Preparation and Structure of Dithioxo- and Diselenoxophosphoranes Stabilized by Intramolecular Coordination with a Dialkylamino Group☆

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Some dithioxophosphoranes **3** stabilized by intramolecular coordination with a dialkylamino group were prepared, and their structures were analyzed by X-ray crystallography involving [2,4-di-*tert*-butyl-6-(isopropylmethylamino)phenyl]- (**3c**), {2,4-di-*tert*-butyl-6-[(dimethylamino)methyl]phenyl}- (**3f**), and {2,4-di-*tert*-butyl-6-[2-(dimethylamino)-1,1-dimethylethyl]phenyl}dithioxophosphorane (**3h**). The bond between the phosphorus atom and the aromatic ring is flexible and the angle narrows with decreasing ring size of the intramolecular coordination. The ^{31}P-NMR signals are shifted to higher field with increasing ring size of the intramolecular coordination or strength of coordination. Similarly, the corresponding diselenoxophosphoranes **4** were prepared. Both their ^{31}P- and ^{77}Se-NMR signals are shifted to higher field with increasing contribution of intramolecular coordination.

Sterically protected phosphorus compounds are of current interest because of their unusual structures and properties[1]. Molecular design utilizing an extremely bulky 2,4,6-tri-*tert*-butylphenyl group (abbreviated as Ar) allowed us to prepare several kinds of stabilized low-coordinated phosphorus compounds such as diphosphene[2], phosphaallenes[3,4], dithioxophosphorane[5], and diselenoxophosphorane[6]. We recently reported on the utilization of the 2,4-di-*tert*-butyl-6-(dimethylamino)phenyl group (abbreviated as Mx)[7], where one of the *o*-*tert*-butyl groups on the phenyl ring is replaced by the dimethylamino group. Using this substituent, we succeeded in preparing MxP=S and MxP=Se for the first time as well as MxP(=S)$_2$ and MxP(=Se)$_2$ as stable compounds[7,8]. Since then, we were interested in the role of the nitrogen lone pair of the Mx group and in modifying the Mx group with respect to the kind of the element as well as the position of the hetero atom. In this paper we therefore report on the utilization of the 2,4-di-*tert*-butyl-6-[(dimethylamino)methyl]phenyl group (abbreviated as Mamx)[9] and the 2,4-di-*tert*-butyl-6-[2-(dimethylamino)-1,1-dimethylethyl]phenyl group (abbreviated as Maar)[10]. Although the role of the dimethylamino group in the Mx group has not been studied in detail, in the Mamx or Maar group it is assumed to be coordinated directly in an intramolecular fashion. Furthermore, an X-ray analysis of the dithioxophosphoranes MamxP(=S)$_2$ and MaarP(=S)$_2$[9,10] revealed that such intramolecular coordination actually exists.

Although we recently reported on a novel stabilizing group, the 2,4-di-*tert*-butyl-6-piperidinophenyl group (abbreviated as Pix), for diselenoxophoshorane PixP(=Se)$_2$[11], dithioxophosphoranes with four-membered ring intramolecular coordination have not been described so far. The coordination ability of the Mx group was expected to be lower than that of the Mamx or Maar group, for which five- or six-membered ring coordination is preferred. Using the 2,4-di-*tert*-butyl-6-(isopropylmethylamino)phenyl group, we succeeded in preparing the corresponding dithioxophosphorane and characterizing it by X-ray analysis. The character of the P−N bond may strongly influence the NMR chemical shifts.

Results and Discussion

Starting from bulky aminobromobenzenes **1**[7−12], we prepared primary phosphanes **2** as shown in Scheme 1, after we had checked the halogen metal exchange reactions of **1b−d** with butyllithium by quenching with water leading to **5b−d**. The phosphanes **2** thus obtained were used for further reactions with sulfur and selenium affording dithioxophosphoranes **3** and diselenoxophosphoranes **4**, respectively.

NMR Study of Dithioxophosphoranes and Diselenoxophosphoranes

Dithioxophosphoranes (**3**) and diselenoxophoranes (**4**) were analyzed by means of NMR. Figure 1 and Table 1 show ^{31}P-NMR data of **3** and **4** with various substituents. As can be seen from the δP data of dithioxophosphoranes **3**, the coordination of N to P causes a high-field shift, probably because the nitrogen lone pairs increase the electron density at the phosphorus atom. The signals due to the dithioxophosphoranes **3b−e** are shifted to higher field by Δδ = 125−130 compared to that of non-coordinated dithioxophosphorane **3a**[5,7,9,10]. Furthermore, the signals due to the dithioxophosphoranes **3f** and **3g** are shifted to higher field by ca. Δδ = 150, and the signal of **3h** is shifted to higher field by Δδ = 165 compared to that of **3a**. The δ_P values for **3f** and **3g** range between **3h** and **3b−e** reflecting

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Scheme 1. **a**: R = *t*Bu; **b**: R = NEt*i*Pr; **c**: R = NMe*i*Pr; **d**: R = $N(CH_2)_5$; **e**: R = NMe_2; **f**: R = CH_2NMe_2; **g**: R = CMe_2NMe_2; **h**: R = $CMe_2CH_2NMe_2$; **i**: R = NH_2; **j**: R = NH*i*Pr; **k**: R = MeO; **l**: R = Me

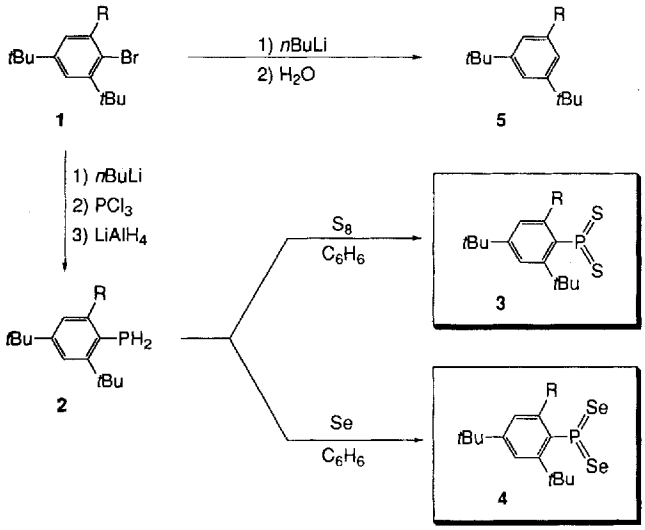
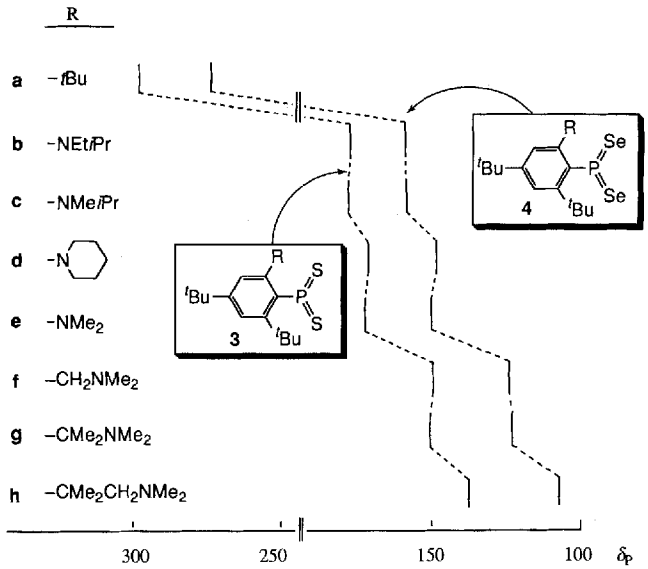
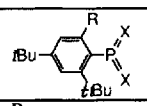


Figure 1. ^{31}P-NMR chemical shifts of dithioxophosphoranes **3** and diselenoxophosphoranes **4**



the efficiency of internal coordination. Thus, the degree of the observed upfield shift corresponds to the ring size of intramolecular coordination.

Table 1. ^{31}P- and ^{77}Se-NMR data of some dithioxophosphoranes **3** and diselenoxophosphoranes **4**



	R	**3** X=S δ_P / ppm	**4** X=Se δ_P / ppm	$^1J_{PSe}$ / Hz	δ_{Se} / ppm[c]
a	*t*Bu	298.2[a]	273.0[b]	855	—[i]
b	NEt*i*Pr	177.2	157.4	806, 817[h]	491.9, 445.3[h]
c	NMe*i*Pr	177.6	157.0	815, 823[h]	454.0, 399.5[h]
d	$N(CH_2)_5$	169.9	147.7[d]	813	397.4
e	NMe_2	170.6[e]	149.6[e]	820	400.0
f	CH_2NMe_2	149.6[f]	123.6	790	195.4
g	CMe_2NMe_2	150.5[g]	121.8	784	353.1
h	$CMe_2CH_2NMe_2$	135.7[g]	108.7	769	210.1

[a] Data taken from ref.[5]. – [b] Data taken from ref.[6]. – [c] External standard, Me_2Se. – [d] Data taken from ref.[11]. – [e] Data taken from ref.[7]. – [f] Data taken from ref.[9]. – [g] Data taken from ref.[10]. – [h] Two values are observed due to nonequivalent selenium atoms (see Experimental). – [i] Data of **4a** are not reported.

Similar phenomena were observed for the ^{31}P-NMR chemical shifts of the corresponding diselenophosphoranes **4a–h** (Figure 1)[6,7,11]. Furthermore, the data in Table 1 show that the coupling constant $^1J_{PSe}$ decreases with increasing ring size of coordination and that a high-field shift of the ^{77}Se-NMR signals is caused by intramolecular coordination, although the relation between the chemical shift and the coordination size does not seem to be linear in the case of diselenoxophosphoranes. It should be mentioned here that the spectra of diselenoxophosphoranes **4b** and **4c** carrying unsymmetrical dialkylamino groups show two signals with two different coupling constants $^1J_{PSe}$, indicating that the two selenium atoms are magnetically non-equivalent. This phenomenon is observed for the methyl protons of the isopropyl groups of the unsymmetrical dialkylamino groups in the ^{1}H-NMR spectrum. In addition, the ^{77}Se-NMR spectra of **4g** and **4f** show broad signals at room temperature in contrast to a sharp doublet for **4b** or **4c**. Tight coordination might cause restricted internal motion including ring flipping involving the internal N–P coordination bond because of steric repulsion of the dimethyl groups in the benzylic position. Furthermore, the methylene protons of **4f** appear as broad signals at room temperature. In the ^{77}Se-NMR spectra recorded at 330 K the signals originating from **4g** and **4f** are slightly sharpend.

The signal of a thermodynamically stabilized compound **6** (δ_P = 243)[13a], reported by Schmidpeter et al., appears at lower field than those of **3b–h**, indicating that there is a large electronic perturbation in **3b–h**.

Furthermore, it should be noted that the ^{31}P-NMR chemical shift of a methoxy-substituted phenyldithioxophosphorane, (2,4-di-*tert*-butyl-6-methoxyphenyl)dithioxophosphorane (**3k**: δ_P = 277.6)[14], is very similar to that of **3a** (δ_P = 298.2)[5c] or similar to that of non-coordinated (2,4-di-*tert*-butyl-6-methylphenyl)dithioxophosphorane (**3l**: δ_P = 285.2)[15], indicating that the intramolecular coordination of the oxygen lone pair to phosphorus is not tight[14]. Furthermore, the dithioxophosphoranes of this type are much less stable than the amino-substituted dithioxophosphoranes.

X-Ray Analysis of Dithioxophosphoranes and Diselenoxophosphoranes

The intramolecular six-membered ring coordination in **3h** and the five-membered ring coordination in **3f**[9] were established by X-ray crystallographic analysis[10].

The four-membered ring coordination in **3c** was unambiguously established by X-ray crystallographic analysis. Figure 2 depicts an ORTEP[16] drawing of **3c**. The atoms C(1), P(1), N(1), and C(6) are almost coplanar within 0.02 Å, and the plane forms an angle of 86.3° with the triangular

plane C(1)–S(1)–S(2). The atom P(1) is 0.264 Å above the triangular plane toward N(1) and the sum of the angles around P(1) [S(1)–P(1)–C(1), S(1)–P(1)–S(2), and C(1)–P(1)–S(2)] is 354.1(3)°, indicating fairly good planarity around the phosphorus atom. The benzene ring C(1) to C(6) is coplanar within 0.015 Å, and the atoms P(1) and N(1) are located almost on the plane, deviating by −0.027 and −0.054 Å, respectively. Some important bond lengths and angles are listed in Table 2. Table 3 compiles bond lengths [*l*(PN), *l*(PS)] and bond angles (∠PCC, ∠SPS) for some dithioxophosphoranes **3c**, **3f**, and **3h** as well as for **3a**[5a] and the corresponding diselenoxophosphorane **4d**[11] determined by X-ray analyses.

Figure 2. Molecular structure for dithioxophosphorane **3c**. Both *o*-*tert*-butyl and *p*-*tert*-butyl groups are disordered, and those with the predominant occupancy factor are displayed. Benzene included as solvent is omitted for clarity

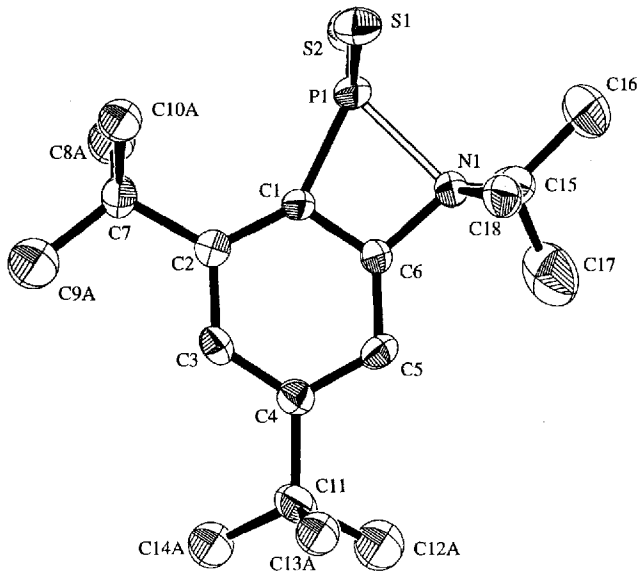
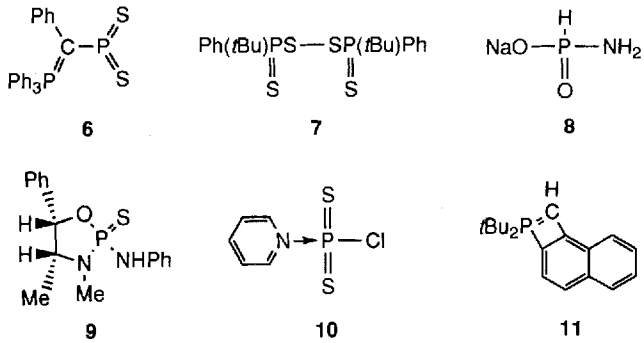


Table 2. Selected bond lengths and angles of **3c**

Bond Length / Å		Bond Angle / °	
S(1)-P(1)	1.931(4)	S(1)-P(1)-S(2)	121.7(2)
S(2)-P(1)	1.936(4)	S(1)-P(1)-C(1)	118.0(3)
P(1)-N(1)	2.023(8)	S(2)-P(1)-C(1)	114.6(3)
P(1)-C(1)	1.811(9)	P(1)-C(1)-C(6)	96.8(7)
N(1)-C(6)	1.46(1)	N(1)-C(6)-C(1)	106.0(8)
C(1)-C(2)	1.41(1)	S(1)-P(1)-N(1)	107.1(3)
C(2)-C(7)	1.53(1)	S(2)-P(1)-N(1)	111.7(3)
C(1)-C(6)	1.37(1)		

The P=S bond lengths in **3c** are 1.931(4) and 1.936(4) Å and are slightly shorter than those in **3h** [1.956(4) and 1.946(4) Å][10] or **3f** [1.944(4) and 1.936(4) Å][9]. The bond angle S–P–S in **3c** is 121.7(2)° and thus almost similar to that in **3h** [120.6(2)°] or **3f** [122.2(2)°]. The most striking feature of **3c** is that the bond angle P(1)–C(1)–C(6) is significantly narrowed to 96.8(7)° to form an intramolecular four-membered ring coordination, while N(1)–C(6)–C(1) is 106.0(5)°. A very similar molecular structure was observed for the corresponding diselenoxophosphorane **4d**[11] which exhibits a four-membered ring coordination. The deformation of the bond angle P–C–C is rather comparable to the value for benzo-λ^5-phosphete **11** with all covalent bonds [87.1(5),de][20]. The corresponding bond angles P–C–C in **3f** and **3h** are 109.7(8) and 119.3(9)°, respectively. Thus, the P–C bond including an sp^2 carbon atom in **3c** is flexible enough to allow distortion of 23° resulting in four-membered ring internal coordination.



The P–N bond lengths in **3h**, **3f**, **3c**, and **4d** are much shorter than the sum of the van der Waals radii, 3.4 Å, and longer than the calculated value for $H_2P–NH_2$ (1.69 Å at the SCF level)[18]. They are longer than the P–N bond lengths in sodium hydrogen phosphoramidate **8** [1.77(2) Å][19a] and 2-anilino-substituted 1,3,2-oxazaphospholane **9** [1.627(3) and 1.632(3) Å][19b] with covalent bonds, and than that in the pyridine adduct of dithiophosphoryl monochloride **10** [1.849(2) Å][19c] with intermolecular coordination, indicating that intramolecular coordination observed in the case of **3h**, **3f**, **3c**, and **4d** are incomplete. Thus, the P–N distance in **3c** is 2.023(8) Å and very similar to that in **4d** [2.039(5) Å], but considerably longer than those in **3f** [1.921(8) Å] and **3h** [1.918(9) Å].

Table 3. Selected bond lengths and angles for some dithioxo- and diselenoxophosphoranes

Compound	Ring size[a]	*l*(PN)/Å	∠PCC[b]/deg	*l*(PS)/Å	∠SPS/deg	ΣAngles[c]
3h[d]	6	1.918(9)	119.3(9)	1.956(4), 1.946(4)	120.6(2)	348.4(2)
3f[e]	5	1.921(8)	109.7(8)	1.944(4), 1.936(4)	122.2(2)	350.7(2)
3c	4	2.023(8)	96.8(7)	1.931(4), 1.936(4)	121.7(2)	354.3(3)
4d[f]	4	2.039(5)	96.3(4)	2.08(5), 2.085(5)[h]	121.80(8)[h]	353.7(2)
3a[g]	—	—	120	1.90, 1.90	126	360

[a] Internal coordination. – [b] The angle of PC(arom.) and a benzene edge (see text). – [c] Sum of the angles ∠SPS, ∠SPC, and ∠CPS or their selenium equivalent. – [d] Data taken from ref.[10]. – [e] Data taken from ref.[9]. – [f] Data taken from ref.[11]. – [g] Data taken from ref.[5a]. – [h] *l*(PSe) or ∠SePSe.

The P=S bonds in **3h**, **3f**, and **3c** (1.93–1.96 Å) are longer than that in **3a** (1.90 Å)[5a] and are significantly shorter than the phosphorus-sulfur single bond length in bis(phosphinothioyl) disulfide **7** [2.153(1) Å][17]. The bond length P–S in the dithioxophosphoranes elongates with increasing ring size, suggesting stronger coordination with decreasing bonding interaction between phosphorus and sulfur. This elongated bond length indicates that the multiplicity of P=S decreases by the coordination. Similar phenomena are observed by the fact that the coupling constants $^1J_{PSe}$ for the diselenoxophosphoranes **4a–h** decrease with decreasing strength for intramolecular coordination or increasing coordination ring size, as can be seen in Table 1. Table 3 shows that the sum of angles around P(1) decreases from 360 to 348° with increasing coordination ring size.

It is interesting to note that an energy-optimized structure calculated by CACheMOPAC[21] using the PM3 SCF-MO method[22] for $MxP(=S)_2$ (**3e**) closely resembles the structure of **3c**: 2.166 Å for the P–N bond length, 98.0° for the P–C–C and 108.3° for the N–C–C bond angles with 0.2° for the P–C–C–N dihedral angle, indicating that the P–C bond is flexible enough to adopt an intramolecular coordination with a nitrogen lone pair.

In summary, we prepared some sterically protected dialkylamino-containing phenyldithioxophosphoranes **3** and -diselenoxophosphoranes **4**. Intramolecular coordination causes in each case a high-field shift as revealed by the ^{31}P- and ^{77}Se-NMR spectra as well as an increase in the coupling constants $^1J_{PSe}$. By X-ray analysis, even four-membered ring coordination was observed resulting in compression of the P–C–C bond angle in **3c** as well as in **4d**.

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Experimental

^{1}H and ^{13}C NMR: Bruker AC-200P (^{1}H, 200.1; ^{13}C, 50.3 MHz) and AM-600 (^{1}H, 600.1; ^{13}C, 150.9 MHz). – ^{31}P and ^{77}Se NMR: Bruker AC-200P (^{31}P, 81.0; ^{77}Se, 38.2 MHz). Standards: $SiMe_4$ (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P), Me_2Se (^{77}Se). Solvent: $CDCl_3$. Temperature: 20°C unless specified otherwise. – UV-Vis: Hitachi-U-3210. – IR: Horiba FT-300. – MS: Jeol HX-110 or Hitachi M-2500S (70 eV). – Melting points: Yanagimoto MP-J3 micromelting point apparatus, uncorrected values. – Reactions were carried out under argon.

2-Bromo-1,5-di-tert-butyl-3-(isopropylamino)benzene (**1j**): 2-Bromo-3,5-di-*tert*-butylaniline (**1i**) was prepared according to a literature method[7]. A suspension of **1i** (1.13 g, 3.98 mmol) and $NaBH_4$ (1.5 g, 39.7 mmol) in 20 ml of THF was added to a solution of acetone (1.5 ml, 20.4 mmol) in THF (20 ml) at 0°C. Sulfuric acid (2 ml) was then added, and the mixture was stirred for 2 h at room temp. An aqueous sodium hydroxide solution was added to the reaction mixture to make it alkaline. The mixture was extracted with ether, the extract washed with brine and dried ($MgSO_4$). The solvent was removed in vacuo to give **1j** (1.31 g, 4.01 mmol, almost quantitative yield) as a colorless oil. – ^{1}H NMR (200 MHz): δ = 1.31 (6H, d, J = 6.3 Hz, CHMe_2), 1.34 (9H, s, *p*-*t*Bu), 1.56 (9H, s, *o*-*t*Bu), 3.70 (1H, sept, J = 6.3 Hz, NCH), 4.55 (1H, br. s, NH), 6.63 (1H, d, J = 2.3 Hz, arom.), 6.87 (1H, d, J = 2.3 Hz, arom.). – ^{13}C{^{1}H} NMR (50 MHz): δ = 23.0 (CHMe_2), 30.1 (CMe_3), 31.3 (CMe_3), 34.8 (*C*Me$_3$), 37.2 (*C*Me$_3$), 44.6 (NMe), 107.6 (arom., CH), 107.9 (arom., CBr), 113.4 (arom., CH), 144.5 (arom.), 147.5 (arom.), 150.0 (arom.). – IR (neat): $\tilde{\nu}$ = 3413 cm^{-1} (NH). – MS, *m/z* (%): 327 (51) [M^+ + 2], 325 (53) [M^+], 312 (100) [M^+ – Me + 2], 310 (91) [M^+ – Me]. – $C_{17}H_{28}{}^{79}BrN$: calcd. 325.1405; found 325.1447 (MS).

2-Bromo-1,5-di-tert-butyl-3-(ethylisopropylamino)benzene (**1b**): A suspension of **1j** (231 mg, 0.708 mmol) and $NaBH_4$ (161 mg, 4.26 mmol) in 10 ml of THF was added to 81% aqueous acetaldehyde (0.45 ml, 7.28 mmol) in THF (10 ml) at 0°C. Sulfuric acid (1.5 ml) was then added, and the mixture was stirred for 2 h at room temp. It was then treated as usual to give **1b** (243 mg, 0.685 mmol, 97% yield) as a colorless oil. – ^{1}H NMR (200 MHz): δ = 0.89 (3H, t, J = 7.0 Hz, CH_2Me), 1.11 (6H, d, J = 6.3 Hz, CHMe_2), 1.31 (9H, s, *p*-*t*Bu), 1.55 (9H, s, *o*-*t*Bu), 3.06 (2H, q, J = 7.0 Hz, NCH_2), 3.27 (1H, sept, J = 6.6 Hz, NCH), 7.04 (1H, d, J = 2.3 Hz, arom.), 7.23 (1H, d, J = 2.4 Hz, arom.). – ^{13}C{^{1}H} NMR (50 MHz): δ = 13.3 (CH_2Me), 20.6 (CHMe_2), 30.3 (CMe_3), 31.4 (CMe_3), 34.7 (*C*Me$_3$), 37.6 (*C*Me$_3$), 39.7 (NCH_2), 53.6 (NCH), 120.6 (arom., CH), 121.0 (arom., CH), 123.4 (arom.), 148.3 (arom.), 148.6 (arom.), 149.2 (arom.). – IR (NaCl): $\tilde{\nu}$ = 1362, 1242, 1020 cm^{-1}. – MS, *m/z* (%): 355 (11) [M^+ + 2], 353 (10) [M^+], 340 (99) [M^+ – Me + 2], 338 (100) [M^+ – Me], 57 (24) [*t*Bu$^+$]. – $C_{19}H_{32}{}^{79}BrN$: calcd. 353.1719; found 353.1712 (MS).

Lithiation of **1b** *with 3.1 Equiv. of Butyllithium:* Butyllithium (0.656 mmol in hexane) was added to a solution of **1b** (76.2 mg, 0.215 mmol) in THF (5 ml) at 0°C, the mixture was stirred for 10 min, then water was added at room temp. to give **5b** (57.4 mg, 0.209 mmol) as a colorless oil in 97% yield after the usual workup. – ^{1}H NMR (200 MHz): δ = 1.19 (6H, d, J = 6.6 Hz, CHMe_2), 1.20 (3H, t, J = 7.0 Hz, CH_2Me), 1.32 (18H, s, *t*Bu), 3.25 (2H, q, J = 7.0 Hz, NCH_2), 4.05 (1H, sept, J = 6.6 Hz, NCH), 6.63 (2H, d, J = 1.5 Hz, arom.), 6.78 (1H, t, J = 1.5 Hz, arom.).

[2,4-Di-tert-butyl-6-(ethylisopropylamino)phenyl]dithioxophosphorane (**3b**): Butyllithium (2.64 mmol in hexane) was added to a THF solution (6 ml) of **1b** (309 mg, 0.872 mmol) over a period of 10 min at 0°C with stirring, the reaction mixture was warmed to room temp., then a solution of PCl_3 (0.50 ml, 5.73 mmol) in THF (6 ml) was added at –78°C. The mixture was stirred for 10 min, then warmed to room temp., and the solvent was evaporated in vacuo. The residue was then dissolved in THF (5 ml), and the solution was added to a THF solution (5 ml) of $LiAlH_4$ (LAH; 100 mg, 2.64 mmol) at 0°C, stirred for 10 min and then for 15 min at room temp. Methanol was added slowly to destroy excess LAH. Insoluble materials were filtered off, and the filtrate was concentrated in vacuo to give *[2,4-di-tert-butyl-6-(ethylisopropylamino)-phenyl]phosphane* (**2b**) as a colorless oil. – ^{1}H NMR (200 MHz): δ = 0.93 (3H, t, J_{HH} = 7.0 Hz, CH_2Me), 1.07 (3H, d, J_{HH} = 6.2 Hz, CHMe_2), 1.16 (3H, d, J_{HH} = 6.7 Hz, CHMe_2), 1.31 (9H, s, *p*-*t*Bu), 1.49 (9H, s, *o*-*t*Bu), 2.9–3.3 (3H, m, NCH, NCH_2), 4.08 (1H, dd, J_{PH} = 212.8, J_{HH} = 10.2 Hz, PH), 4.19 (1H, dd, J_{PH} = 215.9, J_{HH} = 10.4 Hz, PH), 7.04 (1H, dd, J_{PH} = 2.1, J_{HH} = 2.1 Hz, arom.), 7.29 (1H, dd, J_{PH} = 2.1, J_{HH} = 2.1 Hz, arom.). – ^{31}P NMR: δ = –140.2 (t, J_{PH} = 215 Hz). – To this oil sulfur (111 mg, 3.47 mmol), benzene (6 ml), and triethylamine (1 ml) were added, and the mixture was stirred for 1 h. The solvent was removed in vacuo and the residue submitted to silica gel column chromatography using benzene as eluent to give **3b** (85.1 mg, 0.230 mmol, 26%) as colorless prisms. M.p. 185–189°C (benzene). – ^{1}H NMR (200 MHz): δ = 1.19 (3H, t, J_{HH} = 7.3 Hz, CH_2Me), 1.31 (9H, s, *p*-

*t*Bu), 1.44 (3H, d, J_{HH} = 6.6 Hz, CH*Me*), 1.46 (3H, d, J_{HH} = 6.6 Hz, CH*Me*), 1.54 (9H, s, *o*-*t*Bu), 3.4–3.8 (2H, m, NCH_2), 4.47 (1H, d of sept, J_{PH} = 6, J_{HH} = 6.6 Hz, NCH), 6.99 (1H, dd, J_{PH} = 2.2, J_{HH} = 1.5 Hz, arom.), 7.50 (1H, dd, J_{PH} = 8.5, J_{HH} = 1.3 Hz, arom.). – $^{13}C\{^1H\}$ NMR (50 MHz): δ = 12.6 (d, J_{PC} = 1.0 Hz, CH_2Me), 18.7 (d, J_{PC} = 2.4 Hz, CH*Me*), 19.0 (d, J_{PC} = 1.8 Hz, CH*Me*), 31.2 (CMe_3), 31.4 (CMe_3), 35.5 (d, J_{PC} = 1.1 Hz, CMe_3), 36.0 (d, J_{PC} = 2.1 Hz, CMe_3), 44.0 (s, CH_2Me), 57.4 (s, $CHMe_2$), 117.6 (d, J_{PC} = 13.2 Hz, *m*-C), 125.6 (d, J_{PC} = 13.8 Hz, *m'*-C), 141.3 (d, J_{PC} = 87.0 Hz, *ipso*-C), 143.2 (d, J_{PC} = 1.2 Hz, arom.), 151.0 (d, J_{PC} = 3.6 Hz, arom.), 155.9 (d, J_{PC} = 3.1 Hz, arom.). – $^{31}P\{^1H\}$ NMR: δ = 177.2. – UV (CH_2Cl_2): λ_{max} (lg ε) 262 nm (3.89). – IR (KBr): $\tilde{\nu}$ = 721 cm^{-1}. – MS, *m/z* (%): 369 (69) [M^+], 336 (100) [M^+ – S – 1], 57 (53) [tBu^+]. – $C_{19}H_{32}NPS_2$: calcd. 369.1714; found 369.1738 (MS).

[2,4-Di-tert-butyl-6-(ethylisopropylamino)phenyl]-diselenoxophosphorane (**4b**): The phenylphosphane **2b** was prepared from **1b** (232 mg, 0.654 mmol) and allowed to react with selenium (204 mg, 2.58 mmol) in a mixture of benzene (7 ml) and triethylamine (1 ml) for 22 h. The solvent was removed in vacuo and the residue submitted to silica gel column chromatography using benzene as eluent to give **4b** (96.1 mg, 0.207 mmol, 32%) as yellow prisms (benzene). M.p. 164–167°C (dec.). – ^1H NMR (200 MHz): δ = 1.21 (3H, t, J_{HH} = 7.4 Hz, CH_2Me), 1.32 (9H, s, *p*-*t*Bu), 1.43 (3H, d, J_{HH} = 6.6 Hz, CH*Me*), 1.49 (3H, d, J_{HH} = 6.6 Hz, CH*Me*), 1.60 (9H, s, *o*-*t*Bu), 3.3–3.8 (2H, m, NCH_2), 4.53 (1H, d of sept, J_{PH} = 4.5, J_{HH} = 6.7 Hz, NCH), 6.94 (1H, dd, J_{PH} = 2.5, J_{HH} = 1.5 Hz, arom.), 7.52 (1H, dd, J_{PH} = 8.2, J_{HH} = 1.5 Hz, arom.). – $^{13}C\{^1H\}$ NMR (50 MHz): δ = 13.0 (s, CH_2Me), 18.8 (d, J_{PC} = 2.1 Hz, CH*Me*), 18.9 (d, J_{PC} = 2.2 Hz, CH*Me*), 31.2 (s, CMe_3), 31.7 (s, CMe_3), 35.5 (d, J_{PC} = 1.0 Hz, CMe_3), 36.4 (d, J_{PC} = 1.6 Hz, CMe_3), 43.4 (s, CH_2Me), 57.4 (d, J_{PC} = 2.3 Hz, $CHMe_2$), 118.5 (d, J_{PC} = 11.5 Hz, *m*-C), 126.0 (d, J_{PC} = 13.0 Hz, *m'*-C), 140.4 (d, J_{PC} = 64.0 Hz, *ipso*-C), 143.4 (d, J_{PC} = 4.1 Hz, arom.), 151.0 (d, J_{PC} = 3.1 Hz, arom.), 155.8 (d, J_{PC} = 3.0 Hz, arom.). – $^{31}P\{^1H\}$ NMR: δ = 157.4 (satellite d, J_{PSe} = 817 Hz). – ^{77}Se NMR: δ = 445.3 (d, J_{PSe} = 817 Hz), 491.9 (d, J_{PSe} = 806 Hz). – UV (CH_2Cl_2): λ_{max} (lg ε) = 285 nm (sh, 3.90), 252 (4.17). – IR (KBr): $\tilde{\nu}$ = 577 cm^{-1}. – MS, *m/z* (%): 465 (7) [M^+], 463 (6) [M^+ – 2], 384 (15) [M^+ – Se – 1], 304 (100) [M^+ – 2 Se – 1]. – $C_{19}H_{32}NP^{80}Se_2$: calcd. 465.0603; found 465.0585 (MS).

2-Bromo-1,5-di-tert-butyl-3-(isopropylmethylamino)benzene (**1c**): A suspension of **1j** (371 mg, 1.14 mmol) and $NaBH_4$ (260 mg, 6.87 mmol) in 10 ml of THF was added to a solution of formalin (0.45 ml, 6.00 mmol) in THF (10 ml) at 0°C, then sulfuric acid (0.5 ml) was added, and the mixture was stirred for 2 h at room temp. It was then treated as usual to give **1c** (349 mg, 1.02 mmol, 90% yield) as colorless crystals. M.p. 74.0–75.0°C. – ^1H NMR (200 MHz): δ = 1.10 (6H, d, *J* = 6.3 Hz, $CHMe_2$), 1.31 (9H, s, *p*-*t*Bu), 1.55 (9H, s, *o*-*t*Bu), 2.64 (3H, s, NMe), 3.40 (1H, sept, *J* = 6.7 Hz, $NCHMe_2$), 7.02 (1H, d, *J* = 2.4 Hz, arom.), 7.21 (1H, d, *J* = 2.4 Hz, arom.). – $^{13}C\{^1H\}$ NMR (50 MHz): δ = 18.3 (br, $CHMe_2$), 30.3 (CMe_3), 31.3 (CMe_3), 33.7 ($CHMe_2$), 34.8 (CMe_3), 37.6 (CMe_3), 53.4 (NMe), 119.2 (arom., CH), 120.2 (arom., CH), 120.6 (arom., CBr), 148.3 (arom.), 149.1 (arom.), 152.1 (arom.). – IR (KBr): $\tilde{\nu}$ = 1404, 1190, 1012, 964 cm^{-1}. – MS, *m/z* (%): 341 (11) [M^+ + 2], 339 (15) [M^+], 326 (97) [M^+ – Me + 2], 324 (100) [M^+ – Me], 57 (29) [tBu^+]. – $C_{18}H_{30}{}^{79}BrN$: calcd. 339.1562; found 339.1567 (MS).

Lithiation of **1c** *with 1.5 Equiv. of Butyllithium:* Butyllithium (0.232 mmol in hexane) was added to a solution of **1c** (52.3 mg, 0.154 mmol) in THF (5 ml) at 0°C, the mixture was stirred for 10 min, and the reaction was quenched with water at room temp. to give **5c** (38.1 mg, 0.146 mmol) as a colorless oil in 95% yield after the usual work-up procedure. – ^1H NMR (200 MHz): δ = 1.18 (6H, d, *J* = 6.6 Hz, $CHMe_2$), 1.33 (18H, s, *t*Bu), 2.76 (3H, s, NMe), 4.08 (1H, sept, *J* = 6.6 Hz, NCH), 6.67 (2H, d, *J* = 1.6 Hz, arom.), 6.82 (1H, t, *J* = 1.6 Hz, arom.). – MS, *m/z* (%): 261 (31) [M^+], 246 (100) [M^+ – Me], 232 (34) [M^+ – 2 Me + 1], 57 (28) [tBu^+]. – $C_{18}H_{31}N$: calcd. 261.2456; found 261.2457 (MS).

[2,4-Di-tert-butyl-6-(isopropylmethylamino)phenyl]dithioxophosphorane (**3c**): Butyllithium (2.56 mmol in hexane) was added to a THF (10 ml) solution of **1c** (573 mg, 1.68 mmol) over a period of 10 min at 0°C with stirring. The mixture was warmed to room temp., added to a solution of PCl_3 (0.60 ml, 6.88 mmol) in THF (6 ml) at –78°C and stirred for 10 min. The reaction mixture was warmed up to room temp., and the solvent was evaporated in vacuo. The residue was then dissolved in THF (10 ml), and the solution was added to a solution of LAH (192 mg, 5.06 mmol) in ether (6 ml) at 0°C, stirred for 10 min and further stirred for 15 min at room temp. Methanol was added slowly to destroy excess LAH. Insoluble materials were filtered off, and the filtrate was concentrated in vacuo to give *[2,4-di-tert-butyl-6-(isopropylmethylamino)-phenyl]phosphane* (**2c**): – ^1H NMR (200 MHz): δ = 1.10 (6H, d, J_{HH} = 6.4 Hz, $CHMe_2$), 1.31 (9H, s, *p*-*t*Bu), 1.49 (9H, s, *o*-*t*Bu), 2.60 (3H, s, Me), 3.16 (1H, sept, J_{HH} = 6.4 Hz, NCH), 4.11 (2H, d, J_{PH} = 214.2 Hz, PH_2), 7.06 (1H, dd, J_{PH} = J_{HH} = 2.2 Hz, arom.), 7.30 (1H, dd, J_{PH} = J_{HH} = 2.1 Hz, arom.). – ^{31}P NMR: δ = –140.0 (t, J_{PH} = 214 Hz). – MS, *m/z* (%): 293 (36) [M^+], 292 (96) [M^+ – 1], 276 (34) [M^+ – Me – 2], 57 (100) [tBu^+]. The phosphane **2c** was allowed to react with sulfur (214 mg, 6.67 mmol) in a mixture of benzene (10 ml) and triethylamine (1 ml), and the mixture was stirred for 3 h. The solvent was removed in vacuo and the residue submitted to silica gel column chromatography using benzene as eluent to give **3c** (279 mg, 0.789 mmol, 47%) as colorless prisms. M.p. 209–211°C (benzene). – ^1H NMR (200 MHz): δ = 1.32 (9H, s, *p*-*t*Bu), 1.45 (3H, d, J_{HH} = 6.2 Hz, CH*Me*), 1.48 (3H, d, J_{HH} = 6.2 Hz, CH*Me*), 1.55 (9H, s, *o*-*t*Bu), 3.05 (3H, d, J_{PH} = 7.9 Hz, NMe), 4.49 (1H, d of sept, J_{PH} = 4.5, J_{HH} = 6.6 Hz, NCH), 7.03 (1H, dd, J_{PH} = 2.5, J_{HH} = 1.5 Hz, arom.), 7.50 (1H, dd, J_{PH} = 8.4, J_{HH} = 1.4 Hz, arom.). – $^{13}C\{^1H\}$ NMR (50 MHz): δ = 18.0 (d, J_{PC} = 2.2 Hz, CHMe), 19.0 (d, J_{PC} = 1.7 Hz, CH*Me*), 31.3 (s, CMe_3), 31.4 (s, CMe_3), 35.6 (s, CMe_3), 36.1 (s, CMe_3), 36.1 (d, J_{PC} = 2.3 Hz, $CHMe_2$), 57.2 (s, NMe), 115.2 (d, J_{PC} = 12.2 Hz, *m*-C), 125.8 (d, J_{PC} = 13.5 Hz, *m'*-C), 139.9 (d, J_{PC} = 87.8 Hz, *ipso*-C), 146.7 (s, arom.), 150.9 (d, J_{PC} = 3.5 Hz, arom.), 156.7 (d, J_{PC} = 3.0 Hz, arom.). – $^{31}P\{^1H\}$ NMR: δ = 177.6. – UV (CH_2Cl_2): λ_{max} (lg ε) = 260 nm (3.95). – IR (KBr): $\tilde{\nu}$ = 725 cm^{-1}. – MS, *m/z* (%): 355 (66) [M^+], 322 (100) [M^+ – S – 1]. – $C_{18}H_{30}NPS_2$: calcd.355.1557; found 355.1577 (MS).

[2,4-Di-tert-butyl-6-(isopropylmethylamino)phenyl]-diselenoxophosphorane (**4c**): The phosphane **2c** was prepared from **1c** (547 mg, 1.61 mmol) and was allowed to react with selenium (508 mg, 6.43 mmol) in a mixture of benzene (10 ml) and triethylamine (1 ml) for 2 h. The solvent was removed in vacuo, and the residue was submitted to silica gel column chromatography using benzene as eluent to give **4c** (340 mg, 0.757 mmol, 47%) as yellow crystals (benzene). M.p. 208–210°C (dec.). – ^1H NMR (200 MHz): δ = 1.31 (9H, s, *p*-*t*Bu), 1.42 (3H, d, J_{HH} = 6.5 Hz, CH*Me*), 1.49 (3H, d, J_{HH} = 6.6 Hz, CH*Me*), 1.58 (9H, s, *o*-*t*Bu), 2.95 (3H, d, J_{PH} = 7.9 Hz, NMe), 4.54 (1H, d of sept, J_{PH} = 4.8 Hz, J_{HH} = 6.6 Hz, $NCHMe_2$), 6.97 (1H, dd, J_{PH} = 2.7, J_{HH} = 1.5 Hz, arom.), 7.51 (1H, dd, J_{PH} = 8.1, J_{HH} = 1.5 Hz, arom.). – $^{13}C\{^1H\}$ NMR (50 MHz): δ = 18.1 (d, J_{PC} = 1.7 Hz, CH*Me*), 18.9 (d, J_{PC} = 2.2 Hz, CH*Me*), 31.3 (s, CMe_3), 31.6 (s, CMe_3), 35.6 (d,

J_{PC} = 1.0 Hz, *C*Me$_3$), 36.0 (d, J_{PC} = 1.4 Hz, *C*HMe$_2$), 36.5 (d, J_{PC} = 1.5 Hz, *C*Me$_3$), 56.9 (d, J_{PC} = 2.5 Hz, NMe), 115.9 (d, J_{PC} = 10.5 Hz, *m*-C), 126.2 (d, J_{PC} = 12.9 Hz, *m'*-C), 139.4 (d, J_{PC} = 64.9 Hz, *ipso*-C), 147.1 (d, J_{PC} = 3.7 Hz, arom.), 151.1 (d, J_{PC} = 3.1 Hz, arom.), 156.7 (d, J_{PC} = 3.0 Hz, arom.). – $^{31}P\{^1H\}$ NMR: δ = 157.0 (satellite d, J_{PSe} = 815 Hz). – ^{77}Se NMR: δ = 399.5 (d, J_{PSe} = 823 Hz), 454.0 (d, J_{PSe} = 815 Hz). – UV (CH_2Cl_2): λ_{max} (lg ε) = 250 nm (4.18), 281 (3.89). – IR (KBr): $\tilde{\nu}$ = 579 cm^{-1}. – MS, *m/z* (%): 451 (23) [M$^+$], 449 (21) [M$^+$ – 2], 370 (25) [M$^+$ – Se – 1], 291 (100) [M$^+$ – Se$_2$]. – $C_{18}H_{30}NP^{80}Se_2$: calcd. 451.0446; found 451.0430 (MS).

Lithiation of 2-Bromo-1,5-di-tert-butyl-3-piperidinobenzene (**1d**) *with Butyllithium:* Compound **1d** was prepared according to the method as previously reported[11]. Butyllithium (0.245 mmol in hexane) was added to a solution of **1d** (70.7 mg, 0.201 mmol) in THF (2 ml) at 0°C, the mixture was stirred for 10 min, then water was added at room temp. The reaction mixture was worked up as usual to give **5d** (46.1 mg, 0.169 mmol, 84% yield) as colorless crystals. M.p. 36.5–39.5°C. – ^1H NMR (200 MHz): δ = 1.34 (18H, s, *t*Bu), 1.57 (2H, br. s, CH$_2$), 1.75 (4H, br. s, CH$_2$), 3.15 (4H, t, *J* = 5.3 Hz, NCH$_2$), 6.85 (2H, d, *J* = 1.6 Hz, arom.), 6.97 (1H, t, *J* = 1.6 Hz, arom.). – $^{13}C\{^1H\}$ NMR (50 MHz): δ = 24.4 (CH$_2$), 26.2 (CH$_2$), 31.5 (C*Me*$_3$), 35.0 (*C*Me$_3$), 51.7 (NCH$_2$), 111.8 (arom., CH), 114.4 (arom., CH), 151.1 (arom.), 152.0 (arom.). – IR (neat): $\tilde{\nu}$ = 2962 cm^{-1}, 2952, 2862, 2798, 2794, 1593. – MS, *m/z* (%): 273 (100) [M$^+$], 83 (10) [(CH$_2$)$_5$N$^+$ – 1]. – $C_{19}H_{31}N$: calcd. 273.2456; found 273.2456 (MS).

(2,4-Di-tert-butyl-6-piperidinophenyl)dithioxophosphorane (**3d**): Butyllithium (0.815 mmol in hexane) was added to a THF (6 ml) solution of **1d** (217 mg, 0.742 mmol) over a period of 10 min with stirring at 0°C. The reaction mixture was warmed gradually to room temp., then cooled and subsequently added to a solution of PCl_3 (0.26 ml, 2.98 mmol) in THF (6 ml) at –78°C with stirring for 10 min. The mixture was warmed up to room temp. and the solvent evaporated in vacuo. The residue consisting of *[2,4-di-tert-butyl-6-piperidinophenyl]phosphonous dichloride* was dissolved in ether (5 ml), and the solution was added to an ethereal solution (5 ml) of LAH (207 mg, 5.45 mmol) at 0°C. The mixture was stirred for 10 min and for further 15 min at room temp. Methanol was added slowly to destroy excess LAH. Insoluble materials were filtered off and the filtrate was concentrated in vacuo to give an oil consisting of *[2,4-di-tert-butyl-6-piperidinophenyl]phosphane* (**2d**) as a colorless oil. – ^1H NMR (200 MHz): δ = 1.31 (9H, s, *p*-*t*Bu), 1.49 (9H, s, *o*-*t*Bu), 1.6–1.9 (6H, br. s, CH$_2$), 2.6–2.8 (2H, br. s, NCH), 2.9–3.1 (2H, br. s, NCH), 4.14 (2H, d, J_{PH} = 214.8 Hz, PH$_2$), 7.06 (1H, dd, J_{PH} = J_{HH} = 2.2 Hz, arom.), 7.32 (1H, dd, J_{PH} = J_{HH} = 2.2 Hz, arom.). – ^{31}P NMR: δ = –141.4 (t, J_{PH} = 215 Hz). – MS, *m/z* (%): 305 (35) [M$^+$], 304 (100) [M$^+$ – 1], 273 (88) [M$^+$ – PH]. – $C_{19}H_{32}NP$: calcd. 305.2272; found 305.2264. – To the oily **2d** sulfur (78.1 mg, 2.44 mmol) and triethylamine (5 ml) were added, and the mixture was stirred for 17 h. The solvent was removed in vacuo and the residue submitted to silica gel column chromatography using benzene as eluent to give **3d** (107 mg, 0.291 mmol, 39% yield) as colorless prisms (benzene). M.p. 278–280°C (dec.). – ^1H NMR (200 MHz): δ = 1.31 (9H, s, *p*-*t*Bu), 1.53 (9H, s, *o*-*t*Bu), 1.5–1.9 (4H, m, CH$_2$), 2.31 (2H, br. q, *J* = 15 Hz, CH$_2$), 3.17 (2H, br. q, *J* = 12 Hz, NCH), 4.11 (2H, br. d, *J* = 11 Hz, NCH), 7.01 (1H, dd, J_{PH} = 2.7, J_{HH} = 1.4 Hz, arom.), 7.48 (1H, dd, J_{PH} = 8.4, J_{HH} = 1.4 Hz, arom.). – $^{13}C\{^1H\}$ NMR (50 MHz): δ = 21.5 (s, CH$_2$), 22.6 (s, CH$_2$), 31.2 (s, C*Me*$_3$), 31.4 (s, C*Me*$_3$), 35.8 (s, *C*Me$_3$), 36.2 (s, *C*Me$_3$), 55.7 (s, NCH$_2$), 112.0 (d, J_{PC} = 11.4 Hz, *m*-C), 126.3 (d, J_{PC} = 13.5 Hz, *m'*-C), 139.6 (d, J_{PC} = 88.9 Hz, *ipso*-C), 146.9 (s, arom.), 151.4 (d, J_{PC} = 3.4 Hz, arom.), 157.3 (d, J_{PC} = 3.0 Hz, arom.). – $^{31}P\{^1H\}$ NMR: δ = 169.9. – UV (CH_2Cl_2): λ_{max} (lg ε) = 259 nm (4.22), 302 (sh, 3.51), 325 (sh, 3.05). – IR (KBr): $\tilde{\nu}$ = 727 cm^{-1}. – MS, *m/z* (%): 367 (29) [M$^+$], 334 (100) [M$^+$ – S – 1], 57 (12) [*t*Bu$^+$]. – $C_{19}H_{30}NPS_2$: calcd. 367.1557; found 367.1556 (MS).

{2,4-Di-tert-butyl-6-[(dimethylamino)methyl]phenyl}-diselen oxophosphorane (**4f**): 2-Bromo-1,5-di-*tert*-butylphenyl-3-[(dimethylamino)methyl]benzene (**1f**) was prepared from 2-bromo-1-(bromomethyl)-3,5-di-*tert*-butylbenzene[23] according to the method reported previously[9] as a colorless oil. – ^1H NMR (200 MHz): δ = 1.32 (9H, s, *t*Bu), 1.55 (9H, s, *t*Bu), 2.31 (2H, s, NMe$_2$), 3.54 (2H, s, CH$_2$), 7.29 (1H, d, *J* = 2.6 Hz, arom.), 7.40 (1H, d, *J* = 2.6 Hz, arom.). – ^{13}C NMR (50 MHz): δ = 30.2 (C*Me*$_3$), 31.3 (C*Me*$_3$), 34.7 (*C*Me$_3$), 37.4 (*C*Me$_3$), 45.7 (NMe$_2$), 65.5 (CH$_2$), 122.4 (arom.), 124.0 (arom., CH), 126.1 (arom., CH), 139.1 (arom.), 147.4 (arom.), 149.0 (arom.). – UV (hexane): λ_{max} (lg ε) = 221 nm (4.09, sh), 272 (2.51, sh), 302 (2.05), 313 (1.98, sh). – MS, *m/z* (%): 327 (10) [M$^+$ + 2], 325 (50) [M$^+$], 283 (7) [M$^+$ + 2 – NMe$_2$], 281 (7) [M$^+$ – NMe$_2$], 246 (8) [M$^+$ – Br], 203 (100) [M$^+$ – Br – NMe$_2$ – 1], 57 (6) [*t*Bu$^+$]. – $C_{17}H_{28}NBr$: calcd. 325.1405; found 325.1369 (MS). – The bromide **1f** (905 mg, 2.77 mmol) was converted to the corresponding primary phosphane **2f**[9] (^{31}P NMR: δ = –143.6, J_{PH} = 205 Hz) which was allowed to react with selenium (832 mg, 10.5 mmol, 3.8 equiv.) in benzene (50 ml) in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene; 0.41 ml, 2.7 mmol, 1 equiv.) at room temp. for 15 h. After chromatography on alumina (chloroform) and trituration of the residue with a mixture of chloroform and hexane, 188 mg of **4f** was obtained as colorless crystals in 16% yield (based on **1f**). M.p. 222.0–224.0°C. – ^1H NMR (200 MHz): δ = 1.31 (9H, s, *t*Bu), 1.78 (9H, s, *t*Bu), 3.11 (6H, d, *J* = 8.2 Hz, NMe$_2$), 4.46 (6H, s, CH$_2$), 7.00 (1H, pseudo t, *J* = 2.2 Hz, arom.), 7.56 (1H, d, J_{HH} = 1.9, *J* = 7.3 Hz, arom.). – ^{13}C NMR (50 MHz): δ = 31.1 (s, C*Me*$_3$), 32.9 (s, C*Me*$_3$), 35.0 (d, J_{PC} = 1.1 Hz, *C*Me$_3$), 38.6 (d, J_{PC} = 1.2 Hz, *C*Me$_3$), 45.6 (d, J_{PC} = 2.5 Hz, NMe$_2$), 61.9 (d, J_{PC} = 8.5 Hz, CH$_2$), 119.5 (d, J_{PC} = 9.3 Hz, *m*-C), 126.3 (d, J_{PC} = 12.4 Hz, *m*-C), 133.6 (d, J_{PC} = 10.5 Hz, *o*-C), 136.0 (d, J_{PC} = 57.6 Hz, *ipso*-C), 152.6 (d, J_{PC} = 10.4 Hz, *o*-C), 154.4 (d, J_{PC} = 3.1 Hz, *p*-C). – ^{31}P NMR: δ = 123.6 (J_{PSe} = 790 Hz). – ^{77}Se NMR ($CDCl_3$, 296 K): δ = 195.4 (d, J_{PSe} = 791 Hz). – UV (CH_2Cl_2): λ_{max} (lg ε): 231 nm (4.18), 274 (3.73). – IR (KBr): $\tilde{\nu}$ = 1465 cm^{-1}, 1442, 821, 609, 588, 547, 512. – MS, *m/z* (%): 437 (33) [M$^+$], 357 (19) [M$^+$ – Se], 277 (100) [M$^+$ – 2 Se], 262 (57) [M$^+$ – 2 Se – Me], 57 (56) [*t*Bu$^+$]. – $C_{17}H_{28}NPSe_2$: calcd. 437.0293; found 437.0287 (MS).

[2,4-Di-tert-butyl-6-[1-(dimethylamino)-1-methylethyl]phenyl]diselenoxophosphorane (**4g**): 2-Bromo-1,5-di-*tert*-butylphenyl-3-[1-(dimethylamino)-1-methylethyl]benzene (**1g**) was prepared from 2-bromo-1-(bromomethyl)-3,5-di-*tert*-butylbenzene[23] according to the method reported previously[10] as colorless crystals. M.p. 72.5–75.0°C. – ^1H NMR (200 MHz): δ = 1.31 (9H, s, *t*Bu), 1.54 (6H, s, C*Me*$_2$NMe$_2$), 1.59 (9H, s, *t*Bu), 2.15 (2H, s, NMe$_2$), 7.34 (1H, d, *J* = 2.5 Hz, arom.), 7.55 (1H, d, *J* = 2.5 Hz, arom.). – ^{13}C NMR (50 MHz): δ = 22.8 (C*Me*$_2$NMe$_2$), 31.0 (C*Me*$_3$), 31.4 (C*Me*$_3$), 34.8 (*C*Mc$_3$), 18.2 (NMe$_2$), 38.33 (*C*Me$_3$), 62.7 (*C*Me$_2$NMe$_2$), 120.8 (arom.), 123.8 (arom., CH), 124.4 (arom., CH), 147.0 (arom.), 147.9 (arom.), 148.7 (arom.). – MS, *m/z* (%): 355 (6) [M$^+$ + 2], 353 (6) [M$^+$], 340 (98) [M$^+$ + 2 – Me], 338 (100) [M$^+$ – Me], 86 (92), [CMe$_2$NMe$_2^+$], 57 (46) [*t*Bu$^+$]. – The bromide **1g** (563 mg, 1.59 mmol) was converted to the corresponding primary phosphane **2g**[10] (^{31}P NMR: δ = –127.4, J_{PH} = 207 Hz) which was allowed to react with selenium (119 mg, 1.51 mmol, 1 equiv.) in benzene (10 ml) in the presence of DBU (0.22 ml, 1.6 mmol, 1.1 equiv.) at room temp. for 8 h. After chromatography on

alumina (chloroform) and trituration of the residue with a mixture of chloroform and hexane, 198 mg of **4g** was obtained in 26% yield (based on **1g**) as colorless crystals. M.p. 239–242°C. – ^{1}H NMR (200 MHz): δ = 1.32 (9H, s, *t*Bu), 1.86 (9H, s, *t*Bu), 2.03 (6H, s, CMe_2NMe_2), 3.04 (6H, d, *J* = 9.0 Hz, NMe_2), 7.02 (1H, dd, J_{HH} = 1.9, J_{PH} = 2.8 Hz, arom.), 7.64 (1H, d, J_{HH} = 1.9, *J* = 7.2 Hz, arom.). – ^{13}C NMR (50 MHz): δ = 28.5 (s, CMe_2NMe_2), 31.1 (s, CMe_3), 33.4 (s, CMe_3), 35.1 (d, J_{PC} = 1.2 Hz, CMe_3), 39.2 (d, J_{PC} = 1.2 Hz, CMe_3), 43.1 (br. d, J_{PC} = 4.0 Hz, NMe_2), 71.9 (d, J_{PC} = 5.7 Hz, CMe_2), 118.1 (d, J_{PC} = 9.6 Hz, *m*-C), 127.1 (d, J_{PC} = 12.5 Hz, *m*-C), 133.0 (d, J_{PC} = 56.9 Hz, *ipso*-C), 144.1 (d, J_{PC} = 11.4 Hz, *o*-C), 152.7 (d, J_{PC} = 11.6 Hz, *o*-C), 154.7 (d, J_{PC} = 3.1 Hz, *p*-C). – ^{31}P NMR: δ = 121.8 (J_{PSe} = 784 Hz). – ^{77}Se NMR (330 K): δ = 353.1 (d, J_{PSe} = 801 Hz). – IR (KBr): $\tilde{\nu}$ = 1596 cm^{-1}, 1471, 1427, 1361, 1145, 705, 609, 570, 509, 495. – MS, *m/z* (%): 465 (18) [M^+], 463 (18) [$M^+ - 2$], 461 (10) [$M^+ - 4$], 385 (18) [$M^+ - Se$], 370 (14) [$M^+ - Se - Me$], 305 (100) [$M^+ - 2\,Se$], 290 (18) [$M^+ - 2\,Se - Me$], 261 (42) [$M^+ - 2\,Se - NMe_2$], 57 (75) [$t Bu^+$]. – $C_{19}H_{32}NPSe_2$: calcd. 465.0606; found 465.0624 (MS).

{2,4-Di-tert-butyl-6-[2-(dimethylamino)-1,1-dimethylethyl}-phenyl}diselenoxophosphorane (**4h**): 2-Bromo-1,5-di-*tert*-butyl-phenyl-3-[2-(dimethylamino)-1,1-dimethylethyl]benzene (**1h**) was prepared from 2-bromo-1-(bromomethyl)-3,5-di-*tert*-butylbenzene[23] according to the method reported previously[10] as a colorless oil. – ^{1}H NMR (200 MHz): δ = 1.31 (9H, s, *t*Bu), 1.57 (9H, s, *t*Bu), 1.60 (6H, s, CMe_2CH_2), 3.08 (2H, s, CH_2), 7.41 (2H, *pseudo* s, arom.). – ^{13}C NMR (50 MHz): δ = 28.6 (CMe_2CH_2), 31.0 (CMe_3), 31.3 (CMe_3), 34.7, 38.2 (CMe_3 or CMe_2CH_2), 43.0 (CMe_3 or CMe_2CH_2), 121.7 (arom.), 123.7 (arom., CH), 125.3 (arom., CH), 146.3 (arom.), 148.3$_1$ (arom.), 148.3$_3$ (arom.). – IR (KBr): $\tilde{\nu}$ = 1589 cm^{-1}, 1317, 1282, 1263, 1240, 1222, 1201, 1157, 1118, 1095, 842, 738. – The bromide **1h** (317 mg, 0.860 mmol) was converted to the corresponding primary phosphane **2h**[10] (^{31}P NMR: δ = –127.4, J_{PH} = 208 Hz) which was allowed to react with selenium (305 mg, 3.85 mmol, 4.5 equiv.) in benzene (5 ml) in the presence of DBU (0.14 ml, 9.5 mmol, 1.1 equiv.) at room temp. for 10 h. After chromatography on alumina (chloroform) and trituration of the residue with a mixture of chloroform and pentane 93.3 mg of **4h** was obtained as a colorless oil in 20% yield (based on **1h**). M.p. 221.0–224.0°C. – ^{1}H NMR (200 MHz): δ = 1.29 (9H, s, *t*Bu), 1.60 (6H, s, CMe_2CH_2), 1.88 (9H, s, *t*Bu), 3.06 (3H, br. s, NMe_2), 3.10 (3H, br. s, NMe_2), 7.16 (1H, dd, J_{HH} = 2.0, J_{PH} = 4.0 Hz, arom.), 7.60 (1H, d, J_{HH} = 2.0, *J* = 4.9 Hz, arom.). – ^{13}C NMR (100 MHz): δ = 31.0 (s, CMe_3), 34.8 (s, CMe_3), 34.9 (s, CMe_3), 35.0 (s, $CMe_2CH_2NMe_2$), 37.1 (d, J_{PC} = 3.1 Hz, CMe_3), 40.7 (d, J_{PC} = 2.3 Hz, $CMe_2CH_2NMe_2$), 43.5–46.5 (br., NMe_2), 66.5 (s, CH_2), 119.3 (d, J_{PC} = 9.9 Hz, *m*-C), 128.6 (d, J_{PC} = 13.7 Hz, *m*-C), 134.1 (d, J_{PC} = 54.9 Hz, *ipso*-C), 142.8 (d, J_{PC} = 5.3 Hz, *o*-C), 152.4 (d, J_{PC} = 3.1 Hz, *p*-C), 156.6 (d, J_{PC} = 13.7 Hz, *o*-C). – ^{31}P NMR: δ = 108.7 (J_{PSe} = 769 Hz). – ^{77}Se NMR (330 K): δ = 210.1 (d, J_{PSe} = 799 Hz). – IR (KBr): $\tilde{\nu}$ = 1596 cm^{-1}, 1481, 1450, 1394, 1363, 1240, 1213, 1162, 1118, 1012, 991, 811, 642, 617, 597, 555, 534, 505. – MS, *m/z* (%): 479 (1) [M^+], 398 (5) [$M^+ - Se - 1$], 336 (4) [$M^+ - 2\,Se$], 58 (100) [$CH_2NMe_2^+$].

X-Ray Structure Determination of **3c**[24]: $C_{18}H_{30}NPS_2 \cdot C_6H_6$, M_r = 433.65. Monoclinic, space group $P2_1/c$, *a* = 10.393(5), *b* = 18.064(5), *c* = 14.519(5) Å; β = 109.42(3)°; *V* = 2570(1) Å^3, *Z* = 4, ρ = 1.120 g cm^{-3}, μ = 2.79 cm^{-1}; 4713 unique reflections with $2\Theta \leq 50.1°$ were recorded with a four-circle diffractometer (Mo-K_α radiation, graphite monochrometer). Of these, 2025 with $I > 3\sigma(I)$ were considered observed. The structure was solved with SHELXS86[25]. The methyl carbon atoms of the *o-tert*-butyl group (C8–C10) and *o-tert*-butyl group (C12–C14) are disordered. These disordered groups were resolved into two positions from the difference maps. The predominant occupancy factor for (C8A–C10A) was refined to 0.64, while that for (C8B–C10B) was 0.36; the predominant occupancy factor for (C12A–C14A) was refined to 0.52, while that for (C12B–C14B) was 0.48. *R* = 0.089, R_w = 0.104.

☆ Dedicated to Prof. Dr. *Marianne Baudler* on the occasion of her 75th birthday.

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