## **Inorganic Chemistry**

# A Series of Homoleptic Linear Trimethylsilylchalcogenido Cuprates, Argentates and Aurates Cat[Me<sub>3</sub>SiE-M-ESiMe<sub>3</sub>] (M = Cu, Ag, Au; E = S, Se)

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**ABSTRACT:** The syntheses and XRD molecular structures of a complete series of silylsulfido metalates  $Cat[M(SSiMe_3)_2]$  (M = Cu, Ag, Au) and corresponding silylselenido metalates  $Cat[M(SeSiMe_3)_2]$  (M = Cu, Ag, Au) comprising lattice stabilizing organic cations (Cat =  $Ph_4P^+$  or  $PPN^+$ ) are reported. Much to our surprise these homoleptic cuprates, argentates, and aurates are stable enough to be isolated even in the absence of any strongly binding phosphines or N-heterocyclic carbenes as coligands. Their metal atoms are coordinated by two silylchalcogenido ligands in a linear fashion. The silyl moieties of all anions show an unexpected *gauche* conformation of the silyl substituents with respect to the central axis Si-[E-M-E]-Si in the solid state. The energetic preference for the *gauche* conformation is



confirmed by quantum chemical calculations and amounts to about 2–6 kJ/mol, thus revealing a rather shallow potential mainly depending on electronic effects of the metal. Furthermore, 2D HMQC methods were applied to detect the otherwise nonobservable NMR shifts of the <sup>29</sup>Si and <sup>77</sup>Se nuclei of the silylselenido compounds. Preliminary investigations reveal that these thermally and protolytically labile chalcogenido metalates are valuable precursors for the precipitation of binary coinage metal chalcogenide nanoparticles from organic solution and for coinage metal cluster syntheses.

#### INTRODUCTION

Species containing highly thiophilic group 11 metal centers M  $(M = Cu^{I}, Ag^{I}, Au^{I})$  and chalcogenolate ligands  $[ER]^{-}$  (E = S, I)Se, Te; R = organic moiety) constitute a class of compounds mainly dominated by oligomeric cluster or coordination polymer structural motifs.<sup>1</sup> On the other hand, hydrosulfide [SH]<sup>-</sup> complexes of transition metals are of interest as a class of its own, but only very few examples of hydrosulfide complexes are known for the coinage metals.<sup>2</sup> The few existing are stabilized by strongly binding coligands; homoleptic hydrosulfide complexes are unknown. The self-assembly of such partially coligand masked polynuclear chalcogen complexes via higher aggregated oligomers and clusters, finally, to nanocrystals can be considered a general trend and aim.<sup>3</sup> Recently, less aggregated, molecular chalcogenide compounds, again typically stabilized by strongly binding coligands such as N-heterocyclic carbenes (NHC) or chelating *tert*.-amines, came into focus of interest: They serve as molecular models for reactive sites of solid state materials, e.g.  $[(NHC-Cu)_2(\mu_2 - \mu_2)]$ (S) (S))<sup>4</sup> as a molecular variant of Cu<sub>2</sub>S, they serve as molecular building blocks such as  $[(\text{tmeda})\text{Zn}(\text{SSiMe}_3)_2]^5$  in the step-bystep bottom-up synthesis of chalcogenide materials, e.g. ZnS, or they provide biomimetic model systems for metalloproteins such as the tetranuclear [4Cu:2S] cluster in the active site of N<sub>2</sub>O reductase.<sup>6</sup> Understanding structure property relations in metalloproteins and other bioactive compounds is challenging: While copper represents the second most abundant transition metal found in organisms, after iron, silver compounds are

commonly used as biocides, not harmful to mammals but deadly to microorganisms.<sup>8</sup> In contrast, molecular gold(I) thiolato complexes are used as metalo pharmaceuticals in commercially established drugs, e.g. for the therapy of arthritis.<sup>9</sup>

Let us focus on the much less investigated, nonbiogenic class of complexes containing trimethylsilylchalcogenido ligands  $[ESiMe_3]^-$  (E = S, Se, Te). From a chemical point of view they are hybrids of organochalcogenolato  $[ER]^-$  and hydrochalcogenido  $[EH]^-$  functional molecules with respect to their labile bonds and potential transformations: Such complexes can be used as a starting point for the preparation of coinage metal chalcogenido clusters of higher complexity or for nanoparticles<sup>10</sup> being of interest due to their photoluminescence behavior.<sup>11,12</sup> The cleavage of the E–Si linkage can be performed with suitable desilylating agents, such as metal acetates or acetato complexes, or by thermally induced intra- or intermolecular elimination of  $E(SiMe_3)_2$ ,<sup>5,10,11</sup> The E–R cleavage barriers grow with increasing sterical demand of the silylchalcogenide or alkylchalcogenolate ligand. Polynuclear compounds such as Au<sub>4</sub>[EC(SiMe\_3)\_3]\_4 (E = S, Se, Te)<sup>13</sup> and

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also mononuclear complexes like  $R_3PAuSSi(SiMe_3),^{14}$   $R_3PAuTeC(SiMe_3),^{13}$  and  $Ph_3PAuSC(SiMe_3)^{14}$  are known examples of reasonable stability at room temperature. The latter has been reported to be of use for the synthesis of clusters  $Au_{108}S_{24}(PPh_3)_{16}^{15}$  and  $Au_{70}S_{20}(PPh_3)_{12}^{16}$  when treated with borohydrides-rather strong E-R cleavage agents compared to e.g. acetates. However, to date, mononuclear neutral compounds containing a coinage metal attached E-SiMe<sub>3</sub> group were made accessible only by applying strongly binding amine, phosphine, or N-heterocyclic carbene auxiliary ligands. While the phosphine compounds of the type  $[R_3P-$ M-ESiMe<sub>3</sub>] are quite difficult to handle,<sup>17</sup> the NHC analogues [NHC-M-ESiMe<sub>3</sub>] and related cyclic alkyl(amino)carbenes (CAAC) [CAAC-M-ESiMe<sub>3</sub>] are of reasonable stability for using them in selective bottom-up syntheses of defined ternary clusters with tunable optical properties.<sup>11,18,19</sup> Finally, NHC masked coinage metal silvlchalcogenido complexes have been used as precursors for the preparation of coinage metal chalcogenide materials  $M_2E$ .<sup>20</sup> These materials are receiving growing interest due to their negligible toxicity and their potential to act as e.g. IR emitters and superionic conductors.<sup>2</sup>

Linearly coordinated organchalcogenolato metalates of the type  $[M(ER)_2]^-$  (M = Cu, Ag, Au; E = S, Se, Te; R = bulky organic ligand) were chosen as the lead structural motif of this study.<sup>1,2,3</sup> In these anions, intermolecular charge repulsion in combination with bulky organic groups and robust E–C bonds are often preventing higher aggregation, but even these anionic complexes can form higher-coordinated or higher-charged polynuclear coinage metalates.<sup>23</sup>

Recently, we discovered a class of thermally and protolytically metastable homoleptic silylchalcogenido metalates Cat- $[M(ESiMe_3)_4]$  (M = Ga, In; E = S, Se)<sup>22a</sup> and Cat[M-(ESiMe\_3)\_3] (M = Sn, Zn; E = S, Se).<sup>22b</sup> They have proven to act as precursors in a solution based low temperature synthesis of ternary and quaternary chalcogenide materials CuInS<sub>2</sub> and Cu<sub>2</sub>ZnSnS<sub>4</sub>, which are members of the PV absorber material classes CIGS and CZTS, respectively.<sup>22</sup> Encouraged by these results, we were motivated to target so far unknown  $[M(ESiMe_3)_2]^-$  (M = Cu, Ag, Au, E = S, Se) precursors for materials synthesis. The challenge was to isolate such thermally and protolytically labile homoleptic complexes with coinage metals having an intrinsically higher lattice energy in the form of their metal chalcogenides compared to the metals of our previous studies. An economically attractive aspect with respect to potential applications seemed to be that the targeted metastable molecular precursors might not rely on strongly binding, expensive, and difficult to recycle PR3 or NHC coligands. A principal aim is that these building blocks for materials synthesis should be accessible in any element combination Cu/Ag/Au-S/Se.

#### RESULTS AND DISCUSSION

**Synthesis.** The principle strategy to synthesize the title compounds follows the route established in our previous reports for other homoleptic silylchalcogenido metalates (Scheme 1). First, an organic cation chloride Cat[Cl] is added to the metal chlorides, here  $[MCl]_n$  (M = Cu, Ag, Au), in order to chop up the solid compound and to yield molecular chlorometalates, Cat[MCl<sub>2</sub>] in this case. Without the need to isolate these intermediates, 2 equiv of LiESiMe<sub>3</sub><sup>24</sup> are added in THF at -78 °C. After slowly warming the reaction mixture to ambient temperature and removal of all volatiles *in vacuo*, the rather lipophilic salts comprising large, nonpolarizing cations

#### Scheme 1. Synthesis of the Title Compounds Cat[M(ESiMe<sub>3</sub>)<sub>2</sub>]

Cat[MCl <sub>2</sub> ]	<sup>2 Li-ESiMe<sub>3</sub></sup> thf, -78°C→rt, 18 h Cat[M(ESiMe <sub>3</sub> ) <sub>2</sub> ]
Cat Cl thf, rt, 18 h MCl	1: M = Cu, E = S, Cat = $Ph_4P^+$ 2: M = Ag, E = S, Cat = $Ph_4P^+$ 3-Cat: M = Au, E = S, Cat = $Ph_4P^+$ / PPN <sup>+</sup> 4-Cat: M = Cu, E = Se, Cat = $Ph_4P^+$ / PPN <sup>+</sup> 5-Cat: M = Ag, E = Se, Cat = $Ph_4P^+$ / PPN <sup>+</sup> 6-Cat: M = Au, E = Se, Cat = $Ph_4P^+$ / PPN <sup>+</sup>

are extracted into diethyl ether, thus being separated from LiCl. The highest yields 84–86% achieved after crystallization are obtained with the  $Ph_4P^+$  cation for 1–3. However, use of  $PPN^+$  was indicated in some cases in order to get single crystals suitable for XRD analysis. These thermally metastable compounds can be handled at ambient temperature for some time, and they can be stored at –30 °C under inert gas for an extended period of time.

By following this low-temperature approach, the complete series of homologues 1-6 displaying two reactive ESiMe<sub>3</sub> moieties was isolated and fully characterized. Even small deviations from this protocol lead to darkening of the reaction mixture and brown-black precipitates. If such side products or unreacted starting material are not desirable, it is beneficial to quench mechanistically plausible partially substituted intermediates [Cl-M-ESiMe<sub>3</sub>]<sup>-</sup> at low temperature by a second equivalent of LiESiMe<sub>3</sub> in THF; otherwise, there is a certain risk (or chance!) of eliminating Me<sub>3</sub>SiCl, if the solution is warming up prior to the second substitution step. All kinetically stabilized molecular products  $Cat[M(ESiMe_3)_2]$ (M = Cu, Ag, Au, E = S, Se) are colorless and crystalline compounds. Any compounds possibly forming upon elimination of  $Me_3Si-X$  (X = Cl,  $ESiMe_3$ ) from thermally unstable, plausible intermediates  $[Cl-M-ESiMe_3]^-$  or from metastable final products [Me<sub>3</sub>Si-M-ESiMe<sub>3</sub>]<sup>-</sup>, e.g. hypothetical polyanionic clusters  $Cat_n[(ME)_n(MESiMe_3)_m]$  or simply their decomposition products M2E, Cat2E and Me3SiX, are expected to change drastically in their optical absorption and emission spectra. The perspective to isolate crystalline intermediates on this decay path into the thermodynamically most stable crystalline phases should be followed up in future research: A trigger for desired or undesired desilylation reactions seems to be the presence or absence of excess of weakly solvated ionic chloride Cat[Cl] in the reaction mixture.

**XRD Structures.** All title compounds crystallize in the triclinic space group  $P\overline{1}$ , 1 with two (Figure 1) and 2–6 with four ion pairs per unit cell (Figure 2, Figure 3, Figure S1, Figure S2, and Figure 4, respectively).

1 reveals only one crystallographically independent anion per unit cell, while 2–6 contain two independent anions. Structural parameters such as E–M–E or Si–E–E–Si dihedral angles of crystallographically independent anions are summarized in Table 1. The largest differences between two independent anions are observed in silylsulfido-argentate 2. While structurally comparable linearly coordinated cuprates and argentates with silylthiolate moieties  $[Cu(SSiPh_3)_2]^{-25}$  and  $[Ag(SSiR_3)_2]^-$  (R = bis(diisopropyl)phenolate (OC<sub>12</sub>H<sub>17</sub>))<sup>26,27</sup> are known, the title compounds comprise the first structurally characterized silylselenido cuprates or argentates and silylchalcogenido aurates.

By analyzing and comparing the observed torsion angles  $\alpha$ (Si-E-E-Si), it became evident that all molecular structures



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Figure 1. Molecular structure of  $Ph_4P[Cu(SSiMe_3)_2]$  (1). Hydrogen atoms are neglected for clarity. Ellipsoids are shown at 50% level. Selected bond lengths (Å) and angles (deg) of the anion in 1: Cu1– S1 2.1412(6), Cu1–S2 2.1475(6), S1–Si1 2.1081(8), S2–Si2 2.1129(7), S1–Cu1–S2 176.63(2), Cu1–S1–Si1 100.34(2), Cu1– S2–Si2 97.14(2), Si1–S1–S2–Si2 48.86(3).



**Figure 2.** Molecular structure of  $Ph_4P[Ag(SSiMe_3)_2]$  (2). Hydrogen atoms are neglected for clarity. Ellipsoids are shown at 50% level. Selected bond lengths (Å) and angles (deg) of the crystallographically inequivalent anions in the reduced cell in 2: Ag1–S1 2.341(1), Ag1– S2 2.356(1), S1–Si1 2.111(1), S2–Si2 2.108(2), S1–Ag1–S2 171.70(4), Ag1–S1–Si1 106.28(5), Ag1–S2–Si2 98.59(5), Si1– S1–S2–Si2 51.27(7), Ag2–S3 2.357(1), Ag2–S4 2.368(1), S3–Si3 2.118(2), S4–Si4 2.099(2), S3–Ag2–S4 175.56(4), Ag2–S3–Si3 100.07(5), Ag2–S4–Si4 98.19(6), Si3–S3–S4–Si4 27.82(7).

of 1-6 display their E-silyl substituent in a quasi-gauche conformation with respect to the linear E-(M)-E axis. First, this seemed to be unexpected, as for steric reasons such molecules might have favored an *anti*-conformation as observed in the aforementioned structurally characterized  $[Cu(SSiPh_3)_2]^{-,25}$   $[Ag(SSiR_3)_2]^{-,26,27}$  and the 1-adamanylthiolato-cuprate  $[Cu(SAd)_2]^{-,28}$  On the other hand organo-thiolates  $[Cu(StBu)_2]^{-29}$  and  $[Au(SeCF_3)_2]^{-30}$  also show this quasi-gauche conformation.

**DFT Calculations.** For a deeper insight into the phenomenon connected with the *gauche*-like conformation, the variation of Si–E–E–Si torsion angle was investigated in density functional calculations employing TURBOMOLE<sup>31</sup> with the TPSS functional<sup>32</sup> and dhf-TZVP basis sets.<sup>33</sup> Structure optimizations were carried out keeping  $\alpha$  fixed at –10, 0, 10, ..., 0.270° and optimizing all other coordinates. This was done for M = Cu, Ag, Au and E = S, Se in



**Figure 3.** Molecular structure of PPN[Au(SSiMe<sub>3</sub>)<sub>2</sub>] (**3-PPN**). Hydrogen atoms are neglected for clarity. Ellipsoids are shown at 50% level. Selected bond lengths (Å) and angles (deg) of the two crystallographically inequivalent anions in the reduced cell in 3: Au1–S1 2.289(1), Au1–S2 2.308(1), S1–Si1 2.107(2), S2–Si2 2.112(2), S1–Au1–S2 178.79(4), Au1–S1–Si1 103.80(5), Au1–S2–Si2 94.71(5), Si1–S1–S2-Si2 62.15(6),Au2–S3 2.299(1), Au2–S4 2.2985(9), S3–Si3 2.119(1), S4–Si4 2.119(1), S3–Au2–S4 176.52(3), Au2–S3–Si3 100.38(5), Au2–S4–Si4 102.44(4), Si3–S3–S4–Si4 77.21(5).



**Figure 4.** Molecular structure of PPN[Au(SeSiMe<sub>3</sub>)<sub>2</sub>] (6-PPN). Hydrogen atoms are neglected for clarity. Ellipsoids are shown at 50% level. Selected bond lengths (Å) and angles (deg) of the crystallographically inequivalent anions in the reduced cell in 6: Au1–Se1 2.3980(6), Au1–Se2 2.4015(6), Se1–Si1 2.255(1), Se2–Si2 2.256(1), Se1–Au1–Se2 175.46(2), Au1–Se1–Si1 101.36(3), Au1–Se2–Si2 97.68(3), Si1–Se1–Se2–Si2 75.21(4), Au2–Se3 2.3956(7), Au2–Se4 2.4139(6), Se3–Si3 2.258(1), Se4–Si4 2.255(1), Se3–Au2–Se4 176.14(3), Au2–Se3–Si3 100.79(3), Au2–Se4–Si4 90.29(3), Si3–Se3–Se4–Si4 72.49(4).

 $[M(ESiMe_3)_2]^-$  as well as for the model compound  $[Cu-(SCl)_2]^-$ . The resulting energy curves are shown in Figure 5.

The experimentally observed preference of torsional angles in the range of about 100° and 250° is visible also in the calculated energy curves, but it is not very large. The maximum difference amounts to 6 kJ/mol and is found between  $\alpha = 0^{\circ}$ and  $\alpha = 100^{\circ}$  for [Cu(SeSiMe<sub>3</sub>)<sub>2</sub>]<sup>-</sup>. For a given M, the results for S and Se are very similar. The impact of the choice of M to Table 1. Comparison of Structural Parameters of Homologue Cuprates, Argentates, and Aurates  $Ph_4P[Cu(SSiMe_3)_2]$  (1),  $Ph_4P[Ag(SSiMe_3)_2]$  (2),  $PPN[Au(SSiMe_3)_2]$  (3-PPN),  $PPN[Cu(SeSiMe_3)_2]$  (4-PPN),  $PPN[Ag(SeSiMe_3)_2]$  (5-PPN), and  $PPN[Au(SeSiMe_3)_2]$  (6-PPN)

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Anion (M/E)	М-Е (Å)	E-Si (Å)	E-M-E (deg)	M-E-Si (deg)	Si-E-E-Si (deg)
1 (Cu/S)	2.1412(6) - 2.1475(6)	2.1081(8) - 2.1129(7)	176.63(2)	97.14(2)-100.34(2)	48.86(3)
2 (Ag/S)	2.341(1) - 2.368(1)	2.099(2) - 2.118(2)	171.70(4)-175.56(4)	98.19(6)-106.28(5)	27.82(7)-51.82(7)
3 (Au/S)	2.289(1) - 2.308(1)	2.107(2) - 2.119(1)	178.79(4)-176.52(3)	94.71(5)-103.80(5)	62.15(6)-77.21(5)
4 (Cu/Se)	2.2613(7) - 2.2836(6)	2.247(1) - 2.2561(8)	174.16(2) - 174.98(3)	88.30(3)-101.97(3)	75.97(3)-77.45(3)
5 (Ag/Se)	2.4487(6) - 2.4745(6)	2.247(2) - 2.256(2)	174.66(3)-175.29(2)	87.93(4)-101.79(4)	73.82(5)-74.75(6)
6 (Au/Se)	2.3956(7)-2.4139(6)	2.255(1) - 2.258(1)	175.46(2)-176.14(3)	90.29(3)-101.36(3)	72.49(4)-75.21(4)



**Figure 5.** Energy as a function of the torsional angle Si–E–E–Si,  $\alpha$ , of  $[M(ESiMe_3)_2]^-$  and Cl–E–E–Cl for  $[Cu(SCl)_2]^-$ , respectively. Energies are given relative to the eclipsed configuration (0°). For  $[Cu(SCl)_2]^-$ , the energies are divided by a factor of 2.

the shape of the curves is larger. The energy difference between  $\alpha = 0^{\circ}$  and  $\alpha = 100^{\circ}$  decreases from Cu via Au to Ag, which is in line with the sequence of the accessibility of the d shell for chemical bonds and thus points to a rationalization involving angle-dependent ( $\pi$ -type) interactions of the d(M) orbitals and the p(E) orbitals. Due to the smallness of the energetic preference of  $\alpha = 100^{\circ}$ , the net effect is expected to be small for all compounds. We thus first discuss the electronic structure of the model compound  $[Cu(SCl)_2]^-$ , which shows a similar shape for E( $\alpha$ ), but with energy differences between  $\alpha = 0^{\circ}$  and  $\alpha = 100^{\circ}$  being twice as large as that for  $[Cu(SeSiMe_3)_2]^-$ . A Walsh-type diagram for the nine highest occupied MOs and angles between  $0^{\circ}$  and  $90^{\circ}$  is shown in Figure 6.

For HOMO, HOMO-1, and HOMO-6 a significant influence of  $\alpha$  on the orbital energies is observed. For  $\alpha = 0^{\circ}$ , the HOMO is a strongly antibonding combination (Mulliken overlap population OP = -0.246 between Cu and S) of  $d_{xz}$ (Cu) and  $p_x$ (S); HOMO-1 is a very weakly bonding combination of  $d_{xy}$ (Cu) and  $p_x$ (S). For  $\alpha = 90^{\circ}$ , both orbitals are essentially nonbonding, which in sum increases the overlap and thus the bond strength. This is enhanced by HOMO-6 ( $d_{yz}$ (Cu) with  $p_z$ (S)), which changes from nonbonding to weakly bonding, accompanied by a lowering of the orbital energy. For this model compound, the preference of  $\alpha = 90^{\circ}$ thus is rationalized by the change of the  $\pi$  interactions in these three MOs, in particular by the decrease of the antibonding character of the HOMO, and reflected by an increase ( $\alpha = 90^{\circ}$ vs  $\alpha = 0^{\circ}$ ) of OP by 0.180 for the sum of these MOs. When



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**Figure 6.** Orbital energies of the highest occupied MOs as a function of the torsional angle Cl–S–S–Cl,  $\alpha$ , of  $[Cu(SCl)_2]^-$ . Orbitals are plotted for  $\alpha = 0^\circ$  (left) and  $\alpha = 90^\circ$  (right). The numbers in the diagram (-0.246 etc.) denote the sum of the Mulliken overlap population between Cu and the two S atoms (negative numbers indicate antibonding character).

summing over all MOs, the OP changes by 0.121 (from 1.143 to 1.264), which shows that the dominant changes indeed arise from the three MOs listed above. For completeness we note that the interaction between Cu and the two Cl atoms is weakly antibonding and only slightly dependent from  $\alpha$ : OP(0°) = -0.134, OP(90°) = -0.152.

For the original compound [Cu(SSiMe<sub>3</sub>)<sub>2</sub>]<sup>-</sup> matters are by far less obvious (shown in the Supporting Information, Figure \$5). As in the case of the model compound, the antibonding character of the HOMO, which is similar to that of the model compound, is reduced, but this stabilization is compensated by changes in several other MOs. As a consequence, the OPs between Cu and the two S atoms are identical for  $\alpha = 90^{\circ}$  and  $\alpha = 0^{\circ}$ , 1.195. Here,  $\pi$  interactions between Cu and S alone do not rationalize the (slight) energetic preference for  $\alpha = 90^{\circ}$ . An explanation rather may be found in the neighbor next neighbor interactions and further in effects of electron correlation, which are beyond the one-electron picture of orbital considerations. This is supported by the fact that in DFT, where these effects are included, the energy difference between  $\alpha = 0^{\circ}$  and  $\alpha = 90^{\circ}$ is 5.6 kJ/mol, whereas at Hartree-Fock level, where such effects are neglected, it is only 2.3 kJ/mol.

So far, the influence of the counterions was neglected. For a rough estimation of this effect we exemplarily calculated the equilibrium structure of  $[Cu(SeSiMe_3)_2]^-$  in the presence of one PPN<sup>+</sup> unit at the DFT level. The coordinates were taken from the X-ray structure and kept fixed for PPN<sup>+</sup> as well as for the Cu atom. For the optimized structure, the gauche-type

conformation is maintained ( $\alpha = 95.2^{\circ}$ ). The eclipsed conformer, which was obtained by additionally fixing  $\alpha$  at 0°, is higher in energy by 9.2 kJ/mol. This is close to the above value for the gas phase, 6 kJ/mol, and also close to the difference of single-point energies for the two structures with PPN<sup>+</sup> being removed, 7.1 kJ/mol. So, the (small) relative stability of the gauche conformation compared to the eclipsed one is not significantly affected by the presence of PPN<sup>+</sup> despite relatively strong ionic interaction between PPN<sup>+</sup> and [Cu(SeSiMe<sub>3</sub>)<sub>2</sub>]<sup>-</sup> amounting to 194 kJ/mol.

**NMR Spectroscopy.** Silylsulfido metalates 1-3 were investigated by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy in THF[d<sub>8</sub>] at ambient temperature. The <sup>1</sup>H NMR signals for the metalate anions range from 0.12 ppm for the argentate 2 to 0.13 ppm for both, the aurate  $3-Ph_4P$  and the cuprate 1. The <sup>13</sup>C NMR signals range from 7.4 ppm for the aurate  $3-Ph_4P$  to 8.6 ppm for the argentate 2, while the chemical shift for the cuprate 1 is at 8.3 ppm. A trend is observed in <sup>29</sup>Si NMR spectra showing an increasingly pronounced low field shift with growing molecular weight. It ranges from 5.2 ppm for the cuprate 1 to 7.7 ppm for the aurate  $3-Ph_4P$  (Figure 7).



Figure 7. <sup>29</sup>Si NMR (59.7 MHz for 1 and 2, 99.4 MHz for 3, THF[d<sub>8</sub>]) spectra of the  $Ph_4P[Cu(SSiMe_3)_2]$  (1, top row),  $Ph_4P[Ag(SSiMe_3)_2]$  (2, middle row), and  $Ph_4P[Au(SSiMe_3)_2]$  (3- $Ph_4P$ , bottom row).

While <sup>1</sup>H and <sup>13</sup>C NMR spectra were routinely recorded for the silylselenido metalates **4**–**6**, detection of <sup>29</sup>Si and the <sup>77</sup>Se signals turned out to be very difficult. We therefore applied two-dimensional <sup>1</sup>H–<sup>29</sup>Si-HMQC<sup>34</sup> and <sup>1</sup>H–<sup>77</sup>Se-HMQC methods at 0 °C utilizing the gradient selective coherence transfer from the proton to the corresponding heteronuclei. At 0 °C, the <sup>1</sup>H NMR shifts of the silylselenido metalate anions are quite similar, ranging from 0.27 ppm for the cuprate 4-Ph<sub>4</sub>P as well as 0.31 ppm for the aurate **6-Ph<sub>4</sub>P**, and 0.30 ppm for the argentate **4-Ph<sub>4</sub>P**. However, clear identification is possible by the <sup>29</sup>Si NMR shifts that are accessible by the 2D-NMR method quite easily. The <sup>29</sup>Si NMR shifts range from 0.2 ppm for the cuprate **4-Ph<sub>4</sub>P** to 2.4 ppm for the aurate **6-Ph<sub>4</sub>P**, while the signal for the argentate **5-Ph<sub>4</sub>P** is at 1.6 ppm (Figure 8).

The specific <sup>77</sup>Se NMR signals in  ${}^{1}\text{H}-{}^{77}\text{Se-HMQC}$  NMR spectra of selenidometalates **4-Ph<sub>4</sub>P**, **5-Ph<sub>4</sub>P**, and **6-Ph<sub>4</sub>P** also allow an identification. The most high-field shifted <sup>77</sup>Se NMR signal (-502.2 ppm) is observed for the argentate **5-Ph<sub>4</sub>P**, while the aurate **6-Ph<sub>4</sub>P** shows the most low-field shifted signal (-377.9 ppm). The <sup>77</sup>Se NMR signal of the cuprate **4-Ph<sub>4</sub>P** is at -469.4 ppm (Figure 9).

Preliminary Study on Reactivity of [M(ESiMe<sub>3</sub>)<sub>2</sub>]<sup>-</sup> Representatives. While silylchalcogenido metalates of the coinage metals turned out to be similar to organochalcogenolato metalates with respect to their structural features, their



Figure 8.  ${}^{1}H{-}^{29}Si{-}HMQC$  NMR (99.4 MHz, THF[d<sub>8</sub>]) spectra of the silylselenido metalates 4-Ph<sub>4</sub>P, 5-Ph<sub>4</sub>P, and 6-Ph<sub>4</sub>P at 273 K.



Figure 9.  ${}^{1}\text{H}-{}^{77}\text{Se-HMQC}$  NMR (500.2 MHz, THF[d<sub>8</sub>]) spectra of the silylselenido metalates 4-Ph<sub>4</sub>P, 5-Ph<sub>4</sub>P, and 6-Ph<sub>4</sub>P at 273 K.

protolytic and thermal reactivity differs drastically. In sharp contrast to organothiolates, all of the title compounds spontaneously precipitate monovalent coinage metal chalcogenides from THF or other organic solutions, when methanol or traces of water are added. Diffusion of protic reactants into colorless solutions of e.g.  $Ph_4P[Ag(SSiMe_3)_2]$  (2) in THF leads to the formation of a brown-black nanocrystalline dispersion containing  $Ag_2S$  (Scheme 2, eqs 1 and 2). S-

Scheme 2. Postulated Protic Decay Paths of Silylsulfido Cuprates, Argentates, and Aurates; Cat = Organic Cation

2 Cat[M(SSiMe <sub>3</sub> ) <sub>2</sub> ] + 4 MeOH ───►				
2 "Cat[(MS)]" + 4 MeOSiMe <sub>3</sub> + 2 H <sub>2</sub> S (1)				
2 "Cat[(MS)]" + $H_2O \longrightarrow M_2E$ + CatSH + CatOH (2)				
n "Cat[(MS)]" + m M <sub>2</sub> S $\longrightarrow$ Cat <sub>n</sub> [(MS) <sub>n</sub> (M <sub>2</sub> S) <sub>m</sub> ] (3)				

Desilylation with formation of RO–SiMe<sub>3</sub> (R = organyl or H) is occurring. As plausible intermediate  $Ph_4P[Ag(SH)_2]$  is not stable at room temperature, it is believed to further condense with loss of H<sub>2</sub>S. Products of the composition "Ph<sub>4</sub>P[(AgS)]" are not known so far, but they might be stabilized by nucleation and condensation with nc-Ag<sub>2</sub>S forming in *statu nascendi* (eq 3). Anionic clusters of the formal composition  $Cat_n[(AgS)_n(Ag_2S)_m]$  might be envisaged, but were not isolated and characterized so far under such protic reaction conditions represented by Scheme 2:

Addition of MeOH to  $Ph_4P[Ag(SSiMe_3)_2]$  leads to the release of  $H_2S$  as indicated by a weak evolution of gas and spontaneous precipitation of a black precipitate, which after 3

h of aging was centrifuged and washed with MeOH. Upon annealing at 140 °C for 3 days, essentially phase pure microcrystalline Ag<sub>2</sub>S was identified *via* PXRD (JCPDS: 14-0072; see supplement, Figure S6). Future studies will have to focus on soluble fractions and the question of whether partially silylated anionic clusters  $Cat_n[(AgS)_n(AgSSiMe_3)_m]$  might be formed as intermediates on the way toward the thermodynamic sink Ag<sub>2</sub>S.

An indication that this is not pure speculation was gained from controlled thermolysis studies under strictly aprotic conditions: The DSC-TGA curve of  $Ph_4P[Cu(SSiMe_3)_2]$  (1) under inert gas reveals a defined melting point at 91 °C (see supplement, Figure S3). Decomposition of this molten ionic liquid starts at an onset temperature of  $T_{onset}$  = 179.2 °C. At this temperature, the robust cations remain intact according to <sup>31</sup>P NMR studies; the anion however starts to decompose prior to cation under elimination of volatile (Me<sub>2</sub>Si)<sub>2</sub>S. Controlled thermolysis of the molten salt 1 in a Schlenk tube at 180 °C for 2 min under  $10^{-2}$  mbar dynamic vacuum led to an orangeyellow waxy solid. This residue was dissolved in the smallest amount of DMF and layered with twice the volume of diethyl ether. After a few days, red single crystals were obtained. An XRD analysis revealed that these were identical with literatureknown  $(Ph_4P)_4[Cu_{12}S_8]$ .<sup>35</sup> The composition of this cubocta-hedral cluster can formally be envisaged as  $\operatorname{Cat}_{n}[(\operatorname{CuS})_{n}(\operatorname{Cu}_{2}\operatorname{S})_{m}]$  with n = 4 and m = 4 (in accord with Scheme 3, eq 3). In our synthesis, cluster nucleating anionic

### Scheme 3. Postulated Thermal Decay Paths of $Cat[Cu(SSiMe_3)_2]$ and Nucleation of $Cat_4[Cu_{12}S_8]$ (Cat = $Ph_4P$ )

12 Cat[Cu(SSiMe <sub>3</sub> ) <sub>2</sub> ] → 12 "Cat[(CuS)]" + 12 (Me <sub>3</sub> Si) <sub>2</sub> S (1)				
8 "Cat[(CuS)]"	→ 4 $Cu_2S$ + 4 $Cat_2S$ (2)			
4 "Cat[(CuS)]" + 4 Cu <sub>2</sub> S	Cat <sub>4</sub> [(CuS) <sub>4</sub> (Cu <sub>2</sub> S) <sub>4</sub> ] (3)			

building blocks "Ph<sub>4</sub>P[(CuS)]" might have formed via selective thermal elimination of  $(Me_3Si)_2S$  at 1. The literature synthesis of  $(Ph_4P)_4[Cu_{12}S_8]$  via complex redox reaction of  $CuCl_2(H_2O)_2$  with 3 equiv of  $[EtS]^-$  in methanol, followed by cooling to -78 °C and addition of  $Li_2S$  and slow warming of the mixture in the presence of  $Ph_4P[Br]$ , offers even more room for speculations about any cluster nucleation mechanism.

The thermally and protolytically labile nature of the E–Si bonds in these molecular precursors 1-6 provides new perspectives for ligand L controlled formation of dispersions of LCu<sub>x</sub>Ag<sub>y</sub>Au<sub>z</sub>S<sub>n</sub>Se<sub>m</sub> nanoparticles from homogeneous organic precursor solutions under adjustable protolytic conditions difficult to provide with other molecular precursors. On the other hand, detailed studies on thermal decay paths under aprotic conditions are opening perspectives to isolate and characterize new family members of unprecedented anionic chalcogenido clusters of these elements in future.

#### CONCLUSION

We described the syntheses and XRD molecular structures of homoleptic silylsulfido and silylselenido cuprates, argentates, and aurates  $[M(SSiMe_3)_2]^-$  (M = Cu (1), Ag (2), Au (3)) and  $[M(SeSiMe_3)_2]^-$  (M = Cu (4), Ag (5), Au (6)) comprising Ph<sub>4</sub>P<sup>+</sup> or PPN<sup>+</sup> cations. All metalate anions exhibit a linear coordination with a *gauche*-like Si-[E-M-E]-Si conformation in the solid state. The energetic preference for the *gauche* 

conformation is confirmed by quantum chemical calculations and amounts to about 2-6 kJ/mol, thus revealing a rather shallow potential mainly depending on electronic effects of the metal. Furthermore, 2D HMQC methods were applied to detect the otherwise nonobservable NMR shifts of the <sup>29</sup>Si and <sup>77</sup>Se nuclei of the silylselenido compounds 4-Ph<sub>4</sub>P, 5-Ph<sub>4</sub>P, and 6-Ph<sub>4</sub>P. We are convinced that metastable metalates of the type introduced here will be valuable precursors for controlled multinary coinage metal chalcogenide cluster or nanoparticle syntheses from organic solution. Prospective veins of gold to investigate are thermally induced, chloride induced, or strong ligand phosphine/NHC induced Me<sub>3</sub>Si-X elimination, nucleation, and condensation reaction paths of 1-6. The nature of more or less polarizing, weakly coordinating organic cations (Cat) and/or the periferically remaining  $-SiR_3^+$ substituent (R = alkyl, aryl) in their compensation of accumulating negative cluster charge upon growth will probably be triggering the existing range of products.

#### EXPERIMENTAL SECTION

All preparative operations were conducted by using standard Schlenk techniques and freshly dried solvents. All solvents were dried according to common procedures<sup>36</sup> and passed through columns of aluminum oxide, R3-11G-catalyst (BASF), or stored over molecular sieves (3 or 4 Å). Other reagents were used as received unless stated otherwise.  $S(SiMe_3)_2$  and  $Se(SiMe_3)_2$  were prepared analogously according to the literature known synthesis of  $S(SiMe_3)_{2i}^{37}$  LiESiMe<sub>3</sub> are known precursors for the introduction of E–SiMe<sub>3</sub> moieties.<sup>24</sup> We prepared these compounds in a slightly simplified way, as described in the Experimental Section.

Elemental analyses (C, H, N, S) were carried out by the service department for routine analysis with a vario MICRO cube (Elementar). Samples for the elemental analysis were weighted into tin capsules inside a nitrogen filled glovebox. <sup>1</sup>H and proton decoupled <sup>13</sup>C NMR spectra were recorded in automation with a Bruker Avance II 300 spectrometer; <sup>29</sup>Si and <sup>77</sup>Se NMR spectra were recorded by the service department for NMR analyses with a Bruker Avance III HD 300, DRX 400, or Avance III 500 spectrometer. All spectra were recorded at ambient temperature, unless stated otherwise. <sup>1</sup>H and <sup>13</sup>C NMR spectra were calibrated using residual proton signals of the solvent (THF[d<sub>8</sub>]:  $\delta_{\rm H}$  3.58 and 1.72 ppm,  $\delta_{\rm C}$  67.21 and 25.31 ppm). <sup>29</sup>Si NMR spectra were referenced externally (SiMe<sub>4</sub>:  $\delta_{\rm Si}$ 0.00 ppm) just as <sup>77</sup>Se NMR spectra (Me<sub>2</sub>Se  $\delta_{\rm Se}$ 0.00 ppm).

The XRD data collection was performed on a Stoe Stadivari diffractometer or a Bruker D8 Quest diffractometer. Details of data collection and refinement are given in the Supporting Information. New data sets were deposited under CCDC codes 1940489–1940503.

Only one representative synthesis procedure of  $Ph_4P[Cu-(SSiMe_3)_2]$  (1) is described here. For all other representative compounds 2–6, selected analytical data are given. The complete data and a general synthetic procedure of all compounds are given in the Supporting Information.

 $Ph_4P[Cu(SSiMe_3)_2]$  (1). A mixture of  $Ph_4P[Cl]$  (0.122 g, 0.32 mmol, 1.00 equiv) and CuCl (0.032 g, 0.32 mmol, 1.00 equiv) was suspended in thf (10 mL) and stirred for 18 h at room temperature to obtain a suspension of  $Ph_4P[CuCl_2]$ . In a separate flask a solution of  $S(SiMe_3)_2$  (0.119 g, 0.67 mmol, 2.1 equiv) in thf (5 mL) was stirred at 0 °C and treated with a 2.9 M solution of *n*-BuLi in hexane (0.22 mL, 0.64 mmol, 2.0 equiv). The pale-yellow reaction mixture was stirred for 30 min at 0 °C and for an additional 30 min at room temperature. All volatiles were removed in fine vacuum until LiSSiMe\_3 is obtained as a colorless waxy solid, and the remaining excess of  $S(SiMe_3)_2$  is removed quantitatively. The residue is diluted in THF (10 mL) and added dropwise to the previously prepared suspension of  $Ph_4P[CuCl_2]$  at -78 °C. The reaction mixture was slowly allowed to reach room temperature within 18 h. All volatiles were removed in

fine vacuum, and the residue was suspended and extracted with diethyl ether (60 mL) and filtrated. The filtrate was stored at -30 °C to obtain the target compound as colorless blocks. The mother liquor can be reused for a second extraction cycle to obtain 1 as colorless crystals with a yield of 0.168 g (0.27 mmol, 84%). <sup>1</sup>H NMR (300.3 MHz, THF[d<sub>8</sub>]):  $\delta$  = 7.93–7.83 (m, 20 H, ( $H_5C_6$ )<sub>4</sub>P<sup>+</sup>), 0.13 (s, 18 H, [Cu(SSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>]<sup>-</sup>) ppm. <sup>13</sup>C NMR (75.5 MHz, THF[d<sub>8</sub>]):  $\delta$  = 136.1 (d, <sup>4</sup> $J_{PC}$  = 3.2 Hz, [(HC(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>C)<sub>4</sub>P]<sup>+</sup>)), 135.6 (d, <sup>3</sup> $J_{PC}$  = 10.4 Hz, [(HC(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>C)<sub>4</sub>P]<sup>+</sup>), 131.3 (d, <sup>2</sup> $J_{PC}$  = 13.2 Hz, [(HC(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>C)<sub>4</sub>P]<sup>+</sup>), 8.3 (s, [Cu(SSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>]<sup>-</sup>) ppm. <sup>29</sup>Si NMR (59.7 MHz, THF[d<sub>8</sub>]):  $\delta$  = 5.2 (s) ppm. Anal. calcd for C<sub>30</sub>H<sub>38</sub>Cu<sub>1</sub>P<sub>1</sub>S<sub>2</sub>Si<sub>2</sub>: C, 58.7; H, 6.2; S, 10.5. Found: C, 58.6; H, 5.8; S, 10.3.

**Ph**<sub>4</sub>**P**[**Ag**(**SSiMe**<sub>3</sub>)<sub>2</sub>] (2). <sup>29</sup>Si NMR (59.7 MHz, THF[d<sub>8</sub>]):  $\delta$  = 5.2 ppm. Anal. calcd for C<sub>30</sub>H<sub>38</sub>AgPS<sub>2</sub>Si<sub>2</sub>: C, 54.8; H, 5.8; S, 9.8. Found: C, 54.7; H, 5.8; S, 10.3.

 $\begin{array}{l} \label{eq:PPN[Au(SSiMe_3)_2] (3-PPN). $^{29}Si NMR (99.4 MHz, THF[d_8]): $\delta$ = 7.6 ppm. Anal. calcd for $C_{42}H_{48}AuNP_2S_2Si_2: $C, 53.3; $H, 5.1; $N, 1.5; $S, 6.8. Found: $C, 53.0; $H, 5.2; $N, 1.7; $S, 6.7. $Ph_4P[Cu(SeSiMe_3)_2] (4-Ph_4P). $^{29}Si NMR (99.4 MHz, THF[d_8]): $\end{array}$ 

**Ph<sub>4</sub>P[Cu(SeSiMe<sub>3</sub>)<sub>2</sub>] (4-Ph<sub>4</sub>P).** <sup>29</sup>Si NMR (99.4 MHz, THF[d<sub>8</sub>]): δ = 0.23 ppm. Extended measurement times were needed to obtain a 1D-<sup>29</sup>Si NMR spectrum. It was not possible to obtain a 1D-<sup>77</sup>Se NMR signal. For convenient detection of <sup>29</sup>Si and <sup>77</sup>Se NMR signals, <sup>29</sup>Si/<sup>1</sup>H- and <sup>77</sup>Se/<sup>1</sup>H-HMQC measurements were performed: <sup>29</sup>Si/<sup>1</sup>H-HMQC NMR (99.4 MHz/500.2 MHz, THF[d<sub>8</sub>]): δ = <sup>1</sup>H 0.27/<sup>29</sup>Si 0.2 ppm. <sup>77</sup>Se/<sup>1</sup>H-HMQC NMR (95.4 MHz/500.2 MHz, THF[d<sub>8</sub>]): δ = <sup>1</sup>H 0.28/<sup>77</sup>Se - 469.4 ppm.

**Ph<sub>4</sub>P[Ag(SeSiMe<sub>3</sub>)<sub>2</sub>] (5-Ph<sub>4</sub>P).** <sup>29</sup>Si NMR (99.4 MHz, THF[d<sub>8</sub>], 273 K): δ = 1.59 (b) ppm. <sup>77</sup>Se NMR (95.4 MHz, THF[d<sub>8</sub>], 273 K): δ = -501.5 (b) ppm. Extended measurement times were needed to obtain a 1D-<sup>29</sup>Si- and 1D-<sup>77</sup>Se NMR spectrum. For a more convenient detection of <sup>29</sup>Si and <sup>77</sup>Se NMR signals, <sup>29</sup>Si/<sup>1</sup>H- and <sup>77</sup>Se/<sup>1</sup>H-HMQC measurements were performed: <sup>29</sup>Si/<sup>1</sup>H-HMQC NMR (99.4 MHz/500.2 MHz, THF[d<sub>8</sub>]): δ = <sup>1</sup>H 0.27/<sup>29</sup>Si 1.6 ppm. <sup>77</sup>Se/<sup>1</sup>H-HMQC NMR (95.4 MHz/500.2 MHz, THF[d<sub>8</sub>]): δ = <sup>1</sup>H 0.29/<sup>77</sup>Se -502.2 ppm. Anal. calcd for C<sub>30</sub>H<sub>38</sub>AgPSe<sub>2</sub>Si<sub>2</sub>: C, 47.9; H, 5.1. Found: C, 47.5; H, 4.9.

**Ph<sub>4</sub>P[Au(SeSiMe<sub>3</sub>)<sub>2</sub>] (6-Ph<sub>4</sub>P).** <sup>29</sup>Si NMR (99.4 MHz, THF[d<sub>8</sub>], 273 K):  $\delta$  = 2.4 (b) ppm. <sup>77</sup>Se (95.4 MHz, THF[d<sub>8</sub>], 273 K):  $\delta$  = -377.1 (b) ppm. Extended measurement times were needed to obtain broad 1D-<sup>29</sup>Si NMR and 1D-<sup>77</sup>Se NMR signals. For the convenient detection of <sup>29</sup>Si and <sup>77</sup>Se NMR signals, <sup>29</sup>Si/<sup>1</sup>H- and <sup>77</sup>Se/<sup>1</sup>H-HMQC measurements were performed: <sup>29</sup>Si/<sup>1</sup>H-HMQC NMR (99.4 MHz/500.2 MHz, THF[d<sub>8</sub>]):  $\delta$  = <sup>1</sup>H 0.27/<sup>29</sup>Si 2.4 ppm. <sup>77</sup>Se/<sup>1</sup>H-HMQC NMR (95.4 MHz/500.2 MHz, THF[d<sub>8</sub>]):  $\delta$  = <sup>1</sup>H 0.31/<sup>77</sup>Se -377.3 ppm. Anal. calcd for C<sub>30</sub>H<sub>38</sub>AuPSe<sub>2</sub>Si<sub>2</sub>: C, 42.9; H, 4.6. Found: C, 42.5; H, 4.5.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02808.

Experimental procedures, spectroscopic, analytic, and crystallographic details, NMR spectra, thermal decomposition behavior (TGA and DSC) of 1, Supporting Information on DFT calculations and a description of preliminary reactivity studies: methanolysis of 2,  $Ag_2S$  precipitation and PXRD analysis, finally the controlled thermolysis of 1 to  $(Ph_4P)_4[Cu_{12}S_8]$  (PDF)

#### Accession Codes

CCDC 1940498–1940503 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### **Author Contributions**

J.G. concept, synthesis of all compounds, and writing the first draft; T.V. all XRD analyses; X.X. correlated HMQC NMR experiments; F.W. quantum chemical calculations; J.S. general concept, writing and editing the final version. All authors have given approval to the final version of the manuscript.

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#### Notes

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