Inorg. Chem. **2004**, *43*, 3453–3460

Inorganic Chemistry
Article

Lithiation of $(^tBuNH)_3PNSiMe_3$ and Formation of Tetraimidophosphate Complexes Containing M_3O_3 Rings (M = Li, K): X-ray Structure of the Stable Radical $\{(Me_3SiN)P(\mu_3\text{-}N^tBu)_3[\mu_3\text{-}Li(THF)]_3(O^tBu)\}$

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Received November 28, 2003

The reaction of $(^tBuNH)_3PNSiMe_3$ (**1**) with 1 equiv of ^nBuLi results in the formation of $Li[P(NH^tBu)_2(N^tBu)(NSiMe_3)]$ (**2**); treatment of **2** with a second equivalent of ^nBuLi produces the dilithium salt $Li_2[P(NH^tBu)(N^tBu)_2(NSiMe_3)]$ (**3**). Similarly, the reaction of **1** and ^nBuLi in a 1:3 stoichiometry produces the trilithiated species $Li_3[P(N^tBu)_3(NSiMe_3)]$ (**4**). These three complexes represent imido analogues of dihydrogen phosphate $[H_2PO_4]^-$, hydrogen phosphate $[HPO_4]^{2-}$, and orthophosphate $[PO_4]^{3-}$, respectively. Reaction of **4** with alkali metal alkoxides MOR (M = Li, R = $SiMe_3$; M = K, R = ^tBu) generates the imido-alkoxy complexes $\{Li_3[P(N^tBu)_3(NSiMe_3)](MOR)_3\}$ (**8**, M = Li; **9**, M = K). These compounds were characterized by multinuclear (^1H, ^7Li, ^{13}C, and ^{31}P) NMR spectroscopy and, in the cases of **2**, **8**, and **9**·3THF, by X-ray crystallography. In the solid state, **2** exists as a dimer with Li–N contacts serving to link the two $Li[P(NH^tBu)_2(N^tBu)(NSiMe_3)]$ units. The monomeric compounds **8** and **9**·3THF consist of a rare M_3O_3 ring coordinated to the $(LiN)_3$ unit of **4**. The unexpected formation of the stable radical $\{(Me_3SiN)P(\mu_3\text{-}N^tBu)_3[\mu_3\text{-}Li(THF)]_3(O^tBu)\}$ (**10**) is also reported. X-ray crystallography indicated that **10** has a distorted cubic structure consisting of the radical dianion $[P(N^tBu)_3(NSiMe_3)]^{\bullet 2-}$, two lithium cations, and a molecule of LiO^tBu in the solid state. In dilute THF solution, the cube is disrupted to give the radical monoanion $[(Me_3SiN)(^tBuN)P(\mu\text{-}N^tBu)_2Li(THF)_2]^{\bullet -}$, which was identified by EPR spectroscopy.

Introduction

In recent years, a great deal of research has been carried out involving the preparation and characterization of imido $[NR]^{2-}$ (R = H, alkyl, aryl) analogues of common oxo-anions such as $[CO_3]^{2-}$, $[SO_3]^{2-}$, and $[PO_4]^{3-}$.[1] The imido group is isoelectronic with the oxo $[O]^{2-}$ substituent; replacement of one or more oxo ligands by an imido group generates a new class of p-block polyanions with significantly different chemical and physical properties than those of their parent oxo-anions. Numerous analogues of phosphorus oxo-anions have been prepared,[2] including both homoleptic systems, in which all the oxo substituents have been replaced by imido groups, and heteroleptic compounds, which contain both oxo and imido moieties. Examples of polyimido-anions include trisimidometaphosphate ions $[P(NR)_3]^-$,[3] bisimidophosphinate ions $[R_2P(NR)_2]^{2-}$,[4] and the tetrakisimidophosphate trianion $[P(NNaph)_4]^{3-}$ (Naph = naphthyl).[5] In some cases, the coordination chemistry of these interesting ligands has been studied extensively; for example, the bisimidophosphite anion $\{[P(NR)_2]_2\}^{2-}$ has been coordinated to a variety of main group and d-block metals, including gallium,[6a] indium,[6b] thallium,[6b] antimony,[7] bismuth,[7] titanium,[8] zirconium,[8] and nickel.[9]

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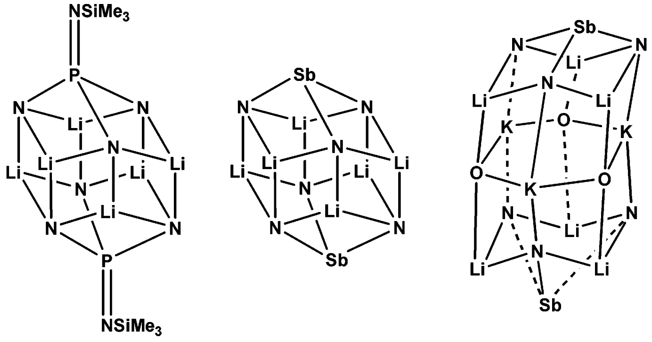
10.1021/ic035377v CCC: $27.50

Though the tetrakisimidophosphate trianion $[\mathrm{P(NNaph)_4}]^{3-}$ has been known for several years,[5] it was only recently that a rational synthesis of such species was reported. In a preliminary communication,[10a] we showed that the reaction of the iminophosphorane $(^t\mathrm{BuNH})_3\mathrm{PNSiMe}_3$ (**1**) with 3 equiv of *n*-butyllithium produces the trilithium salt of the trianion $[\mathrm{P(NR)_3(NR')}]^{3-}$ (R = ^{t}Bu; R′ = $\mathrm{SiMe_3}$) in good yield. In this article, we describe the stepwise lithiation of **1** to form the mono- and dilithiated species, $\mathrm{Li[P(N^tBu)(NH^tBu)_2(NSiMe_3)]}$ (**2**) and $\mathrm{Li_2[P(N^tBu)_2(NH^tBu)(NSiMe_3)]}$ (**3**), which represent the first imido analogues of dihydrogen phosphate $[\mathrm{H_2PO_4}]^-$ and hydrogen phosphate $[\mathrm{HPO_4}]^{2-}$, respectively. The stepwise lithiation of the tetraanilino phosphonium cation $[\mathrm{P(NPh)_4}]^+$ by *n*-butyllithium has been reported recently by Russell and co-workers.[10b]

By analogy with the diverse coordination chemistry that is known for the orthophosphate trianion $[\mathrm{PO_4}]^{3-}$,[11] a rich ligand chemistry can be envisaged for the isoelectronic species $[\mathrm{P(NR)_4}]^{3-}$. However, it is expected that the steric bulk of the imido groups will hinder aggregation, resulting in the formation of much smaller molecules than the extended networks that are characteristic of metal−phosphate complexes. One aspect of the coordination chemistry of the trilithiated tetrakisimidophosphate $\mathrm{Li_3[P(N^tBu)_3(NSiMe_3)]}$ (**4**) is explored in this study.

Previously, we reported that, in the solid state, **4** exists as a centrosymmetric dimer with two $\mathrm{PNSiMe_3}$ groups capping the hexagonal faces of a $\mathrm{Li_6N_6}$ cyclic ladder.[10] Several years ago, Wright and co-workers reported the synthesis of the trisimidostibinite trianion $[\mathrm{Sb(NCy)_3}]^{3-}$ (Cy = cyclohexyl), which is isoelectronic with $[\mathrm{SbO_3}]^{3-}$.[12] In the solid state, the trilithium salt of this anion $\{\mathrm{Li_3[Sb(NCy)_3]}\}_2$ (**5**) exists as a dimer which is isostructural with **4** (Figure 1). Further work in this area showed that when **5** is reacted with potassium *tert*-butoxide, rather than the anticipated transmetalation reaction, a cage expansion occurs, producing $\{\mathrm{Li_3[Sb(NCy)_3)]}\}_2(\mathrm{KO^tBu})_3\cdot\mathrm{C_6H_5CH_3}$ (**6**).[13] This compound consists of a planar six-membered $\mathrm{K_3O_3}$ ring sandwiched between two $\mathrm{Li_3[Sb(NCy)_3]}$ moieties (Figure 1).

As potassium alkoxides commonly exist as dimers, tetramers, hexamers, or polymers,[14] the presence of a trimeric potassium *tert*-butoxide moiety is a rare structural feature. Similarly, lithium alkoxides typically exist in the form $(\mathrm{LiOR})_x$ ($x = 2, 4, 6, 4$),[15,16] and only a handful of complexes are known that contain a six-membered $(\mathrm{LiOR})_3$ ring.[17−20] In such complexes, sterically demanding aryl substituents such as (2,6-diphenyl)(3,5-di-*tert*-butyl)phenyl are employed to prevent the formation of larger oligomers or polymers.[18] In light of the close structural relationship between **4** and **5**, reactions of **4** with alkali metal alkoxides were undertaken in order to determine whether the trilithiated tetrakisimidophosphate trianion is capable of trapping trimeric $(\mathrm{MOR})_3$ rings.



4 **5** **6**

Figure 1. Cluster frameworks of **4**, **5**, and **6**. ^{t}Bu groups on cluster N atoms of **4** and O atoms of **6** are omitted; Cy groups on N atoms of **5** and **6** are omitted.

Experimental Section

Reagents and General Procedures. All experiments were carried out under an argon atmosphere using standard Schlenk techniques. The solvents toluene, tetrahydrofuran (THF), *n*-pentane, and *n*-hexane were dried over Na/benzophenone, distilled, and stored over molecular sieves prior to use. Lithium trimethylsilanolate, potassium *tert*-butoxide (95%), and *n*-butyllithium (2.5 M solution in hexanes) were used as received from Aldrich; $(^t\mathrm{BuNH})_3\mathrm{PNSiMe_3}$ and $\mathrm{Li_3[P(N^tBu)_3(NSiMe_3)]}$ were prepared as described previously.[10]

Instrumentation. ^{1}H NMR spectra were obtained using a Bruker AM-200 spectrometer; chemical shifts are reported relative to $\mathrm{Me_4Si}$ in $\mathrm{CDCl_3}$. ^{7}Li, ^{13}C, and ^{31}P NMR spectra were collected on a Bruker DRX-400 spectrometer with chemical shifts reported relative to 1.0 M LiCl in $\mathrm{D_2O}$, $\mathrm{Me_4Si}$ in $\mathrm{CDCl_3}$, and 85% $\mathrm{H_3PO_4}$ in $\mathrm{D_2O}$, respectively. All spectra were collected at 22 °C. Infrared spectra were recorded as Nujol mulls on KBr plates using a Nicolet Nexus 470 FTIR spectrometer in the range 4000−400 $\mathrm{cm^{-1}}$. EPR spectra were recorded on a Bruker EMX 113 spectrometer; spectral simulations were carried out by using the WINEPR SimFonia

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program provided by Bruker. Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Synthesis of $\{Li[P(N^tBu)(NH^tBu)_2(NSiMe_3)]\}$ (2). A solution of *n*-butyllithium in *n*-hexane (1.2 mL, 2.5 M, 3.0 mmol) was added to a stirred solution of $(^tBuNH)_3PNSiMe_3$ (1.015 g, 3.034 mmol) in hexane (15 mL) at 22 °C, resulting in a cloudy white solution. After 3 h, the solvent was removed in vacuo, leaving a sticky white solid. The product was washed with *n*-hexane (5 mL) to give **2** as a white powder (0.450 g, 1.32 mmol, 44%). X-ray quality crystals were obtained by recrystallization from *n*-pentane at −18°C. ^1H NMR (C_6D_6, δ): 1.90 (br, 2 H, NH), 1.38 (s, 9 H, N^tBu), 1.35 (s, 18 H, NH^tBu), 0.46 (s, 9 H, $SiMe_3$). ^7Li NMR (C_6D_6, δ): 1.62 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 51.68 [d, $NCMe_3$, $^2J(^{13}C-^{31}P) = 16.1$ Hz], 51.20 [d, $NHCMe_3$, $^2J(^{13}C-^{31}P) = 12.6$ Hz], 34.43 [d, $NCMe_3$, $^3J(^{13}C-^{31}P) = 39.4$ Hz], 32.82 [d, $NHCMe_3$, $^3J(^{13}C-^{31}P) = 13.7$ Hz], 6.83 [d, $SiMe_3$, $^3J(^{13}C-^{31}P) = 12.9$ Hz]. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): −0.80 (s). Anal. Calcd for $C_{15}H_{38}LiN_4PSi$: C, 52.91; H, 11.25; N, 16.45. Found: C, 51.27; H, 10.95; N, 15.61.

IR (cm^{-1}): 3284, 3339 (N−H stretch.). Very small amounts of **1** and **3** were evident in the ^1H and ^{31}P NMR spectra of the recrystallized product.

Synthesis of $\{Li_2[P(N^tBu)_2(NH^tBu)(NSiMe_3)]\}$ (3). A solution of *n*-butyllithium in *n*-hexane (1.20 mL, 2.5 M, 3.00 mmol) was added to a stirred cloudy solution of $Li[P(N^tBu)(NH^tBu)_2(NSiMe_3)]$ (1.034 g, 3.04 mmol) in hexane (25 mL) at 22 °C, resulting in a white slurry. After 3 h, the volume of the reaction mixture was reduced to 10 mL, and the white solid was allowed to settle to the bottom of the flask. The supernatant liquid was decanted, and the last traces of solvent were removed via dynamic vacuum, leaving **3** as a white powder (0.971 g, 2.80 mmol, 93%). ^1H NMR (d_8-THF, δ): 1.55 (br, d, 1 H, NH), 1.31 (s, 9 H, NH^tBu), 1.23 (s, 18 H, N^tBu), −0.01 (s, 9 H, $SiMe_3$). ^7Li NMR (C_6D_6, δ): 2.16 (s), 1.65 (s). $^{13}C\{^1H\}$ NMR (d_8-THF δ): 50.98 [d, $NHCMe_3$, $^2J(^{13}C-^{31}P) = 14.9$ Hz], 50.64 [d, $NCMe_3$, $^2J(^{13}C-^{31}P) = 9.2$ Hz], 36.37 [d, $NCMe_3$, $^3J(^{13}C-^{31}P) = 40.7$ Hz], 32.82 [d, $NHCMe_3$, $^3J(^{13}C-^{31}P) = 15.2$ Hz], 6.13 [d, $SiMe_3$, $^3J(^{13}C-^{31}P) = 8.8$ Hz]. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 0.16 (s). Anal. Calcd for $C_{15}H_{37}Li_2N_4PSi$: C, 52.01; H, 10.77; N, 16.17. Found: C, 50.92; H, 10.14; N, 15.97.

IR (cm^{-1}): 3345 (N−H stretch).

Synthesis of $\{Li_3[P(N^tBu)_3(NSiMe_3)](LiOSiMe_3)_3\}$ (8). A solution of *n*-butyllithium in *n*-hexane (1.0 mL, 2.5 M, 2.5 mmol) was added to a cloudy pale yellow solution of $(^tBuNH)_3PNSiMe_3$ (0.293 g, 0.876 mmol) and $LiOSiMe_3$ (0.253 g, 2.632 mmol) in toluene (15 mL) at 22 °C with constant stirring. After 11 h, the solvent was removed via dynamic vacuum, leaving **8** as a yellow powder (0.450 g, 0.701 mmol, 80%). Colorless X-ray quality crystals of **8** were obtained from a solution of the product in *n*-pentane. ^1H NMR (C_6D_6, δ): 1.42 (s, 27 H, ^tBu), 0.70 (s, 9 H, $NSiMe_3$), 0.19 (s, 27 H, $OSiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 52.70 [d, CMe_3, $^2J(^{13}C-^{31}P) = 15.2$ Hz], 34.50 [d, CMe_3, $^3J(^{13}C-^{31}P) = 34.4$ Hz], 5.77 (s, $NSiMe_3$), 3.80 (s, $OSiMe_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 6.92 (s). Anal. Calcd for $C_{24}H_{63}Li_6N_4O_3P_1Si_4$: C, 44.99; H, 9.91; N, 8.74. Found: C, 45.35; H, 10.29; N, 9.04.

Synthesis of $\{Li_3[P(N^tBu)_3(NSiMe_3)](KO^tBu)_3\}\cdot(C_4H_8O)_3$ (9·3THF). A solution of KO^tBu (0.244 g, 2.17 mmol) in toluene/THF (5 mL/1.5 mL) was added to a stirred white slurry of $Li_3[P(N^tBu)_3(NSiMe_3)]$ (0.255 g, 0.723 mmol) in toluene (10 mL) at 22 °C, resulting in a bright orange solution. After 1 h, the volume of the reaction mixture was reduced to 5 mL. Colorless X-ray quality crystals of **9**·3THF (0.450 g, 0.497 mmol, 69%) formed after 48 h at −18°C. ^1H NMR (C_6D_6, δ): 3.53 (m, 12 H, THF), 1.55 (m, 12 H, THF), 1.39 (s, 27 H, O^tBu), 1.24 (s, 27 H, N^tBu), 0.52 (s, 9 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 67.81 (s, THF), 51.82 (s, $OCMe_3$), 50.92 (s, $NCMe_3$), 37.00 (s, $OCMe_3$), 36.59 (s, $NCMe_3$), 25.68 (s, THF), 7.19 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 10.01 (s). Anal. Calcd for $C_{39}H_{87}K_3Li_3N_4O_6PSi$: C, 51.74; H, 9.69; N, 6.19. Found: C, 50.26; H, 9.87; N, 6.47. The low C and high N values appear to result from the partial loss of THF during manipulation of the sample.

Table 1. Crystallographic Data

	2	**8**	**9**·3THF	**10**
formula	$C_{30}H_{76}Li_2N_8P_2Si_2$	$C_{24}H_{63}Li_6N_4O_3PSi_4$	$C_{39}H_{87}K_3Li_3N_4O_6PSi$	$C_{31}H_{69}Li_3N_4O_4PSi$
fw	680.99	640.75	905.31	641.78
space group	$P2_12_12_1$	$R3$	$P\bar{1}$	$P2_1/n$
a, Å	13.4399(3)	16.1620(4)	12.469(2)	15.289(3)
b, Å	15.7195(5)	16.1620(4)	20.744(4)	14.788(3)
c, Å	20.3644(5)	13.7560(4)	20.810(3)	18.542(5)
α, deg	90	90	95.188(11)	90
β, deg	90	90	90.085(10)	107.057(10)
γ, deg	90	120	96.317(12)	90
V, Å^3	4302.4(2)	3111.81(14)	5327.7(15)	4007.8(16)
Z	4	3	4	4
T, K	173(2)	173(2)	173(2)	173(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
d_{calcd}, g cm^{-3}	1.051	1.026	1.129	1.064
μ, mm^{-1}	0.18	0.208	0.35	0.13
$F(000)$	1504	1044	1968	1412
R^a	0.051	0.0463	0.067	0.053
$R_w{}^b$	0.115	0.095	0.110	0.121

[a] $R = [\sum||F_o| - |F_c||]/[\sum|F_o|]$ for reflections with $I > 2.00\sigma(I)$. [b] $R_w = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$ for all reflections.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

P(1)−N(1)	1.564(3)	N(4)−Li(2)	2.017(6)
P(1)−N(4)	1.615(2)	N(4)−Li(1)	2.071(6)
P(2)−N(5)	1.563(3)	N(5)−Li(2)	1.991(6)
P(2)−N(8)	1.622(3)	N(8)−Li(1)	2.030(6)
N(1)−Li(1)	2.004(6)	N(8)−Li(2)	2.053(6)
N(1)−P(1)−N(4)	106.45(14)	P(2)−N(5)−Li(2)	89.9(2)
N(1)−P(1)−Li(1)	52.81(16)	P(2)−N(8)−Li(1)	131.1(2)
N(5)−P(2)−N(8)	105.76(15)	N(1)−Li(1)−N(4)	77.3(2)
P(1)−N(1)−Li(1)	88.7(2)	N(8)−Li(1)−N(4)	108.0(3)
P(1)−N(4)−Li(2)	130.7(2)	N(5)−Li(2)−N(8)	77.8(2)
Li(2)−N(4)−Li(1)	68.3(2)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **8**

Si(1)−N(1)	1.652(4)	O(1)−Li(2)	1.868(5)
Si(2)−O(1)	1.6193(19)	O(1)−Li(1)	1.877(5)
P(1)−N(1)	1.552(4)	O(1)−Li(1)* [a]	1.907(5)
P(1)−N(2)	1.683(2)	Li(1)−O(1)′	1.907(5)
N(2)−Li(1)	2.094(5)	Li(2)−N(2)*	2.065(5)
P(1)−N(1)−Si(1)	180.0	Li(2)−N(2)−Li(1)	71.9(2)
Li(2)−N(2)−Li(2)′	135.0(3)	N(2)−P(1)−N(2)′	101.21(9)
P(1)−N(2)−Li(1)	120.08(16)	N(1)−P(1)−N(2)*	116.83(8)

[a] Symmetry transformations used to generate equivalent atoms: *, $-y$, $x - y$, z; ′, $-x + y$, $-x$, z.

X-ray Analyses. X-ray quality crystals of **10**·3THF were obtained from the blue solution produced upon air oxidation of a mixture of **4** and lithium *tert*-butoxide in THF after layering with *n*-hexane and cooling to −18 °C. Colorless crystals of **3**, **8**, **9**·3THF, and **10** were coated with Paratone 8277 oil and mounted on a glass fiber. All measurements were made on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation. Crystallographic data are summarized in Table 1. Bond lengths and angles are available in Tables 2−5. The structures were solved by direct methods[21] and refined by full-matrix least-squares methods with SHELXL-97.[22] Hydrogen atoms were included at geometrically idealized positions and were not refined; the non-

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **9**·3THF

K(1)−O(1)	2.626(3)	P(1)−N(2)	1.678(3)
K(1)−O(2)	2.648(3)	Si(1)−N(1)	1.639(4)
P(1)−N(1)	1.567(4)	O(1)−Li(1)	1.834(7)
P(1)−N(4)	1.675(3)	N(2)−Li(1)	1.972(8)
P(1)−N(3)	1.676(4)	N(2)−Li(3)	2.046(8)
O(1)−K(1)−O(2)	119.59(9)	P(1)−N(2)−Li(3)	86.1(2)
N(4)−P(1)−N(3)	102.00(17)	Li(1)−N(2)−Li(3)	116.4(3)
K(1)−O(1)−K(3)	108.67(10)	O(1)−Li(1)−N(2)	133.0(4)
P(1)−N(1)−Si(1)	178.4(3)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **10**

P(1)−N(4)	1.5546(19)	O(4)−Li(3)	1.903(5)
P(1)−N(1)	1.6594(19)	O(4)−Li(2)	1.916(5)
P(1)−N(3)	1.6714(19)	O(4)−Li(1)	1.917(4)
P(1)−N(2)	1.6908(19)	N(1)−Li(1)	2.051(5)
Si(1)−N(4)	1.641(2)	N(1)−Li(2)	2.212(5)
O(1)−Li(1)	2.017(4)	N(2)−Li(3)	2.134(5)
O(2)−Li(2)	1.995(4)	N(2)−Li(1)	2.302(5)
O(3)−Li(3)	2.034(4)	N(3)−Li(2)	2.093(5)
O(4)−C(28)	1.412(3)	N(3)−Li(3)	2.231(5)
N(1)−P(1)−N(3)	101.66(10)	P(1)−N(2)−Li(1)	86.47(14)
N(3)−P(1)−N(2)	100.51(10)	Li(2)−N(3)−Li(3)	73.25(17)
P(1)−N(1)−Li(1)	96.07(16)	P(1)−N(3)−Li(2)	92.86(14)
Li(1)−N(1)−Li(2)	73.43(17)	P(1)−N(4)−Si(1)	179.51(14)
Li(2)−O(4)−Li(1)	83.50(19)	O(4)−Li(1)−N(1)	103.97(19)
Li(3)−O(4)−Li(2)	85.1(2)	N(1)−Li(1)−N(2)	72.81(15)
O(4)−Li(2)−N(3)	102.8(2)	O(4)−Li(3)−N(3)	98.34(19)
O(4)−Li(2)−N(1)	98.25(18)		

hydrogen atoms were refined anisotropically. The methyl groups of one OSiMe$_3$ group in **8** were disordered, with each carbon atom disordered over two sites with partial occupancy factors of 0.55(2) and 0.45(2). A carbon atom in one of the solvating THF molecules in **9**·3 THF was disordered over two sites; this was included in the refinements using partial site occupancy factors.

Results and Discussion

Lithiation of (^{t}BuNH)$_3$PNSiMe$_3$. The reaction of (^{t}BuNH)$_3$PNSiMe$_3$ (**1**) with 1 equiv of *n*-butyllithium in hexane results in the formation of Li[P(N^{t}Bu)(NH^{t}Bu)$_2$(NSiMe$_3$)] (**2**) over a reaction time of approximately 3 h. While this reaction gives only a moderate yield (ca. 45%), it should be noted that **2** is somewhat soluble in both polar and nonpolar organic solvents; consequently, a substantial amount of product is lost during workup of the reaction. In contrast, the dilithium salt Li$_2$[P(N^{t}Bu)$_2$(NH^{t}Bu)(NSiMe$_3$)] (**3**), prepared via the reaction of **2** with 1 equiv of *n*-butyllithium, is soluble only in polar solvents such as THF. Consequently, **3** is isolated in much higher yield (>90%) than **2** over a similar reaction time. Attempts to generate **3** by the direct reaction of **1** with 2 equiv of *n*-butyllithium were not successful, as multinuclear NMR data (^{1}H and ^{31}P) indicated that they resulted in a mixture of products.

Perhaps the most interesting aspect of these lithiation reactions is the facility with which they occur. Although mono- and di-lithium derivatives of the (trisamino)phosphate OP(NH^{t}Bu)$_3$ have been isolated and characterized, complete deprotonation of this heteroleptic species could not be achieved regardless of the reaction conditions.[10a] In contrast, **2**, **3**, and **4** can be prepared at room temperature using a variety of organic solvents such as THF, *n*-hexane, and toluene, in only a few hours.

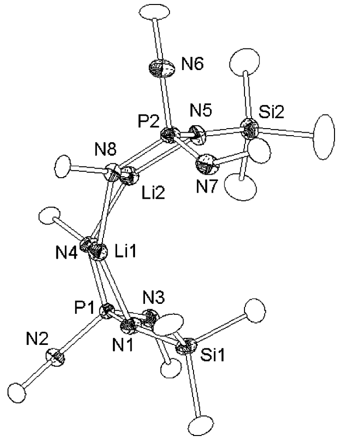

Figure 2. Thermal ellipsoid plot of **2** (30% probability ellipsoids). Only the α-carbon atoms of the ^{t}Bu groups are shown.

The lithiation of **1** is readily monitored by ^{31}P NMR spectroscopy, as the single resonance is observed to shift further downfield with each subsequent deprotonation. When reacted with 1 equiv of *n*-butyllithium, the ^{31}P signal changes from δ −13.6 (**1**) to δ −0.80 (**2**); addition of a second equivalent of *n*-butyllithium results in a singlet at δ 0.16, which is characteristic of **3**. Finally, when a third equivalent of *n*-butyllithium is added, a resonance is observed at δ 4.19 indicating the presence of THF-solvated **4**.

The ^{1}H NMR data of **2** indicate the presence of one N^{t}Bu group (δ 1.38), two equivalent NH^{t}Bu groups (δ 1.35) slightly upfield of the N^{t}Bu group, and a NSiMe$_3$ substituent. A significant downfield shift is observed in the SiMe$_3$ resonance of **2** (δ 0.46) as compared to the corresponding signal in **1** (δ −0.01), which is rationalized below. The ^{13}C NMR spectrum displayed the four resonances expected for the two types of ^{t}Bu groups, as well as a singlet at δ 6.83 ppm attributed to the SiMe$_3$ group. Only one resonance was observed in each of the ^{7}Li (δ 1.62) and ^{31}P (δ −0.80) NMR spectra.

The dilithiated compound **3** was also thoroughly characterized by multinuclear NMR spectroscopy and elemental analysis. Only one signal is observed in the ^{31}P NMR spectrum (δ 0.16) of **3**, suggesting that it has a highly symmetrical structure as opposed to the irregular structures often associated with the isoelectronic hydrogen phosphate salts.[11] The ^{1}H and ^{13}C NMR spectra confirm the presence of two N^{t}Bu substituents and a NH^{t}Bu group, in addition to the SiMe$_3$ resonance at δ −0.01.

X-ray Structure of Li[P(N^{t}Bu)(NH^{t}Bu)$_2$(NSiMe$_3$)] (2). While imido analogues of numerous phosphorus oxoanions have been reported previously,[2] complex **2** is the first imido derivative of dihydrogen phosphate [H$_2$PO$_4$]$^-$ to be characterized in full. In contrast to the extended structures typically found in metal complexes of the [H$_2$PO$_4$]$^-$ anion, an X-ray structural analysis revealed that **2** exists as a dimer in the solid state (Figure 2). This observation is consistent with

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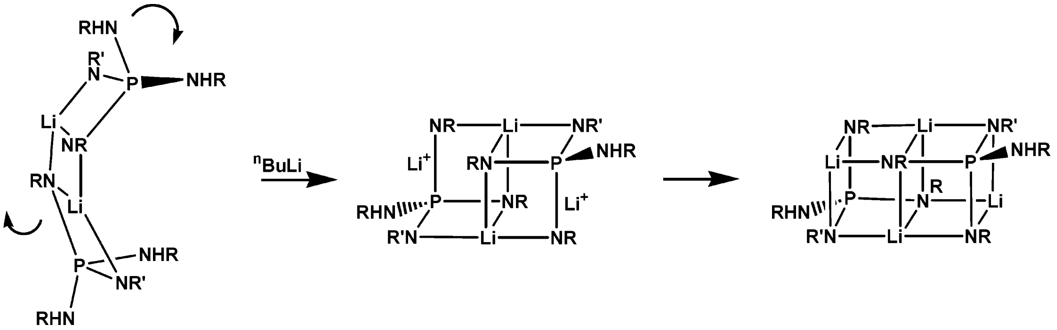
(22) Sheldrick, G. M. *SHELXL-97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

Scheme 1. Conversion of the Dimer **2** to a Dilithiated Double-Cubane **3** (R = ^{t}Bu; R′ = $SiMe_3$)



previous findings that alkali-metal derivatives of polyimido-anions of p- or d-block elements consistently form smaller oligomers than their oxo-anion counterparts, as the steric bulk of the $[NR]^{2-}$ ligands hinders aggregation.[1]

In the solid state, **2** dimerizes via lithium−nitrogen interactions resulting in the formation of a ladder-type structure with four rungs. The Li−N bonds involving the two N^tBu groups produce a nonplanar Li_2N_2 ring which serves to link the two Li[P(N^tBu)(NH^tBu)$_2$($NSiMe_3$)] units. The fold ("butterfly") angle between the Li(1)−N(4)−Li(2) and Li(1)−N(8)−Li(2) planes is 22.0(4)°. Li−$NSiMe_3$ bonds are also present (average distance 2.00 Å), resulting in the formation of two PN_2Li rings, each of which shares an NLi unit with the Li_2N_2 ring. The two P−N bonds adopt a *cis* conformation with respect to the Li_2N_2 ring. The lithium−nitrogen bond distances in the Li_2N_2 ring are all quite similar, ranging from 2.02 to 2.07 Å, with an average Li−N distance of 2.04 Å. Identical ∠LiNLi bond angles of 68.3(2)° are observed at the two nitrogen centers in the Li_2N_2 ring, while the ∠NLiN angles within the ring differ slightly with values of 108.0(3)° and 109.3(3)° at Li(1) and Li(2), respectively. Similar bond angles are observed for the Li_2N_2 ring in the related phosphorus(III) complex [^{t}BuP(NH^tBu)(N^tBu)Li]$_2$.[23] Like the Li_2N_2 rings, the PN_2Li units are quite symmetrical, with similar ∠PNLi angles observed at all four nitrogen atoms (average ∠PNLi 87.5°).

The phosphorus−nitrogen distances are as expected, with shorter distances observed for the P═$NSiMe_3$ bonds (average 1.56 Å) than for the P−NH^tBu bonds (average 1.67 Å), while intermediate bond lengths are observed for the P−N^tBu moieties (average 1.62 Å). These distances are comparable to those found in **1**, which contains a slightly shorter P═$NSiMe_3$ bond (1.55 Å), while the P−N^tBu distances are somewhat longer (1.70 Å) than those found in **2**. The bond angles about the phosphorus center range from 99.95(16)° to 118.76(17)° with an average value of 109.5°.

An interesting feature of this structure is the average ∠PNSi bond angle of 157.2°. While this value is considerably larger than the idealized 120° bond angle that is expected for an sp^2 nitrogen atom, it is significantly smaller than the 180° bond angle observed in both **1** and **4**.[10] The linearity of the PNSi moiety in **1** and **4** was attributed to steric crowding about the phosphorus atom; replacement of the bulky N^tBu groups with smaller NCy groups was found to alleviate this strain, resulting in a reduction of ∠PNSi to 131.7(2)°.[10] In the instance of **2**, the presence of lithium−nitrogen bonds involving the $NSiMe_3$ groups renders these nitrogen atoms three-coordinate, whereas the $NSiMe_3$ nitrogens are two-coordinate in both **1** and **4**. This difference in the geometry about the N atom in **2** is expected to generate a nonlinear PNSi arrangement and may account for the downfield shift of the $SiMe_3$ protons observed in the ^1H NMR spectrum of **2**. Other factors, such as hyperconjugation, involving the σ^* orbital of the $SiMe_3$ group may also contribute to the latter observation.

Though X-ray quality single crystals of the dilithiated amino(bisimido)phosphate **3** could not be obtained despite numerous attempts, some information regarding its structure in solution can be inferred from the NMR data. The observation of only one resonance in the ^{31}P NMR spectrum and only one set of resonances in the ^1H/^{13}C NMR spectra for the N^tBu, $NSiMe_3$, and NH^tBu groups suggests that **3** has a symmetrical structure. The dilithium salt of a bis(imido)amidophosphate {Li_2[OP(N^tBu)$_2$(NH^tBu)]}$_2$ (**7**), which differs from **3** only in the replacement of an oxo substituent by the trimethylsilyl imido group, exists as a centrosymmetric dimer with a face-sharing double-cubane structure, containing a central Li_2O_2 ring.[10a] The isoelectronic relationship between **3** and **7** suggests that they may have similar cluster structures. The solution NMR data for **7** are consistent with the solid-state structure.[10a] The conversion of the dimer **2** upon lithiation to a double-cubane arrangement like that of **7** can readily be envisaged (Scheme 1). The observation of two singlets at δ 1.65 and 2.15 in the ^7Li NMR spectrum of **3** in C_6D_6 is consistent with this structural proposal.

Formation and Structures of {Li_3[P(N^tBu)$_3$($NSiMe_3$)]-(MOR)$_3$} (8, M = Li, R = $SiMe_3$; 9, M = K, R = ^{t}Bu). Initial investigations of the reaction of **4** with lithium trimethylsilanolate resulted in the formation of a mixture of products. An alternate synthetic approach was adopted which entailed the reaction of (^{t}BuNH)$_3$P$NSiMe_3$ with 3 equiv of *n*-butyllithium in the presence of $LiOSiMe_3$. This methodology was found to produce the half-sandwich complex {Li_3[P(N^tBu)$_3$($NSiMe_3$)]($LiOSiMe_3$)$_3$} (**8**) in 80% yield. The ^1H NMR spectrum of **8** displays one signal for each of the N^tBu, $NSiMe_3$, and $OSiMe_3$ groups, and a single resonance is observed at δ 6.92 in the ^{31}P NMR spectrum. An X-ray structural analysis of **8** (Figure 3) showed that, in this

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[23] Bauer, T.; Schulz, S.; Nieger, M.; Kessler, U. *Organometallics*, **2003**, *22*, 3134.

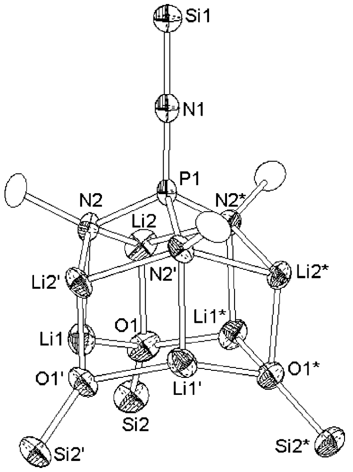

Figure 3. Thermal ellipsoid plot of **8** (25% probability ellipsoids). Only α-carbon atoms of the ^tBu groups are shown; methyl groups attached to the Si atoms are also omitted.

complex, the trilithiated tetrakisimidophosphate trianion acts to entrap 3 equiv of $LiOSiMe_3$, resulting in the formation of a rare trimeric Li_3O_3 ring. Lithium trimethylsilanolate has not been structurally characterized, but the related compounds $LiOSiMe_2{}^tBu$[24] and $LiOSiMe^tBu_2$[25] are hexameric and tetrameric, respectively. The structure of **8** can be viewed as a hybrid of the classical "ring-stacked" Li_6O_6 and Li_6N_6 structures involving Li_3O_3 and Li_3N_3 rings.[26]

A closer look at the crystallographic data reveals the presence of strong interactions between the Li_3O_3 ring and the Li_3N_3 ring of the trilithiated tetrakisimidophosphate. The lithium−nitrogen distances involving $LiOSiMe_3$ lithium atoms (2.09 Å) are similar to those within the Li_3N_3 ring (2.04 Å), as are the lithium−oxygen distances between the two rings [$Li(1)-O(1) = 1.89$ Å; $Li(2)-O(1) = 1.87$ Å]. These lithium−oxygen distances are comparable to those found in other trimeric lithium alkoxides (range 1.91−2.02 Å).[20] The generation of **8** is presumably driven by the formation of these strong Li−N and Li−O bonds. The P−N(2) distance (1.68 Å) in this complex is slightly shorter than the corresponding bond lengths in **4** (1.70 Å), while the bond angle $\angle N(2)-P(1)\text{-}N(2)$ in **8** [101.21(9)°] is comparable to that found in **4** [102.14(4)°].[10] As is observed in both **1** and **4**, the PNSi unit in **8** is linear. Agostic interactions are observed between each Li(2) atom and a methyl group on the neighboring *tert*-butyl group, with an observed Li⋯C(H) distance of 2.61 Å. Similar interactions are observed in the dimeric compound $\{Li_3[Sb(N^tBu)_3]\}_2$ (**5**) (average Li⋯C(H) 2.65 Å).[27]

The reaction of **4** with 3 equiv of potassium *tert*-butoxide produces the imido-alkoxy complex $\{Li_3[P(N^tBu)_3(NSiMe_3)](KO^tBu)_3\}(THF)_3$ (**9**·3THF). The structure of **9**·3THF (Figure 4) is closely related to that of **8**; it consists of a trilithiated $[P(N^tBu)_3(NSiMe_3)]^{3-}$ trianion which serves to trap a trimeric K_3O_3 ring via the formation of lithium−oxygen bonds. In contrast to the strong Li−N contacts in **8**, very weak K−N interactions with an average K−N distance of 3.37 Å are present in **9**·3THF. This disparity can be attributed to the smaller size and stronger polarizing power of Li^+ as compared to K^+. Also, the coordination of one THF, a strong electron donor, to each potassium (average K−O 2.71 Å), and the strong K−O bonds (average K−O 2.64 Å) within the K_3O_3 ring, reduce the electrophilicity of the K^+ ions. These potassium−oxygen distances are typical of those found in other potassium alkoxides (range 2.64−2.93 Å).[28] Agostic interactions between one methyl carbon of the N^tBu groups and the neighboring potassium atom were found to be present, with a mean distance of 3.21 Å; weaker intermolecular contacts (average K⋯C(H) 3.49 Å) were also identified, with one methyl group on each $SiMe_3$ moiety interacting with the three potassium atoms in the adjacent molecule.

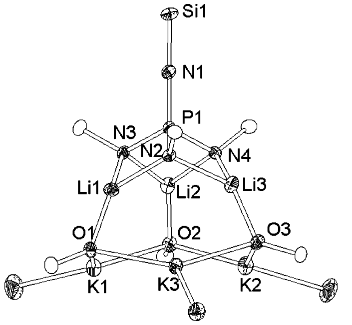

Figure 4. Thermal ellipsoid plot of **9**·3THF (30% probability ellipsoids). Only oxygen atoms of THF molecules are shown. Only α-carbon atoms of the ^tBu groups are shown; methyl groups attached to the Si atom are also omitted.

The presence of a trimeric potassium *tert*-butoxide unit in **9**·3THF is a rare structural feature, as KO^tBu is known to be tetrameric in the solid state.[14] An example of a related cluster that contains this ring system is $\{Li_3[Sb(NCy)_3)]\}_2(KO^tBu)_3\cdot C_6H_5CH_3$ (**6**),[13] in which the K_3O_3 ring is sandwiched between two trilithiated $[Sb(NCy)_3]^{3-}$ trianions. A striking difference between the structures of **9**·3THF and **6** is the conformation of the K_3O_3 ring; whereas it is planar in **6**, this heterocycle adopts a more conventional chair configuration in **9**·3THF. While both these complexes contain strong lithium−oxygen bonds (average Li−O = 1.84 Å and 1.90 Å in **9**·3THF and **6**, respectively), the K−N bonds (average 2.85 Å) in **6** are considerably stronger than those found in **9**·3THF, while the K−O bonds (2.90 Å) are substantially weaker than those observed in **9**·3THF (2.64 Å).

In view of the isolation of the antimony compound **6**, it was thought that the reaction of **4** with 1.5 equiv of potassium *tert*-butoxide in the absence of THF or other coordinating solvents would lead to the formation of the 2:1 complex $\{Li_6[P(N^tBu)_3(NSiMe_3)]_2(KO^tBu)_3\}$. However, ^{31}P NMR

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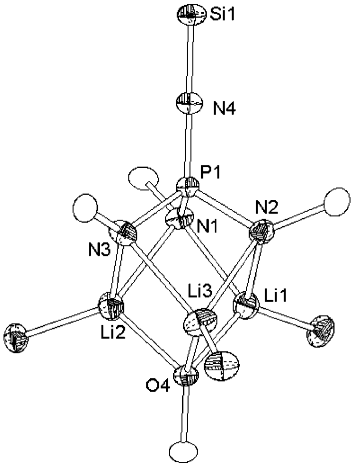

Figure 5. Thermal ellipsoid plot of **10** (30% probability ellipsoids). Only oxygen atoms of THF molecules are shown. Only α-carbon atoms of the ^{t}Bu groups are shown; methyl groups attached to the Si atom are also omitted.

monitoring of this reaction indicated that, in fact, a mixture of products is formed. When a similar reaction was attempted with LiOSiMe$_3$, the 1:1 complex **8** was produced, and unreacted **4** and lithium trimethylsilanolate were recovered. Thus, in contrast to the 2:1 complexes produced by the hexadentate ligand Li$_3$[Sb(NCy)$_3$] and trimeric alkali-metal alkoxides, the phosphorus analogue Li$_3$[P(N^{t}Bu)$_3$(NSiMe$_3$)] forms only 1:1 complexes with M$_3$O$_3$ rings.

Formation and X-ray Structure of {(Me$_3$SiN)P(μ$_3$-N^{t}Bu)$_3$[μ$_3$-Li(THF)]$_3$(O^{t}Bu)} (10). In light of the successful syntheses of **8** and **9**·3THF, similar reactions were attempted using potassium trimethylsilanolate and lithium *tert*-butoxide. The reaction of **4** with 3 equiv of KOSiMe$_3$ resulted in a mixture of products, while in the case of LiO^{t}Bu, no reaction was observed regardless of the solvent or reaction conditions. However, when a mixture of lithium *tert*-butoxide and **4** in THF was exposed briefly to atmospheric oxygen, the solution was observed to turn a deep blue, suggesting the formation of a radical species. Removal of the solvent under vacuum and recrystallization from THF/*n*-hexane afforded blue paramagnetic crystals which were identified as {(Me$_3$SiN)P(μ$_3$-N^{t}Bu)$_3$[μ$_3$-Li(THF)]$_3$(O^{t}Bu)} (**10**) by X-ray crystallography. These crystals are stable for several weeks under THF/*n*-hexane, while blue solutions of **10** dissolved in THF persist for months.

An X-ray crystal structure (Figure 5) of the blue crystals showed that, in the solid state, the cluster **10** exists as a distorted PN$_3$Li$_3$O cube similar to the PN$_3$Li$_3$I cube observed in the isovalent halide-containing radical{(Me$_3$SiN)P(μ$_3$-N^{t}Bu)$_3$[μ$_3$-Li(THF)]$_3$I}.[29] These paramagnetic species are composed of the dianion radical [P(N^{t}Bu)$_3$(NSiMe$_3$)]$^{\bullet 2-}$, which is formed via the one-electron oxidation of the trianion [P(N*t*Bu)$_3$(NSiMe$_3$)]$^{3-}$ in **4**, and is stabilized by two Li$^+$ cations. This dilithiated tetrakisimidophosphate radical acts to entrap a monomeric unit of LiX, where X = O^{t}Bu in the case of **10**.

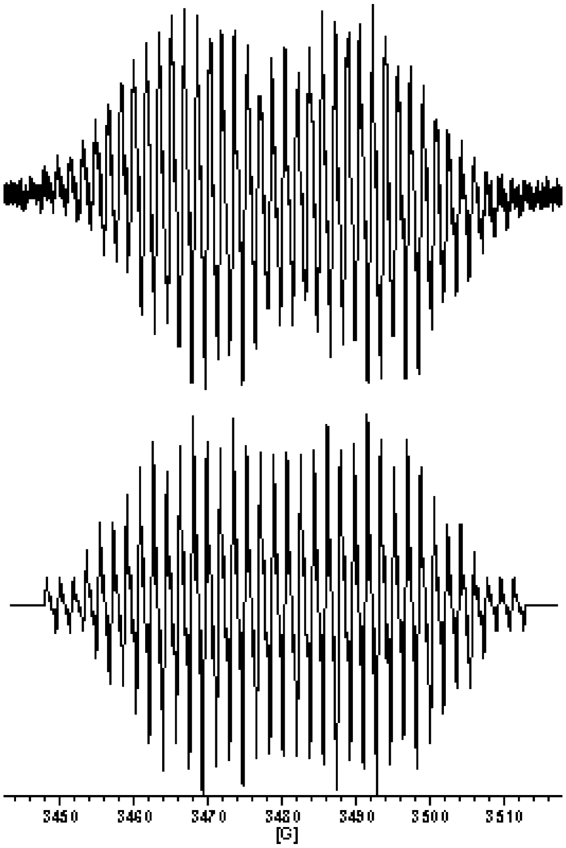

Figure 6. Experimental (top) and simulated (bottom) EPR spectrum of **10** in THF at 23 °C.

The geometry of the cube is distorted, with bond angles within the cluster ranging between 73° and 101°. The bond lengths within the cube range from a mean value of 1.67 Å for the P−N bonds to an average value of 2.17 Å for the lithium−nitrogen distances. The Li−O bonds within this cage are strong with a mean value 1.91 Å. The *exo*-cluster P−N bond length of 1.55 Å and the linearity of the P−N−Si arrangement [179.5(1)°] are reminiscent of the corresponding structural parameters in **4**.[10a] A molecule of THF is coordinated to each of the three lithium cations. The stability of this radical is attributed to a combination of the steric protection provided by the N^{t}Bu and NSiMe$_3$ groups and the delocalization of the unpaired electron over the cluster.

An EPR spectrum of a sample of solid **10** exhibited a single broad resonance; in THF solution, a complex spectrum was obtained (Figure 6) due to hyperfine coupling (hfc) of the unpaired electron to phosphorus (^{31}P, $I = {}^1/_2$, 100%), nitrogen (^{14}N, $I = 1$, 99.6%), and lithium (^{7}Li, $I = {}^3/_2$, 92.6%). The best resolution of the EPR spectrum was obtained by using very dilute solutions and a low modulation amplitude. The *g* value of this radical is 2.00452. A good simulation of this spectrum was obtained by including hyperfine coupling to one phosphorus atom ($a_P = 23.5$ G), two equivalent nitrogen centers ($a_N = 5.40$ G), two unique nitrogen atoms with hfcs of 7.20 and 1.80 G, respectively, and one lithium nucleus ($a_{Li} = 0.31$ G). The presence of coupling to only one lithium nucleus and the three different nitrogen hfcs is reminiscent of the behavior that was observed for dilute THF solutions of the analogous halide-containing

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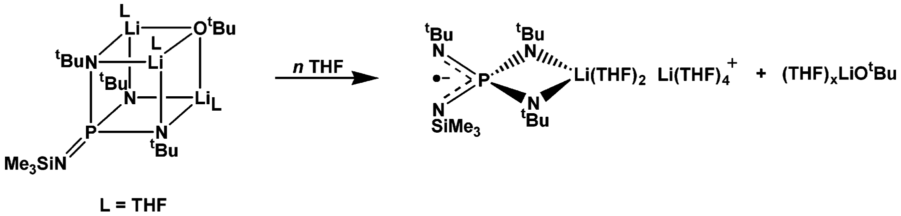
Scheme 2. Dissociation of the Cubic Radical **10** in Dilute THF Solution



radicals $\{(Me_3SiN)P(\mu_3\text{-}N^tBu)_3[\mu_3\text{-}Li(THF)]_3X\}$ (X = Br, I) for which the hfcs were $a_P = 23.1$ G, $a_N = 5.38$ G (×2), 7.38 G, and 1.93 G, and $a_{Li} = 0.30$ G.[29] In that case, the solution behavior was interpreted in terms of the disruption of the cubic radicals upon solvation by THF with the release of $(THF)_3LiX$ which was isolated for X = I. The congruence of the EPR parameters indicates that a similar process occurs for **10** generating the same cyclic radical monoanion as obtained for the halide-containing systems (Scheme 2). However, we have not been able to isolate $(THF)_xLiO^tBu$, the expected byproduct of this solvation process.

The formation of **10** by the method described above did not generate a pure product reproducibly. Consequently, alternative synthetic approaches to **10** were investigated. The attempted direct oxidation of **4** with di-*tert*-butylperoxide in THF resulted in no reaction at room temperature over an 18 h period. In another attempt, **1** was trilithiated with *n*-butyllithium in the presence of half an equivalent of $^tBuOO^tBu$. A dark blue paste was isolated, but this product was not stable in the solid state; it decomposed after only a few days at 22 °C.

Conclusion

The neutral compound $(^tBuNH)_3PNSiMe_3$ is mono-, di-, or trilithiated by reactions with a stoichiometric amount of ^nBuLi at room temperature generating imido analogues of the $[H_2PO_4]^-$, $[HPO_4]^{2-}$, and $[PO_4]^{3-}$ ions, respectively. Lithium salts of tetrakisimidophosphate anions $[P(NSiMe_3)(N^tBu)_3]^{x-}$ (x = 2, 3) possess a unique coordination chemistry, as evidenced by their ability to trap either monomeric and trimeric alkali metal alkoxide fragments. Investigations of the ligand behavior of the trilithiated tetrakisimidophosphate toward other element-oxygen ring systems are in progress.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for funding.

Supporting Information Available: X-ray crystallographic files in CIF format for **2**, **8**, **9**·3THF, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035377V