Syntheses and structures of N,C,N-stabilized antimony chalcogenides

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Dedicated to Prof. G. van Koten on the occasion of his 75th birthday

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Abstract

The oxidation reactions of ArSb [Ar = 2,6-(HC=N-*t*-Bu)₂C₆H₃] with S₈, grey Se and Te as well as E₂Ph₂ (E = S, Se, Te) are demonstrated. The reactions of ArSb with elemental sulfur and selenium occurred at elevated temperatures and yielded ArSbE (E = S, **1**; Se **2**), whereas the reactions with E₂Ph₂ proceeded at room temperature with subsequent formation of the corresponding insertion complexes ArSb(EPh₂)₂ (E = S **3**; Se **4**). In addition, ArSb(TePh)₂ (**5**) was formed at very low temperature and showed a temperature-dependent reversible equilibrium with ArSb and Te₂Ph₂ between – 80 °C to 20 °C. The formation and structure of compounds **1** – **4**, which were isolated in good yields, are assigned through multinuclear NMR (¹H, ¹³C, ⁷⁷Se), IR spectroscopy and microanalyses data. In addition, the molecular structures of **2** – **4** are further confirmed by single crystal X-ray diffraction studies.

Keywords: Pincer ligand, chalcogens, subvalent compounds, oxidation

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1. Introduction

The chemistry of organoantimony(I) compounds has been continuously studied for decades. They were mainly synthesized by reduction reactions of organoantimony(III)dihalides of the general type RSbX_2 ($\text{X} = \text{C}, \text{Br}, \text{I}$) with alkali and alkaline earth metals. For a long time only oligomeric species $(\text{RSb})_n$ ($\text{R} = \text{alkyl or aryl}, n = 3 - 6$) could be isolated and their structures were determined by single crystal X-ray diffraction. Their solution structures are often complicated by present ring-ring equilibrium as was demonstrated by in situ NMR spectroscopic studies.[1] The development of bulky ligands providing sufficient kinetic protection of reactive centers, e.g. by the groups of Power or Tokitoh,[2,3] also allowed the isolation of the first examples of distibenes containing a $\text{Sb}=\text{Sb}$ double bond.[4] In addition, one of us recently succeeded in the synthesis of the Ga-substituted distibene $[\text{L}(\text{NMe}_2)\text{Ga}]_2\text{Sb}_2$ ($\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]_2$), which was obtained from the reduction reaction of $\text{Sb}(\text{NMe}_2)_3$ with the corresponding monovalent gallanediyl complex LGa . [5] Distibines of the general type Sb_2R_4 revealed an interesting reactivity including oxidation with elemental chalcogens, leading to a rich spectrum of antimony chalcogenides,[6] as well as dichalcogenanes $\text{E}_2\text{R}'_2$ ($\text{E} = \text{S}, \text{Se}, \text{Te}; \text{R}' = \text{alkyl}, \text{aryl}$), leading to compounds of the general type $\text{R}_2\text{Sb-ER}'$, [7] which have been studied due to their thermochromic behavior. Nevertheless, the stabilization of terminal $\text{Sb}=\text{E}$ bonds ($\text{E} = \text{S}, \text{Se}, \text{Te}$) was not successful even with the use of sterically demanding ligands. However, the elusive monomeric stibinidenes RSb have been synthesized quite recently and the presence of N,C,N-pincer type ligand was crucial for their stabilization.[8] Bertrand and Hudnall independently showed that stibinidenes may be also stabilized using carbene ligands,[9] but their chemistry was not, to the best of our knowledge, further developed. By contrast, we have demonstrated in a preliminary communication that N,C,N-chelated stibinidenes are promising ligands for transition metals[10] and we have also demonstrated, that N,C,N-pincer ligands are able to support terminal $\text{Sb}=\text{E}$ bonds.[11]

Our long term interest in the reactivity of monovalent, monomeric stibinidenes of the general type RSb prompted us to investigate the oxidation reactions of stibinidene ArSb (**1**) [$\text{Ar} = 2,6\text{-(HC=N-}t\text{-Bu)}_2\text{C}_6\text{H}_3$] with elemental chalcogens E ($\text{E} = \text{S}, \text{Se}, \text{Te}$) to prove their potential to trap terminal $\text{Sb}=\text{E}$ bonds. Furthermore, its reactivity toward dichalcogenanes E_2Ph_2 ($\text{E} = \text{S}, \text{Se}$) is included, because the reactivity of isolated stibinidenes with dichalcogenanes E_2Ph_2 has not been investigated to date despite these dichalcogenanes showed interesting reactivity with many low-valent main group elements.[12] For instance, reactions of the comparable Bi(I) complex $\text{Ar}''\text{Bi}$ [$\text{Ar}'' = 2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$] as well as Sb(I) complex $\text{Ar}'''\text{Sb}$ ($\text{Ar}''' = o\text{-}$

(CH=N-2,6-*i*-Pr₂-C₆H₃)]C₆H₄), which adopts a tetrameric form in the solid state, with E₂Ph₂ (E = S, Se, Te) occurred with insertion into the E-E bond and subsequent formation of Ar^{''}Bi(EPh)₂ and Ar^{'''}Sb(EPh)₂, [12a] respectively. These reactions occurred with formation of the ArSb(III)E complexes containing terminally bonded chalcogenides as well as with insertion of ArSb into the E-E bond and formation of ArSb(EPh)₂, respectively.

2. Results and Discussion

The oxidation reactions of ArSb [10] [L = 2,6-(HC=N-*t*-Bu)₂C₆H₃] with S₈ and grey Se at 80-85 °C yielded the chalcogenide derivatives ArSbE (E = S, **1**; Se **2**) as red crystalline solids in moderate yields, whereas the analogous reaction with elemental Te did not yield the Te-analogue of **1** and **2**. Furthermore, ArSb was found to readily insert into the E-E bond of E₂Ph₂ (E = S, Se) at ambient temperature, resulting in the formation of ArSb(EPh)₂ (E = S **3**; Se **4**) in 73-79 % yield. In contrast, we were not able to isolate the Te-analogue ArSb(TePh)₂ (**5**) of the equimolar reaction of ArSb with Te₂Ph₂ in C₆D₆ at ambient temperature. Instead, the resulting solution only showed broad signals of the Ar ligand in the ¹H NMR spectrum (Figure S19). To further investigate this reaction in more detail, a variable temperature ¹H NMR experiment was carried out with the 1:1 mixture of ArSb and Te₂Ph₂ in toluene-*d*₈ between – 80 °C to 80 °C (Figure 1). The ¹H NMR spectrum of the reaction mixture showed only the signals corresponding to **5** below – 60 °C whereas a mixture of ArSb, Te₂Ph₂ and **5** was observed between – 40 °C to 20 °C. At higher temperatures there are no interaction between ArSb and Te₂Ph₂.

We also investigated the reaction of ArSb with E₂Et₄ (E = Sb, Bi) in order to prove if this might allow a controlled extension of the weakly bonded E-E unit by insertion of one ArSb moiety as was previously observed in analogous reactions of group 13 diyls LM (M = Al, Ga, In) with the distibine Sb₂Et₄ and dibismuthine Bi₂Et₄. [13] Unfortunately, these reactions completely failed, which is in remarkable contrast to previously described reactions of cyclostibines with distibines, which resulted in the formation of catenastibines. However, these were found to be only stable in solution. [1b, 1m]

Scheme 1. Synthesis of **1** – **4**.

Figure 1. Variable temperature ^1H NMR experiment of an equimolar mixture of ArSb and Te_2Ph_2 in $\text{toluene-}d_8$. The signals corresponding to HC=N- and $p\text{-C}_6\text{H}_3$ groups of ArSb (*) and **5** (#) are marked.

Compounds **1** – **4** are slightly sensitive towards air- and moisture but can be stored at room temperature under argon atmosphere for several days without any decomposition. Compounds **1** and **2** are only poorly soluble in benzene and toluene, whereas **3** and **4** dissolve well. The ^1H NMR spectra of **1** – **4** in C_6D_6 exhibit characteristic resonances for the *t*-Bu [singlet at 1.38 (**1**), 1.41 (**2**), 1.30 (**3**), 1.33 (**4**) ppm], HC=N- [singlet at 8.12 (**1**), 8.17 (**2**), 8.03 (**3**), 8.06 (**4**) ppm], and C_6H_3 [multiplet at 7.21 (**1**), 7.22 (**2**), 7.37 (**3**), 7.49 (**4**) ppm] groups. In addition, **3** and **4** show additional resonances for the S-*Ph* (multiplet 6.83 – 6.99 ppm) and Se-*Ph*

(multiplet 6.89 – 7.14 ppm). The ^{13}C NMR spectra of **1** – **4** in C_6D_6 exhibit the distinct $\text{HC}=\text{N}$ - carbon signals in the high frequency range [159.26 (**1**); 159.78 (**2**); 160.53 (**3**); 160.74 (**4**) ppm], while the *t*-Bu carbons appear at lower frequencies [31.66, 61.20 (**1**); 31.90, 61.47 (**2**); 31.47, 61.04 (**3**); 31.65, 61.34 (**4**) ppm]. A solution of **2** in C_6D_6 surprisingly did not show any signal in the ^{77}Se NMR spectrum, while comparable compounds $\text{Ar}'\text{SbSe}$ [$\text{Ar}' = 2,6\text{-(C(Me)=N-2,6-Me}_2\text{-C}_6\text{H}_3)_2\text{C}_6\text{H}_3$] and $\text{Ar}''\text{SbSe}$ [$\text{Ar}'' = 2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$] show sharp resonances at -140 ppm [11c] and -197 ppm,[11a] respectively. The Ar ligand retains its tridentate mode of coordination towards Sb in **1** – **4** and NMR and elemental analysis data of **1** – **4** are consistent with the expected formulae.

The molecular structures of **2** – **4** were confirmed by single crystal X-ray diffraction analysis and the solid state structures are shown in Figures 2 – 4 along with selected geometric parameters. Single crystals of **2** were formed while slowly cooling the warm benzene solution of **2** to room temperature, whereas crystals of **3** and **4** were obtained by slow diffusion of *n*-hexane into saturated toluene solutions at 0 °C. **2** and **3** crystallize in the monoclinic space groups $P2_1/n$ and $C2/c$ and **4** crystallizes in the triclinic space group $P-1$. The crystal of the **3** contains two independent molecules in the unit cell with very similar molecular parameters and one of the molecules is depicted in Figure 3 and discussed below.

The molecular structure of **2** closely resembles that of $\text{Ar}'\text{SbSe}$ [11c] and $\text{Ar}''\text{SbSe}$. [11a] The Sb atoms in both compounds adopt severely distorted trigonal bipyramidal coordination geometries with the *ipso*-C, Se and the electron lone pair of the Sb in the equatorial positions and two nitrogen atoms in the axial positions, even though the N-Sb-N bond angle [144.22(4)°] largely deviates from linearity due to significant ligand rigidity. In contrast, the $\text{C}_{ipso}\text{SbE}_2$ moieties in **3** and **4**, possess T-shaped geometry as was previously observed in ArMX_2 (M = Sb, Bi; X = halides).[14] The overall geometry at the Sb center in **3** and **4** is best described as distorted square pyramidal, with the *ipso*-C adopting the apical position. The EPh moieties in **3** and **4** are bonded to the Sb atoms in trans positions and the E-Sb-E angles of **3** [S(12)-Sb(1)-S(11) 161.897(13)°] and **4** [Se(2)-Sb(1)-Se(1) 163.431(6)°] are close to linear. The Sb-E bond distances of **3** [Sb(1)-S(11) 2.6724(5) Å, Sb(1)-S(12) 2.6603(5) Å] and **4** [Sb(1)-Se(2) 2.7861(3) Å, Sb(1)-Se(1) 2.8387(3) Å] are within the typical range observed for Sb-E single bonds, while the Sb-Se bond length in **2** [2.4497(4) Å], which is comparable to those reported for the analogous compounds $\text{Ar}'\text{SbSe}$ [2.4329(5) Å][11c] and $\text{Ar}''\text{SbSe}$ [2.4396(7) Å],[11a] is significantly shorter than the sum of the covalent radii (Sb = 1.40 Å; Se = 1.16 Å).[15] The Sb-N bond distances in **2** – **4** [2.3909(11) Å, 2.5488(11) Å, **2**;

2.3964(14) Å, 2.4564(14) Å and 2.3881(14), 2.4455(14) Å, **3**; 2.3946(11) Å, 2.4427(11) Å, **4**] are comparable to those observed in Ar'Sb [2.346(3) Å, 2.352(3) Å], Ar'SbSe [2.395(2) Å, 2.393(2) Å] and Ar''SbSe [2.461(3), 2.518(3) Å], indicating the presence of strong intramolecular (dative) Sb-N interactions in **2** – **4**, except for one Sb-N bond in **2** [2.5488(11) Å], which is elongated compared to the other Sb-N bond lengths. The N-Sb-N angles in **2** – **4** [144.22(4)° (**2**), 145.64(4)° (**3**), 145.49(4)° (**4**)] are also comparable to those observed in Ar'SbSe [145.01(8)°] and Ar''SbSe [145.14(12)°] and more acute than the E-Sb-E angles of **3** and **4** [161.897(13), E = S, **3**; 163.431(6), E = Se, **4**]. In addition, the C(1)-Sb(1)-Se(2) bond angle (99.49(3)°) in **2** deviates significantly from the ideal value 120° as was previously observed for Ar'SbSe [102.90(11)°] and Ar''SbSe [105.96(7)°], and the two fused five-membered SbC₃N rings and the Ph backbone in **2** – **4** are planar [rms deviation from best plane 0.0450 Å(**2**), 0.0229 and 0.0446 Å (**3**), 0.0345 Å (**4**)].

Figure 2. Solid state structure of **2** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity.

Figure 3. Solid state structure of **3** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity. Only one independent molecules displayed.

Figure 4. Solid state structure of **4** (thermal ellipsoids are shown at 50% probability levels); H atoms and solvent molecule are omitted for clarity.

Table 1: Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] of **2–4**.

	2	3	4
Sb–C	2.1285(12)	2.1143(15)	2.1093(13)
		2.1077(15)	
Sb–N	2.3909(11), 2.5488(11)	2.3964(14), 2.4564(14)	2.3946(11), 2.4427(11)
		2.3881(14), 2.4455(14)	
Sb–E	2.4497(4)	2.6603(5), 2.6724(5)	2.7861(3), 2.8387(3)
		2.6557(5), 2.6880(5)	
N–C _s	1.2867(16), 1.2801(17)	1.279(2), 1.279(2)	1.2772(19), 1.2806(18)
		1.285(2), 1.279(2)	

N–C _R	1.4946(16), 1.4802(16)	1.496(2), 1.490(2)	1.4902(18), 1.4969(16)
		1.489(2), 1.486(2)	
C–Sb–N	73.55(4), 70.90(4)	73.17(5), 72.46(5)	73.32(4), 72.44(5)
		72.58(5), 73.56(5)	
C–Sb–E	99.49(3)	79.17(4), 83.32(4)	81.93(3), 82.04(3)
		78.73(4), 80.96(4)	
N–Sb–N	144.22(4)	145.64(4)	145.49(4)
		146.13(4)	
N–Sb–E	92.99(3), 96.68(3)	82.53(4), 91.14(4), 88.06(4), 87.94(4)	81.67(3), 89.48(3), 89.73(3), 89.67(3)
		83.14(4), 89.87(4), 85.69(4), 89.49(4)	
E–Sb–E	–	161.897(13)	163.431(6)
		158.900(13)	
C–N–C	121.98(11), 122.75(11)	122.02(15), 120.61(14)	122.62(11), 119.66(11)
		121.14(14), 123.50(14)	
Sb–N–C _S	112.27(8), 110.55(8)	112.66(11), 111.69(11)	111.66(9), 112.12(9)
		111.51(11), 112.13(10)	
Sb–N–C _R	125.72(8), 126.69(8)	125.32(10), 127.28(10)	125.71(9), 128.06(8)
		127.09(10), 124.36(10)	

C_S Carbon atom of the side-arm of the ligand, C_R Carbon atom of the residual group of the ligand.

The oxidation of low-valent main group metal complexes with elemental chalcogens is well established and has been observed in reactions of monovalent and divalent group 13 ([MR]_x, M₂R₄; M = Al, Ga, In), group 14 ([M'R]_x, M'R₂; M' = Ge, Sn) and group 15 metal complexes ([M''R]_x, M''₂R₄; M = Sb, Bi).[16] While most of these reactions yielded oligomeric, chalcogen-bridged compounds, only a very few examples containing terminal-bonded chalcogen atoms with a formal metal-chalcogen double bond are known.[2b] These compounds almost exclusively contained sterically extremely bulky organic substituents or chelating groups. The easy formation of **1** and **2** as described herein now further expands the knowledge on compounds of the desired type and allows to study their reactivity in the future in more detail. Initial oxidation reactions of **1** and **2** were performed with an excess of sulfur and selenium, but unfortunately, these reactions did not yield the corresponding stiboranes of the general type ArSb(E)₂.

In addition, dichalcogenanes E₂R₂ are also suitable oxidizing reagents in reactions with monovalent group 13 and divalent group 14 metal complexes. These reactions often occurred at milder reaction conditions compared to reactions with elemental chalcogens, most likely

since the dichalcogenanes are readily soluble in organic solvents and therefore the reactions take place in homogeneous phase rather than at the solution-solid interfaces as is the case for reactions with insoluble chalcogens. The reactions typically proceeded with insertion of the low-valent metal complex into the E-E bond, yielding complexes of the type $\text{RM}(\text{ER})_2$ ($\text{M} = \text{Al, Ga, In}$)[17] and $\text{R}_2\text{M}'(\text{ER})_2$ ($\text{M}' = \text{Ge, Sn}$).[18] We herein demonstrated that monovalent stibinidenes RSb also easily react with insertion into the E-E bond ($\text{E} = \text{S, Se}$). While **3** and **4** were isolated at crystalline solids, which are thermally stable in solution and in their isolated crystalline form at ambient temperature, the corresponding tellurium derivative $\text{ArSb}(\text{TePh})_2$ **5** was only formed in solution at very low temperature ($-60\text{ }^\circ\text{C}$), whereas it was found to decompose to the starting reagents ArSb and Te_2Ph_2 upon heating to ambient temperature. Interestingly, $\text{ArSb}(\text{TePh})_2$ (**5**) showed a reversible temperature-dependent equilibrium with ArSb and Te_2Ph_2 between $-80\text{ }^\circ\text{C}$ to $20\text{ }^\circ\text{C}$. These findings clearly result from the decreasing Sb-E bond strength with increasing atomic number of the chalcogen atom.

In summary, chalcogenide complexes of the general form $\text{ArSb}=\text{E}$ and $\text{ArSb}(\text{EPh})_2$ ($\text{E} = \text{S, Se}$) containing either Sb-E single or Sb=E double bonds were synthesized by reaction of ArSb with elemental chalcogenes E or E_2Ph_2 and partly structurally characterized. In contrast, the corresponding tellurium derivative $\text{ArSb}=\text{Te}$ did not form while reacting LSb with elemental Te , whereas $\text{ArSb}(\text{TePh})_2$ (**5**) can only be synthesized at low reaction temperatures due to its tendency to form a reversible temperature-dependent equilibrium with ArSb and Te_2Ph_2 between $-80\text{ }^\circ\text{C}$ to $20\text{ }^\circ\text{C}$. Furthermore, the reaction with E_2Et_4 ($\text{E} = \text{Sb, Bi}$) also did not occur with insertion into the weak E-E bond as was previously observed in analogous reactions with LM ($\text{M} = \text{Al, Ga, In}$) even under different reactions conditions.

3. Experimental Section

3.1. General Considerations

The reactions were performed using standard Schlenk and glove-box techniques under purified argon atmosphere. Benzene was carefully dried over sodium under argon and degassed prior to use. Hexane and toluene were collected from M-Braun solvent purification system. Deuterated solvents were stored over activated molecular sieves ($4\text{ \AA}$) and degassed prior to use. Karl Fischer titration of the dry solvents showed values below 3 ppm. Elemental sulfur, selenium and tellurium powders and E_2Ph_2 ($\text{E} = \text{S, Se, Te}$) are commercially available (Acros Organics; Sigma-Aldrich) and were used as received, while E_2Et_4 ($\text{E} = \text{Sb, Bi}$) [19] and ArSb were prepared according to literature methods.[10] ^1H (300 MHz), $^{13}\text{C}\{^1\text{H}\}$ (75.5

MHz) and $^{77}\text{Se}\{^1\text{H}\}$ (57 MHz) NMR (δ in ppm) spectra were recorded using a Bruker Avance DPX-300 spectrometer and the spectra were referenced to internal $\text{C}_6\text{D}_5\text{H}$ (^1H : $\delta = 7.154$; ^{13}C : $\delta = 128.39$) and ^{77}Se NMR spectra were referenced to tetramethylsilane.[20] Microanalyses were performed at the elemental analysis laboratory of the University of Duisburg-Essen. IR spectra were measured in an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The FT-IR spectrometer was placed in an argon-filled glovebox to avoid any oxidation or hydrolysis of the samples during measurement.

3.1. Synthesis of 1 - 4

Synthesis of ArSbS (1). In a schlenk tube, a mixture of ArSb (80 mg, 0.219 mmol) and S_8 (7 mg, 0.027 mmol) in 0.5 mL of toluene was heated at 85 °C for 24 h. The solution was slowly cooled to room temperature and allowed to stand at this temperature for 1 day to afford red-orange crystals of **1**. The crystals were washed with 1 mL of benzene. Yield: 56 mg (0.141 mmol, 64 %). Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{SSb}$: C, 48.38; H, 5.84; N, 7.05; S, 8.07. Found: C, 48.80; H, 5.47; N, 6.92; S, 8.17 %. IR (neat): ν 2966 (w), 2924 (w), 2894 (w), 2852 (w), 1615 (w), 1555 (w), 1459 (w), 1375 (w), 1225 (w), 1201 (m), 1063 (w), 1020 (w), 960 (w), 912 (w), 816 (w), 780 (w), 708 (w), 636 (w), 522 (w), 492 (w), 390 (s) cm^{-1} . ^1H NMR (C_6D_6 , 300 MHz): δ 1.38 (s, 18H, $\text{NC}(\text{CH}_3)_3$), 7.21 (m, 3H, *m*, *p*- C_6H_3), 8.12 (s, 2H, - $\text{CH}=\text{N}^t\text{Bu}$). ^{13}C NMR (C_6D_6 , 75.5 MHz): δ 31.66 ($\text{NC}(\text{CH}_3)_3$), 61.20 ($\text{NC}(\text{CH}_3)_3$), 132.43 (C_6H_3), 137.92 (C_6H_3), 140.99 (C_6H_3), 159.26 (- $\text{CH}=\text{N}^t\text{Bu}$).

Synthesis of ArSbSe (2). In a schlenk tube, a mixture of ArSb (50 mg, 0.137 mmol) and Se (10 mg, 0.127 mmol) in 0.5 mL of benzene was heated at 80 °C for 24 h. The solution was slowly cooled to room temperature and allowed to stand at this temperature for 1 day to afford red crystals of **2**. The crystals were washed with 1 mL of benzene. Yield: 36 mg (0.081 mmol, 59 %). Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{SbSe}$: C, 43.27; H, 5.22; N, 6.31. Found: C, 43.09; H, 5.34; N, 6.42 %. IR (neat): ν 2966 (w), 2925 (w), 2901 (w), 2860 (w), 1612 (w), 1565 (w), 1459 (w), 1370 (w), 1311 (w), 1234 (m), 1187 (m), 1116 (m, br), 1063 (m), 980 (m), 951 (w), 910 (w), 786 (m), 744 (w), 715 (m), 644 (w), 520 (w), 490 (w) cm^{-1} . ^1H NMR (C_6D_6 , 300 MHz): δ 1.41 (s, 18H, $\text{NC}(\text{CH}_3)_3$), 7.18-7.27 (m, 3H, *m*, *p*- C_6H_3), 8.17 (s, 2H, - $\text{CH}=\text{N}^t\text{Bu}$). ^{13}C NMR (C_6D_6 , 75.5 MHz): δ 31.90 ($\text{NC}(\text{CH}_3)_3$), 61.47 ($\text{NC}(\text{CH}_3)_3$), 132.48 (C_6H_3), 140.95 (C_6H_3), 159.78 (- $\text{CH}=\text{N}^t\text{Bu}$). ^{77}Se NMR (C_6D_6 , 57 MHz): No signal was observed.

Synthesis of ArSb(SPh)₂ (3). ArSb (50 mg, 0.137 mmol) in 0.5 mL of toluene was added dropwise to the well-stirred toluene (0.5 mL) solution of S_2Ph_2 (30 mg, 0.137 mmol) and the

stirring was continued for 1 h at room temperature. The resulting brown solution was layered with 0.5 mL of hexane and kept at 0 °C for 3 days to yield red crystals of **3**. Yield: 58 mg (0.099 mmol, 73 %). Anal. Calcd. for C₂₈H₃₃N₂S₂Sb: C, 57.64; H, 5.70; N, 4.80; S, 10.99. Found: C, 57.49; H, 5.78; N, 4.92; S, 11.10 %. IR (neat): ν 3054 (w), 2960 (w), 2925 (w), 2860 (w), 1660 (w), 1612 (w), 1571 (m), 1471 (m), 1429 (w), 1370 (w), 1234 (w), 1193 (w), 1122 (w), 1075 (m), 1051 (m), 1022 (m), 957 (w), 909 (w), 797 (m), 732 (m), 685 (m), 472 (w), 425 (w) cm⁻¹. ¹H NMR (C₆D₆, 300 MHz): δ 1.30 (s, 18H, NC(CH₃)₃), 6.83-6.99 (m, 10H, -SPh), 7.37 (m, 3H, *m*, *p*-C₆H₃), 8.03 (s, 2H, -CH=N*t*-Bu). ¹³C NMR (C₆D₆, 75.5 MHz): δ 31.47 (NC(CH₃)₃), 61.04 (NC(CH₃)₃), 123.19, 128.93, 129.67, 133.06, 134.04, 139.48, 146.05, 153.70 (C₆H₃ & -S-C₆H₅), 160.53 (-CH=N*t*-Bu).

Synthesis of ArSb(SePh)₂ (4). **4** was prepared using the same procedure as described for **3** by reaction of ArSb (50 mg, 0.137 mmol) and Se₂Ph₂ (43 mg, 0.137 mmol). Yield: 73 mg (0.108 mmol, 79 %). Anal. Calcd. for C₂₈H₃₃N₂SbSe₂: C, 49.66; H, 4.91; N, 4.14. Found: C, 49.90; H, 4.87; N, 4.35 %. IR (neat): ν 3066 (w), 2972 (w), 2924 (w), 2860 (w), 1612 (w), 1565 (w), 1465 (m), 1429 (w), 1370 (w), 1234 (w), 1193 (w), 1063 (m), 1022 (w), 980 (w), 957 (w), 910 (w), 786 (w), 732 (m), 691 (m), 661 (m), 508 (w), 461 (m) cm⁻¹. ¹H NMR (C₆D₆, 300 MHz): δ 1.33 (s, 18H, NC(CH₃)₃), 6.89-7.14 (m, 10H, -SePh), 7.48-7.51 (m, 3H, *m*, *p*-C₆H₃), 8.06 (s, 2H, -CH=N*t*-Bu). ¹³C NMR (C₆D₆, 75.5 MHz): δ 31.65 (NC(CH₃)₃), 61.34 (NC(CH₃)₃), 124.11, 126.03, 128.52, 128.84, 129.66, 133.18, 136.41, 137.57, 139.45 (C₆H₃ & -Se-C₆H₅), 160.74 (-CH=N*t*-Bu). ⁷⁷Se NMR (C₆D₆, 57 MHz): δ 318.15.

3.3. X-ray Structure Solution and Refinement.

Crystals of **2** - **4** were mounted on nylon loops in inert oil. Crystallographic data of **2** - **4** are summarized in Table 1. Figures 2 - 4 show the solid state structures of **2** - **4** including selected bond lengths and angles. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated MoK α radiation, λ = 0.71073 Å) at 100(1) K. The structures were solved by Direct Methods (SHELXS-97)[21] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2014).[22] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Baker AXS APEX2.). Non-hydrogen atoms were refined anisotropically where possible and hydrogen atoms were refined using a riding model or rigid methyl groups. **4** contains a toluene molecules disordered over a centre of inversion.

Crystallographic data of **2** - **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1520205 (**2**), 1520206 (**3**), 1520207 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internal) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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