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Formation and Rearrangement of Dithioxo- and Diselenoxophosphoranes Carrying Bulky 4-*t*-Butyl-2,6-bis(methoxyalkyl)phenyl Groups

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Abstract—[4-*t*-Butyl-2,6-bis(1-methoxy-1-methylethyl)phenyl]phosphine, [4-*t*-butyl-2,6-bis(2-methoxy-1,1-dimethylethyl)phenyl]phosphine, and [4-*t*-butyl-2,6-bis(3-methoxy-1,1-dimethylpropyl)phenyl]phosphine were prepared and allowed to react with sulfur or selenium, to give heterocyclic compounds containing phosphorus–oxygen bond, via rearrangement of the methyl moiety of the methoxy group.

Compounds with multiple-bonded heavier main-group elements, such as phosphorus, are currently of interest.[1] By utilizing an extremely bulky 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated as Ar; Chart 1) as a sterically protecting auxiliary, we and others have successfully prepared various types of multiple bonded phosphorus compounds, such as diphosphene **1** (Chart 2),[2] dithioxophosphorane (thioxophosphine sulfide) **2**,[3] and diselenoxophosphorane (selenoxophosphine selenide) **3**.[4] Recently, we have developed some novel substituents, such as the 2,4-di-*t*-butyl-6-(dimethylamino)phenyl group (abbreviated as Mx),[5] the 2,4-di-*t*-butyl-6-methoxyphenyl group (abbreviated as Mox),[6] the 2,4-di-*t*-butyl-6-(dimethylaminomethyl)phenyl group (abbreviated as Mamx),[7] the 2,4-di-*t*-butyl-6-(methoxymethyl)phenyl group (abbreviated as Momx),[8] the 4-*t*-butyl-2,6-bis(dimethylaminomethyl)phenyl group (abbreviated as Mamt),[9] and the 2,4-di-*t*-butyl-6-[1,1-dimethyl-2-(dimethylamino)ethyl]phenyl group (abbreviated as Maar),[10] having both a bulky *t*-butyl group and an electron donating part at the *o*-positions.

Dithioxo- and diselenoxophosphorane derivatives **4** and **5**,[5] bearing the Mx group, are highly stabilized, mainly by intramolecular coordination (compared with the kinetically stabilized 'genuine' dithioxophosphorane **2** and diselenoxophosphorane **3**). The intramolecular coordination in the solid state was confirmed by X-ray crystallography in the case of the compounds bearing the Mx-type substituents[11] as well as the compounds with the Mamx[7] and the Maar substituents.[10]

Contrary to this, the Mox-substituted dithioxophosphorane **6** was not stable, suggesting a weak intramolecular interaction within the molecule. When a solution of **6** was concentrated, the compound dimerized to **7** (Scheme 1).[6a] On heating, the monomeric dithioxophosphorane **6** was regenerated from the dimer **7**.[6b] As for a selenium congener of **6**, we have not been successful in preparation of the Mox-substituted diselenoxophosphorane **8**. An attempted preparation of **8** by the reaction of $MoxPH_2$ with selenium in the presence of a base, according to the preparative method of diselenoxophosphoranes with the Mx-type substituents, resulted in the formation of a heterocyclic compound **9**.[6c]

This striking difference in the stabilizing abilities between the Mx group and the Mox group prompted us to examine the effect of oxygen-functional group on the $-P(=S)_2$ and $-P(=Se)_2$ moieties by using other type of substituents. As a part of our investigation on the modified 2,4,6-tri-*t*-butylphenyl group, we now report the introduction of 4-*t*-butyl-2,6-bis(1-methoxy-1-methylethyl)phenyl group (**a** in Chart 3), 4-*t*-butyl-2,6-bis(2-methoxy-1,1-dimethylethyl)phenyl group (**b**) and 4-*t*-butyl-2,6-bis(3-methoxy-1,1-dimethylpropyl)phenyl group (**c**).

Results and Discussion

Preparation of 2-bromo-5-*t*-butyl-1,3-bis(methoxyalkyl) benzenes

In order to introduce a bulky 4-*t*-butyl-2,6-bis(methoxyalkyl)phenyl moiety into a molecule, the corresponding bromobenzenes **10a**–**c** were prepared as follows. Bromobenzene **10a** was prepared by a route shown in Scheme 2.

Keywords: phosphorus heterocycles; phosphines; rearrangements; steric and strain effects.

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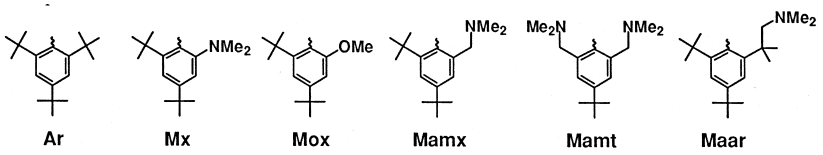


Chart 1.

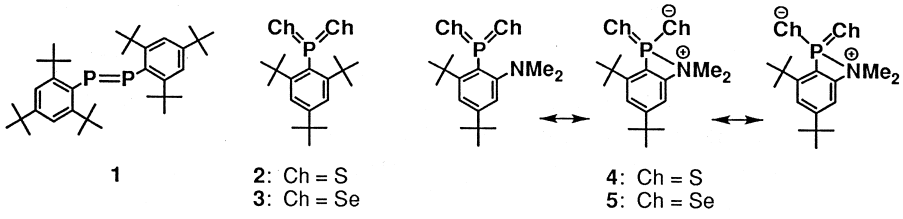
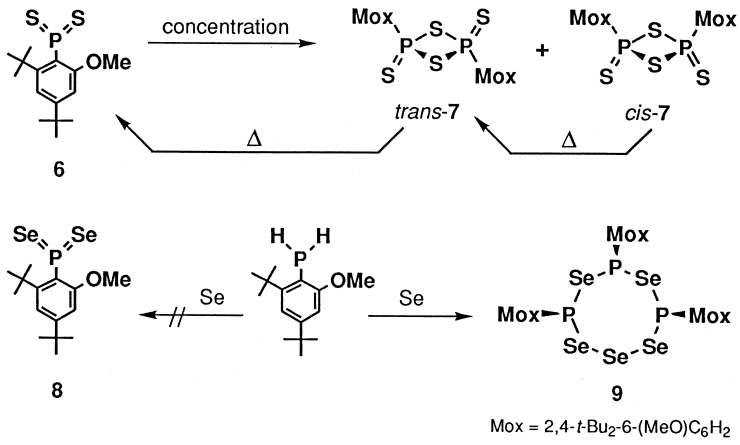


Chart 2.



Scheme 1.

Oxidation of 2-bromo-5-*t*-butyl-1,3-dimethylbenzene (**11**)[12a] afforded the isophthalic acid derivative **12**,[12b] which was then converted to the corresponding dimethyl ester **13**. The ester **13** was then allowed to react with methylmagnesium bromide to give 2-bromo-5-*t*-butyl-1,3-bis(1-hydroxy-1-methylethyl)benzene (**14**) in 64% yield. Methylation of **14** afforded **10a** in 92% yield.

Bromobenzene **10b** was prepared as shown in Scheme 3. 2-Bromo-1,3-bis(bromomethyl)-5-*t*-butylbenzene (**15**)[13] was allowed to react with potassium cyanide in acetonitrile in the presence of 18-crown-6 to afford the dicyano derivative **16** in 89% yield. Methylation at the benzyl position[14] of **16** with MeI/KOH in dimethyl sulfoxide gave 2-bromo-5-*t*-butyl-1,3-bis(1-cyano-1-methylethyl)benzene (**17**) in 65% yield. Successive reduction of the cyano group in **17** with diisobutyl aluminum hydride and lithium aluminum hydride afforded the dihydroxy derivative **19** via the diformyl derivative **18**. While methylation of **19** with an excess of dimethyl sulfate gave the mono-methoxy derivative **20** (Chart 4) as a major product (59%) with only a trace amount (3%) of the desired dimethoxy derivative **10b**, methylation of **19** using MeI/NaH afforded **10b** in good yield (93%).

Similarly, bromobenzene **10c** was prepared from a synthetic intermediate **18** by a route as shown in Scheme 4. Thus, the Wittig reaction of the diformyl derivative **18** with methylenetriphenylphosphorane afforded **21** (91%). Hydroboration of **21** gave diol **22** as a major product (72%) along with the Markovnikov-type product **23** (24%, Chart 4). Then **22** was methylated with MeI/NaH to give **10c** almost quantitatively.

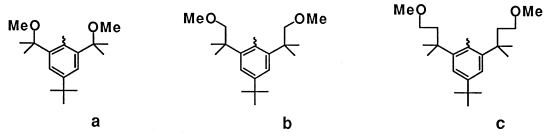
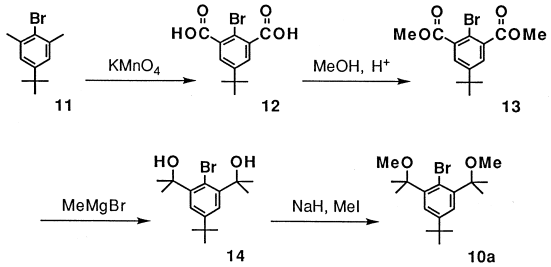
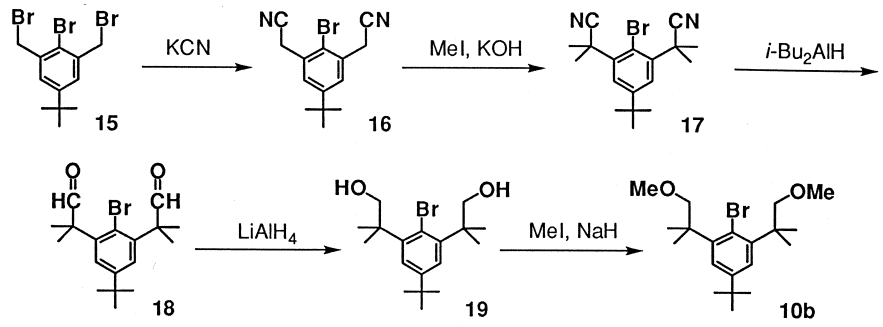


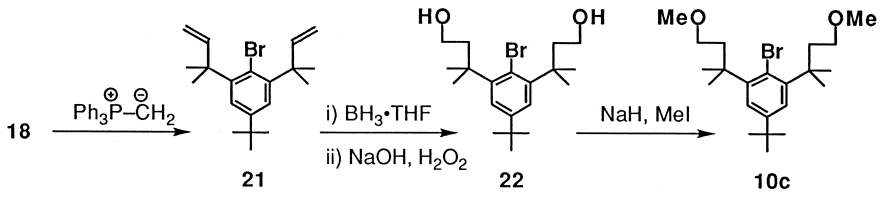
Chart 3.



Scheme 2.



Scheme 3.



Scheme 4.

Preparation of primary phosphines and diphosphenes

Since bromobenzenes **10a**–**c** were prepared as described above, attempted preparation of primary phosphines bearing the substituents **a**–**c** were made by a normal procedure via phosphonous dichlorides (Scheme 5). At first, appropriate reaction conditions were determined for metallation of bromobenzenes **10a**–**c** with butyllithium in THF. As for compounds **10a**,**b**, the best results were obtained at room temperature and the corresponding benzene derivatives **25a**,**b** were formed in good yields (96 and 92%, respectively), after quenching of the reaction mixtures with water. Although lithiation of **10c** proceeded effectively (97% yield of **25c**) at −78°C, attempted lithiation of **10c** at room temperature gave a complex mixture of products.

Then, bromobenzenes **10a**–**c** were lithiated with butyllithium in THF under the conditions mentioned above, and the resulting mixtures were allowed to react with PCl_3 (Scheme 6). However, only **10c** gave satisfactory results to afford the corresponding phosphonous dichloride **26c**. In the cases of **10a**,**b**, intramolecular cyclization of intermediary phosphonous dichlorides **26a**,**b** proceeded. Compounds **27a**,**b** were observed by ^{31}P NMR spectroscopic monitoring during the reaction [**27a**: δ_P (THF–C_6D_6)=166; **27b**: δ_P (THF–C_6D_6)=156]. Intermediates **26a**,**b** were not detected by this monitoring, indicating that the cyclization reactions are rapid. When compounds **27a**,**b** were allowed to react with methanol in the presence of triethylamine, compounds **29a**,**b** were obtained via **28a**,**b** [**28a**: δ_P (THF–C_6D_6)=164 (m); **28b**: δ_P ($CDCl_3$)=144.6 (br. s)].

On the other hand, the relatively stable phosphonous dichloride **26c** reacted with methanol to give **31** via **30** [δ_P (THF–C_6D_6)=175 (m)]. It should be noted that successive reaction of **24c** with PCl_3 and methanol in acetonitrile (instead of THF) afforded **29c** [δ_P ($CDCl_3$)=28.3 (dd, $^1J_{PH}$=586 Hz and $^3J_{PH}$=21 Hz] via intramolecularly cyclized intermediates **27c** [δ_P (MeCN–C_6D_6)=164 (br. s)] and **28c** [δ_P (MeCN–C_6D_6)=164 (m)]. Thus, the cyclization reaction is largely affected by the solvent.

As an alternative method, the phosphorus atom was introduced by use of diethyl phosphorochloridite as a phosphorus source. Thus, bromobenzenes **10a**,**b** were lithiated with butyllithium and the resulting phenyllithiums **24a**,**b** were allowed to react with diethyl phosphorochloridite to form **32a**,**b** [**32a**: δ_P (THF–C_6D_6)=170.9, **32b**: δ_P (THF–C_6D_6)=168.2]. The reaction mixtures were worked up, and ethyl phosphinates **33a**,**b** were obtained in 63 and 45% yield, respectively, after column chromatographic treatment. Phosphonous dichloride **26c** and ethyl phosphinate **33a**,**b** were reduced with $LiAlH_4$ in THF at 0°C, to form the desired phosphines **34a**–**c** (Scheme 7). Although phosphine **34a** was isolated, attempted isolations of **34b**,**c** have been unsuccessful due to the oxidation reaction during the isolation process.

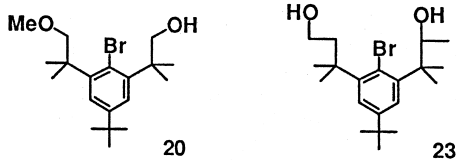
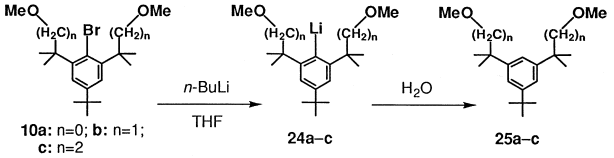
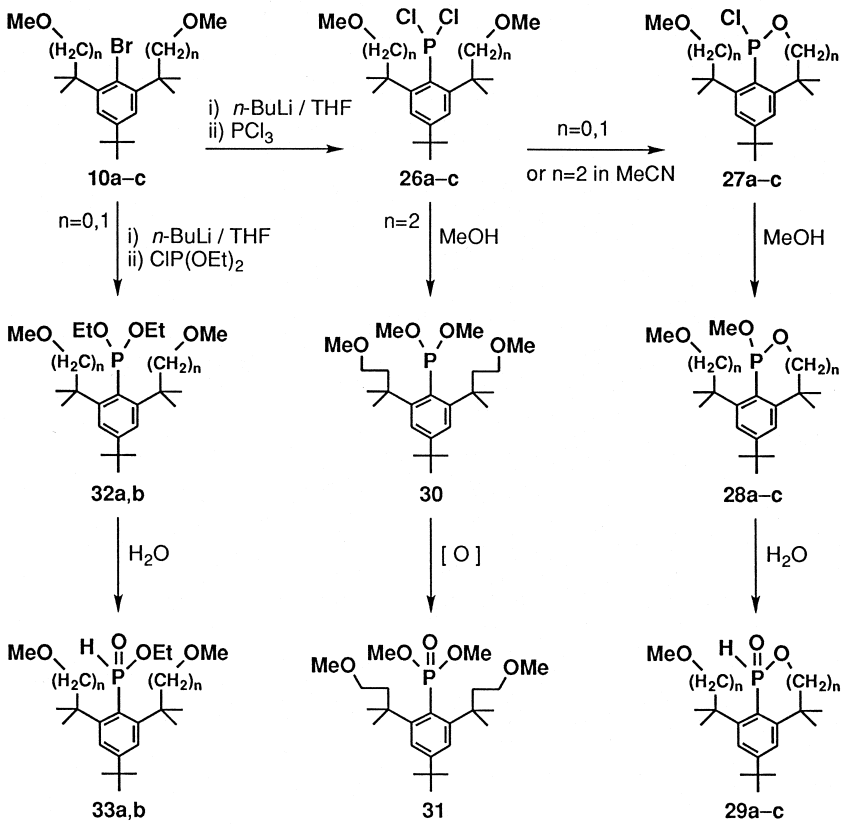


Chart 4.



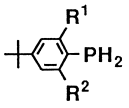
Scheme 5.



Scheme 6.

Furthermore, phosphonous dichloride **26c** was converted to the corresponding diphosphene **35c** by addition of lithium naphthalenide. Although diphosphene **35c** was formed as a major product (indicated by ^{31}P NMR spectrum of the reaction mixture), the isolated yield of **35c** was only 4% due to the decomposition during the aluminum column-chromatographic treatment. It should be noted that phosphonous dichloride **26b** reacted (before formation of **27b**) with *t*-butyllithium at −78°C to form diphosphene **35b** (diphosphene **35b** was decomposed during the isolation process). Contrary to this, in the reaction of **26a** with *t*-butyllithium at −78°C, a signal due to diphosphene was not observed by ^{31}P NMR spectroscopic monitoring, probably because the cyclization reaction of **26a** to **27** was rapid.

Table 1. ^{31}P NMR data for primary phosphines

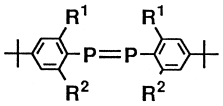


R^1	R^2		δ (J_{PH}/Hz) in $CDCl_3$
CMe_2OMe	CMe_2OMe	**34a**	−129.1 (216.6)
CMe_2CH_2OMe	CMe_2CH_2OMe	**34b**	−129.4 (209.3)
$CMe_2CH_2CH_2OMe$	$CMe_2CH_2CH_2OMe$	**34c**	−130.2 (209.2)
t-Bu	*t*-Bu	**34d**	−129.9[a] (210.6)
t-Bu	Me	**34e**	−143.0[b] (203.0)
t-Bu	OMe	**34f**	−155.4[c] (207.4)
t-Bu	NMe_2		−141.6[d] (213.7)
t-Bu	CH_2NMe_2		−143.6[e] (203.6)
t-Bu	CMe_2NMe_2		−134.5[f] (206.8)
t-Bu	$CMe_2CH_2NMe_2$		−127.4[f] (208)
CH_2NMe_2	CH_2NMe_2		−148.7[g] (207.4)

[a] Data taken from Ref. 15.
[b] Data reported in Ref. 16: −149.9 (J_{PH}=201.1 Hz) in C_6D_6.
[c] Data taken from Ref. 6a, measured in C_6D_6.
[d] Data taken from Ref. 5a.
[e] Data taken from Ref. 7.
[f] Data taken from Ref. 10.
[g] Data taken from Ref. 9.

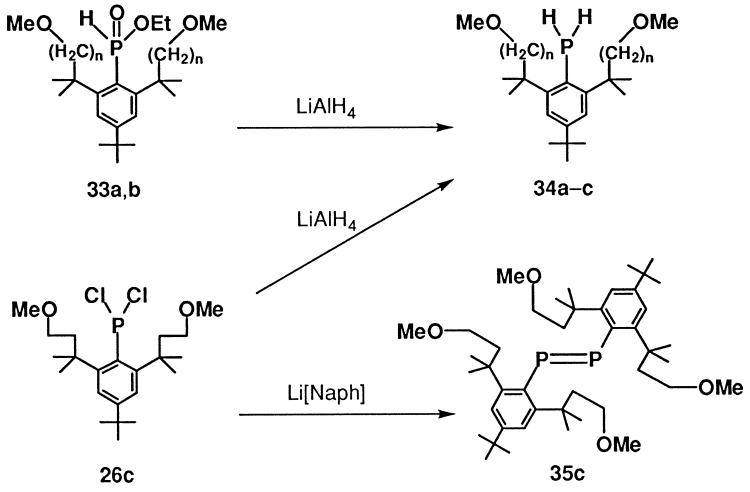
Tables 1 and 2 show ^{31}P NMR chemical shifts of phosphines **34a**–**c**, diphosphenes **35b**,**c**, and some related compounds. The chemical shifts of **34a**–**c** are very similar to that of $ArPH_2$ (**34d**) and considerably different from those of (2,4-di-*t*-butyl-6-methylphenyl)phosphine (**34e**) and $MoxPH_2$ (**34f**). Similarly, the chemical shifts for **35b**,**c** are very close to that for diphosphene **1**, probably because the steric hindrance around the phosphorus atom plays an

Table 2. ^{31}P NMR data for diphosphenes

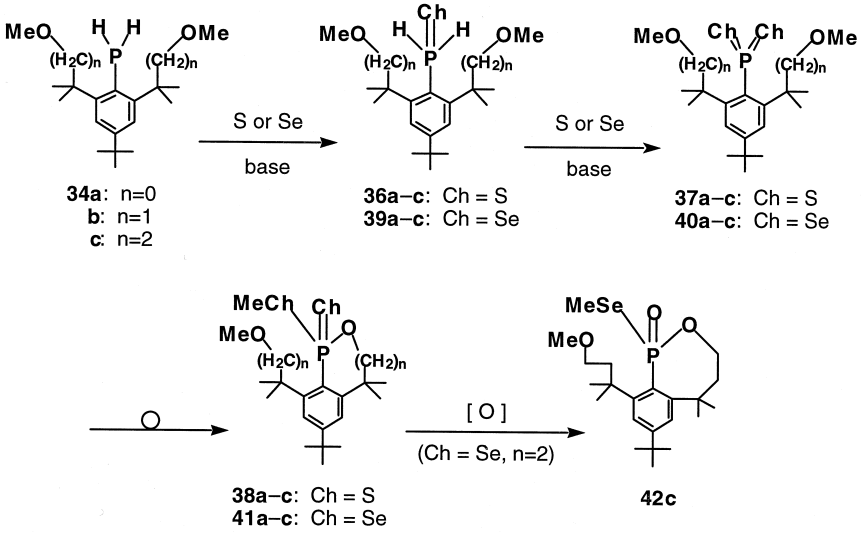


R^1	R^2		δ in $CDCl_3$
CMe_2CH_2OMe	CMe_2CH_2OMe	**35b**	493.7
$CMe_2CH_2CH_2OMe$	$CMe_2CH_2CH_2OMe$	**35c**	493.8
t-Bu	*t*-Bu	**1**	492.4[a]
t-Bu	NMe_2		428.2[b]

[a] Data taken from Ref. 2, measured in C_6D_6.
[b] Data taken from Ref. 5a, measured in THF–C_6D_6.



Scheme 7.



Scheme 8.

important role in the chemical shift of these compounds and electronic effects of the methoxy groups of **34a**–**c** on the chemical shift are relatively small.

Reaction of the phosphines with sulfur or selenium

We have reported that the sterically protected (2,4,6-tri-*t*-butylphenyl)phosphine ($ArPH_2$) reacted with elemental sulfur in the presence of a base such as 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) to give dithioxophosphorane **2**.[3a] Thus, the reactions of phosphines **34a**–**c** with elemental sulfur were carried out in order to investigate the effect of the methoxy groups on the phosphorus center in the corresponding dithioxophosphoranes. When phosphine **34c** was allowed to react with S_8 in benzene in the presence of a catalytic amount of DBU at room temperature, a signal due to dithioxophosphorane **37c** was observed (δ_P=295.2), along with some signals of precursors such as phosphine sulfide **36c** [δ_P=−25.0 (t, $^1J_{PH}$=465 Hz)], by ^{31}PNMR spectroscopic monitoring during the reaction (Scheme 8). The chemical shift for **37c** is very close to that for $ArPS_2$ (**2**) [δ_P ($CDCl_3$)=298.2].[3a]

However, dithioxophosphorane **37c** changed to compound **38c** in the reaction mixture, which was isolated in 26% yield after column chromatographic treatment. Similar results were obtained in the case of the reaction of the phosphines **34a**,**b**, giving **38a**,**b**, although intermediary dithioxophosphoranes **37a**,**b** were not observed by ^{31}P NMR spectroscopic monitoring during the reaction.

When phosphine **34c** was allowed to react with elemental selenium in benzene in the presence of a catalytic amount of DBU at room temperature, a signal due to diselenoxophosphorane **40c** was observed at δ_P=267.4, along with some signals due to the precursors such as phosphine selenide **39c** [δ_P=−52.3 (t, $^1J_{PH}$=458 Hz), satellite d, $^1J_{SeP}$=736 Hz], by ^{31}PNMR spectroscopy. The chemical shift for **40c** was similar to that for $ArPSe_2$ (**3**) [δ_P ($CDCl_3$)=273.0].[4] However, the reaction was complicated and the product isolated after

column chromatography was **42c** (11% yield based on **10c**), probably via intramolecular rearrangement of **40c** to **41c** followed by oxidation of **41c** during the isolation process performed in the air.

In the reaction of phosphine **34a** with selenium, formation of **41a** was observed as a major product by ^{31}P NMR monitoring, however, **41a** was isolated in very low yield (3%), due to decomposition during the isolation procedure. When **34b** was allowed to react with selenium under similar conditions, the reaction became more complicated than the case of **34a** and only trace amount of **41b** was obtained. In these reactions of **34a**,**b**, intermediary diselenoxophosphoranes **40a**,**b** were not observed by ^{31}P NMR spectroscopic monitoring during the reaction, and products of the **42c**-type were not isolated because of difficulties in separation from other decomposition products.

Although the chemical shift of the dithioxophosphorane **37c** is similar to that of $MoxPS_2$ (**6**) [δ_P (C_6D_6)=277.6],[6a] **37** and **6** behave differently in reactivities. Compound **37** afforded a rearranged compound rather than a dimeric compound.[6a,b,17] In the case of **37**, the methoxy group seems to interact with the phosphorus atom more effectively than observed in **6**, due to the conformational flexibility. Because sulfur is more electronegative than phosphorus, the phosphorus atom in the $-P(=S)_2$ moiety has a partially cationic character. In the case of dithioxophosphoranes bearing aniline-type ligands such as $MxPS_2$ (**4**), this cationic character causes intramolecular coordination of the nitrogen atom as shown in Chart 1. When the oxygen atom in **37** coordinates to the phosphorus atom, the carbon atom of the methoxy group may become positive to be attacked by the sulfur atom of the $-P(=S)_2$ moiety. The situation in the diselenoxophosphorane **40** seems to be similar.

In conclusion, interaction between the methoxy group and the phosphorus atom is relatively small in the primary phosphine **34** and diphosphene **35**, while there is a large interaction in the dithioxophosphoranes **37** and diselenoxophosphoranes **40**. This interaction causes methyl-group migration in **37** and **40**, to give the cyclized products **38** and **41**, respectively. Thus, benzene-fused five- to seven-membered ring heterocyclic compounds (**29**, **38**, **41**, and **42**) containing the *endo*-cyclic phosphorus–oxygen bond were obtained in this study. Detailed mechanistic studies of the sulfurization reaction and the selenation reaction, as well as studies on properties of the heterocycles, are in progress.

Experimental

Melting points were measured on a Yanagimoto MP-J3 micro melting points apparatus and were uncorrected. ^1H (200 MHz) and ^{31}P (81 MHz) NMR spectra were taken on a Bruker AC-200P spectrometer. UV–Vis spectra were obtained on a Hitachi U-3210 spectrometer. IR spectra were recorded on a Horiba FT-300 spectrometer and mass spectra were taken on a JEOL HX-110 spectrometer. All experiments, except for the work-up and chromatographic treatment, were carried out under argon with anhydrous and deoxygenated solvents unless otherwise noted.

2-Bromo-5-*t*-butylisophthalic acid (12)[12b]. To a mixture of 2-bromo-5-*t*-butyl-1,3-dimethylbenzene (**11**, 4.51 g, 18.7 mmol),[12a] aqueous potassium hydroxide (113 mmol of KOH in 45 mL of water), and pyridine (90 mL) was added $KMnO_4$ (31.1 g, 197 mmol) at 100°C over a 9-h period. The resulting mixture was stirred for a further 11 h, then cooled to room temperature. An appropriate amount of aqueous $NaHSO_3$ was added to the reaction mixture at 0°C, in order to consume unreacted $KMnO_4$. Then the resulting mixture was acidified with aqueous H_2SO_4 to form colorless precipitates. The precipitates, which consisted of **12** and half-oxidized compound 2-bromo-5-*t*-butyl-3-methylbenzoic acid (**43**), were filtered off and the filtrate was extracted with Et_2O. The organic phase was washed with saturated aqueous NaCl, dried over $MgSO_4$, then the solvent was removed under reduced pressure to give 951.4 mg (17%) of **12**.

12: Colorless prisms, mp 260–262°C (AcOEt); ^1H NMR (200 MHz, CD_3OD) δ 1.34 (9H, s, *t*-Bu) and 7.75 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, CD_3OD) δ 32.1 (CMe_3), 36.5 (CMe_3), 116.2 (arom., CBr), 130.7 (arom., CH), 138.4 (arom.), 153.1 (arom.), and 171.1 (C=O); IR (KBr) 3600–2500 (br.), 2968, 1722, 1699, 1402, 1248, 1225, 908, and 688 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 302 (M^++2; 21), 300 (M^+; 22), 287 (M^+−Me+2; 99), and 285 (M^+−Me; 100). Found: *m/z* 299.9994. Calcd for $C_{12}H_{13}BrO_4$: M, 299.9997.

43: Colorless prisms, mp 182–183°C (AcOEt); ^1H NMR (200 MHz, $CDCl_3$) δ 1.33 (9H, s, *t*-Bu), 2.49 (3H, s, Me), 7.43 (1H, d, ^4J=2.5 Hz, arom.), 7.74 (1H, d, ^4J=2.5 Hz, arom.), and 9.4–10.3 (1H, br. s, OH); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 24.1 (Me), 31.0 (CMe_3), 34.5 (CMe_3), 120.6 (arom., CBr), 126.4 (arom., CH), 131.5 (arom.), 131.6 (arom., CH), 139.5 (arom.), 150.0 (arom.), and 172.9 (C=O); IR (KBr) 3200–2200 (br.), 2968, 1701, 1684, 1585, 1460, 1425, 1311, 1284, 1248, 1192, 1032, 937, 887, 715, and 644 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 272 (M^++2; 23), 270 (M^+; 24), 257 (M^+−Me+2; 100), and 255 (M^+−Me; 100).

Dimethyl 2-bromo-5-*t*-butylisophthalate (13). A mixture of **12** (5.19 g), methanol (50 mL), sulfuric acid (5 mL) was heated under reflux for 3 h and then cooled to room temperature. The reaction mixture was poured into 200 mL of water and the resulting suspension was neutralized by addition of solid $NaHCO_3$. Then the mixture was extracted with ether and the combined organic phase was dried over $MgSO_4$. The solvent was removed in vacuo and the residue was recrystallized from hexane to give **13** (3.43 g, 60%).

13: Colorless plates, mp 100–101°C (hexane); ^1H NMR (200 MHz, $CDCl_3$) δ 1.32 (9H, s, *t*-Bu), 3.95 (6H, s, OMe), and 7.69 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 30.8 (CMe_3), 34.7 (CMe_3), 52.6 (OMe), 115.6 (arom., CBr), 129.4 (arom., CH), 134.9 (arom.), 150.7 (arom.), and 167.3 (C=O); IR (KBr) 1734, 1716, 1475, 1442, 1433, 1365, 1338, 1292, 1267, 1254, 1216, 1196, 1177, 1155, 984, 968, 877, 795, 715, and 647 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 330 (M^++2; 20), 328 (M^+; 20), 315 (M^+−Me+2; 100), and 313 (M^+−Me; 100).

Found: *m*/*z* 328.0301. Calcd for $C_{14}H_{17}BrO_4$: M, 328.0310.

2-Bromo-5-*t*-butyl-1,3-bis(1-hydroxy-1-methylethyl)-benzene (14). To a solution of **13** (299.8 mg, 0.911 mmol) in THF (15 mL) was added 9.3 mmol of methylmagnesium bromide (0.93M in THF) at 0°C. The resulting mixture was stirred at ambient temperature for 18 h. The reaction was quenched by addition of aqueous NH_4Cl at 0°C. Then the resulting suspension was extracted using ether and saturated aqueous $NaHCO_3$ and the organic phase was dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by chromatographic treatment (SiO_2/$CHCl_3$) afforded 193.1 mg (64%) of **14**.

14: Colorless crystals, mp 135–137°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (9H, s, *t*-Bu), 1.81 (12H, s, CMe_2), 3.06 (2H, br. s, OH), and 7.66 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 30.2 (C*Me*$_3$), 31.2 (C*Me*$_2$O), 34.9 (*C*Me$_3$), 74.8 (*C*Me$_2$O), 116.6 (arom., CBr), 123.9 (arom., CH), 146.6 (arom.), and 149.9 (arom.); IR (KBr) 3334, 3018, 2929, 2870, 1477, 1458, 1400, 1362, 1255, 1213, 1178, 1136, 1011, 956, 901, 760, and 737 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 330 (M^++2; 14), 328 (M^+; 14), 315 (M^+−Me+2; 96), 313 (M^+−Me; 100), 297 (M^+−2OH+3; 24), 295 (M^+−2OH+1; 21), and 57 (*t*-Bu$^+$; 44). Found: *m*/*z* 328.1041. Calcd for $C_{16}H_{25}BrO_2$: M, 328.1038.

2-Bromo-5-*t*-butyl-1,3-bis(1-methoxy-1-methylethyl)-benzene (10a). A solution of **14** (1.34 g, 4.07 mmol) in THF (50 mL) was added to ca. 25 mmol of NaH at 0°C over a 5-min period. The resulting mixture was stirred at 0°C for 5 min, and 24.1 mmol of iodomethane was added. The reaction mixture was warmed to room temperature and stirred for 21 h. The reaction was quenched by addition of methanol and the solvent was removed in vacuo. The residue was worked up using hexane and aqueous Na_2SO_3 and the organic phase was dried over $MgSO_4$. Removal of the solvent gave 1.33 g (92%) of **10a**.

10a: Colorless crystals, mp 62–65°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (9H, s, *t*-Bu), 1.76 (12H, s, CMe_2), 3.12 (6H, s, OMe), and 7.43 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 27.5 (C*Me*$_2$O), 31.2 (C*Me*$_3$), 34.6 (*C*Me$_3$), 50.5 (OMe), 79.6 (*C*Me$_2$O), 117.9 (arom., CBr), 125.3 (arom., CH), 143.8 (arom.), and 148.9 (arom.); IR (KBr) 1477, 1396, 1375, 1360, 1171, 1068, 1012, 879, 850, and 748 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 358 (M^++2; 11), 356 (M^+; 11), 343 (M^+−Me+2; 100), 341 (M^+−Me; 99), 247 (M^+−Br–OMe+1; 27), 72 (CMe_2OMe^+; 55), and 57 (*t*-Bu$^+$; 17). Found: *m*/*z* 356.1354. Calcd for $C_{18}H_{29}BrO_2$: M, 356.1351.

2-Bromo-5-*t*-butyl-1,3-bis(cyanomethyl)benzene (16). To a mixture of 2-bromo-1,3-bis(bromomethyl)-5-*t*-butylbenzene (**15**, 17.0 g, 42.5 mmol)[13] and 18-crown-6 (2.92 g, 11.0 mmol) in acetonitrile (200 mL) was added potassium cyanide (8.16 g, 125 mmol) and water (33 mL), then the resulting mixture was refluxed for 3.5 h. The reaction mixture was extracted with ether and saturated aqueous NaCl, and then the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo and the residue was recrystallized from ethanol to give 11.0 g (89% yield) of **16**.

16: Colorless needles, mp 145–146°C (EtOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.35 (9H, s, *t*-Bu), 3.87 (4H, s, CH_2), and 7.51 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 25.7 (CH_2), 31.0 (C*Me*$_3$), 34.9 (*C*Me$_3$), 116.7 (CN), 121.6 (arom., CBr), 127.0 (arom., CH), 130.8 (arom.), and 152.2 (arom.); UV (CH_3CN) 220 (sh, log ϵ 3.99), 235 (sh, 3.67), 261 (sh, 2.47), 268 (2.57), and 280 nm (sh, 2.24); IR (KBr) 2254, 1481, 1458, 1412, 1363, 1149, 1028, and 889 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 292 (M^++2; 13), 290 (M^+; 15), 277 (M^+−Me+2; 100), and 275 (M^+−Me; 99). Found: C, 57.50; H, 5.49; Br, 27.20; N, 9.47%. Calcd for $C_{14}H_{15}BrN_2$: C, 57.75; H, 5.19; Br, 27.44; N, 9.62%.

2-Bromo-5-*t*-butyl-1,3-bis(1-cyano-1-methylethyl)benzene (17). To a solution of **16** (5.10 g, 17.5 mmol) in dimethyl sulfoxide (50 mL) was added 1.0 mL of water and 14.1 g (251 mmol) of powdered KOH. The resulting dark solution was cooled using an ice-bath and 15.0 mL (240 mmol) of iodomethane was added. Then the mixture was warmed to room temperature and stirred for 41 h. The reaction mixture was extracted with ether, washed with saturated aqueous NaCl, and then the organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was treated with column chromatography (SiO_2/$CHCl_3$) to give 3.96 g (65%) of **17**.

17: Colorless fine needles, mp 222–222.5°C (EtOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33 (9H, s, *t*-Bu), 1.94 (12H, s, CMe_2), and 7.48 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 28.3 (C*Me*$_2$), 31.1 (C*Me*$_3$), 35.1 (*C*Me$_3$), 38.3 (*C*Me$_2$), 120.8 (arom., CBr), 123.5 (CN), 124.3 (arom., CH), 140.0 (arom.), and 150.9 (arom.); UV (hexane) 224 (sh, log ϵ 3.59), 228 (3.58), 234 (sh, 3.53), 269 (2.22), and 278 nm (2.10); IR (KBr) 2231, 1415, 1371, 1020, and 739 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 348 (M^++2; 18), 346 (M^+; 18), 333 (M^+−Me+2; 100), 331 (M^+−Me; 100), and 57 (*t*-Bu$^+$; 30). Found: *m*/*z* 346.1056. Calcd for $C_{18}H_{23}BrN_2$: M, 346.1044.

2-Bromo-5-*t*-butyl-1,3-bis(1-formyl-1-methylethyl)benzene (18). To a solution of **17** (4.24 g, 12.2 mmol) in benzene (260 mL) was added 30.3 mmol of diisobutylaluminum hydride (1.01 M solution in toluene) and the resulting mixture was stirred at ambient temperature for 4 h. The resulting mixture was cooled using an ice-bath and 5% aqueous sulfuric acid was added to the mixture. After being stirred for 20 min, the reaction mixture was worked up using benzene and saturated aqueous NaCl. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to give **18** (4.29 g, 99% yield).

18: Colorless powder, mp 142.5–145.0°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.36 (9H, s, *t*-Bu), 1.53 (12H, s, CMe_2), 7.42 (2H, s, arom.), and 9.78 (2H, s, CHO); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 23.8 (C*Me*$_2$), 31.2 (C*Me*$_3$), 35.0 (*C*Me$_3$), 52.7 (*C*Me$_2$), 121.6 (arom., CBr), 125.3 (arom., CH), 143.5 (arom.), 150.9 (arom.), and 203.0 (CHO); UV (hexane) 223 (sh, log ϵ 4.02), 232

(3.79), 267 (2.54), 280 (2.39), and 306 nm (2.07); IR (KBr) 2962, 2803, 2705, 1722, 1587, 1469, 1389, and 1016 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 352 (M^+; 0.2), 323 (M^+-CHO; 5), 273 (M^+-Br; 37), and 57 (*t*-Bu^+; 100).

2-Bromo-5-*t*-butyl-1,3-bis(2-hydroxy-1,1-dimethylethyl)-benzene (19). A THF (80 mL) solution of **18** (1.61 g, 4.50 mmol) was added dropwise to a suspension of $LiAlH_4$ (473 mg, 12.5 mmol) in THF (10 mL) at 0°C. Then the resulting mixture was stirred at room temperature for 1.5 h and treated with MeOH. The reaction mixture was extracted with ether, washed with saturated aqueous NaCl, and then the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo, then the residue was treated with column chromatography (SiO_2/$CHCl_3$–Et_2O) to afford 1.10 g (68%) of **19**.

19: Colorless powder, mp 210.5–213.5°C (hexane); ^1H NMR (200 MHz, $CDCl_3$) δ 1.32 (9H, s, *t*-Bu), 1.42 (2H, br. s, OH), 1.57 (12H, s, CMe_2), 4.10 (4H, s, CH_2), and 7.45 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 26.7 (C*Me*$_2$), 31.2 (C*Me*$_3$), 34.9 (*C*Me$_3$), 44.0 (*C*Me$_2$), 69.9 (CH_2), 120.8 (arom., CBr), 126.5 (arom., CH), 144.4 (arom.), and 148.7 (arom.); UV (CH_2Cl_2) 235 nm (sh, log ϵ 3.74); IR (KBr) 3330, 2958, 2881, 1475, 1411, 1394, 1363, and 1031 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 307 ($M^+-Me-2OH$; 10), 276 (M^+-Br-1; 5), 267 (M^+-t-Bu–2OH; 7), 259 ($M^+-Br-OH-1$; 27), 245 ($M^+-Br-2OH$; 55), and 57 (*t*-Bu^+; 100) (molecular ion peak was not observed in the mass spectrum).

2-Bromo-5-*t*-butyl-1,3-bis(2-methoxy-1,1-dimethylethyl)-benzene (10b). Method A: A THF (25 mL) solution of **19** (1.12 g, 3.14 mmol) was added to ca. 9.9 mmol of sodium hydride at 0°C and the resulting mixture was stirred for 15 min at 0°C. To this suspension was added 1.2 mL (19 mmol) of iodomethane at 0°C and the reaction mixture was stirred for 6 h at ambient temperature. Then the mixture was treated with methanol and the solvent was evaporated. The residue was worked up using hexane and aqueous $NaHSO_4$, and the organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure to give 1.13 g (93%) of **10b**.

Method B: To a solution of **19** (180.3 mg, 0.505 mmol) and benzyltriethylammonium chloride (3.2 mg, 0.014 mmol) in benzene (45 mL) was added 50% aqueous NaOH (2.0 mL) and the reaction mixture was vigorously stirred for 30 min. Then the mixture was cooled over an ice-bath and 1.15 mL (12.1 mmol) of dimethyl sulfate was added. After being stirred for 6 h, the reaction mixture was treated with 29% aqueous ammonia, and the resulting mixture was stirred at room temperature for 30 min. Then the mixture was extracted with benzene, the organic phase was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was treated with column chromatography (SiO_2/$CHCl_3$) to give 6.4 mg (3%) of **10b**, 110.3 mg (59%) of 2-bromo-5-*t*-butyl-1-(2-hydroxy-1,1-dimethylethyl)-3-(2-methoxy-1,1-dimethylethyl)benzene (**20**), and 49.2 mg (27% recovery) of the starting **19**. Attempted reaction of the isolated **20** with dimethyl sulfate under similar conditions with longer reaction time (1 day) gave **10b** in only 15% yield, indicating that the second methylation proceeded slowly.

10b: Colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.33 (9H, s, *t*-Bu), 1.58 (12H, s, CMe_2), 3.35 (6H, s, OMe), 3.79 (4H, s, CH_2), and 7.37 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 26.2 (C*Me*$_2$), 31.3 (C*Me*$_3$), 34.6 (*C*Me$_3$), 42.7 (*C*Me$_2$), 59.0 (s, OMe), 81.1 (CH_2), 121.3 (arom., CBr), 125.5 (arom., CH), 145.4 (arom.), and 148.2 (arom.); UV (hexane) 233 nm (sh, log ϵ 3.90); IR (neat) 1590, 1479, 1462, 1392, 1363, 1198, 1109, 1012, 966, and 736 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 339 (M^+-CH_2OMe; 12), 305 (M^+-Br; 28), 245 ($M^+-Br-2OMe+2$; 9), and 57 (*t*-Bu^+; 100) (molecular ion peak was not observed in the mass spectrum).

20: Colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.32 (9H, s, *t*-Bu), 1.57 (12H, s, CMe_2), 3.35 (3H, s, OMe), 3.78 (2H, s, C*H*$_2$OMe), 4.10 (2H, s, C*H*$_2$OH), 7.40 (1H, d, $^4J_{HH}$=2.5 Hz, arom.), and 7.41 (1H, d, $^4J_{HH}$=2.5 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 26.3 (C*Me*$_2$CH$_2$OH), 26.7 (C*Me*$_2$CH$_2$OMe), 31.3 (C*Me*$_3$), 34.8 (*C*Me$_3$), 42.7 (*C*Me$_2$CH$_2$OH), 44.0 (*C*Me$_2$CH$_2$OMe), 59.0 (s, OMe), 70.0 (CH_2OH), 81.1 (*C*H$_2$OMe), 121.0 (arom., CBr), 125.9 (arom., CH), 126.2 (arom., CH), 144.2 (arom.) 145.6 (arom.), and 148.5 (arom.); UV (hexane) 235 nm (sh, log ϵ 3.62); IR (neat) 3432, 2964, 2873, 1590, 1477, 1461, 1392, 1363, 1108, 1041, 1012, 879, and 736 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 339 (M^+-OMe; 2), 291 (M^+-Br; 3), 259 ($M^+-Br-OMe-1$; 45), 245 ($M^+-Br-OMe-OH+2$; 67), and 57 (*t*-Bu^+; 100) (molecular ion peak was not observed in the mass spectrum).

2-Bromo-5-*t*-butyl-1,3-bis(1,1-dimethyl-2-propenyl)benzene (21). To a solution of methyltriphenylphosphonium bromide (7.80 g, 21.8 mmol) in THF (60 mL) was added 22.0 mmol of sodium bis(trimethylsilyl)amide (1.00 M solution in THF) and the resulting mixture was heated to reflux for 3 h. Then the reaction mixture was cooled to room temperature, and to this mixture was added a THF (50 mL) solution of **18**. The resulting mixture was stirred at ambient temperature for 2 h. Then the reaction was quenched by addition of water. The mixture was extracted with ether and the organic phase was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was treated with column chromatography (SiO_2/hexane–$CHCl_3$) to give 2.03 g (91%) of **21**.

21: Colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.34 (9H, s, *t*-Bu), 1.60 (12H, s, CMe_2), 4.91 (2H, dd, ^3J=17.6 Hz and ^2J=0.8 Hz, CH_2), 5.00 (2H, dd, ^3J=10.6 Hz and ^2J=0.8 Hz, CH_2), 6.24 (2H, dd, ^3J=17.6 Hz and ^3J=10.6 Hz, C*H*=CH_2), and 7.43 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 29.7 (C*Me*$_2$), 31.3 (C*Me*$_3$), 34.9 (*C*Me$_3$), 44.1 (*C*Me$_2$), 110.7 (CH_2), 122.4 (arom., CBr), 124.0 (arom., CH), 147.6 (arom.), 148.5 (arom.), and 148.8 (*C*H=CH_2); UV (hexane) 240 (log ϵ 3.62) and 266 nm (2.47); IR (neat) 3082, 2966, 1633, 1465, 1408, 1362, 1173, 1016, 989, 903, 879, 742, and 676 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 350 (M^++2; 39), 348 (M^+; 38), 335 (M^+-Me+2; 49), 333 (M^+-Me; 48), and 57 (*t*-Bu^+; 100). Found: *m/z* 348.1455. Calcd for $C_{20}H_{29}Br$: M, 348.1453.

2-Bromo-5-*t*-butyl-1,3-bis(3-hydroxy-1,1-dimethylpropyl)-benzene (22). To a THF (25 mL) solution of **21** (199 mg, 0.570 mmol) was added 3.40 mmol of borane–THF complex (1.0 M solution in THF) at 0°C, and the reaction mixture was stirred at room temperature for 45 min. The resulting solution was cooled to 0°C, and the reaction was quenched by addition of water. Aqueous NaOH (5.46 mmol), 30% aqueous hydrogen peroxide (5.3 mmol) were added successively to the reaction mixture at 0°C, and the resulting mixture was stirred at room temperature for 3 h. Then the reaction mixture was extracted with ether, the organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was treated with column chromatography (SiO_2/Et_2O) to give 157.6 mg (72%) of **22** and 52.8 mg (24%) of 2-bromo-5-*t*-butyl-1-(2-hydroxy-1,1-dimethylpropyl)-3-(3-hydroxy-1,1-dimethylpropyl)benzene (**23**).

22: Colorless plates, mp 123–125°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30 (9H, s, *t*-Bu), 1.39 (2H, br. s, OH), 1.58 (12H, s, CMe_2), 2.42 (4H, t, ^3J=7.5 Hz, C*H*$_2$CH$_2$O), 3.41 (4H, t, ^3J=7.5 Hz, CH$_2$O), and 7.33 (2H, s, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 30.5 (C*Me*$_2$), 31.2 (C*Me*$_3$), 34.8 (*C*Me$_3$), 40.3 (*C*Me$_2$), 42.5 (*C*H$_2$CH$_2$O), 60.4 (CH$_2$O), 121.5 (arom., CBr), 124.8 (arom., CH), 146.1 (arom.), and 148.7 (arom.); IR (neat) 3292, 2960, 2927, 2871, 1591, 1479, 1463, 1404, 1385, 1363, 1061, 1039, 1028, 1014, 985, 879, 775, and 740 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 339 (M$^+$−CH$_2$CH$_2$OH; 0.3), 259 (M$^+$−Br–CH$_2$CH$_2$OH−1; 17), 219 (M$^+$−Br–CMe$_2$CH$_2$CH$_2$OH+1; 42), and 57 (*t*-Bu$^+$; 100) (molecular ion peak was not observed in the mass spectrum). Found: C, 62.55; H, 8.57%. Calcd for $C_{20}H_{33}BrO_2$: C, 62.33; H, 8.63%.

23: Colorless crystals, mp 148–149°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.06 (3H, d, ^3J=6.4 Hz, CH*Me*), 1.30 (9H, s, *t*-Bu), 1.54 (3H, s, CMe_2), 1.57 (3H, s, CMe_2), 1.58 (6H, s, CMe_2), 2.33-2.49 (2H, m, C*H*$_2$CH$_2$O), 3.41 (2H, t, ^3J=7.5 Hz, CH$_2$O), 5.20 (1H, q, ^3J=6.4 Hz, C*H*Me), 7.35 (1H, d, ^4J=2.4 Hz, arom.), and 7.40 (1H, d, ^4J=2.4 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 17.6 (CH*Me*), 24.4 (C*Me*$_2$), 30.4 (C*Me*$_2$), 30.6 (C*Me*$_2$), 31.2 (C*Me*$_3$), 34.8 (*C*Me$_3$), 40.2 (*C*Me$_2$CH$_2$), 42.6 (*C*H$_2$CH$_2$O), 46.6 (*C*Me$_2$CO), 60.6 (CH$_2$O), 69.4 (*C*HMe), 120.9 (arom., CBr), 125.1 (arom., CH), 126.0 (arom., CH), 145.9 (arom.), 146.4 (arom.), and 148.6 (arom.); IR (neat) 3325, 2966, 2929, 2879, 1475, 1458, 1412, 1402, 1392, 1362, 1311, 1149, 1095, 1068, 1059, 1030, 1012, 901, 881, 744, and 636 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 368 (M$^+$−OH+1; 0.3), 366 (M$^+$−OH−1; 0.3), 341 (M$^+$−CH(OH)Me+2; 3), 339 (M$^+$−CH(OH)Me; 2), and 261 (M$^+$−CH(OH)Me–Br; 100) (molecular ion peak was not observed in the mass spectrum).

2-Bromo-5-*t*-butyl-1,3-bis(3-methoxy-1,1-dimethylpropyl)-benzene (10c). A THF (100 mL) solution of **22** (2.02 g, 5.24 mmol) was added to sodium hydride (31 mmol) at 0°C over a 15-min period. The resulting mixture was stirred at 0°C for 5 min, and to this mixture was added 32.1 mmol of iodomethane at 0°C. The reaction mixture was warmed to room temperature and stirred for 72 h. Appropriate amount of methanol was added to the mixture in order to quench the unreacted NaH. Then the solvent was evaporated and the residue was extracted with hexane. The organic phase was dried over $MgSO_4$, and the solvent was removed to give 2.16 g (99%) of **10c**.

10c: Colorless crystals, mp 42–43°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31 (9H, s, *t*-Bu), 1.58 (12H, s, CMe_2), 2.40 (4H, t, ^3J=7.5 Hz, C*H*$_2$CH$_2$O), 3.11 (4H, t, ^3J=7.5 Hz, CH$_2$O), 3.19 (6H, s, OMe), and 7.33 (2H, s, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 30.4 (C*Me*$_2$), 31.2 (C*Me*$_3$), 34.8 (*C*Me$_3$), 39.4 (*C*H$_2$CH$_2$O), 40.3 (*C*Me$_2$), 58.4 (OMe), 70.5 (CH$_2$O), 121.6 (arom., CBr), 124.8 (arom., CH), 146.1 (arom.), and 148.3 (arom.); IR (neat) 1589, 1477, 1462, 1387, 1363, 1205, 1119, 1012, 966, and 879 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 414 (M$^+$+2; 0.4), 412 (M$^+$; 0.4), 275 (M$^+$−Br–*t*-Bu−1; 52), 243 (M$^+$−Br–*t*-Bu–OMe−2; 81), and 57 (*t*-Bu$^+$; 100). Found: *m*/*z* 412.1981. Calcd for $C_{22}H_{37}BrO_2$: M, 412.1977.

General procedure for the lithiation of the bromobenzenes 10a–c. To a solution of **10** (0.08 mmol) in THF (3 mL) was added 0.09 mmol of butyllithium (1.54M in hexane) at room temperature (for **10a**,**b**) or at −78°C (for **10c**) and the resulting mixture was further stirred at those temperatures for 20 min. Then the reaction was quenched by addition of water. The reaction mixture was extracted using ether and the organic phase was dried over $MgSO_4$. Removal of the solvent afforded **25**.

25a (96% yield): Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34 (9H, s, *t*-Bu), 1.54 (12H, s, CMe_2), 3.07 (6H, s, OMe), 7.24 (1H, t, ^4J=1.6 Hz, arom.), and 7.32 (2H, d, ^4J=1.6 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 28.1 (C*Me*$_2$), 31.5 (C*Me*$_3$), 34.8 (*C*Me$_3$), 50.5 (OMe), 77.1 (*C*Me$_2$), 120.3 (arom., CH), 121.1 (arom., CH), 145.1 (arom.), and 150.7 (arom.); IR (neat) 1599, 1462, 1435, 1377, 1362, 1242, 1173, 1076, 877, 816, 760, and 719 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 278 (M$^+$; 3), 263 (M$^+$−Me; 100), and 247 (M$^+$−OMe; 10). Found: *m*/*z* 278.2246. Calcd for $C_{18}H_{30}O_2$: M, 278.2246.

25b (92% yield): Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33 (9H, s, *t*-Bu), 1.34 (12H, s, CMe_2), 3.33 (6H, s, OMe), 3.40 (4H, s, CH_2), 7.22 (1H, t, ^4J=1.7 Hz, arom.), and 7.30 (2H, d, ^4J=1.7 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 26.1 (C*Me*$_2$), 31.5 (C*Me*$_3$), 34.9 (*C*Me$_3$), 39.3 (*C*Me$_2$), 59.3 (OMe), 82.9 (CH$_2$), 120.6 (arom., CH), 120.7 (arom., CH), 146.4 (arom.), and 149.9 (arom.); IR (neat) 1597, 1477, 1456, 1362, 1194, 1111, 964, 874, and 714 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 306 (M$^+$; 8), 261 (M$^+$−CH$_2$OMe; 100), 215 (M$^+$−2CH$_2$OMe−1; 11), and 57 (*t*-Bu$^+$; 11). Found: *m*/*z* 306.2558. Calcd for $C_{20}H_{34}O_2$: M, 306.2559.

25c (97% yield): Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33 (9H, s, *t*-Bu), 1.35 (12H, s, CMe_2), 1.94 (4H, t, ^3J=7.8 Hz, C*H*$_2$CH$_2$O), 3.20 (4H, t, ^3J=7.8 Hz, CH$_2$O), 3.24 (6H, s, OMe), 7.14 (1H, t, ^4J=1.7 Hz, arom.), and 7.20 (2H, d, ^4J=1.7 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 29.3 (C*Me*$_2$), 31.5 (C*Me*$_3$), 34.9 (*C*Me$_3$), 36.8 (*C*Me$_2$), 43.4 (*C*H$_2$CH$_2$O), 58.4 (OMe), 70.1 (CH$_2$O), 119.8 (arom., CH), 120.1 (arom., CH), 147.8 (arom.), and 150.1 (arom.); IR (neat) 1597, 1460, 1363, 1117, and

715 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 334 (M^+; 20) and 276 (M^+-t-Bu^+-1; 100). Found: *m/z* 334.2865. Calcd for $C_{22}H_{38}O_2$: M, 334.2872.

Attempted preparation of the phosphonous dichlorides 26a,b. To a solution of bromobenzene **10a** (39.4 mg, 0.110 mmol) in THF (4 mL) was added 0.123 mmol of butyllithium at room temperature and the resulting solution was stirred for 10 min. The solution was cooled to 0°C and 0.287 mmol of PCl_3 was added. Then the reaction mixture was warmed to room temperature. Formation of the cyclized product **27a** was observed by ^{31}P NMR spectroscopy. To this solution was added 1.0 mL of methanol at room temperature and the solvent was evaporated. The residue was worked up with hexane and saturated aqueous NaCl, the organic phase was dried over $MgSO_4$, and the solvent was removed in vacuo. Chromatographic treatment of the residue afforded 8.3 mg (24%) of 5-*t*-butyl-3,3-dimethyl-7-(1-methoxy-1-methylethyl)-2-oxa-1-phosphaindan 1-oxide (**29a**). Similarly, 6-*t*-butyl-4,4-dimethyl-8-(2-methoxy-1,1-dimethylethyl)-2-oxa-1-phospha-1,2,3,4-tetrahydronaphthalene 1-oxide (**29b**) was obtained from **10b** in 41% yield.

29a: Colorless crystals, mp 139–142°C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.35 (9H, s, *t*-Bu), 1.60 (3H, s, CMe_2OP), 1.61 (6H, s, CMe_2OMe), 1.75 (3H, s, CMe_2OP), 3.43 (3H, s, OMe), 7.13 (1H, pseudo-t, $^4J_{PH}$=$^4J_{HH}$=1.5 Hz, arom.), 7.29 (1H, dd, $^4J_{PH}$=5.5 Hz, $^4J_{HH}$=1.5 Hz, arom.), and 7.96 (1H, d, $^1J_{PH}$=631.8 Hz, PH); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 24.1 (s, CMe_2), 28.6 (s, CMe_2), 30.5 (d, J_{PC}=4.0 Hz, CMe_2), 31.1 (s, CMe_2), 31.2 (s, CMe_3), 35.3 (d, J_{PC}=0.7 Hz, CMe_3), 49.4 (s, OMe), 77.8 (d, J_{PC}=1.0 Hz, CMe_2), 87.0 (d, J_{PC}=0.8 Hz, CMe_2), 116.9 (d, J_{PC}=13.2 Hz, arom., CH), 121.1 (d, J_{PC}=126.6 Hz, arom., CP), 121.7 (d, J_{PC}=10.4 Hz, arom., CH), 151.6 (d, J_{PC}=7.7 Hz, arom.), 154.3 (d, J_{PC}=20.9 Hz, arom.), and 157.5 (d, J_{PC}=2.6 Hz, arom.); ^{31}PNMR (81 MHz, $CDCl_3$) δ 34.6 (d, $^1J_{PH}$=632.9 Hz); IR (KBr) 2393, 1603, 1460, 1383, 1363, 1240, 1223, 1066, 980, 881, 773, and 557 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 310 (M^+; 3), 295 (M^+−Me; 65), 280 (M^+−2Me; 100), and 263 (M^+−Me−OMe−1; 80). Found: *m/z* 310.1718. Calcd for $C_{17}H_{27}O_3P$: M, 310.1698.

29b: Colorless oil, ^1H NMR (200 MHz, $CDCl_3$) δ 1.32 (9H, s, *t*-Bu), 1.34 (3H, s, CMe_2), 1.40 (3H, s, CMe_2), 1.60 (3H, s, CMe_2), 1.61 (3H, s, CMe_2), 3.34 (3H, s, OMe), 3.60 (1H, d, $^2J_{HH}$=10.2 Hz, CH_2OMe), 3.97 (1H, dd, $^3J_{PH}$=15.1 Hz and $^2J_{HH}$=11.3 Hz, CH_2OP), 4.01 (1H, d, $^2J_{HH}$=10.2 Hz, CH_2OMe), 4.30 (1H, dd, $^3J_{PH}$=13.9 Hz and $^2J_{HH}$=11.3 Hz, CH_2OP), 7.34 (1H, dd, $^4J_{PH}$=3.6 Hz and $^4J_{HH}$=1.8 Hz, arom.), 7.49 (1H, dd, $^4J_{PH}$=5.0 Hz and $^4J_{HH}$=1.8 Hz, arom.), and 7.68 (1H, d, $^1J_{PH}$=586.5 Hz, PH); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 26.9 (s, CMe_2), 28.0 (s, CMe_2), 28.2 (s, CMe_2), 28.6 (s, CMe_2), 30.9 (s, CMe_3), 35.1 (s, CMe_3), 37.7 (d, $^3J_{PC}$=4.6 Hz, CMe_2), 43.1 (d, $^3J_{PC}$=1.9 Hz, CMe_2), 59.0 (s, OMe), 71.1 (d, $^2J_{PC}$=5.7 Hz, CH_2OP), 82.1 (s, CH_2OMe), 121.7 (d, $^1J_{PC}$=111.4 Hz, arom., CP), 121.8 (d, $^3J_{PC}$=10.0 Hz, arom., CH), 124.8 (d, $^3J_{PC}$=12.6 Hz, arom., CH), 151.2 (s, arom.), 151.3 (d, $^2J_{PC}$=4.9 Hz, arom.), and 154.9 (d, $^2J_{PC}$=2.7 Hz, arom.); ^{31}PNMR (81 MHz, $CDCl_3$) δ 22.3 (d, $^1J_{PH}$=585.0 Hz); IR (neat) 1726, 1601, 1473, 1396, 1365, 1238, 1232, 1106, 1010, 941, 821, and 756 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 338 (M^+; 6), 323 (M^+−Me; 11), 306 (M^+−OMe−1; 5), 293 (M^+-CH_2OMe; 31), and 57 (t-Bu^+; 100). Found: *m/z* 338.2012. Calcd for $C_{19}H_{31}O_3P$: M, 338.2011.

Formation of [4-*t*-Butyl-2,6-bis(3-methoxy-1,1-dimethylpropyl)phenyl]phosphonous dichloride (26c). To a solution of **10c** (33.6 mg, 0.0813 mmol) in THF (5 mL) was added 0.0882 mmol of butyllithium (1.47 M in hexane) at −78°C, and the resulting solution was stirred at that temperature for 20 min. Phosphorus trichloride (0.138 mmol) was added to the solution and the resulting mixture was stirred at −78°C for 20 min. Aliquots of the reaction mixture were occasionally removed and analyzed by ^{31}P NMR spectroscopy and a signal due to **26c** [δ_P (THF–C_6D_6)=152.7] was observed as a single product. The reaction mixture was stirred for an additional hour. Triethylamine (0.10 mL) and methanol (0.80 mL) were added to the solution and the resulting mixture was warmed to room temperature. ^{31}P NMR spectrum of the reaction mixture indicated the formation of **30**. The solvent was removed in vacuo and the residue was worked up using ether and saturated aqueous NaCl, dried over $MgSO_4$, and the solvent was evaporated. Chromatographic treatment of the residue afforded 13.9 mg (39%) of dimethyl [4-*t*-butyl-2,6-bis(3-methoxy-1,1-dimethylpropyl)phenyl]phosphonate (**31**).

31: Colorless crystals, mp 68–71°C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.29 (9H, s, *t*-Bu), 1.56 (12H, s, CMe_2), 2.02 (4H, t, $^3J_{HH}$=7.6 Hz, CH_2CH_2O), 2.92 (4H, t, $^3J_{HH}$=7.6 Hz, CH_2O), 3.16 (6H, s, OMe), 3.55 (6H, d, $^3J_{PH}$=11.0 Hz, POMe), and 7.39 (2H, d, $^4J_{PH}$=5.1 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 30.2 (s, CMe_2), 30.9 (s, CMe_3), 34.6 (d, $^5J_{PC}$=1.5 Hz, CMe_3), 41.7 (d, $^3J_{PC}$=3.8 Hz, CMe_2), 47.3 (s, CH_2CH_2O), 52.2 (d, $^2J_{PC}$=7.2 Hz, POMe), 58.4 (s, CH_2OMe), 69.7 (s, CH_2O), 120.5 (d, $^1J_{PC}$=99.9 Hz, arom., CP), 123.5 (d, $^3J_{PC}$=15.6 Hz, arom., CH), 152.7 (d, $^4J_{PC}$=4.2 Hz, arom.), and 157.0 (d, $^2J_{PC}$=8.8 Hz, arom.); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 23.3; IR (KBr) 1591, 1460, 1394, 1362, 1232, 1207, 1173, 1122, 1061, 1047, 1020, 829, 762, and 638 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 442 (M^+; 0.1), 427 (M^+−Me; 1), 411 (M^+−OMe; 2), 397 (M^+-CH_2OMe; 2), 384 ($M^+-CH_2CH_2OMe+1$; 21), and 275 (M^+-t-Bu−P(O)$(OMe)_2$−1; 100).

Preparation of the ethyl phosphinates 33a,b. To a solution of bromobenzene **10a** in THF (25 mL) was added 1.62 mmol of butyllithium at room temperature, and the resulting solution was stirred for 10 min. Then the solution was cooled to 0°C, and 6.18 mmol of diethyl phosphorochloridite was added to the solution. The resulting mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, the residue was worked up using hexane and water, the organic phase was dried over $MgSO_4$, and the solvent was evaporated. Chromatographic treatment of the residue afforded 331.4 mg (63%) of ethyl [4-*t*-butyl-2,6-bis(1-methoxy-1-methylethyl)phenyl]phosphinate (**33a**). Compound **33b** was obtained from **10b** by a similar procedure in 45% yield.

33a: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30 (9H, s, *t*-Bu), 1.37 (3H, t, $^3J_{HH}$=7.0 Hz, CH_2*Me*), 1.65 (12H, br. s, CMe_2), 3.28 (6H, s, OMe), 3.9–4.3 (2H, m, C*H*$_2$Me), 7.24 (2H, d, $^4J_{PH}$=4.4 Hz, arom.), and 7.92 (1H, d, $^1J_{PH}$=585.1 Hz, PH); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 16.2 (d, $^3J_{PC}$=7.7 Hz, CH_2*Me*), 27.9 (s, C*Me*$_2$), 28.6 (s, C*Me*$_2$), 30.9 (s, C*Me*$_3$), 34.6 (s, *C*Me$_3$), 49.6 (s, OMe), 62.6 (d, $^2J_{PC}$=4.8 Hz, CH_2), 79.1 (d, $^3J_{PC}$=3.1 Hz, *C*Me$_2$), 122.7 (d, $^3J_{PC}$=12.6 Hz, arom., CH), 124.3 (d, $^1J_{PC}$=138.8 Hz, arom., CP), 152.6 (d, $^2J_{PC}$=8.8 Hz, arom.), and 153.6 (d, $^4J_{PC}$=3.0 Hz, arom.); ^{31}PNMR (81 MHz, $CDCl_3$) δ 23.3 (d, $^1J_{PH}$=585.3 Hz); IR (neat) 2447, 1603, 1464, 1381, 1362, 1190, 1211, 1171, 1068, 1020, 935, 879, 781, 752, and 623 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 370 (M^+; 2), 369 (M^+-1; 10), 338 ($M^+-OMe-1$; 100), 309 ($M^+-2OMe+1$; 96), and 295 ($M^+-OMe-OEt+1$; 84). Found: *m*/*z* 370.2254. Calcd for $C_{20}H_{35}O_4P$: M, 370.2273.

33b: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31 (9H, s, *t*-Bu), 1.33 (3H, t, $^3J_{HH}$=7.0 Hz, CH_2*Me*), 1.56 (6H, s, CMe_2), 1.58 (6H, s, CMe_2), 3.34 (6H, s, OMe), 3.60 (2H, d, $^2J_{HH}$=9.3 Hz, C*H*$_2$OMe), 3.64 (2H, d, $^2J_{HH}$=9.3 Hz, C*H*$_2$OMe), 3.9–4.2 (2H, m, C*H*$_2$Me), 7.50 (2H, d, $^4J_{PH}$=4.5 Hz, arom.), and 8.11 (1H, d, $^1J_{PH}$=569.1 Hz, PH); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 15.7 (d, $^3J_{PC}$=7.1 Hz, CH_2*Me*), 29.0 (d, $^4J_{PC}$=11.2 Hz, C*Me*$_2$), 30.9 (s, C*Me*$_3$), 34.9 (d, $^5J_{PC}$=1.1 Hz, *C*Me$_3$), 42.8 (d, $^3J_{PC}$=4.2 Hz, *C*Me$_2$), 58.9 (s, OMe), 62.3 (d, $^2J_{PC}$=6.1 Hz, *C*H$_2$Me), 82.9 (s, *C*H$_2$OMe), 124.8 (d, $^3J_{PC}$=13.5 Hz, arom., CH), 126.0 (d, $^1J_{PC}$=127.0 Hz, arom., CP), 152.6 (d, $^2J_{PC}$=9.2 Hz, arom.), and 152.7 (d, $^4J_{PC}$=3.3 Hz, arom.); ^{31}P NMR (81 MHz, $CDCl_3$) δ 27.9 (d, $^1J_{PH}$=568.6 Hz); IR (neat) 2466, 1599, 1461, 1396, 1363, 1222, 1108, 1025, 944, 750, and 619 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 398 (M^+; 3), 383 (M^+-Me; 6), 353 (M^+-OEt; 34), 261 ($M^+-P(O)H(OEt)-CH_2OMe+1$; 100), and 57 (*t*-Bu$^+$; 41). Found: *m*/*z* 398.2586. Calcd for $C_{22}H_{39}O_4P$: M, 398.2586.

Preparation of the phosphines 34a–c. A THF (5 mL) solution of the phosphinate **33a** (52.0 mg, 0.140 mmol) was added to 0.261 mmol of $LiAlH_4$ at 0°C and the resulting mixture was stirred for 1 h. An appropriate amount of methanol was added to the mixture and the solvent was removed in vacuo. Hexane was added to the residue and insoluble materials were filtered off. Removal of the solvent under reduced pressure followed by chromatographic treatment (SiO_2/$CHCl_3$) afforded 11.7 mg (27%) of [4-*t*-butyl-2,6-bis(1-methoxy-1-methylethyl)phenyl]phosphine (**34a**). [4-*t*-Butyl-2,6-bis(2-methoxy-1,1-dimethylethyl)phenyl]-phosphine (**34b**) [δ_P ($CDCl_3$)=−129.4 (t, $^1J_{PH}$=209.3 Hz)] was formed from **33b** by a similar procedure, however, attempted isolation of **34b** resulted in decomposition. Similarly, attempted isolation of [4-*t*-butyl-2,6-bis(3-methoxy-1,1-dimethylpropyl)phenyl]phosphine (**34c**) [δ_P ($CDCl_3$)=−130.2 (t, $^1J_{PH}$=209.2 Hz)], formed by the reaction of phosphonous dichloride **26c** with $LiAlH_4$, resulted in decomposition of **34c**.

34a: Colorless crystals; mp 124–125°C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30 (9H, s, *t*-Bu), 1.68 (12H, s, CMe_2), 3.17 (6H, s, OMe), 4.16 (2H, d, $^1J_{PH}$=216.4 Hz, PH), and 7.16 (2H, d, $^4J_{PH}$=2.2 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 28.3 (s, C*Me*$_2$), 31.2 (s, C*Me*$_3$), 34.4 (s, *C*Me$_3$), 50.3 (d, J_{PC}=5.4 Hz, OMe), 80.0 (d, $^3J_{PC}$=1.9 Hz, *C*Me$_2$), 122.8 (d, $^3J_{PC}$=1.0 Hz, arom., CH), 126.2 (d, $^1J_{PC}$=27.5 Hz, arom., CP), 148.1 (d, $^2J_{PC}$=4.2 Hz, arom.), and 149.0 (d, $^4J_{PC}$=1.1 Hz, arom.); ^{31}P NMR (81 MHz, $CDCl_3$) δ −129.1 (t, $^1J_{PH}$=216.6 Hz); IR (KBr) 2355, 2339, 1598, 1462, 1415, 1377, 1360, 1240, 1182, 1169, 1068, 877, 847, 816, 735, and 606 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 310 (M^+; 4), 278 (M^+-PH_2+1; 100), and 263 (M^+-PH_2-Me+1; 85). Found: *m*/*z* 310.2051. Calcd for $C_{18}H_{31}O_2P$: M, 310.2062.

1,2-Bis[4-*t*-butyl-2,6-bis(3-methoxy-1,1-dimethylpropyl)-phenyl]diphosphene (35c). Phosphonous dichloride **26c** was prepared from 201.2 mg (0.487 mmol) of the bromobenzene **10c** by a method described above, then the solvent and unreacted PCl_3 was removed under reduced pressure. THF (20 mL) was added to the residue and the solution was cooled to −78°C. To the solution was added 1.0 mmol of lithium naphthalenide at the same temperature and the resulting mixture was stirred for 30 min. Then the reaction mixture was warmed to room temperature, and the solvent was removed in vacuo. Hexane was added to the residue, the insoluble material was removed by filtration, and the solvent was evaporated. Chromatographic treatment (Al_2O_3/hexane–benzene) of the residue afforded 6.9 mg (4%) of the diphosphene **35c**.

35c: Yellow crystals, mp 116–117°C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.35 (18H, s, *t*-Bu), 1.47 (24H, s, CMe_2), 2.10 (8H, t, $^2J_{HH}$=7.3 Hz, C*H*$_2$CH$_2$O), 3.06 (8H, t, $^2J_{HH}$=7.3 Hz, CH_2O), 3.17 (12H, s, OMe), and 7.33 (4H, br. s, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 31.2 (C*Me*$_3$), 32.6 (C*Me*$_2$), 34.6 (*C*Me$_3$), 40.4 (*C*Me$_2$), 44.9 (*C*H$_2$CH$_2$O), 58.4 (OMe), 70.0 (CH_2O), 122.6 (arom., CH), 138.4 (arom., CP), 149.4 (arom.), and 152.1 (arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 493.8; UV (hexane) 291 (log ϵ 4.0), 343 (3.6), and 466 nm (2.8); IR (neat) 1589, 1460, 1360, 1196, 1113, 962, 879, and 746 cm^{-1}; FAB-MS *m*/*z* (rel intensity) 365 ($M^+/2+1$; 100), 349 ($M^+/2-Me$; 21), 333 ($M^+/2-OMe$; 21), 306 ($M^+/2-t$-Bu−1; 52), and 274 ($M^+/2-2CH_2OMe$; 25) (molecular ion peak was not observed in the mass spectrum).

General procedure for the reaction of phosphines 34a–c with sulfur. Phosphine **34** was formed in situ by the method described above. To a mixture of phosphine **34a–c** (0.17 mmol) and elemental sulfur (0.6 mg-atom) were added successively benzene (10 mL) and DBU (0.02 mmol), then the resulting mixture was stirred at room temperature for 1–3 days. The solvent was removed under reduced pressure and the residue was washed with hexane. Chromatographic treatment (SiO_2/$CHCl_3$) of the washings afforded **38a–c**.

38a (53% yield): mp 115–117°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34 (9H, s, *t*-Bu), 1.60 (3H, s, CMe_2OP), 1.67 (6H, br. s, C*Me*$_2$OMe), 1.74 (3H, s, CMe_2OP), 2.39 (3H, d, $^3J_{PH}$=15.8 Hz, SMe), 3.39 (3H, s, OMe), 7.09 (1H, pseudo t, $^4J_{PH}$=$^4J_{HH}$=1.7 Hz, arom.), and 7.36 (1H, dd, $^4J_{PH}$=6.5 Hz and $^4J_{HH}$=1.7 Hz, arom.); ^{13}C{^{1}H}NMR (50 MHz, $CDCl_3$) δ 14.5 (d, $^2J_{PC}$=4.2 Hz, SMe), 25.9 (s, C*Me*$_2$), 26.9 (d,

J_{PC}=1.0 Hz, C*Me*$_2$), 29.5 (d, J_{PC}=1.6 Hz, C*Me*$_2$), 30.8 (d, J_{PC}=2.7 Hz, C*Me*$_2$), 31.1 (s, C*Me*$_3$), 35.2 (d, $^5J_{PC}$=1.1 Hz, *C*Me$_3$), 48.1 (s, OMe), 78.0 (d, $^3J_{PC}$=0.8 Hz, *C*Me$_2$OMe), 87.7 (d, $^2J_{PC}$=4.2 Hz, *C*Me$_2$OP), 117.1 (d, $^3J_{PC}$=14.2 Hz, arom., CH), 123.0 (d, $^3J_{PC}$=11.4 Hz, arom., CH), 124.9 (d, $^1J_{PC}$=107.2 Hz, arom., CP), 151.0 (d, $^2J_{PC}$=8.4 Hz, arom.), 152.4 (d, $^2J_{PC}$=23.2 Hz, arom.), and 156.7 (d, $^4J_{PC}$=3.1 Hz, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 106.4; IR (KBr) 1603, 1456, 1377, 1363, 1252, 1224, 1190, 1144, 1072, 1061, 947, 916, 901, 877, 847, 802, 775, 698, 611, and 559 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 372 (M^+; 46), 342 (M^+−OMe+1; 12), 340 (M^+−S; 12), 325 (M^+−SMe; 20), and 295 (M^+−SMe−S+2; 100). Found: *m*/*z* 372.1345. Calcd for $C_{18}H_{29}O_2PS_2$: M, 372.1347.

38b (11% yield): Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.32 (9H, s, *t*-Bu), 1.35 (3H, s, CMe$_2$), 1.42 (3H, s, CMe$_2$), 1.75 (6H, s, CMe$_2$), 2.35 (3H, d, $^3J_{PH}$=15.2 Hz, SMe), 3.32 (3H, s, OMe), 3.67 (1H, d, $^2J_{HH}$=9.6 Hz, C*H*$_2$OMe), 3.97 (1H, dd, $^3J_{PH}$=22.5 Hz and $^2J_{HH}$=11.2 Hz, CH$_2$OP), 4.09 (1H, d, $^2J_{HH}$=9.6 Hz, C*H*$_2$OMe), 4.48 (1H, dd, $^3J_{PH}$=13.9 Hz and $^2J_{HH}$=11.2 Hz, CH$_2$OP), 7.34 (1H, dd, $^4J_{PH}$=4.4 Hz and $^4J_{HH}$=2.0 Hz, arom.), and 7.59 (1H, dd, $^4J_{PH}$=6.2 Hz and $^4J_{HH}$=2.0 Hz, arom.); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 13.8 (d, $^2J_{PC}$=3.6 Hz, SMe), 27.0 (s, C*Me*$_2$), 29.4 (s, C*Me*$_2$), 30.2 (s, C*Me*$_2$), 30.8 (s, C*Me*$_2$), 30.9 (s, C*Me*$_3$), 35.1 (s, *C*Me$_3$), 38.1 (d, $^3J_{PC}$=4.6 Hz, *C*Me$_2$), 44.1 (d, $^3J_{PC}$=2.3 Hz, *C*Me$_2$), 59.0 (s, OMe), 72.6 (d, $^2J_{PC}$=8.5 Hz, CH$_2$OP), 82.6 (s, *C*H$_2$OMe), 123.1 (d, $^3J_{PC}$=11.0 Hz, arom., CH), 126.1 (d, $^1J_{PC}$=91.6 Hz, arom., CP), 126.9 (d, $^3J_{PC}$=13.9 Hz, arom., CH), 151.1 (d, $^2J_{PC}$=12.5 Hz, arom.), 151.2 (d, $^2J_{PC}$=6.7 Hz, arom.), and 154.3 (d, $^4J_{PC}$=3.2 Hz, arom.); ^{31}P{^{1}H}NMR (81 MHz, $CDCl_3$) δ 97.4; IR (neat) 1600, 1469, 1107, 1041, 812, 701, and 684 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 400 (M^+; 0.4), 385 (M^+−Me; 10), 367 (M^+−S; 7), 353 (M^+−SMe; 100), 321 (M^+−SMe−S; 11), and 57 (*t*-Bu$^+$; 17). Found: *m*/*z* 400.1666. Calcd for $C_{20}H_{33}O_2PS_2$: M, 400.1660.

38c (26% yield): Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.17 (3H, s, CMe$_2$), 1.30 (9H, s, *t*-Bu), 1.59 (1H, m, C*H*$_2$CH$_2$O), 1.62 (3H, s, CMe$_2$), 1.62 (3H, s, CMe$_2$), 1.84 (3H, s, CMe$_2$), 1.91 (3H, d, $^3J_{PH}$=15.3 Hz, SMe), 2.18 (1H, m, C*H*$_2$CH$_2$O), 2.39 (1H, m, C*H*$_2$CH$_2$O), 2.91 (1H, m, CH$_2$O), 3.03 (1H, m, CH$_2$O), 3.11 (1H, m, C*H*$_2$CH$_2$O), 3.17 (3H, s, MeO), 4.19 (1H, m, CH$_2$OP), 4.70 (1H, m, CH$_2$OP), 7.31 (1H, dd, $^4J_{PH}$=4.5 Hz and $^4J_{HH}$=2.1 Hz, arom.), and 7.36 (1H, dd, $^4J_{PH}$=5.9 Hz and $^4J_{HH}$=2.1 Hz, arom.); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 13.5 (d, $^2J_{PC}$=4.5 Hz, SMe), 27.6 (s, C*Me*$_2$), 30.9 (s, C*Me*$_3$), 32.4 (d, $^4J_{PC}$=6.2 Hz, C*Me*$_2$), 34.7 (d, $^5J_{PC}$=1.4 Hz, *C*Me$_3$), 37.2 (s, C*Me*$_2$), 39.9 (d, $^3J_{PC}$=2.6 Hz, *C*H$_2$CH$_2$OP), 42.1 (d, $^3J_{PC}$=3.2 Hz, *C*Me$_2$), 42.6 (d, $^3J_{PC}$=2.6 Hz, *C*Me$_2$), 45.9 (s, *C*H$_2$CH$_2$OMe), 58.4 (s, OMe), 63.9 (d, $^2J_{PC}$=6.5 Hz, CH$_2$OP), 70.0 (s, *C*H$_2$OMe), 123.1 (d, $^3J_{PC}$=13.3 Hz, arom., CH), 125.2 (d, $^3J_{PC}$=14.9 Hz, arom., CH), 131.9 (d, $^1J_{PC}$=99.3 Hz, arom., CP), 152.3 (d, $^4J_{PC}$=4.5 Hz, arom.), 154.1 (d, $^2J_{PC}$=11.8 Hz, arom.), and 157.6 (d, $^2J_{PC}$=6.6 Hz, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 101.9; IR (neat) 1591, 1464, 1389, 1363, 1169, 1117, 1066, 1038, 985, 781, 677, and 600 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 428 (M^+; 2), 413 (M^+−Me; 24), 396 (M^+−S; 82), 381 (M^+−SMe; 83), 371 (M^+−*t*-Bu; 55), 355 (M^+−*t*-Bu−Me−1; 93), 323 (M^+−*t*-Bu−SMe−1; 93), and 57 (*t*-Bu$^+$; 100). Found: *m*/*z* 428.1971. Calcd for $C_{22}H_{37}O_2PS_2$: M, 428.1973.

Typical procedure for the reaction of phosphines 34a–c with selenium. Phosphine **34a**–**c** was formed in situ by the method described above. To a mixture of phosphine **34a**–**c** (0.18 mmol) and elemental selenium (0.58 mg-atom) were added successively benzene (10 mL) and a base (0.03 mmol), then the resulting mixture was stirred at room temperature for 1–3 days. The solvent was removed under reduced pressure and the residue was washed with hexane. The hexane-insoluble material was removed by filtration, and the filtrate was treated with column chromatography to give **41** and/or **42**.

41a (3% yield): Colorless crystals, mp 150–151°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34 (9H, s, *t*-Bu), 1.59 (3H, s, CMe$_2$), 1.66 (3H, s, CMe$_2$), 1.68 (3H, s, CMe$_2$), 1.74 (3H, s, CMe$_2$), 2.37 (3H, d, $^3J_{PH}$=13.6 Hz, SeMe), 3.43 (3H, s, OMe), 7.07 (1H, pseudo-t, $^4J_{PH}$=$^4J_{HH}$=1.9 Hz, arom.), and 7.31 (1H, dd, $^4J_{PH}$=6.5 Hz and $^4J_{HH}$=1.6 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 8.2 (d, $^2J_{PC}$=4.2 Hz, SeMe), 25.9 (s, C*Me*$_2$), 26.8 (d, J_{PC}=1.1 Hz, C*Me*$_2$), 29.6 (s, C*Me*$_2$), 30.8 (d, J_{PC}=2.5 Hz, C*Me*$_2$), 31.2 (s, C*Me*$_3$), 35.1 (d, $^5J_{PC}$=1.1 Hz, *C*Me$_3$), 47.5 (s, OMe), 78.1 (s, *C*Me$_2$OMe), 89.5 (d, $^2J_{PC}$=7.2 Hz, *C*Me$_2$OP), 117.1 (d, $^3J_{PC}$=13.7 Hz, arom., CH), 122.9 (d, $^3J_{PC}$=10.9 Hz, arom., CH), 126.6 (d, $^1J_{PC}$=83.5 Hz, arom., CP), 150.5 (d, $^2J_{PC}$=7.9 Hz, arom.), 150.7 (d, $^2J_{PC}$=22.0 Hz, arom.), and 156.6 (d, $^4J_{PC}$=3.1 Hz, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 70.6, satellite, $^1J_{SeP}$=841.9 and 436.6 Hz; IR (KBr) 1600, 1458, 1377, 1362, 1190, 1070, 947, 914, 899, 877, 845, 771, 642, 570, 536, and 521 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 468 (M^+; 17), 373 (M^+−SeMe; 24), and 293 (M^+−SeMe−Se; 100). Found: *m*/*z* 468.0216. Calcd for $C_{18}H_{29}O_2PSe_2$: M, 468.0236.

41b (trace): ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 82.9, satellite, $^1J_{PSe}$=832.4 and 420.4 Hz.

42c (11% yield): Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26 (3H, s, CMe$_2$), 1.30 (9H, s, *t*-Bu), 1.56 (3H, s, CMe$_2$), 1.70 (3H, s, CMe$_2$), 1.78 (3H, s, CMe$_2$), 1.91 (3H, d, $^3J_{PH}$=11.8 Hz, SeMe), 2.0–2.2 (2H, m, C*H*$_2$CH$_2$O), 2.7–2.9 (3H, m, C*H*$_2$CH$_2$O and CH$_2$O), 3.1–3.2 (1H, m, CH$_2$O), 3.17 (3H, s, OMe), 4.1–4.3 (1H, m, CH$_2$O), 4.5–4.6 (1H, m, CH$_2$O), 7.30 (1H, dd, $^4J_{PH}$=4.6 Hz and $^4J_{HH}$=2.0 Hz, arom.), and 7.43 (1H, dd, $^4J_{PH}$=5.6 Hz and $^4J_{HH}$=2.0 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 5.0 (d, $^2J_{PC}$=4.9 Hz, SeMe), 28.3 (s, C*Me*$_2$), 30.8 (s, C*Me*$_3$), 31.7 (s, C*Me*$_2$), 34.7 (d, $^5J_{PC}$=1.5 Hz, *C*Me$_3$), 35.8 (s, C*Me*$_2$), 40.1 (s, *C*H$_2$CH$_2$OP), 41.7 (d, $^3J_{PC}$=3.8 Hz, *C*Me$_2$), 41.8 (d, $^3J_{PC}$=3.4 Hz, *C*Me$_2$), 46.7 (s, *C*H$_2$CH$_2$OMe), 58.3 (s, OMe), 64.3 (d, $^2J_{PC}$=7.1 Hz, CH$_2$OP), 69.9 (s, *C*H$_2$OMe), 122.7 (d, $^3J_{PC}$=13.7 Hz, arom., CH), 125.4 (d, $^3J_{PC}$=15.2 Hz, arom., CH), 129.1 (d, $^1J_{PC}$=119.4 Hz, arom., CP), 152.7 (d, $^4J_{PC}$=4.2 Hz, arom.), 154.1 (d, $^2J_{PC}$=13.4 Hz, arom.), and 155.8 (d, $^2J_{PC}$=8.4 Hz, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ (42.2, satellite, $^1J_{SeP}$=424.2 Hz; IR (neat) 1593, 1463, 1223, 1117, 1068, 985, 757, and 609 cm^{-1}; MS (70 eV)

m/*z* (rel intensity) 445 (M^+-Me; 1) and 365 (M^+-SeMe; 100) (molecular ion peak was not observed in the mass spectrum).

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