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The crystal structure of $MoO_2Cl_2[(CH_3OCH_2CH_2)_2P(O)CH_2CH_2P(O)(CH_2CH_2OCH_3)_2]$

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Abstract

1,2-Bis[bis(methoxyethyl)phosphino]ethane dioxide ($tmepeO_2$) (**1**) and its molybdenum(VI) complex, MoO_2Cl_2 ($tmepeO_2$) (**2**) are resistant to acidic hydrolysis in ambient temperatures. The crystal structure of **2** has been determined by X-ray diffraction methods and refined by a full-matrix least-squares technique to $R = 0.0395$ for 2393 independent non-zero reflections. Crystals are monoclinic, space group $P2_1/c$, with four complex molecules in the unit cell of dimensions: $a = 14.655(13)$, $b = 8.298(10)$, $c = 20.644(28)$ Å, $\beta = 108.97(9)°$.

1. Introduction

It is characteristic for moieties with two methylene group chains to be susceptible to degradation. Supposedly because of the β-elimination reaction rearrangements such Grignard reagents as $CH_3OCH_2CH_2MgX$ [1], $XMgCH_2CH_2MgX$ [2] (where X = Cl, Br or I) and $Ph_2PCH_2CH_2MgCl$ [3] have not been prepared. On the other hand, Grignard reagents such as $XMgCH_2MgX$ [4], CH_3OCH_2MgCl [1], $CH_3OCH_2CH_2CH_2MgCl$ [6] and $Ph_2PCH_2CH_2CH_2MgCl$ [3] are obtainable without difficulty. However, $BrMgCH_2CH_2CH_2MgBr$, not obtainable in a direct reaction, is stable when prepared [5].

In a previous paper, we discussed the case of fast hydrolytic degradation of the $CH_3OCH_2CH_2P(H)$– moiety and concluded that the unstability of this group depends probably on the intramolecular bifurcated hydrogen bonds than on the carbon–carbon chain length [7]. To prove this, we examined the behaviour of the oxidized form of that unstable diphosphine, 1,2-bis[bis(methoxyethyl)phosphino]ethane dioxide ($tmepeO_2$), in acidic conditions.

2. Experimental section

1,2-Bis[bis(methoxyethyl)phosphino]ethane dioxide ($tmepeO_2$) was prepared by stirring a DMSO solution of tmepe or $[tmepeH_2](HSO_4)_2$ at 60°C or by boiling their THF solutions when exposed on air. The product, a white amorphous powder, was separated only from THF solution by solvent evaporation. The dioxide was treated with HCl solutions (range from 1 to 5 N) directly in DMSO solution and THF suspension, and in the solid state, for over 24 h with stirring at room temperature. Solutions were then evaporated *in vacuo* and ^1H and ^{31}P NMR spectra were recorded on 300-MHz Nicolet and Varian VRX 300 spectrometers using DMSO-d_6 as solvent. Pale-green crystals of the

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TABLE 1. Final atomic parameters with e.s.d. s in parentheses for $MoO_2Cl_2[(CH_3OCH_2CH_2)_2P(O)CH_2CH_2P(O)(CH_2CH_2OCH_3)_2]$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	0.23453(5)	0.45527(7)	0.69350(3)	0.0683(4)	0.0436(3)	0.0566(3)	0.0001(3)	0.0075(3)	0.0068(4)
Cl(1)	0.21343(16)	0.58272(24)	0.79146(8)	0.1099(17)	0.0778(14)	0.0514(10)	0.0028(9)	0.0228(11)	0.0041(13)
Cl(2)	0.25237(17)	0.39409(29)	0.58570(10)	0.0956(17)	0.1060(16)	0.0783(14)	−0.0364(12)	0.0220(13)	0.0113(14)
P(1)	0.06643(14)	0.77169(19)	0.62281(8)	0.0641(13)	0.0419(9)	0.0456(9)	0.0001(7)	0.0092(9)	0.0037(9)
P(2)	0.32860(16)	0.83978(23)	0.68341(9)	0.0712(15)	0.0595(11)	0.0582(11)	−0.0022(9)	0.0146(11)	−0.0122(11)
O(1)	0.1293(3)	0.6249(5)	0.63461(19)	0.061(4)	0.050(3)	0.048(3)	0.003(3)	0.013(3)	0.011(3)
O(2)	0.3260(4)	0.6592(6)	0.6942(3)	0.060(4)	0.061(3)	0.078(4)	−0.005(3)	0.022(3)	0.000(3)
O(3)	0.3340(4)	0.3453(6)	0.7392(3)	0.072(4)	0.064(4)	0.091(4)	0.005(3)	−0.003(3)	0.014(3)
O(4)	0.1399(4)	0.3198(6)	0.6860(3)	0.082(4)	0.039(3)	0.086(4)	0.002(3)	0.006(3)	−0.006(3)
O(5)	0.0878(4)	0.8387(6)	0.4758(3)	0.105(5)	0.053(3)	0.062(3)	−0.004(3)	0.032(4)	−0.004(4)
O(6)	−0.1245(6)	0.5874(10)	0.6303(4)	0.130(7)	0.121(7)	0.144(7)	−0.034(6)	0.078(6)	−0.036(6)
O(7)	0.3957(6)	0.9212(8)	0.8412(3)	0.148(7)	0.105(6)	0.067(4)	0.005(4)	0.016(5)	0.016(5)
O(8)	0.4809(7)	0.9103(11)	0.5986(4)	0.123(7)	0.162(9)	0.144(7)	−0.021(6)	0.037(6)	−0.014(7)
C(1)	0.1348(6)	0.9557(8)	0.6345(4)	0.079(6)	0.045(4)	0.064(5)	0.010(4)	0.007(4)	−0.002(5)
C(2)	0.2305(6)	0.9523(8)	0.6950(4)	0.070(5)	0.050(4)	0.062(4)	−0.005(4)	0.009(4)	−0.008(5)
C(11)	−0.0181(5)	0.7669(8)	0.5377(3)	0.061(5)	0.053(4)	0.054(4)	0.005(4)	0.006(4)	0.003(4)
C(12)	0.0267(6)	0.7146(8)	0.4843(4)	0.093(7)	0.051(4)	0.047(4)	−0.001(4)	0.008(4)	−0.005(5)
C(13)	0.1336(7)	0.7970(12)	0.4271(4)	0.148(10)	0.118(8)	0.070(6)	−0.013(6)	0.058(7)	0.005(8)
C(14)	−0.0008(6)	0.7847(9)	0.6821(4)	0.080(6)	0.077(6)	0.058(5)	−0.006(4)	0.022(5)	0.023(5)
C(15)	−0.0518(7)	0.6288(12)	0.6895(5)	0.113(9)	0.092(7)	0.104(8)	0.014(6)	0.053(7)	−0.001(7)
C(16)	−0.2097(7)	0.6589(16)	0.6208(6)	0.104(10)	0.236(18)	0.160(12)	−0.080(12)	0.050(9)	−0.009(12)
C(21)	0.4373(6)	0.9239(10)	0.7410(4)	0.085(7)	0.094(7)	0.079(6)	−0.012(5)	0.009(5)	−0.015(6)
C(22)	0.4608(7)	0.8620(13)	0.8121(5)	0.091(8)	0.113(8)	0.076(6)	−0.011(6)	0.003(6)	0.003(7)
C(23)	0.4130(9)	0.8605(14)	0.9072(5)	0.261(17)	0.151(11)	0.073(7)	0.019(7)	0.038(9)	0.051(12)
C(24)	0.3243(7)	0.8864(14)	0.5964(4)	0.105(9)	0.150(10)	0.072(6)	0.011(6)	0.034(6)	0.002(8)
C(25)	0.4000(9)	0.8141(17)	0.5742(6)	0.135(12)	0.207(15)	0.114(9)	−0.060(10)	0.039(9)	−0.033(12)
C(26)	0.5625(8)	0.8520(15)	0.5810(6)	0.139(12)	0.160(13)	0.163(12)	−0.017(10)	0.071(11)	−0.007(11)
				U_{iso}					U_{iso}
H(13)	0.182(4)	0.697(5)	0.446(2)	0.15	H(11)	−0.048	0.886	0.525	0.08
H(131)	0.175(4)	0.902(5)	0.424(4)	0.15	H(111)	−0.075	0.684	0.537	0.08
H(132)	0.085(4)	0.767(7)	0.377(2)	0.15	H(12)	−0.030	0.692	0.436	0.08
H(16)	−0.186(3)	0.782(3)	0.619(3)	0.15	H(121)	0.068	0.606	0.501	0.08
H(161)	−0.265(2)	0.631(5)	0.573(2)	0.15	H(14)	−0.055	0.878	0.664	0.08
H(162)	−0.239(2)	0.647(6)	0.662(2)	0.15	H(141)	0.049	0.817	0.732	0.08
H(23)	0.364(3)	0.899(8)	0.934(3)	0.15	H(15)	−0.083	0.644	0.730	0.12
H(231)	0.486(2)	0.884(7)	0.939(1)	0.15	H(151)	0.001	0.533	0.703	0.12
H(232)	0.404(5)	0.733(3)	0.897(4)	0.15	H(21)	0.429	1.053	0.742	0.10
H(26)	0.622(2)	0.932(5)	0.604(3)	0.15	H(211)	0.496	0.895	0.722	0.10
H(261)	0.555(5)	0.833(7)	0.528(1)	0.15	H(22)	0.533	0.900	0.842	0.11
H(262)	0.576(5)	0.738(4)	0.608(3)	0.15	H(221)	0.457	0.732	0.811	0.11
H(1)	0.091	1.052	0.643	0.08	H(24)	0.329	1.016	0.592	0.12
H(10)	0.151	0.980	0.588	0.08	H(241)	0.256	0.846	0.562	0.12
H(2)	0.254	1.075	0.706	0.08	H(25)	0.377	0.809	0.519	0.15
H(20)	0.215	0.902	0.739	0.08	H(251)	0.416	0.694	0.595	0.15

compound 2 were isolated from a slowly evaporated, air-saturated water/methanol solution of $Cs_3[MoCl_6]$ and $[tmepeH_2](HSO_4)_2$ (1 : 2). Crystalline material was recrystalized from a 5 N HCl solution. Multi-faced crystals for X-ray examination were taken directly from the mother liquor.

3. Crystallography

Crystal data were $(C_{14}H_{32}O_6P_2)Cl_2MoO_2$, $M = 557.2$, $a = 14.655(13)$, $b = 8.298(10)$, $c = 20.644(28)$ Å, $\beta = 108.97(9)°$, $U = 2374(5)$ Å^3, $D_c = 1.559(4)$ g cm^{-3}, $F(000) = 1144$, space group $P2_1/c$, $Z = 4$, Cu Kα radiation, $\lambda = 1.5418$ Å, $\mu = 83.7$ cm^{-1}, $T = 293(2)$ K.

A KM4 four-circle diffractometer (κ-geometry) was used. Cell parameters were obtained from a least-squares fit of the setting angles of 22 reflections in the range $20 < 2\theta < 30°$. The diffraction data were collected by the θ–2θ scan technique with graphite monochromatized Cu Kα radiation; 5718 reflections up to $\theta = 82°$ were collected. The intensities of three standard reflections, which were monitored after 100 intensity scans, decreased by approximately 20% over the period of data collection. The data were rescaled on the intensities of the standards and corrected for Lorentz polarization effects; 2496 reflections with $I > 3\sigma(I)$ were used for the structure analysis; $R_{\mathrm{merg}} = 0.017$. The structure was solved by the heavy atom method and refined by full-matrix least-squares [8]. The H atoms from methyl groups were located from a difference Fourier synthesis and refined with the constraint that $d(\mathrm{C–H}) = 1.08$ Å. All other H-atoms were included in geometrically calculated positions. Neutral atom scattering factors were utilized and were corrected for real and imaginary components [9]. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w = 1/\sigma^2(F_o)$. An absorption correction following the DIFABS [10] procedure was applied; minimum and maximum absorption corrections were 0.917 and 1.310, respectively. The final R and R_w values were 0.0395 and 0.0373 for 2393 merged reflections. For the last cycle of the refinement, the maximal value of the Δ/σ ratio was 0.17 and the final difference map showed a general background within -0.66 and 0.53 e Å^{-3}. The final atomic parameters are given in Table 1.

4. Results and discussion

1,2-Bis[bis(methoxyethyl)phosphino]ethane dioxide was easily obtainable by direct oxidation of the diphosphine but such a product was always impure and ^{31}P NMR spectra, in spite of the signal characteristic for phosphine oxides [11], showed several small signals belonging to impurities. Clear spectra (^{1}H, ^{31}P NMR) were obtained when diphosphine or its hydrosulfate had been oxidized in DMSO at 60°C and/or in boiling THF. The resulting dioxide showed one resonance peak in the ^{31}P NMR spectrum at 46.7 ppm. When the solution (DMSO) or suspension (ether) of $tmepeO_2$ was treated at room temperature with diluted and moderately concentrated HCl solution, no changes were observed after 24 h. When 1 was treated with concen-

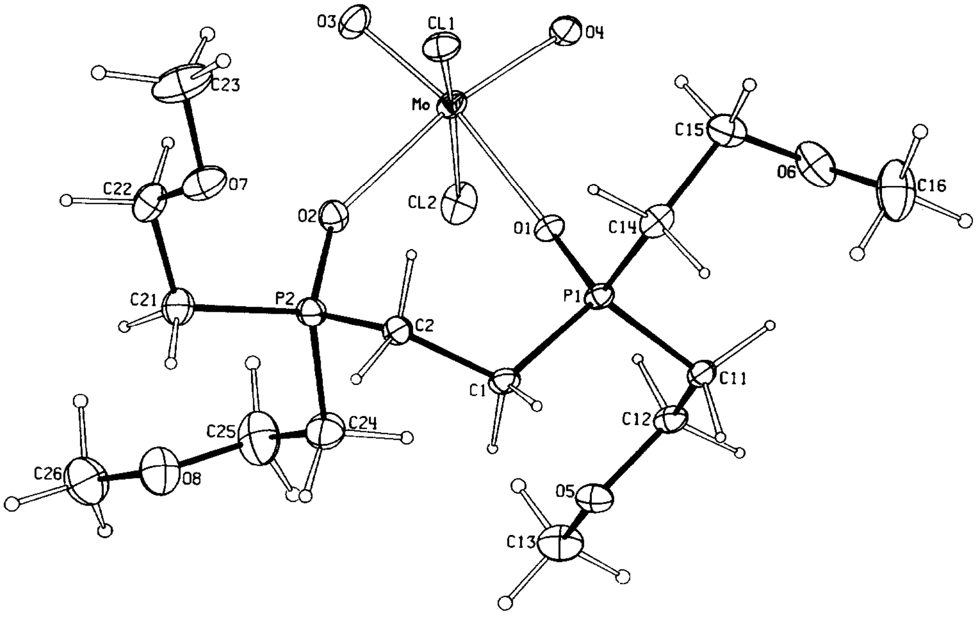

Fig. 1. The molecular structure of the $MoO_2Cl_2(tmepeO_2)$ complex.

trated hydrochloric acid (12 N) for over 24 h, some unsoluble (DMSO) white material appeared which was apparently a hydrolytic product. Solutions and/or suspensions of tmepeO_2 remained unchanged when saturated with gaseous HCl for a prolonged period of time. ^1H NMR spectra registered from tmepeO_2 before and after HCl treatment were identical [7, Fig. 1(c)] and confirm that the compound is resistant to hydrolysis (acidolysis). Compound **1** is also resistant to hydrolysis when coordinated to the metal. The complex MoO_2Cl_2 (tmepeO_2) does not undergo hydrolysis and could be recrystallized from HCl solution (5 N) in order to improve crystalline features.

Compound **2** is a monomeric *cis*-dioxo molybdenum(VI) complex with a distorted octahedral coordination sphere. The overall view of one molecule is shown in Fig. 1. The chlorine atoms are mutually *trans* with Mo–Cl distances of 2.390(3) and 2.378(3) Å (Table 2), typical for *cis*-dioxomolybdenum(VI) complexes [12]. The Cl–Mo–Cl angle is 166.0(1)°. This distorsion from 180° in an ideal octahedron is caused by the repulsive influence of a bulky ligand. The bond lengths of Mo–O(3) and Mo–O(4) are short, 1.719(5) and 1.753(5) Å, respectively, and correspond well with terminal Mo–O(oxo) fragments [12–14]. These bond lengths as well as the O(3)–Mo–O(4) angle [102.4(3)°] are typical for *cis*-dioxomolybdenum(VI) complexes [15–17], where they usually have magnitudes of 1.68(3)–1.77(3) Å and 102(1)°, respectively. The remarkable angle widening is caused by a strong repulsion of shortly bonded terminal oxygen atoms [15]. The terminal Mo–O(oxo) bonds have a strong *trans* influence on the Mo–O(1) and Mo–O(2) bond lengths, 2.149(4) and 2.157(7) Å, respectively. There are also examples of even greater bond elongation [18].

The P–O bonds (Table 2) are of typical length for

TABLE 2. Selected bond lengths (Å), bond angles (°) and torsion angles for $MoO_2Cl_2[(CH_3OCH_2CH_2)_2P(O)CH_2CH_2P(O)(CH_2CH_2OCH_3)_2]$

Mo–Cl(1)	2.390(3)	Mo–Cl(2)	2.378(3)
Mo–O(1)	2.149(4)	Mo–O(2)	2.157(7)
Mo–O(3)	1.719(5)	Mo–O(4)	1.753(5)
P(1)–O(1)	1.498(5)	P(2)–O(2)	1.517(7)
P(1)–C(1)	1.799(7)	P(2)–C(2)	1.794(8)
P(1)–C(11)	1.791(6)	P(2)–C(21)	1.792(8)
P(1)–C(14)	1.808(8)	P(2)–C(24)	1.819(8)
O(5)–C(12)	1.413(9)	O(6)–C(15)	1.379(12)
O(5)–C(13)	1.422(11)	O(6)–C(16)	1.337(14)
O(7)–C(22)	1.372(12)	O(8)–C(25)	1.381(16)
O(7)–C(23)	1.397(11)	O(8)–C(26)	1.441(16)
Cl(1)–Mo–Cl(2)	166.0(1)	O(1)–Mo–O(2)	79.6(2)
Cl(1)–Mo–O(1)	85.5(2)	Cl(2)–Mo–O(1)	83.5(2)
Cl(1)–Mo–O(2)	84.1(2)	Cl(2)–Mo–O(2)	85.2(2)
Cl(1)–Mo–O(3)	95.2(2)	Cl(2)–Mo–O(3)	93.9(2)
Cl(1)–Mo–O(4)	92.4(2)	Cl(2)–Mo–O(4)	96.0(2)
O(1)–Mo–O(3)	169.4(3)	O(2)–Mo–O(3)	89.9(3)
O(1)–Mo–O(4)	88.2(2)	O(2)–Mo–O(4)	167.5(3)
O(3)–Mo–O(4)	102.4(3)		
Mo–O(1)–P(1)	156.1(3)	Mo–O(2)–P(2)	145.0(5)
O(1)–P(1)–C(1)	112.4(3)	O(2)–P(2)–C(2)	115.8(4)
O(1)–P(1)–C(11)	109.5(3)	O(2)–P(2)–C(21)	110.3(4)
O(1)–P(1)–C(14)	112.4(3)	O(2)–P(2)–C(24)	111.2(5)
C(1)–P(1)–C(11)	109.2(4)	C(2)–P(2)–C(21)	106.7(4)
C(1)–P(1)–C(14)	105.1(4)	C(2)–P(2)–C(24)	104.4(4)
C(11)–P(1)–C(14)	108.0(4)	C(21)–P(2)–C(24)	108.1(5)
P(1)–C(1)–C(2)	114.4(5)	P(2)–C(2)–C(1)	117.3(5)
C(12)–O(5)–C(13)	112.0(6)	C(15)–O(6)–C(16)	115.8(9)
C(22)–O(7)–C(23)	111.5(8)	C(25)–O(8)–C(26)	113.5(10)
C(13)–O(5)–C(12)–C(11)	179.1(11)	C(16)–O(6)–C(15)–C(14)	−83.4(17)
C(23)–O(7)–C(22)–C(21)	177.6(14)	C(26)–O(8)–C(25)–C(24)	179.4(19)
O(5)–C(12)–C(11)–P(1)	−70.8(10)	O(6)–C(15)–C(14)–P(1)	−66.3(16)
O(7)–C(22)–C(21)–P(2)	−69.9(22)	O(8)–C(25)–C(24)–P(2)	−82.1(17)
C(12)–C(11)–P(1)–O(1)	−43.0(12)	C(15)–C(14)–P(1)–O(1)	−47.9(14)
C(22)–C(21)–P(2)–O(2)	−44.7(19)	C(25)–C(24)–P(2)–O(2)	−56.8(16)
O(1)–P(1)–C(1)–C(2)	−39.2(15)	O(2)–P(2)–C(2)–C(1)	−81.2(13)
P(1)–C(1)–C(2)–P(2)	74.7(13)		

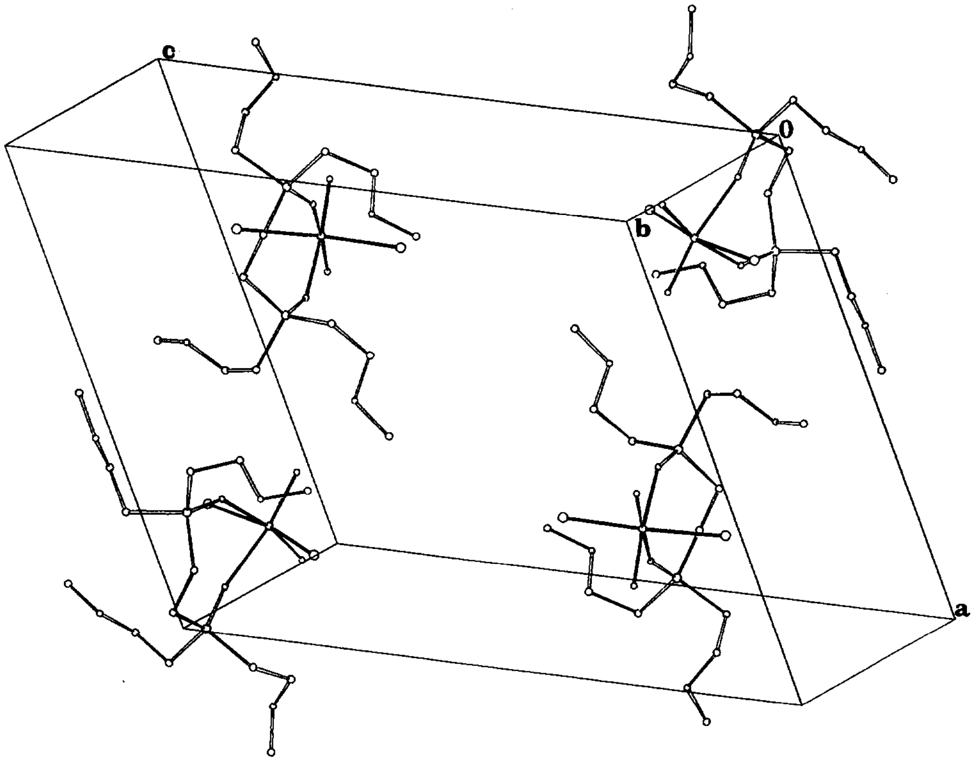

Fig. 2. The crystal packing of $MoO_2Cl_2[(CH_3OCH_2CH_2)_2P(O)CH_2CH_2P(O)(CH_2CH_2OCH_3)_2]$.

phosphine oxides coordinated to the metal centres and the small elongation in respect of free phosphine oxide is a result of coordination [19,20].

The diphosphine dioxide is a bidentate ligand which, when not coordinated, may have been centrosymmetrical, similar to the isostructural ethanediylbis(diphenylphosphonium)–PH, P′H′ cation described earlier [21]. In complex **2**, the structure of tmepeO_2 is strongly deformed to be capable of bidentate coordinating. The degree of the deformation can be judged by a comparison of suitable torsion angles. Thus, the P(1)–C(1)–C(2)–P(2) torsion angle of 74.7(13)° shows the extent of the ethylene bridge twist, while the others, O(1)–P(1)–C(1)–C(2) of −39.2(15)° and O(2)–P(2)–C(2)–C(1) of −81.2(13)° show the direction and extent that P–O moieties are bent up to adjacent octahedral corners. It is interesting that the greater torsion angle of the latter is related to the greater bend of the P–O–Mo fragment [smaller angle, 145.0(5)°] whereas the smaller one refers to the smaller bend of P–O–Mo [wider angle, 156.1(3)°]. In the diphosphine dioxide, three of its four methoxyethyl substituents are structurally similar having local *trans* geometry. The last one has a methyl group perpendicular to the plain defined by three atoms, O(6), C(15), and C(14) [torsion angle C(16)–O(6)–C(15)–C(14) −83.4(17)°] (see also Fig. 1). This may be caused by ligand–ligand interactions and crystal packing forces (see Fig. 2).

References

1 F. Runge, E. Taeger, C. Fiedler and E. Kahlert, *J. Pract. Chem.*, *19* (1963) 37; B. Castro, *Bull. Soc. Chim. Fr.*, (1967) 1533.
2 N.J.R. Van Eikema Hommes, F. Bickelhaupt and G.W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, *107* (1988) 393 (in this paper detection of $BrMgCH_2CH_2MgBr$ is reported).
3 S.O. Grim and R.C. Bart, *J. Organomet. Chem.*, *94* (1975) 327.
4 B.J.J. Van de Heisteeg, G. Schat, O.S. Akkerman and F. Bickelhaupt, in B.J. King and J.J. Eish (eds.), *Organometallic Syntheses*, Elsevier, Amsterdam, 389; F. Bertini, P. Grasselli, Z. Zubiani and G. Cainelli, *Tetrahedron*, *26* (1970) 1281; J. Yoshimura, K. Sato, H. Wakai and M. Funabashi, *Bull. Chem. Soc. Jpn.*, *49* (1976) 1169.
5 W.E. McEwen, A.B. Janes, J.W. Knapczyk, V.L. Kyllingstad, W.-I. Shian, S. Shore and J.H. Smith, *J. Am. Chem. Soc.*, *100* (1978) 7304.
6 F. Bickelhaupt, in H. Werner and G. Erker (eds.), *Organometallics in Organic Synthesis 2*, Springer-Verlag, Berlin, 1989; L.C. Costa and G.M. Whitesides, *J. Am. Chem. Soc.*, *99* (1977) 2390.
7 A. Herbowski and E.A. Deutsch, *J. Organomet. Chem.*, *460* (1993) 19.
8 G.M. Sheldrick, SHELX 76, Program for Crystal Structure Solution, University of Cambridge, UK, 1976.
9 *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, 1974.
10 N. Walker and D. Stuart, *Acta Crystallogr. Sect. A*, *39* (1983) 158.

11 D.G. Gorenstein, *Phosphorus-31 NMR, Principles and Applications*, Academic Press, New York, 1984.

12 T. Głowiak, *Problemy i Metody Chemii Koordynacyjnej*, PWN, Warszawa-Wrocław 1981, pp. 253–280.

13 C.D. Garner, N.C. Howlander, F.E. Mabbs, A.T. McPhail and K.D. Onan, *J. Chem. Soc., Dalton Trans.*, (1978) 1848.

14 C.D. Garner, P. Lambert, F.E. Mabbs and T.J. King, *J. Chem. Soc., Dalton Trans.*, (1977) 1191.

15 L.R. Florian and E.R. Corey, *Inorg. Chem.*, *7* (1968) 723.

16 F.A. Cotton, S.M. Morehouse and J.S. Wood, *Inorg. Chem.*, *3* (1964) 1603; F.A. Cotton and R.M. Wing, *Inorg. Chem.*, *4* (1965) 872; F.A. Cotton and S.M. Morehouse, *Inorg. Chem.*, *4* (1965) 1377.

17 L.O. Atovmyan, Yu.A. Sokolova and V.V. Tkachev, *Dokl. Akad. Nauk SSSR*, *195* (1970) 1355; L.O. Atovmyan and O.N. Krasochka, *J. Chem. Soc., Chem. Commun.*, *12* (1969) 649.

18 M.G.B. Drew and J.D. Wilkins, *J. Chem. Soc., Dalton Trans.*, (1975) 1984.

19 S.Z. Goldberg and K.N. Raymond, *Inorg. Chem.*, *12* (1973) 2927.

20 G. Bandoli, G. Bartolozzo, D.A. Clemente, U. Croatto and Panaltoni, *J. Chem. Soc. A*, (1970) 2778.

21 A. Herbowski and T. Lis, *Polyhedron*, *4* (1985) 127.