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Metal Complexes of Cyanamides and their Alkylation to Cyanamidium Salts. A General Synthesis of Highly Substituted Ureas, Isoureas, and Guanidines

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The complexes **3a** – **p** were prepared from disubstituted cyanamides and Lewis acids. According to a X-ray structural analysis, the antimony pentachloride complex **3a** is neither a σ nor a π complex (∢ C≡N – Sb 133°). The complexes **3** with $SbCl_5$ and $FeCl_3$ can be alkylated with tertiary alkyl chlorides, affording crystalline cyanamidium salts (**5a** – **m**) which were characterized by reactions with water, primary or secondary alcohols to give ureas (**11**) and uronium salts (**8a** – **z**), respectively. The guanidinium salts **9a** – **s** were obtained with ammonia, primary and secondary amines.

Metallkomplexe von Cyanamiden und ihre Alkylierung zu Cyanamidiumsalzen. Eine allgemeine Synthese hochsubstituierter Harnstoffe, Isoharnstoffe und Guanidine

Aus disubstituierten Cyanamiden und Lewis-Säuren werden die Komplexe **3a** – **p** erhalten. Nach einer Röntgenstrukturanalyse hat der Antimonpentachlorid-Komplex **3a** weder σ- noch π-Symmetrie (∢ C≡N – Sb 133°). Die Komplexe **3** mit $SbCl_5$ oder $FeCl_3$ können mit tertiären Alkylchloriden zu den kristallinen Cyanamidiumsalzen **5a** – **m** alkyliert werden. Mit Wasser, primären oder sekundären Alkoholen reagieren die Verbindungen **5** zu Harnstoffen (**11**) bzw. Uroniumsalzen (**8a** – **z**), mit Ammoniak, primären oder sekundären Aminen zu Guanidiniumsalzen (**9a** – **s**).

Disubstituted cyanamides react with many metal centres to form stable complexes. There have to be considered three sites at a cyanamide to which the metal may be coordinated: a lone pair of electrons at each nitrogen and the nitrile π-electrons. The spectral properties of the known cyanamide complexes seem to be consistent with coordination to the nitrile group only. Usually, an increase in the energy of the nitrile antisymmetric stretching vibration (e.g. dimethylcyanamide: ν_{CN} = 2221 cm^{-1}; 0.1 M in CCl_4 [1]) on complexation is taken as evidence for a coordination to the nitrile lone pair (σ complex) (e.g. $(CH_3)_2NCN \cdot BF_3$: ν_{CN} = 2307 cm^{-1}; 0.1 M in CCl_4 [1]), while a shift to smaller wave numbers is believed to demonstrate complexation to the nitrile π system (π complex) (e.g. **1**: ν_{CN} = 2008 cm^{-1}; KBr [2]). The Cr(0) complex **2** of diethylcyanamide has been shown by an X-ray structural analysis to be a σ complex[3]. Similar complexes with other transition metals are known[4,5]. On the other hand, in the nitrile complex **1**[6] and related compounds[7,8] the nitrile group acts as a four electron donor forming a σ bond to one metal atom and a π bond to an other. In such cases there is no simple relation between the position of ν_{CN} in the IR spectra and the structure of the cyanamide complex. Therefore, the classifi-

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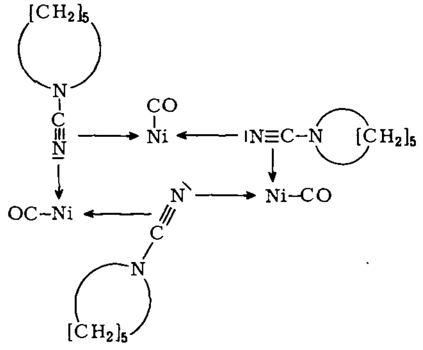
cation of the cyanamide complexes $R^2NCN \cdot X$ with X = $Al(C_2H_5)_3$[9], BF_3, $(SnCl_4)_{1/2}$[1,10,11], $(NiCl_2)_{1/3}$, $(CoCl_2)_{1/3}$[12], $TiCl_4$, $(ZrCl_4)_{1/2}$[11] as σ complexes from IR arguments alone has to be regarded with caution.



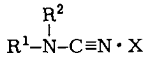
1

$(C_2H_5)_2N{-}C{\equiv}N{\rightarrow}Cr(CO)_5$

2

In the course of our work on cyanamidium salts (**5**)[13,14] the complexes **3a – p** were prepared. A bathochromic shift of ν_{CN} of diisopropylcyanamide (ν_{CN} = 2180 cm^{-1}; 0.1 M in $CHCl_3$) to 2170 cm^{-1} is observed on complexation with antimony pentachloride. But for the boron trifluoride complex a hypsochromic shift of ν_{CN} to 2310 cm^{-1} was found. To find out whether this may be due to a dimeric ionic structure of the antimony pentachloride compound[15] an X-ray structural analysis of **3a** was undertaken.

3a-p



$R^1{-}\overset{R^2}{\overset{|}{N}}{-}C{\equiv}N \cdot X$

3	R^1	R^2	X	3	R^1	R^2	X
a	$(CH_3)_2CH$	$(CH_3)_2CH$	$SbCl_5$	**i**	CH_3	CH_3	$SbCl_5$
b	$(CH_3)_2CH$	$(CH_3)_2CH$	BF_3	**j**	CH_3	$(CH_3)_2CH$	$SbCl_5$
c	$(CH_3)_2CH$	$(CH_3)_2CH$	$FeCl_3$	**k**	CH_3	c-C_6H_{11}	$SbCl_5$
d	$(CH_3)_2CH$	$(CH_3)_2CH$	$AlCl_3$	**l**	CH_3	C_6H_5	$SbCl_5$
e	$(CH_3)_2CH$	$(CH_3)_2CH$	$TiCl_4$	**m**	$-[CH_2]_5-$		$SbCl_5$
f	$(CH_3)_2CH$	$(CH_3)_2CH$	$ZnCl_2$	**n**	$-[CH_2]_2O[CH_2]_2-$		$SbCl_5$
g	$(CH_3)_2CH$	$(CH_3)_2CH$	1/2 $ZnCl_2$	**o**	C_6H_5	C_6H_5	$SbCl_5$
h	$(CH_3)_2CH$	$(CH_3)_2CH$	1/2 $SnCl_4$	**p**	C_6H_5	c-C_6H_{11}	$SbCl_5$

X-Ray Diffraction Analysis of 3a*)

3a, $C_7H_{14}N_2 \cdot SbCl_5$, orthorhombic, space group $P2_12_12_1$ (No. 19[16]) $Z = 4$, $a = 986\,(1)$, $b = 1207\,(1)$, $c = 1342\,(1)$ pm, $V = 1598 \cdot 10^6$ pm^3, $d_{calc.} = 1.77$ gcm^{-3}, $\mu_{Mo\text{-}K_\alpha} = 25.5$ cm^{-1}, $T = 298$ K, ω-scan, $\Delta\omega = 1.1°$, $3 < \dot{\omega} < 29.3°\,\text{min}^{-1}$, $2 \leqslant 2\Theta < 44°$, 1061 independent significant reflections ($I \geqslant 2\sigma$). The cell constants and the reflection intensities were determined on a Syntex

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*) Further details of the structural analysis can be obtained referring to this paper and to the registration number CSD 50494 from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen.

P3 diffractometer (graphite monochromator, $\lambda_{\text{Mo-}K_\alpha} = 71.069$ pm). The structure was solved by direct methods using the programme SHEL-XTL[17]. Hydrogen atoms were fixed on calculated geometrically ideal positions. Atomic factors of neutral atoms were used. The anisotropic refinement led to final agreement factors $R_1 = 0.038$ and $R_2 = 0.041$.

$$R_1 = [\Sigma|F_o - |F_c||] \cdot [\Sigma F_o]^{-1/2},\ R_2 = [\Sigma w \cdot (F_o - |F_c|)^2]^{1/2} \cdot [\Sigma w \cdot F_o^2]^{-1/2}$$

A list of atomic coordinates with LS-computed standard deviations is given in Table 1. In Table 2 the bond angles and selected torsional angles of **3a** are listed. Fig. 1 shows a molecular drawing and the bond lengths.

Table 1. Fractional Atomic Coordinates and Temperature Parameters of **3a**[a)]

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Sb	1.11891(8)	-0.00167(9)	1.04292(6)	N2	0.838(1)	0.0686(9)	0.8113(8)
Cl1	1.2449(4)	0.1464(4)	0.9786(4)	C2	0.697(1)	0.021(1)	0.818(1)
Cl2	0.9415(4)	0.1207(3)	1.0839(3)	C21	0.614(2)	0.088(2)	0.890(2)
Cl3	0.9788(4)	-0.1525(3)	1.0870(3)	C22	0.709(2)	-0.106(2)	0.841(2)
Cl4	1.2855(4)	-0.1257(4)	0.9875(4)	C3	0.860(2)	0.166(1)	0.743(1)
Cl5	1.2110(4)	0.0128(5)	1.2023(3)	C31	0.971(2)	0.242(1)	0.789(2)
N1	1.029(1)	-0.0185(9)	0.8982(8)	C32	0.894(2)	0.122(2)	0.642(2)
C1	0.938(1)	0.025(1)	0.859(1)				

atom	U11	U22	U33	U23	U13	U12
Sb	0.0407(4)	0.0371(4)	0.0595(5)	-0.0022(6)	0.0001(4)	-0.0001(6)
Cl1	0.069(3)	0.060(3)	0.112(4)	-0.005(3)	0.024(3)	-0.024(2)
Cl2	0.074(3)	0.046(2)	0.089(3)	-0.006(2)	0.018(2)	0.012(2)
Cl3	0.063(2)	0.041(2)	0.092(3)	0.009(2)	0.010(2)	-0.005(2)
Cl4	0.052(2)	0.069(3)	0.101(4)	-0.013(3)	-0.001(3)	0.017(2)
Cl5	0.086(3)	0.104(3)	0.073(2)	-0.012(4)	-0.021(2)	-0.002(4)
N1	0.031(6)	0.044(7)	0.071(7)	0.003(7)	0.003(6)	0.012(6)
C1	0.051(8)	0.032(8)	0.049(8)	-0.004(7)	0.015(7)	-0.011(7)
N2	0.048(7)	0.057(7)	0.059(7)	0.012(7)	-0.004(7)	0.001(6)
C2	0.045(7)	0.05(1)	0.074(9)	0.005(9)	0.001(7)	-0.011(8)
C21	0.06(1)	0.11(1)	0.15(2)	0.01(2)	0.02(1)	0.01(1)
C22	0.07(1)	0.09(1)	0.18(2)	0.05(2)	-0.04(2)	-0.03(1)
C3	0.06(1)	0.09(1)	0.09(1)	0.05(1)	0.01(1)	0.03(1)
C31	0.14(2)	0.06(1)	0.14(2)	0.06(1)	0.01(2)	-0.02(1)
C32	0.09(1)	0.17(2)	0.09(1)	0.06(2)	0.03(1)	0.02(2)

[a)] The anisotropic temperature parameters are defined by the equation:
$T = \exp(-2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*])$.

The crystals of **3a** consist of monomeric nonionic complexes of one molecule of antimony pentachloride with one molecule of the cyanamide. The complex has neither a σ nor a π symmetry. Because of a C1 – N1 – Sb bond angle of 133° and a torsional angle C3 – N2 – N1 – Sb of 95° the moiety $\rangle$N – C≡N – Sb shows approximate C_s symmetry. But the nitrogen N1 is not sp^2 hybridized as might be supposed from the allene like geometry of **3a**. The lengths of the C1 – N1 "triple bond" (117 pm) and of the N2 – C1 "single bond" (129 pm) in **3a** are similar to those of an cyanamidium salt (116 and 125 pm, respectively[13,18]) and are clearly different from the N=C=N double bond lengths (about 122 pm[19]) in carbodiimides. The complex of acetonitrile and antimony

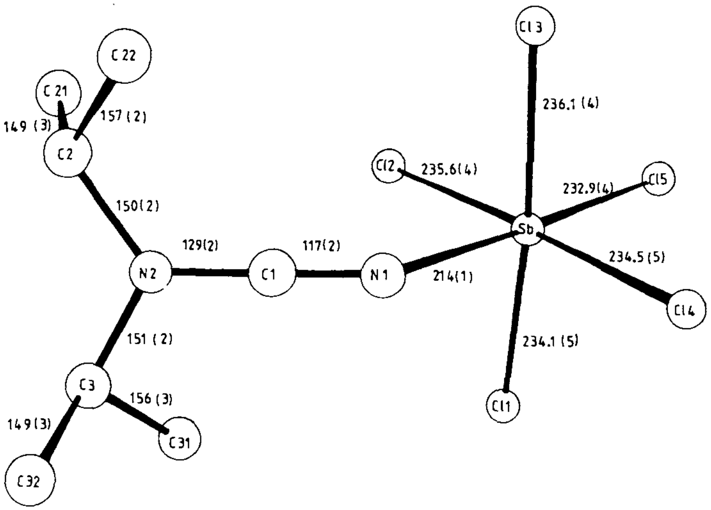
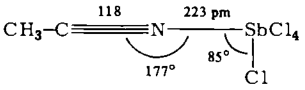


Fig. 1. Molecular Drawing and Bond Lengths (pm) of **3a**

Table 2. Bond Angles and Selected Torsional Angles [°] of **3a**

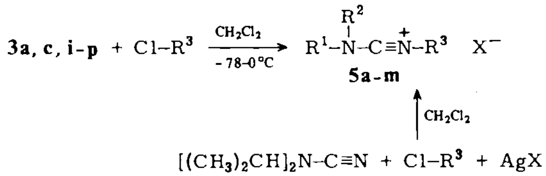
N2-C1-N1	177(1)	Cl1-Sb-Cl2	90.1(2)
C1-N1-Sb	133(1)	Cl1-Sb-Cl3	172.5(2)
C2-N2-C1	121(1)	Cl1-Sb-Cl4	89.9(2)
C3-N2-C1	121(1)	Cl1-Sb-Cl5	94.2(2)
C2-N2-C3	118(1)	Cl2-Sb-Cl3	89.5(1)
C21-C2-N2	110(1)	Cl2-Sb-Cl4	174.6(2)
C22-C2-N2	109(1)	Cl2-Sb-Cl5	91.6(2)
C21-C2-C22	117(2)	Cl3-Sb-Cl4	89.8(2)
C31-C3-N2	108(1)	Cl3-Sb-Cl5	93.2(2)
C32-C3-N2	108(2)	Cl4-Sb-Cl5	93.8(2)
C31-C3-C32	114(2)		
N1-Sb-Cl1	87.6(3)	C2-N2-N1-Sb	-90
N1-Sb-Cl2	87.9(3)	C3-N2-N1-Sb	+95
N1-Sb-Cl3	84.9(3)	C1-N1-Sb-Cl1	-84
N1-Sb-Cl4	86.7(3)	C22-C2-N2-C1	-28
N1-Sb-Cl5	178.1(3)	C32-C3-N2-C1	+88

pentachloride (**4**) is linear (C_{4v} framework symmetry) and has a longer N – Sb bond distance than **3a**. In both cases the N – Sb – *cis*-Cl bond angle is smaller than 90°[20]. The complex of cyanogen chloride with antimony pentachloride, Cl – CN → $SbCl_5$, which according to X-ray powder photographs is isomorphous to **4**[21], shows nuclear quadrupole resonance spectra indicating a bent C_s symmetry[22]. Apparently, the bending potential around the nitrile nitrogen atom in these complexes is shallow[23].



4

Recently, we described the preparation of cyanamidium hexachloroantimonates **5** by alkylation of disubstituted cyanamides with tert. alkyl chlorides in the presence of antimony pentachloride[13]. We now found that these sensitive compounds could be obtained in a purer and more stable state by the reaction of some of the isolated complexes **3** with tert. alkyl chlorides. The crystalline cyanamidium hexachloroantimonates **5a – j** and the tetrachloroferrate **5k** were prepared in this way while **5l, m** were obtained from diisopropylcyanamide, *tert*-butyl chloride, and $AgBF_4$ or $AgSbF_6$, respectively.



5	R¹	R²	R³	X
a	$(CH_3)_2CH$	$(CH_3)_2CH$	$(CH_3)_3C$	$SbCl_6$
b	$(CH_3)_2CH$	$(CH_3)_2CH$	1-adamantyl*)	$SbCl_6$
c	CH_3	CH_3	$(CH_3)_3C$	$SbCl_6$
d	CH_3	CH_3	1-adamantyl*)	$SbCl_6$
e	$-[CH_2]_5-$		$(CH_3)_3C$	$SbCl_6$
f	$-[CH_2]_5-$		1-adamantyl*)	$SbCl_6$
g	$-[CH_2]_2O[CH_2]_2-$		$(CH_3)_3C$	$SbCl_6$
h	C_6H_5	C_6H_5	$(CH_3)_3C$	$SbCl_6$
i	C_6H_5	$c\text{-}C_6H_{11}$	$(CH_3)_3C$	$SbCl_6$
j	CH_3	$c\text{-}C_6H_{11}$	$(CH_3)_3C$	$SbCl_6$
k	$(CH_3)_2CH$	$(CH_3)_2CH$	$(CH_3)_3C$	$FeCl_4$
l	$(CH_3)_2CH$	$(CH_3)_2CH$	$(CH_3)_3C$	BF_4
m	$(CH_3)_2CH$	$(CH_3)_2CH$	$(CH_3)_3C$	SbF_6

*) 1-adamantyl =

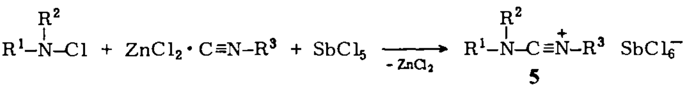
The salts **5** can only be obtained from the complexes **3** containing antimony pentachloride or iron trichloride. The $AlCl_3$ complex (**3d**) and *tert*-butyl chloride form the cyanamidium salt **5a** (X = $AlCl_4$) in an equilibrium as can be seen from the ^1H NMR spectra of the solutions (e.g. **3d**: CH δ = 3.64 (sept., J = 7 Hz), $[(CH_3)_2CH]_2NC\overset{+}{N}C(CH_3)_3$ $AlCl_4^-$: CH δ = 3.86 (sept., J = 7 Hz)). No reactions were observed between the complexes **3b, e – h** and *tert*-butyl chloride. No reactions, too, were observed between the antimony pentachloride complexes **3a, i – p** and alkyl chlorides like benzyl chloride or isopropyl chloride.

Other nitriles are known to be alkylated by secondary and even primary alkyl chlorides in the presence of strong Lewis acids although more sluggish than with tert. alkyl chlorides[24]. The mechanism of the alkylation of nitriles still remains unknown. Considering the mechanism of a nucleophilic substitution on an octahedron it would seem likely that the uncomplexed nitrile is the species that is alkylated. The experiments with **3d** indicate that the whole reaction is reversible.

$$\underset{\mathbf{3}}{R^1{-}C{\equiv}N\cdot X} + Cl{-}R^2 \rightleftharpoons R^1{-}C{\equiv}N| + X\cdots Cl{-}R^2 \rightleftharpoons \underset{\mathbf{5}}{R^1{-}C{\equiv}\overset{+}{N}{-}R^2} + XCl^-$$

Contrary to other nitriles (R^1 = ⪫C) for cyanamides (R^1 = >N) the first equilibrium lies far to the left. Strong Lewis acids X shift the second equilibrium to the right but the first equilibrium to the left side.

Cyanamidium salts **5**, except for tert. alkyl substituents R^3, also can be obtained from isocyanides and *N*-chlorodialkylamines in the presence of antimony pentachloride and mercury chloride or zinc chloride[14].



$$R^1{-}\overset{R^2}{\overset{|}{N}}{-}Cl + ZnCl_2\cdot C{\equiv}N{-}R^3 + SbCl_5 \xrightarrow[-\,ZnCl_2]{} R^1{-}\overset{R^2}{\overset{|}{N}}{-}C{\equiv}\overset{+}{N}{-}R^3\ SbCl_6^-$$

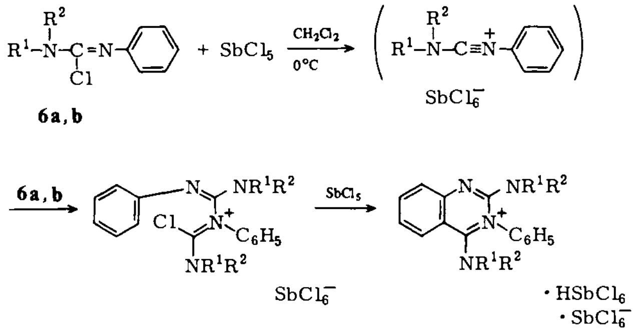
5

R^1, R^2 = alkyl, R^3 = alkyl, aryl, benzyl

The cyanamidium salts **5a – m** are moisture sensitive colourless compounds which can be stored for some time below 0 °C; the thermal lability increases if R^1, R^2 are aryl or methyl. The IR spectra of the salts **5** show characteristic strong and broad bands between 2200 and 2300 cm^{-1}, which may be assigned to the antisymmetric stretching vibration of $C{\equiv}\overset{+}{N}$. The ^{13}C NMR resonances of the nitrilium carbons appear between 115 and 120 ppm as weak and broad signals.

Preliminary attempts to prepare cyanamidium salts **5** from chloroformamidines **6** and antimony pentachloride proved to be fruitless. Trialkyl-substituted chloroformamidines with bulky alkyl groups, which can be expected to give stable cyanamidium salts **5**, are not easily accessible and suffer from von Braun cleavage[24], affording disubstituted cyanamides and alkyl chlorides.

The N^2-phenyl-substituted chloroformamidines **6a, b** react with antimony pentachloride to give the quinazolinium salts **7a, b**[25].



6a, b

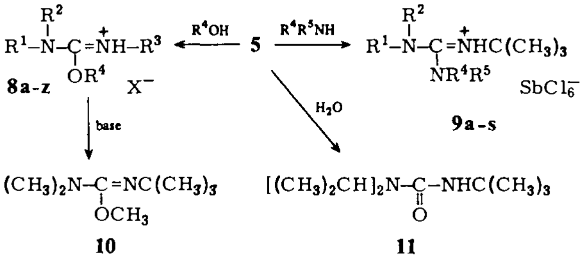
a: R^1, R^2 = $-[CH_2]_5-$

b: R^1, R^2 = $-[CH_2]_2O[CH_2]_2-$

7a, b

The cyanamidium salts **5** react under mild conditions with primary or secondary alcohols, bringing about the uronium salts **8a – z**, a class of compounds of considerable synthetic value[26,27]. From tert. alcohols the cyanamidium salts **5** eliminate water giving trisubstituted ureas[26]. These compounds (e.g. **11**) can be formed directly by hydrolysis of **5**[27].

With thiols the cyanamidium salts **5** do not give thiuronium salts. Apparently, the thiols are alkylated by **5** to sulfides. This reaction and the corresponding reactions with phenols and sulfides are presently under investigation.



8	R¹	R²	R³	R⁴	X
a	*i*Pr	*i*Pr	*t*Bu	CH_3	BF_4
b	*i*Pr	*i*Pr	*t*Bu	CH_3	SbF_6
c	*i*Pr	*i*Pr	*t*Bu	C_2H_5	$FeCl_4$
d	*i*Pr	*i*Pr	*t*Bu	*i*Pr	$SbCl_6$
e	*i*Pr	*i*Pr	*t*Bu	*n*Bu	$SbCl_6$
f	*i*Pr	*i*Pr	*)	CH_3	$SbCl_6$
g	CH_3	CH_3	*t*Bu	CH_3	$FeCl_4$
h	CH_3	CH_3	*t*Bu	C_2H_5	$SbCl_6$
i	CH_3	CH_3	*t*Bu	*i*Pr	$SbCl_6$
j	CH_3	CH_3	*)	CH_3	$SbCl_6$
k	C_6H_5	C_6H_5	*t*Bu	CH_3	$SbCl_6$
l	C_6H_5	*c*-C_6H_{11}	*t*Bu	CH_3	$SbCl_6$
m	CH_3	*c*-C_6H_{11}	*t*Bu	CH_3	$SbCl_6$
n	CH_3	*t*Bu	*t*Bu	CH_3	$SbCl_6$
o	$-[CH_2]_5-$		*t*Bu	CH_3	$SbCl_6$
p	$-[CH_2]_5-$		*t*Bu	C_2H_5	$SbCl_6$
q	$-[CH_2]_5-$		*t*Bu	*i*Pr	$SbCl_6$
r	$-[CH_2]_5-$		*)	CH_3	$SbCl_6$
s	$-[CH_2]_2O[CH_2]_2-$		*t*Bu	CH_3	$SbCl_6$
t	$-[CH_2]_2O[CH_2]_2-$		*t*Bu	C_2H_5	$SbCl_6$
u	CH_3	*i*Pr	*t*Bu	CH_3	$SbCl_6$
v	CH_3	*i*Pr	*t*Bu	C_2H_5	$SbCl_6$
w	CH_3	C_6H_5	*t*Bu	CH_3	$SbCl_6$
x	CH_3	C_6H_5	*t*Bu	C_2H_5	$SbCl_6$
y	CH_3	C_6H_5	*t*Bu	*i*Pr	$SbCl_6$
z	*i*Pr	*i*Pr	H	CH_3	$SbCl_6$

9	R¹	R²	R⁴	R⁵
a	*i*Pr	*i*Pr	H	H
b	*i*Pr	*i*Pr	*t*Bu	H
c	*i*Pr	*i*Pr	C_6H_5	H
d	*i*Pr	*i*Pr	$-[CH_2]_2O[CH_2]_2-$	
e	*i*Pr	*i*Pr	C_2H_5	C_2H_5
f	*i*Pr	*i*Pr	*i*Pr	CH_3
g	CH_3	CH_3	$C_6H_5CH_2$	H
h	CH_3	CH_3	*i*Pr	H
i	CH_3	CH_3	*t*Bu	H
j	CH_3	CH_3	*i*Pr	*i*Pr
k	CH_3	CH_3	$-[CH_2]_5-$	
l	CH_3	CH_3	$-[CH_2]_2O[CH_2]_2-$	
m	$-[CH_2]_5-$		$-[CH_2]_2O[CH_2]_2-$	
n	$-[CH_2]_5-$		*t*Bu	H
o	$-[CH_2]_5-$		$-[CH_2]_5-$	
p	$-[CH_2]_2O[CH_2]_2-$		$-[CH_2]_2O[CH_2]_2-$	
q	CH_3	C_6H_5	CH_3	CH_3
r	CH_3	C_6H_5	C_6H_5	H
s	CH_3	C_6H_5	*t*Bu	H

*) 1-adamantyl = 

The uronium salt **8z** resulted from silylation of **3a** with chlorotrimethylsilane and subsequent addition of methanol. With base the isoureas (e.g. **10**) can be obtained from the uronium salts **8**. Finally, the cyanamidium salts **5** were characterized by transformation into the guanidinium salts **9a**–s with ammonia, primary or secondary amines.

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Experimental Part

IR spectra: Perkin-Elmer IR 299. – ^{1}H and ^{13}C NMR spectra: Jeol JNM-MH-100 and Bruker WM-250 spectrometer, internal reference tetramethylsilane. – The melting points are uncorrected.

Antimony Pentachloride-Diisopropylcyanamide (**3a**): To antimony pentachloride (5.98 g, 20 mmol) in dry dichloromethane (20 ml) was added dropwise with stirring at –78°C a solution of diisopropylcyanamide (2.53 g, 20 mmol) in dry dichloromethane (20 ml). Stirring was continued for 1 h at –78°C and then for 2 h at +22°C. The solvent was evaporated under reduced pressure to a volume of 5 ml. Dry pentane (50 ml) was added slowly and the precipitate isolated and washed with pentane affording a moisture sensitive yellow powder (8.08 g, 95%) which can be recrystallized from dry dichloromethane; m.p. 94–96°C. – ^{1}H-NMR ($CDCl_3$): CH_3 δ = 1.55 (d, J = 7 Hz), CH 3.71 (sept., J = 7 Hz). – ^{13}C-NMR ($CDCl_3$, 280 K, TMS external): CH_3 δ = 23.2, CH 57.7, CN 130.6. – IR ($CHCl_3$): 2170 cm^{-1}.

$[C_7H_{14}N_2]SbCl_5$ (425.2) Calcd. C 19.77 H 3.32 N 6.59 Found C 19.74 H 3.24 N 6.37

Boron Trifluoride-Diisopropylcyanamide (**3b**): From boron trifluoride etherate (2.84 g, 20 mmol) as described for **3a**. Yield 3.57 g (92%) of a colourless hygroscopic oil which solidified below –10°C. – ^{1}H-NMR ($CDCl_3$): CH_3 δ = 1.36 (d, J = 7 Hz), CH 3.49 (sept., J = 7 Hz). – ^{13}C-NMR ($CDCl_3$, 263 K): CH_3 δ = 21.2, CH 53.3, CN 111.6. – IR ($CHCl_3$): 2309 cm^{-1}.

$[C_7H_{14}N_2]BF_3$ (194.0) Calcd. C 43.33 H 7.27 N 14.44 Found C 43.39 H 7.47 N 14.14

Iron Trichloride-Diisopropylcyanamide (**3c**): From dry iron trichloride (3.24 g, 20 mmol) as described for **3a**. Yield 4.85 g (84%) of a hygroscopic brown oil. – IR ($CHCl_3$): 2220 cm^{-1}.

$[C_7H_{14}N_2]FeCl_3$ (288.4) Calcd. C 29.15 H 4.89 N 9.72 Found C 29.02 H 4.83 N 9.60

Aluminium Trichloride-Diisopropylcyanamide (**3d**): From dry aluminium trichloride (2.67 g, 20 mmol) as described for **3a**. Yield 4.78 g (92%) of a hygroscopic pale brown oil which slowly eliminated diisopropylcyanamide at 0.1 Torr. – ^{1}H-NMR ($CDCl_3$): CH_3 δ = 1.43 (d, J = 7 Hz), CH 3.64 (sept., J = 7 Hz). – ^{13}C-NMR ($CDCl_3$, TMS external): CH_3 δ = 23.0, CH 56.1, CN 122.6. – IR ($CHCl_3$): 2250 cm^{-1}.

$[C_7H_{14}N_2]AlCl_3$ (259.5) Calcd. C 32.39 H 5.44 N 10.80 Found C 32.10 H 5.53 N 10.83

Titanium Tetrachloride-Diisopropylcyanamide (**3e**): From titanium tetrachloride (3.79 g, 20 mmol) as described for **3a**. Yield 6.13 g (97%) of a hygroscopic yellow powder; m.p. 72–73°C. – ^{1}H-NMR ($CDCl_3$): CH_3 δ = 1.40 (d, J = 7 Hz), CH 3.49 (sept., J = 7 Hz). – ^{13}C-NMR ($CDCl_3$): CH_3 δ = 21.9, CH 53.8, CN 121.8. – IR ($CHCl_3$): 2215 cm^{-1}.

$[C_7H_{14}N_2]TiCl_4$ (315.9) Calcd. C 26.61 H 4.47 N 8.87 Found C 26.57 H 4.53 N 8.74

Zinc Dichloride-Diisopropylcyanamide (**3f**): From dry zinc chloride (2.73 g, 20 mmol) as described for **3a**. Yield 5.20 g (99%) of a hygroscopic colourless oil which solidified below –10°C and quickly eliminated diisopropylcyanamide under reduced pressure. The compound quickly took up one mol of water. – ^{1}H-NMR ($CDCl_3$): CH_3 δ = 1.35 (d, J = 7 Hz), CH 3.50

(sept., J = 7 Hz). – ^{13}C-NMR ($CDCl_3$, 273 K, TMS external): CH_3 δ = 23.1, CH 54.0, CN 119.5. – IR ($CHCl_3$): 2240 cm^{-1}.

$[C_7H_{14}N_2]ZnCl_2 \cdot H_2O$ (280.5) Calcd. C 29.97 H 5.75 N 9.99
Found C 30.10 H 5.51 N 9.91

Zinc Dichloride-Bis(diisopropylcyanamide) (**3g**): From dry zinc chloride (1.36 g, 10 mmol) and diisopropylcyanamide (2.53 g, 20 mmol) as described for **3a**. Yield 3.54 g (91%) of colourless prisms; m.p. 58 – 60°C. – ^{1}H-NMR ($CDCl_3$): CH_3 δ = 1.34 (d, J = 7 Hz), CH 3.39 (sept., J = 7 Hz). – ^{13}C-NMR ($CDCl_3$, 273 K, TMS external): CH_3 δ = 23.0, CH 53.8, CN 118.6. – IR ($CHCl_3$): 2250 cm^{-1}.

$[C_{14}H_{28}N_4]ZnCl_2$ (388.7) Calcd. C 43.26 H 7.26 N 14.42 Found C 43.10 H 7.35 N 14.34

Tin Tetrachloride-Bis(diisopropylcyanamide) (**3h**): From tin(IV) chloride (2.61 g, 10 mmol) as described for **3g**. Yield 4.87 g (95%) of a hygroscopic colourless powder; m.p. 65 – 68°C. – ^{1}H-NMR ($CDCl_3$): CH_3 δ = 1.42 (d, J = 7 Hz), CH 3.53 (sept., J = 7 Hz). – ^{13}C-NMR ($CDCl_3$, 263 K, TMS external): CH_3 δ = 21.5, CH 53.6, CN 123.2. – IR ($CHCl_3$): 2201 cm^{-1}.

$[C_{14}H_{28}N_4]SnCl_4$ (512.9) Calcd. C 32.78 H 5.50 N 10.93 Found C 32.50 H 5.58 N 10.75

Antimony Pentachloride-Dimethylcyanamide (**3i**): From dimethylcyanamide (1.40 g, 20 mmol) as described for **3a**. Yield 7.01 g (95%) of a yellow powder; m.p. 136 – 138°C. – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 3.33. – IR (CH_2Cl_2): 2180 cm^{-1}.

$[C_3H_6N_2]SbCl_5$ (369.1) Calcd. C 9.76 H 1.64 N 7.59 Found C 9.88 H 1.81 N 7.42

Antimony Pentachloride-Isopropylmethylcyanamide (**3j**): From isopropylmethylcyanamide (1.96 g, 20 mmol) as described for **3a**. Yield 7.71 g (97%) of a yellow powder; m.p. 76 – 78°C. – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.50 (d, J = 7 Hz), 3.27, CH 3.65 (sept., J = 7 Hz). – IR (CH_2Cl_2): 2170 cm^{-1}.

$[C_5H_{10}N_2]SbCl_5$ (397.2) Calcd. C 15.12 H 2.54 N 7.06 Found C 15.11 H 2.65 N 6.82

Antimony Pentachloride-Cyclohexylmethylcyanamide (**3k**): From cyclohexylmethylcyanamide (2.76 g, 20 mmol) as described for **3a**. Yield 8.48 g (97%) of a yellow powder; m.p. 103 – 105°C. – ^{13}C-NMR (CD_2Cl_2, 273 K): CH_2 δ = 24.8, 24.9, 30.8, CH_3 38.1, CH 64.2, CN 132.7.

$[C_8H_{14}N_2]SbCl_5$ (437.2) Calcd. C 21.98 H 3.23 N 6.41 Found C 22.13 H 3.29 N 6.27

Antimony Pentachloride-Methylphenylcyanamide (**3l**): From methylphenylcyanamide (2.64 g, 20 mmol) as described for **3a**. Yield 8.19 g (95%) of orange prisms (from dichloromethane); m.p. 140°C. – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 3.69.

$[C_8H_8N_2]SbCl_5$ (431.0) Calcd. C 22.28 H 1.87 N 6.50 Found C 22.36 H 1.90 N 6.40

Antimony Pentachloride-1-Piperidinecarbonitrile (**3m**): From 1-piperidinecarbonitrile (2.20 g, 20 mmol) as described for **3a**. Yield 7.77 g (95%) of a yellow powder; m.p. 142 – 143°C (dec.). – IR (CH_2Cl_2): 2165 cm^{-1}.

$[C_6H_{10}N_2]SbCl_5$ (409.2) Calcd. C 17.61 H 2.46 N 6.85 Found C 17.76 H 2.58 N 6.73

Antimony Pentachloride-1-Morpholinecarbonitrile (**3n**): From 1-morpholinecarbonitrile (2.24 g, 20 mmol) as described for **3a**. Excess of antimony pentachloride adds to the oxygen. Yield 7.81 g (95%) of a yellow powder; m.p. 142 – 147°C (dec.). – IR (CH_2Cl_2): 2210 cm^{-1}.

$[C_5H_8N_2]SbCl_5$ (411.2) Calcd. C 14.61 H 1.96 N 6.82 Found C 14.83 H 2.07 N 6.78

Antimony Pentachloride-Diphenylcyanamide (**3o**): From diphenylcyanamide (3.89 g, 20 mmol) as described for **3a**. Yield 8.88 g (90%) of an olive-green powder; dec. above 93°C. – IR (CH_2Cl_2): 2220 cm^{-1}.

$[C_{13}H_{10}N_2]SbCl_5$ (493.3) Calcd. C 31.65 H 2.04 N 5.68 Found C 31.49 H 2.52 N 5.48

Antimony Pentachloride-Cyclohexylphenylcyanamide (**3p**): From cyclohexylphenylcyanamide (4.01 g, 20 mmol) as described for **3a**. Yield 8.99 g (90%) of a brown powder; dec. above 95 °C. – IR (CH_2Cl_2): 2180 cm^{-1}.

$[C_{13}H_{16}N_2]SbCl_5$ (499.3) Calcd. C 31.27 H 3.23 N 5.61 Found C 31.08 H 3.52 N 5.33

3-tert-Butyl-1,1-diisopropylcyanamidium Hexachloroantimonate (**5a**): To **3a** (8.50 g, 20 mmol) in dry dichloromethane (20 ml) was added dropwise with stirring at – 15 °C a solution of *tert*-butyl chloride (5 ml) in dry dichloromethane (10 ml). Stirring was continued for 1 h at + 5 °C. The solution was concentrated under reduced pressure to a volume of 3 ml. The product was precipitated by slow addition of dry pentane (30 ml) at 0 °C affording a colourless powder (31.23 g, 95%); m.p. 113 – 116 °C (dec.). – The IR and NMR spectra were identical with those of an authentic specimen[14)].

1,1-Diisopropyl-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)cyanamidium Hexachloroantimonate (**5b**): From **3a** (8.50 g, 20 mmol) and 1-chloroadamantane (3.76 g, 22 mmol) as described for **5a**. The reaction mixture was stirred for 12 h at + 22 °C. After addition of dry ether (50 ml) the colourless precipitate was collected (10.13 g, 85%) and recrystallized from dry dichloromethane/dry ether; m.p. 210 °C (dec.). – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.48 (d, J = 7 Hz), CH 3.87 (sept., J = 7 Hz). – ^{13}C-NMR (CD_2Cl_2, 263 K): CH_3 δ = 21.8, CHN 56.7, adamantyl C 29.8, 35.2, 43.7, 66.3, NCN 119.4. – IR (CH_2Cl_2): 2210 cm^{-1}.

$[C_{17}H_{29}N_2]SbCl_6$ (595.9) Calcd. C 34.26 H 4.91 N 4.70 Found C 34.45 H 4.91 N 4.58

3-tert-Butyl-1,1-dimethylcyanamidium Hexachloroantimonate (**5c**): From **3i** (7.38 g, 20 mmol) as described for **5a**. The reaction mixture was stirred for 1 h at 0 °C and then cooled to – 40 °C. Precipitation with dry ether (50 ml) afforded a colourless hygroscopic powder (7.39 g, 80%) which decomposed in solution but which could be kept in the solid state below 0 °C for some days; m.p. 90 – 95 °C (dec.). – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.68, 3.38. – ^{13}C-NMR (CD_2Cl_2, 263 K): CH_3 δ = 30.2, 41.9, C 65.5, NCN 114.9. – IR (CH_2Cl_2): 2270, 2320 cm^{-1}.

$[C_7H_{15}N_2]SbCl_6$ (461.7) Calcd. C 18.21 H 3.28 N 6.07 Found C 18.45 H 3.31 N 6.09

1,1-Dimethyl-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)cyanamidium Hexachloroantimonate (**5d**): From **3i** (7.38 g, 20 mmol) and 1-chloroadamantane (6.83 g, 40 mmol) as described for **5c**. Yield 9.93 g (92%) of a colourless powder; m.p. 160 – 165 °C (dec.). – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 3.38. – ^{13}C-NMR (CD_2Cl_2, 273 K): CH_3 δ = 42.1, adamantyl C 29.8, 35.3, 43.2, 65.5, NCN 115.9. – IR (CH_2Cl_2): 2280, 2320 cm^{-1}.

$[C_{13}H_{21}N_2]SbCl_6$ (539.8) Calcd. C 28.92 H 3.92 N 5.19 Found C 28.90 H 4.01 N 4.99

N-tert-Butyl-1-piperidinecarbonitrilium Hexachloroantimonate (**5e**): From **3m** (8.18 g, 20 mmol) as described for **5c**. Yield 9.73 g (97%) of a colourless instable powder; m.p. 103 – 106 °C (dec.). – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.67. – ^{13}C-NMR (CD_2Cl_2, 273 K): NCN δ = 114.5. – IR (CH_2Cl_2): 2260, 2310 cm^{-1}.

$[C_{10}H_{19}N_2]SbCl_6$ (501.8) Calcd. C 23.94 H 3.82 N 5.59 Found C 24.06 H 3.83 N 5.43

N-(Tricyclo[3.3.1.1^{3,7}]dec-1-yl)-1-piperidinecarbonitrilium Hexachloroantimonate (**5f**): From **3m** (8.18 g, 20 mmol) as described for **5d**. Yield 8.12 g (70%) of a colourless powder; m.p. 170 – 175 °C (dec.). – IR (CH_2Cl_2): 2240 cm^{-1}.

$[C_{16}H_{25}N_2]SbCl_6$ (579.9) Calcd. C 33.14 H 4.35 N 4.83 Found C 33.17 H 4.32 N 4.57

N-tert-Butyl-1-morpholinecarbonitrilium Hexachloroantimonate (**5g**): From **3n** (8.22 g, 20 mmol) and *tert*-butyl chloride (10 ml) as described for **5c**. Yield 8.06 g (80%) of a colourless powder of low solubility in dichloromethane; m.p. 110 – 113 °C (dec.). – IR (CH_2Cl_2): 2280 cm^{-1}.

[$C_9H_{17}N_2O$]$SbCl_6$ (503.7) Calcd. C 21.46 H 3.40 N 5.56 Found C 21.57 H 3.29 N 5.81

3-tert-Butyl-1,1-diphenylcyanamidium Hexachloroantimonate (**5h**): From **3o** (9.87 g, 20 mmol) as described for **5g**. Yield 10.43 g (89%) of a green instable powder; m.p. 105 °C (dec.). In dichloromethane an equilibrium **5h** ⇌ **3o** + *tert*-butyl chloride is observed. – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.82 (**5h**), 1.60 (*tert*-butyl chloride).

[$C_{17}H_{19}N_2$]$SbCl_6$ (585.8) Calcd. C 34.85 H 3.27 N 4.78 Found C 34.59 H 3.32 N 4.70

3-tert-Butyl-1-cyclohexyl-1-phenylcyanamidium Hexachloroantimonate (**5i**): From **3p** (9.99 g, 20 mmol) as described for **5g**. Yield 7.34 g (62%) of a brown instable powder which decomposes in dichloromethane to an equilibrium with the starting materials; m.p. 110 °C (dec.). – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.71 (**5i**), 1.59 (*tert*-butyl chloride). – IR (CH_2Cl_2): 2270 cm^{-1}.

[$C_{17}H_{25}N_2$]$SbCl_6$ (591.9) Calcd. C 34.50 H 4.26 N 4.73 Found C 34.53 H 4.30 N 4.57

3-tert-Butyl-1-cyclohexyl-1-methylcyanamidium Hexachloroantimonate (**5j**): From **3k** (8.74 g, 20 mmol) as described for **5g**. Yield 10.28 g (97%) of a colourless powder; m.p. 83 – 84 °C. – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 2.65, 3.34. – ^{13}C-NMR (CD_2Cl_2, 273 K): CH_3 δ = 30.4, 38.6, CH_2 24.8, 24.9, 30.9, CH 63.9, C 65.8, NCN 117.1. – IR (CH_2Cl_2): 2240 cm^{-1}.

[$C_{12}H_{23}N_2$]$SbCl_6$ (529.8) Calcd. C 27.20 H 4.38 N 5.29 Found C 27.52 H 4.40 N 5.14

3-tert-Butyl-1,1-diisopropylcyanamidium Tetrachloroferrate (**5k**): To dry iron(III) chloride (3.24 g, 20 mmol) in dry dichloromethane (20 ml) was added dropwise with stirring at – 78 °C a solution of diisopropylcyanamide (2.52 g, 20 mmol) in dry dichloromethane (20 ml). After stirring for 30 min at – 78 °C *tert*-butyl chloride (10 ml) was added dropwise. Stirring was continued for 30 min at – 78 °C and then for 12 h at + 22 °C. The reaction mixture was filtered and concentrated under reduced pressure to a volume of about 15 ml. After cooling to – 10 °C the product was precipitated by slow addition of dry ether (70 ml) affording a brownish powder (7.01 g, 92%) which was recrystallized from dichloromethane/ether; m.p. 55 – 56 °C. – IR (CH_2Cl_2): 2230 cm^{-1}.

[$C_{11}H_{23}N_2$]$FeCl_4$ (381.0) Calcd. C 34.68 H 6.09 N 7.36 Found C 34.53 H 6.01 N 7.41

3-tert-Butyl-1,1-diisopropylcyanamidium Tetrafluoroborate (**5l**): To silver tetrafluoroborate (3.98 g, 20 mmol) in dry dichloromethane (20 ml) at – 78 °C was added dropwise with stirring a solution of diisopropylcyanamide (2.52 g, 20 mmol) in dry dichloromethane (20 ml) followed by *tert*-butyl chloride (2.78 g, 30 mmol). Stirring was continued for 30 min at – 78 °C and then for 2 h at – 25 °C. The reaction mixture was filtered with exclusion of moisture and cooled to – 20 °C. Precipitation by addition of dry ether (100 ml) afforded a colourless powder which was dissolved in dry dichloromethane (15 ml) and precipitated at – 20 °C by addition of dry ether (50 ml) giving a hygroscopic powder (3.51 g, 65%); m.p. 46 – 47 °C. – ^{1}H-NMR ($CDCl_3$): CH_3 δ = 1.45 (d, J = 7 Hz), 1.68, CH 3.93 (sept., J = 7 Hz). – ^{13}C-NMR ($CDCl_3$, 273 K): CH_3 δ = 21.0, 29.9, CH 55.4, C 65.3, NCN 119.0. – IR (CH_2Cl_2): 2220 cm^{-1}.

[$C_{11}H_{23}N_2$]BF_4 (270.1) Calcd. C 48.91 H 8.58 N 10.37 Found C 47.15 H 8.83 N 10.31

3-tert-Butyl-1,1-diisopropylcyanamidium Hexafluoroantimonate (**5m**): From silver hexafluoroantimonate (6.87 g, 20 mmol) as described for **5l**. Yield 3.19 g (38%) of a colourless hygroscopic powder which was recrystallized at – 40 °C from dichloromethane (20 ml)/ether (100 ml); m.p. 122 – 123 °C. – ^{13}C-NMR (CD_2Cl_2, 273 K): CH_3 δ = 21.2, 30.2, CH 56.1, C 66.0, NCN 118.6. – IR (CH_2Cl_2): 2220 cm^{-1}.

[$C_{11}H_{23}N_2$]SbF_6 (419.1) Calcd. C 31.53 H 5.53 N 6.69 Found C 31.81 H 5.32 N 6.67

3-Phenyl-2,4-dipiperidinoquinazolinium Bis(hexachloroantimonate) (**7a**): To a solution of *N*-phenyl-1-piperidinecarbimidoyl chloride (**6a**)[28] (4.45 g, 20 mmol) in dry dichloromethane (20 ml) was added at −78 °C antimony pentachloride (5.98 g, 20 mmol). The mixture was warmed up to 0 °C over a period of 2 h. Slow addition of dry ether (100 ml) resulted in precipitation of a pale yellow powder (8.35 g, 80%); m.p. 180 – 185 °C (dec.).

$[C_{24}H_{30}N_4]2\,SbCl_6$ (1043.5) Calcd. C 27.62 H 2.90 N 5.37
Found C 27.94 H 2.87 N 5.36

2,4-Dimorpholino-3-phenylquinazolinium Bis(hexachloroantimonate) (**7b**): From *N*-phenyl-1-morpholinecarbimidoyl chloride[29] (4.49 g, 20 mmol) as described for **7a**. Yield 10.45 g (100%) of a yellow powder; m.p. 180 – 185 °C (dec.).

$[C_{22}H_{26}N_4O_2]2\,SbCl_6$ (1047.4) Calcd. C 25.23 H 2.50 N 5.35
Found C 25.06 H 2.66 N 5.11

Uronium Salts **8**, *General Procedure:* To a solution of the corresponding cyanamidium salt **5** (20 mmol, freshly prepared, with or without isolation) in dichloromethane (25 ml) was added dropwise with stirring at −10 °C the dry alcohol (15 ml). Stirring was continued for 1 – 3 h at +22 °C until the IR spectra of the reaction mixture no longer showed a nitrilium band around 2300 cm^{-1}. The solvent was evaporated under reduced pressure. The solid residue was stirred under ether (30 ml) and isolated by filtration. Alternatively, the reaction mixture was cooled to −20 °C and the product was precipitated by slow addition of ether (50 – 100 ml).

3-tert-Butyl-1,1-diisopropyl-2-methyluronium Tetrafluoroborate (**8a**): Recrystallization from dichloromethane (5 ml)/ether (25 ml) afforded 2.78 g (46%) of a colourless powder; m.p. 144 – 145 °C. – ^{1}H-NMR ($CDCl_2$): CH_3 δ = 1.39 (d, J = 7 Hz), 1.49, 4.14, CH 3.97 (sept., J = 7 Hz), NH 6.45. – ^{13}C-NMR ($CDCl_3$, 273 K): $(CH_3)_2$ δ = 21.0, $(CH_3)_3$ 29.5, OCH_3 63.3, CH 50.7, C 57.1, NCN 162.4.

$[C_{12}H_{27}N_2O]BF_4$ (302.2) Calcd. C 47.70 H 9.01 N 9.27 Found C 47.78 H 9.21 N 9.22

3-tert-Butyl-1,1-diisopropyl-2-methyluronium Hexafluoroantimonate (**8b**): Recrystallization from dichloromethane (30 ml)/ether (150 ml) at −10 °C afforded a colourless powder (2.03 g, 45%); m.p. 102 – 103 °C.

$[C_{12}H_{27}N_2O]SbF_6$ (451.1) Calcd. C 31.95 H 6.03 N 6.21 Found C 32.21 H 6.07 N 6.19

3-tert-Butyl-2-ethyl-1,1-diisopropyluronium Tetrafluoroferrate (**8c**): Yield 8.29 g (97%). Recrystallization from chloroform (60 ml)/ether afforded green needles; m.p. 183 °C.

$[C_{13}H_{29}N_2O]FeCl_4$ (427.0) Calcd. C 36.56 H 6.84 N 6.56 Found C 36.52 H 6.87 N 6.45

3-tert-Butyl-1,1,2-triisopropyluronium Hexachloroantimonate (**8d**): Yield 8.32 g (72%) of a colourless powder; m.p. 125 °C. – ^{13}C-NMR (CD_2Cl_2, 263 K): $(CH_3)_2$ δ = 21.3, 22.3, $(CH_3)_3$ 30.3, CH 50.5, OCH 83.3, C 57.4, NCN 159.8.

$[C_{14}H_{31}N_2O]SbCl_6$ (577.9) Calcd. C 29.10 H 5.41 N 4.85 Found C 29.28 H 5.49 N 4.74

2-Butyl-3-tert-butyl-1,1-diisopropyluronium Hexachloroantimonate (**8e**): Yield 8.88 g (75%). Recrystallization from dichloromethane/ether afforded a colourless powder; m.p. 159 – 160 °C.

$[C_{15}H_{33}N_2O]SbCl_6$ (591.9) Calcd. C 30.44 H 5.62 N 4.73 Found C 30.53 H 5.75 N 4.67

1,1-Diisopropyl-2-methyl-3-(tricyclo[3.3.1.$1^{3,7}$]dec-1-yl)uronium Hexachloroantimonate (**8f**): Yield 10.68 g (85%). Recrystallization from dichloromethane/ether afforded a colourless powder; m.p. 170 – 171 °C. – ^{13}C-NMR (CD_2Cl_2): CH_3 δ = 21.3, OCH_3 64.6, adamantyl C 30.2, 35.9, 43.2, 59.2, NCN 162.3.

$[C_{18}H_{33}N_2O]SbCl_6$ (628.0) Calcd. C 34.43 H 5.30 N 4.46 Found C 34.49 H 5.38 N 4.39

3-tert-Butyl-1,1,2-trimethyluronium Tetrachloroferrate (**8g**): Yield 6.57 g (92%) of a yellow powder; m.p. 67 °C.

$[C_8H_{19}N_2O]FeCl_4$ (356.9) Calcd. C 26.92 H 5.37 N 7.85 Found C 27.31 H 5.16 N 7.90

3-tert-Butyl-2-ethyl-1,1-dimethyluronium Hexachloroantimonate (**8h**): Recrystallization from dichloromethane (15 ml)/ether afforded colourless prisms (9.34 g, 92%); m.p. 144 – 146 °C. – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.49, 1.58 (t, J = 7 Hz), 3.22, CH_2 4.52 (q, J = 7 Hz).

$[C_9H_{21}N_2O]SbCl_6$ (507.8) Calcd. C 21.29 H 4.17 N 5.52 Found C 21.27 H 4.20 N 5.45

3-tert-Butyl-2-isopropyl-1,1-dimethyluronium Hexachloroantimonate (**8i**): Recrystallization from dichloromethane/ether afforded a colourless powder (7.62 g, 73%); m.p. 120 – 122 °C.

$[C_{10}H_{23}N_2O]SbCl_6$ (521.8) Calcd. C 23.02 H 4.44 N 5.37 Found C 23.07 H 4.53 N 5.36

1,1,2-Trimethyl-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)uronium Hexachloroantimonate (**8j**): Yield 9.26 g (81%) of a colourless powder; m.p. 166 °C.

$[C_{14}H_{25}N_2O]SbCl_6$ (571.8) Calcd. C 29.40 H 4.41 N 4.90 Found C 29.50 H 4.46 N 4.81

3-tert-Butyl-2-methyl-1,1-diphenyluronium Hexachloroantimonate (**8k**): Yield 9.02 g (73%) of a yellow powder which was recrystallized from dichloromethane/ether; m.p. 117 – 120 °C. – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.47, 3.91, NH 6.07. – ^{13}C-NMR (CD_2Cl_2): CH_3 δ = 29.4, OCH_3 63.4, C 58.2, NCN 162.6, aromatic C 126.3, 130.2, 131.6, 139.3.

$[C_{18}H_{23}N_2O]SbCl_6$ (617.9) Calcd. C 34.99 H 3.75 N 4.54 Found C 35.18 H 3.79 N 4.52

3-tert-Butyl-1-cyclohexyl-2-methyl-1-phenyluronium Hexachloroantimonate (**8l**): Recrystallization from dichloromethane (35 ml)/ether afforded colourless prisms (7.49 g, 60%); m.p. 135 °C (dec.).

$[C_{18}H_{29}N_2O]SbCl_6$ (623.9) Calcd. C 34.65 H 4.69 N 4.49 Found C 34.59 H 4.69 N 4.42

3-tert-Butyl-1-cyclohexyl-1,2-dimethyluronium Hexachloroantimonate (**8m**): Yield 9.44 g (84%) of a colourless powder; m.p. 137 °C. – ^{13}C-NMR (CD_2Cl_2, 273 K): CH_3 δ = 29.9, CH_2 25.1, 25.6, 30.2, NCH_3 32.7, OCH_3 64.1, CH 60.5, C 57.3, NCN 163.1.

$[C_{13}H_{27}N_2O]SbCl_6$ (561.8) Calcd. C 27.79 H 4.84 N 4.99 Found C 27.65 H 4.83 N 4.71

1,3-Di-tert-butyl-1,2-dimethyluronium Hexachloroantimonate (**8n**): Yield 10.18 g (95%) of a colourless powder; m.p. 199 °C. – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.50, 1.53, 3.07, 4.15, NH 5.76.

$[C_{11}H_{25}N_2O]SbCl_6$ (535.8) Calcd. C 24.66 H 4.70 N 5.23 Found C 24.88 H 4.86 N 5.22

tert-Butyl(methoxypiperidinomethylen)ammonium Hexachloroantimonate (**8o**): Recrystallization from dichloromethane (10 ml)/ether at –50 °C afforded colourless prisms (10.57 g, 99%); m.p. 144 – 146 °C.

$[C_{11}H_{23}N_2O]SbCl_6$ (533.8) Calcd. C 24.75 H 4.34 N 5.25 Found C 25.00 H 4.46 N 5.23

tert-Butyl(ethoxypiperidinomethylen)ammonium Hexachloroantimonate (**8p**): Yield 8.33 g (76%) of a colourless powder; m.p. 169 – 171 °C.

$[C_{12}H_{25}N_2O]SbCl_6$ (547.8) Calcd. C 26.31 H 4.60 N 5.12 Found C 26.55 H 4.47 N 5.03

tert-Butyl(isopropoxypiperidinomethylen)ammonium Hexachloroantimonate (**8q**): Yield 10.11 g (90%) of a colourless powder; m.p. 128 – 130 °C.

$[C_{13}H_{27}N_2O]SbCl_6$ (561.8) Calcd. C 27.79 H 4.84 N 4.99 Found C 27.92 H 4.71 N 4.94

(Methoxypiperidinomethylene)tricyclo[3.3.1.1^{3,7}]dec-1-ylammonium Hexachloroantimonate (**8r**): Yield 7.34 g (60%) of a colourless powder; m.p. 152 °C.

$[C_{17}H_{29}N_2O]SbCl_6$ (611.9) Calcd. C 33.37 H 4.78 N 4.58 Found C 33.68 H 4.78 N 4.39

tert-Butyl(morpholinomethoxymethylen)ammonium Hexachloroantimonate (**8s**): Yield 8.79 g (82%) of a yellow powder; m.p. 146 – 151 °C (dec.). – ^{13}C-NMR ([D$_6$]acetone, 253 K): CH_3 δ = 29.4, OCH_3 63.6, CH_2 48.6, 66.0, C 56.5, NCN 163.4.

$[C_{10}H_{21}N_2O_2]SbCl_6$ (535.8) Calcd. C 22.42 H 3.95 N 5.23 Found C 22.45 H 3.99 N 5.15

tert-Butyl(ethoxymorpholinomethylen)ammonium Hexachloroantimonate (**8t**): Yield 9.24 g (84%) of a yellow powder; m.p. 166 – 168 °C.

$[C_{11}H_{23}N_2O_2]SbCl_6$ (549.8) Calcd. C 24.03 H 4.22 N 5.10 Found C 24.13 H 4.05 N 5.18

3-tert-Butyl-1-isopropyl-1,2-dimethyluronium Hexachloroantimonate (**8u**): Recrystallization from dichloromethane (25 ml)/ether (200 ml) afforded a pale yellow powder (9.39 g, 90%); m.p. 135 – 137 °C.

$[C_{10}H_{23}N_2O]SbCl_6$ (521.8) Calcd. C 23.02 H 4.44 N 5.37 Found C 22.86 H 4.53 N 5.60

3-tert-Butyl-2-ethyl-1-isopropyl-1-methyluronium Hexachloroantimonate (**8v**): Yield 10.18 g (95%) of a pale yellow powder which was recrystallized from ethanol (140 ml); m.p. 144 – 146 °C. – ^{1}H-NMR ([D$_6$]acetone): CH_3 δ = 1.35 (d; J = 7 Hz), 1.51, 1.59 (t; J = 7 Hz), 3.11, CH_2 4.65 (q; J = 7 Hz), NH 7.36.

$[C_{11}H_{25}N_2O]SbCl_6$ (535.8) Calcd. C 24.66 H 4.70 N 5.23 Found C 24.87 H 4.74 N 5.11

3-tert-Butyl-1,2-dimethyl-1-phenyluronium Hexachloroantimonate (**8w**): Recrystallization from dichloromethane (50 ml)/ether afforded yellow prisms (8.45 g, 76%); m.p. 114 – 115 °C.

$[C_{13}H_{21}N_2O]SbCl_6$ (555.8) Calcd. C 28.09 H 3.81 N 5.04 Found C 28.05 H 3.68 N 4.81

3-tert-Butyl-2-ethyl-1-methyl-1-phenyluronium Hexachloroantimonate (**8x**): Yield 8.66 g (76%) of a yellow powder; m.p. 110 °C (dec.).

$[C_{14}H_{23}N_2O]SbCl_6$ (569.8) Calcd. C 29.51 H 4.07 N 4.92 Found C 29.45 H 4.05 N 4.82

3-tert-Butyl-2-isopropyl-1-methyl-1-phenyluronium Hexachloroantimonate (**8y**): Yield 7.82 g (67%) of a yellow powder; m.p. 111 °C (dec.).

$[C_{15}H_{25}N_2O]SbCl_6$ (583.8) Calcd. C 30.86 H 4.32 N 4.80 Found C 30.74 H 4.27 N 4.71

1,1-Diisopropyl-2-methyluronium Hexachloroantimonate (**8z**)[30]: To **3a** (2.13 g, 5.0 mmol) in dry dichloromethane (10 ml) was added dropwise at – 15 °C a solution of chlorotrimethylsilane (1.09 g, 10 mmol) in dry dichloromethane (5 ml). Stirring was continued for 1 h at + 22 °C, after which dry methanol (7 ml) was added dropwise. The solution was stirred for 12 h at + 22 °C. The solvent was evaporated under reduced pressure. The oily residue crystallized after addition of a little ether at – 25 °C affording colourless prisms (1.48 g, 60%); m.p. 105 – 110 °C.

$[C_8H_{19}N_2O]SbCl_6$ (493.7) Calcd. C 19.46 H 3.88 N 5.68 Found C 19.55 H 3.73 N 5.64

3-tert-Butyl-1,1-diisopropylurea (**11**): A mixture of **5a** (8.50 g, 20 mmol) in dry dichloromethane (140 ml) and 10% aqueous potassium hydroxide (100 ml) was stirred for 1 h at – 10 °C and then for 2 h at + 22 °C. The organic layer was separated, washed with water, and dried over magnesium sulfate. Evaporation of the solvent afforded a colourless oil (2.84 g, 71%). – ^{1}H-NMR (CDCl$_3$): CH_3 δ = 1.20 (d, J = 7 Hz), 1.35, CH 3.91 (sept., J = 7 Hz), NH 4.10.

$C_{11}H_{24}N_2O$ (200.3) Calcd. C 65.95 H 12.08 N 13.99 Found C 66.07 H 12.00 N 13.73

3-tert-Butyl-1,1,2-trimethylisourea (**10**): A mixture of **8g** (7.14 g, 20 mmol) in dichloromethane (60 ml) and 10% aqueous potassium hydroxide (100 ml) was stirred at 0 °C for 3 h. The organic layer was separated, washed with water, and dried over magnesium sulfate. Evaporation of the solvent and distillation afforded a colourless oil (1.96 g, 62%); b.p. 59 – 60 °C/13 Torr. – ^{1}H-NMR (CCl$_4$): CH_3 δ = 1.08, 2.52, 3.53.

$C_8H_{18}N_2O$ (158.2) Calcd. C 60.72 H 11.47 N 17.71 Found C 60.91 H 11.67 N 17.75

2-tert-Butyl-1,1-diisopropylguanidinium Hexachloroantimonate (**9a**)

a) Dry gaseous ammonia was introduced into a solution of **5a** (10.36 g, 20 mmol) in dry dichloromethane (50 ml) at −78 °C until the mixture started to turn yellow (a few min). Warming to −50 °C and precipitating with dry ether (100 ml) afforded a colourless powder (8.88 g, 83%) which was recrystallized from dichloromethane; m.p. 228–230 °C (dec.). – ^{13}C-NMR (CD_2Cl_2/[D_6]acetone, 253 K): $(CH_3)_2$ δ = 21.5, $(CH_3)_3$ 29.8, CH 49.1, C 54.2, NCN 154.8.

[$C_{11}H_{26}N_3$]$SbCl_6$ (534.8) Calcd. C 24.70 H 4.90 N 7.86 Found C 24.97 H 4.91 N 7.65

b) To **3a** (8.50 g, 20 mmol) in dry dichlormethane (20 ml) was added dropwise at −78 °C a solution of *tert*-butylamine (1.46 g, 20 mmol) in dry dichloromethane (20 ml) followed by a solution of hydrogen chloride in dry ether (10 ml, 80 g HCl in 100 ml ether). The mixture was stirred for 3 d at +22 °C. Evaporation of the solvent and crystallization of the residue from dichloromethane (50 ml)/ether (25 ml) afforded a colourless powder (5.35 g, 50%); m.p. 228–230 °C (dec.).

Guanidinium Hexachloroantimonates **9**, *General Procedure:* To the cyanamidium salt **5** (freshly prepared, with or without isolation, 20 mmol) in dry dichloromethane (20 ml) was added dropwise with stirring at −78 °C a solution of the amine (20 mmol) in dry dichloromethane (10 ml). The mixture was stirred for 1 h at +22 °C. After cooling to −10 °C **9** was precipitated by addition of ether (100 ml).

2,3-Di-tert-butyl-1,1-diisopropylguanidinium Hexachloroantimonate (**9b**): Yield 11.58 g (98%) of a colourless powder which was recrystallized from dichloromethane/ether; m.p. 210–212 °C. – ^{13}C-NMR (CD_2Cl_2, 273 K): $(CH_3)_2$ δ = 22.7, $(CH_3)_3$ 30.5, CH 51.4, C 56.5, NCN 157.6.

[$C_{15}H_{34}N_3$]$SbCl_6$ (590.9) Calcd. C 30.49 H 5.80 N 7.11 Found C 30.43 H 5.92 N 6.71

2-tert-Butyl-1,1-diisopropyl-3-phenylguanidinium Hexachloroantimonate (**9c**): Yield 11.97 g (98%) of a brown powder which was dissolved in dichloromethane (20 ml). The solution was decanted from a tarry impurity and filtrated with charcoal. With ether yellow-brown crystals were precipitated; m.p. 155–156 °C. – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.22 (d, J = 7 Hz), 1.55, CH 3.82, NH 5.46, 6.46. – ^{13}C-NMR (CD_2Cl_2, 253 K): $(CH_3)_2$ δ = 21.4, $(CH_3)_3$ 30.7, CH 50.9, C 56.3, NCN 155.4, aromatic C 124.0, 127.9, 130.6, 136.7.

[$C_{17}H_{30}N_3$]$SbCl_6$ (610.9) Calcd. C 33.42 H 4.95 N 6.88 Found C 33.57 H 4.87 N 6.74

N^2-tert-Butyl-N^1,N^1-diisopropyl-1-morpholinecarboxamidinium Hexachloroantimonate (**9d**): Yield 11.01 g (91%) of a yellow powder which was recrystallized from dichloromethane/ether; m.p. 203–210 °C (dec.).

[$C_{15}H_{32}N_3O$]$SbCl_6$ (604.9) Calcd. C 29.78 H 5.33 N 6.95 Found C 30.10 H 5.38 N 6.91

2-tert-Butyl-1,1-diethyl-3,3-diisopropylguanidinium Hexachloroantimonate (**9e**): Yield 10.64 g (90%) of a colourless powder which was recrystallized from dichloromethane/ether; m.p. 215–220 °C (dec.). – ^{13}C-NMR ([D_6]acetone): CH_3 δ = 12.5, $(CH_3)_2$ 22.7, $(CH_3)_3$ 29.8, CH_2 46.2, CH 52.1 (broad), C 58.1, NCN 161.3.

[$C_{15}H_{34}N_3$]$SbCl_6$ (590.9) Calcd. C 30.49 H 5.80 N 7.11 Found C 30.58 H 5.77 N 7.03

2-tert-Butyl-1,1,3-triisopropyl-3-methylguanidinium Hexachloroantimonate (**9f**): Recrystallization from dichloromethane/ether afforded a colourless powder (9.69 g, 82%); m.p. 207–209 °C (dec.). – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.32 (d, J = 7 Hz), 1.39 (d, J = 7 Hz), 1.46 (d, J = 7 Hz), 1.50, 2.88, CH 3.73 (2H, sept., J = 7 Hz, broad), 4.04 (sept., J = 7 Hz), NH 5.22.

[$C_{15}H_{34}N_3$]$SbCl_6$ (590.9) Calcd. C 30.49 H 5.80 N 7.11 Found C 30.27 H 5.84 N 6.97

No reaction was observed between **5a** and diisopropylamine.

3-Benzyl-2-tert-butyl-1,1-dimethylguanidinium Hexachloroantimonate (**9g**): Yield 10.01 g (88%) of a pale yellow powder which was recrystallized from dichloromethane/ether; m.p. 130 – 132°C.

$[C_{14}H_{24}N_3]SbCl_6$ (568.8) Calcd. C 29.56 H 4.25 N 7.39 Found C 29.74 H 4.20 N 7.29

2-tert-Butyl-3-isopropyl-1,1-dimethylguanidinium Hexachloroantimonate (**9h**): Yield 8.54 g (82%) of a colourless powder which was recrystallized from dichloromethane/ether; m.p. 153 – 157°C.

$[C_{10}H_{24}N_3]SbCl_6$ (520.8) Calcd. C 23.06 H 4.65 N 8.07 Found C 22.74 H 4.76 N 8.14

2,3-Di-tert-butyl-1,1-dimethylguanidinium Hexachloroantimonate (**9i**): Yield 7.70 g (72%) of a colourless powder which was recrystallized from dichloromethane/ether; m.p. 135 – 145°C (dec.). – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.50, 3.14.

$[C_{11}H_{26}N_3]SbCl_6$ (534.8) Calcd. C 24.70 H 4.90 N 7.86 Found C 24.72 H 4.84 N 7.79

2-tert-Butyl-1,1-diisopropyl-3,3-dimethylguanidinium Hexachloroantimonate (**9j**): Yield 10.36 g (92%) of a colourless powder; m.p. 220 – 227°C (dec.).

$[C_{13}H_{30}N_3]SbCl_6$ (562.9) Calcd. C 27.74 H 5.37 N 7.47 Found C 27.75 H 5.26 N 7.26

N^2-tert-Butyl-N^1,N^1-dimethyl-1-piperidinecarboxamidinium Hexachloroantimonate (**9k**): Yield 7.77 g (71%) of a pale yellow powder which was recrystallized from dichloromethane (30 ml)/ether (20 ml); m.p. 190 – 193°C.

$[C_{12}H_{26}N_3]SbCl_6$ (546.8) Calcd. C 26.36 H 4.79 N 7.69 Found C 26.53 H 4.97 N 7.51

N^2-tert-Butyl-N^1,N^1-dimethyl-1-morpholinecarboxamidinium Hexachloroantimonate (**9l**): Yield 8.78 g (80%) of a yellow powder which was recrystallized from dichloromethane (260 ml)/ ether (450 ml); m.p. 225 – 228°C.

$[C_{11}H_{24}N_3O]SbCl_6$ (548.8) Calcd. C 24.07 H 4.41 N 7.66 Found C 24.15 H 4.48 N 7.56

tert-Butyl(morpholinopiperidinomethylen)ammonium Hexachloroantimonate (**9m**): Yield 10.01 g (85%) of a pale yellow powder which was recrystallized from dichloromethane/ether; m.p. 197 – 200°C (dec.).

$[C_{14}H_{28}N_3O]SbCl_6$ (588.9) Calcd. C 28.55 H 4.79 N 7.14 Found C 28.45 H 4.72 N 6.99

N^1,N^2-Di-tert-butyl-1-piperidinecarboxamidinium Hexachloroantimonate (**9n**): Yield 9.20 g (80%) of a colourless powder; m.p. 155 – 157°C.

$[C_{14}H_{30}N_3]SbCl_6$ (574.9) Calcd. C 29.25 H 5.26 N 7.31 Found C 29.55 H 5.16 N 7.24

tert-Butyl(dipiperidinomethylen)ammonium Hexachloroantimonate (**9o**): Yield 8.57 g (73%) of a yellow powder; m.p. 103 – 105°C.

$[C_{15}H_{30}N_3]SbCl_6$ (586.9) Calcd. C 30.70 H 5.15 N 7.16 Found C 31.05 H 5.11 N 7.05

tert-Butyl(dimorpholinomethylen)ammonium Hexachloroantimonate (**9p**): Yield 10.87 g (92%) of a yellow poorly soluble powder; m.p. 225 – 226°C (dec.).

$[C_{13}H_{26}N_2O_2]SbCl_6$ (590.8) Calcd. C 26.43 H 4.44 N 7.11 Found C 26.64 H 4.55 N 7.27

2-tert-Butyl-1,1,3-trimethyl-3-phenylguanidinium Hexachloroantimonate (**9q**)

a) The preparation from **5c** and *N*-methylaniline afforded a yellow powder (9.44 g, 83%) which was recrystallized from dichloromethane/ether; m.p. 153 – 155°C (dec.). – ^{1}H-NMR (CH_2Cl_2): CH_3 δ = 1.31, 3.07 (6H, broad), 3.45, NH 5.44.

$[C_{14}H_{24}N_3]SbCl_6$ (568.8) Calcd. C 29.56 H 4.25 N 7.39 Found C 29.41 H 4.30 N 7.27

b) The preparation from **3l** with *tert*-butyl chloride and dimethylamine afforded the same compound (6.83 g, 60%); m.p. 153 – 155°C (dec.).

2-tert-Butyl-1-methyl-1,3-diphenylguanidinium Hexachloroantimonate (**9r**): The preparation from **31**, *tert*-butyl chloride and aniline (without isolation of the instable cyanamidium salt) afforded orange prisms (7.40 g, 60%) which were recrystallized from dichloromethane/ether; m.p. 171 °C (dec.).

$[C_{18}H_{24}N_3]SbCl_6$ (616.9) Calcd. C 35.04 H 3.92 N 6.81 Found C 34.96 H 3.86 N 6.64

2,3-Di-tert-butyl-1-methyl-1-phenylguanidinium Hexachloroantimonate (**9s**): The preparation from **31**, *tert*-butyl chloride and *tert*-butylamine afforded an orange powder (8.36 g, 70%) which was recrystallized from dichloromethane/ether; m.p. 165 °C.

$[C_{16}H_{28}N_3]SbCl_6$ (596.9) Calcd. C 32.19 H 4.73 N 7.04 Found C 32.12 H 4.80 N 6.93

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