Inorganic Chemistry

Article

pubs.acs.org/IC

Main Group Tellurium Heterocycles Anchored by a $P^{V}_{2}N_{2}$ Scaffold and Their Sulfur/Selenium Analogues

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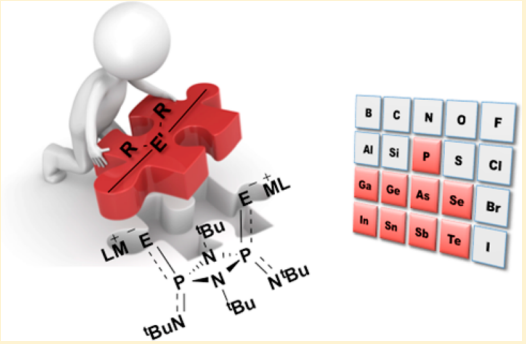
Supporting Information

ABSTRACT: A comprehensive investigation of reactions of alkali-metal derivatives of the ditelluro dianion $[TeP^{V}(N^{t}Bu)(\mu\text{-}N^{t}Bu)]_{2}^{2-}$ ($\mathbf{L}^{2-}$, E = Te) with p-block element halides produced a series of novel heterocycles incorporating $P^{V}_{2}N_{2}$ 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 $\mathbf{L}^{2-}$ (E = S, Se). In the case of group 13 trihalides MCl_3 (M = Ga, In), neutral spirocyclic complexes (**L**)M[N^{t}Bu(Te)P^{V}(μ-N^{t}Bu)$_2P^{III}N(H)^{t}Bu$)] (M = Ga, In) comprised of a Te,Te′-chelated ligand $\mathbf{L}^{2-}$ and a N,Te-bonded ligand resulting from loss of Te and monoprotonation were obtained. In reactions with $RPCl_2$ (R = ^{t}Bu, Ad, $^{i}Pr_2N$) 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**)$Sn^{t}Bu_2$ (E = Te, **12a**); E = Se, **12aSe**, E = S, **12aS**) and (**L**)(μ-SeSe) (E = Te, **16**).



INTRODUCTION

Cyclodiphosphazanes, for example, $[ClP^{III}(\mu\text{-}NR)]_2$, are saturated, four-membered $P^{III}_{2}N_2$ 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, for example, $[^{t}BuN(H)P^{III}(\mu\text{-}N^{t}Bu)]_2$, are readily oxidized by sulfur or selenium.[8] Subsequent double deprotonation of the resulting P^{V}/P^{V}dichalcogenides $[^{t}BuN(H)(E)\{P^{V}(\mu\text{-}N^{t}Bu)\}]_2$ 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** (Chart 1) or in a side-on mode (bis-N,E) for the lithium analogues;[9,10] dimethylaluminum derivatives also adopt bis-N,E chelation.[11] Monodeprotonation of $[^{t}BuN(H)(E)\{P^{V}(\mu\text{-}N^{t}Bu)\}]_2$ (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 $P^{V}_{2}N_2$ rings.[12] In the case of E = Se this oxidation also gives rise to the bridging tetraselenide $[^{t}BuN\{P^{V}(\mu\text{-}N^{t}Bu)\}]_2(\mu\text{-SeSeSeSe})$ (**3**) (Chart 1), which is more conveniently prepared by metathesis of **2** with Se_2Cl_2.[12]

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

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 produces the cyclic tritelluride

Received: January 26, 2015
Published: February 26, 2015

DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043−3054

Chart 1

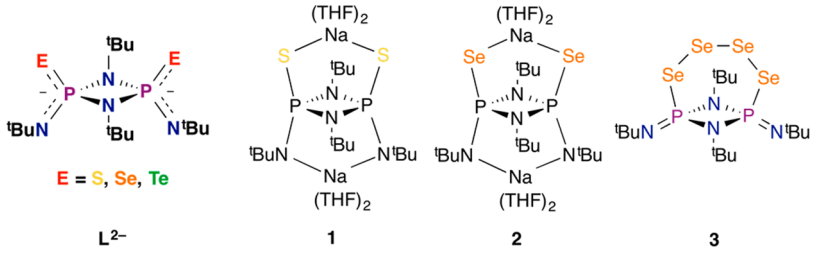
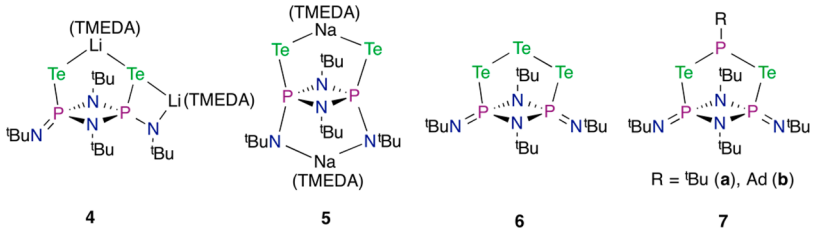


Chart 2



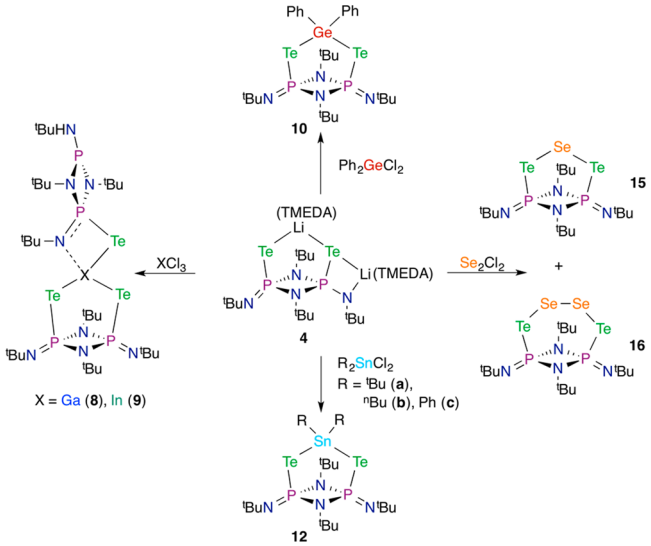
[^{t}BuN{P^V(μ-N^{t}Bu)}]$_2$(μ-TeTeTe) (**6**, Chart 2), which is obtained in higher yield by metathesis of **5** with $TeCl_2$·TMTU (TMTU = tetramethylthiourea).[15a] Furthermore, metathesis of **4** with $RPCl_2$ (R = ^{t}Bu, Ad) generates the $P^V_2N_2$-supported heterocycles **7a**,**b** (Chart 2), which were among the first examples of structurally characterized phosphorus(III)−tellurium ring systems.[15b] The unusual ditellurido-bridged P_2N_2 ring [(μ-NTer)P]$_2$(μ-TeTe) has also been reported recently.[16]

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. To determine the scope and limitations of the ditelluro dianion L^{2-} (E = Te) as a reagent for the synthesis of such heterocycles, we performed 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, ^{n}Bu, Ph), $RMCl_2$ (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$_2$N). 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 performed 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 $GaCl_3$ and $InCl_3$ 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).[17] The indium derivative **9** is considerably less prone to decomposition than the gallium analogue **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 of 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 ^2J(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

DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043−3054

third resonance at −133 and −135 ppm in **8** and **9**, respectively, which also displays satellites (^1J(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 from 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 P^{III} and P^V centers.

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

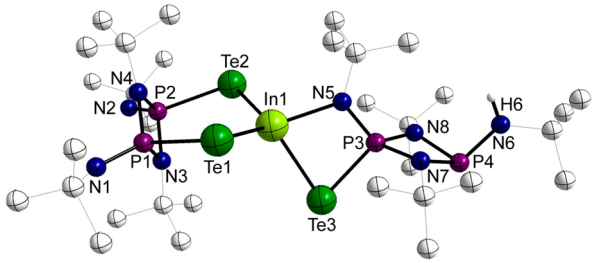


Figure 1. Molecular structure of **9**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Te1−In1 2.7270(16), Te1−P1 2.485(4), Te2−In1 2.7210(16), Te2−P2 2.499(3), Te3−In1 2.7959(6), Te3−P3 2.4526(10), In1−N5 2.174(3), P1−N1 1.559(12), P1−N3 1.699(13), P1−N4 1.662(12), P3−N5 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).

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 monotelluro monoanion $[(^t\text{BuN(Te)P}^V(\mu\text{-N}^t\text{Bu})_2\text{P}^{III}\text{N(H)}^t\text{Bu})]^-$, which presumably results from the loss of tellurium from $\mathbf{L}^{2-}$ (E = Te) and monoprotonation.[17]

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 $\{\text{In}(\mu\text{-Te})[\text{N}(^i\text{Pr}_2\text{PTe})_2]\}_3$.[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.

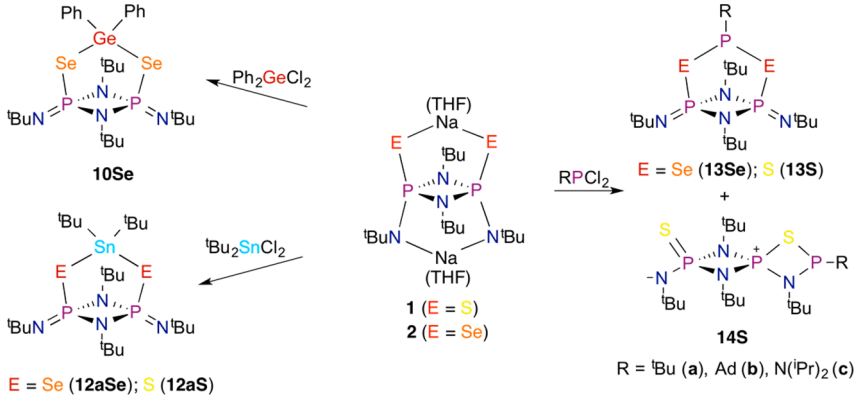
Synthesis, NMR Spectra, and Crystal Structures of Ph_2Ge Complexes. The reaction of **4** with Ph_2GeCl_2 produces the diphenylgermanium derivative **10** in 39% isolated yield (Scheme 1); no decomposition was observed in the solid state after 3 d of exposure to moist air. By contrast, the formation of the selenium analogue **10Se** (Scheme 2) was accompanied by the diprotonated derivative $H_2\mathbf{L}$ (E = Se) (**11Se**), which precluded the isolation of pure **10Se** due to their similar solubilities.[19]

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(P,Te) = 1103 Hz) strongly suggests symmetrical coordination of the ligand $\mathbf{L}^{2-}$ (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).

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 $[(2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2)_2\text{GeTe}_2]_2$ and 2.580(1) Å in $[(2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2)_4\text{Ge}_4\text{Te}_6]$.[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 analogue **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 ^1J(P,Se) = 470 Hz and ^2J(P,P) = 60 Hz. Consistently, the ^{77}Se NMR spectrum is comprised of a doublet of doublets centered at 137.6 ppm with ^1J(P,Se) = 470 Hz and ^3J(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**

Scheme 2



DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043−3054

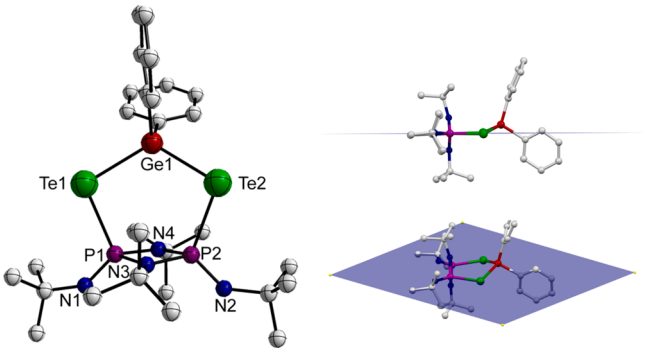


Figure 2. Molecular structure and side view of **10**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Te1–Ge1 2.577(3), Te2–Ge1 2.565(3), Te1–P1 2.508(6), Te2–P2 2.508(6), P1–N1 1.525(17), P1–N3 1.715(18), P1–N4 1.686(17), P2–N3 1.733(17), P2–N2 1.521(16), P2–N4 1.693(18); 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).

were isolated, they were not of sufficient quality for the crystal structure to be determined.

Synthesis, NMR Spectra, and Crystal Structures of R_2Sn Complexes. Metathetical reactions of **4** with R_2SnCl_2 (R = ^{t}Bu, ^{n}Bu, Ph) were performed 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 3 d, whereas the $^n Bu_2Sn$ (**12b**) and Ph_2Sn (**12c**) analogues 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).

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

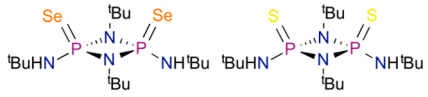
compound	**12a**	**12b**	**12c**	**12aSe**	**12aS**
E	Te	Te	Te	Se	S
R	^{t}Bu	^{n}Bu	Ph	^{t}Bu	^{t}Bu
$\delta(^{31}P)$	−141.6	−140.4	−141.1	−77.0	−48.7
$^1J(^{31}P,E)$[c]	1183	1102	1140	500	
$^2J(^{31}P,^{119}Sn)$	52	60	51	42	35
$\delta(^{119}Sn)$	34.2 (t)	−156.1 (t)	−84.7 (t)	69.8 (t)	66.4 (t)
$^1J(^{119}Sn,E)$[c]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

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 [^1J(P,Te) = 1183 Hz and ^2J(P,P) = 3.4 Hz]. Furthermore, tin satellites corresponding to ^2J(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 ^1J(Sn,Te) ≈ 3390 Hz. The ^{125}Te NMR spectrum consists of a doublet of doublets attributed to the ^1J(Te,P) and ^3J(Te,P) couplings. In addition, satellites confirming the ^1J(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, that is, Te,Te′ chelation, for this series of R_2Sn (R = ^{n}Bu, Ph, ^{t}Bu) derivatives (Table 1).

To assess the influence of the chalcogen on the stability of R_2Sn derivatives of the dianions $\mathbf{L}^{2-}$ (**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 coformation of **11Se** and **11S**[19] (Chart 3).

Chart 3



11Se **11S**

The ^{31}P NMR spectrum of **12aSe** exhibits a singlet at −77.0 ppm with two sets of satellites, ^1J(P,Se) = 500 Hz and ^2J(P,Sn) = 42 Hz. Similar to the observations for the tellurium analogue **12a**, the ^{119}Sn NMR spectrum of **12aSe** shows a triplet at 69.8 ppm (^1J(Sn,Se) = 691 Hz) and the ^{77}Se NMR spectrum exhibits a doublet of doublets at 77.3 ppm, which arises from the ^1J(P,Se) and ^3J(P,Se) couplings (Table 1). For comparison, the ^{31}P NMR spectrum of the tin(IV) complex [Sn{(Se)C-(PPh_2Se)$_2$}$_2$] shows a singlet at 61.6 ppm with ^1J(P,Se) = 536 Hz[21] and the tin(II) complex [Sn{$NSeP^iPr_2$}$_2$-Se,Se′}$_2$] exhibits a singlet at 58.8 ppm with ^1J(P,Se) = 550 Hz and a ^2J(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 (^2J(P,Sn) = 35 Hz) and the ^{119}Sn NMR spectrum reveals a triplet at 66.4 ppm confirming the ^2J(P,Sn) values observed in the ^{31}P NMR spectrum (Table 1). 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 3, and structural parameters are compared in Table 2.

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** was characterized previously for Me_2SnL (E = S).[23] In that case, however, the isomer formed was predetermined by the synthetic approach, which involved oxidation of the two P^{III} centers in the N,N′-chelated complex [(^{t}BuNP^{III}(μ-N^{t}Bu)$_2$P^{III}N^{t}Bu)(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

DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043–3054

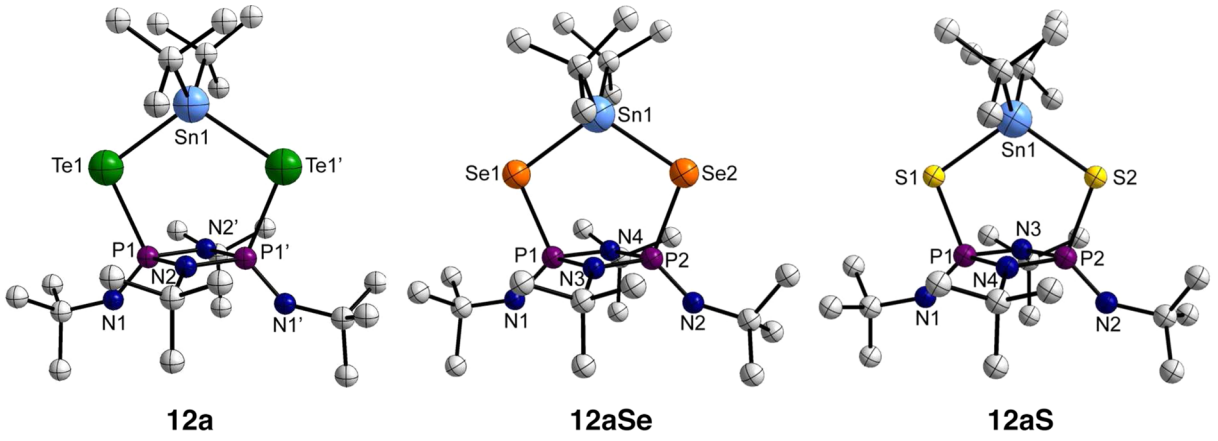


Figure 3. Molecular Structures of **12a**, **12aSe**, and **12aS**.

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.

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 $[Sn\{NSeP^iPr_2\}_2\text{-}Se,Se']_2]$.[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, for example, 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,[15b] we have now investigated the reactions of **1** and **2** with $RPCl_2$ (R = ^{t}Bu, Ad, $^iPr_2N$) 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%, 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 **L**P^{t}Bu (E = Se); the symmetrical Se,Se′-coordination to the ^{t}BuP group was confirmed by a well-modeled disordered crystal structure (see Supporting Information).

The NMR spectra of **13aSe** and **13bSe** exhibit patterns similar to those of the tellurium analogues **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 4). 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 ^2J(P,P) = 58 Hz, as expected for the chemically equivalent, but magnetically inequivalent, phosphorus atoms of the $P^V_2N_2$ ring. The large difference in ^1J(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

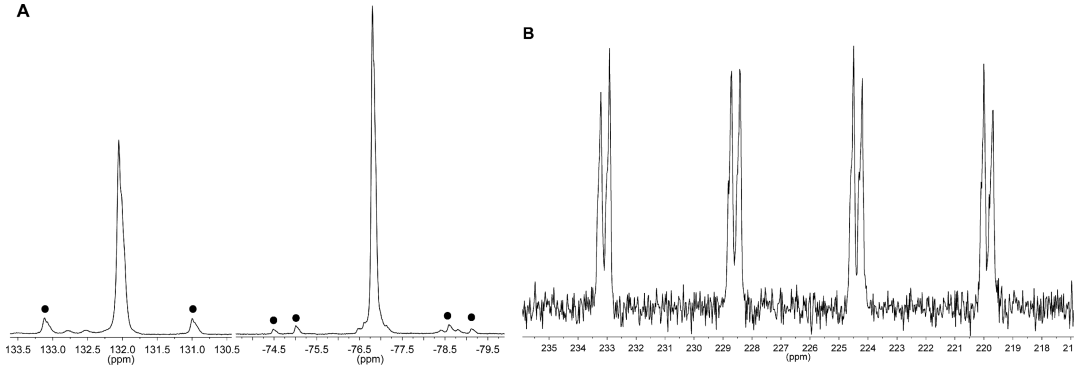


Figure 4. (**A**) ^{31}P NMR and (**B**) ^{77}Se NMR spectra of **13bSe**.

DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043–3054

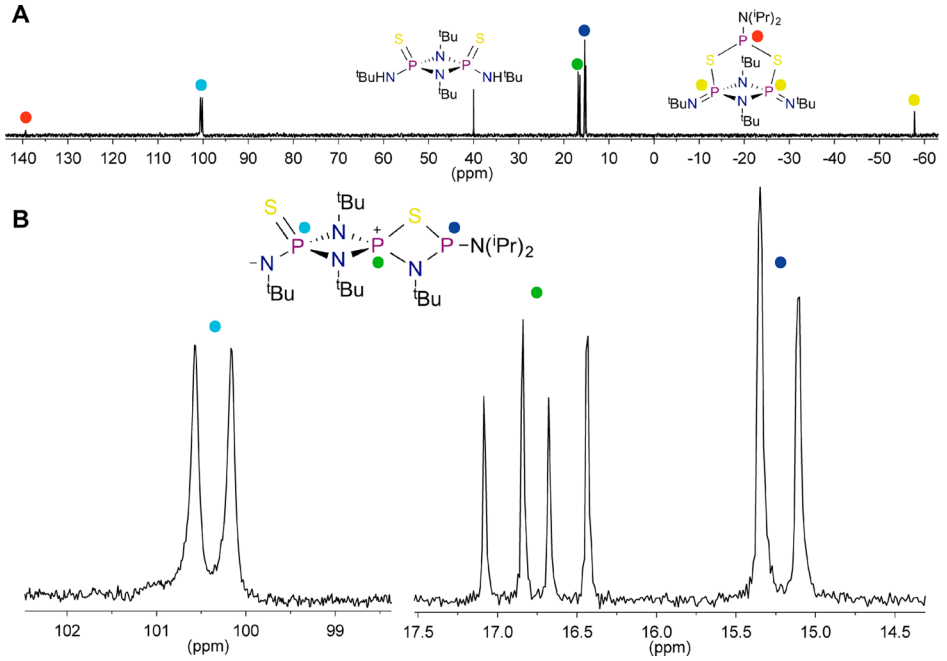


Figure 5. ^{31}P NMR spectrum of the reaction of **1** with $^{i}Pr_2NPCl_2$. (A) Complete spectrum. (B) Expanded spectrum for the N,S-chelated complex **14cS**.

aforementioned ^{1}J(P,Se) couplings and a ^{3}J(Se,P) coupling of 15.6 Hz (Figure 4).

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 electrospray ionization (EI) mass spectra and a detailed analysis of the ^{31}P NMR spectra. As a typical example, Figure 5A 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 analogues **13aSe** and **13bSe**.

The expanded ^{31}P NMR spectrum of **14cS** (Figure 5B) reveals three distinct phosphorus environments resulting from the N,S-chelation of the ligand 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 (^{2}J(P,P) = 44 Hz) for the terminal P^{V} center, (b) a doublet of doublets at 16.8 ppm ($^{2}J(P^{V},P^{V})$ = 45 Hz, $^{2}J(P^{V},P^{III})$ = 26 Hz) for the spirocyclic P^{V} environment, and (c) a doublet at 15.2 ppm ($^{2}J(P^{III},P^{V})$ = 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-} toward an RP^{2+} unit was unexpected; the only previous examples of N,S-chelation of the dianion L^{2-} (E = S) were found in the tetrahydrofuran (THF)-solvated dilithium[10] and dimethylaluminum derivatives.[11] 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.

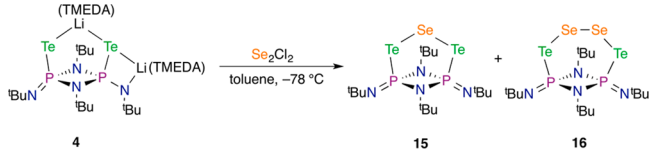
Table 3. ^{31}P NMR Chemical Shifts and ^{2}J(P,P) for 14a−c[a]

compound	**14aS**	**14bS**	**14cS**
$\delta(^{31}P)$ (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)
$^{2}J(P^{V},P^{III})$	27	27	26
$^{2}J(P^{V},P^{V})$	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 as 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,

Scheme 3



DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043−3054

^{125}Te) NMR spectra, the X-ray structure of a single crystal of **16** was determined.

The molecular structure of **16** is illustrated in Figure 6 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 **6**.

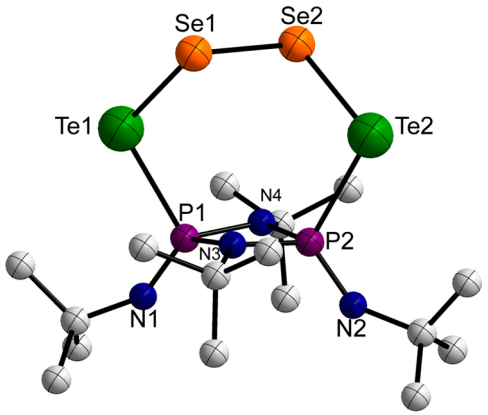


Figure 6. Molecular structure of **16**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Te1–Se1 2.4919(18), Te1–P1 2.483(3), Te2–Se2 2.5356(17), Te2–P2 2.501(3), Se1–Se2 2.391(2), P1–N1 1.502(10), P1–N3 1.688(9), P1–N4 1.701(9); Se1–Te1–P1 104.20(8), Se2–Te2–P2 101.64(8), 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 7 compares the ring conformations of the two trichalcogenides **6**[15] and **15**[15a] and the two tetrachalcogenides **3**[12] and **16**, all of which are supported by *cyclo*-$P^V_2N_2$ scaffolds. The extent of puckering is clearly very similar for the two trichalcogenides and the two tetrachalcogenides.

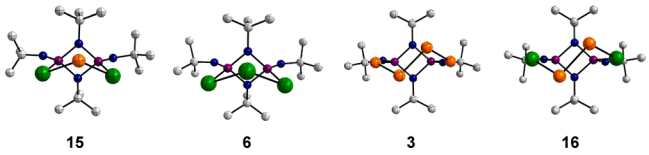


Figure 7. Conformations of *cyclo*-$P^V_2N_2$-supported polychalcogenides; Te atoms are shown in green, and Se atoms are in orange.

As indicated in Table 4, the previously reported NMR data for the tetraselenide **3**[12] and tritelluride **6**[15a] 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, ^1J(P,Te) = 1025 Hz and ^2J(P,Se) = 29 Hz, cf. −134.5 ppm and ^1J(P,Te) = 1029 Hz for **6**.[15a] The ^{77}Se NMR spectrum of **15** reveals a 1:2:1 triplet at 240.9 ppm (^2J(P,Se) = 29 Hz), and the ^{125}Te NMR spectrum shows a resonance at 870.3 ppm appearing as a doublet of doublets (^1J(P,Te) = 1025 Hz and ^3J(Te,P) = 34 Hz).

Table 4. Structural and NMR Parameters for *cyclo*-$P^V_2N_2$-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)
δ (^{31}P)	−121.0	−134.5	−50.8	−68.6
^1J(P,E)	1025	1029	524	1287
^2J(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 7 to compare analogous bond lengths in the tri- and tetrachalcogenide systems.

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 ^1J(P,Te) value of 1287 Hz for **16** is substantially larger than the value of 1029 Hz found for the tritelluride **6**,[15a] 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 (^2J(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(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 (^1J(P,Te) = 1289 Hz and ^3J(P,Te) = 42 Hz).

The homoleptic tellurium(II) complex $[Te\{^tBu(H)N(Se)\text{-}P^V(\mu\text{-}N^tBu)_2P^V(Se)^tBuN\text{-}N,Se\}_2]$ (**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.

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 $^tBu_2Sn$ 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 L^{2-} (E = Se) is considerably more hydrolytically sensitive than the tellurium analogue; however, the complete series (**L**)Sn^{t}Bu$_2$ (E = S, Se, Te) could be isolated enabling a structural comparison to be

DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043–3054

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 × 0.10 × 0.01	0.17 × 0.07 × 0.02	0.10 × 0.10 × 0.10
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 (deg)	90.0000	87.895(6)	90.0000
β (deg)	99.789(4)	80.914(6)	94.354(7)
γ (deg)	90.0000	89.309(6)	90.0000
volume ($Å^3$)	2384.5(7)	1697.6(6)	2678.4(13)
space group	$P2_1$	$P\bar{1}$	$P21/c$
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 Kα) (cm^{-1})	2.459	2.703	5.025
No. of reflections measured	32 486	13 435	15 644
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

made. Organophosphorus(III) complexes of L^{2-} (E = S, Se) evinced a significant structural difference. As in the previous work with L^{2-} (E = Te),[15b] 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 L^{2-} (E = Se) with silver(I) or gold(I) halides produces macrocycles that incorporate the monoprotonated ligand HL^-.[39]

The comprehensive survey of the reactions of the *cyclo*-$P_2^VN_2$-supported dianion L^{2-} (E = Te) with p-block element halides in this and previous work[15] 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 semiconducting 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 (1 × 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 were used without further purification unless otherwise stated. The products were stored in a glovebox 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}, 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. Tetramethylsilane 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, and 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. The data for **9** and **12aSe** were collected using a Rigaku FRX RA generator, Dectris P200 detector and Oxford cryostream low-temperature device. All data were collected with Mo Kα radiation (λ = 0.710 73 Å) and corrected for Lorentz and polarization 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, while hydrogen

DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043−3054

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)	0.24 × 0.18 × 0.03	0.10 × 0.03 × 0.03	0.15 × 0.09 × 0.03
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 (deg)	90.0000	90.0000	90.0000
β (deg)	90.0000	90.608(4)	119.829(17)
γ (deg)	90.0000	90.0000	90.0000
volume ($Å^3$)	7031.2(8)	3336.2(13)	3359.2(14)
space group	*Fdd*2	*Cc*	$P2_1/c1$
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 Kα) (cm^{-1})	2.462	3.062	0.998
No. of reflections measured	14 705	21 515	25 146
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

atoms were refined using the riding model. All calculations were performed using CrystalStructure[52] crystallographic software package and SHELXL-97.[53] Despite several crystals being examined, thin plates of **10**, **12aS**, and **16** 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 Tables 5 and 6.

General Procedure for Metathetical Reactions. The reagent **1**,[10] **2**,[10] **4**,[14] or **5**[15a] (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 −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, 0.590 mmol) and $GaCl_3$ (53 mg, 0.30 mmol, 0.5 equiv) 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, ^1J(P,Te) = 1233 Hz), −133.3 (s, ^1J(P,Te) = 1130 Hz, ^3J(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 equiv) (179 mg, 0.590 mmol) and **4** (500 mg, 0.590 mmol) in toluene (20 mL). 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, ^2J(P,P) = 3.4 Hz), −41.2 (d, ^1J(P,Te) = 1251 Hz, ^2J(P,P) = 3.4 Hz), −135.1 (s, ^1J(P,Te) = 1113 Hz, ^2J(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). Anal. 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, 0.590 mmol) and Ph_2GeCl_2 (176 mg, 0.590 mmol) in toluene (20 mL). Yield of red crystals = 39%. ^1H 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, ^1J(P,Te) = 1103 Hz, ^2J(P,P) = 20 Hz). ^{125}Te NMR (85.24 MHz, [D_8]toluene): δ = 162.4 (^1J(P,Te) = 1105 Hz, ^3J(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. Anal. 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, 0.600 mmol, 1 equiv) and Ph_2GeCl_2 (178 mg, 0.600 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, 0.590 mmol) and **4** (500 mg, 0.590 mmol) in toluene (25 mL). Yellow crystals of **12a** isolated in 34% yield. ^1H 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^+-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, 0.590 mmol) and **1** (500 mg, 0.590 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): 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 =

DOI: 10.1021/acs.inorgchem.5b00161
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−141.1 (s, ^{1}J(P,Te) = 1140 Hz, ^{2}J(P,Sn) = 51 Hz). ^{119}Sn NMR (100.75 MHz, [D$_8$]toluene): δ = −84.7 (^{2}J(P,Sn) = 52 Hz, ^{1}J(Sn,Te) = 3288 Hz). ^{125}Te NMR (85.24 MHz, [D$_8$]toluene): δ = 6.7 (dd, ^{1}J(P,Te) = 1137 Hz, ^{3}J(P,Te) = 26 Hz).

Synthesis of ***12c***. Reagents: Ph_2SnCl_2 (203 mg, 0.590 mmol) and **4** (500 mg, 0.590 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, ^{1}J(P,Te) = 1102 Hz, ^{2}J(P,Sn) = 60 Hz, ^{2}J(P,P) = 6.5 Hz). ^{119}Sn NMR (100.75 MHz, [D$_8$]toluene): δ = −156.1 (^{2}J(P,Sn) = 62 Hz). ^{125}Te NMR (85.24 MHz, [D$_8$]toluene): δ = 23.4 (^{1}J(P,Te) = 1102 Hz, ^{3}J(P,Te) = 26 Hz).

Synthesis of ***12aSe***. Reagents: **2** (500 mg, 0.600 mmol) and $^{t}Bu_2SnCl_2$ (182 mg, 0.600 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, ^{1}J(P,Se) = 500.0 Hz, ^{2}J(P,Sn) = 42.3 Hz). ^{119}Sn NMR (100.75 MHz, [D$_8$]THF): δ = 69.8 (^{2}J(P,Sn) = 43.1 Hz, ^{1}J(Sn,Se) = 690.5 Hz). ^{77}Se NMR (51.52 MHz, [D$_8$]THF): δ = 77.3 (^{1}J(P,Se) = 498.2 Hz, ^{3}J(P,Se) = 12.0 Hz). EIMS, *m*/*z*: 723.1 (M$^+$−CH$_3$), calcd 723.1. Anal. 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, 0.680 mmol) and $^{t}Bu_2SnCl_2$ (207 mg, 0.680 mmol) 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, ^{2}J(P,Sn) = 35.2 Hz). ^{119}Sn NMR (100.75 MHz, [D$_8$]THF): δ = 66.4 (^{2}J(P,Sn) = 33.9 Hz). EIMS, *m*/*z*: 629.2 (M$^+$−CH$_3$), calcd 629.2. Anal. 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 $^{t}BuPCl_2$ (95 mg, 0.60 mmol) and **2** (500 mg, 0.590 mmol) in toluene (25 mL). Estimated yields from the ^{31}P NMR spectrum were **13aSe** (40%) and **11Se** (20%), which cocrystallized as colorless crystals.[37] NMR data for **13aSe**: ^{31}P NMR (109.37 MHz, [D$_8$]THF): δ = 139.5 (^{1}J(P,Se) = 234.1 Hz), −78.0 (^{1}J(P,Se) = 447.3 Hz, ^{2}J(P,P) = 58.0 Hz). ^{77}Se NMR (51.52 MHz, [D$_8$]THF): δ = 256.0 (^{1}J(Se,P^{V}) = 450.8 Hz, ^{1}J(Se,P^{III}) = 234.4 Hz, ^{3}J(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. Anal. 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, 0.600 mmol) and **2** (500 mg, 0.590 mmol) in toluene (25 mL). Yield of **13bSe** estimated from integration of the ^{31}P NMR spectrum ca. 79% **13bSe** formed colorless cocrystals with the byproduct **11Se**.[37] NMR data for **13bSe**: ^{31}P NMR (109.37 MHz, [D$_8$]THF): δ = 132.0 (^{1}J(P,Se) = 231.8 Hz), −76.8 (^{1}J(P,Se) = 449.5 Hz, ^{2}J(P,P) = 58.0 Hz). ^{77}Se NMR (51.52 MHz, [D$_8$]THF): δ = 226.5 (ddd, ^{1}J(Se,P^{V}) = 449.0 Hz, ^{1}J(Se,P^{III}) = 232.1 Hz, ^{3}J(Se,P) = 15.6 Hz).

Synthesis of ***13aS*** *and* ***14aS***. Reagents: **1** (500 mg, 0.680 mmol) and $^{t}BuPCl_2$ (107 mg, 0.680 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_6D_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_6D_6-capillary): δ = 116.9 (d, ^{2}J(P,P) = 42.3 Hz), 17.2 (dd, ^{2}J(P,P) = 42.5 Hz, ^{2}J(P,P) = 27.1 Hz), 14.4 (d, ^{2}J(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, 0.680 mmol) and $AdPCl_2$ (159 mg, 0.680 mmol, 1 equiv) in toluene (25 mL). Estimated yields 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_6D_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, ^{2}J(P,P) = 43.4 Hz), 17.3 (dd, ^{2}J(P,P) = 43.4 Hz, ^{2}J(P,P) = 26.9 Hz), 14.6 (d, ^{2}J(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, 0.680 mmol) and (^{i}Pr)$_2$NPCl$_2$ (159 mg, 0.680 mmol) in toluene (25 mL). Estimated yields 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, ^{2}J(P,P) = 4.3 Hz), −57.7 (d, ^{2}J(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, ^{2}J(P,P) = 44.4 Hz), 16.8 (dd, ^{2}J(P,P) = 44.6 Hz, ^{2}J(P,P) = 25.9 Hz), 15.2 (d, ^{2}J(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, 0.590 mmol) and **1** (500 mg, 0.590 mmol) in toluene (25 mL). NMR data for the major product **15**: ^{31}P NMR (109.37 MHz, [D$_8$]toluene): δ = −121.0 (^{1}J(P,^{125}Te) = 1025 Hz; ^{2}J(P,^{77}Se) = 29 Hz; ^{2}J(P,P) = 23 Hz). ^{77}Se NMR (51.52 MHz, [D$_8$]toluene): δ = 240.9 (t, ^{2}J(P,^{77}Se) = 30 Hz) ppm. ^{125}Te NMR (85.24 MHz, [D$_8$]toluene): δ [ppm] = 870.3 (dd, ^{1}J(P,^{125}Te) = 1025 Hz; ^{3}J(P,^{125}Te) = 34 Hz). NMR data for **16**: ^{31}P NMR (109.37 MHz, [D$_8$]toluene): δ = −68.6 (^{1}J(P,^{125}Te) = 1287 Hz; ^{2}J(P,P) = 47 Hz; ^{1}J(P,^{77}Se) = 14 Hz) ppm). ^{77}Se NMR (51.52 MHz, [D$_8$]toluene): δ = 465.6 (pseudo-t, ^{2}J(P,^{77}Se = 14 Hz). ^{125}Te NMR (85.24 MHz, [D$_8$]toluene): δ = 711.6 (dd, ^{1}J(P,^{125}Te) = 1289 Hz; ^{3}J(P,^{125}Te) = 42 Hz). A few red crystals of **16** were isolated;. Anal. 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 byproduct in the ^{31}P and ^{125}Te NMR spectra.[15a] ^{31}P NMR (109.37 MHz, [D$_8$]toluene): δ = −134.6 (^{1}J(P,^{125}Te) = 1028 Hz; ^{2}J(P,P) = 31 Hz). ^{125}Te NMR (126.43 MHz, [D$_8$]toluene): δ = 442.8 (dd, ^{1}J(P,Te) = 1031 Hz, ^{3}J(P,Te) = 41 Hz), 361.9 (t, ^{1}J(^{125}Te,^{123}Te) = 1254 Hz, ^{2}J(P,Te) = 35 Hz).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format for compounds **9**, **10**, **12a**, **13aSe**, **12b**, **12c**, **16**, and **18Se**. Synthesis of **18**, **18Se**, **18S**, and **19**. X-ray crystallography, featuring structural drawings of **13aSe** and **18Se**. Additional references. 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.

■ ACKNOWLEDGMENTS

The authors are grateful to the EPSRC, the EPSRC National Mass Spectrometry Service Centre (NMSSC) Swansea, the School of Chemistry St. Andrews, EaStCHEM, and NSERC Canada for financial support.

■ REFERENCES

(1) Chivers, T.; Manners, I. *Inorganic Rings and Polymers of the p-Block Elements: From Fundamentals to Applications;* RSC Publishing: Cambridge, U.K., 2009; pp 231−236.

(2) For reviews, see (a) Balakrishna, M. S.; Eisler, D. J.; Chivers, T. *Chem. Soc. Rev.* **2007**, *36*, 650. (b) Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203. (c) Balakrishna, M. S.; Reddy, V. S.; Krishnamurthy, S. S.; Nixon, J. F.; Burckett St Laurent, J. C. T. R. *Coord. Chem. Rev.* **1994**, *129*, 1. (d) Keat, R. *Top. Curr. Chem.* **1982**, *102*, 89.

(3) For a review, see Calera, S. G.; Wright, D. S. *Dalton Trans.* **2010**, *39*, 5055 and references cited therein.

(4) Balakrishna, M. S. *J. Organomet. Chem.* **2010**, *695*, 925.

DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043−3054

(5) Siddiqui, M. M.; Mobin, S. M.; Senkovska, I.; Kaskel, S.; Balakrishna, M. S. *Chem. Commun.* **2014**, *50*, 12273.
(6) Garcia, F.; Goodman, J. M.; Kowenicki, R. A.; Kuzu, I.; McPartlin, M.; Silva, M. A.; Riera, L.; Woods, A. D.; Wright, D. S. *Chem.—Eur. J.* **2004**, *10*, 6066.
(7) Chandrasekharan, P.; Mague, J. T.; Balakrishna, M. S. *Dalton Trans.* **2009**, 5478.
(8) Briand, G. G.; Chivers, T.; Krahn, M. *Coord. Chem. Rev.* **2002**, *233*−*234*, 237 and references cited therein.
(9) Chivers, T.; Krahn, M.; Parvez, M. *Chem. Commun.* **2000**, 463.
(10) Chivers, T.; Krahn, M.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 2547.
(11) Lief, G. R.; Carrow, C. J.; Stahl, L. *Organometallics* **2001**, *20*, 1629.
(12) Nordheider, A.; Chivers, T.; Thirumoorthi, R.; Vargas-Baca, I.; Woollins, J. D. *Chem. Commun.* **2012**, *48*, 6346.
(13) For a review of main group derivatives of the P^{III}/P^{III} dianion $[^tBuNP^{III}(\mu\text{-}N^tBu)]_2^{2-}$ see Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203.
(14) Briand, G. G.; Chivers, T.; Parvez, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3468.
(15) (a) Nordheider, A.; Chivers, T.; Thirumoorthi, R.; Athukorala Arachchige, K. S.; Slawin, A. M. Z.; Woollins, J. D.; Vargas-Baca, I. *Dalton Trans.* **2013**, *42*, 3291. (b) Nordheider, A.; Chivers, T.; Schön, O.; Karaghiosoff, K.; Athukorala Arachchige, K. S.; Slawin, A. M. Z.; Woollins, J. D. *Chem.—Eur. J.* **2014**, *20*, 704.
(16) Hinz, A.; Kuzora, R.; Rosenthal, U.; Schulz, A.; Villinger, A. *Chem.—Eur. J.* **2014**, *45*, 14659.
(17) The lability of the P−Te bond, especially in the presence of organolithium reagents, is common feature of phosphorus(V)-tellurium chemistry that gives rise to low yields. For recent examples, see (a) Daniliuc, C.; Druckenbrodt, C.; Hrib, C. G.; Ruthe, F.; Blaschette, A.; Jones, P. G.; du Mont, W.-W. *Chem. Commun.* **2007**, 2060. (b) Ritch, J. S.; Chivers, T. *Dalton Trans.* **2008**, 957. (c) Konu, J.; Tuononen, H. M.; Chivers, T. *Inorg. Chem.* **2009**, *48*, 11788. (d) Elder, P. J. W.; Chivers, T.; Thirumoorthi, R. *Eur. J. Inorg. Chem.* **2013**, 2867. (e) Jeremias, L.; Babiak, M.; Kubát, V.; Calhorda, M. J.; Trávníček, Z.; Novosad, J. *RSC Adv.* **2014**, *4*, 15428.
(18) Copsey, M. C.; Chivers, T. *Chem. Commun.* **2005**, 4938.
(19) In a previous investigation the formation of **11Se** ($\delta(^{31}P)$ = 26.7 ppm, ^1J(P,Se) = 880 Hz) and **11S** ($\delta(^{31}P)$ = 40.0 ppm) was proposed to be the result of a radical process. Semi-empirical MO calculations of the model system $[Me(H)N(S)P^V(\mu\text{-}NMe)_2P^V(S)NMe]^\bullet$ indicated a nitrogen-based SOMO (spin population at nitrogen = 0.957) in preference to the formation of a sulfur-based radical. Such nitrogen-based radicals will abstract hydrogen atoms from the solvent to form **11S** (or **11Se**). This prediction was supported by the detection of a N-centered radical intermediate by EPR spectra in the reaction of $Li[^tBuN(S)P^V(\mu\text{-}N^tBu)_2P^V(S)N(H)^tBu]$ with $TeCl_4$, which produces **11S** as one of the products. Briand, G. G.; Chivers, T.; Schatte, G. *Inorg. Chem.* **2002**, *41*, 1958.
(20) Ramaker, G.; Saak, W.; Haase, D.; Weidenbruch, M. *Organometallics* **2003**, *22*, 5212.
(21) Konu, J.; Chivers, T. *Chem. Commun.* **2010**, *46*, 1431.
(22) Rufino-Felipe, E.; Osorio, E.; Merino, G.; Muñoz-Hernández, M.-A. *Dalton Trans.* **2013**, *42*, 11180.
(23) Linti, G.; Nöth, H.; Schneider, E.; Storch, W. *Chem. Ber.* **1993**, *126*, 611.
(24) (a) Puff, H.; Breuer, B.; Schuh, W.; Sievers, R.; Zimmer, R. *J. Organomet. Chem.* **1987**, *332*, 279. (b) You, Z.; Bergunde, J.; Gerke, B.; Pöttgen, R.; Dehnen, S. *Inorg. Chem.* **2014**, *53*, 12512.
(25) Bhattacharyya, P.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2001**, 300.
(26) Hua, G.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *Angew. Chem., Int. Ed.* **2008**, *47*, 2857.
(27) Silvestru, C.; Haiduc, I.; Klima, S.; Thewalt, U.; Gielen, M.; Zuckerman, J. J. *J. Organomet. Chem.* **1987**, *327*, 181.
(28) Casas, J. S.; Castiñeiras, A.; Rodríguez-Argüelles, M. C.; Sánchez, A.; Sordo, J.; Vázquez-López, A.; Vázquez-López, E. M. *J. Chem. Soc., Dalton Trans.* **2000**, 4056.
(29) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Mullins, F. P. *Inorg. Chem.* **1981**, *20*, 2172.
(30) Sladky, F.; Bildstein, B.; Rieker, C.; Gieren, A.; Betz, H.; Hübner, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1800.
(31) Collins, M. J.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1987**, *26*, 1476.
(32) Ogawa, S.; Yoshimura, S.; Nagahora, N.; Kawai, Y.; Mikata, Y.; Sato, R. *Chem. Commun.* **2002**, 1918.
(33) An inverse correlation between d(P−Te) and ^1J(P,Te) values for *cyclo*-P_2N_2 derivatives with a terminal Te substituent has previously been discussed. Briand, G. G.; Chivers, T.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2003**, *42*, 525.
(34) The tellurium(II) complex $[Te\{^tBu(H)N(Se)P^V(\mu\text{-}N^tBu)_2P^V(Se)^tBuN\text{-}N,Se\}_2]$ was previously prepared by the reaction of 2 equiv of the monoanion HL^- (E = Se) with $TeCl_4$, and the X-ray structure revealed bis-N,Se chelation. Briand, G. G.; Chivers, T.; Schatte, G. *Inorg. Chem.* **2002**, *41*, 1958.
(35) In the current work the structure of the minor byproduct $[Te\{^tBu(H)N(Se)P^V(\mu\text{-}N^tBu)_2P^V(Se)^tBuN\text{-}N,Se\}_2]$ was determined, and the structural parameters were similar to the reported values.[34] The formation of P^V−Se linkages in this reaction indicates significant decomposition of the ditelluro ligand 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 performed. Although the solution ^{31}P NMR spectra were consistent with the formation of Te,Te′-chelated complexes of L^{2-}, the lability of these derivatives (extrusion of Te) precluded further characterization (see Supporting Information).
(37) (a) Separation of **10Se** from **11Se** ($\delta(^{31}P)$ = 26.7 ppm, ^1J(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..
(38) Hill, T. G.; Haltiwanger, R. C.; Thompson, M. L.; Katz, S. A.; Norman, A. D. *Inorg. Chem.* **1994**, *33*, 1770.
(39) Nordheider, A.; Hüll, K.; Athukorala Arachchige, K. S.; Slawin, A. M. Z.; Woollins, J. D.; Thirumoorthi, R.; Chivers, T. *Dalton Trans.* **2015**, DOI: 10.1039/c5dt00159e.
(40) For a review, see Chivers, T.; Ritch, J. R.; Robertson, S. D.; Konu, J.; Tuononen, H. M. *Acc. Chem. Res.* **2010**, *43*, 1053.
(41) Group 10: (a) Levesanos, N.; Robertson, S. D.; Maganas, D.; Raptopoulou, C. P.; Terzis, A.; Kyritsis, P.; Chivers, T. *Inorg. Chem.* **2008**, *47*, 2949. (b) Robertson, S. D.; Ritch, J. S.; Chivers, T. *Dalton Trans.* **2009**, 8582.
(42) Group 11: (a) Copsey, M. C.; Panneerselvam, A.; Afzaal, M.; Chivers, T.; O'Brien, P. *Dalton Trans.* **2007**, 1528. (b) Eisler, D. J.; Robertson, S. D.; Chivers, T. *Can. J. Chem.* **2009**, *87*, 39.
(43) Group 12: (a) Chivers, T.; Eisler, D. J.; Ritch, J. S. *Dalton Trans.* **2005**, 2675. (b) Garje, S. S.; Ritch, J. S.; Eisler, D. J.; Afzaal, M.; O'Brien, P.; Chivers, T. *J. Mater. Chem.* **2006**, *16*, 966.
(44) Lanthanides and actinides: (a) Gaunt, A. J.; Scott, B. L.; Neu, M. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 1638. (b) Ingram, K. I. M.; Kaltsoyannis, N.; Gaunt, A. J.; Neu, M. P. *J. Alloys Compd.* **2007**, *444*−*445*, 369. (c) Gaunt, A. J.; Reilly, S. D.; Enriquez, A. E.; Scott, B. L.; Ibers, J. A.; Sekar, P.; Ingram, K. I. M.; Kaltsoyannis, N.; Neu, M. P. *Inorg. Chem.* **2008**, *47*, 29. (d) Ingram, K. I. M.; Tassell, M. J.; Gaunt, A. J.; Kaltsoyannis, N. *Inorg. Chem.* **2008**, *47*, 7824.
(45) Ritch, J. S.; Afzaal, M.; Chivers, T.; O'Brien, P. *Chem. Soc. Rev.* **2007**, *36*, 1622.
(46) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 6th ed.; Butterworth-Heinemann: Oxford, U.K., 2009.
(47) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M. *Organometallics* **2010**, *29*, 2176.
(48) (a) Fuller, A. L.; Scott-Hayward, L. A. S.; Li, Y.; Bühl, M.; Slawin, A. M. Z.; Woollins, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 5799−5802. (b) *CrystalClear 2.0*; Rigaku Corporation: Texas, U.S., 2012. (c) Pflugrath, J. W. *Acta Crystallogr.* **1999**, *D55*, 1718.

DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043−3054

(49) Altomare, A.; Burla, M.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.
(50) Beurskens, P. T.; Admiraal, G.; Behm, H.; Beurskens, G.; Smits, J. M. M.; Smykalla, C. *Z. Kristallogr.* **1991**, *Suppl. 4*, 99.
(51) Beuerskens, P. T.; Admiraal, G.; Beuerskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 program system;* Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1999.
(52) (a) *CrystalStructure 3.8.1:* Crystal Structure Analysis Package; Rigaku and Rigaku/MSC, The Woodlands, TX, 2000−2006. (b) *CrystalStructure 4.0:* Crystal Structure Analysis Package; Rigaku Corporation: Tokyo, Japan, 2000−2010; pp 196−8666.
(53) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

DOI: 10.1021/acs.inorgchem.5b00161
Inorg. Chem. 2015, 54, 3043−3054