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Homoleptic Pnictogen-Chalcogen Coordination Complexes

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Abstract: The synthesis and structural characterization of dicationic selenium and tellurium analogues of the carbodiphosphorane and triphosphenium families of compounds is 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 P→Ch 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 As→Ch 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 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**) and the related anionic dichalcogenido-imidophosphinates (**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 centre 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, 6**).²¹⁻²⁶

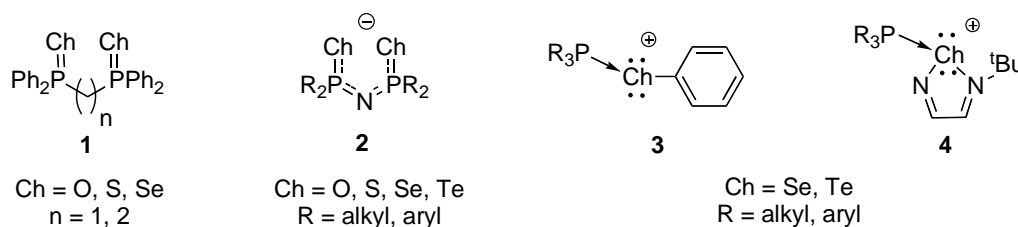
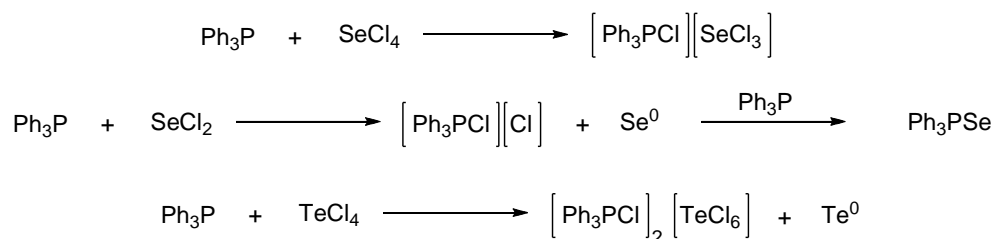


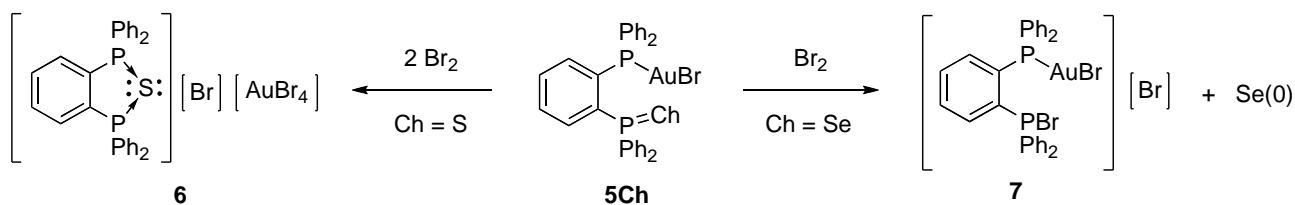
Figure 1: Structures of the common phosphine chalcogenides (**1**), dichalcogenido-imidophosphinates (**2**), and the examples of phosphines binding to electrophilic chalcogen centers (**3,4**).

The lack of activity in this area is surprising given the readily available sources of Lewis acidic group 16 centers as the di- (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 addition of excess phosphine.



Scheme 1. Redox reactions between Ph_3P and the electrophilic selenium and tellurium halides.

It was recently reported that the bromination of $(\text{dppbzS})\text{AuBr}$ (**5S**) ($\text{dppbz} = 1,2$ -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, 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 ($\text{X} = \text{Cl}, \text{Br}$), followed by halide abstraction reactions to generate the chelates. However, this is not viable as the aforementioned redox reactions dominate, rather than formation of $\text{P} \rightarrow \text{ChX}_2$ coordination complexes.



Scheme 2. Synthesis of the first P-S-P chelate via gold oxidation.

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 $[\text{Ch}]^{2+}$ (**8**, **9Ch**).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 As \rightarrow Ch coordination compounds (**11Ch**) were also prepared from 1,2-bis(diphenylarsino)ethane (dpAs), representing the first As \rightarrow Ch coordinative bond. A theoretical evaluation of the electronic structure and bonding in this class of compounds accompanies the experimental data.

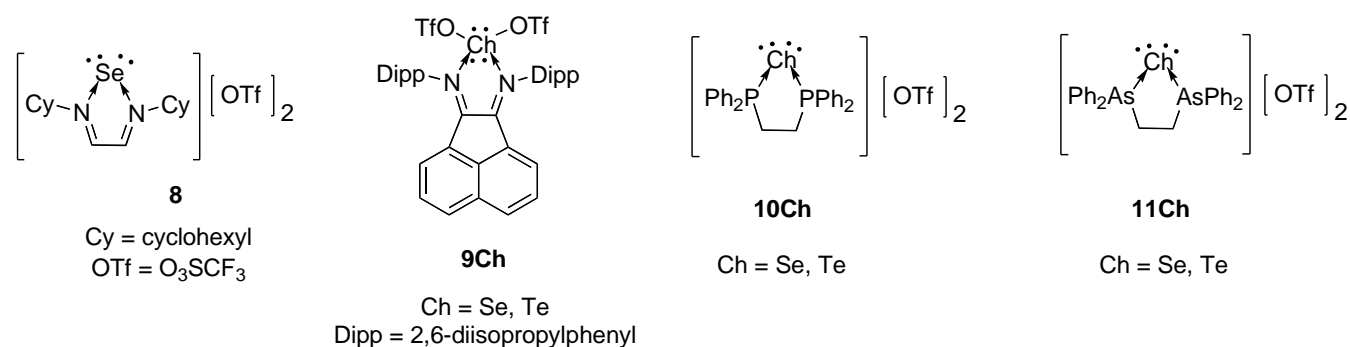


Figure 2: Suitable $\text{Ch}(\text{OTf})_2$ (Ch = Se, Te) transfer reagents (**8**, **9Ch**), and the compounds reported in this work (**10Ch**, **11Ch**).

Experimental Section:

Synthetic Procedures: All inert atmosphere syntheses were performed in a nitrogen-filled MBraun Labmaster 130 glove box 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. Solvent Purification System or an MBraun Solvent Purification system. Dried solvents were collected under vacuum and stored under a nitrogen atmosphere in Strauss flasks or in the glove box over 4Å molecular sieves. CD₃CN was dried with CaH₂, vacuum distilled, and stored in the glove box over 3Å molecular sieves. Solution ¹H, ¹³C{¹H}, ¹⁹F{¹H}, ³¹P{¹H}, ⁷⁷Se{¹H} NMR spectroscopy were recorded on a Varian INOVA 400 MHz spectrometer (¹H 400.09 MHz, ¹³C{¹H} 100.52 MHz, ¹⁹F{¹H} 376.15 MHz ³¹P{¹H} 161.82 MHz, ⁷⁷Se{¹H} 76.28 MHz). All ¹H and ¹³C{¹H} NMR spectra were referenced to residual solvent protons relative to Si(CH₃)₄ (CHD₂CN; ¹H δ_H = 1.95, ¹³C{¹H} δ_C = 1.32, 118.26). Chemical shifts for ³¹P{¹H} and ⁷⁷Se{¹H} NMR spectroscopy were referenced to an external standard (85% H₃PO₄; δ_P = 0.0, saturated SeO₂ solution in D₂O; δ_{Se} = -1302). FT-IR spectroscopy were collected on samples as KBr pellets using a Bruker Tenser 27 FT-IR spectrometer with a resolution of 4 cm⁻¹. FT-Raman spectroscopy 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 hours, precluding the collection of satisfactory microanalytical data. Proton 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 ⁷⁷Se{¹H} and ¹²⁵Te{¹H} NMR spectroscopic data.

X-Ray Crystallography Details: Single crystals for X-ray diffraction studies were grown by vapour diffusion of Et₂O 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-K α radiation ($\lambda = 0.71073\text{\AA}$) at the Western University X-Ray Facility. The Nonius and Bruker instruments operate SMART,³⁰ and COLLECT³¹ 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 5-membered dicationic ring was present, refining to 15% occupancy, with all atoms being refined anisotropically (Figure S8 Supporting Information). One of the triflate anions was also disordered and modeled leaving all atoms isotropic; attempting to treat these atoms anisotropically lead to unstable refinement. Similar disorder to **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 6.3³⁵ and Gaussian09.³⁶ Geometries of the studied systems were optimized using the PBE1PBE density functional³⁷⁻⁴⁰ in combination with the def2-TZVP basis sets.^{41,42} The nature of stationary points found

was assessed by calculating full Hessian matrices at the respective level of theory. Atomic charges were calculated with the 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; CH₂Cl₂ 3 mL) was added to a slurry of **8**²⁹ (0.100 g, 0.168 mmol; CH₂Cl₂ 5 mL) resulting in the immediate generation of a pale yellow solution with a small amount of colorless precipitate. After 5 minutes *n*-pentane (10 mL) was added giving further precipitation of colorless powder. The powder was allowed to settle and the supernatant decanted. The powder was washed with Et₂O (3 x 5 mL) and dried *in vacuo* giving **10Se** as a colorless powder. Yield 0.060 g, 46%; d.p. powder turns grey at 225°C; ¹H NMR (CD₃CN, δ ppm) 3.93 (multiplet; -CH₂); 7.96 – 7.78 (overlapping multiplets; Ph-H); ¹³C{¹H} NMR (CD₃CN, δ ppm) 30.5 (d, ¹J_{31P-13C} = 37.6 Hz), 117.7 (d, ¹J_{31P-13C} = 76.0 Hz), 131.8 (d, ²J_{31P-13C} = 14.9 Hz), 135.5, 138.0; ¹⁹F{¹H} NMR (CD₃CN, δ ppm) - 78.5; ³¹P{¹H} NMR (CD₃CN, δ ppm) 74.7 (¹J_{77Se-31P} = 382 Hz); ⁷⁷Se{¹H} NMR (CD₃CN, δ ppm) - 91.5 (¹J_{77Se-31P} = 382 Hz); Elemental analysis calc'd (found) C 43.35 (43.71), H 3.12 (4.03); 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).

Synthesis of 10Te: A solution of dppe (0.056 g, 0.140 mmol; CH₂Cl₂ 3 mL) was added to a slurry of **9Te**²⁸ (0.129 g, 0.140 mmol; CH₂Cl₂ 5 mL) resulting in the immediate generation of a pale yellow precipitate. After 5 minutes Et₂O (10 mL) was added. The powder was allowed to settle and the supernatant decanted. The powder was washed with Et₂O (3 x 5 mL) and dried *in vacuo* giving **10Te** as an off-white powder. Yield 0.102 g, 89%; d.p. powder turns grey at 125°C; ¹H NMR (CD₃CN, δ ppm) 3.65 (multiplet; -CH₂), 7.90 – 7.74 (multiplets; Ph-H); ¹⁹F{¹H} NMR (CD₃CN, δ ppm) - 78.5; ³¹P{¹H}

NMR (CD₃CN, δ ppm) 43.0 ($^1J_{125\text{Te}-31\text{P}} = 1020$ Hz); Elemental analysis calc'd (found) C 40.79 (38.63), H 2.94 (2.56); 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)⁺

Synthesis of **11Se**: A solution of dpAse (0.072 g, 0.149 mmol; CH₂Cl₂ 5 mL) was added to a slurry of **9Se**²⁹ (0.131 g, 0.149 mmol; CH₂Cl₂ 5 mL) resulting in the immediate darkening of the solution. After 15 minutes pentane (10 mL) was added. The white powder was allowed to settle and the supernatant decanted. The powder was washed with Et₂O (3 x 5 mL) and dried *in vacuo* giving **11Se** as an off-white powder. Yield: 35%, 45 mg; d.p. powder turns grey at 146°C; ¹H NMR (CD₃CN, δ ppm): 3.97 (s, 4H, -CH₂), 7.70-7.74 (m, 8H, Ph-H), 7.78-7.85 (m, 12H, Ph-H); ¹³C{¹H} NMR (CD₃CN δ ppm): 58.7, 131.8, 132.1, 133.3, 133.6; ¹⁹F{¹H} NMR (CD₃CN 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; CH₂Cl₂ 3 mL) was added to a slurry of **9Te**²⁸ (0.092 g, 0.0988 mmol; CH₂Cl₂ 5 mL) resulting in the immediate generation of a light brown precipitate. After 15 minutes pentane (10 mL) was added. The powder was allowed to settle and the supernatant decanted. The powder was washed with Et₂O (3 x 5 mL) and dried *in vacuo* giving **10Te** as a light brown powder. Yield: 70%, 63 mg; d.p. powder turns grey at 206°C; ¹H NMR (CD₃CN, δ ppm): 3.66 (s, 4H, -CH₂), 7.72-7.76 (m, 8H, Ph-H), 7.82-7.88 (m, 12H, Ph-H); ¹³C{¹H} NMR (CD₃CN δ ppm): 37.5, 124.7, 131.7, 133.7, 135.5; ¹⁹F{¹H} NMR (CD₃CN, δ ppm): -78.5; FT-IR (cm⁻¹ (ranked

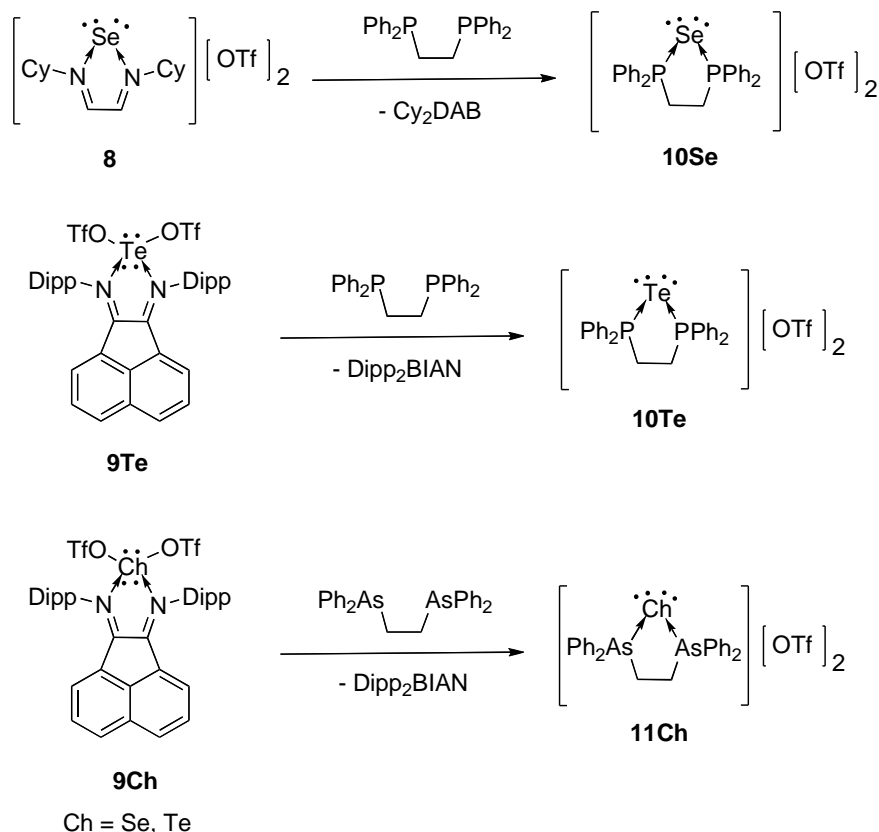
intensity)): 466 (9), 516 (10), 574 (12), 636 (4), 688 (7), 744 (6), 771 (14), 997 (11), 1023 (3), 1076 (13), 1165 (5), 1234 (1), 1286 (2), 1440 (8), 2918 (15).

Results and Discussion:

The 1:1 stoichiometric reaction of dppe (1,2-bis(diphenylphosphino)ethane) with **8** or **9Ch** in CH₂Cl₂ immediately resulted in the production of yellow solutions; colorless powders were obtained after precipitation with *n*-pentane and washing with Et₂O. Samples of the solids were redissolved in CD₃CN for analysis by multinuclear NMR spectroscopy, where the ³¹P{¹H} 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 (⁷⁷Se; 7.6%) and tellurium (¹²⁵Te; 7.1%), were clearly visible in the spectra with ¹J_{77Se-31P} and ¹J_{125Te-31P} values of 380 Hz and 1020 Hz for **10Se** and **10Te**, respectively. The ¹H NMR spectrum revealed a set of resonances for one dppe molecule and the methylene protons shifted downfield compared to the free ligand (**10Se**: Δδ_H = 1.85; **10Te**: Δδ_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 Ch(II) atoms found in the P,P chelate of the ligand (**10Ch**; Scheme 1).

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 as compared to the corresponding diphosphine. Compounds **11Ch** were prepared by using a similar strategy for the preparation of **10Ch**. In the case of selenium it was found that dpAse (1,2-bis(diphenylarsino)ethane) would not undergo ligand exchange with **8** and instead **9Se** had to be used. After precipitating the product from the reaction mixture, subsequent ¹H NMR spectra revealed resonances consistent with a single dpAse ligand with methylene protons shifted downfield (**11Se**: Δδ_H

= 1.91; **11Te**: $\Delta\delta_{\text{H}} = 1.54$). These compounds are significantly less stable than **10Ch** in solution, with elemental Se or Te observed to precipitate after one hour 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**.



Scheme 3: Synthesis of compounds **10Ch** and **11Ch** *via* ligand exchange reactions.

X-Ray Crystallography:

Single crystals suitable for X-ray diffraction studies were grown by vapour diffusion of Et_2O 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 Ch-P coordination complexes, and are significantly longer than the Ch-P 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** 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 the dppe derivative, crystallizing in the same space group with slightly larger unit cell parameters. However, there is disorder about the core 5-membered ring as well as one of the triflate anions that was successfully modeled (Figure S-8) but the deviation between the two prevents the 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 lengths in **10Te** while the As – Te – As bond angle is slightly larger at 84-86°. The Te-As bond distances is comparable to a standard Te – As single bond,⁴⁹ however this structure represents the first example where the arsenic-tellurium 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, H₃COTf ($\delta_F = -75.0$), and an ionic triflate, [NOct₄][OTf] ($\delta_F = -79.0$ in CH₂Cl₂, $\delta_F = -78.5$ in MeCN) is quite distinguishable. These data provide insight on whether the triflate oxygen 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 [R₃POPR₃][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 short P – O bond lengths of

1.54 Å and a very wide bond angle of 164° for the P – O – P fragment indicating that the P – O bond orders could be greater than one.⁵² Cyclic species have also been reported but not structurally characterized.⁵³

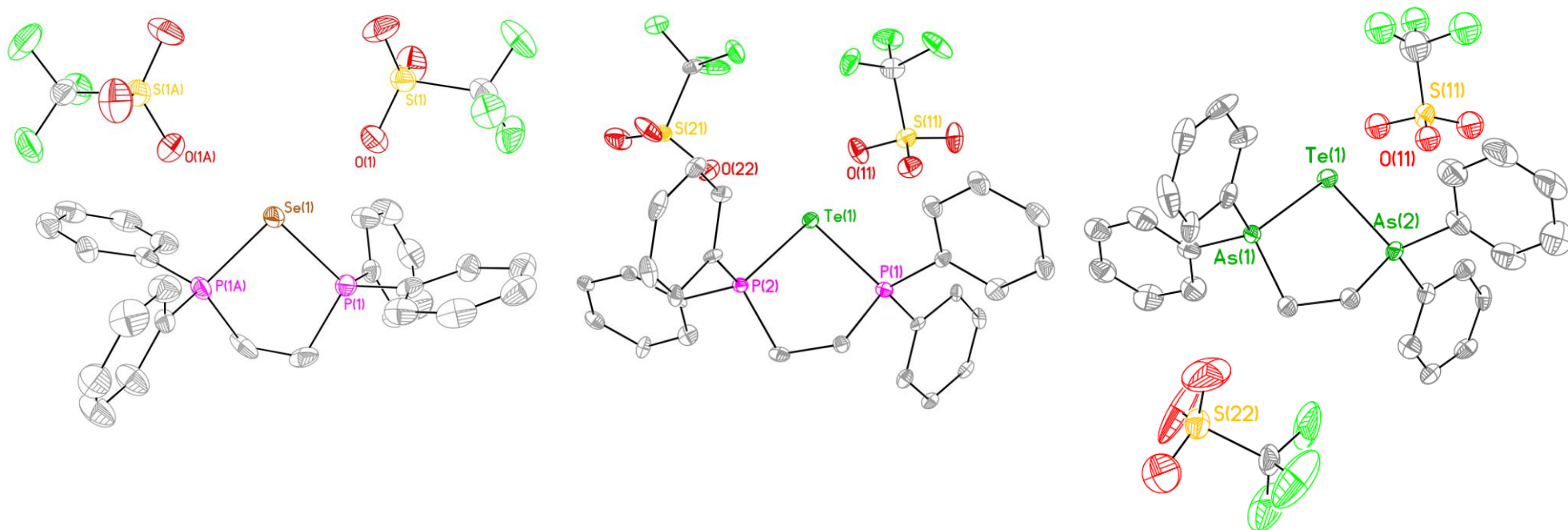


Figure 3. Solid-state structures of **10Se** (left), **10Te** (center), and **11Te** (right). Thermal ellipsoids are displayed at the 50% probability level and hydrogen atoms are omitted. For **10Te** and **11Te** acetonitrile solvate is removed for clarity. For **11Te** the disordered ring and triflate are removed for clarity, a full view is provided in the supporting information (Figure S8). Selected bond lengths (Å) and angles (°); calculated values in square brackets: **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].

Table 1: X-ray details for **10Se**, **10Te**, **11Te**.

Compound	10Se	10Te	11Te
Empirical formula	C ₂₈ H ₂₄ F ₆ O ₆ P ₂ S ₂ Se ₁	C ₂₈ H ₂₄ F ₆ O ₆ P ₂ S ₂ Te ₁	C ₂₈ H ₂₄ As ₂ F ₆ O ₆ S ₂ Te ₁
		1/3 (C ₂ H ₃ N)	1/3 (C ₂ H ₃ N)
FW (g/mol)	775.49	836.81	924.71
Crystal system	Monoclinic	Trigonal	Trigonal
Space group	C2/c	R3	R3
<i>a</i> (Å)	15.014	24.418	24.603
<i>b</i> (Å)	9.896	24.418	24.603
<i>c</i> (Å)	21.02	13.727	13.890
α (deg)	90	90	90
β (deg)	99.97	90	90
γ (deg)	90	120	120
<i>V</i> (Å ³)	3076	7088	7281
<i>Z</i>	4	9	9
<i>D_c</i> (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)
<i>R</i> 1[<i>I</i> >2 σ] ^a	0.0416	0.0722	0.0543
<i>wR</i> 2(<i>F</i> ²) ^a	0.1079	0.1716	0.1007
GOF (<i>S</i>) ^a	1.121	1.045	1.028

^a $R1(F[I > 2(I)]) = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2(F^2 [all data]) = [w(F_o^2 - F_c^2)^2]^{1/2}$; $S(all data) = [w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (*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.

Electronic Structures:

Compounds **10Ch** can be considered dicationic analogues of the carbodiphosphorane (**12**) and, in particular, cyclictriphosphenium (**13**) families of compounds. 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 C⁰ 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 one (dative bond **13a**, or single bond, **13b**), 1.5 (**13c**), or two (**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.

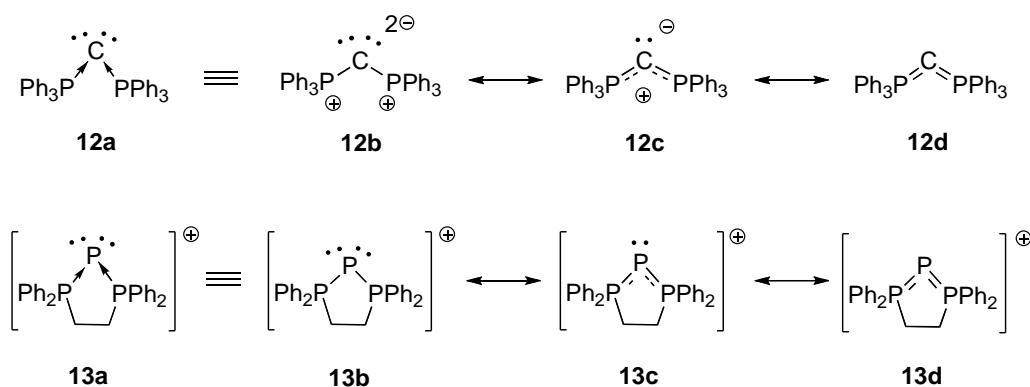


Figure 4: Resonance structures of carbodiphosphorane **12**, and cyclic triphosphenium cation, **13**.

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; 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** (Figure 5, Figure S-9, S-10 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 $p\pi$ -lone pair orbital is localized, which indicates the absence of π -type bonding within the P – Ch – P and As – Ch – As moiety, in good agreement with the determined structural parameters. Natural population analysis assigns the positive charge in the dications mostly on the pnictogen atoms and that the chalcogen centers are essentially electroneutral; the range of calculated values extending from -0.10 for **11Se** to $+0.25$ for **10Te** (Supporting Information). However, the calculated electrostatic potential yields a much more even distribution of positive charge in **10Ch** and **11Ch** (Figure S11 Supporting Information). For all systems investigated, the Wiberg bond index, calculated in the natural atomic orbital basis, of the Ch – P and Ch – As bonds is roughly 0.95. A similar picture of these interactions is drawn by the analysis of the electron localization function which reveals significant depopulation of the disynaptic $V(\text{Ch,P})$ and $V(\text{Ch,As})$ basins from the ideal value of a single electron pair.

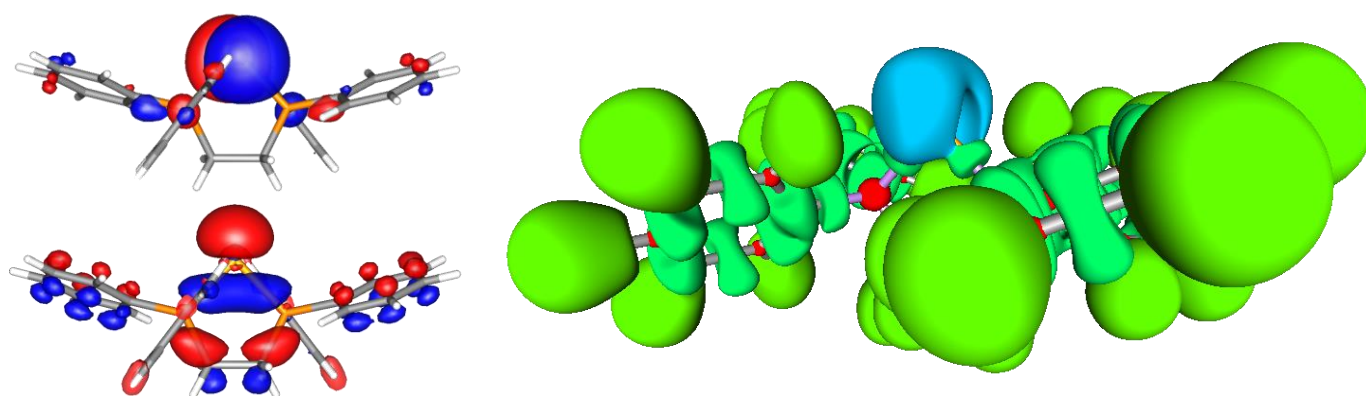


Figure 5: Frontier Kohn-Sham orbitals (left) and electron localization function (right) of **10Se**. Colour code: monosynaptic valence basin (blue), disynaptic valence basin (green), core basin (red).

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 one (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** as this also takes into account the 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 over interpreted, 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 dative bonding model and rare donor→acceptor pnictogen→chalcogen coordination complexes, **A**. The fact that the triflate anion weakly coordinates to the Ch 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 chalcogen–pnictogen interaction with a covalent bond parallels with their chemical behavior, that is, decomposition by reduction of the chalcogen atom to an elemental state.

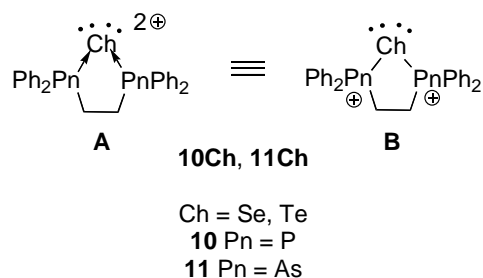


Figure 6: Depictions of **10Ch** and **11Ch** using the dative bonding model (**A**) and the corresponding Lewis Structure (**B**).

Conclusions:

We have described a facile synthesis of cyclic diphosphachalcogenium dications, using $[\text{Ch}]^{2+}$ synthons, which cannot be accessed using the traditional electrophilic Ch(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 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.

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Supporting Information Available.

Supporting information including NMR spectra, cif files, and computational details is available on the WWW free of charge.

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