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Facile Synthesis of Hyper-Branched Tetraphosphanes and Tetraphosphane Chalcogenides

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Novel families of hyper-branched tertiary tetraphosphanes, tetraphosphane sulfides, and tetraphosphane selenides were synthesized in 72–97 % yield by treating secondary phosphanes, phosphane sulfides, and phosphane selenides with the tetravinyl ether of pentaerythritol (UV irradiation, room temp. or AIBN, 65 °C).

Introduction

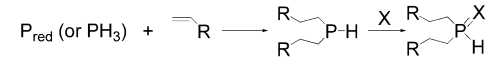
The chemistry of organophosphorus compounds containing two or more phosphane moieties is now rapidly developed. Diphosphanes such as dipamp, duphos, prophos, xyliphos, xantphos, josiphos, biphep, binap, bpe, dppe, and dppf are widely used ligands for organometallic catalysts,[1] anticancer drugs,[2] and fluorescent sensors for heavy metals.[3] Triphosphanes are ligands of catalysts for homogeneous olefin polymerization[4] and hydrogenolysis of benzothiophene.[5] They are also employed in Wittig reactions.[6] Among the triphosphanes, polydentate phosphane arms[7] are applied for the preparation of radiopharmaceutical imaging agents.[8]

Less accessible and hence less understood are the tetraphosphanes and particularly the corresponding tetraphosphane chalcogenides, though some of them are used as pincer ligands, capable of forming dimetallocycled molecules.[7c,9] Also, such dinuclear organometallic complexes attract special attention due to their possible applications as building blocks for new types of catalysts and materials with magnetic, nonlinear optical (NLO), or liquid crystalline properties.[10] Tetrapodal phosphanes, including chiral ones,[9a,9b] act as ligands in Rh-catalyzed asymmetric hydrogenation of arylenamides,[11] highly regioselective isomerization of olefins,[12] alkylation[13] and amination,[14] Mo- or W-catalyzed N–N bond cleavage of organohydrazines,[15] and Heck,[16] Negishi,[17] Sonogashira,[18] and Suzuki[19] couplings and for other important syntheses.[20] Particularly promising are the branched tetraphosphanes with longer and flexible spacers containing other heteroatoms between the phosphane moieties and bulky hydrophobic substituents that make them more adjustable and hemilabile ligands in the metallocomplex formation as well as convenient scaffolds for supramolecular nanostructured materials. Generally, phosphanes and phosphane chalcogenides with bulky organic surrounding are now the subjects of special interest, as they often dramatically change the activity and other properties of organometallic catalysts.[21]

The known syntheses of tetraphosphanes are based on hazardous phosphorus halides and alkali metals, and the procedures are often multistep, laborious, and chemical- and solvent-consuming.[9b,22] Therefore, the search for a more straightforward and atom-economic ("green") route to tertiary tetraphosphanes is justifiable.

Results and Discussion

Here we report a facile, one-pot synthesis of novel families of hyper-branched tetraphosphanes and tetraphosphane chalcogenides by free-radical addition of secondary phosphanes **1** and **2**, phosphane sulfides **3** and **4**, and phosphane selenides **5** and **6** to the tetravinyl ether of pentaerythritol **7**. The secondary phosphanes and phosphane chalcogenides belong to the still-rare classes of phosphorus hydrides that contain both aliphatic chain $(CH_2)_2$ and aromatic moieties in the bulky substituents. Recently, they became available by a one-pot synthesis from red phosphorus or PH_3 and styrenes[23] (Scheme 1).



R = Ph, 4-*t*BuC$_6$H$_4$; X = S, Se

Scheme 1. Synthesis of bis(2-arylethyl)phosphanes and phosphanes chalcogenides.

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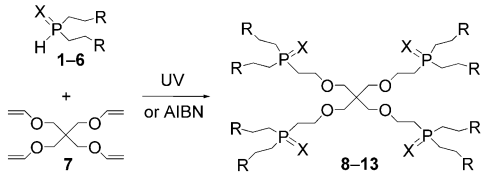
The choice of tetravinyl ether **7** is not occasional. This ether is produced by industrially feasible direct vinylation of pentaerythritol with acetylene.[24]

It is known that divinyl ethers of glycols, when treated with PH-addends under free-radical conditions, do not give the expected diadducts, but undergo cyclization and/or telomerization.[25] Therefore, it might be expected that the addition of secondary phosphanes **1** and **2**, phosphane sulfides **3** and **4**, and phosphane selenides **5** and **6** to tetravinyl ether **7**, which contains two 1,3-glycol divinyl ether moieties, will be complicated by similar cycloadditions, telomerization, oligomerization, and cross-linking reactions.

Meanwhile, we found the conditions under which the above side reactions practically do not occur. To our surprise, when addends **1**–**6** and tetravinyl ether **7** (molar ratio 4:1) were allowed to react under UV irradiation (method A) or in the presence of AIBN at 65 °C (method B), tetraadducts **8**–**13** were readily formed in 72–97% yields (Table 1). They were easily purified by passing the reaction mixture through a thin layer of alumina.

Table 1. Exhaustive addition of phosphorus hydrides **1**–**6** to tetravinyl ether **7**.



PH-addend	R	X	Method[a]/ Time [h]	Product[b]	Yield[c] [%]
1	Ph	none	A/5 B/8	**8**	90 (94) 90 (98)
2	4-*t*BuC$_6$H$_4$	none	A/5 B/7	**9**	88 (90) 80 (85)
3	Ph	S	A/3 B/10	**10**	97 (99) 97 (99)
4	4-*t*BuC$_6$H$_4$	S	A/3	**11**	75 (96)
5	Ph	Se	A/4 B/14	**12**	75 (95) 35 (45)
6	4-*t*BuC$_6$H$_4$	Se	A/4	**13**	72 (82)

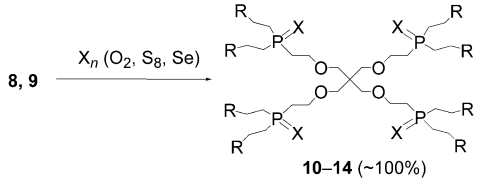
[a] Standard reaction conditions: molar ratio **1**–**6**/**7** = 4:1. Experiments were carried out under an inert atmosphere (argon). Method A: UV, room temp., dioxane. Method B: AIBN (1.5–2 wt.-% of the reactants' mass), 65 °C, dioxane. [b] The crude product was purified by column chromatography on alumina (Et_2O/hexane). [c] Isolated yield (NMR yield parentheses).

As seen from Table 1, the UV-initiated addition (method A) was preferred over AIBN-initiated addition (method B): the yields of tetraadducts were always higher and the reaction times were shorter. Besides, in the case of method B, the reaction with phosphane selenide **5** was accompanied by the precipitation of elemental selenium, which sharply decreased the yield of adduct **12** (35%) apparently as a result of the elevated temperature (65 °C). Generally, as we observed here (Table 1), for phosphane selenides the adduct yields are about 20% lower than with the corresponding phosphanes and phosphane sulfides, obviously owing to selenium extrusion.

Amazingly, incomplete addition products (mono-, di-, and triadducts) were not discernible (^{1}H, ^{13}C, ^{31}P NMR) in the crude product. This implies that incomplete adducts, despite the growing steric hindrance in the vicinity of the remaining vinyl groups, are almost as active towards the addends as starting ether **7**.

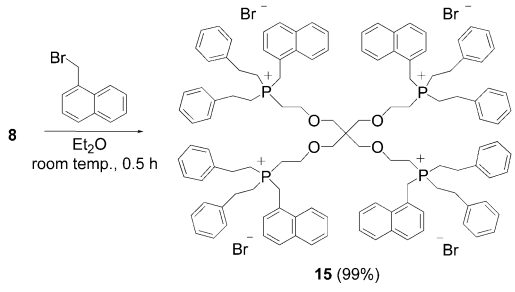
Interestingly, the corresponding reactions with secondary phosphane oxides and tetravinyl ether **7** gave practically no adducts under the conditions of both methods (A and B). This is in agreement with literature data that lower activity of secondary phosphane oxides in radical additions is often observed.[26]

To check the reactivity of the phosphane centers in the hyper-branched surroundings of the adducts we used tetraphosphanes **8** and **9** in typical phosphane reactions. It was found that tetraphosphanes **8** and **9** were smoothly oxidized by air (room temp., 40 h, acetone) or elemental sulfur and selenium (50 °C, 1 h, toluene) to quantitatively give the corresponding tetraphoshane chalcogenides **10**–**14** (Scheme 2).



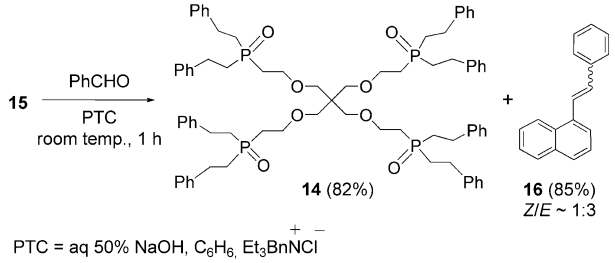
Scheme 2. Oxidation of tetraphosphanes **8** and **9**.

It is astounding that all four phosphane centers in tetraphosphane **8** are easily accessible, even for bulky electrophiles such as 1-(bromomethyl)naphthalene. The corresponding tetraphosponium salt **15** is formed in quantitative yield under mild conditions (room temp., 0.5 h, Et_2O) (Scheme 3).



Scheme 3. Exhaustive reaction of tetraphosphane **8** with 1-(bromomethyl)naphthalene.

Moreover, this salt is capable of being efficiently involved in Wittig–Horner-type reactions. For example, when salt **15** was treated with benzenecarbaldehyde (aq. 50% NaOH, benzene, EtBnNCl, room temp., 1 h), expected stilbenoid **16** (85%) and tetraphosphane oxide **14** (82%) were formed (Scheme 4).



Scheme 4. Wittig–Horner reaction between salt **15** and benzenecarbaldehyde.

Conclusions

To conclude, a facile synthesis of novel families of hyperbranched tetraphosphanes and tetraphosphane chalcogenides was accomplished by using free-radical addition of secondary phosphanes and phosphane chalcogenides to the tetravinyl ether of pentaerythritol. These specific tetraphosphanes and tetraphosphane chalcogenides of dendrimer-like structure thus synthesized are promising pincer ligands for novel organometallic catalysts as well as reagents for organic synthesis and building blocks to design new types of supramolecular architectures with special magnetic, NLO, or liquid crystalline properties.

Experimental Section

General: IR spectra were obtained with a Bruker IFS-25 spectrometer (400–4000 cm^{-1}, KBr pellets). ^1H (400.13 MHz), ^{13}C NMR (101.6 MHz), and ^{31}P NMR (161.98 MHz) spectra were recorded with a Bruker DPX 400 instrument in $CDCl_3$ solutions and referenced to internal hexamethyldisiloxane (^1H NMR) and external 85% H_3PO_4 (^{31}P NMR). Phosphanes **1** and **2** were prepared from red phosphorus and styrenes.[23a,23c] Phosphane chalcogenides **3**–**6** were prepared by reaction of phosphanes **1** and **2** with elemental sulfur or selenium.[23c,27] Ether **7** was synthesized from pentaerythritol and acetylene in the system KOH/DMSO.[24]

General Procedures for the Preparation of Tetraphosphanes 8 and 9 and Tetraphosphane Chalcogenides 10–13

Method A: A solution of PH-addend **1**–**6** (0.4 mmol) and ether **7** (0.1 mmol) in dioxane (0.5 mL) was irradiated (200-W Hg arc lamp) in a quartz ampoule (reaction times are given in Table 1).

Method B: A solution of PH-addend **1**–**6** (0.6 mmol) and ether **7** (0.15 mmol) in dioxane (5 mL) in the presence of AIBN (1–2 wt.-% of the total mass of reactants) was stirred at 65 °C in a sealed ampoule (reaction times are given in Table 1).

The reaction was monitored by ^{31}P NMR spectroscopy by disappearance of the signal of the starting PH-addends (the –70 to –68 region for phosphanes **1** and **2**; the 2 to 23 interval for phosphane chalcogenides **3**–**6**) and appearance of a new resonance in the –32 to –30 and 36 to 49 regions, corresponding to tertiary tetraphosphanes **8** and **9** and tetraphosphane chalcogenides **10**–**13**. Crude products **8**–**13** were purified by column chromatography (Al_2O_3; hexane/diethyl ether, 1:1). All steps of the experiments were carried out under an atmosphere of argon.

Tetra{2-[bis(2-phenethyl)phosphanyl]ethoxy}neopentane (8): Colorless oil. Yield: 109 mg, 90% (Methods A and B). IR: $\tilde{\nu}$ = 3105, 3083, 3061, 3025, 3000 [*ν*=CH(Ph)], 2929, 2892, 2862, 2880 (νCH), 1603, 1583, 1495 [νC=C(Ph)], 1452 (δCH_2), 1365, 1201, 1179, 1166 [δCH(Ph)], 1099 (νC–O), 1030, 1004 [δCH(Ph)], 754 [νP–C, δCH(Ph)], 698 [δCH(Ph)], 495 (δCPC) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.22–7.13 (m, 40 H, Ph), 3.53–3.47 (m, 8 H, OC$H_2$$CH_2$P), 3.37 (s, 8 H, CH_2C), 2.72–2.66 (m, 16 H, CH_2Ph), 1.74–1.70 (m, 24 H, CH_2P) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 142.94 (d, $^3J_{P,C}$ = 11.1 Hz, C-*i*), 128.53 (C-*m*), 128.20 (C-*o*), 126.05 (C-*p*), 69.95 (*C*H_2C), 69.46 (d, $^2J_{P,C}$ = 19.4 Hz, CH_2O), 45.36 (*C*CH_2), 32.34 (d, $^2J_{P,C}$ = 15.9 Hz, CH_2Ph), 29.37 (d, $^1J_{P,C}$ = 14.0 Hz, PCH_2), 27.57 (d, $^1J_{P,C}$ = 14.3 Hz, P*C*$H_2$$CH_2$O) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.77 ppm. $C_{77}H_{96}O_4P_4$ (1209.48): calcd. C 76.46, H 8.00, P 10.24; found C 76.65, H 8.02, P 9.98.

Tetra(2-{bis[2-(4-*tert*-butyl)phenethyl]phosphanyl}ethoxy)neopentane (9): Colorless oil. Yield: 146 mg, 88% (Method A); 199 mg, 80% (Method B). IR: $\tilde{\nu}$ = 3091, 3054, 3022 [ν=CH(Ph)], 2960, 2926, 2906, 2868 (νCH), 1613, 1516 [νC=C(Ph)], 1463, 1411, 1393 (δCH_2), 1364 (δCH_3), 1107 (νC–O), 817 [δCH(Ph)], 562 (δCPC) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.29–7.08 (m, 32 H, C_6H_4), 3.68 (m, 8 H, OC$H_2$$CH_2$P), 3.53 and 3.42 (m, 8 H, CH_2C), 2.68 (m, 16 H, C$H_2$$C_6H_4$), 1.74–1.72 (m, 24 H, CH_2P), 1.28 (s, 64 H, Me) ppm. ^{13}C NMR (101.6 MHz, $CDCl_3$): δ = 148.83 (C-*p*), 139.78 (d, $^3J_{P,C}$ = 10.1 Hz, C-*i*), 127.76 (C-*m*), 125.32 (C-*o*), 69.43 (*C*H_2C), 67.09 (CH_2O), 45.01 (*C*CH_2), 34.35 (CMe), 32.18 (d, $^1J_{P,C}$ = 17.0 Hz, CH_2Ph), 31.39 (Me), 29.22 (d, $^2J_{P,C}$ = 11.6 Hz, CH_2P), 27.51 (P*C*$H_2$$CH_2$O) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.84 ppm. $C_{109}H_{160}O_4P_4$ (1658.33): calcd. C 78.94, H 9.72, P 7.47; found C 78.65, H 9.52, P 7.68.

Tetra{2-[bis(2-phenethyl)phosphorothioyl]ethoxy}neopentane (10): Light-yellow oil. Yield: 130 mg, 97% (Method A); 191 mg, 95% (Method B). IR: $\tilde{\nu}$ = 3106, 3084, 3060, 3025, 3001 [=CH(Ph)], 2918, 2904, 2863 (=CH), 1602, 1583, 1496 [C=C(Ph)], 1453, 1401 (δCH_2), 1099 (C-O), 752, 697 [δCH(Ph)], 598 (P=S) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.26–7.16 (m, 40 H, Ph), 3.54–3.50 (m, 8 H, CH_2O), 3.14 (s, 8 H, CH_2C), 2.90–2.89 (m, 16 H, CH_2Ph), 2.14–2.13 and 1.99–1.98 (m, 24 H, CH_2P) ppm. ^{13}C NMR (101.6 MHz, $CDCl_3$): δ = 140.43 (d, $^3J_{P,C}$ = 19.6 Hz, C-*i*), 128.43 (C-*m*), 127.97 (C-*o*), 126.30 (C-*p*), 69.61 (*C*H_2C), 65.21 (CH_2O), 44.70 (*C*CH_2), 33.18 (d, $^1J_{P,C}$ = 54.8 Hz, CH_2P), 30.95 (d, $^1J_{P,C}$ = 55.2 Hz, P*C*$H_2$$CH_2$O), 28.33 ($CH_2$Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 48.35 ppm. $C_{77}H_{96}O_4P_4S_4$ (1337.74): calcd. C 69.13, H 7.23, P 9.26, S 9.59; found C 69.35, H 7.32, P 8.98, S 9.35.

Tetra(2-{bis[2-(4-*tert*-butyl)phenethyl]phosphorothioyl}ethoxy)neopentane (11): Colorless powder. Yield: 134 mg, 75% (Method A). M.p. 159–160 °C (hexane). IR (KBr): $\tilde{\nu}$ = 3091, 3055, 3024 [=CH(C_6H_4)], 2961, 2905, 2855 (=CH), 1626, 1515 [C=C(C_6H_4)], 1463, 1393 (δCH_2), 1364, 1269 (δCH_3), 1107 (C–O), 818 [δCH(C_6H_4)], 565, 552 (sh., P=S) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.28–7.22 and 7.10–7.09 (m, 32 H, C_6H_4), 3.70–3.66 (m, 8 H, CH_2O), 3.31 (m, 8 H, CH_2C), 2.86 (m, 16 H, C$H_2$$C_6H_4$), 2.12–2.05 (m, 24 H, CH_2P), 1.26 (s, 72 H, Me) ppm. ^{13}C NMR (101.6 MHz, $CDCl_3$): δ = 149.46 (C-*p*), 137.42 (d, $^3J_{P,C}$ = 20.2 Hz, C-*i*), 127.91 (C-*m*), 125.55 (C-*o*), 70.63 (*C*H_2C), 65.58 (CH_2O), 45.22 (*C*CH_2), 34.41 (*C*Me), 33.66 (d, $^1J_{P,C}$ = 50.7 Hz, CH_2P), 31.38 (Me), 30.75 (d, $^1J_{P,C}$ = 53.9 Hz, P*C*$H_2$$CH_2$O), 27.99 (*C*$H_2$$C_6H_4$) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 47.80 ppm. $C_{109}H_{160}O_4P_4S_4$ (1786.59): calcd. C 73.28, H 9.03, P 6.93, S 7.18; found C 73.30, H 9.02, P 6.80, S 7.16.

Tetra{2-[bis(2-phenethyl)phosphoroselenoyl]ethoxy}neopentane (12): Light-yellow oil. Yield: 114 mg, 75% (Method A); 80 mg, 35% (Method B). IR: $\tilde{\nu}$ = 3103, 3083, 3059, 3024, 3000 [=CH(Ph)], 2897,

2904, 2863 (=CH), 1602, 1583, 1495 [C=C(Ph)], 1453, 1400 (δCH_2), 1099 (C–O) 750, 697 [δCH(Ph)], 573 (P=Se) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.24–7.18 (m, 40 H, Ph), 3.62–3.48 (m, 8 H, CH_2O), 3.23 and 3.13 (m, 8 H, CH_2C), 2.91–2.89 (m, 16 H, CH_2Ph), 2.27–2.26 (m, 16 H, CH_2P), 2.09–2.08 (m, 8 H, PCH_2CH_2O) ppm. ^{13}C NMR (101.6 MHz, $CDCl_3$): δ = 140.50 (d, $^3J_{P,C}$ = 14.5 Hz, C-*i*), 128.85 (C-*m*), 128.35 (C-*o*), 126.67 (C-*p*), 69.79 (CH_2C), 66.27 (CH_2O), 45.28 (CCH_2), 33.23 (d, $^1J_{P,C}$ = 43.2 Hz, CH_2P), 30.71 (d, $^1J_{P,C}$ = 49.2 Hz, PCH_2CH_2O), 29.44 (CH_2Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 36.85 ppm. $C_{77}H_{96}O_4P_4Se_4$ (1525.32): calcd. C 60.63, H 6.34, P 8.12, Se 20.71; found C 60.45, H 6.23, P 8.18, Se 20.35.

Tetra(2-{bis[2-(4-*tert*-butyl)phenethyl]phosphoroselenoyl}ethoxy)neopentane (13): Colorless powder. Yield: 142 mg, 72% (Method A). M.p. 159–160 °C (hexane). IR (KBr): $\tilde{\nu}$ = 3091, 3054, 3021 [=CH(C_6H_4)], 2961, 2904, 2865 (=CH), 1626, 1516 [C=C(C_6H_4)], 1463, 1394 (δCH_2), 1363, 1268 (δCH_3), 1107, (C–O), 818 [δCH(C_6H_4)], 564, 551 (sh., P=Se) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.27–7.10 (m, 32 H, C_6H_4), 3.80–3.60 (m, 8 H, CH_2O), 3.47–3.23 (m, 8 H, CH_2C), 2.87 (m, 16 H, $CH_2C_6H_4$), 2.24 (m, 24 H, CH_2P), 1.27 (s, 72 H, Me) ppm. ^{13}C NMR (101.6 MHz, $CDCl_3$): δ = 149.46 (C-*p*), 137.20 (d, $^3J_{P,C}$ = 14.5 Hz, C-*i*), 127.92 (C-*m*), 125.56 (C-*o*), 70.59 (CH_2C), 66.44 (CH_2O), 45.08 (CCH_2), 34.38 (CMe), 33.27 (d, $^1J_{P,C}$ = 45.2 Hz, CH_2P), 31.34 (Me), 29.82 (d, $^1J_{P,C}$ = 37.9 Hz, PCH_2CH_2O), 28.82 ($CH_2C_6H_4$) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 37.46 ppm. $C_{109}H_{160}O_4P_4Se_4$ (1974.17): calcd. C 66.31, H 8.17, P 6.28, Se 16.0; found C 66.45, H 8.23, P 6.18, Se 16.35.

Synthesis of Salt 15: A solution of phosphane **8** (420 mg, 0.35 mmol) and 1-(bromomethyl)naphthalene (310 mg, 1.4 mmol) in diethyl ether (5 mL) was stirred under an argon atmosphere at 23–25 °C for 0.5 h. The solvent was removed in vacuo, and the residue was precipitated from $CHCl_3$ (1 mL) in pentane (7 mL) to give phosphonium bromide **15** (725 mg, 99%).

Tetra{2-[bis(2-phenethyl)(1-naphthylmethyl)phosphonio]ethoxy}neopentane Tetrabromide (15): Colorless powder. Yield: 725 mg, 99%. M.p. 109–110 °C. IR (KBr): $\tilde{\nu}$ = 3006, 3085, 3058, 3027, 3000 [=CH(Ph)], 2921, 2872 (=CH), 1602, 1510, 1499 [C=C(Ph)], 1455, 1396 (δCH_2), 1106 (C–O), 810, 778, 749, 670 [δCH(Ph)] cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 8.45–8.43 and 7.86–7.00 (m, 68 H, naph, Ph), 4.80–4.76 (d, $^1J_{P,H}$ = 18.8 Hz, 8 H, CH_2naph), 3.89–3.85 (m, 8 H, CH_2O), 3.55 (m, 8 H, CH_2C), 2.92 (m, 24 H, PCH_2CH_2O, CH_2Ph), 2.51 (m, 16 H, CH_2P) ppm. ^{13}C NMR (101.6 MHz, $CDCl_3$): δ = 138.62 (d, $^3J_{P,C}$ = 13.3 Hz, C-*i*), 134.00 (C^2), 131.99 (C^{11}), 129.45 (C^6), 129.14 (C^{10}), 128.69 (C-*m*), 128.28 (C-*o*), 127.67 (C^3), 126.89 (C-*p*), 126.59 (C^5), 125.62 (C^8), 125.14 ($C^{4,7}$), 124.08 (C^9), 70.29 (CH_2C), 64.14 (CH_2O), 44.91 (CCH_2), 27.58 (CH_2Ph), 25.01 (d, $^1J_{P,C}$ = 45.2 Hz, CH_2naph), 21.66 (d, $^1J_{P,C}$ = 38.7 Hz, CH_2P), 21.11 (d, $^1J_{P,C}$ = 50.0 Hz, PCH_2CH_2O) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 31.99 ppm. $C_{121}H_{132}Br_4O_4P_4$ (2093.85): calcd. C 69.41, H 6.35, Br 15.26, P 5.92; found C 69.53, H 6.32, Br 15.16, P 5.98.

Wittig–Horner Reaction: A mixture of tetrabromide **15** (220 mg, 0.105 mmol), benzenecarbaldehyde (446 mg, 0.42 mmol), $Et_3BzN^+Cl^-$ (≈0.001 mg), NaOH (700 mg), benzene (5.0 mL), and H_2O (2 mL) was stirred vigorously under an argon atmosphere at 23–25 °C for 1 h. The organic part was separated, washed with water (3 × 0.5 mL), and dried with K_2CO_3. Benzene was removed in vacuo, and the residue was dissolved in $CHCl_3$ (1 mL) and precipitated with ether (10 mL). The sediment (colorless oil) was separated and dried in vacuo to furnish phosphane oxide **14** (110 mg, 82%). Removal of chloroform and ether from the extract gave 2-phenylethenylnaphthalene **16** (*Z*/*E* = 1:4, 82 mg, 85%) as a colorless oil. Spectral characteristics of **16** correspond to the reference data.[28]

Tetra{2-[bis(2-phenethyl)phosphoryl]ethoxy}neopentane (14): Colorless oil. Yield: 110 mg, 82%. IR: $\tilde{\nu}$ = 3065, 3026 [=CH(Ph)], 2950, 2871 (CH), 1604, 1563, 1493 [C=C(Ph)], 1452 (δCH_2), 1403, 1369, 1220 [δCH(Ph)], 1100 (CO), 1158 (P=O), 995 [δCH(Ph)], 754 [P–C, δCH(Ph)], 702 [δCH(Ph)], 493 (δCPC) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.26–7.14 (m, 40 H, Ph), 3.51–3.44 (m, 8 H, CH_2O), 3.21 (m, 8 H, CH_2C), 2.89–2.83 (m, 16 H, CH_2Ph), 2.02–1.83 (m, 24 H, CH_2P) ppm. ^{13}C NMR (101.6 MHz, $CDCl_3$): δ = 140.40 (d, $^3J_{P,C}$ = 23.1 Hz, C-*i*), 128.30 (C-*m*), 127.59 (C-*o*), 126.12 (C-*p*), 69.52 (CH_2C), 64.47 (CH_2O), 44.48 (CCH_2), 30.35 (d, $^1J_{P,C}$ = 68.8 Hz, CH_2P), 28.43 (d, $^1J_{P,C}$ = 68.8 Hz, PCH_2CH_2O), 27.19 (CH_2Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 46.90 ppm. $C_{77}H_{96}O_8P_4$ (1273.48): calcd. C 72.62, H 7.60, P 9.73; found C 72.65, H 7.56, P 9.68.

Supporting Information (see footnote on the first page of this article): Characterization data of **8**–**13** and copies of the ^1H, ^{13}C, and ^{31}P NMR spectra of new compounds.

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