

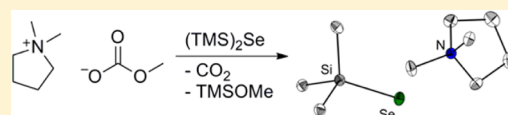
Synthesis of Organic (Trimethylsilyl)chalcogenolate Salts Cat[TMS-E] (E = S, Se, Te): the Methylcarbonate Anion as a Desilylating Agent[†]

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Supporting Information

ABSTRACT: A high-yield synthesis of the class of (trimethylsilyl)-chalcogenolate organic salts [Cat][TMS-E] (E = S, Se, Te; Cat = BMPyr, DMPyr, NMe₄, nBu₃MeP) is presented. The title compounds have been prepared by the strictly aprotic reaction between the respective bis-(trimethylsilyl)chalcogenide (TMS₂E) and methylcarbonate ionic liquids (ILs). This constitutes a novel reaction behavior of methylcarbonate ILs, acting as a nucleophilic desilylating agent and a Lewis base instead of as a Brønsted base. Thus prepared silylchalcogenolate salts represent an activated form of the multifunctional TMS₂E reactant series. Pyrrolidinium TMS-S salts have proven to be excellent precursors for the synthesis of pyrrolidinium hexasulfides. The scope of the desilylation reaction can be extended to other silyl-bearing synthons such as (trimethylsilyl)azide and (trimethylsilyl)cyanide.

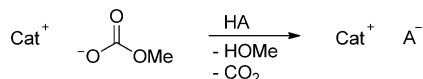


INTRODUCTION

Organic methylcarbonate salts¹ offer by far the most attractive route for a strictly water- and halide-free production of ionic liquids (ILs). While other halide-free procedures often include toxic reagents, involve highly reactive and unstable intermediates, or demand laborious workup,² the *green* reagent dimethylcarbonate is easily available and nontoxic.³ The preparation of methylcarbonate salts can start from a wide range of nucleophiles and is high yielding and reliable. This particular atom-efficient variant is, however, limited to at least one methyl substituent at the cation, resulting from methylation of the nucleophilic cation precursor with dimethylcarbonate. Subsequently, the methylcarbonate salts can easily be transformed into a variety of further ILs by reaction with Brønsted acidic reagents. Methanol and carbon dioxide (CO₂) are the volatile and only side products of this transformation. So far, this method was limited to Brønsted acidic reaction partners. A comparatively low acidity (e.g., NH₄⁺ ions) is sufficient though. That means that even a pK_a value higher than the one of methylcarbonic acid (5.61⁴) will allow the equilibrium to shift to the product side because of irreversible decay to methanol and CO₂.^{1d,5}

It turned out that methylcarbonate ILs can also act as mild and selective desilylating agents (Scheme 1). On the one hand, this significantly extends the applicability of methylcarbonate ILs; on the other hand, an easy to prepare, strictly aprotic, and long-term stable desilylating agent becomes available. Com-

Scheme 1. Reaction of Methylcarbonate ILs with Brønsted Acids (pK_a ≤ 5.61)



parable aprotic desilylating agents are, e.g., alkali alkoxides or tetraalkylammonium fluorides like TMAF⁶ and TBAF.⁷ While TBAF is not storable in a pure form because of E2-type elimination and decomposition reactions and has to be freshly prepared, TMAF and most alkali alkoxides suffer from a decreased solubility. Because of the extreme nucleophilicity and basicity of the weakly solvated fluoride ion, side reactions are likely and the toxicity of the fluoride ion may not be neglected. Furthermore, fluoride anions only tolerate very few organic cations in a solvate-free form, thereby limiting the variability of the reagent. In contrast, for methylcarbonate salts, a huge variety of cations are possible, which allows adjustment of the solubility.

Our present investigations primarily focused on the synthesis of silylchalcogenolate salts, which present more stable and completely aprotic alternatives to the corresponding hydrochalcogenide salts⁸ and may serve as an activated form of the charge-neutral bis(trimethylsilyl)chalcogenides (TMS₂E). These are versatile reagents that are employed most notably as starting materials for transition-metal chalcogenide clusters,⁹ chalcogenide semiconductors, and quantum dots¹⁰ and in a range of organic syntheses.¹¹ The only published example of an uncoordinated (trimethylsilyl)thiolate anion was prepared by reacting TMS₂S with TMAF.¹² Alkali-metal salts of (trimethylsilyl)chalcogenolate anions have been accessed, e.g., by reductive cleavage of the TMS₂E precursors with sodium in liquid ammonia¹³ or nBuLi in tetrahydrofuran (THF).¹⁴ However, the application of methylcarbonate salts as desilylating agents can also be transferred to other silylated compounds, which will be exemplified in the last paragraph.

Received: July 23, 2015

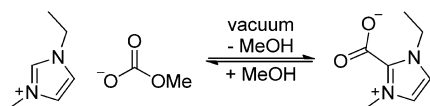
Published: September 15, 2015

RESULTS

The preparation of organic methylcarbonate salts is usually performed in a methanol solution. For imidazolium salts, the presence of methanol has proven vital in order to prevent side and follow-up reactions,^{1a,c} which lead to a series of imidazolium carboxylate zwitterions.¹⁵ We noticed that also the synthesis of ammonium and phosphonium methylcarbonate ILs appears to proceed more smoothly in the presence of methanol and conducted all syntheses of methylcarbonate ILs in methanol under solvothermal conditions at 130 °C. In order to employ the substances under strictly aprotic conditions in the following reactions, all methylcarbonate salts were thoroughly dried in fine vacuum and recrystallized from a mixture of acetonitrile and diethyl ether. The products form hygroscopic colorless solids, which can be stored indefinitely if they are kept under an inert atmosphere. Only tributylmethylphosphonium methylcarbonate was isolated as a slightly yellow, very viscous oil.

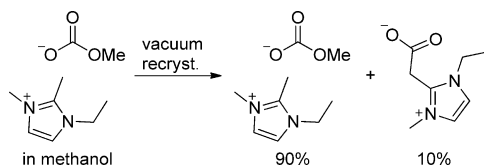
This work-up is, however, not transferable to imidazolium cations because the methanol-free methylcarbonates are not accessible. The reaction, which leads to the imidazolium 2-carboxylates, does not solely occur at elevated temperatures, but equilibrium between imidazolium methylcarbonate and imidazolium-2-carboxylate plus methanol is already observed at ambient temperature (Scheme 2).

Scheme 2. Equilibrium between [EMIm]-methylcarbonate and 1-Ethyl-2-methylimidazolium 2-Carboxylate at Ambient Temperature



Removing methanol from an imidazolium methylcarbonate solution in vacuum results in formation of the corresponding carboxylate; upon the addition of methanol, the methylcarbonate salt is regenerated. When attempting to employ a C2-methylated imidazolium ion in order to prevent this reaction, we found that the equivalent phenomenon can also be observed for these systems, although to a lesser extent. Apparently the methyl group is deprotonated, leading to a ketene-*N,N*-diacetal or *N*-heterocyclic olefin (NHO) intermediate,^{2g,16} which attacks the forming CO₂, resulting in a CH₂-spaced zwitterion (Scheme 3). This is formed as a nonremovable impurity

Scheme 3. Formation of an NHO–CO₂ Adduct upon Drying of 1-Ethyl-2,3-dimethylimidazolium Methylcarbonate

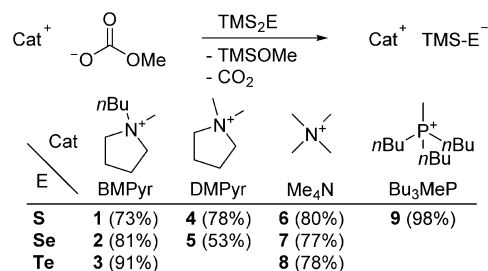


between 5 and 10% (according to ¹H NMR spectroscopy). Details concerning the synthesis, characterization, and reactivity of the respective imidazolium carboxylates will be published in due course.

However, the methanol-free ammonium and phosphonium methylcarbonates were used in subsequent reactions with a series of bis(trimethylsilyl)chalcogenides (TMS₂E; E = S, Se,

Te), yielding the almost unstudied class of organic TMS-E salts (Scheme 4). So far, the only known example, [NMe₄][TMS-S⁻], was prepared and characterized by Nieboer et al.¹²

Scheme 4. Synthesis of (Trimethylsilyl)chalcogenolate Organic Salts 1–9^a



^aYields in parentheses (mol %) refer to the methylcarbonate precursor as the limiting reagent.

Slowly adding the TMS₂E reagent to a cooled solution of the methylcarbonate precursor in acetonitrile and warming the mixture to ambient temperature to complete the reaction yields the respective (trimethylsilyl)chalcogenolate salts in a very simple procedure. The initially formed methyl(trimethylsilyl) carbonate is unstable at ambient temperature and decomposes to CO₂ and methyl(trimethylsilyl) ether. The substances are isolated in overall good yield by either removal of all volatile components and recrystallization or direct precipitation of the product from the reaction mixture by the addition of diethyl ether and cooling to –25 °C. All substances are highly sensitive toward moisture, which decomposes the salts in a matter of seconds. The silylselenolate and silyltelluroolate compounds are, furthermore, very liable to oxidation, forming intense green (selenium) or violet (tellurium) polychalcogenides.

All ammonium salts were isolated as colorless solids and investigated with respect to their melting points. None of them showed a true melting point; instead, all substances slowly decomposed during melting. As anticipated, the respective decomposition temperatures generally increase in the series BMPyr < DMPyr < NMe₄. However, no distinctive trend could be observed concerning the series of TMS-E anions. For example, TMS-S⁻ and TMS-Se⁻ show almost identical decomposition temperatures in combination with the DMPyr cation (*T*_{dec} = 167 and 168 °C, respectively); with the BMPyr cation, the TMS-Se⁻ salt is apparently more stable (TMS-S⁻, *T*_{dec} = 121 °C; TMS-Se⁻, *T*_{dec} = 128 °C). In combination with the tetramethylammonium cation, all salts show a remarkable stability, decomposing at 184 °C. Decomposition of the NMe₄ salts is accompanied by an instantaneous vaporization. Trimethylamine and methyl(trimethylsilyl)sulfide were found as the major components after condensation of the volatile decomposition products. The phosphonium salt 9, which was isolated as a slightly yellow oil, substantiates that, with careful choice of the cation, also room temperature ILs are accessible.

Thus prepared (trimethylsilyl)chalcogenolate salts were investigated in detail utilizing ¹H, ¹³C, and heteronuclear NMR spectroscopy. Table 1 summarizes the NMR data for the bis(trimethylsilyl)chalcogenides and (trimethylsilyl)chalcogenolate anions (Cat = [BMPyr]).¹⁷ As anticipated, the ⁷⁷Se and ¹²⁵Te NMR spectra of the (trimethylsilyl)chalcogenolate anions show strongly high-field-shifted resonance signals compared to the neutral TMS₂E starting

Table 1. NMR Data for the [TMS-E] Anions (Cat = [BMPyr]) and the Neutral TMS₂E Precursors

substance	δ_{H}	δ_{C}	δ_{Si}	$\delta_{\text{Se/Te}}$	$^1J_{\text{Si-E}}$
TMS ₂ S ^a	0.29	4.3	15.0		
TMS-S ^{-b}	-0.07	8.9	-0.7		
TMS ₂ Se ^a	0.37	4.7	10.8	-330.8	108
TMS-Se ^{-b}	0.09	9.2	-4.7	-417.5	175
TMS ₂ Te ^a	0.50	5.7	-5.7	-858.5	277
TMS-Te ^{-b}	0.32	10.1	-27.0	-1142.0	468

^aIn C₆D₆, ^bIn DMSO-*d*₆. δ values are in ppm and *J* values in Hz.

materials. An analogous trend can be observed in the respective ²⁹Si NMR spectra. Furthermore, the signals in the silicon NMR spectra are shifted to high field upon going from sulfur to tellurium for the neutral as well as anionic molecules. The local effects resulting from a decrease in the electronegativity of the chalcogenide substituent apparently dominate the shielding. The ¹J_{Si-E} coupling constants increase significantly upon going from the neutral precursor to the silylchalcogenolate anion. All values are in good agreement with literature values of the bis(trimethylsilyl)chalcogenides and alkali-metal salts of oligosilylchalcogenolates.¹⁸ The ¹H and ¹³C NMR shifts of the TMS moieties show an opposing trend, being shifted to lower field with increasing atomic number of the chalcogen. This is also observed for the respective lithium salts,¹⁴ the copper and zinc TMS-E complexes,¹⁹ and the isoelectronic series of (trimethylsilyl)halides.²⁰ So far, no definite explanation for this antipodal trend has been provided. While Harris and Kimber²⁰ and Drake et al.²¹ conclude that anisotropic and more intricate factors than plain inductive substituent effects may be responsible, Tran and Corrigan,^{19a} in contrast, trace the phenomenon back to inductive effects. We strongly agree with the former approach because the trend concerning the chemical shift of the ¹³C resonance is reversed in the series of bis(dihydromethylsilyl)chalcogenides (H₂MeSi)₂E.²¹

The IR spectra of all (trimethylsilyl)chalcogenolate salts are dominated by several distinct bands in the range from 400 to 1500 cm⁻¹, with the band at \approx 820 cm⁻¹ in all cases being the most intense. The Si-S stretching vibration of the TMS-S anion is the only silicon chalcogen vibration within the range of the recorded mid-IR spectra, leading to a band at 500–507 cm⁻¹. By comparison with the spectra of (trimethylsilyl)halides, the bands at ca. 630, 670, 740, and 820 cm⁻¹ can be assigned to Si-C stretching vibrations.²² According to the intensive theoretical studies, the latter three are overlapped with CH₃ rocking vibrations. In contrast to the (trimethylsilyl)halide spectra, where no distinctive alteration in these vibration frequencies is observed, they are shifted to higher wavenumbers with increasing atomic number of the chalcogen substituent. The band at \approx 630 cm⁻¹ shows the opposite trend, appearing at 633–637 cm⁻¹ for TMS-S⁻ salts, at 621–632 cm⁻¹ for TMS-Se⁻, and at 616–625 cm⁻¹ for the TMS-Te⁻ anions. Whether these trends are to be explained by a substituent effect on the reduced mass or can be traced back to an alteration in the Si-C bond strength, which might correlate with the ¹³C and ¹H NMR shifts of the methyl groups, is not yet elucidated.

In addition, the (trimethylsilyl)chalcogenolate salts [DMPyr][TMS-Se] (**5**) and [NMe₄][TMS-S] (**6**) could be structurally characterized by single-crystal X-ray diffraction (XRD), proving the ionic structure in the solid state. **5** (Figure 1) crystallized in the monoclinic space group *P*₂₁/*c* and features two ion pairs in the asymmetric unit. The Si-Se bond lengths

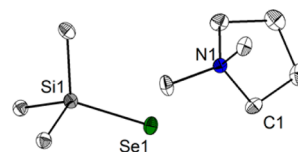


Figure 1. Molecular structure of **5**. Hydrogen atoms were omitted for clarity; only one of two independent ion pairs in the unit cell is displayed. $d(\text{Se1-Si1}) = 2.220(1)$ Å and $d(\text{Se2-Si2}) = 2.216(1)$ Å.

are 2.220(1) and 2.216(1) Å and thereby well in the range of Si-Se distances found in copper phosphine TMS-Se complexes^{19a} but significantly shorter than those in zinc complexes bearing a TMS-Se ligand.^{19b}

6 (Figure 2) crystallized in the monoclinic space group *P*₂₁/*m* with one molecule of acetonitrile as the crystal solvate. The

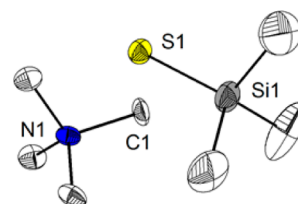


Figure 2. Molecular structure of **6**. Hydrogen atoms and one molecule of acetonitrile solvate were omitted for clarity. $d(\text{S1-Si1}) = 2.052(1)$ Å.

asymmetric unit contains half an ion pair and half a molecule of acetonitrile. The structure was treated as a nonmerohedral twin, whose components were freely refined to a ratio of 49% to 51%. The S-Si bond length [2.052(1) Å] is significantly shorter than that in the neutral parent molecule TMS₂S [2.152(2) Å]²³ and also shorter than those in copper and zinc TMS-S complexes [2.078(1)–2.119(2) Å].¹⁹

The corresponding organic salts of chalcogenide dianions (Cat)₂E proved to be inaccessible by a 2-fold desilylation of 1 equiv of TMS₂E with 2 jointly or consecutively applied equiv of the methylcarbonate precursor. While no reaction occurred at lower temperatures, elevated temperatures (>60 °C) led to decomposition of the chalcogenide anion to unknown side products. In each case, the methylcarbonate anion was detected in the product mixture by NMR spectroscopy.

Nevertheless, the (trimethylsilyl)thiolates have proven to be excellent starting materials for the preparation of organic hexasulfides (Scheme 5). The reaction proceeds most conveniently in THF, in which the TMS-S⁻ salt and sulfur are partly soluble. The product is almost insoluble and precipitates as a fine bright-red solid, which can be isolated by filtration or centrifugation and is usually obtained in an analytically pure form after washing with THF and drying in fine vacuum. Bis(trimethylsilyl)sulfide is formed as the only side product. The hexasulfide apparently represents the thermodynamically most stable member of this series of pyrrolidinium polysulfides. The attempted synthesis of di- or tetrasulfides by variation of the reaction stoichiometry only led to decreased yields of the hexasulfides. The hexasulfide **11** was structurally characterized by single-crystal XRD (Figure 3; monoclinic *P*₂₁/*c*; two cations and one dianion per asymmetric unit). The sulfur chain adopts a helical structure and is disordered over two positions (ratio 93:7), which exhibit opposing rotating directions. The S-S bond lengths differ significantly along the chain. The longest bond is situated at the

Table 2. Crystal Data for 5, 6·CH₃CN, 11, [BMPyr]₂Se₃, and [DMPyr]₄Te₁₂

	[DMPyr][TMS-Se] (5)	[NMe ₄][TMS-S]·CH ₃ CN (6)	[DMPyr] ₂ S ₆ (11)	[BMPyr] ₂ Se ₃	[DMPyr] ₄ Te ₁₂
formula	C ₁₈ H ₄₆ N ₂ Se ₂ Si ₂	C ₉ H ₂₄ N ₂ SSi	C ₁₂ H ₂₈ N ₂ S ₆	C ₃₆ H ₈₀ N ₄ Se ₆	C ₂₄ H ₅₆ N ₄ Te ₁₂
fw/g·mol ⁻¹	504.67	220.45	392.72	1042.80	1931.92
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>m</i>	<i>P</i> ₂ / <i>c</i>	<i>Cc</i>	<i>P</i> ₂ / <i>n</i>
color, habit	colorless block	colorless plate	red block	dark-green block	dark-violet plate
cryst size/mm ³	0.25 × 0.1 × 0.05	0.24 × 0.175 × 0.14	0.14 × 0.10 × 0.10	0.23 × 0.11 × 0.06	0.28 × 0.13 × 0.03
<i>a</i> /Å	12.2500(8)	7.6236(11)	13.9975(10)	14.0988(8)	9.5497(7)
<i>b</i> /Å	10.8215(7)	7.6281(11)	12.2771(9)	24.8538(12)	18.7183(14)
<i>c</i> /Å	19.3331(12)	13.2227(18)	12.6705(8)	14.4105(8)	13.2276(10)
<i>α</i> /deg	90	90	90	90	90
<i>β</i> /deg	90.166(3)	104.094(4)	115.568(2)	116.435(2)	107.817(2)
<i>γ</i> /deg	90	90	90	90	90
<i>V</i> /Å ³	2562.9(3)	745.80(18)	1964.2(2)	4521.6(4)	2251.1(3)
<i>Z</i>	4	2	4	4	2
<i>D</i> _{calc} /g·cm ⁻³	1.308	0.982	1.328	1.532	2.850
abs corrn	multiscan	multiscan	multiscan	multiscan	multiscan
min/max transmn	0.7452/0.6204	0.7460/0.5002	0.7455/0.5398	0.7455/0.5006	0.7452/0.5263
<i>μ</i> /cm ⁻¹	29.83	2.68	6.90	48.83	76.68
<i>F</i> (000)	784	244	840	2112	1704
<i>T</i> /K	100(2)	100(2)	100(2)	100(2)	100(2)
<i>θ</i> range/deg	2.16–25.37	2.76–30.31	2.31–27.17	2.84–27.78	2.18–25.34
<i>h, k, l</i> indices	–14:14, –13:13, –23:23	–10:10, 0:10, 0:18	–16:17, –15:15, –16:15	–18:16, 0:31, 0:18	–11:11, –22:22, –15:14
reflns coll	38995	2198	18591	5047	35122
reflns indep	4683	2198	4304	5047	4100
reflns [<i>I</i> > 2σ(<i>I</i>)]	4335	1545	3075	4199	3923
data/restraint/ param	4683/0/228	2198/0/77	4304/36/240	5047/23/437	4100/0/185
<i>R</i> _{int}	0.0730	–(<i>hklf</i> 5)	0.0862	–(<i>hklf</i> 5)	0.0385
<i>R</i> ₁ (obs)	0.0306	0.0784	0.0551	0.0616	0.0280
<i>wR</i> ₂ (all)	0.0692	0.1505	0.1275	0.1114	0.0630
GOF (<i>F</i> ₂)	1.117	1.100	1.035	1.145	1.291
residual electron density (min/ max)	–0.550/0.521	–0.439/0.508	–0.411/0.569	–1.001/1.014	–0.867/1.495
CCDC	1413729	1413730	1413731	1413732	1413733

Scheme 5. Synthesis of Pyrrolidinium Hexasulfides 10 and 11

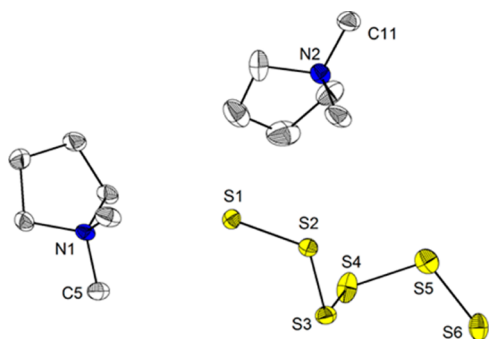
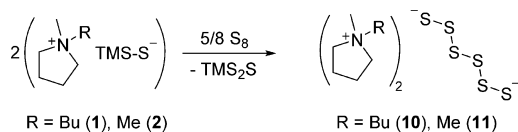


Figure 3. Molecular structure of 11. Hydrogen atoms were omitted for clarity; only the sulfur chain with the higher site occupancy is shown.

central position [$d(\text{S3-S4}) = 2.085(1) \text{ \AA}$]; toward the final atoms, the bond lengths decrease stepwise [e.g., $d(\text{S4-S5}) = 2.040(2) \text{ \AA}$ and $d(\text{S5-S6}) = 2.031(2) \text{ \AA}$]. The helical S₆ structure is the predominant conformation among comparable crystal structures. Also, the S–S bond lengths lie in a similar range, with the central bond always being the weakest.²⁴ The torsion within the S₆ chain varies over a large range, resulting in differences in the total chain length of almost 1 Å (e.g., 7.60 Å in [NBu₄]₂S₆^{24a} vs 6.63 Å in [enH₂]₂S₆^{24b}). The present dimethylpyrrolidinium hexasulfide shows an intermediate distance of 7.04 Å between S1 and S6.

While pure (trimethylsilyl)selenolate and -tellurolate salts are colorless and storable without decomposition at 25 °C in the dark under an inert atmosphere, solutions of them, especially in the presence of silicon grease or traces of air, show some decomposition, resulting in intensely green and violet solutions. The colors clearly indicate the presence of polyselenides and polytellurides, respectively. For the silylselenolates and -tellurolates, a lability similar to those of H₂Se and H₂Te and the hydroselenide and hydrotelluride anions, which are prone to homolytic dissociation to hydrogen and the elemental chalcogen, has to be expected. During crystallization, previously colorless solutions of [BMPyr][TMS-Se] and [DMPyr][TMS-Te] yielded green and violet-black single crystals suitable for X-

ray structure determination; the substances could be identified as $[\text{BMPyr}]_2\text{Se}_3$ and $[\text{DMPyr}]_4\text{Te}_{12}$. Preliminary experiments indicate that polyselenides and polytellurides can be synthesized analogously to the polysulfides from TMS-E^- and E_n . A more detailed investigation is still underway though and will be published in due course.

The triselenide (Figure 4) crystallized in the monoclinic space group Cc comprising four cations and two dianions in the

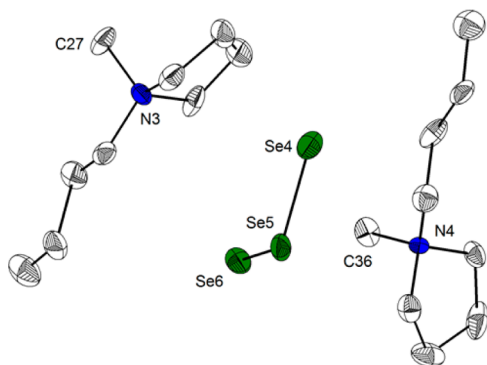


Figure 4. Molecular structure of $[\text{BMPyr}]_2\text{Se}_3$. Hydrogen atoms were omitted for clarity; only one of two ion pairs in the asymmetric unit is displayed.

asymmetric unit. The structure was treated as a nonmerohedral twin, whose components were freely refined to a ratio of 51% to 49%; additionally, one of the triselenide anions is disordered over two positions with a freely refined ratio of 91% to 9%. Considering only the nondisordered anion, the Se–Se bond lengths are 2.352(2) and 2.356(2) Å, while the triatomic structure is bent at an angle of 113.4(1)°. Similar bond lengths are found in other triselenides; the best agreement persists with Cs_2Se_3 [2.358(1) Å].²⁵ The Se–Se distances in the closer-related structure with distinctively separated ions ($[\text{Mn}(\text{en})_3]\text{Se}_3$; en = ethylenediamine) are considerably shorter [2.3394(4) Å].²⁶ The angles in the known triselenide structures are smaller by approximately 10°. The structural diversity of polyselenides was recently reviewed and classified.²⁷

The polytelluride (Figure 5) crystallized in the monoclinic space group $P2_1/n$; the asymmetric unit comprises two cations and a Te_6 chain. Two neighboring Te_6 chains form a tetraanionic tricyclic structure. A related tetraanion was

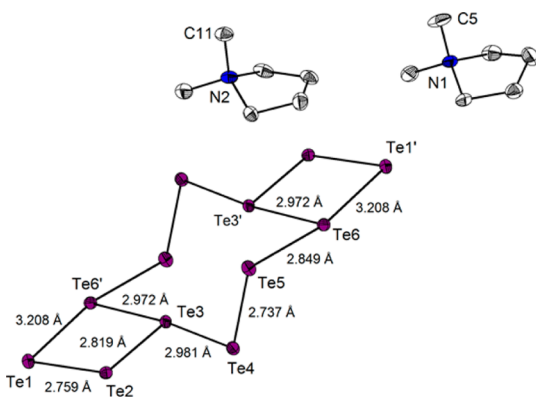
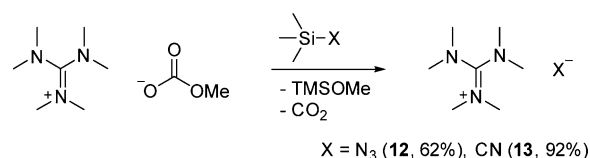


Figure 5. Molecular structure of $[\text{DMPyr}]_4\text{Te}_{12}$. Hydrogen atoms and two symmetry-equivalent cations were omitted for clarity. Symmetry operation: $'$, $2 - x, -y, -z$.

observed by Feldmann and Okrut, who synthesized the corresponding $\text{Li}(12\text{-crown-4})_2$ salt from elemental tellurium and lithium antimonide.²⁸ The present structure is not disordered though, allowing a higher precision in comparison with the previous structure report. As pointed out by Feldmann and Okrut, two different Te–Te bonding modes can be observed in the anion structure. Te_2 units with a pseudotetrahedral coordination geometry show short Te–Te distances typical of polytelluride chains [$d(\text{Te4–Te5}) = 2.737(1)$ Å and $d(\text{Te1–Te2}) = 2.759(1)$ Å]. T-shaped Te_4 units with a pseudo-trigonal-bipyramidal coordination of the central, hypervalent atom show distinctively longer distances, e.g., $d(\text{Te2–Te3}) = 2.819(1)$ Å, $d(\text{Te3–Te4}) = 2.981(1)$ Å, and $d(\text{Te3–Te6}') = 2.972(1)$ Å. The particularly elongated Te–Te bond between Te1 and Te6' [3.208(1) Å] in the second T-shaped fragment points to a secondary interaction. Nevertheless, Te6 can be regarded as hypervalent, judging from the bonding geometry and the anisotropic displacement parameters of the neighboring atoms: The four three-coordinate tellurium atoms are formally Te^- , which can be regarded as pseudo-I. The largest polytelluride with organic cations known so far is the dodecatelluride dianion found in $(\text{NEt}_4)_2\text{Te}_{12}$;²⁹ other structurally characterized polytellurides with organic cations include Te_2^{2-} ,^{8a} Te_3^{2-} ,²⁹ Te_4^{2-} ,³⁰ and Te_5^{2-} .^{24a,31} For an extensive overview, the attentive reader is referred to the excellent reviews by Smith and Ibers³² and Sheldrick.^{27a}

After successfully implementing methylcarbonate ILs as desilylating agents for bis(trimethylsilyl)sulfide, -selenide, and -telluride, we were curious whether this procedure is transferable to other TMS-substituted reagents. As may be expected, no reaction occurs with the lightest homologue of the series, TMS_2O . Apparently, the formation of a Si–O bond is needed as the driving force for the reaction. Accordingly, (trimethylsilyl)azide and (trimethylsilyl)cyanide react selectively with hexamethylguanidinium methylcarbonate to form hexamethylguanidinium azide and cyanide (Scheme 6).

Scheme 6. Synthesis of Hexamethylguanidinium Azide (12) and Cyanide (13) by Methylcarbonate-Induced Desilylation



This provides an elegant access to these organic salts, whose synthesis is usually challenging because of unfavorable solubility equilibria for alkali halide salt metathesis reactions and the very high toxicity of the corresponding free acids. The completely aprotic procedure allows total exclusion of highly hazardous and volatile HCN and HN_3 . The preparation of organic silylchalcogenolate salts and the additional examples demonstrate the attractive desilylation potential of organic methylcarbonate salts. These readily available reagents supplement the typically weakly coordinated fluoride salts, e.g., cesium, TBAF, and TMAF, whose desilylation behavior has been well-known for decades.³³

CONCLUSION AND OUTLOOK

A series of nine quaternary ammonium and phosphonium (trimethylsilyl)thiolates, -selenolates, and -tellurolates $[\text{TMS-E}]$ were synthesized by a new method of mild

desilylation of the respective bis(trimethylsilyl)chalcogenides TMS_2E (E = S, Se, Te) with known methylcarbonate ILs. Our synthesis is based on the observed desilylating capability of the highly nucleophilic methylcarbonate anion, followed by irreversible decarboxylation. This method offers a high yield and, in terms of cation and anion variability, broad access to well-soluble and pure silylchalcogenolates with purely organic cations. Upon exploration of the scope of this method, desilylation could be extended to representative C- and N-silyl derivatives, allowing a safe access to organic azide and cyanide salts, difficult to obtain in pure form by other methods. The new ionic chalcogenides were investigated regarding their decomposition temperatures and spectroscopic properties (NMR and IR). The crystal structures of **6** and **5** constitute the first structurally characterized examples of uncoordinated (trimethylsilyl)chalcogenolate anions. These are highly valuable precursors for the synthesis of polychalcogenides with purely organic cations, as demonstrated by the selective synthesis of pyrrolidinium hexasulfides via a redox reaction with elemental sulfur. The XRD structural characterization of the side products $[\text{BMPyr}]_2\text{Se}_3$ and $[\text{DMPyr}]_4\text{Te}_{12}$ demonstrates that this strategy can be extended to the higher homologues. We are confident that the now readily available title compounds $\text{Cat}[\text{TMS-E}]$ (E = S, Se, Te) will expand the starting material basis for many chemists working in the topical areas of metal chalcogenide clusters, (silyl)chalcogenidometallates, metal chalcogenide semiconductor materials, and polychalcogenide redox mediators.

EXPERIMENTAL SECTION

Details of solvothermal syntheses and isolation of methylcarbonate salts and other starting materials, e.g., TMS_2Te , as well as synthetic procedures for compounds **4–10** are submitted as [Supporting Information](#). Representative procedures:

Synthesis of N-Butyl-N-methylpyrrolidinium (Trimethylsilyl)thiolate ([BMPyr][TMS-S], 1). N-Butyl-N-methylpyrrolidinium methylcarbonate (617 mg, 2.84 mmol, 1.00 equiv) was dissolved in acetonitrile (5 mL), and the solution was cooled to 0 °C. TMS_2S (688 mg, 3.86 mmol, 1.36 equiv) was added dropwise, and the mixture was stirred for 1 h at 0 °C and a further 30 min at ambient temperature. The solution was concentrated in fine vacuum to two-thirds of its original volume, and diethyl ether (2 mL) was added. Storage at –25 °C yielded colorless crystals. The precipitate was filtered over a precooled frit, washed with diethyl ether (10 mL), and dried in fine vacuum. $[\text{BMPyr}][\text{TMS-S}]$ was isolated as a colorless solid. Yield: 514 mg (2.08 mmol, 73%). Mp: 120.9–121.9 °C (5 K/min, dec, MeCN/Et₂O). Elem anal. Calcd for $\text{C}_{12}\text{H}_{29}\text{N}_1\text{S}_1\text{Si}_1$: C, 58.2; H, 11.8; N, 5.7; S, 12.95. Found: C, 58.3; H, 12.2; N, 5.8; S, 12.5. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2938 (m), 1478 (w), 1384 (w), 1231 (m), 1030 (w), 1007 (w), 937 (w), 814 (vs), 735 (m), 663 (m), 633 (s), 499 (s). ¹H NMR (300.1 MHz, DMSO-*d*₆): δ –0.07 (s, 9H, TMS-S), 0.93 (t, ³J_{HH} = 7.5 Hz, 3H, CH₂CH₃), 1.25–1.38 (m, 2H, CH₂CH₃), 1.62–1.73 (m, 4H), 2.08 (br s, 4H), 3.01 (s, 3H, NMe), 3.33–3.39 (m, 2H), 3.44–3.56 (m, 4H). ¹³C NMR (75.5 MHz, DMSO-*d*₆): δ 8.9 (3C, TMS-S), 13.4 (1C), 19.2 (1C), 21.0 (1C), 24.9 (1C), 47.4 (br s, 2C), 62.7 (br s, 2C), 63.3 (br s, 1C). ²⁹Si NMR (99.4 MHz, DMSO-*d*₆): δ –0.7 (s).

Synthesis of N-Butyl-N-methylpyrrolidinium (Trimethylsilyl)selenolate ([BMPyr][TMS-Se], 2). N-Butyl-N-methylpyrrolidinium methylcarbonate (997 mg, 4.59 mmol, 1.00 equiv) was dissolved in acetonitrile (10 mL), and the solution was cooled to 0 °C and degassed three times. TMS_2Se (1.24 g, 5.50 mmol, 1.20 equiv) was added dropwise, and the mixture was stirred for 1 h at 0 °C and a further 30 min at ambient temperature. The solution was concentrated in fine vacuum to half of the original volume and stored at –20 °C. The resulting suspension was filtered over a precooled frit, and the precipitate was washed with diethyl ether (10 mL) and dried in fine vacuum. A second crop of material was obtained analogously by

cooling the combined mother liquor and washings to –20 °C. $[\text{BMPyr}][\text{TMS-Se}]$ was isolated as a colorless solid. Yield: 1.10 g (3.74 mmol, 81%). Mp: 127.8–128.4 °C (5 K/min, dec, MeCN/Et₂O). Elem anal. Calcd for $\text{C}_{12}\text{H}_{29}\text{N}_1\text{Se}_1\text{Si}_1$: C, 49.0; H, 9.9; N, 4.8. Found: C, 48.5; H, 9.8; N, 5.3. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2941 (m), 2889 (w), 1465 (w), 1383 (w), 1231 (m), 1004 (w), 931 (w), 818 (vs), 735 (m), 667 (m), 621 (m). ¹H NMR (300.1 MHz, DMSO-*d*₆): δ 0.09 (s, 9H, TMS-Se), 0.93 (t, ³J_{HH} = 7.5 Hz, 3H, CH₂CH₃), 1.25–1.38 (m, 2H, CH₂CH₃), 1.62–1.73 (m, 4H), 2.08 (br s, 4H), 2.99 (s, 3H, NMe), 3.29–3.35 (m, 2H), 3.39–3.54 (m, 4H). ¹³C NMR (75.5 MHz, DMSO-*d*₆): δ 9.2 (3C, TMS-Se), 13.4 (1C), 19.2 (1C), 21.0 (1C), 24.9 (1C), 47.5 (br s, 2C), 62.8 (br s, 2C), 63.3 (br s, 1C). ²⁹Si NMR (59.7 MHz, DMSO-*d*₆): δ –4.7 (s). ⁷⁷Se NMR (57.3 MHz, DMSO-*d*₆): δ –417.5 (s).

Synthesis of N-Butyl-N-methylpyrrolidinium (Trimethylsilyl)telluroate ([BMPyr][TMS-Te], 3). N-Butyl-N-methylpyrrolidinium methylcarbonate (1.00 g, 4.60 mmol, 1.00 equiv) was dissolved in acetonitrile (8 mL), and the solution was cooled to 0 °C and degassed three times. TMS_2Te (1.28 g, 4.66 mmol, 1.01 equiv) was added dropwise, whereupon the solution turned slightly red. The mixture was stirred for 30 min at 0 °C and a further 60 min at ambient temperature. All volatile components were removed in vacuo, and a reddish-gray solid remained, which proved to be pure according to elemental analysis. $[\text{BMPyr}][\text{TMS-Te}]$ was isolated in a yield of 1.44 g (4.19 mmol, 91%). Mp: 120.4–121.2 °C (5 K/min, dec, MeCN). Elem anal. Calcd for $\text{C}_{12}\text{H}_{29}\text{N}_1\text{Te}_1\text{Si}_1$: C, 42.0; H, 8.5; N, 4.1. Found: C, 42.4; H, 8.7; N, 4.5. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2939 (m), 2880 (w), 1461 (w), 1230 (m), 1060 (w), 933 (w), 822 (vs), 738 (m), 672 (m), 616 (s). ¹H NMR (300.1 MHz, DMSO-*d*₆): δ 0.32 (s, 9H, TMS-Te), 0.92 (t, ³J_{HH} = 7.4 Hz, 3H, CH₂CH₃), 1.25–1.38 (m, 2H, CH₂CH₃), 1.61–1.75 (m, 4H), 2.08 (br s, 4H), 3.01 (s, 3H, NMe), 3.32–3.41 (m, 2H), 3.44–3.56 (m, 4H). ¹³C NMR (75.5 MHz, DMSO-*d*₆): δ 10.1 (3C, TMS-Te), 13.4 (1C), 19.2 (1C), 21.0 (1C), 24.9 (1C), 47.5 (br s, 2C), 62.7 (br s, 2C), 63.3 (br s, 1C). ²⁹Si NMR (79.5 MHz, DMSO-*d*₆): δ –27.0 (s). ¹²⁵Te NMR (126.2 MHz, DMSO-*d*₆): δ –1142.0 (s).

Synthesis of Bis(N,N-dimethylpyrrolidinium)hexasulfide ([DMPyr]₂Se₆, 11). A suspension of sulfur (201 mg, 6.27 mmol, 4.95 equiv) in THF (20 mL) was added to $[\text{DMPyr}][\text{TMS-S}]$ (520 mg, 2.53 mmol, 2.00 equiv). The mixture immediately turned bright red and was stirred for 3 days, after which a fine red precipitate had formed. The solid was filtered, washed with THF (10 mL), and dried in fine vacuum. **11** was isolated in a yield of 485 mg (1.23 mmol, 98%). Mp: 128.2–128.8 °C (5 K/min, dec, THF). Elem anal. Calcd for $\text{C}_{12}\text{H}_{28}\text{N}_2\text{S}_6$: C, 36.7; H, 7.2; N, 7.1; S, 50.0.³⁴ Found: C, 36.9; H, 7.3; N, 8.4; S, 52.51. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2982 (w), 1459 (w), 1000 (w), 975 (w), 935 (w), 818 (w), 503 (vs), 439 (w). ¹H NMR (300.1 MHz, DMSO-*d*₆): δ 2.12 (br s, 4H, CH₂), 3.14 (s, 6H, NMe₂), 3.51 (br s, 4H, NCH₂). ¹³C NMR (75.5 MHz, DMSO-*d*₆): δ 22.1 (2C, CH₂), 52.3 (br s, 2C, NMe₂), 65.8 (br s, 2C, NCH₂).

Synthesis of Hexamethylguanidinium Azide ([Me₆Gua][N₃], 12). Hexamethylguanidinium methylcarbonate (288 mg, 1.31 mmol, 1.00 equiv) was dissolved in acetonitrile (8 mL) and the mixture cooled to 0 °C. (Trimethylsilyl)azide (189 mg, 1.64 mmol, 1.25 equiv) was added dropwise, whereupon gas evolution could be witnessed. The mixture was stirred at 0 °C for 20 min and at ambient temperature for 30 min. Trace amounts of solid residue were removed by syringe filtration, and all volatile components were removed in fine vacuum. The solid residue was recrystallized from a mixture of acetonitrile and diethyl ether at –25 °C. $[\text{Me}_6\text{Gua}][\text{N}_3]$ was isolated in a yield of 152 mg (0.816 mmol, 62%) as colorless crystals. Mp: 299.9–300.7 °C (5 K/min, dec, MeCN/Et₂O). Elem anal. Calcd for $\text{C}_7\text{H}_{18}\text{N}_6$: C, 45.1; H, 9.7; N, 45.1. Found: C, 45.1; H, 9.5; N, 45.5. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3288 (w), 3000 (w), 2898 (w), 2803 (w), 1994 (vs), 1596 (vs), 1477 (m), 1402 (vs), 1254 (m), 1147 (m), 1069 (m), 895 (m), 630 (w), 536 (w). ¹H NMR (300.1 MHz, DMSO-*d*₆): δ 2.87 (s, 18H, Me). ¹³C NMR (75.5 MHz, DMSO-*d*₆): δ 39.4 (6C, Me), 162.3 (1C, C_{quart}).

Synthesis of Hexamethylguanidinium Cyanide ([Me₆Gua][CN], 13). Hexamethylguanidinium methylcarbonate (210 mg, 0.958 mmol, 1.00 equiv) was dissolved in acetonitrile (8 mL) and the

mixture cooled to 0 °C. (Trimethylsilyl)cyanide (120 mg, 1.21 mmol, 1.26 equiv) was added dropwise. The mixture was stirred at 0 °C for 15 min and at ambient temperature for 60 min. Trace amounts of solid residue were removed by syringe filtration, all volatile components were removed, and the residue was thoroughly dried in vacuo. [Me₆Gua][CN] was isolated in a yield of 149 mg (0.875 mmol, 92%) as a colorless powder. Mp: 258.5–259.9 °C (5 K/min, dec, MeCN). Elem anal. Calcd for C₆H₁₈N₄: C, 56.4; H, 10.7; N, 32.9. Found: C, 56.3; H, 10.7; N, 33.4. IR ($\nu_{\max}/\text{cm}^{-1}$): 3003 (w), 2898 (w), 2809 (w), 1600 (vs), 1480 (m), 1407 (vs), 1257 (m), 1152 (m), 1073 (m), 898 (m), 537 (w). ¹H NMR (300.1 MHz, DMSO-*d*₆): δ 2.87 (s, 18H, Me). ¹³C NMR (75.5 MHz, DMSO-*d*₆): δ 39.4 (6C, Me), 162.3 (1C, C_{quat}), 166.8 (1C, CN⁻).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01665.

X-ray crystallographic data in CIF format (CIF)

Details concerning devices, methods, and starting materials, further synthetic procedures and analytical data of new compounds, details concerning crystal structure determination, notes concerning elemental analysis, and representations of NMR and IR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the “Fonds der Chemischen Industrie” (doctoral fellowship for L.H.F.) and the DFG, GRK 1782 “Functionalization of Semiconductors”, for financial support. For his advice with crystal structure refinement, we are very grateful to Dr. K. Harms and thank J. Guschlbauer for his synthetic contribution. The analytical service department is thanked for their continued efforts.

■ DEDICATION

†Dedicated to Professor Herbert W. Roesky on the occasion of his 80th birthday.

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(34) For a discussion of the deviation in *N* and *S* values, refer to the [Supporting Information](#).