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O,*S*-Heterocyclic Stannylenes: Synthesis and Reactivity

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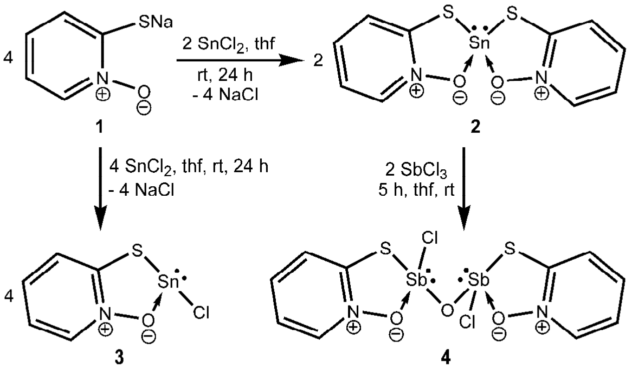
Commercially available *N*-oxide (2-mercaptopyridine-*N*-oxide) is used as a ligand instead of an oxidizing agent to stabilize compounds of main group elements in low-valent states. The isolated compounds [($C_5H_4NOS)_2Sn$ (2), (C_5H_4NOS)SnCl (3) and [(C_5H_4NOS)GeCl] (5)] are the first structurally characterized examples of *O*,*S*-heterocyclic stannylenes and germylene with interesting bonding features, respectively. Further, a reaction of compound 2 with $SbCl_3$ afforded a rare dichlorodiantimony oxide [{(C_5H_4NOS)SbCl}$_2$O] (4) unprecedentedly.

Novel structural aspects and applications of compounds with divalent germanium (germylenes) and -tin (stannylenes) atoms in small molecule activation, catalysis, and isolation of interesting compounds with M=E bonds (M = Ge, Sn; E = O, S, Se, Te), and so forth, have attracted the attention of chemists and led to the enormous growth in the chemistry of these heavier carbene analogues.[1-5] Due to the reactive nature of germylenes and stannylenes, they are mostly stabilized through bulky substituents/ligands. Though these substituents/ligands usually have a spectator role, the atom(s) in them that bind(s) with the Ge(II)/Sn(II) center and the kinetic and/or electronic stabilization offered by them are crucial in dictating the nature of the resultant germylene or stannylene.[1-4,6] Quite common are the substituents/ligands which bind through carbon, or nitrogen, or a combination of carbon and nitrogen atoms. There are ligands which bind through other atoms such as oxygen, silicon, phosphorous, and so forth.[7] Nevertheless, there is no example of a structurally characterized germylene or stannylene stabilized by a ligand that binds through a combination of oxygen and any one of its heavier analogues (such as sulfur, selenium). As this feature is there in the commercially available 2-mercaptopyridine-*N*-oxide (2-mpno), we wanted to use this simple ligand for the stabilization of Sn(II) and Ge(II) centers. Further, as *N*-oxides are known to oxidize the low-valent group 14 elements,[5a,h,8] it would be very interesting to see, how the oxygen in 2-mpno will behave after the binding of sulfur to the low-valent atom. Will it oxidize the Ge(II)/Sn(II) atoms or coordinatively bind to them? Therefore, the reactions of tin(II) chloride with two and one equivalents of sodium salt of 2-mpno were tried and it was found that the oxygen of 2-mpno prefers coordination with Sn(II) center, over oxidative addition reaction, to afford the first *N*-oxide stabilized *O*,*S*-heterocyclic stannylenes [(2-mpno)$_2$Sn] (**2**) and [(2-mpno)SnCl] (**3**) with novel Sn(II)-O(0) bonds, respectively (scheme 1). The reaction of tin(II) chloride with two equivalents of sodium salt of 2-mpno at an elevated temperature (60 °C) also afforded compound **2** only. Since oxygen in the *N*-oxide is a potential oxidizing agent and can oxidize the tin(II) to tin(IV) atom, isolation of compounds **2** and **3** without such process is very interesting. Thus, these compounds are unique examples where a main group element in a low-valent state is bonded to oxygen atom(s) in formal zero-valent state. Formation of compounds **2** and **3** without oxidative addition can be explained by saying that the oxidative addition may involve ring contraction and increase the strain in the system.



Scheme 1. Synthesis of 2-mercaptopyridine-*N*-oxide stabilized stannylenes **2** and **3**, and the reaction of compound **2** with $SbCl_3$

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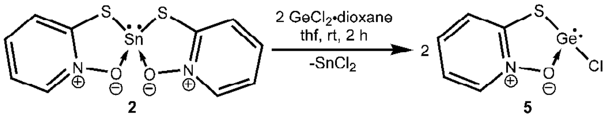
† Dedicated to (**to be added later**).

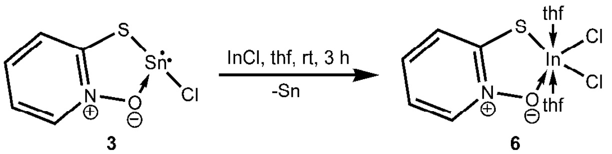
Electronic Supplementary Information (ESI) available: Details of experimental procedures, figures (S1-S3), crystallographic data, and coordinates of the optimized geometries of compounds **2**, **3**, and **5**. See DOI: 10.1039/x0xx00000x

After the isolation of compound **2**, we checked its stability under ambient conditions and found that compound **2** does not decompose in air and moisture for about a week. This may be due to the reduced electrophilicity of the Sn(II) atom as a result of high electron donation from the ligands to the vacant orbitals of tin.[9] But, we also found that white crystals of compound **2** grown in an open vessel, when kept for 3-4 weeks in the mother liquor (without separation) turned yellow. The yellow crystals were characterized through single-crystal X-ray diffraction studies as tin(IV) tetrakis(2-mpno) [$(C_5H_4NOS)_4Sn$] (**7**) (Figure S1, see the ESI). Since the low-valent tin atom in compound **2** did not undergo oxidative addition with oxygen of the ligand, it would be interesting to look at the reactivity of compound **2** with oxygen sensitive reagents. Accordingly, compound **2** was treated with equimolar $SbCl_3$ in tetrahydrofuran at room temperature. It resulted in an unexpected diantimony oxide [$\{(C_5H_4NOS)SbCl\}_2O$] (**4**) in 89% yield (Scheme 1) through an unusual reaction. HSAB interactions may be the driving force for the metathesis reaction involved as one of the steps in the conversion of compound of **2** to **4**. The by-product of this reaction was an insoluble material, and therefore, its characterization was not possible. Interestingly, compound **4** contains one Sb(III)-O(II)-Sb(III) and two Sb(III)-O(0) formal bonds. For the formation of the Sb(III)-O(II)-Sb(III) bond, the source of the oxygen atom may be the ligand (2-mpno), tetrahydrofuran, adventitious moisture, or traces of antimony oxychloride in the reagent. The reaction that affords compound **4** was also tried in $CDCl_3$ and it was found that compound **4** is the major product as seen in the reaction using tetrahydrofuran. This rules out tetrahydrofuran as the source of oxygen.



Scheme 2. Synthesis of 2-mercaptopyridine-*N*-oxide stabilized germylene **5**

Then, a reaction of compound **2** with two equivalents of $GeCl_2$·(1,4)-dioxane in tetrahydrofuran was attempted. Contrary to the reaction of compound **2** with $SbCl_3$, only metathesis reaction occurred and gave the first *N*-oxide stabilized monochlorogermylene [(2-mpno)GeCl] (**5**) in a high yield of 96% (Scheme 2). It is important to note that apart from the interesting Ge(II)-O(0) bond, the *O*,*S*-heterocyclic germylene **5** does not have any steric protection at the low-valent germanium center but still it is monomeric. This suggests that the *N*-oxide ligand acts as a strong electron donor and provides sufficient electronic stabilization to the low-valent germanium atom. To study the reactivity of monochlorostannylene **3**, it was treated with indium(I) chloride in an equimolar ratio in tetrahydrofuran at room temperature. It also gave a metathesis reaction that resulted in dichloroindium(III) complex [$(2\text{-mpno})InCl_2\cdot(thf)_2$] (**6**) with two coordinating tetrahydrofuran molecules in a high yield (95%) (Scheme 3). Dias and co-workers observed such metathesis reaction when tetracoordinate stannylene [$(Me_2ATI)_2Sn$] (**8**) was treated with indium(I) chloride.[10]



Scheme 3. Reaction of stannylene **3** with In(I)Cl

All the compounds **2**-**6** are stable at ambient temperature under a dry N_2 atmosphere. Compound **2**, apart from being stable in air and moisture (vide supra), is also stable under hydrous conditions for about a week. This was checked by adding D_2O in the solution of compound **2** in $CDCl_3$ and monitoring its ^1H NMR spectrum periodically (Figure S2, see the ESI). Compounds **2** and **4**-**6** are moderately soluble in tetrahydrofuran, dichloromethane, and chloroform. Compound **3** is sparingly soluble in tetrahydrofuran, freely soluble in dimethylsulfoxide, and poorly soluble in chloroform.

In the ^1H NMR spectrum of compound **2**, two triplets (6.86 and 7.15 ppm) and two doublets (7.55 and 8.14 ppm) were observed for protons of the pyridyl ring. A similar pattern was observed in the ^1H NMR spectra of compounds **3**-**6**. Signals for the two tetrahydrofuran molecules in compound **6** were observed at 1.89-1.93 and 3.90 ppm. In the ^{13}C NMR spectra, signals for the carbon atoms of pyridyl ring in compounds **2**-**6** were observed between 117.90-159.08 ppm. Two additional signals at 25.58 and 69.02 ppm appeared for tetrahydrofuran in compound **6**. In the ^{119}Sn NMR spectra of compounds **2** and **3**, signals at −261.0 and −288.6 ppm were observed, respectively, and these values are comparable to the one observed for a tin(IV) compound [$(2\text{-mpno})_2SnMe_2$] (**9**) (-172 ppm) containing similar ligand (i.e., 2-mpno).[11] The characterization of compound **7** in the solution state could not be done due to its insolubility in the common organic solvents.

In the molecular structure of compound **2**, the tin atom has a distorted tetragonal pyramidal geometry (Figure 1). The average O-Sn-S, O-Sn-O, and S-Sn-S bond angles are 74.6(1), 149.2(1), and 92.8(1)°, respectively. These are almost similar to the C-Sn-O (73.2(3)°), O-Sn-O (145.1(2)°), and C-Sn-Cl (91.1(2)°) bond angles in a pincer ligand stabilized five-membered heterocyclic stannylene [$\{(CH_3C_6H_4SO_2)_2C_6H_3\}SnCl$] (**10**)[12], respectively. The average O-Sn-S bond angle is almost similar to that in the tin(IV) compound $(2\text{-mpno})_2SnMe_2$ (**9**) (72.8°),[11] whereas, the O-Sn-O and S-Sn-S bond angles are smaller than those in compound **9**, (O-Sn-O: 136.7° and S-Sn-S: 77.8°). The average Sn-O bond length (2.263(2) Å) is shorter than those in the tin(II) complex **10** (2.458(7) and 2.543(7) Å) and tin(IV) compound **9** (2.383_{av} Å) which suggests a strong coordination of oxygen with tin in compound **2**. However, it is longer than that in a tin(II) compound with formal Sn=O bond (2.079(2) Å).[5f] The average Sn-S bond length (2.579(1) Å) is longer than that in a tin(IV) compound [$\{((2,4,6\text{-}Bu^t_3C_6H_2)P(S)CCl)_2SnS\}_2$] (**11**) ($2.413(1)_{av}$ Å)[13] and comparable to that in compound **9** (2.551_{av} Å). This can be attributed to the lower oxidation state of the tin atom in compound **2** (+2) than that in compounds **11** and **9** (+4).

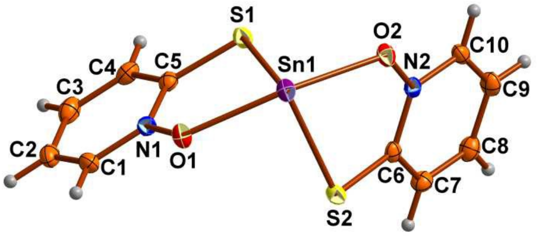


Figure 1. Molecular structure of compound **2**. Selected bond lengths (Å) and angles (°): Sn(1)-O(1) 2.265(2), Sn(1)-O(2) 2.260(2), Sn(1)-S(1) 2.578(1), Sn(1)-S(2) 2.579(1); O(1)-Sn(1)-S(1) 74.7(1), O(2)-Sn(1)-S(2) 74.6(1), O(2)-Sn(1)-O(1) 149.2(1), S(1)-Sn(1)-S(2) 92.8(1).

In compound **3**, the tin atom has a distorted trigonal pyramidal geometry (Figure S3, see the ESI). The sum of the bond angles around the tin atom is 261.5(1)°. The O-Sn-S bond angle (77.3(1)°) is almost similar to the O-Sn-N bond angle (76.7(1)°) in $[(CH_3)_2N(CH_2)_2O]_2Sn$ (**12**)[14], but, greater than the N-Sn-N bond angle (73.9(2)°) in $[(Pr^i)_2ATI]SnCl$ (**13**).[15] The Sn-O bond length (2.181(4) Å) is shorter than that in compound **2** (2.263(2) Å). The Sn-Cl bond (2.567(2) Å) is slightly longer than the same in compound **13** (2.542(2) Å). In compound **4**, both the antimony atoms have distorted tetragonal pyramidal geometry with the two Sb-Cl bonds making a dihedral angle of 98.5(1)° (Figure 2). The bridging oxygen in the Sb-O-Sb moiety has a bent geometry with Sb-O-Sb bond angle of 128.7(2)° which is smaller than that in $[(2\text{-}Me_2CH_2)C_6H_4SbCl]_2O$ (**14**) (130.7(1)°).[16] The average Sb-Cl bond length (2.558(1) Å) is similar to that in compound **14** (2.557(2) Å), whereas, the Sb-S bond length (2.476(1) Å) is in between those found in $[(2\text{-}Me_2CH_2)C_6H_4SbClS]_2$ (**15**) (2.425(1) and 2.534(1) Å).[16] The average Sb-$O_{bridging}$ bond length (1.940(4) Å) is shorter than the average Sb-O_{ligand} bond length (2.193(5) Å), but, almost similar to the same in compound **14** (1.951(3) Å).

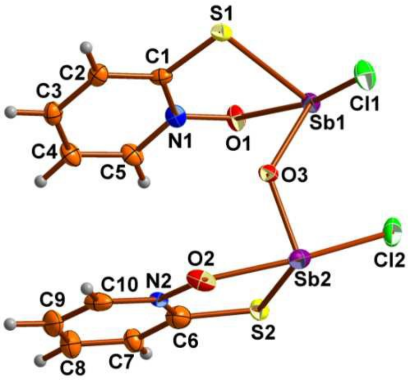


Figure 2. Molecular structure of compound **4**. Selected bond lengths (Å) and angles (°): Sb(1)-O(1) 2.226(4), Sb(2)-O(2) 2.160(5), Sb(1)-O(3) 1.949(4), Sb(2)-O(3) 1.931(4), Sb(1)-S(1) 2.483(2), Sb(2)-S(2) 2.468(2), Sb(1)-Cl(1) 2.522(2), Sb(2)-Cl(2) 2.593(2); O(1)-Sb(1)-S(1) 75.7(1), O(3)-Sb(1)-O(1) 83.9(2), O(3)-Sb(1)-Cl(1) 88.7(1), S(1)-Sb(1)-Cl(1) 87.4(1), Sb(2)-O(3)-Sb(1) 128.7(2), O(2)-Sb(2)-S(2) 77.9(1), O(3)-Sb(2)-O(2) 84.8(2), O(3)-Sb(2)-Cl(2) 87.1(1), S(2)-Sb(2)-Cl(2) 80.0(1).

Molecular structure of compound **5** is similar to that of compound **3**. In compound **5**, the sum of bond angles around the germanium(II) atom is 268.9(2)° (Figure 3). The O-Ge-S bond angle in the five-membered ring is 81.5(2)° which is comparable to the N-Ge-N bond angle (80.0(1)°) in the five-membered ring of $[(Bu^i)_2ATI]GeCl$ (**16**)[17] but smaller than the O-Ge-N bond angle (84.7(2)°) in the five-membered ring of $[(CH_3)_2N(CH_2)_2O]GeCl$ (**17**).[18] The Ge-O and Ge-Cl bonds (2.023(5) and 2.435(2) Å) are longer than the same bonds present in compound **17** (1.820(4) and 2.330(2) Å), respectively. The Ge-S bond (2.437(2) Å) is longer than that in $[(Bu^i)_2ATI]GeSPh$ (**18**) (2.367(1) Å) and $[(Bu^i)_2ATI]GeSSiMe_3$ (**19**) (2.220(1)$_{avg}$ Å).[5c,6e]

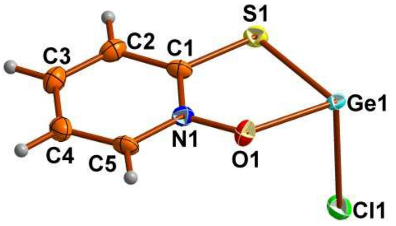
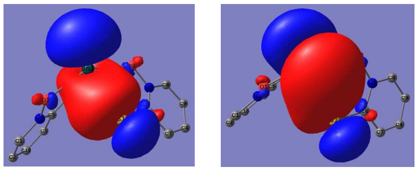


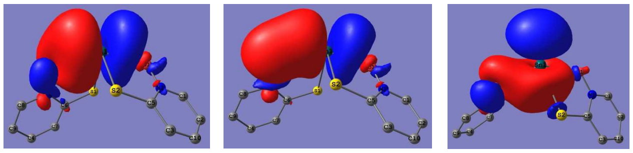
Figure 4. Molecular structure of compound **5**. Selected bond lengths (Å) and angles (°): Ge(1)-O(1) 2.023(5), Ge(1)-S(1) 2.437(2), Ge(1)-Cl(1) 2.435(2); O(1)-Ge(1)-S(1) 81.5(2), O(1)-Ge(1)-Cl(1) 90.8(1), Cl(1)-Ge(1)-S(1) 96.6(1).

Apart from the coordination of *N*-oxide to the low-valent atoms in compounds **2**-**5**, the molecular structure of compound **6** reveals that the *N*-oxide ligand can be used to stabilize the Lewis-acidic group-13 elements also in their usual oxidation state (Figure S4, see the ESI). The indium atom in compound **6** has distorted octahedral geometry with the two coordinated tetrahydrofuran molecules *trans* to each other. The O_{thf}-In-O_{thf} bond angle is almost linear (174.8(1)°), whereas the O-In-S and Cl-In-Cl bond angles are 77.9(1) and 99.9(1)°, respectively. The length of In-O_{ligand} bond (2.174(2) Å) is shorter than the average length of In-O_{thf} bonds (2.270(2) Å). The In-O_{thf} is similar to that in $[KInCl_2(OCH(CF_3)_2)_2(THF)_3]_n$ (**20**) (2.272(3) Å).[10a] The In-S bond length is 2.530(1) Å, whereas, the average In-Cl bond length is 2.423(1) Å that is slightly longer than that in $[(Me)_2ATI]_2InCl$ (**21**) (2.417(1) Å)[10b] and $[CyNC(Bu^t)NCy]_2InCl$ (**22**) (2.405(1) Å)[19], respectively. In the molecular structure of compound **7**, the tin atom bound with four ligands (2-mpno) is octacoordinate (Figure S1, see the ESI). Its bond lengths and angles are comparable with those in compounds **2** and **3.**

To get an insight of the frontier molecular orbitals of compounds **2**, **3**, and **5**, DFT calculations were carried out (Figure S5). The highest occupied molecular orbital (HOMO) of compound **2** can be described as a non-bonding orbital and is primarily composed of s-orbital of tin and p-orbitals of sulfur atoms, whereas, the lowest unoccupied molecular orbital (LUMO) is a π-type antibonding orbital diffused on the six-membered ring atoms. The HOMO-LUMO energy gap (approximated as the difference in energies of HOMO and LUMO) is 374.4 kJ/mol. In compound **3**, the non-bonding s-orbital of tin and p-orbitals of sulfur and chlorine have the major contribution to the HOMO. The LUMO is a π-antibonding orbital diffused on all the ring atoms except the tin atom. The nature of HOMO and LUMO of compound **5** resembles the corresponding orbitals of compound **3**. The HOMO-LUMO energy gaps in compounds **3** and **5** are 400.7 and 403.9 kJ/mol, respectively. Thus, the substitution of chlorine atom attached to the tin(II) atom in compound **3** by 2-mpno (to give compound **2**) reduced the HOMO-LUMO energy gap by 26.3 kcal/mol. Further, NBO second order perturbation theory analysis was performed on compound **2** to understand the nature of interactions between the ligand and divalent tin atom. A σ-interaction stabilized by 67.92 kcal/mol is seen between $sp^{6.70}$-orbital of sulfur and $sp^{8.58}$-orbital of tin (Figure 4a). Another σ-interaction between $sp^{6.70}$-orbital of sulfur and p-orbital of tin is stabilized by 32.28 kcal/mol (Figure 4b). The $sp^{2.92}$-orbital of oxygen interacts axially with p-orbital of tin and this interaction is stabilized by 29.27 kcal/mol (Figure 4c). The interaction between $sp^{0.83}$-orbital of oxygen and p-orbital of tin is stabilized by 11.46 kcal/mol (Figure 4d). Similarly, an interaction between $sp^{2.92}$-orbital of oxygen and $sp^{8.58}$-orbital of tin is also seen, which is stabilized by 10.48 kcal/mol (Figure 4e). Thus, these interactions provide the strong electronic stabilization for the divalent tin atom in compound **2**. The lone-pair of the tin atom is accommodated in an orbital ($sp^{0.12}$) that is essentially s in character.



(a) 67.92 kcal/mol (b) 32.28 kcal/mol



(c) 29.27 kcal/mol (d) 11.46 kcal/mol (e) 10.48 kcal/mol

Figure 4. NBOs of compound **2** showing interactions (along with stabilization energies) between: (a) $sp^{6.70}$-orbital of S and $sp^{8.58}$-orbital of Sn (b) $sp^{6.70}$-orbital of S and p-orbital of Sn (c) $sp^{2.92}$-orbital of O and p-orbital of Sn (d) $sp^{0.83}$-orbital of O and p-orbital of Sn and (e) $sp^{2.92}$-orbital of O and $sp^{8.58}$-orbital of Sn.

In summary, the commercially available 2-mercaptopyridine-*N*-oxide (2-mpno, **1**) was reacted with $SnCl_2$ in 2:1 and 1:1 ratios afforded the first *O,S*-heterocyclic stannylenes $(C_5H_4NOS)_2Sn$ (**2**) and $(C_5H_4NOS)SnCl$ (**3**). In these compounds, the oxygen atom of the *N*-oxide acts as a Lewis base and did not oxidatively add to the tin(II) atom in these compounds. The structural analysis and NBO studies on the stannylene **2** revealed that the oxygen atom of the *N*-oxide (2-mpno) acts as a strong σ-donor. These qualities of 2-mpno were further evident when diantimony oxide $\{(C_5H_4NOS)SbCl\}_2O$ (**4**) and the first *O,S*-heterocyclic germylene $(C_5H_4NOS)GeCl$ (**5**) were obtained as stable products from the reaction of stannylene **2** with $SbCl_3$ and $GeCl_2$·dioxane complex, respectively.

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