Preparation and Properties of Stabilized Thioxophosphine Sulfides Bearing the 4-*t*-Butyl-2,6-bis(dialkylaminomethyl)phenyl or the 2,4-Di-*t*-butyl-6-(dialkylaminomethyl)phenyl Substituents

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Stabilized thioxophosphine sulfides bearing the 4-*t*-butyl-2,6-bis(dialkylaminomethyl)phenyl or the 2,4-di-*t*-butyl-6-(dialkylaminomethyl)phenyl group, as well as their ^{15}N labeled analogs, were prepared. Intramolecular interaction between the nitrogen and the phosphorus atoms was investigated, mainly by means of ^{31}P NMR and ^{1}H NMR spectroscopic studies.

Phosphorus compounds bearing bulky substituents are of current interest.[1] The 2,4,6-tri-*t*-butylphenyl group is one of the most powerful bulky stabilizing groups; by utilizing this substituent, we and others have successfully prepared various types of multiple-bonded phosphorus compounds, such as diphosphenes,[2] phosphacumulenes,[3] and phospharadialenes.[4] In the course of our study for developing new stabilizing groups, we have examined various groups having an electron donating part within their moieties, in order to stabilize reactive phosphorus-chalcogen multiple bonds.

Thus, we have developed several stabilizing groups, such as 2,4-di-*t*-butyl-6-(dialkylamino)phenyl,[5] 2-alkoxy-4,6-di-*t*-butylphenyl,[6] 2,4-di-*t*-butyl-6-(dimethylaminomethyl)phenyl,[7] 2,4-di-*t*-butyl-6-(methoxymethyl)phenyl,[8] and 2,4-di-*t*-butyl-6-[1,1-dimethyl-2-(dimethylamino)ethylphenyl.[9] Comparison of properties of the phosphorus compounds bearing such stabilizing groups with those with the 2,4,6-tri-*t*-butylphenyl group is of interest from the viewpoint of heteroatom chemistry, in terms of the element–element interactions. We report here the utilization of the 4-*t*-butyl-2,6-bis(dialkylaminomethyl)phenyl[10] and the 2,4-di-*t*-butyl-6-(dialkylaminomethyl)phenyl groups, as well as their ^{15}N labeled derivatives, for the study of phosphorus–nitrogen intramolecular donor–acceptor interactions in the stabilized thioxophosphine sulfides.

Results and Discussion

First of all, 2-bromo-5-*t*-butyl-1,3-bis(dialkylaminomethyl)benzenes were prepared from 2-bromo-1,3-bis(bromomethyl)-5-*t*-butylbenzene (**1A**)[11] by a method similar to that for 2-bromo-5-*t*-butyl-1,3-bis(dimethylaminomethyl)-benzene (**2a**).[10] Thus, **1A** was treated with amines, such as diethylamine or diisopropylamine, to give the corresponding bromobenzene **2b** or **2c** (Scheme 1). Similarly, 2-bromo-1,5-di-*t*-butyl-3-(dialkylaminomethyl)benzenes **2f—h** were prepared, from 2-bromo-1-bromomethyl-3,5-di-*t*-butylbenzene (**1B**).[8]

Lithiation of bromobenzenes **2b,c**, followed by the reaction with phosphorus trichloride, formed phosphonous dichlorides **3b,c**, which were then reduced by $LiAlH_4$ to give the corresponding primary phosphines **4b,c**. The phosphines **4b,c** were then allowed to react with elemental sulfur in benzene at an ambient temperature. Formation of the corresponding thioxophosphine sulfides **5b,c** was observed by ^{31}P NMR spectroscopy. Although the attempted isolation of **5c** was unsuccessful, compound **5b** was isolated in 15% yield. Seemingly, the diisopropylamino derivative **5c** is less stable than the diethylamino derivative **5b**. This fact indicates that the intramolecular coordination (see below) of the nitrogen to the phosphorus atom in **5c** is not so effective as those in **5b** and **5a**[10a] (Chart 1), probably because of the steric hindrance of the isopropyl groups.

A similar tendency was found in the case of **5f—h**. Although thioxophosphine sulfide **5f** was isolated in 12% yield,[7] attempted preparations of **5g** and **5h** resulted in the formation of a complex mixture of products. Although formation of **5h** was not confirmed by ^{31}P NMR monitoring, compound **5g** was detected in the reaction mixture.

Table 1 lists the ^{31}P NMR data for phosphines **4b,c,f—h** and thioxophosphine sulfides **5b,c,f**, and **g** as well as those for the related compounds **4e,4j**, **5e**, and **5j** (see below), **4a,k—m**, and **5a**, **k—m** (Chart 1). The phosphorus atoms of phosphines **4a—c**, **e—h,j** exhibit a slightly upfield shift by 1—11 ppm compared with that of 2,4-di-*t*-butyl-6-methylphenylphosphine **4l**. This difference in chemical shifts is smaller than that between **4l** and (2,4,6-tri-*t*-butylphenyl)-phosphine **4m**. Thus, the interaction between the phosphorus atom and the nitrogen atom in **4a—c,e—h,j** seems to be small. However, in the case of **5**, compounds **5a—c,e—h,j**, containing amino groups within the molecules, show a large upfield shift compared with **5l** by 125—144 ppm, while the chemical shifts for **5l** and **5m** are very close in value (a

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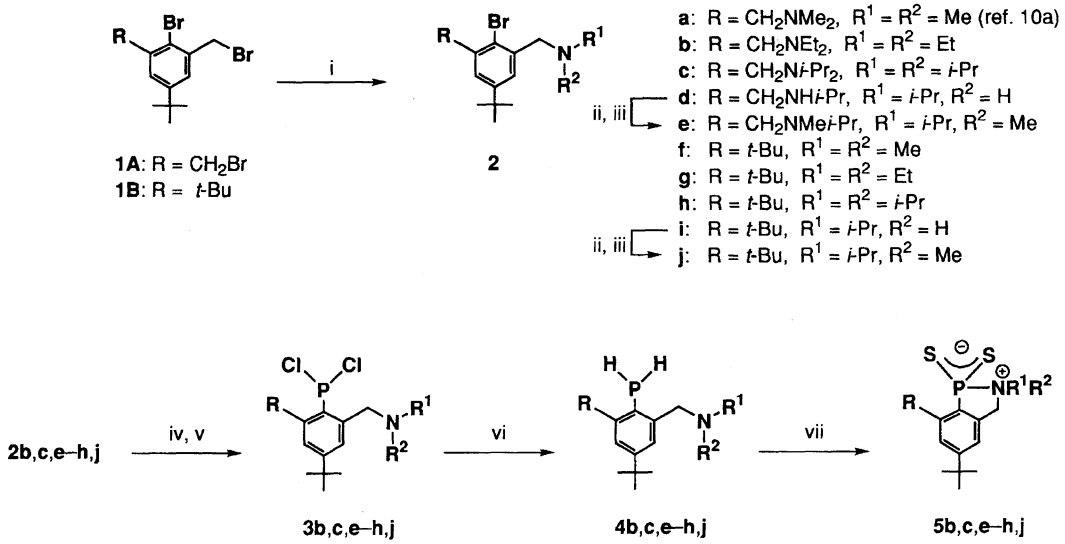


i, R^1R^2NH; ii, HCHO; iii, $NaBH_3CN$; iv, *n*-BuLi; v, PCl_3; vi, $LiAlH_4$; vii, S_8.

Scheme 1.

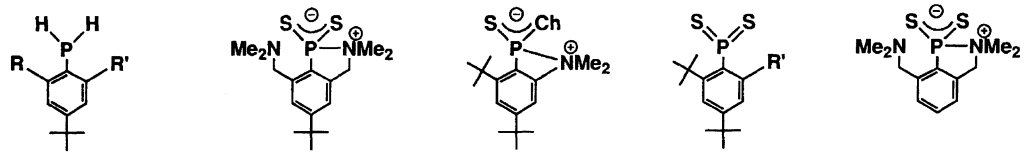


Chart 1.

Table 1. ^{31}P NMR Data (81 MHz) of Phosphines **4** and Thioxophosphine Sulfides **5**

Compound	Substituent at the *o*-positions		4		5
	R	R′	δ_P in $CDCl_3$	($^1J_{PH}$/Hz)	δ_P in $CDCl_3$
a	CH_2NMe_2	CH_2NMe_2	−148.7[a]	(207.4)	145.3[a]
b	CH_2NEt_2	CH_2NEt_2	−147.3	(204.6)	149.1
c	$CH_2N(i\text{-Pr})_2$	$CH_2N(i\text{-Pr})_2$	−153.5	(207.5)	163.6[b]
e	$CH_2N(Me)i\text{-Pr}$	$CH_2N(Me)i\text{-Pr}$	−147.0	(205.7)	151.8
f	*t*-Bu	CH_2NMe_2	−143.6	(203.6)	149.6
g	*t*-Bu	CH_2NEt_2	−143.2	(207.2)	153.0
h	*t*-Bu	$CH_2N(i\text{-Pr})_2$	−146.9	(205.4)	—[c]
j	*t*-Bu	$CH_2N(Me)i\text{-Pr}$	−142.5	(207.3)	156.0
k	*t*-Bu	NMe_2	−141.6[d]	(213.7)	170.6[d]
l	*t*-Bu	Me	−143.0[e]	(203.0)	289.4[f]
m	*t*-Bu	*t*-Bu	−129.9[g]	(210.6)	298.2[h]

a) Data taken from Ref. 10a. b) Measured in C_6D_6. c) Not detected. d) Data taken from Ref. 5a. e) The reported value in Ref. 12: −149.9 ($^1J_{PH}$ = 201.1 Hz, in C_6D_6). f) Data taken from Ref. 13a. g) Data taken from Ref. 14. h) Data taken from Ref. 15.

difference of only 9 ppm). The relative stabilities of **5a—c** and the tendency of the upfield shift seem to correlate, i.e. the signal due to a more stable derivative appears at a higher field than those of the less stable compounds. This is also true in the relation between **5f** and **5g**.

Table 2 shows IR data of the amino-containing thioxophosphine sulfides **5a**,**b**,**f**,**k** and 2,4,6-tri-*t*-butylphenyl substituted thioxophosphine sulfide **5m**. The absorption due to the phosphorus–sulfur double bond of **5a**,**b**,**f**,**k** shifts to lower wavenumber, compared with that of **5m**. This phenomenon suggests that the phosphorus–sulfur double bond in **5a**,**b**,**f**, **k** is weaker than that of **5m**.

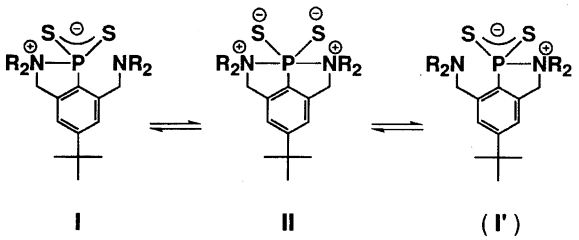
These facts indicate that there are strong interactions between the nitrogen atoms and the phosphorus centers in **5a—c**,**e—h**,**j**, i.e. an intramolecular coordination of the nitrogen to the phosphorus atom is suggested to operate, as

Table 2. IR Data (KBr) of Thioxophosphine Sulfides **5**

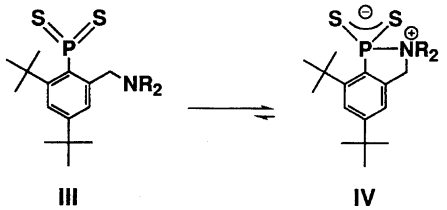
Compound	Substituent at the *o*-positions		$\nu_{(P=S)}$ / cm^{-1}	
	R	R′		
5a	CH_2NMe_2	CH_2NMe_2	714[a]	635[a]
5b	CH_2NEt_2	CH_2NEt_2	715	642
5f	*t*-Bu	CH_2NMe_2	713	634
5k	*t*-Bu	NMe_2	725[b]	653[b]
5m	*t*-Bu	*t*-Bu	792[c]	660[c]

a) Data taken from Ref. 10a. b) Data taken from Ref. 5a.
c) Data taken from Ref. 15.

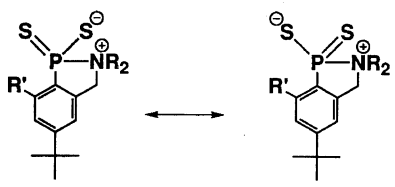
shown in Schemes 2 and 3. The intramolecularly coordinated system can be alternatively represented by a resonance hybrid, as shown in Scheme 4. This type of coordination gives donor–acceptor interaction on the phosphorus atom of the intrinsically polarized $P^{\delta+}=S^{\delta-}$ bond. The more effective coordination causes the molecule to be more stable, by delocalization of charge, to lead the phosphorus atom to be more electron-rich. The chemical shifts for **5a**,**b**,**e** (δ_P = 145—152) are similar to those for **5f**,**g**,**j** (δ_P = 149—156). A signal due to the bis(dialkylaminomethyl)phenyl derivative appears at a higher field, but only by 4 ppm, as compared with that for the corresponding mono(dialkylaminomethyl)phenyl derivative (for example, the difference in the chemical shifts of **5a** and **5f** is only 4.3 ppm). Moreover, the IR absorptions [ν(P=S)] for **5a**,**b** were very similar to those for **5f** (Table 2). In fact, **5f** showed nearly the same wavenumbers as those for **5a** (in KBr). These facts may suggest that the contribution of structure **I** is more important than the trigonal bipyramidal structure (**II**),[16] as shown in Scheme 2.



Scheme 2.



Scheme 3.



Scheme 4.

In order to obtain further information about the intramolecular coordination, we prepared some compounds containing unsymmetrically substituted amino groups. Thus, the bromobenzene **1A** was allowed to react with isopropylamine to give **2d**. Reductive methylation of **2d** using formaldehyde and $NaBH_3CN$ afforded **2e**. Similarly, **1B** was treated with isopropylamine to give **2i**, which was converted to the *N*-methylated derivative **2j**. Phosphines **4e**,**j** and the stabilized thioxophosphine sulfides **5e**,**j** were prepared by procedures similar to that described above (Scheme 1). Table 1 also lists ^{31}P NMR data for **4e**,**j** and **5e**,**j**. In the ^1H NMR spectrum (200 MHz, 295 K) of **5j**, the two methylene protons appeared non-equivalent. This fact suggests that the nitrogen atom coordinates on the phosphorus atom (**IV** in Scheme 3) in solution, at least on the NMR time scale at 295 K, as has been indicated in the solid state structure by X-ray crystallographic analysis of **5f** (Fig. 1).[7] It should be noted that similar magnetic non-equivalency, caused by coordination, was observed in the case of thioxophosphine selenide **6k** (Chart 1).[5b] In the ^1H NMR spectrum of **6k**, the methyl protons on the nitrogen atom appeared as magnetically non-equivalent, indicating that the nitrogen atom coordinates to the phosphorus atom and that rotations around the P–C bond and/or N–C(phenyl) bond are restricted.

In contrast, methylene protons of **5e** appeared equivalent in the ^1H NMR spectrum at room temperature. This may suggest that rapid P–N bond dissociation and bond reformation are alternating to allow inversion at the free nitrogen

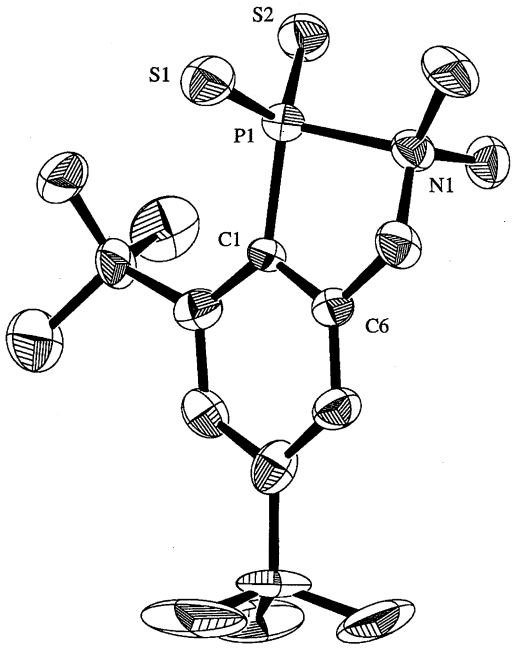


Fig. 1. Molecular structure for **5f**.[7] The crystal data for **5f** were deposited at the Cambridge Crystallographic Data Centre (The CCDC refcode: YEHJEA). Benzene involved as a recrystallizing solvent is omitted for clarity. Some important bond lengths (Å) and angles (°): P1–S1, 1.944(4); P1–S2, 1.936(4); P1–N1, 1.921(8); P1–C1, 1.820(9); P1–C1–C6, 109.7(8).

center. More likely, a rapid exchange exists between the structures **I** and **I′** in solution, as indicated in Scheme 2, to cause bond-switching rather than taking a resonance structure of **II**. ^{1}H NMR spectrum of **5e** at lower temperatures (down to 170 K) suggested that the benzyl protons (δ = 4.1 at 298 K) are de-coalesced at 180 K; however, line shape-analysis was not possible because the methin protons (δ = 3.9) and one of the de-coalesced broad peak of the benzyl protons (δ = 3.8 at 170 K) overlapped each other in the spectrum (averaged chemical shift of all benzyl protons: δ = 3.95 at 170 K).

In order to get insight on this phenomenon, we prepared ^{15}N-labeled compounds, **4a***,**f*** and **5a***,**f***. As for ^{15}N NMR (20 MHz, C_6D_6) spectroscopy, compound **5a*** (δ_N = −363.3, relative to nitromethane) showed a downfield shift compared with that of **4a*** (δ_N = −389.3), probably because the electron density on the nitrogen atom in **5a** was decreased by interaction with the phosphorus center. On the other hand, **4f*** was prepared in situ and immediately converted to **5f***, without measurement of its ^{15}N NMR spectrum because of the instability of **4f***. A signal due to **5f*** (δ_N = −341.8) appeared at a lower field than that of **5a***, which suggests that the phosphorus-nitrogen interaction in **5f*** is stronger than that in **5a***.

^{31}P NMR data of the ^{15}N-labeled compounds are shown in Table 3. The spin–spin coupling constants (J_{PN}) for **5a*** and **5f*** (15—30 Hz) are much larger than those for **4a*** and **4f*** (3—6 Hz), indicating that a significant interaction between the nitrogen atom and the phosphorus atom in **5** is operating. Typical values of spin–spin coupling constants ($^1J_{PN}$) for the P^V–N^{III} bonds are 10—40 Hz and those for the P^{III}–N^{III} bonds are 50—90 Hz.[17] The J_{PN} value for **5f*** (31 Hz) is almost twice the value for **5a*** (15 Hz). This difference in their J_{PN} values indicates that the nitrogen–phosphorus interaction in **5f*** (larger J_{PN}) is stronger than in **5a*** (smaller J_{PN}).

Attempted analysis of crystal structures for the isolated thioxophosphine sulfides **5a**,**b** failed because of lacking appropriate single crystals for X-ray crystallography. A molecular orbital calculation (PM3) of the model compound **5n** (Chart 1) indicated that the structure **II** (Scheme 2) is not at an energy minimum. Thus, the structure **II** seems to be a transition state rather than an intermediate. Figure 2 shows an optimized conformation of **5n**, whose structure corresponds to the structure **I** as shown in Scheme 2. A bond switch in N–S···N system has been described for 1-aminomethyleneamino-1,2,4-thiadiazole system.[18] Moreover, existence of a similar exchange of amine ligands has been reported in the case of 2,6-bis(dimethylaminomethyl)phenyl-substituted

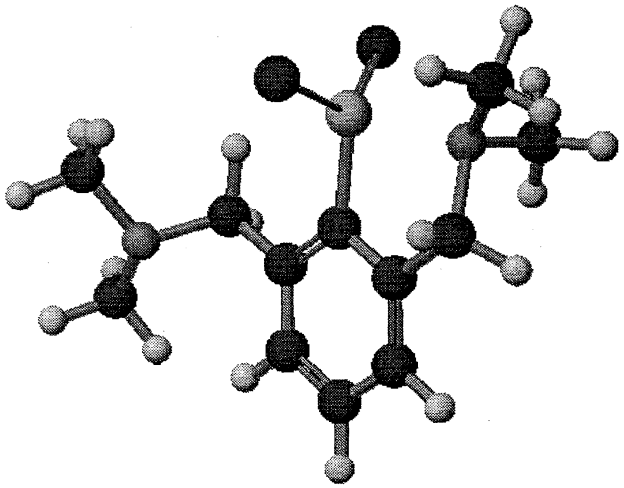


Fig. 2. Optimized structure of **5n** calculated by PM3 method. The total energy was −2531.4329 eV. Some important bond lengths (Å) and angles (°): P–N, 2.081; P···N, 4.396; P–S,1.939 and 1.940; P–C(*ipso*), 1.846; P–C(*ipso*)–C(*o*), 112.45.

silicon compound[10b] as well as 2-[2,6-bis(dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane.[19] In the latter case, exchange via an S_N2-type mechanism has been demonstrated. A competing dissociation of the S_N1-type was also assumed in the case of the dioxaborolane; however, it is unlikely that such dissociation occurs in compound **5**, at least at an ambient temperature. ^{1}H NMR measurement of **5j** at an elevated temperature (393 K in toluene-d_8) showed no significant change, indicating that activation energy for P–N bond dissociation in **5j** is very high.

In summary, we have prepared some stabilized thioxophosphine sulfides bearing the 4-*t*-butyl-2,6-bis(dialkylaminomethyl)phenyl or the 2,4-di-*t*-butyl-6-(dialkylaminomethyl)phenyl group as well as their ^{15}N labeled analogs. In the 2,4-di-*t*-butyl-6-(dialkylaminomethyl)phenyl derivatives, effective coordination of the nitrogen atom to the phosphorus center was suggested. On the other hand, in the 4-*t*-butyl-2,6-bis(dialkylaminomethyl)phenyl derivatives, switching of the amine ligand was suggested to take place.

Experimental

Melting points were taken on a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. ^{1}H NMR spectra and ^{13}C NMR (50 MHz) spectra were recorded on either a Bruker AC-200P or AM-600 spectrometer at 295 K, unless otherwise specified. ^{31}P NMR (81 MHz) spectra were obtained with a Bruker AC-200P spectrometer at 295 K using 85% H_3PO_4 as an external standard, unless otherwise specified. ^{15}N NMR (20 MHz) spectra were

Table 3. ^{31}P NMR Data (81 MHz) of ^{15}N-Labeled Phosphines **4a***,**f***, and Thioxophosphine Sulfides **5a***,**f***

Compound	Substituent at the *o*-positions		**4**[a]		**5**[b]	
	R	R′	δ_P	(J_{PN}/Hz)	δ_P	(J_{PN}/Hz)
a*	$CH_2N^*Me_2$	$CH_2N^*Me_2$	−151 (t)	(5.3)	145 (t)	(15.3)
f*	*t*-Bu	$CH_2N^*Me_2$	−145 (d)	(3.9)	150 (d)	(31.4)

a) Measured in C_6D_6. b) Measured in $CDCl_3$.

recorded on a Bruker AC-200P spectrometer at 295 K using formamide (90% solution in dimethyl sulfoxide, $\delta = -298$ referenced to nitromethane at 0 ppm) as an external standard, and the chemical shifts relative to nitromethane were calculated. UV spectra were measured on a Hitachi U-3210 spectrometer. IR spectra were obtained on a Horiba FT-300 spectrometer. MS (70 eV) spectra were taken on either JEOL HX-110 or Hitachi M-2500S spectrometer. MOPAC PM3 calculation[20] was performed using the CAChe program package available from CAChe Scientific, Co., Ltd.

2-Bromo-5-*t*-butyl-1,3-bis(diethylaminomethyl)benzene (2b). A solution of 2-bromo-1,3-bis(bromomethyl)-5-*t*-butylbenzene (**1A**, 397 mg, 1.00 mmol) and diethylamine (5 mL, 48 mmol) in *N*,*N*-dimethylformamide (30 mL) was stirred at room temperature for 30 min, and then 100 mL of water was added. The mixture was extracted twice with 100 mL of hexane and the combined organic phase was dried with $MgSO_4$. Removal of the solvent in vacuo afforded 370 mg (97%) of **2b**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.05 (12H, t, J = 7.1 Hz, $CH_2\underline{CH_3}$), 1.32 (9H, s, *t*-Bu), 2.57 (8H, q, J = 7.1 Hz, $\underline{CH_2}CH_3$), 3.64 (4H, s, benzyl), and 7.49 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 12.2 ($CH_2\underline{CH_3}$), 31.4 ($C\underline{Me_3}$), 34.6 ($\underline{C}Me_3$), 47.3 ($\underline{CH_2}CH_3$), 58.1 (benzyl), 122.7 (arom.-Br), 125.7 (arom.-CH), 138.8 (arom.), and 149.3 (arom.); IR (NaCl) 1464, 1454, 1385, 1371, 1360, 1203, and 1068 cm^{-1}; MS (70 eV, EI) *m/z* (rel intensity) 384 (M^++2; 42), 382 (M^+; 42), 367 (M^+−Me; 59), 310 (M^+−NEt_2; 67), 239 (M^+−2NEt_2−1; 79), and 86 ($CH_2NEt_2^+$; 100). Found: *m/z* 382.2023. Calcd for $C_{20}H_{35}BrN_2$: M, 382.1983.

2-Bromo-5-*t*-butyl-1,3-bis(diisopropylaminomethyl)benzene (2c). A solution of **1A** (1.21 g, 3.03 mmol) and diisopropylamine (8 mL, 57 mmol) in acetonitrile (60 mL) was stirred at room temperature for 6 h, and then 200 mL of water was added. The mixture was extracted twice with 200 mL of hexane and the combined organic phase was dried with $MgSO_4$. Removal of the solvent in vacuo followed by column chromatographic treatment (Al_2O_3/hexane) afforded 1.11 g (92%) of **2c**: Colorless crystals, mp 62.0—63.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.04 (24H, d, J = 6.6 Hz, $CH\underline{Me_2}$), 1.31 (9H, s, *t*-Bu), 3.06 (4H, sept, J = 6.6 Hz, $C\underline{H}Me_2$), 3.69 (4H, s, benzyl), and 7.65 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 21.0 ($CH\underline{Me_2}$), 31.4 ($C\underline{Me_3}$), 34.7 ($\underline{C}Me_3$), 48.5 (benzyl), 48.6 ($\underline{C}HMe_2$), 121.1 (arom.-Br), 125.1 (arom.-CH), 140.6 (arom.), and 148.9 (arom.); IR (KBr) 1477, 1466, 1404, 1392, 1381, 1363, 1205, 1180, 1140, 1119, and 1014 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 440 (M^++2; 11), 438 (M^+; 9), 423 (M^+−Me; 100), 338 (M^+−N(*i*-Pr)$_2$; 14), and 239 (M^+−2N(*i*-Pr)$_2$+1; 31). Found: *m/z* 438.2603. Calcd for $C_{24}H_{43}BrN_2$: M, 438.2609.

2-Bromo-5-*t*-butyl-1,3-bis(isopropylaminomethyl)benzene (2d). A solution of **1A** (334.4 mg, 0.838 mmol) and isopropylamine (0.36 mL, 4.18 mmol) in *N*,*N*-dimethylformamide (8 mL) was stirred at room temperature for 3 h. The mixture was worked up using hexane and water as usual, then the organic phase was dried over $MgSO_4$. Removal of the solvent in vacuo afforded 278.5 mg (94%) of **2d**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.12 (12H, d, J = 6.2 Hz, $CH\underline{Me_2}$), 1.31 (9H, s, *t*-Bu), 2.84 (2H, sept, J = 6.2 Hz, $C\underline{H}Me_2$), 3.86 (4H, s, benzyl), and 7.29 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 22.8 ($CH\underline{Me_2}$), 31.2 ($C\underline{Me_3}$), 34.4 ($\underline{C}Me_3$), 48.0 ($\underline{C}HMe_2$), 52.4 (benzyl), 122.6 (arom.-Br), 126.4 (arom.-CH), 139.3 (arom.), and 150.1 (arom.); IR (NaCl) 1465, 1436, 1378, 1363, 1172, 1016, 879, 740, and 715 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 356 (M^++2; 5), 354 (M^+; 6), 341 (M^+−Me+2; 91), 339 (M^+−Me; 100), 298 (M^+−NH-*i*-Pr+2; 55), 296 (M^+−NH*i*-Pr; 61), 275 (M^+−Br; 6), 255 (M^+−*i*-Pr−*t*-Bu+2; 18), 253 (M^+−*i*-Pr−*t*-Bu; 17), 241 (M^+−2NH*i*-Pr+3; 32), 239 (M^+−2NH*i*-Pr+1; 35), and 57 (*t*-Bu$^+$; 13). Found: *m/z* 354.1675. Calcd for $C_{18}H_{31}BrN_2$: M, 354.1670.

2-Bromo-5-*t*-butyl-1,3-bis(*N*-isopropyl-*N*-methylaminomethyl)benzene (2e). 2-Bromo-5-*t*-butyl-1,3-bis(isopropylaminomethyl)benzene (**2d**) was prepared from 550.1 mg (1.37 mmol) of **1A** by the method described above, and used for the following reaction without isolation. To a solution of **2d** in acetonitrile (20 mL) were added successively 1.14 mL of formalin (37% aqueous formaldehyde solution, ca. 14 mmol of HCHO) and $NaBH_3CN$ (4.4 mmol). Then the reaction mixture was treated with 0.5 mL of acetic acid, and the resulting mixture was stirred at room temperature for 1 h. Again, 0.5 mL of acetic acid was added, and the resulting mixture was stirred at room temperature for 30 min. The reaction mixture was worked up using Et_2O and aqueous KOH. The organic phase was washed with a saturated aqueous NaCl solution, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure to give 402.9 mg (77% yield based on **1A**) of **2e**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.09 (12H, d, J = 6.6 Hz, $CH\underline{Me_2}$), 1.33 (9H, s, *t*-Bu), 2.21 (6H, s, NMe), 2.98 (2H, sept, J = 6.6 Hz, $C\underline{H}Me_2$), 3.63 (4H, s, benzyl), and 7.42 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 17.9 ($CH\underline{Me_2}$), 31.3 ($C\underline{Me_3}$), 34.5 ($\underline{C}Me_3$), 36.5 ($\underline{C}HMe_2$), 53.6 (NMe), 58.2 (benzyl), 123.4 (arom.-Br), 126.1 (arom.-CH), 138.5 (arom.), and 149.4 (arom.); IR (NaCl) 1461, 1382, 1361, 1220, 1178, 1130, 1072, 1018, 964, and 889 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 384 (M^++2; 7), 382 (M^+; 7), 369 (M^+−Me+2; 100), 367 (M^+−Me; 98), 312 (M^+−NMe*i*-Pr+2; 19), 310 (M^+−NMe*i*-Pr; 20), 241 (M^+−2NMe*i*-Pr+3; 24), 239 (M^+−2NMe*i*-Pr+1; 26), and 57 (*t*-Bu$^+$; 8). Found: *m/z* 382.1986. Calcd for $C_{20}H_{35}BrN_2$: M, 382.1983.

2-Bromo-1,5-di-*t*-butyl-3-(dimethylaminomethyl)benzene (2f). To a solution of 2-bromo-1-bromomethyl-3,5-di-*t*-butylbenzene (**1B**, 5.77 g, 15.9 mmol) and dimethylamine hydrochloride (6.49 g, 79.6 mmol) in *N*,*N*-dimethylformamide (150 mL) was added 65 mL of triethylamine. The resulting mixture was heated under reflux for 45 min. The reaction mixture was extracted using hexane and washed with a saturated aqueous $NaHCO_3$ solution. The organic phase was dried with $MgSO_4$. Removal of the solvent in vacuo, followed by chromatographic treatment (Al_2O_3/hexane–Et_2O), afforded 4.95 g (95%) of **2f**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.32 (9H, s, *t*-Bu), 1.55 (9H, s, *t*-Bu), 2.31 (6H, s, NMe_2), 3.54 (2H, s, benzyl), 7.29 (1H, d, J = 2.6 Hz, arom.), and 7.40 (1H, d, J = 2.6 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 30.2 ($C\underline{Me_3}$), 31.3 ($C\underline{Me_3}$), 34.7 ($\underline{C}Me_3$), 37.4 ($\underline{C}Me_3$), 45.7 (NMe_2), 65.5 (benzyl), 122.4 (arom.-Br), 124.0 (arom.-CH), 126.1 (arom.-CH), 139.1 (arom.), 147.4 (arom.), and 149.0 (arom.); IR (NaCl) 1456, 1396, 1363, and 1014 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 327 (M^++2; 50), 325 (M^+; 50), 281 (M^+−NMe_2; 7), 246 (M^+−Br; 8), 203 (M^+−NMe_2−Br+1; 100), and 57 (*t*-Bu$^+$; 6). Found: *m/z* 325.1369. Calcd for $C_{17}H_{28}BrN$: M, 325.1405.

2-Bromo-1,5-di-*t*-butyl-3-(diethylaminomethyl)benzene (2g). A solution of **1B** (7.32 g, 20.1 mmol) and diethylamine (10.5 mL, 101.5 mmol) in benzene (15 mL) was heated under reflux for 40 min. The reaction mixture was extracted using ether and washed with a saturated aqueous $NaHCO_3$ solution. The organic phase was dried with $MgSO_4$. Removal of the solvent in vacuo afforded 6.75 g (95%) of **2g**: Colorless crystals, mp 45—46 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.06 (6H, t, J = 7.1 Hz, $CH_2\underline{CH_3}$), 1.33 (9H, s, *t*-Bu), 1.55 (9H, s, *t*-Bu), 2.58 (4H, q, J = 7.1 Hz, $\underline{CH_2}CH_3$), 3.66 (2H, s, benzyl), 7.37 (1H, d, J = 3.6 Hz, arom.), and 7.57 (1H, d, J = 3.6 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 12.3

($CH_2\underline{C}H_3$), 30.3 ($C\underline{Me}_3$), 31.4 ($\underline{C}Me_3$), 34.8 ($\underline{C}Me_3$), 37.4 ($\underline{C}Me_3$), 47.5 ($\underline{C}H_2CH_3$), 59.3 (benzyl), 121.7 (arom.-Br), 123.4 (arom.-CH), 125.4 (arom.-CH), 140.6 (arom.), 147.0 (arom.), and 148.9 (arom.); IR (KBr) 1475, 1461, 1425, 1294, 1265, 1230, 1203, 1168, 1066, 1014, and 879 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 355 (M^++2; 18), 353 (M^+; 21), 338 (M^+−Me; 61), 281 (M^+−NEt_2; 48), and 57 (*t*-Bu^+; 100). Found: *m/z* 353.1675. Calcd for $C_{19}H_{32}BrN$: M, 353.1718. Found: C, 64.17; H, 8.93; N, 3.97%. Calcd for $C_{19}H_{32}BrN$: C, 64.40; H, 9.10; N, 3.95%.

2-Bromo-1,5-di-*t*-butyl-3-(diisopropylaminomethyl)benzene (2h). A solution of **1B** (4.70 g, 13.0 mmol) and diisopropylamine (5.4 mL, 38.5 mmol) in *N*,*N*-dimethylformamide (200 mL) was heated under reflux for 2 h. The reaction mixture was extracted using ether and washed with a saturated aqueous $NaHCO_3$ solution. The organic phase was dried with $MgSO_4$. Removal of the solvent in vacuo, followed by chromatographic treatment (Al_2O_3/hexane), afforded 4.42 g (89%) of **2h**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.05 (6H, d, J = 6.5 Hz, CH$\underline{Me}_2$), 1.32 (9H, s, *t*-Bu), 1.56 (9H, s, *t*-Bu), 3.06 (2H, sept, J = 6.5 Hz, C$\underline{H}$Me$_2$), 3.70 (2H, s, benzyl), 7.34 (1H, d, J = 2.7 Hz, arom.), and 7.76 (1H, d, J = 2.7 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 21.0 (CH$\underline{Me}_2$), 30.2 ($C\underline{Me}_3$), 31.2 ($C\underline{Me}_3$), 34.9 ($\underline{C}Me_3$), 37.3 ($\underline{C}Me_3$), 48.7 ($\underline{C}HMe_2$), 50.8 (benzyl), 121.1 (arom.), 123.1 (arom.-CH), 125.3 (arom.-CH), 142.6 (arom.), 146.5 (arom.), and 148.7 (arom.); IR (NaCl) 1425, 1321, 1290, 1265, 1137, 1116, 952, and 879 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 383 (M^++2; 12), 381 (M^+; 12), 368 (M^+−Me+2; 100), 366 (M^+−Me; 99), 283 (M^+−*i*-Pr_2N+2; 25), 281 (M^+−*i*-Pr_2N; 25), and 57 (*t*-Bu^+; 24). Found: *m/z* 381.2060. Calcd for $C_{21}H_{36}BrN$: M, 381.2031.

2-Bromo-1,5-di-*t*-butyl-3-(isopropylaminomethyl)benzene (2i). A solution of **1B** (599.2 mg, 1.67 mmol) and isopropylamine (0.35 mL, 4.14 mmol) in *N*,*N*-dimethylformamide (12 mL) was stirred at room temperature for 3 h. The mixture was worked up using hexane and water as usual; then the organic phase was dried over $MgSO_4$. Removal of the solvent in vacuo gave 515.7 mg (92%) of **2i**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.13 (6H, d, J = 6.2 Hz, CH$\underline{Me}_2$), 1.31 (9H, s, *t*-Bu), 1.54 (9H, s, *t*-Bu), 2.85 (1H, sept, J = 6.2 Hz, C$\underline{H}$Me$_2$), 3.88 (2H, s, benzyl), 7.26 (1H, d, J = 2.6 Hz, arom.), and 7.40 (1H, d, J = 2.6 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 22.9 (CH$\underline{Me}_2$), 30.2 ($C\underline{Me}_3$), 31.2 ($C\underline{Me}_3$), 34.6 ($\underline{C}Me_3$), 37.3 ($\underline{C}Me_3$), 48.2 ($\underline{C}HMe_2$), 53.7 (benzyl), 121.8 (arom.-Br), 124.3 (arom.-CH), 125.7 (arom.-CH), 140.5 (arom.), 147.5 (arom.), and 149.4 (arom.); IR (KBr) 1589, 1467, 1396, 1363, 1174, 1014, 877, 744, 725, and 651 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 341 (M^++2; 7), 339 (M^+; 8), 326 (M^+−Me+2; 98), 324 (M^+−Me; 100), 283 (M^+−NH*i*-Pr+2; 64), 281 (M^+−NH*i*-Pr; 64), and 57 (*t*-Bu^+; 43). Found: *m/z* 339.1555. Calcd for $C_{18}H_{30}BrN$: M, 339.1562.

2-Bromo-1,5-di-*t*-butyl-3-(*N*-isopropyl-*N*-methylaminomethyl)benzene (2j). To a solution of **2i** (342.0 g, 1.01 mmol) in acetonitrile (15 mL) were added successively 0.41 mL of formalin (ca. 5 mmol of HCHO) and $NaBH_3CN$ (1.9 mmol). Then the reaction mixture was treated with 0.3 mL of acetic acid, and the resulting mixture was stirred at room temperature for 1 h. Again, 0.3 mL of acetic acid was added, and resulting mixture was stirred at room temperature for 30 min. The reaction mixture was treated with Et_2O and an aqueous KOH solution. The organic phase was washed with a saturated aqueous NaCl solution, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. Chromatographic separation (SiO_2/Et_2O) of the residue afforded 265 mg (74%) of **2j**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.39 (6H, d, J = 6.4 Hz, CH$\underline{Me}_2$), 1.32 (9H, s, *t*-Bu), 1.55 (9H, s, *t*-Bu), 2.22 (3H, s, NMe), 2.96 (1H, sept, J = 6.4 Hz, C$\underline{H}$Me$_2$), 3.63 (2H, s, benzyl), 7.37 (1H, d, J = 2.4 Hz, arom.), and 7.46 (1H, d, J = 2.4 Hz, arom.); $^{13}C\{^1H\}$NMR (50 MHz, $CDCl_3$) δ = 18.0 (CH$\underline{Me}_2$), 30.3 ($C\underline{Me}_3$), 31.4 ($C\underline{Me}_3$), 34.7 ($\underline{C}Me_3$), 36.8 ($\underline{C}HMe_2$), 37.4 ($\underline{C}Me_3$), 53.5 (NMe), 59.1 (benzyl), 122.0 (arom.-Br), 123.6 (arom.-CH), 125.5 (arom.-CH), 140.1 (arom.), 147.1 (arom.), and 148.9 (arom.); IR (NaCl) 1477, 1461, 1427, 1394, 1382, 1363, 1230, 1014, 966, and 879 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 355 (M^++2; 15), 353 (M^+; 15), 340 (M^+−Me+2; 100), 338 (M^+−Me; 100), 283 (M^+−NM*e*i-Pr+2; 27), 281 (M^+−NM*e*i-Pr; 28), 241 (M^+−2*t*-Bu+2; 4), 239 (M^+−2*t*-Bu; 4), and 57 (*t*-Bu^+; 26). Found: *m/z* 353.1715. Calcd for $C_{19}H_{32}BrN$: M, 353.1718.

General Procedure for the Preparation of the 4-*t*-Butyl-2,6-bis(dialkylaminomethyl)phenylphosphine 4. To a solution of **2** (0.57 mmol) in diethyl ether (30 mL) was added butyllithium (0.96 mmol); the resulting mixture was stirred for 10 min. This solution was added dropwise to a solution of phosphorus trichloride (3.44 mmol) in diethyl ether (15 mL) at −78 °C over a 15-minute period. Then the resulting solution was stirred at −78 °C for 30 min and warmed to room temperature. The solvent was removed in vacuo and again 10 mL of diethyl ether was added. To this solution was added a suspension of $LiAlH_4$ (1.52 mmol) and diethyl ether (20 mL) and the reaction mixture was stirred for 15 min. An appropriate amount of methanol was added and the resulting mixture was stirred for 10 min. Removal of the solvent under reduced pressure followed by column chromatographic treatment (Al_2O_3/CH_2Cl_2) afforded **4**. Compounds **4e—h,j** were not isolated because of the decomposition during column chromatographic procedure.

4b: (45% yield), colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.00 (12H, t, $^3J_{HH}$ = 7.1 Hz, $CH_2C\underline{H}_3$), 1.30 (9H, s, *t*-Bu), 2.49 (8H, s, $^3J_{HH}$ = 7.1 Hz, $C\underline{H}_2CH_3$), 3.61 (4H, s, benzyl), 3.67 (2H, d, $^1J_{PH}$ = 204.6 Hz, PH), and 7.24 (2H, d, $^4J_{PH}$ = 2.0 Hz, arom.); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 11.2 (s, $CH_2\underline{C}H_3$), 31.3 (s, $C\underline{Me}_3$), 34.2 (s, $\underline{C}Me_3$), 45.8 (s, $\underline{C}H_2CH_3$), 59.1 (d, J_{PC} = 2.6 Hz, benzyl), 124.8 (d, $^3J_{PC}$ = 2.3 Hz, *m*-arom.), 128.5 (d, $^1J_{PC}$ = 18.2 Hz, *ipso*-arom.), 142.5 (d, $^2J_{PC}$ = 9.6 Hz, *o*-arom.), and 148.9 (s, *p*-arom.); UV (hexane) 238 (sh, log ε 4.0) and 270 nm (sh, 3.2); IR (NaCl) 2266 (PH), 1464, 1385, 1369, 1362, 1203, 1167, and 1066 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 336 (M^+; 13), 263 (M^+−NEt_2−1; 30), 234 (M^+−NEt_2−Et−1; 100), and 191 (M^+−2NEt_2−1; 27). Found: *m/z* 336.2714. Calcd for $C_{20}H_{37}N_2P$: M, 336.2695.

4c: (26% yield), colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.03 (24H, d, $^3J_{HH}$ = 6.6 Hz, CH$\underline{Me}_2$), 1.31 (9H, s, *t*-Bu), 3.00 (4H, sept, $^3J_{HH}$ = 6.6 Hz, C$\underline{H}$Me$_2$), 3.71 (2H, d, $^1J_{PH}$ = 207.5 Hz, PH), 3.72 (4H, br.s, benzyl), and 7.48 (2H, d, $^4J_{PH}$ = 2.1 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 20.6 (s, CH$\underline{Me}_2$), 31.3 (s, $C\underline{Me}_3$), 34.5 (s, $\underline{C}Me_3$), 48.0 (s, $\underline{C}HMe_2$), 48.6 (s, benzyl), 124.1 (d, $^3J_{PC}$ = 2.6 Hz, *m*-arom.), 125.6 (d, $^1J_{PC}$ = 16.4 Hz, *ipso*-arom.), 143.8 (d, $^2J_{PC}$ = 6.5 Hz, *o*-arom.), and 149.3 (s, *p*-arom.); UV (hexane) 238 (sh, log ε 4.1) and 272 nm (sh, 3.1); IR (KBr) 2281 (PH), 1464, 1392, 1381, 1362, 1203, 1176, and 1119 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 392 (M^+; 12), 360 (M^+−PH_2+1; 21), 345 (M^+−PH_2−Me+1; 5), and 161 (M^+−PH_2−2N(*i*-Pr)$_2$+2; 31). Found: *m/z* 392.3332. Calcd for $C_{24}H_{45}N_2P$: M, 392.3321.

General Procedure for the Preparation of the Intramolecular Base Stabilized Thioxophosphine Sulfides 5. A mixture of **4** (0.5 mmol), sulfur (1.2 mg-atom), and benzene (10 mL) was stirred at an ambient temperature for 1 h. Removal of the solvent in vacuo followed by chromatographic treatment (Al_2O_3/AcOEt) afforded **5**. As mentioned in the general preparative procedure for **4**, the starting phosphines **4e—h,j** were not isolated. Thus,

these reactive phosphines were prepared in situ and subjected to the sulfurization reaction. Attempted isolation of **5c,e,g,h,j** by flash column chromatography (Al_2O_3/AcOEt) resulted in decomposition of **5**. ^{13}C NMR and UV spectra for **5b** were poor in quality because of partial decomposition in solution.

5b: (15% yield based on **4b**), colorless powder, mp 144.0—147.0 °C (decomp); ^1H NMR (200 MHz, $CDCl_3$) δ = 1.21 (12H, t, $^3J_{HH}$ = 7.1 Hz, $CH_2C\underline{H}_3$), 1.30 (9H, s, *t*-Bu), 3.06 (8H, m, $C\underline{H}_2CH_3$), 4.12 (4H, br.s, benzyl), and 7.34 (2H, d, $^4J_{PH}$ = 4.6 Hz, arom.); IR (KBr) 1601, 1475, 1452, 1396, 1041, 1003, 970, 939, 893, 715, 625, and 600 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 398 (M^+; 31), 369 (M^+-Et; 100), and 292 ($M^+-S-Et-3Me$; 54). Found: *m/z* 398.1969. Calcd for $C_{20}H_{35}N_2PS_2$: M, 398.1979.

5f: (12% yield based on **2f**), colorless silky needles, mp 236.0—237.0 °C; ^1H NMR (200 MHz, $CDCl_3$) δ = 1.30 (9H, s, *t*-Bu), 1.73 (9H, s, *t*-Bu), 3.09 (6H, d, J_{PH} = 7.6 Hz, NMe_2), 4.47 (2H, d, J_{PH} = 5.0 Hz, benzyl), 7.00 (1H, dd, $^4J_{PH}$ = 2.6 Hz and $^4J_{HH}$ = 1.8 Hz, arom.), and 7.54 (1H, dd, $^4J_{PH}$ = 7.3 Hz and $^4J_{HH}$ = 7.8 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 31.0 (s, $C\underline{Me}_3$), 32.4 (s, $C\underline{Me}_3$), 35.0 (s, $\underline{C}Me_3$), 38.1 (d, $^4J_{PC}$ = 1.3 Hz, $\underline{C}Me_3$), 45.3 (d, J_{PC} = 3.1 Hz, NMe_2), 62.3 (d, J_{PC} = 8.7 Hz, benzyl), 119.7 (d, $^3J_{PC}$ = 10.1 Hz, *m*-arom.), 125.7 (d, $^3J_{PC}$ = 12.9 Hz, *m'*-arom.), 133.7 (d, $^2J_{PC}$ = 12.2 Hz, *o*-arom.), 134.5 (d, $^1J_{PC}$ = 86.6 Hz, *ipso*-arom.), 152.2 (d, $^2J_{PC}$ = 10.9 Hz, *o'*-arom.), and 154.0 (d, $^4J_{PC}$ = 3.0 Hz, *p*-arom.); UV (CH_2Cl_2) 254 (log ε 3.8), 284 (sh, 3.5), and 302 nm (sh, 3.1); IR (KBr) 1601, 1463, 1446, 1396, 1363, 987, 827, 713, and 634 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 341 (M^+; 18), 308 (M^+-S-1; 100), 265 ($M^+-S-NMe_2$; 6), and 57 (*t*-Bu^+; 12). Found: *m/z* 341.1409. Calcd for $C_{17}H_{28}NPS_2$: M, 341.1401.

5e: ^1H NMR (200 MHz, CD_2Cl_2–CS_2 (1 : 1)) at 298 K, δ = 1.3 (12H, d, J_{HH} = 6.6 Hz, $CH\underline{Me}_2$), 1.4 (9H, s, *t*-Bu), 2.5 (6H, d, J_{PH} = 3.4 Hz, NMe), 3.9 (2H, d of sept, J_{HH} = 6.6 Hz and J_{PH} < 1 Hz, $C\underline{H}Me_2$), 4.1 (4H, s, benzyl), and 7.4 (2H, s, arom.); at 170 K, δ = 1.3 (12H, br s, $CH\underline{Me}_2$), 1.3 (9H, s, *t*-Bu), 2.3 (6H, br s, NMe), 3.8 (2H, br s, benzyl), 3.9 (2H, br s, $C\underline{H}Me_2$), 4.1 (2H, br s, benzyl'), and 7.4 (2H, br s, arom.).

5j: ^1H NMR (200 MHz, toluene-d_8) at 393 K, δ = 0.72 (3H, d, J_{HH} = 6.8 Hz, $CH\underline{Me}$), 1.22 (9H, s, *t*-Bu), 1.33 (3H, d, J_{HH} = 8.2 Hz, $CH\underline{Me}'$), 1.83 (9H, s, *t*-Bu), 2.28 (3H, d, J_{PH} = 6.9 Hz, NMe), 3.26 (1H, dd, J_{HH} = 13.4 Hz and J_{PH} = 10.2 Hz, benzyl), 4.17 (1H, d, J_{HH} = 13.4 Hz, benzyl), 4.52 (1H, m, $C\underline{H}Me_2$), 6.68 (1H, br s, arom.), and 7.57 (1H, br d, J = 5.7 Hz, arom.).

^{15}N Labeled Compounds. Dimethylamine-^{15}N hydrochloride (> 99 atom% ^{15}N) was purchased from Isotec Inc. and used as a starting material. The bromobenzenes **2a***,**f*** with enriched ^{15}N contents were prepared by a similar method described above. Thus, **2a*** was prepared, in 72% yield, from a reaction of **1A** (392.5 mg, 0.98 mmol) with 2.0 mmol of dimethylamine-^{15}N hydrochloride in the presence of 6 mmol of triethylamine. Reaction of **1B** (362.2 mg, 1.0 mmol) with dimethylamine-^{15}N hydrochloride (1.1 mmol) in the presence of triethylamine (3 mmol) gave **2f*** in 47% yield. Then the bromobenzenes thus prepared were converted to **5a***, **f*** via **4a***,**f***. Because of our fear of the loss of the reaction products during column chromatographic procedures, these compounds were used for the NMR studies without thorough purification.

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