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Synthesis and X-ray Structures of Dilithium Complexes of the Phosphonate Anions $[\mathrm{PhP(E)(N^tBu)_2}]^{2-}$ (E = O, S, Se, Te) and Dimethylaluminum Derivatives of $[\mathrm{PhP(E)(N^tBu)(NH^tBu)}]^{-}$ (E = S, Se)

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The dilithium salts of the phosphonate dianions $[\mathrm{PhP(E)(N^tBu)_2}]^{2-}$ (E = O, S, Se) are generated by the lithiation of $[\mathrm{PhP(E)(NH^tBu)_2}]$ with *n*-butyllithium. The formation of the corresponding telluride (E = Te) is achieved by oxidation of $\{\mathrm{Li_2[PhP(N^tBu)_2]}\}$ with tellurium. X-ray structural determinations revealed dimeric structures $\{\mathrm{Li(THF)_2[PhP(E)(N^tBu)_2]}\}_2$ in which the monomeric units are linked by Li–E bonds. In the case of E = Se or Te, but not for E = S, transannular Li–E interactions are also observed, resulting in a six-rung ladder. By contrast, for E = O, this synthetic approach yields the $\mathrm{Li_2O}$-templated tetramer $\{\mathrm{(THF)Li_2[PhP(O)(N^tBu)_2]}\}_4\cdot\mathrm{Li_2O}$ in THF or the tetramer $\{\mathrm{(Et_2O)_{0.5}Li_2[PhP(O)(N^tBu)_2]}\}_4$ in diethyl ether. The reaction of trimethylaluminum with $\mathrm{PhP(E)(NH^tBu)_2}$ produces the complexes $\mathrm{Me_2Al[PhP(E)(N^tBu)(NH^tBu)]}$ (E = S, Se), which were shown by X-ray crystallography to be N,E-chelated monomers.

Introduction

Investigations of polyimido analogues of common main-group oxo anions have led to interesting multidentate ligands that, as their alkali-metal derivatives, form novel cluster structures.[1] Recent studies of polyimido-phosphorus systems have uncovered a family of anions: $[\mathrm{P(NR)_2}]^-$,[2] $[\mathrm{R_2P(NR')_2}]^-$,[3] $[\mathrm{P(NR)_3}]^-$,[4] $[\mathrm{P(NR)_4}]^{3-}$,[5] and $[\mathrm{HP(NR')_3}]^{2-}$,[6] that are isoelectronic to the corresponding oxo-anions of phosphorus. Examples of all of the foregoing anions have been structurally characterized as their alkali-metal (usually lithium) derivatives. In addition, the in situ formation of the phenylphosphonate analogue $\mathrm{Li_2[PhP(N^iPr)_3]}$ has been inferred on the basis of derivative chemistry.[7]

Polydentate anions involving a combination of hard (N) and soft (S or Se) donor sites attached to a P(V) center display versatile coordination behavior. For example, the dianions $[\mathrm{^tBuN(E)P(\mu\text{-}N^tBu)_2P(E)N^tBu}]^{2-}$ (E = S, Se), which are formally dimers of the metaphosphates $[\mathrm{EP(N^tBu)_2}]^-$, adopt a different bonding mode toward $\mathrm{Li^+}$ than that observed for $\mathrm{Na^+}$ or $\mathrm{K^+}$.[8] Bis(N,E)-chelation is observed for $\mathrm{Li^+}$, whereas the large alkali-metal cations $\mathrm{Na^+}$ and $\mathrm{K^+}$ coordinate in an N,N′ and E,E′ bonding mode. In addition to these structural variations, the P−E bonds within these anions are more labile than the P−N bonds. This can result in unexpected transformations, e.g., the formation of $[\mathrm{(THF)LiP(N^tBu)_3}]_2$ from the reaction of $[\mathrm{P(S)(NH^tBu)_3}]$ with alkyllithium reagents[9] and the generation of the P(III)/P(V) monoanion $[\mathrm{^tBuN(Se)P(\mu\text{-}N^tBu)_2PNH^tBu}]^-$ [8b] from $[\mathrm{(^tBuNH)(Se)P(\mu\text{-}N^tBu)_2P(Se)(NH^tBu)}]$ and $\mathrm{Li^nBu}$ in boiling THF.

As a further contribution to the chemistry of polydentate phosphorus(V)-centered anionic ligands, we have investigated the reactions of chalcogenidobis(amido)phosphonates, $[\mathrm{PhP(E)(NH^tBu)_2}]$ (**1a**, E = O; **1b**, E = S; **1c**, E = Se),

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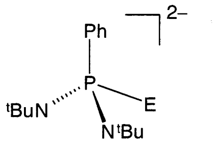
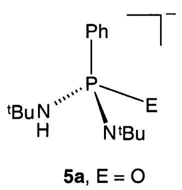
with both alkyllithium and alkylaluminum reagents. Since **1d** (E = Te) could not be prepared (vide infra), the oxidation of {Li$_2$[PhP(N^{t}Bu)$_2$]} with elemental tellurium was also studied. Herein we report the synthesis and X-ray structures of the dimers {Li(THF)$_2$[PhP(E)(N^{t}Bu)$_2$]}$_2$ (**2b**, E = S; **2c**, E = Se; **2d**, E = Te), the Li$_2$O-templated tetramer {(THF)-Li$_2$[PhP(O)(N^{t}Bu)$_2$]}$_4$·Li$_2$O (**2a**·Li$_2$O), and the tetramer {(Et$_2$O)$_{0.5}$Li$_2$[PhP(O)(N^{t}Bu)$_2$]}$_4$ (**2a′**), all of which contain tetrahedral dianions [PhP(E)(N^{t}Bu)]$^{2-}$ (**3a**−**d**). The synthesis and structures of the dimethylaluminum complexes {Me$_2$-Al[PhP(E)(N^{t}Bu)(NH^{t}Bu)]} (**4b**, E = S; **4c**, E = Se), which involve the monoanions [PhP(E)(NH^{t}Bu)(N^{t}Bu)]$^-$ (**5b**, E = S; **5c**, E = Se), are also reported.



3a, E = O
3b, E = S
3c, E = Se
3d, E = Te



5a, E = O
5b, E = S
5c, E = Se

Experimental Section

Reagents and General Procedures. Solvents were dried and distilled prior to use: toluene, tetrahydrofuran, diethyl ether, pentane, and *n*-hexane (Na/benzophenone). *n*-Butyllithium (2.5 M solution in hexanes, Aldrich), trimethylaluminum (2.0 M solution in hexanes, Aldrich), *tert*-butyl hydroperoxide (5.0−6.0 M, Aldrich), sulfur (99.5%, Aldrich), selenium (99.5%, Aldrich), and tellurium (99.5%, Matheson) were used as received. The compounds [PhP-(NH^{t}Bu)$_2$][10] and {Li$_2$[PhP(N^{t}Bu)$_2$]}$_2$[11] were prepared by literature procedures. The reactions and handling of air- and moisture-sensitive reagents were performed under an atmosphere of argon gas by using Schlenk techniques or a glovebox.

Instrumentation. With the exception of **2d**, solution NMR data were recorded at 23 °C. ^{1}H NMR spectra were collected on a Bruker AM-200 spectrometer and chemical shifts are reported relative to Me$_4$Si in CDCl$_3$. ^{31}P and ^{7}Li NMR spectra were obtained on a Bruker AMX 300 spectrometer; chemical shifts are reported relative to 85% H$_3$PO$_4$ and 1 M LiCl in D$_2$O, respectively. ^{77}Se NMR and ^{125}Te NMR were obtained on a Bruker DRX 400 spectrometer; chemical shifts are reported relative to Ph$_2$Se$_2$ (+463 ppm relative to Me$_2$Se) and neat Me$_2$Te, respectively. For the thermally unstable complex **2d** all solution NMR data were recorded on a Bruker DRX 400 spectrometer at −63 °C. Solid-state NMR spectra were collected on a Bruker AMX 300 spectrometer. Infrared spectra were recorded as Nujol mulls on KBr plates on a Nicolet Nexus 470 FTIR in the range 4000−350 cm^{-1}. Mass spectra were obtained with a VG micromass spectrometer VG7070 (70 eV). Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Synthesis of [PhP(O)(NH^{t}Bu)$_2$] (1a). A 5.0−6.0 M solution of ^{t}BuOOH in decane (4.4 mL, 22.00−26.40 mmol) was added dropwise to a stirred solution of PhP(NH^{t}Bu)$_2$ (5.609 g, 22.22 mmol) in toluene (45 mL) at 0 °C. A white precipitate formed immediately. After 2 h, the volume of solvent was reduced to 15 mL under vacuum. The product **1a** was obtained as a white crystalline solid (4.651 g, 17.33 mmol, 78%) after 24 h at −15 °C. ^{1}H NMR (C$_6$D$_6$, δ): 7.1−8.1 (m, 5 H, C$_6$H$_5$), 2.18 [*d*, 2 H, NH, $^2J(^1\mathrm{H}-^{31}\mathrm{P})$ = 7.4 Hz], 1.24 [d, 18 H, N^{t}Bu,$^4J(^1\mathrm{H}-^{31}\mathrm{P})$ = 0.5 Hz]. ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 11.6 (s); (solid state): 14.8 (s). IR (cm^{-1}): 3396 (N−H), 3227 (N−H). MS [EI, *m/z* (rel int)]: 268 (4) (M$^+$). Mp 182−185 °C. Anal. Calcd for C$_{14}$H$_{25}$N$_2$OP: C, 62.66; H, 9.39; N, 10.44. Found: C, 62.07; H, 9.99; N, 10.33.

Synthesis of [PhP(S)(NH^{t}Bu)$_2$] (1b). Hexane (40 mL) was added to a mixture of sulfur (1.323 g, 41.26 mmol) and PhP(NH^{t}Bu)$_2$ (10.412 g, 41.26 mmol) at 0 °C. A white precipitate formed immediately. The hexane was decanted from the product to give **1b** as a white crystalline solid (11.065 g, 38.90 mmol, 94%). ^{1}H NMR (C$_6$D$_6$, δ): 7.1−8.2 (m, 5 H, C$_6$H$_5$), 2.12 [*d*, 2 H, NH, $^2J(^1\mathrm{H}-^{31}\mathrm{P})$ = 4.6 Hz], 1.25 [d, 18 H, N^{t}Bu, $^4J(^1\mathrm{H}-^{31}\mathrm{P})$ = 0.7 Hz]. ^{31}P-{^{1}H} NMR (C$_6$D$_6$, δ): 50.9 (s). IR (cm^{-1}): 3383 (N−H), 3339 (N−H). MS [EI, *m/z* (rel int)]: 284 (30) (M$^+$). Mp 99−101 °C. Anal. Calcd for C$_{14}$H$_{25}$N$_2$SP: C, 59.13; H, 8.86; N, 9.85. Found: C, 58.00; H, 8.12; N, 9.47.

Synthesis of [PhP(Se)(NH^{t}Bu)$_2$] (1c). Hexane (45 mL) was added to a mixture of selenium (3.195 g, 40.46 mmol) and PhP-(NH^{t}Bu)$_2$ (10.210 g, 40.46 mmol) at 0 °C. The reaction mixture was refluxed in hexane at 65 °C for 18 h. While still hot, the solution was decanted from a small amount of unreacted Se and concentrated to 20 mL. Storage at −15 °C for 24 h yielded gray crystals of **1c** (10.947 g, 33.05 mmol, 82%). ^{1}H NMR (C$_6$D$_6$, δ): 7.1−8.2 (m, 5 H, C$_6$H$_5$), 2.20 [d, 2 H, NH, $^2J(^1\mathrm{H}-^{31}\mathrm{P})$ = 4.1 Hz], 1.24 (s, 18 H, N^{t}Bu). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 46.7 [s, $^1J(^{31}\mathrm{P}-^{77}\mathrm{Se})$ = 787 Hz]. ^{77}Se NMR (C$_6$D$_6$, δ): −154.5 [d, $^1J(^{31}\mathrm{P}-^{77}\mathrm{Se})$ = 785 Hz]. IR (cm^{-1}): 3377 (N−H), 3323 (N−H). MS [EI, *m/z* (rel int)]: 331 (19) (M$^+$). Mp 95−98 °C. Anal. Calcd for C$_{14}$H$_{25}$N$_2$-SeP: C, 51.07; H, 7.04; N, 8.51. Found: C, 51.03; H, 7.20; N, 8.35.

Synthesis of {(THF)Li$_2$[PhP(O)(N^{t}Bu)$_2$}4·Li$_2$O (2a·Li$_2$O). *n*-Butyllithium (1.50 mL, 3.75 mmol) was added dropwise to a stirred solution of PhP(O)(NH^{t}Bu)$_2$ (0.502 g, 1.87 mmol) in THF (25 mL) at 23 °C. After 18 h, the volume of the reaction mixture was reduced to 5 mL and layered with pentane (2 mL). Colorless X-ray quality crystals of **2a**(THF)$_4$·Li$_2$O (0.194 g, 0.135 mmol, 29%) formed after 3 days at 23 °C.^{1}H NMR (THF-*d*$_8$, δ): 7.2−8.1 (m, 5 H, C$_6$H$_5$), 3.58 (m, THF), 1.76 (m, THF), 1.14 (s, 18 H, N^{t}Bu). ^{31}P{^{1}H} NMR (THF-*d*$_8$, δ): 23.8 (s). ^{7}Li NMR (C$_6$D$_6$, δ): −0.20 (sh), −0.87 (br). Anal. Calcd for C$_{72}$H$_{124}$N$_8$O$_9$P$_4$Li$_{10}$: C, 60.09; H, 8.68; N, 7.79. Found: C, 59.88; H, 8.33; N, 8.08.

Synthesis of {(Et$_2$O)0.5Li$_2$[PhP(O)(N^{t}Bu)$_2$]}$_4$ (2a′). *n*-Butyllithium (2.433 mL, 6.083 mmol) was added dropwise to a stirred solution of PhP(O)(NH^{t}Bu)$_2$ (0.816 g, 3.041 mmol) in diethyl ether (25 mL) at 23 °C. After 3 h, the solvent was removed in vacuo and the white product was redissolved in a minimal amount of pentane (6 mL). Colorless X-ray quality crystals of **2a**(Et$_2$O)$_2$ (0.620 g, 1.954 mmol, 64%) formed after 24 h at 23 °C.^{1}H NMR (C$_6$D$_6$, δ): 7.2−8.2 (m, 5 H, C$_6$H$_5$), 3.27 (q, Et$_2$O), 1.10−1.90 (br m, 18 H, N^{t}Bu), 1.12 (t, Et$_2$O). ^{31}P NMR (solid state, δ): 25.6, 22.5, 13.2, 6.5. ^{7}Li NMR (solid state, δ): 2.48, 2.23, 1.71, 1.45, 1.15. Anal. Calcd for C$_{64}$H$_{112}$N$_8$O$_6$P$_4$Li$_8$: C, 60.57; H, 8.90; N, 8.83. Found: C, 58.34; H, 9.11; N, 9.34.

Synthesis of {(THF)$_2$Li$_2$[PhP(S)(N^{t}Bu)$_2$]}$_2$ (2b). *n*-Butyllithium (2.81 mL, 7.03 mmol) was added dropwise to a stirred solution of PhP(S)(NH^{t}Bu)$_2$ (1.000 g, 3.516 mmol) in THF (25 mL) at 23 °C. After 3 h, the volume of solvent was reduced to 8 mL under vacuum and hexane (5 mL) was added. Colorless X-ray quality crystals of **2b** (1.056 g, 2.397 mmol, 68%) formed after 24 h at 23 °C.^{1}H NMR (THF-*d*$_8$, δ): 7.1−8.3 (m, 5 H, C$_6$H$_5$), 3.61 (m, THF), 1.76

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Table 1. Crystallographic Data for **2a**·Li_2O, **2a′**, **2b**, **2c**, **2d,** and **4c**

	2a·Li2O	**2a′**	**2b**	**2c**	**2d**	**4c**
formula	$C_{77}H_{136}Li_{10}N_8O_9P_4$[c]	$C_{64}H_{112}Li_8N_8O_6P_4$	$C_{22}H_{39}Li_2N_2O_2PS$	$C_{22}H_{39}Li_2N_2O_2PSe$	$C_{22}H_{39}Li_2N_2O_2PTe$	$C_{16}H_{30}AlN_2PSe$
fw	1511.22	1269.02	440.46	487.36	536.00	387.33
space group	*P*1	$P2_1/a$	$P2_1/c$	*P*1	*P*1	Cc
a, Å	15.8348(2)	16.9725(3)	9.70790(10)	9.41300(10)	9.2017(2)	15.9353(4)
b, Å	15.9927(2)	20.8445(3)	28.8250(4)	10.2438(2)	10.1328(2)	14.6635(4)
c, Å	20.2186(3)	21.5041(4)	10.3105(2)	15.1293(2)	15.8982(4)	8.8872(2)
α, deg	102.2300(10)			89.0090(10)	94.6527(7)	
β, deg	111.6290(10)	94.6600(6)	115.3140(6)	73.1940(10)	104.7860(8)	101.7208(12)
γ, deg	99.7310(10)			66.3900(10)	110.9496(9)	
V, $Å^3$	4476.27(10)	7582.6(2)	2608.15(7)	1271.54(3)	1313.89(5)	2033.35(9)
Z	2	4	4	2	2	4
T, K	173(2)	170(2)	173(2)	173(2)	170(2)	170(2)
λ, Å	0.71069	0.71069	0.71069	0.71069	0.71073	0.71069
d_{calcd}, g cm^{-3}	1.121	1.112	1.122	1.273	1.355	1.265
μ, mm^{-1}	0.14	0.15	0.204	1.558	1.21	1.97
F(000)	1632	2736	952	512	548	808
R[a]	0.066	0.053	0.051	0.037	0.049	0.030
R_w[b]	0.196	0.15	0.137	0.098	0.150	0.080

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. [c] Contains one molecule of pentane.

(m, THF), 1.06 (s, 18 H, N^tBu). $^{31}P\{^1H\}$ NMR (THF-d_8, δ): 39.5 (s). ^7Li NMR (THF-d_8, δ): 2.14 [s]. Anal. Calcd for $C_{22}H_{39}N_2O_2PSLi_2$: C, 59.99; H, 8.92; N, 6.36. Found: C, 59.35; H, 8.98; N, 6.69.

Synthesis of {$(THF)_2Li_2[PhP(Se)(N^tBu)_2]$}$_2$ (2c). *n*-Butyllithium (2.42 mL, 6.05 mmol) was added dropwise to a stirred solution of $PhP(Se)(NH^tBu)_2$ (1.000 g, 3.018 mmol) in THF (25 mL) at 23 °C. After 3 h, the volume of solvent was reduced to 8 mL under vacuum. Pale yellow X-ray quality crystals of **2c** (1.243 g, 2.550 mmol, 85%) formed after 24 h at 23 °C. ^1H NMR (THF-d_8, δ): 7.1−8.3 (m, 5 H, C_6H_5), 3.61 (m, THF), 1.76 (m, THF), 1.08 [d, 18 H, N^tBu, $^4J(^1H-^{31}P) = 0.68$ Hz]. $^{31}P\{^1H\}$ NMR (THF-d_8, δ): 27.6 [s, $^1J(^{31}P-^{77}Se) = 514$ Hz]. ^{77}Se NMR (THF-d_8, δ): −45.7 [d, $^1J(^{31}P-^{77}Se) = 513$ Hz]. ^7Li NMR (THF-d_8, δ): 1.92 [s]. Anal. Calcd for $C_{22}H_{39}N_2O_2PSeLi_2$: C, 54.22; H, 8.07; N, 5.75. Found: C, 54.02; H, 8.35; N, 6.12.

Synthesis of {$(THF)_2Li_2[PhP(Te)(N^tBu)_2]$}$_2$ (2d). A mixture of {$Li_2[PhP(N^tBu)_2]$}$_2$ (0.250 g, 0.946 mmol) and Te powder (0.121 g, 0.946 mmol) in THF (6 mL) was heated to 70 °C for 3 h. After cooling to 23 °C, the mixture was centrifuged and the supernatant was decanted to remove unreacted tellurium. The solvent was removed under vacuum and the product was dissolved in diethyl ether (6 mL). After filtration, the solution was concentrated (ca. 2 mL) to give yellow needles of **2d** (0.069 g, 0.14 mmol, 14%) after 4 days at 23 °C. ^1H NMR (THF-d_8, 235 K, δ): 7.0−8.3 (m, 5 H, C_6H_5), 3.62 (m, THF), 1.77 (m, THF), 1.12 [d, $^4J(^1H-^{31}P) = 1$ Hz, 18 H, N^tBu]. $^{31}P\{^1H\}$ NMR (THF-d_8, 235K, δ): −14.4 [s, $^1J(^{31}P-^{125}Te = 1209$ Hz)]. ^{125}Te NMR (THF-d_8, 235K, δ): −333 [d, $^1J(^{125}Te-^{31}P = 1212$ Hz). Anal. Calcd for $C_{22}H_{39}Li_2N_2O_2PTe$: C, 49.30; H, 7.33; N, 5.23. Found: C, 49.57; H, 7.92; N, 5.45.

Synthesis of {$Me_2Al[PhP(S)(N^tBu)(NH^tBu]$} (4b). Trimethylaluminum (0.88 mL, 1.76 mmol) was added dropwise to a solution of $PhP(S)(NH^tBu)_2$ (0.50 g, 1.76 mmol) in toluene (25 mL) at 23 °C. The reaction mixture was refluxed at 130 °C for 18 h to give an orange solution. The solvent was removed in vacuo and the oily product was redissolved in a minimal amount of pentane (5 mL). Pale yellow X-ray quality crystals of **4b** (0.46 g, 1.35 mmol, 77%) formed after 24 h at −15 °C. ^1H NMR (C_6D_6, δ): 7.1−8.0 (m, 5 H, C_6H_5), 2.38 [d, 1 H, NH, $^2J(^1H-^{31}P) = 6.0$ Hz], 1.28 (s, 9 H, N^tBu), 1.08 [d, 9 H, N^tBu, $^4J(^1H-^{31}P) = 0.86$ Hz], −0.01 (s, 3 H, Me), −0.03 (s, 3 H, Me). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 38.4 (s). Anal. Calcd for $C_{16}H_{30}N_2PSAl$: C, 56.45; H, 8.88; N, 8.23. Found: C, 54.61; H, 8.88; N, 8.78.

Synthesis of {$Me_2Al[PhP(Se)(N^tBu)(NH^tBu]$} (4c). Pale yellow X-ray quality crystals of **4c** (0.36 g, 0.93 mmol, 62%) were obtained from the reaction of trimethylaluminum (0.75 mL, 1.51 mmol) and $PhP(Se)(NH^tBu)_2$ (0.50 g, 1.51 mmol) in toluene (25 mL) by the procedure described above for **4b**. ^1H NMR (C_6D_6, δ): 7.0−8.1 (m, 5 H, C_6H_5), 2.35 [d, 1 H, NH, $^2J(^1H-^{31}P) = 3.2$ Hz], 1.28 [d, 9 H, N^tBu, $^4J(^1H-^{31}P) = 0.51$ Hz], 1.08 [d, 9 H, N^tBu, $^4J(^1H-^{31}P) = 0.86$ Hz], 0.10 (s, 3 H, Me), 0.07 (s, 3 H, Me). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 29.1 [s, $^1J(^{31}P-^{77}Se) = 499$ Hz]. ^{77}Se NMR (C_6D_6, δ): −102.4 (d, $^1J(^{31}P-^{77}Se) = 497$ Hz]. Anal. Calcd for $C_{16}H_{30}N_2PSeAl$: C, 49.61; H, 7.81; N, 7.23. Found: C, 47.54; H, 7.58; N, 6.77.

X-ray Analyses. Crystals of **2a**·Li_2O·C_5H_{12}, **2a′**, **2b**, **2c**, **2d,** and **4c** were coated with Paratone oil and mounted on a glass fiber. All measurements were made on a Nonius Kappa CCD FR540C diffractometer. Crystallographic data are summarized in Table 1. Structures were solved by direct methods (SIR-92)[12a] and refined by full-matrix least-squares methods on F^2 with SHELXL-97.[12b] Unless otherwise stated the non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at geometrically idealized positions but not refined.

2a·Li_2O·C_5H_{12}: The C atoms of a molecule of pentane solvate were allowed isotropic displacement parameters as they were disordered and showed large vibrational parameters.

2a′: The non-hydrogen atoms were refined anisotropically except for the smaller fractions of the disordered atoms, which were allowed isotropic displacement parameters.

2b: One of the THF ligands had three disordered C atoms, which were included in the refinements with partial site occupancy factors.

2c: The C atoms of one THF ligand were disordered over two sites with partial occupancy factors.

Results and Discussion

Preparation of Lithium Imido/Chalcogenido Phosphonates. The preparation of bis(*tert*-butylamido)phenylphosphine chalcogenides, $[PhP(E)(NH^tBu)_2]$ (**1a**, E = O; **1b**, S; **1c**, Se), was first reported by Lane et al. in 1967.[10] The reaction of $[PhP(NH^tBu)_2]$ with *tert*-butyl hydroperoxide,

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

elemental sulfur, or selenium produces **1a**−**c**, respectively, in good yields. The ^{1}H NMR spectra for all three compounds exhibit the expected resonances for phenyl protons at δ 7.1−8.1, $\mathrm{N^tBu}$ groups at δ 1.24−1.25 with $^4J(^{31}\mathrm{P}-^1\mathrm{H}) = 0.0-0.7$ Hz, and the NH protons in the range δ 2.12−2.18 with $^2J(^{31}\mathrm{P}-^1\mathrm{H}) = 4.1-7.4$ Hz. The ^{31}P NMR spectra reveal singlets at δ 11.6 (**1a**), 50.9 (**1b**), and 46.7 (**1c**). The ^{77}Se NMR spectrum of **1c** consists of a doublet centered at δ −154.5 [$^1J(^{77}\mathrm{Se}-^{31}\mathrm{P}) = 785$ Hz] [cf. −153 ppm and 765 Hz for $\mathrm{Ph_2P(Se)N(SiMe_3)_2}$].[13]

Dilithiation of **1a**−**c** with *n*-butyllithium occurs readily in THF at room temperature (eq 1). The products are obtained in good yields and, unlike the lithiation of $\mathrm{SP(NH^tBu)_3}$[9] or $[(^t\mathrm{BuNH})(\mathrm{Se})\mathrm{P}(\mu\text{-}\mathrm{N^tBu})_2\mathrm{P(Se)(NH^tBu)}]$[8b] by ^{n}BuLi, no indication of P−S or P−Se bond cleavage was observed.

$$(x/2)[\mathrm{PhP(E)(NH^tBu)_2}] + x\,{}^n\mathrm{BuLi} \xrightarrow[-2^n\mathrm{BuH}]{\mathrm{THF}} (1/2)\{[\mathrm{Li(THF)}]_2[\mathrm{PhP(E)(N^tBu)_2}]\}_x \tag{1}$$

$$\begin{array}{c}\mathbf{2a},\ \mathrm{E} = \mathrm{O},\ x = 4\\ \mathbf{2b},\ \mathrm{E} = \mathrm{S},\ x = 2\\ \mathbf{2c},\ \mathrm{E} = \mathrm{Se},\ x = 2\end{array}$$

The analogous phosphine telluride $[\mathrm{PhP(Te)(NH^tBu)_2}]$ **1d** cannot be obtained by oxidation of $[\mathrm{PhP(NH^tBu)_2}]$ with elemental tellurium, even in boiling toluene. However, we have recently described a new approach to the synthesis of metalated amidophosphine tellurides that involves carrying out the metalation step prior to oxidation with elemental tellurium.[14] As a further example, we find that the reaction of $\mathrm{Li_2[PhP(N^tBu)_2]}$[11] with elemental tellurium in THF at 70 °C produces the dilithium salt **2d** (eq 2).

$$2\mathrm{Li_2[PhP(N^tBu)_2]} + 2\mathrm{Te} \xrightarrow{\mathrm{THF}} \{[\mathrm{Li(THF)}]_2[\mathrm{PhP(Te)(N^tBu)_2}]\}_2 \tag{2}$$

$$\mathbf{2d}$$

X-ray Structures and NMR Characterization of $\{(\mathrm{THF})\mathrm{Li_2[PhP(O)(N^tBu)_2]}\}_4\cdot\mathrm{Li_2O}$ (2a·Li$_2$O) and $\{(\mathrm{Et_2O})0.5\mathrm{Li_2[PhP(O)(N^tBu)_2]}\}4$ (2a′). Two different products were isolated from the lithiation of $\mathrm{PhP(O)(NH^tBu)_2}$ with $\mathrm{Li^nBu}$, depending on the solvent. In THF, the complex $\{(\mathrm{THF})\mathrm{Li_2[PhP(O)(N^tBu)_2]}\}_4\cdot\mathrm{Li_2O}$ (**2a**·Li$_2$O), in which a tetramer encapsulates a molecule of Li$_2$O, is formed. By contrast, in diethyl ether a tetramer $\{(\mathrm{Et_2O})_{0.5}\mathrm{Li_2[PhP(O)(N^tBu)_2]}\}_4$ (2a′) without the Li$_2$O template is obtained. The molecular geometry and atomic numbering schemes for these two complexes are shown in Figures 1 and 2; pertinent structural parameters are summarized in Tables 2 and 3, respectively. The X-ray structural analysis of **2a**·Li$_2$O reveals a 27-atom $\mathrm{P_4N_8O_5Li_{10}}$ cluster including a central oxide coordinated in an octahedral fashion to six lithium cations. The four phosphonate dianions are on the periphery of the cluster with their phenyl substituents pointing away from the center. Four of the lithium cations are also on the outer surface linking the phosphonate units, and each of these Li$^+$ ions is solvated by one molecule of THF. The remaining four lithium cations and a molecule of Li$_2$O comprise the inner pseudo-octahedral μ_6-$\mathrm{OLi_6}^{4+}$ core. The four phosphonate dianions display two different coordinaton modes. In each of the two modes, the phosphonate ligands coordinate five different lithium cations through the two imido nitrogen atoms and the single oxygen atom. The phosphonate ligands centered at P11 and P31 are (N,N′)-chelated to one lithium ion, while the phosphonate ligands centered at P21 and P41 are (N,O)-chelated to one lithium ion; further coordination occurs through both the oxygen and nitrogen atoms to four other lithium ions. As a result there is a pair of three-coordinate and a pair of four-coordinate oxygen atoms in the peripheral 16-membered $\mathrm{P_4N_4O_4Li_4}$ ring. The four nitrogens in this ring are four-coordinate, whereas the remaining four nitrogen atoms are five-coordinate. Altogether, each phosphonate dianion coordinates three lithium ions of the central Li$_6$O core and two lithium ions that link the phosphonate dianion with two adjacent dianions.

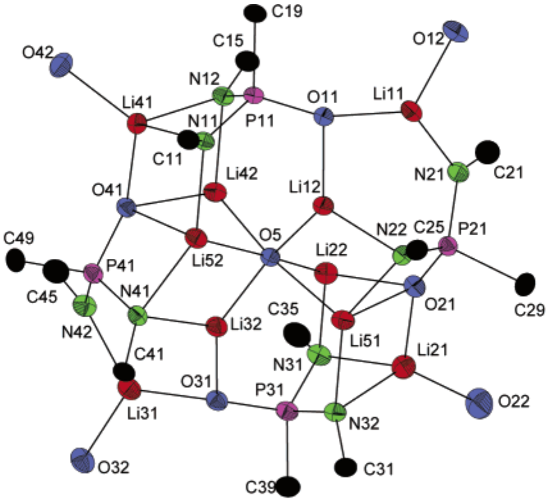

Figure 1. X-ray structure of $\{(\mathrm{THF})\mathrm{Li_2[PhP(O)(N^tBu)_2]}\}_4\cdot\mathrm{Li_2O}$ (**2a**·Li$_2$O) showing the numbering scheme (30% probability ellipsoids). Only the α-carbons of the ^{t}Bu groups, the ipso-carbons of the phenyl groups, and the oxygen atoms of THF molecules are shown.

The oxygen-scavenging properties of alkali-metal complexes, especially those that contain lithium, are reasonably well understood.[15] Several examples exist in which trace amounts of moisture, introduced either purposely or unintentionally, have resulted in a similar μ_6-OLi$_6$ core.[16] The cluster **2a**·Li$_2$O is unique in exhibiting both three- and four-coordinate Li$^+$ ions in the OLi$_6$ core. As expected, the Li−O distances involving three-coordinate Li$^+$ ions are significantly shorter than those involving four-coordinate ions, 1.852(4)−1.985(4) Å vs 2.099(4)−2.166(4) Å. The geometry around

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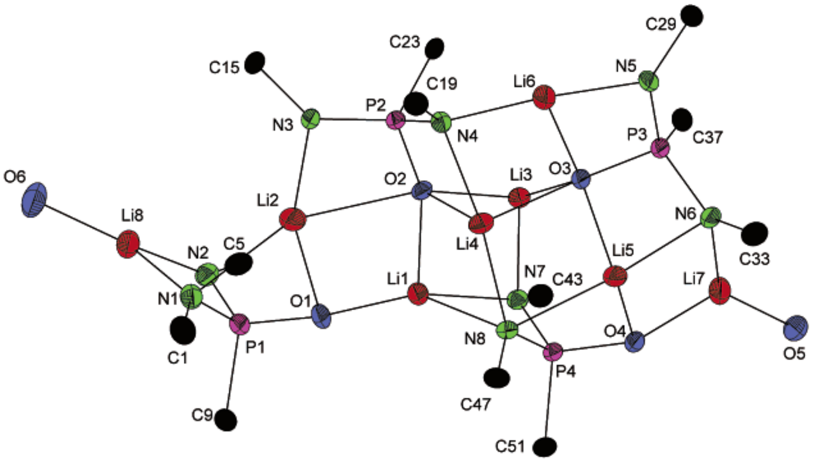

Figure 2. X-ray structure of $\{(Et_2O)_{1/2}Li_2[PhP(O)(N^tBu)_2]\}_4$ (**2a′**) showing the numbering scheme (30% probability ellipsoids). Only the α-carbons of the ^{t}Bu groups, the ipso-carbons of the phenyl groups, and the oxygen atoms of Et_2O molecules are shown.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $\{(THF)Li_2[PhP(O)(N^tBu)_2]\}_4{\cdot}Li_2O$ (**2a**·Li_2O)

Li(11)−O(11)	1.890(4)	P(21)−N(21)	1.6087(18)
Li(11)−N(21)	1.989(4)	P(21)−N(22)	1.6123(17)
Li(12)−O(5)	1.852(4)	O(21)−Li(51)	2.166(4)
Li(12)−O(11)	1.924(4)	N(22)−Li(51)	2.094(4)
Li(12)−N(22)	2.036(4)	Li(31)−O(31)	1.881(4)
P(11)−O(11)	1.5371(15)	Li(31)−N(42)	1.989(4)
P(11)−N(11)	1.6190(18)	Li(32)−O(5)	1.856(4)
P(11)−N(12)	1.6219(17)	Li(32)−O(31)	1.935(4)
N(11)−Li(41)	2.122(4)	Li(32)−N(41)	2.055(4)
N(11)−Li(52)	2.189(4)	P(31)−O(31)	1.5343(16)
N(12)−Li(41)	2.026(4)	P(31)−N(31)	1.6181(19)
N(12)−Li(42)	2.099(4)	P(31)−N(32)	1.6240(19)
Li(21)−O(21)	1.899(4)	N(32)−Li(51)	2.200(4)
Li(21)−N(31)	2.040(5)	Li(41)−O(41)	1.904(4)
Li(21)−N(32)	2.090(4)	Li(42)−O(5)	1.904(4)
Li(22)−O(5)	1.906(4)	Li(42)−O(41)	1.984(4)
Li(22)−O(21)	1.985(4)	P(41)−O(41)	1.5515(15)
Li(22)−N(31)	2.080(4)	P(41)−N(42)	1.6102(18)
P(21)−O(21)	1.5500(15)	P(41)−N(41)	1.6177(18)
O(41)−Li(52)	2.151(4)	O(5)−Li(51)	2.099(4)
N(41)−Li(52)	2.081(4)	O(5)−Li(52)	2.136(4)
Li(12)−O(5)−Li(32)	152.33(19)	Li(32)−O(5)−Li(51)	88.80(17)
Li(12)−O(5)−Li(42)	98.18(17)	Li(42)−O(5)−Li(51)	170.89(17)
Li(32)−O(5)−Li(42)	98.62(18)	Li(22)−O(5)−Li(51)	69.76(16)
Li(12)−O(5)−Li(22)	98.91(18)	Li(12)−O(5)−Li(52)	77.40(16)
Li(32)−O(5)−Li(22)	98.24(17)	Li(42)−O(5)−Li(52)	69.53(15)
Li(42)−O(5)−Li(22)	103.73(17)	Li(22)−O(5)−Li(52)	171.00(17)
Li(12)−O(5)−Li(51)	77.05(16)	Li(51)−O(5)−Li(52)	117.60(15)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $\{(Et_2O)_{1/2}Li_2[PhP(O)(N^tBu)_2]\}_4$ (**2a′**)

Li(1)−O(1)	1.848(5)	Li(6)−N(5)	1.956(5)
Li(1)−O(2)	2.011(5)	Li(6)−N(4)	1.977(5)
Li(1)−N(7)	2.087(5)	Li(6)−O(3)	1.995(5)
Li(1)−N(8)	2.319(5)	Li(7)−O(4)	1.835(5)
Li(2)−N(3)	1.983(5)	Li(7)−N(6)	2.068(6)
Li(2)−O(1)	2.066(5)	Li(8)−N(2)	1.953(6)
Li(2)−N(1)	2.361(6)	Li(8)−N(1)	1.964(6)
Li(2)−O(2)	2.450(6)	P(1)−O(1)	1.5388(18)
Li(3)−O(3)	1.967(5)	P(1)−N(2)	1.600(2)
Li(3)−O(2)	1.975(5)	P(1)−N(1)	1.617(2)
Li(3)−N(7)	2.045(5)	P(2)−O(2)	1.5680(17)
Li(4)−O(2)	1.944(5)	P(2)−N(3)	1.574(2)
Li(4)−N(4)	2.114(5)	P(2)−N(4)	1.625(2)
Li(4)−N(8)	2.125(5)	P(3)−O(3)	1.5821(17)
Li(4)−O(3)	2.143(5)	P(3)−N(5)	1.582(2)
Li(5)−O(4)	1.924(5)	P(3)−N(6)	1.613(2)
Li(5)−O(3)	1.968(5)	P(4)−O(4)	1.5421(18)
Li(5)−N(6)	2.074(5)	P(4)−N(7)	1.610(2)
Li(5)−N(8)	2.255(5)	P(4)−N(8)	1.637(2)
O(1)−P(1)−N(2)	116.48(12)	O(3)−P(3)−N(5)	102.75(10)
O(1)−P(1)−N(1)	111.67(11)	O(3)−P(3)−N(6)	105.26(11)
N(2)−P(1)−N(1)	99.84(12)	N(5)−P(3)−N(6)	126.39(12)
O(2)−P(2)−N(3)	107.98(10)	O(4)−P(4)−N(7)	115.81(11)
O(2)−P(2)−N(4)	102.65(10)	O(4)−P(4)−N(8)	110.14(11)
N(3)−P(2)−N(4)	122.80(12)	N(7)−P(4)−N(8)	101.70(11)

the central oxide is a very distorted octahedron with ∠LiOLi bond angles in the range 69.5(2)° − 117.6(2)°.

Complex **2a′**, which was formed in diethyl ether under identical conditions to those used for the isolation of **2a**·Li_2O, is also tetrameric but, in the absence of encapsulated Li_2O, the symmetry of the cluster is low (Figure 2). It is a 24-atom $P_4N_8O_4Li_8$ cluster in which only two lithium ions are solvated by a molecule of diethyl ether. Like **2a**·Li_2O, the lithium and oxygen atoms in **2a′** reside in the inner part of the cluster, while the phenyl substituents are on the periphery. The predominant features are the numerous four-membered rings, including a central Li_2O_2 ring. There are also two six-membered (Li_2O_2PN) rings. As in **2a**·Li_2O, there are two modes of coordination for the phosphonate dianions in which each dianion coordinates to a total of five unique lithium ions. The phosphonates at P2 and P3 coordinate two lithium ions in a bis(N,O) coordination mode, while the phosphonates at P1 and P4 coordinate two lithium ions via (N,N′) and (N,O) chelation. Coordination to three additional lithium ions occurs through both the oxygen and nitrogen atoms.

In the cluster **2a′** there are three- and four-coordinate lithium ions, three- and five-coordinate oxygen atoms, and three-, four-, and five-coordinate nitrogen centers. Consequently, there is a broader range of Li−N and Li−O distances in **2a′** compared to those in **2a**·Li_2O [the ranges for Li−N and Li−O distances are 1.953(6)−2.319(5) Å and 1.835(5)−2.450(6) Å compared with 1.989(4)−2.200(4) Å and 1.881(4)−2.166(4) Å, respectively].

Both clusters were characterized by multinuclear NMR studies. For **2a**·Li_2O the NMR data indicate a higher symmetry in solution than in the solid state. Thus the ^{1}H NMR spectrum in THF-d_8 at 23 °C reveals a single N^{t}Bu environment, while the ^{31}P NMR spectrum exhibits a singlet at δ 23.8. The ^{7}Li NMR spectrum consists of a broad resonance at δ −0.87 with a shoulder at δ −0.20. The

Scheme 1

$$[Li_2PhP(O)(N^tBu)_2] + H_2O \longrightarrow LiOH + [LiPhP(O)(NH^tBu)(N^tBu)]$$

$$5\,[Li_2PhP(O)(N^tBu)_2] + LiOH \longrightarrow \{Li_2[PhP(O)(N^tBu)_2\}_4{\cdot}Li_2O + [LiPhP(O)(NH^tBu)(N^tBu)]$$

Net reaction:

$$6\,[Li_2PhP(O)(N^tBu)_2] + H_2O \longrightarrow \{Li_2[PhP(O)(N^tBu)_2\}_4{\cdot}Li_2O + 2\,[LiPhP(O)(NH^tBu)(N^tBu)]$$

solution NMR data for **2a**′ are not very informative. Both the ^1H and ^{31}P NMR spectra in THF-d_8 at 23 °C exhibit a multitude of resonances, suggesting that dissociation to give a mixture of oligomers occurs.[17] However, the solid-state ^{31}P NMR spectrum shows four distinct resonances at δ 25.6, 22.5, 13.2, and 6.5, consistent with the X-ray structure. In the solid-state ^7Li NMR spectrum only five resonances are observed, rather than the eight expected from the X-ray structure, likely as a result of overlap of resonances for Li^+ ions in similar environments.

The mechanism of formation of the Li_2O-encapsulated cluster merits further discussion. In three separate experiments crystals of the product of the reaction of **1a** with 2 equiv of ^{n}BuLi could not be obtained from THF solution until a minimum of 3 days had elapsed. In all three cases the crystals were shown by determination of unit cell parameters to be **2a**·Li_2O. Junk et al. report that the deliberate addition of water was necessary to grow crystals of $[(C_5H_3NMeN(H)Li)_6(Et_2O)_2{\cdot}Li_2O]$.[16f] Similarly, $Li_4[^nBuC(N^tBu)_2]_4{\cdot}Li_2O$ is formed when a stoichiometric amount of water is added to a THF solution of $Li[^nBuC(N^tBu)_2]$.[16e] In the current work the reaction of $Li_2[PhP(O)(N^tBu)_2]$ with a stoichiometric amount of water was monitored by ^{31}P NMR, which revealed the presence of $Li[PhP(O)(NH^tBu)(N^tBu)]$ [δ ^{31}P (C_6D_6) = 7.6 (s)] as an intermediate. An authentic sample of this monolithiated complex of **5a** was prepared by the reaction of **1a** with 1 equiv of ^{n}BuLi. Thus we suggest that, by analogy with the formation of $Li_4[^nBuC(N^tBu)_2]_4{\cdot}Li_2O$,[16e] the cluster **2a**·Li_2O is generated by the two-step process shown in Scheme 1. The net reaction requires only traces of water, which may be present in THF solvent or the glassware.

X-ray Structures and NMR Characterization of $\{(THF)_2Li_2[PhP(S)(N^tBu)_2]\}_2$ (2b), $\{(THF)_2Li_2[PhP(Se)(N^tBu)_2]\}_2$ (2c) and $\{(THF)_2Li_2[PhP(Te)(N^tBu)_2]\}_2$ (2d). The molecular geometry and atomic numbering schemes for **2b** and **2c** are shown in Figures 3 and 4. The structure of **2d** is similar to that of **2c**. Pertinent structural parameters for **2b**−**d** are compared in Table 4. All three compounds form dimers that are linked through Li−E (E = S, Se, Te) interactions. The selenide and telluride, **2c** and **2d**, contain central transoid Li_2E_2 rings, while the sulfide **2b** has only very weak transannular interactions. The structures all contain (N,N′)- and (N,E)-chelated lithium ions. The (N,N′)-chelated lithium is solvated by one molecule of THF, while a second molecule of THF bridges these two lithium ions.

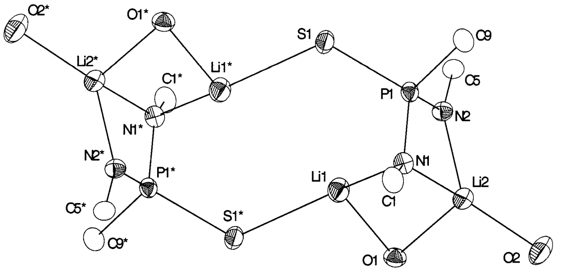

Figure 3. X-ray structure of $\{(THF)_2Li_2[PhP(S)(N^tBu)_2]\}_2$ (**2b**) showing the numbering scheme (30% probability ellipsoids). Only the α-carbons of the ^{t}Bu groups, the ipso-carbons of the phenyl groups, and the oxygen atoms of THF molecules are shown. Symmetry transformations used to generate equivalent atoms: $-x + 1, -y, -z$.

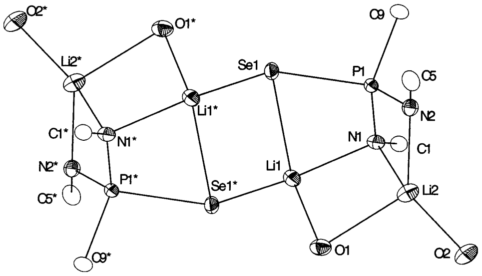

Figure 4. X-ray structure of $\{(THF)_2Li_2[PhP(Se)(N^tBu)_2]\}_2$ (**2c**) showing the numbering scheme (30% probability ellipsoids). Only the α-carbons of the ^{t}Bu groups, the ipso-carbons of the phenyl groups, and the oxygen atoms of THF molecules are shown. Symmetry transformations used to generate equivalent atoms: $-x, -y, -z$.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $\{(THF)_2Li_2[PhP(S)(N^tBu)_2]\}_2$ (**2b**), $\{(THF)_2Li_2[PhP(Se)(N^tBu)_2]\}_2$ (**2c**), and $\{(THF)_2Li_2[PhP(Te)(N^tBu)_2]\}_2$ (**2d**)

	2b	**2c**	**2d**
E(1)−P(1)	2.040(5)	2.2371(5)	2.4935(12)
E(1)−Li(1)*	2.406(4)	2.564(4)	2.792(9)
E(1)−Li(1)	3.172(5)	2.637(4)	2.848(9)
P(1)−N(2)	1.6092(16)	1.6011(17)	1.597(4)
P(1)−N(1)	1.6256(16)	1.6198(17)	1.619(4)
O(1)−Li(1)	2.065(4)	2.034(4)	2.104(9)
O(1)−Li(2)	2.087(4)	2.235(5)	2.140(10)
O(2)−Li(2)	1.936(4)	1.938(4)	1.937(9)
N(1)−Li(1)	2.058(4)	2.027(4)	2.010(10)
N(1)−Li(2)	2.060(4)	2.066(4)	2.106(9)
N(2)−Li(2)	1.960(4)	2.006(4)	2.005(9)
P(1)−E(1)−Li(1)*	124.68(10)	118.51(9)	115.24(18)
P(1)−E(1)−Li (1)	55.86(8)	67.53(8)	63.00(18)
Li(1)−E(1)−Li(1)*	69.35(14)	67.46(13)	64.6(3)
N(2)−P(1)−N(1)	98.82(8)	104.31(9)	105.1(2)
N(2)−P(1)−E(1)	115.81(7)	112.82(7)	113.29(15)
N(1)−P(1)−E(1)	115.00(7)	108.19(7)	106.68(15)
Li(1)−O(1)−Li(2)	76.51(15)	82.09(15)	82.8(4)
P(1)−N(1)−Li(1)	90.72(13)	96.27(13)	100.8(3)
P(1)−N(1)−Li(2)	89.74(12)	86.40(13)	85.4(3)
Li(1)−N(1)−Li(2)	77.25(16)	86.61(17)	86.0(4)
P(1)−N(2)−Li(2)	93.90(13)	88.97(14)	89.5(3)
N(1)−Li(1)−E(1)*	143.7(2)	124.43(17)	126.6(4)
N(1)−Li(1)−E(1)	69.07(15)	83.69(13)	85.0(3)
E(1)*−Li(1)−E(1)	110.65(16)	112.54(13)	115.4(3)
N(2)−Li(2)−N(1)	75.29(14)	77.31(15)	76.8(3)

The P−E distances of 2.040(5), 2.2371(5), and 2.4935(12) Å for **2b**, **2c**, and **2d**, respectively, are all closer to single bond values rather than double bonds.[18−25] The P−N bond lengths are in the narrow range 1.60−1.62 Å for all three compounds. The transannular Li−E distance is slightly

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[17] Dissociation of the tetrameric cluster $\{Li[P(N^tBu)_2]\}_4$ into smaller aggregates has been established by VT NMR studies. Brask, J. K.; Chivers, T.; Krahn, M. L.; Parvez, M. *Inorg. Chem.* **1999**, *38*, 290.

longer than the Li−E* distance for **2c** and **2d**, whereas this difference is ca. 0.77 Å for the sulfide **2b**. Consistently, the N(1)−P(1) −E(1) bond angle is substantially larger for the sulfide [115.00(7)°, **2b**; 108.19(7)°, **2c**; 106.68(15)°, **2d**]. No structural information is available for the alkali-metal derivatives of the related [PhP(N^{t}Bu)$_3$]$^{2-}$ dianion for comparison,[7] although the structure of a spirocyclic tellurium(IV) complex has been reported.[26]

The ^{1}H NMR spectra for **2b**−**d** in THF-d_8 at room temperature all show single N^{t}Bu resonances at δ 1.06, 1.08, and 1.12, respectively, in addition to the resonances for the phenyl substituents and coordinated THF molecules. The ^{31}P NMR spectra consist of singlets at δ 39.5, 27.6, and −14.4 for **2b**, **2c,** and **2d**, respectively. The ^{77}Se and ^{125}Te NMR spectra reveal doublets at δ −45.7 and −333 for **2c** and **2d**, with $^1J(^{31}\text{P}-^{77}\text{Se}) = 513$ Hz and $^1J(^{31}\text{P}-^{125}\text{Te}) = 1212$ Hz, respectively. The decrease in the value of $^1J(^{31}\text{P}-^{77}\text{Se})$ by 273 Hz in **2c** compared to **1c** indicates a substantially lower P−Se bond order as expected from the structural data. Taken together, the NMR data suggest that **2b**−**d** have a higher degree of symmetry in solution than in the solid state. Since only one N^{t}Bu resonance is observed in the ^{1}H NMR spectra of **2b**−**d**, even at −100 °C, and only one ^{7}Li NMR environment is indicated, it is likely that a facile fluxional process involving exchange between Li(1)−N(1) and Li(1)−N(2) interactions occurs. Such fluxional processes are common for polycylic species involving polyimido anions of p-block elements.[1a]

Synthesis and X-ray Structures of {Me$_2$Al[PhP(S)(N^{t}Bu)(NH^{t}Bu]} (4b) and {Me$_2$Al[PhP(Se)(N^{t}Bu)(NH^{t}Bu]} (4c). Stahl et al. have shown that cyclodiphosph(V)azanes *cis*-[^{t}Bu(H)N(E)P(μ-N^{t}Bu)$_2$P(E)N(H)^{t}Bu] (E = O, S, Se) react with trimethylaluminum to form the bis(dimethylaluminum) complexes {(Me$_2$Al)[^{t}BuN(E)P(μ-N^{t}Bu)$_2$P(E)N^{t}Bu](AlMe$_2$)} in which the ligand is bis(N,E)-chelated to aluminum.[27] Related mononuclear dimethylaluminum complexes have been prepared from [Me$_2$Si(μ-N^{t}Bu)$_2$P(E)(NHPh)] and trimethylaluminum.[28] In the present work it was of interest to determine whether the reaction of PhP(E)(NH^{t}Bu)$_2$ (**1b**, E = S; **1c**, E = Se) with trimethylaluminum results in double deprotonation to give the dianions **3b**,**c** or monodeprotonation to give the monoanions **5b**,**c**.

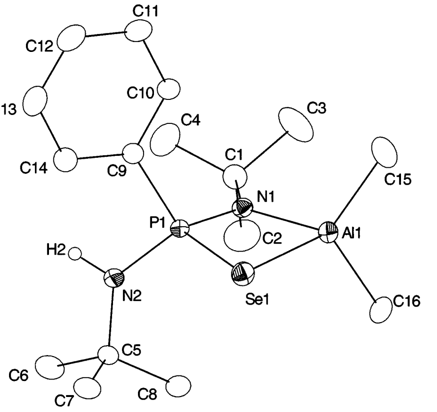

Figure 5. X-ray structure of {Me$_2$Al[PhP(Se)(N^{t}Bu)(NH^{t}Bu]} (**4c**) showing the numbering scheme (30% probability ellipsoids). Only the carbon atoms of the ^{t}Bu, phenyl, and methyl groups are shown.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for {Me$_2$Al[PhP(Se)(N^{t}Bu)(NH^{t}Bu]} (**4c**)

Se(1)−P(1)	2.1865(7)	Al(1)−N(1)	1.900(3)
Se(1)−Al(1)	2.5103(10)	Al(1)−C(16)	1.959(4)
P(1)−N(1)	1.611(2)	Al(1)−C(15)	1.965(4)
P(1)−N(2)	1.653(3)		
P(1)−Se(1)−Al(1)	72.94(3)	N(2)−P(1)−Al(1)	135.44(10)
N(1)−P(1)−N(2)	117.91(14)	Se(1)−P(1)−Al(1)	58.86(3)
N(1)−P(1)−Se(1)	99.55(9)	N(1)−Al(1)−Se(1)	81.75(8)
N(2)−P(1)−Se(1)	116.02(10)	P(1)−N(1)−Al(1)	105.70(13)
N(1)−P(1)−Al(1)	40.72(9)	C(5)−N(2)−P(1)	131.1(2)

The reaction of **1b** or **1c** with 1 equiv of trimethylaluminum in boiling toluene for 18 h yields the complexes **4b** and **4c**, which exhibit similar NMR spectra. The ^{1}H NMR spectra contain two equally intense resonances in the N^{t}Bu region (δ 1.28 and 1.08, **4b** and **4c**), two equally intense methylaluminum resonances (δ −0.01 and −0.03, **4b**; 0.10 and 0.07, **4c**), and an amido NH resonance (δ 2.38, **4b**; 2.35, **4c**), suggesting formation of a monodeprotonated complex. The ^{31}P NMR spectra reveal singlets at δ 38.4 (**4b**) and δ 29.1 (**4c**); the latter resonance shows selenium satellites. The ^{77}Se NMR spectrum of **4c** contains a doublet at δ −102.4 with $^1J(^{31}\text{P}-^{77}\text{Se}) = 497$ Hz (cf. 468 and 463 Hz for {[MeP(N(TMS)$_2$)(N^{t}Bu)(Se)](AlMe$_2$)} and {MeP[N(TMS)(^{t}Bu)][(N^{t}Bu)(Se)](AlMe$_2$)}, respectively).[29,30]

The X-ray structure of **4c** is shown in Figure 5 and pertinent structural parameters are summarized in Table 5. In view of the congruence in the NMR spectra, it is likely that **4b** has a similar structure. Consistent with the NMR data, the monoanion **5c** coordinates the dimethylaluminum fragment through (N,Se)-chelation. The methyl groups on aluminum are oriented perpendicular to the plane of the distorted AlNPSe ring. The ^{t}Bu substituent of the exocyclic N(H)^{t}Bu group is in an exo position with respect to the PNAlSe ring.

The P−Se distance of 2.1865(7) Å is significantly shorter than that observed in **2c** (2.2371(5) Å), indicating a higher

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(18) The P═S double bond in SPPh$_2$NHPh$_2$PS[19] is 1.936(1) Å and a typical single bond value is 2.100(1) Å. Corbridge, D. E. C. In *The Structural Chemistry of Phosphorus*; Elsevier: New York, 1994.

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P−Se bond order in **4c**. However, the values of $^1J(^{31}P-^{77}Se)$ exhibit the opposite trend (497 Hz, **4c**; 513 Hz, **2c**). The reasons for this discrepancy are not clear, but it is apparent that the correlation between bond length (or bond order) and the value of $^1J(^{31}P-^{77}Se)$ is only approximate for this series of compounds. The endocyclic P−N distance of 1.611(2) Å is significantly shorter than the exocyclic P−N distance of 1.653(3) Å. The disparity of ca. 0.6 Å in the Al−Se and Al−N distances results in a distorted four-membered AlNPSe ring with endocyclic bond angles ∠P−Se−Al = 72.94(3)° and ∠P−N−Al = 105.70(13)°. The Al−Se distance of 2.510(1) Å is somewhat longer than the range of values (2.34−2.44 Å) found for recently reported four-coordinate aluminum complexes.[31−33] The Al−N distance of 1.900(3) Å can be compared with values in the range 1.84−1.89 Å for four-coordinate aluminum complexes.[34,35] Thus the structural data indicate, as expected, that the selenium atom is less strongly bonded than nitrogen to the aluminum center.

Conclusions

The dilithium salts of the phosphonate dianions **3a−c** are generated by the lithiation of the appropriate chalcogenido bis(amido)phosphonate **1a−c** with Li^{n}Bu. The preparation of the corresponding telluride requires lithiation of PhP(NH^{t}Bu)$_2$ prior to oxidation with elemental tellurium. The formation of a Li_2O-templated complex provides another example of the creation of a cluster with a central OLi_6 core caused by the presence of adventitious water. Isostructural dimethylaluminum complexes of the monoanions **5b**,**c** can be generated by the reactions of trimethylaluminum with **1b**,**c**, respectively. The novel polydentate dianions **3b−d** and **5b,c** are potentially versatile tripodal or bidentate ligands with both hard (N) and soft (S, Se, Te) donor centers that merit further investigation, especially in the context of transition-metal complexes.

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Supporting Information Available: X-ray crystallographic files, in CIF format for complexes **2a**·Li_2O, **2a′**, **2b**, **2c**, **2d,** and **4c**. This material is. avaliable free of charge via the Internet at http://pubs.acs.org.

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