Inorg. Chem. **2009**, *48*, 1722−1730

Donor−Acceptor Chemistry at Heavy Chalcogen Centers

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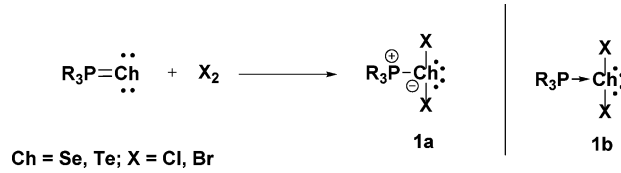
Received October 2, 2008

A series of coordination complexes, where a heavy chalcogen (Se, Te) acts as the acceptor site, using a variety of electron rich Lewis bases (phosphine, imine, *N*-heterocyclic carbene), have been synthesized and comprehensively characterized. Each derivative is a representative example of a E→Ch coordinative bond, characterizing an efficient E-E bond forming methodology and a systematic investigation into the coordination chemistry of the chalcogens. The complexes are susceptible to classic ligand exchange reactions, verifying the dative E→Ch bonding motif.

Introduction

Coordination compounds are ubiquitous across the periodic table for just about every element, featuring wide ranging examples from the s-, d-, and p-blocks. This includes less obvious Lewis acidic element centers such as carbon, phosphorus, halogens, and even the noble gases.[1−8] Despite this almost universal bonding motif, it is remarkable that complexes of the chalcogens (Ch = S, Se, Te) where the chalcogen acts as the acceptor have not been the subject of extensive study for their propensity to undergo ligand exchange, despite their ability to act as Lewis acids.[9−12] The limited development of such chemistry for the group 16 elements is even more surprising when one considers their electropositive nature, vast array of potential oxidation states, and available orbitals with which to accept a donor pair of electrons from a Lewis base. A primary reason for the limited study of coordinative E→Ch bonding is that electrophilic Group 16 element centers often undergo reduction to the elemental form in the presence of two electron donors.[12,13] There have been several reports of base stabilized ChX_2 (Ch = Se, Te; X = Br, I) species where the base is a *N*-heterocyclic carbene or phosphine; however, synthetic access to these compounds is not through coordination but rather through the oxidative addition of X_2 or the interhalogen IBr to the phosphine chalcogenides or chalcoureas (e.g., **1a**, **2a**, Schemes 1, 2).[14−21] Although these compounds may be represented using a dative bonding model (e.g., **1b**, **2b**), there

Scheme 1



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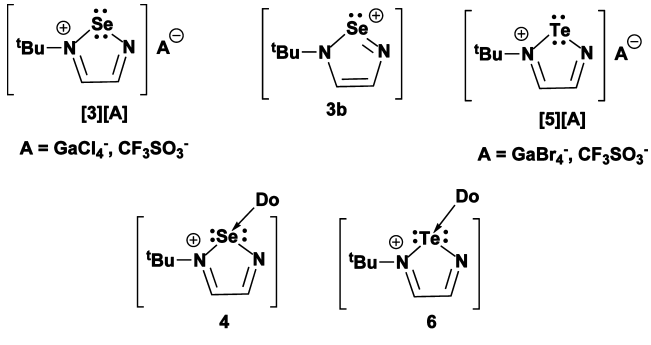
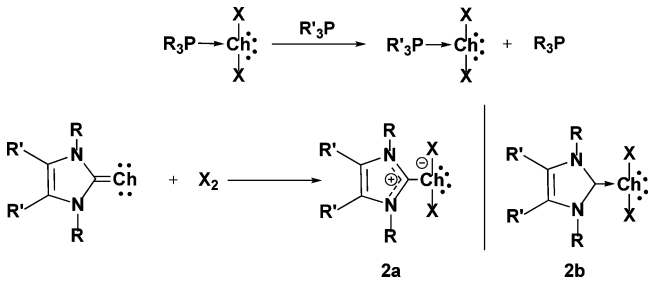
10.1021/ic801883e CCC: $40.75
Published on Web 01/14/2009

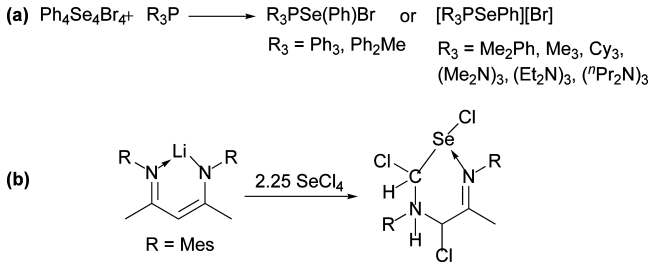
Scheme 2



Scheme 3



Scheme 4



has been no evidence of ligand exchange, a hallmark of the coordinative interaction (Scheme 3).

Godfrey et al. has taken advantage of $Ph_4Se_4X_4$ (X = Br, I), which acts as a source of a Se(II)-like synthon "PhSeX" (Scheme 4a). This work has clearly shown that resilient coordinative P→Ch bonding in solution is possible.[22,23] In a similar vein, Richards et al. have demonstrated that N→Se bonding is also viable by employing the NacNac class of ligands; however, the moderate to low yields, as well as chlorination of the ligand set, underscores the propensity for chalcogen halides to undergo redox chemistry in the presence of strong Lewis bases (Scheme 4b).[24,25]

This tendency for reduction in the presence of neutral donors, as well as a lack of suitable precursor molecules, has likely been the main barrier to a systematic examination of the acceptor abilities of the group 16 elements and subsequent utilization in E-Ch bond forming reactions. The requirements for such a useable compound are that it must contain a Lewis acidic group 16 element center yet be resistant to reduction in the presence of strongly Lewis basic sites. We have recently reported a cationic Se−N five membered ring (1,2,5-selenadiazolium cation) where the Se is formally in the +2 oxidation state and electron rich, carrying two "lone pairs" of electrons (**[3][A];** A = $GaCl_4^-$, $CF_3SO_3^-$(OTf)).[26] However, a dominant resonance contributor for the cation (**3b**) indicates the potential for an enhanced Lewis acidity at selenium, making the cation $\mathbf{3}^+$ an ideal candidate with which to attempt coordination chemistry and subsequent ligand exchange at a heavy chalcogen. In this context, we have examined the reactions between salts of $\mathbf{3}^+$ with a variety of neutral two electron donors (phosphine, imine, carbene) and report examples of heteroatom→selenium coordination complexes (**4**), representing bonding arrangements that are unattainable via any other synthetic route. Furthermore, we have clearly demonstrated that these complexes are indeed susceptible to classic ligand exchange reactions, with limited evidence for decomposition/reduction of the chalcogen. To demonstrate that the same rationale can be extended to tellurium, we have synthesized the cationic tellurium analogue (1,2,5-telluradiazolium; $\mathbf{5}^+$), which also exhibits significant Lewis acidic behavior toward neutral ligands (**6**), as well as the propensity for ligand exchange. This series of compounds (**4**; **6**) represents the first systematic examination of coordinative E→Ch bonds, and the ligand exchange reaction is a novel route for E-Ch bond formation, offering a new paradigm for the chemistry of the chalcogens.

Experimental Details

Manipulations were performed in an N_2 filled MBraun Labmaster 130 glovebox in 4 dr. vials affixed with Teflon lined screw caps, or using standard Schlenk techniques. Dichloromethane, THF, MeCN, Et_2O, *n*-pentane, and *n*-hexane were obtained from Caledon Laboratories and dried using an Innovative Technology Inc. Controlled Atmospheres Solvent Purification System that utilizes dual-alumina columns. The dried solvents were stored in Strauss flasks under an N_2 atmosphere or over 4 Å molecular sieves in the glovebox. Solvents for NMR spectroscopy ($CDCl_3$, CD_3CN) were purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH_2, distilled prior to use, and stored in the glovebox over 4 Å molecular sieves. Selenium tetrachloride, 4-dimethylaminopyridine, SeO_2, $TeBr_4$, H_6TeO_6, Et_3P, $^nBu_3P$, $GaBr_3$, and $(CH_3)_3Si$-OTf were purchased from Alfa Aesar and used as received (OTf = triflate; trifluoromethanesulphonate). Triphenylphosphine, Cy_3P and $GaCl_3$ were purchased from the Aldrich Chemical Co. and used as received. The 1,4-di(*tert*-butyl)-1,4-diaza-1,3-butadiene(*tert*-butyl-DAB) ligand, 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidine ($Dipp_2IM$), **[3][GaCl$_4$]** and **[3][OTf]** were prepared using literature methods.[26−29]

NMR spectra were recorded using a Varian INOVA 400 MHz spectrometer. (^{31}P = 161.83 MHz; ^{77}Se = 76.26 MHz; ^{125}Te = 126.12 MHz; ^{13}C = 100.52 MHz). Phosphorus-31, $^{77}Se\{^1H\}$, $^{125}Te\{^1H\}$ were externally referenced to 85% H_3PO_4 (δ = 0.00

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ppm), Me_2Se ($\delta = 0.00$ ppm using SeO_2 in D_2O, $\delta = -1302$ ppm), and Me_2Te ($\delta = 0.00$ ppm using H_6TeO_6 in D_2O, $\delta = 712$ ppm), respectively. Proton and $^{13}C\{^1H\}$ NMR spectra were referenced relative to Me_4Si using the NMR solvent (^1H: $CHCl_3$, $\delta = 7.26$ ppm; $\delta = 7.15$ ppm; CHD_2CN, $\delta = 1.96$ ppm; $^{13}C\{^1H\}$: $CDCl_3 = 77.2$ ppm). Fluorine-19 spectra were referenced relative to $CFCl_3$ ($\delta = 0.00$ ppm) using neat Ph-CF_3 ($\delta = -62.8$ ppm) as an external standard.

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}. FT-IR 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 Paratone-N oil and mounted on nylon loops and immediately placed in a cold stream of N_2 (150 K). Data were collected on a Bruker Nonius Kappa CCD X-ray diffractometer using graphite monochromated Mo$-K_\alpha$ radiation ($\lambda = 0.71073$ Å). The solution and subsequent refinement of the data were performed using the SHELXTL suite of programs.

Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

General Synthesis of 4PR$_3$. R_3P (neat for R = Et, ^{n}Bu, 3 mL CH_2Cl_2 solution for R = Ph, Cy) was added to an equimolar solution of **3a** (CH_2Cl_2; 3 mL), resulting in a slightly yellow reaction mixture. After stirring for 15 min at room temperature the solvent was removed in vacuo giving **4PR$_3$** as a slightly yellow powder (R = Et, Ph, Cy) or a light yellow oil (R = ^{n}Bu). X-ray quality crystals were grown from CH_2Cl_2 solutions of the bulk powders via vapor diffusion of Et_2O (**4PPh$_3$**) or *n*-hexane (**4PCy$_3$**) at room temperature.

4PPh$_3$. Using 0.0922 mmol **[3][GaCl$_4$]** (0.037 g), Ph_3P (0.024 g); Yield 0.060 g, 95%; mp 122−123 °C; ^1H NMR ($CDCl_3$; δ ppm) 9.26 (d, $^4J_{H-P} = 2.8$ Hz, 1H), 8.74 (d, $^4J_{H-P} = 23.6$ Hz, 1H), 7.76 (m), 7.64(m), 1.47 (s, 9H); $^{31}P\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 12.7 (−80 °C $^1J_{Se-P} = 305$ Hz); $^{77}Se\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 754 ($^1J_{Se-P} = 305$ Hz);$^{13}C\{^1H\}$ NMR (CH_2Cl_2, δ ppm) 153.9, 152.1, 133.7 ($^2J_{P-C} = 11.45$ Hz), 133.1, 129.9 ($^3J_{P-C} = 11.45$ Hz) 62.4, 30.9; Elemental analysis: Found (Calcd) C 43.24 (43.42), H 4.20 (3.92), N 4.10 (4.22); FT-Raman (cm^{-1}(ranked intensity)): 120(15), 152(5), 166(6), 192)(11), 251(10), 344(2), 371(12), 426(8), 504(17), 518(13), 545(7), 999(1), 1027(9), 1096(14), 1521(16), 1585(3), 3061(4); FT-IR (cm^{-1}(ranked intensity)): 118(3), 134(7), 159(1), 217(18), 370(2), 507(4), 690(5), 723(11), 751(10), 864(16), 951(9), 998(13), 1105(8), 1199(12), 1296(17), 1336(20), 1372(14), 1438(6), 1482(19), 2980(15); ESI-MS (*m*/*z*): $[M]^+ = 452$.

4PCy$_3$. Using 0.0935 mmol **[3][GaCl$_4$]** (0.038 g), Cy_3P (0.026 g); Yield 0.064 g, 100%; d.p. = 143−145 °C; ^1H NMR ($CDCl_3$, δ ppm) 9.13 (d, $^4J_{H-P} = 2.4$ Hz, 1H), 8.45 (d, $^4J_{H-P} = 14.4$ Hz, 1H), 2.66 (m, 3H), 1.96 (m, 9H), 1.81 (m, 3H), 1.61 (m, 6H), 1.42 (s, 9H), 1.35(m, 6H); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, δ ppm) 46.3 ($^1J_{Se-P} = 369$ Hz); $^{77}Se\{^1H\}$ NMR (CH_2Cl_2, δ ppm) 577 ($^1J_{Se-P} = 371$ Hz); $^{13}C\{^1H\}$ NMR (CH_2Cl_2, δ ppm) 154.0, 149.4, 60.8, 31.6 (d, $^1J_{C-P} = 24.1$ Hz), 30.0, 27.6, 26.5 (d, $^3J_{C-P} = 11.5$ Hz), 25.3; Elemental analysis: Found (Calcd) C 42.51 (42.24), H 5.87 (6.50), N 4.26 (4.11); FT-Raman (cm^{-1}(ranked intensity)): 119(7), 152(5), 196(3), 320(18) 344(4), 375(13), 393(14), 440(20), 541(16), 817(11), 847(19), 1029(10), 1281(17), 1297(9), 1345(15), 1444(8), 1530(12), 2857(2), 2880(6), 2941(1); FT-IR (cm^{-1}(ranked intensity)): 168(3), 179(2), 375(1), 478(19), 511(7), 523(9), 737(15), 820(11), 853(12), 950(8), 1008(13), 1040(16), 1117(18), 1177(14), 1264(17), 1299(20), 1370(10), 1449(5), 2866(6), 2941(4); ESI-MS (*m*/*z*): $[M - PCy_3]^+ = 191$, $[M]^+ = 471$.

4PBu$_3$. Using 0.0885 mmol **[3][GaCl$_4$]** (0.036 g), $^nBu_3P$ (0.018 g); Yield 0.052 g, 97%; ^1H NMR ($CDCl_3$, δ ppm) 8.90 (d, $^4J_{H-P} = 1.6$ Hz, 1H), 8.32 (d, $^4J_{H-P} = 16.2$ Hz, 1H), 2.19 (m, 6H), 1.54 (m, 6H), 1.45 (m, 6H), 1.41 (s, 9H), 0.92 (t, $^3J_{H-H} = 7.2$ Hz, 9H); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, δ ppm) 38.7 ($^1J_{Se-P} = 350$ Hz); $^{77}Se\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 607 ($^1J_{Se-P} = 352$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ ppm) 153.5 (d, $^3J_{C-P} = 14.9$ Hz), 149.1 (d, $^3J_{C-P} = 12.7$ Hz), 60.3, 29.5, 23.8, 23.0 (d, $^3J_{C-P} = 14.9$ Hz), 20.0 (d, $^3J_{C-P} = 137.6$ Hz), 12.5 (d, $^3J_{C-P} = 9.2$ Hz); ESI-MS (*m*/*z*): $[M]^+ = 392$.

4PEt$_3$. Using 0.0947 mmol **[3][GaCl$_4$]** (0.038 g), Et_3P (0.011 g); Yield 0.047 g, 94%; d.p. 61−63 °C; ^1H NMR ($CDCl_3$, δ ppm) 9.07 (d, $^4J_{H-P} = 2.4$ Hz, 1H), 8.41 (d, $^4J_{H-P} = 15.0$ Hz, 1H), 2.44 (m, 6H), 1.41(s, 9H), 1.25 (m, 9H); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, δ ppm) 47.2 ($^1J_{Se-P} = 353$ Hz); $^{77}Se\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 588 ($^1J_{Se-P} = 356$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ ppm) 153.7 (d, $^3J_{C-P} = 14.4$ Hz), 149.0 (d, $^3J_{C-P} = 9.8$ Hz), 60.4, 29.5, 13.3 (d, $^1J_{C-P} = 33.3$ Hz), 6.0 (m); FT-Raman (cm^{-1}(ranked intensity)): 117(6), 150(3), 252(2), 344(1), 381(13), 424(15), 533(9), 567(16), 628(14), 819(11), 1230(18), 1300(12), 1342(19), 1462(10), 1543(7), 2881(17), 2909(4), 2940(5), 2983(8); FT-IR (cm^{-1}(ranked intensity)): 109(3), 127(7), 148(11), 155(1), 163(10), 175 (6), 377(2), 524(17), 635(19), 750(18), 768(4), 855(16), 950(12), 1042(5), 1210(13), 1309(20), 1409(14), 1460(9), 1619(15), 2978(8); ESI-MS (*m*/*z*): $[M]^+ = 308$.

Synthesis of 4DMAP. A solution of DMAP (4-dimethylaminopyridine; 0.025 g, 0.207 mmol; CH_2Cl_2 3 mL) was added to a slurry of **[3][OTf]** (0.07 g, 0.207 mmol; CH_2Cl_2 3 mL) immediately resulting in light yellow solution. After 60 s *n*-pentane (15 mL) was added giving a light yellow precipitate. The solvent was decanted, and the remaining solids dried in vacuo giving **4DMAP** as a light yellow powder. Yield 0.078 g, 82%; Single crystals for X-ray diffraction studies were grown from a CH_2Cl_2 solution via vapor diffusion of Et_2O at −30 °C. d.p. 89−90 °C; ^1H NMR ($CDCl_3$, δ ppm) 9.67 (s, 1H), 9.58 (s, 1H), 8.30 (d, $^3J_{H-H} = 6$ Hz, 2H), 6.66 (d, $^3J_{H-H} = 6$ Hz, 2H), 3.14 (s, 6H), 1.80 (s, 9H); $^{19}F\{^1H\}$ NMR (CH_2Cl_2, δ ppm) −78.9; $^{77}Se\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 1168;$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ ppm) 156.1, 153.4, 152.6, 144.1, 107.4, 65.7, 39.8, 32.1; Elemental analysis: Found (Calcd) C 36.17 (36.44), H 4.20 (4.58), N 11.74 (12.14); FT-Raman (cm^{-1}(ranked intensity)): 111(7), 194(4), 251(1), 312 (11), 348(9), 559(14), 602(17), 760(2), 824(13), 950(18), 1004(16), 1032(3), 1062(6), 1221(12), 1339(15), 1441(5), 1612(8), 2920(19), 2996(20), 3064(10); FT-IR (cm^{-1}(ranked intensity)): 153(1), 519(12), 601(19), 639(5), 811(11), 840(17), 1007(8), 1029(4), 1063(13), 1148(10), 1166(9), 1224(7), 1258(2), 1270(3), 1378(20), 1394(15), 1439(16), 1534(18), 1550(14), 1625(6); ESI-MS (*m*/*z*): $[M]^+ = 313$.

Synthesis of 4IM. A solution of 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidine (0.035 g, 0.090 mmol; THF 3 mL) was added to a slurry of **[3][OTf]** (0.030 g, 0.090 mmol; THF 3 mL) resulting in a light yellow solution. After 10 min the solvent was removed in vacuo giving **4IM** as an off-white powder. Yield 0.065 g, 100%; single crystals for X-ray diffraction studies were grown from a CH_2Cl_2 solution of the bulk powder via vapor diffusion of Et_2O at room temperature. d.p. 120 °C; ^1H NMR ($CDCl_3$, δ ppm) 8.58 (s, 1H), 8.24 (s, 1H), 7.83 (s, 2H), 7.53 (t, $^3J_{H-H} = 7.6$ Hz, 2H), 7.30 (d, $^3J_{H-H} = 7.6$ Hz, 4H), 2.45 (sept, $^3J_{H-H} = 6.8$ Hz, 4H), 1.24 (d, $^3J_{H-H} = 6.8$ Hz, 12H), 1.19 (m, 21H (NHC doublet overlaps *tert*-butyl singlet)); $^{19}F\{^1H\}$ NMR (CH_2Cl_2, δ ppm) −78.9; $^{77}Se\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 704; $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ ppm) 151.2, 150.14, 150.08, 145.1, 131.7, 131.0, 126.6, 124.5, 60.7, 30.3, 29.2, 24.8, 23.0; Elemental Analysis: Found (Calcd) C 55.82

(56.10), H 6.11 (6.50), N 7.48 (7.70); FT-Raman (cm^{-1}(ranked intensity)): 136(9), 189(8), 314(20), 349(14), 613(17), 885(13), 1030(1), 1042(11), 1237(19), 1305(15), 1377(4), 1445(18), 1469(16), 1522(5), 1544(10), 1592(12), 2868(7), 2911(2), 2929(3), 2969(6); FT-IR (cm^{-1}(ranked intensity)): 517(5), 539(13), 573(10), 638(1), 760(7), 767(16), 812(11), 822(17), 951(14), 1030(2), 1060(12), 1158(4), 1211(18), 1225(9), 1266(3), 1330(20), 1372(15), 1471(8), 2931(19), 2969(6); ESI-MS (*m*/*z*): $[M - IM]^+ = 190$.

Synthesis of [5][OTf]. A solution of *tert*-butyl-DAB (0.100 g, 0.595 mmol; THF 5 mL) was added to a slurry of $TeBr_4$ (0.266 g, 0.595 mmol; THF 5 mL) giving an orange slurry. After 5 min neat TMS-OTf (214 uL, 1.19 mmol) was added, and the solution was allowed to stir at RT for 2.5 h over which time a yellow precipitate formed. The mixture was centrifuged, the supernatant decanted, and the solids were washed (3 × 10 mL) with a 50:50 mixture of pentane and THF. The solids were dried in vacuo giving **[5][OTf]** as a yellow powder. Yield 0.052 g, 23%; d.p. 180 °C; ^{1}H NMR (CD_3CN, δ ppm) 10.62 (s, 1H), 10.18 (s, 1H), 1.70 (s, 9H); Elemental analysis: Found (Calcd) C 20.08 (21.68), H 2.30 (2.86), N 6.31 (7.22); FT-Raman; compound decomposes; FT-IR (cm^{-1}(ranked intensity)): 345(20), 518(6), 533(18), 565(11), 574(10), 644(3), 759(15), 886(16), 967(9), 1032(2), 1060(12), 1166(4), 1191(5), 1247(1), 1351(17), 1376(7), 1433(8), 1477(13), 2983(19), 3056(14) ESI-MS (*m*/*z*): $[M - tert\text{-butyl}]^+ = 183$, $[M]^+ = 239$, $[M_2OTf]^+ = 627$.

Synthesis of [5][GaBr$_4$]. Solid KBr (0.050 g, 0.42 mmol) was added to a slurry of **[5][OTf]** (0.030 g, 0.094 mmol; CH_3CN, 5 mL) giving a black/green mixture. After 10 min the mixture was centrifuged, and the solution decanted. The volatiles were stripped from the solution in vacuo giving a black/green solid. Dichloromethane (5 mL) was added, and the mixture stirred for 10 min, and then centrifuged, resulting in a yellow solution over the residual black solids. The solution was decanted, and a solution of $GaBr_3$ (0.043 g, 0.141 mmol; CH_2Cl_2, 5 mL) was added resulting in the immediate precipitation of a bright yellow powder. The precipitate was allowed to settle, and the solution decanted. The solids were washed with CH_2Cl_2 and then dried in vacuo giving **[5][GaBr$_4$]** as a yellow powder. Yield 0.031 g, 64%; single crystals for X-ray diffraction studies were grown from a CH_3CN solution of the bulk powder via vapor diffusion of Et_2O at −30 °C. d.p. 160 °C; ^{1}H NMR (CD_3CN, δ ppm) 10.43 (s, 1H), 10.17 (s, 1H), 1.70 (s, 9H); ^{125}Te NMR (CH_3CN; δ ppm) 2231; Elemental analysis: Found (Calcd) C 11.65 (11.46), H 1.41 (1.77), N 4.32 (4.46); FT-Raman: Compound decomposes; FT-IR (cm^{-1}(ranked intensity)): 157(1), 279(2), 304(14), 535(11), 567(4), 765(20), 828(16), 842(7), 966(3), 1033(19), 1058(9), 1179(5), 1227(18), 1290(10), 1349(17), 1376(8), 1437(6), 1459(12), 2970(15), 3048(13); ESI-MS (*m*/*z*): $[M - tert\text{-butyl}]^+ = 183$, $[M - CH_3]^+ = 224$, $[M]^+ = 239$, $[M_2Br]^+ = 559$.

Synthesis of 6PCy$_3$. A solution of Cy_3P (0.028 g, 0.099 mmol; CH_2Cl_2 3 mL) was added to a slurry of **[5][OTf]** (0.039 g, 0.099 mmol; CH_2Cl_2 3 mL) giving a yellow slurry. The reaction mixture was centrifuged to remove residual solids, and the supernatant decanted. Pentane (10 mL) was added resulting in a yellow precipitate. The mother liquor was decanted, and the solids dried in vacuo giving **PCy$_3$** as a light yellow powder. Yield, 0.037 g, 56%; single crystals for X-ray diffraction studies were grown from a saturated Et_2O solution of the bulk powder at −30 °C. d.p. 72−75 °C; ^{1}H NMR ($CDCl_3$, δ ppm) 10.35 (d, $^4J_{H-P} = 2.8$ Hz, 1H), 9.50 (d, $^4J_{H-P} = 20.4$ Hz, 1H), 2.15 (m), 1.57 (s, 9H), 1.50 (m), 0.94 (m); ^{31}P{^{1}H} NMR (CH_2Cl_2, δ ppm) 23.1 ($^1J_{P-Te} = 780$ Hz); ^{125}Te{^{1}H} NMR (CH_2Cl_2, δ ppm) 1290 (d, $^1J_{Te-P} = 782$ Hz); ^{13}C{^{1}H} NMR (CH_2Cl_2, δ ppm) 156.0, 155.7, 62.5, 31.7, 31.4 (d, $^1J_{C-P} = 16.1$ Hz), 29.0, 26.9 (d, $^3J_{C-P} = 10.4$ Hz), 25.7; FT-Raman (cm^{-1}(ranked intensity)): 85(5), 141(3), 178(8), 219(12), 311(13), 347(18), 431(16), 704(20), 753(17), 817(11), 1030(2), 1222(15), 1275(14), 1297(10), 1347(19), 1445(9), 1520(7), 2853(4), 2879(6), 2930(1); FT-IR (cm^{-1}(ranked intensity)): 170(1), 176(4), 517(9), 573(16), 637(2), 668(15), 852(14), 1006(12), 1031(3), 1112(13), 1155(6), 1223(11), 1262(5), 1450(10), 2855(8), 2934(7); ESI-MS (*m*/*z*): $[M - PCy_3]^+ = 239$, $[M]^+ = 519$.

Synthesis of 6IM. A solution of $Dipp_2IM$ (0.070 g, 0.180 mmol; THF 3 mL) was added to a slurry of **[5][OTf]** (0.070 g, 0.180 mmol; THF 3 mL) giving a yellow solution, which was stirred at RT for 5 min. Pentane (10 mL) was added resulting in precipitation of a white solid. The mother liquor was decanted, and the solids then dried in vacuo giving **6IM** as an off-white powder. Yield 0.090 g, 64%; d.p. 150−160 °C; ^{1}H NMR ($CDCl_3$, δ ppm) 9.83 (s, 1H), 9.11 (s, 1H), 7.61 (s, 2H), 7.53 (t, $^3J_{H-H} = 7.8$ Hz, 2H), 7.29 (d, $^3J_{H-H} = 7.8$ Hz, 4H), 2.49 (m, $^3J_{H-H} = 6.6$ Hz, 4H), 1.32 (s, 9H), 1.19 (m, $^3J_{H-H} = 6.6$ Hz, 24H); ^{125}Te{^{1}H} NMR (CH_2Cl_2, δ ppm) 1388; ^{13}C{^{1}H} NMR ($CDCl_3$, δ ppm) 155.6, 152.9, 151.1, 145.3, 132.3, 131.5, 126.1, 131.5, 126.1, 124.4, 62.1, 31.5, 29.1, 25.1, 23.0; Elemental analysis: Found (Calcd) C 51.98 (52.60), H 6.18 (6.10), N 7.06 (7.22); FT-Raman (cm^{-1}(ranked intensity)): 134(19), 183(7), 309(18), 882(17), 1031(5), 1042(12), 1236(16), 1375(6), 1444(13), 1462(11), 1491(4), 1546(9), 1591(8), 2719(20), 2869(3), 2912(1), 2964(2), 3036(16), 3072(14), 3170(15); FT-IR (cm^{-1}(ranked intensity)): 154(1), 162(12), 178(19), 517(8), 573(15), 638(2), 759(7), 807(16), 1032(3), 1060(17), 1109(14), 1153(6), 1224(9), 1264(4), 1281(5), 1374(13), 1387(18), 1421(16), 2873(20), 2968(11); ESI-MS (*m*/*z*): $[M]^+ = 629$.

Generation of 6PPh$_3$. A solution of Ph_3P (0.012 g, 0.048 mmol; $CDCl_3$ 1 mL) was added to a slurry of **[5][GaBr$_4$]** (0.030 g, 0.048 mmol; $CDCl_3$ 1 mL) giving a yellow solution. A 1 mL aliquot was transferred to an NMR tube for ^{1}H, ^{31}P{^{1}H}, and ^{125}Te{^{1}H} NMR spectroscopy. ^{1}H NMR ($CDCl_3$, δ ppm) 10.57 (s, 1H), 9.57 (d, $^4J_{H-P} = 21.9$ Hz, 1H), 7.63−7.51 (overlapping multiplets), 1.63 (s, 9H); ^{31}P{^{1}H} NMR ($CDCl_3$, δ ppm) −11.7; ^{125}Te{^{1}H} NMR ($CDCl_3$, δ ppm) 1610 (d, $^1J_{Te-P} = 533$ Hz).

Procedure for Phosphine Ligand Exchange Reactions. A 1 mL CH_2Cl_2 solution of R_3P was added to a 1 mL CH_2Cl_2 solution of **4PR′$_3$** or **6PR$_3$′** in a 1:1 stoichiometry. After five minutes an aliquot was removed for ^{31}P{^{1}H} NMR spectroscopy to confirm production of **4PR$_3$** or **6PR$_3$** and liberation of R'_3P. Upon complete work up, both **4PR$_3$** or **6PR$_3$** were isolated quantitatively.

Procedure for the Reaction of Dipp$_2$IM with 4PPh$_3$. A 1 mL THF solution of $Dipp_2IM$ was added to 1 mL THF solution of **4PPh$_3$** (as a OTf^- salt) and stirred for 5 min. *N*-pentane (5 mL) was then added giving a white precipitate. The supernatant was decanted, the powder washed with 2 × 3 mL of *n*-pentane, and dried in vacuo. Proton-NMR spectroscopy of the powder confirmed its identity as **4IM** isolated in a quantitative yield. An identical procedure is followed for the ligand exchange reaction of $Dipp_2IM$ with **6PCy$_3$**.

Results and Discussion

Although many aspects of the chemistry of the chalcogens are well developed, the resilience of intermolecular Lewis acid/base adducts, specifically their tendency toward ligand exchange, are essentially unknown and therefore, poorly understood. Numerous Ch(II) synthons play important roles

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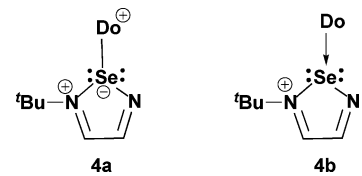
in coordination chemistry as ligands on transition metals or as main group Lewis acids.[30−32] Given the electron rich ("lone pair" bearing) nature of these elements, this may not be surprising; however, many Ch(II) starting materials are used in a variety of organic transformations because of their inherent electrophilicity and electropositive nature.[33−37] In this context, it is remarkable that the acceptor capabilities of these elements have not been thoroughly harnessed for the formation of E→Ch coordination complexes. Examples of such bonding environments have been identified over the past five decades featuring S→Se, N→Se, S→Te, O→Te, P→Se, and recently N→Te coordination, indicating that the isolation of such compounds is achievable.[9,12,38−45] In addition, the chalcogen atom transfer from one organophosphine to a more basic organophosphine (R_3P = Ch to R'_3P = Ch), could be described as a ligand exchange indicative of the coordinative bond, yet this is restricted to Ch-P bond formation only, with no functionality on the heavy chalcogen.[46,47]

The 1:1 stoichiometric reaction between organophosphine (R_3P; R = Et, ^{n}Bu, Cy, Ph) and **[3][GaCl$_4$]** in CH_2Cl_2 immediately results in the formation of clear, colorless solutions. Aliquots of the reaction mixtures were sampled for $^{31}P\{^1H\}$ NMR spectroscopy revealing one signal in each case (δ (ppm) = 46, R = Cy; 47, R = Et; 39, R = ^{n}Bu; 13, R = Ph). As one would expect for a P−Se bond, ^{77}Se satellites were visible for the reactions that involved Cy_3P, Et_3P, and $^nBu_3P$ ($^1J_{Se-P}$ = 370, 355, and 350 Hz, respectively). The chemical shifts observed in the Et_3P and $^nBu_3P$ spectra are similar to those found in the respective phosphine selenides (R_3P = Se); however, the Se−P coupling constants are much smaller (R_3PSe, $^1J_{Se-P} \approx 700$ Hz).[48] In the case of Ph_3P the $^{31}P\{^1H\}$ signal (δ = 14.7 ppm) appeared broadened and no satellites were detected; however, a spectrum obtained at −60 °C sharpened the signal and allowed for observation of the P−Se coupling and a slightly shifted resonance than that observed at room temperature (δ = 12.7 ppm; $^1J_{Se-P}$ = 315 Hz). The $^{77}Se\{^1H\}$ NMR spectra of the same samples revealed doublets at δ = 577, 512, 638, and 714 ppm for R = Cy, Et, ^{n}Bu, Ph, respectively, with identical Se−P coupling constants obtained from $^{31}P\{^1H\}$ NMR spectroscopy. The $^{77}Se\{^1H\}$ signals were shifted well upfield as compared to the singlet resonance for $\mathbf{3}^+$ (δ = 1315 ppm).[26] Removal of the volatiles yielded light yellow powders for R = Et, Cy, Ph, and a light yellow oil for R = ^{n}Bu. Samples of all derivatives were redissolved in $CDCl_3$ for ^{1}H NMR spectroscopy, which indicated sets of signals consistent with the intact framework of $\mathbf{3}^+$, albeit containing additional resonances from the required protons on the phosphine side groups. In addition $^4J_{H-P}$ couplings were apparent (1.5−24 Hz), all indicating resilient Se−P connectivity in solution, and on the basis of this evidence, the new compounds were assigned as having a P→Se bond (**4PR$_3$**).

Single crystals of **4PPh$_3$**, and **4PCy$_3$** were grown from concentrated CH_2Cl_2 solutions of the powders via vapor diffusion of Et_2O. Subsequent X-ray diffraction studies revealed the structures to be as proposed, which are obtained in essentially quantitative yield. Single crystals could not be obtained for compounds **4PBu$_3$** and **4PEt$_3$** as the former is an oil, and the latter is a highly unstable solid, decomposing within hours in solution at −30 °C or in the solid state at room temperature.

The 1:1 stoichiometric reaction of **[3][GaCl$_4$]** with 4-dimethylaminopyridine (DMAP) results in the liberation of chloride from the anion, giving a neutral chlorinated derivative of **3** and a DMAP→$GaCl_3$ adduct, inferred by ^{1}H NMR spectroscopy.[26,49] The same reaction but using **[3][OTf]** instead, with a stoichiometric amount of 4-DMAP (in CH_2Cl_2) or the NHC $Dipp_2IM$ (in THF), immediately results in the formation of a slightly yellow reaction mixture from which a yellow (4-DMAP) or white ($Dipp_2IM$) precipitate can be generated upon the addition of *n*-pentane. A ^{1}H NMR spectrum of redissolved samples of the isolated powders in $CDCl_3$ revealed a single product, containing the required signals arising from $\mathbf{3}^+$ and the Lewis base, albeit shifted (for DMAP $\Delta\delta$ (ppm) 0.09, 0.20, 0.18; for NHC endocyclic protons $\Delta\delta$ = 1.29 ppm) and the $^{77}Se\{^1H\}$ NMR spectra have only one singlet shifted to high field relative to free $\mathbf{3}^+$ (δ = 1168 ppm, 4-DMAP; 704 ppm, $Dipp_2IM$; c.f. 1315 ppm, $\mathbf{3}^+$), where all of these data point toward successful coordination. Single crystals were grown from CH_2Cl_2 solutions of the bulk powders via vapor diffusion of *n*-hexane (4-DMAP; −30 °C) or Et_2O ($Dipp_2IM$; RT). Subsequent X-ray diffraction studies confirmed the generation of **4DMAP** and **4IM**, obtained in 81% and 100% isolated yields, respectively.

There are two possible bonding models for the cation in **4Do** (Do = Lewis base), which can be described as an ylide (**4a**), or as a P→Se coordination complex (**4b**), using a dative bond. If **4b** is the best bonding description, then the reaction of a given complex with a more strongly donating Lewis base should result in ligand exchange.[50]



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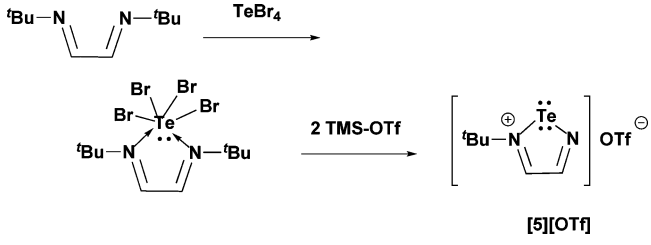
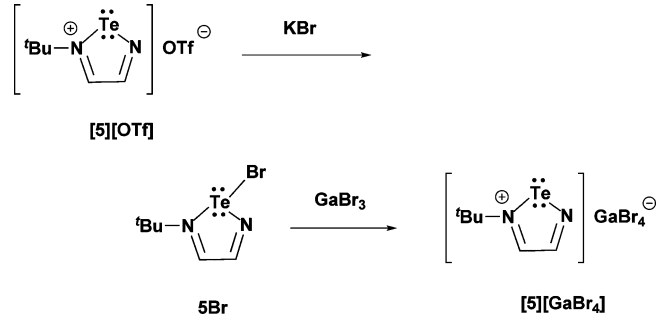
In this context, the addition of one stoichiometric equivalent of $^{n}Bu_3P$ to a CH_2Cl_2 solution of **4PPh$_3$** results in no visible change. Phosphorus-31 NMR spectroscopy of a sample of the reaction mixture revealed two signals: $\delta = 39$ with a $^{1}J_{P-Se} = 350$ Hz, indicative of the production of **4PBu$_3$**, and $\delta = -5$ ppm reminiscent of free Ph_3P, indicating successful ligand exchange at Se for the formation of a new P→Se bond. Identical results are obtained if a stronger Lewis base is employed (e.g., Cy_3P, Et_3P, or $Dipp_2IM$), thus representing a new approach to E→Se bond formation and the discovery of new reactivity for the chalcogens.

Tellurium Analogue. The reaction of *tert*-butyl-DAB with $TeBr_4$ in THF results in the quantitative generation of the simple *tert*-butyl-DAB adduct to $TeBr_4$, in stark contrast to the redox behavior observed in the corresponding selenium systems, which result in cationic Se(II)-N rings (**[3]$_2$[SeX$_6$]**).[29] A corresponding 1,2,5-telluradiazolium analogue of $\mathbf{3}^+$ would be ideal to evaluate the potential of such a tellurium center to act as a Lewis acid. We now report the synthesis of such a cation via the reaction of the *tert*-butyl-DABTeBr_4 adduct with a 2-fold excess of TMS-OTf in THF, resulting in the formation of a bright yellow precipitate. Although the powder was found to be highly insoluble in most organic solvents, a sufficient quantity could be dissolved in CD_3CN to obtain ^{1}H and $^{19}F\{^{1}H\}$ NMR spectra. The ^{1}H NMR spectrum revealed three resonances at $\delta = 10.6$, 10.2, and 1.70 ppm in a 1:1:9 ratio by integration, and the $^{19}F\{^{1}H\}$ NMR spectrum showed one signal at $\delta = -79$ ppm, indicating the presence of an ionic trflate. This same sample was analyzed by positive ESI-mass spectrometry, which showed three major signals at $m/z = 627$, 239, and 183. The masses, and isotope patterns were consistent with $[M_2OTf]^+$, $[M]^+$, and $[M - {}^{t}Bu]^+$, respectively. Negative detection ESI-MS showed only one tellurium containing signal, at $m/z = 537$ for the $[MOTf_2]^-$ cluster.



These data allowed us to tentatively assign the identity of the compound as **[5][OTf]**; however, all attempts to grow single crystals for X-ray diffraction analysis resulted in precipitation of bulk powder only. This was coupled with the difficulty in obtaining other key NMR spectroscopic data ($^{125}Te\{^{1}H\}$, $^{13}C\{^{1}H\}$) because of the limited solubility of the compound, prevented a conclusive assignment of its structure and bonding. In this context, we sought to synthesize a derivative of the cation paired with a different anion to facilitate the growth of single crystals. The brominated derivative was synthesized via the reaction of **[5][OTf]** with an excess of KBr in CH_3CN, which upon workup gives a green solid, **5Br**. A sample of the isolated powder from the bromination reaction was redissolved in $CDCl_3$, and ^{1}H NMR spectroscopy revealed signals at $\delta = 10.67$, 9.54, and 1.67 ppm, in the same ratio by integration as was observed in **[5][OTf]**. Unfortunately, the compound decomposes upon standing in solution and prevented the growth of single crystals for X-ray analysis. The compound may be used in situ to regenerate the cationic heterocycle via halide abstraction using $GaBr_3$, which immediately results in the precipitation of a yellow solid. A sample of the yellow powder redissolved in CD_3CN revealed an essentially identical ^{1}H NMR spectrum as was observed for **[5][OTf]**. Single crystals suitable for X-ray diffraction studies were grown from the NMR sample via vapor diffusion of Et_2O at −30 °C and confirmed the identity of the compound as being **[5][GaBr$_4$]**, obtained in 60% yield based on **[5][OTf]**.



The Lewis acidic chemistry of the cation **5** has been examined in reactions with a selection of neutral two electron ligands. The 1:1 stoichiometric reaction of **[5][OTf]** with Cy_3P, Ph_3P (CH_2Cl_2) or $Dipp_2IM$ (THF) results in light yellow slurries or a yellow solution, respectively. Solids obtained after the reaction work up were redissolved in $CDCl_3$ for multinuclear NMR spectroscopic analysis. In the case of the Cy_3P a single resonance was observed in the $^{31}P\{^{1}H\}$ NMR spectrum at $\delta = 23.1$ ppm, and satellites to ^{125}Te were visible ($^{1}J_{P-Te} = 780$ Hz). The $^{125}Te\{^{1}H\}$ NMR spectra of the same sample revealed a doublet at $\delta = 1290$ ppm with the same P−Te coupling, and the corresponding proton NMR spectrum showed an upfield shift of the backbone protons in the Te−N heterocycle ($\Delta\delta = 0.23$ and 0.91 ppm), all of which are indicative of P→Te coordination. In the case of $Dipp_2IM$, the ^{1}H NMR spectrum of the redissolved solids revealed a clean product, with the required signals from the tellurium heterocycle and the carbene. Similar to the Cy_3P case, the resonances arising from the

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(50) The IUPAC Compendium of Chemical Terminology (2006) defines a dative bond as "The coordination bond formed upon interaction between molecular species, one of which serves as a donor and the other as an acceptor of the electron pair to be shared in the complex formed. In spite of the analogy of dative bonds with covalent bonds, in that both types imply sharing a common electron pair between two vicinal atoms, the former as distinguished by their significant polarity, lesser strength, and greater length. The distinctive feature of dative bonds is that their minimum-energy rupture in the gas phase or in inert solvent follows the heterolytic bond cleavage path." In the present report, the heterolytic cleavage of the bond is induced by the presence of a stronger Lewis base.

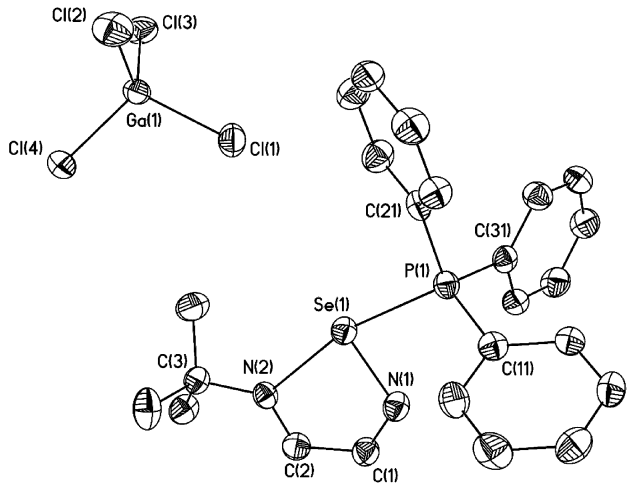

Figure 1. Solid-state structure of **4PPh$_3$**. Ellipsoids are drawn to 50% probability, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Se(1)−P(1) 2.327(1), Se(1)−N(1) 1.863(3), Se(1)−N(2)2.339(2),N(1)−C(1)1.278(4),C(1)−C(2)1.466(4),N(1)−Se(1)−P(1) 86.21(8), N(2)−Se(1)−P(1) 165.57(7), N(1)−Se(1)−N(2) 79.4(1).

backbone protons of the Te−N heterocycle were shifted upfield, whereas those from the backbone protons of the carbene are deshielded, reminiscent of **4IM** ($\Delta\delta$ = 1.07 ppm). Only one signal was detected in the ^{125}Te{^{1}H} NMR spectrum at δ = 1388 ppm. Using Ph$_3$P as a ligand gives a highly unusual resonance in the ^{31}P{^{1}H} NMR spectrum and indicates a single product. This chemical shift is *upfield* from that of free Ph$_3$P (δ = −11.7 ppm), a phenomenon we cannot provide an explanation for at this time but is reproducible upon repeated reaction attempts. A telling component of this system ascertained from the proton NMR spectrum of the same sample is the observed coupling between the backbone protons in the Te−N heterocycle with the phosphorus nuclei ($^4J_{H-P}$ = 21.9 Hz). Although definitive $^1J_{P-Te}$ coupling is not observed in the ^{31}P{^{1}H} NMR spectrum, the ^{125}Te{^{1}H} NMR spectrum clearly reveals a doublet at 1610 ppm with a $^1J_{Te-P}$ = 532 Hz. Furthermore, the Ph$_3$P can be subsequently liberated in a quantitative fashion during a ligand exchange by the reaction of **6PPh$_3$** with Cy$_3$P to regenerate **6PCy$_3$** or Dipp$_2$IM to give **6IM**. Therefore, we believe that a Ph$_3$P complex to Te is indeed formed, although structural evidence for this has remained elusive.

Single crystals suitable for X-ray diffraction studies of **6PCy$_3$** were grown from a saturated Et$_2$O solution of the powder at −30 °C and confirmed the production of a P→Te bond. Unfortunately all efforts to grow single crystals of **6IM** resulted in weakly diffracting material and no data sets of sufficient quality for resolution of the molecule were obtained. However, based on the other data obtained, the identity of a carbene adduct to the Lewis acidic Te center is clear.

X-ray Crystallography. Compounds **4PPh$_3$**, **4PCy$_3$**, **4DMAP**, **4IM**, **[5][GaBr$_4$]**, and **6PCy$_3$** have been characterized by single crystal X-ray diffraction studies, and views of the solid state structures may be found in Figures 1−7. Solution and refinement data are listed in Table 1, and key metrical parameters are summarized in Table 2.

Table 1. Crystal Data for Compounds **4**−**6**

	4PPh$_3$	**4PCy$_3$**	**4IM**	**4DMAP**	**[5][GaBr$_4$]**	**6PCy$_3$**
empirical formula	$C_{24}H_{26}Cl_4Ga_1N_2P_1Se_1$	$C_{24}H_{44}Cl_4GaN_2P_1Se_1$	$C_{34}H_{47}F_3N_4O_3S_1Se_1$	$C_{14}H_{21}F_3N_4O_3S_1Se_1$	$C_6H_{11}Br_4Ga_1N_2Te_1$	$C_{29}H_{54}F_3N_2O_4P_1S_1Te_1$
formula weight	663.92	682.06	727.78	461.37	628.13	741.36
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	11.879(2)	11.032(2)	14.172(3)	7.805(2)	9.520(2)	14.836(3)
b (Å)	11.763(2)	36.409(7)	12.451(3)	7.4665(15)	11.837(2)	22.948(5)
c (Å)	20.177(4)	15.717(3)	21.470(4)	33.101(7)	13.909(3)	10.459(2)
α (deg)	90	90	90	90	90	90
β (deg)	94.38(3)	99.22(3)	103.83(3)	95.31(3)	101.89(3)	97.67(3)
λ (deg)	90	90	90	90	90	90
V (Å^3)	2811.1(10)	6232(2)	3679(1)	1920.7(7)	1533.9(5)	3529(1)
Dc (mg m^{-3})	1.569	1.454	1.314	1.596	2.720	1.397
Z	4	8	4	4	4	4
radiation, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temp. (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
$R[I > 2\sigma I]^a$	0.0408	0.0450	0.0493	0.0530	0.0442	0.0446
$wR2(F^2)^b$	0.1079	0.1196	0.1288	0.1312	0.1167	0.1210
goodness of fit (S)^a	1.072	1.078	1.036	1.068	1.029	1.103

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

Table 2. Selected Bond Lengths and Angles for Compounds **3**, **4**, and **6**^{a}

	[3][GaCl$_4$]	**4PPh$_3$**	**4PCy$_3$**	**4DMAP**	**4IM**	**[5][GaBr$_4$]**	**6PCy$_3$**
Ch(1)−N(1)	1.780(7)	1.863(3)	1.867(3)	1.801(4)	1.858(2)	2.018(5)	2.032(3)
Ch(1)−N(2)	1.880(7)	2.339(2)	2.570(3)	1.979(4)	2.387(2)	2.161(5)	2.365(3)
Ch(1)−E	N/A	2.327(1)	2.284(1)	2.205(4)	1.960(3)	N/A	2.604(1)
N(1)−C(1)	1.295(1)	1.287(4)	1.271(5)	1.292(5)	1.273(4)	1.291(8)	1.291(4)
N(2)−C(2)	1.289(1)	1.274(4)	1.256(5)	1.285(6)	1.263(3)	1.288(8)	1.281(4)
C(1)−C(2)	1.400(1)	1.466(4)	1.466(5)	1.423(6)	1.459(4)	1.443(9)	1.465(5)
N(1)−Ch(1)−N(2)	87.5(3)	79.4(1)	76.3(1)	85.7(2)	78.70(9)	77.0(2)	76.32(11)
N(1)−Ch(1)−E	N/A	86.21(8)	86.07(9)	86.5(2)	87.6(1)	N/A	83.47(9)
N(2)−Ch(1)−E	N/A	165.57(7)	161.95(7)	172.0(1)	164.17(9)	N/A	159.75(7)

^{a} E = P for **4PPh$_3$**, **4PCy$_3$**, **6PCy$_3$**; E = N for **4DMAP**; E = C for **4IM**.

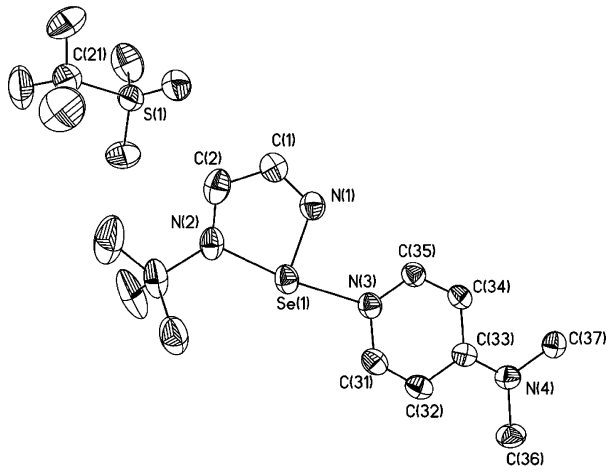

Figure 2. Solid-state structure of **4DMAP**. Ellipsoids are drawn to 50% probability, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg):Se(1)−N(3) 2.205(3), Se(1)−N(1) 1.801(4), Se(1)−N(2)1.979(4),N(1)−C(1)1.292(5),C(1)−C(2)1.423(6),N(1)−Se(1)−N(2) 85.7(2), N(2)−Se(1)−N(3) 172.0(2), N(1)−Se(1)−N(3) 86.5(2).

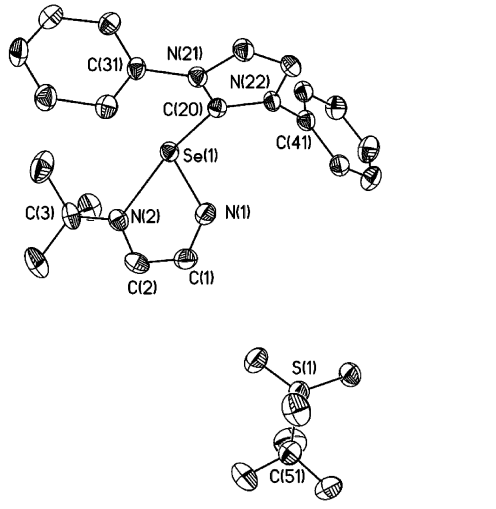

Figure 3. Solid-state structure of **4IM**. Ellipsoids are drawn to 50% probability; isopropyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Se(1)−C(20) 1.960(3), Se(1)−N(1) 1.858(2), Se(1)−N(2) 2.387(2), N(1)−C(1) 1.273(4), C(1)−C(2) 1.459(4),N(1)−Se(1)−C(20)87.6(1),N(1)−Se(1)−N(2)78.70(9),C(20)−Se(1)−N(2) 164.17(9).

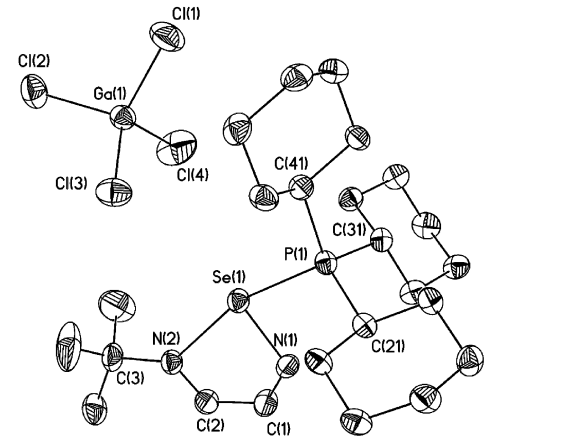

Figure 4. Solid-state structure of **4PCy$_3$**. Ellipsoids are drawn to 50% probability, and hydrogen atoms are omitted for clarity. One of two independant molecules within the asymmetric unit are shown. Selected bond lengths (Å) and angles (deg): Se(1)−P(1) 2.284(1), Se(1)−N(1) 1.867(3), Se(1)−N(2)2.570(3),N(1)−C(1)1.271(5),C(1)−C(2)1.466(5),N(1)−Se(1)−P(1) 86.07(9), N(2)−Se(1)−P(1) 161.95(7), N(1)−Se(1)−N(2) 76.3(1).

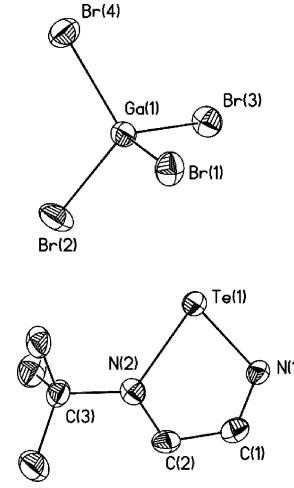

Figure 5. Solid-state structure of **[5][GaBr$_4$]**, showing only the asymmetric unit. Ellipsoids are drawn to 50% probability, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Te(1)−N(1) 2.018(5), Te(1)−N(2) 2.161(5), N(1)−C(1) 1.291(8), N(2)−C(2) 1.288(8), C(1)−C(2) 1.443(9), N(2)−Te(1)−N(1) 77.0(2).

An examination of the metrical parameters for **4PPh$_3$** shows a P−Se bond length (2.327(1) Å) slightly elongated with respect to derivatives of **1** (≈ 2.25 Å).[51] The Se−N bonds are significantly lengthened from **[3][GaCl$_4$]**, especially N(2)−Se(1), which is 2.339(2) Å versus 1.851(3) Å in the free cation. The geometry about selenium is essentially T-shaped, and the endocylic SeN_2C_2 atoms plus P(1) are planar (mean deviation = 0.0162 Å). This is consistent with AX_3E_2 electron pair geometry, indicating selenium retains two "lone pairs" of electrons, and this bonding arrangement about selenium is mimicked in all derivatives. The solid state structure of **4PCy$_3$** reveals a somewhat shorter Se−P bond length of 2.284(1) Å; however, the Se−N bond distances are more dramatically lengthened from the free cation to 2.570(3) Å (Se(1)−N(2)) and 1.867(3) Å (Se(1)−N(1)). The elongation is a consequence of the strong phosphine Lewis base populating the Lewis acidic σ^* orbital corresponding to the ^{t}BuN−Se bond, thus lowering the bond order.[52] The greater degree to which this is observed in **4PCy$_3$** is related to the stronger σ donor ability of Cy_3P versus Ph_3P.

The bonding for the cation in **4DMAP** is analogous to the phosphine derivatives exhibiting the T-shaped geometry. The Se(1)−N(3) bond is 2.205(4) Å, significantly longer than the endocyclic Se−N bonds (Se−N(1) = 1.801(4) Å, Se−N(2) = 1.979(4) Å), which are only slightly elongated from the parent cation. The SeN_2C_2 ring and the entire DMAP moiety are found in the same plane (mean deviation = 0.0241 Å).

Unlike the DMAP adduct, the imidazole ring in **4IM** is titled entirely out of the plane of the SeN_2C_2 ring, to allow for the sterically demanding *tert*-butyl and 2,6-diisopropylphenyl groups to achieve maximum separation. The Se(1)−C(20) bond length is 1.960(3) Å, slightly longer than other reported Se-imidazolium bonds (1.88−1.92 Å).[13,16,18] The Se(1)−N(2) bond is significantly lengthened (2.387(2) Å) as compared to the free cation but not to the extent that

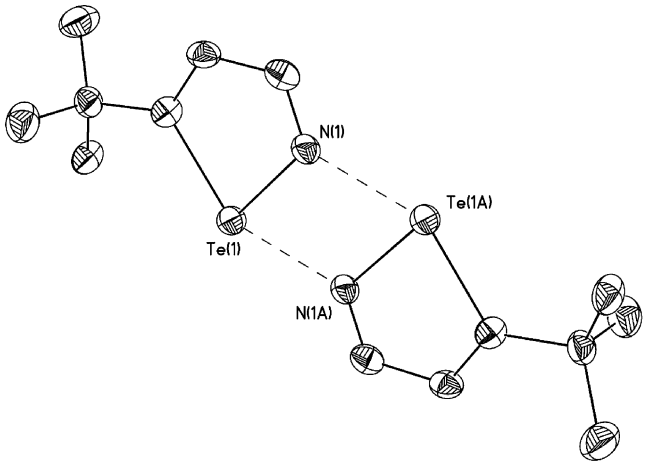

Figure 6. Solid-state structure of **[5][GaBr$_4$]**, showing the dimer formed by two cations. The $GaBr_4$ anions are omitted. Ellipsoids are drawn to 50% probability, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Te(1)−N(1A) 2.301(5).

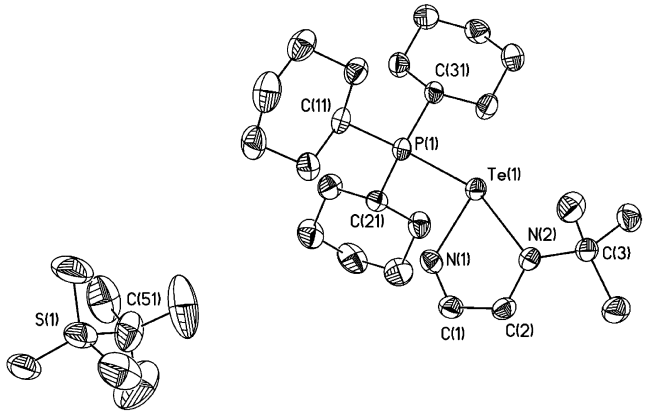

Figure 7. Solid-state structure of **6PCy$_3$**. Ellipsoids are drawn to 50% probability; hydrogen atoms and Et_2O solvate are omitted for clarity. Selected bond lengths (Å) and angles (deg): Te(1)−P (1) 2.604(1), Te(1)−N(1) 2.032(3), Te(1)−N(2) 2.365(3), N(1)−C(1) 1.291(4), C(1)−C(2) 1.465(5), N(1)−Te(1)−N(2) 76.32(11), N(1)−Te(1)−P(1)−Te(1)−P(1) 83.47(9), N(2)−Te(1)−P(1) 159.75(7).

was observed for **4PCy$_3$**, as the steric bulk of the carbene prevents a complete interaction despite its very strong σ donor ability.

Two of the tellurium analogues have been characterized by X-ray crystallography, the cation (**[5][GaBr$_4$]**) and the Cy_3P adduct as a triflate salt (**6PCy$_3$**). The salt **[5][GaBr$_4$]** is the second example of a 1,2,5-telluradiazolium ring and is isostructural with its selenium counterpart **[3][GaCl$_4$]**.[53] The Te−N bond lengths are 2.018(5) Å (Te(1)−N(1)) and 2.161(5) Å (Te(1)−N(2)), both in the range of Te−N single bonds.[54,55] The endocyclic C−N linkages are consistent with mostly double bond character (1.291(8) Å and 1.288(8) Å), and the endocyclic C−C bond length (1.443(9) Å) is essentially identical to that reported for the free *tert*-butyl-DAB ligand.[56] As was the case for **[3][GaCl$_4$]**, the cation forms a dimer in the solid-state via short Te−N secondary bonding interactions (2.301(5) Å), generating a Te_2N_2 core. This is a common phenomenon for chalcogen(II) compounds found in an N−Ch−N bonding arrangement and has been evaluated in considerable detail.[54] The contacts in **[5][GaBr$_4$]** are significantly shorter than those reported for the neutral telluradiazole systems (2.77 Å), likely owing to the greater Lewis acidity conferred onto the heterocycle by the positive charge. The N−Te−N bond angle is 77.02(7)° compared with the N−Se−N angle of 87.6(1)° in the selenium analogue. The increased acuteness of this angle is simply a function of the greater distance of the central atom from the organic backbone of the heterocycle.

The Te(1)−P(1) bond in **6PCy$_3$** is a rare example of a P→Te bond, the distance is 2.6045(11) Å, substantially longer than other reports of trialkyl phosphines bound to Te(II) fragments, which are on the order of approximately 2.48 Å.[17] As in the selenium congeners, the Te(1)−N(2) bond is the longer than the corresponding contact in the free cation (2.365(3) Å vs 2.161(5) Å). The N(1)−Te(2)−N(1) bond angle is 76.3(1)°, and the angle of N(2)−Te(1)−P(1) is 159.75(7) °, defining a distorted T-shaped geometry.

Conclusions

We have described a facile synthetic route to a family of compounds that can be described as coordination complexes of the chalcogens. The coordinative bonding model was confirmed by a series of ligand exchange reactions, where the donor molecule could be displaced by a superior Lewis base forming a new complex in essentially quantitative yield. The ability to perform ligand exchange opens a new paradigm for the chemistry of the heavier chalcogens in that a systematic study of donor−acceptor complexes has remained elusive until now.

Acknowledgment. We would like to thank the Natural Sciencess and Engineering Research Council (NSERC) of Canada, Canada Foundation for Innovation, the Ontario Ministry of Research and Innovation Early Researcher Award (OMRI-ERA) and The University of Western Ontario for generous financial support.

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

IC801883E

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