$\frac{1}{2} + y$, $-1 - z$) 2·733 Å. The C—O distance in the solvated molecule is unacceptably long at 1·63 Å; however, the electron density associated with the carbon position is not well defined.

Although the conformation of the phenyl ring and the attached atoms is similar to that of the A and B rings in estrone and estradiol, the conformation of the remainder of the 14-membered ring differs considerably from the perimeter atom arrangement in the steroids. The functional groups and their geometric relationship must be of importance in active-site binding; however, the 14-membered ring is flexible and the solid-state conformation may differ significantly from that in solution. Nevertheless, it should be noted that the O(3)···O(17) and O(3)···O(18) separations in estradiol and its derivatives (Duax & Norton, 1975) average 11·0 and 8·6 Å while the O(14)···O(7) and O(14)···C(17) distances in α-zearalenol are 10·03 and 8·43 Å respectively. The relationships between C(18), O(17) and C(7), O(7) are not comparable.

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Structure of 1,1,1-Tris[(diphenylphosphino)methyl]ethane (Triphos)

BY C. MEALLI

Istituto di Stereochimica di Coordinazione del CNR, 27 via D. Guerrazzi, Firenze, Italy

Abstract. $C_{41}H_{39}P_3$, $M_r = 624\cdot69$, triclinic, $P\bar{1}$, $a = 13\cdot487$ (5), $b = 13\cdot573$ (5), $c = 10\cdot484$ (5) Å, $\alpha = 104\cdot73$ (9), $\beta = 106\cdot37$ (8), $\gamma = 97\cdot73$ (8)°, $V = 1736\cdot4$ Å^3, $Z = 2$, $F(000) = 660$, $D_c = 1\cdot19$, $D_m = 1\cdot19$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1\cdot58$ mm^{-1}; $R = 0\cdot077$, $R_w = 0\cdot093$ for 3073 unique reflections. The structure is composed of isolated molecules. The three-armed molecule has neither crystallographic nor pseudo threefold symmetry as the conformation of one of the three aliphatic chains markedly differs from that of the other two. A comparison between the geometries of uncoordinated and coordinated triphos shows that

only a minor rearrangement of the chains, such as a crossing of the torsional barrier from one staggered conformation to an equivalent one, is sufficient to coordinate most metal atoms.

Introduction. 1,1,1-Tris[(diphenylphosphino)methyl]ethane, triphos, has been shown to be a ligand which can stabilize a great variety of coordination compounds (Sacconi & Mani, 1982). At least 16 X-ray structure determinations of such compounds have been carried out in recent years in this laboratory (Bianchini, Dapporto & Meli, 1979; Bianchini, Dapporto, Meli &

Sacconi, 1980; Bianchini, Mealli, Meli & Sacconi, 1979; Dapporto, Fallani & Sacconi, 1974; Dapporto, Midollini, Orlandini & Sacconi, 1976; Dapporto, Midollini & Sacconi, 1975; Ghilardi, Midollini, Orlandini & Sacconi, 1980; Ghilardi, Midollini & Sacconi, 1980; Mealli, Midollini, Moneti & Sacconi, 1980, 1981; Mealli, Midollini & Sacconi, 1975, 1978). In terms of the electronic structure of the complexes a high stability is gained through π back donation from the metal to the empty P d orbitals. In this respect the (triphos)M fragment is similarly or even more isolobal [see Elian, Chen, Mingos & Hoffmann (1976) for the isolobality concept] than the classical hemioctahedral $M(CO)_3$ fragment. It is also worthwhile noticing that in order to allow sufficient back donation to the ligand the metal is required to have a minimum number of d electrons and in no case is a (triphos)M fragment formed with metals having less than six d electrons. Geometrically, the ligand, in spite of its bulkiness, does not seem to suffer any major steric impediment to setting the three P atoms at the vertices of an octahedron face; moreover, the chelating effect associated with the specific umbrella conformation further justifies the stability of the (triphos)M fragments in coordination compounds. In order to evaluate directly the geometrical rearrangements which the ligand undergoes on coordinating a metal atom, the structural analysis of the uncoordinated triphos has been performed.

The title compound, prepared as previously described (Cloyd & Meek, 1972), was recrystallized from ethanol and obtained as transparent prismatic crystals.

A prismatic crystal of dimensions $0.30 \times 0.07 \times 0.09$ mm was randomly mounted on the goniometer of a Philips PW 1100 automated diffractometer. Routine work to find a set of 18 centering reflections allowed the determination of the orientation matrix **UB** and also of the lattice parameters. Intensities were collected by the θ–2θ scanning technique and counted with a scintillation counter. 3073 unique reflections, collected within a reciprocal-sphere radius of 0.50, had intensity values greater than 3σ, where σ is the e.s.d. of the intensity calculated from counting statistics. Three standard reflections were checked at intervals of 2 h during data collection and no deterioration of the crystal was observed. An absorption correction was applied although the effect seemed almost irrelevant, the transmission factors being in the range 0.94–0.96. Direct-methods and full-matrix least-squares techniques were used for structure determination and refinement. The routines used belonged to the *SHELX* system (Sheldrick, 1976). In the final stages of refinement the H atoms were introduced at calculated positions. In order to reduce the number of least-squares variables the phenyl C atoms were treated as isotropic spheres at variance with the other non-hydrogen atoms which were allotted anisotropic tem-

perature factors. However, no rigid-body D_{6h} constraint was applied to the phenyl groups to prevent any geometrical bias of the structure. The function minimized was $\sum w(F_o - |F_c|)^2$ with $w = 1/\sigma^2$. The final standard weighted and unweighted R factors, defined as $[\sum w(F_o - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ and $\sum (F_o - |F_c|)/\sum F_o$ respectively, are 0.093 and 0.077. In the final difference Fourier map the highest peak was less than 0.2 e Å^{-3}. Final atom parameters are given in Table 1.*

Table 1. *Final positional parameters* $(\times 10^4)$ *and isotropic thermal parameters* $(\times 10^3)$

Atoms P(1)–P(3) and C(1)–C(5) were refined anisotropically; $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}/U (Å^2)
P(1)	1734 (1)	5272 (1)	7408 (2)	42 (1)
P(2)	5290 (1)	7681 (1)	9192 (2)	41 (1)
P(3)	1522 (1)	7872 (1)	9061 (2)	44 (1)
C(1)	2497 (5)	5900 (5)	9287 (6)	44 (4)
C(2)	2843 (5)	7698 (5)	8978 (7)	43 (4)
C(3)	4200 (5)	6597 (5)	8993 (6)	44 (4)
C(4)	3338 (4)	6900 (4)	9612 (6)	39 (4)
C(5)	3817 (5)	7350 (5)	11211 (6)	49 (4)
C(6)	2450 (5)	4250 (5)	6942 (6)	41 (2)
C(7)	2722 (5)	3576 (5)	7694 (8)	59 (2)
C(8)	3283 (6)	2836 (6)	7302 (8)	67 (2)
C(9)	3572 (6)	2763 (7)	6128 (8)	73 (2)
C(10)	3315 (6)	3420 (6)	5370 (9)	77 (2)
C(11)	2746 (6)	4163 (6)	5759 (8)	60 (2)
C(12)	547 (5)	4487 (5)	7489 (6)	38 (2)
C(13)	−352 (5)	4204 (5)	6332 (7)	51 (2)
C(14)	−1252 (6)	3555 (6)	6260 (8)	66 (2)
C(15)	−1292 (7)	3196 (6)	7355 (8)	69 (2)
C(16)	−417 (6)	3491 (6)	8531 (9)	71 (2)
C(17)	505 (6)	4138 (5)	8597 (7)	56 (2)
C(18)	6243 (5)	6941 (5)	8685 (6)	42 (2)
C(19)	6046 (6)	5884 (6)	8074 (7)	60 (2)
C(20)	6834 (6)	5406 (7)	7748 (8)	68 (2)
C(21)	7811 (6)	5990 (6)	7972 (8)	67 (2)
C(22)	8016 (7)	7035 (6)	8556 (8)	73 (2)
C(23)	7229 (6)	7515 (6)	8917 (8)	61 (2)
C(24)	4772 (5)	8068 (5)	7625 (6)	41 (2)
C(25)	4512 (5)	7412 (5)	6280 (7)	52 (2)
C(26)	4131 (6)	7754 (6)	5132 (8)	65 (2)
C(27)	3996 (6)	8756 (6)	5319 (9)	74 (2)
C(28)	4237 (6)	9417 (7)	6630 (8)	69 (2)
C(29)	4633 (5)	9083 (5)	7786 (7)	52 (2)
C(30)	1183 (6)	8457 (6)	7647 (8)	58 (2)
C(31)	305 (7)	7896 (8)	6490 (10)	89 (3)
C(32)	12 (10)	8218 (9)	5277 (13)	117 (4)
C(33)	668 (9)	9046 (8)	5349 (13)	114 (3)
C(34)	1478 (9)	9685 (10)	6370 (12)	112 (3)
C(35)	1734 (8)	9343 (8)	7652 (11)	95 (3)
C(36)	1753 (5)	8974 (5)	10598 (6)	40 (2)
C(37)	2721 (6)	9573 (5)	11539 (7)	59 (2)
C(38)	2801 (7)	10368 (6)	12716 (8)	68 (2)
C(39)	1899 (6)	10590 (6)	12962 (8)	68 (2)
C(40)	923 (7)	10005 (6)	12059 (8)	74 (2)
C(41)	870 (6)	9208 (6)	10917 (8)	60 (2)

Scattering factors for the various atoms were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The structure of triphos consists of discrete molecules with the configuration shown in Fig. 1. The shortest intermolecular contacts, not less than 3·44 Å, involve, with no exception, the C atoms of the C(30)–C(35) phenyl ring. These atoms have the highest thermal parameters, indicating a certain amount of disorder in the arm of the molecule centered on the P(3) atom. Selected bond distances and angles are given in Table 2. The magnitudes reported in this table are worth a few comments. All the C—C distances in the aliphatic chains closely approach the value of 1·54 Å expected for C—C single bonds; the P—C distances are slightly but significantly shorter for phenyl C atoms on account of some participation of the P atoms in the conjugation of the phenyl rings; the C—P—C angles have average values of 101·4 (0·4), 101·2 (1·0) and
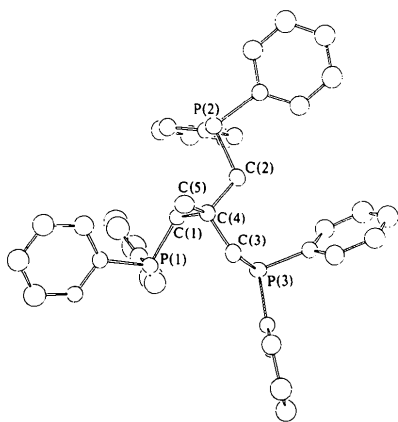

Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the molecule.

Table 2. *Selected bond lengths (Å) and angles (°)*

P(1)—C(1)	1·853 (6)	C(1)—P(1)—C(6)	101·2 (3)
P(2)—C(2)	1·859 (6)	C(1)—P(1)—C(12)	101·5 (3)
P(3)—C(3)	1·851 (5)	C(6)—P(1)—C(12)	100·5 (3)
C(4)—C(1)	1·542 (8)	C(2)—P(2)—C(18)	100·8 (3)
C(4)—C(2)	1·536 (7)	C(2)—P(2)—C(24)	102·6 (3)
C(4)—C(3)	1·540 (8)	C(18)—P(2)—C(24)	100·1 (3)
C(4)—C(5)	1·537 (8)	C(3)—P(3)—C(30)	97·1 (3)
P(1)—C(6)	1·838 (6)	C(3)—P(3)—C(36)	106·6 (3)
P(1)—C(12)	1·836 (6)	C(30)—P(3)—C(36)	102·3 (3)
P(2)—C(18)	1·844 (6)	P(1)—C(1)—C(4)	114·7 (4)
P(2)—C(24)	1·832 (6)	P(2) C(2)- C(4)	116·8 (4)
P(3)—C(30)	1·831 (7)	P(3)—C(3)—C(4)	118·7 (4)
P(3)—C(36)	1·815 (6)	C(1)—C(4)—C(2)	108·4 (4)
		C(1)—C(4)—C(3)	109·5 (4)
		C(2)—C(4)—C(3)	109·5 (4)
		C(5)—C(4)—C(1)	106·9 (4)
		C(5)—C(4)—C(2)	109·9 (5)
		C(5)—C(4)—C(3)	110·9 (5)

102 (3·8)° at P(1), P(2) and P(3) respectively; in spite of the large standard deviation associated with the latter value, a trend is observable for a more pronounced pyramidalization at P atoms in this polyphosphane molecule than in the triphenylphosphine molecule itself [C—P—C average angle 103·0 (0·6)° in the latter structure] (Daly, 1964). Even more significant in this respect is the different displacement of the P atom from the plane of the three bonded C atoms in this and the Daly structure [0·825 (15) Å (ave.) *vs* 0·785 Å, respectively]. In terms of the Valence-Shell Electron-Pair Repulsion (VSEPR) model (Gillespie, 1972), a greater pyramidalization means a larger extension of the lone pair at the P atom which is not unlikely when an electron-donating alkyl group is substituted for a phenyl group.

As already mentioned, the main interest of this work was to establish the overall conformation of triphos. It is noteworthy that the molecule has neither real crystallographic nor pseudo threefold symmetry. This can immediately be seen by comparing the intramolecular P—P separations. The P(1)—P(3) distance (3·60 Å) is shorter than the other two P—P contacts (*ca* 5·0 Å). In the hemioctahedral (triphos)*M* fragments all the P—P contacts are equivalent and usually in the range 3·1–3·3 Å. Moreover, at variance with coordinated triphos, the C(4)—C(5) vector is not orthogonal to the plane of the three P atoms but forms with it an angle of about 33°. This is due to the unique conformation of the aliphatic chain leading to the P(3) atom. The torsional angle at the C(4)—C(3) bond has a value of 175·5°, while it is −78·5 and −65·5°, respectively, for the chains leading to P(1) and P(2). In any case, however, an almost staggered conformation is approached at any C—C bond. The observed overall asymmetric conformation of the molecule can be attributed to solid-state effects. Conversely, the torsion angles at C—C bonds are almost invariably in the range 170–180° for coordinated triphos. This means that, at maximum, only a torsional barrier from one staggered conformation to an almost equivalent one must be crossed over by the arms of the ligand. No other energy-demanding process, such as angle bending, is experienced by coordinated triphos.

A final comment must be devoted to the conformation angles at the P—C(phenyl) bonds, defined with respect to the plane of the phenyl group and the direction of the P lone-pair orbital. These values in the present structure are spread in the range 9–50·5° and practically cover the entire range 0–90° in the 16 complexes of triphos referenced in this paper. Owing to the symmetry of the phenyl ring and the energetic equivalence of the right- and left-handed conformation, the unique range of rotation of each ring about the P—C axis is just 90°. The prediction of the existence of a number of equally probable conformations was made by Pratt Brock & Ibers (1973) through a con-

formational analysis of the triphenylphosphine molecule in the free and solid states. Our finding, that the azimuth of the phenyl group about the P—C(phenyl) bond is arbitrary, confirms the earlier observations of Horrocks & Greenberg (1971).

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6-*exo*-Hydroxy-2-*exo*-methylbicyclo[2.2.1]heptane-2,6-carbolactone

By Derek J. Chadwick

Department of Organic Chemistry, Robert Robinson Laboratories, University of Liverpool, Liverpool L69 3BX, England

and W. Bernd Schweizer, Paul Seiler and Stephen N. Whittleton

Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, 8092 Zürich, Switzerland

Abstract. $C_9H_{12}O_3$, $M_r = 168.18$, orthorhombic, *Pbca*, $a = 16.361$ (3), $b = 10.390$ (3), $c = 9.757$ (4) Å, $U = 1658.6$ Å^3, $Z = 8$, $D_x = 1.35$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.71 mm^{-1}. $R = 0.031$, $R_w = 0.035$ for 1094 unique diffractometer data. The title compound exists as the closed hydroxy-lactone form in the solid, with appreciable distortions from the idealized geometry.

Introduction. The title compound (1) (m.p. 401–402 K) was prepared by methylation of the ester acetal (2) followed by hydrolysis of the acetal and ester groups (Whittleton, 1980).

(1)   (2)
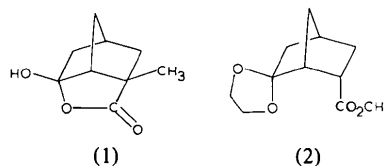
Intensities of 1806 reflexions ($2\theta \leq 54°$) were measured for a crystal of edges $0.4 \times 0.3 \times 0.3$ mm, grown by slow evaporation of a solution in ethyl acetate–cyclohexane, with an Enraf–Nonius CAD-4 diffractometer and graphite-monochromatized Mo $K\alpha$ radiation. Equivalent reflexions were merged to give