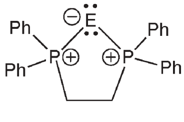
The direct reaction of the ^{t}Bu-DAB ligand with $SeCl_4$: a redox route to selenium–nitrogen heterocycles†

Jason L. Dutton, Jocelyn J. Tindale, Michael C. Jennings and Paul J. Ragogna*

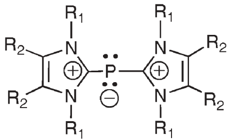
Received (in Berkeley, CA, USA) 13th March 2006, Accepted 10th April 2006
First published as an Advance Article on the web 3rd May 2006
DOI: 10.1039/b603777a

The reaction of $SeCl_4$ with the ubiquitous *tert*-butyl-substituted diazabutadiene ligand results in the isolation of a rare example of a 1,2,5-selenadiazolium cation, representing a novel route to Se–N ring formation; these heterocycles can be derivatised at selenium, which has led to the identification of a short Se···N secondary bonding interaction.

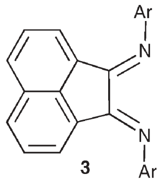
Low oxidation state main group chemistry has been highlighted by sequestered P(I) or As(I) cations from the reaction of diphosphines or carbenes with EI_3 or PCl_3 (E = P, As; *e.g.*, **1** or **2**).[1,2] This methodology has been extended to include the diimine ligand 1,2-bis(arylimino)acenaphthene **3** (aryl = 2,6-diisopropylphenyl), revealing an uncommon intramolecular charge transfer process.[3] In each case, the reductive elimination of X_2 has been identified during the synthesis of **1** (X = I)[1,3] and **2** (X = Cl).[2] Analogous chemistry, employing bidentate diimine ligands and group 16 element chlorides (ECl_4) to achieve E–N bond formation has remained unreported, in contrast to the many recent developments in selenium–nitrogen chemistry. The high reactivity of the Se–N bond can be exploited in a variety of synthetic and self assembly applications, however its inherent lability renders the isolation of new Se–N systems a significant challenge.[4–6]



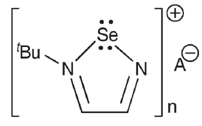
1a; E = P
1b; E = As



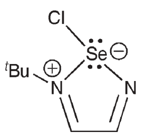
2
R_1 = Et, ^{i}Pr. ^{t}Bu, 1-Ad, Mes;
R_2 = Me, H



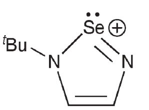
3
R = Dipp



[4]$_2$[SeCl$_6$]; A = $SeCl_6^{2-}$; n = 2
[4] [GaCl$_4$]; A = $GaCl_4^{-}$; n = 1



4Cl



4a

In this context, we report the synthesis and comprehensive characterisation of a series of unusual cationic (**[4]$_2$[SeCl$_6$]** and **[4][GaCl$_4$]**) and neutral (**4Cl**) Se(II)–N heterocycles, which result from the direct reaction of $SeCl_4$ with the 1,4-di(*tert*-butyl)-1,4-diaza-1,3-butadiene ligand (*tert*-butyl-DAB).‡ This represents a novel route to functionalised selenium–nitrogen rings. They are rare examples of structurally characterised 1,2,5-selenadiazolium heterocycles, and in the case of **[4][GaCl$_4$]**, we have identified a short Se···N secondary bonding interaction.[7]

The 2 : 3 stoichiometric reaction between *tert*-butyl-DAB and $SeCl_4$ at room temperature in THF immediately results in the formation of a bright yellow precipitate. Proton NMR spectroscopy of the redissolved powder in acetonitrile-d_3 revealed two distinct signals for the backbone protons on the ligand (9.49 and 9.39 ppm; $^{3}J_{H–H}$ = 0.6 Hz), as well as a singlet consistent with ^{t}Bu (1.76 ppm). However, their integration ratio was found to be 1 : 1 : 9, and not the expected 1 : 1 : 18. Crystals from the bulk powder were grown from concentrated acetonitrile solutions at −30 °C, and X-ray diffraction studies of the crystalline material revealed the compound to be **[4]$_2$[SeCl$_6$]**, featuring two C_2N_2Se heterocyclic cations with a $SeCl_6^{2-}$ counter-dianion (Fig. 1).

The precise mechanism for the formation of **[4]$_2$[SeCl$_6$]** is still under investigation, however, in light of the studies involving P and As, we postulate that reduction of the two Se centres in the cations of **[4]$_2$[SeCl$_6$]** are each partnered by the loss of Cl_2 and *tert*-butylchloride, with concomitant abstraction of the remaining chlorides by $SeCl_4$, forming the $SeCl_6^{2-}$ dianion. The ^{1}H NMR spectra of the supernatant from the reaction of *tert*-butyl-DAB and $SeCl_4$ in THF-d_8 revealed the presence of multiple products. However, a prominent singlet at 1.62 ppm was consistent with the formation of *tert*-butylchloride.[8,9] The NMR sample was subsequently doped with 2-chloro-2-methylpropane (*tert*-butylchloride) and a corresponding increase in the signal at 1.62 ppm was observed.

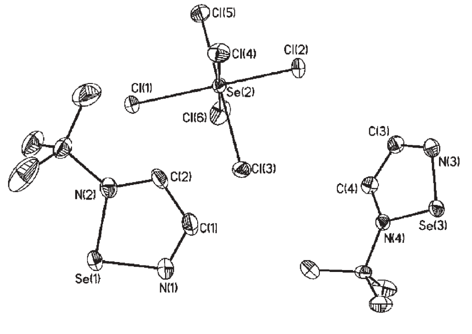


Fig. 1 Solid-state structure of **[4]$_2$[SeCl$_6$]**·MeCN. Ellipsoids are drawn to 50% probability, hydrogen atoms and MeCN solvate are removed for clarity, and atoms of interest labelled. Selected bond lengths (Å) and angles (°): Se(1)–N(1) 1.780(7), Se(1)–N(2) 1.880(7), N(1)–C(1) 1.295(1), N(2)–C(2) 1.289(1), C(1)–C(2) 1.400(1), Se(3)–N(3) 1.766(7), Se(3)–N(4) 1.852(7), N(3)–C(3) 1.315(1), N(4)–C(4) 1.298(1), C(3)–C(4) 1.416(1), N(1)–Se(1)–N(2) 87.5(3), N(3)–Se(3)–N(4) 88.4(3).

Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7. E-mail: pragogna@uwo.ca; Fax: +1 519-661-3022; Tel: +1 519-661-2111

† Electronic supplementary information (ESI) available: Tables of X-ray crystallographic data. See DOI: 10.1039/b603777a

This journal is © The Royal Society of Chemistry 2006

The addition of a CH_2Cl_2 solution containing Ph_3P (4 equivalents) to a CH_2Cl_2 slurry of **[4]$_2$[SeCl$_6$]** immediately gave a clear, pale yellow reaction mixture. Addition of *n*-hexanes resulted in the precipitation of a fine white powder (**4Cl**, 90%), which has been identified as the chloride derivative, based on ^1H NMR spectroscopy and single crystal X-ray diffraction studies (Fig. 2). The formation of **4Cl** results from the liberation of chloride from $SeCl_6^{2-}$ by Ph_3P, which is subsequently trapped by the cationic heterocycle. Phosphorus-31 NMR spectroscopy of the reaction mixture reveals two by-products, consistent with the formation of Ph_3PSe (36 ppm; $^1J_{P-Se}$ = 737 Hz) and $[Ph_3PCl]^+$ (66 ppm).[10,11]

The solid state structures of **[4]$_2$[SeCl$_6$]** and **4Cl** reveal planar C_2N_2Se rings in all cases (mean deviation from planarity 0.006 Å for **4Cl**, and 0.010 and 0.0081 Å for **[4]$_2$[SeCl$_6$]**). The cation in **[4]$_2$[SeCl$_6$]** has a sharply bent geometry about Se (87.5(1) and 88.4(3)°). The $SeCl_6^{2-}$ dianion is essentially octahedral with a stereochemically-inactive lone pair of electrons.[12] Compound **4Cl** exhibits a classical T-shaped AX_3E_2 geometry. The N–Se bond lengths in **[4]$_2$[SeCl$_6$]** are significantly shorter than in **4Cl**, which is likely to be a result of the low coordination environment about Se in **[4]$_2$[SeCl$_6$]**. The Se(1)–N(1) bond lengths in both compounds, as well as the Se(3)–N(3) bond length in **[4]$_2$[SeCl$_6$]**, are between 1.766(7) and 1.807(2) Å, which is close to the outer limit for Se–N multiple bonds.[7b,8,13] In comparison, the predicted value for a Se=N double bond is 1.65 Å,[7b] and those that have been experimentally measured are 1.679(8) Å in AdN=Se=NAd (Ad = adamantyl) and 1.710(3) Å in $SnCl_4[(^tBuN)_2Se](THF)_2]$.[13] Furthermore, the metrical parameters of the N–C–C–N backbone are similar to those reported for the free *tert*-butyl-DAB ligand,[14] with short endocyclic C–N bonds (1.295(1) to 1.315(1) Å). Therefore, the bonding in the heterocycle is best described as containing two C=N functionalities, with a contribution from the resonance form **4a**.[15] In addition, $^{77}Se\{^1H\}$ NMR spectroscopic data for all compounds fall within the range for Se(II) rather than Se(IV). For example, diimido Se(IV) compounds are shifted significantly further downfield (*e.g.*, $^tBuN=Se=N^tBu$ = 1655 ppm).[6] These combined data support the necessary reduction from Se(IV) to Se(II) rather than a reduction of the ligand.

The solubility of **[4]$_2$[SeCl$_6$]** is marginal in common organic solvents, thereby limiting our ability to study its chemistry. Compound **4Cl** provides a readily-accessible starting material for the derivatisation of the Se–N heterocycle, thus allowing the synthesis of analogues of greater solubility. A stoichiometric reaction of **4Cl** with $GaCl_3$ in CH_2Cl_2 resulted in a clear, colourless solution. Addition of hexanes yielded a white powder (**[4][GaCl$_4$]**, 92%), which gave ^1H NMR characteristics consistent with **[4]$_2$[SeCl$_6$]** and **4Cl**. X-ray diffraction studies on single crystals grown from the bulk powder revealed the structure to be the $GaCl_4^-$ salt of the selenadiazolium heterocycle (Fig. 3). The structural features of this heterocyclic cation are consistent with those of the **[4]$_2$[SeCl$_6$]** and **4Cl**. Further analysis of the structure revealed a short Se···N secondary bonding interaction (2.605(3) Å),[7] creating a 4-membered Se_2N_2 ring, which is directed by the apparent steric bulk of the *tert*-butyl groups. This may have implications for the application of these ring systems in molecular self-assembly. This phenomenon is not observed in the solid-state structure of **4Cl** as the presence of Cl on Se interferes with the potential alignment of a second ring. In the case of **[4]$_2$[SeCl$_6$]**, there is a much longer Se···N contact (3.714(7) Å), which falls outside of the sum of the van der Waals radii (3.54 Å). We are in the process of investigating the impact of these contacts on the solid state arrangement of the heterocycles, the details of which will be reported in a full paper.

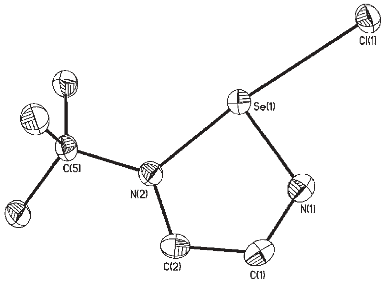


Fig. 2 Solid-state structure of **4Cl**. Ellipsoids are drawn to 50% probability, hydrogen atoms are removed for clarity, and atoms of interest labelled. Selected bond lengths (Å) and angles (°): Se(1)–N(1) 1.807(2), Se(1)–N(2) 1.948(2), Se(1)–Cl(1) 2.6051(8), N(1)–C(1) 1.303(3), N(2)–C(2) 1.297(3), C(1)–C(2) 1.418(4), N(1)–Se(1)–N(2) 85.9(1), N(2)–Se(1)–Cl(1) 173.3(1), N(1)–Se(1)–Cl(1) 87.6(1).

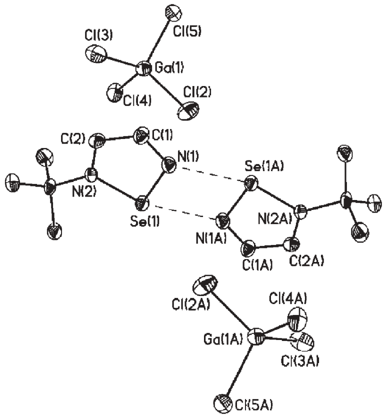


Fig. 3 Solid-state structure of **[4][GaCl$_4$]**. Ellipsoids are drawn to 50% probability, hydrogen atoms are removed for clarity, and atoms of interest labelled. Selected bond lengths (Å) and angles (°): Se(1)–N(1) 1.787(3), Se(1)–N(2) 1.851(3), N(1)–C(1) 1.301(4), N(2)–C(2) 1.317(4), C(1)–C(2) 1.420(5), N(1)–Se(1)–N(2) 87.5(1).

We have identified a facile route to the synthesis of rare, functionalised 1,2,5-selenadiazolium derivatives, which offers the opportunity to further study the chemistry of these unusual compounds. This occurs through a redox process reminiscent of that reported for P and As, which may be indicative of a general trend across the p-block. We are currently investigating the redox and Lewis acid–base properties of these novel heterocycles, as well as pursuing the synthesis of S and Te analogues.

We would like to thank the Natural Science and Engineering Research Council of Canada (NSERC) and the University of Western Ontario for their generous financial support, and Dr C. W. Kirby and Mr K. Pollard for their help with the acquisition of $^{77}Se\{^1H\}$ NMR spectra.

Notes and references

‡ Multi-nuclear NMR chemical shifts are reported in ppm and coupling constants in Hz. $^{77}Se\{^1H\}$ NMR spectra were externally referenced to SeO_2, relative to neat Me_2Se.[6] NMR spectra were recorded in acetonitrile-*d*$_3$

unless otherwise indicated. X-ray diffraction data were collected on a Nonius Kappa-CCD area detector using Mo-Kα radiation (λ = 0.71073 Å). Single crystals of **[4]$_2$[SeCl$_6$]**, **4Cl** and **[4][GaCl$_4$]** were selected under oil, mounted on glass fibers, then immediately placed in a cold stream of N_2. Structures were solved by direct methods and refined using full-matrix, least-squares on F^2.

Compound **[4]$_2$[SeCl$_6$]**: A Schlenk tube was charged with $SeCl_4$ (2.00 g, 9.06 mmol), the contents dissolved in THF (30 mL), and a THF (10 mL) solution of *tert*-butyl-DAB (1.00 g, 5.95 mmol) added at RT. After 5 min, the yellow precipitate was collected and washed with THF (50 mL). The yellow powder was dried *in vacuo*, giving **[4]$_2$[SeCl$_6$]**. Yield 0.686 g, 36%. d.p. 80 °C. ^{1}H NMR: 9.49 (1 H), 9.39 (1 H) and 1.76 (9 H). ^{13}C{^{1}H} NMR: 154.4, 152.0, 67.5 and 31.6. ^{77}Se{^{1}H} NMR was not observed because of low solubility. ESI-MS (*m/z*): [$M^+ - SeCl_6$] 191. Crystal data: $C_{14}H_{25}Cl_6N_5Se_3$, M = 712.97 g mol^{-1}, monoclinic, $P2_1/c$, a = 14.5099(4), b = 10.4455(2), c = 16.7518(7) Å, β = 93.718(2)°, V = 2533.61(14) Å^3, T = 150(2) K, Z = 4, D_c = 1.869, measured reflections = 25379, unique = 4477 (R_{int} = 0.069), refined parameters = 254, $R[I > 2\sigma(I)]$ = 0.0532, w$R_2(F^2)$ = 0.1230, R_1(all data) = 0.0686, wR_2(all data) = 0.1276. CCDC 601830.

Compound **4Cl**: In a N_2 filled dry box, a vial was charged with Ph_3P (0.048 g, 0.178 mmol), the contents dissolved in CH_2Cl_2 (2 mL), and then added to a RT CH_2Cl_2 (2 mL) slurry of **[4]$_2$[SeCl$_6$]** (0.030 g, 0.0447 mmol). After 1 min, hexanes (20 mL) were added and the resulting suspension centrifuged. The solids were washed with hexanes (4 × 10 mL) and the volatiles removed, giving **4Cl** as a white powder. Yield 0.018 g, 90%. d.p. 70 °C. ^{1}H NMR: 9.38 (1 H), 9.16 (1 H) and 1.66 (9 H). ^{13}C{^{1}H} NMR: 153.7, 152.8, 65.2 and 31.7. ^{77}Se{^{1}H} NMR: 1190. Crystal data: $C_6H_{11}ClN_2Se$, M = 225.58 g mol^{-1}, monoclinic, $P2_1/c$, a = 9.1855(7), b = 9.2467(7), c = 10.3396(6) Å, β = 104.012(4)°, V = 852.07(10) Å^3, T = 150(2) K, Z = 4, D_c = 1.758, measured reflections = 10131, unique = 2110 (R_{int} = 0.060), refined parameters = 91, $R[I > 2\sigma(I)]$ = 0.0326, w$R_2(F^2)$ = 0.0682, R_1(all data) = 0.0507, wR_2(all data) = 0.0738. CCDC 601829.

Compound **[4][GaCl$_4$]**: $GaCl_3$ (0.008 g, 0.044 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of **4Cl** (0.011 g, 0.044 mmol) in CH_2Cl_2 (5 mL) at RT. After 40 min, hexanes (10 mL) were added and the resulting suspension centrifuged. The solids were washed with hexanes (3 × 10 mL) and the volatiles removed, giving **[4][GaCl$_4$]** as a white powder. Yield 0.018 g, 92%. d.p. 139–142 °C. ^{1}H NMR: 9.52 (1 H), 9.46 (1 H) and 1.79 (9 H). ^{77}Se{^{1}H} NMR: 1315. ESI-MS (*m/z*): [M^+] 191, [M_2A^+] 593 and [A^-] 210. Crystal data: $C_6H_{11}Cl_4Ga_1N_2Se$, M = 401.65 g mol^{-1}, monoclinic, $P2_1/c$, a = 12.7117(5), b = 9.9671(4), c = 11.0754(4) Å, β = 99.724(2)°, V = 1383.09(9) Å^3, T = 150(2) K, Z = 4, D_c = 1.929, measured reflections = 6048, unique = 3174 (R_{int} = 0.0429), refined parameters = 128, $R[I > 2\sigma(I)]$ = 0.0377, w$R_2(F^2)$ = 0.0900, R_1(all data) = 0.0567, wR_2(all data) = 0.0968. CCDC 601831. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603777a

1 B. D. Ellis, M. Carlesimo and C. L. B. Macdonald, *Chem. Commun.*, 2003, 1946.

2 B. D. Ellis, C. A. Dyker, A. Decken and C. L. B. Macdonald, *Chem. Commun.*, 2005, 1965.

3 G. Reeske, C. R. Hoberg, N. J. Hill and A. H. Cowley, *J. Am. Chem. Soc.*, 2006, **128**, 2800.

4 T. Chivers, *A Guide to Chalcogen-Nitrogen Chemistry*, World Scientific, Hackensack, NJ, 2005.

5 K. B. Sharpless, T. Hori, L. K. Truesdale and C. O. Dietrich, *J. Am. Chem. Soc.*, 1976, **98**, 269.

6 T. Maaninen, T. Chivers, R. Laitinen, G. Schatte and M. Nissinen, *Inorg. Chem.*, 2000, **39**, 5341.

7 (*a*) A. F. Cozzolino, I. Vargas-Baca, S. Mansour and A. H. Mahmoudkhani, *J. Am. Chem. Soc.*, 2005, **127**, 3184; (*b*) M. Björgvinsson and H. W. Roesky, *Polyhedron*, 1991, **10**, 2353.

8 Loss of *tert*-butyl has been observed during the synthesis of other Se and Te heterocycles. For examples, see: H. W. Roesky, K. Weber, U. Seseke, W. Pinkert, M. Noltemeyer, W. Clegg and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1985, 565 and ref. 9. This phenomenon is even more likely from an imine upon reaction with a Lewis acid (*e.g.*, $SeCl_4$).

9 T. Chivers, X. Gao and M. Parvez, *Inorg. Chem.*, 1996, **35**, 9.

10 (*a*) G. M. Kosolapoff and L. Maier, *Organic Phosphorus Compounds*, Wiley-Interscience, New York, 1972, vol. **4**; (*b*) K. B. Dillon, R. J. Lynch, R. N. Reeve and T. C. Waddington, *J. Inorg. Nucl. Chem.*, 1974, **36**, 815.

11 Ph_3PSe and [Ph_3PCl][$SeCl_3$] have been isolated from the reaction of $SeCl_4$ and excess Ph_3P, which gives a consistent ^{31}P{^{1}H} NMR signature with the reaction mixture for the synthesis of **4Cl**.

12 Reports of crystallographically-characterised monomeric $SeCl_6^{2-}$ dianions are rare. A Cambridge Structural Database search gave the following three references: (*a*) P. D. Boyle, S. M. Godfrey and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1999, 4245; (*b*) W. Czado, M. Maurer and V. Muller, *Z. Anorg. Allg. Chem.*, 1998, 1871; (*c*) U. Muller and B. Eckhoff, *Z. Kristallogr.–New Cryst. Struct.*, 1999, 505.

13 (*a*) T. Maaninen, R. Laitinen and T. Chivers, *Chem. Commun.*, 2002, 1812; (*b*) J. Gindl, M. Björgvinsson, H. W. Roesky, C. Freire-Erdbrügger and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1993, 811.

14 M. Haaf, A. Schmiedl, T. A. Schmedake, D. R. Powell, A. J. Millevolte, M. Denk and R. West, *J. Am. Chem. Soc.*, 1998, **120**, 12714.

15 A survey of the Cambridge Structural Database for 1,2,5-selenadiazoles, of which solid-state structures are rare, revealed bond length ranges of: N–Se (1.816–1.766 Å), endocyclic C–N (1.309–1.335 Å) and endocyclic C–C (1.452–1.411 Å).