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Cycloaddition of di(2-pyridyl) diselenide to styrene activated with antimony pentachloride

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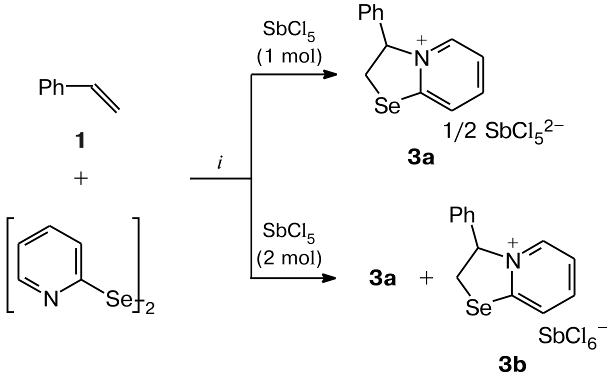
A reaction of styrene with the di(2-pyridyl) diselenide—antimony pentachloride system furnishes 2,3-dihydro[1,3]selenazolo[3,2-*a*]pyridinium chloroantimonates(III) and (V), the products of cycloaddition of the selenylating agent at the multiple bond.

Key words: di(2-pyridyl) diselenide, antimony pentachloride, alkenes, polar cycloaddition, X-ray diffraction analysis.

It is known that diorganyl diselenides can be activated in the reactions with alkenes with such oxidants as ammonium persulfate,[1—6] *m*-nitrobenzenesulfonyl peroxide,[7], diacetoxyiodobenzene,[8] tin(IV),[9,10] copper(II),[11] lead(IV),[11] and cerium(IV)[12] salts. These reactions usually result in the formation of 1,2-addition products of seleno-centered electrophiles generated under indicated conditions to alkenes, the former are solvoadducts, products of conjugated addition of various nucleophilically active additives, 1,2-bis(selenides), or products of cyclization with the ring closure involving an electron-donating atom from the functional group of the unsaturated compound. However, it should be noted that these studies were limited only to the reactions of such simple model reactants, as dimethyl diselenide and diphenyl diselenide.

In the present work, we for the first time studied reactions of styrene (**1**) with di(2-pyridyl) diselenide (**2**) bearing potentially nucleophilic nitrogen atom in the hetaryl fragment, whereas antimony pentachloride was used as an activating additive. It was found that the reaction of alkene **1** with the antimony pentachloride—diselenide **2** system in dichloromethane at −40 °C leads to the products of cyclization with the ring closure involving nitrogen atom of the pyridine ring in the starting reactant. When the ratio alkene : diselenide : antimony pentachloride is 2 : 1 : 1, the reaction leads to the formation of bis(3-phenyl-2,3-dihydro[1,3]selenazolo[3,2-*a*]pyridinium) pentachloroantimonate(III) (**3a**) in virtually quantitative yield (Scheme 1). When the ratio alkene : diselenide : antimony pentachloride is 2 : 1 : 2, 3-phenyl-2,3-dihydro[1,3]selenazolo[3,2-*a*]pyridinium hexachloroantimonate(V) (**3b**) was obtained in 63% yield together with the salt **3a** (32% yield).

Scheme 1



i. CH_2Cl_2, −40 °C.

The structures of compounds **3a** and **3b** were established by X-ray crystallography (Figs 1 and 2). Selected bond distances and bond angles are given in Tables 1 and 2.

Compound **3a** and **3b** are the salts containing pyridinium cation and $SbCl_5^{2-}$ and $SbCl_6^{-}$ anions, respectively. The five-membered heterocycle of the cation adopts the

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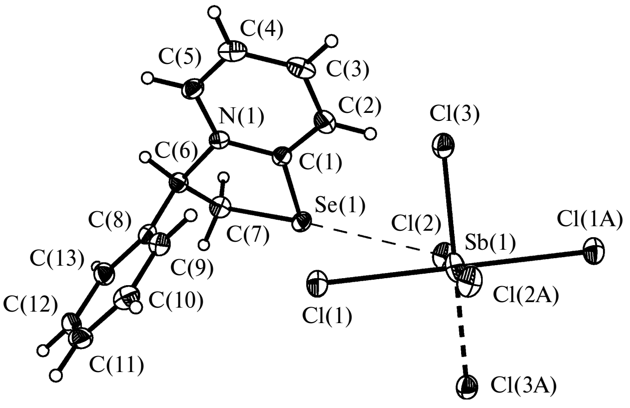


Fig. 1. Molecular structure of compound **3a**. The dashed line in bold shows an alternative position of the vertex of the tetragonal-pyramidal $SbCl_5^{2-}$ anion, the normal dashed line, the short Se...Cl contact.

envelop conformation, with the C(7) carbon atom coming out of the plane, passing through the rest of the atoms of the ring, by 0.597(3) and 0.611(2) Å, respectively. The phenyl substituent occupies the most energetically preferable equatorial position. The $SbCl_5^{2-}$ anions in compound **3a** adopt slightly distorted tetragonal-pyramidal configuration (the bond angles Cl—Sb—Cl are within 86.94(3)—93.06(3)°). The equatorial bond distances between the antimony atom and the chlorine atoms placed in the pyramid base (an average value 2.6011(5) Å) are considerably longer than the length of the axial bond between the antimony atom and the chlorine atom in its vertex (2.2947(11) Å). Such a structure is characteristic[13—16] of the isolated $SbCl_5^{2-}$ anion and is explained by the effect of stereochemically active lone pair of electrons on the antimony(III) atom occupying *trans*-position with respect to the short (axial) Sb—Cl bond and supplementing the antimony(III) atom surrounding to the octahedral. The $SbCl_6^{-}$ anions in compound **3b** have slightly distorted octahedral structure (the average bond distances Sb—Cl are 2.3670(4) Å, the bond angles Cl—Sb—Cl are within 89.116(15)—91.507(14)°).

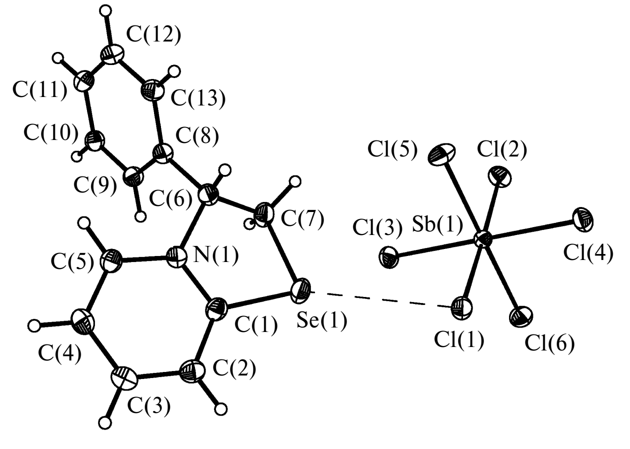


Fig. 2. Molecular structure o compound **3b**. The dashed line shows the short Se...Cl contact.

Table 1. Selected bond distances (*d*) in the crystals of compounds **3a** and **3b**

d/Å	**3a**	**3b**
Se(1)—C(1)	1.875(2)	1.876(2)
Se(1)—C(7)	1.965(2)	1.959(2)
N(1)—C(1)	1.346(3)	1.351(2)
N(1)—C(5)	1.360(3)	1.358(2)
N(1)—C(6)	1.485(3)	1.511(2)
C(6)—C(7)	1.521(3)	1.530(2)
Sb(1)—Cl(1)	2.6046(5)	2.3611(4)
Sb(1)—Cl(2)	2.5976(5)	2.3709(4)
Sb(1)—Cl(3)	2.2947(11)	2.3682(4)
Sb(1)—Cl(4)*	2.6046(5)	2.3576(4)
Sb(1)—Cl(5)*	2.5976(5)	2.3796(4)
Sb(1)—Cl(6)	—	2.3647(4)

* In the structure of **3a**, the chlorine atoms Cl(4) and Cl(5) are equivalent to the chlorine atoms Cl(1) and Cl(2), respectively, *i.e.* to the atoms Cl(1A) and Cl(2A).

The selenium atoms in compounds **3a** and **3b** form additional short contacts with the chlorine atoms of the anions with the distances 3.4923(6) Å (Se(1)...Cl(2)) and 3.4247(4) Å (Se(1)...Cl(1) [$-x$, $1-y$, $1-z$]), respectively, thus acquiring a distorted three-coordinated surround-

Table 2. Selected bond angles (ω) in the crystals of **3a** and **3b**

ω/deg	**3a**	**3b**
C(1)—Se(1)—C(7)	85.81(9)	85.760(6)
Se(1)—C(1)—N(1)	113.30(2)	113.690(11)
Se(1)—C(7)—C(6)	105.18(13)	105.750(10)
C(1)—N(1)—C(6)	116.20(2)	116.080(12)
N(1)—C(6)—C(7)	106.00(2)	105.640(12)
Cl(1)—Sb(1)—Cl(2)	89.28(2)	178.693(14)
Cl(1)—Sb(1)—Cl(3)	89.24(3)	89.599(13)
Cl(1)—Sb(1)—Cl(4)*	180.00	89.430(13)
Cl(1)—Sb(1)—Cl(5)*	90.72(2)	89.974(14)
Cl(1)—Sb(1)—Cl(6)	–	90.639(14)
Cl(2)—Sb(1)—Cl(3)	86.94(3)	89.451(14)
Cl(2)—Sb(1)—Cl(4)*	90.72(2)	91.507(14)
Cl(2)—Sb(1)—Cl(5)*	180.00	89.116(15)
Cl(2)—Sb(1)—Cl(6)	–	90.270(15)
Cl(3)—Sb(1)—Cl(4)*	90.76(2)	178.758(15)
Cl(3)—Sb(1)—Cl(5)*	93.06(2)	89.311(15)
Cl(3)—Sb(1)—Cl(6)	–	90.628(15)
Cl(4)*—Sb(1)—Cl(5)*	89.28(2)	89.914(15)
Cl(4)—Sb(1)—Cl(6)	–	90.158(15)
Cl(5)—Sb(1)—Cl(6)	–	179.383(15)

* In the structure of **3a**, the chlorine atoms Cl(4) and Cl(5) are equivalent to the chlorine atoms Cl(1) and Cl(2), respectively, *i.e.* to the atoms Cl(1A) and Cl(2A).

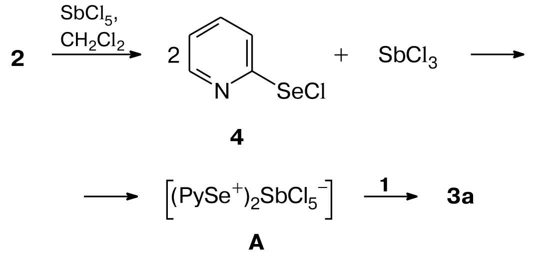
ing of the *swing* type. Due to the indicated attractive interactions Se...Cl, cation-anionic associates are formed in the crystals of compounds **3a** and **3b** in the proportions 2 : 1 and 1 : 1, respectively (Figs 3 and 4).

The cation-anionic associates in the crystal of compound **3a** are packed in stacks along the axis *a* (see Fig. 3), whereas in the crystal of compound **3b** they form the zigzag chains along the axis *b* through the nonvalent interactions Cl...Cl with the distances 3.3320(5) Å (Cl(3)...Cl(5) [$-x$, $1/2 + y$, $1/2 - z$]) (see Fig. 4).

The cation of compounds **3a** and **3b** has an asymmetric carbon atom C(6); crystals of both compounds are racemates.

Based on the results obtained from the studies of reactions of styrene **1** with the antimony pentachloride—di(2-pyridyl) diselenide **2** system, the following schemes for the formation of products **3a** and **3b** can be suggested. As it is known, antimony pentachloride is an efficient chlorinating agent and a source of molecular chlorine.[17—23] Apparently, in the processes under consideration chlorination of diselenide **2** with antimony pentachloride occurs initially to furnish 2-pyridineselenenyl chloride (**4**) and antimony trichloride. Further reaction of these compounds with the equimolar ratio of diselenide and antimony pentachloride apparently leads to the complexes of the type **A**, which react with styrene to yield the salts **3a** (Scheme 2). Obtaining compound **3a** in a nearly quantitative yield, in our opinion, can serve as an indirect confirmation of the indicated scheme.

Scheme 2



When a two-fold excess of antimony pentachloride with respect to diselenide **2** is used, apparently, a competitive

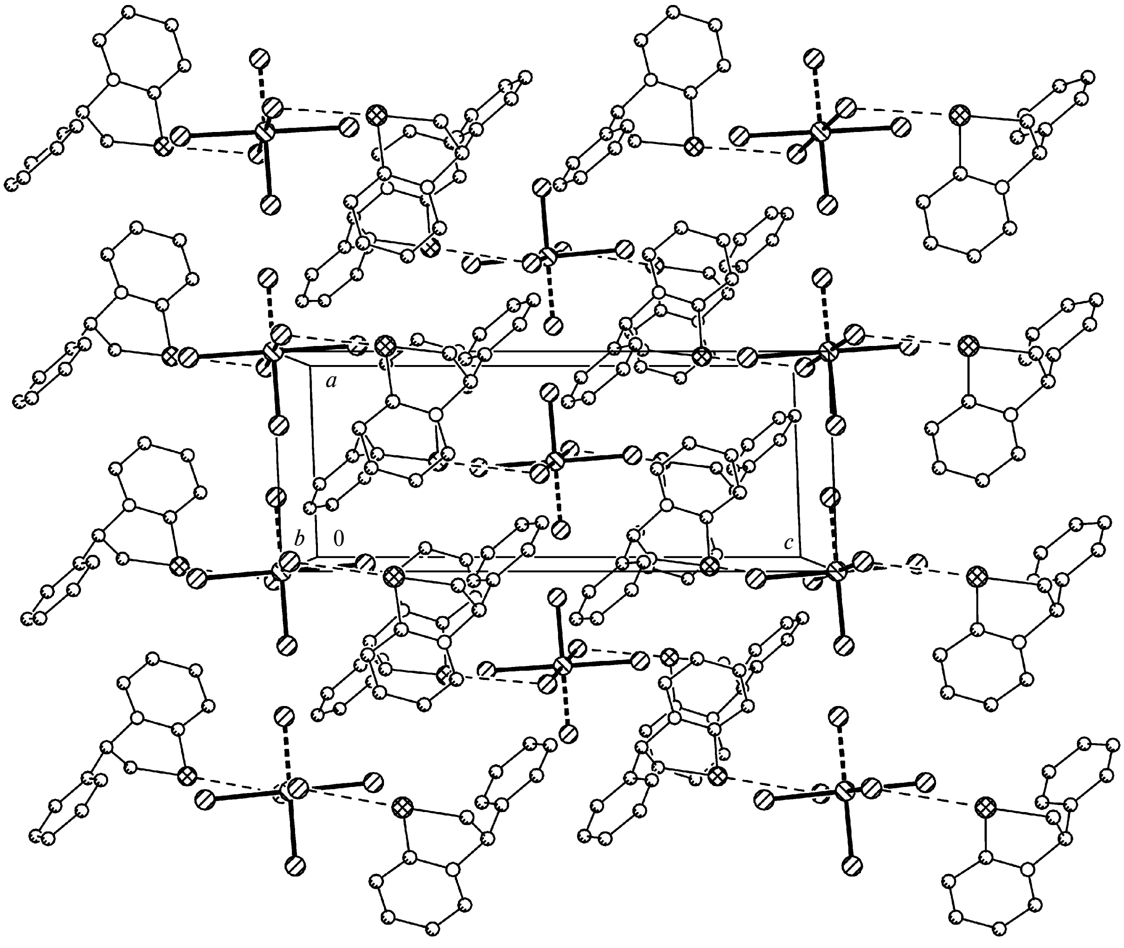


Fig. 3. Crystal packing of compound **3a**. Hydrogen atoms are not shown. The dashed lines in bold show alternative positions of the vertices of the tetragonal-pyramidal $SbCl_5^{2-}$ anions, the normal dashed lines, the attractive nonvalent interactions Se...Cl.

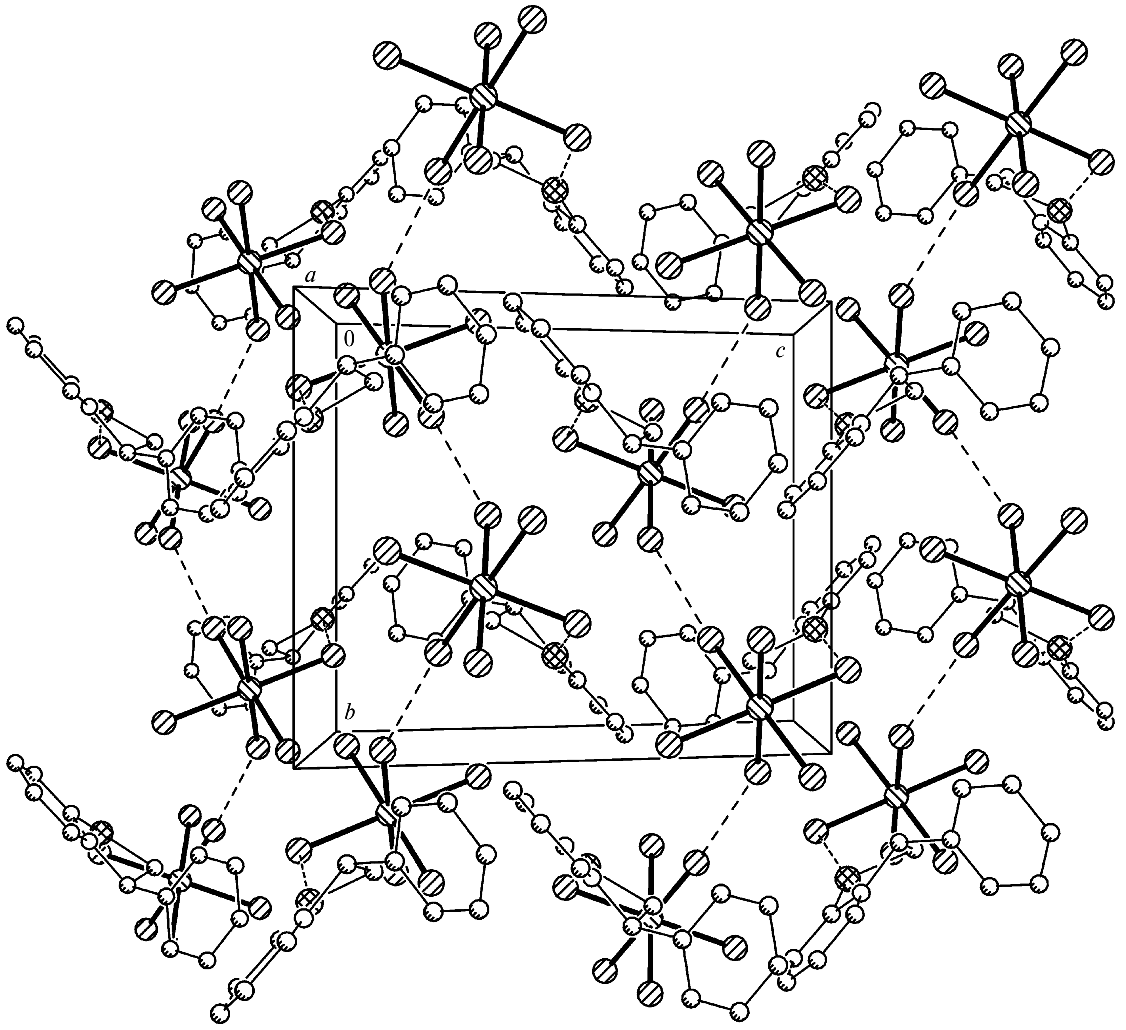
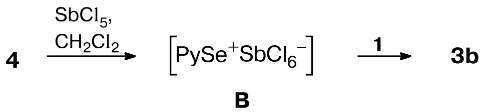


Fig. 4. Crystal packing of compound **3b**. Hydrogen atoms are not shown. The dashed lines show the attractive nonvalent interactions Se...Cl and Cl...Cl.

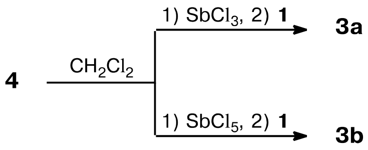
combination of the generated selenenyl chloride **4** occurs with both antimony trichloride and pentachloride to form, along with the complexes of the type **A**, the intermediate reactants of the type **B** (Scheme 3). Therefore, a mixture of Sb^{III} and Sb^{V} salts is formed in this case.

Scheme 3



The results of the following experiments can be considered as a strong argument in favor of the mechanism suggested for the formation of compounds **3a** and **3b** in the reactions of styrene with diselenide **2** activated with antimony pentachloride. Thus, we found that when antimony trichloride (CH_2Cl_2, −40 °C) and alkene **1** are sequentially added to the pre-prepared selenenyl chloride **4**, compound **3a** is formed in 92% yield. Similarly, when antimony pentachloride is used the salt **3b** was obtained in 93% yield (Scheme 4).

Scheme 4



Experimental

^{1}H NMR spectra were recorded on a Bruker Avance 600 spectrometer (600 MHz) in DMSO-d_6. Dichloromethane used as a solvent was purified by distillation over P_2O_5. Styrene (**1**) was used freshly distilled. Di(2-pyridyl) diselenide (**2**) (m.p. 48—49 °C) and 2-pyridineselenenyl chloride (**4**) (m.p. 118—119 °C) were synthesized according to the known procedures.[24]

Reaction of styrene 1 with the antimony pentachloride—di(2-pyridyl) diselenide 2 system (general procedure). A solution of $SbCl_5$ (0.075 g, 0.25 mmol) in anhydrous CH_2Cl_2 (10 mL) was added to a solution of diselenide **2** (0.079 g, 0.25 mmol) in CH_2Cl_2 (10 mL) at –40 °C with stirring under dry argon. Formation of white amorphous precipitate was observed. The reaction mixture was stirred for 15 min at –40 °C, followed by a dropwise addition of a solution of styrene **1** (0.052 g, 0.5 mmol) in CH_2Cl_2 (5 mL), then the mixture was stirred at this temperature for 30 min until the precipitate was completely dissolved. The mixture was warmed to room temperature, the solvent was evaporated *in vacuo*. After recrystallization of the residue from CH_2Cl_2, compound **3a** (0.20 g, 97%) was obtained.

Reactions with the ratio alkene : diselenide : antimony pentachloride equal to 2 : 1 : 2 was performed similarly. After heating the reaction mixture to room temperatures, the solvent was half evaporated *in vacuo*, the thus formed crystals of compound **3b** were filtered off. The mother liquor was concentrated, the residue was recrystallized from CH_2Cl_2 to obtain compound **3a**.

Bis(3-phenyl-2,3-dihydro[1,3]selenazolo[3,2-*a*]pyridinium-4) pentchloroantimonate(III) (3a). Light yellow crystals, m.p. 238—240 °C. Found (%): C, 37.89; H, 2.87. $C_{26}H_{24}Cl_5N_2SbSe_2$. Calculated (%): C, 38.02; H, 2.94. ^1H NMR, δ: 3.81 (dd, 1 H, H(2), J = 10.3 Hz, J = 7.3 Hz); 4.29 (dd, 1 H, H(2), J = 10.3 Hz, J = 7.3 Hz); 6.61 (t, 1 H, H(3), J = 7.3 Hz); 7.40 (m, 2 H, Ph); 7.48 (m, 3 H, Ph); 7.74 (dd, 1 H, H(6), J = 7.3 Hz, J = 5.9 Hz); 8.32 (dd, 1 H, H(7), J = 8.8 Hz, J = 7.3 Hz); 8.42 (d, 1 H, H(8), J = 8.8 Hz); 8.51 (d, 1 H, H(5), J = 5.9 Hz).

3-Phenyl-2,3-dihydro[1,3]selenazolo[3,2-*a*]pyridinium-4 hexachloroantimonate(V) (3b). Yellow crystals, m.p. 188—190 °C. Found (%): C, 26.12; H, 1.97. $C_{13}H_{12}Cl_6NSbSe$. Calculated (%): C, 26.21; H, 2.03. The ^1H NMR spectrum of the salts **3b** is identical to the spectrum of compound **3a**.

Reaction of styrene 1 with 2-pyridineselenenyl chloride 4 in the presence of antimony chlorides (general procedure). A solution of $SbCl_3$ (0.057 g, 0.25 mmol) in anhydrous CH_2Cl_2 (10 mL) was added to a suspension of finely powdered 2-pyridineselenenyl chloride (**4**) (0.096 g, 0.5 mmol) in CH_2Cl_2 (15 mL) at –40 °C with stirring under dry argon. Formation of white amorphous precipitate was observed. The reaction mixture was stirred for 15 min at –40 °C, followed by a dropwise addition of a solution of styrene **1** (0.052 g, 0.5 mmol) in CH_2Cl_2 (5 mL), then the mixture was stirred at this temperature for 30 min until the precipitate was completely dissolved. The mixture was warmed to room temperatures, the solvent was evaporated *in vacuo*. Recrystallization of the residue from CH_2Cl_2 yielded compound **3a** (0.189 g, 92%).

The reaction of selenenyl chloride **4** with styrene in the presence of $SbCl_5$ was performed similarly.

X-ray diffraction studies of compounds 3a and 3b. Parameters of the unit cells and intensities of reflections for compounds **3a** and **3b** were measured on a Bruker APEX-II CCD automatic three-circle diffractometer with a two-coordinate detector (T = 100 K, Mo-Kα radiation, graphite monochromator, φ- and ω-scanning). Allowance for the absorption of X-ray radiation was made for the data obtained using the SADABS program.[25] The principal crystallographic data are given in Table 3.

Table 3. Principal crystallographic data and parameters of refinement for compounds **3a** and **3b**

Compound	**3a**	**3b**
Molecular formula	$C_{26}H_{24}N_2Se_2SbCl_5$	$C_{13}H_{12}NSeSbCl_6$
Molecular weight	821.40	595.65
T/K	100	100
Crystal system	Monoclinic	
Space group	$P2_1/n$	$P2_1/c$
a/Å	6.7822(3)	13.5164(4)
b/Å	12.1732(6)	10.9651(3)
c/Å	17.1401(8)	13.5804(4)
α/deg	90	90
β/deg	92.143(1)	111.453(1)
γ/deg	90	90
V/Å^3	1414.12(11)	1873.29(9)
Z2	4	
d_{calc}/g cm^{-3}	1.929	2.112
F(000)	796	1136
μ/mm^{-1}	4.043	4.265
2θ$_{max}$/deg	60	65
Number of measured reflections	17498	27401
Number of independent reflections	4100	6833
R_{int}	0.034	0.029
Number of reflections with $I > 2\sigma(I)$	3445	6198
Number of refined parameters	169	199
R_1 ($I > 2\sigma(I)$)	0.0263	0.0215
wR_2 (all the data)	0.0594	0.0537
GOF	1.001	1.007
Transmission, T_{min}/T_{max}	0.582/0.643	0.415/0.567

The structures of compounds **3a,b** were solved by the direct method and refined by the full-matrix least squares method in the anisotropic approximation for nonhydrogen atoms. The antimony atom in the structure of **3a** occupies a particular position in the center of inversion, resulting in the $SbCl_5^{2-}$ anion being disordered over two positions with the equal populations. All the hydrogen atoms, whose positions were calculated geometrically, were included into the refinement in the isotropic approximation with the fixed positional (the riding model) and thermal ($U_{iso}(H) = 1.2U_{eq}(C)$) parameters. All the calculations were performed using the SHELXTL program package.[26]

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