Unique Approach to Copper(I) Silylene Chalcogenone Complexes

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Supporting Information

ABSTRACT: Silylene-S-thione $[PhC(NtBu)_2Si(=S)N(SiMe_3)_2]$ (2) and silylene-Seselone $[PhC(NtBu)_2Si(=Se)N(SiMe_3)_2]$ (3) compounds were prepared from the silylene $[PhC(NtBu)_2SiN(SiMe_3)_2]$ (1) with 1 equiv of 1/8 S₈ and 1 equiv of Se powder, respectively, in high yields. Furthermore, compounds 2 and 3 reacted with CuCl and CuBr and yielded $[{PhC(NtBu)_2}Si(=S\rightarrow CuX)N(SiMe_3)_2]$ (X = Cl (4), Br (5)) and $[{PhC(NtBu)_2}Si(=Se\rightarrow CuX)N(SiMe_3)_2]$ (X = Cl (6), Br (7)), respectively. Complexes 4–7 can also be obtained from the direct reaction of sulfur and selenium with the corresponding silylene copper complexes $[{PhC(NtBu)_2}Si(=Sample CuX)_2Si(=Sample CUX)_2Si(=Sam$



 $\{N(SiMe_3)_2\}_2Cu_2X_2 (X = Cl (8), Br (9)).$ The latter route avoids the preparation of the highly reactive silvlene chalcogenones. For comparison purposes the silvlene $PhC(NtBu)_2SiN(SiMe_3)_2$ in 2 and 3 was replaced by NHC (1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene) (10). The resulting products NHC=S (thione 11) and NHC=Se (selenone 12) react with CuBr and lead to the expected complexes (NHC=S→CuBr) (13) and (NHC=Se→CuBr) (14). However, unlike silvlene complexes, 13 and 14 cannot be prepared by reacting NHC-CuBr (15) with chalcogens.

INTRODUCTION

Ketones are one of the most important functional groups in organic chemistry. However, the heavier double-bonded compounds between silicon and chalcogen are highly reactive due to poor $p\pi - p\pi$ overlap between chalcogens and silicon atoms.¹ In 1989, Corriu et al. reported the first stable diaryl-Sithiones and diaryl-Si-selones Ia-Ic (Chart 1).² Subsequently, Tokitoh, Okazaki, and their co-workers synthesized and characterized a series of kinetically stable heavier diaryl Si chalcogenones IIa-c using sterically hindered aromatic groups.³ Since then numerous examples of compounds containing a Si chalcogen double bond have been reported, thanks to extensive work from the groups of Kira (III), West (IV), Driess (V and VI), and others.⁴ With these compounds in hand, one can envisage using these Si chalcogenones as ligands in transition-metal chemistry. It has also been known for some time that aldehydes and ketones can serve as ligands in transition-metal complexes.⁵ In fact, the frequent use of acetone often led to serendipitous acetone complexes such as $[(\eta^5 C_5H_5)Re(NO)(PPh_3)(\eta^{l}-(CH_3)_2C=O)]^+PF_6^-$ and [Fe- $(C_{19}H_{25}N_5)(C_3H_6O)(H_2O)_2](BF_4)_2 \cdot 2C_3H_6O.^6$ There are several reports where Si=O double-bonded compounds were isolated as adducts with transition metals;⁷ however, other Si= E (E = S, Se, Te) bonded compounds were not explored for such complexation. The only available report on a Si= $S \rightarrow LA$ type (LA = Lewis acid) linkage is observed in the monomeric silicon disulfide (SiS₂) VII⁸ stabilized by the Lewis acid GaCl₃ (Chart 2). The same ligand system was further used to isolate the germanium analogue of VII.9

In 2007, we synthesized and characterized a silicon thioester with the Si(=S)-S skeleton by using the benzamidinato chlorosilylene [PhC(NtBu)₂SiCl].¹⁰ Furthermore, this silylene was utilized to prepare the functionalized silylene [PhC- $(NtBu)_2SiN(SiMe_3)_2$ ¹¹ (1) in high yield. However, 1 has yet to be explored for preparing Si chalcogenones. The first aim of our investigation focused on the reactivity of 1 toward chalcogens (E = S, Se). When we observed that compound 1 can smoothly afford the formation of silylene-S-thione (2) and silvlene-Se-selone (3), we investigated the donating abilities of the Si chalcogenones toward transition metals. The reaction of CuCl and CuBr resulted in the monomeric Lewis acid-base adducts 4-7, respectively. It must be noted here that this is the first report on sterically encumbered silicon-based silathione and silaselenone donor ligands for the synthesis of lowcoordinate transition-metal complexes. Moreover, the present study pointed to a distinctly superior donating ability of silvlene chalcogenones over silvlenes, as the latter were found to form dimeric complexes with transition metals from analogous reactions.¹²

RESULT AND DISCUSSION

Our efforts began by exploring the reactivity of 1 with chalcogens (E = S, Se). Treatment of 1 in toluene with 1/8 equiv of S₈ at room temperature for 12 h afforded a pale yellow solution of 2 (66% isolated yield) (Scheme 1). Similarly, 3 was

Received: November 26, 2016

Chart 1. Reported Compounds with a Double Bond Involving Chalcogens and Silicon Atoms



Chart 2. Lewis Acid-Base Adduct with Si Bis-Thione



synthesized in 70% yield by reacting 1 with 1 equiv of selenium powder (Scheme 1). The reaction mixture turned from yellow to colorless. Products 2 and 3 were isolated as colorless crystalline solids with good solubility in toluene, THF, and dichloromethane. After the isolation of 2 and 3, we explored the donor properties of the Si chalcogenones. We were able to prepare the Lewis acid–base adducts $[{PhC(NtBu)}_2]Si(=S \rightarrow$

CuX)N(SiMe₃)₂] (X = Cl (4), Br (5)), [{PhC(NtBu)₂}Si(= Se→CuX)N(SiMe₃)₂] (X = Cl (6), Br (7)) by using Si chalcogenones 2 and 3, respectively. Alternatively, the reactions of silylene copper complexes [{PhC(NtBu)₂}Si{N-(SiMe₃)₂}]₂Cu₂X₂ (X = Cl (8), Br (9))¹² with chalcogens also resulted in the formation of products 4–7.

The ¹H NMR spectra of **2** and **3** each display a sharp singlet at δ 1.30 and 1.34 ppm for 18 *t*Bu protons, which are shifted downfield in comparison to those of **1** (δ 1.23 ppm). The ²⁹Si NMR spectra of both **2** and **3** display three resonances (**2**, δ -16.82, 1.69, 6.26 ppm; **3**, δ -20.22, 2.78, 8.40 ppm). The resonances at δ -16.82 and -20.22 ppm for **2** and **3** respectively correspond to the central silicon atom, which are shifted upfield in comparison with that of **1** (δ -8.07 ppm). The other two resonances for both **2** and **3** are assigned to the two SiMe₃ groups. A sharp resonance is exhibited at δ -458.42 ppm for **3** in the ⁷⁷Se NMR spectrum. In the HRMS spectrum,

Scheme 1. Reactions of 1 with Chalcogens (S, Se) and Copper Halides (CuCl, CuBr)



the most abundant ion was observed at m/z 452.2405 for 2 and m/z 500.1852 for 3 with the highest relative intensity (100%).

The ORTEP diagrams of **2** and **3** are shown in Figures 1 and 2 with their structural parameters. **2** crystallizes in the



Figure 1. Molecular structure of 2 with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (deg): Si1–S1 1.987(2), Si1–N3 1.716(4), Si1–N2 1.816(4), Si1–N1 1.834(4); N3–Si1–S1 119.04(17), N2–Si1–S1 117.13(14), N1–Si1–S1 113.32(16).



Figure 2. Molecular structure of 3 with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (deg): Se1–Si1 2.1369(9), N3–Si1 1.715(2), N2–Si1 1.815(2), N1–Si1 1.827(2); N3–Si1–Se1 121.86(8), N2–Si1–Se1 113.23(8), N1–Si1–Se1 114.48(8).

monoclinic space group $P2_1/c$, whereas 3 crystallizes in the triclinic space group $P\overline{1}$.¹³ Both crystals were obtained in toluene at -30 °C in a freezer. The silicon center in both 2 and 3 is four-coordinate, and each exhibits a distorted-tetrahedral geometry. The two sites are occupied by the N atoms from the amidinato ligand: one site is occupied by the N atom of the N(TMS)₂ moiety, and the other site is connected with the chalcogens (S, 2; Se, 3). The Si=S bond length in 2 is 1.987(2) Å, which is in good agreement with the previously reported Si=S double bond in [{PhC(NtBu)₂}Si(S)StBu] (1.984(8) Å).¹⁰ The Si=S bond length in 2 is slightly longer than those in IIa (1.948(4) and 1.952(4) Å, as two nonidentical molecules of IIa were present in the unit cell)^{3a,b} and IIIa (1.957(2) Å),^{4a} respectively, but shorter than that of the base stabilized Si thione Ia² (2.013(3) Å). Similarly, the Si=Se bond

distance in 3 is 2.1369(9) Å, which is longer than those of III and V (2.096(1) and 2.117(1) Å) but shorter than those of IV and VI (2.153(1) and 2.146(1) Å). The average Si–S–N bond angle is 116.50°, which matches with an average Si–Se–N bond angle (116.52°).

The reactions of **2** and **3** with 1 equiv of CuCl in toluene afforded colorless crystalline solids of **4** and **6** with approximately 60–61% yield (Scheme 1). The coordination of the Si chalcogens to CuX is observed by a shift in the respective ²⁹Si NMR spectrum, while the resonance for the central Si atom is exhibited at δ –14.96 and –19.79 ppm for **4** and **6**, respectively. These resonances are shifted downfield in comparison with those of their parent compounds **2** and **3**. The ⁷⁷Se NMR spectrum of **6** shows a sharp singlet at δ –466.68 ppm, which is shifted upfield in comparison to **3** (δ –458.42 ppm).

Compounds 4 and 6 were further characterized by singlecrystal X-ray diffraction analysis shown in Figures 3 and 4, and



Figure 3. Molecular structure of 4 with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (deg): Si1–S1 2.039(2), Cu1–S1 2.1260(18), Cu1–Cl1 2.092(2), Si1–N3 1.692(5), Si1–N2 1.819(5), Si1–N1 1.804(5); Cl1–Cu1–S1 175.00(9), Si1–S1–Cu1 99.64(9), N3–Si1–S1 115.13(19), N2–Si1–S1 115.83(18), N1–Si1–S1 112.66(18).



Figure 4. Molecular structure of 6 with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (deg): Si1–Sel 2.1903(8), Cu1–Sel 2.2412(5), Cu1–Cl1 2.0953(9), Si1–N3 1.694(2), Si1–N2 1.821(2), Si1–N1 1.808(2); Cl1–Cu1–Sel 174.15(4), Si1–Sel–Cu1 98.96(2), N3–Si1–Sel 115.14(8), N2–Si1–Sel 115.22(8), N1–Si1–Sel 113.20(8).

selected bond parameters are given in the legends of the figures. Both complexes crystallize in the orthorhombic space group Pbca. The silicon center is tetracoordinate for compounds 4 and 6. In both cases, the chalcogens are dicoordinate: one site is connected with the silicon center, and the other site is coordinated with the copper center of the CuCl moiety. In 4, the Si=S bond length is 2.039(2) Å, which is longer than that of 2 due to coordination with the Lewis acid CuCl and also closely matches with that of the previously reported VII (2.106(2) Å),⁸ where S donates its lone pair of electrons to the Lewis acid of GaCl₃. The S \rightarrow Cu bond length is 2.1260(18) Å. S-Cu-Cl exhibits an angle of 175.00(9)°, while the Si-S-Cu angle is $99.64(9)^{\circ}$. Similarly, in the case of 6, the Si=Se bond length is 2.1903(8) Å, which is slightly longer than that of the precursor. The Se \rightarrow Cu bond length is 2.2412(5) Å. Here, as in the previous case the Se, Cu, and Cl are arranged in the same plane with a bond angle of $174.15(4)^{\circ}$.

Similarly, compounds **5** and 7 were obtained in good yield (60–62%) from the reaction of **2** and **3** with 1 equiv of CuBr in toluene at room temperature (Scheme 1). The ¹H and ²⁹Si NMR spectra of **5** and 7 reflect the coordination of S and Se centers via one of their lone pair of electrons to the CuBr moiety. The resonances for the silicon center were observed at δ –17.19 ppm (**5**) and δ –19.93 ppm (7). The slight upfield shift in the resonance of **5** is unexpected, as there should be an electron density shift from Si to S upon coordination with the Lewis acid (CuX). However, this unusual behavior can be attributed to the domination of a Si–S σ -bonding MO, which was previously reported for the Si=S \rightarrow GaCl₃ compound VII.⁸

The solid-state structures of 5 and 7 are the bromide analogues of 4 and 6 (Figures 5 and 6). 5 crystallizes in the



Figure 5. Molecular structure of 5 with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (deg): Si1–S1 2.0491(10), S1–Cu1 2.1304(8), Cu1–Br1 2.2316(4), Si1–N3 1.702(2), Si1–N2 1.814(2), Si1–N1 1.816(2); S1–Cu1–Br1 175.79(3), Si1–S1–Cu1 105.79(4), N3–Si1–S1 115.00(8), N2–Si1–S1 112.80(8), N1–Si1–S1 114.64(8).

monoclinic space group $P2_1/c$, and 7 crystallizes in the orthorhombic space group Pbca.¹³ For all of the complexes, the silicon center is tetracoordinate. Furthermore, each of the dicoordinate chalcogen atoms is bound to the Lewis acid CuBr. Compounds **5** and 7 show Si=E (E = S, Se) bond lengths of 2.0491(10) and 2.1902(18) Å, respectively. The E \rightarrow Cu (E = S, Se) bond lengths are 2.1304(8) and 2.2460(11) Å for **5** and 7, respectively. The S1-Cu1-Br1 angle of 175.79(3)° in **5** and



Figure 6. Molecular structure of 7 with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (deg): Se1–Si1 2.1901(18), Se1–Cu1 2.2460(11), Cu1–Br1 2.2194(11), Si1–N3 1.696(5), Si1–N2 1.811(5), Si1–N1 1.817(5); Se1–Cu1–Br1 173.22(5), Si1–Se1–Cu1 99.55(6), N3–Si1–Se1 114.93(19), N2–Si1–Se1 113.32(18), N1–Si1–Se1 115.38(18).

the Se1-Cu1-Br1 angle of $173.22(5)^{\circ}$ in 7 indicate that Cu, Cl, and E (E = S, Se) are arranged in the same plane.

Compounds 4–7 can also be prepared by the insertion of E (E = S, Se) into the Si→Cu bond of the complexes [PhC(NtBu)₂SiN(SiMe₃)₂CuCl]₂ (8) and [PhC(NtBu)₂SiN(SiMe₃)₂CuBr]₂ (9), respectively. Complexes 8 and 9 can be prepared by a modified literature procedure.¹² The reactions of complexes 8 and 9 with chalcogens (E = S, Se) resulted in the Lewis acid-base adducts 4–7, respectively. This is another useful route to synthesize Lewis acid-base adducts from the Si^{II}→CuX (X = Cl, Br) coordination complexes. DFT calculations reveal that the Si→CuBr bond (WBI = 0.68) is much weaker in comparison to the Si=S bond (WBI = 1.55). Therefore, the formation of a stronger Si-S (Si-Se) bond is at the expense of a weaker Si-Cu bond that renders the thermodynamic driving force for the aforementioned process.

For comparison reasons we further investigated the reactivity of an N-heterocyclic carbene instead of silvlene with chalcogens to explore their coordination behavior (see the Supporting Information for the experimental details and crystal structures). For this purpose, we prepared the previously reported sterically demanding N-heterocyclic carbene 1,3-bis(2,6-bis-(diphenylmethyl)-4-methylphenyl)
imidazol-2-ylidene $\ \ {\rm (10)}^{.14}$ Treating 10 with sulfur and selenium afforded the thione 11 and the previously reported selenone 12,15 respectively. Subsequently, these chalcogenones act as a Lewis base to form adducts 13 and 14 (Scheme 2). We have also prepared the carbene CuBr complex 15 and subsequently attempted to react the latter with chalcogens (E = S, Se). However, unlike 8 and 9, no reaction between 15 and chalcogens was observed. Therefore, this synthetic protocol did not lead to the formation of 13 and 14, which was explained by density functional theory (DFT) calculations. The theoretical study was performed using isodesmic reactions (see the Supporting Information for details), and a comparison of the solvent-corrected Gibbs free energies of these isodesmic reactions shows that carbene-S \rightarrow CuBr formation is 51.6 kcal/mol more endergonic than silylene-S→CuBr formation. Compounds 11 and 13–15 were characterized by state of the art spectroscopic tools and singlecrystal X-ray diffraction analysis. Although X-ray diffraction on

Scheme 2. Reaction of 10 with Chalcogens and CuBr^a



 a Ar*= 4-Me-C₆H₂-2,6-(CHPh₂)₂.

a single crystal unambiguously established the connectivity of 11 and 13–15, we refrain from a discussion of their bonding parameters because of the low quality of the data (see Figures S1-S3 in the Supporting Information for the crystal structures).

In order to obtain a deeper insight into the electronic structure of the silicon-chalcogen double bonds, we have carried out density functional theory (DFT) calculations on model compounds (see Computational Details in the Supporting Information) $[PhC(NMe)_2Si(=S)N(SiMe_3)_2]$ (2m) and $[PhC(NMe)_2Si(=Se)N(SiMe_3)_2]$ (3m). The calculated structural parameters are fairly consistent with the crystallographic data, and the geometry optimized structure of 2m is shown in Figure 7. The Si=S bond length in 2m is found



Figure 7. Molecular geometry optimized structure and relevant molecular orbitals of 2m.

to be 1.997 Å, which is close to the experimentally measured value of 1.987 Å in **2**. The Wiberg bond index (WBI) for the Si \equiv S bond is found to be 1.55, which indicates that the Si \equiv S bond has a multiple bonding character in addition to a contribution from the charge-separated canonical forms (vide infra; NPA calculations). An inspection of the molecular orbitals (MOs) confirms the bonding picture. MO analysis shows both σ - and π -bonding interactions between the Si and the S atoms. As illustrated in Figure 7, the HOMO is a lone pair on the S atom and HOMO-1 is a π -type bonding orbital (concentrated on the Si-S bond), while HOMO-4 clearly

shows the σ -bonding interaction between Si and S. NBO analysis suggests that the Si–S σ -bonding orbital is polarized toward the S atom (64% of NBO density on S). The calculated NPA charges on Si and S atoms are 1.829 and -0.802, consistent with a polarized Si–S bond. Furthermore, at the second-order perturbation level, a donor–acceptor interaction is found between the lone pairs of S atom and the empty p orbitals of Si (interaction energy sums up to 105.8 kcal/mol), which is in support of the back-bonding picture.

The bonding situation in **3m** is found to be similar to that in **2m** with a calculated WBI of 1.59. MO analysis shows that both σ - and π -bonding interactions are present in the Si=Se bond (Figure 8). The Si=Se σ -bonding orbital is polarized toward



Figure 8. Molecular geometry optimized structure and relevant molecular orbitals of 3m.

the Se atom (60.5% of NBO density on Se). However, as expected from the relatively smaller electronegativity of the Se in comparison to S, the Si=Se bond is slightly less polarized than the Si=S bond; the NPA charges on Si and Se atoms are 1.747 and -0.709 ($\Delta q = 2.456$ vs 2.631 in **2m**). Furthermore, the Se \rightarrow Si back-donation is confirmed by NBO analysis, which suggests a donor-acceptor interaction between the lone pairs of Se and the empty p orbitals of Si.

The coordinate bonded 1:1 complexes between Si chalcogenones and CuX (X = Cl, Br) have also been subjected to computational analysis. Geometry optimized structures of these complexes (4m-7m) are depicted in Figure S4 in the Supporting Information. Our results indicate that in all the complexes, silicon-chalcogen double bonds are elongated in comparison to those in the Si chalcogenones. For example, the Si=S bond in 5m is elongated to 2.064 Å (computed 1.997 Å in 2m), while the WBI is reduced to 1.22 (1.55 in 2m). This can be explained by the electron donation from S to Cu. In fact, NBO analysis shows that a significant donor-acceptor interaction is found between a lone pair of the S atom and an empty s orbital in Cu (at the second-order perturbation level the interaction energy amounts to 104.9 kcal/mol).

Apart from the bonding analysis, we also posed a few questions which we tried to answer from DFT calculations. For example, silylene copper halide complexes 8 and 9 are dimeric, while silachalcogenone copper halides complexes 4-7 are monomeric. The free energy of dimerization of $Si=S\rightarrow$ CuBr (Sm) is endergonic by 7.4 kcal/mol, while dimerization of $Si\rightarrow$ CuBr is almost thermoneutral in toluene. It is also interesting to note that sulfur and selenium insert into the Si–Cu bond but

not into the C–Cu bond. To rationalize this observation of why 13 and 14 cannot be afforded from 15, we have formulated a couple of isodesmic reactions through which we aim to examine the propensity of the formation of (silylene/carbene)- $S \rightarrow CuBr$ complexes from (silylene/carbene)-CuBr complexes. For construction of the isodesmic equations, H_2Si : and H_2C : are used as reference molecules and the equations are

 $Si \rightarrow CuBr + H_2Si = S \rightarrow Si = S \rightarrow CuBr + H_2Si$: (1)

$$C \rightarrow CuBr + H_2C = S \rightarrow C = S \rightarrow CuBr + H_2C:$$
 (2)

A comparison of the solvent-corrected Gibbs free energies of these isodesmic reactions shows that the carbene-S \rightarrow CuBr formation is 51.6 kcal/mol more endergonic than the silylene-S \rightarrow CuBr formation. This result is consistent with the experimental findings.

In summary, we have done a systematic study of the synthesis and characterization of Si chalcogenones 2 and 3 and their transition-metal-based Lewis acid-base adducts 4-7 of composition $Si=E \rightarrow LA$ (E = S, Se) with electron-deficient CuX (X = Cl, Br). In addition to the Si=S-based complexes 4-7, we also prepared thione 11 and their Lewis acid-base adducts 13 and 14 from sterically hindered carbene 10 to compare them with their silicon analogues. On comparison, we observed that Si chalcogen based Lewis acid-base adducts 4-7 can also be obtained from the reaction of silylene copper complexes 8 and 9 with chalcogens; however, this route does not work for the carbene copper complex 15, as the latter does not react with chalcogens to form 13 and 14. The dichotomy was rationalized by theoretical calculations, which reveal that carbene-S→CuBr formation is 51.6 kcal/mol more endergonic than silylene-S \rightarrow CuBr formation.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02833.

Experimental, crystal, and theoretical data (PDF)

Crystal data (CIF) Crystal data (CIF)

- Crystal data (CIF)
- Crystal data (CIF)

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Notes

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ACKNOWLEDGMENTS

S.K. thanks the SERB (India), DST-FIST, and IISER Pune for financial support. N.P. and S.P. thank the UGC for providing fellowships. H.W.R. thanks the Deutsche Forschungsgemeinschaft for financial support.

DEDICATION

Dedicated to Professor Ionel Haiduc on the occasion of his 80th birthday.

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