

Lewis Base Sequestered Chalcogen Dihalides: Synthetic Sources of ChX_2 ($\text{Ch} = \text{Se}, \text{Te}$; $\text{X} = \text{Cl}, \text{Br}$)

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Abstract: The synthesis and comprehensive characterization of a series of base-stabilized ChX_2 ($\text{Ch} = \text{Se}, \text{Te}$; $\text{X} = \text{Cl}, \text{Br}$) is reported using aryl-substituted diazabutadiene and 2,2'-bipyridine (bipy) as the ligands. In stark contrast to free ChX_2 the complexes display excellent thermal stability. Their use as

viable ChX_2 reagents that may be stored for later use is demonstrated in principle. The syntheses are simple and

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high-yielding from commercially available or easily synthesized reagents. The bipy complexes are exceedingly rare examples of this ubiquitous ligand being utilized within Group 16 chemistry; the Se examples are the first to be characterized by X-ray crystallography, and the Te species are only the second.

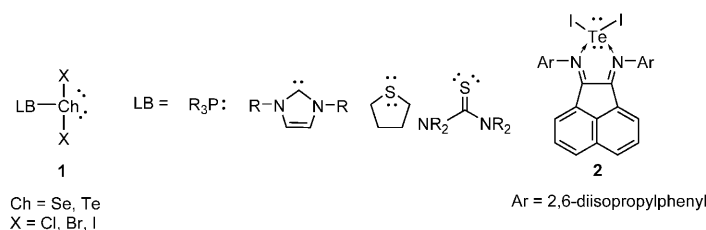
Introduction

The coordination chemistry of the heavy chalcogens is underdeveloped when compared with the majority of the periodic table.^[1] The primary reason for this lack of activity is likely because the obvious electrophilic Group 16 starting reagents, the tetrahalides (ChX_4 ; $\text{Ch} = \text{Se}, \text{Te}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), typically undergo redox reactions in the presence of common ligands (imine, phosphine, N-heterocyclic carbene).^[2] These processes result in a reduction of the chalcogen atom to the +2 oxidation state, coupled with the elimination of reactive X_2 . The released dihalogen often participates in undesirable side reactions, leading to difficulty in controlling the reaction outcome.^[3,4] The X_2 can be sequestered by the addition of a third species (i.e., cyclohexene, SnCl_2), provided the additional reagent does not interfere with the targeted reactions.^[5,6] Within our laboratory we have found that starting with a Ch^{II} source appears to largely circumvent this problem.^[7,8] Unfortunately, the selenium dihalides (SeX_2 ; $\text{X} = \text{Cl}, \text{Br}$) are highly unstable with respect to disproportionation. Selenium dichloride must be synthesized and used within a matter of hours, and SeBr_2 is stable

for only mere minutes before substantial decomposition ensues, rendering these reagents very difficult to use in a straightforward fashion.^[9] There exist several different methods for making SeX_2 and all suffer from the drawback that the resultant selenium dihalide must be used in situ, and cannot be stored for later use.^[9–11] Complicating matters, there is no simple method of readily ascertaining exactly what is present in solution—that is, how pure the SeCl_2 is after, for example, 4 or 5 h. Selenium-77 NMR spectroscopy is relatively simple using modern spectrometers, but obtaining a reasonable ^{77}Se NMR spectrum in a short timeframe is not as facile as it is for other routine nuclei (e.g., ^1H , ^{13}C , ^{31}P , ^{19}F). Moreover, a 5–10% impurity is not easily observed in a routine sample analyzed by ^{77}Se NMR spectroscopy, even though it may be a significant detriment to any attempted transformations. Another restriction is that SeX_2 is only compatible with certain organic solvents (e.g., THF, MeCN), whereas other common solvents such as CH_2Cl_2 cannot be used.

Base-stabilized SeX_2 derivatives have been reported and include the products from the oxidative addition of X_2 to phosphine selenides or selenoureas, which formally contain a SeX_2 fragment (e.g., **1**; Scheme 1).^[12–17] Direct reaction of S-based ligands with SeX_2 has also been used to sequester this reactive fragment.^[9,18,19] To the best of our knowledge, no further chemistry has been described using any of these as a source of SeX_2 . The corresponding tellurium binary halides are known only as transient species in the gas phase.^[20,21] Base-stabilized TeX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; for example, **1**, **2**) compounds have also been reported but they have not

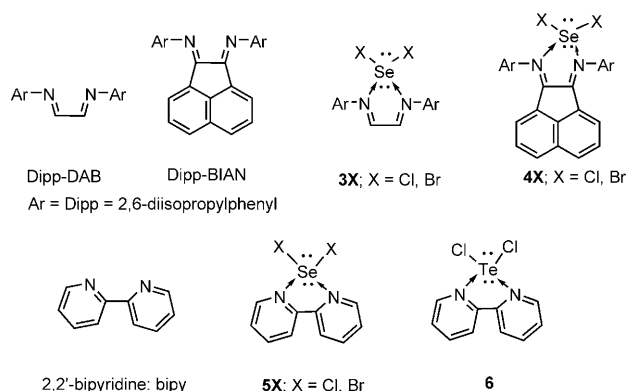
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Scheme 1. Representative examples of known base-stabilized ChX_2 species.

yet been utilized in the delivery of the tellurium dihalide, with the exception of a hydrated thiourea-ligated TeCl_2 fragment.^[4,22–25]

These combined issues call for a system in which a functional equivalent of ChX_2 can be stored for an indefinite period of time, its purity easily ascertained, and demonstrates the ability to cleanly deliver the chalcogen dihalide. In this context, we have discovered that α -diimine ligands featuring aryl N-substituents (Dipp-DAB, Dipp-BIAN; Dipp = 2,6-diisopropylphenyl; DAB = diazabutadiene; BIAN = bisaryliminoacenaphthene) or the 2,2'-bipyridyl (bipy) ligand can easily sequester ChX_2 in a stable form (**3–6**). If one views the Ch–N linkage as a formally dative inter-



action, it has an intrinsic lability and should therefore be inclined to quantitative release of the ChX_2 fragment, which can be utilized as a synthetic equivalent of the chalcogen dihalide. The syntheses may easily be performed on a large scale, thus they are amenable to preparatory reactions. Although 2,2'-bipyridine has been synonymous with a wide range of transition metal and p-block complexes, compounds **5** and **6** are exceedingly rare examples of this ubiquitous ligand being utilized within Group 16 chemistry.^[26,27] Indeed, the Se-bipy complexes are the first structurally characterized bipy chelates of that element, and a derivative of **6** represents only the second example of a Te-bipy molecule characterized by X-ray diffraction studies.^[28]

Results and Discussion

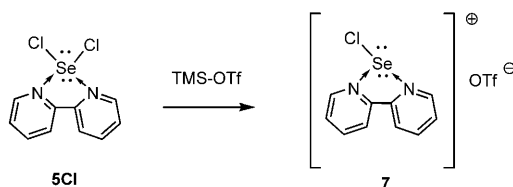
The 1:1 stoichiometric reaction of Dipp-DAB or Dipp-BIAN with SeCl_2 (prepared from Se^0 and SO_2Cl_2) in THF results in a red solution. Removal of the solvent in vacuo gives a bright orange (Dipp-DAB) or deep red (Dipp-BIAN) powder. A sample of each of the powders redissolved in CDCl_3 for ^1H NMR spectroscopy revealed a set of signals indicative of a single, pure diazabutadiene-containing product, with an apparent retention of the ligand symmetry. The diagnostic resonance arising from the protons in the ligand backbones were shifted downfield from the free ligand in both cases (Dipp-DAB: $\Delta\delta = 0.7$ ppm; Dipp-BIAN: $\Delta\delta = 0.14$ ppm). Single crystals for X-ray diffraction studies were obtained for the Dipp-BIAN analogue, which revealed the Dipp-BIAN chelate of SeCl_2 (**4Cl**). Despite many repeated efforts, we were unable to obtain single crystals from solutions of the bulk powder. Elemental analysis (C, H, N) gave results indicative of a molecular formula containing only Dipp-DAB and SeCl_2 ($\text{C}_{26}\text{H}_{36}\text{N}_2\text{Cl}_2\text{Se}$), which is also consistent with the total mass of material recovered from the reaction (96% yield). Based on these data, the compound was assigned as being the Dipp-DAB chelate of SeCl_2 (**3Cl**).

The same compounds may also be made from SeCl_2 generated in situ from SeCl_4 and SbPh_3 in THF, in which the Ph_3SbCl_2 byproduct is easily removed by washing with Et_2O , and the complexed SeCl_2 remains insoluble. Both **3Cl** and **4Cl** are stable in the solid state (>1 year under an N_2 atmosphere) at room temperature, and for days in solution, which is in distinct contrast to free SeCl_2 , which readily disproportionates. Remarkably, the compounds show no evidence of decomposition in the solid state until after at least sixty days if left open to the ambient atmosphere of the laboratory, as monitored by FT-Raman spectroscopy, whereas molecular SeCl_2 reacts almost instantaneously if exposed to the open air. In solution, **3Cl** and **4Cl** decompose within five minutes of exposure to ambient conditions. The materials are also compatible with a range of common organic solvents (alkanes (insoluble), ethers such as Et_2O (insoluble) and THF (soluble), arenes (slight soluble), chloroalkanes (soluble), MeCN (soluble)), provided the solvents are dried to the typical standards required for handling moderately moisture-sensitive materials ($\text{H}_2\text{O} < 100$ ppm).

Selenium dibromide is considered to be significantly less stable than SeCl_2 ; however, the successful trapping of SeCl_2 indicated that it might be possible to do the same for the bromide congener. The 1:1 stoichiometric reaction of SeBr_2 with Dipp-DAB or Dipp-BIAN in THF results in the immediate generation of a very dark red solution. Removal of the THF under vacuum gave dark brown (Dipp-DAB) or purple (Dipp-BIAN) solids. The proton NMR spectra of samples of both solids were essentially identical to those observed for **3Cl** and **4Cl**, and indicated successful complexation of the SeBr_2 . Single crystals for X-ray diffraction analysis were obtained for the Dipp-BIAN analogue, which revealed the expected Dipp-BIAN chelate to SeBr_2 (**4Br**). Al-

ternatively, the compounds can be prepared in quantitative yields by means of halide metathesis of **3Cl** or **4Cl** using $(\text{CH}_3)_3\text{SiBr}$. Compound **4Br** shows no signs of decomposition if stored under N_2 at room temperature; **3Br** decomposes within 2 weeks at room temperature under inert conditions. In contrast with the chlorine derivatives, both bromine analogues are quite sensitive to the ambient atmosphere of the laboratory in the solid state, decomposing in minutes.

The 1:1 stoichiometric reaction of a freshly prepared solution of SeX_2 ($\text{X}=\text{Cl}, \text{Br}$) with 2,2'-bipyridine resulted in the immediate precipitation of yellow solids. The solids were separated from the supernatant, washed with Et_2O , and dried in vacuo. For $\text{X}=\text{Cl}$, the material was found to be insoluble in a variety of solvents for NMR spectroscopy (C_6D_6 , CDCl_3 , CD_3CN), but was sufficiently soluble in $[\text{D}_6]\text{acetone}$, enabling the acquisition of ^1H NMR spectroscopic data. The spectrum showed a set of resonances consistent with a single product containing the bipy framework. The yield of material recovered was essentially equal to the total expected based on SeCl_2 and bipy, and therefore the identity of the compound was tentatively assigned as the bipy chelate of SeCl_2 (**5Cl**). Decomposition of a solution of the compound in acetone was observed within minutes (<20 min), which precluded the growth of single crystals for X-ray analysis, and a definitive assignment of the bonding. The bromine derivative was found to be significantly more soluble, with single crystals readily grown from a solution of the bulk powder in CH_2Cl_2 . Subsequent X-ray diffraction studies revealed the $[\text{Se}(\text{bipy})\text{Br}_2]$ complex (**5Br**). A more soluble derivative of **5Cl** was generated by means of halide abstraction (Scheme 2) using one stoichiometric equivalent

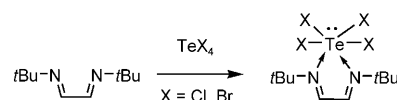


Scheme 2. Derivation of **5Cl** by means of halide metathesis.

of TMS-OTf (TMS-OTf = trimethylsilyltrifluoromethanesulfonate), in CH_2Cl_2 , which resulted in a color change of the solid from pale yellow to colorless. After isolation, a sample of the powder was dissolved in CD_3CN for ^1H NMR spectroscopy. The resonances were consistent with a single product containing the bipy ligand. To obtain definitive identification of the material single crystals were grown from a saturated solution of the bulk powder in CH_3CN by means of vapor diffusion of Et_2O . X-ray diffraction studies revealed the compound to be the salt $[\text{Se}(\text{bipy})\text{Cl}][\text{OTf}]$ (OTf = triflate) (**7**), with the Se atom found in the N,N' -chelate of the bipyridine ligand. Compounds **5Cl** and **5Br** are indefinitely stable in the solid state at room temperature under an N_2 at-

mosphere, but they do decompose within an hour if opened to ambient air.

In contrast with the reactivity observed for Se, the direct reaction of alkyl-substituted DAB ligands and TeX_4 does not result in a reduction of the Te atom from Te^{IV} to Te^{II} . Instead simple $[\text{Te}(\text{dab})\text{X}_4]$ coordination complexes are formed (Scheme 3).^[6] Unfortunately, all attempts to reduce

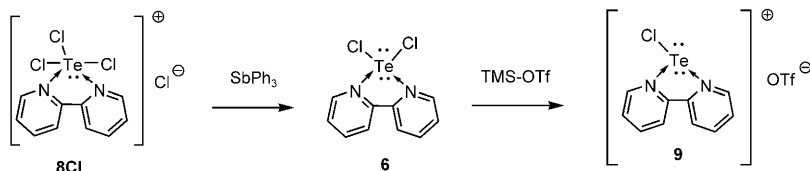


Scheme 3. Previous synthesis of TeX_4 -diimine coordination complex using the *tert*-butyl DAB ligand.

the Te to the +2 oxidation state in these compounds resulted in the immediate deposition of elemental tellurium. Cowley et al. showed that the direct reaction of the Dipp-BIAN ligand with TeI_4 did result in a redox process, generating the TeI_2 chelate of Dipp-BIAN.^[23] This compound appears to have the potential to be used as a Te^{II} source although no further chemistry utilizing the compound as a TeI_2 synthon has been reported. Very recently our group has reported the use of a Dipp-BIAN-stabilized pseudohalide of Te ($\text{Te}(\text{OTf})_2$) to generate a series of Te-centered dications.^[29] However, a viable source of TeCl_2 remains unknown. We have found that the direct reaction of TeX_4 ($\text{X}=\text{Cl}, \text{Br}$) with either Dipp-DAB or Dipp-BIAN gives a complicated mixture of products, and trying to mediate the redox process using SbPh_3 or SnCl_2 also results in complex mixtures with concomitant deposition of Te metal. Given the successful complexation of SeX_2 using the bipy ligand, we were prompted to investigate the use of bipy as a potential stabilizing agent for TeX_2 .

The 1:1 stoichiometric reaction of TeX_4 ($\text{X}=\text{Cl}, \text{Br}$) with bipy results in the immediate generation of a yellow ($\text{X}=\text{Cl}$) or bright orange ($\text{X}=\text{Br}$) precipitate. After separation from the supernatant and drying under vacuum, bright yellow ($\text{X}=\text{Cl}$) or orange ($\text{X}=\text{Br}$) powders are isolated. Both solid materials are highly insoluble in all common NMR spectroscopic solvents, with the exception of $[\text{D}_6]\text{acetone}$; ^1H NMR spectra of both materials in $[\text{D}_6]\text{acetone}$ showed resonances indicative of a single bipy-containing product. As in the above case with SeCl_2 , the compounds decompose readily in acetone. Results from CHN combustion analysis allowed the assignment of the compounds as bipy chelates of TeX_4 (**8Cl** and **8Br**). Related compounds of the formula $\text{RTeCl}_3\text{bipy}$ ($\text{R}=\textit{o}$ -cresol, \textit{m} -cresol, \textit{p} -cresol, \textit{o} -chlorophenol) have been described as a cation-anion pair ($[\text{Te}(\text{bipy})\text{Cl}_2\text{R}][\text{Cl}]$).^[27] No structural evidence was obtained, but conductivity measurements were consistent with a 1:1 electrolyte. Conductivity experiments on **8Cl** and **8Br** in acetone showed similar conductivity as the above report, therefore an ionic formula ($[\text{Te}(\text{bipy})\text{X}_3][\text{X}]$) is also proposed for these compounds.

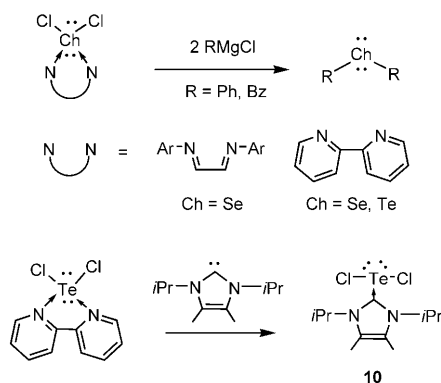
No reaction is detectable between bipy and TeI_4 , which was also observed in attempted reactions with alkyl-substituted diazabutadiene ligands. The TeCl_4 congener may be cleanly reduced to the TeCl_2 species (**6**) using Ph_3Sb , which gives a green powder upon workup (Scheme 4). The powder



Scheme 4. Reduction of **8Cl**, which gave a base-stabilized form of TeCl_2 (**6**) and subsequent derivation by halide abstraction for positive identification.

may be dissolved in CD_3CN in sufficient quantities for ^1H NMR spectroscopic studies, which gave a clean spectrum of a single bipy-containing compound, and combustion analysis of the bulk powder was consistent with the molecular formula containing TeCl_2 and bipy. Although this material is stable in acetonitrile, we have been unable to obtain crystals of sufficient quality for X-ray diffraction analysis. A halide-abstraction reaction from the TeCl_2 using one stoichiometric equivalent of TMS-OTf gives a derivative for which single crystals could be obtained. X-ray diffraction analysis of a single crystal revealed the expected $[\text{Te}(\text{bipy})\text{Cl}]^+$ cation paired with a triflate anion (**9**), thereby allowing us to infer that the formulation of **6** was indeed correct.

Preliminary reactivity studies: The above compounds represent novel complexes within chalcogen–nitrogen chemistry, but to act as functional equivalents of ChX_2 , they must cleanly release the chalcogen dihalide and the ligand byproduct must be readily removed from the new material. Aryl Grignard reagents react with SeCl_2 in a 2:1 stoichiometry to give the corresponding aryl selenides.^[30] This appeared to be an ideal reaction to test our ability to use the above compounds as a source of SeCl_2 (Scheme 5). The reaction of **4Cl** with two equivalents of PhMgCl in THF at -78°C gives



Scheme 5. Selected reactions utilizing the base-stabilized ChX_2 species as synthetic equivalents of ChX_2 .

a yellow slurry. After warming the mixture to room temperature, the THF was removed in vacuo and the residue was extracted with *n*-hexane. After filtration and removal of the *n*-hexane, an ^1H NMR spectrum of the gel-like material showed resonances arising from the free Dipp-BIAN ligand,

as well as other overlapping signals in the phenyl region. A $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of the same sample revealed only one signal at $\delta = 416$ ppm, consistent with SePh_2 . The phenylselenide may be easily separated from the Dipp-BIAN by column chromatography (silica gel; 98.5:1.5 hexane/ethyl acetate) and recovered in an overall yield of 70–75%, which is com-

parable to the literature report for the direct reaction. An essentially identical procedure may be used to generate SeBz_2 from BzMgCl ($\text{Bz} = -\text{CH}_2\text{Ph}$), with the exception that **3Cl** was used as the SeCl_2 source. The $[\text{Se}(\text{bipy})\text{Cl}_2]$ complex **5** also reacts with the Grignard reagents to form aryl selenides. The primary difference from the DAB congeners is that the released bipy ligand forms an insoluble complex with the MgCl_2 byproduct, thereby eliminating the need for column chromatography.^[31] Most interesting is that compound **6** serves as a functional equivalent of TeCl_2 . This is a significant discovery as the free binary halide is unknown in the condensed phase, and thus the reactivity of the tellurium dihalides is completely unexplored. Diaryl telluriides may be formed by the reaction of **6** with either PhMgCl or BzMgCl in good yields with only a simple workup (60–70%). Compound **6** may also be utilized as a TeCl_2 synthon in a ligand-exchange reaction with a stronger Lewis base (e.g., N-heterocyclic carbene; $\text{NHC} = 2,5$ -diisopropylimidazole-3,4-dimethyl-2-ylidene). The reaction of one equivalent of NHC with **6** in THF gives compound **10** in a good yield (70%) after a short workup. A previous investigation by Kuhn and co-workers generated the I_2 congener of this compound through the direct reaction of TeI_4 with the carbene, coupled with the reductive elimination of I_2 .^[4] They were unable to synthesize the lighter halide analogues due to the much higher reactivity of the released Cl_2 or Br_2 , which gave complex mixtures. Using a source of Te^{II} rather than Te^{IV} appears to have circumvented this issue, highlighting the possible utility of **6** as an effective source of TeCl_2 .

X-ray crystallography: Compounds **4**, **5Br**, **7**, **9**, and **10** have been characterized by single-crystal X-ray diffraction studies. Views of the solid-state structures are shown in Figures 1 to 6, and pertinent refinement details may be found in Table 1. Key bond lengths and angles are summarized in Table 2.

An examination of the metrical parameters for **4Cl** reveals a square-planar Se center (Figure 1), which is consistent with an AX_4E_2 electron-pair geometry, indicative of two lone pairs at Se, and retention of the +2 oxidation of

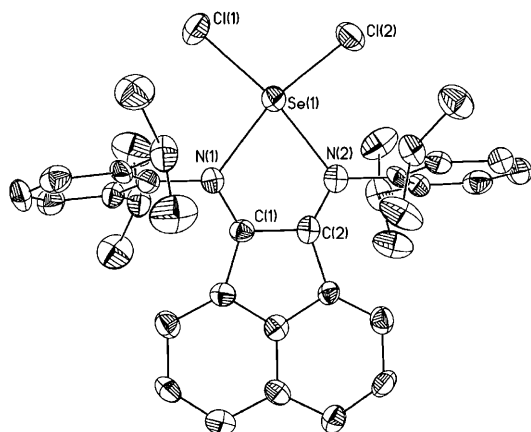


Figure 1. Solid-state structure of **4Cl**. Ellipsoids are drawn to 50 % probability level and hydrogen atoms are omitted for clarity.

the metal. The Se–N bonds are considerably elongated (Se(1)–N(1), 2.263(3); Se(1)–N(2), 2.314(5) Å) relative to a typical Se–N single bond (1.8–1.9 Å).^[32] These bonds are best designated as coordinative in nature, which is supported by their labile character, and thus the ease with which diorganoselenides could be synthesized. The Se–Cl bonds were also elongated by virtue of the coordination of the ligand into the Se–Cl σ^* orbitals (Se(1)–Cl(1), 2.293(2); Se(1)–Cl(2), 2.326(2) Å).^[33] The endocyclic N–C bonds are short (1.286–1.301 Å), reflective of their imine character, and the C–C bond in the N_2C_2Se heterocycle is consistent with a single bond (1.490(9) Å). This is in contrast to what is reported for coordination of Dipp-BIAN or Dipp-DAB with the pnictogen halides, whereby an internal two-electron transfer from the central element into the LUMO of the DAB ligand imposes a pnictenium architecture containing N–C and C=C functionalities.^[34,35]

Compound **4Br** (Figure 2) is isostructural with **4Cl**, where the main difference was even longer Se–N bonds (Se(1)–N(1), 2.290(3); Se(1)–N(2), 2.358(3) Å). Compounds **5Br** and **7** represent the first structurally characterized Se com-

Table 2. Selected bond lengths [Å] and angles [°] for compounds **4**, **5Br**, **7**, and **9**.

	4Cl	4Br	5Br	7	9
Ch(1)–N(1)	2.263(3)	2.290(3)	2.099(6)	1.970(3)	2.171(6)
Ch(1)–N(2)	2.314(5)	2.358(3)	2.090(5)	N/A	2.288(6)
Ch(1)–X(1)	2.293(2)	2.4367(7)	2.673(1)	2.710(1)	2.492(2)
Ch(1)–X(2)	2.326(2)	2.4677(8)	2.640(1)	N/A	N/A
N(1)–C(1)	1.301(8)	1.286(5)	1.360(8)	1.359(5)	1.36(1)
N(2)–C(2)	1.286(8)	1.279(5)	1.348(8)	N/A	1.347(9)
C(1)–C(2)	1.490(9)	1.496(6)	1.45(1)	1.451(8)	1.46(1)
X(1)–Ch(1)–X(2)	98.56(8)	97.91(2)	94.51(4)	N/A	N/A
X(2)–Ch(1)–N(2)	95.1(2)	95.96(8)	94.36(15)	N/A	N/A
N(2)–Ch(1)–N(1)	74.4(2)	73.6(1)	77.0(2)	80.1(2)	73.1(2)
N(1)–Ch(1)–X(1)	91.9(2)	92.54(9)	94.19(15)	94.1(1)	88.9(2)

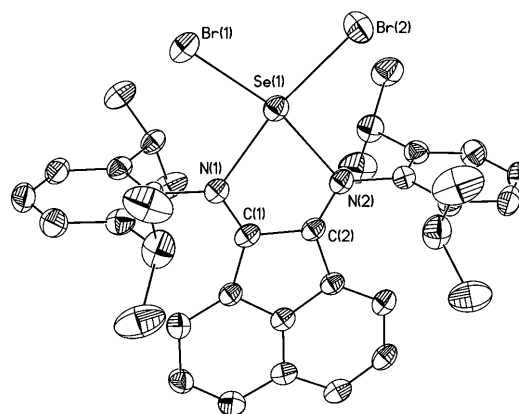


Figure 2. Solid-state structure of **4Br**. Ellipsoids are drawn to 50 % probability level and hydrogen atoms are omitted for clarity.

plexes of the 2,2'-bipyridine ligand. In **5Br** (Figure 3), the square-planar N_2SeBr_2 motif is again observed, and the Se–N bonds (Se(1)–N(1), 2.099(5); Se(1)–N(2), 2.090(5) Å) are significantly shorter as compared with those in **4Br**, which reflects the greater Lewis basicity of the less sterically encumbered bipy ligand. The Se–Br bonds are long (Se(1)–Br(1), 2.673(1); Se(1)–Br(2), 2.640(1) Å) and likely reflect a

Table 1. Crystal data for compounds **4**, **5Br**, **7**, **9**, and **10**.

	4Cl	4Br	5Br	7	9	10
formula	$C_{36}H_{40}Cl_2N_2Se_1$	$C_{36}H_{40}Br_2N_2Se_1$	$C_{10}H_8Br_2N_2Se_1$	$C_{11}H_8Cl_1F_3N_2O_3S_1Se_1$	$C_{11}H_8Cl_1F_3N_2O_3S_1Te_1$	$C_{11}H_{20}Cl_2N_2Te_1$
M_r	650.56	739.48	394.96	419.66	468.30	378.79
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$Pbca$	$Pbca$	$P2_1/c$	$I2/m$	$P2_1/c$	$C2/c$
a [Å]	11.5069(5)	11.602(2)	8.649(2)	5.794(1)	9.586(2)	10.846(2)
b [Å]	21.4507(8)	21.673(4)	10.005(2)	12.932(3)	38.269(8)	12.207(2)
c [Å]	27.0071(8)	27.103(5)	13.623(3)	19.246(4)	8.510(2)	12.046(2)
α [°]	90	90	90	90	90	90
β [°]	90	90	100.54(3)	93.76(3)	109.90(3)	110.37(3)
γ [°]	90	90	90	90	90	90
V [Å ³]	6666.2(4)	6815(2)	1159.0(4)	1439.0(5)	2935(1)	1495.2(5)
ρ_{calcd} [mg m ^{−3}]	1.296	1.441	2.264	1.937	2.119	1.683
R [$I > 2\sigma(I)$] ^[a]	0.0716	0.0508	0.0593	0.0426	0.0623	0.0262
$wR2$ (F^2) ^[b]	0.1971	0.1367	0.1588	0.0981	0.1788	0.0670

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

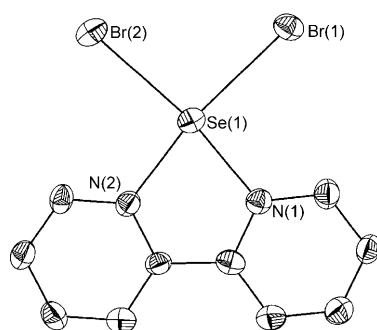


Figure 3. Solid-state structure of **5Br**. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are omitted.

degree of ionic character for the molecule. For compound **7** (Figure 4), a dicationic dimer is formed between two {Se-(bipy)Cl} moieties by means of very long Se–Cl interactions (2.710(1) Å). Within the asymmetric unit, the Se center is T-

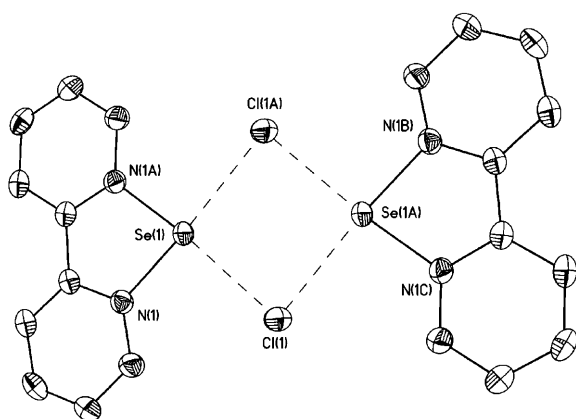


Figure 4. Solid-state structure of **7** showing the dicationic dimer formed by two units. Thermal ellipsoids are drawn to the 50% probability level; hydrogen atoms and triflate anions are omitted.

shaped (AX_3E_2), and the chloride atom from the neighboring unit fills the vacant coordination site, imposing a square-planar geometry. The Se–N bonds are somewhat shortened in comparison with **5Br** at 1.970(3) Å. No significant cation–anion interactions are present between the Se centers and the OTf anions. The solid-state structure of compound **9** (Figure 5) is very different from that of the selenium analogue, in that no dimeric arrangement is formed; rather a long contact is present between the Te center and an O atom from the triflate anion (Te(1)–O(1), 2.836(6) Å). The Te–N bonds are asymmetric (Te(1)–N(1), 2.171(6); Te(1)–N(2), 2.288(6) Å), reflecting the *trans* influence of the chlorine atom bound to Te (Te(1)–Cl(1), 2.492(2) Å). The overall geometry about Te is T-shaped, which is consistent with the assignment of the +2 oxidation state for the tellurium center. Compound **9** represents only the second Te–bipy compound to be characterized by X-ray diffraction studies.^[26]

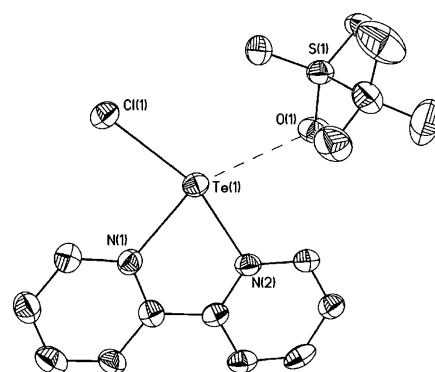


Figure 5. Solid-state structure of **9**. One of two independent cation–anion pairs in the asymmetric unit is shown. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are omitted.

Compound **10** (Figure 6) is isostructural with its recently reported Se counterpart.^[2] The Te–C bond is 2.103(3) Å, similar to other representative Te–C single bonds,^[36] and the

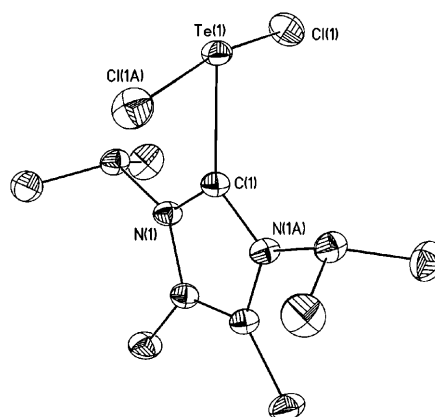


Figure 6. Solid-state structure of **10**. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Te(1)–C(1) 2.103(3), Te–Cl(1) 2.5522(9); C(1)–Te(1)–Cl(1) 85.69(2), Cl(1)–Te(1)–Cl(1A) 171.38(3).

Te–Cl bonds are slightly elongated from those in **9** at 2.5522(9) Å.^[34] Unlike the TeI_2 analogue reported by Kuhn et al. and the Et_3P-TeX_2 species by Chivers et al., there are no significant Te–X intermolecular contacts in the solid state.^[4,22]

Conclusion

We have described a facile synthetic route to diimine sequestered forms of ChX_2 , which show remarkable stability in contrast to the free binary halides. Furthermore we have demonstrated that, in principle, these compounds may act as a source of Ch^{II} for further transformations, possibly opening new opportunities in the study of low-valent chalcogen chemistry. This report underscores the utility of binary

chalcogen halides as electrophilic reagents, which has remained largely unexplored due to their instability (Se) or complete unavailability (Te).

Experimental Section

Manipulations were performed using an N₂-filled MBRAUN Labmaster 130 glove box in 4 dr. vials affixed with Teflon-lined screw caps, or using standard Schlenk techniques. Dichloromethane, THF, Et₂O, *n*-pentane, and *n*-hexane were obtained from Caledon Laboratories and dried using an MBRAUN SPS. The dried solvents were stored in Strauss flasks under an N₂ atmosphere, or over 4 Å molecular sieves in the glove box. Solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, dried by stirring for 3 d over CaH₂, distilled prior to use, and stored in the glove box over 4 Å molecular sieves. Selenium tetrachloride, SeBr₄, TeCl₄, TeBr₄, TMS-OTf, benzyl magnesium chloride, and 2,2'-bipyridine were purchased from Alfa Aesar and used as received. Phenyl magnesium chloride, SO₂Cl₂, SbPh₃, and elemental selenium were obtained from the Aldrich Chemical Company. The Dipp-DAB and Dipp-BIAN ligands, as well as SeCl₂ and SeBr₂ were prepared according to literature procedures.^[9–11,37,38]

Nuclear magnetic resonance spectra were recorded using an INOVA 400 MHz spectrometer (⁷⁷Se = 76.26 MHz; ¹³C = 100.52 MHz) at room temperature (25 °C). ⁷⁷Se NMR spectra were externally referenced to Me₂Se (δ = 0.00 ppm using SeO₂ in D₂O; δ = −1302 ppm), and ¹²⁵Te{¹H} NMR spectra were referenced to Me₂Te (δ = 0.00 ppm using H₂TeO₄ in D₂O; δ = 712 ppm). Proton and ¹³C{¹H} NMR spectra were referenced relative to Me₄Si using the NMR spectroscopic solvent (¹H: CHCl₃, δ = 7.26 ppm; ¹³C{¹H}: CDCl₃, δ = 77.2 ppm).

Samples for FT-Raman spectroscopy were packed in capillary tubes, flame-sealed, and data were collected using a Bruker RFS 100/S spectrometer with a resolution of 4 cm^{−1}. FTIR spectra were collected on samples as CsI pellets using a Bruker Tensor 27 spectrometer with a resolution of 4 cm^{−1}. Decomposition/melting points were recorded in flame-sealed capillary tubes using a Gallenkamp Variable Heater. Suitable single crystals for X-ray diffraction studies were individually selected under oil (Paratone-N), mounted on nylon loops, and immediately placed in a cold stream of N₂ (150 K). Data were collected using a Bruker Nonius Kappa CCD X-ray diffractometer using graphite-monochromated MoK α radiation (λ = 0.71073 Å). The solution and subsequent refinement of the data were performed using the SHELXTL suite of programs.^[39]

Synthesis of 3Cl: A freshly prepared solution of SeCl₂ (7.33 mmol; THF 10 mL) was added to a solution of Dipp-DAB (2.89 g, 7.33 mmol; THF 15 mL) at −78 °C, which resulted in an orange slurry. The mixture was allowed to warm to room temperature, which gave a red solution. After stirring at RT for 20 min, the THF was removed in vacuo, which gave **3Cl** as a bright orange powder. Yield: 3.88 g (96 %); decomposition point (d.p.) 145 °C; ¹H NMR (CDCl₃): δ = 8.78 (brs, 2H), 7.23 (br, overlaps residual CHCl₃ signal), 2.83 (br, 4H), 1.22 ppm (d, ³J_{H,H} = 6.4 Hz, 24H); FT-Raman (ranked intensity): $\tilde{\nu}$ = 84 (10), 121 (15), 143 (3), 169 (11), 189 (12), 236 (1), 308 (13), 582 (9), 841 (19), 888 (20), 1040 (18), 1052 (17), 1175 (4), 1243 (5), 1355 (7), 1488 (2), 1588 (6), 2868 (14), 2961 (16), 3061 cm^{−1} (8); FTIR (ranked intensity): $\tilde{\nu}$ = 212 (8), 279 (19), 453 (17), 579 (20), 722 (14), 755 (6), 801 (3), 867 (15), 939 (18), 1058 (11), 1100 (10), 1176 (9), 1266 (13), 1325 (7), 1354 (5), 1364 (2), 1377 (1), 1486 (4), 1589 (16), 3057 cm^{−1} (12); elemental analysis calcd (%) for **3Cl**: C 58.87, H 7.19, N 5.73; found: C 59.30, H 6.90, N 5.32.

Synthesis of 4Cl: A freshly prepared solution of SeCl₂ (0.626 mmol; THF 10 mL) was added to a solution of Dipp-BIAN (0.407 g, 0.626 mmol; THF 15 mL) at room temperature, which resulted in a red solution. After stirring at RT for 20 min, the THF was removed in vacuo, which gave **4Cl** as a deep red powder. Yield: 0.503 g (100 %); d.p. 189 °C; ¹H NMR (CDCl₃): δ = 8.03 (d, ³J_{H,H} = 8 Hz, 2H), 7.47 (t, ³J_{H,H} = 8 Hz, 2H), 7.37 (t, ³J_{H,H} = 8 Hz, 6H), 6.67 (d, ³J_{H,H} = 8 Hz, 2H), 3.02 (sept, ³J_{H,H} = 8 Hz, 4H), 1.34 (d, ³J_{H,H} = 8 Hz, 12H), 0.94 ppm (d, ³J_{H,H} = 8 Hz, 12H); ⁷⁷Se{¹H} NMR (CDCl₃): δ = 1523 ppm; ¹³C{¹H} NMR (CH₂Cl₂):

δ = 163.0, 141.5, 141.2, 138.6, 132.3, 130.9, 128.8, 128.3, 126.9, 125.4, 123.3, 68.0, 29.2, 23.9 ppm; FT-Raman (ranked intensity): $\tilde{\nu}$ = 89 (4), 145 (3), 204 (6), 236 (1), 273 (10), 290 (18), 443 (19), 508 (14), 625 (12), 686 (20), 831 (16), 957 (9), 1047 (15), 1127 (17), 1187 (11), 1244 (7), 1436 (8), 1576 (2), 1597 (5), 1661 cm^{−1} (13); FTIR (ranked intensity): $\tilde{\nu}$ = 266 (4), 760 (7), 781 (3), 799 (5), 833 (10), 936 (16), 1050 (11), 1086 (17), 1187 (12), 1252 (14), 1286 (9), 1324 (13), 1365 (6), 1377 (2), 1435 (1), 1575 (8), 1641 cm^{−1} (15); elemental analysis calcd (%) for **4Cl**: C 67.16, H 5.75, N 4.82; found: C 66.44, H 6.20, N 4.92.

Synthesis of 3Br: A freshly prepared solution of SeBr₂ (0.572 mmol; THF 5 mL) was added to a solution of Dipp-DAB (0.214 g, 0.572 mmol; THF 5 mL) immediately, which resulted in a color change to deep red. The mixture was stirred for 15 min. The solvent was then removed in vacuo, which gave **3Br** as a brown powder. Yield: 0.351 g (100 %); d.p. 86 °C; ¹H NMR (CDCl₃): δ = 8.16 (br, 2H), 7.55 (br), 7.22 (br) 2.95 (br, 4H), 1.22 ppm (br, 24H); FT-Raman (ranked intensity): $\tilde{\nu}$ = 109 (4), 142 (2), 160 (5), 218 (12), 236 (3), 503 (16), 535 (15), 575 (19), 836 (18), 867 (13), 887 (20), 1001 (11), 1045 (9), 1173 (6), 1242 (7), 1353 (10), 1492 (1), 1587 (8), 2960 (17), 3054 cm^{−1} (14); FTIR (ranked intensity): $\tilde{\nu}$ = 291 (10), 457 (13), 682 (8), 728 (3), 754 (9), 800 (5), 995 (16), 1059 (20), 1175 (19), 1328 (12), 1353 (15), 1365 (7), 1386 (18), 1436 (2), 1466 (6), 1475 (4), 1492 (14), 2870 (17), 2928 (11), 2960 cm^{−1} (1).

Synthesis of 4Br: A freshly prepared solution of SeBr₂ (2.47 mmol; THF 5 mL) was added to a solution of Dipp-BIAN (1.236 g, 2.47 mmol; THF 15 mL), which immediately resulted in a color change to deep purple. The mixture was allowed to stir for 15 min. The solvent was then removed in vacuo, which gave **4Br** as a very deep purple powder. Yield: 1.60 g (100 %); d.p. 189 °C; ¹H NMR (CDCl₃): δ = 7.91 (d, ³J_{H,H} = 8.4 Hz, 2H), 7.38 (t, ³J_{H,H} = 7.2 Hz, 2H), 7.27 (overlaps residual CHCl₃ signal), 6.66 (d, ³J_{H,H} = 7.2 Hz, 2H), 3.02 (sept, ³J_{H,H} = 7.2 Hz, 4H), 1.24 (d, ³J_{H,H} = 7.2 Hz, 12H), 0.95 ppm (d, ³J_{H,H} = 6.6 Hz, 12H); ¹³C{¹H} NMR (CH₂Cl₂): δ = 162.19, 142.78, 138.03, 133.66, 131.47, 130.83, 128.53, 127.7, 125.30, 124.22, 29.19, 23.93 ppm; FT-Raman (ranked intensity): $\tilde{\nu}$ = 89 (8), 108 (10), 125 (7), 160 (9), 183 (2), 206 (6), 216 (4), 507 (18), 622 (19), 830 (20), 956 (13), 1000 (12), 1122 (17), 1187 (14), 1243 (15), 1435 (11), 1578 (1), 1596 (3), 1611 (6), 3055 cm^{−1} (12); FTIR (ranked intensity): $\tilde{\nu}$ = 457 (12), 541 (13), 683 (5), 729 (4), 760 (9), 781 (3), 799 (13), 833 (7), 995 (16), 1053 (10), 1188 (11), 1257 (19), 1286 (8), 1328 (15), 1364 (18), 1385 (17), 1436 (1), 1579 (6), 2868 (20), 2962 cm^{−1} (2); elemental analysis calcd (%) for **4Br**: C 58.45, H 5.45, N 3.79; found: C 58.37, H 5.59, N 3.81.

Synthesis of 5Cl: A solution of bipy (0.071 g, 0.452 mmol; THF 5 mL) was added to a freshly prepared solution of SeCl₂ (0.452 mmol; THF 5 mL), which resulted in the immediate precipitation of a light yellow solid. The supernatant was decanted and the solids washed with Et₂O (2 × 5 mL), then dried in vacuo, which gave **5Cl** as a pale yellow powder. Yield: 0.117 g (85 %); d.p. 260–270 °C; ¹H NMR (C₂D₆O): δ = 9.04 (br, 2H), 8.90 (br, 2H), 8.43 (br, 2H), 7.91 ppm (br, 2H); FT-Raman (ranked intensity): $\tilde{\nu}$ = 128 (2), 218 (5), 266 (12), 365 (7), 766 (10), 1016 (4), 1056 (11), 1161 (13), 1251 (15), 1275 (14), 1329 (3), 1494 (8), 1557 (6), 1604 (1), 3073 cm^{−1} (9); FTIR (ranked intensity): $\tilde{\nu}$ = 635 (13), 655 (12), 711 (9), 761 (1), 995 (15), 1013 (3), 1153 (11), 1168 (10), 1310 (7), 1431 (4), 1446 (2), 1468 (5), 1526 (14), 1584 (6), 1600 cm^{−1} (8); elemental analysis calcd (%) for **5Cl**: C 39.64, H 2.43, N 9.01; found: C 39.22, H 2.64, N 9.15.

Synthesis of 5Br: A solution of bipy (0.140 g, 0.900 mmol; THF 5 mL) was added to a freshly prepared solution of SeBr₂ (0.900 mmol; THF 5 mL), which resulted in the immediate precipitation of a yellow solid. The supernatant was decanted and the solids washed with Et₂O (2 × 5 mL), then dried in vacuo, which gave **5Br** as a bright yellow powder. Yield: 0.325 g (90 %); d.p. 232–236 °C; ¹H NMR (CDCl₃): δ = 9.00 (d, ³J_{H,H} = 4.8 Hz, 2H), 8.43 (d, ³J_{H,H} = 8 Hz, 2H), 7.98 (t, ³J_{H,H} = 7.2 Hz, 2H), 7.46 ppm (t, ³J_{H,H} = 4.8 Hz, 2H); FT-Raman (ranked intensity): $\tilde{\nu}$ = 86 (7), 108 (10), 127 (13), 168 (3), 202 (8), 765 (12), 1013 (5), 359 (6), 1057 (14), 1159 (15), 1326 (2), 1393 (11), 1557 (4), 1602 (1), 3069 cm^{−1} (9); FTIR (ranked intensity): $\tilde{\nu}$ = 412 (14), 631 (9), 650 (10), 710 (6), 764 (1), 1009 (2), 1107 (13), 1160 (8), 1169 (7), 1248 (15), 1311 (5), 1425 (11), 1442 (3), 1464 (12), 1598 cm^{−1} (4); elemental analysis calcd (%) for **5Br**: C 30.41, H 1.93, N 6.99; found: C 30.39, H 2.04, N 7.09.

Synthesis of 6: A solution of Ph_3Sb (0.090 g, 0.255 mmol; CH_2Cl_2 5 mL) was added to a slurry of **8Cl** (0.108 g, 0.255 mmol; CH_2Cl_2 5 mL), which resulted in an immediate color change from yellow to dark green. Et_2O (10 mL) was added and the supernatant was decanted. The solids were washed with Et_2O (2×5 mL) and the solids dried in vacuo, which gave **6** as a dark green powder. Yield: 0.065 g (72%); d.p. 225 °C; ^1H NMR (CD_3CN): δ = 9.31 (brs, 2H), 8.59 (d, $^3J_{\text{HH}}$ = 8.4 Hz, 2H), 8.36 (t, $^3J_{\text{HH}}$ = 7.6 Hz, 2H), 7.85 ppm (t, $^3J_{\text{HH}}$ = 6.4 Hz, 2H); FT-Raman (ranked intensity): $\tilde{\nu}$ = 81 (1), 122 (3), 141 (2), 358 (7), 762 (9), 1010 (5), 1319 (6), 1485 (8), 1555 (11), 1598 (4), 3069 cm^{-1} (10); FTIR (ranked intensity): $\tilde{\nu}$ = 414 (8), 634 (12), 649 (11), 717 (5), 766 (1), 1010 (3), 1068 (14), 1114 (13), 1164 (9), 1248 (15), 1310 (7), 1439 (2), 1468 (6), 1597 (4), 3100 cm^{-1} (10); elemental analysis calcd (%) for **8Cl**: C 34.26, H 2.27, N 7.14; found: C 33.84, H 2.27, N 7.90.

Synthesis of 7: Neat TMS-OTf (80.1 μL , 0.448 mmol) was added to a slurry of **5Cl** (0.137 g, 0.448 mmol; CH_2Cl_2 5 mL) and stirred at room temperature for 10 min, which gave a colorless slurry. The solids were allowed to settle, and the supernatant was decanted. The solids were then dried in vacuo, which gave **7** as a colorless powder. Yield: 0.152 g (81%); d.p. 200–210 °C; ^1H NMR (CD_3CN): δ = 9.61 (d, $^3J_{\text{HH}}$ = 6.0 Hz, 2H), 8.84 (d, $^3J_{\text{HH}}$ = 8.4 Hz, 2H), 8.57 (t, $^3J_{\text{HH}}$ = 8.4 Hz, 2H), 8.11 ppm (t, $^3J_{\text{HH}}$ = 6.4 Hz, 2H); FT-Raman (ranked intensity): $\tilde{\nu}$ = 85 (3), 124 (1), 260 (8), 322 (6), 381 (11), 667 (12), 767 (10), 1030 (2), 1058 (13), 1337 (7), 1505 (5), 1557 (9), 1608 (4), 3083 cm^{-1} (14); FTIR (ranked intensity): $\tilde{\nu}$ = 518 (8), 574 (11), 638 (3), 664 (14), 784 (5), 1027 (2), 1057 (12), 1134 (15), 1158 (6), 1182 (4), 1224 (7), 1261 (1), 1428 (13), 1470 (9), 1607 cm^{-1} (10); ESI-MS: m/z : 271 $[\text{M}]^+$.

Synthesis of 8Cl: A solution of bipy (0.059 g, 0.371 mmol; THF 5 mL) was added to a solution of TeCl_4 (0.100 g, 0.371 mmol; THF 5 mL), which resulted in the precipitation of a yellow solid over five minutes. The solution was stored at -30°C for one hour. The supernatant was then decanted and the solids dried in vacuo, which gave **8Cl** as a bright yellow powder. Yield: 0.145 g (90%); d.p. 210 °C (solid turns brown); ^1H NMR ($\text{C}_2\text{D}_6\text{O}$): δ = 9.11 (brs, 2H), 8.83 (d, $^3J_{\text{HH}}$ = 7.6 Hz, 2H), 8.60 (t, $^3J_{\text{HH}}$ = 8.0 Hz, 2H), 8.06 ppm (t, $^3J_{\text{HH}}$ = 6.0 Hz, 2H); FT-Raman (ranked intensity): $\tilde{\nu}$ = 113 (3), 225 (7), 275 (4), 360 (13), 765 (15), 995 (6), 1020 (14), 1236 (11), 1302 (10), 1319 (2), 1446 (9), 1482 (12), 1572 (5), 1593 (1), 3074 cm^{-1} (8); FTIR (ranked intensity): $\tilde{\nu}$ = 412 (7), 636 (3), 646 (4), 713 (11), 763 (2), 1012 (1), 1062 (12), 1097 (13), 1247 (14), 1314 (5), 1441 (6), 1367 (9), 1494 (10), 1561 (15), 1593 cm^{-1} (8); elemental analysis calcd (%) for **8Cl**: C 26.21, H 2.14, N 5.97; found: C 28.20, H 1.89, N 6.58; molar conductivity: 59 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

Synthesis of 8Br: A solution of bipy (0.026 g, 0.164 mmol; THF 5 mL) was added to a slurry of TeBr_4 (0.074 g, 0.164 mmol; THF 5 mL), which resulted in the precipitation of an orange solid over five minutes. The mixture was stored at -30°C for one hour, and then the supernatant was decanted. The solids were dried in vacuo, which gave **8Br** as a bright orange powder. Yield: 0.080 g (80%); d.p. 205 °C; ^1H NMR ($\text{C}_2\text{D}_6\text{O}$): δ = 9.20 (brs, 2H), 8.85 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H), 8.60 (t, $^3J_{\text{HH}}$ = 7.6 Hz, 2H), 8.05 ppm (brs, 2H); FT-Raman (ranked intensity): $\tilde{\nu}$ = 105 (5), 155 (1), 166 (2), 351 (7), 410 (15), 764 (14), 1015 (6), 1062 (9), 1156 (12), 1270 (13), 1314 (3), 1492 (11), 1562 (10), 1591 (4), 3066 cm^{-1} (8); FTIR (ranked intensity): $\tilde{\nu}$ = 408 (8), 449 (12), 632 (3), 645 (6), 713 (4), 762 (1), 969 (15), 1006 (2), 1063 (10), 1243 (14), 1310 (7), 1437 (5), 1463 (9), 1490 (13), 1589 cm^{-1} (11); elemental analysis calcd (%) for **8Br**: C 19.89, H 1.18, N 4.55; found: C 19.89, H 1.34, N 4.64; molar conductivity: 110 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

Synthesis of 9: Neat TMS-OTf (19 μL , 0.107 mmol) was added to a slurry of **6** (0.038 g, 0.107 mmol; CH_2Cl_2 5 mL). The mixture was stirred for two hours, and then the volatiles were stripped in vacuo. Acetonitrile (5 mL) was added and the mixture was centrifuged. The yellow supernatant was decanted and Et_2O (15 mL) was added, which resulted in a yellow precipitate. The solids were allowed to settle, the supernatant was decanted, and the solids were dried in vacuo, which gave **9** as a yellow powder. Yield: 0.033 g (66%); m.p. 198–200 °C; ^1H NMR (CD_3CN): δ = 9.47 (d, $^3J_{\text{HH}}$ = 5.6 Hz, 2H), 8.81 (d, $^3J_{\text{HH}}$ = 7.6 Hz, 2H), 8.46 (t, $^3J_{\text{HH}}$ = 8.4 Hz, 2H), 8.00 ppm (t, $^3J_{\text{HH}}$ = 7.6 Hz, 2H); $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN): δ = -78.4 ppm; FT-Raman (ranked intensity): $\tilde{\nu}$ = 142 (12), 211 (11), 258 (7),

348 (15), 370 (8), 765 (6), 1018 (1), 1064 (10), 1181 (13), 1275 (14), 1325 (3), 1495 (4), 1558 (5), 1603 (2), 3089 cm^{-1} (9); FTIR (ranked intensity): $\tilde{\nu}$ = 412 (14), 517 (8), 573 (13), 634 (2), 712 (12), 768 (6), 1025 (4), 1065 (15), 1168 (5), 1230 (1), 1293 (3), 1321 (11), 1445 (7), 1476 (9), 1603 cm^{-1} (10).

Synthesis of 10: A solution of NHC (0.050 g, 0.280 mmol; THF 5 mL) was added to a slurry of **6** (0.099 g, 0.2804 mmol; THF 5 mL), which resulted in the immediate generation of a black slurry. After stirring for 10 min, the solvent was stripped in vacuo. The solids were then washed with Et_2O (2×5 mL), and then CH_2Cl_2 (10 mL) was added. The dark mixture was centrifuged, which gave a yellow solution over a small amount of black solid. The solution was decanted and the CH_2Cl_2 was removed in vacuo, which gave **10** as a green-yellow powder. Yield: 0.072 g (68%); d.p. 205 °C (solid turns brown); ^1H NMR (CDCl_3): δ = 5.77 (br, 2H), 2.39 (s, 6H), 1.69 ppm (d, $^3J_{\text{HH}}$ = 7.2 Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CH_2Cl_2): δ = 128.1, 59.4, 20.9, 10.2 ppm; $^{125}\text{Te}\{^1\text{H}\}$ NMR (CH_2Cl_2): δ = 902 ppm; FT-Raman (ranked intensity): $\tilde{\nu}$ = 108 (7), 142 (10), 247 (1), 282 (3), 889 (12), 1279 (6), 1360 (15), 1408 (11), 1446 (8), 1572 (13), 1590 (14), 1618 (9), 2936 (2), 2963 (5), 2982 cm^{-1} (4); FTIR (ranked intensity): $\tilde{\nu}$ = 750 (9), 765 (12), 906 (11), 1025 (15), 1114 (5), 1138 (10), 1217 (4), 1335 (14), 1370 (2), 1382 (3), 1412 (1), 1443 (6), 1618 (8), 2935 (13), 2980 cm^{-1} (7); ESI-MS: m/z : 304 $[\text{TeIM}]^-$, 414 $[\text{TeIMCl}_3]^-$, 793 $[\text{Te}_2\text{IM}_2\text{Cl}_3]^-$.

Synthesis of Ph_2Se from 4Cl: A solution of PhMgCl (1.22 mL, 2 M in THF, 2.44 mmol) was added to a solution of **4Cl** (0.7932 g, 1.22 mmol; THF 50 mL) at -78°C , which resulted in the generation of a light orange slurry over 30 min. The mixture was allowed to warm to room temperature, and the solvent was removed in vacuo, which gave a sticky orange gel. Hexane (50 mL) was added and the mixture was filtered. The filtrate was reduced in volume to approximately 3 mL and was loaded onto a silica gel column (eluent: 98.5:1.5 *n*-hexane/ethyl acetate). The yellow Ph_2Se eluted first and a yellow oil was recovered (0.206 g, 72%) after removal of the solvent under vacuum. Purity and identity were confirmed by ^1H and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectroscopy.^[40]

Synthesis of Ph_2Se from 5Cl: A solution of PhMgCl (0.432 mL, 2 M in THF, 0.866 mmol) was added to a solution of **4Cl** (0.132 g, 0.433 mmol; THF 5 mL) at -78°C and was allowed to warm to room temperature, which resulted in a yellow slurry. The mixture was centrifuged and the solution was decanted. The THF was stripped in vacuo giving a sticky yellow gel. The gel was washed with *n*-pentane (3×5 mL), the washings were combined, and the solvent was removed in vacuo, which gave a yellow oil. The oil was dissolved in CH_2Cl_2 (2 mL) and passed through a small plug of silica gel. The CH_2Cl_2 was removed in vacuo, which gave Ph_2Se as a yellow oil. The amount of Ph_2Se recovered was 0.082 g (82%).

Synthesis of Bz_2Se from 3Cl: A solution of BzMgCl (2.3 mL, 1.2 M in THF, 2.76 mmol) was added to a solution of **3Cl** (0.725 g, 1.38 mmol; THF 50 mL) at -78°C , which resulted in the generation of a light orange slurry over 30 min. The mixture was allowed to warm to room temperature, and the solvent was removed in vacuo, which gave a yellow gel. Hexane (50 mL) was added and the mixture was filtered. The filtrate was reduced in volume to approximately 3 mL and was loaded onto a silica gel column (eluent: 50:50 *n*-hexane/ CH_2Cl_2). The yellow Bz_2Se eluted first and a yellow powder was recovered (0.128 g, 48%) after removal of the solvent under vacuum. Purity was confirmed by ^1H and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectroscopy.^[40]

Synthesis of Bz_2Se from 5Cl: A solution of BzMgCl (1.09 mL, 1.2 M in THF, 1.358 mmol) was added to a solution of **4Cl** (0.207 g, 0.679 mmol; THF 5 mL) at -78°C and allowed to warm to room temperature, which resulted in a dark brown slurry. The THF was stripped in vacuo, which gave a brown solid. The solid was washed with Et_2O (2×15 mL), the washings were combined, and the solvent was removed in vacuo, which gave Bz_2Se as a light yellow powder. The amount of Bz_2Se recovered was 0.147 g (83%).

Synthesis of Ph_2Te from 6: A solution of PhMgCl (0.436 mL, 2 M in THF, 0.873 mmol) was added to a slurry of **6** (0.155 g, 0.436 mmol; THF 5 mL) at -78°C and allowed to warm to room temperature resulting in a yellow slurry. The mixture was centrifuged and the solution was decanted. The THF was stripped in vacuo, which gave a sticky yellow gel.

The gel was washed with *n*-pentane (3 × 5 mL), the washings were combined, and the solvent was removed in vacuo, which gave Ph₂Te as a yellow oil (0.085 g, 70%). Purity and identity were confirmed by ¹H and ¹²⁵Te{¹H} NMR spectroscopy.^[41]

Synthesis of Bz₂Te from 6: A solution of BzMgCl (0.360 mL, 1.2 M in THF, 0.420 mmol) was added to a slurry of **6** (0.075 g, 0.211 mmol; THF 10 mL) at –78 °C and allowed to warm to room temperature, which gave a dark red solution. The solvent was removed in vacuo, which gave a dark red gel. The gel was washed with *n*-pentane (3 × 5 mL) and the washings were combined. The volume of *n*-pentane was reduced to approximately 2 mL in vacuo and cooled to –60 °C, which resulted in the precipitation of a light yellow powder. The mother liquor was decanted and the precipitate was dried, which gave Bz₂Te as a yellow powder (0.038 g, 58%). Purity and identity were confirmed by ¹H NMR spectroscopy.^[42] The ¹²⁵Te{¹H} chemical shift of Bz₂Te was found to be δ = 608 ppm.

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