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Lithiation of Tris(alkyl- and arylamido)orthophosphates $EP[N(H)R]_3$ ($E = O, S, Se$): Imido Substituent Effects and P═E Bond Cleavage

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In the solid state, $OP[N(H)Me]_3$ (**1a**) and $OP[N(H)^tBu]_3$ (**1b**) have hydrogen-bonded structures that exhibit three-dimensional and one-dimensional arrays, respectively. The lithiation of **1b** with 1 equiv of ^nBuLi generates the trimeric monolithiated complex $(THF)\{LiOP(N^tBu)[N(H)^tBu]_2\}_3$ (**4**), whereas reaction with an excess of ^nBuLi produces the dimeric dilithium complex $\{(THF)_2Li_2OP(N^tBu)_2[N(H)^tBu]\}_2$ (**5**). Complex **4** contains a Li_2O_2 ring in an open-ladder structure, whereas **5** embraces a central Li_2O_2 ring in a closed-ladder arrangement. Investigations of the lithiation of tris(alkyl or arylamido)thiophosphates, $SP[N(H)R]_3$ (**2a**, R = ^{i}Pr; **2b**, R = ^{t}Bu; **2c**, R = *p*-tol) with ^nBuLi reveal interesting imido substituent effects. For the alkyl derivatives, only mono- or dilithiation is observed. In the case of R = ^{t}Bu, lithiation is accompanied by P–S bond cleavage to give the dilithiated cyclodiphosph(V/V)azane $\{(THF)_2Li_2[(^tBuN)_2P(\mu\text{-}N^tBu)_2P(N^tBu)_2]\}$ (**9**). Trilithiation occurs for the triaryl derivatives $EP[N(H)Ar]_3$ (E = S, Ar = *p*-tolyl; E = Se, Ar = Ph), as demonstrated by the preparation of $\{(THF)_4Li_3[SP(Np\text{-}tol)_3]\}_2$ (**10**) and $\{(THF)_4Li_3[SeP(NPh)_3]\}_2$ (**11**), which are accompanied by the formation of small amounts of **10**·$[LiOH(THF)]_2$ and **11**·$Li_2Se_2(THF)_2$, respectively.

Introduction

Isoelectronic analogues of common phosphorus(V) oxo anions, e.g., orthophosphate $[PO_4]^{3-}$,[1] metaphosphate $[PO_3]^-$,[2] and phosphonate $[RPO_3]^{2-}$,[3] in which the oxygen atoms are replaced by imido (NR) groups and/or chalcogen (S, Se, or Te) atoms, are potentially versatile multidentate ligands involving a combination of hard (N) and soft (S, Se, or Te) donor sites. Whereas metal complexes of the most common phosphorus(V) oxoanion, $[PO_4]^{3-}$, typically form open-framework three-dimensional polymeric clusters composed of metal−oxygen interactions, the steric bulk of the imido substituents precludes the formation of large aggregates, as illustrated by the dimeric structure of the tetrakis(imido)-phosphate complex $\{Li_3[P(N^tBu)_3(NSiMe_3)]\}_2$.[1b] The $[P(NR)_4]^{3-}$ anion (R = 1-naph) has also been characterized as a monomeric ion-separated complex.[4]

This paper provides a full account of our attempts to generate the heteroleptic orthophosphate analogues $[EP(NR)_3]^{3-}$ (E = O, S, Se; R = alkyl, aryl) by lithiation of the neutral precursors $EP(NHR)_3$.[5] Issues of interest include (a) the effect of alkyl and aryl substituents on the lithiation process, (b) the competition between Li-E and Li−N(R) modes of interaction in the structures of lithium derivatives, (c) the steric influence of the R substituent on aggregation, and (d) the factors leading to and consequences of P═E bond cleavage (if observed).

This investigation begins with a description of improved methods for the syntheses of $OP[N(H)R]_3$ (**1a**, R = Me; **1b**, R = ^{t}Bu), $SP[N(H)R]_3$ (**2a**, R = ^{i}Pr; **2b**, R = ^{t}Bu; **2c**, R = *p*-tol), and $SeP[N(H)Ph]_3$ (**3**). The X-ray structures of **1a** and **1b** were determined to probe the influence of the R substituent on the hydrogen-bonded networks. The lithiation of **1b** with ^nBuLi gives only mono- or dilithiated products, whereas the lithiation of the thiophosphate analogue **2b** is

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accompanied by P−S bond cleavage. By contrast, trilithiation occurs for the aryl derivatives **2c** and **3** to give the first examples of tris(imido)thio- and selenophosphate trianions $[EP(NAr)_3]^{3-}$ (E = S, Ar = *p*-tol; E = Se, Ar = Ph).

Experimental Section

Reagents and General Procedures. Solvents were dried and distilled prior to use: toluene, tetrahydrofuran, diethyl ether, *n*-hexane (Na/benzophenone), and *n*-pentane (Na). *n*-Butyllithium (2.5 M solution in hexanes, Aldrich), *tert*-butylamine (98%, Aldrich), *iso*-propylamine (99.5%, Aldrich), *para*-toluidine (99%, Aldrich), methylamine (1 M solution in THF, Aldrich), aniline (99%, Aldrich), phosphoryl chloride (99%, Aldrich), thiophosphoryl chloride (99%, Aldrich), TMEDA (99.5%, Aldrich), and selenium (99.5%, Aldrich) were used as received. The compounds $(Et_2O)LiN(SiMe_3)_2$,[6] $LiN(H)^tBu$,[7] and $P(NHPh)_3$,[8] were prepared by literature procedures.

Caution: Selenium compounds are potentially toxic. All reactions should be carried out in a well-ventilated fume hood. The use of protective latex gloves is recommended.

Instrumentation. Unless stated otherwise, NMR data were recorded at 23 °C. ^1H NMR spectra were collected on a Bruker ACT-200 spectrometer, and chemical shifts are reported relative to Me_4Si in $CDCl_3$. ^{31}P and ^7Li NMR spectra were obtained on a Bruker AMX2−300 spectrometer; chemical shifts are reported relative to 85% H_3PO_4 and 1 M LiCl in D_2O, respectively. ^{77}Se NMR spectra were obtained on a Bruker Advance DRX 400 spectrometer; chemical shifts are reported relative to Ph_2Se_2 (+463 ppm relative to Me_2Se). Solid-state NMR spectra were collected on a Bruker AMX2-300 spectrometer. Infrared spectra were recorded as Nujol mulls on KBr plates on a Nicolet Nexus 470 FTIR spectrometer in the range 4000−350 cm^{-1}. Mass spectra were obtained with a VG Micromass spectrometer VG7070 (70 eV). Elemental analyses were obtained with a Control Equipment Corporation model 440 instrument by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Preparation of $OP[N(H)Me]_3$ (1a). The following is a modified literature procedure.[9] Phosphoryl chloride (3.06 mL, 5.11 g, 33.3 mmol) was added dropwise to an excess of methylamine (100 mL, 6.21 g, 200 mmol) in hexane (250 mL) at 0 °C. A white precipitate formed, and the solution was slowly warmed to 23 °C and stirred for 2 h. Hexane was removed in vacuo, and chloroform (250 mL) was added to the sticky white solid. Methylammonium chloride was filtered on a Buchner funnel and a potassium hydroxide/methanol solution was added dropwise until pH > 7. Potassium chloride was removed by filtration, and the volume of the solution was reduced to 50 mL. Dilute hydrochloric acid (2 M) was added to the solution until pH = 5−6, and then toluene (150 mL) was added. After 2 days at 23 °C, the solution was filtered, and the volume of the filtrate was reduced to 50 mL. Hexane (10 mL) was added to the concentrated solution, and after 1 day at 23 °C, crystals of **1a** formed (2.75 g, 20.1 mmol, 60%). Anal. Calcd for $C_3H_{12}N_3OP$: C, 26.28; H, 8.82; N, 30.64. Found: C, 26.56; H, 9.00; N, 29.16. ^1H NMR ($CDCl_3$, δ): 2.55 [d, 9H, Me, $^3J(^1H-^{31}P) = 12$ Hz], 2.38 (s, 3H, NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 18.5 (s). mp 65−68 °C. IR (cm^{-1}): 3372 [ν(N−H)]. MS [EI, *m/z* (rel int)]: M^+ 137(23). [cf. lit. 41% yield.[9a] ^1H NMR (C_6D_6, δ): 2.7 [d, $^3J(^1H-^{31}P) = 12$ Hz]. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 22.8 (s).]

Preparation of $OP[N(H)^tBu]_3$ (1b). The following is a modified literature procedure.[10] Phosphoryl chloride (10 mL, 16.71 g, 0.109 mol) was added dropwise to an excess of *tert*-butylamine (100 mL, 69.6 g, 0.952 mol) in toluene (350 mL) at 0 °C. A white precipitate formed and the solution was slowly warmed to 23 °C and stirred for 3 h. *tert*-Butylammonium chloride was removed by filtration, and the volume of the solution was reduced to 75 mL. Hexane (25 mL) was added, and after 1 day at −15 °C, white crystals formed. Sublimation at 120 °C/10^{-2} Torr gave **1b** (25.55 g, 0.097 mol, 89%). Anal. Calcd for $C_{12}H_{30}N_3OP$: C, 54.73; H, 11.47; N, 15.96. Found: C, 54.16; H, 11.65; N, 15.64. ^1H NMR ($CDCl_3$, δ): 2.20 [d, 3H, NH, $^2J(^1H-^{31}P) = 6$ Hz], 1.26 (s, 27H, N^tBu). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 5.5 (s). IR (cm^{-1}): 3286 [ν(N−H)]. MS [EI, *m/z* (rel int)]: M^+ 263(15). [cf. lit. ^1H NMR ($CDCl_3$, δ): 2.57 (s, 3H, NH), 1.22 (s, 27H, N^tBu).[10]]

Preparation of $SP[N(H)^iPr]_3$ (2a). The following is a modified literature procedure.[11] Thiophosphoryl chloride (17.89 mL, 29.8 g, 0.176 mol) was added dropwise to an excess of *iso*-propylamine (90 mL, 62.48 g, 1.057 mol) in diethyl ether (200 mL) at 0 °C. A white precipitate formed, and the solution was slowly warmed to 23 °C and stirred for 3 h. *iso*-Propylammonium chloride was removed by filtration and washed with diethyl ether (200 mL) and toluene (100 mL). The volume of the filtrate was reduced to 100 mL; hexane (50 mL) was added; and after 1 day at −15 °C, a white solid formed that contained mostly **2a** mixed with a small amount of $[^iPrNH(S)P(\mu\text{-}N^iPr)_2P(S)NH^iPr]$. Sublimation of the mixture at 90 °C/10^{-2} Torr yielded **2a** [19.97 g, 0.084 mol, 48% (cf. lit. 11%)].[11] mp 92−94 °C. Anal. Calcd for $C_9H_{24}N_3PS$: C, 45.54; H, 10.19; N, 17.70. Found: C, 45.46; H, 9.95; N, 17.57. ^1H NMR (C_6D_6, δ): 3.45 (septet, 3H, $CH(CH_3)_2$), 2.05 (br s, 3H, NH), 1.01 [d, 18H, $CH(CH_3)_2$, $^3J(^1H-^1H) = 6$ Hz]. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 56.3 (s) (lit. 58.6);[12] solid-state (10 kHz): 51.2 (s). IR (cm^{-1}): 3389, 3231 [ν(N−H)]. MS [EI, *m/z* (rel int)]: M^+ 237(8). The unsublimed residue was identified as $[^iPrNH(S)P(\mu\text{-}N^iPr)_2P(S)NH^iPr]$ (4.24 g, 0.012 mol, 14%) by comparison of ^1H and ^{31}P NMR spectra with literature data..[12b]

Preparation of $SP[N(H)^tBu]_3$ (2b). The following is a modified literature procedure.[12] Thiophosphoryl chloride (15.00 mL, 25.01 g, 0.1477 mol) was added dropwise to an excess of *tert*-butylamine (110 mL, 76.58 g, 1.047 mol) in diethyl ether (250 mL) at 0 °C. The workup procedure was similar to that described above for **2a** and gave white crystals of **2b** (32.87 g, 0.118 mol, 80%). mp 115−118 °C. Anal. Calcd for $C_{12}H_{30}N_3PS$: C, 51.58; H, 10.82; N, 15.04. Found: C, 51.73; H, 10.73; N, 14.89. ^1H NMR (C_6D_6, δ): 2.25 [d, 3H, NH, $^2J(^1H-^{31}P) = 4$ Hz], 1.36 [d, 27H, ^tBu, $^4J(^1H-^{31}P) = 0.7$ Hz]. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 46.3 (s) (lit. 60.4); solid-state (10 kHz): 46.0 (s). IR (cm^{-1}): 3398 [ν(N−H)]. MS [EI, *m/z* (rel int)]: M^+ 279(61).

Preparation of $SP[N(H)p\text{-}tol]_3$ (2c). The following is a modified literature procedure.[13] Thiophosphoryl chloride (10.00 mL, 16.67 g, 0.09847 mol) was added dropwise to an excess of *para*-toluidine

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(80.00 g, 0.7465 mol) in toluene (250 mL) at 0 °C. A brown slurry formed, and the mixture was slowly warmed to 23 °C and stirred for 2 h. Solvent was removed in vacuo, and dilute HCl (100 mL) was added to the brown solid to dissolve *para*-tolylammonium chloride. The product was separated by filtration and redissolved in THF (100 mL). Pentane (50 mL) was added to the filtrate, and after 1 day at −15 °C, tan-colored microcrystalline **2c** (15.87 g, 0.0416 mol, 42%) was obtained. ^{1}H NMR (d_8-THF, δ): 7.11 [d, 6H, Ph-*m*, $^3J(^1\text{H}-^1\text{H}) = 8$ Hz], 6.93 [d, 6H, Ph-*o*, $^3J(^1\text{H}-^1\text{H}) = 9$ Hz], 3.58 (m, THF), 2.20 (s, 9H, Ph-*Me*), 1.76 (m, THF). ^{31}P{^{1}H} NMR (d_8-THF, δ): 44.5 (s) (cf. lit. 43.9).[13] IR (cm^{-1}): 3394 [ν(N−H)]. MS [EI, *m*/*z* (rel int)]: M$^+$ 381(26).

Preparation of SeP[N(H)Ph]$_3$ (3). Diethyl ether (25 mL) was added to a mixture of P(NHPh)$_3$ (1.165 g, 3.79 mmol), elemental selenium (0.299 g, 3.79 mmol), and aniline (1−2 mL) at 23 °C. The solution was stirred for 2 days and then filtered to remove residual selenium. X-ray-quality crystals of **3** (0.864 g, 2.24 mmol, 59%) were obtained from a concentrated diethyl ether/pentane solution after 24 h at −15 °C. Anal. Calcd for $C_{18}H_{18}N_3PSe$: C, 55.97; H, 4.90; N, 10.88. Found: C, 55.77; H, 5.15; N, 11.10. ^{1}H NMR (d_8-THF, δ): 7.27−7.09 (m, 12H, Ph-*m*, Ph-*o*), 6.83 (t, 3H, Ph-*p*, $^3J(^1\text{H}-^1\text{H}) = 7$ Hz), 2.42 (s, 3H, NH). ^{31}P{^{1}H} NMR (C_6D_6, δ): 33.4 [s, $^1J(^{31}\text{P}-^{77}\text{Se}) = 854$ Hz]. ^{77}Se NMR (d_8-THF, δ): −205.0 [d, $^1J(^{77}\text{Se}-^{31}\text{P}) = 853$ Hz]. IR (cm^{-1}): 3354 [ν(N−H)].

Preparation of (THF){LiOP(N^{t}Bu)[N(H)^{t}Bu]$_2$}$_3$ (4). (Et$_2$O)-LiN(SiMe$_3$)$_2$ (0.458 g, 1.897 mmol) in THF (10 mL) was added slowly to a stirred solution of OP[N(H)^{t}Bu]$_3$ (0.500 g, 1.897 mmol) in THF (15 mL) at 23 °C. After 18 h, removal of the solvent and washing with pentane (2 × 5 mL) yielded a white amorphous solid (0.480 g, 0.546 mmol, 86%). X-ray-quality crystals of **4** were obtained from a concentrated THF/hexane solution in 24 h at 23 °C. Anal. Calcd for $C_{42}H_{98}N_9Li_3O_{4.5}P_3$: C, 55.07; H, 10.89; N, 13.76. Found: C, 53.91; H, 10.86; N, 13.62. ^{1}H NMR (d_8-THF, δ): 3.58 (m, [O(C*H*$_2$)$_2$(CH$_2$)$_2$]), 1.90 (s, 2H, NH), 1.74 (m, [O(CH$_2$)$_2$(C*H*$_2$)$_2$]), 1.29 (s, 18H, NH^{t}Bu), 1.18 (s, 9H, N^{t}Bu). ^{31}P{^{1}H} NMR (d_8-THF, δ): 5.8 (s); solid-state (δ): 6.2 (s), 4.0 (s), 3.3 (s) (1:1:1). ^{7}Li NMR (d_8-THF, δ): −1.80 (s). IR (cm^{-1}): 3430, 3385, 3339 [ν(N−H)].

Formation of {(THF)$_2$Li$_2$[(^{t}BuN)$_2$P(μ-N^{t}Bu)$_2$P(N^{t}Bu)$_2$] (9). *n*-Butyllithium (1.43 mL, 0.229 g, 3.58 mmol) was added dropwise to a solution of SP[N(H)^{t}Bu]$_3$ (0.500 g, 1.79 mmol) in THF (25 mL) at 23 °C. After 2 h, the solvent was concentrated and layered with hexane at 23 °C to give X-ray-quality crystals of **9** (86.8 mg, 0.134 mmol, 15%). Reliable CHN data could not be obtained because of facile loss of coordinated THF, but the purity of **9** was established by multinuclear NMR data. ^{1}H NMR (d_8-THF, 23 °C, δ): 3.58 (m, THF), 1.73 (m, THF), 1.53 (s, 18H, N^{t}Bu), 1.28 (s, 36H, N^{t}Bu). ^{31}P{^{1}H} NMR (d_8-THF, δ): −21.6 (s); solid-state (13 kHz, δ): −20.3. ^{7}Li NMR (C_6D_6, δ): −1.43 (s).

Preparation of {(THF)$_4$Li$_3$[SP(N*p*-tol)$_3$]}$_2$ (10) and 10·[LiOH-(THF)]$_2$. *n*-Butyllithium (3.17 mL, 0.508 g, 7.93 mmol) was added dropwise to a solution of SP[N(H)*p*-tol]$_3$ (1.008 g, 2.64 mmol) in THF (25 mL) at 23 °C. After 18 h, the solvent was concentrated to 10 mL, and hexane was layered onto the THF solution at 23 °C to give X-ray-quality crystals of **10** (1.44 g, 1.047 mmol, 79%). Anal. Calcd for $C_{37}H_{53}N_3O_4PSLi_3$: C, 64.62; H, 7.77; N, 6.11. Found: C, 63.52; H, 7.86; N, 6.64. ^{1}H NMR (d_8-THF, δ): 6.83 [d, 6H, Ph-*m*, $^3J(^1\text{H}-^1\text{H}) = 7$ Hz], 6.53 [d, 6H, Ph-*o*, $^3J(^1\text{H}-^1\text{H}) = 8$ Hz], 3.61 (m, 16H, THF), 2.03 (s, 9H, Ph-*Me*), 1.76 (m, 16H, THF). ^{31}P{^{1}H} NMR (d_8-THF, δ): 36.4 (s); solid-state (10 kHz, δ): 35.2, 33.4 (s). ^{7}Li NMR (d_8-THF, δ): 0.74 (s, $\Delta w_{1/2} = 9$ Hz); solid-state (13.9 kHz, δ): 1.54 (s).

In a preliminary experiment, a few single crystals of **10**·[LiOH-(THF)]$_2$ were obtained from the first fraction of a recrystallization at −15 °C after 3 days, and an X-ray structure was determined.

Preparation of {(THF)$_4$Li$_3$[Se(NPh)$_3$]}$_2$ (11) and 11·Li$_2$Se$_2$-(THF)$_2$. *n*-Butyllithium (1.95 mL, 0.313 g, 4.88 mmol) was added dropwise to a solution of SeP[N(H)Ph]$_3$ (0.626 g, 1.62 mmol) in THF (25 mL) at 23 °C. After 18 h, the solvent was concentrated to 10 mL, and hexane was layered onto the red THF solution at 23 °C to give **11** (0.847 g, 1.22 mmol, 75%).[14] Anal. Calcd for $C_{34}H_{47}N_3O_4PSeLi_3$: C, 58.72; H, 6.84; N, 6.07. Found: C, 59.08; H, 6.93; N, 6.20. ^{1}H NMR (d_8-THF, δ): 6.91 (br d, 6H, Ph-*m*, $^3J(^1\text{H}-^1\text{H}) = 6$ Hz), 6.66 [t, 6H, Ph-*o*, $^3J(^1\text{H}-^1\text{H}) = 8$ Hz], 6.13 (t, 3H, Ph-*p*, $^3J(^1\text{H}-^1\text{H}) = 7$ Hz), 3.58 (m, 16H, THF), 1.75 (m, 16H, THF). ^{31}P{^{1}H} NMR (d_8-THF, δ): 21.4 (br s, $\Delta w_{1/2} = 499$ Hz); solid-state (10 kHz, δ): 23.3, 21.2 (s). ^{77}Se NMR (d_8-THF, −80 °C, δ): −59.1 [d, $^1J(^{31}\text{P}-^{77}\text{Se}) = 499$ Hz]. ^{7}Li NMR (d_8-THF, δ): 0.65 (br s, $\Delta w_{1/2} = 12$ Hz).

In a preliminary experiment, a few single crystals of **11**·Li$_2$Se$_2$-(THF)$_2$ were obtained from the first fraction of a recrystallization at 23 °C after 1 day, and an X-ray structure was determined.

X-ray Analyses. Measurements were made on the following instruments: Nonius Kappa CCD diffractometer {**1a**, **1b**, **3**, **10**, **10**·[LiOH(THF)]$_2$, **11**·Li$_2$Se$_2$(THF)$_2$}, Bruker AXS P4/RA/SMART 1000 CCD diffractometer (**4** and **7**), Bruker SMART APEX CCD diffractometer (**9**). The crystallographic data are summarized in Tables 1 and 2.

Structures were solved by direct methods (SIR-92[15a] or SHELXS-97[15b]) and refined by full-matrix least-squares methods on F^2 with SHELXL-97.[16a] In structures **1a** and **1b**, the refined absolute structure parameters [0.49(12) and 0.6(2)] were neither unity nor nil and were used as scaling parameters in the racemic twin refinement.[16b] Unless otherwise stated, the non-hydrogen atoms were refined anisotropically, hydrogen atoms were included at geometrically idealized positions but not refined; displacement ellipsoids are plotted at the 30% probability level, except for **9**, **10**·[LiOH(THF)]$_2$, and **11**·Li$_2$Se$_2$(THF)$_2$, which are at the 20% probability level.

Full details of the structure solutions and refinements are given in the Supporting Information. Brief comments on the treatment of disorder problems in various structures are included here.

The P and O atoms in **1b** were disordered over two sites with occupancy factors 0.923(3) and 0.077(3). The non-hydrogen atoms were refined anisotropically except for the smaller fractions of the P and O atoms, which were allowed isotropic displacement factors. The carbon atoms of one ^{t}Bu group [C(81), C(82), C(83)] in **4** were disordered over two sites with partial occupancy factors of 0.61(2) and 0.40(2). The carbon atoms of the THF molecule were also disordered over two positions with partial occupancy factors of 0.73-(1) and 0.27(1). The carbon atoms of a coordinating THF molecule in **7**, labeled C1−C4 and C1′−C4′, were disordered with partial occupancy factors of 0.5 each. The carbon atoms C27 and C39 from two different THF molecules in **10**·[LiOH(THF)]$_2$ were disordered over two sites each. Two carbon atoms of a THF solvent

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[14] The formula unit is assumed to contain four molecules of THF, on the basis of the integration of the ^{1}H NMR spectrum and CHN analyses.

[15] (a) For SIR-92, see: Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343. (b) For SHELXS-97, see: Sheldrick, G. M. *Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

[16] (a) For SHELXL-97, see: Sheldrick, G. M. *Program for the Refinement of Crystal Structures;* University of Göttingen: Göttingen, Germany, 1997. (b) Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908.

Table 1. Crystallographic Data for **1a**, **1b**, **3**, and **4**

	1a	**1b**	**3**	**4**
formula	$C_3H_{12}N_3OP$	$C_{12}H_{30}N_3OP$	$C_{18}H_{18}N_3PSe$	$C_{40}H_{95}Li_3N_9O_4P_3$
fw	137.13	263.36	386.28	879.89
space group	$P\bar{4}2_1c$	$P6_1$	$P2_1/n$	Pbca
a, Å	12.5497(2)	9.5570(2)	9.3044(2)	20.940(3)
b, Å	12.5497(2)	9.5570(2)	11.2562(2)	19.282(3)
c, Å	8.9196(3)	29.6910(8)	16.7247(4)	27.461(3)
α, °	90	90	90	90
β, °	90	90	104.7660(8)	90
γ, °	90	120	90	90
V, $Å_3$	1404.79(6)	2348.54(9)	1693.77(6)	11088(2)
Z	8	6	4	8
T, K	170(2)	173(2)	170(2)	193(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
d_{calcd}, g cm^{-3}	1.297	1.117	1.515	1.054
μ, mm^{-1}	0.31	0.17	2.31	0.149
F(000)	592	876	784	3872
R^a	0.030	0.049	0.028	0.0439
$R_w{}^b$	0.082	0.114	0.075	0.1250

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

Table 2. Crystallographic Data for **7**, **9**, **10**, **10**·[LiOH(THF)]$_2$, and **11**·Li_2Se_2(THF)$_2$

	7	**9**	**10**	**10·[LiOH(THF)]$_2$**	**11·Li_2Se_2(THF)$_2$**
formula	$C_{21}H_{54}Li_2N_7PS$	$C_{32}H_{70}Li_2N_6O_2P_2$	$C_{74}H_{112}Li_6N_6O_8P_2S_2$	$C_{49}H_{78}Li_4N_3O_8PS$	$C_{38}H_{55}Li_4N_3O_5PSe_2 \cdot 0.5C_4H_8O$
fw	481.62	646.76	1381.40	926.96	886.55
space group	P$\bar{1}$	Cm	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.687(1)	11.917(6)	15.33(1)	11.6036(3)	11.0786(5)
b, Å	12.393(2)	16.255(8)	16.88(2)	16.1164(3)	14.1834(7)
c, Å	14.357(2)	11.025(5)	18.71(3)	16.2421(5)	16.460(1)
α, °	86.402(3)	90	86.645(5)	64.238(1)	112.555(2)
β, °	75.281(2)	108.760(5)	73.522(4)	81.685(1)	100.183(2)
γ, °	71.642(3)	90	64.607(5)	73.172(1)	93.590(2)
V, Å^3	1581.9(4)	2022(2)	4181(7)	2617.8(1)	2326.5(2)
Z	2	2	2	2	2
T, K	193(2)	298(2)	173(2)	173(2)	170(2)
λ, Å	0.71073	0.71073	0.71073	0.71069	0.71073
d_{calcd}, g cm^{-3}	1.011	1.062	1.097	1.177	1.266
μ, mm^{-1}	0.172	0.140	0.153	0.140	1.67
F(000)	532	712	1484	998	918
R^a	0.0619	0.0422	0.1865	0.084	0.076
$R_w{}^b$	0.1634	0.1060	0.5145	0.269	0.221

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

molecule in **11**·Li_2Se_2(THF)$_2$ were disordered and allowed isotropic displacement parameters.

Results and Discussion

Synthesis and X-ray Structures of OP[N(H)R]$_3$ (1a, R = Me; 1b, R = ^{t}Bu). Tris(alkyl- or arylamido)orthophosphates have been known for over a century. In addition to OP(NHMe)$_3$ (**1a**)[9] and OP(NH^{t}Bu)$_3$ (**1b**),[10] the derivatives OP[N(H)R]$_3$ with R = H,[17] ^{n}Pr,[18] ^{i}Pr,[19] ^{n}Bu,[18] ^{sec}Bu,[19] ^{i}Bu,[20] cyclohexyl,[21] Ph,[21] Bz,[21] *o*-tol,[21] *m*-tol,[22] *p*-tol,[23,21] C_6H_4-OC_2H_5,[21] and $CH_2CH{=}CH_2$[24] have been prepared. The general synthetic methods involve reactions of phosphoryl chloride with an excess of primary amine either alone or in the presence of another HCl scavenger.

The main challenge in these reactions is the separation of the tris(amido)phosphate from the alkylammonium chloride byproduct. In the synthesis of **1a**, several steps, including aqueous workup and pH adjustment, are required to obtain the tris(amido)phosphate free of methylammonium chloride. The ^{t}Bu derivative **1b** not only requires sublimation to completely separate it from *tert*-butylammonium chloride, but it also more readily undergoes a thermal condensation reaction to produce a dimer.[25] In this work, the literature procedures have been refined to give improved yields of **1a** and **1b** (60 and 89%, respectively).

Recently, there has been growing interest in crystal engineering employing the subtle manipulation of hydrogen bonding in solid-state structures.[26] For example, Gong et al. have shown that *N,N′*-bis(alkyl or aryl)sulfamides O_2S-[N(H)R]$_2$ consist of two-dimensional hydrogen-bonded networks assembled through NH···O intermolecular inter-

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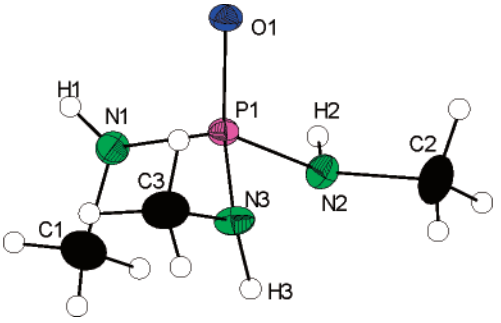

Figure 1. Molecular structure of a monomeric unit of OP[N(H)Me]$_3$ (**1a**).

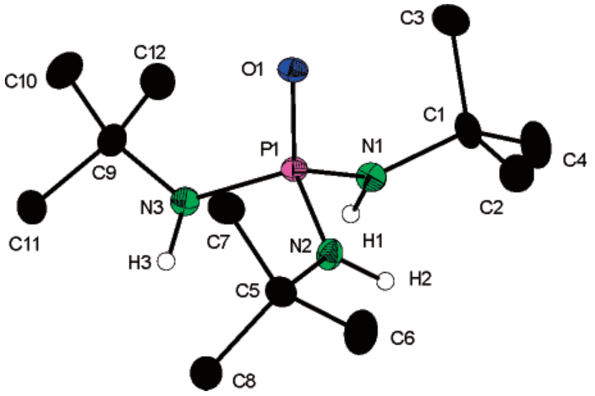

Figure 2. Molecular structure of a monomeric unit of OP[N(H)^{t}Bu]$_3$ (**1b**). Protons attached to methyl carbons have been omitted for clarity.

actions.[27] Of the numerous known tris(alkyl- or arylamido)phosphates, structures have been determined only for OP[N(H)R]$_3$ (R = H, *m*-tol, and *p*-tol). In the aryl derivatives, cocrystallization of donor solvents or arylammonium chloride precludes extended hydrogen-bonding networks.[22,23b] However, in the structure of phosphoric triamide, OP(NH$_2$)$_3$, all six of the hydrogen atoms take part in a three-dimensional network of NH···O and NH···N hydrogen bonding, with each oxygen atom participating in four hydrogen bonds.[17]

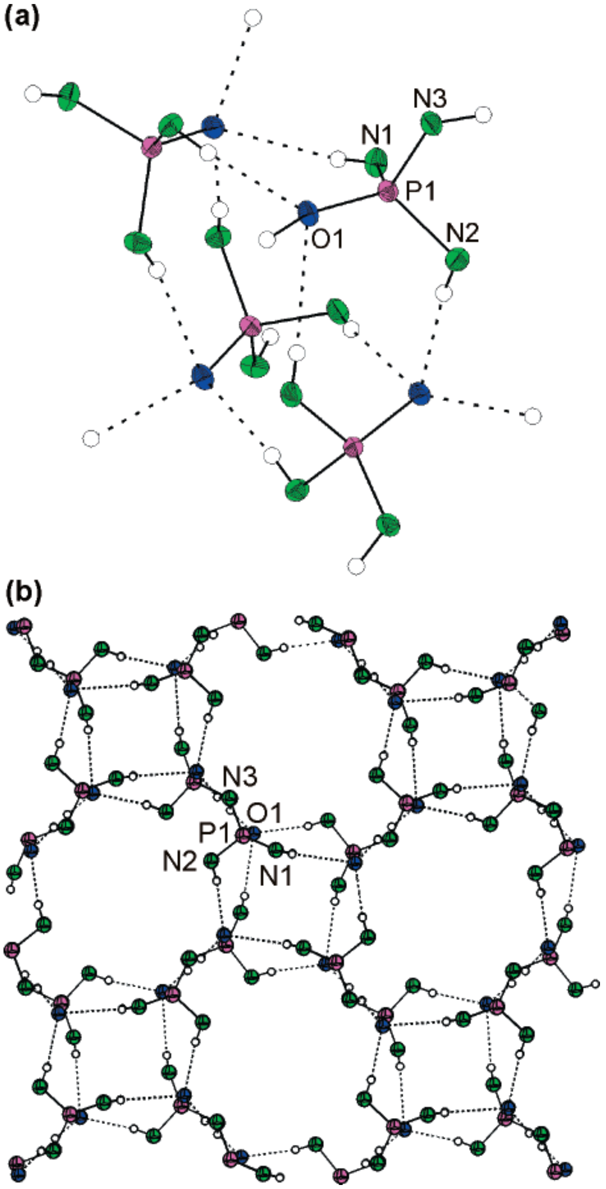

Figure 3. Molecular structure of {OP[N(H)Me]$_3$}$_n$ (**1a**) showing (a) the tetrameric building block and (b) part of the layer network composed of tetramers. For clarity, the methyl substituents have been omitted.

Because the tris(amido)phosphates have only one oxygen acceptor and three NHR groups, the impact on the hydrogen-bonding network of changing the R substituent might be more profound than that observed for *N*,*N′*-bis(alkyl- or arylamido)sulfamides. To investigate the structural influence of the R group, the X-ray structures of **1a** and **1b** were determined. The amido hydrogens of **1a** were refined isotropically, whereas those in the more highly disordered structure of **1b** were included at geometrically idealized positions and not refined. The monomeric units of **1a** and **1b** differ with respect to the orientation of the N(H)R groups (Figures 1 and 2). In **1b**, the N(H)^{t}Bu groups are arranged such that the N−H substituents all point in a similar direction away from the oxo ligand, whereas in **1a**, the N(H)Me groups are oriented randomly. This discrepancy presumably accommodates the steric repulsion between the ^{t}Bu substituents in **1b**. As a consequence, the NH···O hydrogen-bonded networks of **1a** and **1b** exhibit different motifs. The methyl derivative **1a** forms a three-dimensional network (Figure 3), whereas the *tert*-butyl derivative **1b** forms a one-dimensional array (Figure 4). There are also significant differences in the range of bond angles around the four-coordinate phosphorus centers: 101.31(8)−118.60(8)° in **1a** and 105.0(1)°−113.7(1)° in **1b**.

The basic building block in the three-dimensional network of **1a** is a tetramer (Figure 3a). All of the amido protons are involved in hydrogen bonding to oxygen atoms of three adjacent phosphates such that each oxygen atom is hydrogen-bonded to three amido protons of three different phosphate molecules. For comparison, the oxygen atoms in OP(NH$_2$)$_3$ are hydrogen-bonded to four amido protons from three different phosphate molecules.[17] Of the six intermolecular interactions per phosphate monomer in **1a**, four extend within the tetrameric cluster, and two link to other tetrameric units.

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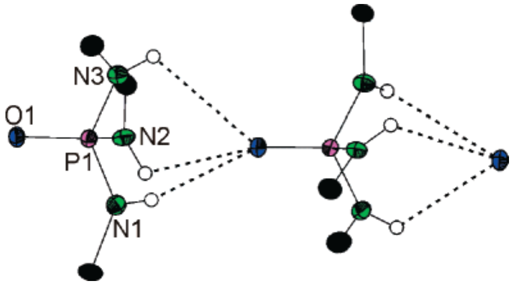

Figure 4. Molecular structure of $\{OP[N(H)^tBu]_3\}_n$ (**1b**) showing the one-dimensional hydrogen-bonding array. For clarity, only the α-carbons of the ^{t}Bu substituents are shown.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **1a** and **1b**

	1a	**1b**
P(1)−O(1)	1.4937(1)	1.474(3)
P(1)−N(1)	1.624(2)	1.638(2)
P(1)−N(2)	1.636(2)	1.638(3)
P(1)−N(3)	1.642(2)	1.635(2)
N(1)−H(1)	0.72(3)	
N(2)−H(2)	0.82(3)	
N(3)−H(3)	0.88(3)	
H(1)···O(1)[a]	2.54(3)	
H(2)···O(1)[a]	2.16(3)	
H(3)···O(1)[a]	2.14(3)	
N(1)···O(1)[a]	3.253(2)	3.159(4)
N(2)···O(1)[a]	2.970(2)	3.295(4)
N(3)···O(1)[a]	2.961(2)	3.255(4)
O(1)−P(1)−N(1)	108.65(8)	112.0(1)
O(1)−P(1)−N(2)	118.60(8)	113.7(1)
O(1)−P(1)−N(3)	110.99(8)	111.3(1)
N(1)−P(1)−N(2)	104.16(9)	105.0(1)
N(1)−P(1)−N(3)	113.0(1)	108.1(1)
N(2)−P(1)−N(3)	101.31(8)	106.4(1)
P(1)−N(1)−H(1)	124(2)	
P(1)−N(2)−H(2)	109(2)	
P(1)−N(3)−H(3)	119(2)	
N(1)−H(1)···O(1)[a]	170(3)	123.0
N(2)−H(2)···O(1)[a]	172(2)	93.4
N(3)−H(3)···O(1)[a]	154(2)	111.1

[a] O(1) is an equivalent oxygen atom of an adjacent molecule.

Figure 3b illustrates the extended structure generated by interactions between these tetramers.

The *tert*-butyl derivative **1b** forms a one-dimensional chain in which all three amido protons are hydrogen-bonded to the same oxygen atom of an adjacent phosphate molecule in a tripodal fashion. Compound **1b** belongs to a hexagonal space group with a 6-fold screw axis through the center of the structure. Thus, the tripodal phosphates are aligned in a staggered conformation. Although the increase in bulkiness of the R substituent significantly changes the mode of hydrogen bonding, it does not affect the number of hydrogen bonds per monomeric unit.

The strength of a hydrogen bond X−H···A (X = O, N) increases as the H···A and X···A distances decrease, as the X−H distance increases, and as the bond angle ∠ XHA approaches linearity (180°).[26] By these criteria, **1a** has more strongly hydrogen-bonded interactions than **1b** [d(O···H)| = 2.28 and 2.85 Å and d|N···O| = 3.061 and 3.236 Å for **1a** and **1b**, respectively; see Table 3]. However, the P−O bond distance of 1.494(1) Å in **1a** is only slightly longer than that in **1b**, d(P−O) = 1.474(3) Å [cf. 1.510 Å in $OP(NH_2)_3$, which has four O−H hydrogen bonds].[17] Although the hydrogen bonding is stronger, the range of N−O distances is greater in **1a** than that in **1b** [2.961(2)−3.253(2) Å, **1a**; 3.159(4)−3.295(4) Å, **1b**]. The N(3)···O(1) interaction, which links adjacent tetramers, has the shortest bond distance and the strongest hydrogen bonding.

Synthesis of $SP[N(H)R]_3$ (2a, R = ^{i}Pr; 2b, R = ^{t}Bu; 2c, R = *p*-tol) and X-ray Structure of $SeP[N(H)Ph]_3$ (3). Tris(amido)thiophosphates have also been known for many years. In 1903, Michaelis reported tris(ethylamido)thiophosphate, $SP[N(H)R]_3$ (R = Et).[28] Since then, numerous derivatives have been described with R = Me;[20] ^{n}Pr;[20] ^{n}Bu;[28] ^{i}Bu;[20] ^{sec}Bu;[11] Bz;[29] *cyclo*-pentyl;[11] *cyclo*-hexyl;[29] *o*-, *m*-tolyl;[13] *o*-, *m*-, *p*-C_6H_3OMe;[12] Ph;[29] 2,4-$C_6H_3F_2$;[30] 2,4-$C_6H_3Cl_2$;[30] and 2,4-$C_6H_3Me_2$.[30] The ^{i}Pr (**2a**),[11] ^{t}Bu (**2b**),[12] and *p*-tol (**2c**)[13] derivatives have also been previously synthesized, but only the ^{31}P NMR shifts were reported. The full characterization of **2a**−**c** is now presented.

The derivatives **2a**−**c** are prepared by treatment of $SPCl_3$ with the appropriate primary amine. The reaction of thiophosphoryl chloride with an excess of *iso*-propylamine in diethyl ether, however, generates both tris(*iso*-propylamido)thiophosphate (**2a**) and the condensation product *trans*-$[^iPrNH(S)P(\mu\text{-}N^iPr)_2P(S)NH^iPr]$ through loss of *iso*-propylamine. Sublimation at 90 °C produces pure **2a** in ca. 50% yield. By contrast, the ^{t}Bu and *p*-tol derivatives form a single product in yields of 80 and 42%, respectively.

The ^{1}H NMR spectra of **2a** and **2b** exhibit the expected ^{i}Pr and ^{t}Bu resonances, in addition to a resonance for the NH protons [δ 2.05 (br s) and 2.25 (d) for **2a** and **2b**, respectively]. The ^{1}H NMR spectrum of **2c** reveals proton resonances for the phenyl protons (δ 7.11−6.93) and the *para*-Me substituent (δ 2.20), but the resonance for the NH protons is not apparent. Although the latter might be obscured by the *para*-Me resonance, the integration and sharpness of the resonance at δ 2.20 suggest otherwise. The ^{31}P NMR spectra for all three compounds reveal singlets that are consistent with the literature values for **2a** and **2c**, but not for **2b**, for which δ ^{31}P 46.3 (in C_6D_6) (cf. 60.4 in $CHCl_3$).[12] This discrepancy in the chemical shifts is too large to be attributed to solvent effects.

As $SePCl_3$ is unknown, a different synthetic strategy must be employed for the synthesis of tris(amido)selenophosphates. Two tris(amido)selenophosphates have been reported. The reaction of phosphorus pentaselenide with *cyclo*-hexylamine generates $SeP[N(H)Cy]_3$ in 10% yield.[31] In a different approach, $SeP[N(H)CH_2CH_2]_3N$ is formed in the reaction of $\{HP[N(H)CH_2CH_2]_3N\}^+(OTf)^-$ with ^{n}BuLi, followed by the addition of red selenium.[32] In this work, $SeP[N(H)Ph]_3$ (**3**) was synthesized in 59% yield by the oxidation of $P[N(H)Ph]_3$[8] with elemental selenium in diethyl ether.

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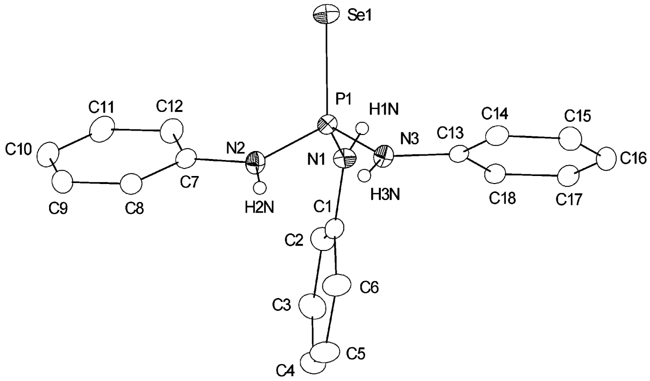

Figure 5. Molecular structure of $SeP[N(H)Ph]_3$ (**3**). Only the carbon atoms of the phenyl substituents are shown.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $SeP[N(H)Ph]_3$ (**3**)

Se(1)−P(1)	2.117(1)
P(1)−N(1)	1.647(2)
P(1)−N(2)	1.654(2)
P(1)−N(3)	1.671(2)
N(1)−P(1)−N(2)	107.92(9)
N(1)−P(1)−N(3)	109.91(8)
N(2)−P(1)−N(3)	97.52(8)
N(1)−P(1)−Se(1)	106.95(6)
N(2)−P(1)−Se(1)	117.94(6)
N(3)−P(1)−Se(1)	116.14(6)

Aniline was added to the reaction mixture to suppress the formation of the condensation product $(PhNH)_2P(\mu\text{-}NPh)P(NHPh)_2$. The ^1H NMR spectrum of **3** exhibits phenyl proton resonances between δ 7.27 and 6.80 and an NH resonance at δ 2.41. The ^{31}P NMR spectrum contains a singlet at δ 33.4, and the ^{77}Se NMR spectrum consists of a doublet centered at δ −205.0, both revealing $^1J(^{31}P-^{77}Se)$ coupling of 854 Hz.

X-ray-quality crystals of **3** were obtained from a diethyl ether/pentane solution, and the first X-ray structure of a tris(alkyl or arylamido)thio- or selenophosphate was determined. The molecular geometry and atomic numbering scheme of **3** are shown in Figure 5; pertinent structural parameters are summarized in Table 4. The P−Se distance of 2.117(1) Å is within the normal range of P−Se double-bond values.[33] The structure of tris(anilido)phosphine[8] can be compared with that of **3**. Two predictable changes occur on oxidation to **3**: the P−N bond lengths are shortened by approximately 0.04 Å, and the mean N−P−N bond angle is widened by ca. 6°. The difference in the P−N bond lengths can be attributed to the difference in covalent radii of P(III) vs P(V), while the larger N−P−N bond angle reflects the smaller repulsions of the electron pairs of the P═Se bond in **3** compared to a lone pair on a P(III) center.

Lithiation of $OP[N(H)^tBu]_3$ (1b). In the attempted preparation of a trilithium salt of $[OP(N^tBu)_3]^{3-}$, stepwise lithiation was investigated to provide a detailed picture of the processes involved. The reaction of **1b** with 1 equiv of ^nBuLi or $LiN(SiMe_3)_2$ generates the monolithium derivative $(THF)\{LiOP(N^tBu)[N(H)^tBu]_2\}_3$ (**4**) in 86% yield, while the treatment of **1b** with ≥2 equiv of ^nBuLi yields the dilithium salt $\{(THF)_2Li_2OP(N^tBu)_2[N(H)^tBu]\}_2$ (**5**) described previously.[1b]

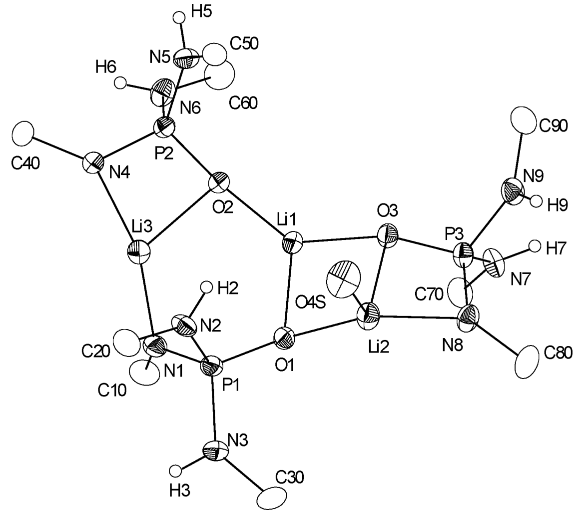

Figure 6. Molecular structure of $(THF)\{LiOP(N^tBu)[N(H)^tBu]_2\}_3$ (**4**). For clarity, only the α-carbons of the ^tBu substituents and oxygen atoms of the THF groups are shown.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**

P(1)−O(1)	1.517(2)	O(1)−Li(2)	1.890(5)
P(1)−N(1)	1.567(2)	N(8)−Li(2)	1.965(5)
P(1)−N(3)	1.654(3)	O(1)−Li(1)	1.992(5)
P(1)−N(2)	1.679(2)	O(2)−Li(1)	1.846(5)
P(2)−O(2)	1.518(2)	O(2)−Li(3)	2.095(5)
P(2)−N(4)	1.573(2)	O(3)−Li(1)	1.856(4)
P(2)−N(5)	1.651(2)	O(3)−Li(2)	2.134(5)
P(2)−N(6)	1.672(2)	N(1)−Li(3)	1.958(6)
P(3)−O(3)	1.512(2)	N(4)−Li(3)	1.964(6)
P(3)−N(8)	1.575(2)	Li(2)−O(4S)	2.045(6)
P(3)−N(7)	1.659(2)	Li(1)−N(1)	3.343(5)
P(3)−N(9)	1.661(2)		
O(1)−P(1)−N(1)	120.1(1)	O(2)−P(2)−N(6)	114.1(1)
O(1)−P(1)−N(3)	108.5(1)	N(4)−P(2)−N(6)	110.1(1)
N(1)−P(1)−N(3)	110.7(1)	N(5)−P(2)−N(6)	100.1(1)
O(1)−P(1)−N(2)	101.7(1)	O(3)−P(3)−N(8)	106.4(1)
N(1)−P(1)−N(2)	102.6(1)	O(3)−P(3)−N(7)	108.5(1)
N(3)−P(1)−N(2)	112.8(1)	N(8)−P(3)−N(7)	119.0(1)
O(2)−P(2)−N(4)	106.0(1)	O(3)−P(3)−N(9)	113.1(1)
O(2)−P(2)−N(5)	109.0(1)	N(8)−P(3)−N(9)	109.6(1)
N(4)−P(2)−N(5)	117.9(1)	N(7)−P(3)−N(9)	100.3(1)
P(1)−O(1)−Li(2)	147.2(2)	O(2)−Li(1)−O(1)	121.3(2)
P(1)−O(1)−Li(1)	116.0(2)	O(3)−Li(1)−O(1)	96.7(2)
Li(2)−O(1)−Li(1)	83.3(2)	N(1)−Li(3)−N(4)	147.8(3)
P(2)−O(2)−Li(1)	170.0(2)	N(1)−Li(3)−O(2)	114.6(2)
P(2)−O(2)−Li(3)	87.9(2)	N(4)−Li(3)−O(2)	74.9(2)
Li(1)−O(2)−Li(3)	99.8(2)	N(1)−Li(3)−N(2)	68.9(2)
P(3)−O(3)−Li(1)	161.3(2)	N(4)−Li(3)−N(2)	141.1(3)
P(3)−O(3)−Li(2)	87.5(2)	O(2)−Li(3)−N(2)	104.7(2)
Li(1)−O(3)−Li(2)	80.3(2)	O(1)−Li(2)−N(8)	139.6(3)
P(1)−N(1)−Li(3)	97.1(2)	O(1)−Li(2)−O(3)	91.0(2)
P(1)−N(2)−Li(3)	77.2(2)	N(8)−Li(2)−O(3)	74.0(2)
P(2)−N(4)−Li(3)	91.2(2)	O(1)−Li(2)−O(4S)	107.0(2)
P(3)−N(8)−Li(2)	92.0(2)	O(4S)−Li(2)−O(3)	112.7(3)
O(2)−Li(1)−O(3)	136.2(3)	N(8)−Li(2)−O(4S)	113.5(2)

The structure of **4** was determined by X-ray crystallography. The molecular geometry and atomic numbering scheme are shown in Figure 6; pertinent structural parameters are summarized in Table 5. The monolithium salt **4** has a trimeric structure consisting of a six-membered O−P−N−Li−O−Li ring in a boat conformation and three four-membered rings. The $[OP(N^tBu)(NH^tBu)_2]^-$ monoanions exhibit two different modes of coordination: two of them

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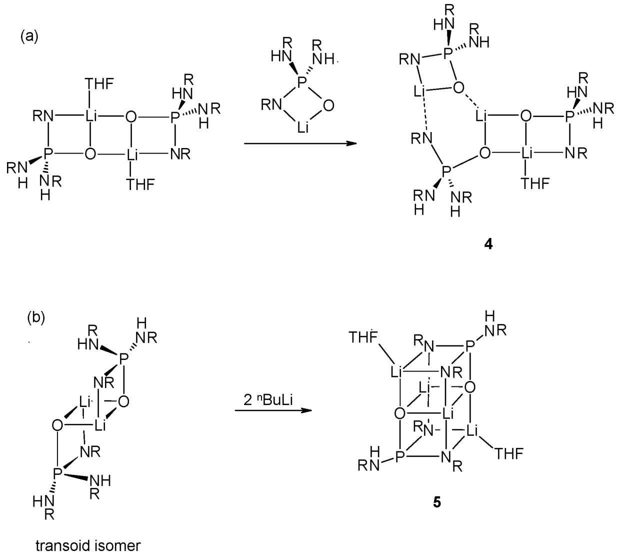
Scheme 1



coordinate one lithium ion by N, O coordination, while the third bridges two lithium ions. All three ligands coordinate to a second lithium ion through the oxygen atom. The lithium ions Li(1) and Li(3) are three-coordinate, whereas Li(2) is four-coordinate as a result of solvation by one THF molecule.

The mean endocyclic P−N distances in **4** are ca. 0.09 Å shorter than those involving the exocyclic NH^{t}Bu groups. The P−O distances are in the range 1.512(2)−1.518(2) Å [cf. 1.474(3) Å in **1b**]. The Li−N distances fall with the narrow range of 1.958(6)−1.965(5) Å, whereas the Li−O bond lengths span a wider range of 1.856(4)−2.134(5) Å [(cf. 1.91(1)−1.96(1) Å for the four-coordinate lithiums in the central Li_2O_2 ring of the tetramer, $\{Ph_2P(O)CH_2Li]_2(TMEDA)\}_2]$.[35]

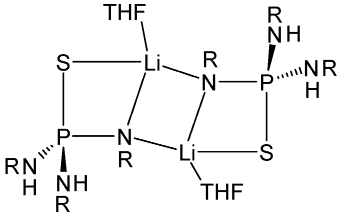
Lateral association to form Li_2O_2 rings and ladders is very common in lithium heterocarboxylates and related clusters.[36] The formation of the trimeric structure of **4** is surprising. It can be envisaged to result from insertion of a monomeric unit into one of the Li−N bonds of a centrosymmetric dimer (Scheme 1a). Apparently this process occurs in preference to the association of dimeric units to give a Li_4O_4 cubane or Li_6O_6 hexagonal prism, which has been observed for lithium derivatives of imido carboxylates.[37]

The NMR spectra of **4** reveal the formation of a symmetrical structure in solution. The ^{1}H NMR spectrum in d$_8$-THF at 23 °C exhibits two singlets, with relative intensities 2:1, in the N^{t}Bu region for the NH^{t}Bu and N^{t}Bu groups, respectively, and a single resonance for the NH protons, indicating a single environment for the $[OP(NH^tBu)_2(N^tBu)]^-$ ligand. Consistently, the ^{31}P NMR spectrum at 23 °C reveals a singlet at δ 5.8 in d$_8$-THF and a singlet at δ 2.7 in C_6D_6. However, at −100 °C, the ^{31}P NMR spectrum in d$_8$-THF exhibits three equally intense singlets at δ 7.0, 6.3, and 5.9, consistent with the X-ray structure, and several other minor resonances. As expected, the solid-state ^{31}P NMR spectrum of **4** also shows three singlets at δ 6.2, 4.0, and 3.3 with approximately equal intensities. Taken together, the NMR data indicate that a more symmetrical structure, e.g., a centrosymmetric dimer, predominates in solution at room temperature. A fluxional process for the trimer **4** might also account for the observation of a single ^{31}P NMR resonance in solution at 23 °C. However, a dimeric monolithiated complex is a plausible precursor for the box-shaped structure of **5** (Scheme 1b).

The use of an excess of organolithium reagent or benzylpotassium did not effect further metalation of **5**, even in boiling THF. Because arylamines have more acidic protons than their alkyl analogues, the lithiation of $OP[N(H)Ar]_3$ (Ar = aryl) should occur more readily than that of **1a** and **1b** and might provide a source of the trianions $\{OP[NAr]_3\}^{3-}$. Consequently, we prepared OP[N(H)*p*-tol]$_3$ by the literature procedure,[22,23] but we were unable to completely remove the byproduct [*p*-tolNH$_3$]Cl. Significantly, the crystal structure of OP[N(H)*m*-tol]$_3$ contains a molecule of hydrogen-bonded [*m*-tolNH$_3$]Cl.[22] We note, however, that the use of aryl derivatives was successful for the generation of $[EP(NAr)_3]^{3-}$ (E = S, Se) (vide infra).

Lithiation of SP[N(H)^{i}Pr]$_3$ (2a) and SP[N(H)^{t}Bu]$_3$ (2b). The reaction of SP[N(H)^{i}Pr]$_3$ (**2a**) with ^{n}BuLi in a 1:1 molar ratio in THF produces the monolithiated derivative {(THF){LiSP(N^{i}Pr)[N(H)^{i}Pr]$_2$}$_2$ (**6**) in 61% yield. The ^{31}P NMR spectrum of **6** in C_6D_6 showed a singlet at δ 47.9 (cf. δ 56.3 for **2a**). When the same reaction is carried out in a 1:2 molar ratio in THF an insoluble product is formed. In the presence of TMEDA, however, this reaction produces the dilithiated complex {[(TMEDA)Li$_2$]SP(N^{i}Pr)$_2$[N(H)^{i}Pr]}$_2$ (**7**) in 56% yield.[1c] Solid-state ^{7}Li and ^{31}P NMR spectra of **7** consist of singlets at δ 1.9 and 45.7, respectively. Attempts to form a trilithium salt were unsuccessful.

The X-ray structure of **6** was described previously.[1c] It consists of a centrosymmetric dimer composed of a step-shaped ladder in the transoid conformation. Aggregation of the two monoanions occurs through the more polar Li−N edges rather than the sterically unencumbered Li−S edges.



6, R = ^{i}Pr

The molecular geometry and atomic numbering scheme of **7** are shown in Figure 7; pertinent structural parameters are summarized in Table 6. Complex **7** has a monomeric

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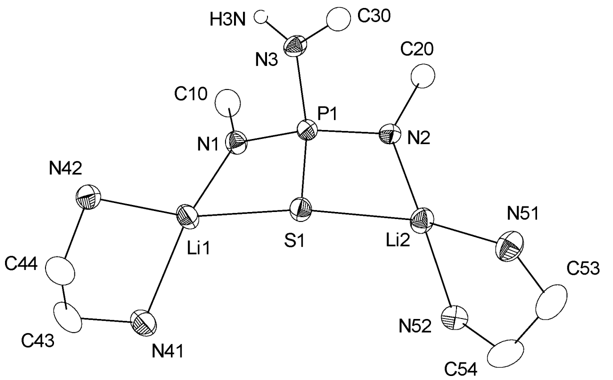


Figure 7. Molecular structure of $\{[(\mathrm{TMEDA})\mathrm{Li}]_2[\mathrm{SP(N^iPr)_2(NH^iPr)}]\}$ (**7**). Only the secondary carbon atoms of the ^{i}Pr groups and the backbone carbon and nitrogen atoms of the TMEDA molecules are shown for clarity.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for **7**

S(1)−P(1)	2.054(1)	N(1)−Li(1)	1.930(6)
S(1)−Li(1)	2.461(5)	N(2)−Li(2)	1.939(6)
S(1)−Li(2)	2.462(5)	N(41)−Li(1)	2.146(6)
P(1)−N(1)	1.609(3)	N(42)−Li(1)	2.142(6)
P(1)−N(2)	1.611(2)	N(51)−Li(2)	2.152(6)
P(1)−N(3)	1.699(3)	N(52)−Li(2)	2.128(7)

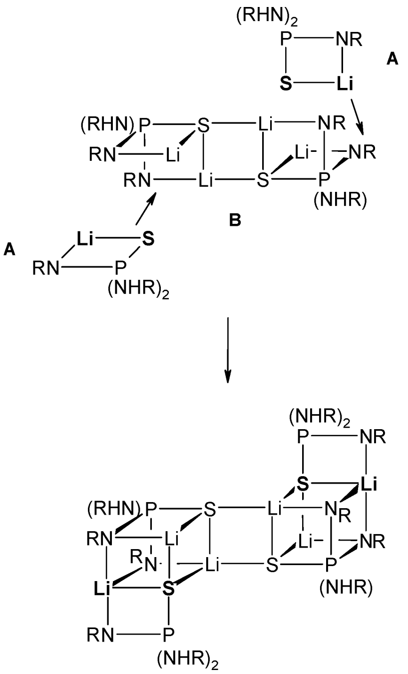
P(1)−S(1)−Li(1)	73.3(1)	N(42)−Li(1)−N(41)	85.3(2)
P(1)−S(1)−Li(2)	73.4(1)	N(52)−Li(2)−N(51)	84.3(2)
Li(1)−S(1)−Li(2)	122.0(2)	N(1)−Li(1)−N(42)	122.6(3)
N(1)−P(1)−N(2)	124.4(1)	N(1)−Li(1)−N(41)	136.8(3)
N(1)−P(1)−N(3)	104.9 (1)	N(42)−Li(1)−S(1)	115.9(2)
N(2)−P(1)−N(3)	107.2(1)	N(41)−Li(1)−S(1)	117.3(3)
N(1)−P(1)−S(1)	104.4 (1)	N(2)−Li(2)−N(52)	123.5(3)
N(2)−P(1)−S(1)	104.6 (1)	N(2)−Li(2)−N(51)	135.2(3)
N(3)−P(1)−S(1)	111.2(1)	N(52)−Li(2)−S(1)	121.3(3)
P(1)−N(1)−Li(1)	99.7(2)	N(51)−Li(2)−S(1)	115.2(2)
P(1)−N(2)−Li(2)	99.5(2)		

structure that contains the dianion $[\mathrm{SP(N^iPr)_2(NH^iPr)}]^{2-}$. Apparently, chelation of $\mathrm{Li^+}$ ions by a TMEDA ligand prevents extensive laddering via Li−N interactions (cf. $\{[p\text{-}\mathrm{CH_3C_6H_4N(H)Li{\cdot}TMEDA}]_2\}$).[7] An unsolvated one-dimensional polymer that aggregates via Li−N edges, in a manner similar to that of **6**, might account for the insolubility of the product obtained in the absence of TMEDA.

The P−S bond length for the three-coordinate sulfur center in **7** is 2.054(1) Å [cf. 1.9927(8) Å for the two-coordinate sulfur center in **6**]; the mean P−N distances for the coordinated imido groups are 1.610 Å for both the three- and four-coordinate nitrogen centers in **6** and **7**. The mean Li−N distances in **7** are 1.930(6) Å, whereas in the dimer **6**, they are 2.129(4) Å for the LiNPS ring and 2.104(4) Å for edge-to-edge dimerization. This difference can be attributed to the different coordination numbers of the nitrogen atoms. By contrast, the Li−S distances are longer in **6** [2.526(4) Å] than in **7** [2.462(5) Å], even though the sulfur centers are two- and three-coordinate, respectively. This might be due, in part, to the difference in anionic charges and the delocalization of those charges. In both complexes, the $\mathrm{Li^+}$ ions achieve a four-coordinate environment through bonding to either THF or TMEDA.

The reaction of $\mathrm{SP[N(H)^tBu]_3}$ with ^{n}BuLi or $\mathrm{LiN(SiMe_3)_2}$ in THF in a 2:3 molar ratio produces the complex $\{[\mathrm{LiSP(N^tBu)(NH^tBu)_2}][(\mathrm{THF})\mathrm{Li_2SP(N^tBu)_2(NH^tBu)}]\}_2$ (**8**) in an optimum yield of 82%. In contrast to the Li−N interactions observed for the *iso*-propyl derivative **6**, an X-ray analysis showed **8** to be a dimer in which the central feature is a cisoid $\mathrm{Li_4S_4}$ ladder (see Scheme 2).[1c] There is a crystallographic 2-fold axis through the middle of the central $\mathrm{Li_2S_2}$ ring. The asymmetric unit of **8** is comprised of an aggregate of the mono- and dilithiated derivatives, $\mathrm{LiSP(N^tBu)(NH^tBu)_2}$ and $\mathrm{Li_2SP(N^tBu)_2(NH^tBu)}$, respectively, linked by Li−S and Li−N bonds to give a distorted $\mathrm{Li_3PS_2N_2}$ cube.

Scheme 2



8, R = ^{t}Bu

The *iso*-propyl substituents in **6** are presumably small enough to allow association to occur via Li−N rather than the sterically unencumbered Li−S edges. For comparison, we note that lithium thioamidates $\{\mathrm{Li[RC(S)NR']}\}_n$ (R = ^{n}Bu, ^{t}Bu; R′ = ^{t}Bu) invariably aggregate through Li−S bonds.[31] Apparently, the influence of steric effects on the aggregation process is quite subtle for these imido thiophosphate systems.

Complex **8** is also generated when the reaction of **2b** with ^{n}BuLi is carried out in a 1:1 molar ratio, suggesting that the production of **8** is favored in the lithiation process. The formation of **8** can be envisaged to occur by the aggregation of two monolithiated monomers **A** and a centrosymmetric dilithiated dimer **B** via Li−S interactions (Scheme 2). In contrast to the behavior of the ^{i}Pr system, however, the use of a 1:2 molar ratio for the reaction of $\mathrm{SP[N(H)^tBu]_3}$ with ^{n}BuLi results in sulfur extrusion (as $\mathrm{LiS^nBu}$) to give the complex $\{(\mathrm{THF})\mathrm{Li[(^tBuN)_2P(\mu\text{-}N^tBu)_2P(N^tBu)_2]Li(THF)}\}$ (**9**) in ca. 15% yield. An X-ray analysis revealed that **9** is a $\mathrm{Li_2N_4P_2}$ cubane with exocyclic $\mathrm{N^tBu}$ groups attached to P, i.e., the dimeric lithium derivative of the tris(imido)metaphosphate anion $[\mathrm{P(N^tBu)_3}]^-$ (Figure 8). Pertinent structural parameters are summarized in Table 7. The mean P−N bond distances in the cubane **9** have three distinct values: 1.733(4) Å within the $\mathrm{P_2N_2}$ ring, 1.647(6) Å for the link between $\mathrm{P_2N_2}$ and $\mathrm{Li_2N_2}$ rings, and 1.526(6) Å for the exocyclic P−N bonds. In the $\mathrm{Li_2N_2}$ ring, $|d(\mathrm{Li{-}N})| = 2.11$-

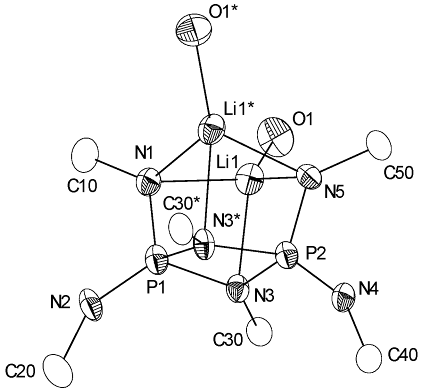


Figure 8. Molecular structure of {(THF)Li[(^{t}BuN)$_2$P(μ-N^{t}Bu)$_2$P(N^{t}Bu)$_2$]Li(THF)} (**9**). Only the α-carbon atoms of the ^{t}Bu groups and the oxygen atoms of the THF molecules are shown.

Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) for **9**

P(1)−N(2)	1.527(6)	P(2)−N(3)^a	1.734(4)
P(1)−N(1)	1.649(6)	P(2)−N(3)	1.734(4)
P(1)−N(3)	1.731(4)	N(1)−Li(1)	2.10(1)
P(1)−N(3)^a	1.731(4)	N(1)−Li(1)^a	2.10(1)
P(2)−N(4)	1.524(6)	N(3)−Li(1)	2.33(1)
P(2)−N(5)	1.644(5)	N(5)−Li(1)^a	2.120(9)
		N(5)−Li(1)	2.120(9)
N(5)−Li(1)−N(3)	73.5(3)	N(5)−P(2)−N(3)	104.3(2)
N(2)−P(1)−N(1)	114.9(3)	N(3)^a−P(2)−N(3)	80.9(3)
N(1)−Li(1)−N(3)	73.8(3)	P(1)−N(1)−Li(1)	95.7(3)
N(2)−P(1)−N(3)	123.3(2)	P(1)−N(1)−Li(1)^a	95.7(3)
N(1)−P(1)−N(3)	104.3(2)	Li(1)−N(1)−Li(1)^a	73.8(5)
N(2)−P(1)−N(3)^a	123.3(2)	P(1)−N(3)−P(2)	97.7(2)
N(1)−P(1)−N(3)^a	104.3(2)	P(1)−N(3)−Li(1)	85.9(3)
N(3)−P(1)−N(3)^a	81.0(3)	P(2)−N(3)−Li(1)	86.2(3)
N(4)−P(2)−N(5)	116.1(3)	P(2)−N(5)−Li(1)^a	95.7(3)
N(4)−P(2)−N(3)^a	122.5(2)	P(2)−N(5)−Li(1)	95.7(3)
N(5)−P(2)−N(3)^a	104.3(2)	Li(1)^a−N(5)−Li(1)	73.2(5)
N(4)−P(2)−N(3)	122.5(2)	N(1)−Li(1)−N(5)	99.4(4)

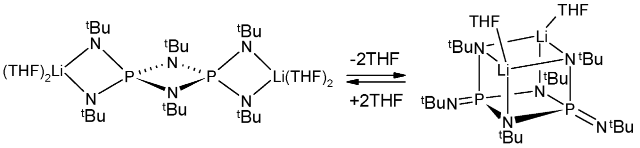
^{a} Symmetry transformations used to generate equivalent atoms: *x*, −*y*, *z*.

(1) Å, whereas the Li−N distance connecting the Li_2N_2 and P_2N_2 rings is longer [2.33(1) Å].

Monomeric analogues of **9**, e.g., the ion-separated complex $[Li(THF)_4]^+$ $[P(NMes^*)_3]^-$, have been reported,[38] but **9** is the first example of a dimeric tris(imido)metaphosphate as its lithium salt. The P(III) analogue {(THF)Li[(^{t}BuN)P(μ-N^{t}Bu)$_2$P(N^{t}Bu)]Li(THF)} also has a cubane structure,[39] which, in the absence of THF ligands, dimerizes via Li−N interactions.[40]

The ^{1}H NMR spectrum in d$_8$-THF at 23 °C contains two resonances at δ 1.28 and 1.53 in a 2:1 ratio in the N^{t}Bu region instead of the expected 1:1:1 ratio. This observation can be attributed to the formation of the bis-spirocyclic complex **9′** in solution at 23 °C through coordination of a second THF molecule to the Li$^+$ ions (Scheme 3). This type of ring-opening has been observed in structurally related rhenium complexes in which the ligands are CO instead of THF molecules.[41] At −50 °C, the resonances at δ 1.28 and 1.53 are still predominant, but new resonances at δ 1.24, 1.27, and 1.49 (1:1:1), attributable to **9**, are evident. At −100 °C, the latter resonances dominate over those of **9′**. These changes in the NMR spectra are reversible. The ^{31}P NMR spectra show a singlet at δ −18.9 through the temperature range from 23 to −100 °C, suggesting that the phosphorus environments of **9** and **9′** cannot be distinguished. The solid-state ^{31}P NMR spectrum of **9** shows a singlet at δ −20.3.

Scheme 3



9′ **9**

Lithiation of Tris(arylamido)thio- and -selenophosphates EP[N(H)R]$_3$ (2c, E = S, R = *p*-tol; 3, E = Se, R = Ph). In contrast to the incomplete lithiation of **2a** and **2b**, the trianion [SP(N*p*-tol)$_3$]$^{3-}$ can be generated by treatment of **2c** with 3 equiv of ^{n}BuLi to give {Li$_3$[SP(N*p*-tol)$_3$]} (**10**) in ca. 80% yield. The corresponding reaction with SeP[N(H)Ph]$_3$ (**3**) produces the trilithium salt {Li$_3$[SeP(NPh)$_3$]}$_2$ **11** in 75% yield. In the syntheses of **10** and **11**, the minor products **10**·[LiOH(THF)]$_2$ and **11**·$Li_2Se_2(THF)_2$, respectively, were also isolated and characterized by X-ray crystallography.

Compounds **10** and **11** represent the first examples of tris(imido)thio- or -selenophosphate trianions. Although crystals of **10** were weakly diffracting and the disorder of the THF solvent molecules resulted in a poorly refined structure, the atom connectivity was established. The central feature of the structure is a $PN_2S_2Li_3$ cube (cf. **8**) in which one of the Li−S edges exhibits a very weak interaction. The two [SP(N*p*-tol)$_3$]$^{3-}$ trianions in **10** display different coordination modes to the Li$^+$ ions. One of the trianionic ligands coordinates to three of the Li$^+$ ions in an (*N*, *S*) fashion and to a fourth Li$^+$ ion via (*N*, *N′*) chelation. The other ligand displays both (*N*, *S*) and (*N*, *N′*) coordination to different Li$^+$ ions. This ligand also interacts via the sulfur atom with two other Li$^+$ ions, as well as through a nitrogen atom with one additional Li$^+$ ion. Three of the nitrogen atoms in **10** are four-coordinate and the other three are three-coordinate; both of the sulfur centers are four-coordinate. The dimeric complex contains eight molecules of THF that solvate six Li$^+$ cations. All six of the Li$^+$ ions are four-coordinate; two are solvated by two terminal THF ligands, two are solvated by one THF ligand, one is solvated by both a bridging and a terminal THF ligand, and one is only solvated only by a bridging THF ligand.

In a preliminary experiment, a few X-ray-quality crystals of **10**·[LiOH(THF)]$_2$ were grown from THF solution at −15 °C. This complex has a centrosymmetric dimeric structure in which the four Li$^+$ ions of each monomeric unit are solvated by five THF molecules (see Figure 9). Two molecules of LiOH reside in the middle of the structure, forming a Li_2O_2 ring that links two {SP[N(H)*p*-tol]$_3$}$^{3-}$

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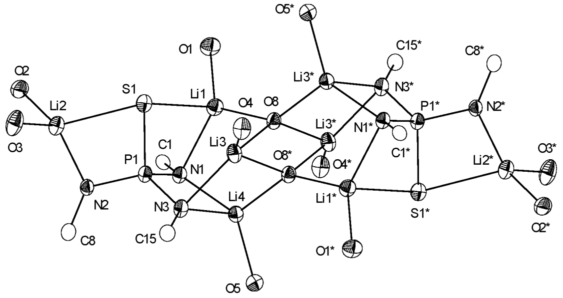
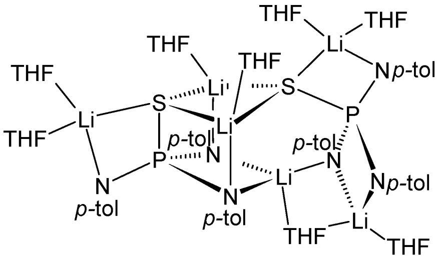


Figure 9. X-ray structure of {$(THF)_4Li_3[SP(Np\text{-tol})_3]\cdot[(THF)LiOH]$}$_2$ {**10**·$[LiOH(THF)]_2$}. Only the ipso carbons of the *p*-tol groups and oxygen atoms of the THF molecules are shown for clarity.



10

anions. The structure contains an eight-rung S-shaped ladder in which the outer rungs are the Li(1)−S(1) and Li(1)*−S(1)*. Two of the three Li^+ ions are chelated in an (*N*, *S*) fashion while the third is (*N*, *N′*)-coordinated by the $[SP(Np\text{-tol})_3]^{3-}$ trianions. This coordination mode, which involves three-coordinate sulfur atoms, differs from those of the trianions in **10**.

The P−S bond length in **10**·$[LiOH(THF)]_2$ is 2.066(2) Å, as indicated in Table 8 [cf. 2.054(1) Å in **7**]. There are two types of P−N bonds, involving three- and four-coordinate nitrogen atoms, N(2) and N(1)/N(3), respectively. The P−N(2) bond length is 1.618(3) Å, whereas the P−N(1) and P−N(3) bond lengths are 1.639(4) and 1.652(3) Å. There are three types of Li−N bonds with mean distances of ca. 1.98, 2.05, and 2.14 Å corresponding to those involving (a) three-coordinate nitrogen atoms, (b) four-coordinate nitrogen atoms not bonded to LiOH, and (c) four-coordinate nitrogen atoms bonded to LiOH, respectively. The Li−O distances are typical of other complexes containing LiOH [$|d(\mathrm{Li{-}O})| = 1.953$ Å; range 1.931(6)−1.970(6) Å (solvent contacts excluded)].[42]

Table 8. Selected Bond Lengths (Å) and Bond Angles (deg) for **10**·$[LiOH(THF)]_2$

S(1)−P(1)	2.066(2)	Li(1)−O(8)	1.944(7)
S(1)−Li(2)	2.458(5)	Li(2)−N(2)	1.976(8)
S(1)−Li(1)	2.532(5)	Li(3)−O(8)^a	1.931(6)
S(1)−Li(3)	2.891(7)	Li(3)−O(8)	1.970(6)
P(1)−N(2)	1.618(3)	Li(3)−N(3)	2.158(6)
P(1)−N(3)	1.639(4)	Li(4)−O(8)^a	1.967(6)
P(1)−N(1)	1.652(3)	Li(4)−N(3)	2.046(6)
Li(1)−N(1)	2.130(7)	Li(4)−N(1)	2.063(8)

P(1)−S(1)−Li(2)	75.6(2)	P(1)−N(1)−Li(4)	93.8(2)
P(1)−S(1)−Li(1)	73.2(2)	P(1)−N(1)−Li(1)	93.2(2)
Li(2)−S(1)−Li(1)	131.6(2)	Li(4)−N(1)−Li(1)	90.8(3)
P(1)−S(1)−Li(3)	69.5(1)	N(1)−Li(1)−S(1)	80.8(2)
Li(2)−S(1)−Li(3)	136.4(2)	P(1)−N(2)−Li(2)	101.3(2)
Li(1)−S(1)−Li(3)	60.5(2)	P(1)−N(3)−Li(4)	94.8(2)
N(2)−P(1)−N(3)	119.2(2)	P(1)−N(3)−Li(3)	98.9(2)
N(2)−P(1)−N(1)	119.6(1)	Li(4)−N(3)−Li(3)	75.4(3)
N(3)−P(1)−N(1)	97.2(1)	N(2)−Li(2)−S(1)	80.5(2)
N(2)−P(1)−S(1)	102.6(1)	N(3)−Li(3)−S(1)	112.0(2)
N(3)−P(1)−S(1)	108.9(1)	Li(3)^a−O(8)−Li(1)^a	90.4(3)
N(1)−P(1)−S(1)	109.1(1)	O(8)−Li(4)−N(3)	102.1(3)
Li(3)^a−O(8)−Li(3)	134.1(3)	Li(3)^a−O(8)−Li(4)	111.7(3)
Li(1)^a−O(8)−Li(3)	110.6(3)	Li(1)^a−O(8)−Li(4)	135.7(3)
O(8)−Li(4)−N(1)	115.9(3)	Li(3)−O(8)−Li(4)	81.6(3)
N(3)−Li(4)−N(1)	73.8(2)		

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z$.

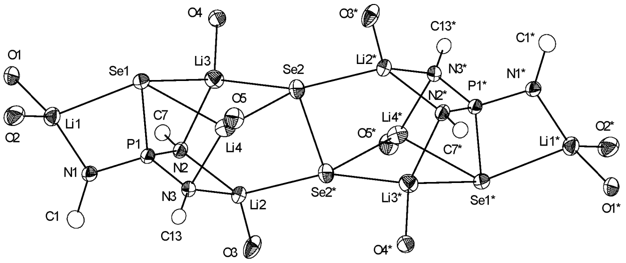


Figure 10. X-ray structure of {$(THF)_4Li_3[SeP(NPh)_3]\cdot[(THF)LiSe]$}$_2$ {**11**·$Li_2Se_2(THF)_2$}. Only the ipso carbons of the phenyl groups and oxygen atoms of the THF molecules are shown for clarity.

The solid-state ^{31}P NMR spectrum of **10** exhibits two resonances at δ 35.2 and 33.4 consistent with the X-ray structure. The solution NMR spectra in d_8-THF of both crystals and amorphous solid suggest a complex of higher symmetry than that observed in the solid state. The ^1H NMR spectrum shows only one *para*-methyl resonance. The solution ^{31}P NMR spectrum contains a singlet at δ 36.4 (cf. δ 44.5 in **2c**). The IR spectrum of **10** does not exhibit an O−H stretch [cf. ν(OH) 3677 cm^{-1} for {$(Li[(^nBu)C(N^t\text{-}Bu)_2])_2\cdot LiOH\cdot THF$}$_2$].[42] The ^7Li NMR spectrum of **10** exhibits a singlet in the solid state. Apparently, the significantly different environments of the four Li^+ ions are not distinguishable. The LiOH-containing complex **10**·$[LiOH(THF)]_2$ was isolated as a minor product in one synthesis of **10**. As for other LiOH complexes,[42] it is presumably formed by partial hydrolysis during the recrystallization process.

The structure of **11**·$Li_2Se_2(THF)_2$ (Figure 10) resembles that of **10**·$[LiOH(THF)]_2$. However, it contains an acyclic LiSeSeLi molecule rather than the cyclic dimer $(LiOH)_2$, and the selenium atoms are four-coordinate, whereas the sulfur atoms in the latter are three-coordinate. The coordination mode of the $[SeP(NPh)_3]^{3-}$ trianion is analogous to that of one of the $[SP(Np\text{-tol})_3]^{3-}$ trianions in **10**. It is involved in (*N*, *Se*) coordination to three Li^+ ions and (*N*, *N′*) coordination to the fourth Li^+ ion. The overall extent of THF solvation is the same as that in **10**·$[LiOH(THF)]_2$, i.e., a terminal bis-solvated Li^+ ion and three monosolvated Li^+ ions. Although dilithium diselenide, Li_2Se_2, has been used as a reagent in a variety of interesting chemistry,[43] it has not been structurally characterized. Attempts to crystallize Li_2Se_2 by using strongly coordinating ligands resulted in the isolation of the $Li_2Se_5(pmdeta)_2$ and the formation of a lithium mirror.[44] To the best of our knowledge, **11**·$Li_2Se_2(THF)_2$ is the first structurally characterized complex incorporating dilithium diselenide.

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Table 9. Selected Bond Lengths (Å) and Bond Angles (deg) for **11**·$Li_2Se_2(THF)_2$

Se(1)−P(1)	2.225(3)	P(1)−N(1)	1.627(6)
Se(1)−Li(1)	2.59(1)	P(1)−N(2)	1.635(7)
Se(1)−Li(3)	2.66(2)	P(1)−N(3)	1.636(7)
Se(1)−Li(4)	2.71(2)	Li(2)−Se(2)[a]	2.62(1)
Se(2)−Se(2)[a]	2.388(2)	N(2)−Li(2)	2.08(2)
Se(2)−Li(4)	2.56(1)	N(2)−Li(3)	2.16(2)
Se(2)−Li(3)	2.59(2)	N(3)−Li(2)	2.06(2)
Se(2)−Li(2)[a]	2.62(1)	N(3)−Li(4)	2.15(2)

P(1)−Se(1)−Li(1)	71.5(3)	N(1)−P(1)−N(3)	121.0(4)
P(1)−Se(1)−Li(3)	70.6(3)	N(2)−P(1)−N(3)	97.5(3)
Li(1)−Se(1)−Li(3)	125.8(4)	N(1)−P(1)−Se(1)	102.4(3)
P(1)−Se(1)−Li(4)	70.3(3)	N(2)−P(1)−Se(1)	108.3(3)
Li(1)−Se(1)−Li(4)	129.9(5)	N(3)−P(1)−Se(1)	108.2(3)
Li(3)−Se(1)−Li(4)	67.8(5)	N(3)−P(1)−Li(3)	97.2(4)
Se(2)[a]−Se(2)−Li(4)	84.1(4)	N(3)−Li(2)−N(2)	123.0(5)
Se(2)[a]−Se(2)−Li(3)	110.4(3)	N(3)−Li(2)−Se(2)[a]	105.1(6)
Li(4)−Se(2)−Li(3)	71.2(5)	N(2)−Li(2)−Se(2)[a]	132.2(7)
Se(2)[a]−Se(2)−Li(2)[a]	86.3(3)	N(2)−Li(3)−Se(1)	80.8(5)
Li(4)−Se(2)−Li(2)[a]	122.7(5)	N(1)−Li(1)−Se(1)	82.2(6)
Li(3)−Se(2)−Li(2)[a]	160.3(5)	Se(2)−Li(3)−Se(1)	105.9(5)
N(1)−P(1)−N(2)	118.9(3)	P(1)−N(1)−Li(1)	103.9(5)

[a] Symmetry transformations used to generate equivalent atoms: $-x, -y + 1, -z + 1$.

The P−Se distance in **11**·$Li_2Se_2(THF)_2$ is elongated to 2.225(3) Å upon trilithiation, as indicated in Table 9 [cf. 2.117(1) Å in **3**]. The mean P−N distance is ca. 0.03 Å shorter than that observed in **3**. The Se−Se distance of 2.388(2) Å is significantly longer than those observed in $Li_2Se_5(pmdeta)_2$ [$|d(Se-Se)| = 2.331$ Å with a range of 2.307(2)−2.360(2) Å].[44] The Li−Se distances in the pentaselenide are 2.56(1) and 2.62(1) Å, comparable to those observed in **11**·$Li_2Se_2(THF)_2$ [2.56(1)−2.62(1) Å]. The mean Li−Se−Se angle in **11**·$Li_2Se_2(THF)_2$ is 93.6° with a range of 84.1−110.4°, significantly smaller than the corresponding bond angle of $Li_2Se_5(pmdeta)_2$ [mean = 109.1°, range = 100.4(3)−117.7(3)°].[44]

The ^{31}P NMR spectrum of **11** in d_8-THF at 23 °C reveals a broad singlet at δ 21.4 ($\Delta w_{1/2} = 500$ Hz), whereas the solid-state ^{31}P NMR spectrum contains two resonances at δ 23.3 and 21.3 (cf. δ 35.2 and 33.4 for **10**). The ^{77}Se NMR spectrum of **11** in d_8-THF at −80 °C exhibits a doublet at δ −59.1 with $^1J(^{31}P-^{77}Se) = 459$ Hz (cf. δ −205.0 and 853 Hz for **3**). No ^{77}Se resonance attributable to the Li_2Se_2 complex was observed.[45] The solution ^7Li NMR spectrum of **11** exhibits a singlet at δ 0.65. In summary, the NMR evidence and elemental analyses (CHN) indicate that **11** is the major product of the reaction of $SeP[N(H)Ph]_3$ with 3 equiv of ^nBuLi. Attempts to grow X-ray-quality crystals of **11** were unsuccessful, but the solid-state NMR spectrum indicates a structure similar to that of the sulfur analogue **10**. The Li_2Se_2 complex is a minor product presumably formed by P═Se bond cleavage at room temperature, a process that was observed previously in the lithiation of $^tBuNH(Se)P(\mu\text{-}N^tBu)_2P(Se)NH^tBu$.[2d] This side reaction can be minimized by carrying out the lithiation at lower temperatures.

Conclusions

The tris(alkylamido)phosphates $OP[N(H)Me]_3$ (**1a**) and $OP[N(H)^tBu]_3$ (**1b**) have solid-state structures that exhibit a three-dimensional network and a one-dimensional array, respectively. Lithiation of **1a** and **1b** with ^nBuLi is limited to the formation of mono- and dilithiated products. Investigations of the reactions of the sulfur analogues, $SP[N(H)R]_3$, with ^nBuLi have provided important insights regarding the generation of heteroleptic imidothiophosphates. For the alkyl derivatives, only mono- or dilithiation is observed, and in the case of R = ^tBu, further lithiation results in P−S bond cleavage. However, trilithiation can be achieved for the triaryl derivatives $EP[N(H)Ar]_3$ (E = S, Se).

In summary, anions of the type $\{EP(NR)[N(H)R]_2\}^-$, $\{EP(NR)_2[N(H)R]\}^{2-}$ (E = O, S; R = alkyl), and $[EP(NAr)_3]^{3-}$ (E = S, Se) are readily generated by the lithiation of tris(alkyl or arylamido)chalcogenidophosphates with the appropriate amounts of ^nBuLi. The ligand behavior of these novel polydentate anions, which have both hard and soft donor centers, toward both main-group and transition-metal ions awaits investigation.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1a**, **1b**, **3**, **4**, **7**, **9**, **10**, **10**·$[LiOH(THF)]_2$, and **11**·$Li_2Se_2(THF)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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