(27)	1.433(23)	C(2)—Mn—P(2)		93.3(5)
C(13)—C(14)	1.381(39)	1.364(33)	C(2)—Mn—P(3)		88.2(6)
C(14)—C(15)	1.367(34)	1.432(33)	C(2)—Mn—P(4)		92.8(5)
C(15)—C(16)	1.434(26)	1.448(28)	P(1)—Mn—P(2)	90.2(1)	92.8(3)
C(16)—C(11)	1.401(20)	1.378(22)	P(1)—Mn—P(3)[P(1)']	176.0(2)	174.5(3)
C(21)—C(22)	1.410(18)	1.384(25)	P(1)—Mn—P(4)	92.5(1)	88.0(3)
C(22)—C(23)	1.422(14)	1.424(21)	P(2)—Mn—P(3)		87.5(3)
C(23)—C(24)	1.369(22)	1.373(29)	P(2)—Mn—P(4)[P(2)']	93.5(1)	174.0(2)
C(24)—C(25)	1.395(23)	1.400(31)	P(3)—Mn—P(4)		92.3(3)

blocked-matrix least-squares techniques resulting in a final conventional R-index of 0.076 with unit weights. A final difference map showed no regions of appreciable electron density and no hydrogen atoms could be placed. The scattering factors, anomalous dispersion coefficients and computer programs are the same as given for the *cis*-isomer. The atomic coordinates and thermal parameters are listed in Table 2 and the bond lengths and angles are given in Table 3.

The molecular configurations of the two cations are illustrated by the perspective drawings in Fig. 1 and 2. A list of the observed and calculated structure factors for both structures is available *. The thermal parameters in Tables 1 and 2 are of the form $T = \exp[-2\pi^2(a^*b^*U_{11} + ... + 2b^*c^*klU_{23})]$.

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* May be obtained from the authors on request (G.J.K.).

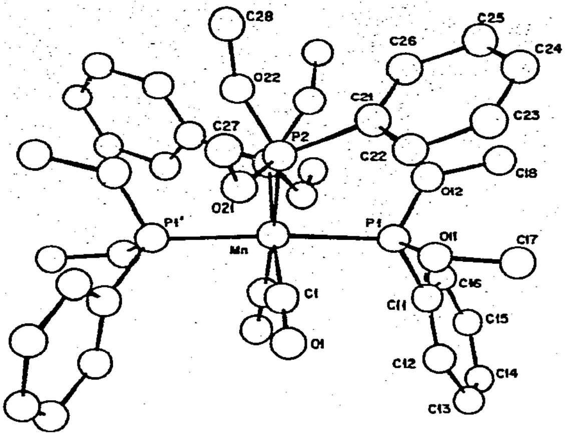

Fig. 1. The molecular structure of the *cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]^+$ cation.

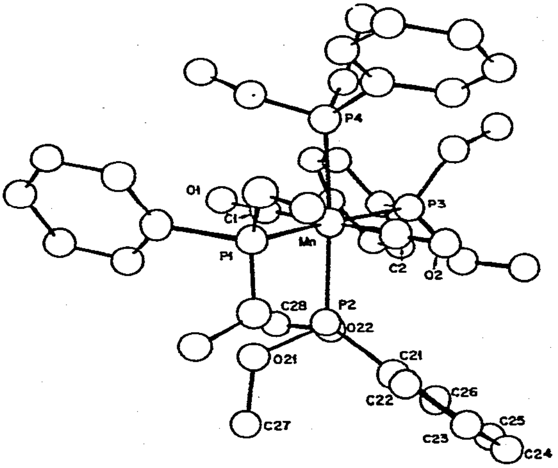

Fig. 2. The molecular structure of the *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]^+$ cation.

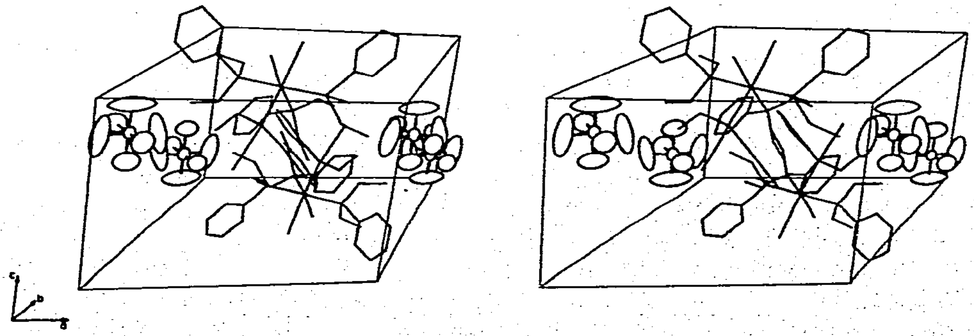

Fig. 3. Stereoscopic view of the unit cell and contents in the *cis*-isomer. The thermal ellipsoids in the cation are not shown for clarity.

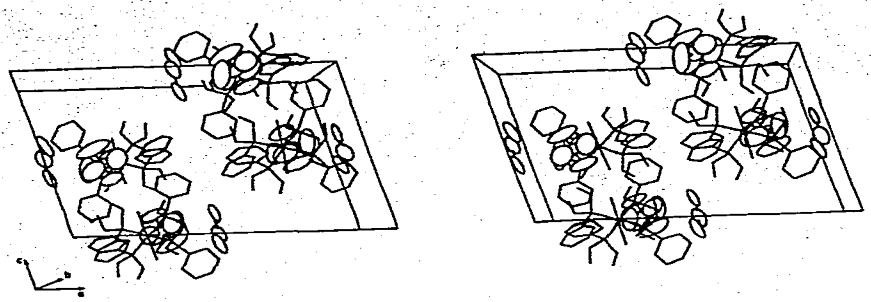

Fig. 4. Stereoscopic view of the unit cell and contents in the *trans*-isomer. The thermal ellipsoids in the cation are not shown for clarity.

Results and discussion

Both crystal structures contain discrete $[Mn(CO)_2\{P(OMe)_2Ph\}_4]^+$ cations and $[PF_6]^-$ anions. The manganese atom of the *cis*-isomer lies on a two-fold rotational axis causing the full cation to have this rotational symmetry. Atoms related by this symmetry are marked with a superscript (′) in Table 3.

Both isomers show slight deviations from the ideal octahedral symmetry of the coordination polyhedron around the manganese atom. In both cases this distortion can be attributed to the steric requirements of the phosphonite groups.

The Mn—P bond lengths are within one standard deviation of the mean value of 2.27 Å and are comparable with those found in the neutral carbonyl complexes [5], *fac*- and *mer*, *trans*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$.

The Mn—C bond lengths of 1.78(1) Å for the *cis*-CO groups and 1.84(2) Å for the mutually *trans*-CO groups in the *cis*- and *trans*-isomers respectively, seem to be in accordance with the structural *trans* effect postulated for other carbonyl compounds [10, 11]. However, the difference of 0.06 Å is hardly greater than the limits of accuracy at which bond lengths could be determined in these structures. Although differences in M—CO bond lengths of this magnitude have previously been considered to be structurally significant in other studies, the contradictory results observed in the comparable crystal structures of *fac*- and *mer*, *trans*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$ [5] and in other compounds [12—14], suggest that a correlation has yet to be shown between M—CO bond lengths and the kinetic *trans* effect. Differences in carbonyl bonding may also be somewhat reduced in complexes containing phosphonite ligands compared to tertiary phosphine ligands due to the greater π-acceptor properties of the phosphonites.

The Mn—C bond lengths in these cationic manganese carbonyl complexes do not differ significantly from those found in *fac*- and *mer*, *trans*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$, although the uncharged complexes undergo carbonyl substitution reactions much more readily. Although decreased metal carbonyl π-bonding may be expected in the cations due to a lower electron density on the metal, recent results [15] indicate that simple π-electron theory may not apply due to a possible direct donation of phosphorus σ electrons into the π orbitals of *cis*-CO groups. Hence the comparable bond lengths found in the cationic and uncharged species may be attributed either to a perturbation of the π-electron system or to the Mn—C bond lengths being insufficiently sensitive to charges in Mn—C bonding.

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