REACTIVITY OF TRANSITION METAL-SUBSTITUTED PHOSPHORANES: CRYSTAL AND MOLECULAR STRUCTURE OF 2-PENTACARBONYLMANGANESE-1,3,2-BENZODIOXAPHOSPHOLE-2-OXIDE

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Summary

The crystal and molecular structure of 2-pentacarbonylmanganese-1,3,2-benzodioxaphosphole-2-oxide, $OC_6H_4OP(O)Mn(CO)_5$, has been determined by single crystal X-ray diffraction. The crystal belongs to the triclinic system with a space group of $P\bar{1}$. The unit cell parameters are: a 6.753(2), b 8.818(3), c 12.004(4) Å, α 106.79(2), β 105.37(2), γ 98.82(2)°, and $Z = 2$. Graphite monochromatic Mo-K_α radiation was used in the intensity measurements. The final disagreement index was 0.073 for 2293 reflections. The Mn and P atoms have distorted octahedral and tetrahedral configurations, respectively. The phenyl ring is essentially planar; however, the dioxaphosphole 5-membered ring is slightly puckered. The P=O has an almost eclipsed conformation with one of the equatorial carbonyls, leading to pseudo mirror symmetry.

Introduction

The hydrolysis of 2-pentacarbonylmanganese-2,2′-spirobi(1,3,2-benzodioxaphosphole) (1) [1] has been investigated during the course of studies on the synthesis and reactivity of transition metal-substituted phosphoranes. It was found that 1 hydrolyzes as follows [2]:
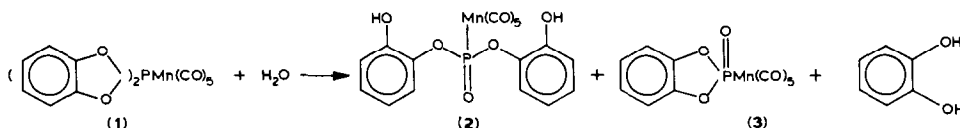
Di(2-hydroxyphenyl)pentacarbonylmanganese phosphonate (2) rearranges either in solution or in the gas phase to give 2-pentacarbonylmanganese-1,3,2-benzodi-

oxaphosphole-2-oxide (3) and catechol. The identity of 2 was confirmed by the single crystal X-ray structural determination [2]. The crystal structure of 3 is reported in this paper. This structure was pursued for the following reasons: first, to confirm the identity of 3; second, although there have been several metal complexes synthesized containing the 1,3,2-benzodioxaphosphole ring [3–8], no structural data are known; and finally, only two structures on the derivatives of 1,3,2-benzodi-oxaphosphole-2-oxide (4 and 5) have been reported. The determination of the crystal structure of 3 provides a means to ascertain the effect of the metal substituent on the geometry and bonding in the $OC_6H_4OP(O)$ system.

(R = Cl , 4 [13] ,
R = OH , 5 [14])
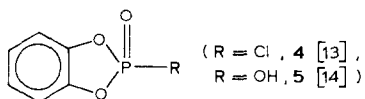
Experimental

The preparation of 3 has been described previously [2] and suitable crystals of 3 were obtained by concentrating the final solution of 3 and catechol in THF. The colorless crystal was sealed in a capillary tube for the X-ray analysis.

The unit cell parameters and intensity data were measured on a Syntex $P2_1$ computer controlled diffractometer. The crystal data are summarized in Table 1. A $\theta/2\theta$ scanning mode with graphite monochromatic Mo-K_α was used in the intensity measurements. Reflections with $I < 0.5\sigma(I)$ were assigned as $I = 0.25\sigma(I)$; $\sigma(I)$, the standard deviation of the intensity, was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, and no absorption corrections were applied.

TABLE 1

CRYSTAL AND EXPERIMENTAL DATA

Formula	$C_{11}H_4O_8PMn$
Formula weight	350.05
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a 6.753(2) Å α 106.79(2)°
	b 8.818(3) Å β 105.37(2)°
	c 12.004(4) Å γ 98.82(2)°
	V 651.9(3) Å^3
Density (calcd.)	1.783 g cm^{-3}
Number of molecules per unit cell	2
X-radiation used for data collection	λ(Mo-K_α) 0.7107 Å
Linear absorption coefficient	μ(Mo-K_α) 10.86 cm^{-1}
Total number of reflections with $2\theta < 50$	2293
Disagreement index, $R = (\Sigma \|F_o\| - \|F_c\|/\Sigma \|F_o\|)$	0.073 for 2293 reflections
Weighted disagreement index, R_w	0.075
Crystal size	$0.5 \times 0.05 \times 0.05$ mm
Weighting scheme	$w = k/\sigma^2(F)$
	($k = 1.285$ in the final refinement cycle)

Structure determination

The structure was determined by the application of direct methods and was refined using SHELX 76 [9] system of programs. The refinements were carried out by the full-matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms. The hydrogen positions were located on a difference Fourier synthesis. Isotropic temperature factors were used for the hydrogen atoms and the positional parameters were varied with constraints on the C–H bond distances. The weighting scheme was $w = k/\sigma^2(F)$, where $\sigma(F)$ is the standard deviation of the structure amplitude as derived from counting statistics. The scale factor k refined to a final value of 1.285. All the reflections were included in the refinements. The final disagreement index, $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.073 for 2293 reflections. The weighted disagreement index, R_w, was 0.075. The atomic scattering factors used for manganese, phosphorous, oxygen, carbon, and hydrogen atoms were those from International Tables for X-ray Crystallography [10]. The final positional parameters are given in Table 2. (Lists of structure factors and anisotropic temperature factors are available upon request from the authors.)

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR NON-HYDROGEN AND ($\times 10^3$) FOR HYDROGEN ATOMS. THE ESTIMATED STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES

	x	y	z	U_{eq}/U^a (Å^2)
Mn	1517(1)	2098(1)	8253(1)	499(5)
C(1)	2100(10)	35(8)	7650(6)	623(40)
O(1)	2467(8)	−1190(6)	7308(5)	904(39)
C(2)	1086(9)	4234(8)	8769(5)	529(36)
O(2)	788(7)	5509(5)	9044(4)	626(28)
C(3)	3600(10)	2424(8)	9706(6)	606(39)
O(3)	4839(8)	2544(6)	10575(4)	860(37)
C(4)	−337(10)	1837(7)	6731(6)	544(36)
O(4)	−1406(7)	1687(5)	5801(4)	662(29)
C(5)	−522(9)	1369(7)	8847(5)	528(36)
O(5)	−1707(8)	895(5)	9205(4)	832(35)
P	3980(2)	3054(2)	7506(1)	526(9)
O(1′)	2992(6)	4371(4)	6867(4)	565(24)
O(2′)	3996(6)	1739(5)	6206(4)	646(27)
O(P)	6103(6)	3644(6)	8301(4)	749(31)
C(1′)	2931(8)	3920(6)	5634(5)	465(31)
C(2′)	3510(9)	2405(7)	5263(5)	538(34)
C(3′)	3622(9)	1758(7)	4088(6)	582(37)
C(4′)	3057(9)	2617(8)	3309(6)	601(39)
C(5′)	2443(9)	4100(8)	3670(6)	619(40)
C(6′)	2383(8)	4776(7)	4860(6)	557(35)
H(C3′)	413	61	379	1109(26)
H(C4′)	308	212	238	1078(25)
H(C5′)	199	474	302	781(14)
H(C6′)	192	594	515	492(13)

^{a} $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

Results and discussion

The identification of the atoms and the configuration of the molecule are shown in the ORTEP drawing [11] in Fig. 1. The bond lengths and bond angles, with their standard deviations, are shown in Table 3. The Mn and P atoms have distorted octahedral and tetrahedral configurations, respectively. The P=O bond length of 1.458(5) Å is in good agreement with that observed in compounds of either transition metal-substituted phosphonates [2,12] or main group species [13,14]. The Mn–P bond length of 2.307(2) Å is in good agreement with that of 2.297(2) Å in 2 [2] and with the values of 2.25–2.30 Å in the other known manganese phosphonate structure [15]. The C–C–C bond angles within the phenyl ring range from 117.4(6) to 122.0(6)°. The deviation of the phenyl ring from the ideal hexagonal configuration is due to the presence of a strained five-membered ring. The C–C–C bond angles are larger at the positions of oxygen substitution [C(1') and C(2')] and at the positions of C(4') and C(5'), while the C–C–C bond angles are contracted at the C(3') and C(6') positions. These deviations have also been observed in 4 [13] and 5 [14].

The least-squares planes of the equatorial carbonyl carbons and the 1,3,2-benzo-dioxaphosphole ring systems are shown in Table 4. The four equatorial carbonyl carbons [C(1), C(2), C(3), and C(4)] lie in a plane; however, the equatorial carbonyl oxygens deviate from the plane toward the side with the phosphorus and the manganese atom deviates from the plane toward the axial carbonyl group. This is similar to many compounds of the type $LM(CO)_5$ and $LM(CO)_4$ where the equatorial carbonyl groups are bent toward the L group [16,17]. The average C_{eq}–Mn–P bond angle of 87.1(2)° is similar to that of 87.6(2)° in 2 [2]. The effect of the bulky $Mn(CO)_5$ group on the bond angles about phosphorous is evident by examination of
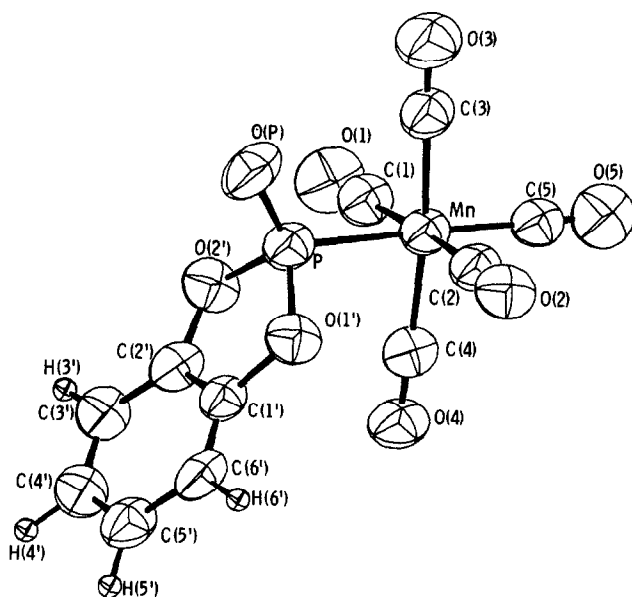

Fig. 1. ORTEP drawing of one molecule of 3.

TABLE 3

INTRAMOLECULAR AND INTERMOLECULAR DISTANCES (Å) AND BOND ANGLES (°) (The estimated standard deviations are given in parenthesis and refer to the last positions of respective values)

Bond lengths

Mn–P	2.307(2)	C(3)–O(3)	1.123(9).
Mn–C(1)	1.864(7)	C(4)–O(4)	1.122(8)
Mn–C(2)	1.874(7)	C(5)–O(5)	1.114(8)
Mn–C(3)	1.860(7)	C(1′)–O(1′)	1.406(7)
Mn–C(4)	1.861(7)	C(2′)–O(2′)	1.395(8)
Mn–C(5)	1.867(6)	C(1′)–C(2′)	1.398(8)
P–O(P)	1.458(5)	C(1′)–C(6′)	1.353(8)
P–O(1′)	1.652(4)	C(2′)–C(3′)	1.385(9)
P–O(2′)	1.657(5)	C(3′)–C(4′)	1.361(9)
C(1)–O(1)	1.109(9)	C(4′)–C(5′)	1.382(10)
C(2)–O(2)	1.125(8)	C(5′)–C(6′)	1.393(9)

Non-bonded intramolecular distances

O(P) ··· C(3)	3.029(9)	O(1′) ··· C(2)	2.929(8)
O(1′) ··· C(4)	3.000(8)	O(2′) ··· C(1)	3.054(8)
O(2′) ··· C(4)	3.154(8)		

Intermolecular distances

O(1)[x,y,z] ··· O(3)[$1-x,-y,2-z$]	3.284(8)
O(2)[x,y,z] ··· O(2)[$-x,1-y,2-z$]	3.093(7)
O(2)[x,y,z] ··· O(3)[$1-x,1-y,2-z$]	3.167(7)
O(2)[x,y,z] ··· O(5)[$-x,1-y,2-z$]	3.171(7)
O(2)[x,y,z] ··· O(P)[$1-x,1-y,2-z$]	3.161(7)
O(2)[x,y,z] ··· O(P)[$-1+x,y,z$]	3.236(7)
O(2)[x,y,z] ··· C(2)[$-x,1-y,2-z$]	3.162(8)
O(2)[x,y,z] ··· C(5)[$-x,1-y,2-z$]	3.210(8)
O(4)[x,y,z] ··· O(2′)[$-1+x,y,z$]	3.269(6)
O(4)[x,y,z] ··· O(2′)[$-x,-y,1-z$]	3.294(6)
O(5)[x,y,z] ··· O(P)[$-1+x,y,z$]	3.223(7)
O(P)[x,y,z] ··· C(2)[$1+x,y,z$]	3.241(8)
O(P)[x,y,z] ··· C(5)[$1+x,y,z$]	3.198(8)
C(1′)[x,y,z] ··· C(5′)[$1-x,1-y,1-z$]	3.248(9)

Bond angles

C(1)–Mn–P	89.1(2)	P–O(1′)–C(1′)	110.8(4)
C(1)–Mn–C(2)	174.3(3)	P–O(2′)–C(2′)	110.5(4)
C(1)–Mn–C(3)	90.1(3)	O(P)–P–O(1′)	112.4(3)
C(1)–Mn–C(4)	89.3(3)	O(P)–P–O(2′)	109.9(3)
C(1)–Mn–C(5)	92.3(3)	O(1′)–P–O(2′)	94.5(2)
C(2)–Mn–P	85.4(2)	O(1′)–C(1′)–C(2′)	111.1(5)
C(2)–Mn–C(3)	90.9(3)	O(1′)–C(1′)–C(6′)	127.0(5)
C(2)–Mn–C(4)	89.2(3)	O(2′)–C(2′)–C(1′)	112.2(5)
C(2)–Mn–C(5)	93.3(3)	O(2′)–C(2′)–C(3′)	127.4(5)
C(3)–Mn–P	88.4(2)	C(2′)–C(1′)–C(6′)	122.0(6)
C(3)–Mn–C(4)	173.7(3)	C(1′)–C(2′)–C(3′)	120.4(6)
C(3)–Mn–C(5)	92.6(3)	C(2′)–C(3′)–C(4′)	117.5(6)
C(4)–Mn–P	85.3(2)	C(3′)–C(4′)–C(5′)	122.0(6)
C(4)–Mn–C(5)	93.8(3)	C(4′)–C(5′)–C(6′)	120.7(6)
C(5)–Mn–P	178.3(2)	C(1′)–C(6′)–C(5′)	117.4(6)
Mn–P–O(P)	119.4(2)		
Mn–P–O(1′)	107.3(2)		
Mn–P–O(2′)	110.5(2)		

TABLE 4

LEAST-SQUARES PLANES AND TORSION ANGLES

Least-squares planes
Equation of planes: $Ax + By + Cz = D$, where x, y, z are in Å

Plane	A	B	C	D
a	−0.824(2)	−0.396(2)	0.671(2)	4.97(2)
b	0.888(1)	0.309(3)	−0.097(3)	2.16(1)
c	0.903(1)	0.328(2)	−0.190(2)	1.58(1)
d	0.8963(9)	0.320(2)	−0.1458(9)	1.933(8)

Displacements (Å) of atoms from the plane [a]

Atoms	Plane a	Atoms	Plane b	Plane c	Plane d
Mn	0.096(4) *	P	0.183(10)*	0.009(2)	0.024(2)
C(1)	0.006(9)	O(1')	0.024(9)*	−0.064(6)	−0.091(6)
C(2)	0.006(9)	O(2')	−0.013(9)*	−0.066(6)	−0.110(6)
C(3)	−0.006(9)	C(1')	0.008(7)	0.049(7)	−0.039(6)
C(4)	−0.007(9)	C(2')	−0.014(8)	0.048(7)	−0.051(7)
O(1)	−0.045(10)*	C(3')	0.014(9)	0.198(10)*	0.040(8)
O(2)	−0.052(10)*	C(4')	−0.001(9)		0.076(8)
O(3)	−0.038(10)*	C(5')	−0.007(9)		0.060(8)
O(4)	−0.108(10)*	C(6')	0.002(9)	0.139(10)*	0.006(8)

Dihedral angles between the least-squares planes (°)
(a) and (b)	143.4(2)
(a) and (c)	148.9(2)
(b) and (c)	174.6(2)

Torsion angles (°)

About the Mn – P bond

C(1)–Mn–P–O(P)	−93.6(3)	C(3)–Mn–P–O(P)	−3.5(3)
C(1)–Mn–P–O(1')	137.1(3)	C(3)–Mn–P–O(1')	−132.8(3)
C(1)–Mn–P–O(2')	35.3(3)	C(3)–Mn–P–O(2')	125.4(3)
C(2)–Mn–P–O(P)	87.6(3)	C(4)–Mn–P–O(P)	177.1(3)
C(2)–Mn–P–O(1')	−141.7(3)	C(4)–Mn–P–O(1')	47.8(3)
C(2)–Mn–P–O(2')	−143.6(3)	C(4)–Mn–P–O(2')	−59.0(3)

The five-membered ring

P–O(1')–C(1')–C(2')	6.4(6)
O(1')–C(1')–C(2')–O(2')	0.0(7)
C(1')–C(2')–O(2')–P	−6.3(6)
C(2')–O(2')–P–O(1')	8.7(4)
O(2')–P–O(1')–C(1')	−8.8(4)

[a] * indicates atoms excluded from the calculation of the least-squares planes.

the bond angles in Table 5. In general, the R–P=O and R–P–O angles are enlarged in **3** compared to **4** and **5**, while the O–P=O and O–P–O angles are contracted. The only apparent exceptions are the R–P–O angles in **3** and **5** which are the same

TABLE 5

BOND ANGLES (°) ABOUT PHOSPHORUS IN 3, 4 AND 5

	R–P=O [a]	R–P–O [a,b]	O–P=O [b]	O–P–O
3	119.4(2)	108.9(4)	111.2(6)	94.5(2)
4	110.0(15)	103.5(15)	118.7 [c]	100.0(10)
5	112.2(2)	108.7(4)	114.0(4)	98.4(2)

[a] R = Mn(CO)$_5$ for 3, Cl for 4, and OH for 5. [b] Average angles. [c] Calculated value, no error limit given.

within experimental error. The 1,3,2-benzodioxaphosphole ring system in 3 is not as nearly planar as those observed in 4 and 5. While the phenyl ring is essentially planar, the five-membered ring shows a slightly puckered conformation. The dihedral angle between the least-squares planes of the two rings is 174.6(2)°. The torsion angles around the five-membered ring shown in Table 4 also indicate the non-planar conformation of the five-membered ring. This non-planarity is due to the small O–P–O intra-ring angle.

The conformation of 3 viewed along the Mn–P direction is shown in Fig. 2 and the torsion angles about the Mn–P bond are shown in Table 4. The molecule has a pseudo-mirror symmetry with respect to the plane containing Mn, P, C(3), C(4) and C(5). The deviation of the phosphoryl oxygen from this plane is 0.075(7) Å and this is also indicated by the torsion angle of 3.5° for C(3)–Mn–P–O(P) bonds. Therefore, the phosphoryl oxygen has an almost eclipsed conformation with one of the carbonyl groups, C(3)–O(3). This is in contrast to that observed in 2, in which the phosphoryl oxygen is staggered between two carbonyl groups resulting in torsion angles of 47.2 and 42.6° [2]. The P=O conformation in 2 is determined by the intra- and intermolecular hydrogen bonding. It might be tempting to attribute the eclipsed conformation in 3 to an electronic interaction of the phosphoryl oxygen with the manganese and/or carbonyl group; however, the similar nonbonded intramolecular O ⋯ C distances in Table 3 suggest that the observed conformation may result from steric effects alone.
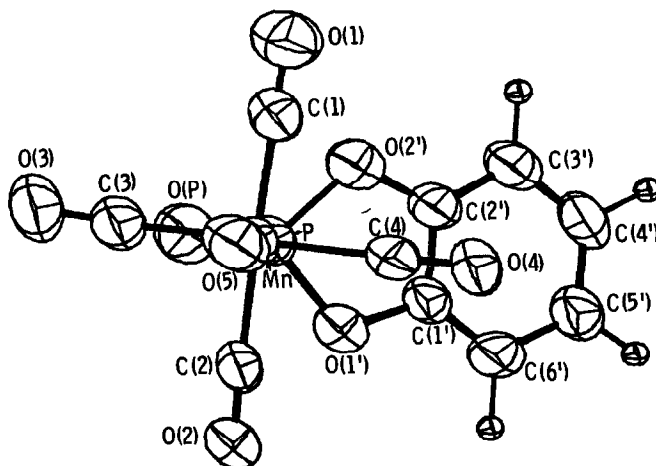

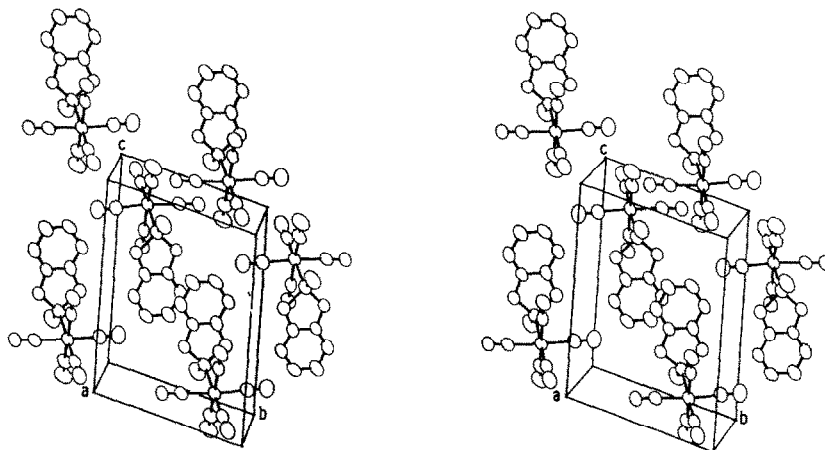Fig. 2. Conformation of 3 viewed along the Mn–P direction.

Fig. 3. The packing of the molecules in a unit cell shown in a stereoscopic drawing.

The packing of the molecules in the unit cell is determined by the Van der Waals forces as shown in a stereoscopic drawing in Fig. 3. The intermolecular distances less than 3.3 Å are shown in Table 3. There are two alternating layers of interactions intercepting the c-axis. In one layer, the interactions are between the carbonyl groups while in the other layer, the interactions are between the phenyl rings. The perpendicular distance between the planes of the two centrosymmetric related phenyl rings is 3.2 Å.

Acknowledgment

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