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Synthesis and transformations of metallacycles

46.* Catalytic cycloalumination reaction in the synthesis of bis(phospholanes)

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An efficient one-pot synthesis of bis(phospholanes) was elaborated, which included a sequential Cp_2ZrCl_2-catalyzed cycloalumination of α,ω-diolefins with $AlEt_3$, giving the corresponding bis(aluminacyclopentanes), and their *in situ* reaction with dihalophosphines to furnish the target α,ω-bis(phospholanes). The reaction of these compounds with H_2O_2 or elementary sulfur gave the corresponding bis(phospholane 1-oxides) and bis(phospholane 1-sulfides).

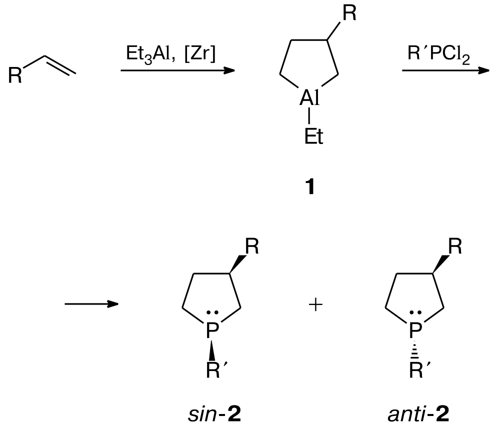
Key words: cycloalumination, organoaluminum compounds, α,ω-diolefins, dichlorophosphines, phospholanes, heterocycles, metal complex catalysis, zirconium complexes.

Bidentate organophosphorus ligands are regarded as occupying a special place in organic synthesis and metal complex catalysis. Nowadays, several hundred of highly efficient catalyst systems based on bis(phospholanes) such as BPE,[2] BINAP,[3] dppe,[4] BisP*,[5] DIOP[6] are used in everyday practice of organic synthesis, and the number of new catalysts on their basis is steadily growing. Apart from that, among the phosphorus-containing bidentate ligands the share of compounds containing phospholane structural fragments, for example, the ligands of DuPhos[7] and TangPhos family,[8] is constantly increasing.

In order to develop approaches to the synthesis of organophosphorus ligands containing two phospholane fragments in the structure, we suggested an idea of a possibility to use for this purpose a catalytic cycloalumination reaction[9] of α,ω-dienes, as well as a developed by us conditions for the replacement of Al atoms in aluminacyclopentanes with P atoms using $RPCl_2$.

Earlier,[10] we have shown that the *in situ* reaction of simple aluminacyclopentanes **1**, obtained by the reaction of terminal alkenes with Et_3Al in the presence of Cp_2ZrCl_2 (5 mol.%) at 20 °C over 12 h, with $RPCl_2$ (R = Me, Ph) in toluene within 30 min leads to the replacement of aluminum atoms by phosphorus atoms with the formation of the corresponding phospholanes **2** in 79—84% yield (Scheme 1).

Scheme 1



[Zr] = Cp_2ZrCl_2; R = Bn, *n*-Bu, *n*-Hex; R′ = Me, Ph

According to this idea on the synthesis of organophosphorus bidentate ligands, initially it seemed important to confirm a possibility to extend this method to the synthesis of α,ω-bis-phospholane compounds by the reaction of dihalophosphines with bis-aluminacyclopentanes obtained *in situ* by the Zr-catalyzed cycloalumination of α,ω-dienes using Et_3Al.

As a first step, we studied a Cp_2ZrCl_2-catalyzed cycloalumination of α,ω-diolefins upon treatment with Et_3Al. It was found that under these conditions 1,7-octadiene reacted with a two-fold excess of Et_3Al in the presence of 10 mol.% Cp_2ZrCl_2 (40 °C, 4 h) without solvent, giving a mixture of mono- and

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* For Part 45, see Ref. 1.

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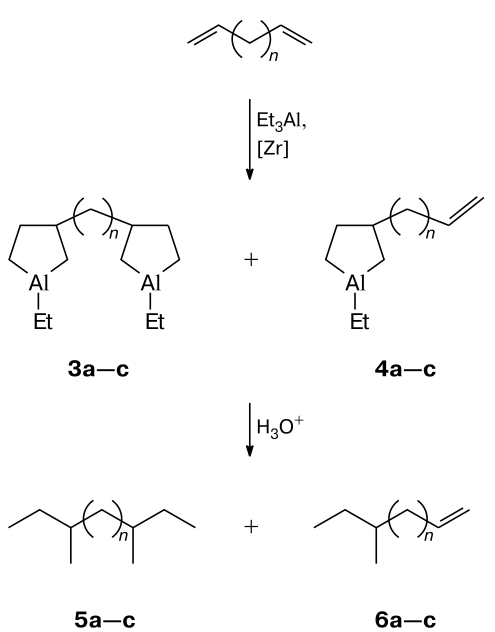
Scheme 2



[Zr] = Cp_2ZrCl_2

n = 2 (**a**), 4 (**b**), 6 (**c**)

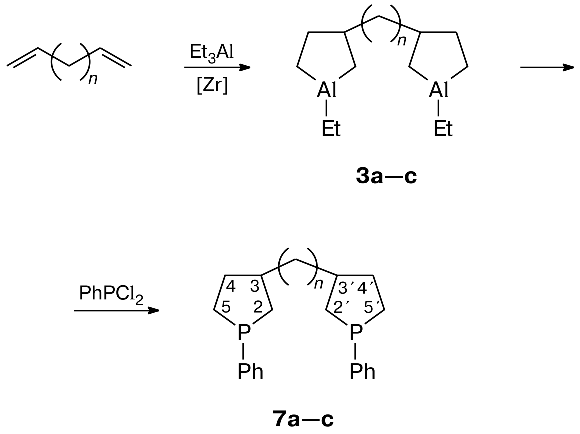
bis(aluminacyclopentanes) (ACP) in 1 : 1 ratio and 89% total yield (Scheme 2).

When the reaction was carried out in toluene, the percentage of bis(aluminacyclopentanes) increased by a factor of 2, with the ratio of mono- and bis(aluminacyclopentanes) being 1 : 2, respectively. An increase in the amount of Et_3Al involved in the reaction also leads to the increase in the percentage of corresponding bis-aluminacyclopentane. Thus, for the ratio of the reaction components 1,7-octadiene : [Al] : [Zr] equal to 1 : 3 : 0.1, in toluene the ratio of mono- and bis(aluminacyclopentanes) was 1 : 3, when the ratio 1,7-octadiene : [Al] : [Zr] was changed to 1 : 6 : 0.1, the content of bis(aluminacyclopentanes) in the reaction mixture increased to 86%. It was shown that cycloalumination of 1,5-hexadiene and 1,9-decadiene under these conditions (α,ω-diene : [Al] : [Zr] = 1 : 6 : 0.1, solvent toluene) with subsequent hydrolysis of the reaction mixture led to the formation of 3,6-dimethyloctane (**5a**) and 3,10-dimethylundecane (**5c**) in 74 and 79% yield, respectively.

Further experiments showed that bis(aluminacyclopentane) **3b**, obtained by cycloalumination of 1,7-octadiene using a six-fold excess of Et_3Al in the presence of 10 mol.% Cp_2ZrCl_2 in toluene, reacted *in situ* with phenyldichlorophosphine with the formation of bisphospholane **7b** as a mixture of *cis*- and *trans*-isomers (1 : 1) in 76% total yield (Scheme 3).

Under the conditions described above, bis-aluminacyclopentanes **3a** and **3c**, obtained by the catalytic cycloalumination of 1,5-hexadiene and 1,9-decadiene, react with phenyldichlorophosphine with the formation of 3,3´-ethane-1,2-bis(1-phenylphospholane) (**7a**) and 3,3´-hexane-1,6-bis(1-phenylphospholane) (**7c**) in 70 and 77% yield, respectively.

Scheme 3

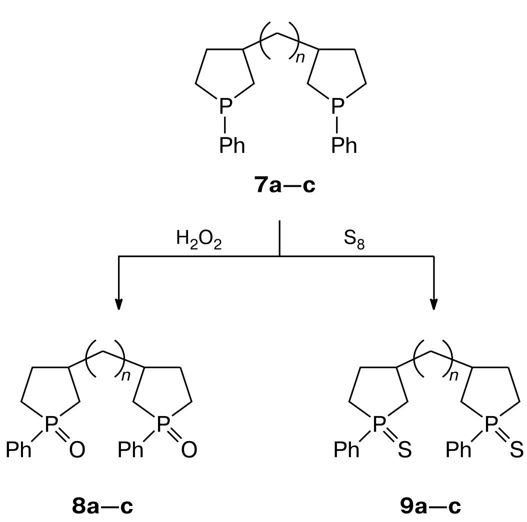


[Zr] = Cp_2ZrCl_2

n = 2 (**a**), 4 (**b**), 6 (**c**)

To reliably establish the structure of bis(phospholanes) **7a—c**, they were involved in the reaction with H_2O_2 in chloroform and with elementary sulfur, which resulted in the formation of bis(phospholane 1-oxides) **8a—c** and bis(phospholane 1-sulfides) **9a,b** in quantitative yields (Scheme 4).

Scheme 4



The structure of new compounds was established using 1D (^1H, ^{13}C, ^{31}P, DEPT 135) and 2D (COSY HH, HSQC, HMBC) homo- and heteronuclear correlation NMR spectroscopy. Thus, the phenyl-substituted bis-

(phospholanes) are characterized by the localization of the ^{31}P NMR signals in the region of δ –14—–13. Because of the presence of a lone pair of electrons (LPE) on the phosphorus atom, the values of the heteronuclear constants for α-carbon atoms of the phospholane ring C(2) and C(5) in the ^{13}C NMR spectra of compounds **7a—c** are $^1J_{\mathrm{P,C}} \approx$ ≈ 10—12 Hz, whereas the corresponding values for bis(phospholane 1-oxides) **8a—c** and bis(phospholane 1-sulfides) **9a—b** increase to ~66—68 Hz. In the ^{31}P NMR spectra of bis(phospholane 1-oxides) **8a—c**, the chemical shift for the phosphorus atom was found in the region of δ ~59, whereas for bis(phospholane 1-sulfides) **9a—b** it was at δ ~57. The spectra of compounds **7a—c**, **8a—c**, **9a—b** exhibit double sets of signals because of the s*yn,anti*-isomerism at the asymmetric phosphorus atom. The ^{13}C NMR spectra of compounds **7a**, **8a**, **9a**, in which the phospholane fragments are bound by two methylene groups, are distinguished by the multiple splitting of signals, obviously, attributed to a mutual influence of the close in space asymmetric centers on the P atoms and restricted rotation around the C—C methylene bonds in the bis(phospholanes) under consideration, binding the phospholane fragments.

In conclusion, we suggested an efficient one-pot synthesis of poorly available bis(phospholanes). The elaborated method is based on the replacement of aluminum atoms in bis-aluminacyclopentanes with the phosphorus atoms, using dichlorophosphines. A possibility of transformation of bis(phospholanes) to bis(phospholane 1-oxides) and bis(phospholane 1-sulfides) was demonstrated. The bis(phospholanes) obtained are of interest as bidentate ligands in metal complex catalysis, monomers in the preparation of phosphorus-containing macrocycles, as well as potential biologically active compounds.

Experimental

Chromatographic analysis was carried out on a Shimadzu GC-9A instrument, a 2000×2-mm column, stationary phase silicon SE-30 (5%) on Chromaton N-AW-HMDS (0.125—0.160 mm), carrier gas helium (30 mL min^{-1}), the temperature was programmed from 50 to 300 °C at the rate of 8 deg min^{-1}. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance-400 spectrometer (100.58 MHz for ^{13}C, 400.00 MHz for ^{1}H, and 161.92 MHz for ^{31}P) in CDCl$_3$. Mass spectra were recorded on a MALDI TOF/TOF Autoflex-III Bruker instrument with 2,5-dihydroxybenzoic acid (2,5-DHB) and α-cyano-4-hydroxycinnamic acids (CHCA) as matrices in the reflective mode with the registration of positive ions. Elemental analysis of the samples was carried out on Karlo Erba, model 1106 elemental analyzer. TLC was carried out on Silufol UV-254 plates in the hexane—ethyl acetate—methanol (5 : 3 : 1) solvent system, visualizing in the iodine vapors. Acros silica gel (0.060—0.200 mm) was used for column chromatography. Product yields were determined using GLC analysis with undecane as an internal standard. The ratio of isomers was determined based on the signal intensities in the ^{1}H and ^{13}C NMR spectra. Reactions with organometallic compounds were carried out under dry argon. Solvents were dried and distilled before use. Phosphines and Cp$_2$ZrCl$_2$ (Acros) and Et$_3$Al (92%) (Sigma-Aldrich) were commercially available.

Synthesis of bis(phospholanes) (general procedure). Toluene (20 mL), Cp$_2$ZrCl$_2$ (0.149 g, 0.5 mmol), α,ω-diolefin (5 mmol), and AlEt$_3$ (5.5 mL, 30 mmol) were sequentially placed into a glass reactor under dry argon at 0 °C with stirring. The temperature was raised to 40 °C, and the reaction mixture was stirred for 4 h and cooled to –5— –10 °C, followed by a dropwise addition of dichlorophenylphosphine (4.1 mL, 30 mmol) and stirring at room temperature for another 30 min. Then, the reaction mixture was treated with saturated aqueous solution of NH$_4$Cl, the reaction products were extracted with diethyl ether and dried with MgSO$_4$. The solvent was evaporated, the volatile fractions were removed by distillation *in vacuo*. The residue was dissolved in some toluene, applied to a short layer of silica gel, and sequentially washed off with hexane and ethyl acetate. The target product was isolated using a hexane—ethyl acetate—methanol solvent mixture (5 : 3 : 1). The solvents were evaporated. All the manipulations were carried out under argon.

3,3´-Ethylene-1,2-bis(1-phenylphospholane) (7a). The yield was 70%. Found (%): C, 74.34; H, 7.92. C$_{22}$H$_{28}$P$_2$. Calculated (%): C, 74.56; H, 7.96. ^{1}H NMR, δ: 1.23—1.60 (m, 16 H, C(2)H$_a$, C(2´)H$_a$, C(4)H$_a$, C(4´)H$_a$, C(6)H$_2$, C(6´)H$_2$); 1.75—1.97 (m, 8 H, C(3)H, C(3´)H, C(5)H$_a$, C(5´)H$_a$); 1.98—2.14 (m, 8 H, C(2)H$_b$, C(2´)H$_b$, C(4)H$_b$, C(4´)H$_b$, C(5)H$_b$, C(5´)H$_b$); 2.15—2.26 (m, 2H, C(5)H$_b$, C(5´)H$_b$); 2.27—2.44 (m, 2H, C(2)H$_b$, C(2´)H$_b$); 7.20—7.26, 7.27—7.35, 7.36—7.44 (all m, 20 H, Ph). ^{13}C NMR, δ: 24.11 (C(5), $^1J_{\mathrm{P,C}}$ = 12.1 Hz); 26.43 (C(5), $^1J_{\mathrm{P,C}}$ = = 10.1 Hz); 26.43 (C(5), $^1J_{\mathrm{P,C}}$ = 10.1 Hz); 32.77, 32.81, 32.83, 32.85, 32.91, 32.94, 32.96, 32.98, 33.06, 33.10, 33.17, 33.21 (C(2)); 33.81, 33.83, 33.85, 33.88 (C(4)); 34.12, 34.16,34.18, 34.20 (C(4)); 34.56, 34.58, 34.62, 34.66, 34.69, 34.81, 34.83, 34.85, 34.87 (C(6)); 41.89, 41.92, 41.93, 41.97, 42.02 (C(3)); 43.07, 43.08, 43.16, 43.17 (C(3)); 126.89 (Ph, $J_{\mathrm{P,C}}$ = 2.0 Hz); 127.91 (Ph, $^3J_{\mathrm{P,C}}$ = 5.0 Hz); 130.00 (Ph, $^2J_{\mathrm{P,C}}$ = 16.1 Hz); 130.02 (Ph, $^2J_{\mathrm{P,C}}$ = 16.1 Hz); 142.25 (br, Ph, $J_{\mathrm{P,C}}$ = 23.1 Hz); 142.71 (br, Ph, $J_{\mathrm{P,C}}$ = 23.1 Hz). ^{31}P NMR, δ: –14.18, –13.56.

3,3´-Tetramethylene-1,4-bis(1-phenylphospholane) (7b). The yield was 76%. Found (%): C, 75.12; H, 8.40. C$_{24}$H$_{32}$P$_2$. Calculated (%): C, 75.37; H, 8.43. ^{1}H NMR, δ: 1.25—1.42 (m, 20 H, C(4)H$_a$, C(4´)H$_a$, C(6)H$_2$, C(6´)H$_2$, C(7)H$_2$, C(7´)H$_2$); 1.42—1.60 (m, 4 H, C(2)H$_a$, C(2´)H$_a$); 1.83—2.01 (m, 8 H, C(3)H, C(3´)H, C(5)H$_a$, C(5´)H$_a$); 2.02—2.18 (m, 8 H, C(2)H$_b$, C(2´)H$_b$, C(4)H$_b$, C(4´)H$_b$, C(5)H$_b$, C(5´)H$_b$); 2.18—2.30 (m, 2 H, C(5)H$_b$, C(5´)H$_b$); 2.33—2.46 (m, 2 H, C(2)H$_b$, C(2´)H$_b$); 7.23—7.28, 7.30—7.36, 7.40—7.47 (all m, 20 H, Ph). ^{13}C NMR, δ: 26.02 (C(5), $^1J_{\mathrm{P,C}}$ = 11.1 Hz); 26.82 (C(5), $^1J_{\mathrm{P,C}}$ = = 9.1 Hz); 28.91, 28.95, 29.02, 29.06 (C(7)); 32.81 (C(2), $^1J_{\mathrm{P,C}}$ = = 12.1 Hz); 33.07 (C(2), $^1J_{\mathrm{P,C}}$ = 11.1 Hz); 33.88 (C(4)); 34.19 (C(4), $^2J_{\mathrm{P,C}}$ = 3.0 Hz); 35.43 (C(6), $^3J_{\mathrm{P,C}}$ = 3.0 Hz); 35.72 (C(6), $^3J_{\mathrm{P,C}}$ = 5.0 Hz); 41.67, 41.69, 41.72, 41.74 (C(3)); 42.87 (C(3)); 126.97, 127.94 (Ph, $^3J_{\mathrm{P,C}}$ = 5.0 Hz); 130.06 (Ph, $^2J_{\mathrm{P,C}}$ = = 16.1 Hz); 130.13 (Ph, $^2J_{\mathrm{P,C}}$ = 16.1 Hz); 142.28 (br, Ph, $J_{\mathrm{P,C}}$ = = 23.1 Hz); 142.72 (br, Ph, $J_{\mathrm{P,C}}$ = 23.1 Hz). ^{31}P NMR, δ: –13.55, –13.18.

3,3´-Hexamethylene-1,6-bis(1-phenylphospholane) (7c). The yield was 77%. Found (%): C, 75.92; H, 8.81. C$_{26}$H$_{36}$P$_2$.

Calculated (%): C, 76.07; H, 8.84. ^{1}H NMR, δ: 1.27—1.47 (m, 28 H, C(4)H$_a$, C(4´)H$_a$, C(6)H$_2$, C(6´)H$_2$, C(7)H$_2$, C(7´)H$_2$, C(8)H$_2$, C(8´)H$_2$); 1.48—1.64 (m, 4 H, C(2)H$_a$, C(2´)H$_a$); 1.83—2.02 (m, 8 H, C(3)H, C(3´)H, C(5)H$_a$, C(5´)H$_a$); 2.03—2.21 (m, 8 H, C(2)H$_b$, C(2´)H$_b$, C(4)H$_b$, C(4´)H$_b$, C(5)H$_b$, C(5´)H$_b$); 2.21—2.33 (m, 2 H, C(5)H$_b$, C(5´)H$_b$); 2.36—2.50 (m, 2 H, C(2)H$_b$, C(2´)H$_b$); 7.25—7.30, 7.33—7.38, 7.40—7.41, 7.43—7.49 (all m, 20 H, Ph). ^{13}C NMR, δ: 27.10 (C(5), $^1J_{\mathrm{P,C}}$ = 11.1 Hz); 27.13 (C(5), $^1J_{\mathrm{P,C}}$ = 11.1 Hz); 27.89 (C(5), $^1J_{\mathrm{P,C}}$ = 9.1 Hz); 27.90 (C(5), $^1J_{\mathrm{P,C}}$ = 9.1 Hz); 29.78, 29.84, 29.89, 29.95 (C(7)); 30.84, 30.91 (C(8)); 34.24 (C(2), $^1J_{\mathrm{P,C}}$ = 12.1 Hz); 34.49 (C(2), $^1J_{\mathrm{P,C}}$ = 11.1 Hz); 35.28 (C(4), $^2J_{\mathrm{P,C}}$ = 3.0 Hz); 35.59 (C(4), $^2J_{\mathrm{P,C}}$ = 4.0 Hz); 36.89, 36.92, 36.96 (C(6)); 37.14, 37.18, 37.23 (C(6)); 43.15 (C(3), $^2J_{\mathrm{P,C}}$ = 4.0 Hz); 43.17 (C(3), $^2J_{\mathrm{P,C}}$ = 4.0 Hz); 44.31, 44. 33, 44.35 (C(3)); 128.31, 129.29 (Ph, $^3J_{\mathrm{P,C}}$ = 5.0 Hz); 131.45 (Ph, $^2J_{\mathrm{P,C}}$ = 15.1 Hz); 131.51 (Ph, $^2J_{\mathrm{P,C}}$ = 16.1 Hz); 143.65 (br, Ph, $^1J_{\mathrm{P,C}}$ = 22.1 Hz); 143.95 (br, Ph, $^1J_{\mathrm{P,C}}$ = 23.1 Hz). ^{31}P NMR, δ: –13.64, -13.23.

Synthesis of bis(phospholane 1-oxides) (general procedure). A 30% aqueous hydrogen peroxide (0.7 mL, 6 mmol) was added slowly dropwise to a solution of bis(phospholane) (3 mmol) synthesized according to the procedure described above in chloroform (8 mL) with vigorous stirring, and the mixture was stirred for 1 h. Then, the mixture was washed with water (3×5 mL), the organic layer was dried with MgSO$_4$. The solvent was evaporated, the residue was subjected to chromatography on silica gel (hexane—ethyl acetate—methanol, 5 : 3 : 1).

3,3´-Ethylene-1,2-bis(1-phenylphospholane 1-oxide) (8a). Found (%): C, 68.11; H, 7.27. $C_{22}H_{28}P_2O_2$. Calculated (%): C, 68.38; H, 7.30. ^{1}H NMR, δ: 1.29—1.65 (m, 12 H, C(2)H$_a$, C(2´)H$_a$, C(4)H$_a$, C(4´)H$_a$, C(6)H$_2$, C(6´)H$_2$); 1.65—1.73 (m, 2 H, C(2)H$_a$, C(2´)H$_a$); 1.73—1.84 (m, 2 H, C(4)H$_a$, C(4´)H$_a$); 1.85—1.95 (m, 2 H, C(5)H$_a$, C(5´)H$_a$); 1.96—2.08 (m, 4 H, C(3)H, C(3´)H, C(5)H$_a$, C(5´)H$_a$); 2.08—2.41 (m, 14 H, C(2)H$_b$, C(2´)H$_b$, C(3)H, C(3´)H, C(4)H$_b$, C(4´)H$_b$, C(5)H$_b$, C(5´)H$_b$); 7.43—7.52, 7.66—7.73 (both m, 20 H, Ph). ^{13}C NMR, δ: 29.36 (C(5), $^1J_{\mathrm{P,C}}$ = 67.4 Hz); 29.39 (C(5), $^1J_{\mathrm{P,C}}$ = 67.4 Hz); 29.44 (C(5), $^1J_{\mathrm{P,C}}$ = 68.4 Hz); 29.46 (C(5), $^1J_{\mathrm{P,C}}$ = 68.4 Hz); 30.44 (C(5), $^1J_{\mathrm{P,C}}$ = 66.4 Hz); 30.84, 30.91, 30.95, 31.01 (C(4)); 32.13, 32.19, 32.26, 32.30 (C(4)); 33.86, 33.99, 34.06, 34.19, 34.25, 34.31, 34.38, 34.45 (C(6)); 35.91 (C(2), $^1J_{\mathrm{P,C}}$ = 67.4 Hz); 35.94 (C(2), $^1J_{\mathrm{P,C}}$ = 67.4 Hz); 35.97 (C(2), $^1J_{\mathrm{P,C}}$ = 66.4 Hz); 36.00 (C(2), $^1J_{\mathrm{P,C}}$ = 66.4 Hz); 36.29 (C(2), $^1J_{\mathrm{P,C}}$ = 68.4 Hz); 36.34 (C(2), $^1J_{\mathrm{P,C}}$ = 68.4 Hz); 36.39 (C(2), $^1J_{\mathrm{P,C}}$ = 68.4 Hz); 36.45 (C(2), $^1J_{\mathrm{P,C}}$ = 68.4 Hz); 38.72, 38.76, 38.80, 38.86, 38.96, 39,05, 30.10, 39.18 (C(3)); 39.75, 39.83, 39.91, 40.09, 40.18 (C(3)); 128.36 (Ph, $^3J_{\mathrm{P,C}}$ = 11.1 Hz); 129.48 (Ph, $^2J_{\mathrm{P,C}}$ = 9.0 Hz); 131.37 (Ph, $^4J_{\mathrm{P,C}}$ = 5.0 Hz); 133.87 (br, Ph, $^1J_{\mathrm{P,C}}$ = 90.5 Hz); 133.95 (br, Ph, $^1J_{\mathrm{P,C}}$ = 89.5 Hz). ^{31}P NMR, δ: 59.15.

3,3´-Tetramethylene-1,4-bis(1-phenylphospholane 1-oxide) (8b). Found (%): C, 69.31; H, 7.75. $C_{24}H_{32}P_2O_2$. Calculated (%): C, 69.55; H, 7.78. ^{1}H NMR, δ: 1.20—1.48 (m, 20 H, C(2)H$_a$, C(2´)H$_a$, C(4)H$_a$, C(4´)H$_a$, C(6)H$_2$, C(6´)H$_2$, C(7)H$_2$, C(7´)H$_2$); 1.52—1.63 (m, 2 H, C(2)H$_a$, C(2´)H$_a$); 1.63—1.75 (m, 2 H, C(4)H$_a$, C(4´)H$_a$); 1.77—1.97 (m, 6 H, C(3)H, C(3´)H, C(5)H$_a$, C(5´)H$_a$); 1.97—2.32 (m, 14 H, C(2)H$_b$, C(2´)H$_b$, C(3)H, C(3´)H, C(4)H$_b$, C(4´)H$_b$, C(5)H$_b$, C(5´)H$_b$); 7.34—7.43, 7.58—7.66 (both m, 20 H, Ph). ^{13}C NMR, δ: 27.41, 27.45, 27.53, 27.56 (C(7)); 29.05 (br, C(5), $^1J_{\mathrm{P,C}}$ = 66.4 Hz); 30.12 (br, C(5), $^1J_{\mathrm{P,C}}$ = 66.4 Hz); 30.45, 30.50, 30.53, 30.56 (C(4)); 31.80 (br, C(4)); 35.49 (br, C(2), $^1J_{\mathrm{P,C}}$ = 67.4 Hz); 35.65, 35.69, 35.77, 35.82 (C(6)); 36.50 (C(2), $^1J_{\mathrm{P,C}}$ = 67.4 Hz); 38.42 (br, C(3)); 39.62 (br, C(3)); 128.26 (Ph, $^3J_{\mathrm{P,C}}$ = 11.1 Hz); 129.41 (Ph, $^2J_{\mathrm{P,C}}$ = 9.0 Hz); 131.25 (Ph, $^4J_{\mathrm{P,C}}$ = 2.0 Hz); 133.92 (br, Ph, $^1J_{\mathrm{P,C}}$ = 91.5 Hz); 134.03 (br, Ph, $^1J_{\mathrm{P,C}}$ = 89.5 Hz). ^{31}P NMR, δ: 59.36. MS (MALDI TOF/TOF), found: *m/z* 413.444 [M – H]$^-$. $C_{24}H_{32}P_2O_2$. Calculated: M = 414.457.

3,3´-Hexamethylene-1,6-bis(1-phenylphospholane 1-oxide) (8c). Found (%): C, 70.44; H, 8.21. $C_{26}H_{36}P_2O_2$. Calculated (%): C, 70.57; H, 8.20. ^{1}H NMR, δ: 1.02—1.45 (m, 28 H, C(2)H$_a$, C(2´)H$_a$, C(4)H$_a$, C(4´)H$_a$, C(6)H$_2$, C(6´)H$_2$, C(7)H$_2$, C(7´)H$_2$, C(8)H$_2$, C(8´)H$_2$); 1.47—1.60 (m, 2 H, C(2)H$_a$, C(2´)H$_a$); 1.60—1.68 (m, 2 H, C(4)H$_a$, C(4´)H$_a$); 1.71—1.80 (m, 2 H, C(5)H$_a$, C(5´)H$_a$); 1.82—2.26 (m, 18 H, C(2)H$_b$, C(2´)H$_b$, C(3)H, C(3´)H, C(4)H$_b$, C(4´)H$_b$, C(5)H$_b$, C(5´)H$_b$); 7.23—7.46, 7.52—7.70 (both m, 20 H, Ph). ^{13}C NMR, δ: 28.68, 28.76 (C(7)); 30.41 (C(5), $^1J_{\mathrm{P,C}}$ = 67.4 Hz); 30.56, 30.75 (C(8)); 31.46 (C(5), $^1J_{\mathrm{P,C}}$ = 67.4 Hz); 31.82, 31.88 C(4)); 33.09, 33.13 (C(4)); 36.80 (C(2), $^1J_{\mathrm{P,C}}$ = 68.4 Hz); 37.14 (br, C(6)); 37.35 (C(2), $^1J_{\mathrm{P,C}}$ = 67.4 Hz); 37.43 (br, C(6)); 39.72, 39.80 (C(3)); 40.96, 41.04 (C(3)); 129.49 (Ph, $^3J_{\mathrm{P,C}}$ = 11.1 Hz); 130.70 (Ph, $^2J_{\mathrm{P,C}}$ = 9.0 Hz); 132.46, 135.37 (br, Ph, $^1J_{\mathrm{P,C}}$ = 89.5 Hz); 135.47 (br, Ph, $^1J_{\mathrm{P,C}}$ = 89.5 Hz). ^{31}P NMR, δ: 59.24. MS (MALDI TOF/TOF), found: *m/z* 441.107 [M – H]$^-$. $C_{26}H_{36}P_2O_2$. Calculated: M = 442.510.

Synthesis of bis(phospholane 1-sulfides) (general procedure). Sulfur (0.192 g, 6 mmol) was added to a solution of bisphospholane (3 mmol) synthesized according to the procedure described above in dichloromethane (10 mL) with cooling. After stirring for 4 h, the reaction mixture was filtered through a short layer of silica gel, the solvent was evaporated.

3,3´-Ethylene-1,2-bis(1-phenylphospholane 1-sulfide) (9a). Found (%): C, 62.93; H, 6.70. $C_{22}H_{28}P_2S_2$. Calculated (%): C, 63.13; H, 6.74. ^{1}H NMR, δ: 1.49—1.71 (m, 10 H, C(4)H$_a$, C(4´)H$_a$, C(6)H$_2$, C(6´)H$_2$); 1.87—2.05 (m, 6 H, C(2)H$_a$, C(2´)H$_a$, C(4)H$_a$, C(4´)H$_a$); 2.14—2.53 (m, 16 H, C(2)H$_b$, C(2´)H$_b$, C(3)H, C(3´)H, C(4)H$_b$, C(4´)H$_b$, C(5)H$_a$, C(5´)H$_a$, C(5)H$_b$, C(5´)H$_b$); 2.58—2.72 (m, 4 H, C(2)H$_b$, C(2´)H$_b$, C(5)H$_b$, C(5´)H$_b$); 7.47—7.56, 7.85—7.93 (both m, 20 H, Ph). ^{13}C NMR, δ: 32.14 (br, C(4)); 33.93 (br, C(4)); 34.16, 34.23, 34.37, 34.49, 35.55 (C(6)); 35.74 (br, C(5), $^1J_{\mathrm{P,C}}$ = 54.3 Hz); 36.61 (br, C(5), $^1J_{\mathrm{P,C}}$ = 53.3 Hz); 39.50, 39.58, 39.66, 39.76, 39.80, 39.84, 39.89, 39.97 (C(3)); 41.36, 41.40, 41.44, 41.46, 41.64, 41.68, 41.71, 41.74 (C(3)); 41.82 (C(2), $^1J_{\mathrm{P,C}}$ = 54.4 Hz); 41.98 (br, C(2), $^1J_{\mathrm{P,C}}$ = 54.4 Hz); 42.47 (C(2), $^1J_{\mathrm{P,C}}$ = 55.4 Hz); 42.60 (br, C(2), $^1J_{\mathrm{P,C}}$ = 55.4 Hz); 128.36 (Ph, $^3J_{\mathrm{P,C}}$ = 12.1 Hz); 129.96 (Ph, $^2J_{\mathrm{P,C}}$ = 10.1 Hz); 131.19 (Ph, J = 3.0 Hz); 133.47 (br, Ph, $^1J_{\mathrm{P,C}}$ = 70.4 Hz); 133.53 (br, Ph, $^1J_{\mathrm{P,C}}$ = 70.4 Hz). ^{31}P NMR, δ: 57.46.

3,3´-Tetramethylene-1,4-bis(1-phenylphospholane 1-sulfide) (9b). Found (%): C, 64.41; H, 7.18. $C_{24}H_{32}P_2S_2$. Calculated (%): C, 64.55; H, 7.22. ^{1}H NMR, δ: 1.29—1.57 (m, 18 H, C(4)H$_a$, C(4´)H$_a$, C(6)H$_2$, C(6´)H$_2$, C(7)H$_2$, C(7´)H$_2$); 1.78—1.98 (m, 6 H, C(2)H$_a$, C(2´)H$_a$, C(4)H$_a$, C(4´)H$_a$); 2.06—2.45 (m, 16 H, C(2)H$_b$, C(2´)H$_b$, C(3)H, C(3´)H, C(4)H$_b$, C(4´)H$_b$, C(5)H$_a$, C(5´)H$_a$, C(5)H$_b$, C(5´)H$_b$); 2.51—2.65 (m, 4 H, C(2)H$_b$, C(2´)H$_b$, C(5)H$_b$, C(5´)H$_b$); 7.41—7.49, 7.80—7.88 (both m, 20 H, Ph). ^{13}C NMR, δ: 28.02 (br, C(7)); 32.14 (C(4), $^2J_{\mathrm{P,C}}$ = 4.0 Hz); 33.89 (C(4), $^2J_{\mathrm{P,C}}$ = 2.0 Hz); 35.47, 35.56, 35.58, 35.67, 35.71, 35.77, 35.83 (C(6)); 35.83 (C(5), $^1J_{\mathrm{P,C}}$ = 53.3 Hz); 36.71 (C(5), $^1J_{\mathrm{P,C}}$ = 53.3 Hz); 39.90, 39.96, 40.02 (C(3)); 41.87 (br, C(3)); 42.23 (C(2), $^1J_{\mathrm{P,C}}$ = 53.3 Hz); 42.58 (C(2), $^1J_{\mathrm{P,C}}$ = 54.3 Hz); 128.30 (Ph, $^3J_{\mathrm{P,C}}$ = 12.1 Hz); 129.93 (Ph, $^2J_{\mathrm{P,C}}$ =

= 10.1 Hz); 131.11 (Ph, J = 3.0 Hz); 133.56 (br, Ph, $^1J_{P,C}$ = 70.4 Hz); 133.62 (br, Ph, $^1J_{P,C}$ = 70.4 Hz). ^{31}P NMR, δ: 57.62.

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