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Article

Experimental and Theoretical Investigations of the Redox Behavior of the Heterodichalcogenido Ligands $[(EP^iPr_2)(TeP^iPr_2)N]^-$ (E = S, Se): Cyclic Cations and Acyclic Dichalcogenide Dimers

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The two-electron oxidation of the lithium salts of the heterodichalcogenidoimidodiphosphinate anions $[(EP^iPr_2)(TeP^iPr_2)N]^-$ (**1a**, E = S; **1b**, E = Se) with iodine yields cyclic cations $[(EP^iPr_2)(TeP^iPr_2)N]^+$ as their iodide salts $[(SP^iPr_2)(TeP^iPr_2)N]I$ (**2a**) and $[(SeP^iPr_2)(TeP^iPr_2)N]I$ (**2b**). The five-membered rings in **2a** and **2b** both display an elongated E−Te bond as a consequence of an interaction between tellurium and the iodide anion. One-electron reduction of **2a** and **2b** with cobaltocene produces the neutral dimers $(EP^iPr_2NP^iPr_2Te-)_2$ (**3a**, E = S; **3b**, E = Se), which are connected exclusively through a Te−Te bond. Two-electron reduction of **2a** and **2b** with 2 equiv of cobaltocene regenerates the corresponding dichalcogenidoimidodiphosphinate anions as ion-separated cobaltocenium salts $Cp_2Co[(EP^iPr_2)(TeP^iPr_2)N]$ (**4a**, E = S; **4b**, E = Se). The ditellurido analogue $Cp_2Co[(TeP^iPr_2)_2N]$ (**4c**) has been prepared in the same manner for comparison. Density functional theory calculations reveal that the preferential interaction of the iodide anion with tellurium is determined by the polarization of the lowest unoccupied molecular orbital [σ^*(E−Te)] of the cations in **2a** and **2b** toward tellurium and that the formation of the dimers **3a** and **3b** with a central Te−Te linkage is energetically more favorable than the structural isomers with either E−Te or E−E bonds. Compounds **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, and **4c** have been characterized in solution by multinuclear NMR spectroscopy and in the solid state by X-ray crystallography.

Introduction

The chemistry of the dichalcogenidoimidodiphosphinates (**I**) has been studied comprehensively since the 1960s.[1] Such compounds are of great interest because they represent inorganic analogues of the common organic chelating ligand acetylacetonate (acac), although the inorganic backbone displays much greater flexibility than the organic counterpart whose planarity is imposed by an array of sp^2-hybridized centers. A considerable variety of different dichalcogenidoimidodiphosphinates are known as a consequence of changing the chalcogens and/or the organic groups bound to phosphorus. The extensive number of O-, S-, and Se-containing derivatives and their complexation chemistry with a number of main-group and transition metals have been comprehensively reviewed.[2−4] Several of these homoleptic metal complexes were shown by O'Brien et al. to be suitable single-source precursors for the generation of semiconducting thin films[5−12] or quantum dots[13] of metal selenides via chemical vapor deposition processes. After a brief hiatus,

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(1) Schmidpeter, A.; Groeger, H. *Z. Anorg. Allg. Chem.* **1966**, *345*, 106.

(2) Haiduc, I. *Compr. Coord. Chem. II* **2003**, 323.

(3) Silvestru, C.; Drake, J. E. *Coord. Chem. Rev.* **2001**, *223*, 117.

(4) Ly, T. Q.; Woollins, J. D. *Coord. Chem. Rev.* **1998**, *176*, 451.

(5) Afzaal, M.; Aucott, S. M.; Crouch, D.; O'Brien, P.; Woollins, J. D.; Park, J.-H. *Chem. Vap. Deposition* **2002**, *8*, 187.

(6) Park, J.-H.; Afzaal, M.; Helliwell, M.; Malik, M. A.; O'Brien, P.; Raftery, J. *Chem. Mater.* **2003**, *15*, 4205.

(7) Crouch, D.; Helliwell, M.; O'Brien, P.; Waters, J.; Williams, D. J. *Dalton Trans.* **2003**, 1500.

(8) Afzaal, M.; Crouch, D.; Malik, M. A.; Motevalli, M.; O'Brien, P.; Park, J.-H. *J. Mater. Chem.* **2003**, *13*, 639.

(9) Crouch, D. J.; Hatton, P. M.; Helliwell, M.; O'Brien, P.; Raftery, J. *Dalton Trans.* **2003**, 2761.

(10) Afzaal, M.; Crouch, D. J.; O'Brien, P.; Raftery, J.; Skabara, P. J.; White, A. J. P.; Williams, D. J. *J. Mater. Chem.* **2004**, *14*, 233.

(11) Afzaal, M.; Ellwood, K.; Pickett, N. L.; O'Brien, P.; Raftery, J.; Waters, J. *J. Mater. Chem.* **2004**, *14*, 1310.

(12) Waters, J.; Crouch, D.; Raftery, J.; O'Brien, P. *Chem. Mater.* **2004**, *16*, 3289.

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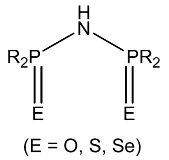
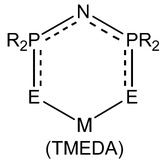
interest in this class of ligand was reinvigorated by the discovery of the first Te-containing examples, which were obtained as alkali metal salts (**1**, E = Te, M = Na, R = Ph,[15] ^{i}Pr[15]). The coordination chemistry of the ditellurido ligand[15] was propelled by the discovery of some alternative bonding modes with respect to the lighter chalcogen derivatives.[16−18] In addition, semiconducting thin films of a variety of metal tellurides were generated by using homoleptic complexes as single-source precursors.[19−21]



(I)



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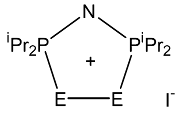

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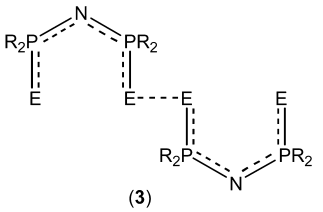

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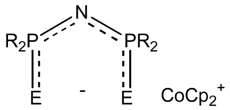

(**4**)

Subsequently, a comprehensive study of the redox chemistry of the dichalcogenidoimidodiphosphinate system was carried out,[22] which resulted in the completion of the sequence of anionic, neutral, and cationic species (−1/0/+1). The cationic derivatives were synthesized as iodide salts [(EP^{i}Pr$_2$)$_2$N]I (**2**, E = Se, Te) by the two-electron oxidation of the corresponding anions with iodine.[23] These five-membered, 6π-electron rings were found to be considerably puckered, in contrast to chalcogen−nitrogen cations such as $[E_3N_2]^{2+}$ (E = S, Se) and $[S_2N_3]^+$, which are planar.[24,25] A structural analysis revealed that these novel ring systems contain elongated chalcogen−chalcogen bonds. On the basis of density functional theory (DFT) calculations, the elongation was attributed to donation of electron density from a lone pair on the iodide anion into the Te−Te σ^* orbital (lowest unoccupied molecular orbital, LUMO) of the cation. Such a lengthening of the chalcogen−chalcogen bond was not evident in ion-separated salts prepared by exchanging I^- for SbF_6^-.[26]

Furthermore, one-electron oxidation of the anions in **1** (E = S, Se, Te) generated neutral dimers (**3**, R = ^{i}Pr, E = Se, Te; R = ^{t}Bu, E = S, Se),[27] formally involving the association of two [E^{i}Pr$_2$PN^{i}Pr$_2$PE]$^\bullet$ radicals through E−E bonds that are elongated with respect to those in the corresponding organic dichalcogenides PhEEPh.[28−30] Calculations showed that the singly occupied molecular orbital (SOMO) of the radicals [TeR$_2$PNR$_2$PTe]$^\bullet$ is based on the two tellurium centers and involves a linear combination of tellurium p orbitals.[22] The calculated energy of dimerization for the methyl-substituted tellurium radical was −80 kJ mol^{-1}; cf. *D*(Te−Te) = 138 kJ mol^{-1} in PhTeTePh, consistent with a significantly weakened Te−Te bonding interaction in **3** (E = Te).

Recently, we described the synthesis of the first heterodichalcogenidoimidodiphosphinate ligands containing tellurium [(EP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N]$^-$ (E = S, Se) as their TMEDA-solvated lithium derivatives.[31] In this paper, we report the results of the investigations of the oxidation of these mixed chalcogen anions with iodine in order to determine (a) the effect of this asymmetry on the cation−iodide interaction of the resulting species [(EP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N]I (E = S, Se) and (b) the preferred chalcogen−chalcogen interaction in the neutral dimers (EP^{i}Pr$_2$NP^{i}Pr$_2$Te)$_2$ (E = S, Se). A series of ion-separated salts, Cp$_2$Co[(EP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N] (E = S, Se, Te), have been prepared in order to determine the structures of the dichalcogenidoimidodiphosphinate anions when they are not coordinated to a cation. Finally, DFT calculations were carried out in order to elucidate the reasons for the observed experimental results in the aforementioned investigations (a) and (b).

Experimental Section

General Procedures. All reactions and manipulations of products were performed under an argon atmosphere by using standard Schlenk techniques or an inert atmosphere glovebox. The reagents (TMEDA)Li[(EP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N] (E = S, Se)[31] and [(TeP^{i}Pr$_2$)$_2$N]I[23] were prepared by literature methods. The solvents *n*-hexane and tetrahydrofuran (THF) were dried by distillation over Na/benzophenone and stored over molecular sieves under an argon atmosphere prior to use. Iodine and cobaltocene were obtained from Aldrich and used as received.

Spectroscopic Methods. The ^{1}H, ^{13}C, ^{31}P, ^{77}Se, and ^{125}Te NMR spectra were obtained in THF-*d*$_8$ on a Bruker DRX 400 spectrometer operating at 399.592, 100.489, 161.765, 76.223, and 126.082 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to the solvent signal. ^{31}P, ^{77}Se, and ^{125}Te NMR spectra are referenced externally to an 85% solution of H$_3$PO$_4$ in D$_2$O, to a solution of (PhSe)$_2$ in CDCl$_3$, and to a solution of (PhTe)$_2$ in CDCl$_3$, respectively. Elemental analyses were performed by Analytical Services, Department of Chemistry, University of Calgary, Calgary, Canada.

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(13) Crouch, D. J.; O'Brien, P.; Malik, M. A.; Skabara, P. J.; Wright, S. P. *Chem. Commun.* **2003**, 1454.
(14) Briand, G. G.; Chivers, T.; Parvez, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3468.
(15) Chivers, T.; Eisler, D. J.; Ritch, J. S. *Dalton. Trans.* **2005**, 2675.
(16) Copsey, M. C.; Chivers, T. *Chem. Commun.* **2005**, 4938.
(17) Copsey, M. C.; Panneerselvam, A.; Afzaal, M.; Chivers, T.; O'Brien, P. *Dalton Trans.* **2007**, 1528.
(18) Eisler, D. J.; Robertson, S. D.; Chivers, T. *Can. J. Chem.* **2009**, *87*, doi: 10.1139-V08-074.
(19) Garje, S. S.; Ritch, J. S.; Eisler, D. J.; Afzaal, M.; O'Brien, P.; Chivers, T. *J. Mater. Chem.* **2006**, *16*, 966.
(20) Garje, S. S.; Copsey, M. C.; Afzaal, M.; O'Brien, P.; Chivers, T. *J. Mater. Chem.* **2006**, *16*, 4542.
(21) Garje, S. S.; Eisler, D. J.; Ritch, J. S.; Afzaal, M.; O'Brien, P.; Chivers, T. *J. Am. Chem. Soc.* **2006**, *128*, 3120.
(22) Chivers, T.; Eisler, D. J.; Ritch, J. S.; Tuononen, H. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4953.
(23) Konu, J.; Chivers, T.; Tuononen, H. M. *Chem. Commun.* **2006**, 1634.
(24) Awere, E. G.; Passmore, J.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1993**, 299.
(25) Herler, S.; Mayer, P.; Noth, H.; Schulz, A.; Suter, M.; Vogt, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3173.
(26) Konu, J.; Chivers, T.; Tuononen, H. M. *Inorg. Chem.* **2006**, *45*, 10678.
(27) Ritch, J. S.; Chivers, T.; Eisler, D. J.; Tuononen, H. M. *Chem.−Eur. J.* **2007**, *13*, 4643.
(28) Steudel, Y.; Wong, M. W.; Steudel, R. *Chem.−Eur. J.* **2005**, *11*, 1281.
(29) Jeske, J.; Martens-Von Saizen, A.; DuMont, W.-W.; Jones, P. G. *Acta Crystallogr., Sect. C* **1998**, *54*, 1873.
(30) Huang, S.-P.; Kantzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 5477.
(31) Robertson, S. D.; Chivers, T. *Dalton Trans.* **2008**, 1765.

Synthesis of [(SP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N]I (2a). A solution of I$_2$ (0.040 g, 0.158 mmol) in 15 mL of THF was cooled to −78 °C and added via a cannula to a −78 °C solution of (TMEDA)Li[(SP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N] (0.085 g, 0.160 mmol) in 25 mL of THF. This was allowed to stir for 1 h at −78 °C and was then warmed to room temperature with stirring. Solvent was evaporated under vacuum, and 50 mL of *n*-hexane was added. This solution was warmed and then filtered through a microfilter [0.45 μm poly(tetrafluoroethylene) (PTFE)]. The solution was reduced in volume to approximately 5 mL and left overnight at −35 °C to yield orange crystals of **2a** (0.086 g, 82%). Elem anal. Calcd (%) for C$_{12}$H$_{28}$P$_2$NSTeI: C, 26.95; H, 5.28; N, 2.62. Found: C, 27.06; H, 5.25; N, 2.67. ^{1}H NMR (THF-*d*$_8$, 23 °C): δ 2.74 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 2.28 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 1.42 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz,$^3J(^1\mathrm{H},^{31}\mathrm{P}) = 18$ Hz, 6H, CH(C*H*$_3$)$_2$], 1.37 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz,$^3J(^1\mathrm{H},^{31}\mathrm{P}) = 21$ Hz, 6H, CH(C*H*$_3$)$_2$], 1.26 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz,$^3J(^1\mathrm{H},^{31}\mathrm{P}) = 18$ Hz, 6H, CH(C*H*$_3$)$_2$], 1.25 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz,$^3J(^1\mathrm{H},^{31}\mathrm{P}) = 18$ Hz, 6H, CH(C*H*$_3$)$_2$]. ^{13}C{^{1}H} NMR: δ 30.31 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 48$ Hz, 1C, *C*H(CH$_3$)$_2$], 30.27 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 48$ Hz, 1C, *C*H(CH$_3$)$_2$], 28.86 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 65$ Hz, 1C, *C*H(CH$_3$)$_2$], 28.83 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 65$ Hz, 1C, *C*H(CH$_3$)$_2$], 17.45 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 2$ Hz, 2C, CH(*C*H$_3$)$_2$], 14.87 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 3$ Hz, 2C, CH(*C*H$_3$)$_2$], 14.65 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 3$ Hz, 2C, CH(*C*H$_3$)$_2$], 14.63 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 2$ Hz, 2C, CH(*C*H$_3$)$_2$]. ^{31}P{^{1}H} NMR: δ 89.9 [d, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 28$ Hz,$^2J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 36$ Hz], 59.2 [d, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 968$ Hz,$^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 28$ Hz]. ^{125}Te NMR: δ 574 [dd, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 968$ Hz, $^2J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 36$ Hz].

Synthesis of [(SeP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N]I (2b). The salt **2b** was obtained as orange crystals (0.066 g, 71%) from the reaction of (TMEDA)Li[(SeP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N] (0.092 g, 0.159 mmol) with I$_2$ (0.040 g, 0.158 mmol) by using a procedure identical with that described above for **2a**. Calcd for C$_{12}$H$_{28}$P$_2$NSeTeI: C, 24.77; H, 4.85; N, 2.41. Found: C, 25.05; H, 5.09; N, 2.75. ^{1}H NMR (THF-*d*$_8$, 23 °C): δ 2.79 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 2.34 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 1.42 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz,$^3J(^1\mathrm{H},^{31}\mathrm{P}) = 18$ Hz, 6H, CH(C*H*$_3$)$_2$], 1.36 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 20$ Hz, 6H, CH(C*H*$_3$)$_2$], 1.28 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 19$ Hz, 6H, CH(C*H*$_3$)$_2$], 1.27 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 18$ Hz, 6H, CH(C*H*$_3$)$_2$]. ^{13}C{^{1}H} NMR: δ 32.38 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 48$ Hz, 1C, *C*H(CH$_3$)$_2$], 32.34 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 48$ Hz, 1C, *C*H(CH$_3$)$_2$], 31.14 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 58$ Hz, 1C, *C*H(CH$_3$)$_2$], 31.10 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 58$ Hz, 1C, *C*H(CH$_3$)$_2$], 19.29 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 2$ Hz, 2C, CH(*C*H$_3$)$_2$], 17.01 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 2$ Hz, 2C, CH(*C*H$_3$)$_2$], 16.88 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 4$ Hz, 2C, CH(*C*H$_3$)$_2$], 16.69 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 3$ Hz, 2C, CH(*C*H$_3$)$_2$]. ^{31}P{^{1}H} NMR: δ 87.1 [d,$^1J(^{77}\mathrm{Se},^{31}\mathrm{P}) = 494$ Hz, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 30$ Hz,$^2J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 30$ Hz], 62.5 [d, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 967$ Hz,$^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 30$ Hz]. ^{77}Se NMR: δ −2 [dd, $^1J(^{77}\mathrm{Se},^{31}\mathrm{P}) = 494$ Hz, $^2J(^{77}\mathrm{Se},^{31}\mathrm{P}) = 9$ Hz]. ^{125}Te NMR: δ 504 [dd, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 967$ Hz, $^2J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 29$ Hz].

Synthesis of (SP^{i}Pr$_2$NP^{i}Pr$_2$Te−)$_2$ (3a). A solution of CoCp$_2$ (0.018 g, 0.095 mmol) in 15 mL of THF was added via a cannula to a solution of **2a** (0.050 g, 0.093 mmol) in 25 mL of THF at room temperature, and this was allowed to stir for 1 h. The resulting brown solution was filtered through a microfilter (0.45 μm PTFE) to remove the obvious fine precipitate, and the solvent was evaporated under vacuum. The remaining dark solid was redissolved in *n*-hexane and left overnight at −35 °C to yield dark crystals of **3a** (0.027 g, 71%). Elem anal. Calcd (%) for C$_{24}$H$_{56}$P$_4$N$_2$S$_2$Te$_2$: C, 35.33; H, 6.91; N, 3.43. Found: C, 35.24; H, 7.07; N, 3.29. ^{1}H NMR (THF-*d*$_8$, 23 °C): δ 2.42 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 4H, C*H*(CH$_3$)$_2$], 1.98 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 4H, C*H*(CH$_3$)$_2$], 1.39 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 18$ Hz, 12H, CH(C*H*$_3$)$_2$], 1.30 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 20$ Hz, 12H, CH(C*H*$_3$)$_2$], 1.15 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 17$ Hz, 12H, CH(C*H*$_3$)$_2$], 1.14 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 18$ Hz, 12H, CH(C*H*$_3$)$_2$]. ^{13}C{^{1}H} NMR: δ 33.71 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 52$ Hz, 2C, *C*H(CH$_3$)$_2$], 33.69 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 52$ Hz, 2C, *C*H(CH$_3$)$_2$], 32.54 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 70$ Hz, 2C, *C*H(CH$_3$)$_2$], 32.51 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 70$ Hz, 2C, *C*H(CH$_3$)$_2$], 20.08 [s, 4C, CH(*C*H$_3$)$_2$], 17.80 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 4$ Hz, 4C, CH(*C*H$_3$)$_2$], 17.51 [s, 4C, CH(*C*H$_3$)$_2$], 17.35 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 3$ Hz, 4C, CH(*C*H$_3$)$_2$]. ^{31}P{^{1}H} NMR: δ 78.2 [d, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 26$ Hz], 40.8 [d, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 1011$ Hz, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 26$ Hz]. ^{125}Te NMR: δ 60 [d, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 1002$ Hz].

Synthesis of (SeP^{i}Pr$_2$NP^{i}Pr$_2$Te−)$_2$ (3b). The compound **3b** was obtained as dark crystals (0.021 g, 54%) from the reaction of **2b** (0.050 g, 0.086 mmol) with CoCp$_2$ (0.016 g, 0.085 mmol) by using a procedure identical with that described above for **3a**. Elem anal. Calcd (%) for C$_{24}$H$_{56}$P$_4$N$_2$Se$_2$Te$_2$: C, 31.69; H, 6.20; N, 3.08. Found: C, 31.36; H, 6.40; N, 3.05. ^{1}H NMR (THF-*d*$_8$, 23 °C): δ 2.41 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 4H, C*H*(CH$_3$)$_2$], 2.05 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 8$ Hz, 4H, C*H*(CH$_3$)$_2$], 1.40 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 18$ Hz, 12H, CH(C*H*$_3$)$_2$], 1.30 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 20$ Hz, 12H, CH(C*H*$_3$)$_2$], 1.16 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 17$ Hz, 12H, CH(C*H*$_3$)$_2$], 1.15 [dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, $^3J(^1\mathrm{H},^{31}\mathrm{P}) = 18$ Hz, 12H, CH(C*H*$_3$)$_2$]. ^{13}C{^{1}H} NMR: δ 33.89 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 52$ Hz, 2C, *C*H(CH$_3$)$_2$], 33.86 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 52$ Hz, 2C, *C*H(CH$_3$)$_2$], 33.07 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 62$ Hz, 2C, *C*H(CH$_3$)$_2$], 33.04 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 62$ Hz, 2C, *C*H(CH$_3$)$_2$], 20.07 [s, 4C, CH(*C*H$_3$)$_2$], 17.99 [s, 4C, CH(*C*H$_3$)$_2$], 17.92 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 5$ Hz, 4C, CH(*C*H$_3$)$_2$], 17.48 [d,$^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 3$ Hz, 4C, CH(*C*H$_3$)$_2$]. ^{31}P{^{1}H} NMR: δ 71.8 [d, $^1J(^{77}\mathrm{Se},^{31}\mathrm{P}) = 639$ Hz, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 26$ Hz], 41.7 [d, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 1012$ Hz,$^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 26$ Hz]. ^{77}Se NMR: δ −177 [d, $^1J(^{77}\mathrm{Se},^{31}\mathrm{P}) = 658$ Hz]. ^{125}Te NMR: δ 72 [d, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 1009$ Hz].

Synthesis of Cp$_2$Co[(SP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N] (4a). A solution of CoCp$_2$ (0.036 g, 0.190 mmol) in 15 mL of THF was added via a cannula to a solution of **2a** (0.050 g, 0.093 mmol) in 25 mL of THF at room temperature, and this was allowed to stir for 1 h. The resulting brown solution was filtered through a microfilter (0.45 μm PTFE) to remove the obvious fine precipitate, and then the solution was reduced in volume to approximately 3 mL. A total of 7 mL of *n*-hexane was added, and this was left overnight at −35 °C to yield dark crystals of **4a** (0.042 g, 76%). Elem anal. Calcd (%) for C$_{22}$H$_{38}$P$_2$NSTeCo: C, 44.25; H, 6.41; N, 2.35. Found: C, 44.06; H, 6.21; N, 2.36. ^{1}H NMR (THF-*d*$_8$, 23 °C): δ 5.83 [br s, 10H, Co(C$_5$H$_5$)$_2$], 2.01 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 1.82 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 1.22−1.11 [m, 24H, CH(C*H*$_3$)$_2$]. ^{13}C{^{1}H} NMR: δ 35.56 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 54$ Hz, 1C, *C*H(CH$_3$)$_2$], 35.52 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 54$ Hz, 1C, *C*H(CH$_3$)$_2$], 33.31 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 75$ Hz, 1C, *C*H(CH$_3$)$_2$], 33.28 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 75$ Hz, 1C, *C*H(CH$_3$)$_2$], 19.62 [s, 2C, CH(*C*H$_3$)$_2$], 18.38 [s, 2C, CH(*C*H$_3$)$_2$], 18.30 [d, $^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 3$ Hz, 2C, CH(*C*H$_3$)$_2$], 18.16 [d, $^2J(^{13}\mathrm{C},^{31}\mathrm{P}) = 3$ Hz, 2C, CH(*C*H$_3$)$_2$]. ^{31}P{^{1}H} NMR: δ 64.3 [d, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 25$ Hz], 19.7 [d, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 1540$ Hz, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 25$ Hz]. ^{125}Te NMR: δ −670 [d, $^1J(^{125}\mathrm{Te},^{31}\mathrm{P}) = 1536$ Hz].

Synthesis of Cp$_2$Co[(SeP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N] (4b). The salt **4b** was obtained as dark crystals (0.038 g, 69%) from the reaction of **2b** (0.050 g, 0.086 mmol) with CoCp$_2$ (0.032 g, 0.170 mmol) by using a procedure identical with that described above for **4a**. Elem anal. Calcd (%) for C$_{22}$H$_{38}$P$_2$NSeTeCo: C, 41.03; H, 5.95; N, 2.18. Found: C, 40.91; H, 6.03; N, 2.30. ^{1}H NMR (THF-*d*$_8$, 23 °C): δ 5.56 [br s, 10H, Co(C$_5$H$_5$)$_2$], 2.04 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 1.87 [2 × sept, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7$ Hz, 2H, C*H*(CH$_3$)$_2$], 1.24−1.12 [m, 24H, CH(C*H*$_3$)$_2$]. ^{13}C{^{1}H} NMR: δ 35.49 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 55$ Hz, 1C, *C*H(CH$_3$)$_2$], 35.46 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 55$ Hz, 1C, *C*H(CH$_3$)$_2$], 34.09 [d, $^1J(^{13}\mathrm{C},^{31}\mathrm{P}) = 66$ Hz, 1C, *C*H(CH$_3$)$_2$],

Table 1. Crystallographic Data for **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, and **4c**[a]

	2a	**2b**	**3a**	**3b**	**4a**	**4b**	**4c**
empirical formula	$C_{12}H_{28}INP_2STe$	$C_{12}H_{28}INP_2SeTe$	$C_{24}H_{56}N_2P_4S_2Te_2$	$C_{24}H_{56}N_2P_4Se_2Te_2$	$C_{22}H_{38}CoNP_2SeTe$	$C_{22}H_{38}CoNP_2SeTe$	$C_{22}H_{38}CoNP_2Te_2$
fw	534.85	581.75	815.91	909.71	597.06	643.96	692.60
cryst syst	orthorhombic	monoclinic	orthorhombic	triclinic	monoclinic	rhombohedral	rhombohedral
space group	*Pbca*	*P*2(1)/*n*	*Pna*2(1)	$P\bar{1}$	*P*2(1)/*c*	$R\bar{3}c$	$R\bar{3}c$
a, Å	8.7937(1)	10.3513(2)	24.5509(6)	7.5584(2)	16.8757(5)	26.156(4)	26.292(4)
b, Å	19.0505(2)	15.5319(3)	8.6486(2)	8.0137(3)	12.3355(3)	26.156(4)	26.292(4)
c, Å	22.7051(3)	13.3861(3)	17.3592(5)	15.0009(5)	13.6601(3)	20.058(4)	20.9914(5)
α, deg	90	90	90	97.474(2)	90	90	90
β, deg	90	112.206	90	96.350(2)	109.931(1)	90	90
γ, deg	90	90	90	92.604(2)	90	120	120
V, $Å^3$	3803.66(8)	1992.53(7)	3685.89(16)	893.72(5)	2673.2(1)	11884(3)	11969(3)
Z	8	4	4	1	4	18	18
T, °C	173	173	173	173	173	173	173
ρ_{calcd}, g/cm^3	1.868	1.939	1.470	1.690	1.484	1.620	1.730
μ(Mo Kα), mm^{-1}	3.453	5.018	1.885	3.864	1.918	3.241	2.925
cryst size, mm	0.40 × 0.30 × 0.20	0.26 × 0.10 × 0.08	0.20 × 0.08 × 0.03	0.20 × 0.08 × 0.04	0.40 × 0.28 × 0.18	0.50 × 0.24 × 0.24	0.24 × 0.04 × 0.04
F(000)	2064	1104	1640	446	1208	5760	6084
θ range, deg	2.79−25.03	2.14−27.68	2.50−25.03	2.74−27.37	2.35−27.51	3.42−25.03	2.58−27.51
reflns collected	56 428	33 864	21 323	15 765	27 193	4457	48 059
unique reflns	3267	4579	6379	4025	6097	2313	3002
R_{int}	0.0758	0.0551	0.0546	0.0537	0.0629	0.0211	0.0596
R1 [$I > 2\sigma(I)$] [b]	0.0273	0.0249	0.0336	0.0301	0.0371	0.0238	0.0328
wR2 (all data) [c]	0.0663	0.0629	0.0741	0.0660	0.1027	0.0607	0.0667
GOF on F^2	1.255	1.080	1.057	1.031	1.078	1.055	1.102
completeness	97.3	98.2	99.1	99.2	99.4	98.9	97.9

[a] λ(Mo Kα) = 0.710 73 Å. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

34.07 [d, $^{1}J(^{13}C,^{31}P) = 66$ Hz, 1C, *C*H(CH$_3$)$_2$], 19.60 [s, 2C, CH(*C*H$_3$)$_2$], 18.73 [s, 2C, CH(*C*H$_3$)$_2$], 18.47 [d, $^{2}J(^{13}C,^{31}P) = 3$ Hz, 2C, CH(*C*H$_3$)$_2$], 18.27 [d, $^{2}J(^{13}C,^{31}P) = 2$ Hz, 2C, CH(*C*H$_3$)$_2$]. $^{31}P\{^{1}H\}$ NMR: δ 57.8 [d, $^{1}J(^{77}Se,^{31}P) = 656$ Hz, $^{2}J(^{31}P,^{31}P) = 25$ Hz], 21.2 [d, $^{1}J(^{125}Te,^{31}P) = 1553$ Hz, $^{2}J(^{31}P,^{31}P) = 25$ Hz]. ^{77}Se NMR: δ −276 [d, $^{1}J(^{77}Se,^{31}P) = 664$ Hz]. ^{125}Te NMR: δ −672 [d, $^{1}J(^{125}Te,^{31}P) = 1599$ Hz].

Synthesis of $Cp_2Co[(TeP^iPr_2)_2N]$ (4c). The salt **4c** was obtained as a dark-red powder (0.060 g, 85%) from the reaction of **2c** (0.064 g, 0.102 mmol) with $CoCp_2$ (0.039 g, 0.206 mmol) by using a procedure identical with that described above for **4a**. Elem anal. Calcd (%) for $C_{22}H_{38}P_2NTe_2Co$: C, 38.15; H, 5.53; N, 2.02. Found: C, 38.49; H, 5.86; N, 1.85. ^{1}H NMR (THF-d_8, 23 °C): δ 1.94 [sept, $^{3}J(^{1}H,^{1}H) = 7$ Hz, 4H, C*H*(CH$_3$)$_2$], 1.22−1.14 [m, 24H, CH(C*H*$_3$)$_2$]. $^{13}C\{^{1}H\}$ NMR: δ 35.28 [d, $^{1}J(^{13}C,^{31}P) = 65$ Hz, 2C, *C*H(CH$_3$)$_2$], 35.22 [d, $^{1}J(^{13}C,^{31}P) = 65$ Hz, 2C, *C*H(CH$_3$)$_2$], 19.13 [s, 4C, CH(*C*H$_3$)$_2$], 17.87 [s, 4C, CH(*C*H$_3$)$_2$]. $^{31}P\{^{1}H\}$ NMR: δ 23.5 [s, $^{1}J(^{125}Te,^{31}P) = 1571$ Hz]. ^{125}Te NMR: δ −680 [d, $^{1}J(^{125}Te,^{31}P) = 1575$ Hz].

X-ray Crystallography. Crystals of **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, and **4c** were coated with Paratone 8277 oil and mounted on a glass fiber. Diffraction data were collected on a Nonius Kappa CCD diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å) at −100 °C. The unit-cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius *DENZO* package. After data reduction, the data were corrected for absorption based on equivalent reflections using *SCALEPACK* (Nonius, 1998). The structure of **3b** was solved by Patterson techniques; all other structures were solved by direct methods using *SHELXS-97*,[32] while refinements were carried out on F^2 against all independent reflections by the full-matrix least-squares method by using the *SHELXL-97* program.[33] The H atoms were calculated geometrically and were riding on their respective atoms, and all non-H atoms were refined with anisotropic thermal parameters.

Crystallographic data are summarized in Table 1. The structures of **2a**, **2b**, **3a**, **3b**, **4a**, and **4c** were well-ordered, and no special considerations were necessary. The structure of **4b** displayed positional disorder of the tellurium and selenium sites, which were modeled as an anisotropic 50:50 mixture.

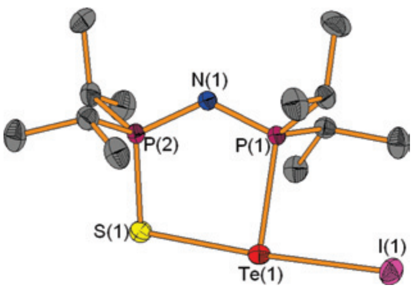

Figure 1. Thermal ellipsoid plot of **2a** (50% probability). All H atoms have been omitted for clarity.

Computational Details. DFT calculations were performed for various geometrical and conformational isomers of compounds **3** (see the text for details). The molecular structures were optimized by using a combination of the PBE exchange-correlation functional[34−36] with Ahlrichs' triple-ζ valence basis set augmented by one set of polarization functions (def-TZVP);[37] for tellurium, the corresponding ECP basis set was used.[38] All calculations were performed with the *Turbomole 5.10* program package.[39] Visualizations for Figure 3 were done with the *gOpenMol* program.[40,41]

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(32) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Determination*; University of Gottingen: Gottingen, Germany, 1997.

(33) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1997.

(34) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(35) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.

(36) Perdew, J. P.; Burke, K.; Ernzerhof, M. *J. Chem. Phys.* **1996**, *105*, 9982.

(37) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

(38) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(39) (a) *TURBOMOLE, Program Package for ab initio Electronic Structure Calculations*, version 5.10; TURBOMOLE GmbH: Karlsruhe, Germany, 2008. (b) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 1659.

(40) Laaksonen, L. *J. Mol. Graphics* **1992**, *10*, 33.

(41) Bergman, D. L.; Laaksonen, L.; Laaksonen, A. *J. Mol. Graphics Modell.* **1997**, *15*, 301.

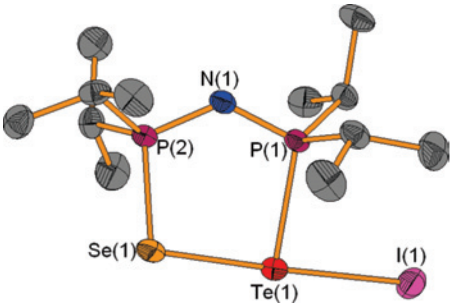


Figure 2. Thermal ellipsoid plot of **2b** (50% probability). All H atoms have been omitted for clarity.

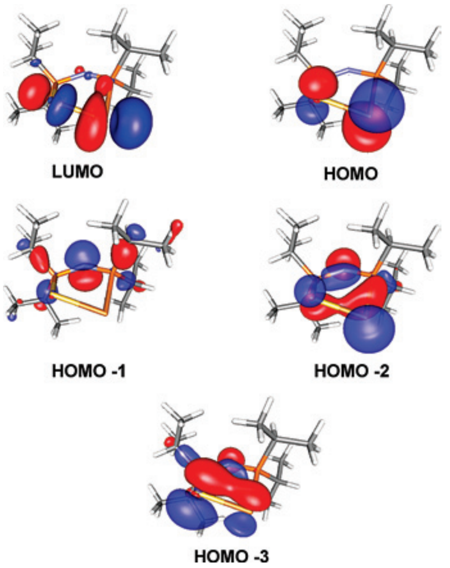


Figure 3. Frontier orbitals in the cyclic cations [(EP^{i}Pr$_2$)(TeP^{i}Pr$_2$)N]$^+$ (E = S, Se). In each case, the Te atom is on the right-hand side of the E−Te linkage.

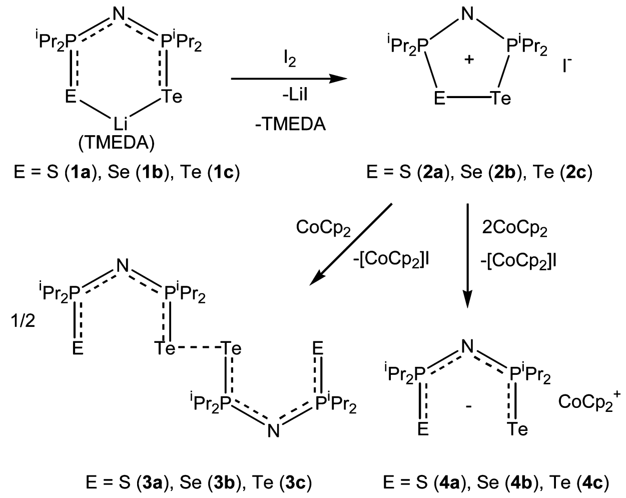
Results and Discussion

Synthesis and Crystal Structures of 2a and 2b. The reaction of the heterodichalcogenidoimidodiphosphinates **1a** and **1b** with 1 equiv of iodine in THF at −78 °C proceeded smoothly to give the salts **2a** and **2b** in good yields according to Scheme 1.

The identity of these new cations was confirmed by multinuclear NMR spectra. The ^{31}P NMR spectrum of **2a** consists of a pair of mutually coupled doublets at 89.9 and 59.2 ppm, which are, as expected, considerably deshielded with respect to those of the corresponding anion **1a** (66.1 and 21.6 ppm).[31] The peak representing the tellurium-bound phosphorus atom (P−Te) displays characteristic ^{125}Te satellites, with ^{1}J(Te−P) = 968 Hz., cf. 1040 Hz for the ditellurido cation in **2c**.[23] The P−S resonance also displays satellites with a separation of 36 Hz, tentatively attributed to a ^{2}J(Te−P) coupling as a consequence of the presence of a S−Te bond. A downfield shift is also observed in the ^{125}Te NMR spectrum of **2a**, for which a doublet of doublets is centered at +574 ppm (cf. −757 ppm in **1a**). The ^{1}J(Te−P) and ^{2}J(Te−P) coupling constants of 968 and 36 Hz, respectively, are consistent with those observed in the ^{31}P NMR spectrum.

The NMR spectra of **2b** are analogous to those of **2a**. The ^{31}P NMR spectrum displays a pair of doublets at 87.1 and 62.5 ppm with selenium (494 Hz) and tellurium (967 Hz) satellites, respectively. The chemical shifts are deshielded and the coupling constants are noticeably smaller than those of the corresponding anion in **1b** [59.0 ppm, ^{1}J(Se−P) = 600 Hz; 23.6 ppm, ^{1}J(Te−P) = 1426 Hz]. While the signal at 87.1 ppm also clearly displays a second set of ^{125}Te satellites with ^{2}J(Te−P) = 30 Hz, the analogous ^{77}Se satellites on either side of the signal at 62.5 ppm are not well-resolved. However, the ^{77}Se NMR spectrum consists of a doublet of doublets centered at −2 ppm with ^{1}J(Se−P) and ^{2}J(Se−P) coupling constants of 494 and 9 Hz, respectively. This ^{77}Se NMR chemical shift is considerably downfield with respect to that of **1b** (−319 ppm).

Scheme 1



X-ray crystallographic analyses confirmed that the structures of **2a** (Figure 1) and **2b** (Figure 2) consist of a cationic five-membered ring and an iodide anion. Selected bond parameters are given in Table 2, along with the corresponding parameters of the ditellurido cation **2c**[23] for comparison. In both cases, the rings are distinctly puckered [E−P−P−Te dihedral angles are 24.74(3)° and 29.04(2)°, respectively], in accordance with the conformation of **2c** but in contrast to the related planar 6π-electron cations [(TeENSN)Cl]$^+$ (E = S, Se).[42−45]

The iodide anion in **2a** displays a much stronger interaction with Te [2.915(1) Å] than with S [3.991(1) Å]. Indeed, this latter distance is close to the sum of the van der Waals radii of S and Te (4.00 Å)[46] and can therefore be considered nonbonding. The Te−I interaction is also evident in the structure of **2b**, where the Te−I distance is 3.005(1) Å. In this derivative, there is clearly no Se−I interaction, with the closest Se−I distance being greater than 6 Å. In both cases, the Te−I interaction is stronger than the corresponding interaction in the ditellurido cation **2c** [3.430(1) Å].

Previous DFT calculations on the homodichalcogenido salts [(EP^{i}Pr$_2$)$_2$N]I (E = Se, Te) showed that donation of

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(42) Haas, A.; Kasprowski, J.; Pryka, M. *Chem. Ber.* **1992**, *125*, 789.
(43) Haas, A.; Pryka, M.; Schafers, M. *Chem. Ber.* **1994**, *127*, 1865.
(44) Dworak, J.; Haas, A.; Hoppmann, E.; Olteanu, A.; Merz, K.; Schafers, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2639.
(45) Konu, J.; Ahlgren, M.; Aucott, S. M.; Chivers, T.; Dale, S. H.; Elsegood, M. R. J.; Holmes, K. E.; James, S. L. M.; Kelly, P. F.; Laitinen, R. S. *Inorg. Chem.* **2005**, *44*, 4992.
(46) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **2a**, **2b**, **2c**, **3a**, **3b**, **3c**, **4a**, **4b**, and **4c** [Calculated Pauling Bond Orders in Square Brackets[45]]

	2a	**2b**	**2c**[23]	**3a**[d]	**3b**[a]	**3c**[22]	**4a**	**4b**[b]	**4c**[c]
Te(1)−P(1)	2.500(1)	2.497(1)	2.396(3)	2.498(1)	2.490(1)	2.489(2)	2.400(1)	2.384(4)	2.401(1)
E(1)−P(2)	2.033(1)	2.205(1)	2.437(3)	1.981(2)	2.152(1)	2.394(2)	2.005(1)	2.169(7)	
P(1)−N(1)	1.591(2)	1.597(2)	1.621(6)	1.578(4)	1.579(2)	1.571(5)	1.585(3)	1.597(1)	1.598(2)
P(2)−N(1)	1.606(2)	1.602(2)	1.552(6)	1.612(4)	1.614(3)	1.623(5)	1.589(3)		
Te(1)−E(1)	2.710(1) [0.38]	2.746(1) [0.51]	2.840(1) [0.72]						
Te(1)−I(1)	2.915(1) [0.50]	3.005(1) [0.37]	3.430(1) [0.09]						
Te(1)−Te(1A)				2.8067(7)[e]	2.893(1)	2.946(1)			
Te(1)•••E(1)				3.296(2)	3.317(1)	3.464(1)	4.434(1)	4.886(9)	4.955(1)
P(1)−N(1)−P(2)	128.5(2)	128.4(2)	133.5(4)	133.3(3)	134.1(1)	135.2(3)	146.9(2)	135.8(2)[f]	136.2(3)[f]
Te(1)−P(1)−N(1)	109.0(1)	109.3(1)	109.6(2)	111.3(2)	112.7(1)	114.1(2)	121.1(1)	120.8(1)	118.9(1)
E(1)−P(2)−N(1)	112.7(1)	111.1(1)	109.4(2)	116.4(2)	114.7(1)	114.5(2)	121.0(1)	117.4(2)	
P(1)−Te(1)−E(1)	82.89(2)	84.68(3)	88.56(5)						
P(2)−E(1)−Te(1)	97.95(3)	92.60(3)	88.36(5)						
Te(1A)−Te(1)−P(1)				98.82(4)[e]	95.01(3)	94.64(4)			
Te(1)−P(1)−P(2)−E(1)	24.74(3)	29.04(2)	25.84(7)	29.13(8)	28.60(3)	29.53(6)	36.45(5)	79.6(2)[f]	77.43(4)[f,h]
P(1)−Te(1)−Te(1A)−P(1A)				131.06(5)[e,g]	180	180			

[a] Symmetry operation: $2 - x$, $1 - y$, $2 - z$. [b] Symmetry operation for the cation: $-x$, $-x + y$, $^1/_2 - z$. Symmetry operation for the anion: $^2/_3 + x - y$, $^1/_3 - y$, $^5/_6 - z$. [c] Symmetry operation: $^2/_3 + x - y$, $^1/_3 - y$, $^5/_6 - z$. [d] The bond parameters for the other half of dimer **3a** are within experimental error of the first half shown above and are not given. [e] Te(1A) = Te(2). [f] P(2) = P(1A). [g] P(1A) = P(3). [h] E(1) = Te(1A).

electron density from the lone pair of the iodide anion into the LUMO σ^*(E−E) of the cationic ring results in elongation of the E−E bond.[23] Simple qualitative molecular orbital theory arguments predict that in the mixed chalcogen systems the LUMO should be polarized toward the more electropositive chalcogen, i.e., tellurium, leading to preferential interaction of the iodide anion with the Te center of the cation. This is borne out by DFT calculations, as illustrated in Figure 3. Because the I−Te contacts in **2a** and **2b** are shorter than those in **2c**, stronger electron donation into the antibonding σ^*(E−Te) orbital (E = S, Se) is expected, resulting in a reduced E−Te bond order and more pronounced elongation of the chalcogen−chalcogen bonds as observed in the crystal structures. The S−Te bond in **2a** [2.710(1) Å] displays an elongation of ca. 12% with respect to typical S−Te bond lengths (2.41−2.43 Å) in compounds where both chalcogens are two-coordinate.[43,45] Likewise, the Se−Te bond is elongated in **2b** by ca. 8% when compared with Se−Te bonds in similar molecules, e.g., [(TeSeNSN)Cl]$^+$ cation (2.53−2.54 Å).[42,45] The calculated Pauling bond orders[47] of these E−Te bonds are 0.38 and 0.51 for **2a** and **2b**, respectively [cf. **2c**; 4% elongation, bond order 0.72]. The trends in the observed lengthening of chalcogen−chalcogen bonds in these cyclic cations are summarized in Table 3.

The stronger Te−I interactions of **2a** and **2b** result in lengthening of the Te−P distance by more than 0.1 Å with respect to that of **2c** [2.500(1) Å (**2a**); 2.497(1) Å (**2b**); 2.396(3) Å (**2c**)]. The Se−P bond of **2b** [2.205(1) Å] is only slightly shorter than the corresponding bond in the diselenido cation [(SeP^{i}Pr$_2$)$_2$N]I [2.229(2) Å],[23] possibly because there is no Se−I interaction in **2b**. The P−N bond lengths are similar in both complexes, and their average values are close to those of **2c**.

Table 3. Elongation of Te−E Bonds in Cyclic Cations (**2**) and Dimers (**3**)

compound	E−E length (Å)	% elongation
2a	2.710(1) (Te−S)	12
2b	2.746(1) (Te−Se)	8
2c[23]	2.840(1) (Te−Te)	4
3a	2.807(1) (Te−Te)	3
3b	2.893(1) (Te−Te)	6
3c[22]	2.946(1) (Te−Te)	8

The P−N−P bond angles of **2a** [128.5(2)°] and **2b** [128.4(2)°] are ca. 5° narrower than that of **2c** [133.5(4)°]. The Te−P−N bond angles are all similar in **2a** and **2b**, falling within the range 109.0(1)−109.6(2)°. Concomitant with the lengthening of the E−Te and E−P bonds going from **2a** to **2c**, the E−Te−P bond angle becomes progressively larger [82.89(2)° (**2a**); 84.68(3)° (**2b**); 88.56(5)° (**2c**)]. This trend is compensated for by successively smaller Te−E−P bond angles [97.95(3)° (**2a**); 92.60(3)° (**2b**); 88.36(5)° (**2c**)].

Synthesis and Crystal Structures of 3a and 3b. The ditelluride dimer **3c** was obtained by the one-electron oxidation of the corresponding anion **1c** with $^1/_2$ equiv of iodine.[22] However, the analogous stoichiometric reaction of **1a** or **1b** with I$_2$ failed to yield the respective dimers **3a** and **3b**. The ^{31}P NMR spectra of these reactions displayed a plethora of peaks, with the principal resonances attributable to the products of a two-electron oxidation (i.e., **2a** and **2b**). Consequently, an alternative synthetic route to **3a** and **3b** was devised, namely, the one-electron reduction of the cations **2a** and **2b** (Scheme 1). Cobaltocene was chosen for this reduction because it is of moderate reducing strength.[48]

The synthetic method employed could potentially give rise to three different dimers through association of the initially formed radicals [EP^{i}Pr$_2$NP^{i}Pr$_2$Te]$^\bullet$, namely, a Te−Te, an E−E, or a Te−E (E = S, Se) bound dimer. The ^{31}P NMR spectra of the products obtained from cobaltocene reductions

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(47) The bond orders were calculated by the Pauling equation $N = 10^{(D-R)/0.71}$,[36] where R is the observed bond length (Å). The single bond length D is estimated from the sums of appropriate covalent radii (Å):[36] Te−S, 2.41; Te−Se, 2.54; Te−Te, 2.74; Te−I, 2.70.

(48) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

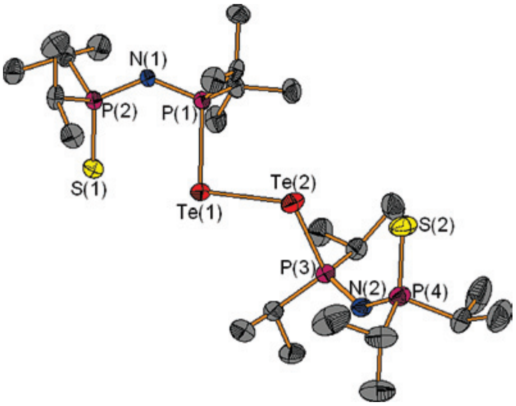

Figure 4. Thermal ellipsoid plot of **3a** (50% probability). All H atoms have been omitted for clarity.

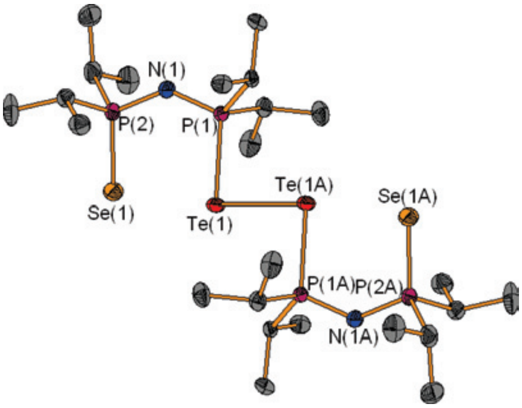

Figure 5. Thermal ellipsoid plot of **3b** (50% probability). All H atoms have been omitted for clarity.

of **2a** and **2b** exhibited a pair of mutually coupled doublets with appropriate Te (and Se in **3b**) satellites, suggesting the formation of only one of these three possible isomers. The ^{1}J(Te−P) coupling constants of **3a** (1011 Hz) and **3b** (1012 Hz.) are of magnitude similar to that of the bridging-Te-bound phosphorus signal in **3c** (1026 Hz),[22] indicating that the product is a Te−Te-bridged dimer [the ^{1}J(Te−P) coupling constant of the terminal Te-bound phosphorus signal in **3c** is 1500 Hz]. Furthermore, the ^{1}J(Se−P) coupling constant of 639 Hz in **3b** is comparable to the value of 642 Hz reported for the terminal P=Se groups in the dimer $(\mathrm{SeP^iPr_2NP^iPr_2Se-})_2$.[27]

The ^{125}Te (and ^{77}Se) NMR spectra of **3a** and **3b** each display appropriate ^{1}J(E−P) coupling constants. The ^{77}Se NMR chemical shift of −177 ppm for **3b** is comparable with the value of −145 ppm for the terminal Se atom in $(\mathrm{SeP^iPr_2NP^iPr_2Se-})_2$ (cf. +242 ppm for bridging Se).[27] The poor solubility of **3c** makes it impossible to compare with the ^{125}Te NMR chemical shifts of **3a** (60 ppm) and **3b** (79 ppm). The ^{77}Se and ^{125}Te NMR chemical shifts in **3a** and **3b** all occur at intermediate values with respect to the corresponding anions **1a** and **1b** and cations **2a** and **2b**.

X-ray crystallographic analyses of **3a** (Figure 4) and **3b** (Figure 5) confirm that the NMR-based assignment of a Te−Te-bound dimer is correct in both cases. Pertinent bond parameters are compared with those of **3c** in Table 2. Like **3c**, the heterodichalcogenido (Se/Te) system **3b** is centrosymmetric and hence displays a P−Te−Te−P dihedral angle of 180°. By contrast, the S/Te derivative **3a**, which is not centrosymmetric, shows a much smaller corresponding dihedral angle [131.06(5)°]. The most interesting feature of these structures is the Te−Te bond length. As indicated in Table 3, the Te−Te bond [2.807(1) Å] in **3a** is elongated by ca. 3% with respect to a Te−Te bond of an organic ditelluride[30] or the $[\mathrm{Te-Te}]^{2-}$ dianion,[49] while the Te−Te bond in **3b** [2.893(1) Å] is elongated by ca. 6% [cf. 2.946(1) Å in **3c**; 8% elongation].[22] The smaller elongation of the central Te−Te bond in the heterodichalcogenido dimers **3a** and **3b** can be attributed to the polarization of the SOMO of the neutral radicals toward the Te centers, cf. the LUMOs of the cyclic cations **2a** and **2b** (Figure 3). The polarization leads to better overlap of the orbitals involved in the Te−Te bond formation and, consequently, to a stronger Te−Te bond. This conclusion is further supported by DFT calculations, which show that the dimers **3a** and **3b** are bound by 131 and 107 kJ mol^{-1} in comparison to two acyclic neutral radicals $[\mathrm{EP^iPr_2NP^iPr_2Te}]^\bullet$ (E = S and Se, respectively); cf. 80 kJ mol^{-1} for E = Te.

A possible minor contribution to the elongation of the Te−Te bond in the centrosymmetric dimers **3b** and **3c** may be attributed to the P−Te−Te−P dihedral angles (both 180°). Calculations have previously shown that Te−Te bonds are moderately elongated (in HTeTeH)[50] when this dihedral angle is either 0 or 180° because the repulsions of the lone pairs on adjacent Te atoms will be maximized in such a conformation.

The Te−P and P−N bond lengths are similar in **3a** and **3b** and in accordance with those reported for **3c**. Like **3c**, the P(2)−N bond lengths of **3a** and **3b** are slightly longer than the P(1)−N bond lengths. The P−S bond of **3a** [1.981(2) Å] is intermediate between the P−S distances of neutral $(\mathrm{SP^iPr_2})_2\mathrm{NH}$ [ave 1.945(1) Å][51] and the cation **2a** [2.033(1) Å]. Likewise, the P−Se bond length in **3b** [2.152(1) Å] falls between the corresponding distances in $(\mathrm{SeP^iPr_2})_2\mathrm{NH}$ [ave 2.099(1) Å][52] and **2b** [2.205(1) Å]. The bond angles in the EPNPTe backbone of **3a** and **3b** are similar, with a minor increase in the P−N−P and Te−P−N angles and a slight decrease in the E−P−N angle along the series **3a**−**3c**.

The four chalcogen atoms of **3a** and **3b** lie in an almost linear arrangement, which is achieved by a distinct twisting of the five-membered EPNPTe backbone as evidenced by the Te−P(1)−P(2)−E dihedral angles [29.13(8)° (**3a**), 28.60(3)° (**3b**)]. This deformation is similar in magnitude to those reported for **3c** [29.53(6)°] and the cationic rings **2a**−**2c**.

Synthesis and Crystal Structures of 4a−4c. The successful one-electron reduction of the cationic species **2a** and **2b** with cobaltocene paves the way for an investigation of the two-electron reduction with 2 equiv of cobaltocene to regenerate the corresponding anions (Scheme 1). Such anions are expected to exist as part of an ion-separated salt with a cobaltocenium cation. The reactions of **2a** and **2b** with

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(49) Bottcher, P.; Getszchmann, J.; Keller, R. *Z. Anorg. Allg. Chem.* **1993**, *619*, 476.

(50) Laitinen, R.; Pakkanen, T. *J. Mol. Struct.* **1985**, *124*, 293.

(51) Cupertino, D.; Keyte, R.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Inorg. Chem.* **1996**, *35*, 2695.

(52) Cupertino, D.; Birdsall, D. J.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chim. Acta* **1999**, *290*, 1.

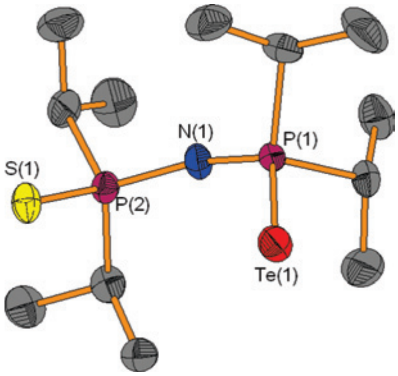

Figure 6. Thermal ellipsoid plot of the anion of **4a** (50% probability). All H atoms have been omitted for clarity.

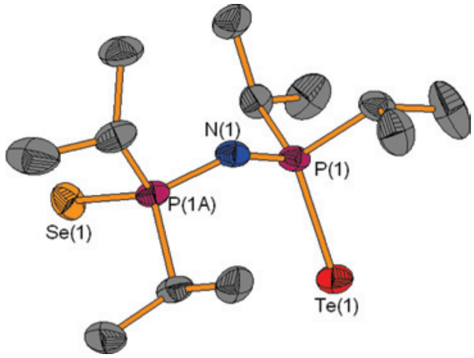

Figure 7. Thermal ellipsoid plot of one of the 50% occupancy models of the anion of **4b** (50% probability). All H atoms have been omitted for clarity.

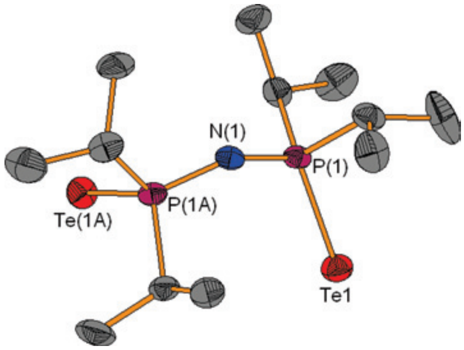

Figure 8. Thermal ellipsoid plot of the anion of **4c** (50% probability). All H atoms have been omitted for clarity.

cobaltocene in a 1:2 molar ratio produce **4a** and **4b** as crystalline materials in good yields; the cobaltocenium salt of the ditellurido anion **4c** is also obtained from the analogous reaction of **2c** with 2 equiv of cobaltocene. The presence of the cobaltocenium cation is confirmed by the ^{1}H NMR spectra of **4a** and **4b**, which each reveal a broad singlet at 5.83 and 5.56 ppm, respectively. The corresponding signal in **4c** is too broad to be observed. The resonance for the $[CoCp_2]^+$ cation in the ^{13}C NMR spectra of all three products is not evident, presumably because it is too broad. ^{31}P NMR analysis of these three products shows chemical shifts similar to those of the contact ion pairs **1a**−**1c**.[31] The ion-separated complexes **4a** and **4b** display a pair of mutually coupled doublets, while **4c** shows the expected singlet. In each case, the chemical shifts are within 2 ppm of those of **1a**−**1c**. The Te satellites in **4a**−**4c** all exhibit a ^{1}J(Te−P) coupling constant (1540−1571 Hz) similar to that of the ion-separated salt $[Me_2Al(TMEDA)][(TeP^iPr_2)_2N]$ (1560 Hz)[53] and intermediate in value between those of the chelated anions (**1a**−**1c**, 1416−1470 Hz) and the monotelluride $Te{=}P^iPr_2N{=}P(H)^iPr_2$ (1654 Hz),[22] which contains a terminal P═Te double bond. These coupling constants reflect the lack of coordination to the anion and suggest that the bond order in solution is intermediate between that of a single and double bond. A similar intermediate ^{1}J(Se−P) coupling constant is found for **4b** (664 Hz; cf. 599 Hz in **1b** and 684 Hz in $Se{=}P^iPr_2N{=}P(H)^iPr_2$).[31] The ^{125}Te (and ^{77}Se) NMR spectra each display the expected doublets with appropriate chalcogen−phosphorus coupling, although the signals are noticeably deshielded with respect to those of the contact ion pairs **1a**−**1c**.

The X-ray crystal structures of compounds **4a**−**4c** confirm that they exist as ion-separated salts (Figures 6−8). Table 2 contains selected bond parameters. The P−N bond lengths are in a narrow range and are consistent with those of the lithium-bound salts **1a**−**1c**. The Te−P bonds are ca. 0.1 Å shorter than those of **1a**−**1c**, in accordance with the conclusion of a higher bond order drawn from the ^{1}J(Te−P) coupling constants (vide supra). The S−P bond of **4a** [2.005(1) Å] is slightly longer than those seen in the limited number of noncoordinated salts containing the $[(SP^iPr_2)_2N]^-$ anion [1.971(2)−1.987(2) Å].[54−58] A similar lengthening is also observed for the Se−P bond of **4b** [2.169(7) Å] when compared with the same bond in the noncoordinated anions $[(SeP^iPr_2)_2N]^-$ [2.128(1) Å][59] and $[(SeP^iPr_2)(OP^iPr_2)N]^-$ [2.140(2) Å].[60]

The P−N−P bond angles in **4b** [135.8(2)°] and **4c** [136.2(3)°] are similar and considerably narrower than that of **4a** [146.9(2)°]. Indeed, **4a** displays a P−N−P bond angle that is 2° larger than that in **1a**, while this angle in **4b** and **4c** is more than 7° narrower than those of the chelated salts **1b** and **1c**. The widening of the P−N−P bond angle in **4a** has an influence on the twisting of the EPNPTe backbone as reflected in the S−P−P−Te dihedral angle of 36.45(5)°, which is ca. 2° smaller than that of **1a** [38.92(5)°]. The narrower P−N−P bond angles in **4b** and **4c** lead to much greater distortion from planarity; the E−P−P−Te dihedral angles are greater than 75°. This increased twisting is substantially greater than that observed in **1b** [41.1(5)°] and **1c** [43.33(6)°], in which the chalcogen atoms are pulled toward one another by the Li cation. These E−P−P−Te dihedral angles in **4b** and **4c** are similar to those reported

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(53) Chivers, T.; Konu, J.; Ritch, J. S.; Copsey, M. C.; Eisler, D. J.; Tuononen, H. M. *J. Organomet. Chem.* **2007**, *692*, 2658.

(54) Ly, T. Q.; Slawin, A. M. Z.; Woollins, J. D. *Main Group Chem.* **2000**, *3*, 73.

(55) Cea-Olivares, R.; Noth, H. *Z. Naturforsch.* **1987**, *426*, 1507.

(56) Haiduc, I.; Cea-Olivares, R.; Hernandez-Ortega, S.; Silvestru, C. *Polyhedron* **1995**, *14*, 2041.

(57) Silvestru, A.; Haiduc, I.; Toscano, R. A.; Breunig, H.-J. *Polyhedron* **1995**, *14*, 2047.

(58) Hernandez-Arganis, M.; Hernandez-Ortega, S.; Toscano, R. A.; Garcia-Montalvo, V.; Cea-Olivares, R. *Chem. Commun.* **2004**, 310.

(59) Ebert, K. H.; Cea-Olivares, R.; Garcia-Montalvo, V.; Espinosa-Perez, G.; Estrada, M. R.; Novosad, J.; Woollins, J. D. *Z. Naturforsch.* **1996**, *51b*, 1145.

(60) Slawin, A. M. Z.; Smith, M. B. *New J. Chem.* **1999**, *23*, 777.

for the neutral complexes $(\mathrm{EP^iPr_2})_2\mathrm{NH}$ (E = S, Se), whose corresponding dihedral angles are 79°[51] and 80°,[52] respectively.

Theoretical Investigations of Structural and Conformational Isomers of 3. Three different conformational isomers have been observed experimentally for the dichalcogenide dimers **3** in the solid state:[22,27,53] one C_2-symmetric conformation (E = Se, R = ^{i}Pr) and two C_i-symmetric conformations (E = Te, R = ^{i}Pr or E = Se, R = ^{t}Bu and E = S, R = ^{t}Bu) that differ by the orientation of the terminal chalcogen atoms. In addition, an interesting structural dichotomy has been established for the all-Te species:[27,53] a Te−Te-bonded dichalcogenide dimer (**3c**) is observed when the substituents at phosphorus are ^{i}Pr groups, whereas a contact ion pair structure (**5**) is obtained for the analogous ^{t}Bu-substituted species. We have recently analyzed the energy hypersurfaces of the homodichalcogenide dimers **3** computationally, and the results showed that (a) the three conformational isomers are generally very close in energy and (b) the stability of the contact ion pair structure **5** increases relative to that of the dichalcogenide structure **3** as one descends the series of chalcogens from S to Te.[27]

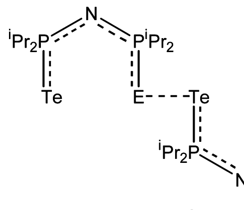
The polarization of the SOMOs of the neutral radicals $[\mathrm{ER_2PNR_2PTe}]^\bullet$ (E = S, Se) toward Te readily explains the preferential dimerization through Te−Te bond formation (vide supra). We have also probed the energetics of the dimerization process by performing geometry optimizations for both **3a** and **3b** as well as for their unknown E−Te and E−E (E = S, Se) bonded structural isomers **3d**−**3g**. The possibility for conformational isomerism was also taken into account in the calculations, and optimizations for all dimers were started from three different conformers analogous to those observed for the known dichalcogenides **3** in the solid state (C_2 and two C_i isomers vide supra).

The calculations correctly identify the experimentally observed Te−Te-bonded isomers **3a** and **3b** as the lowest energy structures on the potential energy hypersurface. Of the three possibilities available, the E−E-bonded dimers **3f** and **3g** are the highest in energy in both series: the energy difference with respect to the corresponding dimers with a Te−Te linkage is found to be 100 and 48 kJ mol^{-1} for S and Se, respectively. The asymmetrically bonded S−Te and Se−Te alternatives are also energetically disfavored though by a much smaller margin. The calculated energy differences are 42 and 22 kJ mol^{-1} for **3d** and **3e**, respectively. For all isomers studied, the C_i-symmetric (or "C_i-like" for **3d** and **3e**) conformer with the two terminal chalcogen atoms significantly twisted away from planarity is always the highest in energy by approximately 50 kJ mol^{-1}. For **3a**, **3b**, **3f**, and **3g**, the C_i-symmetric conformer with a linear chalcogen "chain" and the structure with a C_2 axis have virtually the same energy because the calculated difference is less than the accuracy of the applied DFT method (only a few kilojoules per mole). In contrast, only the "C_2-like" conformer could be found for the asymmetrically bonded **3d** and **3e**.

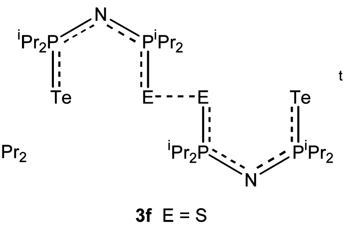
Previous experimental work established the existence of the intriguing contact ion pair structure **5** for the ditelluride dimer when the substituents on the P atoms are changed from ^{i}Pr to the more bulky ^{t}Bu groups.[27] DFT calculations of this structural dichotomy showed that the contact ion pair structure **5** is indeed more energetically favorable (by −20 kJ mol^{-1}) than the ditelluride structure **3** (E = Te, R = ^{t}Bu), whereas there is no clear structural preference for the corresponding all-Se systems and the disulfide structure is more stable for the all-S derivative.[27] This raises the interesting question of whether a contact ion pair structure is energetically preferred for the mixed chalcogen systems **3a** and **3b** when the substituents on the P atoms are ^{t}Bu rather than ^{i}Pr. Interestingly, DFT calculations predict that the contact ion pair structure is 10 kJ mol^{-1} lower in energy than the Te−Te-bonded dimer for the mixed chalcogen (Se/Te) system, whereas for the S/Te system, the Te−Te-bonded dimer is lower in energy by a very small margin (ca. 3 kJ mol^{-1}).

Conclusions

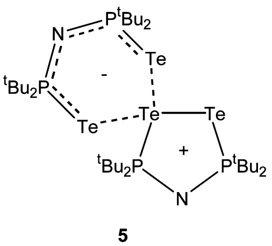
The interaction of the iodide anion and the Te atom of the cyclic heterodichalcogenido cations $[(\mathrm{EP^iPr_2})(\mathrm{TeP^iPr_2})\mathrm{N}]^+$ (E = S, Se) is stronger than that found in the ditellurido salt $[(\mathrm{TeP^iPr_2})_2\mathrm{N}]\mathrm{I}$. A major consequence of this interaction is the lengthening of the E−Te bond by up to 12%. On the basis of DFT calculations, the pronounced elongation of the E−Te bonds is attributed to the polarization of the LUMO σ^*(E−Te) toward tellurium in the cations. Dimers of the type $(\mathrm{EP^iPr_2NP^iPr_2Te}-)_2$ (E = S, Se) are obtained by the novel route of reducing the corresponding cations with cobaltocene. A combination of multinuclear NMR and X-ray crystallographic studies revealed that these dimers exist solely as the Te−Te-bonded isomer in solution and in the solid state. The central Te−Te bond length decreases along the series E = Te, Se, S as a result of the polarization of the SOMO of the neutral radicals $[\mathrm{EP^iPr_2NP^iPr_2Te}]^\bullet$ toward Te when E = S, Se, resulting in stronger Te−Te overlap. DFT calculations of relative energies confirm that the formation of Te−Te-bonded dimers is significantly more favorable than



3d E = S
3e E = Se



3f E = S
3g E = Se



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the structural isomers involving E−Te or E−E bonds. Interestingly, however, a change of the substituents on phosphorus from ^{i}Pr to ^{t}Bu is predicted to tip the energy balance in favor of a contact ion pair structure for the Te−Te-bonded dimer when E = Se. Two-electron reduction of the cations $[(EP^{i}Pr_2)(TeP^{i}Pr_2)N]^+$ (E = S, Se, Te) with cobaltocene regenerates the corresponding anions as ion-separated cobaltocenium salts. The structural analysis of these salts represents the first systematic study of a series of ion-separated dichalcogenidoimidodiphosphinate anions with a common cation.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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