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Extending the Series: Synthesis and Characterization of a Dicationic N-Heterocyclic Selenium Carbene Analogue

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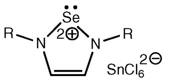
The first report of a “bottleable” carbene by Arduengo et al. has had a significant impact on organic and inorganic chemistry.[1] Since that time, there have been extensive efforts to isolate, comprehensively characterize, and examine the reactivity of the isovalent p-block analogues, collectively known as “main group carbenoids”. These compounds have been successfully synthesized for many of the p-block elements from group 13 to group 15 (Chart 1).[2a−n] In each case, the main group element center is two coordinate, electron rich (bears a “lone pair” of electrons), and can formally be anionic (group 13), neutral (group 14), or cationic (group 15) .

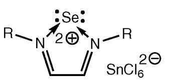
The change in formal charge at the central element has a profound impact on the spectroscopic properties and the reactivity of the carbenoid, in that they can range from being highly nuclelophilic (group 13 and 14) to amphiphilic (group 15), each with a vigorously developing chemistry.[2a,3a−e]

To extend the N-heterocyclic carbenoid series to group 16 would necessitate the central element to formally carry a dicationic charge. These compounds are predicted to be extremely electrophilic and exhibit novel reactivity, and are therefore highly sought-after synthetic targets. Any reports of such N-heterocyclic carbenoid-bonding arrangements for the chalcogens have so far remained absent.[4a−e]

In this context, we report the quantitative, room-temperature synthesis and comprehensive characterization of an N-heterocyclic selenium “carbene” **[1][SnCl$_6$]** (see Supporting Information). To our knowledge, this represents the first example of such a dicationic species in the classical NHC bonding arrangement and is a unique representative of a dicationic Se−N heterocycle.



[1][SnCl$_6$]



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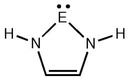
R = 2,6-diisopropylphenyl



3a: E = C, 3b: E = Ga$^-$
3c: E = Ge, 3d: E = As$^+$
3e: E = Se^{2+}, 3f: E = Br^{3+}

Chart 1. Known N-Heterocyclic p-Block Carbenoids, and Their Unknown Chalcogen Analogues (boxed)

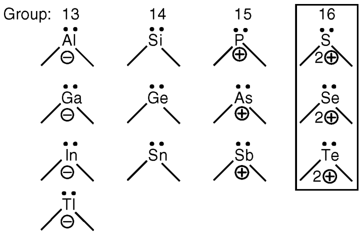


Table 1. Selected Parameters for Related Period 4, p-Block Carbenoids

	E–N[a]	C–N[a]	C–C[a]	δ[b]
3a[1]	1.358 (1.366−1.373)	1.383 (1.382−1.386)	1.349 (1.338)	6.91
3b[2f,j,k]	1.983 (1.983−1.985)	1.379 (1.367−1.423)	1.358 (1.347−1.380)	6.13−6.82
3c[2i]	1.871 (1.856)	1.371 (1.384)	1.354 (1.364)	7.05
3d[2a]	1.810 (1.809−1831)	1.348 (1.339−1.393)	1.370 (1.351−1.375)	8.22
[1^{2+}]	1.870 (1.890)	1.321 (1.293)	1.400 (1.415)	10.58
3e	1.813	1.310	1.418	−
3f	1.872	1.285	1.480	−

[a] Bond distances in (Å), experimental values in parentheses. [b] Experimental ^{1}H NMR chemical shifts (ppm) of the endocyclic C−C ring protons.

The reaction between a stoichiometric mixture of Dipp$_2$DAB (Dipp$_2$DAB = 1,4-(2,6-diisopropyl)phenyl-1,4-diaza-1,3-butadiene) and SnCl$_2$ with one equivalent of SeCl$_4$ in THF solution at room temperature results in the immediate formation of a red precipitate, which gradually (30 min) dissolves to give a deep, orange-red solution. Removal of the solvent in vacuo yields a deep, orange-red powder. Proton NMR spectra of a sample of the redissolved powder in CDCl$_3$ identified a remarkably pure product, with characteristic signals and consistent integration values for the Dipp$_2$DAB ligand. The most striking feature in the spectrum was a highly deshielded singlet ($\delta = 10.58$ ppm; 2H) representing the backbone protons on the ligand framework. The chemical shift of these protons appears to be related to and distinctly diagnostic of the formal charge at the central atom (Table 1). Selenium-77 NMR spectra of the same sample revealed a single selenium signal ($\delta =$ 1268 ppm). Single crystals of the material were grown from the bulk powder via vapor diffusion (CH$_2$Cl$_2$/*n*-pentane), and X-ray diffraction studies of the crystalline sample identified the product to be the two-coordinate, dicationic, N-heterocyclic selenium carbenoid **[1][SnCl$_6$]** (Figure 1).

Although the precise mechanism for the quantitative formation of **[1][SnCl$_6$]** is not yet known, the reaction can be considered to proceed through the reduction of SeCl$_4$ by SnCl$_2$. The resulting intermediate [SeCl$_2$] is sequestered by the Dipp$_2$DAB ligand followed by an intramolecular 2-electron transfer from selenium to the energetically accessible LUMO of the ligand, with concomitant abstraction of the remaining two chlorides by SnCl$_4$. This redox process is consistent with recent reports by Cowley et al. involving diimine ligands with EX$_3$ (E = P, As; X = Cl, I).[2b,c] Although compound **[1][SnCl$_6$]** exhibits the expected bonding arrangement for a p-block carbenoid, there are several noteworthy features of the heterocycle. The endocyclic C−N bonds are shortened (1.293(7) Å), and the C−C bond in the ligand backbone is elongated (1.415(10) Å) with respect to related NHC’s. Furthermore, the Se−N bond lengths are consistent with Se−N single bonds (1.890(4) Å), rather than that of an intermediate single or double Se−N

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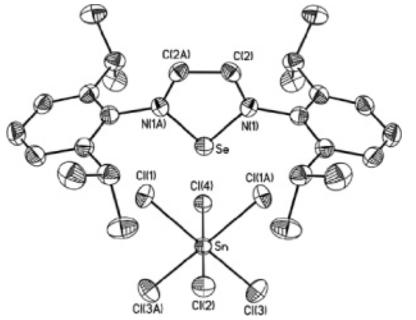

Figure 1. Solid-state structure of **[1][SnCl$_6$]**. Ellipsoids are drawn to 50% probability, hydrogen atoms and CH$_2$Cl$_2$ solvate are removed for clarity. Selected bond lengths (Å) and angles (deg): Se−N(1) 1.890(4), N(1)−C(2) 1.293(7), C(2)−C(2A) 1.415(10), Sn−Cl(1) 2.496(2), Sn−Cl(2) 2.393(2), Sn−Cl(3) 2.386(2), Sn−Cl(4) 2.415(2), Se···Cl(1) 2.742(2), N(1)−Se−N(1A) 81.8(3), Cl(2)−Sn−Cl(4) 173.8(1), Cl(1)−Sn−Cl(3A) 93.0(1), Cl(3)−Sn−Cl(4) 91.4(1), Cl(3)−Sn−Cl(1) 179.2(1), Cl(2)−Sn−Cl(1)87.6(1), Cl(4)−Sn−Cl(1) 88.0(1), Cl(2)−Sn−Cl(3) 93.0(1).

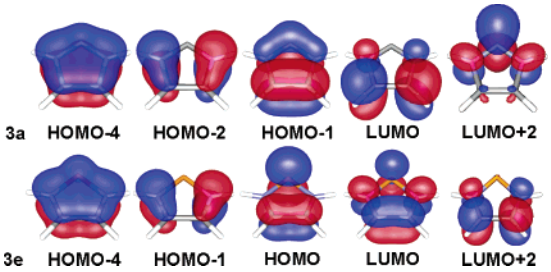

Figure 2. π-Symmetric frontier KS-orbitals of **3a** and **3e**.

bond, which is likely influenced by the close Se···Cl cation−anion contacts (2.742(2) Å).

To garner a more complete understanding of the electronic structure of the heterocyclic ring **[1][SnCl$_6$]**, we have performed a computational investigation of the title compound and for a model of the related p-block carbenoids (**3a**−**f**) (see Supporting Information). Results from the calculations for **[1^{2+}]** and **3a**−**f** revealed metrical parameters in good agreement with those determined experimentally (Table 1). The computational studies for **3e** indicate short endocyclic C−N and long C−C bonds relative to the parent NHC and related p-block carbenoids. A comparison of the frontier orbitals for the parent NHC and **[1^{2+}]** show little evidence for π-delocalization in the N−Se−N linkage in **[1^{2+}]** and are reminiscent of single bonds (Figure 2). Consequently, this imposes enhanced multiple-bond character in the endocyclic C−N linkage, while the endocyclic C−C bond is elongated. This phenomenon is even more apparent in the hypothetical brominenium trication (**3f**) where the endocyclic C−N and C−C bonds further shorten and elongate, respectively.

Given these data, **[1][SnCl$_6$]** may be considered as a Se^{2+} dication sequestered by a chelating diimine (**2**), rather than having undergone the intramolecular charge transfer as reported for the pnictogen (Pn) analogues (Pn = P, As).[2a,b] A sequestered Se^{2+} cation is reminiscent of the base stabilized, low oxidation state P(I) or As(I) cations.[5a,b] The reduction process for the synthesis of **[1][SnCl$_6$]** is related to that reported for the production of monocationic Se−N rings using neutral DAB ligands. However in this case, the Dipp$_2$DAB ligand remains resilient, giving a Se−N dicationic heterocycle, as opposed to the loss of one alkyl substituent in the ^{t}Bu analogue, which results in the formation of monocationic Se−N rings.[5c]

The bonding model in **2** is supported by the topological analysis of the electron localization function, which shows two monosynaptic basins for Se in **[1][SnCl$_6$]**, indicating that selenium carries two "lone pairs" of electrons instead of the expected one. This is corroborated by the results from atoms-in-molecules and MO analyses which show two local maxima in the Laplacian of the electron density around the Se nucleus and the presence of two σ-symmetric lone-pair-type MOs on the Se atom, respectively. However, an understanding of the true nature of the selenium "carbenoid" will require a combination of structure and reactivity studies. We are currently investigating the Lewis acid/base properties of **[1][SnCl$_6$]**, including its propensity to form complexes with transition metals.

In summary, we have identified a simple, quantitative, room-temperature synthesis of a dicationic N-heterocyclic selenium "carbenoid". This represents the first report of a chalcogenium dication mimicking the ubiquitous Arduengo-type carbene.

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Supporting Information Available: Experimental details for the synthesis and characterization of **[1][SnCl6]**, multinuclear NMR spectra, computational details; crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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