Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 4681–4686 **4681**
DOI: 10.1021/ic1005055

Synthesis, Multinuclear NMR Spectra, and X-ray Structures of $^{t}Bu_2PNP(I)^{t}Bu_2$ and $EPR_2NP(I)R_2$ (E = Se, Te; R = ^{i}Pr, ^{t}Bu)

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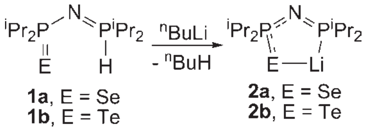
Received March 17, 2010

Two synthetic routes to bifunctional P(V)/P(V) compounds of the type $EPR_2NP(I)R_2$ have been developed. The reaction of $Li[EP^iPr_2NP^iPr_2]$ with one molar equivalent of I_2 produces $EP^iPr_2NP(I)^iPr_2$ (**3a**-I, E = Se; **3b**-I, E = Te). Alternatively, the oxidation of $Na[N(P^tBu_2)_2]$ with I_2 in tetrahydrofuran (THF) generates the P(III)/P(V) compound $^tBu_2PNP(I)^tBu_2$ (**6′**-I) which, on treatment with elemental selenium or tellurium in THF, yields $EP^tBu_2NP(I)^tBu_2$ (**3a′**-I, E = Se; **3b′**-I, E = Te). The acyclic compounds **3a**-I, **3a′**-I, **3b**-I, **3b′**-I, and **6′**-I have been characterized in solution by multinuclear (^1H, ^{31}P, ^{77}Se, and ^{125}Te) NMR spectroscopy and in the solid state by X-ray structural determinations.

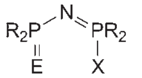
Introduction

In recent studies we have developed a convenient synthetic route to lithium derivatives of the monoanions $[EP^iPr_2NP^iPr_2]^-$ (**2a**, E = Se,[1] **2b**, E = Te[2]) via deprotonation of the corresponding P−H species $[EP^iPr_2NP(H)^iPr_2]$ (**1a** and **1b**, respectively) using *n*-butyl-lithium (see Scheme 1). The reactions of **2a** with tellurium and **2b** with sulfur produce the monoanions $[EP^iPr_2NP^iPr_2Te]^-$ (E = S, Se) in high purity, and the redox chemistry of these mixed dichalcogeno species has been investigated.[3,4] The coordination chemistry of the *P*, *Te*-centered ligand **2b** with group 10, 11, 12 metals has also been probed.[2,5,6] The most interesting finding was the facile insertion of an oxygen atom (using air or, preferably, Me_3NO) or a chalcogen atom (with the reagents *cyclo*-S_8 or red Se) into the Cu−P bond of the trimeric complexes $\{Cu(TeP^iPr_2NP^iPr_2)\}_3$ to generate the mixed chalcogen complexes $\{Cu(TeP^iPr_2NP^iPr_2E)\}_3$ (E = O, S, Se).[5]

Scheme 1



In related studies of the two-electron oxidation of the dichalcogeno anions $[EPR_2NPR_2E]^-$ (E = Se, Te),[7] we found that the reaction of the sodium salt of the phenyl derivative $[SePPh_2NPPh_2Se]^-$ with 1 equiv of I_2 produces the acyclic compound $SePPh_2NP(I)Ph_2$, in addition to the iodide salt of the cationic six-membered ring $[N(PPh_2Se)_2(\mu\text{-}Se)]^+$.[7b] The mixed selenide/iodide $SePPh_2NP(I)Ph_2$ was identified on the basis of multinuclear NMR spectra and by conversion to the μ-oxo derivative $\{[N(PPh_2)_2Se]_2(\mu\text{-}O)\}$ upon hydrolysis. The related acyclic species $SeP^iPr_2NP(Cl)^iPr_2$ (**3a**-Cl), which was formed from the reaction of the sodium salt of the monoanion $[SeP^iPr_2NP^iPr_2Se]^-$ with $SeCl_2$, was structurally characterized by X-ray crystallography.[7b,8]



E = Se	E = Te
3a-Cl, R = ^iPr, X = Cl	
3a-I, R = ^iPr, X = I	**3b**-I, R = ^iPr, X = I
3a'-I, R = ^tBu, X = I	**3b'**-I, R = ^tBu, X = I

In view of the potential uses of the reactive P-halogen functionality in reagents of the type **3** for the construction of chains or as precursors to cations via halide abstraction, we decided to develop reliable synthetic routes to this unusual class of bifunctional compound. In this contribution we report the

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(8) The syntheses of the following related acyclic compounds $EPR_2NP(X)R_2$ (E = chalcogen; X = halogen) have been reported without structural characterization: $[SPPh_2NP(Cl)Ph_2]$,[9a] $[SPPh_2NP(Br)Ph_2]$,[9b] and $[OPPh_2NP(Cl)Ph_2]$.[9c]
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synthesis, multinuclear NMR spectra, and X-ray structures of the derivatives EPR$_2$NP(I)R$_2$ (**3a**-I, E = Se, R = ^{i}Pr; **3b**-I, E = Te, R = ^{i}Pr; **3a′**-I, E = Se, R = ^{t}Bu; **3b′**-I, E = Te, R = ^{t}Bu), as well as the P(III)/P(V) iodide ^{t}Bu$_2$PNP(I)^{t}Bu$_2$ (**6′**-I).[10]

Experimental Section

Reagents and General Procedures. All solvents were dried and distilled from Na/benzophenone and stored over 4 Å molecular sieves prior to use. Deuterated solvents for NMR studies were degassed using at least three freeze−pump−thaw cycles and stored over 4 Å molecular sieves prior to use. The reagents Li[TeP^{i}Pr$_2$NP^{i}Pr$_2$][2] and NaN(P^{t}Bu$_2$)$_2$[11] were prepared according to the literature methods; other reagents were obtained from commercial sources and used as received. All manipulations were performed under an inert atmosphere of argon using standard glovebox and Schlenk techniques.

Instrumentation. ^{1}H, ^{31}P{^{1}H}, ^{77}Se{^{1}H}, and ^{125}Te{^{1}H} NMR spectra were recorded on either a Bruker DRX-400 or an AMX-300 NMR spectrometer. Chemical shifts are reported in parts per million (ppm), relative to the external standards Me$_4$Si (^{1}H), 85% H$_3$PO$_4$ (^{31}P), Ph$_2$Se$_2$ (^{77}Se), and Ph$_2$Te$_2$ (^{125}Te). Elemental analyses were performed by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Synthesis of SeP^{i}Pr$_2$NP(I)^{i}Pr$_2$ (3a-I). ^{n}BuLi (0.2 mL, 2.5 M in hexanes, 0.5 mmol) was added via syringe to a solution of SeP^{i}Pr$_2$NP(H)^{i}Pr$_2$ (0.162 g, 0.5 mmol) in THF (20 mL) at −78 °C. A solution of I$_2$ (0.126 g, 0.5 mmol) in THF (10 mL) at −78 °C was added via cannula, and the resulting yellow solution was stirred for 30 min at −78 °C before being allowed to warm to room temperature. THF was removed in vacuo, and the residue was dissolved in Et$_2$O (20 mL). The solution was filtered through Celite over a 0.45 μm pore size filter disk to remove LiI, and the Et$_2$O was removed in vacuo. The resulting pale yellow powder was recrystallized overnight from Et$_2$O/hexanes at −18 °C to give **3a**-I as colorless crystals (0.159 g, 71%). Elemental analysis calcd (%) for $C_{12}H_{28}INP_2Se$: C, 31.73; H, 6.21; N, 3.08; found: C, 31.51; H, 6.30; N, 2.94. ^{1}H NMR (d_8-THF, 23 °C): δ 2.45 [2 × sept, $^{3}J(^{1}H,^{1}H) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 2.04 [2 × sept, $^{3}J(^{1}H,^{1}H) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 1.31 [dddd, $^{3}J(^{1}H,^{31}P) = 21$ Hz, $^{3}J(^{1}H,^{1}H) = 7$ Hz, 12H, CH(C*H*$_3$)$_2$], 1.15 [dd, $^{3}J(^{1}H,^{31}P) = 18$ Hz, $^{3}J(^{1}H,^{1}H) = 7$ Hz, 12H, CH(C*H*$_3$)$_2$]; ^{31}P{^{1}H} NMR (d_8-THF, 23 °C): δ 70.0 [d, $^{1}J(^{77}Se,^{31}P) = 724$ Hz, $^{2}J(^{31}P,^{31}P) = 42$ Hz, *P*−Se], 51.4 [d, $^{2}J(^{31}P,^{31}P) = 42$ Hz, *P*−I]; ^{77}Se NMR (d_8-THF, 23 °C): δ −313 [d, $^{1}J(^{77}Se,^{31}P) = 725$ Hz]. X-ray quality crystals of **3a**-I were grown by slow diffusion of an Et$_2$O solution layered with hexanes and stored at −35 °C.

Synthesis of TeP^{i}Pr$_2$NP(I)^{i}Pr$_2$ (3b-I). This derivative was prepared using the same method as described for **3a**-I using Li[TeP^{i}Pr$_2$NP^{i}Pr$_2$] (1.33 mmol) and I$_2$ (0.337 g, 1.33 mmol). The filtered product was concentrated to 10 mL and stored at −30 °C. After 2 h, dark orange crystals of **3b**-I were obtained (0.197 g, 29% yield, ca. 85% purity). Elemental analysis (%) calcd for $C_{12}H_{28}INP_2Te$: C, 28.66; H, 5.61; N, 2.79; found: C, 29.01; H, 5.82; N, 2.80. ^{1}H NMR (d_8-THF, 23 °C): δ 2.68−2.43 [m, 2 H, C*H*(CH$_3$)$_2$], 2.05−1.88 [m, 2 H, C*H*(CH$_3$)$_2$], 1.44−1.02 [m, 24 H, CH(C*H*$_3$)$_2$]; ^{31}P{^{1}H} NMR (d_8-THF, 23 °C): δ 68.0 [s, 10 mol %, [(TeP^{i}Pr$_2$)$_2$N]I], 51.5 [d, $^{2}J(^{31}P,^{31}P) = 42$ Hz, *P*−I], 34.9 [d, $^{2}J(^{31}P,^{31}P) = 42$ Hz, $^{1}J(^{125}Te,^{31}P) = 1763$ Hz, *P*−Te]; ^{125}Te NMR (d_8-THF, 23 °C): δ −723 [d, $^{1}J(^{125}Te,^{31}P) = 1758$ Hz]. X-ray quality crystals of **3b**-I were obtained from a saturated Et$_2$O solution stored at room temperature.

Synthesis of SeP^{t}Bu$_2$NP(I)^{t}Bu$_2$ (3a′-I). An orange solution of **6′**-I (0.541 g, 1.25 mmol) in THF (20 mL) was added to a suspension of gray Se powder (0.100 g, 1.27 mmmol) in THF (15 mL). The resulting pale yellow suspension was stirred at room temperature for 3.5 h, and then filtered through a 0.45 μm pore size filter disk (to remove any unreacted Se) to yield a clear pale yellow solution. Removal of the volatiles under vacuum afforded a pale-yellow powder (0.562 g, 88%). Elemental analysis (%) calcd for $C_{16}H_{36}INP_2Se$: C, 37.66; H, 7.11; N, 2.74; found: C, 38.31; H, 7.19; N, 2.74. ^{1}H NMR (d_8-THF, 23 °C): δ 1.55 [d, $^{3}J(^{1}H,^{31}P) = 19$ Hz, 18H, ^{t}Bu], 1.39 [d, $^{3}J(^{1}H,^{31}P) = 16$ Hz, 18H, ^{t}Bu]; ^{31}P{^{1}H} NMR (d_8-THF, 23 °C): δ 83.3 [d, $^{2}J(^{31}P,^{31}P) = 61$ Hz, $^{1}J(^{77}Se,^{31}P) = 729$ Hz, *P*−Se], 71.3 [d, $^{2}J(^{31}P,^{31}P) = 61$ Hz, *P*−I]; ^{77}Se{^{1}H} NMR (d_8-THF, 23 °C): δ −256 [d, $^{1}J(^{77}Se,^{31}P) = 729$ Hz]. X-ray quality crystals of **3a′**-I were obtained from a saturated pentane solution stored at room temperature.

Synthesis of TeP^{t}Bu$_2$NP(I)^{t}Bu$_2$ (3b′-I). The compound **3b′**-I was obtained as an orange powder (0.578 g, 89%) from the reaction of **6′**-I (0.500 g, 1.16 mmol) in THF (20 mL) with tellurium powder (0.149 g, 1.18 mmol) in 15 mL of THF by using a procedure identical to that described above for **3a′**-I. Elemental analysis (%) calcd for $C_{16}H_{36}INP_2Te$: C, 34.38; H, 6.49; N, 2.51; found: C, 34.04; H, 5.99; N, 2.36. ^{1}H NMR (d_8-THF, 23 °C): δ 1.54 [d, $^{3}J(^{1}H,^{31}P) = 19$ Hz, 18H, ^{t}Bu], 1.40 [d, $^{3}J(^{1}H,^{31}P) = 16$ Hz, 18H, ^{t}Bu]; ^{31}P{^{1}H} NMR (d_8-THF, 23 °C): δ 66.6 [d, $^{2}J(^{31}P,^{31}P) = 61$ Hz, *P*−I], 54.7 [d, $^{2}J(^{31}P,^{31}P) = 61$ Hz, $^{1}J(^{125}Te,^{31}P) = 1749$ Hz, *P*−Te]; ^{125}Te{^{1}H} NMR (d_8-THF, 23 °C): δ −596 [d, $^{1}J(^{125}Te,^{31}P) = 1750$ Hz]. X-ray quality crystals of **3b′**-I were obtained from a concentrated solution of the product in THF layered with hexanes at −20 °C.

Synthesis of ^{t}Bu$_2$PNP(I)^{t}Bu$_2$ (6′-I). A cold (0 °C) solution of I$_2$ (0.472 g, 1.86 mmol) in THF (20 mL) was added to a cold (−78 °C) solution of NaN(P^{t}Bu$_2$)$_2$ (0.572 g, 1.75 mmol) in THF (30 mL), resulting in a yellow suspension which was stirred at −78 °C for 15 min, and then for 1 h at room temperature. After removal of the volatiles and addition of hexanes (30 mL), the mixture was filtered through Celite over glass wool and a 0.45 μm pore size filter disk, affording a clear yellow solution. Removal of the volatiles yielded an orange-yellow solid (0.545 g, 72%). Elemental analysis (%) calcd for $C_{16}H_{36}INP_2$: C, 44.55; H, 8.41; N, 3.25; found: C, 44.42; H, 8.66; N, 3.09. ^{1}H NMR (d_8-THF, 23 °C): δ 1.49 [d, $^{3}J(^{1}H,^{31}P) = 18$ Hz, 18H, ^{t}Bu], 1.12 [d, $^{3}J(^{1}H,^{31}P) = 11$ Hz, 18H, ^{t}Bu]; ^{31}P{^{1}H} NMR (d_8-THF, 23 °C): δ 86.4 [d, $^{2}J(^{31}P,^{31}P) = 20$ Hz, ^{t}Bu$_2$*P*−I)], 76.1 [(d, $^{2}J(^{31}P,^{31}P) = 20$ Hz, ^{t}Bu$_2$*P*]. X-ray quality crystals of **6′**-I were obtained from a concentrated solution of the product in hexanes at −35 °C.

X-ray Crystallography. A suitable crystal of the compound was coated in Paratone 8277 oil (Exxon) and mounted on a glass fiber. Data were collected at 173 K with ω and φ scans on either a Nonius KappaCCD diffractometer using Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and the Nonius COLLECT program[12] or a Bruker Apex II diffractometer using Cu$_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) with Bruker SMART software.[13] The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out by using either the Nonius DENZO package[14] or Bruker APEX 2 and SAINT[15] programs, respectively. After reduction, the data were corrected for absorption based on equivalent reflections using SCALEPACK[14] or scaled and corrected for absorption effects using SADABS.[16] The structures were solved by direct methods with

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[10] Compound numbering scheme: In addition to the compound numbers, the letters **a** and **b** are used for Se and Te derivatives, respectively. The ^{i}Pr, ^{t}Bu, and Ph derivatives are represented by no prime, superscript prime, and superscript double prime, respectively. The halide substituent (Cl or I) is distinguished by using the chemical symbol as a suffix.

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[15] *SAINT, Data Reduction Software*; Bruker AXS, 1999.

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Table 1. Crystallographic Data for **3a**-I, **3b**-I, **3a′**-I, **3b′**-I, and **6′**-I[a]

	3a-I	3b-I	3a′-I	3b′-I	6′-I
chemical formula	$C_{12}H_{28}INP_2Se$	$C_{12}H_{28}INP_2Te$	$C_{16}H_{36}INP_2Se$	$C_{16}H_{36}INP_2Te$	$C_{16}H_{36}INP_2$
formula weight	454.15	502.79	510.26	558.90	431.30
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	1.54178
crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
a [Å]	7.4672(3)	7.5215(15)	8.3650(17)	8.1071(16)	13.8624(3)
b [Å]	17.2825(9)	17.514(4)	13.832(3)	14.262(3)	9.3548(2)
c [Å]	14.2260(5)	14.323(3)	18.646(4)	18.862(4)	15.9801(4)
α [deg]	90	90	90	90	90
β [deg]	102.665(3)	101.00(3)	90	90	91.7590(10)
γ [deg]	90	90	90	90	90
V [Å^3]	1791.22(14)	1852.1(7)	2157.4(8)	2180.8(8)	2071.32(8)
Z	4	4	4	4	4
D_{calcd} [g cm^{-3}]	1.684	1.803	1.571	1.702	1.383
μ [mm^{-1}]	3.983	3.431	3.316	2.923	13.536
R_{int}	0.0844	0.0291	0.0493	0.0249	0.0465
R_1 [$I > 2\sigma(I)$][b]	0.0366	0.0334	0.0422	0.0302	0.0449
wR_2 (all data)[c]	0.0653	0.0790	0.0871	0.0819	0.1308
GOF on F^2	1.034	1.061	1.151	1.162	1.092

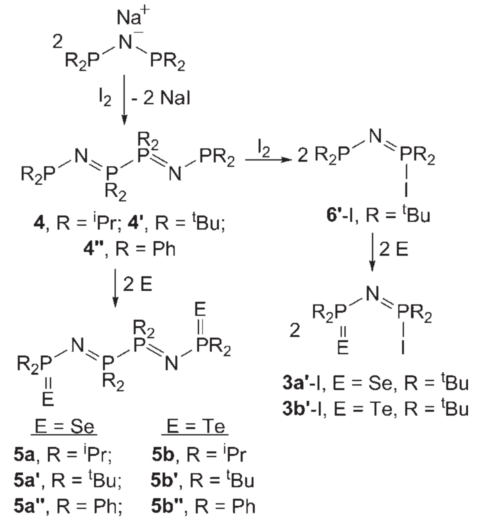
[a] T = 173(2) K. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

SHELXS-97[17] and refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method by using the SHELXL-97 program.[18] Hydrogen atoms were calculated geometrically and were riding on their respective atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data are summarized in Table 1. In the case of **3b′**-I the Flack parameter refined to a value of 0.15(2), indicating the presence of racemic twinning (i.e., both right- and left-handed helical packing forms); the complex **3a′**-I had a Flack parameter of 0.002(19).

Results and Discussion

Synthesis and NMR Spectra of 3a-I, 3b-I, 3a′-I, 3b′-I, and 6′-I. Our initial approach to compounds of the type $EP^iPr_2NP(I)^iPr_2$ (E = Se, Te) was the two-electron oxidation of the corresponding lithium reagents $Li[EP^iPr_2NP^iPr_2]$ (**2a**, E = Se; **2b**, E = Te) with 1 equiv of I_2. This methodology worked well for the selenium derivative $SeP^iPr_2NP(I)^iPr_2$ (**3a**-I), which was isolated as colorless crystals in 71% yield. In the case of the tellurium analogue $TeP^iPr_2NP(I)^iPr_2$ (**3b**-I), however, the known cationic ring system $[(TeP^iPr_2)_2N]I$ was also identified as a byproduct (singlet at $\delta(^{31}P)$ = 68.0).[7] Consequently, the isolated yield of **3b**-I, as dark orange crystals, was limited to 29% after several recrystallizations. The one-electron iodine oxidation of the P(III)/P(III) anion $[N(PPh_2)_2]^-$ has been shown by Braunstein et al. to result in the P−P bonded product **4″** in high yields (see Scheme 2).[19] In a subsequent study Woollins et al. showed that both phosphorus(III) centers in **4″** can be oxidized by selenium to give the corresponding bis(phosphine selenide), for example, **5a″** (see Scheme 2).[20,21]

Scheme 2



An alternative route to **3b**-I involves the reaction of the isopropyl derivative of the bis(phosphine telluride) **5b** with one molar equivalent of I_2. However, the preparation of the P−P bonded precursor **4** by oxidation of $Na[N(P^iPr_2)_2]$ with I_2 in either benzene or THF at −78 °C produced an oil that contained a significant amount of the byproduct $HN(P^iPr_2)_2$, possibly as a result of hydrogen abstraction by the intermediate neutral radical $[N(P^iPr_2)_2]^{\bullet}$ from either $-CH(CH_3)_2$ substituents or the solvent.[23] Consequently, we turned our attention to the preparation of the *tert*-butyl derivative **4′** by oxidation of $Na[N(P^tBu_2)_2]$ with I_2 in a 2:1 molar ratio in benzene.[23] This reaction produced an orange-yellow solid that contained only about 5 mol % of

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[21] We obtained a few crystals of the analogous bis(phosphine telluride) **5b″** during attempted recrystallizations of $(TMEDA)Na[TePPh_2NPPh_2Te]$ and determined the crystal structure.[22] Briand, G. G.; Parvez, M; Chivers, T. unpublished observations, 2002.

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[23] We have previously observed hydrogen abstraction with formation of $HN(SP^iPr_2)_2$ in the oxidation of the dithio monoanion $[SP^iPr_2NP^iPr_2S]^-$ with I_2 in either THF or benzene, whereas the corresponding *tert*-butyl derivative $[SP^tBu_2NP^tBu_2S]^-$ formed an S-S bonded dimer in good yields under similar conditions.[11]

Table 2. NMR Data for $EPR_2NP(X)R_2$ (δ in ppm, J in Hz)

	E = Se			E = Te	
	3a-Cl	**3a**-I	**3a′**-I	**3b**-I	**3b′**-I
	R = ^{i}Pr, X = Cl	R = ^{i}Pr, X = I	R = ^{t}Bu, X = I	R = ^{i}Pr, X = I	R = ^{t}Bu, X = I
δ (^{31}P)	67.2, 66.0	70.0, 51.4	83.3, 71.3	51.5, 34.9	66.6, 54.7
^2J (^{31}P,^{31}P)	37	42	61	42	61
δ(^{77}Se)	−308	−313	−256		
δ(^{125}Te)				−723	−596
^1J(^{31}P,^{77}Se)	722	725	729		
^1J(^{31}P,^{125}Te)				1763	1750

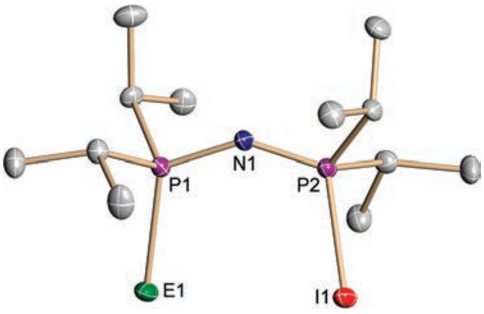

Figure 1. Thermal ellipsoid plot (30% probability) of **3b**-I as representative of compounds **3a**-I (E = Se) and **3b**-I (E = Te). Hydrogen atoms are omitted for clarity.

$HN(P^tBu_2)_2$ as determined from the ^{31}P NMR spectrum. However, the major product exhibited two mutually coupled doublets at δ 86.4 and 76.1 [$^2J(^{31}P,^{31}P)$ = 20.0 Hz] rather than the second order pattern anticipated for the P−P bonded product **4′**,[19] suggesting that it embodied only one P−N−P fragment. This conclusion was supported by CHN analyses and confirmed by a single crystal structure determination that revealed the identity of the product to be $^tBu_2PNP(I)^tBu_2$ (**6′**-I). The compound **6′**-I can be obtained in 72% yield by carrying out the reaction of $Na[N(P^tBu_2)_2]$ with iodine in a 1:1 molar ratio in THF (Scheme 2). Literature reports of P(III)/P(V) compounds of the type $R_2PNP(X)R_2$ are sparse. For example, the derivatives $[(Me_3Si)_2N](R)PNP(X)^tBu_2$ (R = ^{i}Pr, X = Br; R = adamantyl, X = I) were described in 1985 as the addition products of an alkyl halide RX with $(Me_3Si)_2NPNP^tBu_2$;[24] these P(III)/P(V) compounds were characterized by ^{1}H and ^{31}P NMR spectroscopy and, in only one case, by X-ray crystallography.[25] Additionally, the unsymmetrical derivatives $R_2PNP(Cl)R'_2$ (R = CF_3, C_3F_7; R′ = CF_3, C_3F_7, C_6H_5, C_2H_5, Cl) were generated via the condensation reaction of R_2PNH_2 with R'_2PCl_3, but no structural data were reported.[26]

The formation of **6′**-I in one step from $Na[N(P^tBu_2)_2]$ provided an obvious and more direct route to **3b′**-I via oxidation of **6′**-I with elemental tellurium. This reaction proceeded at room temperature to produce **3b′**-I as an orange powder in 89% yield. The selenium analogue **3a′**-I was prepared in the same manner from **6′**-I and elemental selenium, and isolated in 88% yield as a pale yellow solid.

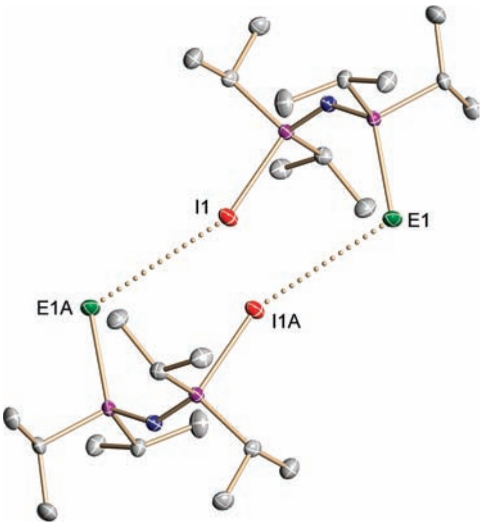

Figure 2. Dimerization modes of compounds **3a**-I and **3b**-I. Symmetry equivalents are generated by a crystallographic inversion center.

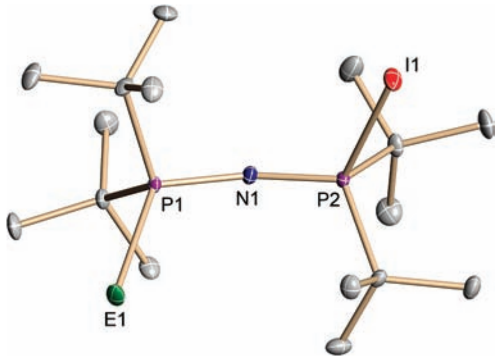

Figure 3. Thermal ellipsoid plot (30% probability) of **3b′**-I as representative of compounds **3a′**-I (E = Se) and **3b′**-I (E = Te). Hydrogen atoms are omitted for clarity.

The NMR data for **3a**-I, **3b**-I, **3a′**-I and **3b′**-I are compared with those for **3a**-Cl[7b] in Table 2 and several general trends are evident. First, the difference in ^{31}P chemical shifts exhibited by the four derivatives containing a P−I bond is much larger (range 11.9−18.6 ppm) compared to the very small disparity of 1.2 ppm observed for the P−Cl compound **3a**-Cl.[7b] The nature of the substituents R attached to phosphorus has a pronounced effect on the two-bond ^{31}P,^{31}P coupling constant in this class of asymmetric PNP compound. For the three isopropyl derivatives, **3a**-Cl, **3a**-I, and **3b**-I, the value of $^2J(^{31}P,^{31}P)$ is about 40 Hz whereas this coupling constant is increased to 61 Hz in the *tert*-butyl derivatives **3a′**-I and

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(24) Markovskii, L. N.; Romanenko, V. D; Klebanskii, E. O.; Chernega, A. N.; Antepin, M. Y.; Struchkov, Y. T.; Boldeskul, I. E. *Z. Obsh. Khim.* **1985**, *55*, 193–194 (engl. transl.).

(25) Chernega, A. N.; Antepin, M. Y.; Struchkov, Y. T.; Boldeskul, E. I.; Klebanskii, E. O.; Romanenko, V. D. *J. Struct. Chem.* **1986**, *27*, 113–120.

(26) Prons, V. N.; Grinblat, M. P.; Klebanskii, A. L. *Z. Obsh. Khim.* **1970**, *40*, 559–564 (engl. transl.).

Table 3. Selected Bond lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in EPR$_2$NP(X)R$_2$

	E = Se			E = Te	
	3a-Cl[a]	**3a**-I	**3a′**-I	**3b**-I	**3b′**-I
	R = ^{i}Pr, X = Cl	R = ^{i}Pr, X = I	R = ^{t}Bu, X = I	R = ^{i}Pr, X = I	R = ^{t}Bu, X = I
E1−P1	2.125(1)	2.134(1)	2.1373(19)	2.378(1)	2.401(1)
X1−P2	2.050(2)	2.444(1)	2.5022(17)	2.451(1)	2.497(1)
P1−N1	1.626(3)	1.634(4)	1.630(6)	1.622(3)	1.627(4)
P2−N1	1.532(3)	1.554(4)	1.542(6)	1.559(3)	1.550(4)
E1−P1−N1	118.1(1)	118.1(1)	118.6(2)	118.2(1)	118.4(1)
P1−N1−P2	147.0(2)	143.9(3)	154.8(4)	143.8(2)	156.1(3)
N1−P2−X1	114.9(1)	116.8(1)	112.7(2)	117.1(1)	113.3(1)
P1−N1−P2−X1	43.5(5)	38.7(5)	−75.4(10)	38.5(4)	67.3(7)
P2−N1−P1−E1	8.3(6)	0.5(5)	−32.4(10)	2.9(4)	35.4(7)

[a] Data taken from ref 7b.

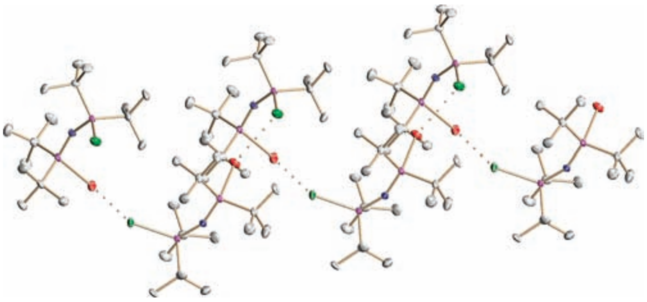

Figure 4. Solid-state packing of **3a′**-I and **3b′**-I along a crystallographic 2$_1$ screw axis in the *y* direction (Red: I; Green: Se or Te; Purple: P; Blue: N; Gray: C).

3b′-I. By contrast, the previously characterized phenyl derivative SePPh$_2$NP(I)Ph$_2$ exhibits only two singlets, that is, the coupling is too small to be resolved.[7b] The values of $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se})$ (722−729 Hz for **3a**-Cl, **3a**-I, and **3a′**-I) and $^{1}J(^{31}\mathrm{P},^{125}\mathrm{Te})$ (1750−1763 Hz for **3b**-I and **3b′**-I) are in the typical range for terminal phosphorus-chalcogen bonds and are significantly larger (by ca. 7%) than those observed for the corresponding hydrido (P−H) species (cf. 681 Hz for **1a**[1] and 1642 Hz for **1b**).[28]

Crystal Structures of 3a-I, 3a′-I, 3b-I, 3b′-I, and 6′-I. The crystal structures of **3a**-I, **3a′**-I, **3b**-I, and **3b′**-I were determined by X-ray crystallography (see Figures 1 and 3) and the structural parameters are compared with those of **3a**-Cl in Table 3. By contrast to the chloro derivative **3a**-Cl, which forms molecular strands connected by Cl---H close contacts in the crystal lattice,[7b] the corresponding iodide **3a**-I forms "head-to-tail" dimers as a result of two very weak Se---I interactions (3.9520(6) Å), compare the sum of van der Waals radii for Se and I = 4.15 Å (see Figure 2).[27] Interestingly, the corresponding telluride **3b**-I adopts a similar centrosymmetric dimeric arrangement with *d*-(Te---I) = 4.000 (1) Å (cf. sum of van der Waals radii for Te and I = 4.35 Å)[27] whereas both *tert*-butyl derivatives **3a′**-I and **3b′**-I exhibit helical packing about a 2$_1$ screw axis (Figure 4) with *d*(Te---I) = 3.795(1) Å and *d*(Se---I) = 3.7975(11) Å, respectively. The P=E bond lengths of 2.12−2.14 Å in **3**-Cl, **3a**-I, and **3a′**-I (E = Se) and about 2.38−2.40 Å in **3b**-I and **3b′**-I (E = Te) are typical values for terminal phosphorus(V)-chalcogen compounds in related compounds.[1,28] The P−I bond distances of **3a-I**, **3a′**-I, **3b-I**, and **3b′-I** (2.441(1) Å, 2.5022(17) Å, 2.451(1) Å, and 2.497(1) Å, respectively) are in the range of P(V)−I distances observed in related compounds. For example, a P−I distance of 2.458(3) Å is reported for the compound [OC(NMe)$_2$)-$\kappa^2 N$]$_2$PI,[29] and the P−I separation in ^{t}Bu$_2$-P(Se)I is 2.4535(14) Å.[30] The longer P−I bond observed in **3a′**-I and **3b′**-I (ca. 0.05 Å greater than those in **3a-I** and **3b-I**) may be the result of the different packing pattern in these compounds, occasioned by the bulky *tert*-butyl substituents on phosphorus, which is in contrast to the dimeric arrangements found for **3a-I** and **3b-I**.

All four derivatives display a *syn* conformation for the terminal chalcogen (E) and halogen (X) atoms. However, there are marked differences in the EPNP and PNPX torsion angles. For the three isopropyl derivatives **3a**-Cl, **3a**-I, and **3b**-I the EPNP unit is close to planarity with torsion angles < 9° whereas the torsion angle ∠PNPX is in the range 38.5(4)−43.5(5)°. The corresponding values of the torsion angles about the P−N bonds for the helical arrangement in the *tert*-butyl derivative **3a′-I** are 75.4(10)° and 32.4(10)°, and those in **3b′-I** are 67.3(7)° and 35.4(7)°.

The difference in the two P−N bond lengths in these P(V)/P(V) compounds is in the range 0.063−0.094 Å indicating a significant contribution from a structure with localized single and double bonds, that is, EP−N=PX, in the acyclic framework. The ∠PNP bond angles of 143.9(3)−147.0(2) Å in the three isopropyl derivatives **3a**-Cl, **3a**-I, and **3b**-I are much wider than those in the corresponding hydrido derivatives, compare 127.5(1)° for **1a**[1] and 127.3(1)° for **1b**.[28] Closer inspection of these values reveals that for the series of selenides, this widening cannot be attributed solely to the larger size of the halogen substituent compared to hydrogen, since ∠PNP is largest for the chloro derivative **3a**-Cl (147.0(2)°),[8] cf. **3a**-I (143.8(3)°). The replacement of Se in **3a**-I or **3a′**-I by Te in **3b**-I or **3b′**-I has no significant effect on ∠PNP. However, changing the ^{i}Pr groups in **3a**-I or **3b**-I to the more bulky ^{t}Bu substituents opens up this bond angle to 154.8(4)° in **3a′**-I and to 156.1(3)° in **3b′**-I. This variation is likely attributable, at least in part, to the different

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(27) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260. The van der Waals radii for Se, Te, and I are 2.00, 2.20, and 2.15 Å, respectively.

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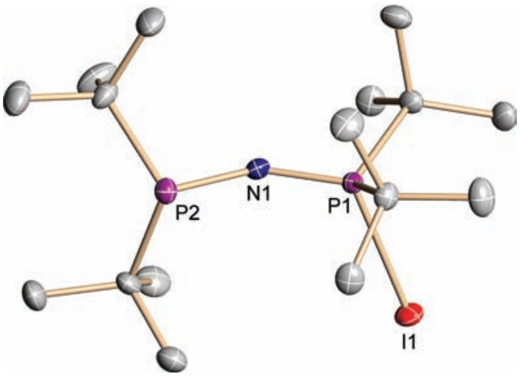

Figure 5. Thermal ellipsoid plot (30% probability) of **6′**-I. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) in ${}^{t}Bu_2P{-}N{=}P(I){}^{t}Bu_2$ (**6′**-I)

P1−I1	2.538(1)	N1−P1−I1	113.8(2)
P1−N1	1.550(4)	P1−N1−P2	139.3(3)
P2−N1	1.686(4)	P2−N1−P1−I1	91.9(4)

packing arrangement in the crystal lattice of the latter, since the ∠PNP bond angle in ${}^{t}Bu_2PNP(I){}^{t}Bu_2$ (**6′**-I), which is monomeric, is only 139.3(3)°.

The crystal structure of **6′**-I is depicted in Figure 5 and confirms the acyclic P(III)NP(V) arrangement, as well as indicating no intermolecular interactions. Relevant structural parameters are summarized in Table 4. The disparity in the PNP bond lengths of 0.136(4) Å is more pronounced than that in the related P(V)NP(V) compounds **3a′**-I and **3b′**-I consistent with localized single and double bonds, that is, ${}^{t}Bu_2P{-}N{=}P(I){}^{t}Bu_2$. The P−N−P−I torsional angle is 91.9(4)°, indicating an *anti*-conformation is preferred between the phosphorus lone pair and iodine center in the absence of van der Waals interactions. The P(V)−I bond length in **6′**-I is about 0.04 Å longer than that in **3a′**-I and **3b′**-I, and with a value of 2.538(1) Å is similar to the distance of 2.511(1) Å in the related compound ${}^{t}Bu_2P(I){-}N{=}P(Ad)(N(SiMe_3)_2)$ (Ad = adamantyl).[25]

Conclusions

Two approaches to mixed halide/chalcogenides of the type $EPR_2NP(I)R_2$ have been established. For the isopropyl derivatives the reaction of $Li[EP^iPr_2NP^iPr_2]$ with I_2 is effective, although the yield of the telluride is modest owing to the concomitant formation of the cyclic cation $[(TeP^iPr_2)_2N]I$. The new P(III)/P(V) reagent ${}^{t}Bu_2PNP(I){}^{t}Bu_2$ has been characterized and subsequently employed for the high-yield synthesis of the *tert*-butyl compounds via reactions with selenium or tellurium. Attempts to convert **3a′**-I or **3b′**-I to the corresponding cation by treatment with $Ag[SbF_6]$ produced ill-defined products that incorporate AgI. Consequently, we have turned our attention to reactions of P(III)/P(V) halides of the type $R_2PNP(X)R_2$ with halide-ion acceptors as a potential source of phosphino-substituted nitrenium ions, for example, $[N(P^tBu_2)_2]^+$.[31]

Acknowledgment. The authors gratefully acknowledge financial support from the Natural Science and Engineering Research Council (Canada), the Alberta Ingenuity Fund (J.S.R.) and the Izaak Walton Killam Memorial Foundation (J.S.R.).

Supporting Information Available: X-ray crystallographic files in CIF format for compounds **3a**-I, **3b**-I, **3a′**-I, **3b′**-I, and **6′**-I. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) For ab initio calculations on this class of nitrenium cation, see: Schoeller, W. W.; Busch, T. *Chem. Ber.* **1990**, *123*, 971–973.