Inorg. Chem. **2002**, *41*, 4348–4354

Inorganic Chemistry
Article

Syntheses and X-ray Structures of Potassium Derivatives and a Paramagnetic Nickel(II) Complex of a Cyclodiphosph(III/V)azane Monoselenide

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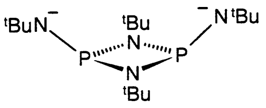
Received March 4, 2002

The cyclodiphosph(III/V)azane monoselenide [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (**6**, H$_2$cdppSe where cdpp = cyclodiphosphazane) is obtained in quantitative yield from the comproportionation reaction of equimolar amounts of H$_2$cdpp (**7**) and H$_2$cdppSe$_2$ (**3**) in toluene at 85 °C. The X-ray structures of **3** and **6** reveal that both the monoselenide and the diselenide adopt a cis,endo,exo arrangement of the ^{t}BuNH groups. Metalation of **6** with 1 equiv of KO^{t}Bu or 2 equiv of KCH$_2$Ph in THF produces $\{$(THF)K[HcdppSe]$\}_2$ (**8**) or $\{$[(THF)$_2$K]$_2$[cdppSe]$\}_2$ (**9**), respectively. The initial deprotonation involves the ^{t}BuNH group attached to the P(V) center in **6**. In the dimeric structure of **8**, both of the monoanionic ligands are bis-N,Se-chelated to the two K$^+$ cations to give a distorted K$_2$N$_2$Se$_2$ octahedron. In the centrosymmetric dimer **9**, the dianionic ligands adopt two different coordination modes to the bis-solvated K$^+$ ions, viz., tridentate N,N′,N′′ coordination and N,Se-chelation involving both exo- and endocyclic nitrogen atoms. The dimer is linked through K–Se interactions. The reaction of 2 equiv of **8** with NiCl$_2$(PMe$_3$)$_2$ in THF produces [Ni(HcdppSe)$_2$], which has a distorted tetrahedral structure and exhibits anomalous ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts owing to the proximity of the paramagnetic Ni(II) center.

Introduction

The coordination chemistry of the dianionic cyclodiphosph(III/III)azane **1** has been studied extensively, especially by Stahl.[1] The interest in this electron-rich N-donor ligand ranges from possible applications in catalysis to the stabilization of unusual geometries at main-group[1] and transition-metal centers.[1,2] We have been investigating the dianionic cyclodiphosph(V/V)azane disulfide **2a** and diselenide **2b** as ambidentate ligands that may function as bridges in the formation of metal-containing coordination polymers.[3] Although the number of examples are limited, the dianions **2a** and **2b** adopt either a "side-on" (N,E) chelation mode for Li[3b] and Al[4] or a "top and bottom" (N,N′ and/or E,E′) chelation mode for Na,[3b] K,[3a] Pt,[3c] and Sn.[5]



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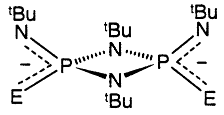

2a (E = S)
2b (E = Se)

An unexpected outcome of these studies was the observation of deselenation of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (**3**) by alkyllithium reagents to form a lithium salt of the monoanion **4** in the attempted synthesis of the dilithium derivative of **2b**.[3b] With a view to the development of the chemistry of anionic cyclodiphosph(III/V)azane ligands **4** and **5**, we now report the synthesis and X-ray structures of the monoselenide [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (**6**), the potassium salts of the corresponding mono- and dianions, **4** and **5**, respectively, and a nickel(II) complex of **4**. The structure of the diselenide **3** was also determined for comparison with that of **6**. Finally, we describe the unexpected outcome of the attempted lithiation of the potassium salt of the monoanion **4**.

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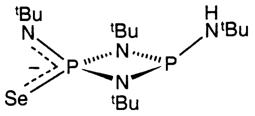

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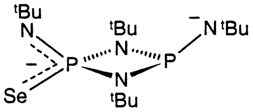

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Experimental Section

Reagents and General Procedures. Solvents were dried and distilled prior to use: tetrahydrofuran, toluene, pentane, and *n*-hexane (Na/benzophenone). *n*-Butyllithium (2.5 M solution in hexanes, Aldrich), Se (99.5%, Aldrich), KO^{t}Bu (95%, Aldrich), and KN(SiMe$_3$)$_2$ (95%, Aldrich) were used as received. The compounds [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (**3**),[3a] [^{t}Bu(H)NP(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (**7**),[6] KCH$_2$Ph,[7] and NiCl$_2$(PMe$_3$)$_2$[8] were prepared by literature procedures. The reactions and handling of air- and moisture-sensitive reagents were performed under an atmosphere of argon gas using Schlenk techniques or a glovebox.

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. ^{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 ^{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 Nicolet Nexus 470 FTIR in the range 4000−350 cm^{-1}. The mass spectra were obtained either with a VG Micromass spectrometer VG7070 (70 eV) or a Bruker Esquire 3000 ESI Ion Trap MS. UV−vis spectra were collected on a Unicam Heλios UV−vis spectrometer in the range 190−720 nm. Magnetic susceptibility measurements were made on an Alfa Aesar Mark 1 magnetic susceptibility balance. Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Synthesis of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (6). A mixture of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (3.80 g, 7.50 mmol) and [^{t}Bu(H)NP(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (2.61 g, 7.50 mmol) in toluene (75 mL) was heated to 85 °C for 18 h. The solvent was removed under vacuum, and the residue was washed with pentane (2 × 10 mL) to give **6** as a white solid (6.24 g, 14.6 mmol, 97%). ^{1}H NMR (C$_6$D$_6$, δ): 3.82 [d, 1H, NH, $^2J(^1\mathrm{H}{-}^{31}\mathrm{P}) = 14$ Hz], 2.93 [d, 1H, NH, $^2J(^1\mathrm{H}{-}^{31}\mathrm{P}) = 7$ Hz], 1.65 (s, 18H, ^{t}Bu), 1.14 (s, 9H, ^{t}Bu), 1.10 (s, 9H, ^{t}Bu). ^{31}P {^{1}H} NMR (THF-*d*$_8$, δ): 80.9 (s), 26.8 [s, $^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se}) = 817$ Hz]. ^{77}Se NMR (THF-*d*$_8$, δ): −80.1 [d, $^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se}) = 818$ Hz]. IR (KBr/Nujol, cm^{-1}): 3377 (NH), 3250 (NH). MS [EI, *m*/*z* (rel int)]: 428 (19) (M$^+$). Anal. Calcd for C$_{16}$H$_{38}$N$_4$P$_2$Se: C, 44.96; H, 8.96; N, 13.11. Found: C, 45.02; H, 8.78; N, 13.00.

Synthesis of {(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]}$_2$ (8). A solution of KO^{t}Bu (0.135 g, 1.20 mmol) in THF (20 mL) was added dropwise to a solution of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]-(0.500 g, 1.17 mmol) in THF (25 mL) at 23 °C. After 3 h, the volume of the solution was reduced to 10 mL, and 3 mL of hexane was added. The solution was stored at −23 °C, and after 24 h, colorless X-ray quality crystals of **8** (0.491 g, 0.913 mmol, 78%) were obtained. ^{1}H NMR (THF-*d*$_8$, δ): 3.58 (m, [O(CH_2)$_2$(CH$_2$)$_2$]), 2.78 [*d*, 1H, NH, $^2J(^1\mathrm{H}{-}^{31}\mathrm{P}) = 6$ Hz], 1.76 (m, [O(CH$_2$)$_2$(CH_2)$_2$]), 1.53 (s, 18H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu), 1.23 (s, 9H, ^{t}Bu). ^{31}P {^{1}H} NMR (THF-*d*$_8$, δ): 75.6 (s), 0.2 [s, $^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se}) = 640$ Hz]. ^{77}Se NMR (THF-*d*$_8$, δ): 14.5 [d, $^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se}) = 638$ Hz]. IR (KBr/Nujol, cm^{-1}): 3377 (NH). Satisfactory CHN analyses could not be obtained owing to facile loss of THF from crystals.

Synthesis of {[(THF)$_2$K]$_2$[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN^{t}Bu]}$_2$ (9). A solution of KCH$_2$Ph (0.321 g, 2.46 mmol) in THF (20 mL) was added dropwise to a solution of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]-(0.500 g, 1.17 mmol) in THF (25 mL) at 23 °C. After 18 h, the solvent was removed from the yellow solution in vacuo, and the residue was washed with pentane (2 × 5 mL) to give **9** as a pale yellow solid (0.631 g, 0.796 mmol, 68%). X-ray quality crystals were obtained from a THF−hexane solution at 23 °C after 24 h. ^{1}H NMR (THF-*d*$_8$, δ): 3.58 (m, [O(CH_2)$_2$(CH$_2$)$_2$]), 2.78 (*d*, 1H, NH), 1.77 (m, [O(CH$_2$)$_2$(CH_2)$_2$]), 1.50 (s, 18H, ^{t}Bu), 1.35 (s, 9H, ^{t}Bu), 1.17 (s, 9H, ^{t}Bu). ^{31}P {^{1}H} NMR (THF-*d*$_8$, δ): 104.3 (d, [$^2J(^{31}\mathrm{P}{-}^{31}\mathrm{P}) = 29$]), 2.4 (d, [$^2J(^{31}\mathrm{P}{-}^{31}\mathrm{P}) = 29$, $^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se}) = 611$ Hz]). ^{77}Se NMR (THF-*d*$_8$, δ): 43.4 [d, $^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se}) = 611$ Hz]. Satisfactory CHN analyses could not be obtained due to facile loss of THF from the crystals.

Synthesis of {Ni[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]$_2$} (10). Benzene (25 mL) was added to a mixture of {(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]}$_2$ (1.00 g, 1.86 mmol) and NiCl$_2$(PMe$_3$)$_2$ (0.262 g, 0.930 mmol) at 23 °C. The color of the solution changed from red to dark green/purple. After 18 h, the solvent was removed in vacuo, and the product was redissolved in hexane. The precipitate of KCl was removed by filtration and the volume of the filtrate was reduced to 10 mL. Green X-ray quality crystals of **10** were obtained after 3 d at −23 °C (0.668 g, 0.733 mmol, 79%). ^{1}H NMR (CDCl$_3$, δ): 21.12 (br s, 18H, ^{t}Bu), −0.68 (s, 18H, ^{t}Bu), −1.22 (br s, 36H, ^{t}Bu), −3.86 (br s, 2H, NH). ^{13}C NMR (CDCl$_3$, δ): 552.84, 52.12, 42.16 [C(CH$_3$)$_3$]; 382.76, 38.57, 31.48 [C(CH_3)$_3$]. ^{31}P {^{1}H} NMR (C$_6$D$_6$, δ): 957.7 (br, s), 22.2 (s). IR (KBr/Nujol, cm^{-1}): 3382 (NH). MS [ESI, *m*/*z*]: 913 (M + H$^+$). UV−vis [CH$_2$Cl$_2$; $\lambda_{\max}$ in nm (ϵ in M^{-1} cm^{-1})]: 323 (2.5 × 10^3), 354 (3.1 × 10^3), 462 (2.8 × 10^3), 592 (1.2 × 10^2). Magnetic moment (μ, 298 K): 3.43 μ_B. Anal. Calcd for C$_{32}$H$_{74}$N$_8$Se$_2$Ni: C, 42.17; H, 8.18; N, 12.29. Found: C, 41.76; H, 8.36; N, 11.50.

Reaction of {(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]}$_2$ with Li^{n}Bu. *n*-Butyllithium (0.379 mL, 0.948 mmol) was added dropwise to a solution of **8** (0.509 g, 0.948 mmol) in THF (25 mL) at 23 °C, and the reaction mixture was refluxed at 75 °C for 18 h. The solvent was removed under vacuum, and the residue was shown by ^{1}H and ^{31}P NMR spectra to be a mixture of **11** and **12**. The two components were separated by washing the residue with hexane (1 × 20 mL) in which **11** is soluble. The volume of the hexane solution was reduced to 5 mL, and colorless crystals of **11** (0.124 g, 0.246 mmol, 52%) were obtained after 1 d at −23 °C. ^{1}H NMR (C$_6$D$_6$, δ): 3.65 (m, THF), 1.57 (s, 18 H, ^{t}Bu), 1.51 (s, 18 H, ^{t}Bu), 1.33 (m, THF). ^{31}P {^{1}H} NMR (C$_6$D$_6$, δ): 158.3 (s) [lit.[6] ^{1}H (C$_6$D$_6$, δ): 3.66 (m), 1.55 (s), 1.49 (s), 1.32 (m). ^{31}P {^{1}H} NMR (C$_6$D$_6$, δ): 159.6 (s)]. Colorless crystals of **12** (0.174 g, 0.218 mmol, 46%) were obtained from a solution of the hexane−insoluble residue in THF (5 mL). ^{1}H (THF-*d*$_8$, δ): 3.58 (m, THF), 1.75 (m, THF), 1.66 (s, 18 H, ^{t}Bu), 1.33 (s, 18 H, ^{t}Bu). ^{31}P {^{1}H} (THF-*d*$_8$, δ): −0.10 [s, $^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se}) = 686$ Hz] [lit.[3a] ^{1}H (THF-*d*$_8$, δ): 3.58 (m), 1.74 (m), 1.66 (s), 1.33 (s). ^{31}P {^{1}H} NMR (THF-*d*$_8$, δ): −0.03 [s, $^1J(^{31}\mathrm{P}{-}^{77}\mathrm{Se}) = 686$ Hz].

X-ray Analyses. Measurements of **3** and **6** were made on a Nonius KappaCCD FR540C diffractometer while those of **8**, **9**, and **10** were made on a Bruker AXS P4/RA/SMART 1000 CCD diffractometer. Crystallographic data are summarized in Table 1.

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Table 1. Crystallographic Data for **3**, **6**, and **8**−**10**

	3	**6**	**8**	**9**	**10**
formula	$C_{16}H_{38}N_4P_2Se_2$	$C_{16}H_{38}N_4P_2Se_1$	$C_{40}H_{90}K_2N_8O_2P_4Se_2$	$C_{64}H_{136}K_4N_8O_8P_4Se_2$	$C_{32}H_{74}N_8NiP_4Se_2$
fw	506.36	427.40	1075.20	1584.00	911.50
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	8.8504(8)	9.5100(1)	10.639(1)	18.481(1)	10.495(2)
b, Å	29.135(3)	15.1320(2)	9.777(1)	13.930(1)	13.201(2)
c, Å	18.620(2)	15.9940(2)	28.036(3)	18.648(1)	16.892(3)
α, deg					76.646(2)
β, deg	99.053(2)	90.6000(5)	94.483(2)	113.814(1)	83.729(2)
γ, deg					87.575(3)
V, Å^3	4741.5(8)	2301.50(5)	2907.4(5)	4392.1(6)	2263.0(6)
Z	8	4	4	4	2
T, K	193(2)	173(2)	193(2)	193(2)	193(2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
d_{calcd}, g cm^{-3}	1.419	1.233	1.228	1.198	1.338
μ, mm^{-1}	3.261	1.776	1.561	1.151	2.209
F(000)	2080	904	1136	1688	956
R^a	0.0548	0.0369	0.0353	0.0576	0.0631
$R_w{}^b$	0.1307	0.0946	0.0917	0.1618	0.1826

^{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).

Structures were solved by direct methods (**9**, SIR-92;[9a] **3**, **6**, **8**, and **10**, SHELXS-97[9b]) and refined by full-matrix least-squares methods on F^2 with SHELX97−2.[10] Unless otherwise stated, the non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at geometrically idealized positions but not refined.

(a) 3. A colorless rodlike crystal of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (0.67 × 0.11 × 0.05 mm) was mounted on a glass fiber. A total of 27 606 reflections was collected, of which 4785 had $I > 2.00\sigma(I)$. The asymmetric unit contains two molecules of **3** with similar bond distances and bond angles. The methyl substituents of one of the ^{t}Bu groups in the second molecule showed severe disorder over two sites with partial occupancy factors of 0.534(15) and 0.466(15) for C71−73 and C71′−73′, respectively.

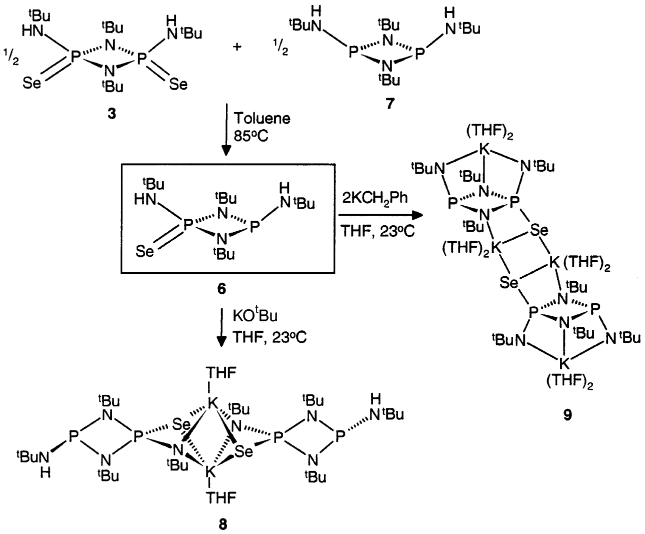
(b) 6. A colorless platelike crystal of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (0.13 × 0.13 × 0.05 mm) was mounted on a cryoloop. A total of 9184 reflections was collected, of which 3359 had $I > 2.00\sigma(I)$. The hydrogen atoms attached to nitrogen centers were located and refined.

(c) 8. A colorless prism-like crystal of {(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]}$_2$ (0.65 × 0.51 × 0.51 mm) was mounted on a glass fiber. A total of 13 461 reflections was collected, of which 4680 had $I > 2.00\sigma(I)$.

(d) 9. A colorless prism-like crystal of {[(THF)$_2$K]$_2$[^{t}BuN(Se)P(μ-^{t}Bu)$_2$PN^{t}Bu]}$_2$ (0.22 × 0.21 × 0.21 mm) was mounted on a glass fiber. A total of 24 273 reflections was collected, of which 3245 had $I > 2.00\sigma(I)$. The carbon atoms of the four coordinated THF molecules were disordered over two sites with partial occupancy factors of 0.63(2) and 0.37(2), 0.54(3) and 0.46(3), 0.714(14) and 0.286(14), 0.56(3) and 0.44(3). In addition, the methyl carbon atoms in one of the ^{t}Bu groups showed a high degree of disorder (C31, C32, C33) and C−C bonds were constrained during the refinement to 1.540(1) and 2.480(1) Å for α−β and β−β carbon distances, respectively. The occupancy factors were refined to 0.59(4) and 0.41(4).

(e) 10. A green prism-like crystal of {Ni[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]$_2$} (0.60 × 0.19 × 0.09 mm) was mounted on a glass fiber. A total of 17 066 reflections was collected, of which 6088 had $I > 2.00\sigma(I)$.

Scheme 1



Results and Discussion

Preparation and X-ray Structure of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (6) and [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (3). The monoselenide [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] **6** is obtained in essentially quantitative yield via a comproportionation reaction of equimolar amounts of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (**3**) and [^{t}Bu(H)NP(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (**7**) in toluene at 85 °C (Scheme 1). Keat et al. have reported the formation of the secondary amido derivatives [R$_2$N(Se)P(μ-N^{t}Bu)$_2$PNR$_2$] (R = Me, Et; R$_2$ = C$_5$H$_{10}$) as a mixture of cis and trans isomers by both a comproportionation reaction and by a mono-oxidation with elemental selenium.[11,12] By contrast, monoselenide **6** is obtained in only one isomeric form (cis with respect to the ^{t}BuNH groups). The related acyclic systems R$_2$P(Se)N(R′)PR$_2$ have received considerably more attention. Cavell et al. have prepared the monoselenide Ph$_2$P(Se)N(Ph)PPh$_2$ by oxidation of Ph$_2$PN(Ph)PPh$_2$ with elemental selenium.[13]

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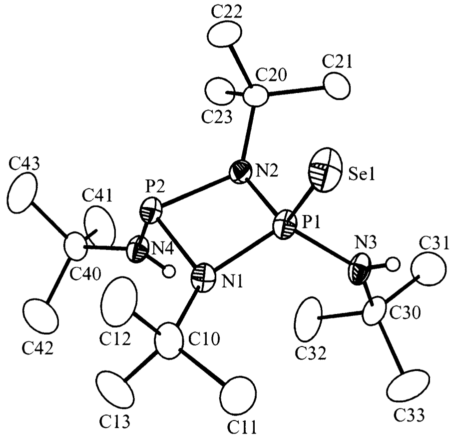

Figure 1. X-ray structure of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (**6**) showing the numbering scheme (30% probability ellipsoids).

Woollins and co-workers have shown that Ph$_2$P(Se)N(H)-PPh$_2$ is formed quantitatively either through mono-oxidation with selenium or by a comproportionation reaction. They found that mono-oxidation is the preferred method.[14] In the present work, however, we were unable to obtain pure **6** by the mono-oxidation route even after recrystallization.

The ^{31}P NMR spectrum does not provide a conclusive identification of **6**. Two singlets with chemical shifts similar to those of the reagents **3** and **7** are observed. The absence of $^2J[^{31}P(V)-^{31}P(III)]$ coupling in **6** is surprising. Typical values of $^2J(^{31}P-^{31}P)$ in acyclic P(III)−N−P(V) systems fall in the range 78−126 Hz (e.g., Ph$_2$P(Se)N(H)PPh$_2$, 93 Hz),[13] while Keat et al. report smaller values (7−10 Hz) for the cyclic systems [R$_2$N(Se)P(μ-N^{t}Bu)$_2$PNR$_2$].[11] The identity of **6** is apparent, however, from the characteristic 2:1:1 ratio of the N^{t}Bu resonances and the two NH resonances in the ^{1}H NMR spectrum. The monoselenide **6** exhibits a doublet in the ^{77}Se NMR at δ −80.1 ppm [$^1J(^{31}P-^{77}Se) = 818$ Hz] (cf. −128 ppm and 877 Hz for **3**).[3a]

The structure of **6** was affirmed by X-ray crystallography, and for comparison, the X-ray structure of the previously reported diselenide **3**[3a] was also determined. The molecular geometry and atomic numbering schemes are shown in Figures 1 and 2, respectively, and pertinent structural parameters are summarized in Table 2. Both **3** and **6** maintain the cis arrangement of the N(H)^{t}Bu groups found in the P(III)/P(III) precursor **7**.[6] Unlike the endo,endo orientation in **7**, however, the exo,endo isomer is observed for both **3** and **6**. The same geometry is also observed in the closely related [Ph(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)Ph].[4]

The P−Se bond lengths of 2.1169(7) and 2.074(3) Å for **6** and **3**, respectively, are similar to those of related compounds.[15] The slightly longer P−Se bond length in **6** is consistent with the $^1J(^{31}P-^{77}Se)$ coupling constants (818 Hz in **6** vs 877 Hz in **3**). The different oxidation states of the two phosphorus centers in **6** give rise to predictable differences in the structural parameters involving P and N atoms.

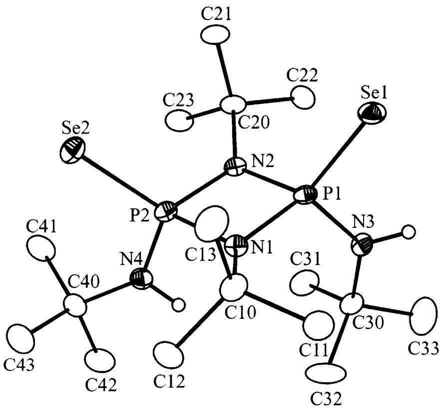

Figure 2. X-ray structure of [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (**3**) showing the numbering scheme (30% probability ellipsoids).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (**6**) and [^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu] (**3**)[a]

	6	**3**		**6**	**3**
Se(1)−P(1)	2.1169(7)	2.078(1)	N(3)−P(1)−Se(1)	105.13(8)	107.3(1)
Se(2)−P(2)		2.070(1)	N(4)−P(2)−Se(2)		113.2(1)
P(1)−N(1)	1.673(2)	1.680(3)	N(1)−P(1)−N(2)	84.2(1)	83.6(2)
P(1)−N(2)	1.671(2)	1.679(2)	N(1)−P(2)−N(2)	79.6(1)	83.2(2)
P(1)−N(3)	1.637(2)	1.624(2)			
P(2)−N(1)	1.750(2)	1.684(3)			
P(2)−N(2)	1.751(2)	1.688(3)			
P(2)−N(4)	1.655(2)	1.617(6)			

[a] Mean bond distances and angles for the two independent molecules in the asymmetric unit.

Thus, the P(III)−N$_{endo}$ distance (1.750(2) Å) is longer than the P(V)−N$_{endo}$ distance (1.672(2) Å); similarly d[P(III)−N$_{exo}$] = 1.655(2) Å and d[P(V)−N$_{exo}$] = 1.637(2) Å (cf. d[|P(V)−N$_{endo}$|] = 1.681(3) Å and d[|P(V)−N$_{exo}$|] = 1.622(1) for **3** and d[P(III)−N$_{endo}$] = 1.726(2) Å and d[P(III)−N$_{exo}$] = 1.664(2) for **7**).[6] The endocyclic ring ∠NPN angles in **6** differ by more than 4°. The exocyclic ∠NPSe bite angle differs depending on the conformation of the N(H)^{t}Bu substituent. For the endo orientation in **3** the angle is 113.1(2)°, while for the exo orientation in **3** and **6** the mean value is 106.3(11)°. This difference presumably reflects the steric influence of the ^{t}Bu group.

Metalation of 6. The metalation of **6** with a variety of potassium salts was investigated in order to (a) compare the structure of the potassium salt of the monoanion **4** with that of the known lithium derivative and (b) generate the dianion **5**. The reaction of **6** with 1 equiv of KO^{t}Bu or KN(SiMe$_3$)$_2$ in THF at 23 °C produced the monopotassium complex {(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]}$_2$ (**8**) in good yields. Attempts to form a dimetalated complex by the reaction of **6** with 2 equiv of KN(SiMe$_3$)$_2$ or KO^{t}Bu in boiling THF were unsuccessful. Formation of the dianion **5** was, however, achieved by using the stronger base benzylpotassium, which dimetalates **6** in THF at 23 °C to form {(THF)$_2$K[^{t}BuN(Se)P(μ-N^{t}Bu)PN^{t}Bu]K(THF)$_2$}$_2$ (**9**) in 68% yield (Scheme 1).

An interesting transformation was observed in an attempt to generate the dianion **5** from the treatment of the monopotassium salt **8** with *n*-butyllithium in boiling THF. The reaction was monitored by both ^{1}H and ^{31}P NMR spectros-

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(13) Balakrishna, M. S.; Klein, R.; Uhlenbrock, S.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1993**, *32*, 5676.

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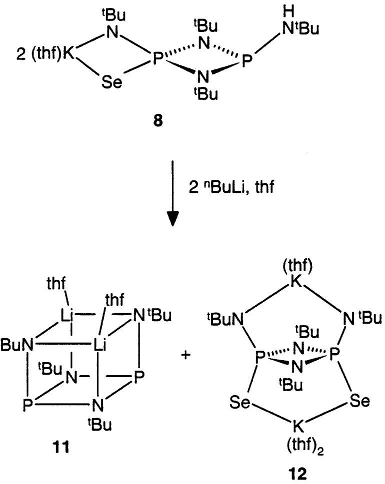
Scheme 2



copy, which revealed that, under these conditions, metalation is accompanied by a redox disproportionation to give the known P(III)/P(III) compound {[(THF)Li[^{t}BuNP(μ-N^{t}Bu)$_2$PN^{t}Bu]Li(THF)] (**11**)[6] and the P(V)/P(V) complex {[(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$P(Se)N^{t}Bu]K(THF)$_2$]$_2$}$_n$ (**12**),[3a] which were separated and identified by their ^{1}H and ^{31}P NMR spectra (Scheme 2). Presumably, the driving force for this transformation is the creation of the stable cubic structure of **11** and the six-membered rings in **12**.

The ^{1}H NMR spectra of both **8** and **9** show three N^{t}Bu resonances with intensities in the ratio 2:1:1; in the case of **8** a signal for the NH proton is also observed. The ^{31}P NMR spectrum of **8** displays two singlets at δ 75.6 and 0.2 for the P(III) and P(V) centers, respectively, whereas that for **9** contains two mutually coupled doublets at δ 104.3 and 2.4 [$^2J(^{31}P-^{31}P) = 29$ Hz]. As expected, the resonances at δ 0.2 and 2.4 show ^{77}Se satellites. The downfield shift of the P(III) signal and upfield shift of the P(V) signal upon metalation are typical for these systems.[3] The ^{77}Se NMR spectra of **8** and **9** display doublets centered at δ 14.5 and 43.4 with $^1J(^{31}P-^{77}Se) = 638$ and 611 Hz, respectively [cf. δ 13.2 and 684 Hz, for **12**].[3a]

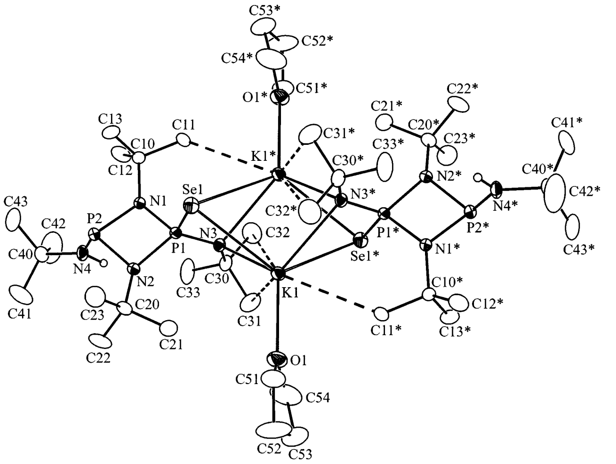


Figure 3. X-ray structure of {(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]}$_2$ (**8**) showing the numbering scheme (30% probability ellipsoids).

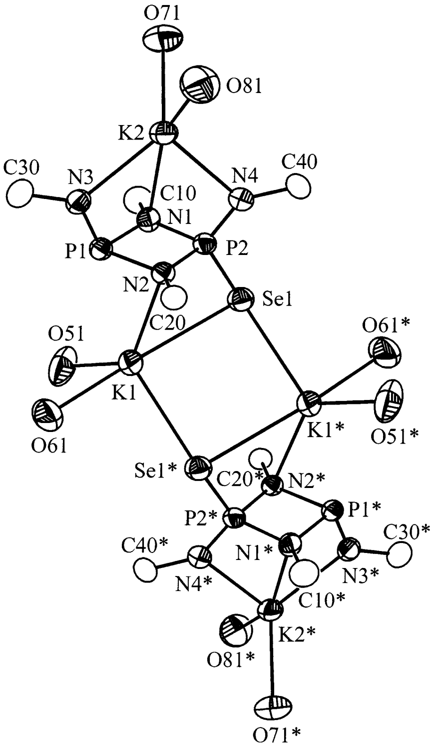


Figure 4. X-ray structure of {(THF)$_2$K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN^{t}Bu]K(THF)$_2$}$_2$ (**9**) showing the numbering scheme (30% probability ellipsoids). Only the α-carbons of the ^{t}Bu groups and the oxygen atoms of THF groups are shown.

X-ray Structures of {(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]}$_2$ (8) and {(THF)$_2$K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN^{t}Bu]K(THF)$_2$}$_2$ (9). The structures of **8** and **9** were established by X-ray crystallography. The molecular geometry and atomic numbering schemes are shown in Figures 3 and 4, and pertinent structural parameters are summarized in Tables 3 and 4, respectively. The X-ray structural analysis of **8** reveals that the proton is abstracted from the amido substituent attached to the P(V) center. Unlike the lithium analogue, {(THF)$_2$Li[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]}, which exists as a monomer,[3b] the structure of **8** is dimeric. Each monoanion is N,Se-chelated to two K$^+$ ions to give a distorted K$_2$N$_2$Se$_2$ octahedron. This dimeric arrangement alleviates the inherent strain in a four-membered PNKSe ring. The only previous example of this ring system occurs in the complex {(THF)K[Ph$_2$P(Se)NSiMe$_3$]}$_2$ (**13**) in which dimerization occurs through K···Se interactions.[16] The K−Se distances of 3.3555(7) and 3.4079(7) Å in **8** are similar to those in **13** [3.366(5)−3.418(4) Å]. The K−N distances of 2.872(2) and 2.965(2) Å in **8** are, however, somewhat longer [cf. 2.77(1) and 2.79(1) Å in **13**], presumably as a result of the increase in coordination of the nitrogen atoms from three to four. The P−Se distance of 2.1650(6) Å in **8** is ca. 0.09 Å longer than that in the neutral precursor **6**. Consistently, the $^1J(^{31}P-^{77}Se)$ coupling constant is reduced from 818 to 638 Hz. The bite angle (∠NPSe) of 106.66(7)° in **8** is similar to that in **6** (105.13(8)°) but much narrower than the value of 114.3(5)° in **13**.

Each potassium ion in **8** is coordinated by a single THF molecule. Additionally, the potassium ions are involved in C(−H)···K agostic interactions in the range 3.432(3)−3.534-

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Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for$\{$(THF)K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]$\}_2$ (**8**)[a] and $\{$Ni[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]$\}_2$ (**10**)[b]

	8	10		8	10
Se(1)−P(1)	2.1650(6)	2.170(2)	P(2)−N(4)	1.668(2)	1.659(3)
M(1)−N(3)	2.872(2)	1.954(4)	M(1)−O(1)	2.664(2)	
M(1)−N(3)*	2.965(2)		M(1)−Se(1)	3.3555(7)	2.479(11)
P(1)−N(1)	1.700(2)	1.683(5)	M(1)−Se(1)*	3.4079(7)	
P(1)−N(2)	1.705(2)	1.672(5)	C(11)−M(1)*	3.432(3)	
P(1)−N(3)	1.574(2)	1.601(5)	C(31)−M(1)	3.501(3)	
P(2)−N(1)	1.735(2)	1.762(11)	C(32)−M(1)*	3.534(3)	
P(2)−N(2)	1.736(2)	1.756(6)			
P(1)−Se(1)−M(1)	79.16(2)	74.31(4)	Se(1)−M(1)−Se(1)*	121.37(2)	
M(1)−Se(1)−M(1)*	58.63(2)		Se(1)−M(1)−Se(2)	123.46(4)	
N(3)−M(1)−Se(1)	57.39(4)	80.8(1)	N(3)−M(1)−N(3)*	110.89(4)	
N(3)*−M(1)−Se(1)	89.35(4)		N(3)−P(1)−Se(1)	106.66(7)	99.5(2)
N(3)−M(1)−Se(2)	120.6(1)		P(1)−N(3)−M(1)	105.99(9)	
N(3)−M(1)−N(5)	136.6(2)		M(1)−N(3)−M(1)*	69.11(4)	

[a] Symmetry transformation used to generate equivalent atoms. *: $-x + 1, -y, -z$. [b] Mean bond distances and angles for the two halves of the molecule.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $\{$(THF)$_2$K[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN^{t}Bu]K(THF)$_2\}_2$ (**9**)[a]

Se(1)−P(2)	2.183(2)	P(1)−N(1)	1.784(5)
Se(1)−K(1)*	3.281(2)	P(1)−N(2)	1.782(5)
Se(1)−K(1)	3.293(2)	P(1)−N(3)	1.591(5)
K(1)−N(2)	3.177(5)	P(2)−N(1)	1.685(5)
K(2)−N(1)	3.154(5)	P(2)−N(2)	1.676(5)
K(2)−N(3)	2.685(5)	P(2)−N(4)	1.558(5)
K(2)−N(4)	2.713(6)		
P(2)−Se(1)−K(1)*	126.93(6)	N(4)−K(2)−N(1)	54.1(1)
P(2)−Se(1)−K(1)	82.40(5)	N(4)−P(2)−Se(1)	117.7(2)
K(1)−Se(1)−K(1)*	91.64(4)	N(2)−P(2)−Se(1)	112.3(2)
N(2)−K(1)−Se(1)*	106.22(9)	P(2)−N(2)−K(1)	94.3(2)
N(2)−K(1)−Se(1)	59.60(9)	P(1)−N(2)−K(1)	78.2(2)
Se(1)*−K(1)−Se(1)	88.36(4)	P(1)−N(3)−K(2)	105.0(3)
N(3)−K(2)−N(4)	98.6(2)	P(2)−N(4)−K(2)	99.5(3)
N(3)−K(2)−N(1)	54.5(1)		

[a] Symmetry transformation used to generate equivalent atoms. *: $-x + 1, -y + 1, -z + 2$.

(3) Å involving the CH$_3$ groups of ^{t}Bu substituents. Previous examples of this type of interaction with C(−H)···K distances in the range 3.103(2)−3.494(4) Å have been reported.[17] Three such interactions involving C11, C31, and C32 are observed in **8**, effectively increasing the coordination number of each potassium ion from five to eight (Figure 3).

The X-ray structural analysis of **9** (Figure 4) reveals a centrosymmetric dimer in which the dianionic ligand adopts two different modes of coordination to the potassium ions. One of the potassium ions is N,N′,N″-chelated by the two exocyclic amido groups and through a weak interaction with one of the endocyclic ring nitrogens. The other potassium is N,Se-chelated via a weak interaction with the other endocyclic ring nitrogen forming a four-membered KNPSe ring. Both pentacoordinate potassium cations are solvated by two THF molecules. Complex **9** is the first alkali metal derivative of a dianionic cyclodiphosph(III/V)azane chalcogenide, although both tin(II) and tin(IV) complexes of a cyclodiphosph(III/V)azane sulfide have been reported previously.[1,5] Although other examples of endocyclic N coordination to metals have been reported for the P(III)/P(III) dianion **1**,[1] the involvement of both bridging nitrogens of the P$_2$N$_2$ ring in coordination is unprecedented.

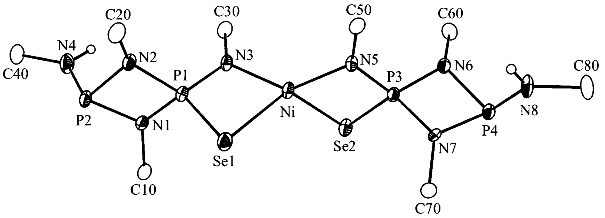

Figure 5. X-ray structure of $\{$Ni[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]$\}_2$ (**10**) showing the numbering scheme (30% probability ellipsoids). Only the α-carbons of the ^{t}Bu groups are shown.

The dimerization of **9** via K−Se interactions is very similar to that of the corresponding P(V)/P(V) system **12**.[3a] In **9**, the K−Se distances within the K$_2$Se$_2$ ring are equal at 3.287(2) Å, forming an almost perfect square, while in **12** the edges are slightly shorter than the rungs 3.312(4) Å vs 3.418(3) Å.[3a] The P−Se bond length of 2.183(2) Å in **9** is similar to that found for **8**.

Synthesis and X-ray Structure of $\{$Ni[^{t}BuN(Se)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu]$_2\}$ (10). In the context of our interest in synthesizing coordination polymers on the basis of a P$_2$N$_2$ template, we have previously described M(II) (M = Ni, Pd) complexes of the P(V)/P(V) monoanion [^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)N(H)^{t}Bu]$^-$.[3c] For comparison, we have prepared the Ni(II) complex of the P(III)/P(V) monoanion **4** by the metathetical process shown in eq 1.

$$\underset{\mathbf{8}}{2\{(\mathrm{THF})\mathrm{K}[^t\mathrm{BuN(Se)P}(\mu\text{-N}^t\mathrm{Bu})_2\,\mathrm{PN(H)}^t\mathrm{Bu}]\}_2} + \mathrm{NiCl_2(PMe_3)_2} \rightarrow \underset{\mathbf{10}}{\{\mathrm{Ni}[^t\mathrm{BuN(Se)P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{PN(H)}^t\mathrm{Bu}]_2\}} + 2\mathrm{KCl} + 2\mathrm{PMe_3} \quad (1)$$

The X-ray structural analysis of the Ni(II) complex **10** reveals bis(N,Se) coordination of the monoanion (Figure 5) in a manner reminiscent of the analogous P(V)/P(V) complex, $\{$Ni[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)N(H)^{t}Bu]$\}_2$ (**13**).[3c] Although there are several known NiNPS heterocycles,[18] **10** is the first structurally characterized NiNPSe heterocycle. The

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nickel center in **10** attains a distorted tetrahedral environment with mean bond angles ∠NNiN = 136.6(2)°, ∠NNiSe = 80.8(1)° and 120.6(7)°, and ∠SeNiSe = 123.46(4)° cf. 145.98(11)°, 80.55(6)° and 116.39(6)°, 122.76(4)°, for the corresponding angles in **13**. The bite angle (∠NPSe) of 99.5(3)° in **10** is comparable to that observed for **13** [101.96(10)°]. The Ni−Se distance of 2.479(1) Å is slightly longer than those observed for both {Ni[(Ph$_2$PSe)$_2$N]$_2$} (**14**) (mean value of 2.350(1) Å),[19] and {Ni[Ph$_2$PSeC(S)NPh]$_2$} (**15**) (2.344(1) Å).[20] However, in both of the aforementioned complexes the nickel(II) center is in a square planar arrangement. The P−Se distance of 2.170(2) Å in **10** falls between those reported for **14** (2.194(2) Å)[19] and **15** (2.145(3) Å).[20] The magnetic moment of **10** at 298 K is 3.43 μ_B (cf. 2.90 μ_B for the related Ni(II) complex **13**).[3c] This value is within the range 3.0−3.5 μ_B, which has been observed for distorted Ni(II) complexes.[18,22]

^{1}H, ^{13}C, and ^{31}P NMR spectra of complex **10** reveal anomalous shifts due to the paramagnetic nickel(II) center. The ^{1}H NMR spectrum shows three N^{t}Bu resonances; one of the signals is shifted downfield to δ 21.12, while the other two appear at δ −0.68 and −1.22. Additionally, there is an NH resonance at δ −3.86. Similarly, the ^{13}C NMR spectrum shows anomalous shifts at 552.84 and 382.76 ppm corresponding to the α and β carbons, respectively, of the nickel-coordinated N^{t}Bu group. The ^{31}P NMR spectrum reveals two resonances of approximately equal intensity, viz. a broad singlet at δ 957.7 and a sharp singlet at δ 22.2. A double-resonance experiment confirmed the connection between the ^{31}P NMR resonance at δ 957.7 and the ^{1}H NMR resonance of δ 21.12. Additionally, an HMQC experiment confirmed the connection between the ^{1}H NMR resonance at δ 21.12 and the ^{13}C NMR resonance of 382.76. The remarkable downfield shifts of these resonance are attributed to the shielding effect of the adjacent, paramagnetic Ni(II) center. The anomalous ^{31}P NMR chemical shift observed for the P(V) center in **10** led us to reinvestigate the ^{31}P NMR spectrum for **13**.[21] ^{31}P NMR chemical shifts in the region observed for **10** and **13** have been observed previously by Kuchen and co-workers for the complexes {Ni[R$_2$P(E)(NR)]$_2$}, δ (^{31}P) −835 (E = O)[18b] and 457.7 (E = S).[18c] Attempts to obtain a ^{77}Se NMR spectrum of **10** were unsuccessful, presumably because the selenium site is directly connected to the paramagnetic Ni(II) center.

Conclusions

The mixed oxidation state monoanion **4** and the dianion **5** can be generated by the reaction of **6** with the appropriate metalating agent. The synthesis of the Ni(II) complex of **4** suggests an alternative approach to P$_2$N$_2$-templated coordination polymers that involves linking the P(III) centers to a metal.

Acknowledgment. We thank the NSERC (Canada) for financial support, Dr. R. MacDonald (University of Alberta) for assistance with the X-ray data collection, and Dr. R. Yamdagni and Ms. Qiao Wu for advice with the determination and interpretation of the NMR spectra of the Ni(II) complexes.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **3**, **6**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) The ^{1}H and ^{31}P NMR spectroscopic data of the nickel(II) complex, {Ni[^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)N(H)^{t}Bu]$_2$} (**13**), described in ref 3c, were reported incorrectly. The revised assignments are as follows. ^{1}H NMR (CDCl$_3$, δ): 14.15 (br s, 18H, ^{t}Bu), 0.09 (s, 18H, ^{t}Bu), −0.09 (br s, 36H, ^{t}Bu), −1.32 (br s, 2H, NH). ^{13}C (CDCl$_3$, δ): 392.12, 55.71, 47.11 [*C*(CH$_3$)$_3$] and 246.51, 31.16, 27.01 [C(*C*H$_3$)$_3$]. ^{31}P NMR (C$_6$D$_6$, δ): 415.9 (br, s), 104.3 (s).

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