Radicals

# Stable Cubic Phosphorus-Containing Radicals[**]

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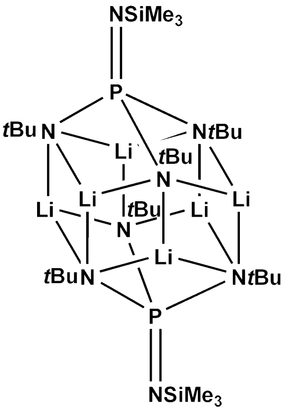
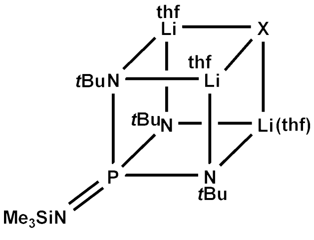
The study of radicals of the heavier main-group elements is an area of significant current interest.[1] Many of the so-called stable radicals[2] are obtained as charged species, that is, ionic radicals. Examples of stable neutral radicals are less common, but several have been structurally characterized recently in the solid state by X-ray crystallography, for example, $CB_{11}Me_{12}^{\bullet}$,[3] $[M(dbdab)_2]$ ($M = Al$, Ga; dbdab = 1,4-di-*tert*-butyl-1,4-diazabutadiene),[4] $[R_2MMR]^{\bullet}$ ($M = Ga$, Al; $R = Si\mathit{t}Bu_3$),[5–7] $R_3SiSi(\mathit{t}Bu)_2^{\bullet}$ [$R = SiMe(\mathit{t}Bu)_2$],[8] $[R_3E]^{\bullet}$ ($E = Si$, Ge; $R = SiMe(\mathit{t}Bu)_2$),[9] and $[Ge(C_6H_3Mes_2\text{-}2,6)]^{\bullet}$ ($Mes = 2,4,6\text{-}(CH_3)_3C_6H_2$).[10] The structure of the phosphorus-centered radical $:P[CH(SiMe_3)_2]_2^{\bullet}$ has been determined in the gas phase by electron diffraction.[11] The diphosphanyl radical $[Mes^*(Me)PPMes^*]^{\bullet}$ ($Mes^* = 2,4,6\text{-}\mathit{t}Bu_3C_6H_2$) has been stabilized by doping into single crystals of $Mes^*(Me)PP(Me)Mes^*$.[12]

An intriguing feature of the chemistry of the lithium derivatives of polyimido anions of p-block elements [13] is the formation of deeply colored persistent radicals[2] upon oxidation of the chalcogen-centered clusters $[\{Li_2[E(N\mathit{t}Bu)_3]\}_2]$ ($E = S$, Se).[14] The solution EPR spectra of these radicals consist of a septet of dectets, which is attributed to coupling of the unpaired electron with three equivalent $^{14}N$ nuclei ($I = 1$, $a \approx 5.5$ G) and three equivalent $^{7}Li$ nuclei ($I = 3/2$, $a \approx 0.8$ G).[15,16] Their solid-state structures have not been determined.

The first tetrakisimidophosphate was obtained as the solvent-separated ion pair $[Li(thf)_4][(thf)_2Li(\mu\text{-}Nnaph)_2P(\mu\text{-}Nnaph)_2Li(thf)_2]$ (naph = 1-naphthyl) by Wright and coworkers in 1997.[17] However, no reactions of this important member of the family of p-block polyimido anions have been reported. Our recent discovery of a simple and versatile route to tetrakisimidophosphates, for example, $[\{Li_3[P(N\mathit{t}Bu)_3(NSiMe_3)]\}_2]$ (**1**),[18] has facilitated investigations of the chemistry of these isoelectronic analogues of the orthophosphate $PO_4^{3-}$ ion. We describe here the synthesis of the stable, neutral radicals $[Me_3SiNP(\mu_3\text{-}N\mathit{t}Bu)_3\{\mu_3\text{-}Li(thf)\}_3X]^{\bullet}$ (**2a**, X = Br; **2b**, X = I) obtained by the oxidation of **1** with halogens. The derivative **2b** has been structurally characterized in the solid state by X-ray crystallography. The solution behavior of these novel radical systems has been investigated by EPR and UV/Vis spectroscopies.



**1**



**2a**: X = Br
**2b**: X = I

The reactions of the dimer **1** with one equivalent of bromine or iodine in a mixture of toluene and THF at 295 K produce deep blue solutions immediately. Removal of the solvents gives **2a** or **2b**, respectively, as blue powders in good yields. Crystals of **2b** suitable for an X-ray structural determination[19] were grown from a supersaturated syrup in THF at 295 K. The molecular structure and pertinent structural parameters for **2b** are depicted in Figure 1. The crystal was composed of **2b** (75%) cocrystallized with the diamagnetic seco-cube $[\{Me_3SiNP(\mu_3\text{-}N\mathit{t}Bu)_3[\mu_3\text{-}Li(thf)]_3\}]$ (25%), that is, a trisolvated monomeric unit of **1**. The molecule has a highly distorted cubic structure similar to that reported by Stalke et al. for the colorless, diamagnetic sulfur(IV) complex $\{S(\mu_3\text{-}N\mathit{t}Bu)_3[\mu_3\text{-}Li(thf)]_3I\}$, which contains the trisimidosulfite dianion $[S(N\mathit{t}Bu)_3]^{2-}$.[15] The absence of iodine in 25% of the molecules in **2b** leads to a more compact lattice compared to the analogous sulfur(IV) complex,[15] as evidenced by several contacts between iodine and THF hydrogen atoms that are less than the sum of the van der Waals radii. The blue, paramagnetic complex **2b** is comprised of the radical dianion $[P(N\mathit{t}Bu)_3(NSiMe_3)]^{2-\bullet}$ (formed by the one-electron oxidation of the $[P(N\mathit{t}Bu)_3(NSiMe_3)]^{3-}$ trianion in **1**), two $Li^+$ counterions and a molecule of lithium iodide. Each of the three $Li^+$ ions is solvated by one THF molecule. The mean bond lengths in the $PN_3Li_3I$ cube are 1.66 (P–N),

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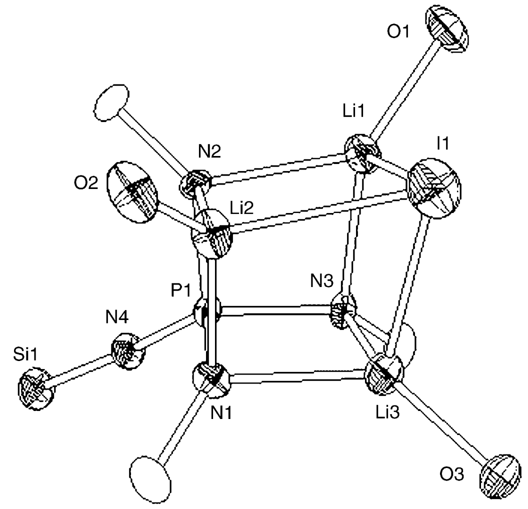


***Figure 1.*** X-ray crystal structure of **2b**. Only the O atoms of THF ligands are shown. Selected bond lengths [Å] and bond angles [°]. Li1-I1 2.704(13), Li2-I1 2.790(13), Li3-I1 2.776(14), P1-N1 1.667(5), P1-N2 1.647(5), P1-N3 1.665(5), P1-N4 1.546(5), Li1-N2 2.046(13), Li1-N3 2.093(14), Li2-N1 2,090(14), Li2-N2 2.071(14), Li3-N1 2.086(13), Li3-N3 2.089(13), Si1-N4 1.650(5); P1-N4-Si1 176.0(4).

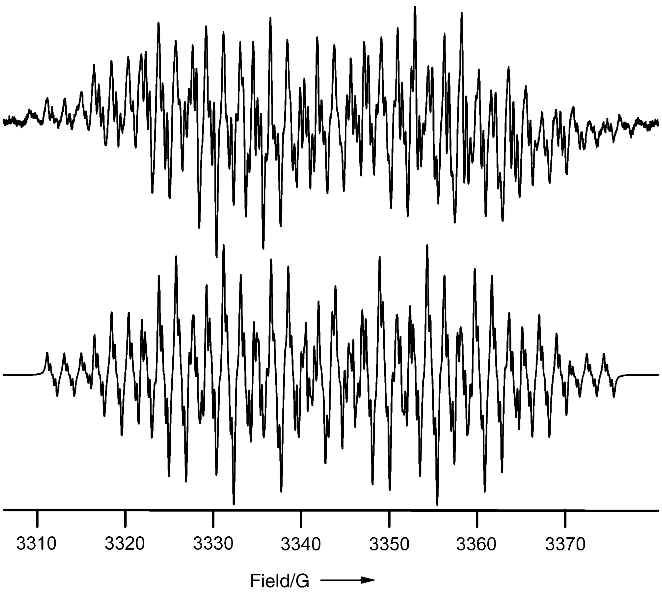
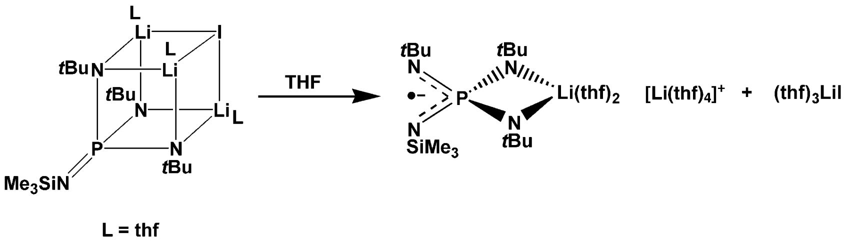


***Figure 2.*** Experimental (top) and simulated (bottom) EPR spectra of a very dilute THF solution of **2b** under vacuum at 295 K.

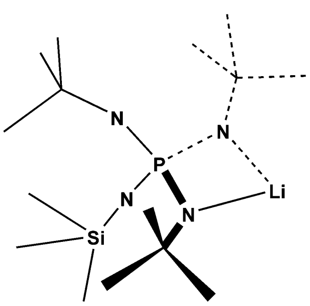


***Scheme 1.*** Solvation of lithium ions in **2b** in very dilute THF solutions.

2.08 (Li–N), and 2.75 Å (Li–I). The Li–I bond length is ≈0.19 Å shorter than the corresponding bond in the analogous sulfur(IV) complex.[15] The exocyclic P–N bond length is 1.542(4) Å, and the P-N-Si arrangement in **2b** is almost linear (176.5°), as was found for **1**.[18]

The radicals **2a** and **2b** dissolve in THF to give intensely blue solutions that persist for several weeks at room temperature. In other solvents, for example hexane, the blue color disappears rapidly. Finely powdered **2b** was dissolved in THF in a T-shaped tube sealed under vacuum, and EPR spectra were recorded as functions of temperature and concentration. A similar study was performed for **2a** and both compounds were found to exhibit similar behavior. Complex spectra with many hyperfine lines that were strongly dependent on both concentration and temperature were obtained. Under high dilution ($<10^{-4}$ M) at 295 K, the spectrum of **2b** stabilized to a limiting pattern (Figure 2). This spectrum could be reasonably well simulated as a monolithium species with the following hyperfine coupling (hfc) values (G): $a_N = 1.93$ to one $^{14}N$, $a_N = 5.38$ to two equivalent $^{14}N$, $a_N = 7.38$ to one $^{14}N$, $a_P = 23.1$ to one $^{31}P$, and $a_{Li} = 0.30$ to one $^{7}Li$ nucleus. We propose that upon dissolution in THF, the cubic cage structure of **2b** is ruptured with the release of solvated lithium iodide and the formation of a solvent-separated ion pair $[Li(thf)_4][(Me_3SiN)(t\mathrm{Bu}N)P(\mu\text{-}Nt\mathrm{Bu})_2Li(thf)_2]$ (**3**) (Scheme 1).

Confirmation of the dissociation of the cube was provided by the isolation of the by-product $(thf)_3LiI$, which was identified by determination of the unit-cell parameters.[20] We have probed possible structures for the radical monoanion in **3** by using AM1 calculations on the corresponding dianion. A reasonable geometry was obtained with $\Delta H_f = -200\ \mathrm{kJ\,mol^{-1}}$ in the gas phase for the monocyclic structure **3'**, in which two *t*BuN groups chelate the single Li$^+$ ion, while the third (noncoordinated) *t*BuN group carries the greater portion of the unpaired spin density. The local $C_s$ symmetry of this cyclic structure is consistent with the EPR spectra of extremely dilute solutions of **2b** described above.[21]The transformation depicted in Scheme 1 implies that the breakdown of the cubic structures of **2a** and **2b** in THF solution will lead to the formation of the same radical species. Indeed, the EPR spectrum of **2a** in very dilute THF solution shows



**3'**

similar features to that of **2b**, and the *g* values are 2.00638 (**2a**) and 2.00632 (**2b**). In addition, the UV/Vis spectra of **2a** and **2b** in THF are essentially identical with broad absorption maxima at ≈640 nm. At higher concentrations, the room-temperature EPR spectra are very complex, but contain components with considerably higher symmetry. At lower temperatures the spectra are simpler, and the EPR spectrum of a solution of **2a** ($\approx 10^{-2}$ M) recorded in a THF gel at 173 K (Figure 3) fits well to a simulation with the following hfc values (G): $a_N = 5.36$ to three equivalent $^{14}N$ and $a_P = 26.0$ to one $^{31}P$ nucleus. This spectrum is consistent with the structure of **2b** (local $C_3$ symmetry) if the hfc to the three Li-bonded nitrogen atoms is significantly larger than that to the unique nitrogen atom that is bonded to the silicon center. Alternative structures containing two (or even one) $Li^+$ ion can be envisaged, but line broadening obscures potentially informative smaller hfcs. EPR spectra of solid **2a** and **2b** are featureless singlets with no detectable hfc.

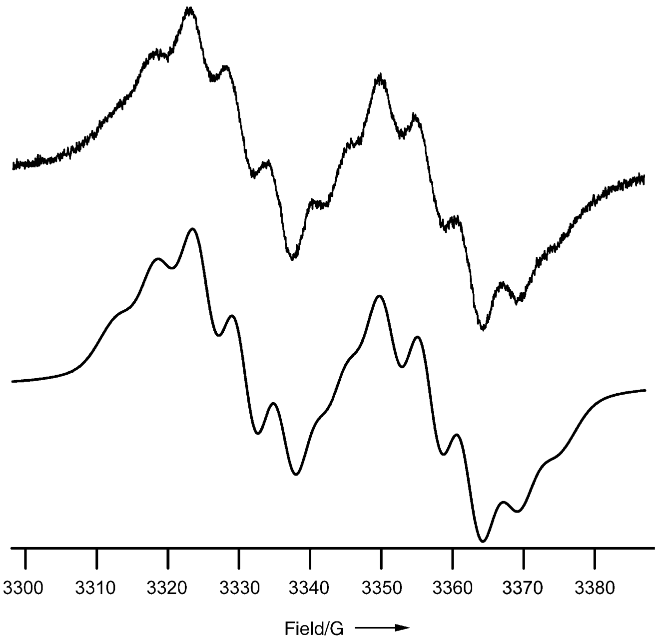


***Figure 3.*** Experimental (top) and simulated (bottom) EPR spectra of **2b** in a THF gel at 173 K.

Surprisingly, the NMR spectra of concentrated, deep-blue solutions of **2a** and **2b** in [D$_8$]THF at room temperature exhibit narrow resonances with normal chemical shifts. The $^1$H, $^7$Li, and $^{31}$P chemical shifts are essentially identical for **2a** and **2b** and only very minor changes in the shifts are observed over the concentration range 0.05–0.16 M. The $^1$H NMR spectra show two resonances for the *t*BuN groups with relative intensities of 2:1, in addition to the resonance for the SiMe$_3$ group. These observations indicate the formation of a diamagnetic species with local $C_s$ or $C_2$ symmetry, presumably by dimerization of the radical monoanion in **3** at these concentrations. Apparently the presence of the radical monoanions in these solutions (deep-blue color) does not have a significant effect on the NMR spectra of the diamagnetic species.

The discovery of the radical dianion $[P(NtBu)_3(NSiMe_3)]^{2-\bullet}$ provides a cogent example of the different behavior of polyimido anions of the p-block elements compared to that of the isoelectronic oxo anions.[22] This radical dianion is stabilized in a distorted cubic framework by two lithium counterions and a molecule of lithium halide. The stability of these deep-blue, neutral radicals is attributed to a combination of electron delocalization over the nitrogen centers within the cube and the steric protection provided by the three N*t*Bu and one NSiMe$_3$ groups. In THF solution, solvation of the lithium centers results in the disruption of the cube with the release of an LiX (X = Br, I) molecule and the formation of $[(Me_3SiN)(tBuN)P(\mu\text{-}NtBu)_2Li(thf)_2]^{-\bullet}$, a monolithium derivative of the radical dianion.

## *Experimental Section*

All reactions and the manipulations of products were carried out under anaerobic and anhydrous conditions using Schlenk techniques and an inert-atmosphere (argon) glove box. EPR spectra were recorded on a Bruker EMX 113 spectrometer equipped with a variable-temperature accessory. A pure Lorentzian line shape and a line width of 0.23 G were employed in the simulation shown in Figure 2 using WINEPR SimFonia, v. 1.25, Bruker Analytische Messtechnik GmbH. A Lorentzian (60%)/Gaussian (40%) line shape and a line width of 5.5 G were used for the simulation shown in Figure 3.

**2a:** A solution of Br$_2$ in toluene (3.7 mL, 0.113 M, 0.419 mmol) was added to a colorless solution of $[\{Li_3[P(NtBu)_3(NSiMe_3)]\}_2]$ (0.295 g, 0.419 mmol) in toluene/THF (5 mL/1 mL) at 295 K, resulting in a deep-blue solution. After 5 min, the solvents were removed via dynamic vacuum to leave **2a** as a bright-blue powder (0.387 g, 0.594 mmol, 71%). UV/Vis (THF): $\lambda_{max}$ 638 nm (br); $^1$H NMR ([D$_8$]THF): $\delta = 1.26$ (s, N*t*Bu, 18H), 1.18 (s, N*t*Bu, 9H), −0.05 ppm (s, SiMe$_3$, 9H); $^7$Li NMR ([D$_8$]THF): $\delta = 0.74$ ppm (s); $^{31}$P{$^1$H} NMR ([D$_8$]thf): $\delta = 6.37$ ppm (s).

**2b:** A solution of I$_2$ in toluene (4.80 mL, 0.071 mmol, 0.342 mmol) was added to a colorless solution of $\{Li_3[P(NtBu)_3(NSiMe_3)]\}_2$ (0.239 g, 0.339 mmol) in toluene/THF (5 mL/0.5 mL) at 295 K, resulting in a deep-blue solution. After 10 min, solvents were removed via dynamic vacuum to leave **2b** as a bright-blue powder (0.339 g, 0.488 mmol, 72%). Elemental analysis calcd (%) for $C_{27}H_{60}ILi_3N_4O_3PSi$: C 46.62, H 8.69, N 8.06; found: C 44.21, H 8.96, N, 8.57; UV/Vis (THF): $\lambda_{max}$ 640 nm (br); $^1$H NMR ([D$_8$]THF): $\delta =$ 1.24 (s, N*t*Bu, 18H), 1.16 (s, N*t*Bu, 9H), −0.06 ppm (s, SiMe$_3$, 9H); $^7$Li NMR ([D$_8$]THF): $\delta = 0.75$ ppm (s); $^{31}$P NMR ([D$_8$]THF): $\delta =$ 6.55 ppm (s). X-ray quality crystals of **2b** were obtained from an extremely concentrated THF solution at 295 K.

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