New trigonal tris(phosphine oxides)

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The reaction of 1,1,1-tris(chloromethyl)propane with diphenylphosphine under phasetransfer conditions afforded 1,1,1-tris(diphenylphosphinomethyl)propane, whose oxidation gave a previously unknown representative of trigonal tris(phosphine oxides), *viz.*, stable 1,1,1-tris(diphenylphosphorylmethyl)propane. Its analogs, *viz.*, bis(diphenylphosphoryl)diphenylphosphinomethane and tris(diphenylphosphoryl)methane, are unstable in air and decompose with the cleavage of the P–C bond.

Key words: bis(diphenylphosphoryl)diphenylphosphinomethane, tris(diphenylphosphoryl)methane, 1,1,1-tris(diphenylphosphinomethyl)propane, 1,1,1-tris(diphenylphosphorylmethyl)propane.

Earlier,¹ linear trisphosphine trioxides have been demonstrated to serve as efficient ligands for actinides and to be superior to the corresponding mono- and bisphosphine oxides in reactivity. The aim of our investigation was to extend the range of the known types of oligophosphine oxides. In the present study, data on the search for a procedure for the synthesis of trigonal triphosphine oxides of the general formula $RC[(CH_2)_nP(O)Ph_2]_3$ containing three phosphoryl groups at the same carbon atom are reported for the first time. We expected that these systems characterized by structural specificity could provide the formation of unusual metal-phosphoryl polyhedra upon coordination to metal ions. This, in turn, could ensure selectivity of separation of metal mixtures by extraction.

The choice of phenyl groups at the phosphorus atom is governed by the known fact that the phosphoryl groups of phosphine oxides, whose phosphorus atoms are bound to two phenyl groups responsible for the orientation of electron-donating atoms, have the highest complexation ability.² The latter atoms form a pincer with open reaction centers, which are capable of coordinating a metal ion without an additional conformational rearrangement of the polydentate reagent. In other words, a hydrophobic "paling" composed of the phenyl rings is formed with the resulting increase in solvation of the reagent, which determines its extraction properties.

First we selected trigonal tris(phosphine oxide) $CH[P(O)Ph_2]_3$ (1) as the subject of studies. Its core is surrounded by three diphenylphosphoryl groups.

We intended to use the reaction of lithium bis(diphenylphosphoryl)methanide (2) with chlorodiphenylphosphine (3) followed by oxidation of phosphinodiphenylphosphine oxide (4) that formed.

The first step of this process has been described earlier³ (Scheme 1).

Scheme 1

$[Ph_2P(O)]_2CHLi + Ph_2PCI \longrightarrow [Ph_2P(O)]_2CH-PPh_2$ **2 3 4**

However, we demonstrated that the reaction performed under the conditions described in the cited study³ did not afford the expected product 4; instead, we prepared its complex with lithium chloride $[Ph_2P(O)]_2CH-PPh_2 \cdot LiCl (5)$, which was confirmed by elemental analysis. The ability of alkylated dioxides to form stable complexes with alkali metal halides during the reaction has been observed earlier.⁴ The possibility of the formation of an analogous complex in the reaction of lithium bis(diphenylphosphino)methanide with alkyl halides has also been mentioned in the study.³ In the present study, alkali metal halide (LiCl) appeared in the reaction mixture as a reaction product of compound 3 with lithium bis(diphenylphosphoryl)methanide (2) as well as with butyllithium, which was not consumed in the lithiation reaction. The latter fact was confirmed by isolation of butyldiphenylphosphine from the reaction mixture. This compound was characterized as the oxidation product.

Complex 5 is unstable in air. In the presence of atmospheric oxygen and moisture, complex 5 decomposes with the cleavage of the P-C bond to give bis(diphenyl-

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phosphoryl)methane (6) and diphenylphosphinic acid. The latter was isolated as complex 7 from an acetone solution of the residue, which has left after extraction of compound 6 with chloroform from a mixture of decomposition products of 5 (Scheme 2).

Scheme 2

$[Ph_{2}P(O)]_{2}CH-PPh_{2} \cdot LiCl$ 5 $O_{2} \downarrow H_{2}O$ $Ph_{2}P(O)-CH_{2}-P(O)Ph_{2} + [Li(Me_{2}CO)(Ph_{2}PO_{2})Ph_{2}PO_{2}H]_{2}$ 6 7

Destruction was monitored by ¹H NMR spectroscopy. The cleavage of the P—C bond was virtually complete in 10 days. The spectrum shows a triplet corresponding to bis-oxide **6**; the ratio between the protons of the methylene fragment and phenyl substituents at the phosphorus atoms is 1 : 10 (2 : 20). A mixture of compound **6** and an authentic sample showed no melting point depression.⁵ The second decomposition product, *viz.*, complex 7, was characterized by X-ray diffraction analysis.

X-ray diffraction study demonstrated that complex 7 has the dimeric [Li(Me₂CO)(Ph₂PO₂)Ph₂PO₂H]₂ structure containing the four-membered Li₂O₂ ring formed through Li...O coordination bonds (Table 1, Fig. 1). The complex includes both the diphenylphosphinic acid molecule and the diphenylphosphinate anion. It should be noted that cocrystallization with diphenylphosphinic acid was not observed in the crystal structures of lithium diarylphosphinates studied earlier.^{6,7} In the crystal structure of complex 7, the molecule occupies a special position, the center of the four-membered Li_2O_2 ring being located in the center of symmetry (see Fig. 1). The coordination sphere of lithium is a distorted tetrahedron formed by two anions, one acetone solvate molecule, and one diphenylphosphinic acid molecule. The endocyclic O(1)-Li(1)-O(1A) angle decreases to 96.4(1)°. The Li...O bond lengths vary in a range of 1.865(3) - 1.966(4) Å and are similar to those observed in the lithium diarylphosphinate complexes studied earlier (1.878(4)-1.991(3) Å).^{6,7}



Fig. 1. Overall view of molecule 7.

Table 1. Selected bond lengths (d) and bond angles (ω) in complex 7

Bond	d∕Å	Angle	ω/deg
P(1) - O(1)	1.498(1)	O(1) - P(1) - O(2)	117.12(7)
P(1) - O(2)	1.505(1)	O(1) - P(1) - C(1)	108.73(8)
P(1) - C(1)	1.807(2)	O(1) - P(1) - C(7)	110.13(8)
P(1) - C(7)	1.804(2)	O(2) - P(1) - C(1)	108.4(1)
P(2)-O(3)	1.482(1)	O(2) - P(1) - C(7)	108.02(9)
P(2)—O(4)	1.541(1)	C(7) - P(1) - C(1)	103.59(8)
P(2)-C(13)	1.794(2)	O(3) - P(2) - O(4)	116.87(8)
P(2)-C(19)	1.795(2)	O(3) - P(2) - C(13)	111.53(8)
O(1) - Li(1)	1.958(3)	O(3) - P(2) - C(19)	109.02(9)
O(1)-Li(1A)	1.930(3)	O(4) - P(2) - C(13)	104.40(9)
O(1S)-Li(1)	1.965(4)	O(4) - P(2) - C(19)	107.98(9)
O(3)-Li(1)	1.865(3)	C(13) - P(2) - C(19)	106.47(8)
		O(1) - Li(1) - O(1S)	113.6(2)
		O(1A) - Li(1) - O(1)	96.3(1)
		O(1A) - Li(1) - O(1S)	112.9(2)
		O(3) - Li(1) - O(1)	115.1(2)
		O(3)-Li(1)-O(1A)	108.3(2)
		O(3) - Li(1) - O(1S)	109.9(2)
		$\frac{\text{Li}(1A)-O(1)-\text{Li}(1)}{}$	83.6(1)

One of the oxygen atoms, O(4), of the diphenylphosphinate anion is coordinated to lithium, whereas the second oxygen atom, O(2), forms a strong intramolecular O...H–O hydrogen bond (O(4)...O(2), 2.424(2) Å; H(O(4))...O(2), 1.50 Å; O(4)–H(O(4))–O(2), 168°) with the P–OH group of the acid molecule. Since the P(1)–O(1) and P(1)–O(2) bond lengths in the diphenylphosphinate anion are virtually equal, it can be concluded that the influence of the strong O–H...O hydrogen bond on the P–O bond lengths in the Ph₂PO₂ fragment is comparable to the influence of two Li...O coordination bonds.

Based on comparison of the geometry of diphenylphosphinic acid in complex 7 with that in the crystal structure of the noncoordinated acid,⁸ it can be concluded that the energy of the hydrogen bond is higher than that of the Li...O interaction. In the crystal structure of the acid, there is also a strong P–O–H...O=P interaction (2.4792(8) Å), due to which the P–OH bond length in complex 7 is virtually equal to that in the crystal of Ph₂PO₂H (1.541(1) and 1.5498(6) Å, respectively). On the contrary, the length of the P=O bond coordinated to the Li cation is substantially shorter (1.482(1) Å) compared to the corresponding bond in the crystal of Ph₂PO₂H (1.5015(5) Å).

An alternative procedure for the preparation of tris(phosphine oxide) 1 involved the reaction of lithium derivative 2 with diphenylphosphinic chloride (8) (Scheme 3).

This reaction also afforded only complex (9) containing trisoxide 1 and two lithium chloride molecules

Scheme 3

$[Ph_2P(O)]_2CHLi + Ph_2P(O)Cl \longrightarrow CH[P(O)Ph_2]_3 \cdot 2LiCl$ **2 8 9**

(1.2LiCl), which was confirmed by elemental analysis. In the presence of atmospheric moisture, complex 9, like the above-described complex 5, decomposes with the cleavage of the P–C bond (decomposition is complete in 15 days). The formation of dioxide 6 upon decomposition was confirmed by ¹H NMR spectroscopy.

Removal of the phosphorus atoms from the central carbon atom would be expected to increase stability of the target compounds. Taking into account this fact, we synthesized 1,1,1-tris(diphenylphosphorylmethyl)propane (11) from the readily accessible and stable 1,1,1-tris(hydroxymethyl)propane using a modified procedure⁹ (Scheme 4).

Scheme 4

$$EtC(CH_2OH)_3 \xrightarrow{SOCl_2} EtC(CH_2Cl)_3 + HPPh_2 \xrightarrow{i} \\ \longrightarrow EtC(CH_2PPh_2)_3 \xrightarrow{H_2O_2} EtC[CH_2P(O)Ph_2]_3 \\ 10 \\ 11$$

i. Phase transfer catalysis.

The reaction of 1,1,1-tris(chloromethyl)propane, which was synthesized from 1,1,1-tris(hydroxymethyl)propane, with diphenylphosphine under phase transfer catalysis (PTC) conditions afforded 1,1,1-tris(diphenylphosphinomethyl)propane (10). The composition and structure of compound 10 were confirmed by elemental analysis and ³¹P{H} NMR spectroscopy. Product 10 is not oxidized with 30% hydrogen peroxide in acetone. The starting compound, which is apparently insoluble in water present in hydrogen peroxide, was recovered from the reaction mixture. Tris(phosphine oxide) 11 was prepared in quantitative yield by oxidation of compound 10 with a solution of anhydrous hydrogen peroxide in tert-butyl alcohol according to a procedure described earlier.¹⁰ Unlike compound 1, product 11, which was isolated as monohydrate, is stable in air.

To summarize, we developed a procedure for the preparation of a new representative of trigonal tris(phosphine oxides), *viz.*, 1,1,1-tris(diphenylphosphorylme-thyl)propane (11). In this compound, all three diphenylphosphoryl groups are separated from the central carbon atom by a methylene fragment. Investigation of the complexation properties of compound 11 is currently underway.

Experimental

NMR spectra were recorded on a Bruker AMX-400 instrument in CDCl₃ or CHCl₃ (c 0.03 mol L⁻¹) using residual signals for the protons of a deuterated solvent as the internal standard (¹H) and 85% H₃PO₄ as the external standard (³P).

X-ray diffraction study. Crystals of 7 ($C_{54}H_{54}Li_2O_{10}P_4$) at 298 K are monoclinic: a = 12.040(2), b = 9.788(2), c =22.915(5) Å, $\beta = 104.39(3)^{\circ}$, V = 2615.9(9) Å³, $d_{calc} =$ 1.271 g cm⁻¹, space group $P2_1/n$, Z = 2, M = 1000.73, F(000) = 1048, $\mu = 2.01$ cm⁻¹. The intensities of 6115 reflections were measured on an automated Nonius CAD-4 diffractometer at 298 K (Mo-Ka radiation, graphite monochromator, $\theta/2\theta$ scanning technique, $2\theta_{max} = 52^{\circ}$), and 5699 observed reflections ($R_{int} = 0.0174$) were used in calculations. The structure was solved by direct methods and refined by the fullmatrix least-squares method in the anisotropic-isotropic approximation against F^2 . The hydrogen atoms were revealed from the difference electron density maps and refined isotropically. The hydrogen atoms of the methyl groups were refined using the riding model. The final reliability factors were $wR_2 = 0.1196$, GOOF = 1.031 based on all reflections ($R_1 = 0.0377$ based on 3930 reflections with $I > 2\sigma(I)$). All calculations were carried out using the SHELXTL PLUS program package.

Bis(diphenylphosphoryl)methane was synthesized according to a procedure described earlier.⁵

Complex of bis(diphenylphosphoryl)diphenylphosphinomethane with lithium chloride (5). A solution of chloride 3 (0.5 g, 2.3 mmol) in benzene (10 mL) was added to a hexane solution of methanide 2, which was prepared from bis(diphenylphosphoryl)methane (0.9 g, 2.16 mmol) and butyllithium (0.15 g, 2.3 mmol).³ The solution was refluxed for 10 h. The precipitate that formed was filtered off (0.9 g) and extracted with chloroform (15 mL). The extract was concentrated to dryness to give complex 5 in a yield of 0.8 g (57.6%), t.decomp. 280 °C. Found (%): Cl, 5.51; P, 14.14. C₃₇H₃₁O₂P·LiCl. Calculated (%): Cl, 5.52; P, 14.47. The benzene-hexane filtrate of the reaction mixture was concentrated to dryness. An additional amount (~0.1 g) of complex 5 was precipitated with diethyl ether from the syrup-like residue (0.35 g). The ethereal filtrate was concentrated and a solution of 30% hydrogen peroxide in acetone was added. Butyldiphenylphosphine oxide was isolated in ~15% yield, m.p. 89–92 °C. $^{31}P{H}$ NMR (CHCl₃), δ: 27.55. Lit. data¹¹: m.p. 89.5–90.5 °C; ³¹P{H} NMR (CHCl₃), δ: 27.60.

Complex of tris(diphenylphosphoryl)methane with lithium chloride (9). A solution of chloride 8 (0.6 g, 2.3 mmol) in benzene (20 mL) was added to a hexane solution of methanide 2, which was prepared from bis(diphenylphosphoryl)methane (0.9 g, 2.16 mmol) and butyllithium (0.15 g, 2.3 mmol). The solution was refluxed for 20 h. The precipitate that formed was filtered off and extracted with chloroform. The extract was concentrated to dryness. The yield of complex 9 was 0.3 g (30%), t.decomp. >300 °C. Found (%): C, 63.07; H, 4.61; Cl, 10.30; P, 13.30. $C_{37}H_{31}O_3P_3 \cdot 2LiCl.$ Calculated (%): C, 63.34; H, 4.42; Cl, 10.13; P, 13.27.

Oxidative destruction of complexes 5 and 9. Complex 5 was kept in air for 10 days and then chloroform (15 mL) was added. One of the decomposition products, viz., bis(diphenylphosphoryl)methane 6, passed into the solution, which was con-

firmed by ¹H NMR spectroscopy of the residue after the removal of the chloroform. ¹H NMR (CDCl₃), δ : 3.51 (t, 2 H, CH₂, ²J_{P,H} = 14.6 Hz); 7.27 (m, 8 H, H_m, Ph); 7.37 (t, 4 H, H_p, Ph, ³J_{H,H} = 7.0 Hz); 7.70 (m, 8 H, H_o, Ph). A mixture of the residue and an authentic sample of **6** had m.p. 180–182 °C (lit. data⁵: m.p. 180–181 °C). The chloroform-insoluble precipitate was dissolved in acetone. The second decomposition product, *viz.*, complex **7**, was isolated after storage of the solution over a long period.

Destruction of complex 9 in the presence of atmospheric oxygen was complete in 15 days. The sample obtained after decomposition was worked up analogously to the sample obtained after destruction of complex 5. One of the decomposition products, *viz.*, compound 6, was isolated from the solution in chloroform. The formation of compound 6 was confirmed by ¹H NMR spectroscopy and m.p. of a mixed sample.

1,1,1-Tris(chloromethyl)propane was synthesized according to a known procedure⁹ from 1,1,1-tris(hydroxymethyl)propane (6.0 g, 45 mmol), thionyl chloride (19.6 g, 160 mmol), and pyridine (2.2 g). The yield was 5.9 g (70%), b.p. 65-67 °C (10 Torr).

1,1,1-Tris(diphenylphosphinomethyl)propane (10).⁹ A solution of NaOH (1.25 g, 22 mmol) in water (1 mL) was added to a mixture of K_2CO_3 (10.5 g, 75 mmol) and diphenylphosphine (3.7 g, 20 mmol) in DMSO (15 mL). After 15 min, 1,1,1-tris(chloromethyl)propane (1.18 g, 0.625 mmol) was added portionwise to the bright-red solution. The reaction mixture was heated at 90 °C for 1 h and then at 120 °C for 1 h until the reaction mixture became colorless. Then water (120 mL) was added and the mixture was vigorously stirred. The solid precipitate that formed was dried *in vacuo* at 80 °C over P_2O_5 for 1 h and recrystallized from ethanol. The yield of trisphosphine **10** was 2.7 g (62.8%), m.p. 105–106 °C. Found (%): C, 78.56; H, 6.52; P, 14.53. $C_{42}H_{41}P_3$. Calculated (%): C, 79.0; H, 6.43; P, 14.58. ³¹P{H} NMR (CHCl₃), δ : –26.1.

1,1,1-Tris(diphenylphosphorylmethyl)propane (11). A mixture of trisphosphine **10** (0.7 g, 1.1 mmol) and 5.7% hydrogen peroxide in *tert*-butyl alcohol (10 mL) was heated at 50 °C for 4 h. Trisphosphine oxide **11** was isolated in a yield of 0.77 g (~100%) as monohydrate, m.p. 178–181 °C. Found (%): C, 71.80; H, 6.30; P, 13.10. $C_{42}H_{41}O_3P_3 \cdot H_2O$. Calculated (%): C, 71.59; H, 6.10; P, 13.21. Drying of a sample of the monohydrate to a constant weight *in vacuo* at 80 °C over P_2O_5 for 3 h led to the loss of the water molecule; the weight loss was ~2.5%, m.p. 181–183 °C. ³¹P{H} NMR (CHCl₃), δ : 31.21.

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