Reactions of 1-Thia-3-azoniabutatriene Salts with Alcohols, Carbonyl Compounds, Diazoalkanes, Nitrile Oxides, Nitrones, Enamines, and Butadienes

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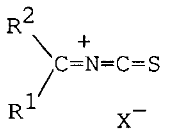
1-Thia-3-azoniabutatriene salts **1** react with alcohols, carbonyl compounds, diazo alkanes, nitrile oxides, nitrones, enamines, and 1,3-butadienes in all cases at the C=S double bond to yield new types of 2-azoniaallene salts (**3**, **9a,b**, **13a,b**, **18**, **22**) and other imines (**2**, **20**). An X-ray diffraction analysis for **9b**, the reaction product of **1b** with 9-diazofluorene, confirms the proposed constitution.

Disregarding the importance of different canonical forms and the geometry of the C=N=C=S unit[1] compounds 1[1–5] will be called 1-thia-3-azoniabutatriene salts throughout this paper.



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1,9	R1	R2	X	Ref.
a	H	Me_2N	$SbCl_6$	2,3)
b	Ph	Me_2N	$SbCl_6$	3)
c	Ph	Me_2N	$AlCl_4$	3)
d	Ph	Ph	$SbCl_6$	1,2)

Little is known about the chemical properties of the new class of bifunctional electrophilic heterocumulenes **1**. The isothiocyanates **1** were treated with simple nucleophiles like water[1] and amines[4,6]. Recently, we described cycloadditions of **1** to azomethines, carbodiimides, and a ketene imine[7].

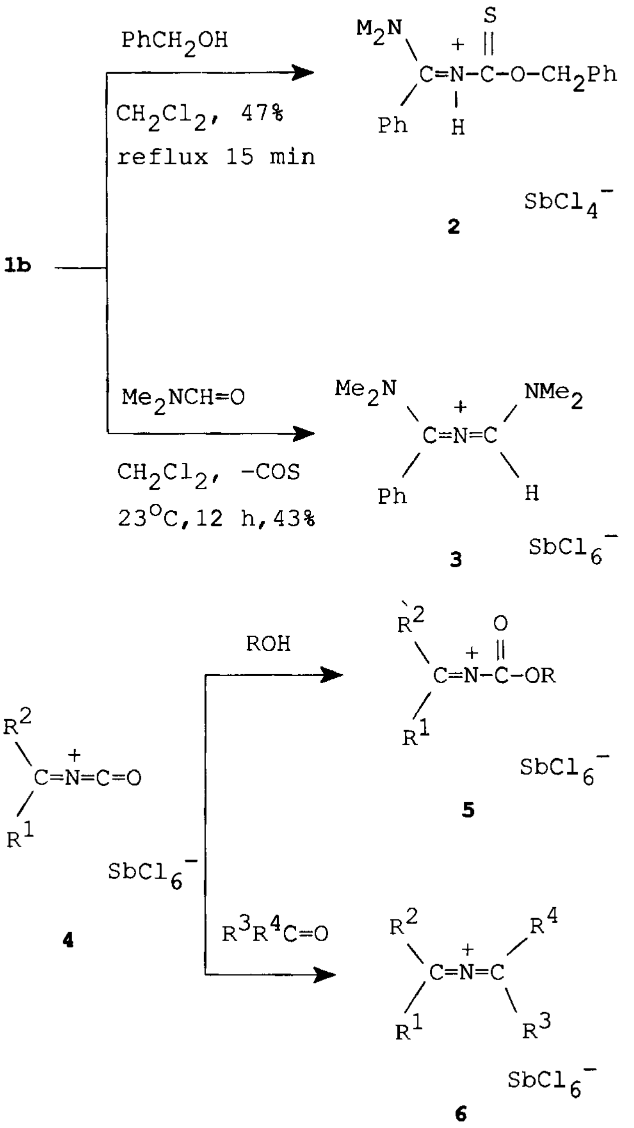
Here we report reactions of **1a–d** with an alcohol, a tertiary amide, with diazo alkanes, nitrile oxides, a nitrone, and with reactive olefins.

Reactions of 1 with Alcohols and Carbonyl Compounds

The salt **1b** reacts with an excess of benzyl alcohol to give the benzamidinium salt **2** in moderate yield. With other alcohols only mixtures of compounds are produced. In contrast, from 1-oxa-3-azoniabutatriene salts **4** and alcohols the acyliminium salts **5** are obtained almost quantitatively[8].

It has been reported that the salts **4** react with ketones, aldehydes, or tertiary carboxamides to furnish 2-azoniaallene salts **6** in high yields[2,9]. However, the 1-thia analogues **1** react only sluggishly with carbonyl groups giving mixtures of compounds. From the reaction of **1b** with dimethylformamide the salt **3** is obtained.

Scheme 1



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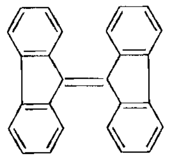
The reactivity of the salts **1** as compared to the oxygen analogue **4** is reduced, just as conventional isothiocyanates are less reactive towards nucleophiles than isocyanates. Furthermore, the reactions of the hexachloroantimonates **1** are complicated by redox processes, e.g. compound **2** is obtained as an antimony(III) salt. Finally, both types of heterocumulenes **1** and **4** are ambident electrophiles, which may be attacked by nucleophiles at the sp- or the sp^2-hybridized carbon atom. While the isocyanates **4** react almost exclusively at the NCO carbon atom the isothiocyanates **1** tend to be attacked at both electrophilic centers. It has been reported, for instance, that **1d** reacts with water to give benzophenone and thiocyanic acid[1].

Reactions of 1 with Diazo Alkanes

New types of sulfur-substituted 2-azoniaallene salts can be obtained by cycloadditions across the C=S double bond of isothiocyanates **1**[7]. Diazo alkanes undergo 1,3-dipolar cycloaddition to the C=S bond of isothiocyanates to produce 1,2,3-thiadiazoles[10–12]. An exception, for which a two-step sequence has been postulated, is the formation of a thiiranimine from the reaction of tosyl isothiocyanate with diazodiphenylmethane[13].

However, when a large excess of 9-diazofluorene is added to a cold (−50°C) solution of **1d** in dichloromethane a vigorous evolution of nitrogen takes place. The isothiocyanate **1d** remains unchanged and 9,9′-bifluorenylidene (**7**) is isolated in 84% yield. Similarly, diazomethane and diazodiphenylmethane quickly decompose in the presence of the isothiocyanate **1a**, and 3-diazo-2,2,4,4-tetramethylpentane is destroyed by the isothiocyanate **1b**. In these cases well-defined products were not isolated. During these reactions the isothiocyanate bands in the IR spectra do not change. Under similar reaction conditions other carbenium hexachloroantimonates, e.g. Gold's salt **8**, do not decompose diazo alkanes.



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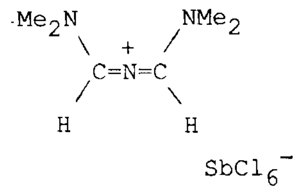

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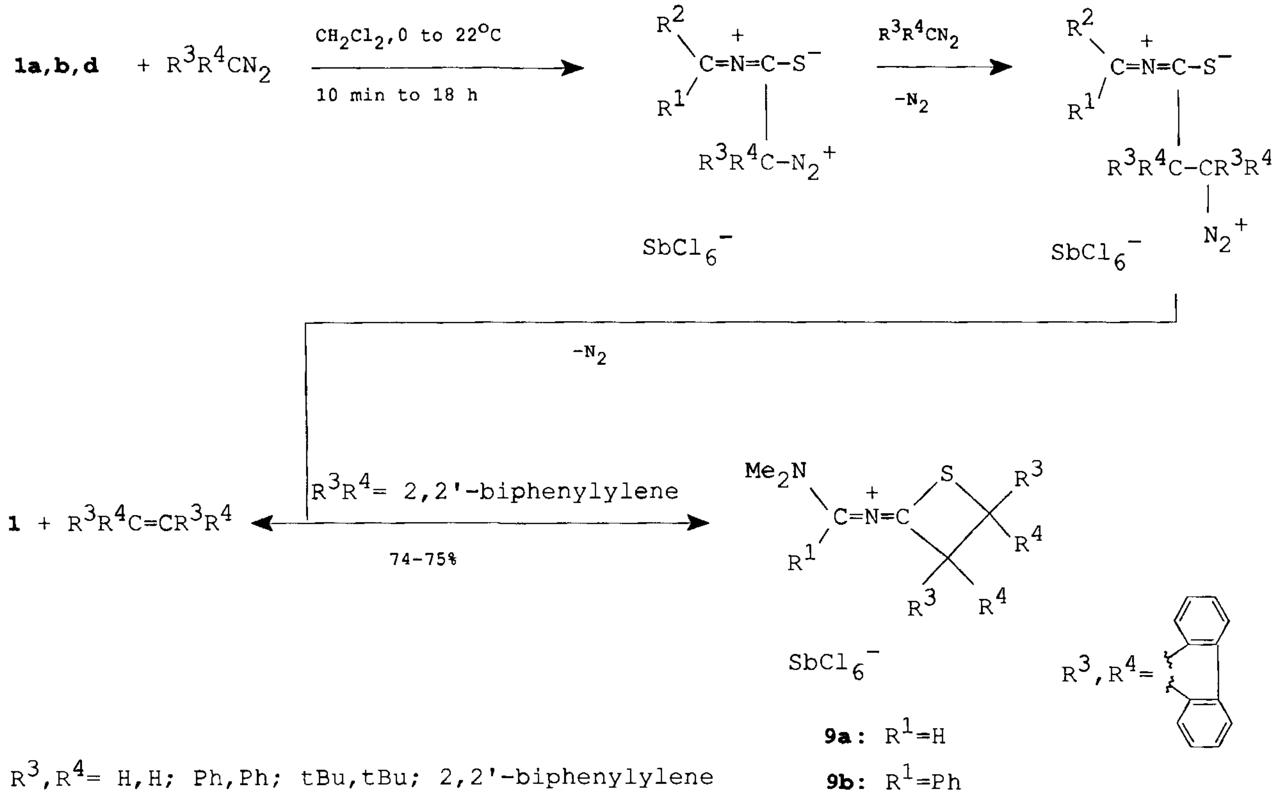
On the other hand, if the isothiocyanates **1a,b** are treated with two equivalents of 9-diazofluorene the addition compounds **9a,b** are formed in high yields. Thietanes of this type seem to be unknown[14]. The pale yellow powders **9a,b** are sparingly soluble in most organic solvents and resist crystallization. The elemental analyses give correct C,H,N values for *hexa*chloroantimonates. Finally, a few prisms suitable for an X-ray diffraction analysis crystallized from a solution of **9b** in a mixture of nitromethane, 1,2-dichloroethane, and ether. The ^{1}H, ^{13}C NMR, and IR spectra of these crystals were identical to those of **9b** before crystallization. However, according to the X-ray results the crystalline compound is a *tetra*chloroantimonate. The origin of this Sb(III)

Scheme 2



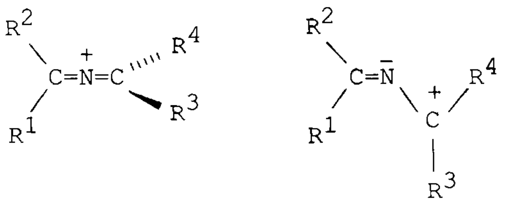
compound remains unclear at the present time. The reactions of the cumulated isothiocyanates **1a,b,d** with diazo alkanes may be rationalized as shown in Scheme 2.

X-ray Diffraction Analysis for 9b[15]

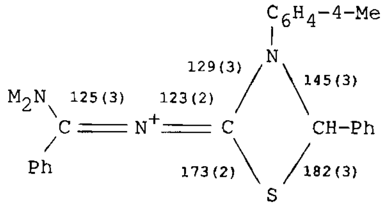
Selected bond lengths, bond angles, and torsional angles for **9b** are given in Table 1. Figure 1 shows a molecular plot for the cation and the anion of **9b**.

The crystal of **9b** consists of discrete $[C_{36}H_{27}N_2S]^+$ cations and $Sb_2Cl_8^{2-}$ anions. Discrete octachlorodiantimonate anions, which crystallize either in a *cis* or in a *trans* form, have only recently been described by Schmidt et al.[16]. The anion of **9b** shows *trans* configuration.

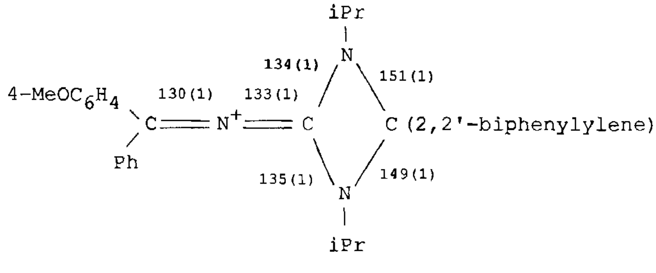
X-ray diffraction data for several organic[1,7,17–30] and metalorganic[31–39] 2-azoniaallene compounds have been published in recent years. For 2-azoniaallene cations qualitative valence-bond arguments suggest two valence tautomeric structures with local D_{2d} (**A**) and C_{2v}-symmetry (**B**), respectively. In the crystal most of the cations show geometries in between. To avoid different names for different molecular geometries, which are mainly determined by the steric requirements of the substituents, we will call these sterically unusually flexible cations 2-azoniaallene ions.



A, local D_{2d} symmetry **B**, local C_{2v} symmetry
α = 180°, β = 90° α = 120°, β = 0°
α: bond angle C=N=C; β: angle between the best planes through N,R^1,C,R^2 and N,R^3,C,R^4



10: α = 122°, β = 6.3°



11: α = 127°, β = 119.5°

Hetero atom-containing substituents bearing free pairs of electrons stabilize geometry **B**. For instance, quantum mechanical calculations predict[24] and X-ray structural analyses confirm[18–21] that 1,1- or 1,3-diamino-substituted 2-azoniaallene cations crystallize in the planar conformation **B**.

The structure of the cation of **9b** may be compared to that of **10**[7] and **11**[29]. Cation **10**, a 1,3-diamino-substituted 2-azoniaallene ion, crystallizes in an almost perfect 2-azaallylium geometry **B** (β = 6.3°). The N–C–N–C–N fragment is W-shaped, the formal heterocumulene unit C=N=C is bent [122(2)°]. In contrast, cation **11**, a 1,1-diamino-substituted 2-azoniaallene ion, deviates from the planar geometry **B** (β = 119.5°). Again, the exocyclic C=N=C unit is bent [127.3(7)°].

For the cation **9b** angles α = 129.0(5)° and β = 104.6° (angle between the best planes through N3–N4–C64–C67 and N3–C63–S2–C50) are found.

The shorter bond lengths for N4–C64 [129.7(8) pm] and N3–C63 [126.7(7) pm] as compared with C64–N3 [136.7(7) pm] indicate considerable double bond character. The positive charge is mainly located in the N4–C64 unit. Amidinium resonance within the N4–C64–N3 fragment is sterically hindered because the planes through N4–C64–N3 and C64–N3–C63 are twisted against each other [torsional angle −119.4(7)° for N4–C64–N3–C63]. The C–S distances in the thietane ring are similar to those found for the cation **10**.

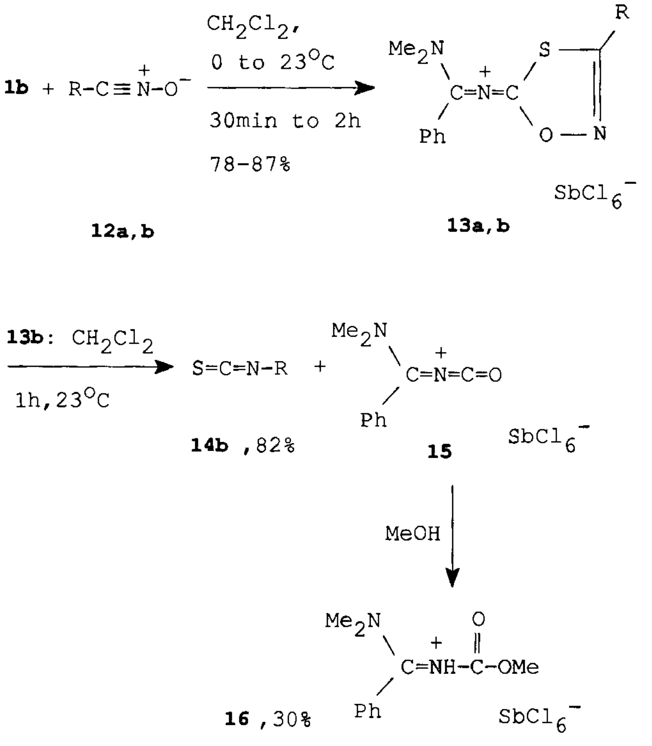
Reactions of 1 with Nitrile Oxides and a Nitrone

Little seems to be known about reactions of nitrile oxides with isothiocyanates[11,40,41]. L'Abbé et al.[42] reported on cycloadditions of nitrile oxides across the C=S double bond of electron-deficient sulfonyl isothiocyanates.

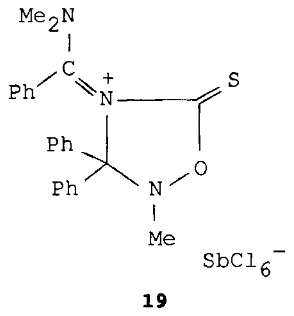
We have found that the extremely electron-deficient isothiocyanates **1a,b** undergo smooth cycloadditions with nitrile oxides across the C=S double bond furnishing the thermally labile and very moisture-sensitive 2-azoniaallene salts **13a,b**. In solution the heterocycles **13** undergo cycloreversion with concomitant rearrangement of the substituent R. For instance, **13b** decomposes in dichloromethane at room temperature within one hour to give the known[43] isothiocyanate **14b** together with the cumulene **15**, which is isolated as the acyliminium salt **16**. Recently, we have described a transformation of isocyanates **4** into isothiocyanates **1**[2]. The reverse transformation **1** → **4** can be accomplished by reaction of **1** with nitrile oxides. Transformations of thiocarbonyl to carbonyl compounds by means of nitrile oxides are well documented[44–47].

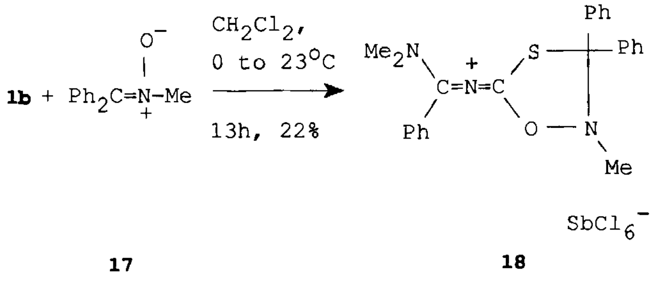
1,3-Dipolar cycloadditions of nitrones both across the C=N and the C=S double bond of isothiocyanates have been described in the literature[48–51]. The nitrone **17** adds to the isothiocyanate **1b** across the C=S bond giving the 2-azoniaallene salt **18** in low yield. The compound shows a characteristic broad 2-azoniaallene IR absorption at 1570 cm^{-1} (in CH_2Cl_2). For benzamidinium salts narrow bands around 1630 cm^{-1} are to be expected. Therefore, the alternative structure **19** for the cation seems unlikely.

Scheme 3



12-14	R
a	$2,4,6\text{-}Me_3C_6H_2$
b	$2,4,6\text{-}(MeO)_3C_6H_2$



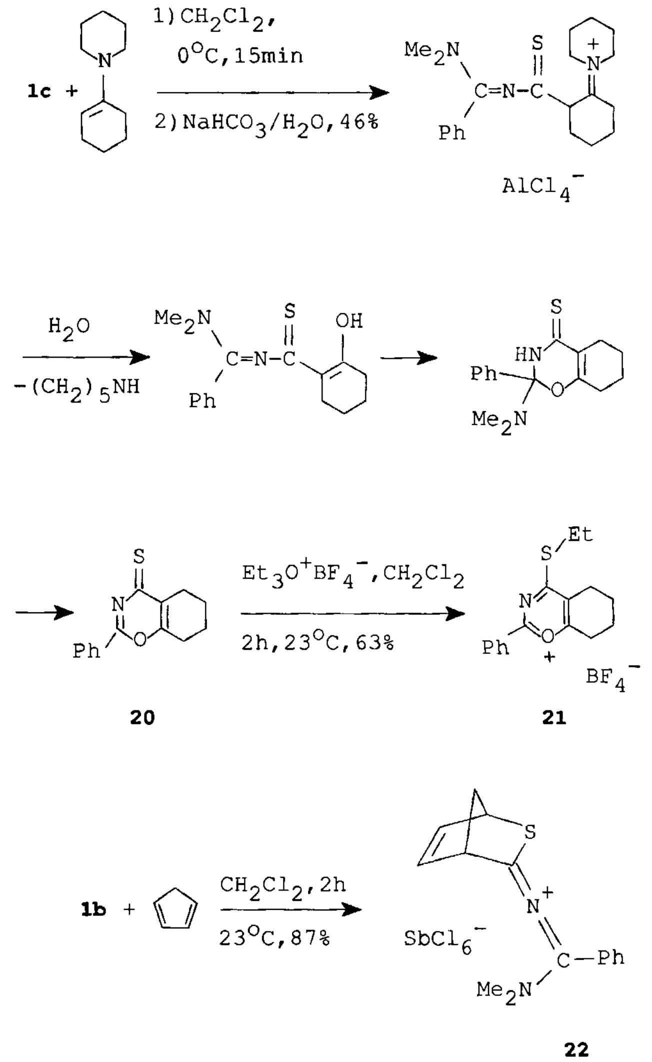


Reactions of 1 with an Enamine and with Cyclopentadiene

Hünig et al.[51] reported that benzoyl isothiocyanate reacts with 1-morpholino-1-cyclohexene to afford the oxazinethione **20**. The same compound is also formed from **1c** and 1-piperidino-1-cyclohexene. It is further characterized as the 1,3-oxazinium derivative **21**.

Compounds **1b** and **1d** do not react with either 1,3-butadiene, isoprene, or norbornadiene in dichloromethane. From cyclopentadiene and **1b** a crystalline product is obtained. Based on a broad and intensive IR absorption at 1600 cm^{-1} assigned to the 2-azoniaallene moiety we propose structure **22**. However, an isomeric structure resulting from cycloaddition of cyclopentadiene across the C=N double bond in **1b** cannot be excluded with certainty.

Scheme 4



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Experimental

IR: Mattson Polaris FT-IR spectrometer; solutions in dichloromethane. – ^1H-, ^{13}C NMR: Bruker WM-250 and AC 250 spectrometers; internal reference tetramethylsilane. – All experiments are carried out with exclusion of moisture. – All solvents are dried by conventional methods.

N^2-[(Benzyloxy)thiocarbonyl]-N^1,N^1-dimethylbenzamidinium Tetrachloroantimonate (**2**): A solution of **1b**[3,7] (5.26 g, 10 mmol) and benzyl alcohol (2.16 g, 20 mmol) in dichloromethane (20 ml) is boiled under reflux for 15 min. After cooling the product is filtered off. Recrystallization from acetonitrile (20 ml) affords yellow needles

Table 1. Selected bond lengths [pm], bond angles, and torsional angles [°] for the cation **9b**

C64-N3	136.7(7)	C64-N3-C63	129.0(5)	S2-C37-C49	116.5(4)	N3-C63-C50-C51	- 60.2(7)
N3-C63	126.7(7)	C67-C64-N3	116.4(5)	S2-C37-C38	116.7(4)	N3-C63-C50-C62	59.9(8)
C67-C64	148.2(8)	N4-C64-N3	119.3(5)	N4-C64-N3-C63	-119.4(7)	C63-S2-C37-C50	- 0.5(3)
N4-C64	129.7(8)	C66-N4-C64	123.1(5)	C64-N3-C63-S2	14(1)	C63-S2-C37-C38	-120.2(5)
C66-N4	147.4(8)	C65-N4-C64	121.3(5)	C67-C64-N3-C63	67.8(7)	C63-S2-C37-C49	118.1(4)
C63-S2	174.1(5)	N3-C63-S2	134.5(4)	C64-N3-C63-C50	-165.7(6)	C63-C50-C51-C52	- 37.8(7)
S2-C37	185.1(5)	N3-C63-C50	126.7(4)	C72-C67-C64-N3	-125.7(6)	S2-C37-C49-C48	- 36.5(7)
C37-C50	165.7(7)	C63-S2-C37	79.2(2)	C66-N4-C64-N3	-171.3(5)	S2-C37-C38-C39	36.8(8)
C50-C63	150.4(7)	S2-C37-C50	89.3(3)	C66-N4-C64-C67	0.9(8)	S2-C37-C50-C51	-121.5(4)
C50-C62	151.5(7)	C37-C50-C63	92.8(4)	C65-N4-C64-N3	13.2(7)	C37-C50-C63-S2	0.6(4)
C50-C51	151.9(7)	C50-C63-S2	98.8(3)	C65-N4-C64-C67	-174.5(5)	C50-C63-S2-C37	0.5(3)
C37-C49	151.4(8)	C63-C50-C62	115.3(4)	N3-C63-S2-C37	-179.5(7)	C50-C37-C49-C48	66.4(7)
C37-C38	150.6(7)	C63-C50-C51	117.3(5)	N3-C63-C50-C37	179.4(6)	C37-C50-C51-C52	69.8(7)

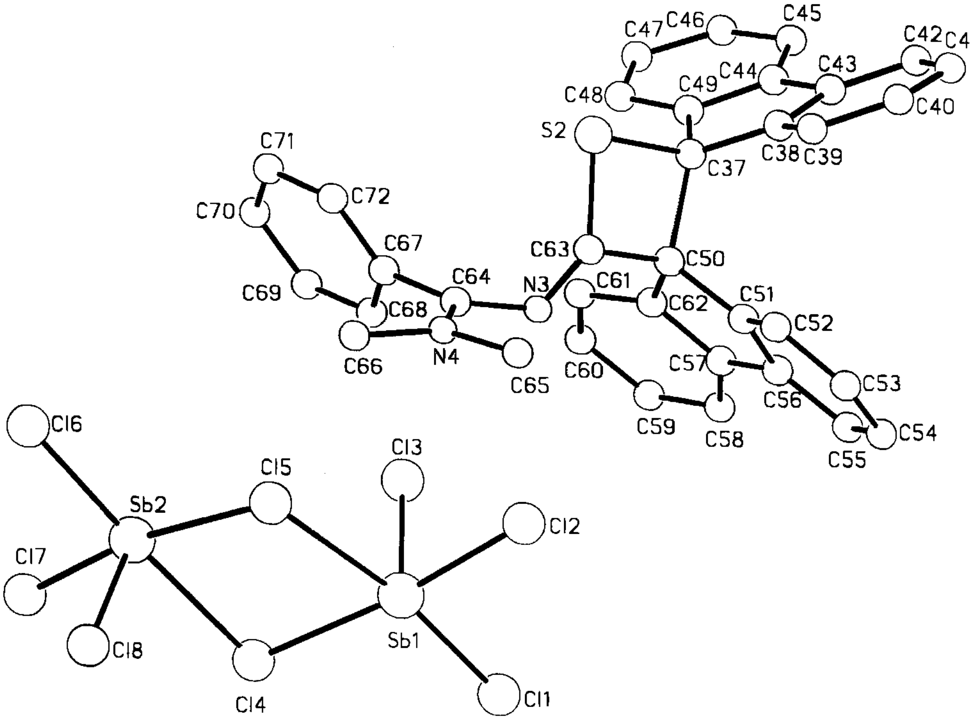

Figure 1. Molecular plot for the cation and anion of **9b**

(2.66 g, 47%), which are sparingly soluble in most organic solvents; m.p. 161–164°C (dec.). – IR: ṽ = 1630, 1770 cm^{-1}. – ^{1}H NMR (CD_3CN): δ = 3.18, 3.49 (CH_3), 5.11 (CH_2). – ^{13}C NMR (CD_3CN): δ = 43.5, 45.1 (CH_3), 70.2 (CH_2).

$C_{17}H_{19}Cl_4N_2OSSb$ (563.0) Calcd. C 36.27 H 3.40 N 4.98
Found C 36.47 H 3.38 N 5.04

1,3-Bis(dimethylamino)-1-phenyl-2-azoniaallene Hexachloroantimonate (**3**): A mixture of dimethylformamide (0.73 g, 10 mmol) and **1b** (5.26 g, 10 mmol) in dichloromethane (30 ml) is stirred at 23°C for 12 h. Filtration, evaporation of the solvent, and recrystallization of the residue from methanol (10 ml) yield yellow prisms (2.32 g, 43%); m.p. 128°C. – IR: ṽ = 1570 (vs), 1650, 1495 cm^{-1}. – ^{1}H NMR (CD_3CN): CH_3 δ = 3.04, 3.09, 3.25 (d, $^4J_{HCNCH}$ = 0.9 Hz), 3.46 (CH_3). – ^{13}C NMR (CD_3CN, 263 K): δ = 37.0, 39.7, 42.5, 42.8 (CH_3), 163.4 (HC=N), 173.1 (C=N).

$C_{12}H_{18}Cl_6N_3Sb$ (538.8) Calcd. C 26.75 H 3.37 N 7.80
Found C 26.88 H 3.38 N 8.05

Reaction of **1d** *with 9-Diazofluorene:* A solution of 9-diazofluorene (1.00 g, 5.2 mmol) in dichloromethane (10 ml) is added dropwise to a stirred solution of **1d**[1,2] (40 mg, 72 mol) in dichloromethane (10 ml) at –50°C. Evolution of nitrogen takes place. In the IR spectrum of the reaction mixture the NCS absorption at 1990 cm^{-1} (CH_2Cl_2) is still observed. The solvent is evaporated under reduced pressure. Crystallization of the residue from $CHCl_3$/ethanol affords red needles (0.72 g, 84%) of **7**; m.p. 175–178°C (ref.[53] 186–187°C).

N^3-{Dispiro[fluorene-9,2'-thietane-3',9''-fluorene]-4'-ylidene}-N^1,N^1-dimethylformamidinium Hexachloroantimonate (**9a**): At 0°C a solution of 9-diazofluorene (3.84 g, 20 mmol) in dichloromethane (30 ml) is added dropwise to a stirred suspension of **1a** in dichlo-

romethane (50 ml). Nitrogen evolves, and a yellow precipitate is produced, which is filtered off and washed with acetonitrile (20 ml). The resulting yellow powder (5.81 g, 75%) is sparingly soluble in most organic solvents; dec. above 160°C. – IR (KBr): ṽ = 1580 (vs, broad), 1600, 1660 cm^{-1}. – ^{1}H NMR (CD$_3$CN): δ = 3.19 (d, $^4J_{HCNCH}$ = 1.2 Hz), 3.54 (CH$_3$), 8.77 (broad, coupled to 3.19, CH).

$C_{30}H_{23}Cl_6N_2SSb$ (778.0) Calcd. C 46.31 H 2.98 N 3.60
Found C 46.80 H 3.34 N 3.53

N^3-{Dispiro[fluorene-9,2'-thietane-3',9''-fluorene]-4'-ylidene}-N^1,N^1-dimethylbenzamidinium Hexachloroantimonate (**9b**): From **1b** (5.26 g, 10 mmol) as described for **9a**. The reaction mixture is stirred at 22°C for 18 h. Slow addition of ether (25 ml)/pentane (25 ml) affords a yellow precipitate (6.30 g, 74%); dec. above 137°C. – IR: ṽ = 1660 (shoulder), 1610 (vs, broad), 1600 (shoulder), 1580 (shoulder) cm^{-1}. – ^{1}H NMR (CD$_3$CN): δ = 3.37, 3.42 (NCH$_3$). – ^{13}C NMR (CD$_3$CN, 263 K): δ = 42.5, 44.7 (NCH$_3$), 66.9, 84.7 (C), 172.0, 191.2 (C=N, C=S), 15 signals for aromatic C's.

$C_{36}H_{27}Cl_6N_2SSb$ (854.1) Calcd. C 50.62 H 3.19 N 3.28
Found C 50.65 H 3.46 N 3.35

X-Ray Diffraction Analysis of **9b**[51]: [$C_{36}H_{27}N_2S$]SbCl$_4$, crystal size 0.3 × 0.4 × 0.5 mm^3, triclinic, space group $P\bar{1}$, $Z = 2$, a = 1037.0(2), b = 1714.8(3), c = 1907.1(2) pm, α = 86.64(1), β = 89.05(1), γ = 79.13(1)°, V = 3324.9 · 10^6 pm^3, d_{calc} = 1.60 gcm^{-3}, T = 209 K, $\mu_{Mo\text{-}K\alpha}$ = 12.5 cm^{-1}, ω scan, 2.2 ≤ ω ≤ 29.3° min^{-1}, 4.0 ≤ 2Θ ≤ 52°, 12671 observed reflections, 9589 independent reflections ($I > 2\sigma$). The cell constants and the intensities of the reflections were measured on a Syntex-P3 diffractometer with a graphite monochromator, $\lambda_{Mo\text{-}K\alpha}$ = 71.069 pm. The structure was solved by the Patterson method using the program SHELXTL[52]. Hydrogen atoms were fixed on calculated geometrically ideal positions. The asymmetric unit contains two cations and one anion $Sb_2Cl_8^{2-}$. The anisotropic refinement led to agreement factors R_1 = 0.047 and R_2 = 0.051. A list of atomic coordinates with thermal factors is given in Table 2.

N^1,N^1-Dimethyl-N^3-(3-mesityl-1,4,2-oxathiazol-5-ylidene)benzamidinium Hexachloroantimonate (**13a**): A solution of **1b** (5.26 g, 10 mmol) and **12a**[54] (1.61 g, 10 mmol) in dichloromethane (40 ml) is stirred at 23°C for 2 h. Cooling to –50°C and slow addition of ether (50 ml) gives a precipitate, which is crystallized from dichloromethane (20 ml)/ether (50 ml) affording a yellow powder (5.36 g, 78%); m.p. 102–104°C (dec.). – IR: ṽ = 1530 (shoulder), 1570 (vs, broad), 1610 (shoulder) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 2.15 (6H), 2.29, 3.56, 3.85 (CH$_3$), 6.92 (*m*-H). – ^{13}C NMR (CDCl$_3$, 263 K): δ = 20.1, 21.3, 42.2, 44.1 (CH$_3$), 162.4, 170.7, 185.0 (C=N).

$C_{20}H_{22}Cl_6N_3OSSb$ (687.0) Calcd. C 34.97 H 3.23 N 6.12
Found C 34.63 H 3.23 N 6.12

N^1,N^1-Dimethyl-N^3-[3-(2,4,6-trimethoxyphenyl)-1,4,2-oxathiazol-5-ylidene]benzamidinium Hexachloroantimonate (**13b**): A suspension of **12b**[55] (2.09 g, 10 mmol) in dichloromethane (10 ml) is added in portions to a cold (0°C) solution of **1b** (5.26 g, 10 mmol) in dichloromethane (10 ml). After stirring at 0°C for 30 min the product is precipitated by slow addition of ether (30 ml). Yield: 6.39 g (87%) of a yellow powder, which quickly decomposes in solution; m.p. 95–98°C (dec.). – IR: ṽ = 1540 (shoulder), 1580 (vs, broad), 1650 (shoulder). – ^{1}H NMR (CDCl$_3$/CD$_3$CN 1:4): δ = 3.42, 3.69, 3.81 (6H), 3.87 (CH$_3$), 6.16 (*m*-H).

$C_{20}H_{22}Cl_6N_3O_4SSb$ (735.0) Calcd. C 32.69 H 3.02 N 5.72
Found C 32.36 H 3.09 N 5.66

2,4,6-Trimethoxyphenyl Isothiocyanate (**14b**): A mixture of **12b** (2.09 g, 10 mmol) and of **1b** (5.26 g, 10 mmol) in dichloromethane (20 ml) is stirred at 23°C for 1 h. After evaporation of the solvent

Table 2. Fractional atomic coordinates and temperature factors [10^4 pm^2] for **9b**

Atom	x/a	y/b	z/c	U [a,b]
Sb1	0.3492(1)	0.2726(1)	0.0858(1)	0.029(1)
Sb2	0.5881(1)	0.2151(1)	-0.0895(1)	0.028(1)
Cl1	0.3941(2)	0.2426(1)	0.2124(1)	0.037(1)
Cl2	0.1465(2)	0.3682(1)	0.1061(1)	0.047(1)
Cl3	0.4663(2)	0.3786(1)	0.0755(1)	0.059(1)
Cl4	0.5950(2)	0.1753(2)	0.0541(1)	0.091(1)
Cl5	0.3126(2)	0.2822(1)	-0.0624(1)	0.045(1)
Cl6	0.5747(2)	0.2566(1)	-0.2170(1)	0.044(1)
Cl7	0.8121(2)	0.1429(1)	-0.0980(1)	0.048(1)
Cl8	0.5039(2)	0.0994(1)	-0.1083(1)	0.062(1)
S1	-0.0924(2)	0.2715(1)	0.1928(1)	0.026(1)
S2	0.8461(2)	0.7891(1)	0.2002(1)	0.038(1)
C1	-0.3451(6)	0.2150(3)	0.3708(3)	0.029(2)
C2	-0.4112(6)	0.1978(3)	0.4326(3)	0.033(2)
C3	-0.3449(6)	0.1765(3)	0.4950(3)	0.035(2)
C4	-0.2091(6)	0.1694(3)	0.4980(3)	0.032(2)
C5	-0.1427(5)	0.1866(3)	0.4364(3)	0.022(2)
C6	-0.0013(5)	0.1775(3)	0.4230(3)	0.023(2)
C7	0.1045(6)	0.1501(3)	0.4670(3)	0.029(2)
C8	0.2303(6)	0.1399(3)	0.4381(3)	0.031(2)
C9	0.2493(6)	0.1550(3)	0.3666(3)	0.030(2)
C10	0.1435(5)	0.1828(3)	0.3228(3)	0.026(2)
C11	0.0178(5)	0.1959(3)	0.3516(3)	0.021(2)
C12	-0.1147(5)	0.2264(3)	0.3161(3)	0.020(1)
C13	-0.2106(5)	0.2111(3)	0.3738(3)	0.019(1)
C14	-0.1267(5)	0.3154(3)	0.2790(3)	0.022(2)
C15	-0.0424(5)	0.3689(3)	0.3060(3)	0.023(2)
C16	0.0910(6)	0.3674(3)	0.2984(3)	0.027(2)
C17	0.1451(6)	0.4253(3)	0.3303(3)	0.035(2)
C18	0.0678(7)	0.4831(3)	0.3688(3)	0.038(2)
C19	-0.0659(6)	0.4863(3)	0.3744(3)	0.034(2)
C20	-0.1220(6)	0.4302(3)	0.3419(3)	0.026(2)
C21	-0.2594(6)	0.4269(3)	0.3304(4)	0.029(2)
C22	-0.3755(7)	0.4776(4)	0.3477(4)	0.043(2)
C23	-0.4921(7)	0.4686(4)	0.3187(4)	0.050(3)
C24	-0.4948(7)	0.4109(4)	0.2708(4)	0.046(2)
C25	-0.3791(6)	0.3580(3)	0.2544(3)	0.033(2)
C26	-0.2641(5)	0.3654(3)	0.2852(3)	0.026(2)
C27	-0.1198(5)	0.1901(3)	0.2465(3)	0.021(2)
N1	-0.1400(4)	0.1207(2)	0.2367(2)	0.023(1)
C28	-0.1235(5)	0.0873(3)	0.1729(3)	0.024(2)
N2	-0.2080(5)	0.0445(3)	0.1554(2)	0.027(1)
C31	-0.0079(5)	0.0965(3)	0.1290(3)	0.026(2)
C32	-0.0247(7)	0.1336(4)	0.0625(3)	0.036(2)
C33	0.0844(7)	0.1444(4)	0.0229(3)	0.041(2)
C34	0.2074(7)	0.1160(4)	0.0480(4)	0.045(2)
C35	0.2259(7)	0.0795(4)	0.1147(4)	0.046(2)
C36	0.1168(6)	0.0707(4)	0.1566(3)	0.040(2)
C29	-0.3293(6)	0.0434(4)	0.1967(3)	0.037(2)
C30	-0.1906(7)	-0.0031(3)	0.0932(3)	0.039(2)
C37	0.8639(6)	0.8214(3)	0.2899(3)	0.026(2)
C38	0.7462(6)	0.8742(3)	0.3204(3)	0.028(2)
C39	0.6133(6)	0.8735(3)	0.3140(4)	0.040(2)
C40	0.5250(7)	0.9292(4)	0.3502(4)	0.052(3)
C41	0.5666(7)	0.9835(4)	0.3907(4)	0.047(2)
C42	0.6989(6)	0.9870(3)	0.3949(3)	0.038(2)
C43	0.7877(6)	0.9319(3)	0.3592(3)	0.027(2)
C44	0.9285(5)	0.9273(3)	0.3465(3)	0.025(2)
C45	1.0120(6)	0.9763(3)	0.3676(3)	0.034(2)
C46	1.1387(7)	0.9644(4)	0.3409(4)	0.040(2)
C47	1.1808(7)	0.9075(4)	0.2926(4)	0.042(2)
C48	1.0970(6)	0.8584(3)	0.2723(3)	0.035(2)
C49	0.9733(5)	0.8667(3)	0.3006(3)	0.025(2)
C50	0.8930(5)	0.7269(3)	0.3194(3)	0.021(2)
C51	0.7988(5)	0.7052(3)	0.3758(3)	0.022(2)
C52	0.6675(6)	0.7004(3)	0.3711(3)	0.029(2)
C53	0.6024(6)	0.6790(3)	0.4320(3)	0.036(2)
C54	0.6674(6)	0.6634(3)	0.4952(3)	0.037(2)
C55	0.7991(7)	0.6663(3)	0.4994(3)	0.035(2)
C56	0.8651(5)	0.6860(3)	0.4392(3)	0.023(2)
C57	1.0057(5)	0.6814(3)	0.4263(3)	0.023(2)
C58	1.1129(6)	0.6540(3)	0.4700(3)	0.031(2)
C59	1.2382(6)	0.6431(3)	0.4409(3)	0.036(2)
C60	1.2557(6)	0.6580(3)	0.3699(3)	0.036(2)
C61	1.1511(6)	0.6848(3)	0.3255(3)	0.029(2)
C62	1.0249(5)	0.6985(3)	0.3544(3)	0.023(2)
C63	0.8809(5)	0.6976(3)	0.2474(3)	0.023(2)
N3	0.8940(5)	0.6259(3)	0.2315(2)	0.029(1)
C64	0.9099(5)	0.5950(3)	0.1668(3)	0.026(2)
N4	0.8233(5)	0.5567(3)	0.1447(2)	0.031(2)
C65	0.6955(7)	0.5600(4)	0.1803(4)	0.042(2)
C66	0.8410(7)	0.5120(4)	0.0804(3)	0.042(2)
C70	1.2715(8)	0.6101(4)	0.0656(4)	0.053(3)
C69	1.2699(7)	0.5759(4)	0.1333(4)	0.053(3)
C68	1.1524(6)	0.5713(4)	0.1656(3)	0.039(2)
C67	1.0353(6)	0.5998(3)	0.1299(3)	0.028(2)
C72	1.0374(7)	0.6344(4)	0.0628(3)	0.040(2)
C71	1.1563(8)	0.6405(4)	0.0310(4)	0.052(3)

[a] The anisotropic temperature factors are defined by the following equation: $T = \exp(-2\pi^2 \cdot [U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*])$ and $U = 1/3(U_{11} + U_{22} + U_{33})$. – [b] Anisotropic refinements for all atoms.

the residue is crystallized from hot methanol (50 ml). The mother liquors are kept for the isolation of **16**. The crystals are dissolved in chloroform (40 ml). Filtration of the turbid solution, evaporation of the solvent, and crystallization of the residue from methanol (20 ml) give yellow needles (1.85 g, 82%); m.p. 159–161°C. – IR: $\tilde{\nu}$ = 2130 (broad), 1598 cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 3.81, 3.86 (6H), (CH$_3$), 6.08 (*m*-H).

$C_{10}H_{11}NO_3S$ (225.3) Calcd. C 53.32 H 4.92 N 6.22
Found C 53.30 H 4.88 N 6.36

N^3-(Methoxycarbonyl)-N^1,N^1-dimethylbenzamidinium Hexachloroantimonate (**16**): The mother liquor of the first crystallization of **14b** is evaporated to dryness. The residue is dissolved in dichloromethane (40 ml). Filtration from an impurity and evaporation of the solvent yield a colorless powder (1.63 g, 30%); m.p. 225–227°C (dec.). – IR: $\tilde{\nu}$ = 1490, 1630, 1790 cm^{-1}. – ^{1}H NMR (CD$_3$CN): δ = 3.18, 3.46, 3.71 (CH$_3$), 9.34 (NH). – ^{13}C NMR (CD$_3$CN): δ = 43.6, 45.1, 55.2 (CH$_3$), 151.3, 166.6 (C=N, C=O).

$C_{11}H_{15}Cl_6N_2O_2Sb$ (541.7) Calcd. C 24.39 H 2.79 N 5.17
Found C 24.25 H 2.56 N 5.15

N^1,N^1-Dimethyl-N^3-(2-methyl-3,3-diphenyl-1,4,2-oxathiazolidin-5-ylidene)benzamidinium Hexachloroantimonate (**18**): A mixture of **1b** (5.26 g, 10 mmol) and **17**[56] in dichloromethane (30 ml) is first stirred at 0°C for 1 h and then at 22°C for 12 h. Filtration after addition of activated carbon and slow addition of ether (50 ml) affords a precipitate, which is crystallized from dichloromethane (30 ml)/ether (40 ml) giving a yellow powder (1.62 g, 22%); m.p. 183–186°C (dec.). – IR: $\tilde{\nu}$ = 1570, 1630 cm^{-1}. – ^{1}H NMR (CD$_3$CN): δ = 3.09, 3.15, 3.52 (CH$_3$). – ^{13}C NMR (CD$_3$CN, 263 K): δ = 32.1, 40.3, 42.4 (CH$_3$), 84.1 (C), 170.8, 171.7 (C=N).

$C_{24}H_{24}Cl_6N_3OSSb$ (737.0) Calcd. C 39.11 H 3.28 N 5.70
Found C 39.56 H 3.40 N 5.76

5,6,7,8-Tetrahydro-2-phenyl-4H-1,3-benzoxazine-4-thione (**20**): A solution of 1-piperidino-1-cyclohexene (1.65 g, 10 mmol) in dichloromethane (10 ml) is added dropwise to a cold (0°C) solution of **1c**[3] (3.60 g, 10 mmol) in dichloromethane (15 ml). After 15 min a saturated solution of NaHCO$_3$ in water (25 ml) is added dropwise to the reaction mixture. The organic phase is separated, the aqueous phase is washed with dichloromethane, and the combined organic phases are washed with water. Drying with sodium sulfate, evaporation of the solvent, and precipitation of the residue from chloroform (15 ml)/pentane (25 ml) afford an orange powder, which after crystallization at –20°C from chloroform (15 ml)/pentane (25 ml) gives red needles (1.12 g, 46%); m.p. 189–191°C (ref.[5] 198–199°C). – IR: $\tilde{\nu}$ = 1640, 1540 cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 1.83 (m, 4H), 2.58 (t), 2.66 (t) (CH$_2$). – ^{13}C NMR (CDCl$_3$): δ = 21.6, 22.2, 26.1, 26.8 (CH$_2$), 200.8 (C=S).

$C_{14}H_{13}NOS$ (243.3) Calcd. C 69.11 H 5.39 N 5.76
Found C 69.10 H 5.33 N 5.68

4-(Ethylthio)-5,6,7,8-tetrahydro-2-phenyl-1,3-benzoxazinium Tetrafluoroborate (**21**): A solution of triethyloxonium tetrafluoroborate (2.43 g, 10 mmol) in dichloromethane (15 ml) is added dropwise to a solution of **20** (2.43 g, 10 mmol) in dichloromethane (25 ml). After 2 h at 23°C the solution is cooled to 0°C, and the product is precipitated by slow addition of pentane (40 ml). Crystallization from dichloromethane (25 ml)/pentane (25 ml) at –20°C affords a pale yellow powder (2.23 g, 63%); m.p. 194–197°C (dec.). – IR: $\tilde{\nu}$ = 1610, 1580 (shoulder) cm^{-1}. – ^{1}H NMR (CD$_3$CN): δ = 1.50 (t, *J* = 7.3 Hz, CH$_3$), 3.62 (q, *J* = 7.3 Hz, CH$_2$). – ^{13}C NMR (CD$_3$CN): δ = 14.1 (CH$_3$), 21.0, 21.1, 23.8, 27.9 (CH$_2$), 164.5, 171.9, 189.9 (C=N, C=O).

$C_{16}H_{18}BF_4NOS$ (359.2) Calcd. C 53.50 H 5.05 N 3.90
Found C 53.36 H 5.12 N 3.90

N^1,N^1-Dimethyl-N^3-(2-thiabicyclo[2.2.1]hept-5-en-3-ylidene)benzamidinium Hexachloroantimonate (**22**): Cyclopentadiene (0.66 g, 10 mmol) in dichloromethane (20 ml) is added dropwise to a solution of **1b** (5.26 g, 10 mmol) in dichloromethane (25 ml). After 2 h of stirring the product is precipitated by slow addition of ether (50 ml) affording a pale brown powder (5.12 g, 87%); m.p. 118–120°C (dec.). – IR: $\tilde{\nu}$ = 1600 (vs, broad), 1560 (shoulder) cm^{-1}. – ^{1}H NMR (CD$_3$CN): δ = 2.17 (m), 2.28 (d, *J* = 9.6 Hz) (CH$_2$), 3.40, 3.43 (NCH$_3$), 4.14 (m), 4.85 (m), 6.43 (m) (CH). – ^{13}C NMR (CD$_3$CN, 263 K): δ = 42.1, 44.8, 59.8, 61.1, 62.4 (CH$_3$, CH$_2$, CH), 130.0, 130.1 (C=C), 128.7, 134.2, 135.9, 144.9 (Ph), 172.9 (C=N), 197.3 (C=S).

$C_{15}H_{17}Cl_6N_2SSb$ (591.9) Calcd. C 30.44 H 2.90 N 4.73
Found C 30.41 H 2.92 N 4.67

CAS-Registry-Nummern

1a: 136357-83-0 / **1b**: 136357-77-2 / **1c**: 136357-84-1 / **1d**: 94224-23-4 / **2**: 136357-79-4 / **3**: 136357-81-8 / **7**: 746-47-4 / **9a**: 136357-88-5 / **9b**: 136357-86-3 / **10**: 136357-72-7 / **11**: 136357-73-8 / **12a**: 2904-57-6 / **12b**: 2904-59-8 / **13a**: 136357-90-9 / **13b**: 136357-92-1 / **14b**: 51675-22-0 / **16**: 136357-94-3 / **17**: 7500-79-0 / **18**: 136357-96-5 / **20**: 5185-14-8 / **21**: 136357-75-0 / **22**: 136357-98-7 / benzylalcohol: 100-51-6 / dimethylformamide: 68-12-2 / 9-diozolfluorene: 832-80-4 / 1-piperidino-1-cyclohexene: 2981-10-4 / cyclopentadiene: 542-92-7

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