Heavier analogues of silaacylium ions 2-4 ([m-TerSiE(NHCH2)2]Cl; m-Ter = 2,6-Mes3C6H3; Mes = 2,4,6-Mes3C6H2; 2 (E = S), 3 (E = Se), 4 (E = Te)) were synthesized by reaction of NHC-stabilized sililylumylidene cation 1 with elemental chalcogens. Fascinating regeneration of 1 from the reaction of 2-4 with AuI was achieved, as successful recovery of a parent Si(II) species from a sila­cyclic Si(IV) compound. Furthermore, unique chalcogen exchange reactions from 4 → 3 → 2 were observed in line with the calculated silicon-chalcogen bond energies.

The Friedel-Craft reaction proved to be indispensable in order to introduce carbonyl functionality in organic backbones. This reaction proceeds through intermediacy of electrophilic acylium cation [RCO]+ (Chart 1a), generated via situ treatment of acyl halides with Lewis acids such as BF3, MF3 (M = P, As, Sb), AlCl3 or ZnCl2. In contrast, examples of respective heavier analogues of acylium cations ([ArCE]+; E = S, Se, Te) are still very sparse, probably due to the limited variety of synthetic methods and the lack of suitable precursors. Theoretical calculations have drawn insight into the highly reactive nature of heavier acyl halides ([XYC=E]; E = Se, Te; X,Y = H, F, Cl, Br and I) by the virtue of small HOMO–LUMO gap. In this context, it is noteworthy to mention that until now only few thio­aroyl cations, ([PhCS][SbF6]3)3b,3c and ([MesCS][C6F5]2B)3a were synthesized either by reacting thio­benzoyl chloride with Ag5B6 or by borinium ion-mediated C–S double bond cleavage of CS2. X-ray crystallographic and DFT studies were carried out to shed light on the different resonance structures of thio­aroyl cations (Chart 1b).3a However, to the best of our knowledge, respective selenium and tellurium analogues still remain inaccessible. Akin to carbon compounds, silicon analogue of these species ([ArSi=E]+; E = S, Se, Te), namely heavier sila­cyclic ions (Chart 1d), are also considered as reactive species and still unprecedented. This is presumably due to the lack of precursor silacylhalides (for example, Ar(X)Si=E; X = F, Cl, Br, I; E = S, Se, Te) along with the large electronegativity difference, weak π-bonding nature and a longer bond length between silicon and heavier chalcogens. Consequently, isolation of such compounds is still challenging.

Recently, we reported the isolation of NHC-stabilized sila­cyclic ions I (Chart 1c) [(RSi(O)(NHCH2)2)Cl; R′ = m-Ter, Tipp; m-Ter = 2,6-Mes3C6H3; Mes = 2,4,6-Mes3C6H2, Tipp = 2,4,6-iPr3-C6H2, NHC = 1,2,3,4-tetramethylimidazol-2-ylidene), by utilizing a bulky terphenyl and tipp group as steric protector and two NHs as external donors.6 In comparison to neutral compounds7, there are only two instances of cationic [RSi=S]+ compounds (II and III) reported in literature (Chart 1d).8 Despite the isolation of oxygen and sulfur analogues of sila­cyclic ions, cationic [RSi=Se]+ and [RSi=Te]+ compounds have not been reported yet, albeit the electronic states and the spectroscopic
properties have been theoretically investigated. Apart from academic and/or experimental interests heavier silicon-chalcogenides showed considerable promise towards silicon-based device fabrications: for instance, the use of SiTe in thermoelectric materials, SiTe$_2$, Si$_2$Te$_3$ in optoelectronics materials, or Si$_2$S and Si$_2$Se as electrocatalytic materials for counter electrodes (CE) in dye-sensitized solar cells (DSSCs). With this incentive, we report the isolation of NHCl-stabilized heavier analogues of silaacylium ions, containing Si=S (2), Si=Se (3) and Si=Te (4) bonds by the reaction of elemental chalcogen with the NHCl-stabilized silyliumlydene (Scheme 1). All compounds were characterized via X-ray crystallography, multinuclear NMR, IR and UV-Vis spectroscopy. Further detailed DFT calculations were carried out to shed light on the electronic and bonding nature of those compounds. Additionally, an alternative pathway to compound 2 is presented by the reaction of carbon disulfide with 1 via facile C=S bond cleavage. With respect to reactivity studies, we showed fascinating regeneration of 1 by treatment of [ArSiE]$^+$ (2, 3 and 4) with Aul and further chalcogen exchange reactions between 2, 3 and 4 (Scheme 2), in good agreement with the bond dissociation energy (BDE) data (Table 1) of the corresponding Si–E bond.

![Scheme 1 Synthesis of compound 2-4 with their possible representation: (A) Two NHCl stabilized heavier silaacylium ion and (B) Zwitterionic form of heavier silaacylium ion, and regeneration of NHCl-stabilized silyliumlydene 1 (R = m-Ter; m-Ter = 2,6-Mes$_2$C$_6$H$_4$; Mes = 2,4,6-Mes$_2$C$_6$H$_4$).](image)

Silyliumlydene ions [RSi]$^+$ bear an unique electronic nature, the central silicon atom possesses a lone pair electron pair as well as vacant p-orbital with a positive charge. Motivated by this electronic feature and our previous report, we thought that silyliumlydene ions would be excellent precursors for the preparation of hitherto unknown silaacylium ions by the reaction with chalcogen atoms. Therefore, we treated 1 with elemental chalcogen in acetonitrile at −78 °C, which resulted in the formation of compounds 2, 3 and 4, with a yield of 85%, 56% and 87% respectively (Scheme 1). All three compounds are stable under inert atmosphere and show high solubility in polar aprotic solvents such as acetonitrile and dichloromethane, but are poorly soluble both in aromatic, aliphatic hydrocarbon and etheral solvents.

Oxidative addition and reductive elimination under regeneration of parent molecules are essential steps in effective catalytic cycles. In this context, recovering a Si(II) compound from its relatively stable Si(IV) complex under mild conditions is considerably challenging. Although there are some reports on the reactivity of compounds containing Si=E bond toward small molecules or alkenes, no interconversion between a Si(II) species and its multiple bonded silachalcogen Si(IV) analogue have been found so far. Even the examples of reversible chalcogen-atom transfer to main group as well as transition metal and actinide complexes are limited. With this in mind, we treated 2-4 with conventional chalcogen scavenger PPPh$_3$$_2$ and P but no chalcogen transfer occurred, probably due to steric reasons. When we treated 2-4 with coinage metal halides, we observed the regeneration of parent silyliumlydene 1 in the case of Aui (Scheme 1). For AgI, we could only regenerate 1 from 2 and 3, which is distinctly different from the reactivity of thio- and selenogermanones [LPhGe=E, E = S, Se], (L = (t-Bu)ATIGePh; ATI = aminotroponimininate) towards AgI. Unfortunately, no reactivity was observed with Cul. The reaction is presumably driven by coordination of the chalcogen to the soft Au and Ag centre through precipitation of free metal and metal-chalcogenide, however, the reaction mechanism is still unclear.

X-ray analysis revealed that all three cations have a central silicon atom that is tetracoordinated by two NHClS and bounded to one m-terphenyl group and the corresponding chalcogen atom (Fig. 1). The Si–Cl distances in 2, 3 and 4 are well above 5 Å, suggesting no direct contact between the silicon and the chlorine atom. In compound 2 (see SI), the Si=S lengths are 2.013(1) Å and 2.018(1) Å for the two independent molecules, which is shorter than the cationic Si–S single bond (2.160 Å) in [(IPrNC(N$_2$)Ni)$_2$SiPh]$_2$PhS$_2$ and nearly close to NHCl or donor stabilized neutral or cationic Si=S bonds reported before (1.96 – 2.00 Å). In compound 3 (Fig. 1a) the Si=Se bond lengths are 2.1516(9) Å and 2.1571(8) Å, which are similar to Lewis base stabilized tetro-coordinated Si=Se double bonded compounds (2.13 to 2.16 Å), but significantly shorter than the cationic Si–Se single bond length (2.308 Å) in [(IPrNC(N$_2$)Ni)$_2$SiPh]$_2$PHSe$_2$. Similarly, the Si=Te bond length of 4 (Fig. 1b) is 2.3941(6) Å and falls in the range of other neutral tetro-coordinated Si=Te compounds (2.38 to 2.39 Å).

![Fig. 1 Molecular structure of a) 3 (only one independent molecule shown) and b) 4. Hydrogen atoms and chloride counterion are omitted for clarity. Ellipsoids are shown at the 50% probability level.](image)

$^{28}$Si NMR spectra of compound 2, 3 and 4 exhibit sharp signals at δ = −36.0 ppm, δ = −41.4 ppm and δ = −72.2 ppm, respectively, which are in good agreement with the calculated data (Table 1, 2 δ = −35.7 ppm, 3 δ = −43.2 ppm and 4 δ = −70.4 ppm) and are close to recently reported heavy silaaldehydes [Ter*(HSiE)NHC$_{Me}$, Ter* = 2,6-Bis(2,4,6-triisopropyphenyl)phenyl]. Compound 2 depicts a significantly upfield shift in comparison to tetro-coordinated cationic silaethonium compounds II (δ = −14.09 ppm) and III (δ = −26.7 ppm) (Chart 1d).
In order to understand the bonding nature of all three compounds, IR spectroscopy has been carried out. In the solid state, the IR spectrum of 2 displayed a strong Si=S absorption band at 645 cm\(^{-1}\), whereas for compounds 3 and 4, strong absorption bands were observed at 524 cm\(^{-1}\) and 475 cm\(^{-1}\) assignable to Si=Se and Si=Te bond, respectively.

Table 1. Calculated values for 2, 3, 4 (a) Bond Dissociation Energy (BDE) in kcal/mol, (b) Natural Population Analysis (NPA) (L1, Si, L2, E), (c) Wiberg Bond Index (WBI), (d) Mayer Bond Order (MBO), (e) IR Stretching in cm\(^{-1}\) and (f) Calculated GIAD \(\delta_3\) NMR shift in ppm of the Si=E bond, E = S, Se, Te.

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<th>BDE((29))</th>
<th>NPA((29))</th>
<th>NPA((29))</th>
<th>WBI((29))</th>
<th>MBO((29))</th>
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<td>-0.47</td>
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</table>

The experimental IR data fits quite well with the calculated values [Calculated B87-D/6-31G(d)[Se,Te:cc-pV2Z-PP] level of theory, \(\tilde{\nu}_{\text{Si=S}} = 643 \text{ cm}^{-1}\), \(\tilde{\nu}_{\text{Si=Se}} = 525 \text{ cm}^{-1}\), \(\tilde{\nu}_{\text{Si=Te}} = 474 \text{ cm}^{-1}\)] and reveals red shifts in comparison to NHC coordinated sila-chalcogen compounds \(\tilde{\nu}_{\text{Si=S}} = 665-683 \text{ cm}^{-1}\), \(\tilde{\nu}_{\text{Si=Se}} = 578-614 \text{ cm}^{-1}\), \(\tilde{\nu}_{\text{Si=Te}} = 595 \text{ cm}^{-1}\).\(^{7,8,19}\) Still, all three absorption bands are large enough to distinguish them from a silicon-chalcogen single bond [for example (MeH\_3)\_2E, \(\tilde{\nu}_{\text{Si=S}} = 461 \text{ cm}^{-1}\), \(\tilde{\nu}_{\text{Si=Se}} = 380 \text{ cm}^{-1}\), \(\tilde{\nu}_{\text{Si=Te}} = 328 \text{ cm}^{-1}\)].\(^{19}\) To get deeper insight into the electronic structure of silicon-chalcogen bonds, we performed DFT calculations employing B97-D/6-31G(d)[Se,Te:cc-pV2Z-PP] level of theory. The HOMO of these compounds (Fig. S19-21) shows mainly the lone pair of chalcogen with some extension to the silicon center which can be considered as an asymmetric \(\pi\) orbital. The LUMO of the compounds is dispersed over the NHC skeletons and is related to the NHC \(\pi\)-system (Fig. S19-21). In addition, the calculated Mayer Bond Order (MBO) of these molecules indicate some multiple-bond character of the Si=E bond (MBO, 2 = 1.64, 3 = 1.36, 4 = 1.26). Equally, Wiberg bond indices (WBI) also support partial Si=E multiple bonding nature (WBI, 2 = 1.40, 3 = 1.41, 4 = 1.39), which is larger than silyl chalcogenide anion [H\(_3\)Si=E\(^-\)], disilyl chalcogenide [H\(_2\)Si=E-SiH\(_3\)] (Table S4-6), NHC stabilized heavy aldehydes ([NHCM\(_{44}\)]=[H\(_3\)Si=E\(^-\)] and ([NHCM\(_{44}\)]=[LHSi=E\(^-\)])\(^{7,8}\) and similar to bis-NHC stabilized terminal Si(V) chalcogenides.\(^{7,8}\) Interestingly, the calculated symmetric valence IR vibrational frequency of reference structures [H\(_2\)Si=E\(^-\)] and [H\(_3\)Si=E-SiH\(_3\)] show much lower values compared to compounds 2-4, while the doubly bonded reference structures [H\(_2\)Si=E\(^-\)] possess only slightly larger IR values. This can also indicate that the double bond resonance structure has considerable contribution to the description of the bonding situation of 2-4. We note that the short bond distance can be partially explained by strong hyperconjugative effects between the lone pair of the chalcogen atoms and the \(\pi^*\)(Si=C) bonds, similar interactions have been found as important factor in other silachalcogenides.\(^{7,8}\) In terms of NBO analysis, the Si atom of these compound possesses a large positive net charge, while the E atom bears a negative charge (see Table 1). This indicates a polarization of the Si=E bond which is responsible for the betaine representation of 2-4 (Scheme 1). Overall, theoretical results lead us to the conclusion to draw both possible resonance structure A and B, for compound 2-4 in Scheme 1, although B may be more relevant.

We performed chalcogen exchange reactions, which display the first example of Si=E scrambling (Scheme 2). Reaction of compound 4 with equimolar amounts of elemental sulfur fully led to compound 2 at room temperature within 8 h. However, the conversion from 4 to 3 with equimolar amounts of elemental Se took prolonged time, 15 days and elevated temperatures to reach an optimized yield of 45%. Similarly, reaction of 3 with sulfur gave 2 in 35% yield after 22 days.

![Scheme 2. Chalcogen Exchange Reactions of 2-4 with Reaction Energies.](image)

Interestingly, no reaction was observed upon treating 3 with same equivalents of tellurium. Likewise, reaction of compound 2 with Se and Te did not form 3 or 4 even after extended reaction time. Here, only unidentified products were observed at elevated temperatures. We calculated the reaction energy of the exchange reactions (Scheme 2, see details in SI) which explain the experimental findings. The exchange reaction energy between 4 and 3 is \(-9.0\) kcal/mol which indicates why only Se to Te exchange can occur. Similarly, the one-way exchange reaction between 3 and 2 is rationalized with the reaction energy of \(-25.0\) kcal/mol. The largest calculated exchange reaction energy is between 4 and 2 (\(-34.0\) kcal/mol) in line with the observed fast and clean exchange reaction. This overall reactivity pattern also follows the Si=E bond strength (BDE, Table 1). The formation of the strong Si=S bond is the driving force of the reaction with S\(_8\) whereas relative stability of Si=Se bond over Si=Te bond may be responsible for the observed one-way Te=Se exchange reaction.

**Conclusions**

In conclusion, we present a simple approach for the synthesis of NHC-stabilized heavier silacyleum ions 2-4 starting from the corresponding NHC-stabilized silylumylidene 1. These complexes are rare examples of cationic silicon compounds with a terminal silicon-chalcogen bond. In addition, we achieved the regeneration of 1, from 2-4 by the treatment with AuI, which represents an unique regeneration of a Si(II) cation from a Si(IV) sila-chalcogen compound. Moreover, intriguing chalcogen exchange reactions were observed, in good agreement with the calculated Si=E bond dissociation energy. Further reactivity of compound 2-4 are currently under investigation in our lab.
Conflicts of interest
There are no conflicts to declare.

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Notes and references