Synthesis of Functional Tripodal Phosphines with Amino and Ether Groups by the Hydrophosphination of Trivinyl Ethers with Secondary Phosphines

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Abstract: A one-pot, atom-economic, metal- and halogen-free synthesis of functional triphosphines with nitrogen and (or) oxygen atoms as additional weaker coordinating sites (new hemilabile ligands) through exhaustive addition of secondary phosphines to available trivinyl ethers of aminotriols and triols has been developed. The reaction proceeds under free-radical conditions (UV irradiation or AIBN, with 3:1 reactant molar ratio) to give chemo- and regioselectively anti-Markovnikov triadducts to all three vinyloxy groups in good to excellent yields.

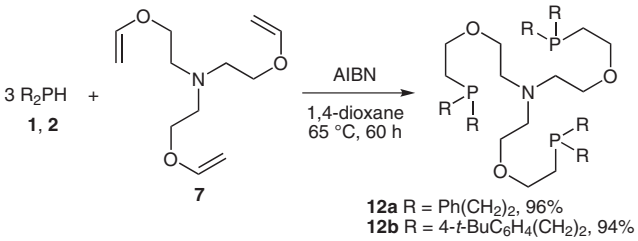
Key words: addition, alkenes, radical reaction, ligands, phosphorylation

Tripodal multidentate phosphines exhibit rich and diverse coordination chemistry and, as such, they have found an integral place in inorganic and organometallic chemistry.[1–3] Among these phosphines, 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) is a versatile ligand that can be used with transition metals in a variety of oxidation states.[2] Its complexes have been applied in the area of catalysis, for example in hydrogenation of esters,[4] alkenes[5] and other substrates.[6,7] Tripodal terdentate phosphines act as ligands in Ru-catalyzed C–O bond cleavage in lignin[8] and dehydrogenation of formic acid (as potential hydrogen storage compound).[9] In addition, these ligands are found to be active stabilizers for noble metal nanoparticles having a small core diameter (< 4 nm) and narrow size distribution.[10,11] Such nanoparticles show good to excellent catalytic activities for various synthetically important C–C coupling reactions, namely Suzuki, Heck, and Sonogashira, which are widely used in organic synthesis.[11]

Over the last decades, research interest has increasingly focused on polydentate ligands with phosphorus and other donor atoms such as oxygen and nitrogen (P,O-,[12] P,N-,[13] and P,N,O-ligands[14]). In these compounds, the metal center is bounded by phosphorus atom, and weak interactions with the other heteroatom (N or O) ensures additional stabilization of the complexes (hemilabile ligands).[14] However, the synthesis of such polydentate ligands presents some difficulties. To our knowledge, functional triphosphines containing amino and ether groups have not been yet described. One of the most straightforward and promising strategies through which to achieve the synthesis of these ligands might be the exhaustive addition of secondary phosphines to trivinyl ethers of triols.

Here, we report on the radical addition of available secondary phosphines **1**–**6**, which are easily prepared from elemental phosphorus and aryl(or hetaryl)ethenes,[15] to trivinyl ethers of aminotriols **7**, **8** and triols **9**–**11**. These trivinyl ethers were chosen because they are efficiently prepared by vinylation of the corresponding triols with acetylene in superbases of the type KOH/dimethyl sulfoxide (DMSO).[16]

We have found that bis(aralkyl)phosphines **1** and **2** can be exhaustively added to *N*,*N*,*N*-tris[2-(vinyloxy)ethyl]amine (**7**) in the presence of a radical initiator (AIBN, 65 °C, 60 h, 1,4-dioxane, argon, the 3:1 reactant molar ratio) in an anti-Markovnikov manner to afford triphosphines **12a** and **12b**, respectively, with amino and ether groups, in almost quantitative yields (Scheme 1). Notably, the reaction proceeds chemo- and regioselectively, and none of the corresponding mono-, di- or Markovnikov adducts, or cyclization or telomerization products were observed (^{1}H and ^{31}P NMR analysis) under these conditions.



Scheme 1 Exhaustive free-radical addition of secondary phosphines **1** and **2** to *N*,*N*,*N*-tris[2-(vinyloxy)ethyl]amine (**7**)

Under similar conditions (AIBN, 75 °C, 72 h, benzene, argon), bis(aralkyl)phosphines **1** and **3** react with the trivinyl ether of aminotriol **8** at a 3:1 molar ratio to give anti-Markovnikov triadducts **13a** and **13b**, respectively, in 92 and 86% yield (Scheme 2).

The efficacy and generality of the elaborated strategy was confirmed by the synthesis of functional triphosphines with ether groups by the exhaustive free-radical addition of secondary phosphines to trivinyl ethers of triols **9**–**11**. Indeed, the free-radical initiation (UV irradiation or

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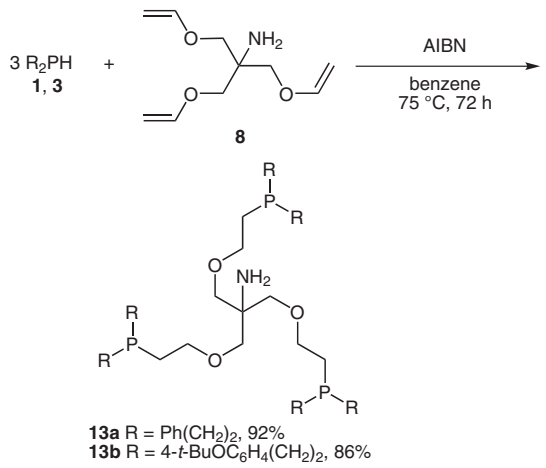


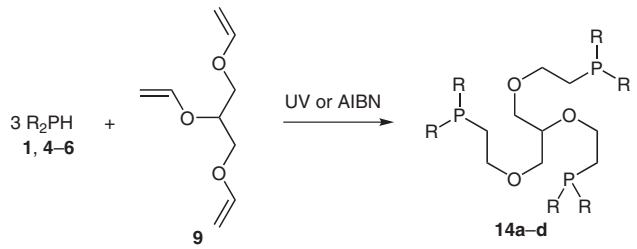
Scheme 2 Synthesis of triphosphines with NH_2 and ether groups from secondary phosphines **1** and **3**, and the trivinyl ether of aminotriol **8**

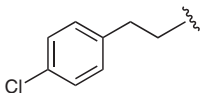
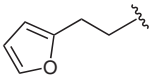
AIBN) proved to be effective for the full hydrophosphination of glycerol trivinyl ether **9** with a diverse range of secondary phosphines **1** and **4**–**6**, bearing aralkyl, hetaralkyl, and phenyl substituents, to afford anti-Markovnikov triadducts **14a**–**d** in 80–90% yield (Table 1). The reaction time was 9 hours in the case of UV irradiation (Table 1, entries 1 and 3), and 24–53 hours when AIBN was employed (Table 1, entries 2, 4, and 5).

Triphosphines **15a**–**d** with ether groups have likewise been synthesized in high yields by the reaction of trivinyl ethers of triols (**10** or **11**) with bis(aralkyl)phosphines **1** or **3** in the presence of AIBN (Table 2). A preliminary application of this strategy was reported with examples of divinyl ethers of diols[17] and the tetravinyl ether of pentaerithritol.[18]

The high chemo- and regioselectivity of the hydrophosphination found deserves special consideration. Indeed, as noted above, neither expected cyclizations nor oligomerizations were discernible in this hydrophosphination. However, in contrast to these results, it was reported that free-radical hydrophosphorylation of divinyl ethers of dioles with dialkylphosphites under similar conditions (AIBN, 67–70 °C) resulted in the formation of cyclic products (ca. 50% yield), and macrocyclic and linear phosphorus-containing telomeres.[19] Furthermore,[20] free-radical addition of diethyl thiophosphite to diallyl ether (AIBN, 60 °C, THF) proceeds as exclusive cyclization to yield *O*,*O*-diethyl (4-methyltetrahydro-3-furanyl)methylthiophosphonate. This occurs because initial intermediate radical-adducts preferentially attack the neighboring double bonds instead of abstracting a hydrogen radical from the phosphite molecule. The astonishing full inhibition of the side cyclization and telomerization reactions during the hydrophosphination with secondary phosphines may be rationalized in terms of the spin exchange between the radical center and lone electron pair of the phosphine moiety in the initial intermediate radical-adduct **A** (Scheme 3). Such a through-space interaction may preclude attack of the intermediate **A** on the neighboring double bonds, instead of abstracting the hydrogen atom from the P–H bond. Since dialkylphosphites do not have the lone electron pair on the phosphorus atom, they cannot participate in the above spin-exchange. Additionally, the P–H bond homolization energy in dialkylphosphites is much higher than that of phosphines (365 and 319 kJ/mol, respectively).[21] Therefore, in case of hydrophosphination, transfer

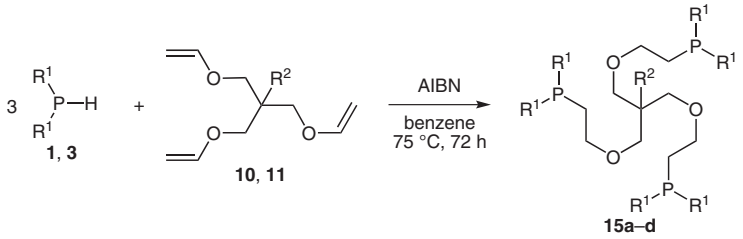
Table 1 Exhaustive Free-Radical Addition of Secondary Phosphines **1** and **4**–**6** to the Trivinyl Ether of Glycerol **9**[a]

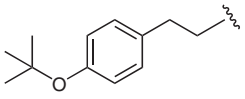
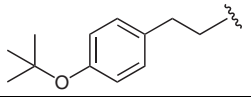


Entry	Phosphine	R	Initiator	Solvent	Temp (°C)	Time (h)	**14**	Yield (%)[b]
1	**1**	$(CH_2)_2Ph$	UV	1,4-dioxane	40[c]	9	**14a**	90
2	**1**	$(CH_2)_2Ph$	AIBN	none	65	24	**14a**	87
3	**4**		UV	1,4-dioxane	40[c]	9	**14b**	88
4	**5**		AIBN	none	65	53	**14c**	80
5	**6**	Ph	AIBN	none	65	48	**14d**	90

[a] Reaction conditions: phosphine (3 equiv.), **9** (1 equiv), argon, UV irradiation (200 W Hg arc lamp) or AIBN (2 wt% of total reactant mass).
[b] Isolated yield.
[c] Heating caused by UV lamp.

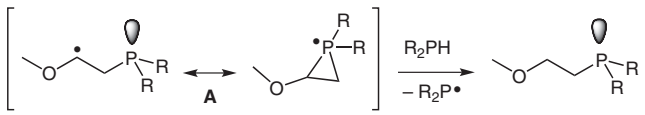
Table 2 Exhaustive Free-Radical Addition of Secondary Phosphines **1** and **3** to Trivinyl Ethers **10** and **11**[a]



Entry	Phosphine	R^1	Trivinyl ether	R^2	Adduct	Yield (%)[b]
1	**1**	$(CH_2)_2Ph$	**10**	Me	**15a**	88
2	**1**	$(CH_2)_2Ph$	**11**	Et	**15b**	82
3	**3**		**10**	Me	**15c**	92
4	**3**		**11**	Et	**15d**	90

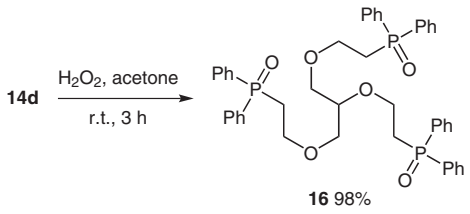
[a] Reaction conditions: phosphine (3 equiv.), **10**/**11** (equiv.), AIBN (2 wt% of the total reactant mass), 75 °C, 72 h, argon.
[b] Isolated yield.

of the hydrogen atom from another phosphine molecule on radical **A** (Scheme 3) appears to be more favorable than intramolecular cyclization of the latter.



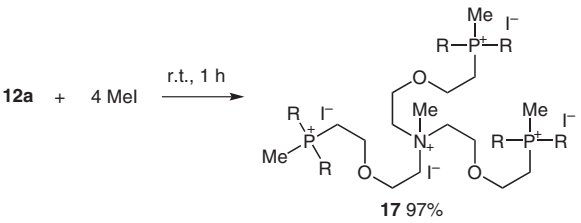
Scheme 3 A through-space stabilization within radical-adduct **A**

Trialkyl- and tris(aralkyl)phosphines are known to be readily oxidized to the corresponding phosphine oxides on exposure to air.[13c,22] Surprisingly, triphosphines **12**–**15** are more resistant to air oxidation. For example, after storage of triphosphine **14a** in an open vessel at room temperature for one month, only traces of its oxide were detected (^{31}P NMR analysis). In contrast, triphoshines are smoothly oxidized by aqueous H_2O_2 (r.t., 3 h, acetone) to give the corresponding triphosphine oxides quantitatively (exemplified by oxidation of triphosphine **14d** to triphosphine oxide **16**; Scheme 4).



Scheme 4 Oxidation of trisphosphine **14d**

Clearly, the stability of the synthesized triphoshines towards air oxidation is advantageous for their handling and applications, particularly as ligands. Moreover, these tripodal phosphines of hemilabile character will likely be used in the design of new metal complexes with diverse and tunable catalytic activity. These compounds are also prospective synthetic intermediates. For instance, triphosphine **12a** easily reacts (r.t., 1 h) with iodomethane to give salt **17** in 97% yield (Scheme 5).



Scheme 5 Exhaustive quaternization of triphosphine **12a** [R = $Ph(CH_2)_2$]

Over the last years, such phosphonium salts have been considered as very promising alternatives to imidazolium-based ionic liquids due to the superior thermal stability of phosphonium analogues and their inertness in basic reaction media.[23]

The novel tripodal phosphines **12**–**15** have been fully characterized by multinuclear (^1H, ^{13}C and ^{31}P) NMR and IR spectroscopy; their composition was also confirmed by elemental analysis data.

In summary, a novel group of functional triphosphines bearing amino and (or) ether groups has been synthesized through exhaustive chemo- and regioselective free-radical addition of secondary phosphines to trivinyl ethers of triols, thereby demonstrating the generality and wide sub-

strate scope of this strategy for the synthesis of tripodal phosphines with extra hemilabile sites. These triphosphines are prospective polydentate ligands that can be used in the design of multipurpose metal complexes and reactive building blocks for organic synthesis, and the primary amino group in triphosphines **13a** and **13b** secures almost unlimited possibilities for the synthesis of a wide range of novel tripodal phosphines with hemilabile sites.

All reactions were carried out under an argon atmosphere. All solvents were dried and purified according to standard procedures. Secondary phosphines **1**–**5** were prepared from the corresponding styrenes and 2-vinylfuran and red phosphorus as previously described.[17] Diphenylphosphine (**6**) was employed as purchased (Aldrich). Trivinyl ethers **7**–**11** were prepared according to a published method.[18] ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded with Bruker DPX 400 or Bruker AV-400 spectrometers (400.13, 100.62, and 161.98 MHz, respectively) at ambient temperature for $CDCl_3$ solutions. Chemical shifts are reported in δ units (ppm) relative to $CDCl_3$ (^{1}H, ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. FTIR spectra were recorded with a Bruker Vertex 70 spectrometer. Microanalyses were performed with a Flash EA 1112 Series elemental analyzer. Melting points were recorded with a Stuart melting-point apparatus and are uncorrected.

Synthesis of Triphosphines 12–15; General Procedure

***Method A*:** A solution of PH-addend **1** or **4** (0.9 mmol) and trivinyl ether **9** (0.3 mmol) in 1,4-dioxane (0.5 mL) was irradiated (200 W Hg arc lamp) in a quartz ampoule (the reaction time is given in Table 1).

***Method B*:** A solution of PH-addend **1**–**6** (0.9 mmol) and trivinyl ether **7**–**11** (0.3 mmol) either with solvent (0.5 mL) or without solvent, in the presence of AIBN (2 wt% of the total mass of reactants) was stirred at 65–75 °C in a sealed ampoule for the given reaction time (Table 1, Table 2, and Scheme 1).

The reaction was monitored by ^{31}P NMR spectroscopy following the disappearance of the peaks of the starting PH-addendes (the –82 to –69 ppm region for phosphines **1**–**5**, and the –39 ppm region for phosphine **7**) and appearance of new peaks in the –32 to –20 ppm region corresponding to triphosphines **12**–**15**. The reaction mixture was dissolved in Et_2O (3 mL), and passed through a layer of Al_2O_3 (activity level II, 0.5 cm), and the latter was additionally washed with *n*-hexane–Et_2O (1:1, 3 mL). The solvents were removed under reduced pressure to give triphosphines **12**–**15**.

***N*,*N*,*N*-Tris[2-(diphenethylphosphino)ethoxyethyl]amine (12a)**
Yield: 275 mg (96%); colorless oil.

IR (KBr): 752 (P–C) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.79–1.83 (m, 18 H, PCH_2), 2.75–2.83 (m, 18 H, $PhCH_2$, NCH_2), 3.52–3.64 (m, 12 H, OCH_2), 7.22–7.33 (m, 30 H, Ph).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.8 (d, $^2J_{P–C}$ = 14.6 Hz, $PhCH_2$), 29.4 (d, $^1J_{P–C}$ = 14.0 Hz, P*C*H_2CH_2O), 32.3 (d, $^1J_{P–C}$ = 14.6 Hz, PCH_2), 54.8 (NCH_2), 68.9 (d, $^2J_{P–C}$ = 20.1 Hz, CH_2O), 69.5 (CH_2O), 126.0 (*p*-C in Ph), 128.2 (*o*-C in Ph), 128.5 (*m*-C in Ph), 142.8 (d, $^3J_{P–C}$ = 10.5 Hz, *ipso*-C in Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –32.3.

Anal. Calcd for $C_{60}H_{78}NO_3P_3$: C, 75.52; H, 8.24; N, 1.47; P, 9.74. Found: C, 75.58; H, 8.33; N, 1.55; P, 9.86.

***N*,*N*,*N*-Tris[2-(bis[4-(*tert*-butyl)phenylethyl]phosphino)ethoxyethyl]amine (12b)**
Yield: 364 mg (94%); colorless oil.

IR (KBr): 771 (P–C) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.34 (s, 54 H, 18 × Me), 1.77–1.85 (m, 18 H, PCH_2), 2.73–2.84 (m, 18 H, $ArCH_2$, NCH_2), 3.53–3.63 (m, 12 H, OCH_2), 7.14–7.35 (m, 24 H, Ar).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.6 (d, $^2J_{P–C}$ = 14.7 Hz, $ArCH_2$), 29.1 (d, $^1J_{P–C}$ = 13.8 Hz, P*C*H_2CH_2O), 31.3 (18 × Me), 31.5 (d, $^1J_{P–C}$ = 14.7 Hz, PCH_2), 54.6 (NCH_2), 68.8 (d, $^2J_{P–C}$ = 20.7 Hz, CH_2O), 69.4 (CH_2O), 77.9 (C in *t*-Bu), 125.4 ($C^{2,6}$ in Ar), 127.6 ($C^{3,5}$ in Ar), 139.6 (d, $^3J_{P–C}$ = 10.8 Hz, C^1 in Ar), 148.6 (C^4 in Ar).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.7.

Anal. Calcd for $C_{84}H_{126}NO_3P_3$: C, 78.16; H, 9.84; N, 1.09; P, 7.20. Found: C, 78.35; H, 9.42; N, 1.14; P, 7.47.

1,1,1-Tris[2-(diphenethylphosphino)ethoxymethyl]methylamine (13a)
Yield: 256 mg (92%); colorless oil.

IR (KBr): 752 (P–C), 3299, 3379 (N–H) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.74–1.78 (m, 18 H, PCH_2), 2.70–2.74 (m, 12 H, $PhCH_2$), 2.91 (s, 2 H, NH_2), 3.33 (s, 6 H, CH_2O), 3.55–3.60 (m, 6 H, CH_2O), 7.18–7.27 (m, 30 H, Ph).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.3 (d, $^2J_{P–C}$ = 14.8 Hz, $PhCH_2$), 29.0 (d, $^1J_{P–C}$ = 14.0 Hz, P*C*H_2CH_2O), 32.0 (d, $^1J_{P–C}$ = 14.6 Hz, PCH_2), 55.6 (CNH_2), 68.1 (d, $^2J_{P–C}$ = 18.8 Hz, CH_2O), 72.8 (O*C*H_2C), 125.71 (*p*-C in Ph), 127.8 (*o*-C in Ph), 128.2 (*m*-C in Ph), 142.5 (d, $^3J_{P–C}$ = 10.7 Hz, *ipso*-C in Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.7.

Anal. Calcd for $C_{58}H_{74}NO_3P_3$: C, 75.22; H, 8.05; N, 1.51; P, 10.03. Found: C, 75.35; H, 8.27; N, 1.63; P, 9.87.

1,1,1-Tris[2-(bis[4-(*tert*-butoxy)phenylethyl]phosphino)ethoxymethyl]methylamine (13b)
Yield: 351 mg (86%); colorless oil.

IR (KBr): 756 (P–C), 3292, 3349 (N–H) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.33 (s, 54 H, 18 × Me), 1.73–1.79 (m, 18 H, PCH_2), 2.69–2.73 (m, 12 H, $ArCH_2$), 3.46–3.65 (m, 14 H, CH_2O, NH_2), 6.89–7.09 (m, 24 H, ArH).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.6 (d, $^2J_{P–C}$ = 14.7 Hz, $ArCH_2$), 28.8 (18 Me), 29.3 (d, $^1J_{P–C}$ = 13.4 Hz, P*C*H_2CH_2O), 31.6 (d, $^1J_{P–C}$ = 14.7 Hz, PCH_2), 55.8 (CNH_2), 69.4 (d, $^2J_{P–C}$ = 18.5 Hz, CH_2O), 72.9 (CH_2O), 78.1 (C in *t*-BuO), 124.1 ($C^{2,6}$ in Ar), 128.3 ($C^{3,5}$ in Ar), 137.6 (d, $^3J_{P–C}$ = 10.4 Hz, C^1 in Ar), 153.4 (C^4 in Ar).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.5.

Anal. Calcd for $C_{82}H_{122}NO_9P_3$: C, 72.48; H, 9.05; N, 1.03; P, 6.84. Found: C, 72.65; H, 9.12; N, 1.17; P, 6.77.

1,2,3-Tris(2-{diphenethylphosphino}ethoxy)propane (14a)
Yield: 242 mg (90%) (method A), 234 mg (87%) (method B); colorless oil.

IR (KBr): 752 (P–C) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.73–1.77 (m, 18 H, PCH_2), 2.69–2.75 (m, 12 H, $PhCH_2$), 3.45–3.62 (m, 10 H, PCH_2CH_2O, CH_2O), 3.75 (m, 1 H, CHO), 7.15–7.28 (m, 30 H, PhH).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.6 (d, $^2J_{P–C}$ = 14.6 Hz, $PhCH_2$), 27.9 (d, $^2J_{P–C}$ = 14.6 Hz, $PhCH_2$), 29.3 (d, $^1J_{P–C}$ = 13.8 Hz, PCH_2), 32.2 (d, $^1J_{P–C}$ = 14.6 Hz, PCH_2), 68.2 (d, $^2J_{P–C}$ = 20.7 Hz, PCH_2CH_2O), 69.3 (d, $^2J_{P–C}$ = 20.3 Hz, PCH_2CH_2O), 70.9 (CH_2O), 77.9 (CHO), 125.9 (*p*-C in Ph), 128.1 (*o*-C in Ph), 128.4 (*m*-C in Ph), 142.7 (d, $^3J_{P–C}$ = 10.4 Hz, *ipso*-C in Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.5 (br s).

Anal. Calcd for $C_{57}H_{71}O_3P_3$: C, 76.31; H, 7.98; P, 10.36. Found: C, 76.54; H, 7.80; P, 10.33.

1,2,3-Tris(2-{bis[4-chlorophenethyl]phosphino}ethoxy)propane (14b)
Yield: 291 mg (88%) (method A); colorless oil.

IR (KBr): 651 (P–C) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.62–1.71 (m, 6 H, PC$H_2$$CH_2O$), 1.96–2.10 (m, 12 H, PCH_2), 2.57–2.67 (m, 4 H, CH_2Ar), 2.78–2.94 (m, 8 H, CH_2Ar), 3.44–3.54 (m, 5 H, CH_2O, CHO), 3.70–3.81 (m, 6 H, PCH_2CH_2O), 7.03–7.11 (m, 12 H, $H^{2,6}$ in Ar), 7.19–7.25 (m, 12 H, $H^{3,5}$ in Ar).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.0 (d, $^2J_{P–C}$ = 15.0 Hz, CH_2Ar), 27.3 (d, $^2J_{P–C}$ = 15.0 Hz, CH_2Ar), 29.1 (d, $^1J_{P–C}$ = 14.2 Hz, PCH_2CH_2O), 31.5 (d, $^1J_{P–C}$ = 14.9 Hz, PCH_2), 68.2 (d, $^2J_{P–C}$ = 20.7 Hz, PCH_2CH_2O), 69.3 (d, $^2J_{P–C}$ = 20.3 Hz, PCH_2CH_2O), 70.9 (CH_2O), 77.9 (CHO), 128.4 ($C^{2,6}$ in Ar), 128.7 ($C^{3,5}$ in Ar), 129.4 (C^4 in Ar), 140.9 (d, $^3J_{P–C}$ = 10.0 Hz, C^1 in Ar).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.5 (br s).

Anal. Calcd for $C_{57}H_{65}Cl_6O_3P_3$: C, 62.03; H, 5.94; Cl, 19.27; P, 8.42. Found: C, 62.21; H, 5.82; Cl, 19.14; P, 8.54.

1,2,3-Tris(2-{bis[2-(2-furyl)ethyl]phosphino}ethoxy)propane (14c)
Yield: 201 mg (80%) (method B); colorless oil.

IR (KBr): 731 (P–C) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.70–1.78 (m, 18 H, PCH_2), 2.71–2.77 (m, 12 H, CH_2Fur), 3.44–3.76 (m, 11 H, CH_2O, CHO), 5.98 (br s, 6 H, H^3 in Fur), 6.25 (br s, 6 H, H^4 in Fur), 7.27 (br s, 6 H, H^5 in Fur).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 20.4 (CH_2Fur), 24.6 (d, $^1J_{P–C}$ = 13.6 Hz, PCH_2), 25.4 (d, $^1J_{P–C}$ = 16.5 Hz, PCH_2), 27.4 (d, $^2J_{P–C}$ = 14.6 Hz, PCH_2CH_2O), 27.7 (d, $^2J_{P–C}$ = 13.2 Hz, PCH_2CH_2O), 68.0 (d, $^2J_{P–C}$ = 22.8 Hz, PCH_2CH_2O), 69.2 (d, $^2J_{P–C}$ = 19.7 Hz, PCH_2CH_2O), 70.9 (CH_2O), 77.9 (CHO), 104.9 (C^3 in Fur), 110.1 (C^4 in Fur), 140.9 (C^5 in Fur), 155.9 (d, $^3J_{P–C}$ = 11.3 Hz, C^2 in Fur).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.9 (br s).

Anal. Calcd for $C_{45}H_{59}O_9P_3$: C, 64.58; H, 7.11; P, 11.10. Found: C, 64.69; H, 7.30; P, 11.27.

1,2,3-Tris[2-(diphenylphosphino)ethoxy]propane (14d)
Yield: 197 mg (90%) (method B); colorless oil.

IR (KBr): 740 (P–C) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.26–2.32 (m, 6 H, PCH_2), 3.27–3.65 (m, 11 H, CH_2O, CHO), 7.23–7.37 (m, 30 H, Ph).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 28.8 (d, $^1J_{P–C}$ = 13.0 Hz, PCH_2), 29.2 (d, $^1J_{P–C}$ = 13.1 Hz, PCH_2), 67.6 (d, $^2J_{P–C}$ = 25.3 Hz, PCH_2CH_2O), 68.7 (d, $^2J_{P–C}$ = 24.5 Hz, PCH_2CH_2O), 70.7 (CH_2O), 77.8 (CHO), 128.4 (*p*-C in Ph), 128.5 (d, $^2J_{P–C}$ = 13.0 Hz, *o*-C in Ph), 132.7 (d, $^3J_{P–C}$ = 19.3 Hz, *m*-C in Ph), 138.4 (d, $^1J_{P–C}$ = 13.0 Hz, *ipso*-C in Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –20.9.

Anal. Calcd for $C_{45}H_{47}O_3P_3$: C, 74.16; H, 6.50; P, 12.75. Found: C, 74.25; H, 6.36; P, 12.88.

1,1,1-Tris[2-(diphenethylphosphino)ethoxymethyl]ethane (15a)
Yield: 244 mg (88%); colorless oil.

IR (KBr): 753 (P–C) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.95 (s, 3 H, Me), 1.71–1.78 (m, 18 H, PCH_2), 2.68–2.72 (m, 12 H, $PhCH_2$), 3.25 (s, 6 H, CH_2O), 3.52–3.56 (m, 6 H, PCH_2CH_2O), 7.23–7.41 (m, 30 H, Ph).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 17.6 (Me), 27.5 (d, $^1J_{P–C}$ = 14.0 Hz, $PhCH_2$), 29.2 (d, $^1J_{P–C}$ = 13.9 Hz, PCH_2CH_2O,), 32.2 (d, $^1J_{P–C}$ = 14.5 Hz, PCH_2), 40.8 (C), 69.4 (d, $^2J_{P–C}$ = 18.9 Hz, PCH_2CH_2O), 73.6 (CH_2O), 125.9 (*p*-C in Ph), 128.0 (*o*-C in Ph), 128.4 (*m*-C in Ph), 142.8 (d, $^3J_{P–C}$ = 11.1 Hz, *ipso*-C in Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.5.

Anal. Calcd for $C_{59}H_{75}O_3P_3$: C, 76.60; H, 8.17; P, 10.04. Found: C, 76.54; H, 8.08; P, 10.21.

1,1,1-Tris[2-(diphenethylphosphino)ethoxymethyl]propane (15b)
Yield: 231 mg (82%); colorless oil.

IR (KBr): 752 (P–C) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.87 (t, $^3J_{H–H}$ = 7.4 Hz, 3 H, Me), 1.42 (q, $^3J_{H–H}$ = 7.6 Hz, 2 H, CH_2Me), 1.77–1.82 (m, 18 H, PCH_2), 2.73–2.79 (m, 12 H, $PhCH_2$), 3.30 (s, 6 H, CH_2O), 3.54–3.60 (m, 6 H, PCH_2CH_2O), 7.19–7.32 (m, 30 H, Ph).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 7.8 (Me), 23.1 (CH_2), 27.5 (d, $^1J_{P–C}$ = 14.5 Hz, $PhCH_2$), 29.3 (d, $^1J_{P–C}$ = 13.9 Hz, PCH_2CH_2O), 32.3 (d, $^1J_{P–C}$ = 14.5 Hz, PCH_2), 43.1 (C), 69.3 (d, $^2J_{P–C}$ = 18.5 Hz, CH_2O), 71.4 (CH_2O), 125.9 (*p*-C in Ph), 128.1 (*o*-C in Ph), 128.4 (*m*-C in Ph), 142.8 (d, $^3J_{P–C}$ = 10.8 Hz, *ipso*-C in Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.4.

Anal. Calcd for $C_{60}H_{77}O_3P_3$: C, 76.73; H, 8.26; P, 9.89. Found: C, 76.69; H, 8.30; P, 9.47.

1,1,1-Tris[2-bis[4-(*tert*-butoxy)phenethyl]phosphinoethoxymethyl]ethane (15c)
Yield: 375 mg (92%); colorless oil.

IR (KBr): 756 (P–C) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.93 (s, 3 H, CH_3), 1.32 (s, 54 H, 18 Me), 1.74–1.78 (m, 18 H, PCH_2), 2.67–2.71 (m, 12 H, $ArCH_2$), 3.27 (s, 6 H, CH_2O), 3.52–3.58 (m, 6 H, PCH_2CH_2O), 6.89–7.08 (m, 24 H, Ar).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 17.6 (CH_3), 27.5 (d, $^1J_{PC}$ = 13.8 Hz, $ArCH_2$), 28.8 (18 Me), 29.3 (d, $^1J_{PC}$ = 13.4 Hz, PCH_2CH_2O), 31.6 (d, $^1J_{PC}$ = 14.7 Hz, PCH_2), 40.8 (*C*Me), 69.4 (d, $^2J_{PC}$ = 19.0 Hz, CH_2O), 73.7 (CH_2O), 78.1 (C in *t*-BuO), 124.1 ($C^{2,6}$ in Ar), 128.4 ($C^{3,5}$ in Ar), 137.7 (d, $^3J_{PC}$ = 10.8 Hz, C^1 in Ar), 153.4 (C^4 in Ar).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.3.

Anal. Calcd for $C_{83}H_{123}O_9P_3$: C, 73.42; H, 9.13; P, 6.84. Found: C, 73.70; H, 9.26; P, 6.72.

1,1,1-Tris[2-bis[4-(*tert*-butoxy)phenethyl]phosphinoethoxymethyl]propane (15d)
Yield: 370 mg (90%); colorless oil.

IR (KBr): 756 (P–C) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.69 (t, ^3J = 7.5 Hz, 3 H, Me), 1.18 (s, 54 H, 18 × Me), 1.25 (q, $^3J_{H–H}$ = 7.5 Hz, 2 H, CH_2Me), 1.58–1.64 (m, 18 H, PCH_2), 2.53–2.59 (m, 12 H, $ArCH_2$), 3.137 (s, 6 H, CH_2O), 3.38–3.44 (m, 6 H, PCH_2CH_2O), 6.74–6.94 (m, 24 H, Ar).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 7.8 (Me), 23.0 (CH_2), 27.5 (d, $^2J_{P–C}$ = 14.2 Hz, $ArCH_2$), 28.8 (18 Me), 29.3 (d, $^1J_{P–C}$ = 13.8 Hz, PCH_2CH_2O), 31.6 (d, $^1J_{P–C}$ = 14.7 Hz, PCH_2), 43.0 (*C*Et), 69.3 (d, $^2J_{P–C}$ = 18.5 Hz, CH_2O), 71.3 (CH_2O), 78.0 (C in *t*-BuO), 124.1 ($C^{2,6}$ in Ar), 128.3 ($C^{3,5}$ in Ar), 137.7 (d, $^3J_{P–C}$ = 11.2 Hz, C^1 in Ar), 153.4 (C^4 in Ar).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.2.

Anal. Calcd for $C_{84}H_{125}O_9P_3$: C, 73.55; H, 9.18; P, 6.77. Found: C, 73.63; H, 9.30; P, 6.84.

Oxidation of Triphosphine 14d with H_2O_2 (Scheme 4); Synthesis of 1,2,3-Tris[2-(diphenylphosphinyl)ethoxy]propane (16)
To a solution of triphosphine **14d** (146 mg, 0.2 mmol) in acetone (5 mL), a 33% aqueous solution of H_2O_2 (1 mL) was added dropwise. The reaction mixture was stirred at 23–25 °C for 3 h, then solvents were evaporated in vacuum and the residue was reprecipitated

from chloroform to hexane and dried in vacuum to give triphosphine oxide **16**.

Yield: 149 mg (96%); white resin.

IR (KBr): 1173 (P=O), 751 (P–C) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.51–2.58 (m, 6 H, PCH_2), 3.07–3.19 (m, 5 H, CH_2O), 3.60–3.77 (m, 6 H, CHO), 7.41–7.76 (m, 30 H, Ph).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 30.5 (d, $^1J_{P-C}$ = 70.7 Hz, PCH_2), 30.9 (d, $^1J_{P-C}$ = 70.3 Hz, PCH_2), 63.5, 64.6 (PCH_2CH_2O), 70.4 (CH_2O), 77.5 (CHO), 128.6 (d, $^3J_{P-C}$ = 11.6 Hz, *m*-C in Ph), 130.7 (d, $^2J_{P-C}$ = 9.5 Hz, *o*-C in Ph), 131.8 (*p*-C in Ph), 132.8 (d, $^1J_{P-C}$ = 100.4 Hz, *ipso*-C in Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 31.04, 31.15.

Anal. Calcd for $C_{45}H_{47}O_6P_3$: C, 69.58; H, 6.10; P, 11.96. Found: C, 69.35; H, 6.15; P, 12.09.

Exhaustive Quaternization of Triphosphine 12a (Scheme 5); Synthesis of Methyl-*N*,*N*,*N*-tris{2-[methyl-bis(phenylethyl)phosphonio]ethoxyethyl}ammonium Tetraiodide (17)

A solution of triphosphine **12a** (204 mg, 0.21 mmol) and MeI (1 mL) in Et_2O (2 mL) was stirred under an argon atmosphere at 23–25 °C for 1 h. The solvent and excess MeI were removed in vacuum, the residue was ground in hexane (7 mL), and the hexane was decanted. The white powder formed was washed with hexane (10 mL) and dried in vacuum (1 Torr, 35–40 °C) to afford salt **17**.

Yield: 310 mg (97%); white powder; mp 68 °C.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.95–2.28 (m, 18 H, PCH_2), 2.08 (d, $^1J_{PH}$ = 11.7 Hz, 9 H, 3 PMe), 2.75–2.90 (m, 18 H, $PhCH_2$, NCH_2), 3.30–3.38 (br s, 3 H, NMe), 3.91–4.04 (m, 12 H, OCH_2), 7.15–7.30 (m, 30 H, Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 32.46.

Anal. Calcd for $C_{64}H_{90}I_4NO_3P_3$: C, 50.51; H, 5.96; I, 33.35; N, 0.92; P, 6.11. Found: C, 50.71; H, 5.95; I, 32.82; N, 1.26; P, 6.18.

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