Main Group-Tellurium Heterocycles Anchored by a $P^V{}_2N_2$ Scaffold and Their Sulfur/Selenium Analogs

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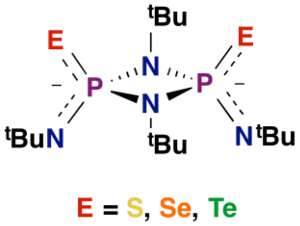
ABSTRACT: A comprehensive investigation of reactions of alkali-metal derivatives of the ditelluro dianion $[TeP^V(N^tBu)(\mu\text{-}N^tBu)]_2{}^{2-}$ (**L**$^{2-}$**,** E = Te) with p-block element halides produced a series of novel heterocycles incorporating $P^V{}_2N_2$ rings, tellurium and group 13-16 elements. The dianion engages in *Te,Te′*-chelation to the metal center in Ph_2Ge and R_2Sn (R = ^{t}Bu, ^{n}Bu, Ph) derivatives; similar behavior was noted for group 14 derivatives of **L**$^{2-}$ (E = S, Se). In the case of group 13 trihalides MCl_3 (M = Ga, In), neutral spirocyclic complexes (**L**)M$[N^tBu(Te)P^V(\mu\text{-}N^tBu)_2P^{III}N(H)^tBu]$ (M = Ga, In) comprised of a *Te,Te′*-chelated ligand **L**$^{2-}$ and a *N,Te*-bonded ligand resulting from loss of Te and monoprotonation were obtained. In reactions with $RPCl_2$ (R = ^{t}Bu, Ad, ^{i}Pr$_2$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 (^{1}H, ^{31}P, ^{77}Se, ^{119}Sn and ^{125}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 Se_2Cl_2 with $\mathbf{L}^{2-}$ (E = Te). Single crystal X-ray structures were obtained for the spirocyclic In complex (**9**), (**L**)$GePh_2$ (E = Te, **10**), (**L**)Sn^tBu_2 (E = Te, **12a**; E = Se, **12aSe,** E = S, **12aS**) and (**L**)(μ-SeSe) (E = Te, **16**).

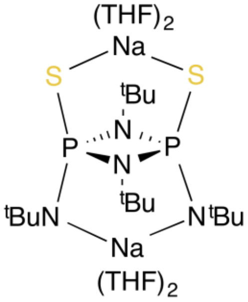
INTRODUCTION

Cyclodiphosphazanes, e.g. $[ClP^{III}(\mu\text{-}NR)]_2$, are saturated four-membered, $P^{III}{}_2N_2$ rings that continue to attract interest from the inorganic chemistry community.[1, 2] 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,[3] as well as those that incorporate coinage metals coordinated to the phosphorus(III) centers.[4] A fascinating recent example is afforded by the Cu_4X_4 clusters linked by P_2N_2 rings that resemble a sodalite framework.[5] In some cases these macrocycles are able to encapsulate halide[6] or perchlorate anions.[7]

The P^{III}/P^{III} systems with terminal alkylamido groups, e.g. $[^tBuN(H)P^{III}(\mu\text{-}N^tBu)]_2$, are readily oxidized by sulfur or selenium.[8] Subsequent double deprotonation of the resulting P^V/P^Vdichalcogenides $[^tBuN(H)(E)\{P^V(\mu\text{-}N^tBu)\}]_2$ produces ambidentate dianions of the type $\mathbf{L}^{2-}$ (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;[9, 10] dimethylaluminum derivatives also adopt *bis-N,E* chelation.[11] Monodeprotonation of $[^tBuN(H)(E)\{P^V(\mu\text{-}N^tBu)\}]_2$ (E = S, Se) generates the corresponding monoanions, which attach to Li^+ in a *mono-N,E* bonding arrangement.[10] Recently, we have shown that the two-electron oxidation of the dianions $\mathbf{L}^{2-}$ (E = S, Se) produces 15-membered macrocycles in which a planar P_6E_6 platform is stabilized by perpendicular $P^V{}_2N_2$ rings.[12] In the case of E = Se this oxidation also gives rise to the bridging tetraselenide [^{t}BuN{P^{V}(μ-N^{t}Bu)}]$_2$(μ-SeSeSeSe) (**3**), which is more conveniently prepared by metathesis of **2** with Se_2Cl_2.[12]



L^{2-}



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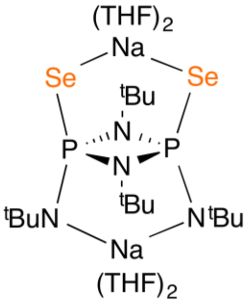

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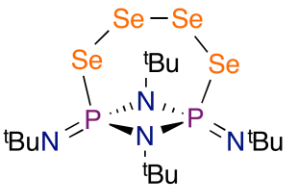

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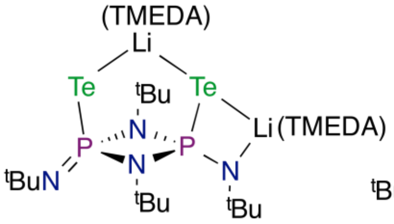
The synthesis of the ditelluro dianion **L**$^{2-}$ (E = Te) requires a different approach because elemental tellurium does not oxidize both P^{III} centers in [^{t}BuN(H)P^{III}(μ-N^{t}Bu)]$_2$. However, if the double deprotonation of this neutral precursor is carried out first,[13] the P^{III} centers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

In contrast to the formation of trimeric macrocycles from the oxidation of alkali-metal derivatives **1** and **2** (*vide supra*),[12] the treatment of **4** with I_2 produced the cyclic tritelluride [^{t}BuN{P^{V}(μ-N^{t}Bu)}]$_2$(μ-TeTeTe) (**6**), which is obtained in higher yield by metathesis of **5** with $TeCl_2$·TMTU (TMTU = tetramethylthiourea).[15] Furthermore, metathesis of **4** with $RPCl_2$ (R = ^{t}Bu, Ad) generates the $P^{V}_2N_2$-supported heterocycles **7a,b**, which were among the first examples of structurally characterized phosphorus(III)-tellurium ring systems.[16]



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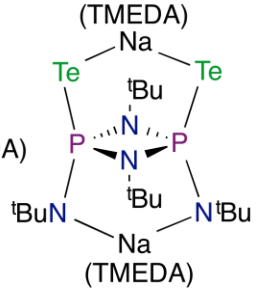

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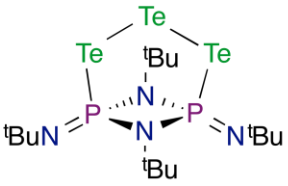

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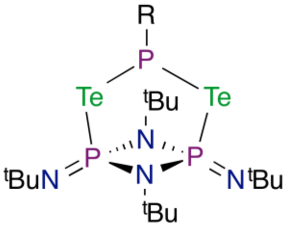

R = ^{t}Bu (**a**), Ad (**b**)

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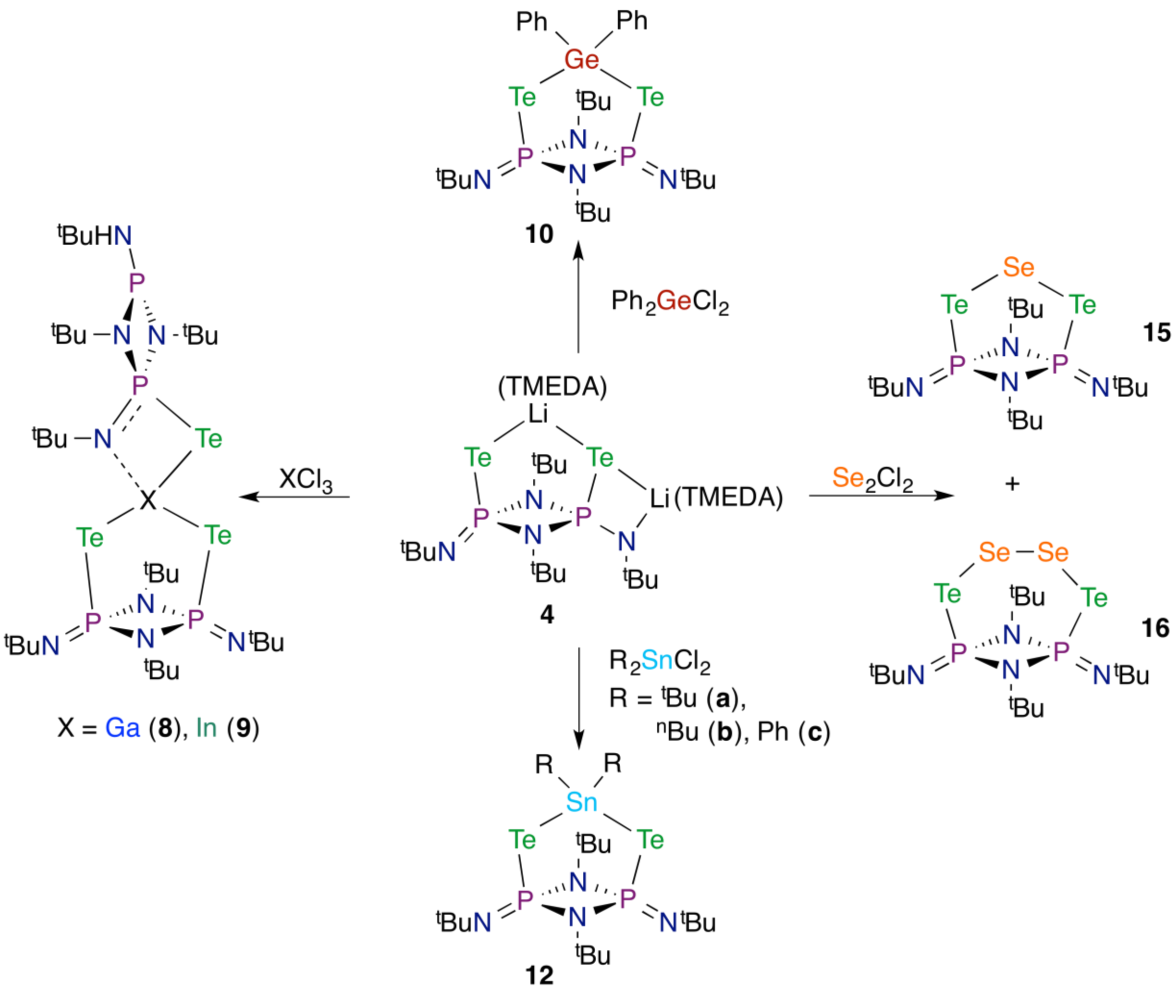
These preliminary results suggest that the $P^{V}_{2}N_{2}$ scaffold plays an influential role in the stabilization of heterocycles that incorporate tellurium and another p-block element. In order to determine the scope and limitations of the ditelluro dianion $\mathbf{L}^{2-}$ (E = Te) as a reagent 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 = ^{t}Bu), $RMCl_2$ (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 = ^{t}Bu, Ad, $^{i}Pr_2N$). The products of these metatheses were characterized by CHN analyses, high-resolution mass spectra and, in solution, by multinuclear NMR spectroscopy (^{1}H, ^{31}P, ^{77}Se, ^{119}Sn and ^{125}Te). Solid-state structures of the spirocyclic In complex (**9**)**,** (**L**)GePh$_2$ (E = Te, **10**), (**L**)Sn^{t}Bu$_2$ (E = Te, **12a**; E = Se, **12aSe,** E = S, **12aS**) and (**L**)(μ-SeSe) (E = Te, **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 °C, followed by warming to room temperature. The crude products were generally recrystallized from *n*-hexane at −40 °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 GaCl₃ and InCl₃ 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).[17] 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}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}Te satellites, the resonance at 77-78 ppm is attributed to a P^{III} center that is no longer attached to tellurium. By contrast, the resonance at 41-45 ppm displays satellites consistent with one-bond ^{31}P-^{125}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 ^{2}J(P,P) = 3.4 Hz, consistent with mutual coupling of inequivalent P environments in the same *cyclo*-$P^{V}_2N_2$ 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 (^{1}J(P,Te) = 1115 and 1130 Hz), is attributed to the symmetrical dianionic ligand $\mathbf{L}^{2-}$ (E = Te). This conclusion is supported by the ^{31}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}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 M^{3+} center in these neutral complexes is symmetrically chelated to a dianionic ligand $\mathbf{L}^{2-}$ (E = Te) and also bonded to a monoanion in which the P_2N_2 platform is comprised of a P^{III} center and a P^{V}=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}P NMR spectra. The spirocyclic structure of **9** is comprised of the dianionic ditelluro ligand $\mathbf{L}^{2-}$ (E = Te) coordinated to indium in a *Te,Te'*-mode and the *Te,N*-chelated *mono*telluro monoanion $[(^{t}BuN(Te)P^{V}(\mu\text{-}N^{t}Bu)_2P^{III}N(H)^{t}Bu)]^{-}$, which presumably results from the loss of tellurium from $\mathbf{L}^{2-}$ (E = Te) and monoprotonation.[17]

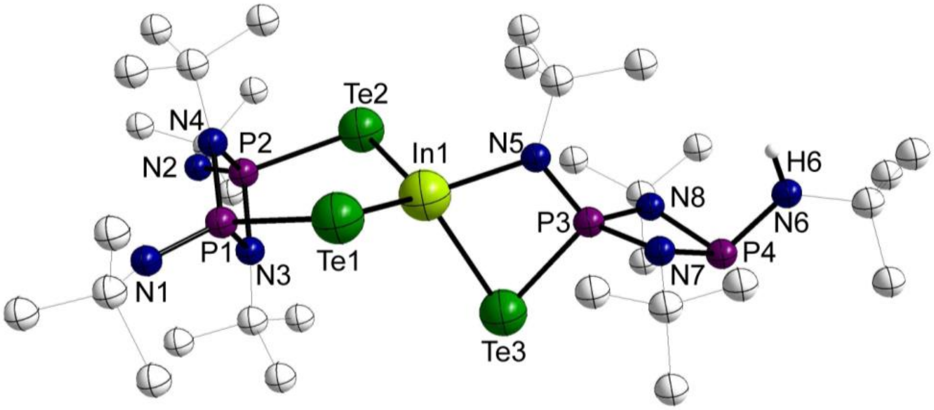
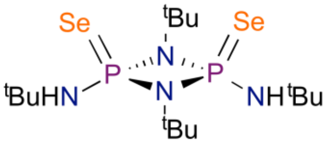


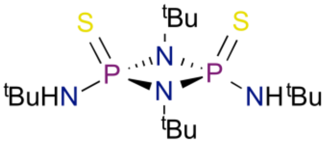
Figure 1. Crystal structure of **9**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–In1 2.7270(16), Te1–P1 2.485(4), Te2–In1 2.7210(16), Te2–P2 2.499(3), Te3–In1 2.7959(6), Te3–P3 2.4526(10), In1–N5 2.174(3), P1–N1 1.559(12), P1–N3 1.699(13), P1–N4 1.662(12), P3–N5 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 $\mathbf{L}^{2-}$ in **9** is comparable to that in the group 15 derivative [cf. 2.510(3) Å in **7b** (R = Ad)],[16] 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 $\{In(\mu\text{-}Te)[N(^iPr_2PTe)_2]\}_3$.[18] The In–Te$_{exo}$ distance of 2.809(1) Å in the latter complex[18] is elongated when compared to the In–Te distances from the dianionic ligand $\mathbf{L}^{2-}$ 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_2GeCl_2 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_2**A** (E = Se) (**11Se)**, which precluded the isolation of pure **10Se** due to their similar solubilities.[19]



11Se



11S

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 ($^{1}J(\mathrm{P,Te})$ = 1103 Hz) strongly suggests symmetrical coordination of the ligand **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_2Ge unit (Figure 2).

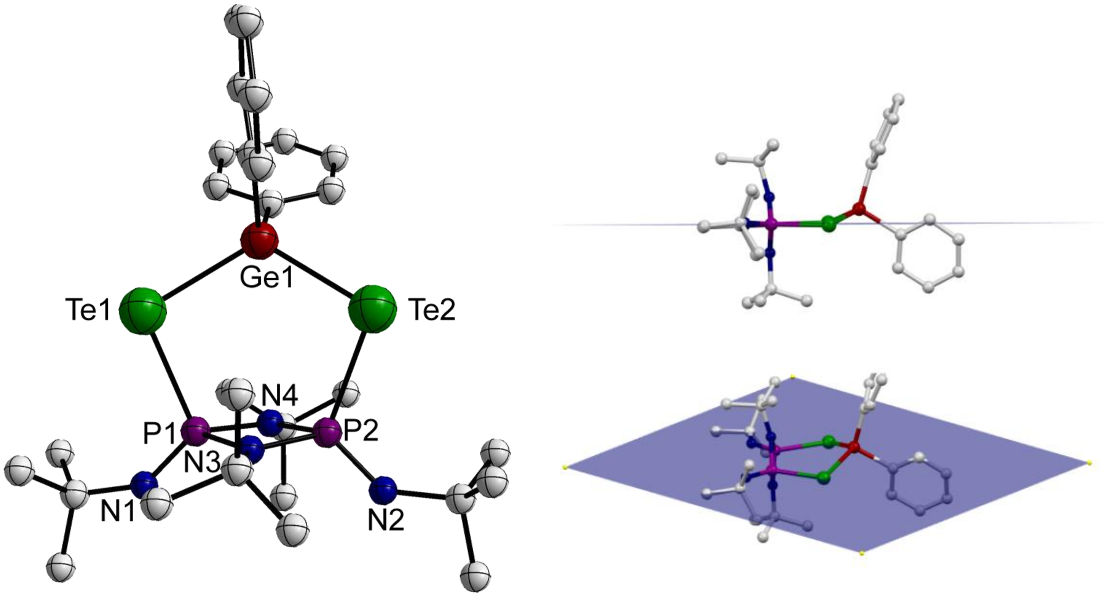


Figure 2. Molecular structure and side view of **10**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–Ge1 2.577(3), Te2–Ge1 2.565(3), Te1–P1 2.508(6), Te2–

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 $[(2,4,6\text{-}^{i}Pr_3C_6H_2)_2GeTe_2]_2$ and 2.580(1) Å in $[(2,4,6\text{-}^{i}Pr_3C_6H_2)_4Ge_4Te_6]$.[20] The Ge atom is located 0.60 Å out of the mean Te1–P1–N1–N2–P2–Te2 plane in **10** and the $P^{V}{}_2N_2$ 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**[14] and <Te–P–Te = 108.81(16)° in **7b**.[16]

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 ^{31}P NMR spectrum consists of a singlet at −80.4 ppm accompanied by a set of satellites revealing $^{1}J(P,Se) = 470$ Hz and $^{2}J(P,P) = 60$ Hz. Consistently, the ^{77}Se NMR spectrum is comprised of a doublet of doublets centered at 137.6 ppm with $^{1}J(P,Se) = 470$ Hz and $^{3}J(P,Se) = 15.6$ Hz. Thus, the NMR data indicate symmetrical coordination of $\mathbf{L}^{2-}$ (E = Se) to the $GePh_2$ 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_2SnCl_2 (R = ^{t}Bu, ^{n}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_2Sn complexes **12a-c** varies dramatically; the $^{t}Bu_2Sn$ derivative **12a** does not deteriorate upon exposure to air in the solid state for three days, whereas the $^{n}Bu_2Sn$ (**12b**) and Ph_2Sn (**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}P NMR spectrum exhibits a singlet accompanied by a doublet of tellurium satellites resulting from the magnetic inequivalence of the phosphorus centers [^{1}J(P,Te) and ^{2}J(P,P)]. Furthermore, tin satellites corresponding to ^{2}J(P,Sn) = 52 Hz are observed. Consistently, the ^{119}Sn NMR spectrum exhibits a triplet attributed to coupling to two equivalent phosphorus centers with satellites showing ^{1}J(Sn,Te) ≈ 3390 Hz. The ^{125}Te NMR spectrum consists of a doublet of doublets attributed to the ^{1}J(Te,P) and ^{3}J(Te,P) couplings. In addition, satellites confirming the ^{1}J(Te,Sn) value from the ^{119}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 R_2Sn (R = ^{n}Bu, Ph, ^{t}Bu) derivatives (Table 1).

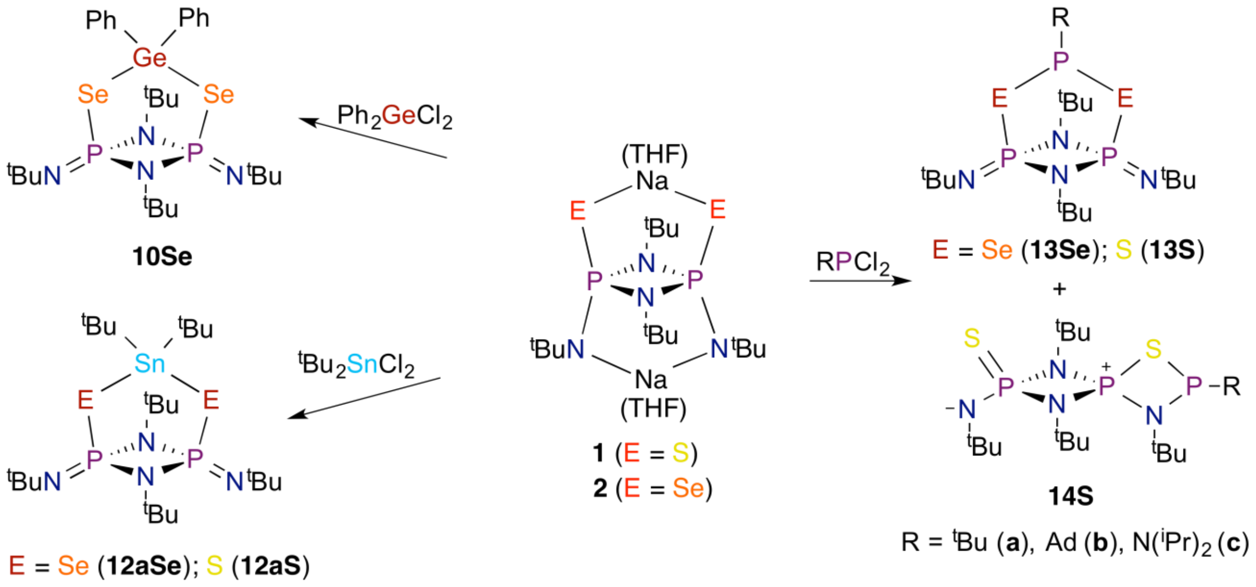
Table 1. Comparison of NMR Parameters for **12a-c, 12aSe** and **12aS**.[a]

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

[a] δ in ppm and J in Hz; t =triplet, dd = doublet of doublets
[b] Poor signal-to-noise ratios in the ^{119}Sn and ^{125}Te NMR spectra
[c] E = ^{77}Se or ^{125}Te

In order to assess the influence of the chalcogen on the stability of R_2Sn derivatives of the dianions **L**$^{2-}$ (**A** = Te, Se, S), the reactions of **1** and **2** with $^{t}Bu_2SnCl_2$ were also conducted. Although the ^{31}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**.[19] The ^{31}P NMR spectrum of **12aSe** exhibits a singlet at −77.0 ppm with two sets of satellites, ^{1}J(P,Se) = 500 Hz and ^{2}J(P,Sn) = 42 Hz. Similar to the observations for the tellurium analog **12a**, the ^{119}Sn NMR spectrum of **12aSe** shows a triplet at 69.8 ppm (^{1}J(Sn,Se) = 691 Hz) and the ^{77}Se NMR spectrum exhibits a doublet of doublets at 77.3 ppm, which arises from the ^{1}J(P,Se) and ^{3}J(P,Se) couplings (Table 1). For comparison, the ^{31}P NMR spectrum of the tin(IV) complex [Sn{(Se)C(PPh$_2$Se)$_2$}$_2$] shows a singlet at 61.6 ppm with ^{1}J(P,Se) = 536 Hz[21] and the tin(II) complex [Sn{NSeP^{i}Pr$_2$)$_2$-Se,Se′}$_2$] exhibits a singlet at 58.8 ppm with ^{1}J(P,Se) = 550 Hz and a ^{2}J(P,Sn) = 55 Hz.[22] The ^{31}P NMR spectrum of **12aS** consists of a single resonance at −48.7 ppm accompanied by ^{119}Sn satellites (^{2}J(P,Sn) = 35 Hz) and the ^{119}Sn NMR spectrum reveals a triplet at 66.4 ppm confirming the ^{2}J(P,Sn) values observed in the ^{31}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 °C. The molecular structures are illustrated in Figure 2 and structural parameters are compared in Table 2.

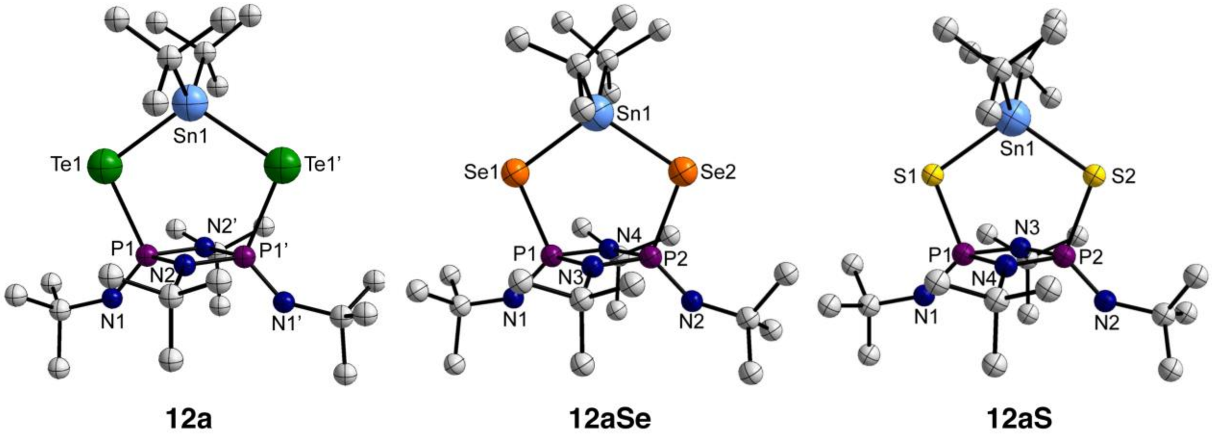


Figure 2. Molecular Structures of **12a**, **12aSe** and **12aS**.

Table 2. Comparison of Structural Data for **12a, 12aSe** and **12aS.**[a]

Compound	12a	12aSe	12aS
d(P–E)	2.504(2)	2.277(3),2.286(3)	2.110(4),2.121(4)
d(E–Sn)	2.7603(7)	2.5687(13),2.5750(14)	2.444(4),2.450(4)
d(P–N_{exo})	1.508(7)	1.521(10),1.507(9)	1.484(10),1.499(10)
d(P–N_{endo})	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)
d(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_{endo}–P	96.2(4)	95.8(5),95.4(5)	95.4(4),95.1(4)
∠ E–P–N_{exo}	115.4(3)	114.3(4),116.1(4)	115.5(4),116.9(5)
∠ E–P–N_{endo}	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)

[a] Bond lengths in Å; bond angles in deg.

The structural determinations confirm the *E,E′* coordination of the ligands $\mathbf{L}^{2-}$ (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_2Sn**L** (E = S).[23] In that case, however, the isomer formed was pre-determined by the synthetic approach, which involved oxidation of the two P^{III} centers in the *N,N′*-chelated complex $[(^tBuNP^{III}(\mu\text{-}N^tBu)_2P^{III}N^tBu)(SnMe_2)]$ with sulfur.[23]

In contrast to the observations for the Ph_2Ge derivative **10**, the –P–Te–Sn–Te–P– framework is perfectly planar in **12a**, **12aSe** and **12aS**; the P_2N_2 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 $(R_2Sn)_3Te_2$ (R = ^{t}Bu,[24a] Fc[24b]). 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^{IV} compound $[Sn\{(Se)C(PPh_2Se)_2\}_2]$[21] and in the Sn^{II} complex $[Sn\{NSeP^iPr_2)_2$-*Se,Se′*$\}_2]$.[22] 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.[25,26] The P–S–Sn–S–P scaffold is well-known, e.g. in diorganotin dithiophosphates $Me_2Sn(S_2PR_2)_2$ (R = Et,[27] Ph,[28] Me[29]). 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,[16] we have now investigated the reactions of **1** and **2** with $RPCl_2$ (R = ^tBu, Ad, $^iPr_2N$) 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 ^{31}P NMR spectra. In both cases colorless crystals were isolated and the CHN analysis of **13aSe** was consistent with the molecular formula **LP**^{t}Bu (E = Se); the symmetrical *Se,Se′*-coordination to the ^tBuP 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**.[16] The ^{31}P and ^{77}Se NMR spectra for the adamantyl derivative **13bSe**, as a representative example, are discussed here (Figure 3). The ^{31}P NMR resonance at 132.0 ppm accompanied by ^{77}Se satellites ($^1J(P,Se) = 232$ Hz) is assigned to the P^{III} center in the bridging SePSe unit. The second resonance at −76.8 ppm shows a doublet of satellites with $^1J(P,Se) =$

449 Hz and ^{2}J(P,P) = 58 Hz, as expected for the chemically equivalent, but magnetically inequivalent, phosphorus atoms of the $P^{V}_{2}N_{2}$ ring. The large difference in ^{1}J(P,Se) values reflects the different formal oxidation states of the P^{III} and P^{V} environments. The ^{77}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 ^{1}J(P,Se) couplings and a ^{3}J(Se,P) coupling of 15.6 Hz (Figure 3).

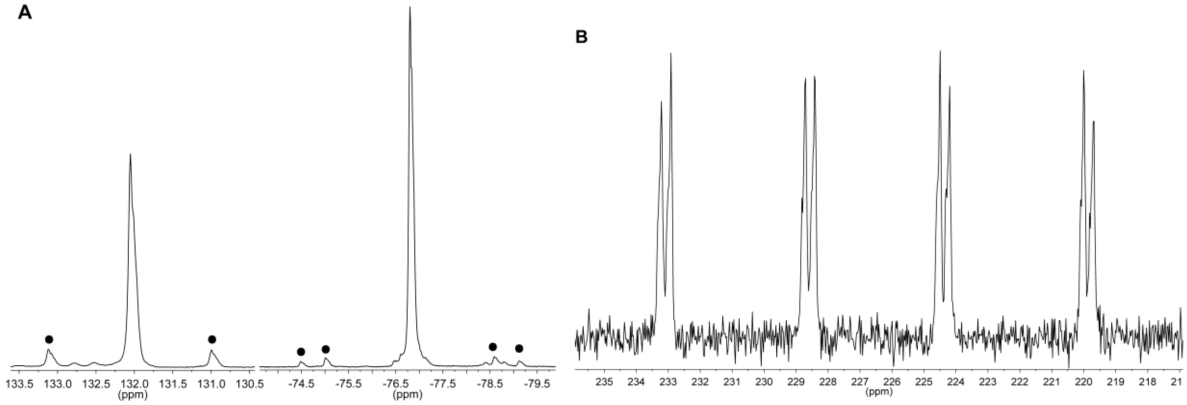


Figure 3. (**A**) ^{31}P NMR and (**B**) ^{77}Se NMR spectra of **13bSe**.

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}P NMR spectra. Instead, the major products from the metathesis of **1** with $RPCl_2$ 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}P NMR spectra. As a typical example, Figure 4A depicts the ^{31}P NMR spectrum of the reaction of **4** with $^{i}Pr_2NPCl_2$ which produces **14cS** as the major product, **13cS** as a very minor product, and **11S**. The ^{31}P NMR spectrum of the *S,S′*-chelated isomer **13cS** exhibits a mutually coupled 1:2:1 triplet and a doublet, attributed to the P^{III} (139.4 ppm) and P^{V} (−57.7 ppm) centers, respectively, with a small ^{2}J(P,P) coupling of 4.3 Hz that was not resolved in the case of the Se analogs **13aSe and 13bSe**.

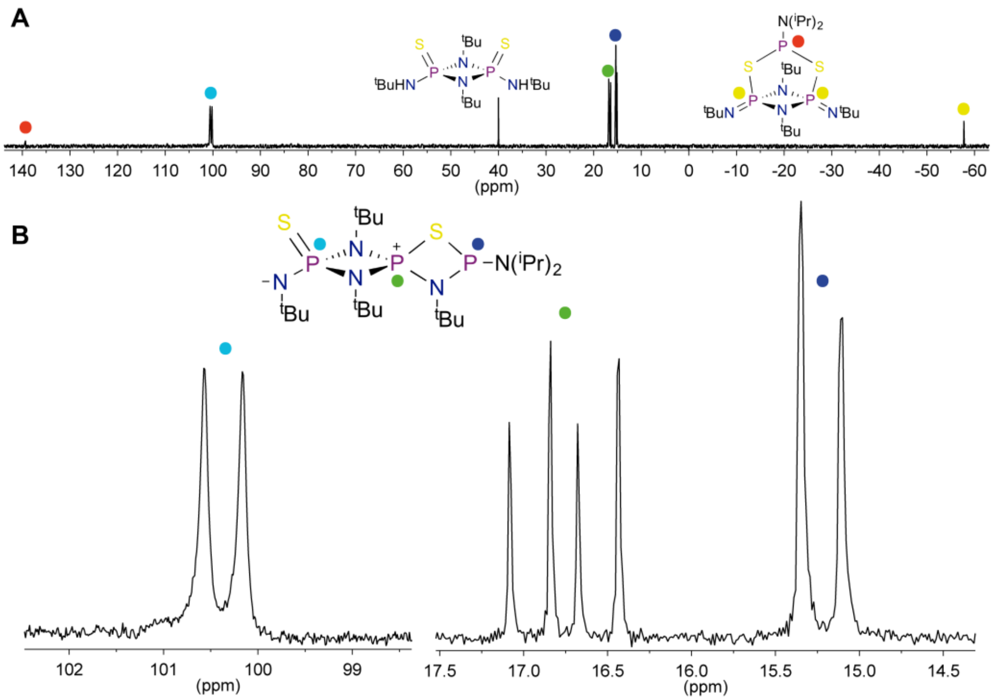


Figure 4. ^{31}P NMR spectrum of the reaction of **1** with $^{i}Pr_2NPCl_2$: (A) Complete spectrum; (B) Expanded spectrum for the *N,S*-chelated complex **14cS**.

The expanded ^{31}P NMR spectrum of **14cS** (Figure 4B) reveals three distinct phosphorus environments resulting from the *N,S*-chelation of the ligand $\mathbf{L}^{2-}$ (E = S) to the RP^{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(P,P) = 44 Hz) for the terminal P^{V} center, (b) a doublet of doublets at 16.8 ppm (^2J(P^V,P^V) = 45 Hz, ^2J(P^V,P^{III}) = 26 Hz) for the spirocyclic P^V environment, and (c) a doublet at 15.2 ppm (^2J(P^{III},P^V) = 26 Hz) for the terminal P^{III} atom. The anomalous chemical shift for the spirocyclic P^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.[10] 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.

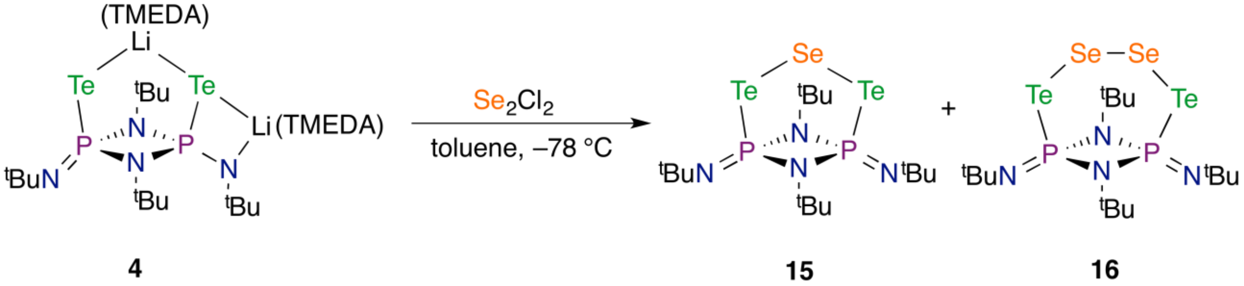
Table 3. ^{31}P NMR Chemical Shifts and ^{2}J(P,P) for **14a-c**.[a]

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

[a] δ 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**[12] and the cyclic tritelluride **6**[15] 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 TsiTeSeSeTeTsi (Tsi = $C(SiMe_3)_3$), but the solid-state structure was not determined;[30] it is also present in the cationic mixed-chalcogen clusters $[Te_2Se_8]^{2+}$ and $[Te_2Se_6]^{2+}$.[31] 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(Se–Te) = 2.523(1)-2.531(1) Å and d(Se–Se) = 2.350 (1) Å.[32] The P–Te bond lengths in **16** are similar to those in **3** and **6**.

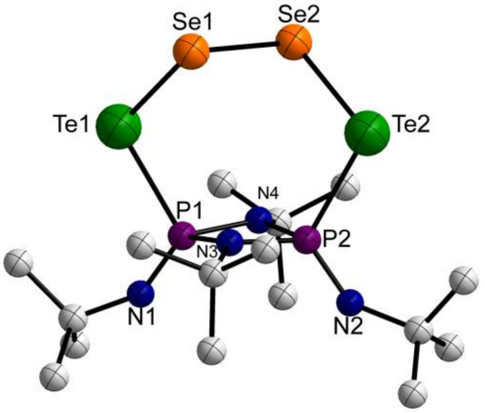
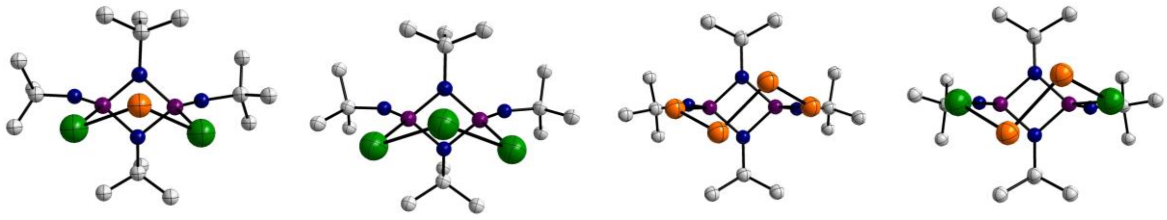


Figure 5. Molecular structure of **16**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–Se1 2.4919(18), Te1–P1 2.483(3), Te2–Se2 2.5356(17), Te2–P2

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**[15] and **15** and the two tetrachalcogenides **3**[12] and **16**, all of which are supported by *cyclo*-$P^{V}_{2}N_{2}$ scaffolds. The extent of puckering is clearly very similar for the two trichalcogenides and the two tetrachalcogenides.



15 **6** **3** **16**

Figure 5. Conformations of *cyclo*-$P^{V}_{2}N_{2}$-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**[12] and tritelluride **6**[15] 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 ^{31}P NMR spectrum of the TeSeTe-bridged derivative **15** appears as a singlet accompanied by both ^{125}Te and ^{77}Se satellites, ^{1}J(P,Te) = 1025 Hz and ^{2}J(P,Se) = 29 Hz, cf. -134.5 ppm and ^{1}J(P,Te) = 1029 Hz for **6**.[15] The ^{77}Se NMR spectrum of **15** reveals a 1:2:1 triplet at 240.9 ppm (^{2}J(P,Se) = 29 Hz) and the ^{125}Te NMR spectrum shows a resonance at 870.3 ppm appearing as a doublet of doublets (^{1}J(P,Te) = 1025 Hz and ^{3}J(Te,P) = 34 Hz).

The chemical shift of −68.6 ppm observed in the ^{31}P NMR spectrum of the TeSeSeTe-bridged derivative **16** is close to the value of −50.8 ppm reported for the tetraselenide **3**,[12] 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 ^{1}J(P,Te) value of 1287 Hz for **16** is substantially larger than the value of 1029 Hz found for the tritelluride **6**,[15] which is consistent with the shorter P–Te distance in **16** (Table 4).[33] The ^{77}Se NMR spectrum exhibits a triplet at 465.6 ppm (^{2}J(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 (^{2}J(P,Se) = 10 Hz).[12] The ^{125}Te NMR spectrum of **16** confirms the P–Te coupling observed in the ^{31}P NMR spectrum by showing a doublet of doublets at 711.6 ppm (^{1}J(P,Te) = 1289 Hz and ^{3}J(P,Te) = 42 Hz).

Table 4. Structural and NMR Parameters for *cyclo*-$P^{V}_{2}N_{2}$-Supported Polychalcogenides.[a,b]

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

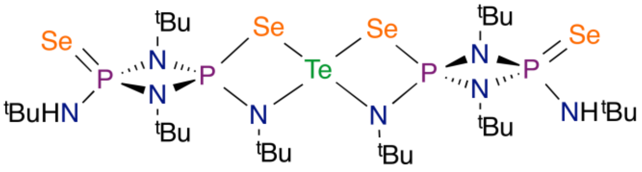
^{2}J(P,E)	29	34	10	14
δ(^{77}Se)	240.9 (t)	-	673.0 (t) 336.7 (dd)	465.6 (t)
δ(^{125}Te)	870.3 (dd)	442.8 (dd) 361.9 (t)	-	711.6 (dd)

[a] Bond lengths in Å;

[b] δ in ppm; J values in Hz; t = triplet, dd = doublet of doublets

[c] 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 [Te{^{t}Bu(H)N(Se)P^{V}(μ-N^{t}Bu)$_2$P^{V}(Se)^{t}BuN-*N,Se*}$_2$] (**17**) was identified as a minor product from the reaction of **4** with Se_2Cl_2;[34,35] a small amount of the cyclic tritelluride **6** was also detected in the ^{31}P NMR spectrum.



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CONCLUSIONS

The thermal and air stability of main group derivatives of the ditelluro dianion **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 Ph_2Ge and $^{t}Bu_2Sn$ derivatives can be handled in air for several days, whereas other R_2Sn (R = ^{n}Bu, Ph) complexes decompose instantly with the formation of elemental tellurium.[36] The lability of the P–Te bond in the ligand **L**$^{2-}$ was also evident in the reactions with MCl_3 (M = Ga, In) to give spirocyclic complexes in which one of the ligands incorporates a P^{III} center, The Ph_2Ge derivative of the diseleno dianion $\mathbf{L}^{2-}$ (E = Se) is considerably more hydrolytically sensitive than the tellurium analog, however the complete series $(\mathbf{L})Sn^tBu_2$ (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),[16] *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 $H\mathbf{L}^{-}$.[39]

The comprehensive survey of the reactions of the *cyclo*-$P^V{}_2N_2$-supported dianion $\mathbf{L}^{2-}$ (E = Te) with p-block element halides in this and previous work[15, 16] 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 $[TeP^VR_2NP^VR_2Te]^-$ (R = ^{i}Pr) have received extensive attention,[40-44] especially with regard to the nature of f-element-tellurium bonds[44] and their use as single-source precursors of semi-conducting metal tellurides in the form of thin films or quantum dots.[45]

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^{-3} 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.[46] 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 °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}H, ^{13}C, $^{31}P\{^{1}H\}$, $^{77}Se\{^{1}H\}$, $^{119}Sn\{^{1}H\}$ NMR and $^{125}Te\{^{1}H\}$ NMR spectra were measured in deuterated solvents or using the reaction mixture and capillaries filled with C_6D_6 at 25 °C. TMS was used as an internal standard for ^{1}H and ^{13}C NMR. 85 % H_3PO_4 was employed as an external standard for $^{31}P\{^{1}H\}$ NMR spectra, Ph_2Te_2 or Me_2Te for $^{125}Te\{^{1}H\}$ NMR spectra, Me_2Se for $^{77}Se\{^{1}H\}$ NMR spectra as well as Me_4Sn for $^{119}Sn\{^{1}H\}$ NMR spectra. All $^{77}Se\{^{1}H\}$, $^{119}Sn\{^{1}H\}$ NMR, $^{125}Te\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra are reported as ^{77}Se, ^{125}Te, ^{119}Sn and ^{31}P NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) relative to the solvent peaks.[47] 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[48] 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-Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarisation effects. The data for all of the compounds were collected and processed using CrystalClear (Rigaku).[48]

The crystal structures were solved using direct methods[49] or heavy-atom Patterson methods[50] and expanded using Fourier techniques.[51] The non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined using the riding model. All calculations were performed using CrystalStructure[52] crystallographic software package and SHELXL-97.[53] **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	**9**	**10**	**16**
Empirical formula	$C_{32}H_{73}InN_8P_4Te_3$	$C_{28}H_{46}GeN_4P_2Te_2$	$C_{16}H_{36}N_4P_2Se_2Te_2$
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^3)	0.10 x 0.10x0.01	0.17x0.07x0.02	0.10x0.10x0.10
Crystal system	monoclinic	triclinic	monoclinic
a (Å)	10.439(2)	9.3375(18)	15.707(5)
b (Å)	13.630(2)	11.603(2)	14.808(4)
c (Å)	17.005(3)	15.879(3)	11.549(3)
α (°)	90.0000	87.895(6)	90.0000
β (°)	99.789(4)	80.914(6)	94.354(7)

γ (°)	90.0000	89.309(6)	90.0000
Volume (Å^3)	2384.5(7)	1697.6(6)	2678.4(13)
Space group	$P\ 2_1$	P -1	P 21/c
Z value	2	2	4
D_{calc} (g/cm^3)	1.659	1.621	1.883
F_{000}	1172.00	816.00	1448.00
μ (Mo-K_α) (cm^{-1})	2.459	2.703	5.025
No. of reflections measured	32486	13435	15644
R_{int}	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: R_1 ($I > 2.00\sigma(I)$)	0.0204	0.1284	0.0780
Residuals: wR_2 (all reflections)	0.0505	0.3008	0.2127
Maximum peak in final diff. map (e$^-$/Å^3)	0.49	2.430	4.980
Minimum peak in final diff. map(e$^-$/Å^3)	−0.38	−1.910	−2.570

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

Compound	**12a**	**12aSe**	**12aS**
Empirical formula	$C_{24}H_{54}N_4P_2SnTe_2$	$C_{24}H_{54}N_4P_2SnSe_2$	$C_{24}H_{54}N_4P_2SnS_2$
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^3)	0.24x0.18x0.03	0.10x0.03x0.03	0.15x0.09x0.03
Crystal system	orthorhombic	monoclinic	monoclinic
a (Å)	20.1157(12)	19.345(4)	11.243(3)
b (Å)	30.241(2)	15.089(3)	30.770(7)
c (Å)	11.5584(7)	11.430(3)	11.193(3)
α (°)	90.0000	90.0000	90.0000
β (°)	90.0000	90.608(4)	119.829(17)
γ (°)	90.0000	90.0000	90.0000
Volume (Å^3)	7031.2(8)	3336.2(13)	3359.2(14)
Space group	$Fdd2$	Cc	$P2_1/c$ 1
Z value	8	4	4
D_{calc} (g/cm^3)	1.577	1.468	1.272
F_{000}	3280.00	1496.00	1352.00
μ (Mo-K_α) (cm^{-1})	2.462	3.062	0.998
No. of reflections measured	14705	21515	25146
R_{int}	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: R_1 ($I > 2.00\sigma(I)$)	0.0373	0.0516	0.0840
Residuals: wR_2 (all reflections)	0.0748	0.1233	0.2759
Maximum peak in final diff. map (e$^-$/Å^3)	0.540	2.87	1.890
Minimum peak in final diff. map(e$^-$/Å^3)	−0.380	−2.00	−1.210

General Procedure for Metathetical Reactions. The reagent **1**,[15] **2**,[15] **4**[16] or **5**[17] (0.60 mmol) was suspended in toluene (10 mL) and cooled to −78 °C. A solution of the p-block element halide R_nMCl_2 ($n = 1, 2$) or MCl_3 (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 °C overnight. The crystals were removed by filtration and dried under vacuum. The resulting filtrate was concentrated and cooled to −40 °C to produce another batch of crystals.

Synthesis of 8. Reagents: **4** (500 mg, 0.59 mmol) and $GaCl_3$ (53 mg, 0.30 mmol, 0.5 eq.) in toluene (20 mL). Red crystals of **8** were isolated from *n*-hexane (yield 8 %). ^{31}P NMR (202.46 MHz, [D_8]toluene): δ = 76.6 (s), −44.7 (s, ^{1}J(P,Te) = 1233 Hz), −133.3 (s, ^{1}J(P,Te) = 1130 Hz, ^{3}J(P,Te) = 184 Hz). Decomposition in toluene or THF precluded the acquisition of a ^{125}Te NMR spectrum.

Synthesis of 9: Reagents: $InCl_3$ (66 mg, 0.30 mmol, 0.5 eq.) (179 mg, 0.59 mmol) and **4** (500 mg, 0.59 mmol) in toluene (20 mL0 Recrystallization from *n*-hexane afforded yellow crystals suitable for X-ray crystallography (yield 12 %). ^{31}P NMR (109.37 MHz, [D_8]toluene): δ = 78.1 (d, ^{2}J(P,P) = 3.4 Hz), −41.2 (d, ^{1}J(P,Te) = 1251 Hz, ^{2}J(P,P) = 3.4 Hz), −135.1 (s, ^{1}J(P,Te) = 1113 Hz, ^{2}J(P,P) = 10.2 Hz). Decomposition during the measurement precluded reliable characterization by ^{125}Te NMR. MS (EI^{+}), *m/z*), 1192.1 (M^{+}), 1177.1 (M^{+}−CH_3). Elemental analysis calcd (%) for $C_{32}H_{73}N_8P_4InTe_3$: 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 Ph_2GeCl_2 (176 mg, 0.59 mmol) in toluene (20 mL). Yield of red crystals = 39 %. ^{1}H NMR (400.13 MHz, [D_8]toluene): δ = 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}P NMR (161.98 MHz, [D_8]toluene): δ = −136.4 (s, ^{1}J(P,Te) = 1103 Hz, ^{2}J(P,P) = 20 Hz). ^{125}Te NMR (85.24 MHz, [D_8]toluene): δ = 162.4 (^{1}J(P,Te) = 1105 Hz, ^{3}J(P,Te) = 26 Hz). HRMS (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 °C.[37] ^{31}P NMR (109.37 MHz, [D$_8$]THF): δ = −80.4 (^1J(P,Se) = 470.3 Hz, ^2J(P,P) = 60.2 Hz). ^{77}Se NMR (51.52 MHz, [D$_8$]THF): δ = 137.6 (dd, ^1J(Se,P) = 470.1 Hz, ^3J(Se,P) = 15.6 Hz). MS (EI$^+$): *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. ^{1}H NMR (270.17 MHz, [D$_8$]toluene): δ = 1.71 (s, 18H, ^{t}Bu) 1.46 (s, 18H, ^{t}Bu), 1.38 (s, 18H, ^{t}Bu). ^{31}P NMR (109.37 MHz, [D$_8$]toluene): δ = −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): δ = 34.2 (^2J(P,Sn) = 52 Hz, ^1J(Sn,Te) = 3385 Hz). ^{125}Te NMR (85.24 MHz, [D$_8$]toluene): δ = −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^+−*t*Bu], 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. ^{1}H NMR (270.17 MHz, [D$_8$]toluene): δ = 1.71 (s, 18H, ^{t}Bu), 1.66-1.47 (m, 4H+4H, ^{n}Bu), 1.44 (s, 18H, ^{t}Bu), 1.32 (s, 4H, ^2J(HH) = 7.6 Hz, ^{n}Bu), 0.90 (t, 6H, ^2J(HH) = 7.6 Hz, ^{n}Bu). ^{31}P NMR (202.46 MHz, [D$_8$]toluene): δ = −141.1 (s, ^1J(P,Te) = 1140 Hz, ^2J(P,Sn) = 51 Hz). ^{119}Sn NMR (100.75 MHz, [D$_8$]toluene): δ = −84.7

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

Synthesis of 12c: Reagents: Ph_2SnCl_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}P NMR (161.98 MHz, [D$_8$]toluene): δ = −140.4 (s, ^1J(P,Te) = 1102 Hz, ^2J(P,Sn) = 60 Hz, ^2J(P,P) = 6.5 Hz). ^{119}Sn NMR (100.75 MHz, [D$_8$]toluene): δ = −156.1 (^2J(P,Sn) = 62 Hz). ^{125}Te NMR (85.24 MHz, [D$_8$]toluene): δ = 23.4 (^1J(P,Te) = 1102 Hz, ^3J(P,Te) = 26 Hz).

Synthesis of 12aSe: Reagents: **2** (500 mg, 0.60 mmol) and $^tBu_2SnCl_2$ (182 mg, 0.60 mmol) in toluene (15 mL). Yield of **12aSe** = 78 % according to the ^{31}P NMR spectrum; yellow crystals were isolated.[37] ^{31}P NMR (109.37 MHz, [D$_8$]THF): δ = −77.0 (s, ^1J(P,Se) = 500.0 Hz, ^2J(P,Sn) = 42.3 Hz). ^{119}Sn NMR (100.75 MHz, [D$_8$]THF): δ = 69.8 (^2J(P,Sn) = 43.1 Hz, ^1J(Sn,Se) = 690.5 Hz). ^{77}Se NMR (51.52 MHz, [D$_8$]THF): δ = 77.3 (^1J(P,Se) = 498.2 Hz, ^3J(P,Se) = 12.0 Hz). EIMS, *m/z*: 723.1 (M^+-CH_3), calcd 723.1. Elemental analysis calcd (%) for $C_{24}H_{54}N_4P_2SnSe_2$: 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 $^tBu_2SnCl_2$ (207 mg, 0.68 mmol, 1 eq) in toluene (25 mL). Yield of **12aS** = 80 % according to the ^{31}P NMR spectrum; colorless crystals were isolated.[38] ^{31}P NMR (109.37 MHz, [D$_8$]toluene): δ = −48.7 (s, ^2J(P,Sn) = 35.2 Hz). ^{119}Sn NMR (100.75 MHz, [D$_8$]THF): δ = 66.4 (^2J(P,Sn) = 33.9 Hz). EIMS, *m/z*: 629.2 (M^+-CH_3), calcd 629.2. Elemental analysis calcd (%) for $C_{24}H_{54}N_4P_2SnS_2$: C 44.80, H 8.46, N 8.71: found: C 44.73, H 8.49, N 8.80.

Synthesis of 13aSe. Reagents $^tBuPCl_2$ (95 mg, 0.60 mmol) and **2** (500 mg, 0.59 mmol) in toluene (25 mL). Estimated yields from the ^{31}P NMR spectrum were **13aSe** (40 %) and **11Se**

(20 %), which co-crystallized as colorless crystals.[37] NMR data for **13aSe**: ^{31}P NMR (109.37 MHz, [D$_8$]THF): δ = 139.5 (^1J(P,Se) = 234.1 Hz), −78.0 (^1J(P,Se) = 447.3 Hz, ^2J(P,P) = 58.0 Hz). ^{77}Se NMR (51.52 MHz, [D$_8$]THF): δ = 256.0 (^1J(Se,P^V) = 450.8 Hz, ^1J(Se,P^{III}) = 234.4 Hz, ^3J(Se,P) = 19.6 Hz). EIMS, *m/z*: 580.1 (M$^+$−CH$_3$+H), calcd 580.1. A few crystals of pure **13aSe** were isolated. Elemental analysis calcd (%) for $C_{20}H_{45}N_4P_3Se_2$: C 40.55, H 7.66, N 9.46; found: C 40.71, H 7.77, N 9.37.

Synthesis of 13bSe. Reagents: AdPCl$_2$ (214 mg, 0.60 mmol) and **2** (500 mg, 0.59 mmol) in toluene (25 mL). Yield of **13bSe** estimated from integration of the ^{31}P NMR spectrum ca. 79 % **13bSe** formed colorless co-crystals with the by-product **11Se**.[37] NMR data for **13bSe**: ^{31}P NMR (109.37 MHz, [D$_8$]THF): δ = 132.0 (^1J(P,Se) = 231.8 Hz), −76.8 (^1J(P,Se) = 449.5 Hz, ^2J(P,P) = 58.0 Hz). ^{77}Se NMR (51.52 MHz, [D$_8$]THF): δ = 226.5 (ddd, ^1J(Se,P^V) = 449.0 Hz, ^1J(Se,P^{III}) = 232.1 Hz, ^3J(Se,P) = 15.6 Hz).

Synthesis of 13aS and 14aS. Reagents: **1** (500 mg, 0.68 mmol) and ^{t}BuPCl$_2$ (107 mg, 0.68 mmol) in toluene (25 mL). Estimated yield of **13aS** and **14aS** were ca. 5% and 67%, respectively, from the integrated ^{31}P NMR spectrum.[38] NMR and MS data for **13aS**: ^{31}P NMR (109.37 MHz, C$_6$D$_6$-capillary): δ = 126.5 (s), −56.9 (s). EIMS, *m/z*: 498.2 (M$^+$), calcd 498.2; 483.1 (M$^+$−CH$_3$), calcd. 438.2. NMR and MS data for **14aS**: ^{31}P NMR (109.37 MHz, C$_6$D$_6$-capillary): δ = 116.9 (d, ^2J(P,P) = 42.3 Hz), 17.2 (dd, ^2J(P,P) = 42.5 Hz, ^2J(P,P) = 27.1 Hz), 14.4 (d, ^2J(P,P) = 27.0 Hz). EIMS, *m/z*: 498.2 (M$^+$), calcd 498.2; 483.1 (M$^+$−CH$_3$), calcd 483.2.

Synthesis of 13bS and 14bS: Reagents: **1** (500 mg, 0.68 mmol) and AdPCl$_2$ (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 ^{31}P NMR spectrum.[38] NMR and MS data for **13bS**: ^{31}P NMR (109.37 MHz, C$_6$D$_6$-capillary): δ = 120.1 (s), −56.2 (s). EIMS, *m/z*: 576.3 (M$^+$), 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): δ = 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.[38] NMR and MS data for **13cS:** ^{31}P NMR (109.37 MHz, C_6D_6-capillary): δ = 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): δ = 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): δ = −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): δ = 240.9 (t, ^2J(P,^{77}Se) = 30 Hz) ppm. ^{125}Te NMR (85.24 MHz, [D$_8$]toluene): δ [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): δ = −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): δ = 465.6 (pseudo-*t*, ^2J(P,^{77}Se = 14 Hz). ^{125}Te NMR (85.24 MHz, [D$_8$]toluene): δ = 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.[15] ^{31}P NMR (109.37 MHz, [D$_8$]toluene): δ = −134.6 (^1J(P,^{125}Te) = 1028 Hz; ^2J(P,P) = 31 Hz).

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

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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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.[34] The formation of P^{V}–Se linkages in this reaction indicates significant decomposition of the ditelluro ligand $\mathbf{L}^{2-}$ (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 ^{31}P NMR spectrum of the reaction mixture.

(36) The reactions of **1**, **2** and **4** with $EtAsI_2$ and $PhSbCl_2$, as representative examples of heavier group 15 elements, were also carried out. Although the solution ^{31}P NMR spectra were consistent with the formation of *Te,Te′*-chelated complexes of $\mathbf{L}^{2-}$, the lability of these derivatives (extrusion of Te) precluded further characterization (see ESI).

(37) (a) Separation of **10Se** from **11Se** ($\delta(^{31}P)$ = 26.7 ppm, $^{1}J(P,Se)$ = 880 Hz)[10] was not possible due to their similar solubility; (b) Separation of **12aS** from **11S** ($\delta(^{31}P)$ = 40.0; cf. lit. value 39 ppm (in [D_8]toluene) = 38.7)[38] was thwarted by their similar solubility.

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SYNOPSIS:

Main Group-Tellurium Heterocycles Anchored by a $P^V_2N_2$ Scaffold and Their Sulfur/Selenium Analogs

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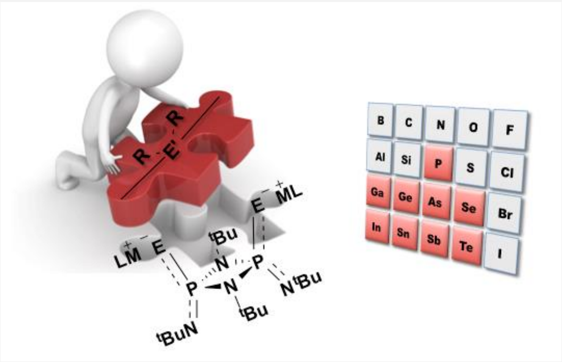

Reactions of the ditelluro dianion $[TeP^V(N^tBu)(\mu\text{-}N^tBu)]_2^{2-}$ and various main group halides produced heterocycles in which the ligand is *Te,Te'*-chelated to heavier p-block elements. For comparison, selenium and sulfur analogs were synthesized from $[EP^V(N^tBu)(\mu\text{-}N^tBu)]_2^{2-}$ (E = S, Se) and group 14 dihalides or $RPCl_2$; in the organophosphorus(III) derivatives the dianionic ligand forms *E,E'*-chelated complexes for selenium and tellurium, but the *N,E*-bonded isomer predominates for sulfur.