Inorg. Chem. **2009**, *48*, 3239−3247

Synthesis of N,C Bound Sulfur, Selenium, and Tellurium Heterocycles via the Reaction of Chalcogen Halides with $-CH_3$ Substituted Diazabutadiene Ligands

Jason L. Dutton, Caleb D. Martin, Michael J. Sgro, Nathan D. Jones, and Paul J. Ragogna*

Department of Chemistry, The University of Western Ontario, 1151 Richmond St., London, Ontario, N6A 5B7, Canada

Received December 3, 2008

A series of N,C bound chalcogen heterocycles from the reaction of chalcogen halides (ChX_n; Ch = S, Se Te; X = Cl, Br; n = 2, 4) with *N*-alkyl or *N*-aryl 1,4-diazabutadiene (DAB) ligands featuring methyl substituents on the backbone C−C linkage are reported. In contrast to what is observed for other p-block elements with the same ligand systems, which typically bind in an *N,N′* fashion, the chalcogens react with the ligand in an unusual manner, forming $N_1C_3Ch_1$ five-membered rings by incorporating a "backbone" methyl group. Solid state structures of the feature compounds have been confirmed by X-ray crystallographic studies. The reaction mechanism was probed by deuterium isotope labeling of the DAB ligand and analyzed using stopped-flow kinetics experiments, which supported attack by the olefin in the enamine form of the DAB ligand with concomitant loss of HX.

Introduction

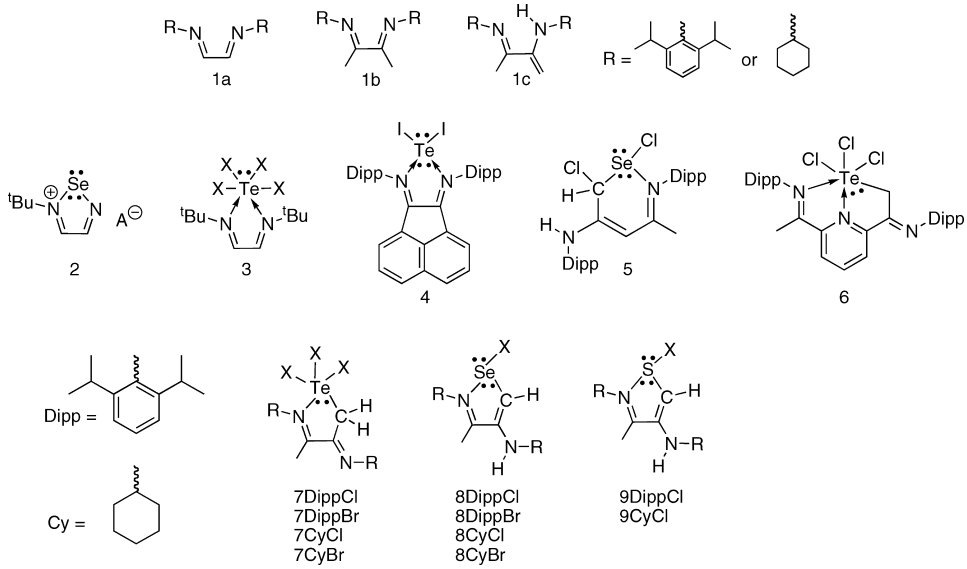
The discovery of new bonding motifs using common ligands (e.g., amines, imines, phosphines) and the heavier chalcogen halides (ChX_4; Ch = S, Se, Te; X = Cl, Br or ChX_2; Ch = S, Se; X = Cl, Br) can be restricted by the propensity for redox processes between the Lewis base and the metal halide.[1] These reactions can result in the undesirable production of Ch^0 or release of reactive X_2 (X = Cl, Br, I), leading to halogenation of any susceptible sites within the system, giving low yields, and causing great difficulty in controlling the outcome of the transformations.[2−4] Despite these issues, a number of recent reports have demonstrated high yielding syntheses of a variety of novel bonding arrangements for selenium and tellurium by employing bifunctional *N,N′* or *N,S* ligands with corresponding chalcogen halides.[2,5−7] In cases where the ligand was based on an α-diimine (**1a**), their reaction with selenium halides resulted in cationic SeN_2C_2 heterocycles. For selenium, this involved the reduction from Se(IV) to Se(II) with concomitant elimination of Cl_2 or Br_2 and the loss of an alkyl substituent from the ligand, generating a 1,2,5-selenadiazolium cation (**2**).[4] In the case of tellurium and *tert*-butyl *N*-substituted DAB ligands, no reduction was observed, where the reactions instead resulted in the formation of simple DAB-TeX_4 adducts (**3**; X = Cl, Br).[2] Analogous chemistry involving the $Dipp_2$-BIAN ligand and TeI_4 or the $Dipp_2$NacNac ligand and SeX_4 (X = Cl, Br) also involved redox processes resulting in a $Dipp_2BIANTeI_2$ (**4**) complex or Se(II)$Dipp_2$NacNac compounds (**5**), where the NacNac ligand was halogenated as a result of X_2 elimination.[3,6] The dependence of the reaction outcome on the specific nature of the ligand is in contrast to what has been reported for analogous group 15 α-diimine chemistry, where an internal charge transfer dominates giving phosphenium or arsenium cations, regardless of the substituents at nitrogen.[8,9]

Nevertheless, there are three separate reports of *N,C* chelation of group 16 centers (Se, **5** and Te, **6**) via the activation of a proximal methyl group on the ligand framework. These represent the first examples of this type of reactivity for the chalcogens; however, analogous chemistry for sulfur has not been reported.[3,6,10]

* To whom correspondence should be addressed. E-mail: pragogna@uwo.ca.

(1) Dutton, J. L.; Tabeshi, R.; Jennings, M. C.; Lough, A.; Ragogna, P. J. *Inorg. Chem.* **2007**, *46*, 8594–8602.
(2) Dutton, J. L.; Sutrisno, A.; Schurko, R. W.; Ragogna, P. J. *Dalton Trans.* **2008**, 3470–3477.
(3) Gushwa, A. F.; Richards, A. F. *Eur. J. Inorg. Chem.* **2008**, 728–736.
(4) Dutton, J. L.; Tindale, J. J.; Jennings, M. C.; Ragogna, P. J. *Chem. Commun.* **2006**, 2474–2476.
(5) Risto, M.; Assoud, A.; Winter, S. M.; Oilunkaniemi, R.; Laitinen, R.; Oakley, R. T. *Inorg. Chem.* **2008**, *47*, 10100–10109.
(6) Reeske, G.; Cowley, A. H. *Chem. Commun.* **2006**, 4856–4858.

10.1021/ic802320s CCC: $40.75
Published on Web 03/02/2009



In this context, we have discovered that utilization of *N*-alkyl or *N*-aryl substituted DAB ligands, which feature methyl substituents in the "backbone" (**1b**; **1Dipp**, R = 2,6-diisopropylphenyl; **1Cy**, R = cyclohexyl), consistently give *N,C* bound group 16 element centers (**7**−**9**) from a variety of chalcogen halide starting materials in moderate to excellent yields. These represent a novel reactivity and coordination mode for α-diimine ligands of this type within the heavier p-block elements. Typically ligands of the form **1b** are the preferred choice as the backbone protons on **1a** are considerably acidic; thus, the ligand is readily deprotonated, where subsequent deleterious reactivity is observed.[11,12] The mechanism for the formation of compounds **7**−**9** has been probed using the reaction of **1Dipp** and $TeCl_4$ as a model, in conjunction with deuterium isotope labeling. Although a definitive mechanism could not be determined, there was a distinct increase in the time required for the reaction to run to completion when **1Dipp-*d*$_6$** was used in place of **1Dipp**, which indicates a primary kinetic isotope effect. Given this observation, we hypothesize that the dominant factor in determining the outcome of these reactions relies on a proton transfer; thus, the presence of the enamine form of the α-diimine ligand (**1c**) is critical. Such a mechanism was postulated for the formation of **5** by Richards et al., albeit using the NacNac class of ligand, rather than a formal C−H bond activation.[3,13,14]

Experimental Section

General Procedures. 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 MBraun Solvent Purification system (MB-SPS). 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, C_5D_5N), D_2O, CH_3CH_2OD, and DCl (35% in D_2O) were purchased from Cambridge Isotope Laboratories; the solvents used for NMR spectroscopy were 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, $SeBr_4$, $TeCl_4$, $TeBr_4$, and 2,3-butanedione were purchased from Alfa Aeasar and used as received. Sulfur monochloride, 2,6-diisopropylaniline, $SbPh_3$ and cyclohexylamine were obtained from the Aldrich Chemical Co. Selenium dichloride, $SeBr_2$, SCl_2, **1Dipp**, **1Cy**, and 2,3-butanedione-d_6 (≈ 95% enrichment) were prepared via literature procedures.[15−19] The $-CD_3$ labeled **1Dipp** was prepared in an identical manner to the unlabeled version, except CH_3CH_2OD was used as the solvent. The SCl_2 was stored under an inert atmosphere at −78 °C, the purity was confirmed by FT-Raman spectroscopy prior to each use. In the formation of $SeCl_2$ from $SeCl_4$ and $SbPh_3$, the resultant (highly soluble) $SbPh_3Cl_2$ is completely removed during workup in all cases.

NMR spectra were recorded on an INOVA 400 MHz spectrometer. (^{77}Se = 76.26 MHz; ^{125}Te = 126.12 MHz; ^{13}C = 100.52 MHz). $^{77}Se\{^1H\}$, and $^{125}Te\{^1H\}$ were externally referenced to Me_2Se (δ = 0.00 ppm using SeO_2 δ = −1302 ppm) and Me_2Te (δ = 0.00 ppm using H_6TeO_6 δ = 712 ppm), respectively. Proton and $^{13}C\{^1H\}$ NMR spectra were referenced relative to Me_4Si using the residual proton signals from the NMR solvent (^1H: $CHCl_3$, δ = 7.26 ppm;

(7) Bacon, C. E.; Eisler, D. J.; Melen, R. L.; Rawson, J. M. *Chem. Commun.* **2008**, 4924–4926.
(8) Reeske, G.; Hoberg, C. R.; Cowley, A. H. *Inorg. Chem.* **2007**, *46*, 1426–1430.
(9) Norton, E. L.; Szekely, K. L. S.; Dube, J. W.; Bomben, P. G.; Macdonald, C. L. B. *Inorg. Chem.* **2008**, *47*, 1196–1203.
(10) Gushwa, A. F.; Karlin, J. G.; Fleischer, R. A.; Richards, A. F. *J. Organomet. Chem.* **2006**, *691*, 5069–5073.
(11) Gudat, D.; Haghverdi, A.; Hupfer, H.; Nieger, M. *Chem.−Eur. J.* **2000**, *6*, 3414–3425.
(12) Martin, C. D.; Jennings, M. C.; Ferguson, M. J.; Ragogna, P. J. *Angew. Chem., Int. Ed.* [Online early access]. DOI: 10.1002/anie200805198. Published Online: **2009**.
(13) Kim, Y. H.; Kim, T. H.; Lee, B. Y. *Organometallics* **2002**, *21*, 3082–3084.
(14) Wik, B. J.; Romming, C.; Tilset, M. *J. Mol. Catal. A: Chem.* **2002**, *189*, 23–32.
(15) Del Bel Belluz, P.; Cordes, A. W.; Kristof, E. M.; Kristof, P. V.; Liblong, S. W.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 9276–9278.
(16) Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B. *Polyhedron* **2004**, *23*, 2789–2795.
(17) Milne, J. *Polyhedron* **1985**, *4*, 65–68.
(18) Plouzennec-houe, I.; Lemberton, J.; Perot, G.; Guisnet, M. *Synthesis* **1983**, 659–661.
(19) Steudel, R.; Jensen, D.; Plinke, B. *Z. Naturforsch.* **1987**, *42b*, 163–168.

CHD_2CN, $\delta = 1.96$ ppm; C_5D_4HN, $\delta = 8.71$ ppm; $^{13}C\{^1H\}$ $CDCl_3$ $\delta = 77.2$ ppm; C_5D_4HN, $\delta = 149.9$ 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}. 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 oil (Paratone-N), mounted on nylon loops, and immediately placed in a cold stream of N_2 (150 K; 193 for **8DippCl** and **9DippCl**). 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.

Combustion analysis (CHN) were performed by Columbia Analytical Services (Tucson, Arizona, U.S.A.). Compounds **7**, **8CyCl**, and **8CyBr** decompose appreciably at room temperature within 24 h and therefore we have been unable to collect the necessary analytical data. As an indication of the level of purity obtained for these compounds, ^1H NMR spectra have been included in the Supporting Information.

Kinetic studies were performed using a Bio-Logic SFM-300 with a TIDAS diode array. Data acquisition was triggered by the hard stop signal of the SFM-300 with an approximate dead time of 2 ms. Three thousand spectra were recorded over 30 s with an integration time of 12 ms and spanning a wavelength range of 302.2 to 1147.5 nm.

Synthesis of 7DippCl. A solution of **1Dipp** (0.136 g, 0.337 mmol; THF 5 mL) was added to a stirred slurry of $TeCl_4$ (0.100 g, 0.337 mmol; THF 5 mL) immediately giving an orange solution, which was allowed to stir for 10 min. The volatiles were then stripped in vacuo giving **7DippCl** as an orange powder. Yield 0.210 g, 98%; single crystals for X-ray diffraction studies were grown from a concentrated CH_2Cl_2 solution of the powder via vapor diffusion into *n*-hexane; d.p. 197 °C; ^1H NMR ($CDCl_3$; δ ppm) 7.39 (m), 7.30 (m), 7.21 (m), 4.21 (s, 2H), 3.02 (sept, 2H, $^3J_{H-H} =$ 6.8 Hz), 2.64 (sept, 2H, $^3J_{H-H} = 6.8$ Hz), 2.32 (s, 3H), 1.23 (overlapping doublets, 12H), 1.09 (overlapping doublets, 12H); $^{125}Te\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 1274; $^{13}C\{^1H\}$ NMR (CH_2Cl_2, δ ppm) 178.6, 162.1, 144.2, 140.5, 138.0, 134.3, 128.6, 125.9, 124.8, 124.3, 123.7, 59.1, 28.6, 24.6, 23.8, 23.2, 22.1, 18.5; ESI-MS (*m*/*z*): 603 $[M - Cl]^+$.

Synthesis of 7DippBr. A solution of **1Dipp** (0.090 g, 0.223 mmol; THF 5 mL) was added to a slurry of $TeBr_4$ (0.100 g, 0.223 mmol; THF 5 mL), which was allowed to stir for 4 h, giving an orange solution. The volatiles were then stripped in vacuo giving **7DippBr** as an orange powder. Yield 0.165 g, 96%; Single crystals for X-ray diffraction studies were grown from a concentrated CH_2Cl_2 solution of the powder via vapor diffusion of Et_2O; d.p. 208 °C; ^1H NMR ($CDCl_3$; δ ppm) 7.36 (m), 7.28 (m), 7.21 (m), 4.55 (s, 2H), 3.14 (sept, 2H, $^3J_{H-H} = 6.8$ Hz), 2.74 (sept, 2H, $^3J_{H-H} = 6.8$ Hz), 2.36 (s, 3H), 1.29 (overlapping doublets, 12H), 1.15 (overlapping doublets, 12H); $^{125}Te\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 1283.

Synthesis of 7CyCl. A solution of **1Cy** (0.050 g, 0.202 mmol; THF 5 mL) was added to a slurry of $TeCl_4$ (0.054 g, 0.202 mmol; THF 5 mL) immediately giving a yellow solution, which was allowed to stir for 10 min. The volatiles were then stripped in vacuo giving a yellow solid. The solids were redissolved in CH_2Cl_2 (2 mL), Et_2O (5 mL) was added, and the mixture stored at −30 °C overnight, giving a colorless precipitate. The supernatant was decanted, and the solids dried in vacuo giving **7CyCl** as a colorless powder. Yield 0.082 g, 84%; single crystals for X-ray diffraction studies were grown from a saturated Et_2O solution of the powder stored at −30 °C for 2 days; d.p. 110 °C; ^1H NMR ($CDCl_3$; δ ppm) 4.31 (s, 2H), 3.87 (m, 1H), 3.54 (m, 1H), 2.46 (s, 3H), 2.15−1.31 (CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ ppm) 175.1, 156.8, 64.0, 62.4, 56.2, 33.3, 32.7, 25.4, 25.0, 24.8, 23.9, 15.6; $^{125}Te\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 1190.

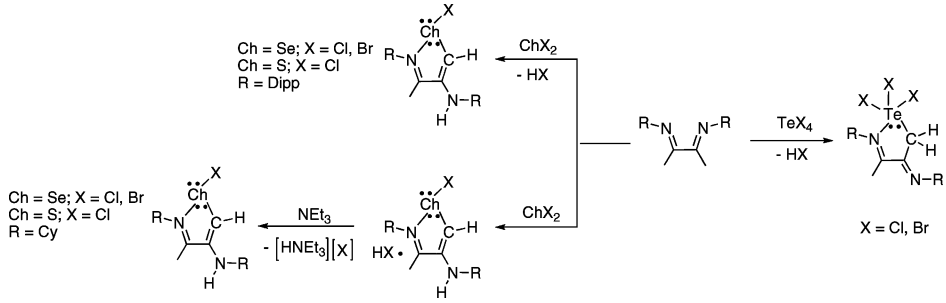
Synthesis of 7CyBr. A solution of **1Cy** (0.100 g, 0.403 mmol; THF 5 mL) was added to a stirred slurry of $TeBr_4$ (0.180 g, 0.403 mmol; THF 5 mL) immediately giving an orange slurry, which was allowed to stir for 10 min. The volatiles were then stripped in vacuo resulting in an orange solid. The powder was washed with Et_2O (2 × 5 mL), and dried yielding **7CyBr** as an orange powder. Yield 0.186 g, 75%; single crystals for X-ray diffraction studies were grown from a concentrated $CHCl_3$ solution of the powder via vapor diffusion of Et_2O; d.p. gradually turns black 135−160 °C; ^1H NMR ($CDCl_3$; δ ppm); 4.58 (s, 2H), 3.80 (m, 1H), 3.56 (m, 1H), 2.44 (s, 3H), 2.20−1.20 (CH_2) $^{125}Te\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 1195.

Synthesis of 8DippCl. A freshly prepared solution of $SeCl_2$ (0.452 mmol; THF 10 mL) was added to a stirred solution of **1Dipp** (0.182 g, 0.452 mmol; THF 10 mL), giving a yellow solution. The mixture was stirred for 1 h, and *n*-pentane (10 mL) was added. The solution stored at −30 °C overnight, resulting in the formation of a bright yellow precipitate. The supernatant was decanted, the solids washed with Et_2O (2 × 5 mL), and the volatiles were removed in vacuo giving **8DippCl** as a yellow powder. Yield 0.201 g, 86%; single crystals for X-ray diffraction studies were grown from a concentrated CH_2Cl_2 solution of the powder via vapor diffusion of Et_2O; d.p. 204 °C; ^1H NMR ($CDCl_3$; δ ppm) 8.30 (s, 1H, $^2J_{Se-H} = 24.0$ Hz), 7.43 (t, 1H, $^3J_{H-H} = 8$ Hz), 7.26 (t, 3H, $^3J_{H-H} = 8$ Hz), 7.20 (m), 4.83 (s, 1H), 3.05 (sept, 2H, $^3J_{H-H} = 6.8$ Hz), 2.36 (sept, 2H, $^3J_{H-H} = 6.8$ Hz), 2.12 (s, 3H), 1.20 (overlapping doublets, 18H), 1.14 (d, 6H, $^3J_{H-H} = 6.8$ Hz); $^{77}Se\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 1013; $^{13}C\{^1H\}$ NMR (CH_2Cl_2, δ ppm) 162.8, 145.2, 144.4, 141.64, 139.9, 135.5, 134.3, 133.5, 131.9, 130.7, 129.8, 127.8, 124.7, 124.6, 28.9, 28.6, 25.2, 24.2, 23.9, 17.0; Elemental analysis (%), Found (Calcd): C 64.83(64.90), H 7.55(7.59), N 5.39(5.41).

Synthesis of 8DippBr. A freshly prepared solution of $SeBr_2$ (0.633 mmol; THF 5 mL) was added to a stirred THF solution of **1Dipp** (0.255 g, 0.633 mmol; THF 10 mL) at room temperature, giving a yellow slurry. After 10 min the mixture was centrifuged and the supernatant decanted. The solvent was removed under vacuum, giving a yellow powder, which was washed with Et_2O (3 × 5 mL). Residual solvent was stripped in vacuo giving **8DippBr** as a yellow powder. Yield 0.275 g, 77%; single crystals for X-ray diffraction studies were grown from a concentrated CH_2Cl_2 solution of the powder via vapor diffusion of Et_2O; d.p. 190 °C; ^1H NMR ($CDCl_3$; δ ppm)); 8.39 (s, 1H, $^2J_{Se-H} = 24.0$ Hz), 7.51 (t, 1H, $^3J_{H-H} = 7.6$ Hz), 7.31 (t, 3H, $^3J_{H-H} = 7.6$ Hz), 7.22 (d, 2H, $^3J_{H-H} = 7.6$ Hz), 4.83 (s, 1H), 3.08 (sept, 2H, $^3J_{H-H} = 6.8$ Hz), 2.40 (sept, 2H, $^3J_{H-H} = 6.8$ Hz), 2.13 (s, 3H), 1.23 (overlapping doublets, 18H), 1.18 (d, 6H, $^3J_{H-H} = 6.8$ Hz); $^{77}Se\{^1H\}$ NMR (CH_2Cl_2; δ ppm) 1023; $^{13}C\{^1H\}$ NMR (CH_2Cl_2, δ ppm) 163.24, 145.20, 144.42, 141.27, 139.52, 135.42, 133.89, 133.61, 131.88, 130.85, 129.83, 127.88, 124.78, 124.65, 28.94, 28.68, 25.20, 24.21, 23.97, 17.21; Elemental analysis (%), Found (Calcd): C 59.46(59.77), H 7.06(6.99), N 4.87(4.98).

Synthesis of 8CyCl·HCl. A freshly prepared solution of $SeCl_2$ (0.452 mmol; THF 5 mL) was added to a THF solution of **1Cy** (0.112 g, 0.454 mmol, THF 5 mL), giving a yellow solution. Normal

Scheme 1



pentane (10 mL) was added, and the reaction mixture was cooled to −30 °C overnight, resulting in the formation of a brown precipitate. The supernatant was decanted, the precipitate washed with Et_2O (2 × 5 mL), and the volatiles were dried in vacuo giving **8CyCl·HCl** as a beige powder. Yield 0.133 g, 74%; d.p. 165−168 °C; ^{1}H NMR (C_5D_5N; δ ppm); 18.00 (bs, 1H), 8.75 (s, 1H, $^2J_{Se-H}$ = 28.0 Hz), 5.17 (bs, 1H), 3.96 (m, 1H), 3.03 (m, 1H), 2.23 (s, 3H), 2.05−1.00 (CH_2); ^{77}Se{^{1}H} NMR (C_5D_5N; δ ppm) 688; ^{13}C{^{1}H} NMR (C_5D_5N, δ ppm): 161.6, 138.7, 127.2, 60.1, 52.5, 34.1, 31.6, 25.0, 24.1, 23.8, 14.6; Elemental analysis (%), Found (Calcd): C 47.52(48.23), H 6.68(7.09), N 6.81(7.04); ESI-MS (*m*/*z*): 327 [M − HCl_2]$^+$

Synthesis of 8CyBr·HBr. A freshly prepared solution of $SeBr_2$ (0.633 mmol; THF 5 mL) was added to a THF solution of **1Cy** (0.157 g, 0.633 mmol; THF 5 mL) at room temperature, resulting in the immediate precipitation of a white solid. The mixture was allowed to stir for 10 min; then the supernatant was decanted. The white solids were washed with Et_2O (2 × 5 mL) and dried in vacuo giving **8CyBr·HBr** as a white powder. Yield 0.240 g, 77%; d.p. 179−181 °C; ^{1}H NMR (C_5D_5N; δ ppm); 12.85 (bs, 1H), 8.65 (s, 1H, $^2J_{Se-H}$ = 28.7 Hz), 5.2 (bs, 1H), 4.10(m, 1H), 3.08 (m, 1H), 2.46(s, 3H), 2.08−1.00 (CH_2); ^{77}Se{^{1}H} NMR (C_5D_5N; δ ppm) 704; ^{13}C{^{1}H} NMR (CH_2Cl_2, δ ppm); 161.7, 139.0, 126.3, 60.3, 52.5, 34.1, 31.4, 24.9, 24.2, 24.0, 23.7, 15.0; Elemental analysis (%), Found (Calcd): C 38.65(39.43), H 5.39(5.80), N 5.64(5.75); ESI-MS (*m*/*z*): 327 [M − HBr_2]$^+$

Synthesis of 8CyCl. Triethylamine (22.3 μL, 0.160 mmol) was added to a THF (5 mL) slurry of **8CyCl·HCl** (0.064 g, 0.160 mmol) resulting in a colorless precipitate within a yellow solution. After 10 min the reaction mixture was centrifuged and the supernatant decanted. The THF was removed in vacuo giving **8CyCl** as a light yellow powder. Yield 0.048 g, 83%; d.p. 150−160 °C (solid blackens); ^{1}H NMR ($CDCl_3$; δ ppm); 8.37 (s, 1H, $^2J_{Se-H}$ = 29.6 Hz), 4.07 (m, 1H), 3.20 (N−H overlaps Cy-ipso, 2H), 2.28 (s, 3H), 2.07−1.15 (CH_2); ^{77}Se{^{1}H} NMR (CH_2Cl_2; δ ppm) 713; ^{13}C{^{1}H} NMR (CH_2Cl_2, δ ppm): 158.1, 137.0, 127.3, 59.3, 50.9, 33.0, 30.4, 23.1, 23.0, 22.5, 22.4, 13.0; ESI-MS (*m*/*z*): 327 [M − Cl]$^+$

Synthesis of 8CyBr. Triethylamine (57 μL, 0.410 mmol) was added to a THF (10 mL) slurry of **8CyBr·HBr** (0.200 g, 0.410 mmol) resulting in a colorless precipitate within a yellow solution. After 10 min the reaction mixture was centrifuged and the supernatant decanted. The solids were washed with THF (2 × 5 mL), and the washings added to the initial supernatant. The THF was removed in vacuo giving **8CyBr** as a light yellow powder. Yield 0.070 g, 42%; d.p. 195−197; ^{1}H NMR ($CDCl_3$; δ ppm); 8.40 (s, 1H, $^2J_{Se-H}$ = 29.4 Hz), 4.08 (m, 1H), 3.29 (s, 1H), 3.12 (m, 1H), 2.29 (s, 3H), 2.10−1.18 (CH_2); ^{77}Se{^{1}H} NMR (C_5D_5N; δ ppm) 720; ^{13}C{^{1}H} NMR (CH_2Cl_2, δ ppm): 158.3, 136.5, 127.5, 59.4, 50.9, 43.5, 32.9, 30.4, 23.3, 22.9, 22.4, 22.3, 13.1; ESI-MS (*m*/*z*): 327 [M − Br]$^+$

Synthesis of 9DippCl. A solution of **1Dipp** (0.100 g, 0.248 mmol; THF 5 mL) was added to a solution of SCl_2 (0.0255 g, 0.248 mmol; THF 5 mL) immediately giving an orange slurry, which was allowed to stir for 10 min. The product was precipitated by the addition of Et_2O (5 mL). The precipitate was washed with Et_2O (2 × 5 mL) and dried in vacuo giving **9DippCl** as a pale yellow powder. Yield 0.080 g, 69%; Crystals for X-ray diffraction studies were grown from a concentrated CH_2Cl_2 solution of the powder via vapor diffusion of Et_2O; d.p. 230−233 °C.^{1}H NMR ($CDCl_3$; δ ppm); 8.32 (s, 1H), 7.57 (t, 1H, $^3J_{H-H}$ = 8.0 Hz), 7.33 (d, 2H, $^3J_{H-H}$ = 8.0 Hz), 7.29 (m, 1H), 7.21 (d, 2H), 6.10 (s, 1H), 3.14 (sept, 2H, $^3J_{H-H}$ = 7.2 Hz), 2.32 (s, 3H), 2.20 (sept, 2H, $^3J_{H-H}$ = 6.8 Hz), 1.15 (m, 24H); ^{13}C{^{1}H} NMR ($CDCl_3$, δ ppm): 158.2, 146.5, 145.9, 142.4, 135.0, 132.1, 131.0, 130.4, 127.8, 124.1, 28.5, 24.9, 24.0, 23.6, 15.7; Elemental analysis (%), Found (Calcd): 71.08(71.38), 8.58(8.35), 5.88(5.95); ESI-MS (*m*/*z*): 435 [M − Cl]$^+$

Synthesis of 9CyCl·HCl. A solution of **1Cy** (0.100 g, 0.406 mmol; 5 mL THF) was added to a solution of SCl_2 (0.0414 g, 0.406 mmol; THF 5 mL) immediately giving a pale beige precipitate, and the reaction mixture was allowed to stir for 10 min. The supernatant was decanted, and the precipitate was washed with THF (5 × 8 mL) and dried in vacuo giving **9CyCl·HCl**. Yield 0.069 g, 49%; d.p. 195−197 °C.^{1}H NMR (CD_3CN; δ ppm); 7.86 (s, 1H), 4.61 (m, 1H), 3.21 (m, 1H), 2.55 (s, 3H), 2.19−1.12 (m, 22H); ^{13}C{^{1}H} NMR (C_5D_5N, δ ppm); 157.4, 142.2, 134.5, 68.2, 62.0, 34.2, 32.9, 26.3, 25.7, 25.6, 25.0, 14.8; Elemental analysis for $SCl_2C_{16}H_{28}$, Found (Calcd): C 53.98(54.68), H 7.39(8.04), N 7.66(7.98); ESI-MS (*m*/*z*): 279 [M − HCl_2]$^+$

Results and Discussion

The 1:1 stoichiometric reaction of **1Dipp** or **1Cy** with TeX_4 (X = Cl, Br) resulted in the formation of a yellow solution, either immediately, or over 4 h (for **1Dipp**; X = Br). Upon no further color change, the volatiles were removed in vacuo affording yellow powders in all cases (Scheme 1). Samples of the material redissolved for ^{1}H NMR spectroscopy revealed signals consistent with a single product; however, it was clear that the symmetry of the ligand framework had been broken. The two methine protons from **1Dipp** were distinct (δ = 3.08 and 2.70 ppm), and the backbone methyl groups were also differentiable, integrating in a 2:3 fashion, rather than the expected 1:1 ratio (**7DippCl**: δ = 4.26 ppm, 2.37 ppm; **7DippBr**: δ = 4.55 ppm, 2.36 ppm; cf. 2.07 ppm in free **1Dipp**). Analogous NMR spectra were obtained when using **1Cy** with an obvious doubling of the cyclohexyl signals and an identical distinction of the backbone methyl groups that was observed when using **1Dipp**. Tellurium-125 NMR spectra of all four samples

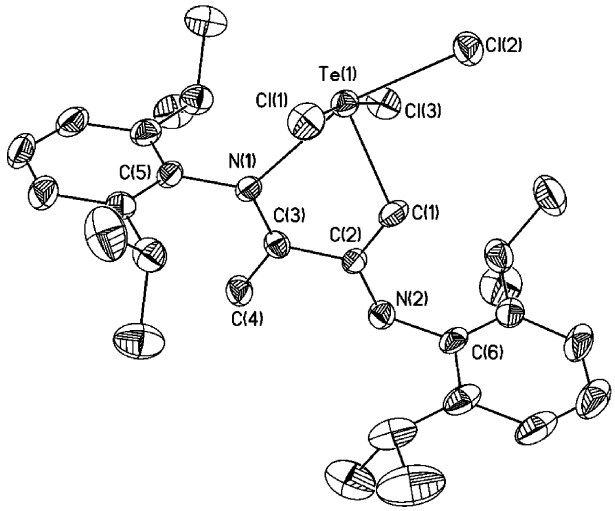


Figure 1. Solid-state structure of **7DippCl**. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are omitted for clarity.

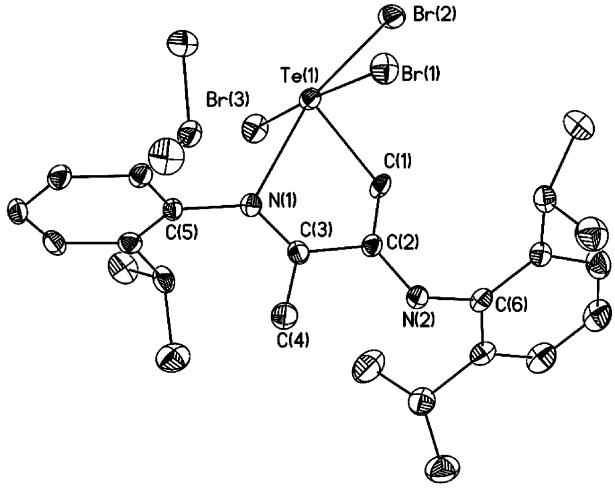


Figure 2. Solid-state structure of **7DippBr**. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are omitted for clarity.

revealed one resonance in all cases, indicating the production of a single tellurium-containing product. Determining the connectivity of these molecules was not possible from an examination of the multinuclear NMR spectra, so single crystals suitable for X-ray diffraction were grown. These experiments revealed parallel products in all cases, where a novel and unexpected $Te_1N_1C_3$ 5-membered ring system was generated by the incorporation of a carbon atom from a methyl group from the ligand backbone (**7**), with three halogen atoms remaining on the Te center, indicating retention of the +4 oxidation state, pointing to the formal loss of HX (Figures 1−4). By repeating these reactions in the presence of Et_3N, it was ascertained that there was indeed a stoichiometric release of the hydrohalide, which was sequestered quantitatively as the $[Et_3NH][X]$ salt, with all products being recovered in yields between 75−98%.

To investigate if this reactivity would be observed with selenium, the reaction of $SeCl_4$ with **1Dipp** in THF was carried out. This immediately resulted a bright yellow solution, which after removal of the THF in vacuo, gave a yellow powder. Unlike the tellurium systems, the ^{1}H NMR spectra of the crude material revealed an apparently complex

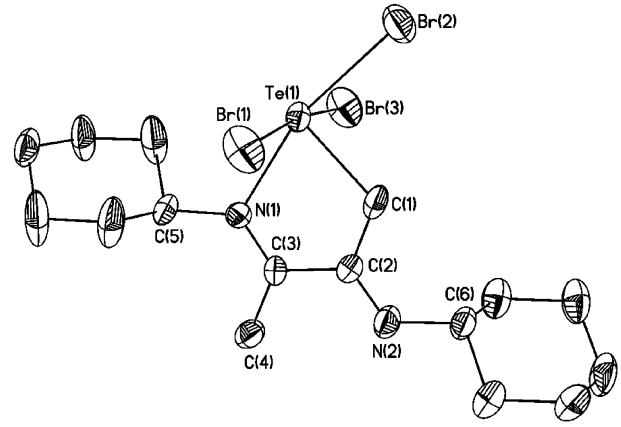


Figure 3. Solid-state structure of **7CyBr**. Thermal ellipsoids are drawn to the 50% probability level, $CHCl_3$ solvate and hydrogen atoms are omitted for clarity.

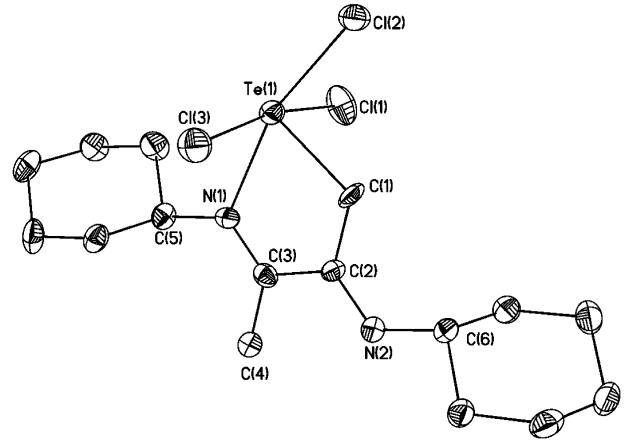


Figure 4. Solid-state structure of **7CyCl**. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are omitted for clarity.

mixture of products. However after work up, the redissolved solids analyzed by ^{1}H NMR spectroscopy, revealed a single compound that appeared to have a framework related to **7Dipp**. Again, the symmetry of the ligand was broken: the methine protons displayed two resonances at $\delta = 3.08$ and 2.39 ppm. A singlet was observed at $\delta = 2.12$ ppm integrating to three protons consistent with a methyl group on the ligand, as well as two signals integrating to one proton each ($\delta = 8.31$ and 4.83 ppm). The resonance at $\delta = 4.83$ ppm was significantly broadened, whereas the signal at $\delta = 8.31$ ppm clearly displayed coupling to ^{77}Se ($^2J_{Se-H} = 24$ Hz). To identify the material conclusively, single crystals were grown for X-ray diffraction, and subsequent solid state studies revealed the compound to feature an *N,C* bound five-membered selenium heterocycle (**8DippCl**), analogous to **7**. However, based on the geometry and coordination environment about the central element, it was apparent that a reduction had taken place, leaving selenium in the +2 oxidation state. The low isolated yield (<20%), combined with the reduction at Se, prompted us to investigate the same chemistry using sources of Se(II) rather than Se(IV).

In this context, the reaction of **1Dipp** with SeX_2 (X = Cl, Br) in THF resulted in the immediate generation of yellow solutions and after workup, bright yellow powders (Scheme 1). For X = Cl, the redissolved ($CDCl_3$) powder showed

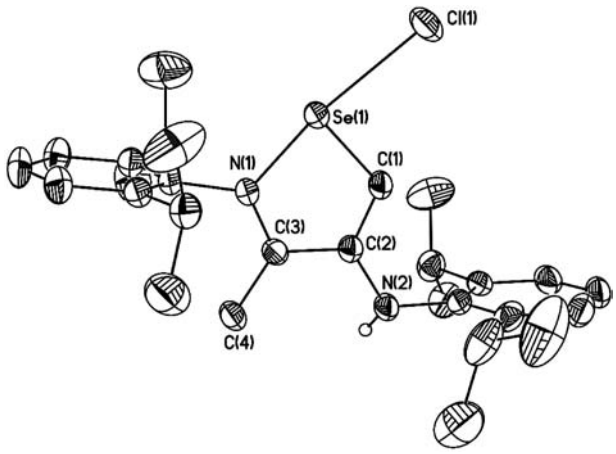


Figure 5. Solid-state structure of **8DippCl**. Thermal ellipsoids are drawn to the 50% probability level and unrefined hydrogen atoms are omitted for clarity.

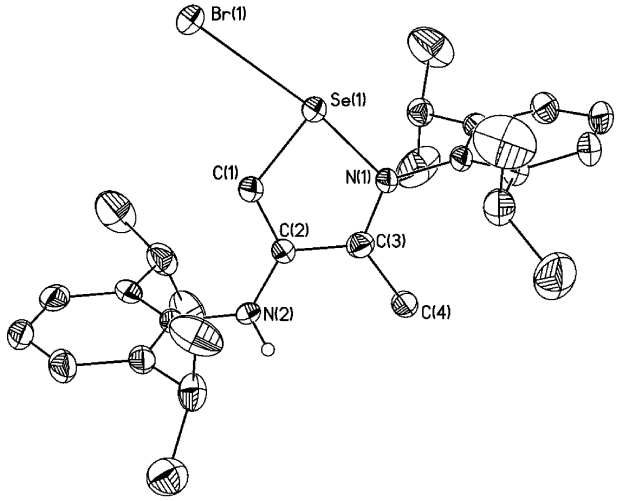


Figure 6. Solid-state structure of **8DippBr**. Thermal ellipsoids are drawn to the 50% probability level and unrefined hydrogen atoms are omitted for clarity.

signals identical to that of **8DippCl** in the ^{1}H NMR spectrum, and X-ray diffraction studies on crystals grown from the bulk powder showed that the material was identical and obtained in a much better yield (ca. 85%; Figure 5). For X = Br, the ^{1}H NMR spectrum was essentially identical to that of **8DippCl**, and X-ray analysis of single crystals grown from the bulk powder confirmed generation of the brominated derivative (**8DippBr**; Figure 6). In both cases there was the formal loss of HX, similar to the tellurium analogues. However unlike the Te chemistry, a proton transfer took place to give an exocyclic amine functionality. A further contrast between the selenium and the tellurium chemistry occurred when an alkyl substituted ligand was employed (**1Cy**) rather than the aryl derivative **1Dipp**. When the reaction was carried out between the selenium(II) halides and **1Cy** under identical reaction conditions, a colorless solid precipitated immediately. The dried powders were found to be completely insoluble in a variety of common solvents used for ^{1}H NMR spectroscopy ($CDCl_3$, C_6D_6, CD_3CN), in stark contrast to the other derivatives (**8DippCl**, **8DippBr**). The powders were soluble in C_5D_5N and the ^{1}H NMR spectra for both X = Cl and Br, revealed a similar break in symmetry for the N-substituents (Cy-ispo; X = Cl, δ = 3.96, 3.03 ppm; X = Br, δ = 4.10, 3.08 ppm) and the backbone methyl group integrated only for 3 protons, as was observed for **8Dipp**. In addition, two signals that integrated to one proton, with one being broad and the other clearly coupling to Se were observed ($^2J_{SeH}$ = 24 Hz). Despite the similarities in the spectroscopic data (^{1}H NMR, FT-IR, and FT-Raman spectra), the extreme differences in solubilities between the Dipp and Cy congeners pointed to some marked dissimilarities. Unfortunately all attempts to grow single crystals of the cyclohexyl analogues for X-ray diffraction studies resulted in the precipitation of bulk powders. Combustion microanalysis (C, H, N) of both derivatives gave results consistent with a molecular formula of $C_{16}H_{28}X_2N_2Se_1$, which indicated that the HX eliminated in the other cases remained in the final product. Upon reexamination of the solution ^{1}H NMR spectra, in the far downfield region a second broad resonance also integrating for one proton was present (δ = 18 ppm, X = Cl; δ = 13 ppm, X = Br). Given that the NMR spectra were collected in pyridine-d_6, we surmised that the insoluble compounds were the HX salts of the *N,C* bound Se(II) heterocycles (**8CyCl·HCl**; **8CyBr·HBr**), which were subsequently deprotonated by the NMR solvent. The HX was eliminated in a facile fashion by adding a stoichiometric equivalent of NEt_3 in THF, which resulted in the immediate precipitation of $[HNEt_3][X]$ and the generation of a yellow solution. Removal of the ammonium salt and volatiles gave light yellow powders. These had solubilites similar to the Dipp analogues, and the ^{1}H NMR spectra in $CDCl_3$ revealed resonances very similar to the hydrogen halide salts, albeit without the broad resonance shifted to low field. All characterization data were consistent with the assignment as the $N_1Se_1C_3$ heterocycles (**8CyCl** or **8CyBr**), isolated in 84% and 40% yields, respectively.

Given these results with Te and Se, we wondered if analogous molecules could be synthesized with sulfur as the central element. Sulfur tetrachloride has been reported; but we have not been able to reproduce its synthesis and SBr_4 is synthetically inaccessible.[20] However, SCl_2 can be prepared via the reaction of S_2Cl_2 with chlorine gas over a catalytic amount of $FeCl_2$ and stored for extended periods (>6 months) under an N_2 atm at −78 °C. Given the known thermal instability of SCl_4, SCl_2 was used as a reagent to generate the sulfur analogues. The 1:1 stoichiometric reaction of **1Dipp** with SCl_2 in THF followed by addition of *n*-pentane after 10 min, gave a yellow powder (Scheme 1). Proton NMR spectroscopy of the isolated solids showed one set of signals, with similar resonances as observed in **8DippCl**. Single crystals suitable for X-ray diffraction studies were grown from a CH_2Cl_2 solution of the bulk material, which revealed the anticipated connectivity of a $N_1S_1C_3$ heterocycle (**9DippCl**), isolated from the reaction in 69%

(20) There have been many reports in the older literature concerning the isolation (and use of) SCl_4 at low temperatures, by reacting liquid Cl_2 with SCl_2. This species is unstable and reported to decompose at temperatures above −30°C (See King, R. B. *Encyclopedia of Inorganic Chemistry*; Wiley: Hoboken, 2005; pp 5364−5367). Our attempts to prepare SCl_4 in situ as CH_2Cl_2 and THF solutions did not reveal any evidence for the formation of SCl_4.

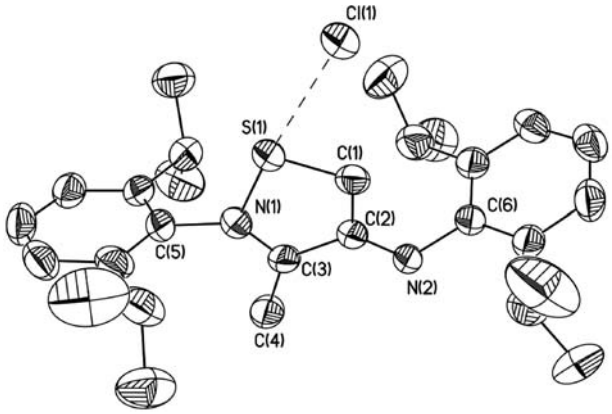


Figure 7. Solid-state structure of **9DippCl** Thermal ellipsoids are drawn to the 50% probability level, CH_2Cl_2 solvate and hydrogen atoms are omitted for clarity.

yield (Figure 7). As was the case for Se, reaction of SCl_2 with **1Cy** in THF resulted in the precipitation of a highly insoluble powder, though sparingly soluble in MeCN. The ^{1}H NMR spectrum gave resonances reminiscent of **8CyCl**, and elemental analysis of the powder was consistent with the hydrochloride salt **9CyCl·HCl**.

X-ray Crystallography. Compounds **7DippCl**, **7DippBr**, **7CyCl**, **7CyBr**, **8DippCl**, **8DippBr**, and **9DippCl** have been characterized by single crystal X-ray diffraction studies. Views of the formula units are shown in Figures 1−7, and key refinement details and a listing of pertinent bond lengths and angles are found in Tables 1 and 2, respectively. All of the tellurium compounds have analogous structural features barring the R substituent on nitrogen and the halide present. The geometry about Te in all cases is a distorted square-based pyramid as described by the AX_5E electron pair formula, where the distortion is imposed by the stereochemically active "lone pair" of electrons. This "lone pair" of electrons and the endocyclic carbon C(1) occupy the axial sites, where the N and remaining three halogen atoms all reside in equatorial positions.

The Te(1)−N(1) (2.298−2.448 Å) and Te(1)−(C1) (av. 2.125 Å) bond lengths are consistent with Te−N or Te−C single bonds.[6,21,22] The endocyclic (N(1)−C(3)) and exocyclic (N(2)−C2)) bonds are relatively short (av. endo: 1.284 Å; av. exo. 1.269 Å), reflective of imine functionalities. Also apparent is the nonplanarity of the $Te_1N_1C_3$ heterocycles: the atoms C(1) are sp^3 hybridized methylene groups with a distorted tetrahedral geometry, which forces a nonplanar five membered ring. This assignment of the bonding is congruent with the ^{1}H NMR data obtained from solution in that there is a methyl and a methylene fragment requiring an integration ratio of 3:2 and there is no evidence of a N−H functionality.

The selenium compounds characterized by X-ray crystallography are isostructural with respect to the 5 membered ring. Given the +2 oxidation state for selenium, a T-shaped geometry is imposed by a AX_3E_2 electron pair formula. The Se(1)−C(1) bonds (**8DippCl**, 1.849(2); **8DippBr**, 1.849(4) Å) are typical Se−C single bond lengths, and the Se(1)−N(1) bond (**8DippCl**, 1.931(1); X = **8DippBr**, 1.942(3) Å) is slightly elongated, indicative of a dative interaction.[1,23] In contrast to the Te rings, C(1)−C(2) clearly form a double bond (**8DippCl**, 1.365(2); **8DippBr**, 1.350(5) Å), and the C(2)−N(2) is elongated (**8DippCl**, 1.386(2); **8DippBr**, 1.388(5) Å). The proton bound to N(2) can be located in the difference map and refined for both **8DippCl** and **8DippBr**. The existence of the N−H functionality is also confirmed by way of the ^{1}H NMR spectra (**8DippCl** and **8DippBr**, δ = 4.83 ppm); as well a distinct N−H stretch observed in IR spectra.

In the case of sulfur (**9DippCl**)), an examination of the metrical parameters reveals a similar N−C bound AX_3E_2 sulfur center as detected for selenium (S(1)−N(1) = 1.709(4) Å, S(1)−C(1) = 1.687(5) Å). The result of a proton transfer is again obviated by the C(1)−C(2) bond length of 1.373(6) Å and the C(2)−N(2) bond at 1.380(6) Å, which is single. A significant deviation from the Se version is the elongated chalcogen-chlorine contact at 2.849(2) Å (S(1)−Cl(1)) as compared to Se(1)−Cl(1) at 2.5965(5) Å. Considering the greater distance, combined with the larger size of selenium, this metrical parameter indicates an ionic character to the sulfur analogue. However, the distance is well within the sum of the van der Waals radii ($\Sigma_{v.d.w.}$ (S−N) = 3.65 Å)[24] and despite this elongation, the chlorine atom still defines a T-shaped geometry about sulfur. This elongation of the S−Cl bond may be a function of hydrogen bonding in the solid state to the proton bound to N(2) of an adjacent molecule (Cl···H = 2.50 Å).

Isotope Labeling. In an effort to garner a greater understanding of this unusual transformation, we have undertaken some additional experiments using the $TeCl_4$/**1Dipp** system as a model.[25] To confirm that the proton eliminated from the reaction (which can be sequestered using NEt_3) originated from within a backbone methyl group, $-CD_3$ labeled **1Dipp** was synthesized from labeled 2,3-butanedione, with an isotopic purity for the $-CD_3$ groups of approximately 95%. The 1:1 stoichiometric reaction of $TeCl_4$ with the labeled ligand (**1Dipp-*d*$_6$**) in THF followed by the addition of NEt_3 results in the precipitation of a colorless powder within a yellow solution. A ^{1}H NMR spectrum of the isolated solid in C_5D_5N indicated the presence of $[DNEt_3]^+$, as the ethyl resonances were identical to that from the analogous $-CH_3$ **1Dipp** experiment, and only a small residual peak was visible for the N−H proton, which arises from the 5% undeuterated material. The ^{1}H NMR spectrum of the **7DippCl-*d*$_5$** recovered revealed the expected spectrum, with approximately 95% disappearance

(21) Furukawa, N.; Sato, S. *Heteroat. Chem.* **2002**, *13*, 406–413.
(22) Kuhn, N.; Abu-Rayyan, A.; Piludu, C.; Steimann, M. *Heteroat. Chem.* **2005**, *16*, 316–319.
(23) Risto, M.; Reed, R. W.; Robertson, C. M.; Oilunkaniemi, R.; Laitinen, R. S.; Oakley, R. T. *Chem. Commun.* **2008**, 3278–3280.
(24) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, 1960.
(25) The kinetics stopped-flow instrumentation requires that all species remain in solution throughout the experiment. Additionally, the stopped-flow system is not compatible with THF. The reaction of $TeCl_4$ and **1Dipp** in toluene gives identical products as the THF reaction, and both the products and the reactants are soluble. In the case of $TeBr_4$, SeX_2 and SCl_2, with **1Dipp**, and all compounds using **1Cy** the products precipitate from toluene. Therefore, we were limited to the $TeCl_4$ system; however, the reactivity of the other analogues appears to be the same.

Table 1. Crystal Data for Compounds **7**−**9**

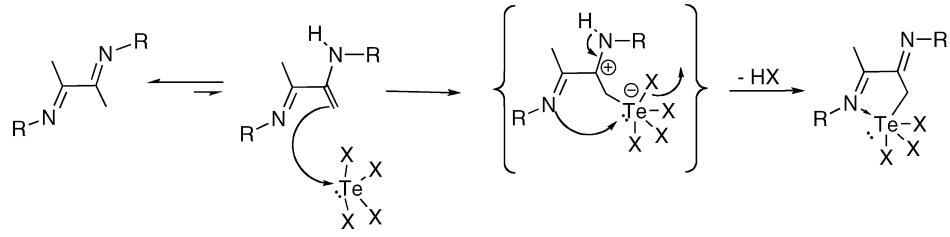
	7DippCl	7DippBr	7CyCl	7CyBr	8DippCl	8DippBr	9DippCl
empirical formula	$C_{28}H_{39}Cl_3N_2Te_1$	$C_{28}H_{39}Br_3N_2Te_1$	$C_{16}H_{27}Cl_3N_2Te_1$	$C_{17}H_{28}Br_3Cl_3N_2Te_1$	$C_{28}H_{39}Cl_1N_2Se_1$	$C_{28}H_{39}Br_1N_2Se_1$	$C_{29}H_{41}Cl_3N_2S_1$
formula weight	637.56	770.94	481.35	734.09	518.02	562.48	556.05
crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	10.236(2)	9.304(2)	9.190(2)	10.697(2)	9.2685(5)	9.306(2)	10.887(2)
b (Å)	16.801(3)	9.630(2)	9.967(2)	10.211(2)	22.653(1)	22.436(5)	19.883(4)
c (Å)	17.921(4)	18.133(4)	11.624(2)	23.173(5)	13.6431(7)	13.720(3)	14.898(3)
α (deg)	90	84.58(3)	84.70(3)	90	90	90	90
β (deg)	94.66(3)	82.27(3)	69.45(3)	100.44(3)	102.3574(7)	100.08(3)	92.75(3)
γ (deg)	90	69.86(3)	75.26(3)	90	90	90	90
V (Å^3)	3072(1)	1509.5(5)	964.1(3)	2489.2(8)	2798.1(2)	2820(1)	3221(1)
D_c (mg m^{-3})	1.247	1.696	1.658	1.959	1.230	1.325	1.147
radiation, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temp. (K)	150(2)	150(2)	150(2)	150(2)	193(2)	150(2)	193(2)
$R[I > 2\sigma I]$[a]	0.0507	0.0389	0.0549	0.0540	0.0323	0.0526	0.0795
$wR2(F^2)$[b]	0.1379	0.1056	0.1294	0.1486	0.0824	0.1241	0.2628
Goodness of fit (S)[a]	0.965	1.044	1.085	1.037	1.062	1.021	1.045

[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 for Compounds **7**−**9**; Ch = Te for **7**, Se for **8**, S for **9**

	7DippCl	7DippBr	7CyCl	7CyBr	8DippCl	8DippBr	9DippCl
Ch(1)−N(1)	2.416(3)	2.448(3)	2.309(4)	2.298(4)	1.931(1)	1.942(3)	1.710(3)
Ch(1)−C(1)	2.124(4)	2.130(3)	2.119(5)	2.127(6)	1.849(2)	1.850(4)	1.686(4)
C(1)−C(2)	1.506(6)	1.505(5)	1.509(7)	1.503(8)	1.365(2)	1.350(5)	1.374(6)
C(2)−C(3)	1.493(6)	1.503(5)	1.494(7)	1.487(7)	1.438(2)	1.441(5)	1.422(6)
C(2)−N(2)	1.267(5)	1.274(4)	1.271(6)	1.265(7)	1.387(2)	1.386(5)	1.377(5)
C(3)−N(1)	1.293(5)	1.278(5)	1.283(6)	1.282(7)	1.314(2)	1.312(5)	1.322(6)
N(1)−C(5)	1.457(5)	1.446(4)	1.474(7)	1.490(7)	1.444(2)	1.443(4)	1.465(5)
N(2)−C(6)	1.440(5)	1.431(4)	1.470(7)	1.454(7)	1.435(2)	1.434(5)	1.442(5)
Ch(1)−X(1)	2.473(1)	2.6589(7)	2.475(2)	2.634(1)	2.5964(5)	2.759(1)	2.848(2)
Ch(1)−X(2)	2.404(1)	2.669(1)	2.447(2)	2.6260(8)			
Ch(1)−X(3)	2.499(1)	2.6610(7)	2.523(2)	2.680(1)			

Scheme 2. Proposed Reaction Pathway for the Generation of the N,C Heterocycles, Using **7DippX** As a Model



of the signals arising from the methyl and methylene protons. This experiment confirmed the assertion that the proton is eliminated from a backbone methyl group, and no other scrambling or rearrangement occurs during the reaction.

Low temperature experiments carried out in THF and monitored by ^{1}H NMR spectroscopy, showed that the reaction initiates at −45 °C, with no species being observed other than **1Dipp** and **7DippCl**. Given the low temperature at which the transformation proceeds and that no intermediates were detected, we hypothesized that the reaction was unlikely to rely on the direct deprotonation of a $-CH_3$ group by a third species in solution.

In an attempt to understand the mechanism of the reaction, a stopped-flow kinetics study was performed on the $TeCl_4$/**1Dipp** system. As suspected from visual observation, the reaction is indeed very fast, going to completion in 1.2 s at a concentration of 0.031 mmol for both reactants. Using $-CD_3$ labeled **1Dipp** the reaction goes to completion 6−7 times slower than using the proteo-ligand, likely indicating a strong primary kinetic isotope effect and that a proton transfer is part of the rate determining step. Also observed was an inverse dependence on the rate with respect to the concentration of $TeCl_4$, likely a result of aggregation of the $TeCl_4$ at higher concentrations. However, we were unable to effectively model the kinetic data to establish a definitive rate law. Nevertheless based on the data obtained, the transformation is proposed to occur via olefin attack on the chalcogen center from the enamine form of the ligand, analogous to the related NacNac system outlined by Richards et al.[3] The carbon-chalcogen bond formation is concomitant with coordination by the imine nitrogen proximal to the tellurium atom, generating the 5 membered ring, and H−X elimination (Scheme 2).

The proton-dependent rate determining process is likely the establishment of the enamine/imine equilibrium for the ligand, with the enamine form being consumed as the reaction proceeds. It must be noted that regardless of the metal starting material used (Se or Te), a distinct increase in the reaction completion time was observed when using the labeled ligand. This gives additional credence to the

assertion that the enamine/imine tautomerization process is the rate limiting step, provided the HX elimination is faster. The reasoning for the preference of the imine (Te) versus enamine (Se, S) tautomer in the final product remains an open question, as it is dependent on either the identity of the central element or the oxidation state it adopts. Unfortunately, attempts to resolve this issue by either reducing the tellurium congeners or oxidizing the Se/S heterocycles were unsuccessful. However, our observations are consistent with those of Cowley et al. in the report of the reaction between $TeCl_4$ and the DIMPY ligand, where Te−C connectivity was observed as well as the imine tautomer remaining resilient.[6]

Conclusion

The reactions of CH_3 substituted α-diimine ligands with *N*-alkyl or *N*-aryl substituents at nitrogen result in the formation of $N_1Ch_1C_3$ ring systems. This is in contrast to what has been reported for the reactions of other main group element halides with analogous DAB ligands or for the chalcogens using non-methylated analogues. By employing a CD_3 substituted version of the ligand, a distinct 6 to 7 fold delay in the completion of the reaction was observed, pointing toward a primary kinetic isotope effect. This lends substantial support to the assertion that the enamine form of the ligand plays a key role the reaction progress and no C−H bond activation is apparent.

Acknowledgment. We thank Natural Sciences and Engineering Research Council (NSERC of Canada), The Canada Foundation for Innovation (CFI), The Ontario Ministry for Research and Innovation (OMRI), and The University of Western Ontario for generous support, Allison Brazeau (UWO) for her assistance with the stopped-flow/kinetic experiments, and Dr. R. McDonald and Dr. M. J. Ferguson (University of Alberta) for the collection of X-ray diffraction data for compounds **8DippCl** and **9DippCl**.

Supporting Information Available: Further details are given in Figures S-1 to S-8 including IR and Raman data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

IC802320S