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Carbones

Syntheses, Structures, and Reactivities of Two Chalcogen-Stabilized Carbones**

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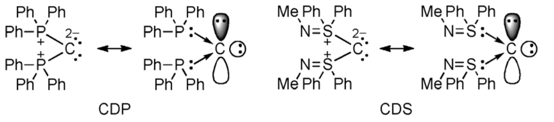
Abstract: *Electronic effects on the central carbon atom of carbone, generated by the replacement of the S^{IV} ligand of carbodisulfane (CDS) with other chalcogen ligands (Ph_2E, $E = S$ or Se), were investigated. The carbones $Ph_2E\rightarrow C\leftarrow SPh_2(NMe)$ [E = S(**1**) or Se(**2**)] were synthesized from the corresponding salts, and their molecular structures and electronic properties were characterized. The carbone **2** is the first carbone containing selenium as the coordinated atom. DFT calculations revealed the electronic structures of **1** and **2**, which have two lone pairs of electrons at the carbon center. The trend in HOMO energy levels, estimated by cyclic voltammetry measurements, for the carbones and CDS follows the order of **2** > **1** > CDS. Analysis of a doubly protonated dication and trication complex revealed that the central carbon atom of **2** behaves as a four-electron donor.*

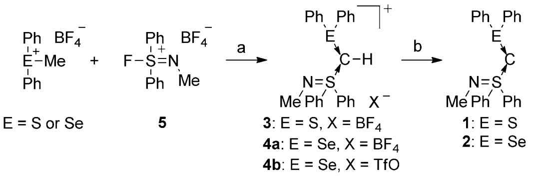
Recent insightful reports proposed that carbodiphosphoranes (CDPs) should be classified as a new class of carbone rather than as a heteroallene.[1] Carbones consist of two ligands (L) coordinated to a central zero-valent carbon atom, which maintains its four valence electrons as two orthogonal lone pairs, and therefore, is also described as carbon complex of the general type L→C←L (Scheme 1).[2]



Scheme 1. Bonding situation in CDP and CDS.

From this view, several examples of carbones have been studied in which one phosphine ligand of CDP is replaced by another ligand such as CN, CO, and carbenes. It has been suggested that reactivities of these carbones depend on the π-acceptor properties of the ligands.[1–3] In contrast, there are still few reports on carbones stabilized by a sulfur ligand.[4] In particular, carbone stabilized by two neutral S^{IV} ligands is restricted, so far, to one example which is defined as a carbodisulfane (CDS; Scheme 1).[5] Replacement of the S^{IV} ligand of CDS by other chalcogen ligands such as Ph_2E ($E = S$, Se) should lead to an increase in the reactivity of the central carbon atom. Herein we report the syntheses, structures, and reactivities of two chalcogen-stabilized carbones [$Ph_2E\rightarrow C\leftarrow SPh_2(NMe)$; E = S(**1**), Se(**2**)] so as to understand the electronic effects on the central carbon atom generated by the replacement of S^{IV} ligand of CDS with either a S^{II} or Se^{II} ligand. We also describe the comparison of these carbones to previously reported CDPs and CDS.

The carbones **1** and **2** were cleanly generated by the deprotonation of the corresponding cationic salts **3** and **4**, which were obtained by the reaction of fluorinated iminosulfonium salt **5**[6] with diphenyl sulfonium and diphenyl selenonium methylide, respectively, using sodium amide ($NaNH_2$) in THF (Scheme 2). They were successfully isolated as yellow crystals in almost quantitative yield. The ^{13}C NMR signals for the central carbon atoms of **1** and **2** appear at $\delta = 35.4$ and 34.4 ppm, respectively, which are shifted to a higher field as compared with that of a CDS carbon atom ($\delta = 38.9$ ppm).[5a,7] In the ^{77}Se NMR spectrum, the signal for **2** is shifted to a lower field ($\delta = 567.9$ ppm) as compared with that for **4a** ($\delta = 554.4$ ppm).



Scheme 2. Synthesis of **1**–**4**. Reagents and conditions (yields in parentheses): a) LDA, THF, −78 °C, then H_2O; **3** (55 %); **4a** (49 %); (**4b** was prepared by the treatment of **4a** with LiOTf); b) $NaNH_2$, THF, −78 °C to RT; **1** (97 %), **2** (97 %). LDA = lithium diisopropylamide, THF = tetrahydrofuran, Tf = trifluoromethanesulfonyl.

The molecular structures of **1**, **2**, **3**, and **4b** were determined by X-ray crystallography (Figure 1).[8] To the best of our knowledge, **2** is the first carbone containing a Se^{II} atom. The $S^{IV}\rightarrow C$ bonds of **1** and **2** (**1**: 1.648 Å, **2**: 1.654 Å) are longer than that in CDS (1.636 Å).[5a] The $E^{II}\rightarrow C$ bonds of **1** and **2** (**1**: 1.707 Å, **2**: 1.876 Å) are slightly longer than that in the salts **3** and **4b**, respectively (**3**: 1.672 Å, **4b**: 1.846 Å; $\Delta_{S\rightarrow C} = 0.035$ Å, $\Delta_{Se\rightarrow C} = 0.030$ Å). The latter observations are in contrast to the trend typically seen in carbones.[2,3,5a,9] Gen-

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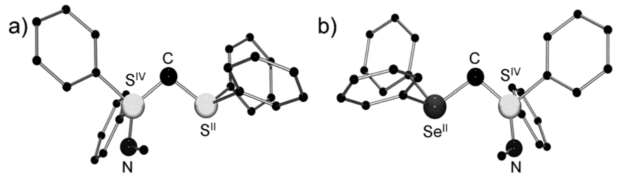


Figure 1. Molecular structures of a) **1** and b) **2**. Ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1**: $S^{II}\rightarrow C$ 1.707(2), $S^{IV}\rightarrow C$ 1.648(2); $S^{II}\rightarrow C\leftarrow S^{IV}$ 106.67(14). **2**: $Se^{II}\rightarrow C$: 1.876(3), $S^{IV}\rightarrow C$ 1.654(3); $Se^{II}\rightarrow C\leftarrow S^{IV}$ 105.48(17).

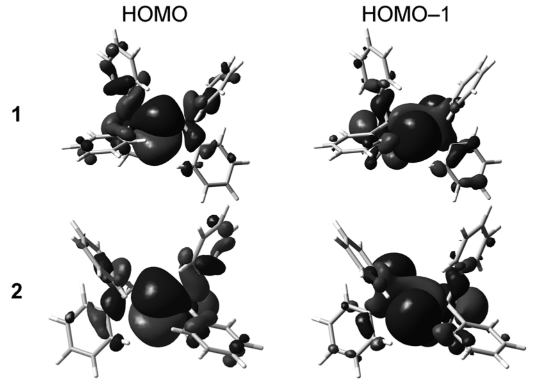


Figure 2. Shape of the two HOMO and HOMO−1 energy levels of **1** and **2**.

erally, the bond distance between the coordinated and central carbon atoms tends to become shorter upon deprotonation because a shorter distance allows the efficient stabilization of the electron pairs at the central carbon atom through an n–σ* interaction. In the case of **1** and **2**, the lone pair on the E^{II} atom favors the antiperiplanar relationship to the electron pairs at the central carbon atom to minimize electronic repulsion. Thus, the orbital overlap between the electron pairs on the central carbon atom and σ* orbitals on the E^{II} atom is significantly reduced. This arrangement explains the small elongation of $E^{II}\rightarrow C$ bond lengths compared to the shortening observed in other carbones upon deprotonation. The $E^{II}\rightarrow C\leftarrow S^{IV}$ fragments of **1** and **2** (**1**: 106.7°, **2**: 105.5°) are significantly bent as compared with those in the salts **3** and **4b**, respectively (**3**: 113.5°, **4b**: 113.8°; $\Delta_{S\rightarrow C\leftarrow S} = 6.8°$, $\Delta_{Se\rightarrow C\leftarrow S} = 8.3°$). In fact, the $Se^{II}\rightarrow C\leftarrow S^{IV}$ fragment is the most bent structure among the acyclic carbones, nearly matching that of a five-membered cyclic CDP (104.8°).[2–5,9,10] The angle tends to become acute upon deprotonation and is in contrast to the trend observed in CDPs, but is similar to the trend observed for CDS.[2–5,9,10]

To gain insight into the electronic structures of **1** and **2**, density functional calculations at the B3PW91/6-311G(d,p) level of theory were performed. The optimized structures closely match the experimental X-ray data (see Figures S1 and S2 in the Supporting Information). The Wiberg bond indices for the carbone $E^{II}\rightarrow C$ (**1**: 1.177, **2**: 1.163) are lower than those for $S^{IV}\rightarrow C$ (**1**: 1.240, **2**: 1.262). Molecular orbital analyses indicate that the central carbon atoms of **1** and **2** have two lone pair orbitals in the HOMO ($n\pi_C$) and HOMO−1 ($n\sigma_C$; Figure 2). Natural bond orbital (NBO) analyses indicate that the $n\sigma_C$ of **1** and **2** has a significantly enhanced *σ* character (**1**: 55%, **2**: 59%), thus indicating a hybridization close to sp, while the $n\pi_C$ lone pair of both carbones has 100% p character. The central carbon atoms of **1** and **2** bear large negative charges (**1**: −1.20 e, **2**: −1.25 e), similar to that of CDP (−1.43 e).[1]

Both carbon lone pairs of **1** are stabilized through interactions with $\sigma^*(S^{IV}–N)$, $\sigma^*(S^{II}–C_{Ph})$, and $\sigma^*(S^{IV}–C_{Ph})$, as determined by NBO second-order perturbation analysis. In particular, $n\pi_C$ interacts with $\sigma^*(S^{IV}–N$; 12.6 kcal mol^{-1}), $\sigma^*(S^{IV}–C_{Ph}$; 21.3 kcal mol^{-1}), and $\sigma^*(S^{II}–C_{Ph}$; 10.1 and 10.8 kcal mol^{-1}). Alternatively, $n\sigma_C$ interacts almost exclusively with $\sigma^*(S^{IV}–N$; 8.0 kcal mol^{-1}), thus indicating that $n\sigma_C$ is much less stabilized by an n–σ* interaction with adjacent substituents compared to $n\pi_C$. The total stabilization energy of n-σ^*S^{II} (20.9 kcal mol^{-1}) is decreased by approximately 40% from that of σ^*S^{IV} (48.4 kcal mol^{-1}), thus indicating that the decrease in valence of the coordinated atom decreases the n–σ* interaction. Thus, the electron-donor abilities of the carbon center can be increased.

The proton affinities (PA) of **1** and **2** were calculated to verify the carbone character. The first and second PA values, PA(1) and PA(2), respectively, are estimated [PA(1) for **1** is 288.0 kcal mol^{-1} and for **2** is 287.1 kcal mol^{-1}; PA(2) for **1** is 184.4 kcal mol^{-1} and for **2** is 187.0 kcal mol^{-1}]. The relatively large values of PA(2) for **1** and **2** clearly indicate carbone character.[1]

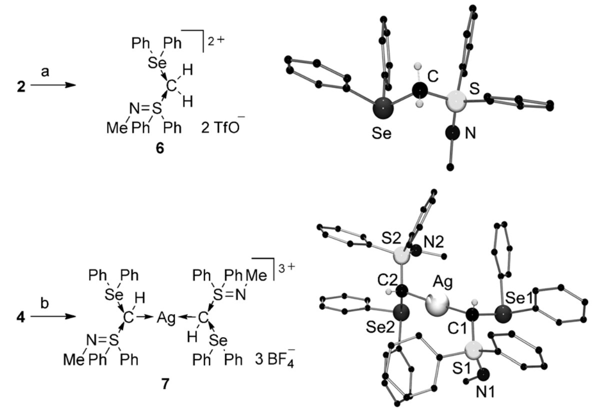
Donor properties of **1** and **2** are assessed by cyclic voltammetry experiments (see Table 1 and Figures S3–S5).[11] The carbones **1** and **2** exhibit an irreversible oxidation process, and the onset potential for oxidation (E^{onset}_{ox}) is observed at −0.73 and −0.92 V (vs. Fc/Fc$^+$), respectively. These values are more negative than that of CDS (−0.45 V). The HOMO energy levels of **1**, **2**, and CDS are estimated to be −4.07, −3.88, and −4.35 eV, respectively. These results demonstrate that the electron-donor ability of these chalcogen-stabilized carbones follows the order of **2** > **1** > CDS.

Table 1: Theoretical and experimental energy levels of the HOMO and HOMO−1, and proton affinities (PA) of **1**, **2**, and CDS.

	HOMO[a] [eV]	HOMO[b] [eV]	HOMO−1[b] [eV]	PA(1)[b] [kcal mol^{-1}]	PA(2)[b] [kcal mol^{-1}]
1	−4.07	−5.08	−5.32	288.0	184.4
2	−3.88	−5.09	−5.36	287.1	187.0
CDS	−4.35	−5.26	−5.56	278.8	182.2

[a] Experimental values. HOMO energy levels were calculated using the following equations:[14] HOMO = [E^{onset}_{ox} + 4.8] eV, where E^{onset}_{ox} is the onset of the first oxidation wave. [b] Theoretical values.

The most interesting feature is that the treatment of **2** with TfOH gave the corresponding dication **6** which is doubly protonated on the central carbon atom (Scheme 3). This double protonation clearly demonstrates the existence of two lone pairs at the carbon center of **2**. In the solid-state structure



Scheme 3. Synthesis and molecular structures of **6** and **7**. Ellipsoids are shown at 50% probability. Hydrogen atoms (except for those on C), triflate anions, and BF_4^- anions are omitted for clarity. Selected bond lengths [Å] and angles [°]: **6**: $Se^{II}\rightarrow C$ 1.967(2), $S^{IV}\rightarrow C$ 1.817(2), $Se^{II}\cdots O1$ 2.993, $Se^{II}\cdots O2$ 3.217; $Se^{II}\rightarrow C\leftarrow S^{IV}$ 105.76(12), **7**: C1→Ag 2.164(4), C2→Ag 2.177(4), Se1→C1 1.936(4), Se2→C2 1.948(5), S1→C1 1.771(5), S2→C2 1.772(5); C1→Ag←C2 172.72(17), Se1→C1←S1 103.8(2), Se2→C2←S2 104.5(2). Reagents and conditions: a) TfOH, MeOH, RT, quantitative; b) $AgBF_4$, CH_2Cl_2, RT, 62%.

of **6**, the $Se^{II}\rightarrow C$ and $S^{IV}\rightarrow C$ bond lengths ($Se^{II}\rightarrow C$: 1.967 Å, $S^{IV}\rightarrow C$: 1.817 Å) are longer than those in **2** and comparable to single bond lengths (Se-C: 1.97 Å, S-C: 1.81 Å).[15] The Se···O interacts with the triflate counterions within the sum of the van der Waals radii (2.993 Å and 3.217 Å; cf. 3.42 Å). In contrast, the ^{19}F NMR spectrum of **6** (−80.3 ppm) suggests a weak interaction between Se and O in solution. The ^{19}F NMR spectra of a covalent triflate, MeTfO ($\delta_F = -75.0$), and an ionic triflate, $[Noct_4][TfO]$ ($\delta_F = -79.0$), are easily distinguished.[16]

These findings prompted us to synthesize the silver complex **7**, which contains the cation **4** as a ligand (Scheme 3). The reaction of the cationic salt **4** and $AgBF_4$ in CH_2Cl_2 gave the trication complex **7**, which was isolated as colorless crystals. The trication **7** is the first example of four-electron donor ligand, such as carbone which is stabilized by two chalcogen atoms. The Ag→C bonds (2.164 Å and 2.177 Å) are shortened as compared with those in the CDP complex (Ag→C 2.209 Å and 2.221 Å).[1a,17] The C1→Ag←C2 angle of **7** is nearly linear (172.7°). The $Se^{II}\rightarrow C\leftarrow S^{IV}$ angles of **7** (103.8° and 104.5°) are more acute than those in **2** and **6**. In contrast, attempts at the double protonation of **1** or the C metalation of **3** were unsuccessful. These results indicate that the replacement of the S^{II} ligand with Se^{II} increases the electron-donor ability of the carbone at the carbon center.

In summary, we successfully synthesized the carbones **1** and **2**, which are stabilized by S^{II} or Se^{II} and S^{IV} ligands. Cyclic voltammetry measurements show that the HOMO energy levels follow the order of **2** > **1** > CDS. The carbone **2** affords the dication **6** and trication **7**, which provides the first experimental proof of carbodichalcogenurane acting as a four-electron donor ligand. These replacements should be considered as new methodologies for tuning the electron-donating ability of carbones at the central carbon atom. Additional reactivities of **1** and **2** with electrophiles and other transition-metal ions are currently under investigation.

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