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THE CRYSTAL AND MOLECULAR STRUCTURES OF *fac*- AND *mer-trans*-BROMOTRICARBONYLBIS(DIMETHOXYPHENYLPHOSPHINE)-MANGANESE(I)

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Summary

The crystal and molecular structures of the *fac*- and *mer-trans*-isomers of bromotricarbonylbis(dimethoxyphenylphosphine)manganese(I), [Mn-$(CO)_3\{P(OMe)_2Ph\}_2Br$], have been determined by single-crystal X-ray diffraction techniques. The *fac*-isomer crystallizes in the orthorhombic system, space group $P2_12_12_1$, a = 17.19(2), b = 16.71(2), c = 8.27(1) Å, Z = 4. Anisotropic refinement by full-matrix least-squares methods gives R = 0.041. The *trans*-isomer crystallizes in the monoclinic system, space group $P2_1/n$, a = 14.94(2), b = 24.94(3), c = 13.34(1) Å, β = 109.6(2)°, Z = 8. One of the two independent molecules in the asymmetric unit exhibits disorder of the bromine atom. Isotropic refinement by full-matrix least-squares methods gives R = 0.116. Intensity data were collected on an automatic diffractometer in both cases. Both structures exhibit slightly distorted octahedral geometry about the manganese with one bromine, two phosphorus and three carbon atoms occupying the coordinate positions. A significant structural *trans*-effect of the carbonyl groups paralleling the known [1] strong carbonyl kinetic *trans*-effect was not observed.

Introduction

Recent studies in these laboratories have investigated the relationship between structure and reactivity in manganese [1] and rhenium [2] carbonyl-bromine systems. We have known [3] that a kinetic *trans*-carbonyl-effect is operative in these systems for mutually *trans*-carbonyl groups and the thermodynamic preference for "all-*cis*"-carbonyl structures limits higher substitution. During the course of this work two crystalline isomers of [Mn-

$(CO)_3\{P(OMe)_2Ph\}_2Br]$ were obtained and it was decided to undertake the structural elucidation of these isomers with the threefold aim of: (*i*) defining unequivocally the *mer-trans*-isomer, (*ii*) seeing if the *cis* ^{31}P—^{31}P coupling observed [1] in *fac*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$ is attributable to molecular distortions from the steric requirements of the ligands affecting the P—Mn—P bond angle, and (*iii*) attempting to establish a correlation between structural *trans*-effects (via Mn—C bond lengths) and the kinetic *trans*-effect.

Experimental

fac-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$

The crystals are prismatic in shape and orange in colour. The space group and preliminary cell dimensions were determined from oscillation and Weissenberg photographs. Accurate cell parameters were obtained from least-squares refinement using twenty five 2θ values measured on a diffractometer.

Crystal data. $MnP_2C_{19}O_7H_{22}Br$, M = 559.0. Orthorhombic, a = 17.19(2), b = 16.71(2), c = 8.27(1) Å, D_m = 1.56(2), Z = 4, D_c = 1.569, $F(000)$ + 1128. Space group $P2_1\,2_1\,2_1$ ($h00$, $H = 2n$; $0k0$, K = 2n; $00l$, $l = 2n$). Mo-K_α radiation. λ = 0.7107 Å, μ(Mo-K_α) = 25.5 cm^{-1}.

Intensity data were collected on a Philips PW1100 single crystal diffractometer fitted with a graphite monochromator to a maximum 2θ value of 44° (ω-2θ scan, scanwidth = 1.2°, scan speed = 0.04° s^{-1}). Background was counted for half the total scanning time on each side of a reflection. Absorption effects were eliminated by using a spherically-ground crystal with radius 0.2 mm for data collection. Of the 1690 independent reflections, 1498 were regarded as observed with $I > 1.65\sigma(I)$. $\sigma^2(I)$ was calculated as $S + B + (0.02S)^2$, where S is the scan count and B the total background count.

Structure solution and refinement. The manganese and bromine positions were located from an origin-removed sharpened Patterson map. The remaining atoms were found from successive Fourier syntheses. Full-matrix least-squares refinement with anisotropic thermal parameters gave a final conventional R of 0.041 and $R_w = [\Sigma w(|F_o|-|F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.048$. The weighting scheme used was $w = (\sin\theta/0.2) \times (70.0/F_o)$ for reflections with $\sin\theta < 0.2$ and/or $F_o > 70.0$. The hydrogen atoms could not be located from a difference Fourier synthesis and they were thus excluded from the structure factor calculations. Since two configurations of the molecule are possible in the space group $P2_1 2_1 2_1$, the inverse structure was also refined and gave a final R = 0.060. The isomer with the lower R was taken to have the correct absolute configuration.

The scattering factors used were those of Cromer and Mann [4] and the components of the anomalous dispersion corrections used for the bromine and manganese atoms were those listed by Cromer and Liberman [5]. All calculations were done using the X-RAY system of crystallographic programs [6]. The thermal ellipsoid drawings were made using the plot program of Johnson [7]. Final positional and thermal parameters are given in Tables 1 and 2 and bond lengths and angles in Tables 3 and 4.

mer-trans-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$

The needle-shaped crystals were orange in colour and many exhibited

TABLE 1

FRACTIONAL COORDINATES WITH E.S.D.'s FOR THE *fac*-ISOMER

Atom	x	y	z
Br	0.3682(1)	0.3828(1)	0.2558(2)
Mn	0.4424(1)	0.3752(1)	−0.0082(2)
P(1)	0.5566(1)	0.3913(1)	0.1321(3)
P(2)	0.4263(1)	0.5085(1)	−0.0710(3)
O(1)	0.2893(5)	0.3398(5)	−0.1556(13)
O(2)	0.4617(5)	0.2025(5)	0.0450(11)
O(3)	0.5205(6)	0.3588(5)	−0.3162(12)
O(11)	0.5763(4)	0.4718(4)	0.2290(9)
O(12)	0.5647(4)	0.3202(4)	0.2599(9)
O(21)	0.3692(4)	0.5637(4)	0.0311(9)
O(22)	0.3928(4)	0.5102(4)	−0.2524(10)
C(1)	0.3467(7)	0.3547(6)	−0.1011(14)
C(2)	0.4538(6)	0.2654(7)	0.0308(13)
C(3)	0.4926(7)	0.3620(7)	−0.2041(19)
C(11)	0.6457(5)	0.3847(5)	0.0163(12)
C(12)	0.6925(5)	0.4514(6)	−0.0100(15)
C(13)	0.7594(7)	0.4442(9)	−0.1086(16)
C(14)	0.7779(7)	0.3719(9)	−0.1779(16)
C(15)	0.7322(8)	0.3047(9)	−0.1525(19)
C(16)	0.6656(7)	0.3121(7)	−0.0563(17)
C(17)	0.5256(6)	0.5052(7)	0.3516(13)
C(18)	0.6341(7)	0.3121(8)	0.3630(15)
C(21)	0.5076(5)	0.5775(5)	−0.0796(12)
C(22)	0.5645(6)	0.5638(6)	−0.1972(12)
C(23)	0.6275(7)	0.6205(8)	−0.2135(15)
C(24)	0.6309(8)	0.6857(8)	−0.1081(19)
C(25)	0.5745(8)	0.6976(6)	0.0053(18)
C(26)	0.5116(6)	0.6443(5)	0.0224(14)
C(27)	0.2854(6)	0.5440(7)	0.0471(18)
C(28)	0.3773(8)	0.5858(7)	−0.3371(17)

twinning. The space group and cell dimensions were determined as described above for the *fac*-isomer.

Crystal data $MnP_2C_{19}O_7H_{22}Br$, M = 559.0. Monoclinic, a = 14.94(2), b = 24.94(3), c = 13.34(1) Å, β = 109.6(2)°, D_m = 1.60(2), Z = 8, D_c = 1.592, $F(000)$ = 2256. Space group $P2_1/n$, ($h0l$, $h+l = 2n$; $0k0$, $k = 2n$). Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 25.8 cm^{-1}.

Intensities were collected on a Philips PW1100 diffractometer under the same conditions as described above for the *fac*-isomer except that the ω-scan mode was used. A crystal ground to spherical shape with radius 0.1 mm was used. Of the 5727 unique reflections measured, 3191 had $I > 1.65\ \sigma(I)$ and were classified as observed. Lorentz and polarization corrections were applied.

Structure solution and refinement. The manganese atoms and one bromine could be placed from a sharpened Patterson synthesis and successive Fourier syntheses revealed the positions of the other atoms. The bromine atom in one of the two independent molecules in the asymmetric unit was disordered with peak heights corresponding to half-atoms above and below the plane through the phosphorus atoms and C(1) and C(2). Packing disorder of this type is possible in this crystal since (*i*) a bromine atom with a covalent radius

TABLE 2

ANISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^3$) WITH E.S.D.'S FOR THE *fac*-ISOMER

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	37(1)	51(1)	51(1)	2(1)	11(1)	9(1)
Mn	25(1)	24(1)	31(1)	−3(1)	0(1)	−1(1)
P(1)	21(1)	24(1)	31(1)	−1(1)	5(1)	0(1)
P(2)	25(1)	27(1)	34(1)	1(1)	−3(1)	1(1)
O(1)	46(5)	68(5)	92(7)	−15(4)	−27(5)	7(5)
O(2)	73(6)	29(4)	77(6)	−3(4)	−10(5)	3(4)
O(3)	72(6)	58(5)	42(5)	−2(4)	15(5)	−12(4)
O(11)	34(3)	36(3)	43(4)	−4(3)	0(4)	−9(3)
O(12)	32(3)	43(4)	43(4)	1(3)	0(4)	13(4)
O(21)	34(4)	33(3)	63(5)	5(3)	7(4)	−4(4)
O(22)	45(4)	45(4)	44(4)	−7(3)	15(4)	14(4)
C(1)	48(7)	35(6)	51(7)	−8(5)	−6(6)	0(5)
C(2)	39(6)	41(7)	47(7)	−10(5)	−12(5)	−14(6)
C(3)	46(7)	40(7)	49(8)	−9(6)	−17(7)	13(6)
C(11)	26(5)	35(5)	40(5)	6(4)	4(5)	9(5)
C(12)	24(5)	52(6)	49(7)	−6(4)	11(6)	13(6)
C(13)	49(7)	87(9)	53(8)	−7(7)	5(7)	21(7)
C(14)	44(7)	89(9)	62(8)	24(8)	18(6)	28(8)
C(15)	58(9)	85(9)	79(9)	22(8)	25(8)	−5(9)
C(16)	51(7)	52(7)	79(9)	12(6)	13(7)	−6(7)
C(17)	56(6)	46(6)	41(6)	15(6)	17(6)	−14(6)
C(18)	40(6)	83(8)	52(7)	5(6)	−21(6)	36(7)
C(21)	30(5)	30(5)	33(5)	1(4)	−11(5)	10(5)
C(22)	36(6)	47(6)	43(7)	−3(5)	4(5)	8(5)
C(23)	46(6)	65(7)	71(9)	−10(7)	2(6)	21(8)
C(24)	54(8)	55(8)	79(9)	−17(7)	−11(9)	27(8)
C(25)	68(8)	41(6)	75(9)	−16(6)	−24(9)	5(7)
C(26)	52(6)	29(5)	48(7)	−6(5)	−14(6)	1(5)
C(27)	22(5)	70(8)	98(9)	16(5)	13(7)	12(8)
C(28)	62(8)	57(7)	69(8)	1(6)	−23(7)	32(7)

of 1.14 Å is comparable in size with a carbonyl group with a carbon atom of radius 0.77 Å and an oxygen atom with radius 0.73 Å at an interatomic distance of 1.15 Å and will hence coincide with the centre of the carbonyl C—O bond; (*ii*) the symmetry of the molecule is such that with the free rotation allowed around the P—Mn—P axis inversion of the molecule can easily occur during crystallization. During the isotropic refinement with full-matrix least-squares methods an approximation to the disorder was made by including the disordered bromine atom in molecule B as two separate atoms with occupancy factors of 0.5 each. The R value converged to 0.121. As the equally disordered third carbonyl group had been ignored before this stage, C(3) and O(3) were included as two half-weight CO groups superimposed on the bromine atoms at calculated positions along the Mn—Br directions. The bromine positions were kept invariant. The final R value was 0.116. Unit weights were used throughout the refinement process since $(\Delta F)^2$ showed very little dependence on sin θ or F_o. Anisotropic refinement was not attempted as the disorder exhibited and the limited number of observed reflections made such refinement meaningless. Final atomic parameters are given in Table 5 and bond lengths and angles in Tables 3 and 4. The computer programs and scat-

TABLE 3

INTRAMOLECULAR DISTANCES (Å)

	fac	*mer trans*	
		Molecule A	Molecule B
Mn—Br	2 532(5)	2.524(7)	2.533(10)
Mn—Br^1			2 530(8)
Mn—P(1)	2.296(4)	2.279(8)	2.258(7)
Mn—P(2)	2 303(4)	2.260(8)	2 259(7)
Mn—C(1)	1 85(1)	1 80(3)	2 00(3)
Mn—C(2)	1 87(1)	1 80(3)	1.84(2)
Mn—C(3)	1.85(1)	1 80(2)	
C(1)—O(1)	1.11(2)	1.18(4)	0.80(3)
C(2)—O(2)	1.07(2)	1.16(4)	1.13(3)
C(3)—O(3)	1.05(2)	1 04(3)	
P(1)—O(11)	1.60(1)	1.61(2)	1.59(2)
P(1)—O(12)	1.60(1)	1.58(2)	1.62(2)
P(1)—C(11)	1 81(1)	1.81(3)	1 85(2)
P(2)—O(21)	1.59(1)	1.59(2)	1.59(2)
P(2)—O(22)	1.61(1)	1.59(2)	1.61(2)
P(2)—C(21)	1.81(1)	1 80(2)	1.85(2)
O(11)—C(17)	1.45(1)	1.45(4)	1.47(3)
O(12)—C(18)	1.47(1)	1.30(4)	1.47(4)
O(21)—C(27)	1.48(1)	1.47(4)	1.46(4)
O(22)—C(28)	1.47(1)	1.47(4)	1.49(3)
C(11)—C(12)	1.39(1)	1 36(3)	1 38(3)
C(12)—C(13)	1.41(2)	1.45(4)	1.44(4)
C(13)—C(14)	1.38(2)	1.36(5)	1.36(5)
C(14)—C(15)	1.39(2)	1.30(4)	1.39(4)
C(15)—C(16)	1 40(2)	1 51(5)	1 48(4)
C(16)—C(11)	1.40(2)	1.39(4)	1.42(4)
C(21)—C(22)	1.40(1)	1.42(3)	1.39(3)
C(22)—C(23)	1.45(2)	1.46(4)	1.40(4)
C(23)—C(24)	1.40(2)	1.35(4)	1.39(5)
C(24)—C(25)	1.36(2)	1 36(3)	1.37(4)
C(25)—C(26)	1.41(2)	1.41(4)	1.42(4)
C(26)—C(21)	1.40(1)	1.35(4)	1 37(4)

tering and dispersion correction factors used are the same as those used during the structure determination of the *fac*-isomer. A list of the observed and calculated structure factors for both structures is available*.

Results and discussion

The results of the structure determinations confirm the *fac*-and *mer-trans*-configurations proposed [1] for the two isomers of $[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$. Perspective drawings of the two structures are given in Figs. 1 and 2 which also illustrate the molecular configurations and numbering systems

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* The observed and calculated structure factor amplitudes may be obtained from the authors on request (G.J.K.).

TABLE 4

INTRAMOLECULAR BOND ANGLES (°)

	fac	*mer trans*	
		Molecule A	Molecule B
Br—Mn—C(1)	85.4(4)	83.9(8)	84.6(9)
Br—Mn—C(2)	87 3(3)	89.4(7)	94 2(10)
Br—Mn—C(3)	175.4(5)	178.5(7)	178.1(6)^a
Br—Mn—P(1)	89 4(2)	86 6(2)	86 6(3)
Br—Mn—P(2)	94.9(1)	94.0(2)	94.2(3)
C(1)—Mn—C(2)	89.0(5)	173.3(10)	178.6(18)
C(1)—Mn—C(3)	91.6(5)	96.1(12)	94.6(9)^a
C(2)—Mn—C(3)	89.5(1)	90.6(11)	86 6(10)^a
P(1)—Mn—P(2)	96.0(1)	178.7(7)	179.1(11)
P(1)—Mn—C(1)	173.2(4)	89.9(9)	90 9(8)
P(1)—Mn—C(2)	86.5(3)	90.1(8)	89.7(9)
P(1)—Mn—C(3)	93 3(4)	91 8(7)	91.7(3)^a
P(2)—Mn—C(1)	88 7(3)	91.4(9)	88 8(8)
P(2)—Mn—C(2)	176.7(4)	88.7(8)	90.6(9)
P(2)—Mn—C(3)	88.5(4)	87.6(7)	87.5(2)^a
Mn—C(1)—O(1)	178(1)	175(2)	172(3)
Mn—C(2)—C(2)	176(1)	179(2)	178(3)
Mn—C(3)—O(3)	176(1)	178(2)	
Mn—P(1)—C(11)	117(1)	117(1)	117(1)
Mn—P(1)—O(11)	122(1)	112(1)	111(1)
Mn—P(1)—O(12)	109(1)	117(1)	119(1)
O(11)—P(1)—O(12)	106(1)	106(1)	106(1)
C(11)—P(1)—O(11)	98(1)	105(1)	107(1)
C(11)—P(1)—O(12)	103(1)	98(1)	96(1)
Mn—P(2)—C(21)	122(1)	116(1)	118(1)
Mn—P(2)—O(21)	121(1)	123(1)	121(1)
Mn—P(2)—O(22)	106(1)	108(1)	109(1)
O(21)—P(2)—O(22)	105(1)	106(1)	104(1)
C(21)—P(2)—O(21)	97(1)	97(1)	98(1)
C(21)—P(2)—O(22)	103(1)	105(1)	104(1)
P(1)—O(11)—C(17)	123(1)	124(2)	121(2)
P(1)—O(12)—C(18)	121(1)	130(3)	118(2)
P(1)—C(11)—C(12)	122(1)	120(2)	120(2)
P(1)—C(11)—C(16)	119(1)	117(2)	114(2)
P(2)—O(21)—C(27)	121(1)	121(2)	122(2)
P(2)—O(22)—C(28)	122(1)	121(2)	123(2)
P(2)—C(21)—C(22)	118(1)	117(2)	119(2)
P(2)—C(21)—C(26)	121(1)	123(2)	119(2)
C(11)—C(12)—C(13)	119(1)	120(3)	117(3)
C(12)—C(13)—C(14)	120(1)	115(3)	118(3)
C(13)—C(14)—C(15)	121(1)	129(3)	126(3)
C(14)—C(15)—C(16)	119(1)	116(3)	117(3)
C(15)—C(16)—C(11)	121(1)	116(2)	115(2)
C(16)—C(11)—C(12)	119(1)	124(2)	126(2)
C(21)—C(22)—C(23)	119(1)	117(2)	120(3)
C(22)—C(23)—C(24)	119(1)	120(2)	118(2)
C(23)—C(24)—C(25)	121(1)	122(3)	123(3)
C(24)—C(25)—C(26)	121(1)	119(3)	119(3)
C(25)—C(26)—C(21)	119(1)	122(2)	118(2)
C(26)—C(21)—C(22)	121(1)	120(2)	122(2)

[a] For molecule B, read B' for C(3) in this table.

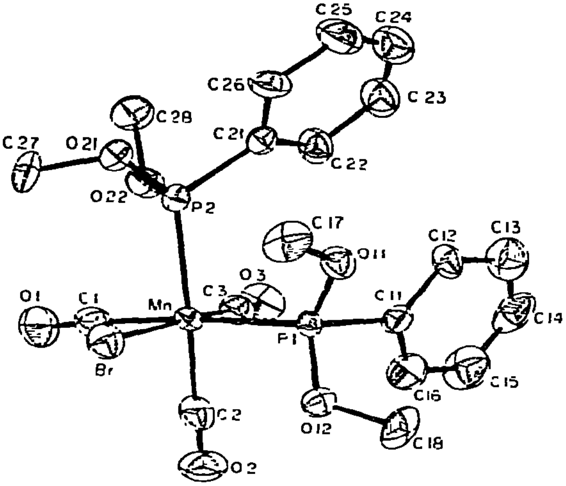
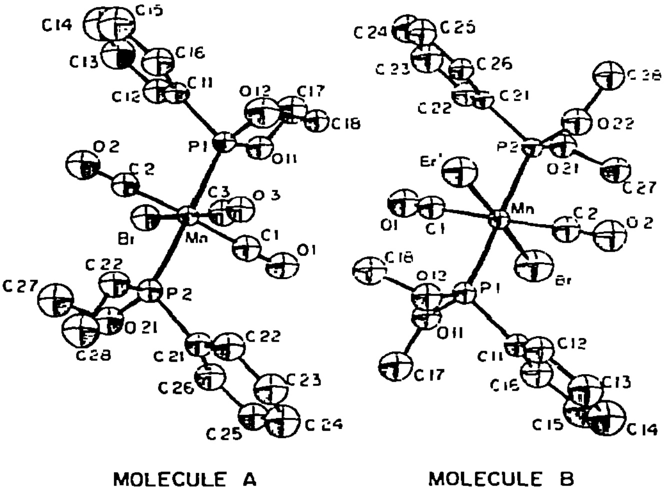


Fig. 1. Molecular structure and nomenclature of the *fac*-isomer.

used. Figure 2 shows the two independent molecules of the *mer-trans*-isomer in the same relative positions as they exist in the crystal. It can be seen from this drawing that the two molecules differ by more than the disorder of the bromine exhibited by molecule B. The substituents in the plane through the manganese atom and perpendicular to the P—Mn—P axis rotate through about 90° relative to the phosphonite ligands going from one molecule to the other.

The disorder in molecule B eliminated all positional detail concerning the carbonyl group *trans* to the bromine and led to physically unreasonable bond lengths in the remaining groups. In the discussion that follows only the bond lengths and angles of molecule A will be referred to.

There is some deviation from ideal octahedral symmetry around the manganese, particularly in the *fac*-isomer. The P—Mn—P angle of 96°, resulting from



MOLECULE A MOLECULE B

Fig. 2. Molecular structure and nomenclature of the *mer-trans*-isomer.

TABLE 5

FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS WITH E.S.D.'S FOR THE *mer-trans*-ISOMER

Atom	x	y	z	$U \times 10^3$
Molecule A				
Br	0.2471(2)	0.1446(1)	0.0494(2)	52(1)
Mn	0.3708(2)	0.1265(1)	0.2286(2)	24(1)
P(1)	0.4259(4)	0.2108(2)	0.2179(5)	32(2)
P(2)	0.3154(4)	0.0435(2)	0.2424(5)	32(2)
O(1)	0.4891(14)	0.0839(8)	0.1063(15)	69(6)
O(2)	0.2383(14)	0.1692(8)	0.3315(16)	72(6)
O(3)	0.5114(12)	0.1097(7)	0.4313(14)	50(5)
O(11)	0.4551(12)	0.2188(7)	0.1131(14)	54(5)
O(12)	0.5144(15)	0.2300(8)	0.3146(16)	73(6)
O(21)	0.2232(12)	0.0186(7)	0.1564(13)	50(5)
O(22)	0.2979(12)	0.0400(7)	0.3536(14)	54(5)
C(1)	0.4396(18)	0.1014(10)	0.1507(20)	45(7)
C(2)	0.2910(16)	0.1529(9)	0.2920(18)	39(6)
C(3)	0.4605(16)	0.1154(9)	0.3566(19)	35(6)
C(11)	0.3471(16)	0.2663(9)	0.2155(18)	37(6)
C(12)	0.2871(17)	0.2845(10)	0.1208(20)	47(7)
C(13)	0.2206(22)	0.3272(12)	0.1190(25)	70(9)
C(14)	0.2237(22)	0.3454(12)	0.2166(26)	75(9)
C(15)	0.2789(23)	0.3306(13)	0.3106(26)	76(9)
C(16)	0.3481(20)	0.2859(11)	0.3135(22)	58(8)
C(17)	0.5033(23)	0.2659(13)	0.0928(25)	77(9)
C(18)	0.6032(26)	0.2169(14)	0.3396(25)	91(9)
C(21)	0.3943(15)	−0.0113(9)	0.2440(17)	30(5)
C(22)	0.4660(17)	−0.0233(10)	0.3419(19)	44(7)
C(23)	0.5315(20)	−0.0666(11)	0.3415(23)	62(8)
C(24)	0.5227(19)	−0.0930(11)	0.2504(21)	53(7)
C(25)	0.4551(18)	−0.0800(10)	0.1565(20)	48(7)
C(26)	0.3873(18)	−0.0405(10)	0.1563(20)	48(7)
C(27)	0.1292(21)	0.0430(12)	0.1337(24)	68(9)
C(28)	0.2594(21)	−0.0085(12)	0.3858(25)	72(10)
Molecule B				
Br	0.8940(3)	0.0904(2)	0.0524(4)	90(2)
Br^{1}	0.8357(2)	0.1559(3)	0.3844(4)	46(1)
Mn	0.8670(2)	0.1243(1)	0.2189(3)	23(1)
P(1)	0.8099(4)	0.0418(2)	0.2323(5)	28(1)
P(2)	0.9227(4)	0.2074(2)	0.2068(5)	29(1)
O(1)	0.6879(14)	0.1579(7)	0.0862(15)	56(5)
O(2)	1.0584(14)	0.0916(8)	0.3604(15)	64(5)
O(3)	0.8997(48)	0.0827(28)	0.0160(56)	250(26)
O(3)^{1}	0.8453(33)	0.1573(19)	0.4124(41)	122(16)
O(11)	0.7265(11)	0.0263(6)	0.1261(12)	43(4)
O(12)	0.7692(10)	0.0296(6)	0.3286(12)	36(4)
O(21)	0.9604(11)	0.2224(6)	0.1124(12)	42(4)
O(22)	1.0111(11)	0.2202(7)	0.3131(13)	48(4)
C(1)	0.7400(20)	0.1473(11)	0.1191(21)	49(7)
C(2)	0.9846(19)	0.1035(10)	0.3079(21)	48(7)
C(3)	0.8867(51)	0.1030(29)	0.1309(60)	97(22)
C(3)^{1}	0.8269(40)	0.1528(24)	0.3255(50)	43(16)
C(11)	0.8960(15)	−0.0142(8)	0.2620(17)	29(5)
C(12)	0.9459(19)	−0.0277(11)	0.3660(21)	52(7)
C(13)	1.0179(20)	−0.0686(12)	0.3839(23)	65(8)
C(14)	1.0320(19)	−0.0911(11)	0.2972(22)	56(7)
C(15)	0.9801(22)	−0.0805(12)	0.1917(25)	74(9)
C(16)	0.9072(20)	−0.0380(11)	0.1702(22)	59(8)
C(17)	0.6766(20)	−0.0254(11)	0.1163(23)	62(8)

(Table to be continued)

TABLE 5 (continued)

Atom	*x*	*y*	*z*	$U \times 10^3$
C(18)	0.6827(22)	0.0576(12)	0.3287(24)	71(9)
C(21)	0.8414(15)	0.2652(9)	0.1935(17)	32(6)
C(22)	0.7955(19)	0.2865(11)	0.0929(21)	54(7)
C(23)	0.7305(20)	0.3286(12)	0.0800(22)	62(8)
C(24)	0.7160(17)	0.3485(10)	0.1706(20)	50(7)
C(25)	0.7613(19)	0.3280(11)	0.2700(21)	54(7)
C(26)	0.8256(17)	0.2844(10)	0.2821(19)	43(6)
C(27)	1.0421(21)	0.1959(12)	0.0977(23)	67(9)
C(29)	1.0669(20)	0.2710(11)	0.3288(23)	61(8)

the steric requirements of the bulky *cis*-bonded $P(OMe)_2Ph$ groups, represents a significant distortion which could give rise to the ^{31}P—^{31}P coupling observed in the ^1H NMR spectrum of *fac*-[$Mn(CO)_3\{P(OMe)_2Ph\}_2Br$] [1].

The Mn—Br distances observed in both isomers compare well with the analogous bond lengths found in *fac*-[$Mn(CO)_3(MeNC)_2Br$] (2.54 Å) [8], *cis*-[$Mn(CO)_4(Ph_3P^+$—C=C$^-$)Br] (2.51 Å) [9], [$(Mn(CO)_3(CNPh)_2$] (2.527 Å) [10] and the α and β isomers of [$Br(CO)_3MnPPh(CH_2CH_2PPh_2)_2Cr(CO)_5$] (2.537 and 2.534 Å) [11].

The Mn—P bond lengths range from 2.260 to 2.303 Å. These are the first Mn—P(phosphonite) bond lengths to be determined and are shorter than the Mn—P(phosphine) bond lengths in *cis*-[$Mn(CO)_4(PPh_3)Cl$] (2.40 Å) [12] and *cis*-[$MeMn(CO)_4(PPh_3)$] (2.31 Å) [13]. This shortening suggests stronger Mn—P π-bonding due to the greater Lewis acidity of $P(OMe)_2Ph$ compared with PPh_3. Differences of a similar magnitude have been observed for the Cr—P distances in the related structures [$Cr(CO)_5L$] (L = PPh_3 and $P(OPh)_3$) [14]. A fractional shortening of the Mn—P bond in the *mer-trans*-isomer (average 2.27 Å), containing mutually *trans*-phosphonite ligands, compared to the *fac*-isomer (average 2.30 Å) in which the ligands are *trans* to the stronger π-accepting carbonyl groups is observed but little physical significance can be attached to bond length differences of this size.

The shortening of the Mn—C bond lengths in the *mer-trans*-isomer (1.79 Å) compared with those in the *fac*-isomer (1.86 Å) is contrary to what might be expected if a correlation existed between thermodynamic parameters and kinetic parameters in these systems. If a parallel structural *trans*-effect was operative we might expect a lengthening of M—C bond lengths in the *mer-trans*-isomer compared with the *fac*-isomer. These differences (0.07 Å), however, are possibly too small to be chemically significant. Furthermore, the Mn—C bond lengths of the CO groups *trans* to Br do not differ from those of the CO groups *cis* to the Br. This absence of meaningful differences in Mn—C bond lengths has been observed in analogous compounds [10, 11], though the β-isomer of [$Br(CO)_3Mn(triphos)Cr(CO)_5$] [11] was found to have the CO group *trans* to the bromine shorter than the other M—C bond lengths.

We have thus been unable to find any thermodynamic correlation with the kinetic *trans*-effect observed in *mer-trans*-[$Mn(CO)_3\{P(OMe)_2Ph\}_2Br$].

References

1 R.H. Reimann and E. Singleton, J. Chem. Soc. Dalton Trans., (1973) 841.
2 R.H. Reimann and E. Singleton, J. Organometal. Chem., 59 (1973) 309.
3 D.J.A. de Waal, R.H. Reimann and E. Singleton, J. Organometal. Chem., 84 (1974) 339.
4 D.T. Cromer and J.B. Mann, Acta Crystallogra. Sect. A, 24 (1968) 321.
5 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
6 J.M. Stewart, G.J. Kruger, H. Ammon, C.H. Dickinson and S.R. Hall, University of Maryland Computer Sci. Tech. Rep. TR-192, College Park, Maryland, 1972.
7 C.K. Johnson, ORTEP, Report ORNL-3784, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
8 A.C. Sarapa and R.F. Fenske, Inorg. Chem., 11 (1972) 3021.
9 S.Z. Goldberg, E.N. Duesler and K.N. Raymond, Inorg. Chem., 11 (1972) 1397.
10 D. Bright and O.S. Mills, J. Chem. Soc. Dalton Trans., (1974) 219.
11 P.H. Bird, N.J. Coville, I.S. Butler and M.L. Schneider, Inorg. Chem., 12 (1973) 2902.
12 H. Vahrenkamp, Chem. Ber., 104 (1971) 449
13 A. Mawby and G.E. Pringle, J. Inorg. Nucl. Chem., 34 (1972) 877.
14 H.J. Plastas, J.M. Stewart and S.O. Grim, Inorg. Chem., 12 (1973) 265