

# Main Group-Tellurium Heterocycles Anchored by a P<sup>V</sup><sub>2</sub>N<sub>2</sub> Scaffold and Their Sulfur/Selenium Analogs

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**ABSTRACT:** A comprehensive investigation of reactions of alkali-metal derivatives of the ditelluro dianion [TeP<sup>V</sup>(N<sup>t</sup>Bu)(μ-N<sup>t</sup>Bu)]<sub>2</sub><sup>2-</sup> (**L**<sup>2-</sup>, E = Te) with p-block element halides produced a series of novel heterocycles incorporating P<sup>V</sup><sub>2</sub>N<sub>2</sub> rings, tellurium and group 13-16 elements. The dianion engages in *Te,Te'*-chelation to the metal center in Ph<sub>2</sub>Ge and R<sub>2</sub>Sn (R = <sup>t</sup>Bu, <sup>n</sup>Bu, Ph) derivatives; similar behavior was noted for group 14 derivatives of **L**<sup>2-</sup> (E = S, Se). In the case of group 13 trihalides MCl<sub>3</sub> (M = Ga, In), neutral spirocyclic complexes (**L**)M[N<sup>t</sup>Bu(Te)P<sup>V</sup>(μ-N<sup>t</sup>Bu)<sub>2</sub>P<sup>III</sup>N(H)<sup>t</sup>Bu)] (M = Ga, In) comprised of a *Te,Te'*-chelated ligand **L**<sup>2-</sup> and a *N,Te*-bonded ligand resulting from loss of Te and monoprotection were obtained. In reactions with RPCl<sub>2</sub> (R = <sup>t</sup>Bu, Ad, <sup>i</sup>Pr<sub>2</sub>N) a significant difference was observed between Se- and S-containing systems. In the former case, *Se,Se'*-chelated derivatives were formed in high yields, whereas the *N,S*-chelated isomers predominated for sulfur. All complexes were characterized by multinuclear (<sup>1</sup>H, <sup>31</sup>P, <sup>77</sup>Se, <sup>119</sup>Sn and <sup>125</sup>Te) NMR spectroscopy; this technique was especially

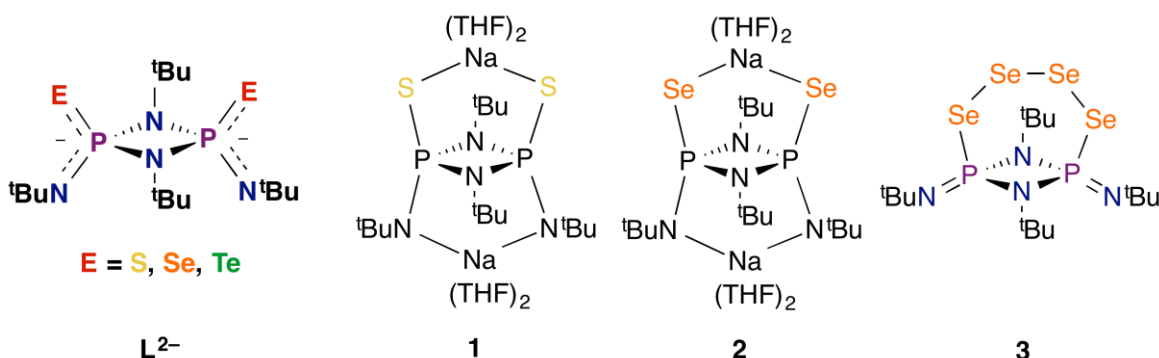
useful in the analysis of the mixture of **(L)**(Se) and **(L)**(SeSe) obtained from the reaction of  $\text{Se}_2\text{Cl}_2$  with  $\text{L}^{2-}$  (E = Te). Single crystal X-ray structures were obtained for the spirocyclic In complex **(9)**, **(L)**GePh<sub>2</sub> (E = Te, **10**), **(L)**Sn<sup>t</sup>Bu<sub>2</sub> (E = Te, **12a**; E = Se, **12aSe**, E = S, **12aS**) and **(L)**( $\mu$ -SeSe) (E = Te, **16**).

## INTRODUCTION

Cyclodiphosphazanes, e.g.  $[\text{ClP}^{\text{III}}(\mu\text{-NR})]_2$ , are saturated four-membered,  $\text{P}^{\text{III}}_2\text{N}_2$  rings that continue to attract interest from the inorganic chemistry community.<sup>1,2</sup> In recent studies they have been used creatively as building blocks in the synthesis of macrocycles with amido (NH) or chalcogenido (O, S, Se) linkers,<sup>3</sup> as well as those that incorporate coinage metals coordinated to the phosphorus(III) centers.<sup>4</sup> A fascinating recent example is afforded by the  $\text{Cu}_4\text{X}_4$  clusters linked by  $\text{P}_2\text{N}_2$  rings that resemble a sodalite framework.<sup>5</sup> In some cases these macrocycles are able to encapsulate halide<sup>6</sup> or perchlorate anions.<sup>7</sup>

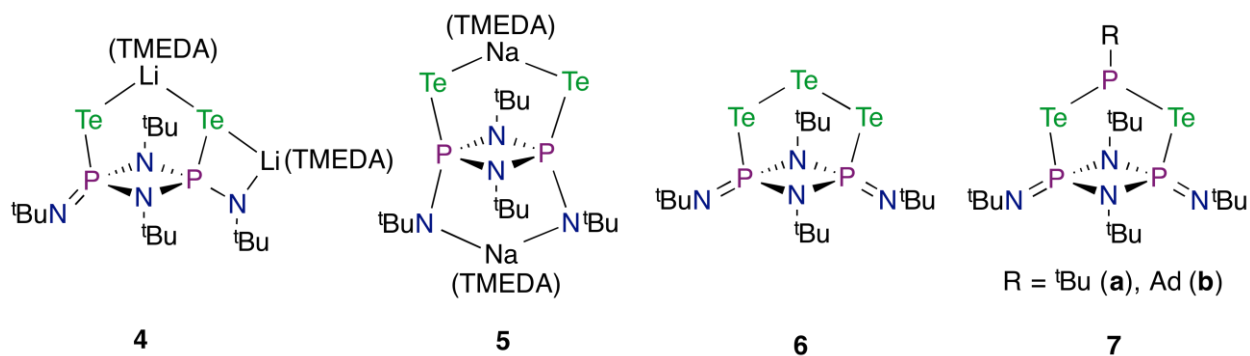
The  $\text{P}^{\text{III}}/\text{P}^{\text{III}}$  systems with terminal alkylamido groups, e.g.  $[\text{tBuN}(\text{H})\text{P}^{\text{III}}(\mu\text{-N}^t\text{Bu})]_2$ , are readily oxidized by sulfur or selenium.<sup>8</sup> Subsequent double deprotonation of the resulting  $\text{P}^{\text{V}}/\text{P}^{\text{V}}$ dichalcogenides  $[\text{tBuN}(\text{H})(\text{E})\{\text{P}^{\text{V}}(\mu\text{-N}^t\text{Bu})\}]_2$  produces ambidentate dianions of the type  $\text{L}^{2-}$  (E = S, Se), which coordinate to alkali metals in either a “top and bottom” fashion (*N,N'* and *E,E'*) for the sodium and potassium derivatives **1** and **2** or in a side-on mode (*bis-N,E*) for the lithium analogs;<sup>9,10</sup> dimethylaluminum derivatives also adopt *bis-N,E* chelation.<sup>11</sup> Monodeprotonation of  $[\text{tBuN}(\text{H})(\text{E})\{\text{P}^{\text{V}}(\mu\text{-N}^t\text{Bu})\}]_2$  (E = S, Se) generates the corresponding monoanions, which attach to  $\text{Li}^+$  in a *mono-N,E* bonding arrangement.<sup>10</sup> Recently, we have shown that the two-electron oxidation of the dianions  $\text{L}^{2-}$  (E = S, Se) produces 15-membered macrocycles in which a planar  $\text{P}_6\text{E}_6$  platform is stabilized by perpendicular  $\text{P}^{\text{V}}_2\text{N}_2$  rings.<sup>12</sup> In the

case of E = Se this oxidation also gives rise to the bridging tetraselenide  $[\text{tBuN}\{\text{P}^{\text{V}}(\mu\text{-N}^{\text{tBu}})\}]_2(\mu\text{-SeSeSeSe})$  (**3**), which is more conveniently prepared by metathesis of **2** with  $\text{Se}_2\text{Cl}_2$ .<sup>12</sup>



The synthesis of the ditelluro dianion  $\text{L}^{2-}$  (E = Te) requires a different approach because elemental tellurium does not oxidize both  $\text{P}^{\text{III}}$  centers in  $[\text{tBuN}(\text{H})\text{P}^{\text{III}}(\mu\text{-N}^{\text{tBu}})]_2$ . However, if the double deprotonation of this neutral precursor is carried out first,<sup>13</sup> the  $\text{P}^{\text{III}}$  centers in the resulting dianion become more nucleophilic and telluration proceeds smoothly to give  $\text{L}^{2-}$  (E = Te) as either dilithium or disodium derivatives, **4** and **5**, respectively.<sup>14,15</sup> As in the case of the dithio analog  $\text{L}^{2-}$  (E = S), the smaller  $\text{Li}^+$  ions in **4** adopt a different coordination mode (*Te, Te'* and *N, Te*)<sup>12</sup> compared to that found for  $\text{Na}^+$  in **5** (*Te, Te'* and *N, N'*).<sup>15</sup>

In contrast to the formation of trimeric macrocycles from the oxidation of alkali-metal derivatives **1** and **2** (*vide supra*),<sup>12</sup> the treatment of **4** with  $\text{I}_2$  produced the cyclic tritelluride  $[\text{tBuN}\{\text{P}^{\text{V}}(\mu\text{-N}^{\text{tBu}})\}]_2(\mu\text{-TeTeTe})$  (**6**), which is obtained in higher yield by metathesis of **5** with  $\text{TeCl}_2 \cdot \text{TMTU}$  (TMTU = tetramethylthiourea).<sup>15</sup> Furthermore, metathesis of **4** with  $\text{R}\text{P}\text{Cl}_2$  (R = <sup>t</sup>Bu, Ad) generates the  $\text{P}^{\text{V}}_2\text{N}_2$ -supported heterocycles **7a,b**, which were among the first examples of structurally characterized phosphorus(III)-tellurium ring systems.<sup>16</sup>



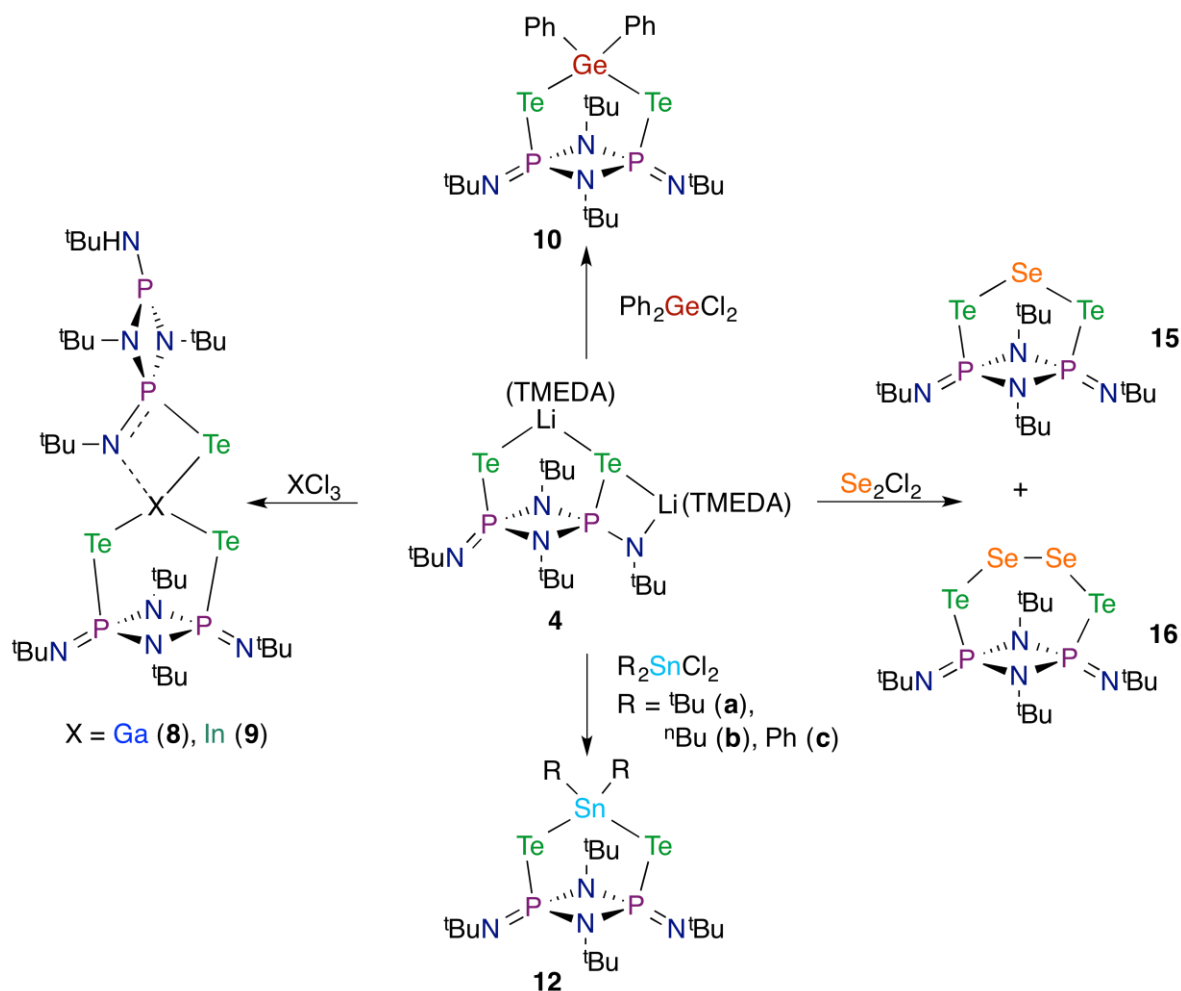
These preliminary results suggest that the  $P^V_2N_2$  scaffold plays an influential role in the stabilization of heterocycles that incorporate tellurium and another p-block element. In order to determine the scope and limitations of the ditelluro dianion  $L^{2-}$  ( $E = Te$ ) as a reagent for the synthesis of such heterocycles, we have carried out a comprehensive investigation of the reactions of **4** and **5** with a variety of group 13, 14, 15 and 16 halides, specifically  $MCl_3$  ( $M = Ga, In$ ),  $R_2MCl_2$  ( $M = Ge, R = Ph$ ;  $M = Sn, R = ^tBu$ ),  $RMCl_2$  ( $M = As, R = Et$ ;  $M = Sb, R = Ph$ ) and  $Se_2Cl_2$ . For comparison, we conducted the reactions of the dithio and diseleno reagents **1** and **2**, respectively, with group 14 dihalides and  $RPCL_2$  ( $R = ^tBu, Ad, ^iPr_2N$ ). The products of these metatheses were characterized by CHN analyses, high-resolution mass spectra and, in solution, by multinuclear NMR spectroscopy ( $^1H, ^{31}P, ^{77}Se, ^{119}Sn$  and  $^{125}Te$ ). Solid-state structures of the spirocyclic In complex (**9**),  $(L)GePh_2$  ( $E = Te, \mathbf{10}$ ),  $(L)Sn^tBu_2$  ( $E = Te, \mathbf{12a}$ ;  $E = Se, \mathbf{12aSe}, E = S, \mathbf{12aS}$ ) and  $(L)(\mu-SeSe)$  ( $E = Te, \mathbf{16}$ ) were determined by single crystal X-ray crystallography.

## RESULTS AND DISCUSSION

**Synthesis, NMR Spectra and Crystal Structure of Group 13 Complexes.** The reactions of **4** and **5** with group 13-16 halides were performed in toluene at  $-78\text{ }^\circ\text{C}$ , followed by warming to room temperature. The crude products were generally recrystallized from *n*-hexane at  $-40\text{ }^\circ\text{C}$  and X-ray structural determinations were carried out when suitable crystals were obtained. In

other cases the identity of the products was based on high-resolution mass spectra and multinuclear NMR spectra. The outcome of these reactions is summarized in Scheme 1.

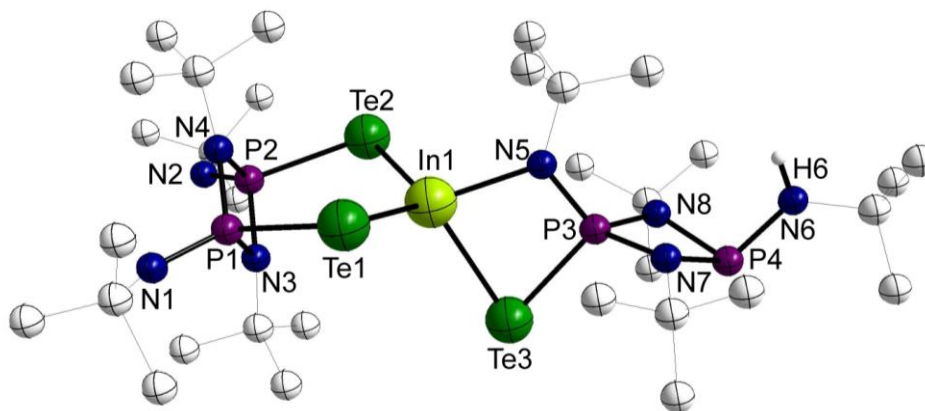
### Scheme 1



The reaction of  $\text{GaCl}_3$  and  $\text{InCl}_3$  with 4 yielded complexes 8 and 9 (Scheme 1) in low isolated yields (8 and 12%, respectively), presumably owing to partial decomposition of the ligand (loss of Te).<sup>17</sup> The indium derivative 9 is considerably less prone to decomposition than the gallium analog 8 and, consequently, it was characterized by CHN analysis, mass spectrometry and a single crystal X-ray structure. The  $^{31}\text{P}$  NMR spectra of 8 and 9 exhibit similar patterns comprised of three resonances in the regions 77-78, -41 to -45, and -133 to -135 ppm with approximate

relative intensities of 1:1:2. On the basis of the high-field chemical shift and lack of  $^{125}\text{Te}$  satellites, the resonance at 77-78 ppm is attributed to a  $\text{P}^{\text{III}}$  center that is no longer attached to tellurium. By contrast, the resonance at 41-45 ppm displays satellites consistent with one-bond  $^{31}\text{P}$ - $^{125}\text{Te}$  coupling (1235-1250 Hz), showing that this P center is still bonded to tellurium. In the case of **9** the resonances at 78.1 and -41.2 ppm both exhibit a well-resolved doublet with  $^2J(\text{P},\text{P}) = 3.4$  Hz, consistent with mutual coupling of inequivalent P environments in the same *cyclo*- $\text{P}^{\text{V}}_2\text{N}_2$  ligand. On the basis of its relative intensity, the third resonance at -133 and -135 ppm in **8** and **9**, respectively, which also displays satellites ( $^1J(\text{P},\text{Te}) = 1115$  and 1130 Hz), is attributed to the symmetrical dianionic ligand  $\text{L}^{2-}$  (E = Te). This conclusion is supported by the  $^{31}\text{P}$  NMR chemical shifts of ca. -136 to -141 ppm observed for the group 14 derivatives **10** and **12a-c** (*vide infra*). In summary, the  $^{31}\text{P}$  NMR spectra for **8** and **9**, together with the CHN data and the observation of the molecular ion at  $m/z = 1192.1$  in the mass spectrum of **9**, indicate that the  $\text{M}^{3+}$  center in these neutral complexes is symmetrically chelated to a dianionic ligand  $\text{L}^{2-}$  (E = Te) and also bonded to a monoanion in which the  $\text{P}_2\text{N}_2$  platform is comprised of a  $\text{P}^{\text{III}}$  center and a  $\text{P}^{\text{V}}=\text{Te}$  functionality.

Yellow platelets of the indium compound **9** were obtained by recrystallization from n-hexane and the structure was determined by X-ray crystallography (Figure 1), which confirmed the conclusions based on the  $^{31}\text{P}$  NMR spectra. The spirocyclic structure of **9** is comprised of the dianionic ditelluro ligand  $\text{L}^{2-}$  (E = Te) coordinated to indium in a *Te,Te'*-mode and the *Te,N*-chelated *monotelluro* monoanion  $[(^t\text{BuN}(\text{Te})\text{P}^{\text{V}}(\mu\text{-N}^t\text{Bu})_2\text{P}^{\text{III}}\text{N}(\text{H})^t\text{Bu})]^-$ , which presumably results from the loss of tellurium from  $\text{L}^{2-}$  (E = Te) and monoprotonation.<sup>17</sup>



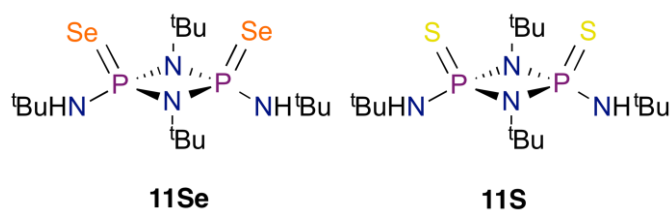
**Figure 1.** Crystal structure of **9**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–In1 2.7270(16), Te1–P1 2.485(4), Te2–In1 2.7210(16), Te2–P2 2.499(3), Te3–In1 2.7959(6), Te3–P3 2.4526(10), In1–N5 2.174(3), P1–N1 1.559(12), P1–N3 1.699(13), P1–N4 1.662(12), P3–N5 1.610(4), P3–N7 1.644(11), P3–N8 1.686(11); In1–Te1–P1 93.37(8), In1–Te2–P2 93.05(8), In1–Te3–P3 71.40(3), Te1–In1–Te2 115.87(3), Te1–In1–Te3 114.25(6), Te1–In1–N5 113.4(4), Te2–In1–Te3 114.25(6), Te2–In1–N5 114.8(4), Te3–In1–N5 79.00(9).

The mean P–Te distance of 2.492(4) Å for the ligand  $L^{2-}$  in **9** is comparable to that in the group 15 derivative [cf. 2.510(3) Å in **7b** (R = Ad)],<sup>16</sup> while the third P–Te bond length of 2.453(1) Å is significantly shorter. The P–Te–In–Te–P scaffold was previously reported in the six-membered ring {In( $\mu$ -Te)[N(<sup>i</sup>Pr<sub>2</sub>P<sub>2</sub>Te)<sub>2</sub>]}<sub>3</sub>.<sup>18</sup> The In–Te<sub>exo</sub> distance of 2.809(1) Å in the latter complex<sup>18</sup> is elongated when compared to the In–Te distances from the dianionic ligand  $L^{2-}$  in **9** (2.721(2)–2.727(2) Å), but comparable to the value of 2.796(1) Å observed for the Te3–In1 distance involving the monoanionic ligand.

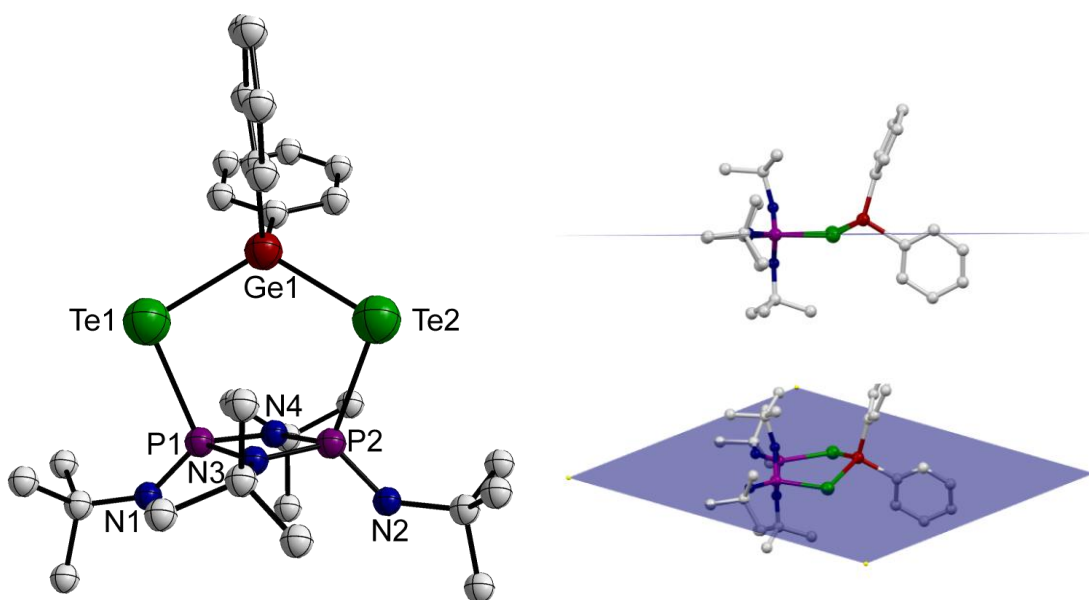
### Synthesis, NMR Spectra and Crystal Structures of Group 14 Complexes.

diseleno ligands  
The reaction of **4** with Ph<sub>2</sub>GeCl<sub>2</sub> produces the diphenylgermanium derivative **10** in 39 % isolated yield (Scheme 1); no decomposition was observed in the solid state after 3 days of exposure to

moist air. By contrast, the formation of the selenium analog **10Se** (Scheme 2) was accompanied by the diprotonated derivative H<sub>2</sub>A (E = Se) (**11Se**), which precluded the isolation of pure **10Se** due to their similar solubilities.<sup>19</sup>



The CHN analysis and the observation of the molecular ion in the high-resolution mass spectrum are consistent with the formation of the expected metathesis product **10**; furthermore, the singlet at  $-136.4$  ppm ( $^1J(\text{P},\text{Te}) = 1103$  Hz) strongly suggests symmetrical coordination of the ligand  $\text{L}^{2-}$  (E = Te) to the group 14 center. Yellow platelets of **10** were isolated from a saturated *n*-hexane solution stored at  $-40$  °C, and an X-ray structural determination confirmed the *Te,Te'*- coordination of the ligand to the Ph<sub>2</sub>Ge unit (Figure 2).



**Figure 2.** Molecular structure and side view of **10**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–Ge1 2.577(3), Te2–Ge1 2.565(3), Te1–P1 2.508(6), Te2–



P2 2.508(6), P1–N1 1.525(17), P1–N3 1.715(18), P1–N4 1.686(17), P2–N3 1.733(17), P2–N2 1.521(16), P2–N4 1.693(18); Ge1–Te1–P1 97.73(14), Ge1–Te2–P2 98.56(14), Te1–Ge1–Te2 115.44(10), Te1–P1–N1 114.0(7), Te1–P1–N3 107.1(7), Te1–P1–N4 109.3(6), Te2–P2–N3 108.5(7), Te2–P2–N2 115.6(7), Te2–P2–N4 107.2(6), N1–P1–N3 120.3(10), N1–P1–N4 117.9(10), N3–P1–N4 84.5(9).

The P–Te–E–Te–P (E = Ge) framework has not been previously reported, although a few examples of structurally characterized compounds incorporating Te–Ge–Te units were described. The mean Te–Ge bond distance in **10** is 2.571(3) Å, *cf.* 2.585(1)–2.600(1) Å in [(2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>GeTe<sub>2</sub>]<sub>2</sub> and 2.580(1) Å in [(2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>4</sub>Ge<sub>4</sub>Te<sub>6</sub>].<sup>20</sup> The Ge atom is located 0.60 Å out of the mean Te1–P1–N1–N2–P2–Te2 plane in **10** and the P<sup>V</sup><sub>2</sub>N<sub>2</sub> ring is exactly perpendicular to this plane (Figure 2). The angle at the bridging Ge atom (<Te–Ge–Te) is 115.44(10)°, *cf.* <Te–Te–Te = 104.50 (1)° in the cyclic tritelluride **6**<sup>14</sup> and <Te–P–Te = 108.81(16)° in **7b**.<sup>16</sup>

The mass spectrum of the selenium analog **10Se** shows a molecular ion at  $m/z = 733.1$  [ $M^+ + H$ ] with a characteristic isotopic pattern. The <sup>31</sup>P NMR spectrum consists of a singlet at –80.4 ppm accompanied by a set of satellites revealing <sup>1</sup>*J*(P,Se) = 470 Hz and <sup>2</sup>*J*(P,P) = 60 Hz. Consistently, the <sup>77</sup>Se NMR spectrum is comprised of a doublet of doublets centered at 137.6 ppm with <sup>1</sup>*J*(P,Se) = 470 Hz and <sup>3</sup>*J*(P,Se) = 15.6 Hz. Thus, the NMR data indicate symmetrical coordination of L<sup>2-</sup> (E = Se) to the GePh<sub>2</sub> unit. Although yellow crystals of **10Se** were isolated, they were not of sufficient quality for the crystal structure to be determined.

Metathetical reactions of **4** with R<sub>2</sub>SnCl<sub>2</sub> (R = <sup>t</sup>Bu, <sup>n</sup>Bu, Ph) were carried out in order to evaluate the influence of the R group on the stability of the products. The air-sensitivity of the R<sub>2</sub>Sn complexes **12a-c** varies dramatically; the <sup>t</sup>Bu<sub>2</sub>Sn derivative **12a** does not deteriorate upon exposure to air in the solid state for three days, whereas the <sup>n</sup>Bu<sub>2</sub>Sn (**12b**) and Ph<sub>2</sub>Sn (**12c**)

analogs decompose instantly with the formation of elemental tellurium (especially in solution), which precluded characterization by elemental analysis and mass spectrometry.

The *Te,Te'*-chelated structure of **12a** was established by an X-ray crystal structure (*vide infra*) and that arrangement is maintained in solution according to the NMR data (Table 1). Accordingly, the  $^{31}\text{P}$  NMR spectrum exhibits a singlet accompanied by a doublet of tellurium satellites resulting from the magnetic inequivalence of the phosphorus centers [ $^1J(\text{P,Te})$  and  $^2J(\text{P,P})$ ]. Furthermore, tin satellites corresponding to  $^2J(\text{P,Sn}) = 52$  Hz are observed. Consistently, the  $^{119}\text{Sn}$  NMR spectrum exhibits a triplet attributed to coupling to two equivalent phosphorus centers with satellites showing  $^1J(\text{Sn,Te}) \approx 3390$  Hz. The  $^{125}\text{Te}$  NMR spectrum consists of a doublet of doublets attributed to the  $^1J(\text{Te,P})$  and  $^3J(\text{Te,P})$  couplings. In addition, satellites confirming the  $^1J(\text{Te,Sn})$  value from the  $^{119}\text{Sn}$  NMR spectra are apparent. Comparison of the NMR data for **12b** and **12c** with those of **12a** strongly suggest a similar framework, i.e. *Te,Te'* chelation, for this series of  $\text{R}_2\text{Sn}$  (R =  $^n\text{Bu}$ , Ph,  $^t\text{Bu}$ ) derivatives (Table 1).

**Table 1.** Comparison of NMR Parameters for **12a-c**, **12aSe** and **12aS**.<sup>a</sup>

Compound	12a	12b	12c	12aSe	12aS
E	Te	Te	Te	Se	S
R	$^t\text{Bu}$	$^n\text{Bu}$	Ph	$^t\text{Bu}$	$^t\text{Bu}$
$\delta(^{31}\text{P})$	-141.6	-140.4	-141.1	-77.0	-48.7
$^1J(^{31}\text{P,E})^c$	1183	1102	1140	500	
$^2J(^{31}\text{P},^{119}\text{Sn})$	52	60	51	42	35
$\delta(^{119}\text{Sn})$	34.2 (t)	-156.1 (t)	-84.7 (t)	69.8 (t)	66.4 (t)
$^1J(^{119}\text{Sn,E})^c$	3385	<i>b</i>	3389	691	-
$\delta(^{125}\text{Te})$	-47.7 (dd)	23.4 (dd)	6.7 (dd)	-	-
$\delta(^{77}\text{Se})$	-	-	-	77.3 (dd)	-
$^3J(^{31}\text{P,E})^c$	25	26	26	12	-

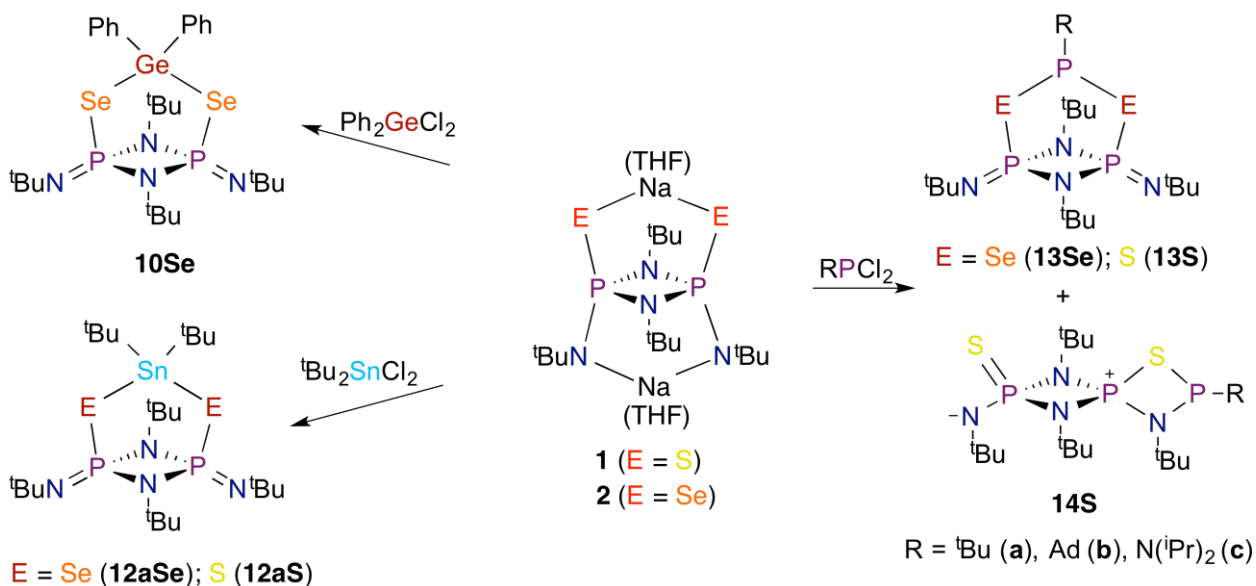
<sup>a</sup>  $\delta$  in ppm and  $J$  in Hz; t = triplet, dd = doublet of doublets

<sup>b</sup> Poor signal-to-noise ratios in the  $^{119}\text{Sn}$  and  $^{125}\text{Te}$  NMR spectra

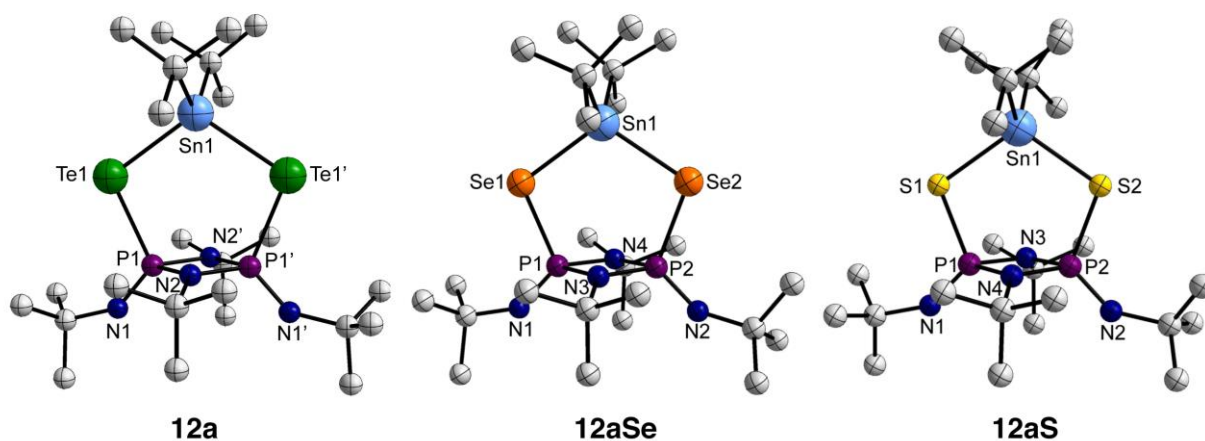
<sup>c</sup> E =  $^{77}\text{Se}$  or  $^{125}\text{Te}$

In order to assess the influence of the chalcogen on the stability of  $\text{R}_2\text{Sn}$  derivatives of the dianions  $\text{L}^{2-}$  (A = Te, Se, S), the reactions of **1** and **2** with  $^t\text{Bu}_2\text{SnCl}_2$  were also conducted. Although the  $^{31}\text{P}$  NMR spectra indicated high yields of **12aS** and **12aSe** in solution (ca. 80%), and analytically pure crystals were obtained, the isolation of large amounts of these products was thwarted by the co-formation of **11Se** and **11S**.<sup>19</sup> The  $^{31}\text{P}$  NMR spectrum of **12aSe** exhibits a singlet at  $-77.0$  ppm with two sets of satellites,  $^1J(\text{P,Se}) = 500$  Hz and  $^2J(\text{P,Sn}) = 42$  Hz. Similar to the observations for the tellurium analog **12a**, the  $^{119}\text{Sn}$  NMR spectrum of **12aSe** shows a triplet at  $69.8$  ppm ( $^1J(\text{Sn,Se}) = 691$  Hz) and the  $^{77}\text{Se}$  NMR spectrum exhibits a doublet of doublets at  $77.3$  ppm, which arises from the  $^1J(\text{P,Se})$  and  $^3J(\text{P,Se})$  couplings (Table 1). For comparison, the  $^{31}\text{P}$  NMR spectrum of the tin(IV) complex  $[\text{Sn}\{(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2\}_2]$  shows a singlet at  $61.6$  ppm with  $^1J(\text{P,Se}) = 536$  Hz<sup>21</sup> and the tin(II) complex  $[\text{Sn}\{\text{NSeP}^i\text{Pr}_2\}_2\text{-Se,Se'}_2]$  exhibits a singlet at  $58.8$  ppm with  $^1J(\text{P,Se}) = 550$  Hz and a  $^2J(\text{P,Sn}) = 55$  Hz.<sup>22</sup> The  $^{31}\text{P}$  NMR spectrum of **12aS** consists of a single resonance at  $-48.7$  ppm accompanied by  $^{119}\text{Sn}$  satellites ( $^2J(\text{P,Sn}) = 35$  Hz) and the  $^{119}\text{Sn}$  NMR spectrum reveals a triplet at  $66.4$  ppm confirming the  $^2J(\text{P,Sn})$  values observed in the  $^{31}\text{P}$  NMR spectrum (Table 1).

## Scheme 2



Yellow (**12a**) and colorless crystals (**12aSe**, **12aS**) suitable for X-ray analysis were isolated after recrystallization from *n*-hexane at  $-40\text{ }^\circ\text{C}$ . The molecular structures are illustrated in Figure 2 and structural parameters are compared in Table 2.



**Figure 2.** Molecular Structures of **12a**, **12aSe** and **12aS**.

**Table 2.** Comparison of Structural Data for **12a**, **12aSe** and **12aS**.<sup>a</sup>

Compound	12a	12aSe	12aS
<i>d</i> (P–E)	2.504(2)	2.277(3),2.286(3)	2.110(4),2.121(4)
<i>d</i> (E–Sn)	2.7603(7)	2.5687(13),2.5750(14)	2.444(4),2.450(4)
<i>d</i> (P–N <sub>exo</sub> )	1.508(7)	1.521(10),1.507(9)	1.484(10),1.499(10)
<i>d</i> (P–N <sub>endo</sub> )	1.696(7),1.693(7)	1.715(9),1.693(9), 1.689(9),1.698(9)	1.704(10),1.696(9), 1.702(9),1.702(10)
<i>d</i> (P···Sn)	4.056	3.808	3.603
∠ P–E–Sn	100.74(6)	102.73(8),103.00(8)	104.34(17),104.31(17)
∠ E–Sn–E	110.84(3)	110.35(4)	109.94(9)
∠ E–P–P	113.87(7)	112.45(13)	110.98(15)
∠ P–N <sub>endo</sub> –P	96.2(4)	95.8(5),95.4(5)	95.4(4),95.1(4)
∠ E–P–N <sub>exo</sub>	115.4(3)	114.3(4),116.1(4)	115.5(4),116.9(5)
∠ E–P–N <sub>endo</sub>	107.3(3)	107.2(3),107.4(3), 106.4(3),106.7(3)	105.7(3),107.4(3), 105.1(3),107.1(3)

<sup>a</sup> Bond lengths in Å; bond angles in deg.

The structural determinations confirm the *E,E'* coordination of the ligands L<sup>2-</sup> (E = S, Se, Te) to the group 14 center in all three derivatives. Interestingly, a *N,N'*-chelated isomer of **12aS** has been characterized previously for Me<sub>2</sub>SnL (E = S).<sup>23</sup> In that case, however, the isomer formed was pre-determined by the synthetic approach, which involved oxidation of the two P<sup>III</sup> centers in the *N,N'*-chelated complex [(<sup>t</sup>BuNP<sup>III</sup>(μ-N<sup>t</sup>Bu)<sub>2</sub>P<sup>III</sup>N<sup>t</sup>Bu)(SnMe<sub>2</sub>)] with sulfur.<sup>23</sup>

In contrast to the observations for the Ph<sub>2</sub>Ge derivative **10**, the –P–Te–Sn–Te–P– framework is perfectly planar in **12a**, **12aSe** and **12aS**; the P<sub>2</sub>N<sub>2</sub> ring is perpendicular to that plane. The Sn–Te bond distance of 2.7603(7) Å in **12a** is comparable to the typical range (2.73–2.76 Å) reported for five-membered rings of the type (R<sub>2</sub>Sn)<sub>3</sub>Te<sub>2</sub> (R = <sup>t</sup>Bu,<sup>24a</sup> Fc<sup>24b</sup>). Although this bond is expectedly 0.19 and 0.32 Å longer than the corresponding distance in **12aSe** and **12aS**, the E–Sn–E bond angle varies by < 1.0° in all three derivatives. Concomitantly, the P–E–Sn bond

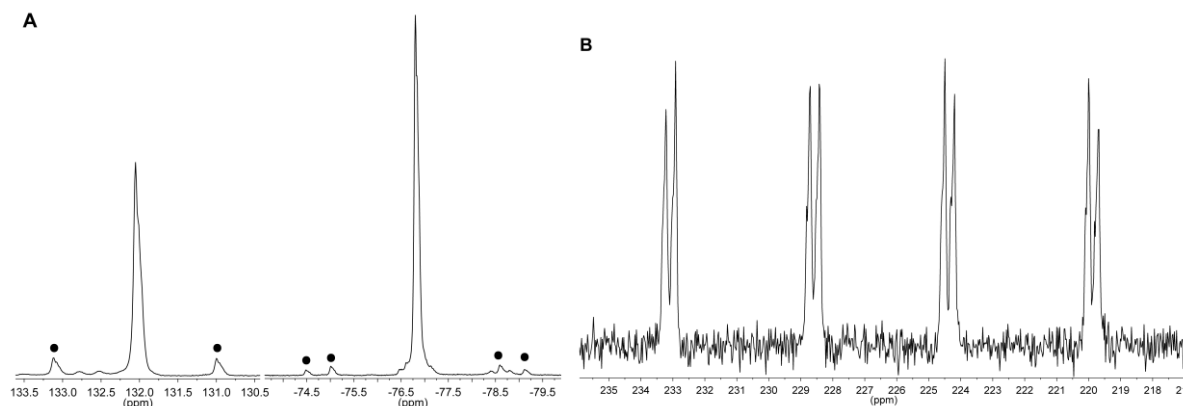
angle increases in the series Te < Se < S from 100.7(1)° to 104.3(2)° consistent with higher p-character in the chalcogen bonds for tellurium. The P–Te distance in **12a** is similar to that in **10**.

The structural motif P–Se–Sn–Se–P has been described in the octahedral Sn<sup>IV</sup> compound [Sn{(Se)C(PPh<sub>2</sub>Se)<sub>2</sub>}<sub>2</sub>]<sup>21</sup> and in the Sn<sup>II</sup> complex [Sn{NSeP<sup>i</sup>Pr<sub>2</sub>)}<sub>2</sub>-Se,Se']<sub>2</sub>.<sup>22</sup> The P–Se distances of 2.277(3) and 2.286(3) Å in **12aSe** are in the typical single-bond range for P–Se rings.<sup>25,26</sup> The P–S–Sn–S–P scaffold is well-known, e.g. in diorganotin dithiophosphates Me<sub>2</sub>Sn(S<sub>2</sub>PR<sub>2</sub>)<sub>2</sub> (R = Et,<sup>27</sup> Ph,<sup>28</sup> Me<sup>29</sup>). The P–S bond distances in **12aS** are slightly longer (by ca. 0.10 Å) than the mean value in diorganotin dithiophosphates, whereas the Sn–S bond lengths are marginally shorter (by 0.02–0.03 Å).

**Synthesis and NMR Spectra of Organophosphorus Derivatives.** In view of our recent synthesis of thermally stable organophosphorus(III)-tellurium heterocycles **7a** and **7b** via metathesis,<sup>16</sup> we have now investigated the reactions of **1** and **2** with RPCl<sub>2</sub> (R = <sup>t</sup>Bu, Ad, <sup>i</sup>Pr<sub>2</sub>N) in order to determine the influence of the chalcogen on the nature of the products. As indicated in Scheme 2, the Se,Se'-coordinated derivatives **13aSe** and **13bSe** are formed for the selenium system in yields of ca. 40% and 79% yields, respectively, on the basis of integrated <sup>31</sup>P NMR spectra. In both cases colorless crystals were isolated and the CHN analysis of **13aSe** was consistent with the molecular formula LP<sup>t</sup>Bu (E = Se); the symmetrical Se,Se'-coordination to the <sup>t</sup>BuP group was confirmed by a well-modeled disordered crystal structure (see ESI).

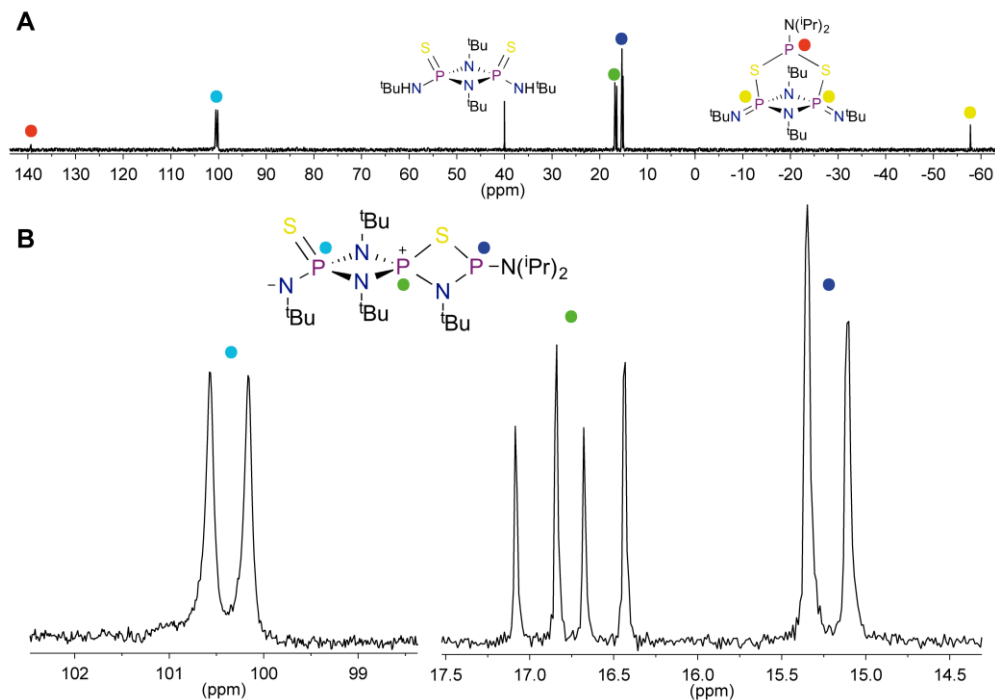
The NMR spectra of **13aSe** and **13bSe** exhibit similar patterns to those of the tellurium analogs **7a** and **7b**.<sup>16</sup> The <sup>31</sup>P and <sup>77</sup>Se NMR spectra for the adamantyl derivative **13bSe**, as a representative example, are discussed here (Figure 3). The <sup>31</sup>P NMR resonance at 132.0 ppm accompanied by <sup>77</sup>Se satellites (<sup>1</sup>J(P,Se) = 232 Hz) is assigned to the P<sup>III</sup> center in the bridging SePSe unit. The second resonance at –76.8 ppm shows a doublet of satellites with <sup>1</sup>J(P,Se) =

449 Hz and  ${}^2J(\text{P},\text{P}) = 58$  Hz, as expected for the chemically equivalent, but magnetically inequivalent, phosphorus atoms of the  $\text{P}^{\text{V}}_2\text{N}_2$  ring. The large difference in  ${}^1J(\text{P},\text{Se})$  values reflects the different formal oxidation states of the  $\text{P}^{\text{III}}$  and  $\text{P}^{\text{V}}$  environments. The  ${}^{77}\text{Se}$  NMR spectrum of **13bSe** consists of a doublet of doublets of doublets centered at 226.5 ppm, which result from the two afore-mentioned  ${}^1J(\text{P},\text{Se})$  couplings and a  ${}^3J(\text{Se},\text{P})$  coupling of 15.6 Hz (Figure 3).



**Figure 3.** (A)  ${}^{31}\text{P}$  NMR and (B)  ${}^{77}\text{Se}$  NMR spectra of **13bSe**.

In distinct contrast to the selenium and tellurium systems, the  $S,S'$ -chelated complexes **13a-cS** were formed in very low (< 5 %) yields, according to  ${}^{31}\text{P}$  NMR spectra. Instead, the major products from the metathesis of **1** with  $\text{RPCl}_2$  were the  $N,S$ -chelated complexes **14a-cS** (Scheme 2). The characterization of these products was based on the observation of the parent ion in the EI mass spectra and a detailed analysis of the  ${}^{31}\text{P}$  NMR spectra. As a typical example, Figure 4A depicts the  ${}^{31}\text{P}$  NMR spectrum of the reaction of **4** with  ${}^1\text{Pr}_2\text{NPCl}_2$  which produces **14cS** as the major product, **13cS** as a very minor product, and **11S**. The  ${}^{31}\text{P}$  NMR spectrum of the  $S,S'$ -chelated isomer **13cS** exhibits a mutually coupled 1:2:1 triplet and a doublet, attributed to the  $\text{P}^{\text{III}}$  (139.4 ppm) and  $\text{P}^{\text{V}}$  (-57.7 ppm) centers, respectively, with a small  ${}^2J(\text{P},\text{P})$  coupling of 4.3 Hz that was not resolved in the case of the Se analogs **13aSe** and **13bSe**.



**Figure 4.**  $^{31}\text{P}$  NMR spectrum of the reaction of **1** with  $i\text{Pr}_2\text{NPCl}_2$ : (A) Complete spectrum; (B) Expanded spectrum for the  $N,S$ -chelated complex **14cS**.

The expanded  $^{31}\text{P}$  NMR spectrum of **14cS** (Figure 4B) reveals three distinct phosphorus environments resulting from the  $N,S$ -chelation of the ligand  $\text{L}^{2-}$  ( $\text{E} = \text{S}$ ) to the  $\text{RP}^{\text{III}}$  center to give a zwitterion (Scheme 2). On the basis of the chemical shifts and coupling patterns, the three resonances can be assigned as follows: (a) a doublet at 100.4 ppm ( $^2J(\text{P},\text{P}) = 44$  Hz) for the terminal  $\text{P}^{\text{V}}$  center, (b) a doublet of doublets at 16.8 ppm ( $^2J(\text{P}^{\text{V}},\text{P}^{\text{V}}) = 45$  Hz,  $^2J(\text{P}^{\text{V}},\text{P}^{\text{III}}) = 26$  Hz) for the spirocyclic  $\text{P}^{\text{V}}$  environment, and (c) a doublet at 15.2 ppm ( $^2J(\text{P}^{\text{III}},\text{P}^{\text{V}}) = 26$  Hz) for the terminal  $\text{P}^{\text{III}}$  atom. The anomalous chemical shift for the spirocyclic  $\text{P}^{\text{V}}$  center is tentatively attributed to the formal positive charge on this atom in the zwitterionic structure of **14cS**. The NMR spectroscopic parameters for the adamantyl (**14bS**) and *tert*-butyl (**14aS**) derivatives, which show similar patterns, are summarized in Table 3.



The observation of different coordination modes of the ligands  $L^{2-}$  towards an  $RP^{2+}$  unit was unexpected; the only previous example of  $N,S$ -chelation of the dianion  $L^{2-}$  ( $E = S$ ) was found in the THF-solvated dilithium derivative.<sup>10</sup> The preferential formation of  $N,E$ -chelated organophosphorus(III) complexes for sulfur, but  $E,E'$ -bonded isomers for selenium and tellurium, may result from a combination of (a) the different bite angles of the two possible modes of chelation and (b) the higher stability of the zwitterionic structure **14S** (Scheme 2) for sulfur.

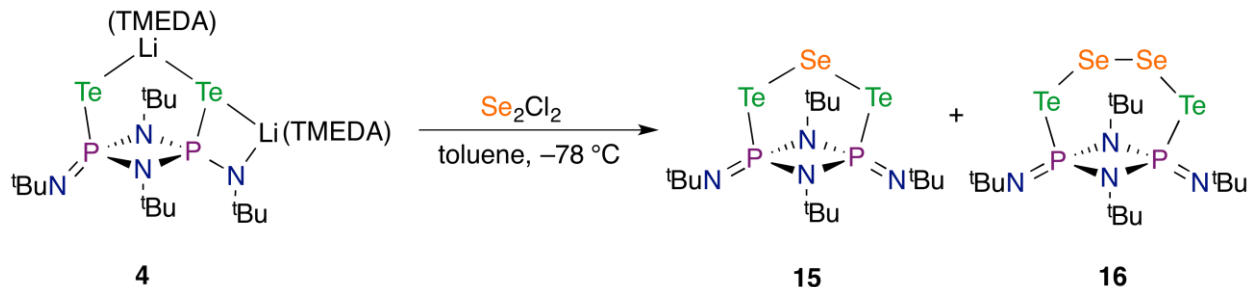
**Table 3.**  $^{31}P$  NMR Chemical Shifts and  $^2J(P,P)$  for **14a-c**.<sup>a</sup>

Compound	14aS	14bS	14cS
$\delta(^{31}P)$ ( $P^V=S$ )	116.9 (d)	111.4 (d)	100.4 (d)
$\delta(^{31}P)$ (spirocyclic $P^V$ )	17.2 (dd)	17.3 (dd)	16.8 (dd)
$\delta(^{31}P)$ ( $P^{III}$ )	14.4 (d)	14.6 (d)	15.2 (d)
$^2J(P^V,P^{III})$	27	27	26
$^2J(P^V,P^V)$	42	43	44

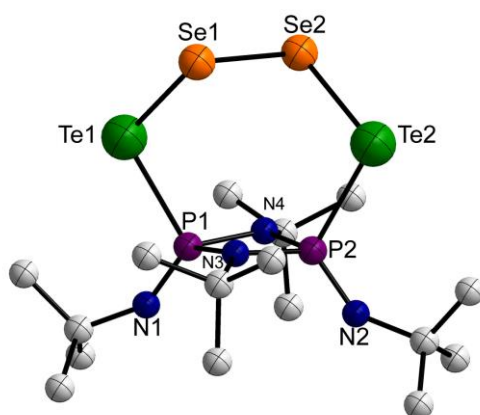
<sup>a</sup>  $\delta$  in ppm and  $J$  in Hz; d = doublet; dd = doublet of doublets.

**Synthesis, NMR Spectra and Crystal Structures of Group 16 Complexes.** Our previous syntheses of the cyclic tetraselenide **3**<sup>12</sup> and the cyclic tritelluride **6**<sup>15</sup> via metathesis, led us to consider whether this approach could be used a source of mixed chalcogenido systems. Accordingly, the ditelluro reagent **4** was treated with  $Se_2Cl_2$  in toluene at  $-78$  °C. This reaction gave a complicated mixture of products, as revealed by  $^{31}P$  NMR spectroscopy. The main components were cyclic derivatives **15** and **16** with  $Se^{2+}$  or  $(Se-Se)^{2+}$  units bridging the ligand  $L^{2-}$  ( $E = Te$ ), respectively (Scheme 3); the former was the major product. In addition to the characterization of these mixed chalcogenides by multinuclear ( $^{31}P$ ,  $^{77}Se$ ,  $^{125}Te$ ) NMR spectra, the X-ray structure of a single crystal of **16** was determined.

### Scheme 3



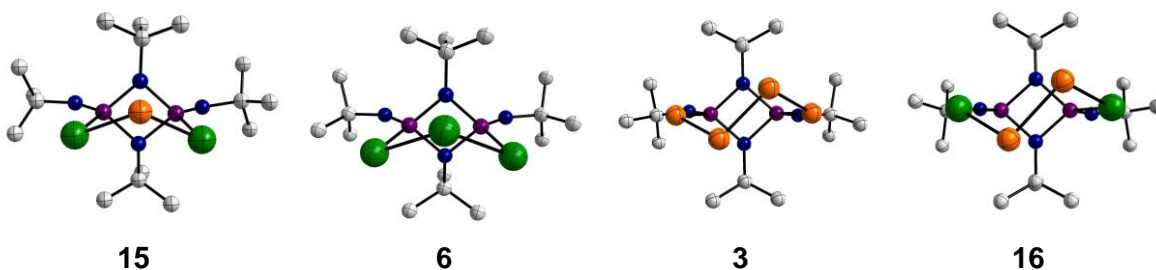
The molecular structure of **16** is illustrated in Figure 5 together with selected structural parameters. The tetrachalcogenide **16** is the first example of a structurally characterized P–Te–Se–Se–Te–P arrangement. The Te–Se–Se–Te unit was described previously by Sladky et al. in the acyclic tetrachalcogenide  $\text{TsiTeSeSeTeTsi}$  ( $\text{Tsi} = \text{C}(\text{SiMe}_3)_3$ ), but the solid-state structure was not determined;<sup>30</sup> it is also present in the cationic mixed-chalcogen clusters  $[\text{Te}_2\text{Se}_8]^{2+}$  and  $[\text{Te}_2\text{Se}_6]^{2+}$ .<sup>31</sup> The Te–Se distances of 2.492(2) and 2.536(2) Å and the Se–Se bond of 2.391(2) Å in **16** are comparable to the values reported for heterocycles in which a trichalcogenido unit bridges a benzene ring,  $d(\text{Se–Te}) = 2.523(1)\text{--}2.531(1)$  Å and  $d(\text{Se–Se}) = 2.350(1)$  Å.<sup>32</sup> The P–Te bond lengths in **16** are similar to those in **3** and **6**.



**Figure 5.** Molecular structure of **16**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Te1–Se1 2.4919(18), Te1–P1 2.483(3), Te2–Se2 2.5356(17), Te2–P2

2.501(3), Se1–Se2 2.391(2), P1–N1 1.502(10), P1–N3 1.688(9), P1–N4 1.701(9); Se1–Te1–P1 104.20(8), Se2–Te2–P2 101.64(8), Te1–Se1–Se2 102.88(7), Te2–Se2–Se1 101.47(7), Te1–P1–N1 113.3(4), Te1–P1–N3 108.1(3), Te1–P1–N4 107.7(3), N1–P1–N3 122.5(5), N1–P1–N4 117.7(5), N3–P1–N4 83.5(5).

Figure 5 compares the ring conformations of the two trichalcogenides **6**<sup>15</sup> and **15** and the two tetrachalcogenides **3**<sup>12</sup> and **16**, all of which are supported by *cyclo*-P<sup>V</sup><sub>2</sub>N<sub>2</sub> scaffolds. The extent of puckering is clearly very similar for the two trichalcogenides and the two tetrachalcogenides.



**Figure 5.** Conformations of *cyclo*-P<sup>V</sup><sub>2</sub>N<sub>2</sub>-supported polychalcogenides; Te atoms are shown in green and Se atoms are in orange.

As indicated in Table 4, the previously reported NMR data for the tetraselenide **3**<sup>12</sup> and tritelluride **6**<sup>15</sup> provide an informative comparison for the assignment of the signals in the multinuclear NMR spectra of **15** and **16**. The resonance at –121.0 ppm in the <sup>31</sup>P NMR spectrum of the TeSeTe-bridged derivative **15** appears as a singlet accompanied by both <sup>125</sup>Te and <sup>77</sup>Se satellites, <sup>1</sup>J(P,Te) = 1025 Hz and <sup>2</sup>J(P,Se) = 29 Hz, cf. –134.5 ppm and <sup>1</sup>J(P,Te) = 1029 Hz for **6**.<sup>15</sup> The <sup>77</sup>Se NMR spectrum of **15** reveals a 1:2:1 triplet at 240.9 ppm (<sup>2</sup>J(P,Se) = 29 Hz) and the <sup>125</sup>Te NMR spectrum shows a resonance at 870.3 ppm appearing as a doublet of doublets (<sup>1</sup>J(P,Te) = 1025 Hz and <sup>3</sup>J(Te,P) = 34 Hz).

The chemical shift of  $-68.6$  ppm observed in the  $^{31}\text{P}$  NMR spectrum of the TeSeSeTe-bridged derivative **16** is close to the value of  $-50.8$  ppm reported for the tetraselenide **3**,<sup>12</sup> cf.  $-121.0$  ppm for **15**. Thus, it appears that ring conformation has a stronger influence than a change of chalcogens (Se vs. Te) on the chemical shift in these examples. The  $^1J(\text{P,Te})$  value of  $1287$  Hz for **16** is substantially larger than the value of  $1029$  Hz found for the tritelluride **6**,<sup>15</sup> which is consistent with the shorter P–Te distance in **16** (Table 4).<sup>33</sup> The  $^{77}\text{Se}$  NMR spectrum exhibits a triplet at  $465.6$  ppm ( $^2J(\text{P,Se}) = 14$  Hz), which can be compared with the triplet observed for the central Se atoms in the tetraselenide **3** at  $673.0$  ppm ( $^2J(\text{P,Se}) = 10$  Hz).<sup>12</sup> The  $^{125}\text{Te}$  NMR spectrum of **16** confirms the P–Te coupling observed in the  $^{31}\text{P}$  NMR spectrum by showing a doublet of doublets at  $711.6$  ppm ( $^1J(\text{P,Te}) = 1289$  Hz and  $^3J(\text{P,Te}) = 42$  Hz).

**Table 4.** Structural and NMR Parameters for *cyclo*-P<sup>V</sup><sub>2</sub>N<sub>2</sub>-Supported Polychalcogenides.<sup>a,b</sup>

	Te1Se3Te2 <b>15</b>	Te1Te3Te2 <b>6</b>	Se1Se3Se4Se2 <b>3</b>	Te1Se3Se4Te2 <sup>c</sup> <b>16</b>
$d(\text{P1-E1})$	-	2.5317(10)	2.280(3)	2.483(3)
$d(\text{P2-E2})$	-	2.5405(10)	2.275(3)	2.501(3)
$d(\text{E1-E3})$	-	2.7155(4)	2.3371(19)	2.4919(18)
$\delta(^{31}\text{P})$	$-121.0$	$-134.5$	$-50.8$	$-68.6$
$^1J(\text{P,E})$	1025	1029	524	1287

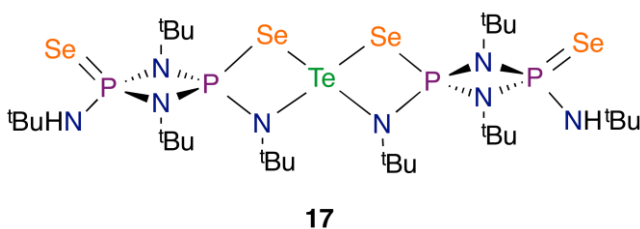
${}^2J(\text{P,E})$	29	34	10	14
$\delta({}^{77}\text{Se})$	240.9 (t)	-	673.0 (t) 336.7 (dd)	465.6 (t)
$\delta({}^{125}\text{Te})$	870.3 (dd)	442.8 (dd) 361.9 (t)	-	711.6 (dd)

<sup>a</sup> Bond lengths in Å;

<sup>b</sup>  $\delta$  in ppm;  $J$  values in Hz; t = triplet, dd = doublet of doublets

<sup>c</sup> The atomic numbering scheme is different from that in Figure 5 in order to compare analogous bond lengths in the tri- and tetra-chalcogenide systems

The homoleptic tellurium(II) complex  $[\text{Te}\{\text{tBu}(\text{H})\text{N}(\text{Se})\text{P}^{\text{V}}(\mu\text{-N}^{\text{tBu}})_2\text{P}^{\text{V}}(\text{Se})\text{tBuN-N,Se}\}_2]$  (**17**) was identified as a minor product from the reaction of **4** with  $\text{Se}_2\text{Cl}_2$ ,<sup>34,35</sup> a small amount of the cyclic tritelluride **6** was also detected in the  ${}^{31}\text{P}$  NMR spectrum.



## CONCLUSIONS

The thermal and air stability of main group derivatives of the ditelluro dianion  $\text{L}^{2-}$  (E = Te) is markedly dependent on both the p-block element in the bridging position and the nature of the organyl groups in that linker. Thus, the  $\text{Ph}_2\text{Ge}$  and  ${}^{\text{tBu}}_2\text{Sn}$  derivatives can be handled in air for several days, whereas other  $\text{R}_2\text{Sn}$  (R =  ${}^{\text{nBu}}$ , Ph) complexes decompose instantly with the formation of elemental tellurium.<sup>36</sup> The lability of the P–Te bond in the ligand  $\text{L}^{2-}$  was also evident in the reactions with  $\text{MCl}_3$  (M = Ga, In) to give spirocyclic complexes in which one of the ligands incorporates a  $\text{P}^{\text{III}}$  center,

The Ph<sub>2</sub>Ge derivative of the diseleno dianion  $\mathbf{L}^{2-}$  (E = Se) is considerably more hydrolytically sensitive than the tellurium analog, however the complete series ( $\mathbf{L}$ )Sn<sup>t</sup>Bu<sub>2</sub> (E = S, Se, Te) could be isolated enabling a structural comparison to be made. Organophosphorus(III) complexes of  $\mathbf{L}^{2-}$  (E = S, Se) evinced a significant structural difference. As in the previous work with  $\mathbf{L}^{2-}$  (E = Te),<sup>16</sup> *E,E'*-chelated complexes were the major products for selenium, but the *N,S*-chelated isomers predominated for the sulfur systems. The formation of *Se,Se'*-chelated complexes with p-block elements contrasts with our recent studies of coinage metal complexes in which attempted metathetical reactions of  $\mathbf{L}^{2-}$  (E = Se) with silver(I) or gold(I) halides produces macrocycles that incorporate the monoprotonated ligand HL<sup>-</sup>.<sup>39</sup>

The comprehensive survey of the reactions of the *cyclo*-P<sup>V</sup><sub>2</sub>N<sub>2</sub>-supported dianion  $\mathbf{L}^{2-}$  (E = Te) with p-block element halides in this and previous work<sup>15,16</sup> provides a benchmark for future studies of transition-metal, lanthanide and actinide complexes of this tellurium-centered ligand, which have not yet been investigated. By contrast, d- and f-block metal complexes of the closely related PNP-bridged ditelluro monoanion [TeP<sup>V</sup>R<sub>2</sub>NP<sup>V</sup>R<sub>2</sub>Te]<sup>-</sup> (R = <sup>i</sup>Pr) have received extensive attention,<sup>40-44</sup> especially with regard to the nature of f-element-tellurium bonds<sup>44</sup> and their use as single-source precursors of semi-conducting metal tellurides in the form of thin films or quantum dots.<sup>45</sup>

## EXPERIMENTAL SECTION

### Reagents and General Procedures.

All synthetic manipulations were performed under an atmosphere of dry argon using standard Schlenk-line techniques and/or a Saffron glovebox operating with argon unless otherwise stated. All glass apparatus was stored in a drying oven (120 °C) and flame dried *in vacuo* (10<sup>-3</sup> mbar)

before use. Dry solvents were collected from an *MBraun* solvent purification system under a nitrogen atmosphere and stored in Schlenk flasks over 4 Å molecular sieves or were dried and purified using common procedures.<sup>46</sup> All chemicals were purchased from *Sigma Aldrich*, *ABCR*, *Acros Organics* and *Strem Chemicals Inc.* and used without further purification unless otherwise stated. The products were stored in a glove box under argon atmosphere or argon fluted Schlenk- or J. Young tubes or flasks. The cooling bath temperature of  $-78\text{ }^{\circ}\text{C}$  was attained by using an acetone/dry ice bath.

### **Spectroscopic Methods.**

NMR spectra were recorded using a *JEOL DELTA EX 270* a *Bruker Avance 360* spectrometer, a *BRUKER Avance II 400* spectrometer, a *BRUKER Avance 500* or a *BRUKER Avance III 500* spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{77}\text{Se}\{^1\text{H}\}$ ,  $^{119}\text{Sn}\{^1\text{H}\}$  NMR and  $^{125}\text{Te}\{^1\text{H}\}$  NMR spectra were measured in deuterated solvents or using the reaction mixture and capillaries filled with  $\text{C}_6\text{D}_6$  at  $25\text{ }^{\circ}\text{C}$ . TMS was used as an internal standard for  $^1\text{H}$  and  $^{13}\text{C}$  NMR. 85 %  $\text{H}_3\text{PO}_4$  was employed as an external standard for  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra,  $\text{Ph}_2\text{Te}_2$  or  $\text{Me}_2\text{Te}$  for  $^{125}\text{Te}\{^1\text{H}\}$  NMR spectra,  $\text{Me}_2\text{Se}$  for  $^{77}\text{Se}\{^1\text{H}\}$  NMR spectra as well as  $\text{Me}_4\text{Sn}$  for  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectra. All  $^{77}\text{Se}\{^1\text{H}\}$ ,  $^{119}\text{Sn}\{^1\text{H}\}$  NMR,  $^{125}\text{Te}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra are reported as  $^{77}\text{Se}$ ,  $^{125}\text{Te}$ ,  $^{119}\text{Sn}$  and  $^{31}\text{P}$  NMR spectra. Chemical shifts ( $\delta$ ) are given in parts per million (ppm) relative to the solvent peaks.<sup>47</sup> Coupling constants ( $J$ ) are given in Hertz (Hz).

Mass spectra were obtained on a *Finnigan MAT 95 XP*, an *Agilent 5975C Inert XL GC/MSD* or a *ThermoFisher LTQ Orbitrap XL* at the EPSRC UK National MS Facility, Swansea. Elemental analysis was performed at the Elemental Analysis Service of the London Metropolitan University (by Mr. S. Boyer).

## X-ray Crystallography.

Crystallographic data were collected by using a Rigaku SCXmini (Mercury2 CCD) or the St Andrews robotic diffractometer<sup>48</sup> at  $-148(1)$  °C or a Rigaku Mo MM007 (dual port) high brilliance generator with Saturn 70 and Mercury CCD detectors, rotating anode/confocal optics and two XStream LT accessories at  $-180(1)$  °C. All data were collected with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and corrected for Lorentz and polarisation effects. The data for all of the compounds were collected and processed using CrystalClear (Rigaku).<sup>48</sup>

The crystal structures were solved using direct methods<sup>49</sup> or heavy-atom Patterson methods<sup>50</sup> and expanded using Fourier techniques.<sup>51</sup> The non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined using the riding model. All calculations were performed using CrystalStructure<sup>52</sup> crystallographic software package and SHELXL-97.<sup>53</sup> **10, 12aS and 16** despite several crystals being examined gave only average quality results and hence only the main features of the structures are discussed above.

Crystallographic data for **9, 10, 12a, 12aSe, 12aS** and **16** are summarized in Table 5.

**Table 5.** Crystallographic Data for **9, 10** and **16**.

Compound	<b>9</b>	<b>10</b>	<b>16</b>
Empirical formula	C <sub>32</sub> H <sub>73</sub> InN <sub>8</sub> P <sub>4</sub> Te <sub>3</sub>	C <sub>28</sub> H <sub>46</sub> GeN <sub>4</sub> P <sub>2</sub> Te <sub>2</sub>	C <sub>16</sub> H <sub>36</sub> N <sub>4</sub> P <sub>2</sub> Se <sub>2</sub> Te <sub>2</sub>
Formula weight	1191.50	828.44	759.55
Temperature (°C)	93	125	93
Crystal color, habit	yellow platelet	yellow platelet	red prism
Crystal dimensions (mm <sup>3</sup> )	0.10 x 0.10x0.01	0.17x0.07x0.02	0.10x0.10x0.10
Crystal system	monoclinic	triclinic	monoclinic
<i>a</i> (Å)	10.439(2)	9.3375(18)	15.707(5)
<i>b</i> (Å)	13.630(2)	11.603(2)	14.808(4)
<i>c</i> (Å)	17.005(3)	15.879(3)	11.549(3)
$\alpha$ (°)	90.0000	87.895(6)	90.0000
$\beta$ (°)	99.789(4)	80.914(6)	94.354(7)



$\gamma$ (°)	90.0000	89.309(6)	90.0000
Volume (Å <sup>3</sup> )	2384.5(7)	1697.6(6)	2678.4(13)
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>Z</i> value	2	2	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.659	1.621	1.883
<i>F</i> <sub>000</sub>	1172.00	816.00	1448.00
$\mu$ (Mo- <i>K</i> $\alpha$ ) (cm <sup>-1</sup> )	2.459	2.703	5.025
No. of reflections measured	32486	13435	15644
<i>R</i> <sub>int</sub>	0.0463	0.1364	0.0512
Min. and max. transmissions	0.683, 0.954	0.480, 0.947	0.414, 0.605
Reflection/parameter ratio	8507 (433)	5948 (334)	4845 (235)
Residuals: <i>R</i> <sub>1</sub> ( <i>I</i> > 2.00 $\sigma$ ( <i>I</i> ))	0.0204	0.1284	0.0780
Residuals: <i>wR</i> <sub>2</sub> (all reflections)	0.0505	0.3008	0.2127
Maximum peak in final diff. map (e <sup>-</sup> /Å <sup>3</sup> )	0.49	2.430	4.980
Minimum peak in final diff. map (e <sup>-</sup> /Å <sup>3</sup> )	-0.38	-1.910	-2.570

**Table 6.** Crystallographic Data for **12a**, **12aSe**, and **12aS**.

Compound	12a	12aSe	12aS
Empirical formula	C <sub>24</sub> H <sub>54</sub> N <sub>4</sub> P <sub>2</sub> SnTe <sub>2</sub>	C <sub>24</sub> H <sub>54</sub> N <sub>4</sub> P <sub>2</sub> SnSe <sub>2</sub>	C <sub>24</sub> H <sub>54</sub> N <sub>4</sub> P <sub>2</sub> SnS <sub>2</sub>
Formula weight	834.56	737.28	643.48
Temperature (°C)	125	93	125
Crystal color, habit	yellow platelet	colorless prism	colorless platelet
Crystal dimensions (mm <sup>3</sup> )	0.24x0.18x0.03	0.10x0.03x0.03	0.15x0.09x0.03
Crystal system	orthorhombic	monoclinic	monoclinic
<i>a</i> (Å)	20.1157(12)	19.345(4)	11.243(3)
<i>b</i> (Å)	30.241(2)	15.089(3)	30.770(7)
<i>c</i> (Å)	11.5584(7)	11.430(3)	11.193(3)
$\alpha$ (°)	90.0000	90.0000	90.0000
$\beta$ (°)	90.0000	90.608(4)	119.829(17)
$\gamma$ (°)	90.0000	90.0000	90.0000
Volume (Å <sup>3</sup> )	7031.2(8)	3336.2(13)	3359.2(14)
Space group	<i>Fdd</i> 2	<i>Cc</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i> 1
<i>Z</i> value	8	4	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.577	1.468	1.272
<i>F</i> <sub>000</sub>	3280.00	1496.00	1352.00
$\mu$ (Mo- <i>K</i> $\alpha$ ) (cm <sup>-1</sup> )	2.462	3.062	0.998
No. of reflections measured	14705	21515	25146
<i>R</i> <sub>int</sub>	0.0712	0.1101	0.1092
Min. and max. transmissions	0.665, 0.929	0.515, 0.912	0.641, 0.971
Reflection/parameter ratio	3097 (150)	5669 (316)	5901 (298)
Residuals: <i>R</i> <sub>1</sub> ( <i>I</i> > 2.00 $\sigma$ ( <i>I</i> ))	0.0373	0.0516	0.0840
Residuals: <i>wR</i> <sub>2</sub> (all reflections)	0.0748	0.1233	0.2759
Maximum peak in final diff. map (e <sup>-</sup> /Å <sup>3</sup> )	0.540	2.87	1.890
Minimum peak in final diff. map (e <sup>-</sup> /Å <sup>3</sup> )	-0.380	-2.00	-1.210

**General Procedure for Metathetical Reactions.** The reagent **1**,<sup>15</sup> **2**,<sup>15</sup> **4**<sup>16</sup> or **5**<sup>17</sup> (0.60 mmol) was suspended in toluene (10 mL) and cooled to -78 °C. A solution of the p-block element halide R<sub>n</sub>MCl<sub>2</sub> (*n* = 1, 2) or MCl<sub>3</sub> (0.59 mmol) in toluene (10 mL) at -78 °C was added dropwise to the suspension of **1**, **2**, **4** or **5** over 15 min by cannula. The reaction mixture was stirred at at -78 °C for 2 h and then warmed to room temperature. After stirring for an additional 1 h, the

precipitate (LiCl or NaCl) was removed by filtration and the solvent was removed under vacuum. The obtained solid was dissolved in *n*-hexane and maintained at  $-40\text{ }^{\circ}\text{C}$  overnight. The crystals were removed by filtration and dried under vacuum. The resulting filtrate was concentrated and cooled to  $-40\text{ }^{\circ}\text{C}$  to produce another batch of crystals.

**Synthesis of 8.** Reagents: **4** (500 mg, 0.59 mmol) and  $\text{GaCl}_3$  (53 mg, 0.30 mmol, 0.5 eq.) in toluene (20 mL). Red crystals of **8** were isolated from *n*-hexane (yield 8 %).  $^{31}\text{P}$  NMR (202.46 MHz,  $[\text{D}_8]$ toluene):  $\delta = 76.6$  (s),  $-44.7$  (s,  $^1J(\text{P},\text{Te}) = 1233$  Hz),  $-133.3$  (s,  $^1J(\text{P},\text{Te}) = 1130$  Hz,  $^3J(\text{P},\text{Te}) = 184$  Hz). Decomposition in toluene or THF precluded the acquisition of a  $^{125}\text{Te}$  NMR spectrum.

**Synthesis of 9:** Reagents:  $\text{InCl}_3$  (66 mg, 0.30 mmol, 0.5 eq.) (179 mg, 0.59 mmol) and **4** (500 mg, 0.59 mmol) in toluene (20 mL). Recrystallization from *n*-hexane afforded yellow crystals suitable for X-ray crystallography (yield 12 %).  $^{31}\text{P}$  NMR (109.37 MHz,  $[\text{D}_8]$ toluene):  $\delta = 78.1$  (d,  $^2J(\text{P},\text{P}) = 3.4$  Hz),  $-41.2$  (d,  $^1J(\text{P},\text{Te}) = 1251$  Hz,  $^2J(\text{P},\text{P}) = 3.4$  Hz),  $-135.1$  (s,  $^1J(\text{P},\text{Te}) = 1113$  Hz,  $^2J(\text{P},\text{P}) = 10.2$  Hz). Decomposition during the measurement precluded reliable characterization by  $^{125}\text{Te}$  NMR. MS ( $\text{EI}^+$ ,  $m/z$ ), 1192.1 ( $M^+$ ), 1177.1 ( $M^+ - \text{CH}_3$ ). Elemental analysis calcd (%) for  $\text{C}_{32}\text{H}_{73}\text{N}_8\text{P}_4\text{InTe}_3$ : C 32.26, H 6.18, N 9.40; found: C 32.32, H 6.20, N 9.59.

**Synthesis of 10.** Reagents: **4** (500 mg, 0.59 mmol) and  $\text{Ph}_2\text{GeCl}_2$  (176 mg, 0.59 mmol) in toluene (20 mL). Yield of red crystals = 39 %.  $^1\text{H}$  NMR (400.13 MHz,  $[\text{D}_8]$ toluene):  $\delta = 7.78$ - $7.75$  (m, 4H, Ph),  $7.12$ - $7.05$  (m, 6H, Ph),  $1.57$  (s, 18H, *t*Bu),  $1.39$  (s, 18H, *t*Bu).  $^{31}\text{P}$  NMR (161.98 MHz,  $[\text{D}_8]$ toluene):  $\delta = -136.4$  (s,  $^1J(\text{P},\text{Te}) = 1103$  Hz,  $^2J(\text{P},\text{P}) = 20$  Hz).  $^{125}\text{Te}$  NMR (85.24 MHz,  $[\text{D}_8]$ toluene):  $\delta = 162.4$  ( $^1J(\text{P},\text{Te}) = 1105$  Hz,  $^3J(\text{P},\text{Te}) = 26$  Hz). HRMS ( $\text{EI}$ ):  $m/z$

Found: 834.0528 ( $M^+$ ), Calcd. for  $C_{28}H_{46}N_4^{74}Ge_1P_2^{130}Te_2$  834.0528. Elemental analysis calcd (%) for  $C_{28}H_{46}GeN_4P_2Te_3$ : C 40.59, H 5.80, N 6.76; found: C 40.65, H 5.65, N 6.84.

**Synthesis of 10Se.** Reagents: **2** (500 mg, 0.60 mmol, 1 eq) and  $Ph_2GeCl_2$  (178 mg, 0.60 mmol) in toluene (25 mL) Yellow prismatic crystals were obtained from *n*-hexane solution at  $-78\text{ }^\circ\text{C}$ .<sup>37</sup>  $^{31}P$  NMR (109.37 MHz,  $[D_8]THF$ ):  $\delta = -80.4$  ( $^1J(P,Se) = 470.3$  Hz,  $^2J(P,P) = 60.2$  Hz).  $^{77}Se$  NMR (51.52 MHz,  $[D_8]THF$ ):  $\delta = 137.6$  (dd,  $^1J(Se,P) = 470.1$  Hz,  $^3J(Se,P) = 15.6$  Hz). MS (EI<sup>+</sup>):  $m/z$  733.1 ( $M^+ + H$ ), calcd: 733.1.

**Synthesis of 12a.** Reagents:  $tBu_2SnCl_2$  (179 mg, 0.59 mmol) and **4** (500 mg, 0.59 mmol) in toluene (25 mL). Yellow crystals of **12a** isolated in 34 % yield.  $^1H$  NMR (270.17 MHz,  $[D_8]toluene$ ):  $\delta = 1.71$  (s, 18H,  $tBu$ ) 1.46 (s, 18H,  $tBu$ ), 1.38 (s, 18H,  $tBu$ ).  $^{31}P$  NMR (109.37 MHz,  $[D_8]toluene$ ):  $\delta = -141.6$  (s,  $^1J(P,Te) = 1183$  Hz,  $^2J(P,Sn) = 52$  Hz,  $^2J(P,P) = 6.1$  Hz).  $^{119}Sn$  NMR (100.75 MHz,  $[D_8]toluene$ ):  $\delta = 34.2$  ( $^2J(P,Sn) = 52$  Hz,  $^1J(Sn,Te) = 3385$  Hz).  $^{125}Te$  NMR (85.24 MHz,  $[D_8]toluene$ ):  $\delta = -47.7$  ( $^1J(P,Te) = 1181$  Hz,  $^3J(P,Te) = 25$  Hz). MS(EI),  $m/z$ : 836.2 ( $M^+$ ), calcd: 836.1; 821.1 [ $M^+ - CH_3$ ], calcd: 821.1. HRMS (EI),  $m/z$ : 783.0260 [ $M^+ - tBu$ ], calcd for  $C_{20}H_{45}N_4P_2Sn_1Te_2$ : 783.0260. Elemental analysis calcd (%) for  $C_{24}H_{54}N_4P_2SnTe_2$ : C 34.54, H 6.52, N 6.71; found: C 34.45, H 6.57, N 6.62.

**Synthesis of 12b:** Reagents:  $nBu_2SnCl_2$  (179 mg, 0.59 mmol) and **1** (500 mg, 0.59 mmol) in toluene (25 mL). Yellow crystals were isolated, but characterization was limited to NMR spectra owing to their extremely air-sensitive nature.  $^1H$  NMR (270.17 MHz,  $[D_8]toluene$ ):  $\delta = 1.71$  (s, 18H,  $tBu$ ), 1.66-1.47 (m, 4H+4H,  $nBu$ ), 1.44 (s, 18H,  $tBu$ ), 1.32 (s, 4H,  $^2J(HH) = 7.6$  Hz,  $nBu$ ), 0.90 (t, 6H,  $^2J(HH) = 7.6$  Hz,  $nBu$ ).  $^{31}P$  NMR (202.46 MHz,  $[D_8]toluene$ ):  $\delta = -141.1$  (s,  $^1J(P,Te) = 1140$  Hz,  $^2J(P,Sn) = 51$  Hz).  $^{119}Sn$  NMR (100.75 MHz,  $[D_8]toluene$ ):  $\delta = -84.7$

( $^2J(\text{P},\text{Sn}) = 52 \text{ Hz}$ ,  $^1J(\text{Sn},\text{Te}) = 3288 \text{ Hz}$ ).  $^{125}\text{Te}$  NMR (85.24 MHz,  $[\text{D}_8]\text{toluene}$ ):  $\delta = 6.7$  (dd,  $^1J(\text{P},\text{Te}) = 1137 \text{ Hz}$ ,  $^3J(\text{P},\text{Te}) = 26 \text{ Hz}$ ).

**Synthesis of 12c:** Reagents:  $\text{Ph}_2\text{SnCl}_2$  (203 mg, 0.59 mmol) and **4** (500 mg, 0.59 mmol) in toluene (25 mL). Yellow crystals were isolated, but characterization was limited to NMR spectra owing to their extremely air-sensitive nature.  $^{31}\text{P}$  NMR (161.98 MHz,  $[\text{D}_8]\text{toluene}$ ):  $\delta = -140.4$  (s,  $^1J(\text{P},\text{Te}) = 1102 \text{ Hz}$ ,  $^2J(\text{P},\text{Sn}) = 60 \text{ Hz}$ ,  $^2J(\text{P},\text{P}) = 6.5 \text{ Hz}$ ).  $^{119}\text{Sn}$  NMR (100.75 MHz,  $[\text{D}_8]\text{toluene}$ ):  $\delta = -156.1$  ( $^2J(\text{P},\text{Sn}) = 62 \text{ Hz}$ ).  $^{125}\text{Te}$  NMR (85.24 MHz,  $[\text{D}_8]\text{toluene}$ ):  $\delta = 23.4$  ( $^1J(\text{P},\text{Te}) = 1102 \text{ Hz}$ ,  $^3J(\text{P},\text{Te}) = 26 \text{ Hz}$ ).

**Synthesis of 12aSe:** Reagents: **2** (500 mg, 0.60 mmol) and  $^t\text{Bu}_2\text{SnCl}_2$  (182 mg, 0.60 mmol) in toluene (15 mL). Yield of **12aSe** = 78 % according to the  $^{31}\text{P}$  NMR spectrum; yellow crystals were isolated.<sup>37</sup>  $^{31}\text{P}$  NMR (109.37 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = -77.0$  (s,  $^1J(\text{P},\text{Se}) = 500.0 \text{ Hz}$ ,  $^2J(\text{P},\text{Sn}) = 42.3 \text{ Hz}$ ).  $^{119}\text{Sn}$  NMR (100.75 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = 69.8$  ( $^2J(\text{P},\text{Sn}) = 43.1 \text{ Hz}$ ,  $^1J(\text{Sn},\text{Se}) = 690.5 \text{ Hz}$ ).  $^{77}\text{Se}$  NMR (51.52 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = 77.3$  ( $^1J(\text{P},\text{Se}) = 498.2 \text{ Hz}$ ,  $^3J(\text{P},\text{Se}) = 12.0 \text{ Hz}$ ). EIMS,  $m/z$ : 723.1 ( $\text{M}^+ - \text{CH}_3$ ), calcd 723.1. Elemental analysis calcd (%) for  $\text{C}_{24}\text{H}_{54}\text{N}_4\text{P}_2\text{SnSe}_2$ : C 39.10, H 7.38, N 7.60; found: C 39.06, H 7.40, N 7.56.

**Synthesis of 12aS:** Reagents: **1** (500 mg, 0.68 mmol, 1 eq) and  $^t\text{Bu}_2\text{SnCl}_2$  (207 mg, 0.68 mmol, 1 eq) in toluene (25 mL). Yield of **12aS** = 80 % according to the  $^{31}\text{P}$  NMR spectrum; colorless crystals were isolated.<sup>38</sup>  $^{31}\text{P}$  NMR (109.37 MHz,  $[\text{D}_8]\text{toluene}$ ):  $\delta = -48.7$  (s,  $^2J(\text{P},\text{Sn}) = 35.2 \text{ Hz}$ ).  $^{119}\text{Sn}$  NMR (100.75 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = 66.4$  ( $^2J(\text{P},\text{Sn}) = 33.9 \text{ Hz}$ ). EIMS,  $m/z$ : 629.2 ( $\text{M}^+ - \text{CH}_3$ ), calcd 629.2. Elemental analysis calcd (%) for  $\text{C}_{24}\text{H}_{54}\text{N}_4\text{P}_2\text{SnS}_2$ : C 44.80, H 8.46, N 8.71; found: C 44.73, H 8.49, N 8.80.

**Synthesis of 13aSe.** Reagents  $^t\text{BuPCl}_2$  (95 mg, 0.60 mmol) and **2** (500 mg, 0.59 mmol) in toluene (25 mL). Estimated yields from the  $^{31}\text{P}$  NMR spectrum were **13aSe** (40 %) and **11Se**

(20 %), which co-crystallized as colorless crystals.<sup>37</sup> NMR data for **13aSe**: <sup>31</sup>P NMR (109.37 MHz, [D<sub>8</sub>]THF):  $\delta = 139.5$  (<sup>1</sup>*J*(P,Se) = 234.1 Hz),  $-78.0$  (<sup>1</sup>*J*(P,Se) = 447.3 Hz, <sup>2</sup>*J*(P,P) = 58.0 Hz). <sup>77</sup>Se NMR (51.52 MHz, [D<sub>8</sub>]THF):  $\delta = 256.0$  (<sup>1</sup>*J*(Se,P<sup>V</sup>) = 450.8 Hz, <sup>1</sup>*J*(Se,P<sup>III</sup>) = 234.4 Hz, <sup>3</sup>*J*(Se,P) = 19.6 Hz). EIMS, *m/z*: 580.1 (M<sup>+</sup>-CH<sub>3</sub>+H), calcd 580.1. A few crystals of pure **13aSe** were isolated. Elemental analysis calcd (%) for C<sub>20</sub>H<sub>45</sub>N<sub>4</sub>P<sub>3</sub>Se<sub>2</sub>: C 40.55, H 7.66, N 9.46; found: C 40.71, H 7.77, N 9.37.

**Synthesis of 13bSe.** Reagents: AdPCl<sub>2</sub> (214 mg, 0.60 mmol) and **2** (500 mg, 0.59 mmol) in toluene (25 mL). Yield of **13bSe** estimated from integration of the <sup>31</sup>P NMR spectrum ca. 79 % **13bSe** formed colorless co-crystals with the by-product **11Se**.<sup>37</sup> NMR data for **13bSe**: <sup>31</sup>P NMR (109.37 MHz, [D<sub>8</sub>]THF):  $\delta = 132.0$  (<sup>1</sup>*J*(P,Se) = 231.8 Hz),  $-76.8$  (<sup>1</sup>*J*(P,Se) = 449.5 Hz, <sup>2</sup>*J*(P,P) = 58.0 Hz). <sup>77</sup>Se NMR (51.52 MHz, [D<sub>8</sub>]THF):  $\delta = 226.5$  (ddd, <sup>1</sup>*J*(Se,P<sup>V</sup>) = 449.0 Hz, <sup>1</sup>*J*(Se,P<sup>III</sup>) = 232.1 Hz, <sup>3</sup>*J*(Se,P) = 15.6 Hz).

**Synthesis of 13aS and 14aS.** Reagents: **1** (500 mg, 0.68 mmol) and <sup>t</sup>BuPCl<sub>2</sub> (107 mg, 0.68 mmol) in toluene (25 mL). Estimated yield of **13aS** and **14aS** were ca. 5% and 67%, respectively, from the integrated <sup>31</sup>P NMR spectrum.<sup>38</sup> NMR and MS data for **13aS**: <sup>31</sup>P NMR (109.37 MHz, C<sub>6</sub>D<sub>6</sub>-capillary):  $\delta = 126.5$  (s),  $-56.9$  (s). EIMS, *m/z*: 498.2 (M<sup>+</sup>), calcd 498.2; 483.1 (M<sup>+</sup>-CH<sub>3</sub>), calcd. 438.2. NMR and MS data for **14aS**: <sup>31</sup>P NMR (109.37 MHz, C<sub>6</sub>D<sub>6</sub>-capillary):  $\delta = 116.9$  (d, <sup>2</sup>*J*(P,P) = 42.3 Hz), 17.2 (dd, <sup>2</sup>*J*(P,P) = 42.5 Hz, <sup>2</sup>*J*(P,P) = 27.1 Hz), 14.4 (d, <sup>2</sup>*J*(P,P) = 27.0 Hz). EIMS, *m/z*: 498.2 (M<sup>+</sup>), calcd 498.2; 483.1 (M<sup>+</sup>-CH<sub>3</sub>), calcd 483.2.

**Synthesis of 13bS and 14bS:** Reagents: **1** (500 mg, 0.68 mmol) and AdPCl<sub>2</sub> (159 mg, 0.68 mmol, 1 eq.) in toluene (25 mL). Estimated yield of **13bS** and **14bS** were ca. 3% and 71%, respectively, from the integrated <sup>31</sup>P NMR spectrum.<sup>38</sup> NMR and MS data for **13bS**: <sup>31</sup>P NMR (109.37 MHz, C<sub>6</sub>D<sub>6</sub>-capillary):  $\delta = 120.1$  (s),  $-56.2$  (s). EIMS, *m/z*: 576.3 (M<sup>+</sup>), calcd 576.3;

561.3 ( $M^+-CH_3$ ), calcd 561.3. NMR and MS data for **14bS**:  $^{31}P$  NMR (109.37 MHz,  $C_6D_6$ -capillary):  $\delta = 111.4$  (d,  $^2J(P,P) = 43.4$  Hz), 17.3 (dd,  $^2J(P,P) = 43.4$  Hz,  $^2J(P,P) = 26.9$  Hz), 14.6 (d,  $^2J(P,P) = 26.8$  Hz). EIMS,  $m/z$ : 576.3 ( $M^+$ ), calcd 576.3; 561.3 ( $M^+-CH_3$ ), calcd 561.3.

**Synthesis of 13cS and 14cS**: Reagents: **1** (500 mg, 0.68 mmol) and  $(iPr)_2NPCl_2$  (159 mg, 0.68 mmol) in toluene (25 mL). Estimated yield of **13cS** and **14cS** were ca. 2% and 93%, respectively, from the integrated  $^{31}P$  NMR spectrum.<sup>38</sup> NMR and MS data for **13cS**:  $^{31}P$  NMR (109.37 MHz,  $C_6D_6$ -capillary):  $\delta = 139.4$  (t,  $^2J(P,P) = 4.3$  Hz),  $-57.7$  (d,  $^2J(P,P) = 4.3$  Hz). EIMS,  $m/z$ : 541.3 ( $M^+$ ), calcd 541.3 ( $M^+$ ); 526.2 ( $M^+-CH_3$ ), calcd 526.2. NMR and MS data for **14cS**:  $^{31}P$  NMR (109.37 MHz,  $[D_8]THF$ ):  $\delta = 100.4$  (d,  $^2J(P,P) = 44.4$  Hz), 16.8 (dd,  $^2J(P,P) = 44.6$  Hz,  $^2J(P,P) = 25.9$  Hz), 15.2 (d,  $^2J(P,P) = 26.2$  Hz). EIMS,  $m/z$ : 541.3 ( $M^+$ ), calcd 541.3 [ $M^+-H$ ]; 526.2 ( $M^+-CH_3$ ), calcd 526.2.

**Synthesis of 15 and 16**: Reagents:  $Se_2Cl_2$  (135 mg, 0.59 mmol) and **1** (500 mg, 0.59 mmol) in toluene (25 mL). NMR data for the major product **15**:  $^{31}P$  NMR (109.37 MHz,  $[D_8]toluene$ ):  $\delta = -121.0$  ( $^1J(P,^{125}Te) = 1025$  Hz;  $^2J(P,^{77}Se) = 29$  Hz;  $^2J(P,P) = 23$  Hz).  $^{77}Se$  NMR (51.52 MHz,  $[D_8]toluene$ ):  $\delta = 240.9$  (t,  $^2J(P,^{77}Se) = 30$  Hz) ppm.  $^{125}Te$  NMR (85.24 MHz,  $[D_8]toluene$ ):  $\delta$  [ppm] = 870.3 (dd,  $^1J(P,^{125}Te) = 1025$  Hz;  $^3J(P,^{125}Te) = 34$  Hz). NMR data for **16**:  $^{31}P$  NMR (109.37 MHz,  $[D_8]toluene$ ):  $\delta = -68.6$  ( $^1J(P,^{125}Te) = 1287$  Hz;  $^2J(P,P) = 47$  Hz;  $^1J(P,^{77}Se) = 14$  Hz) ppm.  $^{77}Se$  NMR (51.52 MHz,  $[D_8]toluene$ ):  $\delta = 465.6$  (pseudo-*t*,  $^2J(P,^{77}Se) = 14$  Hz).  $^{125}Te$  NMR (85.24 MHz,  $[D_8]toluene$ ):  $\delta = 711.6$  (dd,  $^1J(P,^{125}Te) = 1289$  Hz;  $^3J(P,^{125}Te) = 42$  Hz). A few red crystals of **16** were isolated; elemental analysis calcd (%) for  $C_{16}H_{36}N_4P_2Te_2Se_2$ : C 25.30, H 4.78, N 7.38; found: C 25.32, H 4.92, N 7.47.

The cyclic tritelluride **6** was identified as a by-product in the  $^{31}P$  and  $^{125}Te$  NMR spectra.<sup>15</sup>  $^{31}P$  NMR (109.37 MHz,  $[D_8]toluene$ ):  $\delta = -134.6$  ( $^1J(P,^{125}Te) = 1028$  Hz;  $^2J(P,P) = 31$  Hz).

$^{125}\text{Te}$  NMR (126.43 MHz,  $[\text{D}_8]\text{toluene}$ ):  $\delta = 442.8$  (dd,  $^1J(\text{P},\text{Te}) = 1031$  Hz,  $^3J(\text{P},\text{Te}) = 41$  Hz),  
361.9 (t,  $^1J(^{125}\text{Te}, ^{123}\text{Te}) = 1254$  Hz,  $^2J(\text{P},\text{Te}) = 35$  Hz).

## ASSOCIATED CONTENT

**Supporting Information.** This material is available free of charge via the Internet at

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### Notes

The authors declare no competing financial interest.

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### Supporting Information Available:

X-ray crystallographic files in CIF format for compounds **9**, **10**, **12a**, **13aSe**, **12b**, **12c**, **16** and **18Se**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- the reported values.<sup>34</sup> The formation of P<sup>V</sup>-Se linkages in this reaction indicates significant decomposition of the ditelluro ligand **L**<sup>2-</sup> (E = Te) (presumably, via Se-Te exchange). Further evidence of that process is provided by the detection of the neutral diselenido precursor **11Se** in the <sup>31</sup>P NMR spectrum of the reaction mixture.
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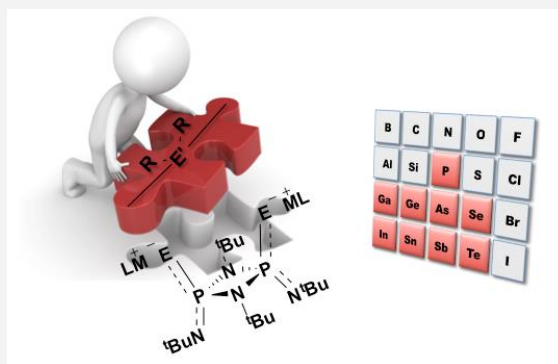
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SYNOPSIS:

## Main Group-Tellurium Heterocycles Anchored by a $P^V N_2$ Scaffold and Their Sulfur/Selenium Analogs

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Reactions of the ditelluro dianion  $[\text{TeP}^{\text{V}}(\text{N}^t\text{Bu})(\mu\text{-N}^t\text{Bu})]_2^{2-}$  and various main group halides produced heterocycles in which the ligand is  $\text{Te}, \text{Te}'$ -chelated to heavier p-block elements. For comparison, selenium and sulfur analogs were synthesized from  $[\text{EP}^{\text{V}}(\text{N}^t\text{Bu})(\mu\text{-N}^t\text{Bu})]_2^{2-}$  ( $\text{E} = \text{S}, \text{Se}$ ) and group 14 dihalides or  $\text{RPCl}_2$ ; in the organophosphorus(III) derivatives the dianionic ligand forms  $\text{E}, \text{E}'$ -chelated complexes for selenium and tellurium, but the  $\text{N}, \text{E}$ -bonded isomer predominates for sulfur.