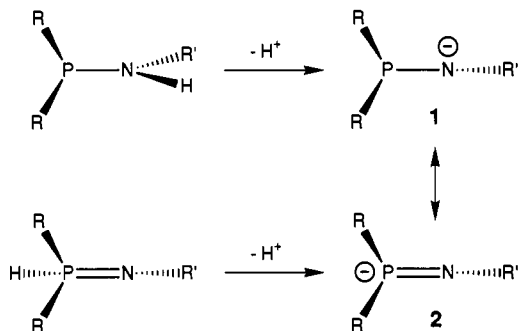


**Synthesis and Molecular Structure of an Iminophosphide/Phosphinoamide Anion: [Li(PhN=PPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>]**

"The P-N bond is one of the most intriguing in chemistry and many of its more subtle aspects still elude a detailed and satisfactory description."<sup>1</sup> Of particular interest are phosphazenes (R<sub>2</sub>P<sup>III</sup>NR', R<sub>4</sub>P<sup>V</sup>NR'<sub>2</sub>) and phosphazenes (RP<sup>III</sup>=NR', R<sub>3</sub>P<sup>V</sup>=NR') and their cyclic analogues.<sup>2</sup> Phosphazenes, because they possess formal P-N double bonds, exhibit comparatively short P-N bond lengths.<sup>3</sup> However, phosphazenes also typically exhibit unexpectedly short P-N bond lengths as well as trigonal planar geometry about their nitrogen atoms.<sup>4</sup> If a phosph(III)azene of the type R<sub>2</sub>RNHR' or a phosph(V)azene of the type R<sub>2</sub>HP=NR' were deprotonated, the resulting anion could in principle be described as a phosphinoamide (1) or an iminophosphide (2).



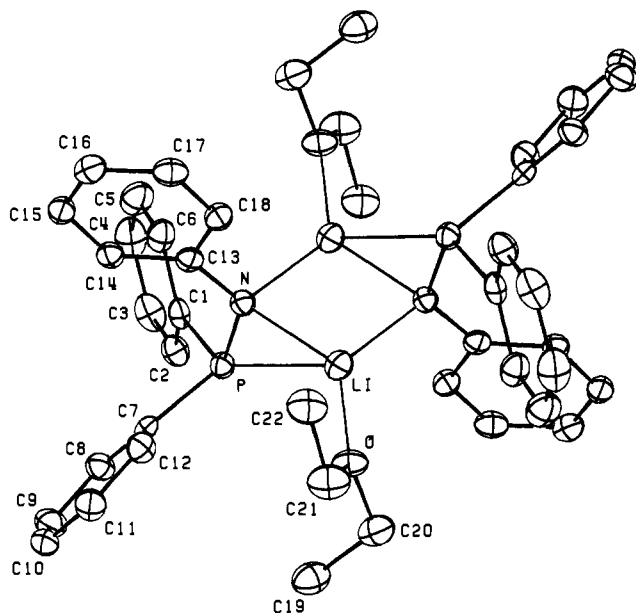
Resonance form 1 yields phosphorus(III) and a formal negative charge on the nitrogen atom, whereas resonance form 2 also yields phosphorus(III), but the formal negative charge is located on the phosphorus atom. Form 1 would be expected to prevail if electronegativity is the dominant factor; however, form 2 would result in additional stabilization as a result of resonance delocalization of the charge and P-N multiple bonding. Form 2 is possible only if phosphorus is capable of expanding its octet. The classical explanation of the way phosphorus violates the octet rule involves phosphorus d orbitals.<sup>5</sup> However, other P-N multiple-bonding schemes have been proposed that do not make use of P d $\pi$  orbitals.<sup>6</sup>

We have synthesized the iminophosphide/phosphinoamide ion Ph<sub>2</sub>PNPh<sup>-</sup> from the corresponding phosphazene Ph<sub>2</sub>PNHPh by treatment with *n*-butyllithium in several ether solvents. When diethyl ether was used as a solvent, well-formed crystals of [Li(PhNPPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>] precipitated.<sup>7</sup> The crystals are air- and

water-sensitive, and they readily lose their solvent of crystallization. Therefore, particular care was required to mount them for a single-crystal X-ray crystallography study.<sup>8</sup> The solid-state structure of the Li(PhNPPh<sub>2</sub>) moiety consists of a centrosymmetric dimer, loosely held together by ion-dipole bonds that are typical of lithium salts (Figure 1).<sup>9</sup> The lithium cations are ligated by both of the heteroatoms of the PhNPPh<sub>2</sub><sup>-</sup> anion. The nitrogen atom bridges both lithium atoms; the observed Li-N distances (2.02 Å) are typical of those found in lithium-amide complexes.<sup>10</sup> In contrast, each phosphorus atom contacts only one lithium atom. Although the Li-N distances are all approximately the same in the molecule, the distance and angle data listed in the caption for Figure 1 demonstrate that the Li<sub>2</sub>N<sub>2</sub>P<sub>2</sub> core of [Li(PhNPPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>] does not have C<sub>s</sub> symmetry. The Li-P and Li'-P distances are 2.684 (4) and 3.004 (4) Å, respectively. The difference between the two Li-P distances is not great; however, the shorter distance is comparable to known Li-P distances.<sup>11</sup> Also, the phosphorus lone pair is clearly oriented toward the lithium ion that exhibits the shorter Li-P distance. These facts suggest that

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- (7) All operations were performed under an atmosphere of purified argon. Diethyl ether was dried over Na/K alloy. To a solution of Ph<sub>2</sub>PNHPh (0.94 g, 3.4 mmol) in ether (15 mL) at -78 °C under argon was added dropwise a hexane solution of *n*-butyllithium (1.36 mL, 2.5 M). After 30 min, the solution was warmed to 0 °C and stirred for 1 h. Voluminous amounts of an off-white precipitate formed, which was presumably [Li(PhNPPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (this solid could be used to resaturate diethyl ether solutions, from which additional crystals of [Li(PhNPPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> could be grown; vide infra). The yellow solution was separated from the solid by transfer to a second flask using a filter cannula. Large pale yellow crystals of [Li(PhNPPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> formed from the diethyl ether solution on standing overnight. The crystals were stored in the solution until they were used in the X-ray study. The high reactivity of [Li(PhNPPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> has so far precluded chemical analysis or estimation of a chemical yield. A direct comparison of the solid-state structure of [Li(PhNPPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> and its structure in diethyl ether solution using NMR methods has proven difficult because [Li(PhNPPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> is virtually insoluble in diethyl ether. However, [Li(PhNPPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> is somewhat more soluble in tetrahydrofuran. <sup>7</sup>Li (external LiBr (D<sub>2</sub>O, 20 °C) δ 0 ppm) and <sup>31</sup>P (external H<sub>3</sub>PO<sub>4</sub> (D<sub>2</sub>O, 20 °C) δ 0 ppm) NMR spectra were recorded in tetrahydrofuran containing 5% benzene-*d*<sub>6</sub> (to lock the instrument) with a Varian XL-300 NMR spectrometer: <sup>7</sup>Li (C<sub>4</sub>H<sub>8</sub>O + 5% C<sub>6</sub>D<sub>6</sub>, 20 °C) δ -2.78 (s) ppm; <sup>7</sup>Li (C<sub>4</sub>H<sub>8</sub>O + 5% C<sub>6</sub>D<sub>6</sub>, -80 °C) δ -2.66 (br) ppm; <sup>31</sup>P (C<sub>4</sub>H<sub>8</sub>O + 5% C<sub>6</sub>D<sub>6</sub>, 20 °C) δ 33.24 (s) ppm; <sup>31</sup>P (C<sub>4</sub>H<sub>8</sub>O + 5% C<sub>6</sub>D<sub>6</sub>, -80 °C) δ 41.69 (s, 50%), 22.49 (s, 50%) ppm. Our failure to observe <sup>7</sup>Li-<sup>31</sup>P coupling suggests there is no strong Li-P interaction in tetrahydrofuran solution. The splitting of the singlet in the <sup>31</sup>P spectrum upon cooling the sample indicates a dynamic process is being frozen out. The dynamic process may be hindered rotation about the P-N bond. Preliminary molecular orbital calculations suggest that the HNPh<sub>2</sub><sup>-</sup> anion exhibits two low-energy conformations of approximately equal total energies. The latter studies will be discussed in more detail in a full paper.
- (8) After growth of the crystals, the ether solvent was removed by cannula and quickly replaced with a low-volatility hydrocarbon oil. Individual crystals were mounted on glass fibers with high-vacuum grease; then they were transferred to the diffractometer, which had been cooled to -110 °C. Only a few attempts were necessary to successfully mount a crystal that proved to be suitable for collecting the X-ray diffraction data. [Li(PhN=PPh<sub>2</sub>)(OEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> crystallizes in the monoclinic space group P2<sub>1</sub>/c with Z = 2, a = 10.076 (3) Å, b = 20.068 (4) Å, c = 10.367 (4) Å, β = 109.66 (3)°, and V = 1974.0 (12) Å<sup>3</sup> at -110 °C. A total of 3773 unique reflections were measured with graphite-monochromated Mo K $\alpha$  radiation on an Enraf-Nonius diffractometer using methods standard in this laboratory. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied, since it was judged to be negligible. After refinement of the non-hydrogen atoms, all of the hydrogen atoms were located in the first difference map. The positional and isotropic thermal parameters of all of the hydrogen atoms were refined. Full-matrix least-squares refinement with 2395 observed reflections ( $|F_o| \geq 3\sigma(F_o)$ ) and 335 variables converged to give R = 0.033, R<sub>w</sub> = 0.038, GOF = 1.14, and final residual = 0.23 e Å<sup>-3</sup>. A full report of the structure determination will be published at a later date.
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**Figure 1.** ORTEP drawing of  $[\text{Li}(\text{PhNPPPh}_2)(\text{OEt}_2)_2]$ . Atoms are represented by thermal vibration ellipsoids at the 50% level, and the labeling scheme is defined (primed labels refer to atoms that are related by a crystallographically imposed inversion center). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): P-C1, 1.843 (2); P-C7, 1.845 (2); P-Li, 2.684 (3); P-Li', 3.004 (4); P-N, 1.672 (2); N-C13, 1.414 (14); N-Li, 2.023 (4); N-Li', 2.024 (4); Li-O, 1.898 (4); Li-Li', 2.478 (2); C1-P-C7, 103.53 (9); C1-P-N, 110.04 (9); C1-P-Li, 144.2 (1); C7-P-Li, 110.6 (1); C7-P-N, 108.9 (1); Li-P-N, 48.8 (1); P-N-C13, 126.7 (1); P-N-Li, 92.7 (1); P-N-Li', 108.4 (1); Li-N-Li', 75.5 (2); N-Li-N', 104.5 (2); N-Li-O, 130.8 (2); N-Li'-O', 124.8 (2).

the Li-P dipole interaction is real, but probably is not very strong. The lithium ions are also ligated by one diethyl ether molecule each: Li-O = 1.90 Å.

Of particular interest with respect to the electronic structure of  $\text{Ph}_2\text{PNPh}^-$  is the relatively short P-N distance observed in  $[\text{Li}(\text{PhNPPPh}_2)(\text{OEt}_2)_2]$  (1.672 (2) Å), which suggests partial P-N multiple-bonding character.<sup>12</sup> A direct comparison of the P-N bond length found for  $[\text{Li}(\text{PhNPPPh}_2)(\text{OEt}_2)_2]$  to related bond lengths found in phosphazanes and phosphazenes is complicated by the apparent sensitivity of P-N bond lengths to substituent effects. Furthermore, there will likely be some influence of the

Li-N and Li-P dipolar interactions on the P-N bond length. Nonetheless, it can be said that the P-N distance observed in  $[\text{Li}(\text{PhNPPPh}_2)(\text{OEt}_2)_2]$  falls somewhere between the expected P-N single- and double-bond lengths.<sup>13</sup> Thus the  $\text{PhNPPPh}_2^-$  ion may be viewed as a resonance hybrid iminophosphide/phosphinoamide ion. To our knowledge, this represents the first such compound to be isolated and characterized by X-ray crystallography. The solid-state structure of  $[\text{Li}(\text{THF})(\text{cyclenphosphoranide})_x]$ , a related phosphorus(V) species, has been characterized by X-ray crystallography.<sup>14</sup> The observed Li-P, Li-N, and Li-O distances in both complexes are remarkably similar.<sup>15</sup> However, whereas the nitrogen and phosphorus atoms of  $[\text{Li}(\text{PhNPPPh}_2)(\text{OEt}_2)_2]$  bind to two lithium atoms and one lithium atom, respectively, the nitrogen and phosphorus atoms of  $[\text{Li}(\text{THF})(\text{cyclenphosphoranide})_x]$  bind to one and two lithium atoms, respectively.

In conclusion, we note that iminophosphide anions are related to the conjugate bases of secondary phosphine chalcogenides ( $[\text{R}_2\text{P}^-\text{X}]^-$ ; X = O, S, Se). The latter species have proven to be popular ligands in part because they exhibit unusual modes of coordination.<sup>16</sup> We are currently exploring the reaction chemistry of iminophosphides, including their coordination chemistry.

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**Supplementary Material Available:** Tables of atomic coordinates of the non-hydrogen atoms and the hydrogen atoms and anisotropic thermal parameters of the non-hydrogen atoms (3 pages); a listing of observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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