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Homoleptic Pnictogen–Chalcogen Coordination Complexes

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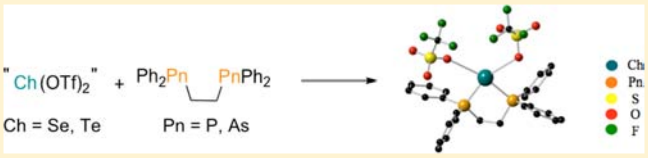
Ⓢ *Supporting Information*



ABSTRACT: The synthesis and structural characterization of dicationic selenium and tellurium analogues of the carbodiphosphorane and triphosphenium families of compounds are reported. These complexes, [Ch(dppe)][OTf]$_2$ [Ch = Se, Te; dppe = 1,2-bis(diphenylphosphino)ethane; OTf = trifluoromethanesulfonate], are formed using [Ch]$^{2+}$ reagents via a ligand-exchange protocol and represent extremely rare examples of homoleptic pnictogen → chalcogen coordination complexes. The corresponding arsenic compounds were also prepared, [Ch(dpAse)][OTf]$_2$ [Ch = Se, Te; dpAse = 1,2-bis(diphenylarsino)ethane], exhibiting the first instance of an arsenic → chalcogen dative bond. The electronic structures of these unique compounds were determined and compared to previously reported chalcogen dications.

■ INTRODUCTION

The broad field of chalcogen–phosphorus (Ch–P) chemistry is an area that is experiencing continuous growth and interest.[1,2] For example, extensive chemistry is known for $R_3P{=}Ch$ compounds, bifunctional phosphine chalcogenides (**1**; Figure 1), and the related anionic dichalcogenidoimidophosphinates (**2**), which act as Lewis bases for a wide variety of elements.[3−7] These types of molecules have recently shown promise as single source precursors for functional materials (i.e., in the formation of metal chalcogenide thin films).[7−20] Far less is known about compounds where the group 16 center acts as the Lewis acid, with the phosphorus being the Lewis base. This is underscored by the fact that there are only three unique systems comprising a total of six reports concerning phosphine ligands binding to chalcogen centers in a classic donor → acceptor mode (**3**, **4**, and **6**).[21−26]

The lack of activity in this area is surprising given the readily available sources of Lewis acidic group 16 centers as dihalides (Ch = S, Se) and tetrahalides (Ch = Se, Te) and the ongoing interest in Ch–P chemistry. The likely reason for this deficiency is that simple reactions between phosphines and chalcogen halides result in redox activity[27] rather than the formation of a P–Ch bond. Reduction of the group 16 element occurs along with halogenation of the phosphine (e.g., between Ph_3P and $SeCl_4$ or $SeCl_2$; Scheme 1). Ultimately, complete reduction of the chalcogen to the phosphine chalcogenide occurs upon the addition of excess phosphine.

It was recently reported that the bromination of (dppbzS)-AuBr [**5S**; dppbz = 1,2-bis(diphenylphosphino)benzene] leads to the formation of a P–S–P dication charge balanced with a bromide and tetrabromoaurate anion (**6**).[25] The compound exists as a halide-bridged dimer in the solid state, with bromine atoms weakly coordinating to the sulfur center. It should be noted that the analogous reaction with the selenium derivative (**5Se**) instead results in the reduction to elemental selenium and no P–Se bond in the final product (**7**). Compound **6** represents the first example of a P–Ch–P chelate bonding motif (Scheme 2); however, the synthetic pathway described above may not be generalized, especially given the result with selenium in place of sulfur. The most straightforward approach to such dicationic compounds would appear to be the binding of a phosphine to the unstable, yet accessible SeX_2 (X = Cl, Br), followed by halide abstraction reactions to generate the chelates. However, this is not viable because the aforementioned redox reactions dominate rather than formation of P → ChX_2 coordination complexes.

Recently, we reported the synthesis of a new class of electrophilic selenium(II) and tellurium(II) reagents as dicationic chalcogen complexes supported by R_2DAB (DAB = diazabutadiene) ligands, which were found to act as ready sources of [Ch]$^{2+}$ (**8** and **9Ch**; Figure 2).[28,29] In this context, we report the applicability of this synthon in the generation of dicationic P–Ch–P compounds **10Ch** via ligand exchange using the 1,2-bis(diphenylphosphino)ethane (dppe) ligand. The analogous arsenic (As) → Ch coordination compounds (**11Ch**) were also prepared from 1,2-bis(diphenylarsino)ethane (dpAse), representing the first As–Ch coordinative bond. A theoretical evaluation of the electronic structure and bonding in this class of compounds accompanies the experimental data.

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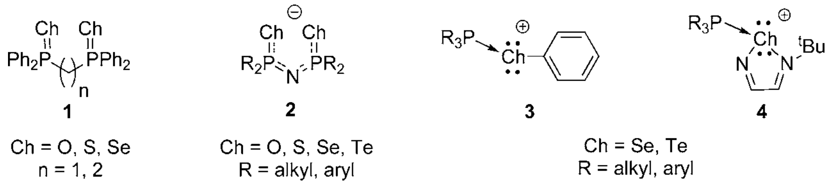
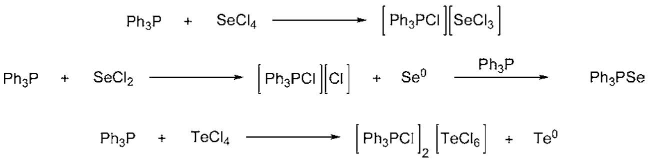


Figure 1. Structures of the common phosphine chalcogenides (**1**) and dichalcogenidoimidophosphinates (**2**) and examples of phosphines binding to electrophilic chalcogen centers (**3** and **4**).

Scheme 1. Redox Reactions between Ph_3P and the Electrophilic Selenium and Tellurium Halides



EXPERIMENTAL SECTION

Synthetic Procedures. All inert-atmosphere syntheses were performed in a nitrogen-filled MBraun Labmaster 130 glovebox or using standard Schlenk-line techniques unless otherwise stated. 1,2-Bis(diphenylphosphino)ethane (dppe) and 1,2-bis(diphenylarsino)-ethane (dpAse) were purchased from Alfa Aesar and Sigma Aldrich, respectively. Solvents were obtained from Caledon Laboratories and dried using an Innovative Technologies Inc. or an MBraun solvent purification system. Dried solvents were collected under vacuum and stored under a nitrogen atmosphere in Strauss flasks or in the glovebox over 4 Å molecular sieves. CD_3CN was dried with CaH_2, vacuum distilled, and stored in the glovebox over 3 Å molecular sieves. Solution ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectroscopies were recorded on a Varian INOVA 400 MHz spectrometer (^1H 400.09 MHz, $^{13}C\{^1H\}$ 100.52 MHz, $^{19}F\{^1H\}$ 376.15 MHz, $^{31}P\{^1H\}$ 161.82 MHz, and $^{77}Se\{^1H\}$ 76.28 MHz). All ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to residual solvent protons relative to $Si(CH_3)_4$ (CHD_2CN; ^1H δ_H 1.95 and $^{13}C\{^1H\}$ δ_C 1.32 and 118.26). Chemical shifts for $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectroscopy were referenced to an external standard (85% H_3PO_4; $\delta_P = 0.0$, saturated SeO_2 solution in D_2O; $\delta_{Se} = -1302$). Fourier transform infrared (FT-IR) spectra were collected on samples as KBr pellets using a Bruker Tenser 27 FT-IR spectrometer with a resolution of 4 cm^{-1}. FT-Raman spectra were collected on samples flame-sealed in glass capillaries using a Bruker RFS 100/s spectrometer, with a resolution of 4 cm^{-1}. Mass spectra were recorded in positive- and negative-ion modes using an electrospray ionization Micromass LCT spectrometer. Melting or decomposition points were determined by sealing the sample in capillaries and heating using a Gallenkamp variable heater.

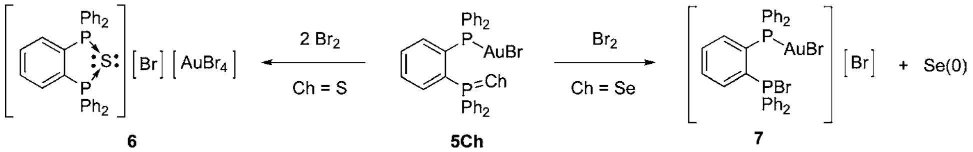
All compounds decompose in the solid state at room temperature within 24 h, precluding the collection of satisfactory microanalytical data. ^1H NMR spectra of these compounds are given in the Supporting Information as an indication of the level of purity obtained. The instability of **10Te** and **11Ch** in solution also did not allow for the collection of $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectroscopic data.

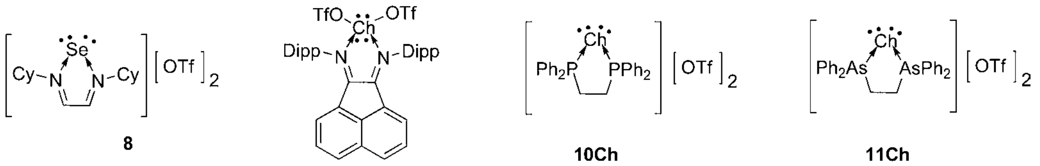
X-ray Crystallography Details. Single crystals for X-ray diffraction studies were grown by vapor diffusion of Et_2O into a saturated solution of the compound in MeCN. Crystals were selected under Paratone-N oil using a nylon loop or a micromount and immediately put under a stream of cold nitrogen gas (150 K) for data to be collected on a Nonius Kappa CCD area detector or Bruker Apex II detector using Mo Kα radiation (λ = 0.71073 Å) at the Western University X-ray Facility. The Nonius and Bruker instruments operate *SMART*[30] and *COLLECT*[31] software, respectively. The unit cell parameters were calculated and refined from the full data set. The absorption correction was applied using *SADABS*[32] or *HKL2000 DENZO-SMN*.[33] The *SHELXTL/PC V6.14* for Windows NT suite of programs was used to solve the structure by direct methods.[34] Subsequent difference Fourier syntheses allowed the remaining atoms to be located while hydrogen atoms were placed in the calculated positions. For **10Se**, all of the non-hydrogen atoms were refined with anisotropic thermal parameters while both the cation and anion were well ordered. For **10Te** and **11Te**, there was warning signs for twinning (both racemic and merohedral). The racemic twinning was refined using TWIN and BASF refined to 0.257 and 0.324 for **10Te** and **11Te**, respectively. No satisfactory twin law could be found to "detwin" the .hkl file and account for the merohedral twinning. For **11Te**, disorder about the five-membered dicationic ring was present, refining to 15% occupancy, with all atoms being refined anisotropically (Figure S-8 in the Supporting Information). One of the triflate anions was also disordered and modeled, leaving all atoms isotropic; attempting to treat these atoms anisotropically leads to unstable refinement. Disorder similar to that of **11Te** was present for **10Te**, refining to less than 10% occupancy, and as such, the disordered component did not refine suitably. As a consequence, the structure of **10Te** presented is that with no disorder refinement. Given the data obtained, the identity of the molecule is not in question, and acceptable standard uncertainties for the key bonds allow for the limited discussion of their significance present in the manuscript. Crystal data and refinement parameters are shown in Table 1, while key bond lengths and angles are presented in the caption of Figure 3.

Computational Details. All calculations were done with the program packages *Turbomole 6.3*[35] and *Gaussian09*.[36] Geometries of the studied systems were optimized using the PBE1PBE density functional[37−40] in combination with the def2-TZVP basis sets.[41,42] The nature of the stationary points found was assessed by calculating full Hessian matrices at the respective level of theory. Atomic charges were calculated with natural population analysis (NPA) using the *NBO 5.9G* code.[43] Calculations of the electron localization function were performed with the *TopMod* program package.[44] The program *gOpenMol* was used for all visualizations of molecular structures and Kohn−Sham orbitals.[45,46]

Synthesis of 10Se. A solution of dppe (0.067 g, 0.168 mmol; CH_2Cl_2 3 mL) was added to a slurry of **8**[29] (0.100 g, 0.168 mmol; CH_2Cl_2 5 mL), resulting in the immediate generation of a pale-yellow solution with a small amount of colorless precipitate. After 5 min, *n*-pentane (10 mL) was added, giving further precipitation of a colorless powder. The powder was allowed to settle and the supernatant

Scheme 2. Synthesis of the First P−S−P Chelate via Gold Oxidation





8

Cy = cyclohexyl
OTf = O_3SCF_3

9Ch

Ch = Se, Te
Dipp = 2,6-diisopropylphenyl

10Ch

Ch = Se, Te

11Ch

Ch = Se, Te

Figure 2. Suitable $Ch(OTf)_2$ (Ch = Se, Te) transfer reagents (**8** and **9Ch**) and the compounds reported in this work (**10Ch** and **11Ch**).

Table 1. X-ray Details for 10Se, 10Te, and 11Te

compound	10Se	10Te	11Te
empirical formula	$C_{28}H_{24}F_6O_6P_2S_2Se_1$	$C_{28}H_{24}F_6O_6P_2S_2Te_1\cdot{}^1/_3C_2H_3N$	$C_{28}H_{24}As_2F_6O_6S_2Te_1\cdot{}^1/_3C_2H_3N$
fw (g/mol)	775.49	836.81	924.71
cryst syst	monoclinic	trigonal	trigonal
space group	$C2/c$	$R3$	$R3$
a (Å)	15.014(3)	24.418(4)	24.606(2)
b (Å)	9.896(2)	24.418(4)	24.606(2)
c (Å)	21.02(4)	13.727(3)	13.921(2)
α (deg)	90	90	90
β (deg)	99.97(3)	90	90
γ (deg)	90	120	120
V (Å^3)	3076(11)	7088(2)	7299(2)
Z	4	9	9
D_c (mg m^{-3})	1.675	1.764	1.893
radiation, λ (Å)	0.71073	0.71073	0.71073
temp (K)	150(2)	150(2)	150(2)
R1 $[I > 2\sigma(I)]^a$	0.0416	0.0722	0.0543
wR2 $(F^2)^a$	0.1079	0.1716	0.1007
GOF $(S)^a$	1.121	1.045	1.028

[a] $R1(F\ [I > 2\sigma(I)]) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2(F^2\ [\text{all data}]) = [w(F_o^2 - F_c^2)^2]^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

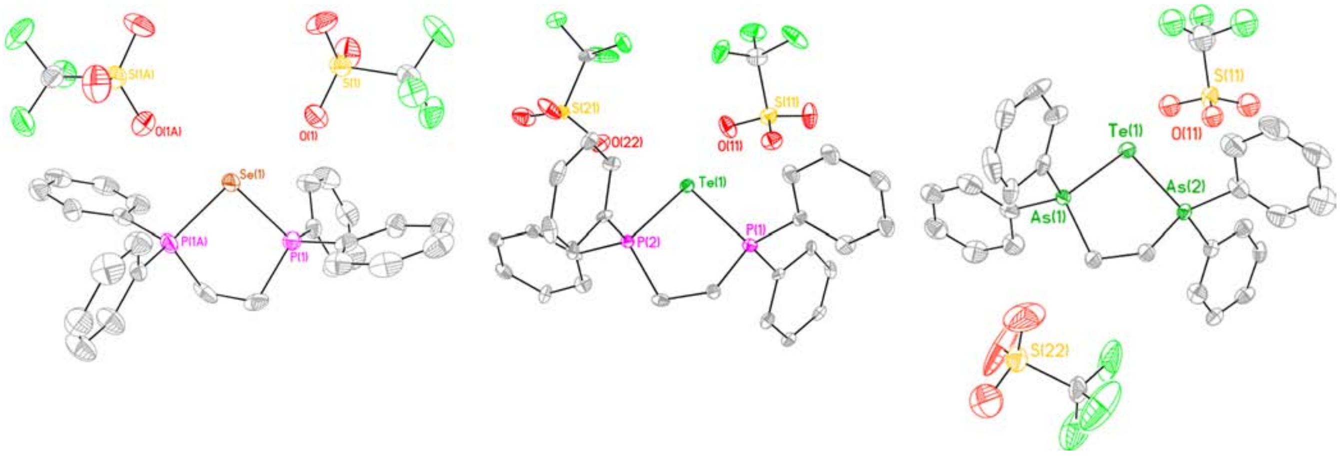


Figure 3. Solid-state structures of **10Se** (left), **10Te** (center), and **11Te** (right). Thermal ellipsoids are displayed at the 50% probability level, and hydrogen atoms are omitted. For **10Te** and **11Te**, the acetonitrile solvate is removed for clarity. For **11Te**, the disordered ring and triflate are removed for clarity; a full view is provided in the Supporting Information (Figure S-8). Selected bond lengths (Å) and angles (deg) [calculated values]: **10Se** Se(1)−P(1) 2.246(1) [2.255], Se(1)···O(1) 2.750(3), P(1)−Se(1)−P(1A) 90.13(6) [91.8]; **10Te** Te(1)−P(1) 2.495(3) [2.472], Te(1)−P(2) 2.465(3) [2.472], Te(1)···O(11) 2.78(1), Te(1)···O(22) 2.88(1), P(1)−Te(1)−P(2) 83.6(1) [86.2]; **11Te** Te(1)−As(1) 2.564(3) [2.570], Te(1)−As(2) 2.560(2) [2.570], Te(1)···O(11) 2.752(11), Te(1)···O(23) 2.856(13), As(1)−Te(1)−As(2) 84.01(9) [86.2], Te(1A)−As(1A) 2.54(2) [2.570], Te(1A)−As(2A) 2.57(2) [2.570], As(1A)−Te(1A)−As(2A) 85.5(5) [86.2].

decanted. The powder was washed with Et_2O (3 × 5 mL) and dried in vacuo, giving **10Se** as a colorless powder: yield 0.060 g, 46%; decomposition point (d.p.) powder turns gray at 225 °C; ^{1}H NMR (CD_3CN, δ ppm) 3.93 (multiplet; $-CH_2$), 7.96−7.78 (overlapping multiplets; Ph−H); $^{13}C\{^1H\}$ NMR (CD_3CN, δ ppm) 30.5 (d, $^1J_{^{31}P-^{13}C}$ = 37.6 Hz), 117.7 (d, $^1J_{^{31}P-^{13}C}$ = 76.0 Hz), 131.8 (d, $^2J_{^{31}P-^{13}C}$ = 14.9

Hz), 135.5, 138.0; ^{19}F{^{1}H} NMR (CD$_3$CN, δ ppm) −78.5; ^{31}P{^{1}H} NMR (CD$_3$CN, δ ppm) 74.7 ($^{1}J_{^{77}\mathrm{Se}-^{31}\mathrm{P}}$ = 382 Hz); ^{77}Se{^{1}H} NMR (CD$_3$CN, δ ppm) −91.5 ($^{1}J_{^{77}\mathrm{Se}-^{31}\mathrm{P}}$ = 382 Hz); FT-Raman [cm^{-1} (ranked intensity)] 121(1), 153(2), 574(9), 759(8), 998(3), 1028(4), 1100(6), 1585(5), 2907(10), 3066(7); FT-IR [cm^{-1} (ranked intensity)] 457(13), 485(12), 515(10), 533(5), 636(3), 686(7), 732(6), 996(11), 1028(2), 1100(9), 1162(4), 1251(1), 1440(8), 2907(14), 2941(15). Elem anal. Calcd (found): C, 43.35 (43.71); H, 3.12 (4.03).

*Synthesis of **10Te**.* A solution of dppe (0.056 g, 0.140 mmol; CH$_2$Cl$_2$ 3 mL) was added to a slurry of **9Te**[28] (0.129 g, 0.140 mmol; CH$_2$Cl$_2$ 5 mL), resulting in the immediate generation of a pale-yellow precipitate. After 5 min, Et$_2$O (10 mL) was added. The powder was allowed to settle and the supernatant decanted. The powder was washed with Et$_2$O (3 × 5 mL) and dried in vacuo, giving **10Te** as an off-white powder: yield 0.102 g, 89%; d.p. powder turns gray at 125 °C; ^{1}H NMR (CD$_3$CN, δ ppm) 3.65 (multiplet; −CH$_2$), 7.90−7.74 (multiplets; Ph−H); ^{19}F{^{1}H} NMR (CD$_3$CN, δ ppm) −78.5; ^{31}P{^{1}H} NMR (CD$_3$CN, δ ppm) 43.0 ($^{1}J_{^{125}\mathrm{Te}-^{31}\mathrm{P}}$ = 1020 Hz); FT-Raman [cm^{-1} (ranked intensity)] 84(2), 106(11), 149(8), 195(6), 224(12), 273(15), 349(9), 614(14), 760(10), 998(3), 1029(1), 1099(5), 1584(4), 2912(13), 3067(7); FT-IR [cm^{-1} (ranked intensity)] 477(14), 515(6), 527(5), 635(3), 688(10), 713(11), 752(9), 807(15), 996(13), 1022(2), 1095(12), 1164(8), 1234(1), 1284(4), 1438(7); ESI-MS (m/z) 527 [(**10Te** − 2 OTf)$^{+}$]. Elem anal. Calcd (found): C, 40.79 (38.63); H, 2.94 (2.56).

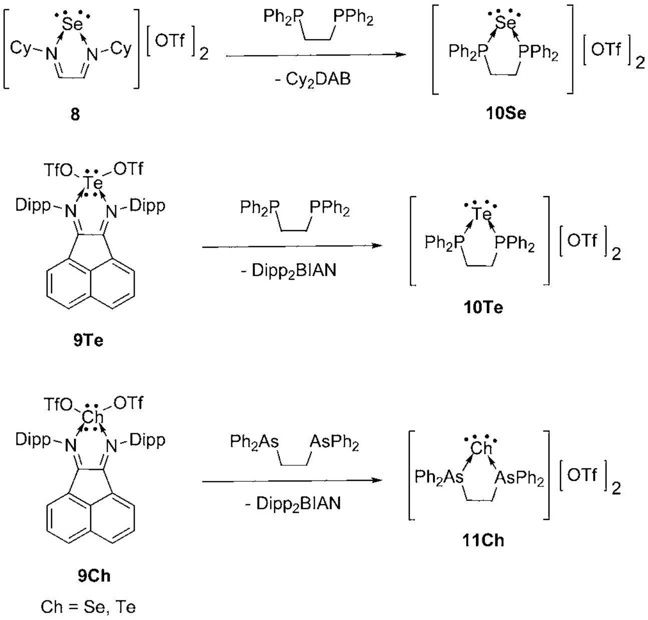
*Synthesis of **11Se**.* A solution of dpAse (0.072 g, 0.149 mmol; CH$_2$Cl$_2$ 5 mL) was added to a slurry of **9Se**[29] (0.131 g, 0.149 mmol; CH$_2$Cl$_2$ 5 mL), resulting in the immediate darkening of the solution. After 15 min, pentane (10 mL) was added. The white powder was allowed to settle and the supernatant decanted. The powder was washed with Et$_2$O (3 × 5 mL) and dried in vacuo, giving **11Se** as an off-white powder: yield 35%, 45 mg; d.p. powder turns gray at 146 °C; ^{1}H NMR (CD$_3$CN, δ ppm): 3.97 (s, 4H, −CH$_2$), 7.70−7.74 (m, 8H, Ph−H), 7.78−7.85 (m, 12H, Ph−H); ^{13}C{^{1}H} NMR (CD$_3$CN δ ppm) 58.7, 131.8, 132.1, 133.3, 133.6; ^{19}F{^{1}H} NMR (CD$_3$CN δ ppm) −78.5; FT-Raman [cm^{-1} (ranked intensity)] 88(2), 112 (8), 206 (5), 314 (13), 353 (12), 582 (7), 616 (14), 678 (11), 762 (9), 946 (15), 1002 (1), 1028 (6), 1084 (10), 1583 (4), 3069 (3); FT-IR [cm^{-1} (ranked intensity)] 460 (11), 516 (8), 573 (12), 635 (3), 684 (6), 741 (5), 997 (9), 1028 (2), 1076 (10), 1158 (4), 1261 (1), 1412 (14), 1444 (7), 1488 (13), 3065 (15).

*Synthesis of **11Te**.* A solution of dpAse (0.048 g, 0.0988 mmol; CH$_2$Cl$_2$ 3 mL) was added to a slurry of **9Te**[28] (0.092 g, 0.0988 mmol; CH$_2$Cl$_2$ 5 mL), resulting in the immediate generation of a light-brown precipitate. After 15 min, pentane (10 mL) was added. The powder was allowed to settle and the supernatant decanted. The powder was washed with Et$_2$O (3 × 5 mL) and dried in vacuo, giving **10Te** as a light-brown powder: yield 70%, 63 mg; d.p. powder turns gray at 206 °C; ^{1}H NMR (CD$_3$CN, δ ppm) 3.66 (s, 4H, −CH$_2$), 7.72−7.76 (m, 8H, Ph−H), 7.82−7.88 (m, 12H, Ph−H); ^{13}C{^{1}H} NMR (CD$_3$CN δ ppm) 37.5, 124.7, 131.7, 133.7, 135.5; ^{19}F{^{1}H} NMR (CD$_3$CN, δ ppm) −78.5; FT-IR [cm^{-1} (ranked intensity)] 466 (9), 516 (10), 574 (12), 636 (4), 688 (7), 744 (6), 771 (14), 997 (11), 1023 (3), 1076 (13), 1165 (5), 1234 (1), 1286 (2), 1440 (8), 2918 (15).

■ RESULTS AND DISCUSSION

The 1:1 stoichiometric reaction of dppe with **8** or **9Ch** in CH$_2$Cl$_2$ immediately resulted in the production of yellow solutions; colorless powders were obtained after precipitation with n-pentane and washing with Et$_2$O. Samples of the solids were redissolved in CD$_3$CN for analysis by multinuclear NMR spectroscopy, where the ^{31}P{^{1}H} NMR spectra displayed a single resonance in both cases (Se, δ_P = 74; Te, δ_P = 43). Satellites, from the spin-active isotopes of selenium (^{77}Se, 7.6%) and tellurium (^{125}Te, 7.1%), were clearly visible in the spectra with $^{1}J_{^{77}\mathrm{Se}-^{31}\mathrm{P}}$ and $^{1}J_{^{125}\mathrm{Te}-^{31}\mathrm{P}}$ values of 380 and 1020 Hz for **10Se** and **10Te**, respectively. The ^{1}H NMR spectrum revealed a set of resonances for one dppe molecule, and the methylene protons shifted downfield compared to the free ligand (**10Se**, $\Delta\delta_H$ = 1.85; **10Te**, $\Delta\delta_H$ = 1.57), consistent with the binding to an electrophilic center. X-ray diffraction studies on single crystals grown from concentrated MeCN solutions of the materials confirmed the compounds to be [dppe-Ch]$^{2+}$ dications, with the chalcogen(II) atoms found in the P,P chelate of the ligand (**10Ch**; Scheme 3).

Scheme 3. Synthesis of Compounds 10Ch and 11Ch via Ligand-Exchange Reactions



While examples of these types of P−Ch interactions are rare, the use of an arsine instead of a phosphine to coordinate an electrophilic chalcogen center is completely absent from the literature. Because of the extremely electrophilic nature of the [Ch]$^{2+}$ reagents **8** and **9Ch**, it was thought that they could also form stable complexes with diarsines, regardless of the weaker Lewis basicity of arsenic compared to the corresponding diphosphine. Compounds **11Ch** were prepared by using a strategy similar to that for the preparation of **10Ch**. In the case of selenium, it was found that dpAse would not undergo ligand exchange with **8**, and instead **9Se** had to be used. After precipitation of the product from the reaction mixture, subsequent ^{1}H NMR spectra revealed resonances consistent with a single dpAse ligand with methylene protons shifted downfield (**11Se**, $\Delta\delta_H$ = 1.91; **11Te**, $\Delta\delta_H$ = 1.54). These compounds are significantly less stable than **10Ch** in solution, with elemental selenium or tellurium observed to precipitate after 1 h of standing at room temperature. X-ray diffraction studies on single crystals grown from a concentrated MeCN solution at −30 °C did confirm the connectivity for **11Te**, while no single crystals suitable for X-ray analysis could be obtained for **11Se**.

X-ray Crystallography. Single crystals suitable for X-ray diffraction studies were grown by vapor diffusion of Et$_2$O into MeCN solutions of the bulk powder at −30 °C for **10Ch** and **11Te** (Table 1). For **10Ch**, the Ch−P bond lengths are 2.246(1) Å (**10Se**) and 2.48 Å (**10Te**, avg), similar to those found in the few other known chalcogen−pnictogen coordination complexes, and are significantly longer than the Ch−P

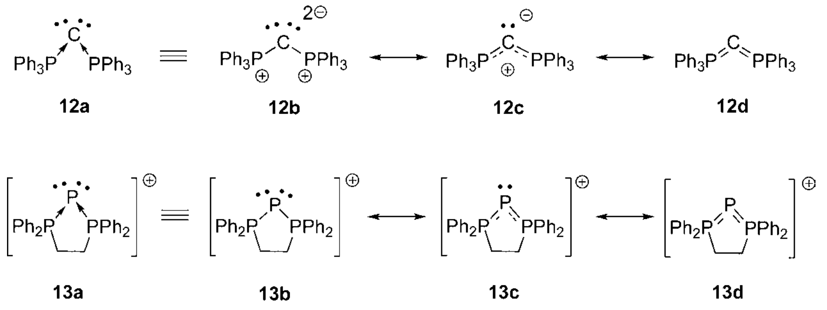


Figure 4. Resonance structures of carbodiphosphorane **12** and cyclic triphosphenium cation **13**.

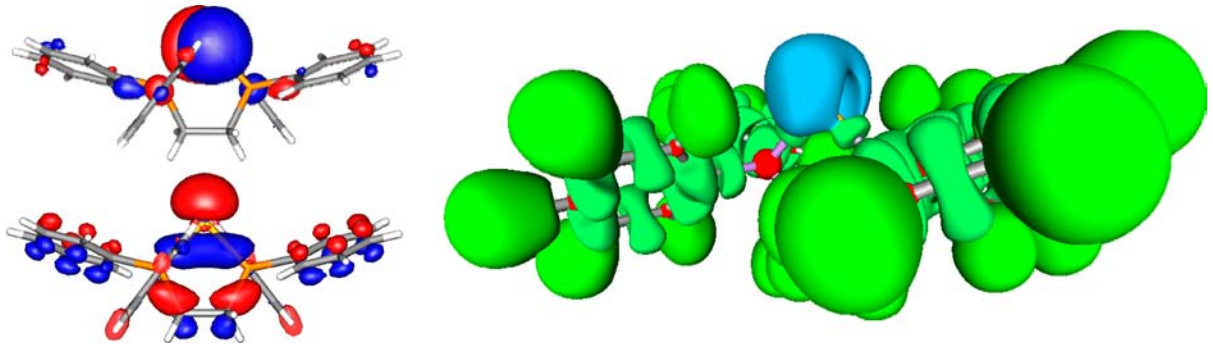


Figure 5. Frontier Kohn−Sham orbitals (left) and electron localization function (right) of **10Se**. Color code: monosynaptic valence basin, blue; disynaptic valence basin, green; core basin, red.

bonds observed in phosphine−chalcogenides (formal bond order = 2; Se−P = 2.07−2.11 Å; Te−P = 2.36−2.38 Å)[47] and dichalcogenophosphinates (formal bond order = 1.5; Se−P = 2.14−2.18 Å; Te−P = 2.38−2.40 Å).[48] This is consistent with a dative bonding description, where **10Ch** compounds are best described as sequestered $[Ch]^{2+}$ dications, or a Ch−P single-bond description, where the formal positive charges lie on the phosphorus centers. The structure of **11Te** is similar to that of the dppe derivative, crystallizing in the same space group with slightly larger unit cell parameters. However, there is disorder about the core five-membered ring as well as one of the triflate anions that was successfully modeled (Figure S-8 in the Supporting Information), but the deviation between the two prevents a detailed discussion of the metrical parameters. For the two dicationic rings, the Te−As bond lengths range from 2.53 to 2.57 Å, which is longer than the Te−P bond length in **10Te**, while the As−Te−As bond angles are slightly larger at 84−86°. The Te−As bond distance is comparable to a standard Te−As single bond;[49] however, this structure represents the first example in which the As−Te bond can also be viewed as a coordinative interaction.

In all cases, there are Ch···O contacts with the triflate counterions within the sum of the van der Waals radii (**10Se**, 2.750(3) Å, cf. 3.42 Å; **10Te**, 2.78(1), 2.88(1) Å; **11Te**, 2.75−2.86 Å, cf. 3.58 Å);[50] however, there is no distortion about the S−O bond lengths in the anions for **10Ch**, consistent with an ionic interaction. For **11Ch**, there is distortion about the S−O bond lengths, with the oxygen atom on the long S−O bond interacting with the tellurium center. This interaction is indicative of the electropositive chalcogen center binding to an oxygen atom of each triflate in the solid state. Fluorine-19 NMR spectroscopy can be quite diagnostic in determining the nature of triflate in solution, where the difference between a covalent triflate, H_3COTf (δ_F = −75.0), and an ionic triflate, $[NOct_4][OTf]$ (δ_F = −79.0 in CH_2Cl_2 and δ_F = −78.5 in MeCN), is quite distinguishable. These data provide insight into whether the triflate oxygen atom is bound or detached from the chalcogen center in solution, where in the cases of **10Ch** and **11Ch**, an ionic triflate is present in all cases.

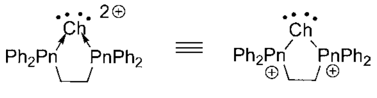
Related dications with the formula $[R_3POPR_3][OTf]_2$ generated from the reaction of phosphine oxides with triflic anhydride are also known and have been used as dehydration reagents in organic reactions.[51] The one structurally characterized example (R = Ph) reveals a short P−O bond length of 1.54 Å and a very wide bond angle of 164° for the P−O−P fragment, indicating that the P−O bond order could be greater than 1.[52] Cyclic species have also been reported but not structurally characterized.[53]

Electronic Structures. Compounds **10Ch** can be considered dicationic analogues of the carbodiphosphorane (**12**) and, in particular, cyclictriphosphenium (**13**) families of compounds (Figure 4). Both are long known[54,55] but have recently been subject to increasing attention;[56−63] carbodiphosphoranes, for example, have been proposed as an alternative to N-heterocyclic carbene ligands for transition metals. The phosphorus analogues have shown Lewis basic properties, forming bonds with strong acceptors such as $[Me]^+$ and $[H]^+$ resulting in dicationic compounds.[64,65]

These molecular architectures have been represented with a variety of bonding models. Carbodiphosphoranes were traditionally portrayed using the resonance forms **12c** and **12d** but have been more recently described as phosphine-stabilized C^0 complexes (**12a**) based on both experimental and theoretical studies.[62,66] The analogous triphosphenium cations have been considered as having the central phosphorus atom in the 1+ oxidation state with formal bond orders to the adjacent phosphorus centers of either 1 (dative bond, **13a**, or single bond, **13b**), 1.5 (**13c**), or 2 (**13d**).[57,67] Given the detailed treatment of both **12** and **13**, an examination of the electronic structures of the dicationic chalcogen analogues was performed.

The molecular geometries of the dications in **10Ch** and **11Ch** were optimized using density functional theory, and the stationary points found were subjected to different electronic structure analyses. The calculated metrical parameters (Figure 3 and the Supporting Information) are in excellent agreement with the X-ray crystallographic data. Examination of the frontier Kohn−Sham orbitals and electron localization function determined for **10Ch** and **11Ch** (Figures 5 and S-9 and S-10 in the Supporting Information) reveals, rather expectedly, the presence of two lone pairs at the chalcogen center. We note, in particular, that, similar to the σ lone pair, the p_π lone pair orbital is localized, which indicates the absence of π-type bonding within the P−Ch−P and As−Ch−As moieties, in good agreement with the determined structural parameters. NPA assigns the positive charge in the dications mostly on the pnictogen atoms, and the chalcogen centers are essentially electroneutral; the range of calculated values extends from −0.10 for **11Se** to +0.25 for **10Te** (see the Supporting Information). However, the calculated electrostatic potential yields a much more even distribution of positive charge in **10Ch** and **11Ch** (Figure S-11 in the Supporting Information). For all systems investigated, the Wiberg bond index, calculated on the natural atomic orbital (NAO) basis, of the Ch−P and Ch−As bonds is roughly 0.95. A similar picture of these interactions is drawn by analysis of the electron localization function, which reveals significant depopulation of the disynaptic V(Ch,P) and V(Ch,As) basins from the ideal value of a single electron pair.

The calculated data can be compared to values reported for cyclic triphosphenium cations **13**, which have a negatively (−0.25) charged dicoordinate phosphorus atom and a P−P Wiberg bond index slightly over 1 (1.10), indicative of a small but noticeable contribution from a π-type back-bonding interaction to their electronic structure.[57] The results for **10Ch** and **11Ch** can also be contrasted with the electronic structure of the dication in **9Te**, which features a highly positive tellurium center (natural charge +1.22) along with two Te−N bonds whose Wiberg bond indices fall significantly short of unity (0.75).[28] Taken as a whole, the electronic structure analyses are consistent with a covalently bound description (Figure 6, **B**), rather than the dative bond description (Figure 6, **A**), for the dications **10Ch** and **11Ch** because this also takes into account localization of the positive charge on the pnictogen atoms. However, both models represent certain features that **10Ch** and **11Ch** possess; therefore, neither structure **A** or **B** should be overinterpreted but rather taken as a guideline for the structural properties and potential reactivity of these compounds. For example, the synthetic details and metrical parameters from the solid-state structures, which are also reproduced from the calculations, are consistent with the dative bonding model and rare donor−acceptor pnictogen−chalcogen coordination complexes, **A**. The fact that the triflate anion weakly coordinates to the chalcogen atom in the solid state provides further evidence for some amount of positive charge or electron deficiency about the chalcogen center. The Lewis depiction, **B**, best takes into account the theoretical NAO charges, those being primarily on the donating pnictogen atom, but analysis of the electrostatic potential shows a more even distribution of charge over the P−Ch−P moiety. Furthermore, representing the Ch−P interaction with a covalent bond parallels with their chemical behavior, that is, decomposition by conversion of the chalcogen atom to an elemental state.



10Ch, **11Ch**

Ch = Se, Te
10 Pn = P
11 Pn = As

Figure 6. Depictions of **10Ch** and **11Ch** using the dative bonding model (**A**) and the corresponding Lewis structure (**B**).

CONCLUSIONS

We have described a facile synthesis of cyclic diphosphachalcogenium dications, using $[\mathrm{Ch}]^{2+}$ synthons, which cannot be accessed using the traditional electrophilic chalcogen(II) sources, the binary halides. The electronic structures were calculated, confirming the presence of two lone pairs on the dicoordinate chalcogen center, with a majority of the charge residing in the donating pnictogen atoms. We are currently investigating the Lewis acidic and basic properties of this new class of compounds as well as synthesizing acyclic derivatives.

ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra, CIF files, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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