Cycloadditions of 1-aza-2-azoniaallene ions to alkenes

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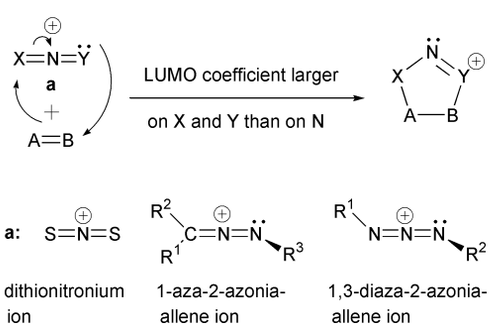
1-Aza-2-azoniaallene salts **3** react with ethene, and mono- to trisubstituted electron-rich alkenes under mild conditions to afford 4,5-dihydro-3*H*-pyrazolium salts **4**. These cycloadditions proceed with complete Markovnikov regioselectivity and retention of the configuration of the alkene. Reactions of salts **3** with norbornene afford cycloadducts without rearrangement of the norbornane moiety. According to these observations, reactions of heteroallenes **3** with alkenes are mechanistically concerted 'reverse electron-demand 1,3-dipolar cycloadditions'. In solution 4,5-dihydro-3*H*-pyrazolium salts **4** with a hydrogen atom in the 5-position tautomerize to 4,5-dihydro-1*H*-pyrazolium salts **6**. A 'general Wagner–Meerwein rearrangement' to the 1*H*-isomer **5y** is observed for compound **4y**. The mechanistic proposals are supported by AM1 calculations. For the salt **4r** and the twofold cycloadduct **4z** X-ray stuctural analyses have been performed.

Introduction

1,3-Dipolar cycloaddition reactions between electrically uncharged 1,3-dipoles and alkenes or alkynes are most important for the construction of five-membered heterocycles.[1,2] Representative are reactions of electron-rich 1,3-dipoles with electron-deficient dipolarophiles. Less frequently encountered are '1,3-dipolar cycloaddition reactions with inverse electron demand', for instance, reactions of nitrones with electron-rich alkenes in the presence of Lewis acids.[3] Only a few reports deal with the extreme case of a cationic four-electron-three-center component acting as a '1,3-dipole' in such reactions. Concerted cycloaddition reactions of protonated aldehyde hydrazones $R^1CH{=}NH^+{-}NR^2R^3\ X^-$ with alkenes are well documented.[4–7] Another striking example is the dithionitronium ion $S{=}N^+{=}S$, which undergoes concerted cycloadditions to the multiple bonds of alkynes, alkenes, nitriles *etc.* (Scheme 1).[8–11] In principle, similar cycloadditions are to be



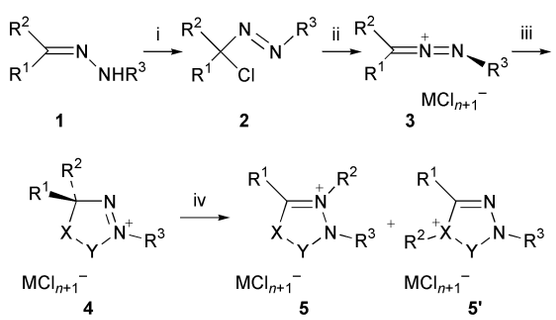
Scheme 1 Inverse electron-demand cycloadditions of 2-azoniaallene cations.

expected for all types of 2-azoniaallene ions **a**, provided that either X or Y carry a lone pair of electrons, and the LUMO coefficients are larger on X and Y than on the central nitrogen atom (Scheme 1).[8] For example, while the first condition is fulfilled for the nitronium ion $O{=}N^+{=}O$, the second is not, that is, the LUMO is larger on the central nitrogen atom than on the oxygen atoms. Thus, in contrast to the dithionitronium ion, the nitronium ion does not react as a cationic 1,3-dipole but acts as a strong N-electrophile effecting, for example, aromatic nitration.

Recently, we reported preparations of 1-aza-2-azoniaallene salts[12–25] and of 1,3-diaza-2-azoniaallene salts[26–29] as reactive intermediates (Scheme 1). These salts were found to react as four-electron-three-center components in cycloadditions with many types of multiple bonds.

Experimental and theoretic arguments had been advanced suggesting that cycloadditions of 1-aza-2-azoniaallene salts **3** to nitriles,[12] isocyanates,[16] isothiocyanates,[22] and carbodiimides[14] are two-step reactions *via* nitrilium or acylium intermediates, while cycloaddition reactions with alkynes[15] and alkenes[13] are likely to be concerted processes.

In most cases studied so far, the primarily formed cycloadducts **4** rearranged spontaneously to salts **5** or **5′** ('generalized Wagner–Meerwein rearrangement'[15]) with the substituent which best stabilizes a positive charge in the transition state migrating exclusively (Scheme 2).[30–38] In the majority of cases



Scheme 2 R^1, R^2 = alkyl, aryl, Cl; R^3 = aryl, CO_2R, Bu^t, $ClCR_2$. *Reagents and conditions*: i, Bu^tOCl, −50 to 23 °C, $CHCl_3$; ii MCl_n ($SbCl_5$, $AlCl_3$, $TiCl_4$, $SnCl_4$), −60 to 23 °C, CH_2Cl_2; iii X=Y: alkenes, alkynes, nitriles, isocyanates, isothiocyanates, carbodiimides; iv in many cases spontaneous rearrangement.

migration to the adjacent nitrogen atom (**5**) took place. However, for cycloadducts **4** of alkynes with **3** rearrangement to **5′** was also observed.[15]

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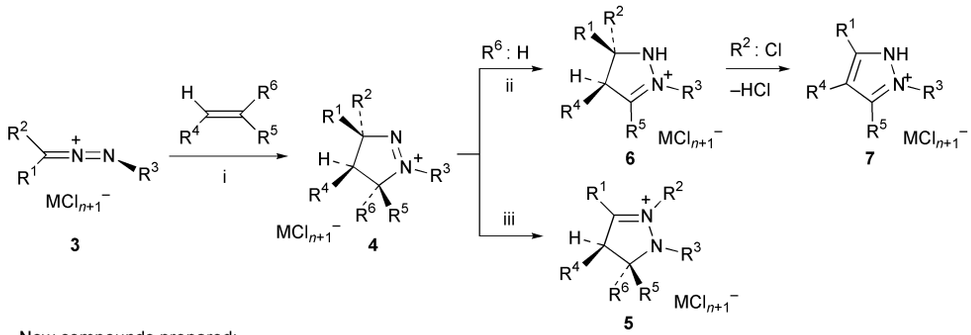
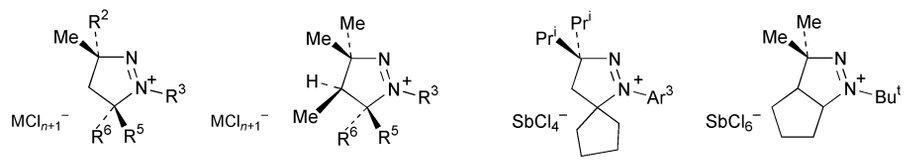


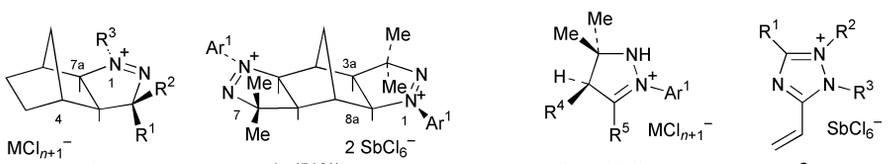
New compounds prepared:



4a-i **4j-o** **4p** (30%) **4q** (39%)

4	R^2	R^3	R^5	R^6	MCl_{n+1}^-	[%][a]
a	Me	Ar^1	H	H	$SbCl_6^-$	89
b	Me	Bu^t	H	H	$SbCl_6^-$	67
c	Me	Ar^1	Bu	H	$SbCl_6^-$	68
d	Me	Ar^1	Cl	H	$SbCl_6^-$	80
e	Me	Bu^t	Cl	H	$SbCl_6^-$	83
f	Me	Ar^1	Me	Me	$AlCl_4^-$	64
g	Me	Bu^t	Me	Me	$SbCl_6^-$	57
h	Pr^i	Ar^1	Me	Me	$SbCl_6^-$	42
i	Pr^i	Ar^2	Me	Me	$SbCl_6^-$	28

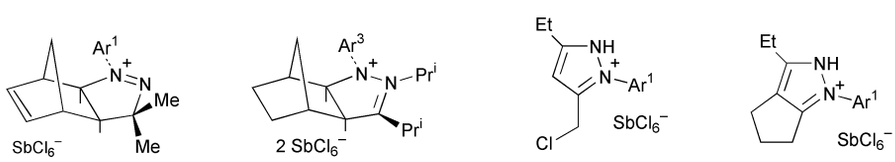
4	R^3	R^5	R^6	MCl_{n+1}^-	[%][a]
j	Ar^1	Me	H	$SbCl_6^-$	17
k	Ar^1	H	Me	$SbCl_6^-$	37
l	Bu^t	H	Me	$SbCl_6^-$	31
m	Ar^1	Me	Me	$AlCl_4^-$	58
n	Ar^1	Et	Me	$AlCl_4^-$	45
o	Ar^1	Me	Et	$AlCl_4^-$	45



4r-y **4z** (59%) **6a,c,d,j,ab** **8**

4	$R^1 = R^2$	R^3	MCl_{n+1}^-	[%][a]
r	Me	Ar^1	$SbCl_6^-$	60
s	Me	Ar^1	$AlCl_4^-$	93
t	Me	Ar^1	Picrate	97
u	Me	Ar^1	1/2 $SnCl_6^{2-}$	54
v	Me	Bu^t	1/2 $TiCl_6^{2-}$	56
w	Et	Ar^3	$SbCl_6^-$	56
x	Et	Ar^2	$SbCl_6^-$	25
y	Pr^1	Ar^3	$SbCl_6^-$	54

6	R^4	R^5	MCl_{n+1}^-	[%][a]
a	H	H	$SbCl_6^-$	66
c	H	Bu	$SbCl_6^-$	56
d	H	Cl	$SbCl_6^-$	63
j	Me	Me	$SbCl_6^-$	24
ab	H	Ph	$AlCl_4^-$	87



4aa (51%) **5y** (60%) **7ac** (73%) **7ad** (52%)

Scheme 3 Substituents of the starting materials **1**–**3** and the alkenes correspond to those of the products **4**–**7**; Ar^1: 2,4,6-$Cl_3C_6H_2$; Ar^2: 2,4-$(NO_2)_2C_6H_3$; Ar^3: 4-$(NO_2)C_6H_4$; [a]: yields after purification. *Reagents and conditions*: i −60 to +23 °C, 3 h, CH_2Cl_2; ii 23 °C, MeCN–CH_2Cl_2; iii, 23 °C.

Reactions of 1-aza-2-azoniaallenes **1** with alkenes have not been studied in detail hitherto. We found that, in contrast to all other unsaturated molecules, most alkenes afford 4,5-dihydro-3*H*-pyrazolium salts **4** (X=Y: $R^1R^2C{=}CR^3R^4$) with no tendency to rearrangement to 4,5-dihydro-1*H*-pyrazolium salts **5**,[13,20] while isolation of the rearranged products **5**, without the 3*H*-pyrazolium salts **4**, were exceptions.[18] The cycloaddition of a salt **3** to (*E*)-hex-3-ene has been found to proceed with complete retention of the configuration of the alkene.[13]

Here we report results of a systematic study of reactions of 1-aza-2-azoniaallene salts **3** with alkenes.

Results and discussion

Ethene and mono-, 1,1-di- as well as 1,2-di- and trisubstituted alkenes were found to react with heterocumulenes **3** under mild conditions to yield the 4,5-dihydro-3*H*-pyrazolium salts **4a**–**aa** (Scheme 3).

For example, at −80 °C at atmospheric pressure ethene was passed into a solution of the chloroazo compound **2a** in dichloromethane (substituents of compounds **1**–**3** correspond to those of the products **4**–**7**, Scheme 3). After addition of antimony pentachloride the mixture was stirred between −60 and +23 °C for three hours. Workup afforded the 4,5-dihydro-3*H*-pyrazolium hexachloroantimonate **4a** in 89% yield. The other compounds **4** were obtained similarly (Scheme 3). Methylenecycloalkenes furnished spiro compounds (**4p**) and cycloalkenes bicyclic heterocycles (**4q**). In most cases, the crude products were isolated almost quantitatively. However, purification often resulted in a precipitous decrease in yields.

Probably because of steric effects, no reactions could be induced between tetrasubstituted alkenes, such as 2,3-dimethylbut-2-ene, and any of the salts **3**.

3*H*-Pyrazolium salts **4** mentioned in the literature have mostly been prepared by alkylation of 4,5-dihydro-3*H*-pyrazoles.[39–42]

Instead of antimony pentachloride other Lewis acids, such as aluminum chloride, tin(IV) chloride or titanium chloride can be used. Highest yields were obtained with $AlCl_3$. The rather hygroscopic tetrachloroaluminates could be transformed into the less hygroscopic picrates (**4t**).

The *N*-substituent R^3 is not limited to aryl or *tert*-butyl but can also be chloroalkyl $ClCR_2$.[20] On the other hand, no reactions could be observed between alkenes and heteroallenes **3** with R^3 = COOEt. A substituent $R^3 = ClCR_2$ can be removed hydrolytically from salts **4** to afford electrically neutral 4,5-dihydro-3*H*-pyrazoles.[20]

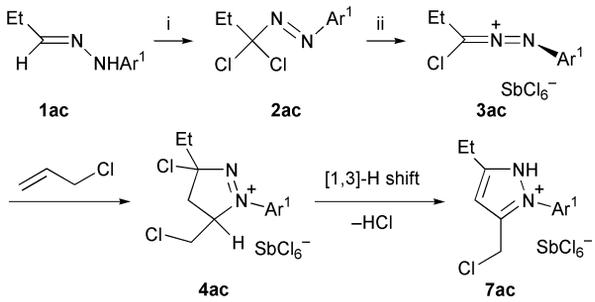
Occasionally, with electron-rich alkenes reduction of the Lewis acid has been observed. Thus, compound **4p** prepared from methylenecyclopentane and **2p** with Sb(V)-chloride turned out to be a Sb(III) salt.

As might be expected for 'inverse electron demand 1,3-dipolar cycloadditions', no reactions were observed between slightly electron-deficient alkenes and heterocumulenes **3**. For instance, while the salt **3a** reacted with isobutene $(CH_3)_2C{=}CH_2$, no cycloaddition took place to the chloro compound $(ClCH_2)_2C{=}CH_2$. Similarly, **3a** underwent cycloaddition to (*E*)- and (*Z*)-but-2-ene but not to (*E*)-1,4-dichlorobut-2-ene. No reactions were observed between α,β-unsaturated carbonyl compounds, *e.g.* coumarin, and heteroallenes **3**. While styrene reacted with **3f** to afford the cycloadduct **6ab**, no reaction could be achieved between a salt **3** and (*Z*)-stilbene. Salts **3a**,**b** and vinyl chloride furnished the cycloadducts **4d**,**e** almost quantitatively but no well defined product was obtained from the reaction of **3a** with acrylonitrile $H_2C{=}CH{-}CN$. On the other hand, we found that heterocumulenes **3** react with allyl cyanide $H_2C{=}CHCH_2{-}CN$.[13] However, the reaction takes place at the nitrile group resulting in the formation of triazolium salts **8** (Scheme 3). Obviously, cycloaddition of **3** across the nitrile group is faster than reaction with an olefinic double bond.

Remarkably, the cycloaddition reactions of 2-azoniaallenes **3** to norbornene and norbornadiene † to furnish compounds **4r**–**aa** went to completion at temperatures below 0 °C essentially within a few minutes with the exclusive production of the *exo* cycloadducts. From norbornadiene with one equivalent of **3a** the monoadduct **4aa** was formed, while with two equivalents of **3a** the bisadduct **4z** was produced. This is in contrast to 1,3-dipolar cycloaddition reactions of diazoalkanes to norbornadiene, which at 4 °C require long times to reach completion.[43–45] Even in the presence of a large excess of the diazoalkane, mixtures of mono- and bisadducts with *endo*- and *exo*-stereochemistry have been obtained.

4,5-Dihydro-3*H*-pyrazolium salts **4** with a hydrogen atom in the 5-position are known to rearrange under mild conditions to the more stable 1*H*-tautomers.[39] Attempts to precipitate the 3*H*-pyrazolium salt **4a** from its solution in acetonitrile with ether resulted in complete rearrangement to the 1*H*-tautomer **6a**. Under similar mild conditions the 3*H*-pyrazolium salts **4c**,**d** were transformed to **6c**,**d**, and compound **6j** was obtained from both **4j** and **4k**. Under conditions for the formation of salts **4**, styrene and the tetrachloroaluminate **3f** afforded the 1*H*-pyrazolium salt **6ab** directly. On the other hand, no [1,3]-H shifts could be induced for the norbornane derivatives **4r**–**aa**.

Moon prepared the dichloro compound **2ac** by treatment of propanal 2,4,6-trichlorophenylhydrazone **1ac** with chlorine in benzene.[17,46] This compound reacted with allyl chloride in the presence of antimony pentachloride to give the pyrazolium salt **7ac**, obviously *via* the dihydropyrazolium salt **4ac** (Scheme 4). Correspondingly, the pyrazolium salt **7ad** was obtained (Scheme 3).



Scheme 4 Ar^1: 2,4,6-$Cl_3C_6H_2$. *Reagents and conditions*: i Cl_2, 0 °C, benzene; ii $SbCl_5$, −60 to +23 °C, CH_2Cl_2.

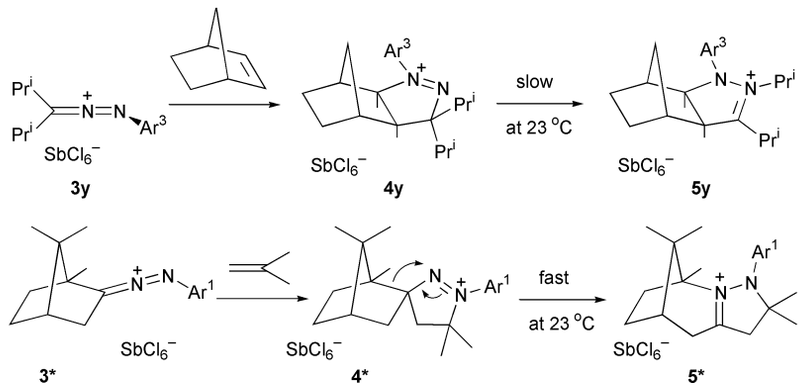
For cycloaddition reactions of 1-aza-2-azoniaallene salts **3** with alkenes the formation of regioisomers **4** has to be considered. All cycloadditions of **3** to alkenes studied so far proceeded with complete Markovnikov regioselectivity. That is, the cations **3** behave as azocarbenium ions undergoing electrophilic attack onto the less substituted end of the olefinic double bond. The observed Markovnikov regioselectivities for cycloadditions of ions **3** to alkenes are in accord with either a nonconcerted mechanism *via* intermediate 3-azopropylium ions $R^3N{=}N{-}CR^1R^2{-}CHR^4{-}C^+R^5R^6$ or with a rather asynchronous concerted mechanism.

The observation that the cycloadditions of cations **3** to alkenes proceed with complete retention of the configuration of the alkene is in better agreement with a concerted mechanism. For example, the reaction of **3a** with (*Z*)-2-methylbut-2-ene afforded a single stereoisomer **4j** clearly different from the single stereoisomer **4k** obtained from reaction of **3a** with (*E*)-2-methylbut-2-ene. In solution both **4j** and **4k** rearranged to the same 1*H*-pyrazol-2-ium salt **6j**. In the ^1H NMR spectrum (CD_3CN) of **4j** a *cis* coupling between H4 and H5 of 7.4 Hz was observed, while **4k** showed a larger *trans* coupling of 11.2 Hz. Similarly, cycloadditions of **3a** to (*Z*)- and (*E*)-3-methylpent-2-ene resulted in the exclusive formation of single stereoisomers **4n**,**o**. Finally, the cycloaddition of a cation **3** to (*E*)-hex-3-ene has been found to proceed with complete retention of the olefinic configuration.[13]

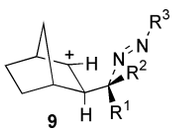
Another argument in favour of a concerted mechanism of the cycloaddition of the cationic 1,3-dipoles **3** to alkenes is the exclusive formation of compounds **4r**–**z** from norbornene and norbornadiene. Namely, if the cycloaddition of a strong electrophile **3** to norbornene were a two-step reaction, a norbornyl cation **9** would have been created as intermediate. Such cations are known to undergo fast Wagner–Meerwein rearrangements and H-shifts.[47] However, we never obtained products resulting from such rearrangements. Therefore, either the two-step cycloadditions leading to **4r**–**z** must be faster than any rearrangement of a norbornyl cation **9**, or the cycloadditions of **3** to norbornene are concerted reactions.[48]

As has been mentioned above, reactions of heterocumulenes **3** with nitriles, isocyanates, isothiocyanates, carbodiimides or

† The IUPAC names for norbornane, norbornene and norbornadiene are bicyclo[2.2.1]heptane, bicyclo[2.2.1]hept-2-ene and bicyclo[2.2.1]-hepta-2,5-diene, respectively.



Scheme 5 Ar^1: 2,4,6-$Cl_3C_6H_2$; Ar^3: 4-$NO_2C_6H_4$.



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alkynes afford cycloadducts **4**, which cannot be isolated but rearrange spontaneously to heterocycles **5** (*cf.* Scheme 2). In contrast, with the exception of **4y**, the pyrazolium salts **4a**–**aa** proved to be thermally stable (Scheme 3). For instance, after ten days at 79 °C the ^{1}H NMR spectra of solutions of the 3,3-diethyl-1-(4-nitrophenyl) compound **4w** or the 3,3-diethyl-1-(2,4-dinitrophenyl) salt **4x** in deuterated acetonitrile showed at the most very small signals, which might be assigned to cations **5w,x**. On the other hand, at 23 °C in CD_3CN the ^{1}H NMR signals of the 3,3-diisopropyl-1-(4-nitrophenyl) salt **4y** soon decreased, while the spectrum of **5y** increased in intensity. After twenty-four hours, the salt **5y** was isolated in 60% yield. A corresponding but even faster rearrangement has been reported for the reaction product **4*** of the camphor‡ derived heteroallene **3*** with isobutene (Scheme 5). In this case, the intermediate **4*** could not be isolated because of fast rearrangement to **5***.[18]

Obviously, rearrangements **4** ⟶ **5** are only observed for salts **4** with an electron deficient pyrazolium ring carrying an electron-withdrawing substituent in the 1-position. Furthermore, the rates of the rearrangements parallel the ability of the migrating group to stabilize a positive charge in the transition state. Thus, compound **4y** rearranges faster than **4w** because the prop-2-ylium ion is more stable than the ethylium ion. Especially effective in stabilizing a positive charge in the transition state is the migrating tertiary alkyl group in the rearrangement **4*** ⟶ **5***.

The fact that some cycloadducts **4** of cations **3** and alkenes do, after all, rearrange to salts **5**, and that the requirements for this rearrangement are the same as those for cycloadducts **4** of cations **3** with nitriles, alkynes *etc.* suggests that all these rearrangements proceed by the same mechanism. If this is accepted, pericyclic [1,5]-sigmatropic mechanisms (van Alphen–Hüttel rearrangement[49–51]), which have been discussed for rearrangements of cycloadducts **4** formed from alkynes or nitriles with cations **3**,[15] can be ruled out because the rearrangement **4y** ⟶ **5y** does not meet the stipulations for such a mechanism. On the other hand, all experimental results are in line with a mechanism corresponding to a Wagner–Meerwein rearrangement $R^1R^2R^3C–C^+R^4R^5 \longrightarrow R^1R^2C^+–CR^3R^4R^5$. A transformation of the type $R^1R^2R^3C–N{=}N^+R^4R^5 \longrightarrow R^1R^2C{=}N^+R^3–NR^4R^5$ may be called a 'generalized Wagner–Meerwein rearrangement'.[15]

The experimental results are supported by AM1 calculations.[52,53] For instance, the energy difference between the HOMO of **3a** and the LUMO of (*Z*)-but-2-ene was calculated to be 15.2 eV, while the energy gap between the LUMO of **3a** and the HOMO of (*Z*)-but-2-ene is only 4.4 eV indicating the dominance of the latter orbital interaction. The largest LUMO orbital coefficient of **3a** was found to be located on the unsaturated C atom, while the largest HOMO coefficient of vinyl chloride is on C2. This explains the regioselectivity of the cycloaddition of **3a** to vinyl chloride affording **4d** exclusively. The cycloaddition of two cations **3a** to norbornadiene could lead to several stereoisomers. The experimentally found C_2-symmetric dication **4z** was calculated to be the most stable isomer.

The cycloaddition of cation **3e** to ethene was computed to be exothermic by 109 kJ mol^{-1}. In the most stable transition structure (activation enthalpy 50 kJ mol^{-1}) the forming C–C bond is shorter than the forming C–N bond. However, a two-step mechanism with a cation $Ar^1–N{=}N–C(Me)_2–CH_2CH_2^+$ as intermediate would require an activation enthalpy of at least 88 kJ mol^{-1}. Thus, the calculations are in conformity with an asynchronous concerted mechanism. On the other hand, for a concerted cycloaddition of **3a** to vinyl chloride an activation enthalpy of 80 kJ mol^{-1} was calculated, while a two-step mechanism requires only 76 kJ mol^{-1}. Thus, at the level of accuracy of AM1 calculations, because of the stability of the cation $Ar^1–N{=}N–C(Me)_2–CH_2CHCl^+$, for the cycloaddition of **3a** to vinyl chloride a two-step process is marginally favoured over a concerted mechanism.

Generalized Wagner–Meerwein rearrangements were calculated for the pyrazolium cations **4k** and **4y**. In conformity with earlier results,[15] the most stable transition structure for a transformation **4k** ⟶ **5k** with a methyl group migrating from C3 of **4k** to N2 is a π-complex of CH_3^+ and the developing NC double bond. The activation enthalpy is high (241 kJ mol^{-1}) and the rearrangement slightly exothermic (12 kJ mol^{-1}). Experimentally, this rearrangement has not been observed. On the other hand, for the observed rearrangement **4y** ⟶ **5y** the corresponding transition structure with isopropyl as migrant is only 108 kJ mol^{-1} higher in energy than the ground state **4y**, and the formation of **5y** is exothermic by 18 kJ mol^{-1}.

The constitutional assignments of the new compounds prepared are essentially based on the NMR spectra and on X-ray crystallographic analyses of salts **4r** and **4z** (Fig. 1 and 2, Tables 1 and 2).

For instance, for the *exo* compound **4r** a H7a–H3a coupling constant of 7.3 Hz was found, and for the *exo*,*exo* dication **4z** similar couplings of 7.4 Hz for H3a–H8a and H4a–H7a (*cf.* Scheme 3). Coupling constants of this magnitude were also taken as being indicative of *exo* configurations of the other norbornane derivatives **4s**–**y**. In the ^{13}C NMR spectrum of compound **4z** seven signals for saturated carbon atoms were observed, in agreement with C_2 symmetry of the dication. If, for example, the dication had a plane of symmetry through C4 and C8, one would expect eight signals for aliphatic carbon atoms.

‡ The IUPAC name for camphor is 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one.

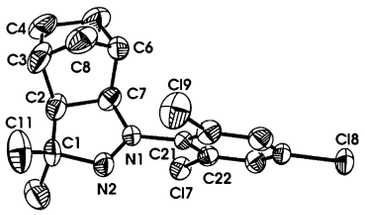

Fig. 1 ORTEP plot for the cation **4r.** The crystal of **4r** contained two independent cations and anions with similar bonding parameters. This figure shows one of the independent cations, and in Table 1 data for this cation are presented.

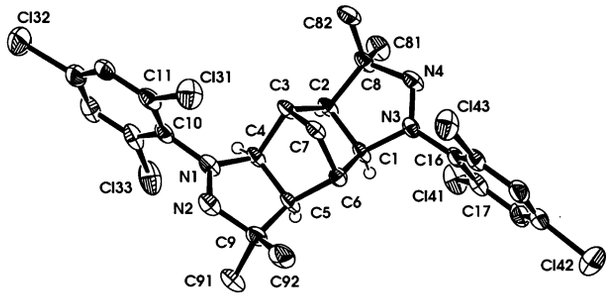

Fig. 2 ORTEP plot of the cation **4z**.

Table 1 Selected bond lengths (pm), bond angles and torsional angles (°) for the cation **4r** [54]

Atoms	Found	Atoms	Found
N1–N2	121.8(9)	C6–C7–N1	111.6(6)
N2–C1	148(1)	N2–C1–C11	106.4(7)
C1–C2	156(1)	C1–C2–C3	120.9(7)
C2–C7	155(1)	N1–N2–C1–C2	−1.8(8)
C7–N1	154(1)	N2–C1–C2–C7	6.0(8)
N1–C21	144.5(9)	C1–C2–C7–N1	−7.3(7)
C1–C11	151(1)	C2–C7–N1–N2	7.3(8)
C2–C3	152(1)	C7–N1–N2–C1	−3.6(8)
C7–C6	152(1)	C1–N2–N1–C21	180.0(6)
N1–N2–C1	110.9(7)	N2–N1–C21–C22	107.7(8)
N2–C1–C2	106.3(6)	N1–N2–C1–C11	−129.0(8)
C1–C2–C7	104.3(7)	N2–N1–C7–C6	118.0(7)
C2–C7–N1	100.7(7)	N2–C1–C2–C3	−106.3(8)
C7–N1–N2	117.2(6)	C1–C2–C3–C8	77(1)
C7–N1–C21	123.0(6)	C1–C2–C3–C4	−173.7(8)

Table 2 Selected bond lengths (pm), bond angles and torsional angles (°) for **4z** [54]

Atoms	Found	Atoms	Found
C1–C2	154(1)	C3–C2–C8	116.5(6)
C2–C8	156.8(9)	C6–C1–N3	111.6(5)
C8–N4	147.8(9)	C1–C2–C8–N4	−7.5(7)
N4–N3	124.3(8)	C2–C8–N4–N3	8.3(8)
N3–C1	149.6(8)	N4–N3–C1–C2	0.4(8)
C4–C5	153(1)	N3–C1–C2–C8	4.5(7)
C4–C3	155.2(9)	C1–C2–C8–C81	102.8(7)
C3–C2	153(1)	C2–C1–N3–C16	179.9(6)
C5–C6	154.0(8)	C1–N3–C16–C17	73.6(8)
C6–C1	153(1)	N4–C8–C2–C3	103.3(7)
C1–C2–C8	103.6(5)	C8–C2–C3–C4	176.7(6)
C2–C8–N4	105.9(5)	C8–C2–C3–C7	−78.6(7)
C8–N4–N3	110.1(5)	N3–C1–C6–C5	−176.6(6)
N4–N3–C1	117.3(6)	C1–C6–C5–C9	175.7(6)
N3–C1–C2	102.4(5)	C2–C3–C4–N1	−176.4(5)

Experimental

Solvents were dried by standard methods. Cycloaddition reactions were carried out with the exclusion of moisture. IR spectra: Perkin-Elmer FTIR 1600 spectrometer. ^{1}H and ^{13}C NMR spectra: Bruker AC-250 and WM-250 spectrometers; internal reference $SiMe_4$; 295 K; δ-scale; J-values are given in Hz.

Yellow prisms suitable for crystallographic analysis of the hexachloroantimonate **4r** were obtained by slow crystallization at 23 °C from CH_2Cl_2–MeCN–Et_2O. Similarly, yellow prisms suitable for crystallographic analysis of the salt **4z** were obtained by slow crystallization at 23 °C from MeCN–Et_2O.

Crystal structure determination of salt 4r [54]

Crystal data. $[C_{16}H_{18}Cl_3N_2]^+[SbCl_6]^-$, $M = 679.1$, monoclinic, $a = 948.7(2)$, $b = 1845.5(4)$, $c = 1428.1(3)$ pm, $\beta = 101.29(3)°$, $V = 2452(1) \times 10^6$ pm^3, $T = 249$ K, space group Pn (no.7), $Z = 4$, μ(Mo-Kα) = 2131 m^{-1}, 5678 reflections measured, 5168 unique ($R_{int} = 0.00$), which were used in all calculations. The final $wR(F^2)$ was 0.0391 (all data).

Crystal structure determination of salt 4z [54]

Crystal data. $[C_{25}H_{24}Cl_6N_4]^+[SbCl_6]_2^-\cdot 5CH_3CN$, $M = 1467.4$, triclinic, $a = 953.7(3)$, $b = 1063.0(4)$, $c = 2793(1)$ pm, $\alpha = 90.85(2)$, $\beta = 92.16(2)$, $\gamma = 89.99(2)°$, $V = 2832(2) \times 10^6$ pm^3, $T = 200$ K, space group $P\bar{1}$ (no.2), $Z = 2$, μ(Mo-Kα) = 1840 m^{-1}, 8815 reflections measured, 8215 unique ($R_{int} = 0.0244$), which were used in all calculations. The final $wR(F^2)$ was 0.3901 (all data).

1-[(1-Chloro-1,2-dimethylpropyl)azo]-2,4-dinitrobenzene 2i

The reaction was carried out with exclusion of light. *tert*-Butyl hypochlorite [56] (1.30 g, 12 mmol) was added dropwise to a cold (−50 °C) solution of **1i** [57] (2.66 g, 10 mmol) in $CHCl_3$ (15 ml). After stirring at 23 °C for 3 d the solvent was removed under reduced pressure to afford *title compound* **2i** as a dark red oil (2.95 g, 98%) (Found: C, 43.72; H, 4.33; N, 18.48. $C_{11}H_{13}ClN_4O_4$ ($M = 300.7$) requires C, 43.94; H, 4.36; N, 18.63%); δ_H(250 MHz; $CDCl_3$) 1.08 (d, J 6.7, CH_3), 1.19 (d, J 6.8, CH_3), 1.89 (CH_3), 2.70 (sept, J 6.7, CH), 7.43 (d, J 8.7, 1 H), 8.56 (dd, J 2.4 and 8.7, 1 H), 8.91 (d, J 2.4, 1 H) (aryl); δ_C(62.9 MHz; $CDCl_3$) 17.6 (2 CH_3), 26.0 (CH_3), 38.8 (CH), 101.4 (CCl), 120.5, 121.3, 128.7, 144.3, 147.6, 149.6 (aryl).

1-[(1-Chloro-1-ethylpropyl)azo]-4-nitrobenzene 2w

From *tert*-butyl hypochlorite (2.17 g, 20 mmol) and **1w** [58] (2.21 g, 10 mmol) in CH_2Cl_2 (30 ml) in the manner described for **2i**. After stirring at 0 °C for 3 h the solvent was removed to afford *title compound* **2w** as an orange oil (2.37 g, 93%) (Found: C, 51.75; H, 5.51; N, 16.40. $C_{11}H_{14}ClN_3O_2$ ($M = 255.8$) requires C, 51.67; H, 5.52; N, 16.43%); δ_H(250 MHz; $CDCl_3$) 0.99 (t, J 7.3, 2 CH_3), 2.33 (m, 2 CH_2), 7.87 (m, 2 H), 8.34 (m, 2 H) (aryl); δ_C(62.9 MHz; $CDCl_3$) 8.4 (2 CH_3), 34.2 (2 CH_2), 101.3 (CCl), 123.5, 124.8, 149.0, 154.3 (aryl).

1-[(1-Chloro-1-ethylpropyl)azo]-2,4-dinitrobenzene 2x

From *tert*-butyl hypochlorite (2.17 g, 20 mmol) and **1x** [59] (2.66 g, 10 mmol) in $CHCl_3$ (25 ml) in the manner described for **2i**. *Title compound* **2x** was obtained as a red oil (2.74 g, 91%) (Found: C, 43.50; H, 4.28; N, 18.50. $C_{11}H_{13}ClN_4O_4$ ($M = 300.7$) requires C, 43.94; H, 4.36; N, 18.63%); δ_H(250 MHz; $CDCl_3$) 1.05 (t, J 7.3, 2 CH_3), 2.35 (m, 2 CH_2), 7.41 (d, J 8.6, 1 H), 8.54 (dd, J 2.3 and 8.6, 1 H), 8.88 (d, J 2.3, 1 H) (aryl); δ_C(62.9 MHz; $CDCl_3$) 8.4 (2 CH_3), 33.9 (2 CH_2), 101.8 (CCl), 120.5, 121.4, 128.6, 144.5, 147.7, 149.5 (aryl).

Preparation of the pyrazolium hexachloroantimonates and tetrachloroaluminates: general procedure

To prepare the pyrazolium hexachloroantimonates a solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a stirred cold (−60 °C) solution of the (chloroalkyl)azo compound **2** (10 mmol) and the alkene (12 mmol) in CH_2Cl_2 (20

ml). In the case of the tetrachloroaluminates the solution of **2** and the alkene in CH_2Cl_2 was added dropwise to a suspension of $AlCl_3$ (1.34 g, 10 mmol) in CH_2Cl_2 (20 ml). The reaction mixture was stirred at −60 °C for 1 h, then at 0 °C for 2 h, and finally at 23 °C for 10 min. The product was precipitated by slow addition of Et_2O or pentane.

4,5-Dihydro-3,3-dimethyl-1-(2,4,6-trichlorophenyl)-3*H*-pyrazolium hexachloroantimonate 4a

At −80 °C ethene (1.12 g, 40 mmol) was condensed into CH_2Cl_2 (20 ml). After addition of **2a**[12] (2.86 g, 10 mmol) followed by a solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) the mixture was stirred according to the general procedure. *Title compound* **4a** was precipitated as a colourless powder (5.46 g, 89%) by slow addition of Et_2O (100 ml); mp 141–143 °C (decomp.) (Found: C, 21.61; H, 2.20; N, 4.61. $C_{11}H_{12}Cl_9N_2Sb$ (M = 613.1) requires C, 21.55; H, 1.97; N, 4.57%); ν_{max}(KBr)/cm^{-1} 1580 (aryl); δ_H(250 MHz; CD_3CN) 1.86 (2 CH_3), 2.61 (t, J 8.2, 2 H4), 5.41 (t, J 8.3, 2 H5), 7.87 (s, aryl); δ_C(62.9 MHz; CD_3CN) 25.9 (2 CH_3), 33.2 (C4), 77.8, 93.2 (C3, C5), 130.9, 131.3, 141.3 (aryl).

1-*tert*-Butyl-4,5-dihydro-3,3-dimethyl-3*H*-pyrazolium hexachloroantimonate 4b

From **2b**[12] (1.63 g, 10 mmol) and ethene (1.12 g, 40 mmol) in the manner described for **4a**. Concentration of the reaction mixture and crystallization at −15 °C afforded colourless prisms (3.30 g, 67%) of *title compound* **4b**; mp 171–173 °C (decomp.) (Found: C, 22.20; H, 4.19; N, 5.66. $C_9H_{19}Cl_6N_2Sb$ (M = 489.7) requires C, 22.07; H, 3.91; N, 5.72%); δ_H(250 MHz; CD_3CN) 1.60 (2 CH_3), 1.68 (3 CH_3), 2.25 (t, J 8.2, 2 H4), 4.98 (t, J 8.2, 2 H5); δ_C(62.9 MHz; CD_3CN) 25.3 (2 CH_3), 27.7 (3 CH_3), 32.5 (C4), 69.5, 76.8, 89.4 (CN).

5-Butyl-4,5-dihydro-3,3-dimethyl-1-(2,4,6-trichlorophenyl)-3*H*-pyrazolium hexachloroantimonate 4c

From **2a** (2.86 g, 10 mmol) and hex-1-ene (1.68 g, 20 mmol). *Title compound* **4c** was precipitated as a colourless powder (4.54 g, 68%) by slow addition of Et_2O (100 ml); mp 130–134 °C (decomp.) (Found: C, 26.92; H, 3.05; N, 4.19. $C_{15}H_{20}Cl_9N_2Sb$ (M = 669.2) requires C, 26.92; H, 3.01; N, 4.19%); ν_{max}(KBr)/cm^{-1} 1560 (br); δ_H(250 MHz; CD_3CN) 0.87 (br, CH_3), 1.32 (m, 2 CH_2), 1.76 (CH_3), 1.80 (m, 1 H), 1.96 (CH_3), 2.03 (m, 1 H), 2.25 (dd, J 8.9 and 13.4, 1 H4), 2.86 (dd, J 8.6 and 13.3, 1 H4), 5.78 (m, H5), 7.89 (s, aryl); δ_C(62.9 MHz; CD_3CN) 13.9, 22.7, 25.7, 27.3, 28.6, 32.5, 38.8 (CH_3, CH_2), 91.8, 91.9 (C3, C5), 131.7, 133.5, 134.2, 141.4 (aryl).

5-Chloro-4,5-dihydro-3,3-dimethyl-1-(2,4,6-trichlorophenyl)-3*H*-pyrazolium hexachloroantimonate 4d

From **2a** (2.86 g, 10 mmol) and vinyl chloride (2.50 g, 40 mmol). *Title compound* **4d** was precipitated as a yellow powder (5.16 g, 80%) by slow addition of Et_2O (80 ml); mp 139–141 °C (decomp.) (Found: C, 20.35; H, 1.81; N, 4.34. $C_{11}H_{11}Cl_{10}N_2Sb$ (M = 647.5) requires C, 20.40; H, 1.71; N, 4.33%); ν_{max}(KBr)/cm^{-1} 1545, 1563 (sh); δ_H(250 MHz; CD_3CN; 273 K) 1.95 (CH_3), 2.04 (CH_3), 2.95 (dd, J 4.0 and 15.1, 1 H4), 3.23 (dd, J 8.3 and 15.1, 1 H4), 7.49 (dd, J 4.0 and 8.3, H5), 7.94 (s, aryl); δ_C(62.9 MHz; CD_3CN; 272 K) 26.6 (CH_3), 27.4 (CH_3), 42.6 (C4), 94.1, 94.8 (C3, C5), 131.7, 142.3 (aryl).

1-*tert*-Butyl-5-chloro-4,5-dihydro-3,3-dimethyl-3*H*-pyrazolium hexachloroantimonate 4e

From **2b** (1.63 g, 10 mmol) and vinyl chloride (1.50 g, 24 mmol). Slow precipitation with Et_2O (20 ml) afforded *title compound* **4e** as a colourless powder (4.33 g, 83%); mp 130–133 °C (decomp.) (Found: C, 20.50; H, 3.75; N, 5.30. $C_9H_{18}Cl_6N_2Sb$ (M = 524.2) requires C, 20.62; H, 3.46; N, 5.34%); δ_H[250 MHz; CD_2Cl_2–CD_3CN (4:1)] 1.77 (CH_3), 1.85 (CH_3), 1.90 (3 CH_3), 2.67 (dd, J 1.6 and 15.1, 1 H4), 2.91 (dd, J 8.3 and 15.1, 1 H4), 6.86 (dd, J 1.6 and 8.3, H5); δ_C[62.9 MHz; CD_2Cl_2–CD_3CN (4:1)] 25.8 (CH_3), 26.3 (CH_3), 29.8 (3 CH_3), 43.0 (CH_2), 80.3, 87.7, 90.4 (CN).

4,5-Dihydro-3,3,5,5-tetramethyl-1-(2,4,6-trichlorophenyl)-3*H*-pyrazolium tetrachloroaluminate 4f

From **2a** (2.86 g, 10 mmol) and isobutene (1.12 g, 20 mmol). Precipitation by slow addition of Et_2O (120 ml) afforded an oil, which crystallized at −15 °C to afford colourless needles (3.08 g, 64%) of *title compound* **4f**; mp 95–97 °C (decomp.) (Found: C, 32.11; H, 3.78; N, 5.60. $C_{13}H_{16}AlCl_7N_2 \cdot \frac{1}{2}\ H_2O$ (M = 484.4) requires C, 32.23; H, 3.54; N, 5.78%); δ_H(250 MHz; CD_3CN) 1.90 (2 CH_3), 1.92 (2 CH_3), 2.57 (s, 2 H4), 7.89 (s, aryl); δ_C(62.9 MHz; CD_3CN) 28.0 (2 CH_3), 29.0 (2 CH_3), 45.9 (C4), 91.5, 105.7 (C3, C5), 131.9, 132.0, 133.5 (br), 141.0 (aryl).

1-*tert*-Butyl-4,5-dihydro-3,3,5,5-tetramethyl-3*H*-pyrazolium hexachloroantimonate 4g

From **2b** (1.63 g, 10 mmol) and isobutene (1.35 g, 24 mmol). Evaporation of the solvent and precipitation of the residue from CH_2Cl_2 (20 ml)–Et_2O (30 ml) afforded *title compound* **4g** as a colourless powder (2.97 g, 57%); mp 175–177 °C (decomp.) (Found: C, 25.38; H, 4.41; N, 5.30. $C_{11}H_{23}Cl_6N_2Sb$ (M = 517.8) requires C, 25.52; H, 4.48; N, 5.41%); δ_H(250 MHz; CD_3CN) 1.64 (2 CH_3), 1.78 (3 CH_3), 1.90 (2 CH_3), 2.27 (s, 2 H4); δ_C(62.9 MHz; CD_3CN) 27.2 (2 CH_3), 29.9 (2 CH_3), 30.3 (3 CH_3), 49.5 (C4), 81.9, 84.4, 100.1 (CN).

4,5-Dihydro-3-isopropyl-3,5,5-trimethyl-1-(2,4,6-trichlorophenyl)-3*H*-pyrazolium hexachloroantimonate 4h

From **2h**[12] (3.14 g, 10 mmol) and isobutene (1.35 g, 24 mmol). *Title compound* **4h** was precipitated as a pale yellow powder (2.80 g, 42%) by slow addition of Et_2O (100 ml); mp 155–159 °C (decomp.) (Found: C, 27.00; H, 2.99; N, 4.19. $C_{15}H_{20}Cl_9N_2Sb$ (M = 669.2) requires C, 26.92; H, 3.01; N, 4.19%); ν_{max}(CH_2Cl_2)/cm^{-1} 1567; δ_H(250 MHz; CD_3CN) 1.11 (d, J 6.8, CH_3), 1.21 (d, J 6.9, CH_3), 1.84 (CH_3), 1.90 (CH_3), 1.94 (CH_3), 2.46 (d, J 13.7, 1 H4), 2.54 (d, J 13.7, 1 H4), 2.63 (sept, J 6.8, CH), 7.89 (s, aryl); δ_C(62.9 MHz; CD_3CN) 17.7 (CH_3), 18.5 (CH_3), 24.1 (CH_3), 28.9 (CH_3), 29.2 (CH_3), 39.1, 41.9 (CH, C4), 98.1, 104.9 (C3, C5), 131.9, 132.0, 133.5 (br), 140.9 (aryl).

1-(2,4-Dinitrophenyl)-4,5-dihydro-3-isopropyl-3,5,5-trimethyl-3*H*-pyrazolium hexachloroantimonate 4i

From **2i** (3.01 g, 10 mmol) and isobutene (1.35 g, 24 mmol). *Title compound* **4i** was precipitated as a brownish powder by slow addition of Et_2O (35 ml). Reprecipitation from CH_2Cl_2 (10 ml)–MeCN (2 ml)–Et_2O (50 ml) afforded a yellow powder (1.84 g, 28%); mp 142–144 °C (decomp.) (Found: C, 27.50; H, 3.30; N, 8.51. $C_{15}H_{21}Cl_6N_4O_4Sb$ (M = 655.8) requires C, 27.47; H, 3.23; N, 8.54%); δ_H(250 MHz; CD_3CN; 313 K) 1.15 (d, J 6.8, CH_3), 1.24 (d, J 6.7, CH_3), 1.79 (CH_3), 1.85 (CH_3), 1.86 (CH_3), 2.46 (sept, J 6.8, CH), 2.59 (AB-q, J 13.6, 2 H4), 8.20 (d, J 8.8, 1 H), 8.86 (dd, J 2.4 and 8.8, 1 H), 9.15 (d, J 2.4, 1 H) (aryl); δ_C(62.9 MHz; CD_3CN; 313 K) 17.7 (CH_3), 18.1 (CH_3), 21.4 (CH_3), 28.5 (CH_3), 39.1, 44.1 (C4, CH), 97.5, 102.9 (C3, C5), 124.3, 130.8, 131.6, 136.4, 144.5, 151.5 (aryl).

cis-4,5-Dihydro-3,3,4,5-tetramethyl-1-(2,4,6-trichlorophenyl)-3*H*-pyrazolium hexachloroantimonate 4j

From **2a** (2.86 g, 10 mmol) and (*Z*)-but-2-ene (2.24 g, 40 mmol). *Title compound* **4j** was precipitated as a colourless powder (1.06 g, 17%) by slow addition of Et_2O (60 ml); mp 117–119 °C (decomp.) (Found: C, 24.37; H, 2.54; N, 4.33. $C_{13}H_{16}Cl_9N_2Sb$

(M = 641.1) requires C, 24.36; H, 2.52; N, 4.37%); ν_{max}(KBr)/cm^{-1} 1553 (br); δ_H(250 MHz; CD_2Cl_2; 263 K) 1.21 (d, J 7.4, CH_3), 1.64 (d, J 7.4, CH_3), 1.88 (CH_3), 1.89 (CH_3), 3.11 (quint, J 7.4, H4), 5.98 (quint, J 7.4, H5), 7.78 (s, aryl); δ_C(62.9 MHz; CD_2Cl_2; 263 K) 10.0 (CH_3), 13.8 (CH_3), 22.3 (CH_3), 25.9 (CH_3), 41.5 (C4), 89.0, 93.4 (C3, C5), 129.9, 130.9, 131.0, 131.4, 132.9, 141.6 (aryl).

trans-4,5-Dihydro-3,3,4,5-tetramethyl-1-(2,4,6-trichlorophenyl)-3_H_-pyrazolium hexachloroantimonate 4k

From **2a** (2.86 g, 10 mmol) and (_E_)-but-2-ene (2.24 g, 40 mmol). _Title compound_ **4k** was precipitated as a yellow powder (2.38 g, 37%) by slow addition of Et_2O (60 ml); mp 123–124 °C (decomp.) (Found: C, 24.07; H, 2.70; N, 4.53. $C_{13}H_{16}Cl_9N_2Sb$ (M = 641.1) requires C, 24.36; H, 2.52; N, 4.37%); ν_{max}(KBr)/cm^{-1} 1560 (br); δ_H(250 MHz; CD_3CN) 1.27 (d, J 6.9, CH_3), 1.57 (CH_3), 1.61 (d, J 6.8, CH_3), 1.95 (CH_3), 2.51 (dq, J 11.2 and 6.9, H4), 5.44 (dq, J 11.2 and 6.8, H5), 7.89 (s, aryl); δ_C(62.9 MHz; CD_3CN) 10.5 (CH_3), 15.6 (CH_3), 19.2 (CH_3), 25.6 (CH_3), 47.6 (C4), 91.0, 93.2 (C3, C5), 130.3–133.5 (several br lines), 141.4 (aryl).

trans-1-_tert_-Butyl-4,5-dihydro-3,3,4,5-tetramethyl-3_H_-pyrazolium hexachloroantimonate 4l

From **2b** (1.63 g, 10 mmol) and (_E_)-but-2-ene (1.35 g, 24 mmol). Slow precipitation with Et_2O (100 ml) and crystallization at −15 °C from CH_2Cl_2 (10 ml)–Et_2O (15 ml) afforded _title compound_ **4l** as a colourless powder (1.60 g, 31%); mp 155–159 °C (decomp.) (Found: C, 25.39; H, 4.43; N, 5.39. $C_{11}H_{23}Cl_6N_2Sb$ (M = 517.8) requires C, 25.52; H, 4.48; N, 5.41%); δ_H(250 MHz; CD_3CN) 1.09 (d, J 7.0, CH_3), 1.34 (CH_3), 1.70 (CH_3), 1.71 (3 CH_3), 1.84 (d, J 6.7, CH_3), 2.18 (dq, J 9.6 and 7.0, H4), 4.86 (dq, J 9.6 and 6.7, H5); δ_C(62.9 MHz; CD_3CN) 11.4 (CH_3), 19.8 (CH_3), 19.9 (CH_3), 25.8 CH_3), 28.4 (3 CH_3), 46.7 (C4), 79.0, 87.9, 88.1 (CN).

4,5-Dihydro-3,3,4,5,5-pentamethyl-1-(2,4,6-trichlorophenyl)-3_H_-pyrazolium tetrachloroaluminate 4m

From **2a** (2.86 g, 10 mmol) and 2-methylbut-2-ene (1.05 g, 15 mmol). Precipitation by slow addition of Et_2O (120 ml) afforded _title compound_ **4m** as a colourless powder (3.26 g, 58%); mp 159–160 °C (decomp.) (Found: C, 30.01; H, 4.71; N, 4.97. $C_{14}H_{18}AlCl_7N_2 \cdot 4H_2O$ (M = 561.5) requires C, 29.94; H, 4.67; N, 4.99%); ν_{max}(CH_2Cl_2)/cm^{-1} 1560 (sh), 1570, 1645 (br); δ_H(250 MHz; CD_3CN) 1.20 (d, J 7.2, CH_3), 1.70 (CH_3), 1.72 (CH_3), 1.86 (CH_3), 1.93 (CH_3), 2.61 (q, J 7.2, CH), 7.88 (s, aryl); δ_C(62.9 MHz; CD_3CN) 9.1, 21.8, 24.1, 27.2, 27.6 (5 CH_3), 47.9 (CH), 93.5, 106.2 (C), 131.7, 131.9, 132.1, 134.0 (br), 140.9 (aryl).

cis-5-Ethyl-4,5-dihydro-3,3,4,5-tetramethyl-1-(2,4,6-trichlorophenyl)-3_H_-pyrazolium tetrachloroaluminate 4n

From **2a** (2.86 g, 10 mmol) and (_Z_)-3-methylpent-2-ene (1.68 g, 20 mmol). Precipitation by slow addition of Et_2O (120 ml) afforded an oil, which crystallized at −15 °C to afford _title compound_ **4n** as colourless prisms (2.26 g, 45%); mp 139–141 °C (decomp.) (Found: C, 36.25; H, 4.38; N, 5.57. $C_{15}H_{20}AlCl_7N_2$ (M = 503.5) requires C, 35.78; H, 4.00; N, 5.56%); ν_{max}(CH_2Cl_2)/cm^{-1} 1560 (sh), 1570; δ_H(250 MHz; CD_3CN) 0.98 (t, J 7.5, CH_3), 1.21 (d, J 7.2, CH_3), 1.72 (CH_3), 1.73 (CH_3), 1.93 (CH_3), 2.24 (m, CH_2), 2.64 (q, J 7.2, CH), 7.88 (s, aryl); δ_C(62.9 MHz; CD_3CN) 8.5, 11.0, 20.5, 22.2, 27.7, 34.2 (5 CH_3, CH_2), 46.8 (CH), 93.8, 110.0 (CN), 131.7, 131.8, 132.0, 132.2, 134.8, 140.9 (aryl).

trans-5-Ethyl-4,5-dihydro-3,3,4,5-tetramethyl-1-(2,4,6-trichlorophenyl)-3_H_-pyrazolium tetrachloroaluminate 4o

From (_E_)-3-methylpent-2-ene (1.68 g, 20 mmol) in the manner described for **4n**. _Title compound_ **4o** was obtained as yellow needles (2.28 g, 45%); mp 139–142 °C (decomp.) (Found: C, 35.49; H, 4.16; N, 5.33. $C_{15}H_{20}AlCl_7N_2$ (M = 503.5) requires C, 35.78; H, 4.00; N, 5.56%); ν_{max}(CH_2Cl_2)/cm^{-1} 1573 (br); δ_H(250 MHz; CD_3CN) 0.98 (t, J 7.4, CH_3), 1.25 (d, J 7.3, CH_3), 1.72 (CH_3), 1.75 (CH_3), 1.91 (CH_3), 2.17 (q, J 7.3, CH_2), 2.65 (q, J 7.3, CH), 7.87 (s, aryl); δ_C(62.9 MHz; CD_3CN) 9.2, 9.8, 22.3, 24.3, 27.6, 28.9 (5 CH_3, CH_2), 49.1 (CH), 93.2, 110.3 (CN), 131.8, 131.9, 132.0 (br), 132.1 (br), 134.7, 140.9 (aryl).

2-Aza-3,3-diisopropyl-1-(4-nitrophenylazonia)spiro[4.4]non-1-ene tetrachloroantimonate 4p

From **2p**[22] (2.84 g, 10 mmol) and methylenecyclopentane (0.99 g, 12 mmol). Precipitation with Et_2O (100 ml) afforded a dark brown powder, which was crystallized at −15 °C from MeCN (20 ml) to furnish _title compound_ **4p** as a dark brown powder (1.65 g, 30%); mp 114–115 °C (decomp.) (Found: C, 38.48; H, 4.50; N, 6.88. $C_{19}H_{28}Cl_4N_3O_2Sb$ (M = 549.0) requires C, 38.42; H, 4.75; N, 7.08%); ν_{max}(CH_2Cl_2)/cm^{-1} 1543, 1594, 1614; δ_H[250 MHz; CD_3CN–CD_2Cl_2 (4:1)] 1.06 (d, J 6.9, 2 CH_3), 1.12 (d, J 6.8, 2 CH_3), 1.89 (m, 4 H), 2.33 (m, 2 H), 2.47 (s, 2 H4), 2.63 (m, 2 H) (CH_2), 2.80 (sept, J 6.9, 2 H, CH), 7.97 (m, 2 H), 8.50 (m, 2 H)(aryl); δ_C[62.9 MHz; CD_3CN–CD_2Cl_2 (4:1)] 18.1 (2 CH_3), 18.5 (2 CH_3), 25.2, 36.7, 39.3, 42.0 (5 CH_2, 2 CH), 101.7, 105.1 (C3, C5), 126.7, 127.7, 143.0, 151.7 (aryl).

1-_tert_-Butyl-3,3a,4,5,6,6a-hexahydro-3,3-dimethylcyclopentapyrazolium hexachloroantimonate 4q

From **2b** (1.63 g, 10 mmol) and cyclopentene (0.82 g, 12 mmol). Evaporation of the solvent and crystallization of the residue at −15 °C from MeCN (5 ml) afforded brown needles of _title compound_ **4q** (2.05 g, 39%); mp 172–175 °C (decomp.) (Found: C, 26.96; H, 4.47; N, 5.26. $C_{12}H_{23}Cl_6N_2Sb$ (M = 529.8) requires C, 27.20; H, 4.38; N, 5.29%); ν_{max}(CH_2Cl_2)/cm^{-1} 1458; δ_H(250 MHz; CD_3CN) 1.55 (CH_3), 1.62 (CH_3), 1.71 (3 CH_3), 1.63–2.48 (several m, 6 H, CH_2), 2.89 (m, H3a), 5.73 (dt, J 5.5 and 8.5, H6a); δ_C(62.9 MHz; CD_3CN) 21.4, 26.6, 28.6, 28.8, 29.2 (3 C), 34.7, 49.0 (CH_3, CH_2, CH), 77.9, 89.2, 92.4 (CN).

(3a_α_,4_α_,7_α_,7a_α_)-3a,4,5,6,7,7a-Hexahydro-3,3-dimethyl-4,7-methano-1-(2,4,6-trichlorophenyl)-3_H_-indazolium hexachloroantimonate 4r

From **2a** (2.86 g, 10 mmol) and norbornene† (1.13 g, 12 mmol). Precipitation with Et_2O (30 ml) afforded a yellow powder. Slow reprecipitation from CH_2Cl_2 (30 ml)–MeCN (30 ml)–Et_2O (120 ml) furnished _title compound_ **4r** as a pale yellow powder (4.04 g, 60%); mp 208–210 °C (decomp.) (Found: C, 28.18; H, 2.69; N, 4.03. $C_{16}H_{18}Cl_9N_2Sb$ (M = 679.2) requires C, 28.30; H, 2.67; N, 4.12%); ν_{max}(KBr)/cm^{-1} 1549 (br); δ_H(250 MHz; CD_3CN; 333 K) 1.26–1.74 (several m, 6 H, CH_2), 1.76 (CH_3), 1.94 (CH_3), 2.60 (br d, J 2.9, 1 H), 2.66 (d, J 7.3, H3a), 2.85 (br d, J 4.3, 1 H), 5.92 (d, J 7.3, H7a), 7.84 (s, aryl); δ_C(62.9 MHz; CD_3CN; 333 K) 20.9, 25.5, 27.7, 31.1, 35.3, 40.0, 42.3, 51.7 (CH_3, CH_2, CH), 95.3, 99.0 (C3, C7a), 131.1 (br), 131.8, 134.7 (br), 141.3 (aryl).

(3a_α_,4_α_,7_α_,7a_α_)-3a,4,5,6,7,7a-Hexahydro-4,7-methano-3,3-dimethyl-1-(2,4,6-trichlorophenyl)-3_H_-indazolium tetrachloroaluminate 4s

From **2a** (2.86 g, 10 mmol) and norbornene (1.13 g, 12 mmol). After addition of Et_2O (120 ml) _title compound_ **4s** crystallized at −15 °C to afford colourless needles (4.92 g, 93%); mp 150–152 °C (decomp.) (Found: C, 36.57; H, 3.92; N, 5.10. $C_{16}H_{18}AlCl_7N_2 \cdot H_2O$ (M = 531.5) requires C, 36.15; H, 3.79; N, 5.27%); ν_{max}(CH_2Cl_2)/cm^{-1} 1630 (br), 1561 (br); δ_H(250 MHz; CD_3CN) 1.25–1.74 (several m, 6 H, CH_2), 1.75 (CH_3), 1.94 (CH_3), 2.59 (br d, J 2.4, 1 H), 2.67 (br d, J 7.4, H3a), 2.84 (br d, J 4.1, 1 H), 5.93 (d, J 7.4, H7a), 7.86 (s, aryl); δ_C(62.9 MHz; CD_3CN) 20.8,

25.4, 27.5, 31.0, 35.2, 39.9, 42.3, 51.4 (CH_3, CH_2, CH), 95.2, 98.7 (C3, C7a), 131.0 (br), 131.4 (br), 131.7, 134.6 (br), 141.0 (aryl).

(3aα,4α,7α,7aα)-3a,4,5,6,7,7a-Hexahydro-4,7-methano-3,3-dimethyl-1-(2,4,6-trichlorophenyl)-3*H*-indazolium picrate 4t

A saturated solution of picric acid (*ca.* 6.87 g, 30 mmol) in EtOH–H_2O (7 : 3) was added to a saturated solution of **4s** (5.32 g, 10 mmol) in EtOH. The precipitate formed was isolated by filtration and washed with EtOH to afford *title compound* **4t** as a yellow powder (5.57 g, 97%); mp 142–144 °C (decomp.) (Found: C, 46.08; H, 3.54; N, 12.05. $C_{22}H_{20}Cl_3N_5O_7$ (M = 572.8) requires C, 46.13; H, 3.52; N, 12.23%); ν_{max}(KBr)/cm^{-1} 1555, 1638 (br); δ_H(250 MHz; $CDCl_3$; 273 K) 1.32–1.79 (several m, 6 H, CH_2), 1.86 (CH_3), 2.01 (CH_3), 2.62 (br, 1 H), 2.84 (d, J 7.3, H3a), 2.91 (br, 1 H), 6.24 (d, J 7.3, H7a), 7.67 (m, 1 H), 7.71 (m, 1 H) ($Cl_3C_6H_2$), 8.79 (2 H, picrate); δ_C(62.9 MHz; $CDCl_3$; 273 K) 20.7, 24.7, 26.9, 30.9, 34.6, 38.9, 41.2, 50.4 (CH_3, CH_2, CH), 94.2, 97.9 (C3, C7a), 125.3, 126.7, 129.9, 130.4, 130.5, 133.2, 140.8, 141.7, 162.2 (aryl).

Bis[(3aα,4α,7α,7aα)-3a,4,5,6,7,7a-hexahydro-4,7-methano-3,3-dimethyl-1-(2,4,6-trichlorophenyl)-3*H*-indazolium] hexachlorostannate 4u

From **2a** (2.86 g, 10 mmol), norbornene (1.13 g, 12 mmol) and $SnCl_4$ (1.30 g, 5 mmol) in the manner described for **4r**. After the stirring procedure the solvent was evaporated and the residue was stirred for 5 h in Et_2O (40 ml). Decantation and slow precipitation of the residue from CH_2Cl_2 (10 ml)–MeCN (2 ml)–Et_2O (40 ml) afforded *title compound* **4u** as a colourless powder (2.74 g, 54%); mp 181–183 °C (decomp.) (Found: C, 37.35; H, 3.60; N, 5.43. $C_{32}H_{36}Cl_{12}N_4Sn$ (M = 1020.8) requires C, 37.65; H, 3.55; N, 5.49%); ν_{max}(KBr)/cm^{-1} 1568, 1580 (sh); δ_H(250 MHz; CD_3CN) 1.28–1.72 (several m, 6 H, CH_2), 1.80 (CH_3), 1.95 (CH_3), 2.49 (br, 1 H), 2.59 (br, 1 H), 2.82 (m, 2 H), 6.04 (m, J 7.4, H7a), 7.87 (s, aryl); δ_C(62.9 MHz; CD_3CN) 20.9, 25.5, 27.6, 31.1, 35.3, 40.0, 42.2, 51.2 (CH_3, CH_2, CH), 95.2, 98.9 (C3, C7a), 131.3, 131.6, 134.7, 140.9 (aryl).

Bis[(3aα,4α,7α,7aα)-1-*tert*-butyl-3a,4,5,6,7,7a-hexahydro-4,7-methano-3,3-dimethyl-3*H*-indazolium] hexachlorotitanate 4v

From **2b** (1.63 g, 10 mmol), norbornene (1.13 g, 12 mmol) and $TiCl_4$ (0.95 g, 5 mmol). Slow precipitation with Et_2O (10 ml) afforded *title compound* **4v** as a yellow crystalline powder (1.98 g, 56%); mp 140–144 °C (decomp.) (Found: C, 47.81; H, 7.36; N, 7.85. $C_{28}H_{50}Cl_6N_4Ti$ (M = 703.3) requires C, 47.80; H, 7.16; N, 7.96%); ν_{max}(CH_2Cl_2)/cm^{-1} 1582; δ_H(250 MHz; CD_3CN) 0.89 (br d, J 11.6, 1 H), 1.18–1.74 (several m, 5 H, CH_2, CH), 1.57 (CH_3), 1.66 (CH_3), 1.75 (3 CH_3), 2.41 (m, 2 H), 3.18 (br d, J 4.6, 1 H), 5.74 (d, J 7.1, H7a); δ_C(62.9 MHz; CD_3CN) 20.9, 25.3, 28.0, 29.1 (3 C), 29.8, 34.0, 39.6, 42.5, 50.9 (CH_3, CH_2, CH), 77.8, 90.3, 94.7 (C-N1, C7a, C3).

(3aα,4α,7α,7aα)-3,3-Diethyl-3a,4,5,6,7,7a-hexahydro-4,7-methano-1-(4-nitrophenyl)-3*H*-indazolium hexachloroantimonate 4w

From **2w** (2.56 g, 10 mmol) and norbornene (1.13 g, 12 mmol). Precipitation with Et_2O (50 ml) afforded a yellow powder, which was crystallized at −15 °C from MeCN (10 ml) to furnish *title compound* **4w** as a yellow powder (3.63 g, 56%); mp 187–189 °C (decomp.) (Found: C, 33.41; H, 3.84; N, 6.49. $C_{18}H_{24}Cl_6N_3O_2Sb$ (M = 648.8) requires C, 33.32; H, 3.73; N, 6.48%); ν_{max}(CH_2Cl_2)/cm^{-1} 1547, 1607; δ_H(250 MHz; CD_3CN) 1.02 (t, J 7.4, CH_3), 1.33 (t, J 7.4, CH_3), 1.37–2.30 (several m, 10 H, CH_2), 2.52 (br, 1 H), 2.60 (dd, J 1.6 and 7.0, 1 H), 2.86 (br d, J 4.8, 1 H), 5.94 (d, J 7.0, H7a), 8.38 (m, 2 H), 8.51 (m, 2 H) (aryl); δ_C(62.9 MHz; CD_3CN) 8.0, 9.0 (CH_3), 25.1, 25.2, 27.9, 32.2, 34.4, 39.3, 42.3, 49.9 (CH_2, CH), 93.2, 98.1 (C3a, C7a), 126.7, 127.5, 142.7, 152.9 (aryl). After heating a solution of **4w** in CD_3CN at 79 °C for 13 d, the ^{1}H NMR spectrum showed at the most traces of (3aα,4α,7α,7aα)-2,3-diethyl-3a,4,5,6,7,7a-hexahydro-4,7-methano-1-(4-nitrophenyl)-1*H*-indazolium hexachloroantimonate **5w**.

(3aα,4α,7α,7aα)-3,3-Diethyl-1-(2,4-dinitrophenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methano-3*H*-indazolium hexachloroantimonate 4x

From **2x** (3.01 g, 10 mmol) and norbornene (1.13 g, 12 mmol). Precipitation with Et_2O (40 ml) afforded *title compound* **4x** as a yellow powder (1.71 g, 25%); mp 146–149 °C (decomp.) (Found: C, 31.44; H, 3.42; N, 8.03. $C_{18}H_{23}Cl_6N_4O_4Sb$ (M = 693.9) requires C, 31.16; H, 3.34; N, 8.07%); ν_{max}(KBr)/cm^{-1} 1545 (br), 1617 (br); δ_H(250 MHz; CD_3CN) 1.10 (t, J 7.4, CH_3), 1.26 (t, J 7.4, CH_3), 1.33–2.26 (several m, 10 H, CH_2, CH), 2.57 (br d, J 2.9, 1 H), 2.68 (m, 2 H), 5.90 (d, J 7.1, H7a), 8.26 (m, 1 H), 8.83 (m, 1 H), 9.07 (m, 1 H) (aryl); δ_C(62.9 MHz; CD_3CN) 7.9, 8.8, 24.7, 25.0, 27.9, 31.0, 34.7, 39.4, 41.7, 50.1 (CH_3, CH_2, CH), 97.1, 100.5 (C3a, C7a), 123.8, 130.7, 131.3, 136.2, 144.5, 152.0 (aryl). After heating a solution of **4x** in CD_3CN at 79 °C for 10 d, the ^{1}H NMR spectrum showed at the most traces of (3aα,4α,7α,7aα)-3,3-diethyl-1-(2,4-dinitrophenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-indazolium hexachloroantimonate **5x**.

(3aα,4α,7α,7aα)-3a,4,5,6,7,7a-Hexahydro-3,3-diisopropyl-4,7-methano-1-(4-nitrophenyl)-3*H*-indazolium hexachloroantimonate 4y

From **2p** (2.84 g, 10 mmol) and norbornene (1.13 g, 12 mmol). Precipitation with Et_2O (50 ml) afforded a yellow powder, which was crystallized at −15 °C from MeCN (10 ml) to furnish *title compound* **4y** as a yellow powder (3.66 g, 54%); mp 106–108 °C (decomp.) (Found: C, 35.47; H, 4.12; N, 6.35. $C_{20}H_{28}Cl_6N_3O_2Sb$ (M = 676.9) requires C, 35.49; H, 4.17; N, 6.21%); ν_{max}(CH_2Cl_2)/cm^{-1} 1595, 1531; δ_H[250 MHz; CD_3CN–CD_2Cl_2 (1 : 4); 273 K] 1.03 (d, J 6.9, CH_3), 1.06 (d, J 6.8, CH_3), 1.37 (d, J 7.0, CH_3), 1.56 (d, J 7.0, CH_3), 1.42–2.90 (several m, 11 H, CH_2, CH), 5.88 (d, J 7.0, H7a), 8.39 (m, 2 H, aryl), 8.58 (m, 2 H, aryl); δ_C[62.9 MHz; CD_3CN–CD_2Cl_2 (1 : 4); 273 K] 19.3, 19.4, 19.8, 20.4, 24.8, 27.9, 33.4, 34.8, 39.6, 40.1, 41.7, 48.8 (CH_3, CH_2, CH), 93.6, 102.5 (C3, C7a), 126.7, 126.8, 141.6, 152.2 (aryl).

(3aα,4α,4aα,7aα,8α,8aα)-3,3a,4,4a,7,7a,8,8a-Octahydro-4,8-methano-3,3,7,7-tetramethyl-1,5-bis(2,4,6-trichlorophenyl)-benzo[1,2-*c*:4,5-*c*′]dipyrazole-1,5-diium bis(hexachloroantimonate) 4z

From **2a** (2.86 g, 10 mmol) and norbornadiene (0.46 g, 5 mmol). After stirring at −60 °C for 1 h and at 0 °C for 2 h, the mixture was stirred at 23 °C for 12 h. Precipitation with Et_2O (120 ml) afforded a yellow powder. Slow reprecipitation from MeCN (60 ml)–Et_2O (120 ml) furnished *title compound* **4z** as a pale yellow powder (3.74 g, 59%); mp 207–208 °C (decomp.) (Found: C, 23.64; H, 1.98; N, 4.37. $C_{25}H_{24}Cl_{18}N_4Sb_2$ (M = 1262.2) requires C, 23.79; H, 1.92; N, 4.44%); ν_{max}(KBr)/cm^{-1} 1558 (br); δ_H(250 MHz; CD_3CN) 1.72 (br, CH_2), 1.79 (2 CH_3), 1.93 (2 CH_3), 2.96 (m, J 7.4, H3a, H7a), 3.21 (br, H4, H8), 6.05 (m, J 7.4, H4a, H8a), 7.93 (s, 4 H, aryl); δ_C(62.9 MHz; CD_3CN; 313 K) 21.2, 30.9, 31.9, 44.7, 48.3 (CH_3, CH_2, CH), 94.5, 96.1 (C3, C7, C4a, C8a), 131.0 (br), 132.1, 134.1, 142.0 (aryl).

(3aα,4α,7α,7aα)-3a,4,7,7a-Tetrahydro-4,7-methano-3,3-dimethyl-1-(2,4,6-trichlorophenyl)-3*H*-indazolium hexachloroantimonate 4aa

From **2a** (2.86 g, 10 mmol) and norbornadiene (0.92 g, 10 mmol). Precipitation with Et_2O (60 ml) afforded a yellow powder, which was reprecipitated from CH_2Cl_2 (10 ml)–MeCN

(20 ml)–Et_2O (60 ml) to furnish *title compound* **4aa** as a pale yellow powder (3.42 g, 51%); mp 167–169 °C (decomp.) (Found: C, 28.21; H, 2.44; N, 4.00. $C_{16}H_{16}Cl_9N_2Sb$ (M = 676.1) requires C, 28.42; H, 2.37; N, 4.14%); ν_{max}(KBr)/cm^{-1} 1560 (br); δ_H(250 MHz; CD_3CN) 1.55–1.80 (m, CH_2), 1.77 (CH_3), 1.94 (CH_3), 2.91 (m, J 2.0 and 7.1, H3a), 3.22 (br, 1 H), 3.57 (br, 1 H) (H4, H7), 5.97 (d, J 7.1, H7a), 6.11 (dd, J 3.3 and 5.6, 1 H), 6.47 (dd, J 3.2 and 5.5, 1 H) (H5, H6), 7.88 (s, aryl); δ_C(62.9 MHz; CD_3CN) 20.5, 31.2 (CH_3), 44.4, 45.9, 48.6, 51.6 (CH_2, CH), 90.7, 99.3 (C3, C7a), 131.2, 131.8 (br), 134.4, 141.2, 144.3 (C=C).

(3aα,4α,7α,7aα)-3a,4,5,6,7,7a-Hexahydro-2,3-diisopropyl-4,7-methano-1-(4-nitrophenyl)-1*H*-indazolium hexachloroantimonate 5y

A solution of **4y** (0.68 g, 1 mmol) in MeCN (12 ml) was stirred at 23 °C for 24 h. After addition of Et_2O (90 ml) crystallization at −15 °C afforded a pale yellow powder (0.53 g, 78%), which was recrystallized at −15 °C from MeCN (10 ml)–Et_2O (20 ml) to furnish *title compound* **5y** as a pale yellow powder (0.42 g, 60%); mp 132–135 °C (decomp.) (Found: C, 36.26; H, 4.31; N, 7.03. $C_{20}H_{28}Cl_6N_3O_2Sb\cdot\frac{1}{2}CH_3CN$ (M = 697.4) requires C, 36.16; H, 4.26; N, 7.03%); ν_{max}(CH_2Cl_2)/cm^{-1} 1532, 1593, 1612; δ_H(250 MHz; CD_3CN) 1.03 (d, J 7.0, CH_3), 1.41 (d, J 7.2, CH_3), 1.48 (d, J 6.8, CH_3), 1.51 (d, J 6.8, CH_3), 1.07–1.72 (several m, 6 H, CH_2), 2.68 (br d, J 3.6, 1 H), 3.00 (br d, J 4.3, 1 H), 3.34 (sept, J 7.0, 1 H), 3.66 (d, J 9.0, 1 H), 3.91 (d, J 9.0, 1 H), 4.61 (sept, J 6.8, 1 H), 7.65 (m, 2 H), 8.34 (m, 2 H) (aryl); δ_C(62.9 MHz; CD_3CN) 19.4, 19.8, 21.1, 22.4, 24.8, 29.2, 30.7, 34.6, 43.1, 45.0, 58.1, 59.9, 75.5 (CH_3, CH_2, CH), 126.6, 128.7 (br), 149.2 (br), 153.1 (aryl), 183.1 (C=N).

4,5-Dihydro-5,5-dimethyl-2-(2,4,6-trichlorophenyl)-1*H*-pyrazol-2-ium hexachloroantimonate 6a

Title compound **6a** was obtained as a colourless powder (4.04 g, 66%) by slow precipitation of **4a** (6.13 g, 10 mmol) from MeCN (30 ml)–Et_2O (100 ml) and workup of the mother liquor; mp 134–136 °C (decomp.) (Found: C, 21.58; H, 2.21; N, 4.51. $C_{11}H_{12}Cl_9N_2Sb$ (M = 613.1) requires C, 21.55; H, 1.97; N, 4.57%); ν_{max}(KBr)/cm^{-1} 1562 (br), 3280 (NH); δ_H(250 MHz; CD_3CN) 1.54 (2 CH_3), 3.55 (d, J 2.1, 2 H4), 7.35 (br, NH), 7.79 (s, aryl), 8.35 (t, J 2.1, H3); δ_C(62.9 MHz; CD_3CN) 27.2 (2 CH_3), 48.6 (C4), 64.6 (C5), 130.5, 130.7, 133.3, 140.5 (aryl), 165.4 (C3).

3-Butyl-4,5-dihydro-5,5-dimethyl-2-(2,4,6-trichlorophenyl)-1*H*-pyrazol-2-ium hexachloroantimonate 6c

A solution of **4c** (6.69 g, 10 mmol) in CH_2Cl_2 (20 ml)–MeCN (10 ml) was stirred at 23 °C for 30 min. *Title compound* **6c** was precipitated as a colourless powder (3.74 g, 56%) by slow addition of Et_2O (100 ml); mp 133–136 °C (decomp.) (Found: C, 26.78; H, 3.14; N, 4.00. $C_{15}H_{20}Cl_9N_2Sb$ (M = 669.2) requires C, 26.92; H, 3.01; N, 4.19%); ν_{max}(KBr)/cm^{-1} 1560, 1570, 1640, 3240 (NH); δ_H(250 MHz; CD_3CN) 0.88 (t, J 7.3, CH_3), 1.34 (m, CH_2), 1.50 (2 CH_3), 1.64 (m, CH_2), 2.53 (t, J 8.0, CH_2), 3.52 (s, 2 H4), 7.07 (br, NH), 7.82 (s, aryl); δ_C(62.9 MHz; CD_3CN) 13.8, 23.2, 27.2, 28.4, 30.4, 49.8 (CH_3, CH_2), 62.4 (C5), 128.8, 131.2, 133.5, 140.7 (aryl), 181.1 (C3).

3-Chloro-4,5-dihydro-5,5-dimethyl-2-(2,4,6-trichlorophenyl)-1*H*-pyrazol-2-ium hexachloroantimonate 6d

A solution of **4d** (6.48 g, 10 mmol) in CH_2Cl_2 (10 ml)–MeCN (4 ml) was stirred at 23 °C for 30 min. *Title compound* **6d** was precipitated as a yellow powder (4.06 g, 63%) by slow addition of Et_2O (60 ml); mp 139–140 °C (decomp.) (Found: C, 20.41; H, 1.92; N, 4.35. $C_{11}H_{11}Cl_{10}N_2Sb$ (M = 647.5) requires C, 20.40; H, 1.71; N, 4.33%); ν_{max}(KBr)/cm^{-1} 1568, 1625, 3240 (NH); δ_H(250 MHz; CD_3CN) 1.61 (2 CH_3), 3.86 (d, J 1.4, 2 H4), 7.52 (br, NH), 7.85 (s, aryl); δ_C(62.9 MHz; CD_3CN) 27.5 (2 CH_3), 51.4 (C4), 64.2 (C5), 127.8, 131.2, 133.2, 141.5 (aryl), 165.2 (C3).

4,5-Dihydro-3,4,5,5-tetramethyl-2-(2,4,6-trichlorophenyl)-1*H*-pyrazol-2-ium hexachloroantimonate 6j

A solution of **4k** (6.41 g, 10 mmol) in CH_2Cl_2 (10 ml)–MeCN (4 ml) was stirred at 23 °C for 30 min. Precipitation by slow addition of Et_2O (60 ml) afforded a brown powder, which was reprecipitated from CH_2Cl_2 (10 ml)–MeCN (4 ml)–Et_2O (40 ml) to afford *title compound* **6j** as a colourless powder (1.54 g, 24%); mp 117–118 °C (decomp.) (Found: C, 24.12; H, 2.50; N, 4.66. $C_{13}H_{16}Cl_9N_2Sb$ (M = 641.1) requires C, 24.36; H, 2.52; N, 4.37%); ν_{max}(KBr)/cm^{-1} 1565, 1578, 1652, 3270 (NH); δ_H(250 MHz; CD_3CN) 1.36 (CH_3), 1.40 (d, J 7.5, CH_3), 1.49 (CH_3), 2.34 (d, J 0.6, CH_3), 3.55 (q, J 7.5, H4), 7.06 (br, NH), 7.81 (s, aryl); δ_C(62.9 MHz; CD_3CN) 10.3 (CH_3), 15.7 (CH_3), 21.2 (CH_3), 26.8 (CH_3), 54.9, 65.5 (C4, C5), 128.6, 131.1, 131.3, 133.5, 133.6, 140.7 (aryl), 181.2 (C3). Correspondingly, compound **6j** was obtained from **4j**.

4,5-Dihydro-5,5-dimethyl-3-phenyl-2-(2,4,6-trichlorophenyl)-1*H*-pyrazol-2-ium tetrachloroaluminate 6ab

From **2a** (2.86 g, 10 mmol) and styrene (1.04 g, 10 mmol). *Title compound* **6ab** was precipitated as a pale yellow powder (4.54 g, 87%) by slow addition of Et_2O (80 ml); mp 130–136 °C (decomp.) (Found: C, 38.94; H, 3.50; N, 5.06. $C_{17}H_{16}AlCl_7N_2$ (M = 523.5) requires C, 39.00; H, 3.08; N, 5.35%); δ_H(250 MHz; CD_3CN) 1.61 (2 CH_3), 4.00 (2 H4), 7.24 (br, NH), 7.45, 7.54, 7.74 (several m, phenyl), 7.80 (s, aryl); δ_C(62.9 MHz; CD_3CN) 27.0 (2 CH_3), 50.1 (C4), 62.4 (C5), 125.0, 130.4, 130.6, 131.0, 131.6, 133.4, 137.1, 140.8 (aryl), 169.8 (C3).

3-(Chloromethyl)-5-ethyl-2-(2,4,6-trichlorophenyl)-1*H*-pyrazol-2-ium hexachloroantimonate 7ac

From **2ac**[46] (3.20 g, 10 mmol) and allyl chloride (0.92 g, 12 mmol). Precipitation with pentane (100 ml) afforded a pale brown powder, which was crystallized at −15 °C from hot $CHCl_3$ (30 ml) (evolution of HCl) to furnish *title compound* **7ac** as a colourless powder (4.83 g, 73%); mp 185–188 °C (decomp.) (Found: C, 21.86; H, 1.65; N, 4.14. $C_{12}H_{11}Cl_{10}N_2Sb$ (M = 659.5) requires C, 21.85; H, 1.68; N, 4.25%); ν_{max}(CH_2Cl_2)/cm^{-1} 1557, 1571, 3199 (br, NH); δ_H[250 MHz; CD_3CN–$CDCl_3$ (1 : 1)] 1.44 (t, J 7.6, CH_3), 3.02 (q, J 7.6, CH_2), 4.55 (s, CH_2), 7.02 (H4), 7.75 (s, aryl), 12.13 (br, NH); δ_C[62.9 MHz; CD_3CN–$CDCl_3$ (1 : 1)] 11.9 (CH_3), 19.9 (CH_2), 33.0 (CH_2), 109.3, 126.3, 130.2, 136.0, 141.1, 148.2, 155.8 (C3, C4, C5, aryl).

3-Ethyl-2,4,5,6-tetrahydro-1-(2,4,6-trichlorophenyl)cyclopentapyrazolium hexachloroantimonate 7ad

From **2ac** (3.20 g, 10 mmol) and cyclopentene (0.82 g, 12 mmol). Precipitation with pentane (200 ml) afforded a dark brown powder, which was crystallized at −15 °C from MeCN (8 ml)–Et_2O (60 ml) to furnish *title compound* **7ad** as a grey powder (3.60 g, 52%); mp 132–134 °C (decomp.) (Found: C, 26.05; H, 2.14; N, 4.19. $C_{14}H_{15}Cl_{10}N_2Sb$ (M = 687.6) requires C, 25.83; H, 2.17; N, 4.30%); ν_{max}(CH_2Cl_2)/cm^{-1} 1506, 1557, 1571, 3232 (br, NH); δ_H(250 MHz; CD_3CN) 1.34 (t, J 7.6, CH_3), 2.59–2.87 (several m, 3 CH_2), 2.88 (q, J 7.6, CH_2), 7.82 (s, aryl), 12.59 (br, NH); δ_C(62.9 MHz; CD_3CN) 11.7 (CH_3), 19.8, 24.0, 25.4, 30.5 (CH_2), 128.8, 129.2, 130.6, 136.1, 140.4, 149.7, 161.3 (C3, C3a, C6a, aryl).

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