

## Syntheses and Molecular Structures of Formal Heterocumulenes with $\text{>S}=\overset{+}{\text{N}}=\overset{-}{\text{C}}=\overset{-}{\text{N}}-$ and $\text{>P}=\overset{+}{\text{N}}=\overset{-}{\text{C}}=\overset{-}{\text{N}}-$ Units

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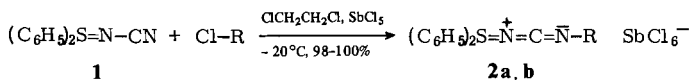
The cyanamides **1** and **3** react with tertiary alkyl chlorides and antimony pentachloride affording formal heterocumulenes  $\text{>S}=\overset{+}{\text{N}}=\overset{-}{\text{C}}=\overset{-}{\text{N}}-$   $\text{SbCl}_6^-$  (**2a, b**) and  $\text{>P}=\overset{+}{\text{N}}=\overset{-}{\text{C}}=\overset{-}{\text{N}}-$   $\text{SbCl}_6^-$  (**4a, b**). X-ray analyses of **2b** and **4b** reveal that in the crystal these compounds are bent pseudocumulenes having structural properties of nitrilium salts (**B**) and of carbodiimides (**D**). With amines and alcohols **2** and **4** react to give compounds **11–17** which are probably not amino-substituted 2-azaallanium salts **E** but guanidines **F**.

### Synthesen und Molekülstrukturen von formalen Heterokumulenen mit

$\text{>S}=\overset{+}{\text{N}}=\overset{-}{\text{C}}=\overset{-}{\text{N}}-$  und  $\text{>P}=\overset{+}{\text{N}}=\overset{-}{\text{C}}=\overset{-}{\text{N}}-$ -Einheiten

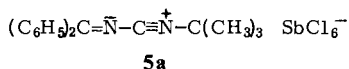
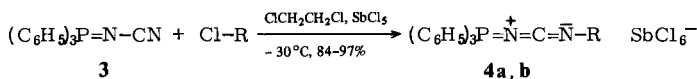
Die Cyanamide **1** und **3** reagieren mit tertiären Alkylchloriden und Antimonpentachlorid zu den formalen Heterokumulenen  $\text{>S}=\overset{+}{\text{N}}=\overset{-}{\text{C}}=\overset{-}{\text{N}}-$   $\text{SbCl}_6^-$  (**2a, b**) und  $\text{>P}=\overset{+}{\text{N}}=\overset{-}{\text{C}}=\overset{-}{\text{N}}-$   $\text{SbCl}_6^-$  (**4a, b**). Nach Röntgenstrukturanalysen von **2b** und **4b** liegen die Verbindungen im Kristall jedoch als gewinkelte Pseudokumule vor, die strukturell Nitriliumsalzen (**B**) und Carbodiimiden (**D**) ähneln. Mit Aminen und Alkoholen reagieren **2** und **4** zu den Verbindungen **11–17**, die wahrscheinlich nicht als aminosubstituierte 2-Azaallaniumsalze **E**, sondern als Guanidine **F** anzusehen sind.

During the course of our search for new heterocumulenes, *N*-cyano-*S,S*-diphenylsulfimide (**1**)<sup>1)</sup> and (cyanimino)triphenylphosphorane **3**<sup>2)</sup> were alkylated with tertiary alkyl chlorides and antimony pentachloride to afford the formal heterocumulenes **2** and **4**, resp.



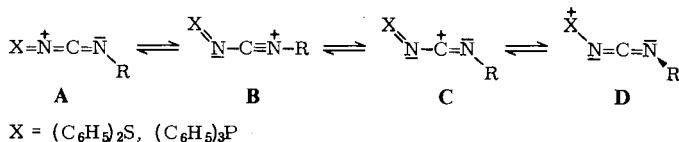
**a:** R = C(CH<sub>3</sub>)<sub>3</sub>

**b:** R = 1-adamantyl



To our knowledge these crystalline, moisture-sensitive substances are the first members of hitherto unknown classes of compounds. They are stable in the solid state but decompose slowly in solution. Attempts to alkylate **1** and **3** with secondary or primary alkyl chlorides failed. Salts **2** and **4** show strong IR absorptions around  $2230\text{ cm}^{-1}$ . In the  $^{13}\text{C}$  NMR spectra very weak signals for NCN can be observed at  $111 - 116\text{ ppm}$ . For the related alkylidenecyanamidium salt **5a** an IR band at  $2270\text{ cm}^{-1}$  and a  $^{13}\text{C}\equiv\text{N}$  resonance at  $103.0\text{ ppm}$  ( $\text{CD}_2\text{Cl}_2$ ,  $273\text{ K}$ ) have been reported<sup>3)</sup>.

For compounds **2** and **4** several valence tautomeric structures can be considered. These substances could either be butatrienes **A** with a linear  $\text{X}=\overset{+}{\text{N}}=\text{C}=\text{N}$  moiety or pseudobutatrienes<sup>4)</sup> with bent units  $\text{X}-\text{N}=\text{C}=\text{N}$ . The achiral cations **B** and **C** are expected to have planar  $\text{XNCN}-\text{R}$  units while the chiral carbodiimide **D** should be nonplanar with a torsional angle  $\text{X}-\text{NCN}-\text{R}$  of  $90^\circ$ . The tautomers **B** and **C** differ in the  $\text{C}-\text{N}-\text{R}$  angles.



To decide between these structures X-ray diffraction analyses of **2b** and **4b** were undertaken.

### X-ray Diffraction Analyses of **2b** and **4b**\*)

**2b**,  $[\text{C}_{23}\text{H}_{25}\text{N}_2\text{S}]^+ [\text{SbCl}_6]^-$ , monoclinic, space group  $Cc$  (No.  $9^5$ ),  $Z = 8$ ,  $a = 2020(1)$ ,  $b = 1240.2(7)$ ,  $c = 2204.9(9)\text{ pm}$ ,  $\beta = 92.58(4)^\circ$ ,  $V = 5518 \cdot 10^6\text{ pm}^3$ ,  $d_{\text{calc.}} = 1.68\text{ g cm}^{-3}$ ,  $\mu_{\text{Mo-K}\alpha} = 16.8\text{ cm}^{-1}$ ,  $T = 228\text{ K}$ ,  $\omega$ -scan,  $\Delta\omega = 1.0^\circ$ ,  $2.6 < \dot{\omega} < 29.3^\circ\text{ min}^{-1}$ ,  $2^\circ < 2\theta < 42^\circ$ , 2884 independent significant reflections ( $I \geq 2\sigma$ ). The cell constants and the reflections were measured on a Syntex-P3-diffractometer with a graphite monochromator,  $\lambda_{\text{Mo-K}\alpha} = 71.069\text{ pm}$ . The structure

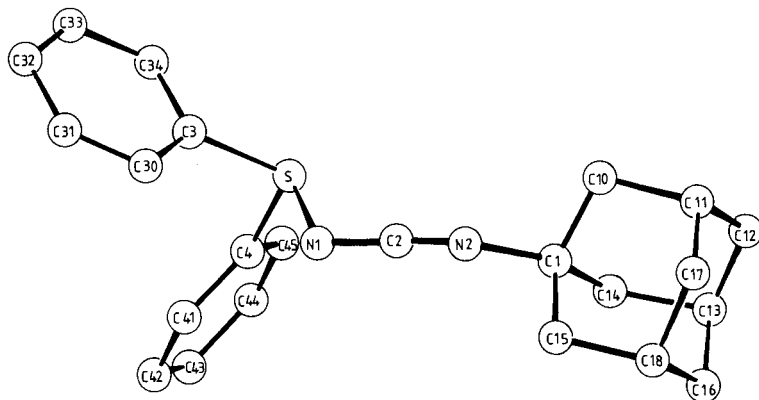


Fig. 1. Molecular drawing of one of the two independent cations of **2b**

\*) Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany), by specifying registry number CSD 50398, author, and the reference to this publication.

Table 1. Fractional atomic coordinates and temperature parameters of 2b<sup>a)</sup>

atom	x/a	y/b	z/c	U11	U22	U33	U23	U13	U12
Sb1	0.04000(0)	0.5393(1)	0.24310(0)	0.0697(9)	0.0583(8)	0.0589(8)	0.0111(6)	0.0107(6)	0.0130(7)
C11	0.1570(2)	0.5638(5)	0.2554(2)	0.061(3)	0.125(4)	0.109(4)	0.018(3)	0.018(3)	0.015(3)
C12	0.0431(3)	0.4219(4)	0.3271(2)	0.089(4)	0.064(3)	0.054(3)	0.014(3)	0.001(3)	0.001(3)
C13	0.0258(2)	0.6885(4)	0.3060(2)	0.099(4)	0.063(3)	0.106(4)	-0.009(3)	0.019(3)	0.008(3)
C14	0.0400(3)	0.6510(4)	0.1569(2)	0.100(4)	0.099(4)	0.095(3)	0.049(3)	0.029(3)	0.029(3)
C15	0.0566(3)	0.3903(4)	0.1790(2)	0.143(5)	0.080(3)	0.068(3)	-0.004(2)	0.006(3)	0.033(3)
C16	-0.0756(2)	0.5201(4)	0.2303(2)	0.076(3)	0.106(4)	0.080(3)	0.023(3)	-0.002(2)	-0.002(3)
Sb2	0.02086(6)	-0.04385(9)	-0.02152(5)	0.0539(7)	0.0547(7)	0.0542(7)	0.0057(6)	-0.0027(5)	0.0030(6)
C17	0.1390(2)	-0.0336(4)	-0.0151(2)	0.041(2)	0.098(3)	0.085(3)	0.001(3)	-0.003(2)	-0.002(2)
C18	0.0190(3)	-0.0815(5)	-0.1022(2)	0.090(4)	0.068(3)	0.072(3)	0.018(3)	-0.008(3)	0.005(3)
C19	0.0286(2)	-0.1877(3)	-0.0904(2)	0.091(3)	0.061(3)	0.074(3)	-0.011(2)	0.006(2)	0.000(2)
C110	0.0153(2)	0.1003(4)	0.0483(2)	0.086(3)	0.075(3)	0.070(3)	-0.012(2)	-0.005(2)	0.005(2)
C111	0.0264(2)	-0.1652(4)	0.0605(2)	0.088(3)	0.082(3)	0.067(3)	0.027(2)	0.003(2)	0.009(3)
C112	-0.0945(2)	-0.0573(4)	-0.0284(2)	0.054(2)	0.094(3)	0.079(3)	0.000(2)	-0.004(2)	0.002(2)
SX	0.6609(2)	-0.1422(4)	0.4722(2)	0.062(3)	0.082(3)	0.085(3)	-0.031(3)	0.007(2)	-0.003(2)
N1X	0.7047(8)	-0.164(1)	0.4122(7)	0.09(1)	0.07(1)	0.09(1)	-0.035(9)	0.006(9)	-0.018(9)
N2X	0.6977(8)	-0.319(1)	0.3464(6)	0.10(1)	0.09(1)	0.07(1)	-0.037(9)	0.014(9)	0.003(9)
S	0.3959(2)	0.3986(3)	0.2861(2)	0.058(2)	0.064(3)	0.065(2)	0.011(2)	-0.008(2)	0.001(2)
N1	0.3959(7)	0.354(1)	0.3328(6)	0.066(9)	0.07(1)	0.075(9)	0.019(8)	-0.001(7)	0.003(8)
N2	0.3698(8)	0.222(1)	0.4121(8)	0.08(1)	0.12(1)	0.11(1)	0.06(1)	0.01(1)	0.00(1)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
C1X	0.6860(7)	-0.386(1)	0.2919(6)	C10X	0.686(1)	-0.501(2)	0.309(1)
C11X	0.679(1)	-0.573(2)	0.251(1)	C12X	0.732(1)	-0.534(2)	0.208(1)
C13X	0.732(1)	-0.425(2)	0.190(1)	C14X	0.742(1)	-0.361(2)	0.2511(8)
C15X	0.6203(9)	-0.350(2)	0.2613(8)	C16X	0.664(1)	-0.395(2)	0.1630(9)
C17X	0.606(1)	-0.534(2)	0.221(1)	C18X	0.607(1)	-0.426(2)	0.2031(8)
C2X	0.6948(8)	-0.245(1)	0.3778(8)	C3X	0.7192(5)	-0.157(1)	0.5320(5)
C30X	0.6998(5)	-0.203(1)	0.5861(5)	C31X	0.7445(5)	-0.210(1)	0.6360(5)
C32X	0.8088(5)	-0.170(1)	0.6319(5)	C33X	0.8282(5)	-0.124(1)	0.5778(5)
C34X	0.7835(5)	-0.117(1)	0.5279(5)	C4X	0.6519(6)	-0.0013(8)	0.4721(4)
C41X	0.6269(6)	0.0470(9)	0.5234(4)	C42X	0.6199(6)	0.1587(8)	0.5259(4)
C43X	0.6378(6)	0.2223(8)	0.4771(4)	C44X	0.6627(6)	0.1740(8)	0.4257(4)
C45X	0.6698(6)	0.0622(8)	0.4232(4)	C1	0.3781(9)	0.127(1)	0.4465(7)
C10	0.4349(9)	0.140(2)	0.4943(8)	C11	0.441(1)	0.034(2)	0.5321(9)
C12	0.4543(8)	-0.056(1)	0.4901(7)	C13	0.4039(9)	-0.075(1)	0.4428(8)
C14	0.394(1)	0.030(2)	0.4036(9)	C15	0.3141(8)	0.100(1)	0.4770(7)
C16	0.3383(9)	-0.093(2)	0.4739(8)	C17	0.379(1)	0.016(2)	0.5626(9)
C18	0.3204(8)	-0.003(1)	0.5170(7)	C2	0.3598(8)	0.283(1)	0.3723(7)
C3	0.3859(5)	0.5357(9)	0.2926(5)	C30	0.3349(5)	0.5830(9)	0.3239(5)
C31	0.3287(5)	0.6950(9)	0.3254(5)	C32	0.3734(5)	0.7597(9)	0.2956(5)
C33	0.4244(5)	0.7124(9)	0.2642(5)	C34	0.4307(5)	0.6004(9)	0.2627(5)
C4	0.3551(4)	0.3760(8)	0.2144(4)	C41	0.2899(4)	0.4085(8)	0.2015(4)
C42	0.2596(4)	0.3874(8)	0.1446(4)	C43	0.2947(4)	0.3340(8)	0.1006(4)
C44	0.3599(4)	0.3015(8)	0.1134(4)	C45	0.3901(4)	0.3225(8)	0.1703(4)

atom	U	atom	U	atom	U	atom	U
C1X	0.052(4)	C10X	0.100(7)	C11X	0.119(7)	C12X	0.114(7)
C13X	0.108(7)	C14X	0.092(6)	C15X	0.084(5)	C16X	0.106(7)
C17X	0.136(9)	C18X	0.082(5)	C2X	0.078(5)	C3X	0.061(4)
C30X	0.085(5)	C31X	0.107(7)	C32X	0.102(6)	C33X	0.100(6)
C34X	0.076(5)	C4X	0.069(4)	C41X	0.079(5)	C42X	0.078(5)
C43X	0.098(6)	C44X	0.106(7)	C45X	0.086(5)	C1	0.069(5)
C10	0.089(5)	C11	0.084(6)	C12	0.074(5)	C13	0.078(5)
C14	0.087(6)	C15	0.075(5)	C16	0.085(5)	C17	0.092(6)
C18	0.072(5)	C2	0.066(4)	C3	0.061(4)	C30	0.084(5)
C31	0.099(6)	C32	0.100(6)	C33	0.088(5)	C34	0.06(1)
C4	0.054(4)	C41	0.063(4)	C42	0.070(4)	C43	0.076(5)
C44	0.079(5)	C45	0.072(5)				

<sup>a)</sup> The anisotropic temperature parameters are defined by the equation:

$$T = \exp(-2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]).$$

was solved using the programme SHEL-XTL<sup>6)</sup> by direct methods. The *S*-phenyl rings were treated as rigid groups. Hydrogen atoms were fixed on calculated geometrically ideal positions. The partially anisotrop refinement with full matrix led to agreement factors  $R_1 = 0.040$  and  $R_2 = 0.047$ .

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

Table 2. Selected bond lengths, bond angles, and torsional angles of **2b**<sup>b)</sup>

C3 - S	172 (1); 174 (1) <sup>b)</sup>	N2 - C1 - C10	110 (2); 110 (1)
C4 - S	177.3 (9); 176 (1)	N2 - C1 - C14	110 (1); 106 (1)
S - N1	161 (2); 164 (2)	N2 - C1 - C15	110 (2); 110 (1)
N1 - C2	127 (2); 127 (2)	C30 - C3 - S - N1	-9.5 (6); -144.7 (6)
C2 - N2	117 (2); 115 (2)	C41 - C4 - S - N1	+49.5 (7); -168.8 (6)
N2 - C1	142 (2); 148 (2)	C30 - C3 - S - C4	+96.0 (4); +109.8 (4)
C1 - C10	153 (3); 148 (3)	C41 - C4 - S - C3	-55.0 (5); -63.1 (5)
C1 - C14	157 (3); 151 (2)	C3 - S - N1 - C2	-131 (1); +114 (2)
C1 - C15	152 (3); 150 (2)	C4 - S - N1 - C2	+125 (1); -143 (1)
C3 - S - N1	101.6 (7); 102.9 (7)	S - N1 - N2 - C1	-97 (1); +115 (1)
C3 - S - C4	100.3 (5); 100.0 (6)	C2 - N2 - C1 - C10	+143 (6); -150 (4)
C4 - S - N1	102.8 (6); 102.6 (7)	C2 - N2 - C1 - C14	+22 (7); + 91 (5)
S - N1 - C2	121 (1); 122 (1)	C2 - N2 - C1 - C15	-96 (6); -29 (5)
N1 - C2 - N2	173 (2); 168 (2)	N2 - C1 - C10 - C11	+179 (2); -176 (2)
C2 - N2 - C1	163 (2); 159 (2)		

<sup>b)</sup> The numbers behind the semicolon refer to the atoms marked with an X.

**4b**,  $[\text{C}_{29}\text{H}_{30}\text{N}_2\text{P}]^+ [\text{SbCl}_6]^-$ , monoclinic, space group  $P2_1/c$  (No. 14<sup>5)</sup>),  $Z = 8$ ,  $a = 2310(2)$ ,  $b = 1611(2)$ ,  $c = 1753(1)$  pm,  $\beta = 94.12(6)^\circ$ ,  $V = 6509 \cdot 10^6$  pm<sup>3</sup>,  $d_{\text{calc}} = 1.58$  gcm<sup>-3</sup>,  $\mu_{\text{Mo-K}\alpha} = 14.2$  cm<sup>-1</sup>,  $T = 228$  K,  $\omega$ -scan,  $\Delta\omega = 1.0^\circ$ ,  $2.4 < \dot{\omega} < 29.3$  min<sup>-1</sup>,  $2^\circ < 2\theta < 40^\circ$ , 4783 independent significant reflections ( $I \geq 2\sigma$ ). Measurements and solution are as described for **2b**, but the *P*-phenyl groups were not treated as rigid groups. The partially anisotropic refinement with full matrix led to agreement factors  $R_1 = 0.059$  and  $R_2 = 0.065$ .

A list of atomic coordinates of **4b** is given in Table 3. In Table 4 selected bond lengths, bond angles, and torsional angles of the two independent cations of **4b** are listed. Fig. 2 shows a molecular drawing of one of the cations **4b**.

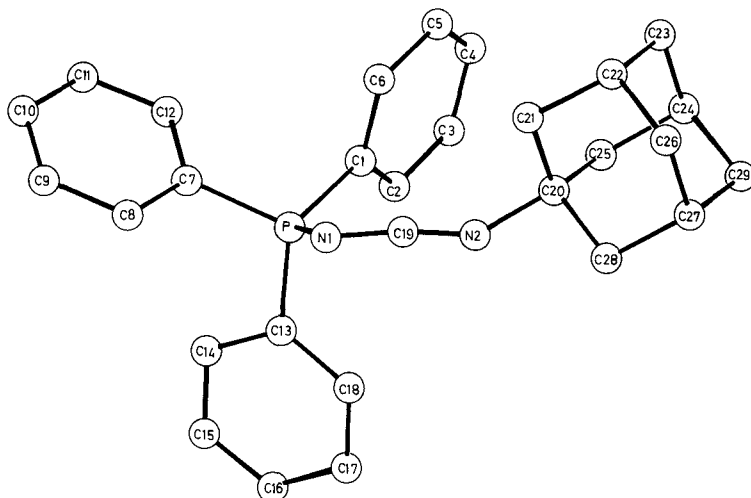


Fig. 2. Molecular drawing of one of the two independent cations of **4b**

Table 3. Fractional atomic coordinates and temperature parameters of **4b**<sup>a</sup>

atom	x/a	y/b	z/c	U11	U22	U33	U23	U13	U12
Sb1	0.11569(4)	0.34980(5)	0.26269(5)	0.0306(5)	0.0360(5)	0.0361(5)	0.0056(4)	-0.0007(4)	-0.0013(4)
Sb2	0.37017(4)	0.93941(6)	0.22902(5)	0.0324(5)	0.0444(5)	0.0447(5)	0.0111(5)	-0.0012(4)	-0.0012(4)
C11	0.1960(2)	0.4224(2)	0.2169(2)	0.042(2)	0.059(3)	0.090(3)	0.012(2)	0.016(2)	-0.012(2)
C12	0.0689(2)	0.3593(3)	0.1388(2)	0.053(2)	0.092(3)	0.041(2)	0.017(2)	-0.007(2)	0.000(2)
C13	0.1584(2)	0.2206(2)	0.2306(2)	0.060(2)	0.047(2)	0.052(2)	-0.002(2)	0.010(2)	0.009(2)
C14	0.1658(2)	0.3407(3)	0.3847(2)	0.061(2)	0.071(3)	0.047(2)	-0.008(2)	-0.019(2)	0.011(2)
C15	0.0729(2)	0.4767(2)	0.2995(2)	0.053(2)	0.039(2)	0.076(3)	0.005(2)	0.008(2)	0.004(2)
C16	0.0352(2)	0.2772(2)	0.3065(2)	0.054(2)	0.046(2)	0.052(2)	-0.002(2)	0.017(2)	-0.015(2)
C17	0.3153(2)	0.8499(3)	0.3054(2)	0.072(3)	0.078(3)	0.074(3)	0.037(2)	0.002(2)	-0.001(2)
C18	0.4260(2)	1.0249(2)	0.1510(2)	0.053(2)	0.049(2)	0.068(2)	0.004(2)	0.028(2)	-0.003(2)
C19	0.4461(2)	0.8411(3)	0.2344(2)	0.074(3)	0.065(3)	0.081(3)	0.009(2)	-0.004(2)	0.030(2)
C110	0.4113(2)	1.0027(3)	0.3414(2)	0.071(3)	0.117(4)	0.060(3)	-0.027(3)	0.007(2)	-0.023(3)
C111	0.2946(2)	1.0371(3)	0.2245(3)	0.057(3)	0.100(4)	0.121(4)	0.060(3)	0.044(3)	0.037(3)
C112	0.3275(2)	0.8760(3)	0.1173(2)	0.078(3)	0.111(4)	0.060(3)	0.005(3)	-0.018(2)	-0.042(3)
P	0.1313(1)	0.8722(2)	0.0555(2)	0.034(2)	0.035(2)	0.024(2)	0.003(1)	0.000(1)	0.002(2)
PX	0.3876(1)	0.3513(2)	0.4311(2)	0.044(2)	0.032(2)	0.024(2)	0.001(2)	-0.002(2)	0.000(2)
N1	0.1364(4)	0.9596(6)	0.1038(5)	0.058(7)	0.039(6)	0.020(5)	0.005(5)	0.007(5)	-0.003(5)
N2	0.1045(5)	0.9806(7)	0.2310(6)	0.084(9)	0.056(8)	0.035(7)	-0.011(6)	0.007(6)	0.010(7)
N1X	0.3875(5)	0.4511(7)	0.4155(5)	0.093(9)	0.044(7)	0.020(6)	0.007(5)	-0.005(6)	0.004(7)
N2X	0.3930(7)	0.5184(8)	0.2966(7)	0.16(1)	0.051(9)	0.055(9)	0.001(7)	0.002(9)	-0.009(9)

atom	x/a	y/b	z/c	U	atom	x/a	y/b	z/c	U
C1	0.1362(5)	0.7840(7)	0.1189(6)	0.031(3)	C1X	0.3812(5)	0.2961(8)	0.3436(7)	0.037(3)
C2	0.0949(5)	0.7217(8)	0.1163(7)	0.040(3)	C2X	0.4292(5)	0.2564(8)	0.3142(7)	0.040(3)
C3	0.1015(6)	0.6548(8)	0.1678(7)	0.048(4)	C3X	0.4235(6)	0.2204(8)	0.2410(7)	0.051(4)
C4	0.1501(6)	0.6512(9)	0.2224(7)	0.051(4)	C4X	0.3691(6)	0.2245(8)	0.1976(7)	0.048(4)
C5	0.1905(6)	0.7161(9)	0.2250(8)	0.051(4)	C5X	0.3228(6)	0.2635(8)	0.2259(7)	0.044(3)
C6	0.1851(5)	0.7829(8)	0.1724(7)	0.040(3)	C6X	0.3275(5)	0.2996(8)	0.2993(7)	0.042(3)
C7	0.1897(5)	0.8701(7)	-0.0064(6)	0.032(3)	C7X	0.3258(5)	0.3274(8)	0.4818(7)	0.043(3)
C8	0.1989(5)	0.9407(8)	-0.0506(7)	0.041(3)	C8X	0.2962(6)	0.3896(9)	0.5220(8)	0.051(4)
C9	0.2445(5)	0.9384(8)	-0.1019(7)	0.047(3)	C9X	0.2441(6)	0.3621(9)	0.5580(8)	0.059(4)
C10	0.2786(5)	0.8676(8)	-0.1058(7)	0.043(3)	C10X	0.2279(7)	0.283(1)	0.5552(8)	0.066(4)
C11	0.2686(6)	0.7976(8)	-0.0615(7)	0.047(4)	C11X	0.2570(6)	0.2203(9)	0.5199(8)	0.063(4)
C12	0.2232(5)	0.7973(8)	-0.0105(7)	0.038(3)	C12X	0.3057(5)	0.2442(8)	0.4801(7)	0.043(3)
C13	0.0638(5)	0.8696(7)	-0.0017(6)	0.032(3)	C13X	0.4533(5)	0.3247(7)	0.4859(6)	0.032(3)
C14	0.0626(6)	0.8427(9)	-0.0786(7)	0.050(4)	C14X	0.4547(6)	0.2522(8)	0.5307(8)	0.050(4)
C15	0.0068(6)	0.8398(9)	-0.1202(8)	0.061(4)	C15X	0.5075(6)	0.2292(9)	0.5741(8)	0.055(4)
C16	-0.0418(6)	0.863(1)	-0.0845(8)	0.064(4)	C16X	0.5565(6)	0.2805(9)	0.5677(8)	0.058(4)
C17	-0.0413(6)	0.8892(9)	-0.0081(8)	0.058(4)	C17X	0.5540(6)	0.3507(9)	0.5228(8)	0.055(4)
C18	0.0133(6)	0.8927(8)	0.0332(7)	0.047(4)	C18X	0.5032(6)	0.3737(9)	0.4809(8)	0.055(4)
C19	0.1220(5)	0.9667(8)	0.1706(7)	0.043(3)	C19X	0.3901(6)	0.4812(8)	0.3535(7)	0.049(4)
C20	0.1139(5)	0.9821(8)	0.3157(7)	0.044(3)	C20X	0.3855(5)	0.5377(8)	0.2123(7)	0.046(4)
C21	0.1764(6)	1.0100(9)	0.3367(8)	0.052(4)	C21X	0.324(1)	0.533(1)	0.189(1)	0.121(7)
C22	0.1842(6)	1.0138(9)	0.4271(8)	0.059(4)	C22X	0.319(1)	0.541(2)	0.091(1)	0.124(8)
C23	0.1751(6)	0.925(1)	0.4584(8)	0.065(4)	C23X	0.3581(9)	0.480(1)	0.062(1)	0.106(7)
C24	0.1137(6)	0.8966(9)	0.4352(8)	0.055(4)	C24X	0.4184(9)	0.494(1)	0.080(1)	0.101(6)
C25	0.1031(6)	0.8922(9)	0.3456(8)	0.051(4)	C25X	0.4226(8)	0.472(1)	0.173(1)	0.098(6)
C26	0.1409(6)	1.0760(9)	0.4566(8)	0.055(4)	C26X	0.3350(8)	0.630(1)	0.090(1)	0.094(6)
C27	0.0769(6)	1.0456(8)	0.4324(7)	0.048(4)	C27X	0.4003(7)	0.644(1)	0.1066(9)	0.082(5)
C28	0.0694(5)	1.0438(8)	0.3436(7)	0.045(3)	C28X	0.4134(8)	0.622(1)	0.200(1)	0.099(6)
C29	0.0678(6)	0.9590(9)	0.4660(8)	0.056(4)	C29X	0.4390(8)	0.582(1)	0.075(1)	0.099(6)

<sup>a</sup> The anisotropic temperature parameters are defined by the equation:

$$T = \exp(-2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]).$$

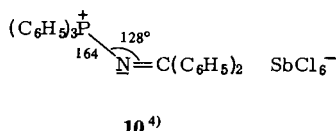
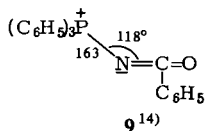
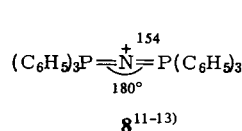
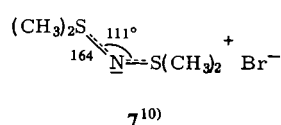
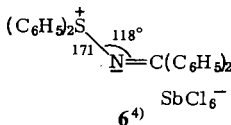
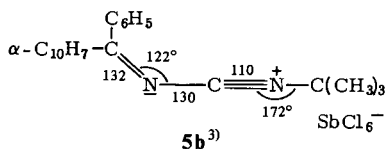
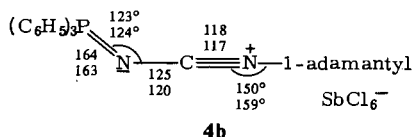
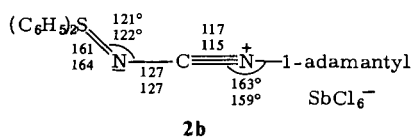
The crystals of **2b** and **4b** consist of discrete  $[C_{23}H_{25}N_2S]^+$  resp.  $[C_{29}H_{30}N_2P]^+$  cations and  $SbCl_6^-$  anions. In both cases the unit cells contain two independent molecules with slightly different shapes. But all cations are bent around N1 with bond angles for X–N1–C of almost 120°. The bond angles around N2 (C–N2–C: 150–163°) are large. Typical bond lengths of nitrilium triple bonds range from 110<sup>3)</sup> to 116 pm<sup>7,8)</sup> while C=N double bonds in carbodiimides have lengths of 120–122 pm<sup>9)</sup>.

Table 4. Selected bond lengths, bond angles, and torsional angles of **4b**<sup>b)</sup>

P - N1	164 (1); 163 (1)	P - N1 - C19	123.3 (9); 124 (1)
N1 - C19	125 (2); 120 (2)	N1 - C19 - N2	173 (1); 173 (2)
C19 - N2	118 (2); 117 (2)	C19 - N2 - C20	150 (1); 159 (1)
N2 - C20	149 (2); 151 (2)	N2 - C20 - C21	108 (1); 108 (1)
P - C1	180 (1); 177 (1)	N2 - C20 - C25	108 (1); 105 (1)
P - C7	179 (1); 178 (1)	N2 - C20 - C28	106 (1); 108 (1)
P - C13	179 (1); 179 (1)	P - N1 - N2 - C20	+92 (1); +34 (1)
C7 - P - N1	107.4 (5); 107.8 (6)	C8 - C7 - P - N1	-48 (1); -19 (1)
C13 - P - N1	109.5 (5); 108.5 (6)	C14 - C13 - P - N1	+136 (1); +156 (1)
C1 - P - N1	111.0 (5); 110.6 (5)	C2 - C1 - P - N1	+127 (1); +104 (1)
C7 - P - C13	108.9 (5); 111.1 (6)	C19 - N2 - C20 - C21	+38 (3); +58 (5)
C7 - P - C1	110.0 (5); 107.7 (6)	C19 - N2 - C20 - C25	-82 (3); -64 (5)
C13 - P - C1	109.9 (5); 111.2 (6)	C19 - N2 - C20 - C28	+158 (2); -178 (4)

b) The numbers behind the semicolon refer to the atoms marked with an X.

For the cations **2b**, **4b** sp C–N bond lengths of 115–118 pm were found. These data together with the torsional angles S–N1–N2–C1 of  $-97^\circ$  and  $+115^\circ$  for **2b** and P–N1–N2–C20 of  $+92^\circ$  and  $+34^\circ$  for **4b** suggest that both molecules are pseudocumulenes with structural features of the valence tautomers **B** and **D** with only small contributions of **A** and **C**. For the alkylidenecyanamidium salt **5b** a shorter  $\text{C}\equiv\text{N}$  triple bond and a longer N–C single bond as compared to **2b**, **4b** were found. The S–N bond in **2b** is shorter than the S–N bond in **6** and perhaps a little shorter than the S–N one and a half bond in **7** suggesting together with the large  $\text{C}\equiv\overset{+}{\text{N}}-\text{C}$  bond angle that the compound **2b** is to be regarded as a nitrilium salt **B** with minor contributions of the form **D**. The positive charge is located mainly on N2 and to a lesser extent on sulfur. The contribution of the carbodiimide form **D** is more pronounced in **4b**. The  $\text{C}\equiv\overset{+}{\text{N}}$  triple bond is longer than in **2b**, the N1–C19 bond shorter. The P–N1 bond has considerable single bond character if compared with the “true”  $\text{P}=\text{N}$  double bond in **8** and is similar to the one and a half bonds in **9** and **10**. Also, the  $\text{C}\equiv\overset{+}{\text{N}}-\text{C}$  bond angle is smaller than that in **2b** leading to the conclusion that the nitrilium form **B** and the

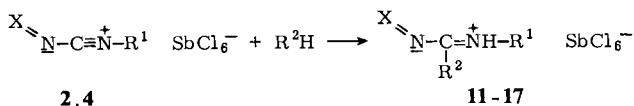


carbodiimide structure **D** have comparable share in the cation **4b** the positive charge density of which being about equal at N2 and P. If contributions of the carbodiimide structure **D** were important one would expect torsional angles X-N1-N2-C of 90°. Actually, torsional angles of +92° and +34° for **4b** and of -97° and +115° for **2b** were found, in agreement with INDO calculations of *Gordon and Fischer*<sup>15)</sup> according to which carbodiimide has a very low barrier to racemization. Transition states of nitrogen inversion and of rotation of one substituent around the N=C=N unit are energetically very similar contrary to other imines.

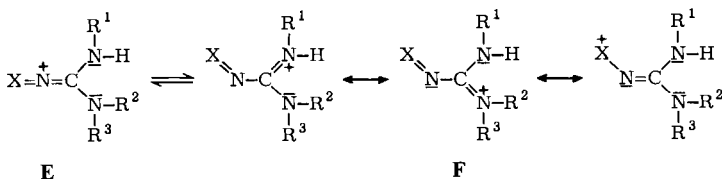
From these data nothing can be said about the structures of **2b** and **4b** in solution. But some indication comes from the <sup>13</sup>C NMR shifts of the nitrilium carbons. For **5a**, which probably has a very short nitrilium C≡N triple bond similar to that of **5b**, a signal at 103 ppm (CD<sub>2</sub>Cl<sub>2</sub>) was observed<sup>3)</sup>. For dialkylcyanamidium salts R<sup>1</sup>R<sup>2</sup>N-C≡N<sup>+</sup>-C(CH<sub>3</sub>)<sub>3</sub> SbCl<sub>6</sub><sup>-</sup> <sup>13</sup>C shifts for NCN at 115–120 ppm were reported<sup>7)</sup> while typical N=C=N shifts of carbodiimides fall in the range 136–143 ppm<sup>16)</sup>. The N<sup>13</sup>CN shifts of **2b** (δ = 116.1, CD<sub>2</sub>Cl<sub>2</sub>) and **4b** (111.8, CDCl<sub>3</sub>) are in agreement with the assumption that these compounds are nitrilium salts also in solution.

### Reactions with Nucleophiles

Salts **2** and **4** are moderately strong electrophiles. Primary and secondary amines and alcohols add readily to the nitrilium carbon at low temperatures affording compounds **11–17** in high yields. With some other nucleophiles only mixtures of compounds were obtained. The structures of **11–17** remain to be elucidated. The compounds can again be cumulenes (e.g. **E**) with linear X=N<sup>+</sup>=C units or pseudocumulenes (e.g. **F**) with bent X=N-C moieties.



	X	R <sup>1</sup>	R <sup>2</sup>
<b>11</b>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S	(CH <sub>3</sub> ) <sub>3</sub> C	(CH <sub>3</sub> ) <sub>3</sub> CNH
<b>12</b>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S	1-adamantyl	(CH <sub>3</sub> ) <sub>3</sub> CNH
<b>13</b>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S	1-adamantyl	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N
<b>14</b>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	(CH <sub>3</sub> ) <sub>3</sub> C	(CH <sub>3</sub> ) <sub>3</sub> CNH
<b>15</b>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	1-adamantyl	(CH <sub>3</sub> ) <sub>3</sub> CNH
<b>16</b>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S	(CH <sub>3</sub> ) <sub>3</sub> C	C <sub>2</sub> H <sub>5</sub> O
<b>17</b>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	1-adamantyl	C <sub>2</sub> H <sub>5</sub> O



Compounds **6** and **10** were shown recently<sup>4)</sup> to be pseudocumulenes having the positive charge located on X. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **11** and **14** show equivalent *tert*-butyl groups at room temperature. In the spectra these compounds have strong

absorptions between 1550 and 1600  $\text{cm}^{-1}$ . Further work is required but it seems likely that compounds **11**–**15** are pseudocumulenes **F** with low barriers to *cis,trans* isomerization<sup>4</sup>).

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## Experimental Part

IR spectra: Perkin-Elmer IR 299 spectrometer. All IR spectra were taken in dichloromethane solution. –  $^1\text{H}$  NMR spectra: Jeol JNM-MH-100 and Bruker WM-250 instruments. –  $^{13}\text{C}$  NMR spectra: Bruker WM-250 spectrometer.  $\delta$ -Scale, internal reference tetramethylsilane. – The melting points are uncorrected.

*N-Cyano-S,S-diphenylsulfimide* (**1**)<sup>1</sup>: To a stirred solution of diphenyl sulfide (9.30 g, 50 mmol) in dry methanol (20 ml) was added dropwise a solution of *tert*-butyl hypochlorite (6.00 g, 55 mmol) in dry methanol (10 ml) at  $-30^\circ\text{C}$  followed by a solution of cyanamide (2.31 g, 55 mmol) and sodium (1.27 g, 55 mmol) in dry methanol (20 ml). Stirring was continued for 1 h at  $-30^\circ\text{C}$  and then for 16 h at  $22^\circ\text{C}$ . After treatment with active charcoal the solution was filtered and concentrated under reduced pressure. The residual oil was purified by chromatography on silica gel (38 cm  $\times$  3.5 cm) with ether as eluent. This purification was repeated with dichloromethane as eluent. The first fractions contained unreacted diphenyl sulfide and were discarded. Work-up afforded 8.00 g (71%) of colourless prisms; m. p.  $59-60^\circ\text{C}$ . –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 263 K): CN  $\delta$  = 120.7, *o*-, *ipso*-C 135.2, 132.8, *m*-, *p*-C 130.0, 127.2.

*3-(tert-Butyl)-1-(diphenylsulfuranylidene)cyanamidium hexachloroantimonate* (**2a**): To **1** (3.40 g, 15 mmol) in 20 ml of dry 1,2-dichloroethane at  $-22^\circ\text{C}$  was added dropwise a solution of antimony pentachloride (4.49 g, 15 mmol) in dry 1,2-dichloroethane (10 ml) followed by the addition of *tert*-butyl chloride (1.67 g, 18 mmol) in dry 1,2-dichloromethane (5 ml). The mixture was stirred for 4 h at  $22^\circ\text{C}$  and then cooled to  $-20^\circ\text{C}$ . Precipitation by slow addition of dry pentane (80 ml) afforded a pink powder (9.35 g, 100%) which was twice recrystallized from chloroform to give colourless, very moisture-sensitive prisms; m. p.  $123-126^\circ\text{C}$  (dec.). –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 263 K):  $\text{CH}_3$   $\delta$  = 1.51. –  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 263 K):  $\text{CH}_3$   $\delta$  = 30.8, C 61.4, NCN 114.5, phenyl C 128.1, 131.4, 131.5, 135.3. – IR:  $\text{CN}^+$  2230  $\text{cm}^{-1}$ .

$[\text{C}_{17}\text{H}_{19}\text{N}_2\text{S}]\text{SbCl}_6$  (617.9) Calc. C 33.04 H 3.10 N 4.53 Found C 32.64 H 3.24 N 4.43

*1-(Diphenylsulfuranylidene)-3-(tricyclo[3.3.1.1<sup>3,7</sup>]dec-1-yl)cyanamidium hexachloroantimonate* (**2b**): From **1** (3.40 g, 15 mmol) and 1-chloroadamantane (2.56 g, 15 mmol) as described for **2a**. The resulting colourless powder (10.22 g, 98%, instable in solution) was crystallized from dry 1,2-dichloroethane/hexane; m. p.  $143-146^\circ\text{C}$  (dec.). –  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): adamantyl C  $\delta$  = 29.9, 35.6, 43.9, 62.0, NCN 116.1, phenyl 128.3, 131.5, 131.6, 135.5. – IR:  $\text{CN}^+$  2200, 2260  $\text{cm}^{-1}$ .

$[\text{C}_{23}\text{H}_{25}\text{N}_2\text{S}]\text{SbCl}_6$  (696.0) Calc. C 39.69 H 3.62 N 4.03 Found C 39.42 H 3.52 N 4.06

*3-tert-Butyl-1-(triphenylphosphoranylidene)cyanamidium hexachloroantimonate* (**4a**): To **3**<sup>2</sup> (3.02 g, 10 mmol) in 30 ml of dry 1,2-dichloroethane was added dropwise at  $-30^\circ\text{C}$  a solution of antimony pentachloride (2.99 g, 10 mmol) in 4 ml of dry 1,2-dichloroethane and subsequently a solution of *tert*-butyl chloride (0.93 g, 10 mmol) in dry 1,2-dichloroethane (2 ml). The mixture was stirred for 1 h at  $0^\circ\text{C}$  and then for 2 h at  $22^\circ\text{C}$ . After cooling to  $-50^\circ\text{C}$  dry pentane (140 ml) was added. An oil precipitated. The supernatant liquid was removed and the oil was crystallized by stirring under dry pentane (70 ml) yielding a colourless powder (6.73 g, 97%) which was recrystallized.



stallized from 1,2-dichloroethane/cyclohexane; m. p. 143–145 °C (dec.) –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\text{CH}_3$   $\delta$  = 1.37. –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\text{CH}_3$   $\delta$  = 31.0, C 60.1, *ipso*-C 121.5 (d,  $J_{31\text{P},^{13}\text{C}}$  = 105 Hz), *o*-C 132.5 (d,  $J$  = 12 Hz), *m*-C 130.5 (d,  $J$  = 14 Hz), *p*-C 135.8 (d,  $J$  = 4 Hz). – IR:  $\text{CN}^+$  2230  $\text{cm}^{-1}$ .

$[\text{C}_{23}\text{H}_{24}\text{N}_2\text{P}]\text{SbCl}_6$  (693.9) Calc. C 39.81 H 3.49 N 4.04 Found C 39.79 H 3.48 N 3.98

*3-(Tricyclo[3.3.1.1<sup>3,7</sup>]dec-1-yl)-1-(triphenylphosphoranylidene)cyanamidium hexachloroantimonate (4b)*: From **3** (3.02 g, 10 mmol) and 1-chloroadamantane (1.71 g, 10 mmol) as described for **4a**. After 2 h at 22 °C the mixture was stirred for 2 h at 45 °C. Half of the solvent was evaporated under reduced pressure and then dry pentane (50 ml) was added at –30 °C. The oily precipitate crystallized when warmed to 22 °C giving a colourless powder (6.49 g, 84%) which was recrystallized from 1,2-dichloroethane/hexane; m. p. 204–206 °C (dec.). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\text{NCN}$   $\delta$  = 111.8 (d,  $J$  = 11 Hz), *ipso*-C 121.5 (d,  $J$  = 104 Hz), *o*-C 132.5 (d,  $J$  = 11 Hz), *m*-C 130.5 (d,  $J$  = 14 Hz), *p*-C 135.7 (d,  $J$  = 3 Hz). – IR:  $\text{CN}^+$  2220  $\text{cm}^{-1}$ .

$[\text{C}_{29}\text{H}_{30}\text{N}_2\text{P}]\text{SbCl}_6$  (772.0) Calc. C 45.12 H 3.92 N 3.63 Found C 44.83 H 3.79 N 3.56

*N,N'-Di-tert-butyl-N''-(diphenylsulfuranylidene)guanidinium hexachloroantimonate (11)*: To **2a** (1.85 g, 3 mmol) in dry dichloromethane (10 ml) at –20 °C was added dropwise a solution of *tert*-butylamine (0.22 g, 3 mmol) in 5 ml of dry dichloromethane. The mixture was stirred for 3 h at 22 °C and then cooled to –20 °C. Slow addition of dry pentane (25 ml) afforded a yellow precipitate (2.05 g, 99%) which was crystallized from dichloromethane/ether; m. p. 154–156 °C (dec.). –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\text{CH}_3$   $\delta$  = 1.48, NH 4.97. –  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\text{CH}_3$   $\delta$  = 30.1, C 54.1,  $\text{NCN}$  159.1, *o,m*-C 127.7, 131.1, *ipso*-C 134.1, 134.4. – IR: C=N 1550  $\text{cm}^{-1}$ .

$[\text{C}_{21}\text{H}_{30}\text{N}_3\text{S}]\text{SbCl}_6$  (691.0) Calc. C 36.50 H 4.38 N 6.08 Found C 36.56 H 4.52 N 6.13

*N-tert-Butyl-N''-(diphenylsulfuranylidene)-N''-tricyclo[3.3.1.1<sup>3,7</sup>]dec-1-yl)guanidinium hexachloroantimonate (12)*: From **2b** (2.09 g, 3 mmol) and *tert*-butylamine (0.22 g, 3 mmol) as described for **11**. After stirring for 3 h at 22 °C the solvent was evaporated under reduced pressure. The residual oil was dissolved in 1,2-dichloroethane (5 ml). Addition of ether (20 ml) afforded an oily precipitate which crystallized on stirring to a yellow powder (1.92 g, 83%) which was recrystallized from 1,2-dichloroethane/ether; m. p. 142–145 °C (dec.). –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\text{CH}_3$   $\delta$  = 1.48, NH 4.87, 5.04. –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\text{CH}_3$ , C, adamantyl C  $\delta$  = 30.0, 36.0, 42.9, 53.7, 54.8,  $\text{NCN}$  158.5, *ipso*-C 134.3, 133.6, *o,m*-C 130.7, 127.5. – IR: 1550, 1590  $\text{cm}^{-1}$ .

$[\text{C}_{27}\text{H}_{36}\text{N}_3\text{S}]\text{SbCl}_6$  (769.1) Calc. C 42.16 H 4.72 N 5.47 Found C 41.93 H 4.69 N 5.56

*N-(Diphenylsulfuranylidene)-N',N'-diethyl-N''-(tricyclo[3.3.1.1<sup>3,7</sup>]dec-1-yl)guanidinium hexachloroantimonate (13)*: From **2b** (2.09 g, 3 mmol) and dry diethylamine (0.22 g, 3 mmol) as described for **11**. After stirring for 2 h at 22 °C pentane (10 ml) was added to the reaction mixture at 0 °C affording a yellow precipitate (2.17 g, 94%) which was recrystallized from chloroform/ether; m. p. 140–143 °C (dec.). –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\text{CH}_3$   $\delta$  = 1.25 (t,  $J$  = 7 Hz),  $\text{CH}_2$  3.31 (q,  $J$  = 7 Hz), NH 5.02. –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\text{CH}_3$   $\delta$  = 13.1, adamantyl C 29.6, 35.9, 42.3, 55.3,  $\text{NCH}_2$  44.9,  $\text{NCN}$  163.9, *ipso,p*-C 135.1, 133.5, *o,m*-C 130.7, 127.3. – IR: C=N 1540  $\text{cm}^{-1}$ .

$[\text{C}_{27}\text{H}_{36}\text{N}_3\text{S}]\text{SbCl}_6$  (769.1) Calc. C 42.16 H 4.72 N 5.47 Found C 41.82 H 4.62 N 5.48

*N,N'-Di-tert-butyl-N''-(triphenylphosphoranylidene)guanidinium hexachloroantimonate (14)*: To **4a** (1.39 g, 2 mmol) in 7 ml of dry dichloromethane at –40 °C was added dropwise a solution of *tert*-butylamine (0.15 g, 2 mmol) in dry dichloromethane (3 ml). After stirring for 3 h at 22 °C and subsequent cooling to –10 °C pentane (25 ml) was added. The colourless precipitate (1.47 g, 96%) was recrystallized from chloroform/hexane; m. p. 180–183 °C (dec.). –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\text{CH}_3$   $\delta$  = 1.31, NH 4.52. –  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\text{CH}_3$   $\delta$  = 29.7, C 53.2,  $\text{NCN}$  155.7,

*ipso*-C 125.7 (d,  $J = 103$  Hz), *o*-C 132.7 (d,  $J = 11$  Hz), *m*-C 130.4 (d,  $J = 13$  Hz), *p*-C 134.7 (d,  $J = 3$  Hz). – IR: C=N 1590, 1570, 1550  $\text{cm}^{-1}$ .

$[\text{C}_{27}\text{H}_{35}\text{N}_3\text{P}]\text{SbCl}_6$  (767.0) Calc. C 42.28 H 4.60 N 5.48 Found C 42.20 H 4.72 N 5.49

*N*-*tert*-Butyl-*N'*-(tricyclo[3.3.1.1<sup>3,7</sup>]dec-1-yl)-*N''*-(triphenylphosphoranylidene)guanidinium hexachloroantimonate (15): From **4b** (0.77 g, 1 mmol) and *tert*-butylamine (0.07 g, 1 mmol) as described for **14**. After stirring for 4 h at 22 °C the solvent was evaporated under reduced pressure. The residue was dissolved in 1,2-dichloroethane (5 ml) and precipitated at –30 °C with pentane (10 ml) affording a colourless powder (0.79 g, 93%) which was recrystallized from 1,2-dichloroethane/hexane; m. p. 198–201 °C (dec.). – <sup>1</sup>H NMR (CDCl<sub>3</sub>): CH<sub>3</sub>  $\delta = 1.30$ , NH 4.42, 4.50. – <sup>13</sup>C NMR (CDCl<sub>3</sub>): CH<sub>3</sub>, CH<sub>2</sub>, C  $\delta = 29.4, 29.6, 36.0, 42.5, 52.9, 53.9$ , NCN 154.9, *ipso*-C 125.4 (d,  $J = 103$  Hz), *o*-C 132.3 (d,  $J = 11$  Hz), *m*-C 130.1 (d,  $J = 13$  Hz), *p*-C 134.4 (d,  $J = 3$  Hz).

$[\text{C}_{33}\text{H}_{41}\text{N}_3\text{P}]\text{SbCl}_6$  (845.1) Calc. C 46.90 H 4.89 N 4.97 Found C 46.81 H 4.94 N 5.04

*1*-*tert*-Butyl-3-(diphenylsulfuranylidene)-2-ethyluronium hexachloroantimonate (16): To **2a** (1.24 g, 2 mmol) in dry dichloromethane (5 ml) at –30 °C was added a solution of dry ethanol (0.18 g, 4 mmol) in dry dichloromethane (5 ml). The mixture was stirred for 6 h at 22 °C and then cooled to –30 °C. Slow addition of pentane (25 ml) afforded an oil which crystallized while warmed to 22 °C (1.25 g, 94%). Recrystallization from dichloromethane/ether/hexane gave a colourless powder; m. p. 143–146 °C (dec.). – <sup>1</sup>H NMR (CDCl<sub>3</sub>): CH<sub>3</sub>  $\delta = 1.51, 1.44$  (t,  $J = 7$  Hz), CH<sub>2</sub> 4.52 (q,  $J = 7$  Hz), NH 5.67. – <sup>13</sup>C NMR (CDCl<sub>3</sub>): CH<sub>3</sub>  $\delta = 14.1, 29.2$ , CH<sub>2</sub> 67.6, C 55.3, NCN 161.5, *ipso*-C 133.9, 133.3, *o,m*-C 130.9, 127.6. – IR: C=N 1560, 1590  $\text{cm}^{-1}$ .

$[\text{C}_{19}\text{H}_{25}\text{N}_2\text{OS}]\text{SbCl}_6$  (664.0) Calc. C 34.37 H 3.80 N 4.22 Found C 34.18 H 3.78 N 4.42

2-Ethyl-1-(tricyclo[3.3.1.1<sup>3,7</sup>]dec-1-yl)-3-(triphenylphosphoranylidene)uronium hexachloroantimonate (17): A solution of **4b** (0.77 g, 1 mmol) and dry ethanol (0.14 g, 3 mmol) in dry 1,2-dichloroethane (7 ml) was refluxed for 2 h. Addition of pentane (10 ml) to the cooled (0 °C) solution afforded a colourless precipitate (0.77 g, 94%) which was recrystallized from 1,2-dichloroethane/ether/hexane; m. p. 188–192 °C (dec.). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): CH<sub>3</sub>  $\delta = 13.9$  (broad), adamantane-C 29.4, 36.0, 41.4, 55.0, OCH<sub>2</sub> 66.6 (broad), NCN 158.5 (broad), *ipso*-C 124.3 (very broad, d,  $J \approx 100$  Hz), *o*-C 132.4 (d,  $J = 11$  Hz), *m*-C 130.1 (broad, d,  $J = 14$  Hz), *p*-C 134.4 (very broad). – IR: C=N 1590, 1570  $\text{cm}^{-1}$ .

$[\text{C}_{31}\text{H}_{36}\text{N}_2\text{OP}]\text{SbCl}_6$  (818.1) Calc. C 45.51 H 4.44 N 3.43 Found C 45.37 H 4.43 N 3.50

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