

1,3-Diaza-2-azoniaallene salts: cycloadditions to alkynes, carbodiimides and cyanamides

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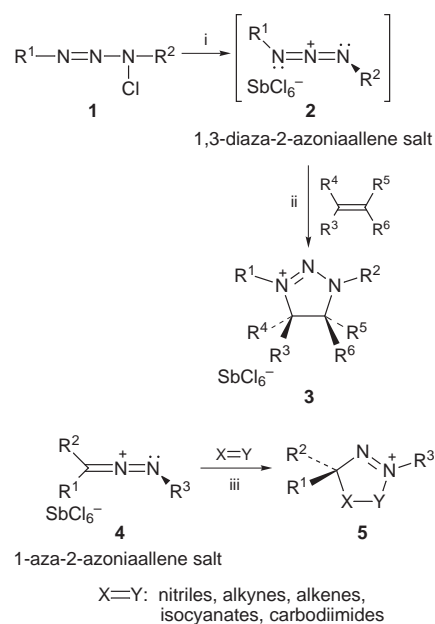
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1,3-Diaza-2-azoniaallene salts **2** react with alkynes **6** to furnish 1,2,3-triazolium salts **7a–m**. According to AM1 calculations, these reactions are concerted [3 + 2] cycloadditions (1,3-dipolar cycloadditions with inverse electron demand). The structure of the triazolium salt **7e** has been confirmed by X-ray crystallographic analysis. With *N,N'*-dialkylcarbodiimides **9** the heteroallene salts **2** undergo cycloaddition to furnish 1,3,4,5-tetra-substituted 4,5-dihydro-tetrazolium salts **11**, which on heating in acetonitrile eliminate an alkene to afford 1,3,5-tri-substituted tetrazolium salts **12**. Furthermore, it has been found that heteroallene salts **2** react with *N,N*-dialkylcyanamides **13** to give 1,3,5-tri-substituted tetrazolium salts **15**. Here, AM1 calculations suggest stepwise cycloaddition mechanisms *via* intermediate nitrilium salts **10** and **14** respectively.

Introduction

The first to encounter the problem of the site (N-1 or N-3) of electrophilic attack on hydrazoic acid HN_3 and organic azides RN_3 was Schmidt who prepared the room temperature stable aminodiazonium hexachloroantimonate $\text{H}_2\text{N}-\text{N}^+\equiv\text{N} \text{SbCl}_6^-$ by protonation of hydrazoic acid with HSbCl_6 . Correspondingly, methyl azide was protonated at N-1 to afford a (methylamino)-diazonium salt, $\text{CH}_3\text{NH}-\text{N}^+\equiv\text{N} \text{SbCl}_6^-$, which above 5°C eliminated nitrogen.^{1–4} Olah *et al.* studied protonation of hydrazoic acid and alkyl azides under superacidic stable ion conditions confirming formation of aminodiazonium ions.^{5,6} According to *ab initio* calculations at the 3-21G level of theory the 1,3-diaza-2-azoniaallene ion $\text{H}-\text{N}=\text{N}^+=\text{N}-\text{H}$ resulting from protonation of hydrazoic acid at N-3 is energetically more than 200 kJ mol^{-1} above the aminodiazonium ion $\text{H}_2\text{N}-\text{N}^+\equiv\text{N}$. Recently, the crystal structure of $\text{H}_2\text{N}-\text{N}^+\equiv\text{N} \text{SbF}_6^-$ has been reported.⁷ Thus, while aminodiazonium ions $\text{R}^1\text{R}^2\text{N}-\text{N}^+\equiv\text{N}$ are well-documented species, 1,3-diaza-2-azoniaallene ions **2** derived from hydrazoic acid by substitution on both N-1 and N-3 are not.

In preceding papers we reported first preparations of open-chain *N*-chlorotriazones **1**, which react with Lewis acids such as antimony pentachloride to give salts **2** (Scheme 1).^{8–10} Below -25°C the orange hexachloroantimonate **2a** (Scheme 2) proved to be stable. At -80°C the salt can be stored for an extended period of time. The structure **2a** follows from the ^1H NMR spectrum (at -35°C in CD_3CN only one singlet at 7.93 ppm), the ^{13}C NMR spectrum (four resonances for two equivalent aryl groups), the IR spectrum (at -50°C in MeCN: strong band at 2018 cm^{-1}), a correct elemental analysis, and from its subsequent reactions with alkenes. In contrast to 1-aza-2-azoniaallene ions **4**,^{11,12} the cation **2a** is only a weak electrophile being neither especially moisture sensitive nor reactive with methanol. However, similar to heteroallenes **4**, 1,3-diaza-2-azoniaallene ions **2** undergo smooth [3 + 2] cycloadditions to both electron-rich and electron-deficient alkenes to afford 4,5-dihydro-1*H*-1,2,3-triazolium salts **3**.⁸ Compounds **3** were formed with complete conservation of the configuration of the alkene. This, and AM1-calculations, suggest that reactions of cations **2** with alkenes are concerted 1,3-dipolar cycloadditions of type III according to Sustmann's classification (1,3-dipolar cycloaddition with inverse electron demand).¹³



Scheme 1 Reagents and conditions: i, SbCl_5 , CH_2Cl_2 , -60°C ; ii, CH_2Cl_2 , -60 to 23°C , 2 h, 43–98%; iii, CH_2Cl_2 , -60 to 23°C , 2 h

Cations of type **2** and **4** can be regarded as aza-substituted allylic cations, for which another pericyclic reaction mode could be envisioned, namely [3 + 4] cycloaddition to butadienes.^{14–16} However, we never observed such a reaction. Instead, cations **2** were again found to undergo 1,3-dipolar cycloaddition to one or both double bonds of buta-1,3-dienes to furnish heterocycles **3**.⁹

While [3 + 2] cycloadditions of organic cations as four-electron components seemed to be unreported, an interesting inorganic example is the cation $\text{S}=\text{N}^+=\text{S}$.^{17–19} In contrast to the familiar nitronium ion $\text{O}=\text{N}^+=\text{O}$, which behaves as a strong electrophile effecting, for instance, aromatic nitration, the dithia analogue $\text{S}=\text{N}^+=\text{S}$ is a cationic 1,3-dipole furnishing cycloadducts with alkenes and other molecules with multiple bonds.

For 1-aza-2-azoniaallene salts **4** cycloadditions not only to alkenes but also to alkynes, isocyanates, carbodiimides and—especially smoothly—to nitriles have been published.^{11,12,20–24} We now set out to study the corresponding reactions of salts **2**, and report here our first results.

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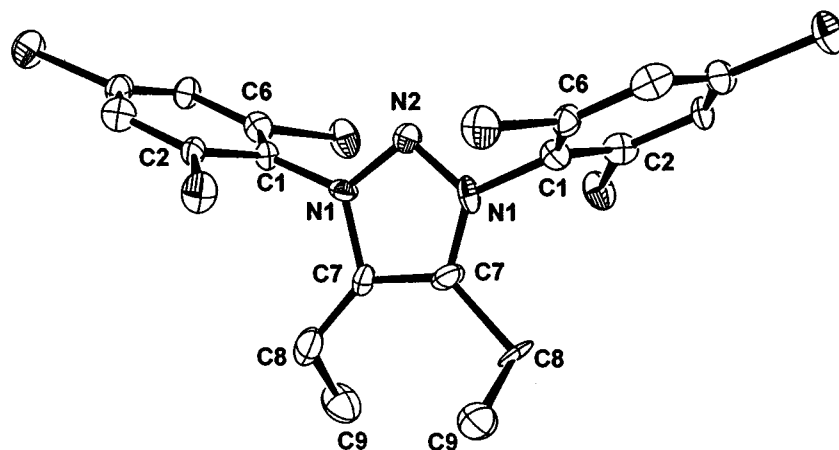
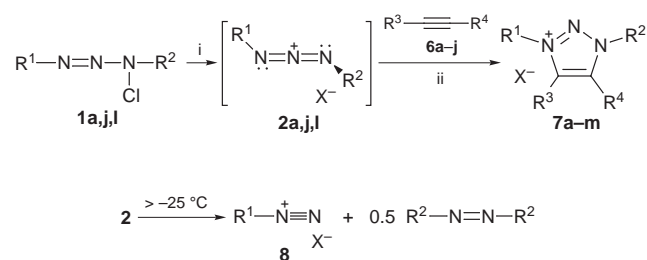


Fig. 1 ORTEP Plot for the cation **7e**; a symmetry transformation was used to generate equivalent atoms: #1 $-x + 1, y, -z + \frac{1}{2}$

Results and discussion

Stirring a mixture of **2a** and an excess of acetylene **6a** between -78 and 23 °C in dichloromethane resulted in formation of the 1,2,3-triazolium hexachloroantimonate **7a** in 83% yield. A small amount of the diazonium salt **8a** was formed as a by-product. Correspondingly, the triazolium salts **7b–m** were prepared in moderate to good yields from mono- and disubstituted alkynes **6b–j** (Scheme 2). Cycloadditions were suc-



1,2,6–8	R ¹	R ²	R ³	R ⁴	X
a	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂	H	H	SbCl ₆ ⁻
b	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂	Bu	H	SbCl ₆ ⁻
c	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂	Bu ^t	H	SbCl ₆ ⁻
d	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂	CH ₂ OH	H	SbCl ₆ ⁻
e	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂	Et	Et	SbCl ₆ ⁻
f	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂	CH ₂ Cl	CH ₂ Cl	SbCl ₆ ⁻
g	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂	Me	Ph	SbCl ₆ ⁻
h	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂	Ph	Ph	SbCl ₆ ⁻
i	2,4,6-Cl ₃ C ₆ H ₂	2,4,6-Cl ₃ C ₆ H ₂	CO ₂ Me	CO ₂ Me	SbCl ₆ ⁻
j	4-ClC ₆ H ₄	4-ClC ₆ H ₄	CH ₂ Cl	H	PF ₆ ⁻
k	4-ClC ₆ H ₄	4-ClC ₆ H ₄	Et	Et	PF ₆ ⁻
l	4-MeC ₆ H ₄	Me	Et	Et	PF ₆ ⁻
m	4-MeC ₆ H ₄	Me	Ph	Ph	PF ₆ ⁻

Scheme 2 Reagents and conditions: i, SbCl₅ or KPF₆, CH₂Cl₂, -78 °C; ii, CH₂Cl₂, -78 to 23 °C, $\frac{1}{4}$ h, 27–83%

cessfully achieved with alkynes with electron-releasing (e.g. **6e**) as well as with electron-withdrawing substituents (**6i**). In contrast, no reactions were observed between 1-aza-2-azoniaallene salts **4** and electron-deficient alkynes, such as dimethyl acetylenedicarboxylate **6i**.²¹

The heteroallenes **2** were prepared *in situ* from *N*-chlorotriazenes **1** with antimony pentachloride or with potassium hexafluorophosphate.

With titanium tetrachloride or tin tetrachloride, hexachlorotitanates and hexachlorostannates **7** were obtained as moisture sensitive brown oils, which could not be purified.

The instability of compounds **1** and **2** even at low temperatures is a limiting factor for the cycloaddition described. For instance, while the chlorotriazene **1a** can be isolated and stored

at 0 °C, the chloro compounds **1j,l** could only be prepared at -60 °C *in situ* by treating the corresponding triazenes with *tert*-butyl hypochlorite.⁸ For the cycloaddition to succeed, the chlorination had to be carried out in the presence of potassium hexafluorophosphate and the alkyne.

Above -25 °C the heteroallenes **2** disproportionate into diazonium salts **8** and azo compounds (Scheme 2).⁸ The rates of disproportionation and of cycloaddition to alkynes seem to be comparable. As a result, the crude triazolium salts **7** were always contaminated with small amounts of diazonium salts **8**, which had to be removed by recrystallization.

The structural assignments of the new compounds prepared are based on their ¹H and ¹³C NMR spectra, IR spectra and elemental analyses. An alternative preparation of triazolium salt **7a** from heteroallene **2a** and vinyl chloride has been reported.⁸ The constitution of the salt **7e** was secured by X-ray crystallographic analysis (Fig. 1, Table 1). In the crystal the cation **7e** showed C₂ rotational symmetry so that one half of the cation had to be generated from the other half by a symmetry operation (#1). Table 1 also contains the structural parameters for the isolated cation **7e** as calculated by the AM1 method.²⁵

The structure **7e** may be discussed in the light of recent arguments in favour of the singlet nitrogen character of 1,3-disubstituted 1,2,3-triazolium salts.²⁷ All structural peculiarities discussed by Boche *et al.* for their 1,2,3-triazolium salts, especially the narrow bond angles N–N–N, also apply to structure **7e** [N1–N2–N1#1: 101.9(2)°].⁹ Boche reached the conclusion that 1,3-disubstituted 1,2,3-triazolium salts are stable nitrogen salts being ‘electronically distinctly different from normal ones’. The stability of cations **7** is essentially a consequence of electronic stabilization of the formally vacant p(π) orbital at the positively charged N2 atom (AM1 calculated charges for **7e**: N1,3: -0.015 , N2: $+0.133$ electrons). As far as we are aware, chemical reactions supporting the idea of a nitrogen character for cations **7** have not been published so far.

AM1 calculations for the cycloaddition of cation **2a** to but-2-yne suggest an exothermic ($\Delta H^0 = -200$ kJ mol⁻¹) concerted reaction with a transition structure (activation enthalpy $\Delta H^\ddagger = 110$ kJ mol⁻¹) with C_{2v} symmetry. This corresponds to the mechanistic scheme of a 1,3-dipolar cycloaddition with inverse electron demand with the 1,3-diaza-2-azoniaallene cation **2a** acting as a ‘1,3-dipole’ (four-electron component) and the alkyne as a dipolarophile (two-electron component).

The cycloaddition of 1,3-diaza-2-azoniaallene salts **2** to alkynes constitutes a new method for the preparation of 1,3-disubstituted 1*H*-1,2,3-triazolium salts **7**, which are conventionally prepared by alkylation of 1*H*-1,2,3-triazoles.²⁸ Recently, the first example of **2** reacting with an alkyne has been published by us.¹⁰

Since 1-aza-2-azoniaallene cations **4** undergo cycloadditions to many nitriles, carbodiimides, isocyanates and other com-

Table 1 Selected bond lengths, bond angles and torsional angles for **7e**^{25,26}

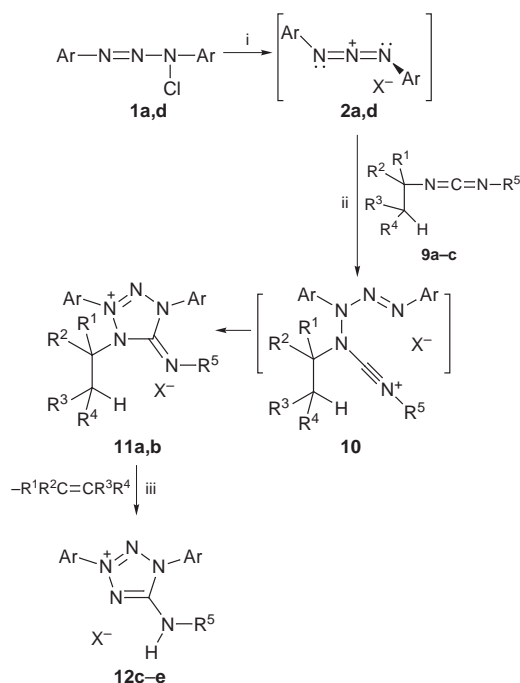
Atoms	Bond length/ pm (exp.)	AMI	Atoms	Angle (°) (exp.)	AMI
N1–N2	131.4(2)	132	N1#1–N2–N1–C7	–0.2(1)	0
N1–C7	136.6(2)	142	N2–N1–C7–C7#1	0.5(2)	0
C7–C7#1	136.8(3)	142	N1#1–N2–N1–C1	–177.5(2)	–179
N1–N2–N1#1	101.9(2)	107	N1–C7–C8–C9	–120.1(2)	–100
N2–N1–C7	114.8(1)	112	N2–N1–C1–C2	96.9(2)	91
N1–C7–C7#1	104.2(1)	105	N2–N1–C7–C8	–179.3(2)	180
N1–C7–C8	123.6(2)	126	C7#1–C7–N1–C1	177.4(2)	179
N2–N1–C1	117.4(1)	123	C8–C7–N1–C1	–2.4(3)	–1
C7–C8–C9	115.3(2)	112	C7#1–C7–C8–C9	60.1(4)	80

pounds with multiple bonds, the question arose whether similar reactions would also be possible for 1,3-diaza-2-azoniaallene cations **2**. However, no reaction could be induced between **2a** and simple nitriles, such as acetonitrile or benzonitrile, or isocyanates (phenyl isocyanate, methyl isocyanate), or isothiocyanates (methyl isothiocyanate, isopropyl isothiocyanate) or azo compounds (azobenzene, 2,3-diazabicyclo[2.2.1]hept-2-ene).

On the other hand, addition at –60 °C of *N,N'*-diisopropylcarbodiimide **9a** to a suspension of the hexachloroantimonate **2a** in dichloromethane afforded after stirring between –60 and 0 °C the 4,5-dihydro-1*H*-tetrazolium salt **11a** as a yellow powder (57% after recrystallization) (Scheme 3). With *N,N*-

ily formed **11c**. With carbodiimides **9a,b** and the heteroallene **2j** (Scheme 2) mixtures of the corresponding tetrazolium salts **11d,e** and **12d,e** were obtained. In boiling acetonitrile the ¹H NMR signals for **11d,e** gradually disappeared while the resonances for **12d,e** increased in intensity. After three hours of boiling under reflux the signals for **11d,e** had completely disappeared, and only signals for **12d,e**, respectively (in the case of **12e** also for cyclohexene), were observed in the ¹H NMR spectra. Work-up afforded the pure tetrazolium salts **12d,e** (77 and 73%). No cycloadditions could be induced between the salt **2a** and aryl substituted carbodiimides, such as *N,N'*-bis(*p*-methoxyphenyl)carbodiimide.

Furthermore, heteroallenes **2** were found to react with electron-rich cyanamides **13a–d** (Scheme 4). Here, the order of

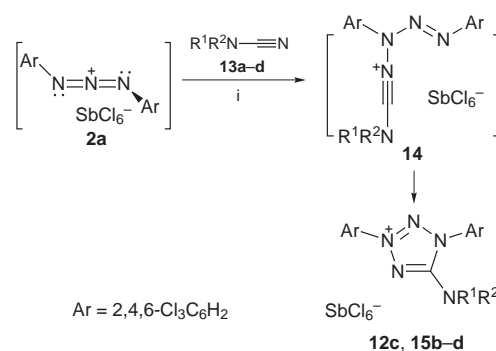


9–12	Ar	R ¹	R ²	R ³	R ⁴	R ⁵	X
a	2,4,6-Cl ₃ C ₆ H ₂	H	Me	H	H	Pr ⁱ	SbCl ₆ ⁻
b	2,4,6-Cl ₃ C ₆ H ₂	H	–(CH ₂) ₄ –	H	H	C ₆ H ₁₁	SbCl ₆ ⁻
c	2,4,6-Cl ₃ C ₆ H ₂	Me	Me	H	H	Bu ^t	SbCl ₆ ⁻
d	4-ClC ₆ H ₄	H	Me	H	H	Pr ⁱ	PF ₆ ⁻
e	4-ClC ₆ H ₄	H	–(CH ₂) ₄ –	H	H	C ₆ H ₁₁	PF ₆ ⁻

Scheme 3 Reagents and conditions: i, SbCl₅ or KPF₆, CH₂Cl₂, –78 °C; ii, CH₂Cl₂, –78 to 23 °C, 1½ h, 57–53%; iii, MeCN, 81 °C, 3 h, 50–77%

dicyclohexylcarbodiimide **9b** and heteroallene **2a** the tetrazolium salt **11b** was obtained (53%).

However, under similar conditions the reaction of *N,N'*-di-*tert*-butylcarbodiimide **9c** with **2a** afforded the 5-*tert*-butylamino substituted tetrazolium salt **12c** instead of the expected tetra-substituted heterocycle **11c**. Obviously, under the reaction conditions, 2-methylpropene was eliminated from primar-



13–15	R ¹	R ²
a	Bu ^t	H
b	Me	Me
c	Me	Pr ⁱ
d	Pr ⁱ	Pr ⁱ

Scheme 4 Reactions and conditions: i, CH₂Cl₂, –78 to 23 °C, 1½ h, 34–71%

mixing of the starting materials proved to be important. Addition, for instance, of antimony pentachloride to a cold (–60 °C) mixture of the chlorotriazene **1a** and the cyanamide **13b** resulted in the exclusive formation of the diazonium salt **8a** and of azo(2,4,6-trichlorobenzene). Apparently, the Lewis acid antimony pentachloride was consumed by complexation with the cyanamide. On the other hand, adding the cyanamide to a cold (–60 °C) suspension of the preformed heteroallene **2a** in dichloromethane afforded the tetrazolium salt **15b** in 61% yield.

At about –30 °C a slow reaction took place between the intermediate **2a** and *tert*-butylcyanamide **13a** to afford the same tetrazolium salt **12c** (34%), which had been obtained already by reaction of **2a** with *N,N'*-di-*tert*-butylcarbodiimide **9c**. As a consequence of the relatively high reaction temperature, the crude salt **12c** was contaminated with the diazonium salt **8a** due to partial decomposition of **2a**. The less sterically encumbered dialkylated cyanamides **13b–d** reacted with the heteroallene **2a** to furnish the 5-(alkylamino)tetrazolium salts **15b–d** (61–71%).

However, only products of decomposition of the heteroallene **2a** were isolated in reactions with less electron-rich cyanamides, such as *N*-cyclohexyl-*N*-phenylcyanamide or *N,N*-diphenylcyanamide or the parent cyanamide.

According to AM1-calculations the cycloaddition of the cation **2a** to *N,N*-dimethylcyanamide **13b** is a two-step reaction with a nitrilium ion **14b** as intermediate. Similarly, nitrilium ions **10** were calculated to be intermediates of the cycloadditions of **2a** to carbodiimides **9**.

Cycloadditions of 1,3-diaza-2-azoniaallene cations to electron-rich carbodiimides and cyanamides constitute new syntheses of tetrazolium salts **11**, **12** and **15**. 5-Amino substituted tetrazolium salts **12**, **15** seem to be unreported in the literature. Conventionally, 1,3,5-trisubstituted tetrazolium salts are prepared by alkylation of 1,5- or 1,3-disubstituted tetrazoles.^{29–32}

Experimental

The solvents were dried by standard methods. The cycloadditions were carried out with exclusion of moisture. IR spectra were obtained with a Perkin-Elmer FTIR 1600 spectrometer. ¹H and ¹³C NMR spectra were obtained with Bruker AC-250 and WM-250 spectrometers; internal reference SiMe₄; 295 K; δ scale; *J* values are given in Hz.

X-Ray structural analysis of **7e**²⁶

Crystal data. [C₁₈H₁₄Cl₆N₃]⁺[SbCl₆]⁻·CH₃CN, *M* = 860.5, monoclinic, space group *C2/c* (No. 15), *a* = 1718.7(2), *b* = 1910(1), *c* = 1061(1) pm, β = 120.2(1)°, *V* = 3009.5(5) × 10⁶ pm³, *Z* = 4, *F*(000) = 1680, *D*_c = 1.899 g cm⁻³, μ (Mo-K α) = 20.0 cm⁻¹, λ = 71.069 pm.

Data collection. Intensity data were collected on an Enraf-Nonius CAD4 four-circle diffractometer using Mo-K α radiation from a graphite monochromator in the θ -range of 2.74–35.32° with a scan width in ω of 0.81° + 0.35 tg θ . The colourless crystal used had dimensions 0.5 × 0.5 × 0.5 mm. Three reference reflections were measured every 1 h which showed no significant variation in intensities throughout data collection. Lorentz and polarization corrections were applied to the data and equivalent reflections were merged to give 4990 unique reflections with $I/\sigma(I) > 2$ (*R*_{int} = 0.014 for all 6357 reflections).

Structure solution and refinement.³³ The structure was solved by the Patterson method. All the non-hydrogen and hydrogen atoms except the three hydrogen atoms of the solvent molecule CH₃CN were located by difference-Fourier synthesis. Cation **7e** contains a C₂ rotational axis so that one half of the molecule was generated by the transformation #1 $-x + 1, y, -z + \frac{3}{2}$. The final cycles of full-matrix least-squares refinement converged to *R* = 0.0290 and *R*_w = 0.0679 for 172 parameters with weights of $1/[\sigma^2(F_o^2) + 0.0338p^2 + 1.61p]$ where $p = [\max(F_o^2, 0) + 2 F_c^2]/3$. In the final difference-Fourier map there were no residual peaks outside the range of $-1.47 \rightarrow 0.57 \times 10^{-6}$ e pm⁻³.

1,3-Bis(2,4,6-trichlorophenyl)-1*H*-1,2,3-triazolium hexachloroantimonate **7a**⁸

A solution of SbCl₅ (2.99 g, 10 mmol) in CH₂Cl₂ (20 ml) was added dropwise to a cold (–78 °C) stirred mixture of acetylene **6a** (2.60 g, 100 mmol) and chlorotriazene **1a** (4.38 g, 10 mmol) in CH₂Cl₂ (40 ml). An orange precipitate was formed. Stirring was continued for 1 h, during which time the temperature rose to –30 °C. After stirring at 0 °C for 30 min and then at 23 °C for 15 min, CCl₄ (40 ml) was added. Filtration afforded a yellow-brown powder (6.34 g, 83%), which was crystallized from CH₂Cl₂ (80 ml)–MeCN (20 ml)–Et₂O (200 ml) to furnish the *title compound 7a* as a crystalline powder, mp 239–241 °C (decomp.) (Found: C, 22.10; H, 0.91; N, 5.39. C₁₄H₆Cl₁₂N₃Sb requires C, 22.03; H, 0.79; N, 5.50%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1566; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 7.91 (aryl), 9.06 (H-4, -5); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 129.9, 130.9, 134.5, 136.5 and 141.4 (aryl, C-4, -5).

4-Butyl-1,3-bis(2,4,6-trichlorophenyl)-1*H*-1,2,3-triazolium hexachloroantimonate **7b**

Prepared from hex-1-yne **6b** (0.99 g, 12 mmol) and the chlorotriazene **1a** (4.38 g, 10 mmol) in the manner described for **7a**. After addition of CCl₄ (120 ml) a pale yellow powder (6.06 g, 74%) was isolated by filtration. Recrystallization at 23 °C from CH₂Cl₂ (20 ml)–MeCN (4 ml)–Et₂O (240 ml) furnished the *title compound 7b* as a powder (5.08 g, 62%), mp 160–162 °C (decomp.) (Found: C, 26.15; H, 1.85; N, 5.22. C₁₈H₁₄Cl₁₂N₃Sb requires C, 26.38; H, 1.72; N, 5.13%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1564; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 0.91 (t, *J* 7.3, CH₃), 1.39 (m), 1.71 (m), 2.83 (t, *J* 7.7) (CH₂), 7.89, 7.92 (aryl), 8.88 (H-5); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 13.8, 22.5, 24.0 and 29.7 (CH₃, CH₂), 127.9, 130.1, 130.9, 131.4, 133.5, 134.4, 134.7, 141.3, 141.8 and 150.4 (aryl, C-4, -5).

4-*tert*-Butyl-1,3-bis(2,4,6-trichlorophenyl)-1*H*-1,2,3-triazolium hexachloroantimonate **7c**

Prepared from 3,3-dimethylbut-1-yne **6c** (0.99 g, 12 mmol) and the chlorotriazene **1a** (4.38 g, 10 mmol) in the manner described for **7a**. After addition of CCl₄ (80 ml) a reddish powder (6.71 g, 82%) was isolated by filtration. Dissolution in CH₂Cl₂ (40 ml) and addition of Et₂O (40 ml) to the solution resulted in precipitation of a small amount of the diazonium salt **8a**, which was removed by filtration. After addition of Et₂O (80 ml) to the filtrate, *title compound 7c* was isolated by filtration as a crystalline powder (5.25 g, 64%), mp 254–258 °C (decomp.) (Found: C, 26.35; H, 1.69; N, 4.81. C₁₈H₁₄Cl₁₂N₃Sb requires C, 26.38; H, 1.72; N, 5.13%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1565; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 1.43 (CH₃), 7.89 and 7.92 (aryl), 8.91 (H-5); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 29.1 (CH₃), 34.1 (C), 129.9, 130.2, 130.9, 131.5, 133.5, 134.3, 135.1, 141.3, 141.9 and 157.5 (aryl, C-4, -5).

4-Hydroxymethyl-1,3-bis(2,4,6-trichlorophenyl)-1*H*-1,2,3-triazolium hexachloroantimonate **7d**

At –60 °C an orange suspension of allene **2a** was prepared by addition of SbCl₅ (2.99 g, 10 mmol) in CH₂Cl₂ (20 ml) to a solution of the chlorotriazene **1a** (4.38 g, 10 mmol) in CH₂Cl₂ (40 ml). A solution of prop-2-ynyl alcohol **6d** (0.67 g, 12 mmol) in CH₂Cl₂ (40 ml) was added. The stirred mixture was warmed to –30 °C in the course of the next 1 h. Stirring was continued at 0 °C for 30 min, then at 23 °C for 15 min. After addition of CCl₄ (40 ml) a small amount of the diazonium salt **8a**⁸ was removed by filtration. Addition of CCl₄ (200 ml) to the filtrate and keeping at –15 °C for 12 h afforded a crystalline powder (6.59 g, 83%), which was recrystallized at 23 °C from CH₂Cl₂ (40 ml)–CCl₄ (120 ml) to give *title compound 7d* as a powder (6.11 g, 77%), mp 140–170 °C (decomp.) (Found: C, 22.71; H, 1.17; N, 5.27. C₁₅H₈Cl₁₂N₃OSb requires C, 22.71; H, 1.02; N, 5.30%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1565, 3534, 3580 (OH); $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 4.06 (t, *J* 6.2, OH), 4.82 (d, *J* 6.1, CH₂), 7.90 and 7.91 (aryl), 8.96 (H-5); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 54.1 (CH₂), 128.7, 130.1, 130.9, 131.1, 133.8, 134.5, 134.6, 141.4, 141.6 and 149.0 (aryl, C-4, -5).

4,5-Diethyl-1,3-bis(2,4,6-trichlorophenyl)-1*H*-1,2,3-triazolium hexachloroantimonate **7e**

Prepared from hex-3-yne **6e** (0.99 g, 12 mmol) and the chlorotriazene **1a** (4.38 g, 10 mmol) in the manner described for **7a**. After addition of CCl₄ (120 ml) a pale yellow powder (6.06 g, 74%) was isolated by filtration. Crystallization at 23 °C from CH₂Cl₂ (20 ml)–Et₂O (40 ml) furnished prisms of the *title compound 7e* (5.41 g, 66%), mp 262–264 °C (decomp.). Crystals suitable for X-ray crystallographic analysis were obtained by slow crystallization at 5 °C from MeCN (Found: C, 26.10; H, 1.74; N, 5.13. C₁₈H₁₄Cl₁₂N₃Sb requires C, 26.38; H, 1.72; N, 5.13%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1563; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 1.23 (t, *J* 7.6, CH₃), 2.92 (q, *J* 7.6, CH₂), 7.91 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 12.5, 17.9 (CH₃, CH₂), 128.4, 131.4, 134.7, 141.7 and 147.5 (aryl, C-4, -5).

4,5-Bis(chloromethyl)-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3-triazolium hexachloroantimonate 7f

From 1,4-dichlorobut-2-yne **6f** (1.48 g, 12 mmol) and chlorotriazene **1a** (4.38 g, 10 mmol) in the manner described for **7a**. Addition of CCl₄ (40 ml), filtration, and addition of further CCl₄ (80 ml) to the filtrate afforded a pale yellow powder (5.33 g, 62%), which was reprecipitated at 23 °C from CH₂Cl₂ (20 ml)–Et₂O (40 ml) to furnish *title compound 7f* as a powder (5.16 g, 60%), mp 226–228 °C (decomp.) (Found: C, 22.17; H, 1.04; N, 4.89. C₁₆H₈Cl₁₄N₃Sb requires C, 22.34; H, 0.94; N, 4.88%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1566; $\delta_{\text{H}}(250 \text{ MHz}, \text{CD}_3\text{CN})$ 4.95 (CH₂), 7.95 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}, \text{CD}_3\text{CN})$ 31.2 (CH₂), 127.4, 131.4, 134.8, 142.4 and 143.5 (aryl, C-4, -5).

4-Methyl-5-phenyl-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3-triazolium hexachloroantimonate 7g

Prepared from 1-phenylpropyne **6g**³⁴ (1.39 g, 12 mmol) and the chlorotriazene **1a** (4.38 g, 10 mmol) in the manner described for **7a**. Addition of CCl₄ (40 ml), filtration, and addition of further CCl₄ (200 ml) to the filtrate and stirring at –20 °C for 1 h afforded a brownish powder (6.15 g, 72%), which was reprecipitated at 23 °C from CH₂Cl₂ (20 ml)–Et₂O (80 ml) to furnish *title compound 7g* as a pale yellow powder (4.87 g, 57%), mp 238–239 °C (decomp.) (Found: C, 29.22; H, 1.69; N, 5.17. C₂₁H₁₂Cl₁₂N₃Sb requires C, 29.55; H, 1.42; N, 4.92%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1571, 1611; $\delta_{\text{H}}(250 \text{ MHz}, \text{CD}_3\text{CN})$ 2.54 (CH₃), 7.51–7.74 (phenyl), 7.80 and 7.95 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}, \text{CD}_3\text{CN})$ 10.2 (CH₃), 121.4, 128.2, 128.8, 130.4, 130.9, 131.2, 131.4, 133.8, 134.7, 134.8, 141.5, 141.8, 143.7 and 144.8 (phenyl, aryl, C-4, -5).

4,5-Diphenyl-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3-triazolium hexachloroantimonate 7h

From diphenylacetylene **6h** (1.78 g, 10 mmol) and the chlorotriazene **1a** (4.38 g, 10 mmol) in the manner described for **7a**. Addition of CCl₄ (80 ml), filtration, and addition of further CCl₄ (40 ml) to the filtrate afforded a pale brown powder (6.68 g, 70%), which was dissolved in CH₂Cl₂ (20 ml). Filtration and addition of Et₂O (40 ml) to the filtrate furnished *title compound 7h* as a powder (6.04 g, 66%), mp 232–236 °C (decomp.) (Found: C, 34.00; H, 1.65; N, 4.53. C₂₆H₁₄Cl₁₂N₃Sb requires C, 34.11; H, 1.54; N, 4.59%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1570, 1608; $\delta_{\text{H}}(250 \text{ MHz}, \text{CD}_3\text{CN}; 313 \text{ K})$ 7.45–7.64 (10 H, phenyl), 7.80 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}, \text{CD}_3\text{CN}; 313 \text{ K})$ 121.0, 128.8, 130.7, 130.8, 131.2, 133.9, 134.8, 141.8 and 144.9 (phenyl, aryl, C-4, -5).

4,5-Bis(methoxycarbonyl)-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3-triazolium hexachloroantimonate 7i

From dimethyl acetylenedicarboxylate **6i** (1.71 g, 12 mmol) and the chlorotriazene **1a** (4.38 g, 10 mmol) in the manner described for **7a**. Filtration and addition of Et₂O (80 ml) to the filtrate afforded a brown precipitate (6.25 g, 71%), which was dissolved in CH₂Cl₂ (40 ml). Filtration from a small amount of the diazonium salt **8a** and addition of Et₂O (120 ml) to the filtrate furnished *title compound 7i* as a powder (5.45 g, 62%), mp 203–205 °C (decomp.) (Found: C, 24.74; H, 1.23; N, 4.65. C₁₈H₁₀Cl₁₂N₃O₄Sb requires C, 24.58; H, 1.15; N, 4.78%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1567, 1759; $\delta_{\text{H}}(250 \text{ MHz}, \text{CD}_3\text{CN})$ 4.02 (CH₃), 7.93 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}, \text{CD}_3\text{CN})$ 56.9 (CH₃), 129.0, 131.2, 134.2, 137.5 and 142.2 (aryl, C-4, -5), 153.8 (CO).

4-Chloromethyl-1,3-bis(4-chlorophenyl)-1H-1,2,3-triazolium hexafluorophosphate 7j

Me₃COCl³⁵ (1.63 g, 15 mmol) was added dropwise under stirring in the dark to a cold (–60 °C) suspension of 1,3-bis(4-chlorophenyl)triazene^{8,36} (2.66 g, 10 mmol), prop-2-ynyl chloride **6j** (1.12 g, 15 mmol) and KPF₆ (3.68 g, 20 mmol) in CH₂Cl₂ (130 ml). Stirring was continued for 4 h. During this time the temperature rose to –10 °C. After stirring at 0 °C for 30 min and then at 23 °C for 15 min the orange suspension was

filtered. The filtrate was evaporated under reduced pressure and the orange residue crystallized at 23 °C from CH₂Cl₂ (30 ml)–MeCN (3 ml)–Et₂O (250 ml) to afford *title compound 7j* as a powder (2.38 g, 49%), mp 232–236 °C (decomp.) (Found: C, 37.17; H, 2.50; N, 9.14. C₁₅H₁₁Cl₃F₆N₃P requires C, 37.18; H, 2.29; N, 8.67%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1560, 1593; $\delta_{\text{H}}(250 \text{ MHz}, \text{CD}_3\text{CN})$ 4.89 (d, *J* 0.4, CH₂), 7.80 (s, 4H), 7.85 (AA'BB' multiplet, 4H) (aryl), 9.05 (H-5); $\delta_{\text{C}}(62.9 \text{ MHz}, \text{CD}_3\text{CN})$ 32.5 (CH₂), 124.9, 128.4, 130.1, 131.7, 131.8, 132.6, 133.5, 134.5, 134.8, 139.2, 139.9 and 143.0 (aryl, C-4, -5).

1,3-Bis(4-chlorophenyl)-4,5-diethyl-1H-1,2,3-triazolium hexafluorophosphate 7k

From Me₃COCl (2.17 g, 20 mmol), 1,3-bis(4-chlorophenyl)triazene (2.66 g, 10 mmol), hex-3-yne **6e** (0.99 g, 12 mmol) and KPF₆ (3.68 g, 20 mmol) in the manner described for **7j**. Evaporation of the solvent afforded a brown residue (4.28 g, 87%), which was precipitated at 23 °C twice from CHCl₃ (15 ml)–Et₂O (130 ml) to furnish *title compound 7k* as a pale yellow powder (3.15 g, 64%), mp 223–226 °C (decomp.) (Found: C, 43.66; H, 3.56; N, 8.49. C₁₈H₁₈Cl₂F₆N₃P requires C, 43.92; H, 3.69; N, 8.54%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1492, 1563, 1594; $\delta_{\text{H}}(250 \text{ MHz}, \text{CD}_3\text{CN})$ 1.14 (t, *J* 7.7, CH₃), 2.79 (q, *J* 7.7, CH₂), 7.60 (AA'BB' multiplet, aryl); $\delta_{\text{C}}(62.9 \text{ MHz}, \text{CD}_3\text{CN})$ 11.7 and 17.0 (CH₃, CH₂), 127.7, 130.3, 132.2, 138.6 and 143.1 (aryl, C-4, -5).

4,5-Diethyl-3-methyl-1-(4-methylphenyl)-1H-1,2,3-triazolium hexafluorophosphate 7l

From Me₃COCl (2.17 g, 20 mmol), 1-(4-methylphenyl)-3-methyltriazene (Fluka) (1.49 g, 10 mmol), hex-3-yne **6e** (0.99 g, 12 mmol) and KPF₆ (3.68 g, 20 mmol) in the manner described for **7j**. The brown solid product was difficult to crystallize. However, very slow addition (1 h) of CCl₄ (100 ml) to a cold (–30 °C) solution in CH₂Cl₂ (15 ml) afforded after further stirring at 0 °C for 5 min *title compound 7l* as a yellow powder (3.04 g, 81%), mp 113–116 °C (decomp.) (Found: C, 44.52; H, 5.34; N, 11.10. C₁₄H₂₀F₆N₃P requires C, 44.81; H, 5.37; N, 11.20%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1513, 1587; $\delta_{\text{H}}(250 \text{ MHz}, \text{CDCl}_3)$ 1.07 (t, *J* 7.6), 1.32 (t, *J* 7.7), 2.45, 4.18 (CH₃), 2.72 (q, *J* 7.6) and 2.89 (q, *J* 7.7) (CH₂), 7.40 (AA'BB' multiplet, aryl); $\delta_{\text{C}}(62.9 \text{ MHz}, \text{CDCl}_3)$ 11.7, 12.3, 16.5, 16.7, 21.3 and 37.4 (CH₃, CH₂), 125.7, 130.7, 131.2, 141.9, 142.4 and 142.7 (aryl, C-4, -5).

3-Methyl-1-(4-methylphenyl)-4,5-diphenyl-1H-1,2,3-triazolium hexafluorophosphate 7m

Prepared from 1-(4-methylphenyl)-3-methyltriazene (1.49 g, 10 mmol) and diphenylacetylene (1.78 g, 10 mmol) in the manner described for **7l**. The brown product was dissolved in CH₂Cl₂ (25 ml). Cooling to –40 °C and slow addition of CCl₄ (75 ml) and pentane (50 ml) afforded a brown powder, which was isolated by decantation (2.07 g, 44%). Reprecipitation from a cold (–30 °C) solution in CH₂Cl₂ (25 ml) by very slow (1 h) addition of CCl₄ (75 ml) afforded *title compound 7m* as a pale yellow powder (1.27 g, 27%), mp 104–110 °C (decomp.) (Found: C, 56.13; H, 4.13; N, 8.73. C₂₂H₂₀F₆N₃P requires C, 56.05; H, 4.28; N, 8.92%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1618, 1581; $\delta_{\text{H}}(250 \text{ MHz}, \text{CD}_3\text{CN})$ 2.41 and 4.22 (CH₃), 7.22–7.64 (phenyl, aryl); $\delta_{\text{C}}(62.9 \text{ MHz}, \text{CD}_3\text{CN})$ 21.4 and 39.5 (CH₃), 123.4–144.0 (14 lines, phenyl, aryl, C-4, -5).

4-Chlorobenzenediazonium hexachloroantimonate 8j³⁷

Me₃COCl (1.63 g, 15 mmol) was added dropwise under stirring in the dark to a cold (–60 °C) suspension of 1,3-bis(4-chlorophenyl)triazene (2.66 g, 10 mmol) and hex-3-yne (0.99 g, 12 mmol) in CH₂Cl₂ (60 ml). The stirred mixture was warmed to –30 °C in the course of the next 1 h. After stirring at 0 °C for 30 min and then at 0 °C for 15 min the solvent was evaporated off. The dark red residue was dissolved in CH₂Cl₂ (20 ml). At –20 °C a solution of SbCl₅ (2.99 g, 10 mmol) in CH₂Cl₂ (10 ml) was added dropwise. After stirring at –20 °C for 15 min, then at

0 °C for 10 min and finally at 23 °C for 10 min a brown powder (4.27 g, 90%) was precipitated by slow addition of CCl₄ (80 ml). Crystallization at -15 °C from CH₂Cl₂ (20 ml)–MeCN (8 ml) afforded prisms of *title compound 8j* (4.03 g, 85%), mp 151–153 °C (decomp.) (Found: C, 14.98; H, 0.86; N, 5.87. C₆H₄Cl₂N₂Sb requires C, 15.20; H, 0.85; N, 5.91%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1561, 2252; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 7.96 and 8.46 (AA'BB' multiplet, aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 113.5 (*i*-C), 133.6 and 134.8 (*m*, *o*-C), 150.6 (*p*-C).

4,5-Dihydro-4-isopropyl-5-isopropylimino-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3,4-tetrazolium hexachloroantimonate 11a

Prepared from the chlorotriazene **1a** (4.38 g, 10 mmol), *N,N'*-diisopropylcarbodiimide **9a** (1.51 g, 12 mmol) and SbCl₅ (2.99 g, 10 mmol) in CH₂Cl₂ (40 ml) in the manner described for **7a**. Evaporation of the solvent afforded a brown foam, which was precipitated from CH₂Cl₂ (20 ml)–Et₂O (140 ml) to give *title compound 11a* as a pale yellow powder (4.92 g, 57%), mp 158–160 °C (decomp.) (Found: C, 26.44; H, 2.03; N, 8.00. C₁₉H₁₈Cl₂N₅Sb requires C, 26.43; H, 2.10; N, 8.11%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1565, 1736; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 1.04 (d, *J* 6.1, 6 H), 1.65 (d, *J* 6.7, 6 H) (CH₃), 3.31 (septet, *J* 6.1), 4.50 (septet, *J* 6.7) (CH), 7.87 and 7.98 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 18.2 and 25.1 (CH₃), 48.1 and 58.3 (CH), 125.8, 127.8, 128.9, 131.2, 132.0, 135.5, 135.9, 141.8 and 144.1 (aryl, C-5).

4-Cyclohexyl-5-cyclohexylimino-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3,4-tetrazolium hexachloroantimonate 11b

Prepared from the chlorotriazene **1a** (4.38 g, 10 mmol) and *N,N'*-dicyclohexylcarbodiimide **9b** (2.48 g, 12 mmol) in the manner described for **11a**. Two precipitations at 23 °C of the product, each from CH₂Cl₂ (20 ml)–Et₂O (350 ml), afforded *title compound 11b* as a pale yellow powder (4.96 g, 53%), mp 115–119 °C (decomp.) (Found: C, 31.48; H, 2.76; N, 7.47. C₂₅H₂₆Cl₂N₅Sb requires C, 31.82; H, 2.78; N, 7.42%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1563, 1648, 1731; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 0.99–2.64 (m, 20 H, CH₂), 2.99 (m, 1 H), 4.13 (tt, *J* 4.1 and 12.0, 1 H) (HCN), 7.88 and 7.98 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 24.3, 25.1, 25.4, 26.1, 27.8 and 35.3 (CH₂), 55.1 and 64.7 (CH), 125.9, 127.7, 128.9, 131.1, 132.1, 135.4, 136.0, 141.7 and 144.1 (aryl, C-5).

5-(*tert*-Butylamino)-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3,4-tetrazolium hexachloroantimonate 12c

(a) Prepared from the chlorotriazene **1a** (4.38 g, 10 mmol) and *N,N'*-di-*tert*-butylcarbodiimide **9c** (1.85 g, 12 mmol) in the manner described for **11a**. Evaporation of the solvent afforded an orange residue, which was stirred at 23 °C for 5 min in CH₂Cl₂ (20 ml). Filtration and addition of Et₂O (60 ml) to the filtrate furnished *title compound 12c* as a powder (4.36 g, 50%), mp 112–115 °C (decomp.) (Found: C, 26.13; H, 2.26; N, 7.75. C₁₇H₁₄Cl₂N₅Sb·0.5Et₂O requires C, 26.15; H, 2.19; N, 8.03%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1567, 1633, 3322, 3380; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 1.49 (9 H, CH₃), 7.20 (br, NH), 7.90 and 7.95 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 27.9 (CH₃), 57.8 (C), 124.7, 130.7, 131.1, 131.4, 134.0, 136.2, 141.9, 142.4 and 157.3 (aryl, C-5).

(b) Prepared from chlorotriazene **1a** (4.38 g, 10 mmol), *tert*-butylcyanamide **13a** (1.55 g, 16 mmol) and SbCl₅ (2.99 g, 10 mmol) in CH₂Cl₂ (80 ml) in the manner described for **7d**. Addition of CCl₄ (40 ml) to the reaction mixture, filtration from a small amount of diazonium salt **8a**, and further addition of CCl₄ (200 ml) to the filtrate afforded a powder (4.64 g, 53%), which was reprecipitated from CH₂Cl₂ (28 ml)–Et₂O (160 ml) to furnish prisms of the *title compound 12c* (3.00 g, 34%), mp 116–118 °C (decomp.).

1,3-Bis(4-chlorophenyl)-5-isopropylamino-1H-1,2,3,4-tetrazolium hexafluorophosphate 12d

Prepared from the chlorotriazene **1j** (2.66 g, 10 mmol) and *N,N'*-dicyclohexylcarbodiimide **9a** (1.51 g, 12 mmol) in the

manner described for **7j**. Evaporation of the solvent afforded a brown foam, which was boiled under reflux for 3 h in MeCN (150 ml). Evaporation of the solvent and crystallization of the residue at 23 °C from MeCN (6 ml)–CCl₄ (210 ml) afforded *title compound 12d* as a pale yellow powder (3.81 g, 77%), mp 208–210 °C (decomp.) (Found: C, 38.69; H, 3.38; N, 13.94. C₁₆H₁₆Cl₂F₆N₅P requires C, 38.89; H, 3.26; N, 14.17%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1588, 1640, 3388; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 1.33 (d, *J* 6.6, 6 H, CH₃), 4.08 (m, CH), 6.60 (br d, *J* 7.6, NH), 7.69–8.18 (m, 8 H, aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 21.9 (CH₃), 49.5 (CH), 123.5, 128.9, 129.9, 131.7, 132.1, 134.9, 139.5 and 139.9 (aryl), 158.0 (C-5).

5-Cyclohexylamino-1,3-bis(4-chlorophenyl)-1H-1,2,3,4-tetrazolium hexafluorophosphate 12e

From the chlorotriazene **1j** (2.66 g, 10 mmol) and *N,N'*-dicyclohexylcarbodiimide **9b** (2.48 g, 12 mmol) in the manner described for **12d**. Crystallization at 23 °C from CH₂Cl₂ (90 ml)–CCl₄ (150 ml) afforded *title compound 12e* as a pale yellow powder (3.90 g, 73%), mp 241–243 °C (decomp.) (Found: C, 42.44; H, 3.76; N, 12.92. C₁₉H₂₀Cl₂F₆N₅P requires C, 42.71; H, 3.77; N, 13.11%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1587, 1640, 3390; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 1.13–2.08 (m, 10 H, CH₂), 3.74 (m, CH), 6.58 (br d, *J* 7.6, NH), 7.68–8.18 (m, 8 H, aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 25.6, 25.9 and 32.6 (CH₂), 56.3 (CH), 123.5, 128.9, 130.0, 131.7, 132.1, 134.9, 139.5 and 140.0 (aryl), 158.0 (C-5).

5-Dimethylamino-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3,4-tetrazolium hexachloroantimonate 15b

Prepared from the chlorotriazene **1a** (4.38 g, 10 mmol) and *N,N*-dimethylcyanamide **13b** (0.84 g, 12 mmol) in the manner described for **7d**. Addition of CCl₄ (40 ml) to the reaction mixture, filtration, and addition of further CCl₄ (120 ml) to the filtrate furnished a colourless powder (5.90 g, 73%), which was crystallized at 23 °C from CH₂Cl₂ (16 ml)–Et₂O (40 ml) to give prisms of the *title compound 15b* (4.93 g, 61%), mp 159–161 °C (decomp.) (Found: C, 21.99; H, 1.36; N, 8.46. C₁₅H₁₀Cl₂N₅Sb requires C, 22.31; H, 1.25; N, 8.67%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1568, 1663; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 3.14 (6 H, CH₃), 7.88 and 7.91 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 41.0 (CH₃), 127.3, 130.7, 131.1, 131.3, 133.9, 135.7, 142.0, 142.1 and 159.3 (aryl, C-5).

5-Isopropyl(methyl)amino-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3,4-tetrazolium hexachloroantimonate 15c

From the chlorotriazene **1a** (4.38 g, 10 mmol) and *N*-isopropyl-*N*-methylcyanamide **13c** (1.18 g, 12 mmol) in the manner described for **15b**. The powder obtained (6.85 g, 82%) was reprecipitated at 23 °C from CH₂Cl₂ (16 ml)–MeCN (1.5 ml)–Et₂O (120 ml) to afford *title compound 15c* as a powder (5.43 g, 65%), mp 188–190 °C (decomp.) (Found: C, 24.19; H, 1.80; N, 8.34. C₁₇H₁₄Cl₂N₅Sb requires C, 24.44; H, 1.69; N, 8.38%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1567, 1640; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 1.31 (d, *J* 6.6, 6 H), 2.86 (3 H) (CH₃), 4.26 (septet, *J* 6.6, CH), 7.89, 7.92 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 19.2 and 31.4 (CH₃), 55.6 (CH), 127.6, 130.7, 131.2, 131.4, 133.9, 135.5, 142.0 and 142.1 (aryl), 158.9 (C-5).

5-Diisopropylamino-1,3-bis(2,4,6-trichlorophenyl)-1H-1,2,3,4-tetrazolium hexachloroantimonate 15d

From the chlorotriazene **1a** (4.38 g, 10 mmol) and diisopropylcyanamide **13d** (1.51 g, 12 mmol) in the manner described for **15b**. The powder (7.60 g, 88%) obtained was reprecipitated at 23 °C from CH₂Cl₂ (28 ml)–MeCN (4 ml)–Et₂O (80 ml) to afford *title compound 15d* as a crystalline powder (6.13 g, 71%), mp 225–227 °C (decomp.) (Found: C, 26.09; H, 2.09; N, 7.95. C₁₉H₁₈Cl₂N₅Sb requires C, 26.43; H, 2.10; N, 8.11%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1567, 1625; $\delta_{\text{H}}(250 \text{ MHz}; \text{CD}_3\text{CN})$ 1.35 (d, *J* 6.7, 12 H, CH₃), 3.86 (septet, *J* 6.7, CH), 7.90 and 7.94 (aryl); $\delta_{\text{C}}(62.9 \text{ MHz}; \text{CD}_3\text{CN})$ 20.1 (CH₃), 52.6 (CH), 128.1, 130.8, 131.2, 131.7, 134.0, 135.2, 141.9 and 142.1 (aryl), 157.2 (C-5).

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