

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

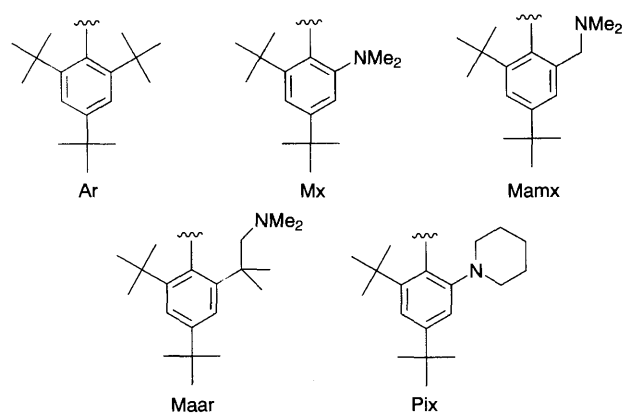
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The 2,4-di-*tert*-butyl-6-(1-piperidino)phenyl group is utilized to stabilize diselenoxophosphorane and the structure determined by X-ray analysis indicates coordination of the nitrogen lone-pair to the P-atom to form a four-membered ring with a remarkably 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<sup>1</sup> and dithioxophosphoranes.<sup>2,3</sup>

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),<sup>4</sup> the 2,4-di-*tert*-butyl-6-(dimethylaminomethyl)phenyl group (Mamx)<sup>5</sup> and the 2,4-di-*tert*-butyl-6-[1,1-dimethyl-2-(dimethylamino)ethyl]phenyl group (Maar),<sup>6</sup> having an electron-donating part within their moieties.



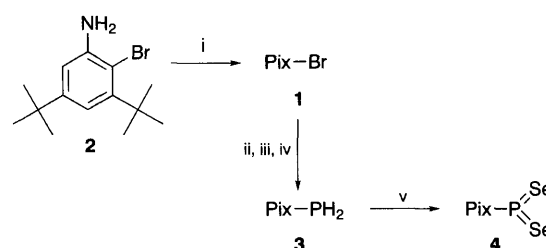
Using these substituents, dithioxophosphoranes as well as selenoxo- and thioxo-phosphines were prepared as stable compounds. In these compounds, the phosphorus–chalcogen bonds are stabilized by both steric protection of the *ortho*-*tert*-butyl group and intramolecular coordination of the amino group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

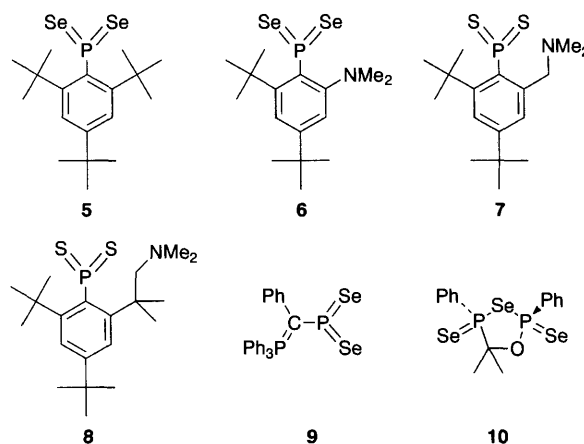
The sterically hindered bromobenzene **1** was prepared from 2-bromo-3,5-di-*tert*-butylaniline **2**<sup>7</sup> and was converted to the corresponding diselenoxophosphorane **4** via an intermediary primary phosphine **3**.<sup>‡</sup> Similarly, diselenoxophosphoranes with the Maar and Mamx groups were prepared, and are expected to form intramolecular six- and five-membered rings upon coordination. <sup>31</sup>P NMR chemical shifts of those compounds together with data for **5**<sup>8</sup> and **6**<sup>4a</sup> are listed in Table 1. Interaction of nitrogen to phosphorus in the diselenoxophosphoranes is clearly shown by <sup>31</sup>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  $\delta_P$

values for **4** and **6** lie between those for **5** and MamxPSe<sub>2</sub> reflecting the efficiency in coordination. This tendency is observed for the corresponding dithioxophosphoranes.<sup>4–6</sup> 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.<sup>5,6</sup>

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



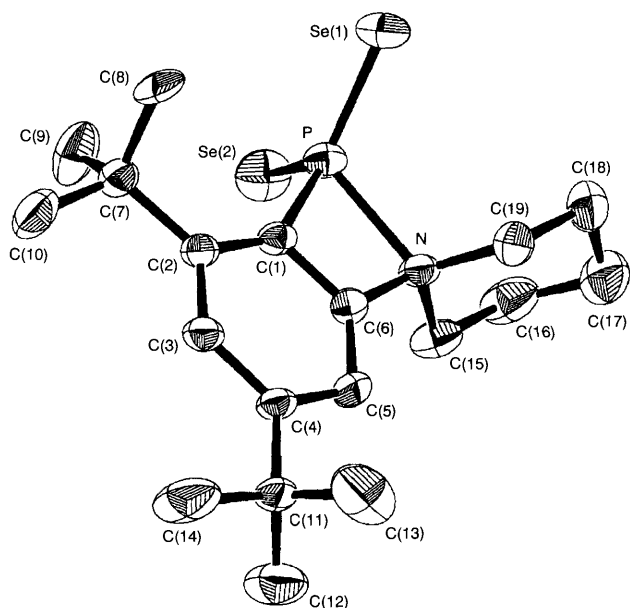
**Scheme 1** Reagents and conditions: i, NaBH<sub>4</sub>–CH<sub>2</sub>(CH<sub>2</sub>CHO)<sub>2</sub>, 73%; ii, Bu<sup>n</sup>Li (1.2 equiv.), Et<sub>2</sub>O, 0 °C; iii, PCl<sub>3</sub> (4.0 equiv.), Et<sub>2</sub>O, –78 °C; iv, LiAlH<sub>4</sub> (3.0 equiv.), Et<sub>2</sub>O; v, Se (4.0 equiv.), 1,8-diazabicyclo[5.4.0]undec-7-ene (*ca.* 1 equiv.), C<sub>6</sub>H<sub>6</sub>, 25 °C, 20 h, 38% from **1**



**Table 1** <sup>31</sup>P NMR data for some diselenoxophosphoranes (81 MHz, CDCl<sub>3</sub>)

Diselenoxophosphorane	$\delta_P$	<sup>1</sup> J <sub>PSe</sub> /Hz
PixPSe <sub>2</sub> <b>4</b>	147.7	813.0
MxPSe <sub>2</sub> <b>6</b> <sup>a</sup>	149.6	819.6
MamxPSe <sub>2</sub>	123.6	789.8
MaarPSe <sub>2</sub>	108.7	769.0
ArPSe <sub>2</sub> <b>5</b> <sup>b</sup>	273.0	854.5

<sup>a</sup> Data taken from ref. 4(a). <sup>b</sup> 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]<sup>10</sup> or **10** [2.081(2) and 2.091(2) Å],<sup>11</sup> but much shorter than the P–Se single bond in **10** [2.258(1) Å].<sup>11</sup> 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<sup>2</sup> 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<sup>¶</sup> using PM3 SCF-MO method<sup>12</sup> for MxPSe<sub>2</sub> **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.<sup>13</sup>

‡ Selected spectroscopic data: **1**. Colourless crystals, mp 56.0–57.5 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.31 (s, 9H, *p*-Bu<sup>t</sup>), 1.55 (s, 9H, *o*-Bu<sup>t</sup>), 1.73 (br s, 4H, CH<sub>2</sub>), 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.); <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>) δ 24.4 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 30.3 (CMe<sub>3</sub>), 31.4 (CMe<sub>3</sub>), 35.0 (CMe<sub>3</sub>), 37.6 (CMe<sub>3</sub>), 54.3 (NCH<sub>2</sub>), 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<sup>+</sup> + 2, 100), 351 (M<sup>+</sup>, 100), 272 (M<sup>+</sup> – Br, 58), 83 [(CH<sub>2</sub>)<sub>5</sub>N<sup>+</sup> – 1, 62]; IR (KBr) 1585 and 1560 cm<sup>-1</sup>. Found: *m/z* 351.1561 calc. for C<sub>19</sub>H<sub>30</sub><sup>79</sup>BrN 351.1561. **3**: <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>) δ –141.4 (t, *J*<sub>PH</sub> 214.8 Hz). Found: *m/z* 305.2264 calc. for C<sub>19</sub>H<sub>32</sub>NP 305.2272. **4**: Yellow prisms, mp 264–266 °C (decomp.); <sup>1</sup>H NMR δ 1.31 (s, 9H, *p*-Bu<sup>t</sup>), 1.57 (s, 9H, *o*-Bu<sup>t</sup>), 1.5–2.0 (m, 4H, CH<sub>2</sub>), 2.39 (br q, *J* 13 Hz, 2H, CH<sub>2</sub>), 3.01 (br q, *J* 13 Hz, 2H, NCH), 4.16 (br d, *J* 13 Hz, 2H, NCH), 6.96 (dd, *J*<sub>PH</sub> 2.7, *J*<sub>HH</sub> 1.3 Hz, 1H, arom.), 7.49 (dd, *J*<sub>PH</sub> 8.2 Hz, *J*<sub>HH</sub> 1.3 Hz, 1H, arom.); <sup>77</sup>Se NMR (38 MHz, CDCl<sub>3</sub>, external standard Me<sub>2</sub>Se) δ 397.4 (d, *J*<sub>PSe</sub> 817.9 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>) δ 21.4 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>), 31.2 (CMe<sub>3</sub>), 31.7 (CMe<sub>3</sub>), 35.8 (CMe<sub>3</sub>), 36.6 (CMe<sub>3</sub>), 55.1 (NCH<sub>2</sub>), 112.6 (d, *J*<sub>PC</sub> 9.7 Hz, arom., CH), 126.7 (d, *J*<sub>PC</sub> 12.5 Hz, arom., CH), 139.2 (d, *J*<sub>PC</sub> 65.8 Hz, *ipso*-arom.), 147.4 (d, *J*<sub>PC</sub> 3.2 Hz, arom.), 151.6 (d, *J*<sub>PC</sub> 3.0 Hz, arom.), 157.3 (d, *J*<sub>PC</sub> 2.7 Hz, arom.); UV (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> 284 nm (sh, log ε 3.91); IR (KBr) 580 cm<sup>-1</sup>; MS *m/z* 463 (M<sup>+</sup>, 20), 382 (M<sup>+</sup> – Se – 1, 22), 303 (M<sup>+</sup> – 2Se, 100), 57 (Bu<sup>t+</sup>, 35). Found: *m/z* 463.0444 calc. for C<sub>19</sub>H<sub>30</sub>NPSe<sub>2</sub> 463.0446.

§ Crystal data for **4**: Recrystallization from benzene. C<sub>19</sub>H<sub>30</sub>NPSe<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>, *M<sub>r</sub>* = 539.46. Monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 15.626(3), *b* = 14.073(2), *c* = 11.565(2) Å; β = 90.89(1)°, *V* = 2542.8(6) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.409 g cm<sup>-3</sup>, μ = 29.83 cm<sup>-1</sup>, 4687 unique reflections with 2θ ≤ 50.0° were recorded on a four-circle diffractometer (Mo-Kα radiation, graphite monochromator). Of these, 3179 with *I* > 3σ(*I*) were judged as observed. The structure was solved with SHELXS86.<sup>9a</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions. *R* = 0.051, *R<sub>w</sub>* = 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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