Heteroatom Chemistry
Volume 15, Number 3, 2004

Design of Novel Podand-Like Compounds with Two Short Diphenylphosphine Oxide Pendant Arms

Rafal Kruszynski and Wanda Wieczorek

Institute of General and Ecological Chemistry, Technical University of Łódź, Łódź, Poland

Received 20 November 2003; revised 12 January 2004

ABSTRACT: *Crystal and molecular structure of 1,3,5-benzene-tris(methylenediphenylphosphine oxide) cyclohexylammonium chloride dibenzene solvate monohydrate has been determined. The overall arrangement of two diphenylphosphine oxide substituents atoms is imposed by intermolecular strong hydrogen bonds,* $O_{(water)}—H\cdots O_{(oxide)}$ *and* $N—H\cdots O_{(oxide,\ water)}$. *Cyclohexylamine exists in almost ideal chair conformation and nitrogen atom is equatorial to the ring. The structure is build up from strong and weak intermolecular hydrogen bonds to form the three-dimensional infinite hydrogen bond network.*

*Crystal and molecular structure of 1,4-*bis*[(diphenylphosphineoxide)methyl]-2,5-*bis*(ethoxymethyl) benzene has been determined. The phenyl rings are inclined at 80.91(7)° within the substituent, and they are involved in weak* $C_{(phenyl)}—H\cdots O_{(oxide)}$ *hydrogen bonds. The arrangement of diphenylphosphine oxide substituents is imposed practically only by steric effects. Two intramolecular weak hydrogen bonds exist between diphenylphosphine oxide and ethoxymethyl substituents, which can provide additional stabilization to molecule, but it has no noticeable influence on overall molecule geometry. Molecules are assembled via weak intermolecular* $C—H\cdots O_{(oxide)}$ *hydrogen bonds to the one-dimensional hydrogen-bonded chain along y axis.* © 2004 Wiley Periodicals, Inc.

Heteroatom Chem 15:233–240, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20008

INTRODUCTION

The design of cation binding compounds for biological, environmental, or recycling purposes is of crucial importance [1]. The development of new technologies, based on binding cations, is restrained by properties of used ligands. Thus, compounds like crown ethers [2], podands, or cryptands [3,4], were recently widely studied [5–7]. Crown ethers and cryptands selectively and specifically bind cations, and their significance, especially for medical purposes, is well known. There is great need of agents which interact with a wider group of compounds. The main disadvantage of podands is their low selectivity [8]. It seems desirable to extend the research to compounds with multiple pendent arms, with a relatively flexible skeleton and large substituents which can restrict the size and geometry of bonded cations. Complexation depends not only on an appropriate topography, but also on neutralizing the charge on the cation. Thus introducing P═O or P═S groups should affect the selectivity of the compound.

The aim of our study was to confirm complexing possibilities of 1,3,5-benzene-tris(methylenediphenylphosphine oxide) (**1**) and propose a new compound which is expected to have more promising complexing properties. Solid state studies if not directly applicable to the solution phase are

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Correspondence to: Rafal Kruszynski; e-mail: kruszyna@p.lodz.pl.

Contract grant sponsor: Ministry of Scientific Research and Information Technology.

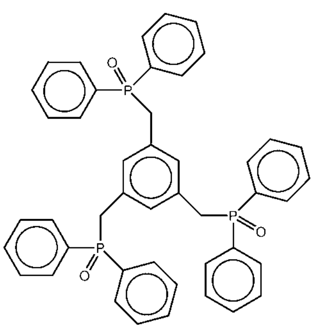
important in this area, as they involve the key molecules, and can confirm the type of cation binding [9]. Compound **1** exist in two polymorphic forms: triclinic *P*1 (**1a**) (CCDC [10] refcode GOKQAY) [11] and monoclinic *Pn* [12] (**1b**). It was shown that molecular geometry of **1** in **1a** and **1b** is almost the same, and differences are mostly crystallographic, not conformational [12]. It was postulated that **1** will exhibit tridentate coordination [Pietrusiewicz, K. M. (Personal communication)]. We decided to verify this supposition introducing cyclohexylammonium chloride to **1**. The ammonium cation fits with size and geometry excellently to cavity of ligand, and, in case of tridentate coordination, should create supramolecular complex via three $N_{(amine)}—H \cdots O_{(diphenylphosphineoxide)}$ interactions.

EXPERIMENTAL SECTION

Synthesis

Compound **1** was synthesized according to Ref. [13]. The complex **1c** was obtained by dissolution of equimolar amounts (0.1 mmol) of **1** and cyclohexylamine hydrochloride in methanol (25 cm^3) in an open vessel. The solvent was allowed to evaporate. The product was dissolved in benzene (12 cm^3), and the solution was kept in open vessel at 277 K. After four months, crystals suitable for X-ray determination had grown.

The 2,5-bis(ethoxymethyl)-1,4-benzene-bis(diphenylphosphineoxide) (**2**) was prepared according to the method of Pietrusiewicz [Pietrusiewicz, K. M. (Unpublished results)]. The product was recrystallized from ethanol giving well shaped crystals after one month.



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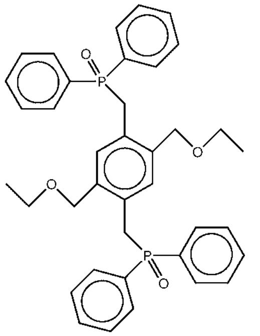

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X-Ray Crystal Structure Analysis

A pyramidal crystal of **1c** was mounted on a Enraf-Nonius CAD-4 automatic four-circle diffractometer and used for data collection. Three-dimensional X-ray intensity data were collected with graphite monochromated CuK_α radiation at room temperature with the ω-2θ scan modes. The unit cell parameters were determined from least-squares calculation from the angular settings of 99 reflections in the θ range 10–50°. Variable scan rate with a maximum scan time 60 s per reflection was applied. Examination of two standard reflections monitored after each 100 reflections measured, showed final coefficient for decay correction 1.504, what corresponds to 33.5% loss of the intensity. During the data reduction the decay correction coefficient was taken into account. A colourless, transparent crystal used for data collection became brown.

A rectangular prism of **2** was mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated MoK_α radiation at room temperature with ω scan mode. A 20 s exposure time was used. A half of Ewald sphere was collected. The unit cell parameters were determined from least-squares refinement of the setting angles of 3628 strongest reflections. Examination of two reference frames monitored after each 50 frames measured showed 62.4% loss of the intensity. During the data reduction above decay correction coefficient was taken into account. A colourless, transparent crystal used for data collection became dark brown.

Details concerning crystal data and refinement for **1c** and **2** are given in Table 1. Lorentz-polarization correction was applied to the intensity data of **1c** and **2**. Numerical absorption correction was used [14]. The structures were solved by direct methods and subsequently completed by the difference Fourier recycling. All the nonhydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent carbon atom with individual isotropic temperature factor equal 1.2 times the value of equivalent temperature factor of the parent carbon atom. Hydrogen atoms positions were idealized after each cycle of refinement. The methyl groups were allowed to rotate about their local threefold axis. The solution and refinements were performed with SHELXS97 [15] and SHELXL97 [16]. The graphical manipulations were performed using the XP routine of the SHELXTL [17], ORTEP [18], and PLUTON [19]. Atomic scattering factors were those incorporated in the computer programs. Interatomic bond distances and angles are listed in Tables 2 and 3 for **1c** and **2** respectively. Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and

TABLE 1 Crystal Data and Structure Refinement Details for Determined Structures

	1c	**2**
Empirical formula	$C_{45}H_{39}O_3P_3 \cdot C_6H_{14}N^+Cl^- \cdot 2C_6H_6 \cdot H_2O$	$C_{38}H_{40}O_4P_2$
Formula weight	1030.54	622.64
Temperature	291(2) K	291(1) K
Wavelength	$\lambda(\mathrm{Cu}K\alpha) = 1.54178$ Å	$\lambda(\mathrm{Mo}K\alpha) = 0.71073$ Å
Crystal system, space group	Triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
Unit cell dimensions	$a = 11.165(2)$	$a = 13.4496(9)$
	$b = 17.380(3)$	$b = 5.7646(4)$
	$c = 17.500(3)$ Å	$c = 21.2340(10)$ Å
	$\alpha = 64.45(3)$	
	$\beta = 72.61(3)$	$\beta = 92.794(5)^\circ$
	$\gamma = 74.75(3)^\circ$	
Volume	2888.0(9) Å^3	1644.35(18) Å^3
Z, Calculated density	2, 1.185 mg/m^3	2, 1.258 mg/m^3
Absorption coefficient	1.730 mm^{-1}	0.172 mm^{-1}
F(000)	1092	660
Crystal size	0.57 × 0.32 × 0.32 mm	0.34 × 0.19 × 0.15 mm
θ range for data collection	2.85 to 74.99°	3.51 to 25.11°
Index ranges	$-13 \leq h \leq 13, -21 \leq k \leq 0, -21 \leq 1 \leq 19$	$-16 \leq h \leq 16, -3 \leq k \leq 6, -21 \leq 1 \leq 25$
Reflections collected/unique	12287/11876	16471/2919
R(int)	0.0393	0.0477
Completeness	to $\theta = 74.99$ 99.9%	to $\theta = 25.11$ 90.0%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Max. and min. transmission	0.419 and 0.665	0.758 and 0.822
Data/restraints/parameters	11876/0/673	2919/0/200
Goodness-of-fit on F^2	1.055	1.095
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0625$, $wR2 = 0.1746$	$R1 = 0.0461$, $wR2 = 0.1243$
R indices (all data)	$R1 = 0.0697$, $wR2 = 0.1836$	$R1 = 0.0547$, $wR2 = 0.1326$
Largest diff. peak and hole	0.656 and −0.578 e Å^{-3}	0.292 and −0.319 e Å^{-3}

equivalent isotropic displacement parameters for nonhydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths, and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under No. CCDC169175 and CCDC169176 for **1c** and **2** respectively.

RESULTS AND DISCUSSION

Description of Compound **1c**

A perspective view of the structure together with the atom numbering scheme is shown in Fig. 1. The displacement ellipsoids plot is depicted in Fig. 2 (the chloride ion, water, and benzene molecules being omitted for clarity). All interatomic distances can be considered as normal. One of the benzene molecules is fully statically disordered (48.5%) and, in addition, shows symptoms of dynamical disorder, which exhibit in rather large thermal motion.

The overall molecular geometry of **1c** is similar to that of **1b** [12]. Main difference is in the arrangement of phenyl rings indicted by C(10), C(22), and C(28) atoms. The weighted r. m. s. deviation for all atoms of ligand **1c** and **1b** is 0.4838 Å. All the phosphorus atoms adopt geometry of distorted tetrahedron, with C—P—C angles equal or smaller than tetrahedral and O—P—C angles greater than tetrahedral (Table 2). The phenyl rings indicated by C(10), C(16), C(28), and C(40) atoms are almost coplanar with the P=O bond. All diphenylphosphine oxide substituents display weak hydrogen bonds $\mathrm{C_{(phenyl)}{—}H \cdots O_{(oxide)}}$ (Table 4), but for two phenyl rings not coplanar with P=O bond, hydrogen bonds are, as expected, the weakest [20]. The overall arrangement of diphenylphosphine oxide substituents (best described by torsion angles, Table 2) indicated by P(1) and P(3) atoms is imposed, like in **1b**, by intermolecular strong hydrogen bonds, $\mathrm{O_{(water)}{—}H \cdots O_{(oxide)}}$ and $\mathrm{N_{(amine)}{—}H \cdots O_{(oxide,\,water)}}$ (for details see Table 4). In this way the 11-membered ring is created, in opposition to **1c**, where 10-membered ring exists. The existence of hydrogen bonds also affect the dihedral angle between central benzene ring and $\mathrm{P\text{-}CH_2C_{(benzene)}}$ which amounts 60.01(14), 52.74(13)° for branches indicated by P1 and P3 atoms, and 68.79(13)° for branch indicated by P2 atom.

The cyclohexylammonium ion exists in almost ideal chair conformation, as shown by asymmetry

TABLE 2 Selected Structural Data for **1c**[a]

P (3)–O (3)	1.487 (2)
P (3)–C (9)	1.812 (2)
P (2)–O (2)	1.480 (2)
P (2)–C (8)	1.814 (2)
P (1)–O (1)	1.494 (1)
P (1)–C (7)	1.797 (2)
C (9)–C (5)	1.515 (3)
C (8)–C (3)	1.510 (3)
C (7)–C (1)	1.515 (3)
Central benzene C–C	1.390 (3)[b]
Phenyl C–C	1.376 (5)[b]
P–C_{Ph}	1.803 (3)[b]
O (3)–P (3)–C (40)	113.0 (1)
O (3)–P (3)–C (34)	110.6 (1)
C (40)–P (3)–C (34)	107.5 (1)
O (3)–P (3)–C (9)	112.1 (1)
C (40)–P (3)–C (9)	109.1 (1)
C (34)–P (3)–C (9)	104.2 (1)
O (2)–P (2)–C (22)	112.8 (1)
O (2)–P (2)–C (8)	113.9 (1)
C (22)–P (2)–C (8)	107.3 (1)
O (2)–P (2)–C (28)	111.6 (1)
C (22)–P (2)–C (28)	105.4 (1)
C (8)–P(2)–C(28)	105.1 (1)
O (1)–P (1)–C (7)	113.9 (1)
O (1)–P (1)–C (16)	111.2 (1)
C (7)–P (1)–C (16)	107.2 (1)
O (1)–P (1)–C (10)	111.4 (1)
C (7)–P (1)–C (10)	106.3 (1)
C (16)–P (1)–C (10)	106.4 (1)
C (5)–C (9)–P (3)	116.3 (1)
C (3)–C (8)–P (2)	112.6 (1)
C (1)–C (7)–P (1)	115.4 (1)
C (4)–C (5)–C (9)	119.2 (2)
C (6)–C (5)–C (9)	121.4 (2)
C (4)–C (3)–C (8)	120.2 (2)
C (2)–C (3)–C (8)	121.1 (2)
C (2)–C (1)–C (7)	119.1 (2)
C (6)–C (1)–C (7)	121.0 (2)
Central benzene C–C–C	120.0 (2)[b]
Phenyl C–C–C	120.0 (3)[b]
P–C_{Ph}–C_{Ph}	117.9 (2);123.1 (2)[b,c]
C (2)–C (1)–C (7)–P (1)	−121.0 (2)
C (1)–C (7)–P (1)–C (10)	167.9 (2)
C (7)–P (1)–C (10)–C (11)	−51.1 (2)
C (7)–P (1)–C (10)–C (15)	129.9 (2)
C (6)–C (1)–C (7)–P (1)	60.9 (2)
C (1)–C (7)–P (1)–C (16)	54.4 (2)
C (7)–P (1)–C (16)–C (17)	−136.7 (2)
C (7)–P (1)–C (16)–C (21)	43.9 (2)
C (1)–C (7)–P (1)–O (1)	−69.1 (2)
O (1)–P (1)–C (10)–C (11)	−175.7 (2)
O (1)–P (1)–C (10)–C (15)	5.4 (2)
O (1)–P (1)–C (16)–C (17)	−11.6 (2)
O (1)–P (1)–C (16)–C (21)	169.0 (2)
C (2)–C (3)–C (8)–P (2)	−110.5 (2)
C (3)–C (8)–P (2)–C (22)	70.2 (2)
C (8)–P (2)–C (22)–C (23)	−152.2 (2)
C (8)–P (2)–C (22)–C (27)	29.8 (2)
C (4)–C (3)–C (8)–P (2)	68.1 (2)
C (3)–C (8)–P (2)–C (28)	−177.9 (2)
C (8)–P (2)–C (28)–C (29)	114.0 (2)
C (8)–P (2)–C (28)–C (33)	−69.7 (3)
C (3)–C (8)–P (2)–O (2)	−55.3 (2)
O (2)–P (2)–C (22)–C (23)	−26.0 (3)
O (2)–P (2)–C (22)–C (27)	156.1 (2)
O (2)–P (2)–C (28)–C (29)	−9.9 (3)
O (2)–P (2)–C (28)–C (33)	166.3 (3)
C (4)–C (5)–C (9)–P (3)	−127.7 (2)
C (5)–C (9)–P (3)–C (34)	168.6 (2)
C (9)–P (3)–C (34)–C (35)	−65.0 (2)
C (9)–P (3)–C (34)–C (39)	110.8 (2)
C (6)–C (5)–C (9)–P (3)	53.4 (2)
C (5)–C (9)–P (3)–C (40)	54.1 (2)
C (9)–P (3)–C (40)–C (41)	20.0 (2)
C (9)–P (3)–C (40)–C (45)	−159.7 (2)
C (5)–C (9)–P (3)–O (3)	−71.8 (2)
O (3)–P (3)–C (34)–C (35)	174.4 (2)
O (3)–P (3)–C (34)–C (39)	−9.8 (2)
O (3)–P (3)–C (40)–C (41)	145.3 (2)
O (3)–P (3)–C (40)–C (45)	−34.3 (2)
C (51)–C (56)	1.503 (4)
C (51)–C (52)	1.516 (4)
C (52)–C (53)	1.522 (6)
C (53)–C (54)	1.482 (8)
C (54)–C (55)	1.535 (9)
C (55)–C (56)	1.513 (5)
N (51)–C (51)	1.479 (3)
N (51)–C–C	108.7 (3)[b]
C (56)–C (51)–C (52)	114.2 (3)
C (51)–C (52)–C (53)	109.0 (4)
C (54)–C (53)–C (52)	111.5 (4)
C (53)–C (54)–C (55)	111.0 (4)
C (56)–C (55)–C (54)	112.7 (5)
C (51)–C (56)–C (55)	109.2 (3)
C (51)–C (52)–C (53)–C (54)	56.6 (5)
C (52)–C (53)–C (54)–C (55)	−56.7 (6)
C (53)–C (54)–C (55)–C (56)	55.1 (6)
C (54)–C (55)–C (56)–C (51)	−52.4 (5)
C (55)–C (56)–C (51)–C (52)	54.4 (4)
C (56)–C (51)–C (52)–C (53)	−56.4 (4)
N (51)–C (51)–C (52)–C (53)	−178.2 (3)
N (51)–C (51)–C (56)–C (55)	176.0 (3)

Continued

TABLE 2 Continued

[a] Distances in Å, angles and torsion angles in °.
[b] Mean value.
[c] Both angles for each phosphorus.

parameters $\Delta C_{S(1)} = 1.403(6)^{\circ}$, $\Delta C_{S(3)} = 2.845(9)^{\circ}$, $\Delta C_{S(5)} = 2.025(7)^{\circ}$, $\Delta C_{2(2)} = 0.499(7)^{\circ}$, $\Delta C_{2(4)} = 3.041(8)^{\circ}$, and $\Delta C_{2(6)} = 3.393(10)^{\circ}$ [21], and nitrogen atom is equatorial to the ring. The structure of **1c** is build up from strong and weak intermolecular hydrogen bonds to form the three-dimensional infinite hydrogen bond network. There are no unusual intermolecular short contacts except hydrogen bonds described in Table 4.

The ammonium ion creates a hydrogen bonded complex with **1** coordinating in monodentate mode. This is mainly caused by steric restraints imposed by large diphenylphosphine oxide substituents. To

TABLE 3 Selected Structural Data for **2**^{a}

P (1)–O (1)	1.479 (1)
P (1)–C (10)	1.807 (2)
P (1)–C (7)	1.810 (2)
P (1)–C (16)	1.812 (2)
O (51)–C (52)	1.408 (4)
O (51)–C (51)	1.413 (3)
C (7)–C (1)	1.513 (3)
C (51)–C (5)	1.514 (3)
C (52)–C (53)	1.414 (6)
Central benzene C–C	1.392 (3)^b
Phenyl C–C	1.378 (4)^b
O (1)–P (1)–C (10)	110.8 (1)
O (1)–P (1)–C (7)	115.3 (1)
C (10)–P (1)–C (7)	106.9 (1)
O (1)–P (1)–C (16)	110.6 (1)
C (10)–P (1)–C (16)	106.6 (1)
C (7)–P (1)–C (16)	106.3 (1)
C (52)–O (51)–C (51)	112.6 (2)
C (1)–C (7)–P (1)	113.6 (1)
O (51)–C (51)–C (5)	112.8 (2)
O (51)–C (52)–C (53)	112.1 (4)
C (6)–C (1)–C (7)	118.7 (2)
C (5)#1–C (1)–C (7)	122.7 (2)
C (6)–C (5)–C (51)	119.8 (2)
C (1)#1–C (5)–C (51)	121.4 (2)
C (17)–C (16)–P (1)	124.7 (2)
C (21)–C (16)–P (1)	116.6 (2)
C (11)–C (10)–P (1)	117.7 (2)
C (15)–C (10)–P (1)	123.2 (2)
Central benzene C–C–C	120.0 (2)^b
Phenyl C–C–C	120.0 (3)^b
C (5)#1–C (1)–C (7)–P (1)	−83.3 (2)
C (1)–C (7)–P (1)–C (10)	−60.8 (2)
C (7)–P (1)–C (10)–C (11)	120.7 (2)
C (7)–P (1)–C (10)–C (15)	−61.2 (2)
C (6)–C (1)–C (7)–P (1)	96.7 (2)
C (1)–C (7)–P (1)–C (16)	−174.4 (1)
C (7)–P (1)–C (16)–C (17)	17.8 (2)
C (7)–P (1)–C (16)–C (21)	−160.1 (2)
C (1)–C (7)–P (1)–O (1)	62.8 (2)
O (1)–P (1)–C (10)–C (11)	−5.6 (2)
O (1)–P (1)–C (10)–C (15)	172.5 (2)
O (1)–P (1)–C (16)–C (17)	143.6 (2)
O (1)–P (1)–C (16)–C (21)	−34.3 (2)
C (6)–C (5)–C (51)–O (51)	−109.0 (2)
C (5)–C (51)–O (51)–C (52)	72.7 (3)
C (51)–O (51)–C (52)–C (53)	−173.8 (5)
C (1)#1–C (5)–C (51)–O (51)	68.7 (3)

Symmetry transformations used to generate equivalent atoms: #1 −x + 1, −y + 2, −z.

^{a}Distances in Å, angles and torsion angles in °.

^{b}Mean value.

release the steric strain there is a great tendency to co-opt to the complex the auxilliary oxygen donors from the adjacent water molecules [22]. Based on elementary considerations of Hancock [23], it was earlier determined [22,24] that the water molecules, which are strongly hydrogen bonded to ligand molecule, play the same role as hydroxylorganic side branch. Taking into account the above considera-

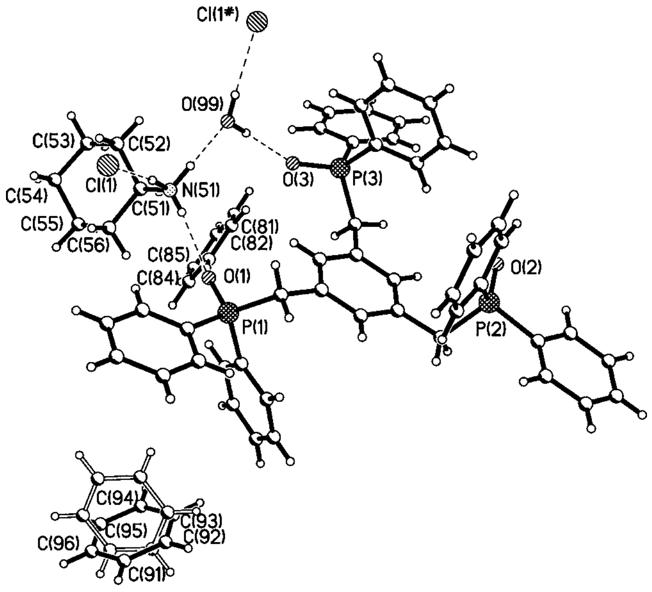

FIGURE 1 The independent part of the unit cell of **1c**. Disordered part of the benzene ring is indicated by double lines. Strong hydrogen bonds are indicated by dashed lines. Atom Cl1# obtained by −x − 1, −y, −z symmetry transformation.

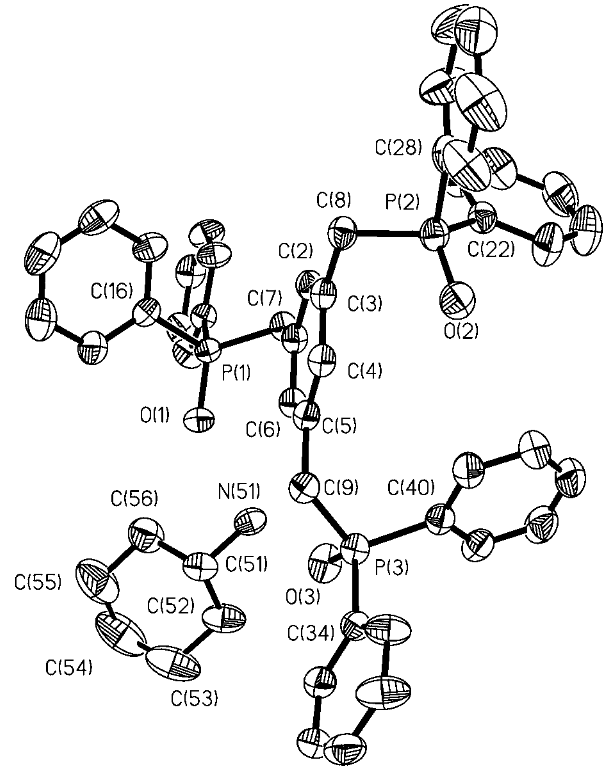

FIGURE 2 The molecular conformation of **1c** plotted with 30% probability of displacement ellipsoids. Chloride ion, benzene rings, water molecule, and hydrogen atoms being omitted for clarity.

TABLE 4 Hydrogen-Bonds for **1c**[a]

D–H···A	*d(D–H)*	*d(H···A)*	*d(D···A)*	*<(DHA)*
C(15)–H(15)···O(1)	0.93	2.60	3.017(3)	107.9
C(17)–H(17)···O(1)	0.93	2.60	3.016(3)	107.4
C(23)–H(23)···O(2)	0.93	2.68	3.063(4)	105.6
C(29)–H(29)···O(2)	0.93	2.57	2.988(4)	107.8
C(39)–H(39)···O(3)	0.93	2.59	3.004(4)	107.1
C(45)–H(45)···O(3)	0.93	2.79	3.121(3)	102.4
N(51)–H(51N)···O(99)	0.93	1.79	2.709(3)	166.9
N(51)–H(51O)···O(1)	0.73	2.10	2.830(2)	174.5
N(51)–H(51P)···Cl(1)	0.95	2.16	3.110(2)	173.5
O(99)–H(99O)···Cl(1)#1	0.84	2.25	3.082(3)	172.4
O(99)–H(99P)···O(3)	0.85	1.82	2.634(3)	160.2
C(2)–H(2)···Cl(1)#3	0.93	2.77	3.636(2)	155.8
C(7)–H(7B)···Cl(1)#3	0.97	2.79	3.731(3)	162.6
C(82)–H(82)···O(3)	0.93	2.56	3.488(4)	174.0
C(86)–H(86)···O(2)#2	0.93	2.60	3.516(4)	169.9

Symmetry transformations used to generate equivalent atoms: #1 −x − 1, −y, −z; #2 −x − 1, −y − 1, −z; #3 −x −2, −y, −z.

[a]Distances in Å, angles in °.

tions the ligand can be regarded as molecule coordinating in bidentate mode, in which one side arm plays indirect (auxiliary) part in the complexation enhancing the coordinative ability of the ligand oxygen donors, but it is impossible to obtain complex with tridentate ligand. Thus we decide to synthesize a new ligand with two diphenylphosphine oxide substituents and two linear side branches (containing oxygen atom). Preliminary complexation studies by means of simple chromatographic test have allowed to select **2** as the most promising ligand exhibiting wide spectrum of complexation abilities.

Description of Compound 2

A perspective view of the structure together with the atom numbering scheme is shown in Fig. 3. The structure is plotted with 50% probability of thermal ellipsoids. The C(54) atom shows some symptoms of disorder and this part of the molecule exhibits rather large thermal motion. All attempts to find model of this disorder were unsuccessful, which can suggest dynamical character of disorder. Because the central benzene ring lies around special position *d* of $P2_1/n$ space group at $1/2$, 0, 0 with site symmetry $\bar{1}$

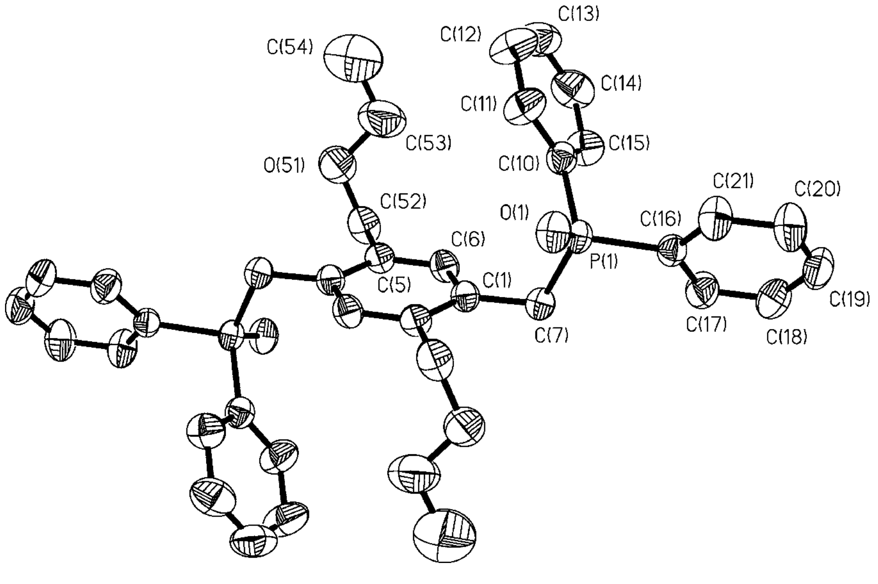

FIGURE 3 The molecular conformation of **2** with atom numbering, plotted with 50% probability of displacement ellipsoids. Hydrogen atoms being omitted for clarity.

TABLE 5 Hydrogen-Bonds for **2**[a]

D–H · · · A	*d(D–H)*	*d(H · · · A)*	*d(D · · · A)*	*< (DHA)*
C(11)–H(11) · · · O(1)	0.93	2.56	2.981(3)	107.9
C(21)–H(21) · · · O(1)	0.93	2.71	3.054(3)	103.1
C(51)–H(51B) · · · O(1)#1	0.97	2.43	3.298(3)	148.9
C(7)–H(7B) · · · O(51)#1	0.97	2.55	3.234(3)	127.4
C(6)–H(6) · · · O(1)#2	0.93	2.54	3.319(2)	141.0
C(7)–H(7A) · · · O(1)#2	0.97	2.40	3.327(2)	159.8

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+2, -z$; #2 $x, y+1, z$.

[a] Distances in Å, angles in °.

[25], the asymmetric unit includes a half of each molecule. All interatomic distances are normal, and benzene rings are planar in range of experimental error.

The conformation of diphenylphosphine oxide substituent is comparable with previously determined compounds **1a–c**, however the dihedral angle between central benzene ring and P-$CH_2C_{(benzene)}$ has a value of 83.29(10)° which is distinctly larger than in compounds **1a–c**. The phenyl rings are inclined at 80.91(7)° within the substituent, and they make the dihedral angles 59.29(9) and 62.41(8)° with the central benzene ring (for the phenyl rings indicated by C(10) and C(16) respectively). All phenyl rings are involved in weak $C_{(phenyl)}$—H · · · $O_{(oxide)}$ hydrogen bond [20] with oxygen atoms (Table 5), and for ring indicated by C(10) atom, coplanar with P═O group, hydrogen bond is considerably stronger. All the phosphorus atoms adopt geometry of distorted tetrahedron, with C—P—C angles smaller than tetrahedral and O—P—C angles greater than tetrahedral (Table 3). These can suggest, as in **1c**, that steric effect imposed by phenyl groups has no greater importance. The phosphorus atom deviate by 0.081(3) and 0.045(3) Å from the phenyl rings indicated by C(10) and C(16) atoms respectively. The arrangement of diphenylphosphine oxide substituents (for describing them torsion angles see Table 3) is imposed, in opposition to **1c**, practically only by steric effects. However, two intramolecular weak hydrogen bonds exist between diphenylphosphine oxide and ethoxymethyl substituents (for details see Table 5), that can provide additional stabilization to the molecule, it has no noticeable influence on overall molecule geometry [20]. Molecules of **2** are assembled via weak intermolecular C—H · · · $O_{(oxide)}$ short contacts, which according to Desiraju and Steiner [20] can be considered as weak hydrogen bonds, to the one-dimensional hydrogen-bonded chain along *y* axis. There are no unusual intermolecular short contacts except hydrogen bonds described in Table 5.

Future Prospects

The preliminary results recognized by us by means of TLC test and mass spectral LSIMS analysis [to be published] showed the capacity of **2** to form stable complexes with wide variety of ions. In the case of **2**, there are two possible structural units capable of taking part in binding cations via supramolecular interactions: (a) oxygen donors of diphenylphosphine oxide substituents (pendant arms), (b) oxygen donors of ethoxymethyl substituents (side arms) and one unit (central benzene ring), (c) which can interact via stacking π electrons. Contacts (b) and (c) can be considered as playing role of strongly structural restrained podand cavity, and interaction (a) as podand arms. These can promise greater selectivity of **2** than is spotted for ordinary podands. In addition, the diphenylphosphine oxide substituent exhibits rather large conformational independence toward central benzene ring ($C_{(phenyl)}$—$C_{(phenyl)}$—C—P torsion angle change value in range 53.4–83.3°). Thus it is expected, that **2** can act selectively as chelating agent for group of compounds and has no disadvantages of cryptands, like to great selectivity, typical for compounds with geometry-restrained three-dimensional cavity.

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