2,4-Di-*tert*-butyl-6-piperidinophenyl as a Sterically and Electronically Stabilizing Group and X-Ray Analysis of the Corresponding Diselenoxophosphorane

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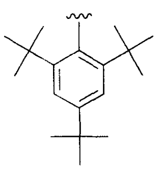
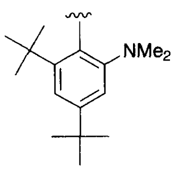
The 2,4-di-*tert*-butyl-6-(1-piperidino)phenyl group is utilized to stabilize diselenoxophosphorane and the structure determined by X-ray analysis indicates coordination of the nitrogen lone-pair to the P-atom to form a four-membered ring with a remarkably distorted P–C–C bond angle.

Kinetic stabilization using bulky substituents is a useful method for the investigation of low-coordinated phosphorus compounds. Utilizing an extremely bulky 2,4,6-tri-*tert*-butylphenyl group (hereafter abbreviated to Ar) as a sterically protecting auxiliary, we and others have been successful in the preparation of various types of multiply bonded phosphorus compounds such as diphosphenes[1] and dithioxophosphoranes.[2,3]

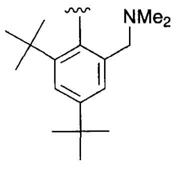
On the other hand, thermodynamic stabilization is an alternative technique for stabilization of such compounds. Recently, we have developed some novel stabilizing groups, such as the 2,4-di-*tert*-butyl-6-(dimethylamino)phenyl group (Mx),[4] the 2,4-di-*tert*-butyl-6-(dimethylaminomethyl)phenyl group (Mamx)[5] and the 2,4-di-*tert*-butyl-6-[1,1-dimethyl-2-(dimethylamino)ethyl]phenyl group (Maar),[6] having an electron-donating part within their moieties.



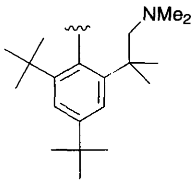
Ar



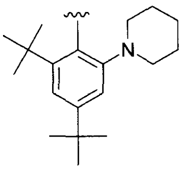
Mx



Mamx



Maar



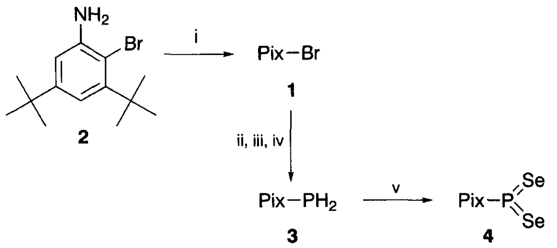
Pix

Using these substituents, dithioxophosphoranes as well as selenoxo- and thioxo-phosphines were prepared as stable compounds. In these compounds, the phosphorus–chalcogen bonds are stabilized by both steric protection of the *o*-*tert*-butyl group and intramolecular coordination of the amino group of the substituents at the *ortho* position.

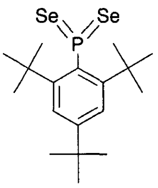
Now we report a novel stabilizing group, the 2,4-di-*tert*-butyl-6-(1-piperidino)phenyl group (Pix = piperidinoxylene derivative), which is expected to have a similar protecting and coordinating ability to the Mx group upon four-membered ring coordination. However, the coordinating ability of the Pix group would be expected to be lower than that of Mamx or Maar, for which five- or six-membered ring coordination is preferred.†

The sterically hindered bromobenzene **1** was prepared from 2-bromo-3,5-di-*tert*-butylaniline **2**[7] and was converted to the corresponding diselenoxophosphorane **4** *via* an intermediary primary phosphine **3**.‡ Similarly, diselenoxophosphoranes with the Maar and Mamx groups were prepared, and are expected to form intramolecular six- and five-membered rings upon coordination. ^{31}P NMR chemical shifts of those compounds together with data for **5**[8] and **6**[4a] are listed in Table 1. Interaction of nitrogen to phosphorus in the diselenoxophosphoranes is clearly shown by ^{31}P NMR spectroscopy. The signals due to the diselenoxophosphoranes **4** and **6** appear at higher field by *ca.* 125 ppm than that of non-coordinated diselenoxophosphorane **5**. This up-field shift is ascribable to the coordination of the nitrogen lone pair to the phosphorus atom in this system. The δ_P values for **4** and **6** lie between those for **5** and MamxPSe$_2$ reflecting the efficiency in coordination. This tendency is observed for the corresponding dithioxophosphoranes.[4–6] In the case of **4**, such internal coordination is achieved by forming a four-membered ring, while five- and six-membered rings are preferably formed in the corresponding dithioxophosphoranes, **7** and **8**, respectively, the structures of which were confirmed by X-ray analysis.[5,6]

The four-membered ring coordination in **4** was unambiguously established by X-ray crystallographic analysis.§ Fig. 1 depicts the molecular structure of **4**.[9b] The P=Se bond length for



Scheme 1 *Reagents and conditions*: i, NaBH$_4$–CH$_2$(CH$_2$CHO)$_2$, 73%; ii, Bu^{n}Li (1.2 equiv.), Et$_2$O, 0 °C; iii, PCl$_3$ (4.0 equiv.), Et$_2$O, −78 °C; iv, LiAlH$_4$ (3.0 equiv.), Et$_2$O; v, Se (4.0 equiv.), 1,8-diazabicyclo[5.4.0]undec-7-ene (*ca.* 1 equiv.), C$_6$H$_6$, 25 °C, 20 h, 38% from **1**



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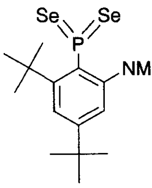

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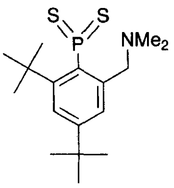

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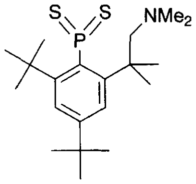

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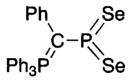

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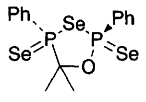

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Table 1 ^{31}P NMR data for some diselenoxophosphoranes (81 MHz, CDCl$_3$)

Diselenoxophosphorane	δ_P	$^1J_{PSe}$/Hz
PixPSe$_2$ **4**	147.7	813.0
MxPSe$_2$ **6**[a]	149.6	819.6
MamxPSe$_2$	123.6	789.8
MaarPSe$_2$	108.7	769.0
ArPSe$_2$ **5**[b]	273.0	854.5

[a] Data taken from ref. 4(*a*). [b] Data taken from ref. 8.

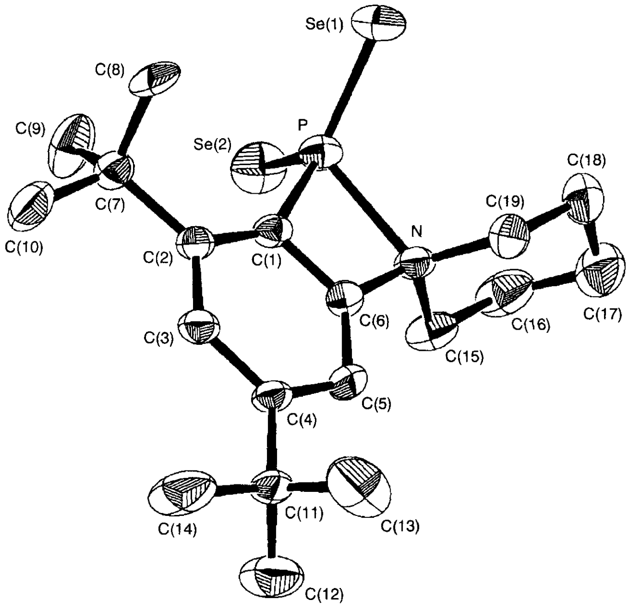

Fig. 1 Molecular structure for **4** showing the atom labelling scheme and thermal ellipsoids at the 50% probability level. Hydrogen atoms and the incorporated benzene molecule are omitted for clarity. Some important bond lengths (Å) and bond and dihedral angles (°): Se(1)–P 2.085(2), Se(2)–P 2.085(2), P–N 2.039(5), P–C(1) 1.814(6), N–C(6) 1.461(7), C(1)–C(2) 1.391(8), C(2)–C(7) 1.521(8), C(1)–C(6) 1.374(8), Se(1)–P–Se(2) 121.80(8), Se(1)–P–C(1) 116.8(2), C(15)–N–C(19) 111.2(5), P–C(1)–C(6) 96.3(4), C(1)–C(2)–C(7) 124.0(5), N–C(6)–C(1) 106.8(5), P–C(1)–C(6)–N 3.1(5)

4 is 2.085(2) Å and is almost identical to those for **9** [2.081(2) Å and 2.079(2) Å][10] or **10** [2.081(2) and 2.091(2) Å],[11] but much shorter than the P–Se single bond in **10** [2.258(1) Å].[11] The bond angle Se–P–Se for **4** is 121.80(8)° and is slightly narrower than that for **9** [124.5(1)°]. The P–N distance for **4** is 2.039(5) Å and is much shorter than the sum of the van der Waals radii, (3.4 Å), but is considerably longer than that for **8** [1.918(9) Å] or **7** [1.921(8) Å]. The most striking feature for **4** is that the bond angle P–C(1)–C(6) is significantly narrowed to 96.3(4)° in forming the four-membered ring, while N–C(6)–C(1) is 106.8(5)°. The corresponding P–C–C bond angles for **7** and **8** are 109.7(8) and 119.3(9)°, respectively. The other bonds in **4** are not so distorted indicating that the P–C bond of sp^2 configuration is flexible enough to allow distortion of 24°. The atoms C(1), P, N and C(6) are almost coplanar within 0.02 Å and the plane makes an angle of 89.3° with the triangle C(1)Se(1)Se(2). The atom P is 0.292 Å above the triangle plane toward N. The benzene ring C(1)–C(6) is coplanar within 0.01 Å and the atoms P and N are almost on the plane, −0.049 and 0.060 Å below and above, respectively. It is interesting to note that an energy-optimized structure calculated by CAChe-MOPAC¶ using PM3 SCF-MO method[12] for $MxPSe_2$ **6** is very similar to the X-ray determined structure for **4** as follows: P–N 2.039 Å, P–C–C 95.9°, N–C–C 106.1°, P–C–C–N 0.2°.

In summary, we have found direct evidence that the nitrogen lone pair is powerful enough to stabilize unstable molecules containing polarizable bonds even when required to form a distorted four-membered ring upon coordination.

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Footnotes

† In fact, there are several organometallic compounds stabilized by internal five- or six-membered ring coordination.[13]

‡ *Selected spectroscopic data*: **1**. Colourless crystals, mp 56.0–57.5 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.31 (s, 9H, *p*-Bu^t), 1.55 (s, 9H, *o*-Bu^t), 1.73 (br s, 4H, CH_2), 2.65 (br s, 2H, NCH), 3.14 (br s, 2H, NCH), 6.99 (d, *J* 2.4 Hz, 1H, arom.), 7.21 (d, *J* 2.4 Hz, 1H, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 24.4 (CH_2), 26.4 (CH_2), 30.3 ($C\mathit{Me}_3$), 31.4 ($C\mathit{Me}_3$), 35.0 ($\mathit{C}Me_3$), 37.6 ($\mathit{C}Me_3$), 54.3 (NCH_2), 116.6 (arom., CH), 119.5 (arom., CBr), 120.2 (arom., CH), 148.3 (arom.), 149.8 (arom.), 152.9 (arom.); MS (70 eV) *m/z* (rel. intensity) 353 ($M^+ + 2$, 100), 351 (M^+, 100), 272 ($M^+ - Br$, 58), 83 [$(CH_2)_5N^+ - 1$, 62]; IR (KBr) 1585 and 1560 cm^{-1}. Found: *m/z* 351.1561 calc. for $C_{19}H_{30}{}^{79}BrN$ 351.1561. **3**: ^{31}P NMR (81 MHz, $CDCl_3$) δ −141.4 (t, $^1J_{PH}$ 214.8 Hz). Found: *m/z* 305.2264 calc. for $C_{19}H_{32}NP$ 305.2272. **4**: Yellow prisms, mp 264–266 °C (decomp.); ^1H NMR δ 1.31 (s, 9H, *p*-Bu^t), 1.57 (s, 9H, *o*-Bu^t), 1.5–2.0 (m, 4H, CH_2), 2.39 (br q, *J* 13 Hz, 2H, CH_2), 3.01 (br q, *J* 13 Hz, 2H, NCH), 4.16 (br d, *J* 13 Hz, 2H, NCH), 6.96 (dd, J_{PH} 2.7, J_{HH} 1.3 Hz, 1H, arom.), 7.49 (dd, J_{PH} 8.2 Hz, J_{HH} 1.3 Hz, 1H, arom.); ^{77}Se NMR (38 MHz, $CDCl_3$, external standard Me_2Se) δ 397.4 (d, $^1J_{PSe}$ 817.9 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 21.4 (CH_2), 22.5 (CH_2), 31.2 ($C\mathit{Me}_3$), 31.7 ($C\mathit{Me}_3$), 35.8 (CMe_3), 36.6 (CMe_3), 55.1 (NCH_2), 112.6 (d, J_{PC} 9.7 Hz, arom., CH), 126.7 (d, J_{PC} 12.5 Hz, arom., CH), 139.2 (d, J_{PC} 65.8 Hz, *ipso*-arom.), 147.4 (d, J_{PC} 3.2 Hz, arom.), 151.6 (d, J_{PC} 3.0 Hz, arom.), 157.3 (d, J_{PC} 2.7 Hz, arom.); UV (CH_2Cl_2) λ_{max} 284 nm (sh, log ε 3.91); IR (KBr) 580 cm^{-1}; MS *m/z* 463 (M^+, 20), 382 ($M^+ - Se - 1$, 22), 303 ($M^+ - 2Se$, 100), 57 (Bu^{t+}, 35). Found: *m/z* 463.0442 calc. for $C_{19}H_{30}NP^{80}Se_2$ 463.0446.

§ *Crystal data* for **4**: Recrystallization from benzene. $C_{19}H_{30}NPSe_2 \cdot C_6H_6$, M_r = 539.46. Monoclinic, space group $P2_1/n$, $a = 15.626(3)$, $b = 14.073(2)$, $c = 11.565(2)$ Å; $\beta = 90.89(1)°$, $V = 2542.8(6)$ Å^3, $Z = 4$, $D_c = 1.409$ g cm^{-3}, $\mu = 29.83$ cm^{-1}, 4687 unique reflections with $2\theta \leqslant 50.0°$ were recorded on a four-circle diffractometer (Mo-Kα radiation, graphite monochromator). Of these, 3179 with $I > 3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86.[9a] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions. $R = 0.051$, $R_w = 0.057$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ The CAChe program is available from CAChe Scientific, Inc.

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