Carbene Analogues

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Ligand-Stabilized Chalcogen Dications**

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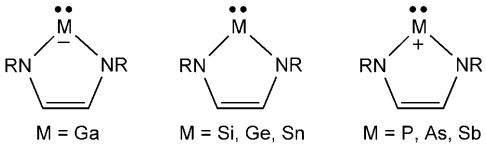
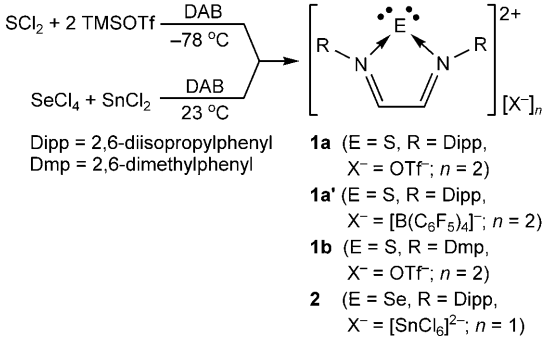
The report of the synthesis of the first stable, crystalline carbene by Arduengo et al. in 1991[1] stimulated a wide range of investigations into the chemistry of N-heterocyclic carbenes (NHCs) in organic transformations and their use as strong σ-donor ligands for transition metals.[2] The challenge of synthesizing the heavier Group 14 congeners[3] as well as the isoelectronic and isovalent analogues from Group 13 (monoanions)[4] and Group 15 (monocations)[5] has also been accomplished. With the possible exception of antimony (see below),[5c] the two-coordinate p-block elements formally accommodate one "lone pair" of electrons (Scheme 1).



Scheme 1. N-heterocyclic p-block carbenoids.

Until recently, Group 16 analogues of NHCs were not accessible. In view of their dicationic charge, the structure and bonding of these species, as well as their potential for unusual reactivity, are of particular interest. The characterization of such highly electrophilic systems is also timely considering the current interest in di- and polycations centered on p-block elements, for example, on B^{III},[6,7] Ge^{II},[8] and P^{V} ions.[9]

In two recent communications Ragogna and co-workers have reported the successful synthesis of stable salts of the dicationic sulfur and selenium analogues of the carbenoid systems represented in Scheme 1.[10,11] The common feature of the synthetic approach is the reaction of a chalcogen dihalide with a 1,4-diaza-1,3-butadiene (DAB). For the sulfur systems (**1a** and **1b**), SCl_2 is converted into the in situ reagent $S(OTf)_2$ (OTf = trifluoromethanesulfonate) by metathesis prior to reaction with the DAB ligand (Scheme 2).[11] The $[B(C_6F_5)]^-$ salt **1a′** is obtained from triflate **1a** by salt metathesis. In the case of the selenium analogue **2**, the thermally unstable



Scheme 2. Synthesis of chalcogen(II) diimine complexes.

reagent $SeCl_2$[12] is generated in situ from an equimolar mixture of $SeCl_4$ and $SnCl_2$ in THF.[10,13]

The salts are obtained in high yield as light orange (**1a, 1a′**, and **1b**) or dark orange (**2**) powders that can be dissolved in $CDCl_3$ or CD_3CN for NMR studies. Conspicuously, the ^{1}H NMR spectra of the chalcogenium dications exhibit highly deshielded resonances ($\delta = 10.2$–10.6 ppm) for the C_2N_2 backbone protons compared to the free ligand ($\delta =$ 8.13 ppm) as well as NHCs and their Group 13–15 analogues ($\delta = 6.91$–8.22 ppm).[3–5] This trend in the ^{1}H NMR chemical shifts presumably reflects an increasing influence of the ring current and, indirectly, the formal charge on the chalcogen atom. X-ray structural determinations of **1a**, **1a′**, **1b**, and **2** all confirm the presence of dicationic heterocycles. The triflate salts **1a** and **1b** both show sulfur···oxygen contacts between the cation and anion, while weak F···S contacts are evident in **1a′**. The structure of **2**, with two ionic Se···Cl contacts of 2.742(2) Å, is shown in Figure 1 as an example.

The endocyclic bond lengths in the essentially planar C_2N_2E rings are consistent with the retention of two C=N bonds and a C–C single bond in the DAB ligand (Table 1). The S–N bond lengths of 1.65–1.70 Å in **1a**, **1a′**, and **1b** are significantly shorter than the typical value of 1.76 Å for a single bond, whereas the Se–N bond length of 1.89 Å in **2** exceeds the value of a Se–N single bond by approximately 0.03 Å, thus reflecting the influence of the short Se···Cl contacts. The square-planar arrangement of the Se–N and Se···Cl contacts in **2** (Figure 1) indicates an AX_4E_2 system, with two lone pairs of electrons completing an octahedral environment around the central selenium atom.

Taken together, these structural parameters imply that these chalcogen–nitrogen heterocycles can be considered as ligand(diimine)-stabilized chalcogen dications in which there

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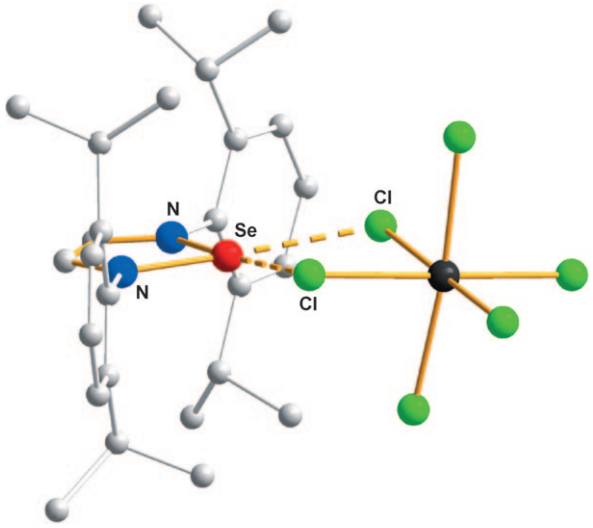

Figure 1. Crystal structure of **2**.

Table 1: Selected bond lengths (in Å) for **1a**, **1a′**, **1b**, and **2**.

	E–N	C–N	C–C
1a[a]	1.697(6)	1.308(9)	1.407(10)
1a′	1.655(3)	1.313(4)	1.396(7)
1b	1.695(3)	1.305(5)	1.390(8)
2	1.890(4)	1.293(7)	1.415(10)

[a] Mean values are reported for **1a**.

is a slightly stronger chalcogen–nitrogen interaction with sulfur than with selenium. In this context, it is noteworthy that treatment of elemental chalcogens with very strong oxidizing agents produces a variety of homocyclic chalcogen dications, for example, E_4^{2+} (E = S, Se), E_8^{2+} (E = S, Se), and Se_{10}^{2+}; however the highest formal oxidation state of the chalcogen is +0.5.[14] Other examples of structurally characterized dicationic sulfur or selenium species include a) a stable salt of an organosulfur(IV) dication[15] and b) the tetracoordinated species $[S(NPMe_3)_4]^{2+}$, which is described as a dication of hexavalent sulfur.[16]

The results of a comprehensive study by Tuononen et al. of the electronic structures of p-block element analogues of NHCs reinforce the conclusions derived from structural data.[17] As illustrated in Figure 2, a unique feature of the Group 16 systems is the presence of an orbital with π symmetry for the lone pair of electrons (highest occupied molecular orbital, HOMO) in addition to the orbital with σ symmetry (HOMO−2)—analogous to that observed for NHCs and their Group 13–15 analogues.[18] Consequently, the behavior of these chalcogen-centered rings as ligands is expected to differ from that of NHC analogues, which have only a single lone pair of electrons and act as strong two-electron σ donors; specifically, the Group 16 systems may act as four-electron (σ and π) donors towards transition metals.

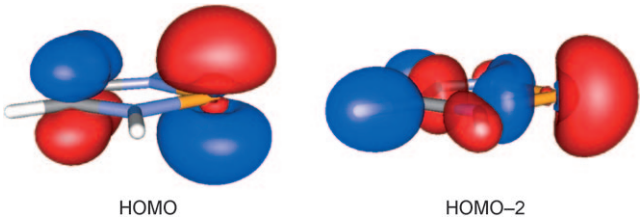

Figure 2. Frontier orbitals in $Se[(NH)_2(CH)_2]^{2+}$ showing the π- and σ-symmetric arrangement of the lone pairs of electrons at the selenium center (HOMO and HOMO−2, respectively).

As is often the case, estimates of the aromaticity in the $[C_2N_2E]^{2+}$ (E = S, Se) rings depend on the criteria used. Although a natural bonding orbital energy analysis showed the chalcogenium systems to have less π stabilization than the Group 13–15 analogues, both magnetic and molecular orbital analyses indicate features characteristic of aromaticity in the Group 16 heterocycles. The calculations also suggest that the likelihood of isolating a stable tellurium analogue of **1** and **2** is questionable in view of the weak bonding between the diimine ligand and the tellurium center as well as the large formal, and calculated, positive charge at the chalcogen center.[17]

The concept of stabilizing cations of electronegative p-block elements by a σ-donor ligand is well-established. A persuasive illustration of this idea is provided by the stabilization of the I^+ ion by nitrogen bases, for example, in bispyridine adducts $I(py)_2^+X^-$ ($X = ClO_4$, NO_3, RCO_2).[19] More recent examples entail the trapping of pnictogen cations E^+ (E = P, As) by *N,N′* or *P,P′* chelating ligands.[13a,b,20,21] An indication of the extraordinary reactions that may be possible with these trapped monoatomic electrophiles is furnished by the report from Driess et al. on the synthesis of the intriguing square-planar phosphonium cation $P[Zr(H)Cp_2]_4^+$, where the dicoordinate P-centred cation $[(Me_2N)_3P]_2P^+$ was used as a source of "P^+" in the reaction with $[Cp_2Zr(H)Cl]$.[22]

To date, the reactions of the novel chalcogenium dications in salts of type **1** and **2** have been limited to a preliminary report of the facile extrusion of the chalcogen from the heterocyclic ring by phosphines to give SPR_3.[11] In addition to their ligand properties (see above), reactions with organic substrates are likely to lead to novel organochalcogen chemistry compared to the well-established behavior of homocyclic chalcogen dications as electrophilic reagents. In addition to the revelations by Passmore and co-workers of the facile addition of these reagents to unsaturated substrates, for example, CF_3-substituted alkynes, to give novel radical cations,[23] homocyclic chalcogen dications are also powerful oxidants towards both aliphatic and aromatic hydrocarbons,[24] as well as of the methyl groups of acetonitrile.[25]

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