Preparation and X-ray Structures of Alkali-Metal Derivatives of the Ambidentate Anions $[^tBuN(E)P(\mu\text{-}N^tBu)_2P(E)N^tBu]^{2-}$ (E = S, Se) and $[^tBuN(Se)P(\mu\text{-}N^tBu)_2PN(H)^tBu)]^-$

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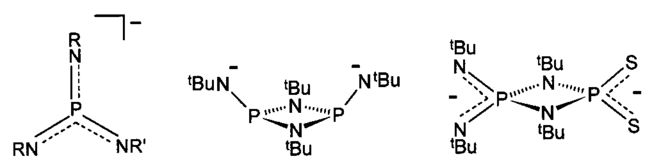
The ambidentate dianions $[^tBuN(E)P(\mu\text{-}N^tBu)_2P(E)N^tBu]^{2-}$ (**5a**, E = S; **5b**, E = Se) are obtained as their disodium and dipotassium salts by the reaction of *cis*-$[^tBu(H)N(E)P(\mu\text{-}N^tBu)_2P(E)N(H)^tBu]$ (**6a**, E = S; **6b**, E = Se), with 2 equiv of $MN(SiMe_3)_2$ (M = Na, K) in THF at 23 °C. The corresponding dilithium derivative is prepared by reacting **6a** with 2 equiv of ^tBuLi in THF at reflux. The X-ray structures of five complexes of the type $[(THF)_xM]_2$-$[^tBuN(E)P(\mu\text{-}N^tBu)_2P(E)N^tBu]$ (**9**, M = Li, E = S, x = 2; **11a**/**11b**, M = Na, E = S/Se, x = 2; **12a**, M = K, E = S, x = 1; **12b**, M = K, E = Se, x = 1.5) have been determined. In the dilithiated derivative **9** the dianion **5a** adopts a bis (*N*,*S*)-chelated bonding mode involving four-membered LiNPS rings whereas **11a**,**b** and **12a**,**b** display a preference for the formation of six-membered MNPNPN and MEPNPE rings, i.e., (*N*,*N*′ and *E*,*E*′)-chelation. The bis-solvated disodium complexes **11a**,**b** and the dilithium complex **9** are monomeric, but the dipotassium complexes **12a**,**b** form dimers with a central K_2E_2 ring and associate further through weak K···E contacts to give an infinite polymeric network of 20-membered $K_6E_6P_4N_4$ rings. The monoanions $[^tBu(H)N(E)P$-$(\mu\text{-}N^tBu)_2P(E)N^tBu)]^-$ (E = S, Se) were obtained as their lithium derivatives **8a** and **8b** by the reaction of 1 equiv of ^nBuLi with **6a** and **6b**, respectively. An X-ray structure of the TMEDA-solvated complex **8a** and the ^{31}P NMR spectrum of **8b** indicate a *N*,*E* coordination mode. The reaction of **6b** with excess ^tBuLi in THF at reflux results in partial deselenation to give the monolithiated P(III)/P(V) complex $\{(THF)_2Li[^tBuN(Se)P(\mu\text{-}N^tBu)_2PN$-$(H)^tBu]\}$ **10**, which adopts a (*N*,*Se)* bonding mode.

Introduction

During the past decade there has been growing interest in the synthesis, cluster structures, and coordination chemistry of homoleptic polyimido anions of p-block elements as their alkali-metal (usually lithium) derivatives.[1] One of the first examples of this class of ligands were monomeric anions of the type $[P(NR)_2(NR')]^-$ **1** isoelectronic with the metaphosphate anion $[PO_3]^-$.[2] The dimeric phosphorus(III) dianions **2** have also attracted attention recently,[3] and the coordination chemistry of this chelating ligand has been explored extensively by Stahl and co-workers for both main group elements and transition metals.[4]

As part of our investigations of heteroleptic imido/oxo (thio) anions with p-block element centers, e.g., $[OS(NR)_2]^{2-}$,[5] $[O_2S(NR)]^{2-}$,[6] $[O_2S(NR)_2]^{2-}$,[7] and $[PhN(SO_2)_2]^{2-}$,[8] we have investigated the reactions of $EPCl_3$ (E = O, S) with an excess of $LiN(H)^tBu$.[9] For E = S we have isolated and structurally characterized the dianion $[(^tBuN)_2P(\mu\text{-}N^tBu)_2PS_2]^{2-}$ **3** as its dilithium derivative.[10]



1a, R = R′ = Mes*
1b, R = Mes*, R′ = ^tBu

2

3

The unsymmetrical dianion **3** can be viewed as a cycloaddition product of the tris(imido)metaphosphate $[P(N^tBu)_3]^-$ (**1**, R = R′ = ^tBu) and the hypothetical dithia(imido)metaphosphate $[S_2P(N^tBu)]^-$. The discovery of the novel bis-chelating dianion **3**, and our prior investigations of hybrid phosphinates of the type $[R_2P(E)(NR')]^-$ **4**,[11] prompted our interest in dianions of the type **5**. These potentially ambidentate ligands are especially interesting as they offer two different modes of coordination:

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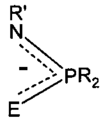
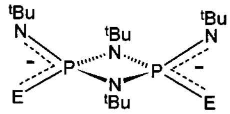
(a) chelation via the "soft" (E,E') and "hard" (N,N') centers forming six-membered rings and (b) bis (N,E)-chelation forming four-membered rings.



4 (E = S, Se)



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

In a preliminary communication[12a] we described the synthesis of disodium and dipotassium salts of **5a** and **5b** and the X-ray structure of the dipotassium salt of **5b**. In the full account of this work we now describe the details of the reactions of *cis*-[^{t}Bu(H)N(E)P(μ-N^{t}Bu)$_2$P(E)N(H)^{t}Bu] (**6a**, E = S; **6b**, E = Se) with Li^{n}Bu, Li^{t}Bu, and MN(SiMe$_3$)$_2$ (M = Na, K) and the X-ray structures of a mono- and dilithiated derivative of **5a**, the disodium and dipotassium complexes of **5a** and **5b**, and the lithium salt of the P(III)/P(V) monoanion [^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]$^-$, formed by deselenation. Stahl and co-workers have very recently reported *N,E*-bonded complexes of aluminum with ligands of the type **5a**,**b**.[12b]

Experimental Section

Reagents and General Procedures. Solvents were dried and distilled over Na/benzophenone prior to use: *n*-hexane, tetrahydrofuran, and toluene. *n*-Butyllithium (2.5 M solution in hexanes, Aldrich), *tert*-butyllithium (1.7 M solution in pentane, Aldrich), TMEDA (Aldrich), Se (99.5%, Aldrich), NaN(SiMe$_3$)$_2$ (95%, Aldrich), and KN(SiMe$_3$)$_2$ (95%, Aldrich) were used as received. The compounds [^{t}Bu(H)NP(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] **7**,[4e] [^{t}Bu(H)N(S)P(μ-N^{t}Bu)$_2$P(S)N(H)^{t}Bu] **6a**,[13] and {(THF)K[(^{t}BuN)(Se)P(μ-N^{t}Bu)$_2$P(Se)(N^{t}Bu)]K(THF)$_2$}$_n$ **12b**[12] were prepared by literature procedures. The handling of air- and moisture-sensitive reagents was performed under an atmosphere of argon gas in a glovebox or by using standard Schlenk techniques.

Instrumentation. ^{1}H NMR spectra were collected on a Bruker AM-200 spectrometer, and chemical shifts are reported relative to Me$_4$Si in CDCl$_3$. ^{7}Li NMR spectra were recorded on a Varian XL-200 instrument operating at 77.75 MHz; chemical shifts are reported relative to 1 M LiCl in D$_2$O. ^{31}P and ^{77}Se NMR spectra were obtained on a Bruker AMX-300 spectrometer (operating at 121.50 and 57.23 MHz, respectively); chemical shifts are reported relative to 85% H$_3$PO$_4$ in D$_2$O and Ph$_2$Se$_2$ in CDCl$_3$ (+463 ppm relative to Me$_2$Se), respectively. Infrared spectra were recorded as Nujol mulls on a Mattson 4030 FTIR spectrometer 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.

Preparation of *cis*-[^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] 6b. A mixture of [^{t}Bu(H)NP(μ-N^{t}Bu)$_2$PN(H)^{t}Bu)] (5.00 g, 14.3 mmol) and elemental selenium (2.28 g, 28.8 mmol) was heated in toluene at 120 °C for 18 h. Unreacted black selenium was removed by filtration to give a yellow solution. The volume of the solution was reduced to 50 mL. Storage at −15 °C yielded two crops of crystals of **6b** (5.91 g, 11.7 mmol, 89%); mp 144−149 °C. ^{1}H NMR (d_8-THF, δ): 4.56 (2H, NH), 1.66 (18H, ^{t}Bu), 1.46 (18H, ^{t}Bu). ^{31}P{^{1}H} NMR (d_8-THF, δ): 26.7 [s, $^1J(^{31}P-^{77}Se)$ = 880 Hz, $^2J(^{31}P-^{31}P)$ = 25 Hz]. ^{77}Se NMR (d_8-THF, δ): −128.6 [d, $^1J(^{31}P-^{77}Se)$ = 877 Hz]. IR (cm^{-1}): 3383 [ν(N−H)], 581 [ν(P=Se)]. MS [EI, *m/z* (rel int)]: M$^+$ 506(3.2). Anal. Calcd for C$_{16}$H$_{38}$N$_4$P$_2$Se$_2$: C, 37.95; H, 7.56, N, 11.06. Found: C, 37.96; H, 7.78; N, 10.89.

Preparation of {(TMEDA)Li[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)NH^{t}Bu]} 8a. A yellow solution of *n*-butyllithium (1.45 mL, 3.64 mmol) in TMEDA (10 mL) was added slowly to a stirred solution of [^{t}Bu(H)N(S)P(μ-N^{t}Bu)$_2$P(S)N(H)^{t}Bu] (1.50 g, 3.64 mmol) in toluene (25 mL) at 23 °C. The reaction mixture was heated for 2.5 h at 75 °C. Removal of the solvent, followed by two washings with hexane (5 mL), yielded **8a** as a pale yellow solid (1.84 g, 3.44 mmol, 95%). X-ray quality crystals were obtained from toluene at 23 °C after 3 days. ^{1}H NMR (C$_6$D$_6$, δ): 3.09 (1H, NH), 2.00 (12H, [(C*H*$_3$)$_2$N(CH$_2$)$_2$N(C*H*$_3$)$_2$]), 1.94 (18H, ^{t}Bu), 1.76 (4H, [(CH$_3$)$_2$N(C*H*$_2$)$_2$N(CH$_3$)$_2$]), 1.54 (9H, ^{t}Bu), 1.41 (9H, ^{t}Bu). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 36.3 (d, $^2J(^{31}P-^{31}P)$ = 21 Hz), 16.7 (unres d). ^{7}Li NMR (C$_6$D$_6$, δ): −1.72 (s). IR (cm^{-1}): 3382 [ν(N−H)].

Preparation of {(THF)$_2$Li[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$P(Se)NH^{t}Bu]} 8b. *n*-Butyllithium (3.95 mL, 9.87 mmol) was added slowly to a stirred solution of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (5.00 g, 9.87 mmol) in THF (50 mL) at −78 °C. The solution was warmed to 23 °C and stirred for 3 h. Removal of the solvent, followed by two washings with pentane (20 mL), yielded **8b** as a white solid (5.85 g, 8.91 mmol, 90%). ^{1}H NMR (d_8-THF, δ): 3.23 (1H, NH), 1.70 (18H, ^{t}Bu), 1.45 (9H, ^{t}Bu), 1.32 (9H, ^{t}Bu). ^{31}P{^{1}H} NMR (d_8-THF, δ): 23.6 [d, $^2J(^{31}P-^{31}P)$ = 8 Hz, $^1J(^{31}P-^{77}Se)$ = 860 Hz], −4.0 [d, $^2J(^{31}P-^{31}P)$ = 8 Hz, $^1J(^{31}P-^{77}Se)$ = 695 Hz]. ^{77}Se NMR (d_8-THF, δ): −81.3 [d,$^1J(^{31}P-^{77}Se)$ = 695 Hz], −131.9 [d, $^1J(^{31}P-^{77}Se)$ = 860 Hz]. ^{7}Li NMR (d_8-THF, δ): 1.8 (br s). IR (cm^{-1}): 3382 [ν(N−H)].

Preparation of {(THF)$_2$Li[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)N^{t}Bu]Li(THF)$_2$} 9. *tert*-Butyllithium (7.10 mL, 12.07 mmol) was added slowly to a stirred solution of [^{t}Bu(H)N(S)P(μ-N^{t}Bu)$_2$P(S)N(H)^{t}Bu] (2.49 g, 6.04 mmol) in THF (30 mL) at 23 °C. The reaction mixture was heated at reflux for 2 d at 65 °C. X-ray quality crystals of **9** were obtained from a THF/hexane solution at 23 °C (2.37 g, 6.64 mmol, 61%). ^{1}H NMR (d_8-THF, δ): 3.58 (m, [O(C*H*$_2$)$_2$(CH$_2$)$_2$]), 1.74 (m, [O(CH$_2$)$_2$(C*H*$_2$)$_2$]), 1.69 (18H, ^{t}Bu), 1.33 (18H, ^{t}Bu). ^{31}P{^{1}H} NMR (d_8-THF, δ): 15.6 (s). ^{7}Li NMR (d_8-THF, δ): 1.4 (s). IR (cm^{-1}): 599 [ν(P−S)].

Preparation of {(THF)$_2$Li[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PNH^{t}Bu]} 10. An excess of *tert*-butyllithium (3.50 mL, 5.95 mmol) was added slowly to a stirred solution of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (1.04 g, 1.98 mmol) in THF (25 mL) at 23 °C. The reaction mixture was heated at reflux for 2 days at 65 °C. X-ray quality crystals of **10** were obtained from a THF/hexane solution at −15 °C (0.89 g, 1.54 mmol, 78%). ^{1}H NMR (d_8-THF, δ): 3.58 (m, [O(C*H*$_2$)$_2$(CH$_2$)$_2$]), 2.8 (1H, NH), 1.74 (m, [O(CH$_2$)$_2$(C*H*$_2$)$_2$]), 1.49 (18H, ^{t}Bu), 1.29 (9H, ^{t}Bu), 1.22 (9H, ^{t}Bu). ^{31}P{^{1}H} NMR (d_8-THF, δ): 74.5 (s), 3.1 [s, $^1J(^{31}P-^{77}Se)$ = 622 Hz]. ^{77}Se (d_8-THF, δ): −64.8 [d, $^1J(^{31}P-^{77}Se)$ = 622 Hz]. ^{7}Li NMR (d_8-THF, δ): 1.5 (s). (**CAUTION**: The byproduct of this reaction, LiSe^{t}Bu, produces an objectionable stench!)

Preparation of {(THF)$_2$Na[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)N^{t}Bu]Na(THF)$_2$} 11a. A solution of NaN(SiMe$_3$)$_2$ (0.468 g, 2.42 mmol) in THF (10 mL) was added slowly to a stirred solution of [^{t}Bu(H)N(S)P(μ-N^{t}Bu)$_2$P(S)N(H)^{t}Bu] (0.500 g, 1.21 mmol) in THF (20 mL) at 23 °C. The reaction mixture was stirred for 2 h at 23 °C to give a faint yellow solution. Removal of the solvent followed by two washings with hexane (5 mL) yielded **11a** as a pale yellow solid (0.579 g, 0.78 mmol, 64%). X-ray quality crystals were obtained from THF at 23 °C. ^{1}H NMR (d_8-THF, δ): 3.58 (m, [O(C*H*$_2$)$_2$(CH$_2$)$_2$]), 1.74 (m, [O(CH$_2$)$_2$(C*H*$_2$)$_2$]), 1.61 (18H, ^{t}Bu), 1.32 (18H, ^{t}Bu). ^{31}P{^{1}H} NMR (d_8-THF, δ): 29.4 (s). IR (cm^{-1}): 565 [ν(P−S)].

Preparation of {(THF)$_2$Na[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$P(Se)N^{t}Bu]Na(THF)$_2$} 11b. A solution of NaN(SiMe$_3$)$_2$ (0.381 g, 1.98 mmol) in THF (10 mL) was added slowly to a stirred solution of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (0.500 g, 0.99 mmol) in THF (20 mL) at 23 °C. The reaction mixture was stirred for 2 h at 23 °C to give a pale yellow solution. Removal of the solvent followed by two washings with hexane (5 mL) yielded **11b** as a white solid (0.538 g, 0.64 mmol, 65%); mp: 200 °C (dec). Crystals were obtained from THF at 23 °C. ^{1}H NMR (d_8-THF, δ): 3.58 (m, [O(C*H*$_2$)$_2$(CH$_2$)$_2$]), 1.74 (m, [O(CH$_2$)$_2$(C*H*$_2$)$_2$]), 1.67 (18H, ^{t}Bu), 1.34 (18H, ^{t}Bu). ^{31}P{^{1}H} NMR (d_8-THF, δ): 3.9 [s, $^1J(^{31}P-^{77}Se)$ = 678 Hz, $^2J(^{31}P-^{31}P)$ = 6 Hz]. ^{77}Se NMR (d_8-THF, δ): −12.4 [d, $^1J(^{31}P-^{77}Se)$ = 677 Hz]. IR (cm^{-1}): 518 [ν(P−Se)].

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Table 1. Crystallographic Data for **8a**, **9·**THF, **10**, **11a**, and **12b**

	8a	**9·**THF	**10**	**11a**	**12b**
formula	$C_{22}H_{53}LiN_6P_2S_2$	$C_{36}H_{76}Li_2N_4O_5P_2S_2$	$C_{48}H_{106}Li_2N_8O_4P_4Se_2$	$C_{32}H_{68}N_4Na_2O_4P_2S_2$	$C_{28}H_{60}K_2N_4O_3P_2Se_2$
fw	534.71	784.97	1155.09	744.94	798.87
cryst size (mm^3)	0.60 × 0.40 × 0.40	0.55 × 0.45 × 0.40	0.28 × 0.22 × 0.21	0.45 × 0.35 × 0.20	0.50 × 0.30 × 0.20
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	10.477(3)	13.172(3)	20.901(2)	10.4015(15)	10.733(11)
b, Å	10.455(4)	16.877(2)	10.1486(9)	21.147(3)	14.085(10)
c, Å	29.375(7)	10.395(2)	30.341(3)	9.9192(12)	26.138(9)
α, deg	91.92(1)	90.314(15)			
β, deg	96.96(3)	90.43(2)	95.4216(18)	94.771(11)	90.99(5)
γ, deg	95.25(1)	100.287(16)			
V, Å^3	3194(2)	2299.9(7)	6407.2(10)	2138.9(5)	3951(5)
Z	4	2	4	2	4
T, °C	−103	−103	−80	−103	−103
λ, Å	0.71069	0.71069	0.71073	0.71069	0.71069
d_{calcd}, g cm^{-3}	1.112	1.133	1.197	1.157	1.343
μ, cm^{-1}	2.87	2.25	12.97	2.56	21.94
F(000)	1168	856	2464	808	1664
R^a	0.0673	0.061	0.0561	0.0551	0.064
$R_w{}^b$	0.1568	0.172	0.1372^c	0.1247	0.1652

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

Preparation of {(THF)K[(^{t}BuN)(S)P(*μ*-N^{t}Bu)$_2$P(S)(N^{t}Bu)]K(THF)}$_n$ 12a. A solution of $KN(SiMe_3)_2$ (1.049 g, 5.00 mmol) in THF (10 mL) was added slowly to a stirred solution of [^{t}Bu(H)N(S)P(*μ*-N^{t}Bu)$_2$P(S)N(H)^{t}Bu] (1.031 g, 2.50 mmol) in THF (20 mL) at 23 °C. The reaction mixture was stirred for 2.5 h at 23 °C to give a yellow solution. Removal of the solvent, followed by two washings with hexane (5 mL), yielded **12a** as a pale yellow solid (1.28 g, 2.02 mmol, 81%). Crystals were obtained from THF at 23 °C. ^{1}H NMR (d_8-THF, *δ*): 3.58 (m, [O(C*H*$_2$)$_2$(CH$_2$)$_2$]), 1.75 (m, [O(CH$_2$)$_2$(C*H*$_2$)$_2$]), 1.60 (18H, ^{t}Bu), 1.31 (18H, ^{t}Bu). ^{31}P{^{1}H} NMR (d_8-THF, *δ*): 26.6 (s). IR (cm^{-1}): 551 [*ν*(P−S)].

X-ray Analyses. All measurements for **8a**, **9·**THF, **11a**, and **12b** were made on a Rigaku AFC6S diffractometer. The measurements for **10** were carried out on a Bruker AXS P4/RA/SMART 1000 CCD diffractometer. Crystallographic data are summarized in Table 1. For structures **8a**, **9·**THF, **11a**, and **12b**, scattering factors were those of Cromer and Waber[14] and allowance was made for anomalous dispersion.[15] All calculations were performed using teXsan[16] and refinements carried out with the aid of SHELXL-97.[17a]

8a. A colorless prismatic crystal of {(TMEDA)Li[^{t}BuN(S)P(*μ*-N^{t}Bu)$_2$P(S) N(H)^{t}Bu]} was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 15 carefully centered reflections in the range 15.72° < 2*θ* < 20.19°. Scans of (0.73 + 0.34 tan *θ*)° were made at a speed of 16.0°/min to a maximum 2*θ* value of 50.1°. The intensities of 5637 unique reflections were measured, of which 2976 had $I > 2.00\sigma(I)$. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods[18] and expanded using Fourier techniques.[19] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The methyl carbon atoms C10−C12 and C22 showed large temperature factors indicating a degree of thermal disorder.

The procedures for data collection, structure solution, and refinement for **9·**THF, **11a**, and **12b** were similar to those described for **8a**. For **9·**THF six carbon atoms of two THF molecules were disordered with inequivalent occupancy factors. The major fractions of these disordered atoms were allowed anisotropic displacement parameters while the minor fractions were allowed isotropic temperature factors. In the case of **10** two independent {(THF)$_2$Li[^{t}BuN(Se)P(*μ*-N^{t}Bu)$_2$PN(H)^{t}Bu]} molecules were present in the asymmetric unit. The bond distances and angles of the two molecules are very similar, and the parameters for only one of these molecules are reported in Table 2. In one of these two molecules the carbon atoms of one of the coordinating THF molecules (C1−C4 and C1′−C4′) are disordered over two sites with partial occupancy factors and its atoms were refined using the SAME, DELU, and SIMU constraints. In the other molecule the methyl groups of one of the ^{t}Bu groups (C81−C83 and C81′−C83′) showed a severe rotational disorder and they could only be refined isotropically. For **12b** the carbon atoms (C18−20) of a THF molecule had large thermal displacement parameters showing thermal disorder.

Results and Discussion

Synthesis and Metalation of *cis*-[^{t}Bu(H)N(E)P(*μ*-N^{t}Bu)$_2$P(E)N(H)^{t}Bu] (6a, E = S; 6b, E = Se). Although the cyclodiphosph(III)azane [^{t}Bu(H)NP(*μ*-N^{t}Bu)$_2$PN(H)^{t}Bu] **7** has been known for many years,[20] the cis arrangement of the exocyclic N(H)^{t}Bu groups was only recently confirmed by X-ray crystallography.[4e,21] Oxidation of **7** with elemental sulfur or selenium in refluxing toluene produces **6a** and **6b** in 97% and 89% yields, respectively (Scheme 1). X-ray structure determinations of **6a**[13] and Ph(H)N(Se)P(*μ*-N^{t}Bu)$_2$P(Se)N(H)Ph,[22] an analogue of **6b**, have shown that the NH hydrogens adopt an endo, exo orientation.

The bis-phosphine sulfide **6a** is both air and moisture stable. The corresponding selenide **6b** is handled under an inert atmosphere due to the lability of the P−Se bond. The ^{31}P{^{1}H} NMR spectrum of **6b** consists of a singlet at 26.7 ppm with two pairs of ^{77}Se satellites attributable to the AA′X spin system of the isotopomer containing one ^{77}Se ($I = ^1/_2$, 7.6%) atom. The A−X [$^1J(^{31}P-^{77}Se)$] coupling is 880 Hz, while the A−A′ [$^2J(^{31}P-^{31}P)$] coupling is 25 Hz [cf. $Ph_2P(Se)NHP(Se)Ph_2$; *δ*-

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(16) *teXsan*: *Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985, 1992.
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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for {(TMEDA)Li[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)NH^{t}Bu]} **8a**, {(THF)$_2$Li[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)N^{t}Bu]Li(THF)$_2$} **9**·THF, and {(THF)$_2$Li[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PNH^{t}Bu]} **10**

	8a (E = S)	**9**·THF (E = S)	**10**[a] (E = Se)
E(1)−P(1)	1.978(2)	2.005(2)	2.1634(15)
E(1)−Li(1)	2.457(11)	2.436(8)	2.605(10)
E(2)−P(2)	1.931(2)	2.000(2)	
E(2)−Li(2)		2.435(9)	
P(1)−N(1)	1.716(5)	1.706(3)	1.696(4)
P(1)−N(2)	1.710(5)	1.718(3)	1.709(5)
P(1)−N(3)	1.571(5)	1.567(4)	1.576(4)
P(2)−N(4)	1.641(5)	1.576(4)	1.678(5)
P(2)−N(2)	1.676(5)	1.720(4)	1.734(4)
P(2)−N(1)	1.677(5)	1.719(3)	1.728(5)
O(1)−Li(1)		1.936(8)	1.966(10)
O(2)−Li(1)		1.982(8)	2.001(12)
O(3)−Li(2)		1.953(9)	
O(4)−Li(2)		1.966(9)	
N(3)−Li(1)	2.021(11)	1.992(8)	1.963(11)
N(4)−Li(2)		2.005(10)	
P(1)−E(1)−Li(1)	74.8(2)	75.31(18)	70.5(2)
P(2)−E(2)−Li(2)		75.7(2)	
N(3)−P(1)−N(1)	120.7(2)	121.83(19)	119.8(2)
N(3)−P(1)−N(2)	118.4(3)	119.90(18)	119.6(2)
N(1)−P(1)−N(2)	81.5(2)	82.73(16)	82.7(2)
N(3)−P(1)−E(1)	107.48(19)	104.69(15)	105.73(17)
N(1)−P(1)−E(1)	112.99(17)	113.28(13)	114.20(16)
N(2)−P(1)−E(1)	114.28(18)	113.85(13)	114.00(16)
N(4)−P(2)−N(2)	108.7(3)	121.04(18)	103.6(2)
N(4)−P(2)−N(1)	108.7(3)	119.92(18)	105.1(2)
N(2)−P(2)−N(1)	83.6(2)	82.28(16)	81.0(2)
N(4)−P(2)−E(2)	112.0(2)	105.33(15)	
N(2)−P(2)−E(2)	120.53(18)	113.36(13)	
N(1)−P(2)−E(2)	120.03(18)	114.14(13)	
P(1)−N(3)−Li(1)	97.7(4)	99.7(3)	102.8(4)
P(1)−N(2)−P(2)	97.2(2)	96.37(17)	97.2(2)
P(1)−N(1)−P(2)	96.9(2)	96.81(17)	98.0(2)
P(2)−N(4)−Li(2)		99.3(3)	
N(3)−Li(1)−E(1)	79.1(4)	79.1(3)	80.9(3)
N(2)−Li(2)−E(2)		79.4(3)	

[a] The bond angles and distances are reported for only one of the two unique molecules in the asymmetric unit. They have very similar bond distances and differ significantly only in the P(2)−N(4) [P(4)−N(8)] bond length: 1.678(5) [1.713(6)].

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for {(THF)$_2$Na[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)N^{t}Bu]Na(THF)$_2$} **11a** and {(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$P(Se)N^{t}Bu]K(THF)$_2$}$_n$ **12b**

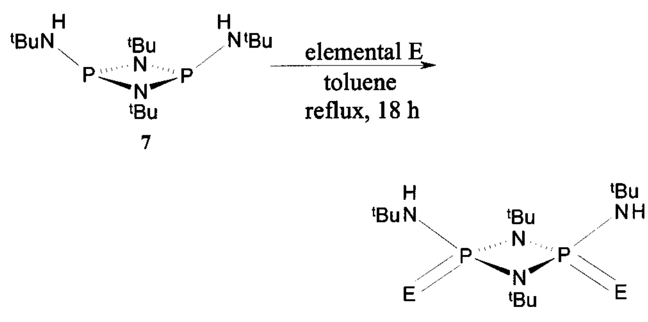
	11a (E = S, M = Na)	**12b** (E = Se, M = K)
E(1)−P(1)	1.994(3)	2.171(4)
E(1)−M(1)	2.873(4)	3.354(3)
E(2)−P(2)	1.991(3)	2.163(4)
E(2)−M(1)	2.832(4)	3.274(4)
P(1)−N(1)	1.715(6)	1.735(9)
P(1)−N(2)	1.706(6)	1.715(10)
P(1)−N(3)	1.559(6)	1.546(10)
P(2)−N(1)	1.719(6)	1.717(19)
P(2)−N(2)	1.705(6)	1.703(8)
P(2)−N(4)	1.565(6)	1.552(10)
M(1)−O(1)	2.369(7)	2.667(11)
M(1)−O(2)	2.301(7)	2.735(10)
M(1)−N(1)	2.756(7)	3.191(11)
M(2)−O(3)	2.413(8)	2.705(11)
M(2)−O(4)	2.374(7)	
M(2)−N(2)	2.916(7)	3.210(10)
M(2)−N(3)	2.461(7)	2.766(11)
M(2)−N(4)	2.423(7)	2.804(10)
P(1)−E(1)−M(1)	82.42(11)	86.66(11)
P(2)−E(2)−M(1)	82.96(12)	87.64(12)
N(3)−P(1)−N(2)	110.8(3)	110.2(5)
N(3)−P(1)−N(1)	112.0(3)	114.4(6)
N(2)−P(1)−N(1)	81.8(3)	82.0(4)
N(3)−P(1)−E(1)	121.0(2)	119.5(4)
N(2)−P(1)−E(1)	113.7(2)	113.7(4)
N(1)−P(1)−E(1)	110.9(2)	111.1(4)
N(4)−P(2)−N(2)	109.7(3)	110.6(5)
N(4)−P(2)−N(1)	113.4(3)	114.0(6)
N(2)−P(2)−N(1)	81.7(3)	82.9(4)
N(4)−P(2)−E(2)	121.0(3)	119.8(4)
N(2)−P(2)−E(2)	113.4(3)	112.2(4)
N(1)−P(2)−E(2)	111.1(2)	111.5(4)
E(2)−M(1)−E(1)	116.84(13)	97.14(8)
N(4)−M(2)−N(3)	104.2(2)	91.2(3)
P(1)−N(1)−P(2)	97.4(3)	96.7(5)
P(1)−N(3)−M(2)	100.7(3)	105.1(5)
P(1)−N(2)−P(2)	98.2(3)	98.0(5)
P(2)−N(4)−M(2)	101.4(3)	104.0(5)

(^{31}P) 53.2 ppm, $^1J(^{31}P-^{77}Se)$ = 786 Hz and $^2J(^{31}P-^{31}P)$ = 29 Hz].[23] The ^{77}Se NMR spectrum of **6b** exhibits the expected doublet at −128.6 ppm [$^1J(^{31}P-^{77}Se)$ = 880 Hz] (cf. Ph$_2$P(Se)NHP(Se)Ph$_2$; δ(^{77}Se) −162.8 ppm, $^1J(^{77}Se-^{31}P)$ = 790 Hz).[24]

As indicated in Scheme 2 the lithiation of **6a** with Li^{n}Bu or Li^{t}Bu produced either a monolithiated or a dilithiated derivative in excellent yields depending on the reaction conditions.[25] Prolonged reflux (2 days) and the use of the stronger base Li^{t}Bu was necessary to achieve dilithiation.[26] The extent of lithiation is readily monitored by ^{31}P NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum of the monolithiated derivative **8a** consists of two mutually coupled doublets centered at δ 36.3 and 16.7 [$^2J(^{31}P-^{31}P)$ = 21 Hz] whereas a singlet is observed at δ 15.6 for the dilithiated complex **9**. In the ^{1}H NMR spectrum, **8** exhibits three resonances in the N^{t}Bu region in the integrated ratio of 2:1:1, and a broad singlet at δ 3.09 (NH), while **9** gives rise to two equally intense resonances for the two pairs of equivalent N^{t}Bu groups.

The reaction of **6b** with Li^{n}Bu at 23 °C produced the monolithiated complex **8b** in excellent yields. The ^{31}P{^{1}H} NMR spectrum of **8b** exhibits two mutually coupled doublets centered at δ 23.6 and δ −4.0 flanked by ^{77}Se satellites [$^1J(^{31}P-^{77}Se)$ = 860 and 695 Hz, respectively; $^2J(^{31}P-^{31}P)$ = 8 Hz]. The ^{77}Se NMR shows two doublets at δ −81.3 and −131.9 [$^1J(^{31}P-^{77}Se)$ = 695 and 860 Hz, respectively] (cf. **6b**, δ (^{77}Se) −128.6 ppm, $^1J(^{31}P-^{77}Se)$ = 877 Hz).

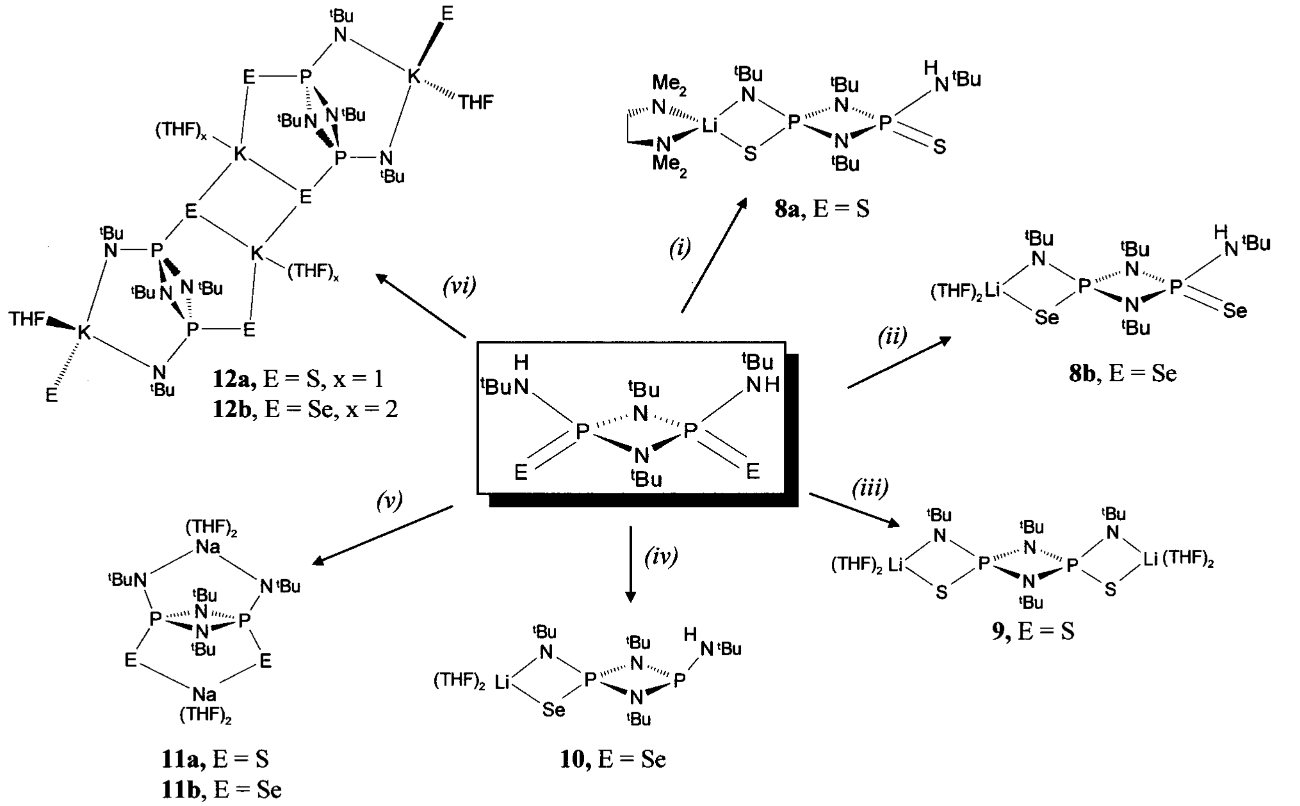
Scheme 1



6a, E = S (97%)
6b, E = Se (81%)

(23) Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2489.
(24) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **1999**, *38*, 5478.
(25) All the alkali-metal derivatives of **6a** and **6b** reported in this paper were spectroscopically pure (^{1}H and ^{31}P NMR) after recrystallization. However, satisfactory CHN analyses could not be obtained owing to a combination of high moisture sensitivity and facile loss of solvent (THF) from crystalline samples.
(26) Stahl and co-workers have reported the generation of dilithium complexes with a bis(*N*,*E*) coordination mode by the treatment of *cis*-[Ph(H)N(E)P(μ-N^{t}Bu)$_2$P(E)N(H)Ph] with 2 equiv of Li^{n}Bu at room temperature (ref 22).

Scheme 2[a]



[a] (i) ⁿBuLi, TMEDA/PhMe, 75 °C, 2.5 h; (ii) ⁿBuLi, THF, −78 °C, 3 h; (iii) 2ᵗBuLi, THF, 65 °C, 2 days; (iv) 3ᵗBuLi, THF, 65 °C, 2 days; (v) $2NaN(SiMe_3)_2$, THF, 23 °C, 2 h; (vi) $2KN(SiMe_3)_2$, THF, 23 °C, 2 h.

Interestingly, an attempt to generate the dilithiated derivative of **5b** resulted in partial deselenation to give the monolithiated complex **10** (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of **10** exhibits two singlets at δ 76.0 and 4.7. The latter resonance is flanked by ^{77}Se satellite peaks [$^1J(^{31}P-^{77}Se) = 622$ Hz]. The chemical shift of the former resonance and the lack of ^{77}Se satellites indicate that reduction of P(V) to P(III) (deselenation) accompanies the lithiation process. The ^{77}Se NMR spectrum of **10** displays a doublet at δ 64.8 [$^1J(^{31}P-^{77}Se) = 622$ Hz]. The reduction in the $^{31}P-^{77}Se$ coupling constant of ca. 250 Hz upon deprotonation of **6b** indicates a decrease in bond order somewhat greater than that observed for related systems [cf. a reduction of ca. 100 Hz upon deprotonation of $Ph_2P(Se)NHP(Se)Ph_2$].[23] The observation of a resonance at δ 166.9 in the ^{77}Se NMR spectrum of the reaction mixture indicates that cleavage of one of the PSe bonds in **6b** by LiᵗBu produces LiSeᵗBu, which is readily obtained from LiᵗBu and elemental selenium.[27]

The reactions of **6a** or **6b** with $MN(SiMe_3)_2$ (M = Na, K) in a 1:1 molar ratio were monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which revealed singlets for the formation of the dianions **5a** or **5b**, in addition to an approximately equally intense resonance for unreacted **6a** or **6b**. The characteristic pattern of two doublets for the monometalated derivatives was only observed in very low intensity in these reaction mixtures. The dimetalated derivatives **11a**,**b** and **12a**,**b** may be obtained in excellent yields when these reactions are carried out in a 1:2 molar ratio in THF (Scheme 2).

The NMR and IR spectroscopic data for **11a**,**b** and **12a**,**b** indicate a substantial decrease in the P−E bond order in the dianions **5a** and **5b** compared to that in the neutral compounds **6a** and **6b**. The ^{31}P NMR spectrum shows a shift to lower frequencies upon deprotonation, from 41.3 in **6a** to 29.4 (**11a**) and 26.7 (**12a**); and from 26.9 in **6b** to 3.9 (**11b**) and 0.0 (**12b**). The coupling constant $^1J(^{31}P-^{77}Se)$ decreases from 880 Hz in **6b** to 678 Hz in **11b** and 686 Hz in **12b** (cf. 786 and 687 Hz for $Ph_2P(Se)NHP(Se)Ph_2$ and its K^+ salt, respectively).[23] The $^2J(^{31}P-^{31}P)$ coupling of the magnetically inequivalent phosphorus centers (A−A′) decreases from 25 Hz in **6b** to 6 Hz (**11b**) (cf. 29 and 6 Hz for $Ph_2P(Se)NHP(Se)Ph_2$ and its K^+ salt, respectively).[23] This coupling could not be resolved for **12b**. The IR stretching frequency ν(P−E) undergoes a corresponding decrease from 614 cm^{-1} in **6a** to 565 (**11a**) and 551 cm^{-1} (**12a**); and from 581 cm^{-1} in **6b** to 518 (**11b**) and 514 cm^{-1} (**12b**). The ^{77}Se NMR chemical shifts show the expected trend to higher frequency upon coordination to metal ions, from −128.6 ppm for **6b** to −12.4 (**11b**) and 13.2 ppm (**12b**), consistent with a shift of δ (^{77}Se) from −153 to −81 ppm for $Ph_2P(Se)N(SiMe_3)_2$ and $K[Ph_2P(Se)N(SiMe_3)]$, respectively.[11a]

X-ray Structures of {(TMEDA)Li[ᵗBuN(S)P(μ-NᵗBu)₂P(S)NHᵗBu]} 8a, ({THF)₂Li[ᵗBuN(S)P(μ-NᵗBu)₂P(S)NᵗBu]Li(THF)₂} 9, and {(THF)₂Li[ᵗBuN(Se)P(μ-NᵗBu)₂PNHᵗBu]} 10. The structures of **8a**, **9**, and **10** are shown in Figures 1−3, and pertinent structural parameters are summarized in Table 2. In all three complexes the anionic ligands are coordinated to lithium ions via *N,E* chelation forming four-membered LiNPE rings.[26] The Li^+ ions are all four-coordinate with either two THF molecules or one TMEDA ligand completing the coordination shell.

In the monolithiated complex **8a** the hydrogen atom of the terminal N(H)ᵗBu group is endo to the P_2N_2 ring. Thus it appears that the N(H)ᵗBu group with the exo hydrogen in **6a** was deprotonated. The terminal P═S bond length of 1.931(2) Å is similar to the mean value of 1.925(1) Å reported for **6a**,[13]

(27) Kawaguchi, H.; Tatsumi, K. *Chem. Commun.* **2000**, 1299.

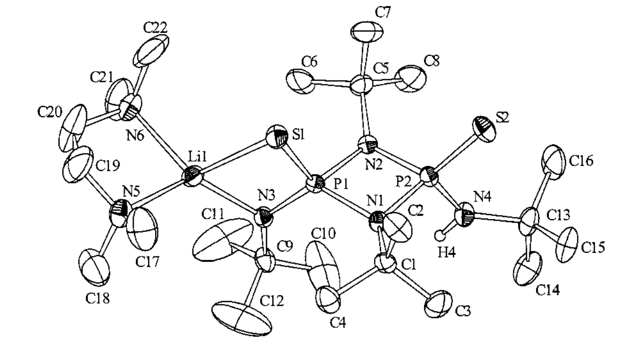


Figure 1. Molecular structure of {(TMEDA)Li[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P-(S)N(H)^{t}Bu]} **8a**. For clarity, the protons are omitted. Displacement ellipsoids are plotted at the 30% probability level.

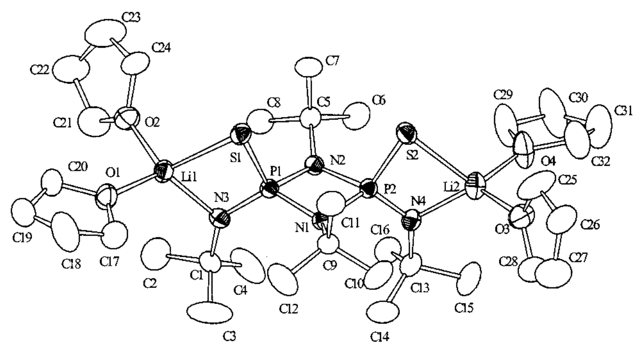


Figure 2. Molecular structure of {(THF)$_2$Li[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)-N^{t}Bu]Li(THF)$_2$} **9**. For clarity, the protons are omitted. Displacement ellipsoids are plotted at the 30% probability level.

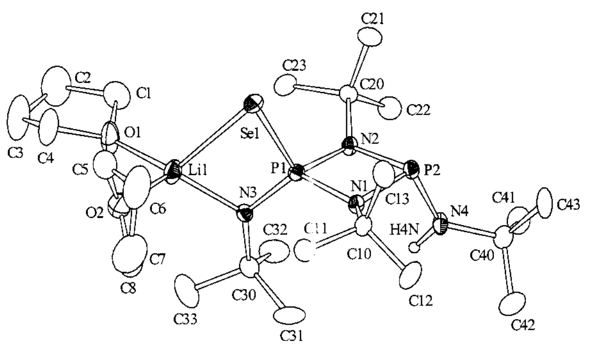


Figure 3. Molecular structure of {(THF)$_2$Li[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN-(H)^{t}Bu]} **10**. Only one of the independent molecules is depicted. For clarity, the protons are omitted. Displacement ellipsoids are plotted at the 30% probability level.

whereas the P−S bond in the LiNPS ring is lengthened to 1.978-(2) Å, consistent with the decrease in bond order implied by the decrease in ν(PS) upon metalation. There is a similar disparity in the P−N bond lengths outside the P_2N_2 ring [1.571-(5) and 1.641(5) Å, respectively; cf. $|d(PN)| = 1.631(3)$ for **6a**].[13] Within the P_2N_2 ring $|d(PN)| = 1.713(5)$ Å for the lithiated side of the molecule compared to 1.685(3) Å for the nonlithiated side. The P_2N_2 ring is significantly more folded than that of **6a**; the dihedral angle between the P(1)−N(1)−N(2) and P(2)−N(1)−N(2) planes is 9.3° (cf. 5.5°, **6a**). The bite angles (∠NPS) are 107.48(19) and 112.0(2) Å for the metalated and nonmetalated sides of **8a**.

The bis THF-solvated dilithiated complex **9** consists of a spirocyclic array of two four-membered LiNPS rings and a central P_2N_2 ring (Figure 2). The metrical parameters for **9** are similar to those of the lithiated side of the molecule in **8a**. For example, the mean exocyclic P−S bond length is 2.003(2) Å; cf. 1.978(2) Å for the corresponding P−S bond in **8a**. The P_2N_2

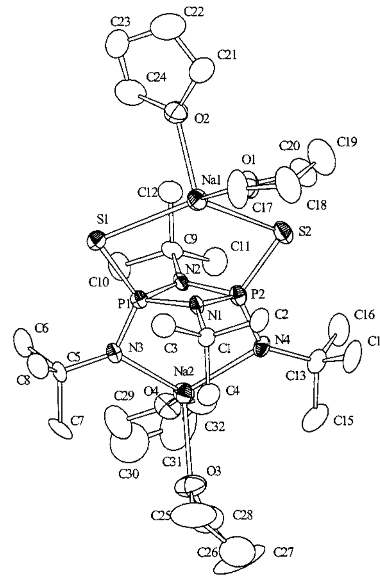


Figure 4. Molecular structure of {(THF)$_2$Na[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)-N^{t}Bu]Na(THF)$_2$} **11a**. For clarity, the protons are omitted. Displacement ellipsoids are plotted at the 30% probability level.

ring in **9** has a dihedral angle of 13.5° (cf. 9.3° for **8a**). The bite angles (∠NPS) are 104.69(15)° and 105.33(15)°; cf. 107.48(19)° in **8a**. These small geometrical distortions can be attributed to the steric congestion in the endo, endo conformation of exocyclic N^{t}Bu groups in **9**.

The P(III)/P(V) complex **10** can be viewed as a selenium analogue of **8a** in which two THF molecules replace the chelating TMEDA ligand and one of the P−Se bonds has been cleaved (see Figure 3). The exocyclic ^{t}BuNH group is trans to selenium with the H atom endo with respect to the P_2N_2 ring. The P−Se bond distance is 2.1634(15) Å [cf. 2.181(5) Å for {K[Ph$_2$P(Se)NSiMe$_3$]·THF}$_2$].[11a] The exocyclic P(III)−N bond length in **10** is 1.696(6) Å (cf. 1.664(2) Å for the cyclodiphosph-(III)azane **7**).[4e] The mean endocyclic P(III)−N bond lengths for **10** and **7** are also similar, 1.731(5) vs 1.726(2) Å.[4e] The dihedral angle P(1)−N(1)−N(2)−P(2) in **10** is 10.4°; cf. 9.3° in **8a**. The replacement of S by Se results in small differences in the geometry of the LiNPE rings in **8a** and **10**. The bond angle ∠PELi is decreased by ca. 4.3° in **10** while ∠PNLi increases by 5.1°. These distortions accommodate a decrease in the Li−N bond distance of 0.06 Å. Interestingly, the bite angle (∠NPSe) of 105.73(17)° in **10** is ca. 8.6° smaller than that in (K[Ph$_2$P-(Se)NSiMe$_3$]·THF)$_2$ as a result of the replacement of K^+ by the smaller Li^+ ion.[11a]

X-ray Structures of {(THF)$_2$Na[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)-N^{t}Bu]Na(THF)$_2$} 11a and {(THF)K[(^{t}BuN)(Se)P(μ-N^{t}Bu)$_2$P-(Se)(N^{t}Bu)]K(THF)$_2$}$_n$ 12b. The structures of compounds **11a**, **11b**, **12a**, and **12b** were all determined by X-ray crystallography. The disodium salts **11a** and **11b** and the dipotassium salts **12a** and **12b** are isostructural. Since the structures of **11b** and **12a** were highly disordered, detailed structural discussion will be restricted to the representative examples **11a** and **12b**. The most significant difference between the structures of **11a**,**b** and **12a**,**b** and that of the dilithiated analogue **9** is the mode of coordination of the dianion to the alkali-metal cation. In contrast to the side-on bis (*N*,*S*)-chelation observed for **9**, the larger Na^+ and K^+ ions are (*N*,*N*′ and *E*,*E*′)-chelated to the top and bottom of the ligand to give six-membered MEPNPE and MNPNPN rings (M = Na, K).

As indicated in Figure 4 for **11a** the disodium salts are monomers with four-coordinate Na^+ ions that are each solvated by two THF molecules. The exocyclic N^tBu groups are exo to the P_2N_2 ring as a consequence of the *N*,*N′* mode of coordination. A side view of the structure along the P−P vector reveals that the sodium ions are not positioned over the center of the P_2N_2 ring, but lie closer to one of the endocyclic nitrogens as found in many imidodiphosphinate systems[28a] and in some metal derivatives of cyclodiphosph(III)azanes and cyclodisilazanes.[28b]

Despite the different modes of coordination, the mean P−S, $P-N_{exo}$, and $P-N_{endo}$ bond lengths for **11a**, 1.993(3), 1.562(6), and 1.711(6) Å, respectively, are similar to the corresponding distances of 2.003(2), 1.572(4), and 1.716(3) Å in **9**. The mean Na−S and Na−N bond lengths in **11a** are 2.853(4) and 2.442(7) Å, respectively. The bond angles ∠SNaS and ∠NNaN are 116.84(13)° and 104.2(2)°, respectively. The P_2N_2 ring in **11a** has a torsion angle of 9.6°; cf. 5.3° in **6a**. The only significant differences in bond angles involve the sulfur atoms. Specifically, $\angle SPN_{exo}$ increases from 110.4(1)° in **6a** to 121.0(3)° in **11a** while $\angle SPN_{endo}$ decreases from 120.0(1)° to 112.27(3)°.

The structure of the dipotassium salt **12b** was described briefly in the preliminary communication.[12] The sulfur analogue **12a** is isostructural with **12b** except that the *S*,*S′*-chelated K^+ ion is monosolvated by THF in **12a** whereas the *Se*,*Se′*-chelated K^+ ion in **12b** is solvated by two THF molecules. In contrast to **11a**,**b**, however, the monomeric units in **12a**,**b** dimerize via K···E interactions (Scheme 2). Furthermore each of these dimers is connected to four other dimers through weaker K···E interactions that involve the mono THF-solvated *N*,*N′*-chelated K^+ ion and the chalcogen atom that is not involved in the dimerization. This results in an extended polymeric network composed of 20-membered $K_6E_6P_4N_4$ rings. These two-dimensional networks are stacked on top of each other in the crystal lattice (Figure 5). There are three different KSe bond distances in **12b**: 3.314(4) Å within the monomeric units (cf. 3.378(5) Å for the dimer $\{K[Ph_2P(Se)NSiMe_3]\cdot THF\}_2$),[11a] 3.418(3) Å for the K_2Se_2 rings (cf. 3.417(4) Å for $\{K[Ph_2P(Se)NSiMe_3]\cdot THF\}_2$),[11a] and 3.644(3) Å for the weak K···Se interactions between dimeric units. Extended structures based on K···E interactions have been reported previously for the unsolvated complexes $\{K[Ph_2P(E)NP(E)Ph_2\}_x$ (E = S,[29] Se).[28a] However, unlike the previously reported extended networks, which are based on "one-sided" monoanionic units, the presence of two K^+ ions per monomeric building block of the dianions allows the formation of extended networks in more than one direction. The bis-solvation of both Na^+ ions in **11a**,**b** apparently prevents the formation of an extended structure for the disodium salts.

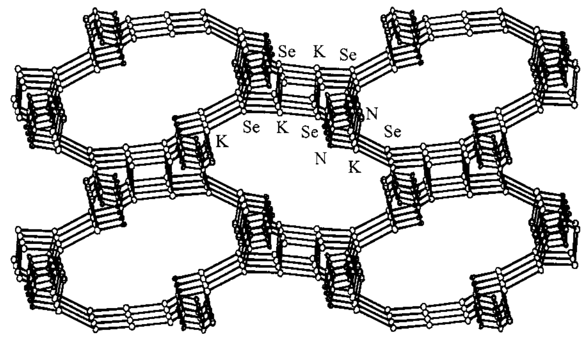


Figure 5. A section of the infinite extended molecular structure of $\{(THF)K[(^tBuN)(Se)P(\mu\text{-}N^tBu)_2P(Se)(N^tBu)]K(THF)_2\}_x$ **12b** as viewed through the $K_6Se_6N_4P_4$ 20-membered pore-like rings. For clarity the ^tBu groups and THF molecules have been omitted.

Many of the bond lengths and bond angles for **12b** follow trends similar to those observed for **11a**. The mean P−Se bond length is 2.167(4) Å (cf. 2.1634(15) Å in **10**). The major differences between the structures of **12b** and **11a** involve the bond angles ∠EME and ∠NMN, which are 97.14(8)° and 91.2(3)°, respectively, for **12b**; cf. 116.84(13)° and 104.2(2)° for **11a**.

Conclusions

Investigations of the alkali-metal derivatives of the ambidentate dianions $[^tBuN(E)P(\mu\text{-}N^tBu)_2P(E)N^tBu]^{2-}$ (E = S, Se) reveal two different modes of coordination. A bis-chelated (*N*,*S*) bonding mode is observed for lithium. By contrast, the larger sodium and potassium ions display a preference for *N*,*N′* and *E*,*E′* bis-chelation. These findings may be significant in future attempts to generate transition-metal-containing polymers based on a P_2N_2 template involving either side-on (*N*,*E*) or top and bottom (*N*,*N′* and *E*,*E′*) coordination.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **8a**, **9**, **10**, **11a**, and **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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