Heteroatom Chemistry
Volume 16, Number 5, 2005

2-Halogeno-1,3,2-diazaarsolenes and 2-Halogeno-1,3,2-diazastibolenes: Examples for Spontaneous E—X Bond Heterolysis or Not?

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Received 12 December 2004; revised 25 January 2005

ABSTRACT: *2-X-1,3,2-diazaarsolenes and 2-X-1,3,2-stibolenes (X = Cl, Br) were prepared from appropriate α-amino-aldimine precursors via transamination with $ClSb(NMe_2)_2$ or via base-induced dehydrohalogenation with EX_3 (E = As, Sb). The products were further converted into 2-iodo-derivatives via halide exchange with Me_3SiI, or into 1,3,2-diazaarsolenium or 1,3,2-stibolenium salts via halide abstraction using $E'X_3$ (E′ = Al, Ga, Sb) or Me_3SiOTf. All compounds synthesized were characterized by spectroscopic data and several of them by single-crystal X-ray diffraction studies. The results of these investigations confirmed that diazaarsolenium or stibolenium cations are stabilized by similar π-delocalization effects as the corresponding diazaphospholenium cations. 2-Halogeno-1,3,2-diazaarsolenes and 2-halogeno-132-stibolenes are best addressed as molecular species whose covalent E—X bonds are as in 2-chloro-diazaphospholenes weakened by intramolecular $\pi(C_2N_2) \rightarrow \sigma^*(E—X)$ and, in the case of the Sb-containing heterocycles, intermolecular $n(X') \rightarrow \sigma^*(E—X)$ hyperconjugation between the σ^* (E—X) orbital and a lone-pair of electrons on the halogen atom of a neighboring molecule. Correlation of structural and spectroscopic data and the evaluation of halide transfer reactions allowed to conclude that the extent of E—X bond weakening in the 2-X-substituted heterocycles decreases and thus the Lewis acidity of the cations increases, with increasing atomic number of the pnicogen atom.* Heteroatom Chem 16:327–338, 2005; DOI 10.1002/hc.20098

INTRODUCTION

Cations containing a positively charged, low-coordinate group-15 element (**I**) have, since the discovery of the first stable phosphenium ions (**I**, E = P) [1,2] some 30 years ago, remained in the focus of research [3]. A great deal of the interest in these species was—and still is—initiated by their capability to act as ligands in transition metal complexes with similar molecular and electronic structures as Fischer-carbene complexes [4], and in particular to stabilize electrophilic complexes with late metal atoms [5,6]. Although the major part of work has been dedicated to phosphenium ions [1], cations with other group-15 elements were also studied, and today stable cations centered at dicoordinate nitrogen (**I**, E = N [7]), arsenic (**I**, E = As [8–10]), antimony (**I**, E = Sb [11]), and bismuth atoms (**I**, E = Bi [11]) are known as well (Scheme 1).

The electronic stabilization of the formally electron deficient two-coordinate central atom in **I** is most easily achieved by interaction with adjacent

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Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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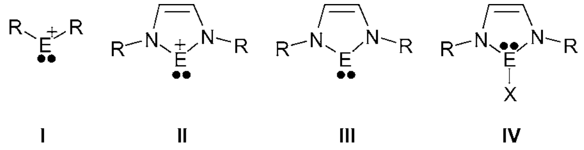


SCHEME 1 Structural types of carbene-analogue cations centered at dicoordinate pnicocen atoms.

π-donor substituents [3,4,12], and practically all stable cations known carry one or two amino (NR'_2) or thiolato (SR') groups. It is known for some time that the mesomeric stabilization in a phosphenium ion can be further enhanced by incorporating the dicoordinate phosphorus atom into the framework of a 1,3,2-diazaphospholenium ring, thus giving rise to cyclic cations **II** (E = P) [14–17] with the same valence electron count, and a closely similar electronic structure, as neutral imidazoyl carbenes (**III**). We have shown recently that, as a consequence of the enhanced π-stabilization, diazaphospholenium cations are more stable and less Lewis acidic than other structural types of phosphenium ions [17], but retain their capability to act as ambiphilic ligands and form carbene-analogue transition metal complexes [18].

Although the adaptation of the imidazoylcarbene like molecular architecture to cations **II** with other elements than phosphorus seems straightforward, few examples of well characterized salts with these cations have in fact been reported so far. Boche et al. described the synthesis and structural characterization of a nitrenium ion (**II**, E = N) [7]. Efforts to access analogous cations with heavier group-15 element are to the best of our knowledge confined to a single report by Cowley et al. [16] who isolated crystals representing a mixture of a pentachlorogermanate salt with a cation **II** (E = As), and a 2-chloro-1,3,2-diazaarsolene (**IV**, E = As, X = Cl), from the reaction of a germylene precursor with $AsCl_3$. Even though the existence of cations **II** (E = As) was in principle established by a single-crystal X-ray diffraction study, the presence of different anionic fragments precluded a clear interpretation of the bonding situation; furthermore, the claimed formation of phosphenium and arsenium cations **II** by spontaneous E–Cl bond heterolysis appears disputable in the light of more recent studies in the phosphenium system [17].

Having recently communicated the synthesis of the first stable stibolenium cation **II** (E = Sb) and its unprecedented oxidative ring cleavage [19], we want in this place to give a full account on the synthesis and structural data of salts of genuine As- and Sb-centered cations of type **II**, and the corresponding 2-halogeno-substituted precursors **IV** (E = As, Sb; X = Cl, Br, I). Structure correlation between different species with related constitution in combination with spectroscopic studies will allow us to discuss trends in E–X bond lengthening and Lewis acidity of the cations **II** (E = As, Sb), and address the question of "spontaneous bond heterolysis" in these compounds in more detail.

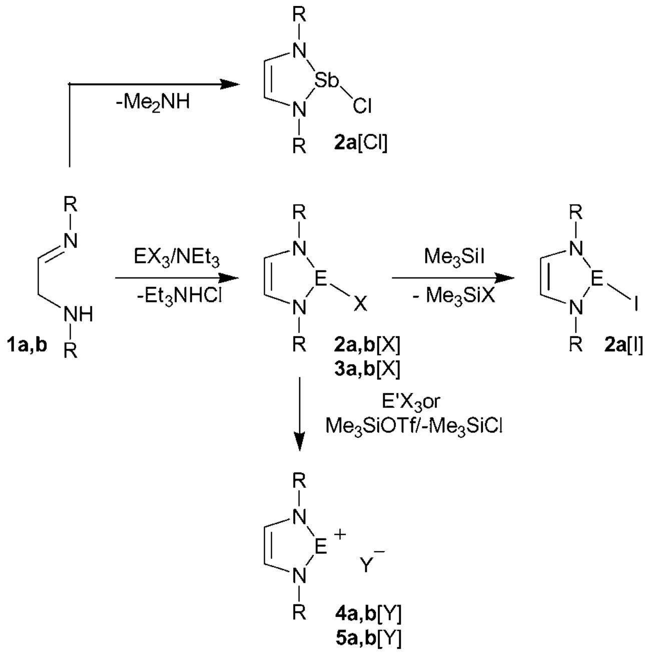
RESULTS AND DISCUSSION

Reactions

Whereas P- and As-containing heterocycles **IV** (E = P, As) are readily prepared from diazadienide metal salts and PCl_3 or $AsCl_3$ via salt elimination [16], reactions of the diazadienides with $SbCl_3$ proceeded in a similar manner as with $SnCl_2$ [20] by electron transfer to give diazadienes and elemental Sb. By analogy to the synthesis of the stannylenes **III** (E = Sn) [20], the 1,3,2-diazastibolenes **2a,b**[Cl] were successfully accessed, however, by transamination of $ClSb(NMe_2)_2$ with the α-aminoaldimines **1a,b**; alternatively, **2a**[Cl] was available from the reaction of **1a** with $SbCl_3$ in the presence of NEt_3 as acid scavenger. Using the same scheme (as in Scheme 2), the 1,3,2-diazaarsolenes **3a,b**[Cl] were prepared from **1a,b** and $AsCl_3/NEt_3$, and reacting the α-aminoaldimine complex **1a**·LiBr with $SbBr_3/NEt_3$ gave the 2-bromo-1,3,2-diazastibolene **2a**[Br]. Finally, the 2-iodo-1,3,2-diazastibolene **2a**[I] was accessed from **2a**[Cl] via halide exchange with Me_3SiI. Treatment of α-aminoaldimines with $BiCl_3/NEt_3$ afforded black reaction mixtures in which diazadienes were identified as the only products detectable by ^1H NMR spectroscopy. All products were isolated in 40–60% yield as orange-red, air and moisture sensitive solids. Conversion of **2a,b**[Cl] and **3a,b**[Cl] into the salts **4a**[Y] (Y = SO_3CF_3, $AlCl_4$, $GaCl_4$, or $SbCl_4$) and **5a,b**[SO_3CF_3], respectively, was achieved by Lewis acid induced As–Cl or Sb–Cl cleavage, using $Me_3SiOSO_2CF_3$, $AlCl_3$, $GaCl_3$, or $SbCl_3$ as chloride acceptor. The salts were isolated in 50–93% yield (after crystallization from Et_2O/MeCN as yellow (Sb-compounds) or colorless (As-compounds), air and moisture sensitive crystalline solids. Characterization of the products was accomplished by analytical and spectroscopic data and, in some cases, by single-crystal X-ray diffraction studies.

Spectroscopic Studies

The ^1H and ^{13}C NMR data (see Experimental section) of **2a,b**[Cl] and **3a,b**[Cl] are closely similar to those of the phosphorus analogues **6a,b**[Cl] [15–17].



	2a, 4a	2b, 4b	3a, 5a	3b, 5b
E	Sb	Sb	As	As
R	tBu	Mes	tBu	Mes

SCHEME 2 Syntheses of 1,3,2-diazastibolene and 1,3,2-diazaarsolene compounds (X = Cl, Br; E′X3 = $AlCl_3$, $GaCl_3$, $SbCl_3$; Y = $AlCl_4$, $GaCl_4$, $SbCl_4$, OTf.

The signals of the hydrogen substituents at the five-membered heterocycles show slight but continuous deshieldings when going from the phosphorus via the arsenic to the antimony compound, whereas formal exchange of the halide substituent in **2a**[X] (X = Cl, Br, I) has hardly any effect. The ^{1}H and ^{13}C NMR signals of the atoms in the endocyclic C_2H_2 moieties of **4a,b**[SO_3CF_3], **5a,b**[SO_3CF_3] display a similar deshielding with respect to the 2-halogeno-substituted precursors as the phosphenium ions **6a,b**[SO_3CF_3] [15,17]. With the exception of the $\delta(^{1}H)$ values for the olefinic protons in *N*-^{t}Bu-substituted cations, which reveal a similar trend as the 2-halogeno-derivatives, formal exchange of the two-coordinate heteroatom in a cation induces only insignificant chemical shift variations.

^{15}N NMR studies disclosed that the chloride abstraction of a from **2a,b**[Cl], **3a,b**[Cl] is likewise accompanied by a deshielding of the ring nitrogen atoms by some 110 ppm, whereas formal exchange of the anion in a salt **4a**[Y] produced smaller, but still significant, variations in $\delta^{15}N$ of some 10 ppm (see Table 1). This anion dependence of $\delta^{15}N$ is complemented by shifts of $\delta^{1}H$ and $\delta^{13}C$ of the atoms in the adjacent C_2H_2 moiety which are still smaller in magnitude, but parallel in direction. Whereas the large decrease in nitrogen shielding upon chloride abstraction is consistent with the presence of improved π-conjugation in the cations, we attribute the anion dependence of $\delta^{15}N$ of the cation **4a** to the presence of residual cation–anion interactions which suggest a certain degree of ion-pairing in solution.

TABLE 1 ^{15}N NMR Data of 1,3,2-Diazastibolene and 1,3,2-Diazaarsolene Derivatives **2a,b**[Cl], **3a,b**[Cl], **4a,b**[Y], **5a,b**[OTf]

	Solvent	*$\delta(^{15}N)$*
2a[Cl]	C_6D_6	−208.9
2b[Cl]	C_6D_6	−219.5
3a[Cl]	C_6D_6	−206.0
3b[Cl]	C_6D_6	−235.7
4a[OTf]	CD_3CN	−84.6
4a[$AlCl_4$]	CD_3CN	−91.8
4a[$GaCl_4$]	CD_3CN	−102.2
4a[$SbCl_4$]	CD_3CN	−94.5
4b[OTf]	CD_3CN	−99.6
5a[OTf]	CD_3CN	−99.6
5b[OTf]	CD_3CN	−116.9

As it had been shown that frequency shifts of the ν(C=C) vibrational mode provide a sensitive probe for monitoring the phosphorus–halogen bonding in the 1,3,2-diazaphospholenes **6a**[X] (X = F, Cl, Br) and helped to distinguish the covalent nature of these compounds from the ionic constitution of the salt **7a**[BF_4][17], we conducted comprehensive IR and Raman spectroscopic studies of **2a**[X] (X = Cl, Br, I), **3a**[Cl], **4a**[Y] (Y = SO_3CF_3, $AlCl_4$, $GaCl_4$, $SbCl_4$), and **5a**[SO_3CF_3]. Comparison of the ν(C=C) values (Table 2) for the cations in the salts

TABLE 2 Wavenumbers of the $\tilde{\nu}$(C=C) Normal Modes (in cm^{-1}) in the IR and Raman Spectra of 1,3,2-Diazastibolene, 1,3,2-Diazaarsolene, and 1,3,2-Diazaphospholene Derivatives

	ν(C=C) (cm^{-1})	
	IR	*Raman*
2a[Cl]	1568[a]	1569
2a[Br]	1558[a]	1559
2a[I]	1539[b]	1549
3a[Cl]	1556[a]	1556
6a[Cl][17]	1560[b]	1560
4a[$AlCl_4$]	1509[a]	1509
4a[$GaCl_4$]	1509[a]	1508
4a[$SbCl_4$]	1512[a]	1513
4a[OTf]	1512[a]	1512
5a[OTf]	1526[a]	1529
7a[BF4][17]		1527

[a] As nujol mull.
[b] As KBr pellet.

4a[SO$_3$CF$_3$]/**5a**[SO$_3$CF$_3$]/**7a**[BF$_4$] showed a systematic shift to lower frequencies with increasing atomic weight of the heteroatom. As the ν(C=C) frequencies in different salts **4a**[Y] show no significant deviations and the band patterns attributable to the anions in **4a**[AlCl$_4$] and **4a**[GaCl$_4$] (see Table 2; assignment was feasible by comparison of the spectra with each other and the literature data of tetrachloroaluminate and tetrachlorogallate salts [21]) gave no evidence for substantial perturbations of the local symmetry, it can be concluded that strong intermolecular interactions in the solid state are presumably absent.

The ν(C=C) bands in the chloro-derivatives **2a**[Cl]/**3a**[Cl]/**6a**[Cl] display marked blue shifts with respect to the corresponding cations; the frequencies of these bands are similar for the P- and As-compounds but still higher for the Sb-compound. Increasing atomic weight of the halogen is associated with red shifts in both the diazaphospholene (**6a**[F]/**6a**[Cl]/**6a**[Br]) and diazastibolene systems (**2a**[Cl]/**2a**[Br]/**2a**[I]) whose variation is much less pronounced than the difference between the halogen-substituted and cationic heterocycles. Although it can currently not be decided if the variations in ν(C=C) between P-, As-, and Sb-containing species reflect simply the change in molecular masses, or changes in C=C force constants resulting from angular distortion of the five-membered rings due the different size of the heteroatom and a varying degree of π-delocalization, the marked difference in ν(C=C) between each cation and the corresponding 2-halogen-substituted heterocycle suggests [17] that the latter must in all cases be considered a molecular compound with a substantial degree of covalent element—halogen bonding. This is corroborated by the appearance of an additional band at 150 cm^{-1} in the Raman spectrum of **2a**[Cl] which was assigned to the ν(Sb—Cl) stretch mode (the ν(Sb—X) modes in **2a**[Br] and **2a**[I] are expected to appear at still lower frequencies and could not be securely identified) [22]; the marked red shift of this absorption as compared to a value of 308 cm^{-1} for ClSb(NMe$_2$)$_2$ [23] suggests a similar weakening of the E—halogen bond in the 1,3,2-diazastibolene (E = Sb) as had previously been established for 1,3,2-diazaphospholenes (E = P) [17]. Although being far from a quantitative interpretation, we believe that the opposite trends in the changes of ν(C=C) for cations and chloro-derivatives (replacement of a lighter by a heavier group-15 element induces a red shift of ν(C=C) in the cations and a blue shift in the chloro-derivatives) indicate that the extent of this bond weakening decreases (i.e. the E—Cl bonds tighten) in the higher homologues.

Crystal Structure Studies

Single-crystal X-ray diffraction studies were carried out for the 2-halogeno-1,3,2-diazastibolenes **2a**[Cl] [19] and **2a**[Br], the 1,3,2-diazaarsolene **3a**[Cl], and the salts **4a**[Y] (Y = SO$_3$CF$_3$, SbCl$_4$) [19] and **5b**[SO$_3$CF$_3$]. Selected bond lengths are listed together with the appropriate data of the phosphorus compounds **6a**[Cl] and **7a**[BF$_4$] [17] in Table 3. A representation of the unit cell of **2a**[Cl] is displayed in Fig. 1, and the molecular structures of individual heterocyclic molecules or ions are shown in Figs. 2–4.

Crystals of **2a**[Cl] and **2a**[Br] are isomorphous (space group *Pbca*, no. 61) and are composed of molecular units whose Sb atoms display intermolecular contacts to a halogen atom of a neighboring

TABLE 3 Selected Bond Distances in 1,3,2-Diazastibolene, 1,3,2-Diazaarsolene, and 1,3,2-Diazaphospholene Derivatives

	E	*E–N*	*N–C*	*C=C*	*E–X*
2a[Cl] [19]	Sb	1.998(4) 2.000(4)	1.407(6) 1.391(6)	1.346(6)	2.6460(15)
2a[Br]	Sb	1.998(2) 1.994(3)	1.386(4) 1.391(4)	1.346(4)	2.9433(4)
4a[OTf] [19]	Sb	2.018(2) 2.020(2)	1.354(3) 1.349(3)	1.364(4)	
4a[SbCl$_4$] [19]	Sb	2.023(2) 2.025(2)	1.356(3) 1.353(3)	1.364(4)	
3a[Cl]	As	1.8045(12) 1.8057(12)	1.382(2) 1.383(2)	1.348(2)	2.6527(4)
5b[OTf]	As	1.8377(14) 1.8271(13)	1.346(2) 1.352(2)	1.362(2)	
6a[Cl] [17]	P	1.6628(8) 1.6651(8)	1.3912(12) 1.3913(12)	1.3485(14)	2.6915(4)
7a[BF$_4$] [17]	P	1.6579(14) 1.6654(14)	1.368(2) 1.370(2)	1.353(2)	

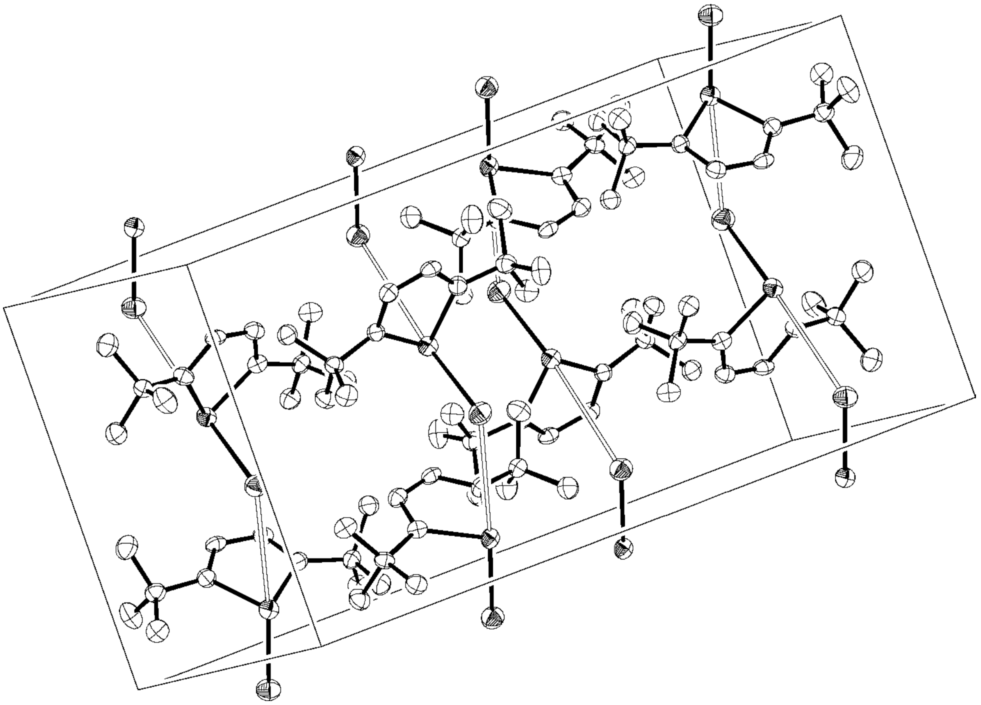


FIGURE 1 Representation of the unit cell of **2a**[Cl]. Hydrogen atoms omitted for clarity. Thin lines represent intermolecular Sb ··· Cl contacts shorter than the sum of van-der-Waals radii.

molecule, leading to the formation of one-dimensional stacks of molecules connected by zig-zag chains of pairs of Sb and halogen atoms (Fig. 1). The secondary Sb···X contacts (**2a**[Cl]: 3.862 Å; **2a**[Br]: 3.581 Å) are longer than the primary Sb—X bond but well below the sum of van-der-Waals radii (Sb···Cl 4.00 Å, Sb···Br 4.15 Å). Quite interestingly, although the individual intra- and intermolecular Sb···X distances differ in both structures, their sums are nearly identical (X···X 6.50 ± 0.05 Å, Sb···Sb 5.50 ± 0.05 Å). The As-compound **3a**[Cl] crystallizes likewise in the same space group as **2a**[Cl], but the two compounds are no isomorphs but differ in the packing of molecules in the crystal. As in **6a**[Cl] [17] there is no evidence for intermolecular interactions shorter than the sum of van-der-Waals radii.

The five-membered C_2N_2E rings (E = As, Sb) in **2a**[Cl], **2a**[Br] (Fig. 2) and **3a**[Cl] (Fig. 3) are planar and resemble in this respect more closely the molecular structure of the cation **7a** rather than neutral **6a**[Cl]. The nitrogen atoms exhibit planar and the antimony and arsenic atoms pyramidal coordination geometries with angles between the E—X bonds and the mean C_2N_2E planes ranging from 99–100° (E = Sb) to 105° (E = As). The endocyclic C=C and C—N distances are similar in all three molecules and differ not significantly from those in **6a**[Cl] (Table 3); as there, the C=C bonds are clearly longer

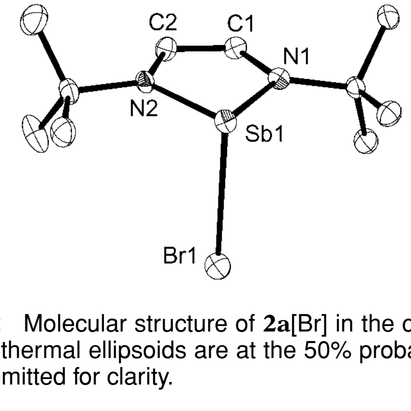


FIGURE 2 Molecular structure of **2a**[Br] in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity.

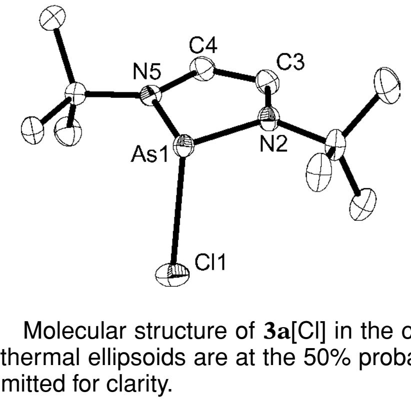


FIGURE 3 Molecular structure of **3a**[Cl] in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity.

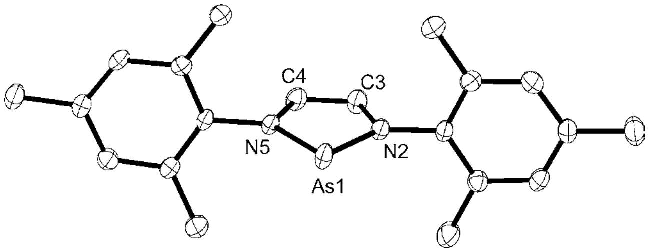


FIGURE 4 Molecular structure of the cation of **5b**[OTf] in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity.

and the C—N bonds shorter as compared to standard distances (C=C 1.322–1.326 Å, C—N 1.457–1.487 Å [24]). The Sb—N bonds in **2a**[X] compare to those in *cyclo*-[$Me_2Si(N\textit{t}Bu)_2SbCl$] (**8**, 1.995(5) Å [11]) and the As—N bonds in **3a**[Cl] lie at the lower end of the known range of As—N distances in diaminochloroarsines (1.84 ± 0.04 Å [25]). In contrast, the E—Cl bond distances in **2a**[Cl] and **3a**[Cl] exceed those in **8** (2.472(3) Å [11]) and the corresponding As-heterocycle, *cyclo*-[$Me_2Si(N\textit{t}Bu)_2AsCl$] (As—Cl 2.345(1) Å [11]), by 7% and 13%, respectively.

The crystals of **4a**[SO_3CF_3] [19] and **5b**[SO_3CF_3] (Fig. 4) are composed of well-separated heterocyclic cations and triflate anions and contain one solvent molecule (CH_2Cl_2 or Et_2O) per formula unit; **4a**[$SbCl_4$] [19] features cations that are indistinguishable from those in the triflate salt, and $Sb_2Cl_8^{2-}$ dianions. The latter are formed by interaction of two $SbCl_4^-$ monoanions via chloride bridges and appear as centrosymmetric dimers whose structural features resemble those of the anions in other known tetrachloroantimonates, e.g. [$\textit{n}Pr_4N$][$SbCl_4$] [26]. The 1,3,2-diazastibolenium ions in **4a**[Y] exhibit several contacts to oxygen and chlorine atoms of adjacent anions or solvent molecules (Sb ⋯ Cl 3.43–3.94 Å, Sb ⋯ O 3.17–3.43 Å) which are shorter than the sum of van-der-Waals radii (Sb ⋯ Cl 4.00 Å, Sb ⋯ O 3.70 Å) but substantially longer than the intermolecular contacts in [*cyclo*-$Me_2Si(N\textit{t}Bu)_2Sb$][$AlCl_4$] (3.04–3.07 Å [11]). The occurrence of a single, rather short, As ⋯ O contact (2.66 Å) in **5b**[SO_3CF_3] is presumably due to electrostatic effects and indicates no specific Lewis acid/base interaction as the As ⋯ O vector lies in the plane of the heterocyclic ring.

The heterocyclic rings in the cations **4a** and **5b** are planar, and the equalization of C=C and C—N bonds (Table 3) is more pronounced than in **2a** and **3a** and exceeds even that in the diazaphospholenium cation **7a** (the results of structural studies in the diazaphospholenium system [17] suggest that the effect of different substituents in the As-compounds can presumably be neglected). The E—N bonds in **4a** and **5b** are slightly longer than in **2a** and **3a** although the deviations are on the verge of being insignificant.

On the whole, the observed structural data indicate that π-conjugation effects in 1,3,2-diazastibolenium and diazaarsolenium cations are of comparable importance and, as judged by the coincidence in the degree of bond length equalization, occur to a similar extent, as in 1,3,2-diazaphospholenium ions. The trend in intermolecular Sb ⋯ Cl interactions in solid **2a**[$SbCl_4$] and [*cyclo*-$Me_2Si(N\textit{t}Bu)_2Sb$][$AlCl_4$] suggests that this enhanced π-conjugation might provide for an enhanced thermodynamic stability, and thus correlate with an appropriate reduction in Lewis acidity, of the cations.

The endocyclic bond lengths in 2-halogeno-substituted 1,3,2-diazastibolenes and 1,3,2-arsolenes **2a**[X] and **3a**[Cl] show a similar deviation from those in genuine cations as had been observed in the diazaphospholene system [17]. This suggests clearly that the diazaarsolene **3a**[Cl] should not be formulated as ionic species [16] but rather as a molecular compound, and that the observed residual equalization of endocyclic C=C and C—N bonds and the lengthening of the exocyclic As—Cl bond is best explained in the same way as for the lighter homologue **6a**[Cl] [17] as a consequence of $\pi(C_2N_2) \rightarrow \sigma^*(E\text{—}X)$ hyperconjugation. Using the same terminology, the solid-state structures of the diazastibolenes **2a**[X] are rationalized as the product of both intramolecular $\pi(C_2N_2) \rightarrow \sigma^*(E\text{—}X)$ and intermolecular $n(X') \rightarrow \sigma^*(E\text{—}X)$ hyperconjugation between the $\sigma^*(E\text{—}X)$ orbital and a lone pair of electrons on the halogen atom of a neighboring molecule. The surprising result that the E—Cl bonds in **2a**[Cl], **3a**[Cl], and **6a**[Cl] become continuously *shorter* with increasing atomic radius of the pnicogen atom may be explained if one assumes that the diazaarsolenium and diazastibolenium ions are stronger chloride acceptors, and thus stronger Lewis acids, than the diazaphospholenium ion.

Determination of Lewis Acidities

Determination of the equilibrium constant K_3 of a halide transfer reaction between a phosphenium ion $[R_2P]^+$ and a halogeno-phosphine $R'_2E\text{—}X$ (E = P, (3) in Scheme 3) offers a possibility for the theoretical [12,13] or experimental [17] evaluation of relative stabilities of the two cations $[R_2P]^+$ and $[R'_2P]^+$, respectively. As the halide transfer can be decomposed into two elementary dissociation reactions ((1), (2) in Scheme 3), the dissociation constant $K^{\mathrm{Diss}}(P\text{—}Cl)$ of one halogeno-phosphine (e.g. $R'_2P\text{—}X$) can be computed if K_3 and the dissociation constant

$$(1)\quad [R_2P]^+ + Cl^- \rightleftharpoons R_2P\text{–}Cl \qquad K_1 = 1/K^{Diss}(P\text{–}Cl)$$

$$(2)\quad R'_2E\text{–}Cl \rightleftharpoons [R'_2E]^+ + Cl^- \qquad K_2 = K^{Diss}(E\text{–}Cl)$$

$$(3)\quad [R_2P]^+ + R'_2E\text{–}Cl \rightleftharpoons R_2P\text{–}Cl + [R'_2E]^+ \qquad K_3 = \frac{c(R_2P\text{–}Cl)\cdot c([R'_2E]^+)}{c(R'_2E\text{–}Cl)\cdot c([R_2P]^+)} = \frac{K^{Diss}(E\text{–}Cl)}{K^{Diss}(P\text{–}Cl)}$$

SCHEME 3 Equations and equilibrium constants of halide transfer and bond dissociation reactions involving $[R_2E]^+$ cations and the corresponding neutral halogen derivatives, $R_2E\text{—}X$.

of the second one (e.g. $R_2P\text{—}X$) are known. Starting from the known dissociation constants of some 2-chloro-diazaphospholenes [17], we have now studied mixed chloride transfer reactions between P-, As-, and Sb-centered cations to assess the chloride acceptor strengths of diazastibolenes and diazaarsolenes. The reactions were simply performed by mixing the appropriate reactants in an inert solvent in an NMR tube. As the exchange rates are fast on the NMR time scale, ^1H (or ^{31}P) NMR spectra of these solutions display a single dynamically averaged set of signals for each $[R_2E]^+/R_2E\text{—}Cl$ pair and evaluating the shift of the observed signals with respect to the resonances of the pure reactants can be directly used to determine relative populations and compute equilibrium constants (see Experimental for a more detailed description).

Qualitative inspection of the spectra of a mixture prepared from equimolar amounts of the diazaphospholene **6a**[Cl] with the diazastibolenium salt **4b**[$AlCl_4$] suggested that complete transfer of a chloride to give **2a**[Cl] and the appropriate diazaphospholenium cation had occurred. Even if quantitative determination of the equilibrium constant K_3 (cf. Scheme 3) was precluded owing to partial decomposition of the sample, the outcome of the reaction allows us to state that the diazastibolenium ion **4b** is a stronger chloride acceptor than the P-centered cation **7a**. Similar results were obtained for the reaction of **6a**[Cl] with the diazaarsolenium salt **5b**[SO_3CF_3]. Here, quantitative evaluation of the equilibrium constant K_3 was feasible and yielded a value of $K^{Diss}(As\text{—}Cl) = 0.12(2) \times 10^{-3}$ mol/L for **3b**[Cl], as compared to $K^{Diss}(P\text{—}Cl) = 2.2(4) \times 10^{-3}$ mol/L for **6a**[Cl] [17]. The observed trend confirms the As-centered cation **5b** to be a stronger chloride acceptor, and thus less stable, than the diazaphospholenium ion **7a**. Even though this is in accord with the conclusions drawn from the molecular structure discussion, it contradicts the results of a previous study [8] where it was shown that diaminophosphenium ions are stronger Lewis acids than the corresponding As-centered cations.

CONCLUSIONS

It has been shown that the structural and spectroscopic properties of 2-halogeno-1,3,2-diazaarsolenes and 2-halogeno-1,3,2-diazastibolenes differ on one hand substantially from those of salts composed of 1,3,2-diazaarsolenium and 1,3,2-diazastibolenium cations and nucleofugic anions, whereas on the other hand each type of compounds shows close similarities to the corresponding 2-halogeno-1,3,2-diazaphospholenes and 1,3,2-diazaphospholenium ions. These findings suggest that (i) the bonding situation in the As- and Sb-containing heterocycles may not only be described as in the lighter homologues in terms of $\pi(C_2N_2) \rightarrow p(E)$ conjugation involving an empty p-orbital at the pnicogen atom in the cations, and in terms of $\pi(C_2N_2) \rightarrow \sigma^*(E\text{—}X)$ hyperconjugation in the 2-halogeno-derivatives but that the extent of π-delocalization in each type of compounds is practically independent of the nature of the pnicogen atom; (ii) 2-halogeno-diazaarsolenes and 2-halogeno-diazastibolenes should not be addressed as ionic species that are formed by spontaneous E—X bond heterolysis but as molecular compounds with a sizeable degree of covalent bonding between the pnicogen and halogen atoms. Although the structural and spectroscopic data give evidence that the E—X bond weakening due to $\pi(C_2N_2) \rightarrow \sigma^*(E\text{—}X)$ hyperconjugation (which is in the Sb-compounds augmented by additional contributions from intermolecular $n(X) \rightarrow \sigma^*(E\text{—}X)$ interactions) is *qualitatively* similar as in diazaphospholenes, a quantitative comparison of spectroscopic and structural data as well as relative chloride acceptor strengths indicates that the Lewis acidities of the heterocyclic cations and the strength of the E—Cl bonds increase with increasing atomic number of the pnicogen atom. Even if an explicit validation is not yet at hand, these findings can be seen as a further example for a growing tendency of species with progressively larger and softer Lewis acidic centers to form adducts with Lewis bases [27].

EXPERIMENTAL SECTION

General Remarks

All manipulations were carried out under dry argon. Solvents were dried by standard procedures. α-Aminoaldimines **1** or their LiX complexes were prepared as described [20]. NMR spectra: Bruker AMX300 (^{1}H: 300.1 MHz, ^{31}P 121.5 MHz, ^{13}C: 75.4 MHz, ^{15}N 30.1 MHz); chemical shifts referenced to ext. TMS (^{1}H, ^{13}C), 85% H_3PO_4 ($\Xi = 40.480747$ MHz), $MeNO_2$ ($\Xi = 10.136767$ MHz); ^{15}N chemical shifts were determined from ^{1}H,^{15}N HMQC spectra; positive signs of chemical shifts denote shifts to lower frequencies, and coupling constants are given as absolute values; prefixes *i*-, *o*-, *m*-, *p*- denote atoms of aryl substituents. MS: Kratos Concept 1H, Xe-FAB, m-NBA matrix. FT-IR spectra: Bruker IFS 113V, in Nujol mulls, KBr, or polethylene. Raman spectra: Bruker RFS 100. Elemental analyses: Heraeus CHNO-Rapid. Melting points were determined in sealed capillaries. Selected NMR and IR data are listed in Tables 1 and 2.

*2-Chloro-1,3-di-t-butyl-1,3,2-diazastibolene (**2a**[Cl])*

A solution of 4.15 g (18.2 mmol) of $SbCl_3$ in 10 mL of toluene was added dropwise to a stirred solution of 3.5 g (16.6 mmol) of **1a** · LiCl and 3.7 g (36.6 mmol) of NEt_3 in 20 mL of toluene. The reddish black solution formed was then stirred for additional 45 min at 50°C. The mixture was allowed to cool to ambient temperature, and volatiles were removed in vacuum. The residue was extracted with 20 mL of hexane and filtered. The filtrate was concentrated and stored overnight at −30°C. The orange-red crystalline precipitate formed was separated from the mother liquor by decantation and dried in vacuum to yield 2.2 g (41%) of **2a**[Cl] of mp 90°C (dec). Analysis: Calcd. For $C_{10}H_{20}N_2SbCl$: C 36.9 H 6.15 N 8.62; found: C 37.0 H 6.53 N 8.45.

^{1}H NMR (C_6D_6): $\delta = 6.60$ (2 H, C**H**), 1.25 (18 H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 119.5$ (C-4/5), 55.2 (**C**(CH$_3$)$_3$), 30.8 (C(**C**H$_3$)$_3$). MS (EI, 16eV, 150°C): *m/e* (%) = 324(85) [M$^+$], 289(85) [M$^+$—Cl], 232(50) [M$^+$—Cl—C$_4$H$_9$]. Raman: $\tilde{\nu} = 150$, 299, 396, 569, 690, 968, 1220, 1262, 1569, 2868, 2905, 2972, 3058 cm^{-1}. IR (KBr): $\tilde{\nu} = 3047$(w), 2955(vs), 1562(w), 1458(s), 1386(s), 1386(vs), 1255(vs), 1145(m), 1058(m), 964(m), 829(m), 686(s), 484 (s) cm^{-1}. IR (Nujol mull): $\tilde{\nu} = 3058$(w), 1568(w, νC=C) cm^{-1}

*2-Bromo-1,3-di-t-butyl-1,3,2-diazastibolene (**2a**[Br])*

A solution of 470 mg (1.30 mmol) of $SbBr_3$ in 10 mL of toluene was added dropwise to a stirred solution of 300 mg (1.17 mmol) of **1a** · LiBr and 270 mg (2.70 mmol) of NEt_3 in 10 mL of toluene. The reddish black solution formed was then stirred for additional 1 h at 50°C. The mixture was allowed to cool to ambient temperature, and volatiles were removed in vacuum. The residue was extracted with 15 mL of hexane and 5 mL of toluene and filtered. The filtrate was concentrated and stored overnight at −30°C. The orange-red crystalline precipitate formed was separated from the mother liquor by decantation and dried in vacuum to yield 200 mg (46%) of **2a**[Cl] of mp 90°C (dec). Analysis: Calcd. For $C_{10}H_{20}N_2SbBr$: C 32.47 H 5.45 N 7.58; found: C 33.52 H 5.75 N 7.56.

^{1}H NMR (C_6D_6): $\delta = 6.62$ (2 H, C**H**), 1.22 (18 H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 122.4$ (C-4/5), 57.3 (**C**(CH$_3$)$_3$), 31.9 (C(**C**H$_3$)$_3$). MS (EI, 16 eV, 150°C): *m/e* (%) = 386(4) [M$^+$], 289(100) [M$^+$—Br], 232(30) [M$^+$—Cl—C$_4$H$_9$]. Raman: $\tilde{\nu} = 157$, 570, 973, 1163; 1205, 1266, 1559, 1862, 2905, 2971, 3048 cm^{-1}. IR (KBr) : $\tilde{\nu} = 2955$(vs), 2850(m), 1595(w), 1546(w), 1497(s), 1488(s), 1313(m), 1210(vs), 1165(m), 1057(m), 1028(w), 704(s), 686(s), 487(m) cm^{-1}. IR (Nujol mull): $\tilde{\nu} = 3044$(w), 1558 (w, νC=C) cm^{-1}.

*1,3-Di-t-butyl-2-iodo-1,3,2-diazastibolene (**2a**[I])*

400 mg (2 mmol) of Me_3SiI was added dropwise via a syringe to a cooled (0°C) and stirred solution of 650 mg (2 mmol) of **2a**[Cl] in 20 mL of THF. The mixture was stirred for further 90 min at ambient temperature, concentrated in vacuum to a final volume of 10 mL and stored overnight at −30°C. The dark red crystalline precipitate was collected by filtration and dried in vacuum to give 300 mg (36%) of **2a**[I], mp 90°C (dec). Analysis: Calcd. For $C_{10}H_{20}N_2SbI$: C 28.81 H 4.83 N 6.72; found: C 28.79 H 5.15 N 6.60.

^{1}H NMR (C_6D_6): $\delta = 6.60$ (2 H, C**H**), 1.18 (18 H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 122.4$ (C-4/5), 56.3 (**C**(CH$_3$)$_3$), 29.4 (C(**C**H$_3$)$_3$). MS (EI, 16 eV, 150°C): *m/e* (%) = 416(9) [M$^+$], 289(100) [M$^+$—I]. Raman: $\tilde{\nu} = 129$, 158, 287, 570, 691, 970, 1042, 1202, 1223, 1262, 1549, 2862, 2903; 2968, 3042 cm−1. IR (KBr): $\tilde{\nu} = 3063$(w), 3028(w), 2952(s), 2850(m), 1539(s), 1458(s), 1387(m), 1358(vs), 1254(m), 1195(vs), 1160(s), 1057(m), 1026(w), 1013(s), 810(m), 710(s), 686(s) cm^{-1}.

*2-Chloro-1,3-dimesityl-1,3,2-diazastibolene (**2b**[Cl])*

4.91 g (20 mmol) of $ClSb(NMe_2)_2$ dissolved in 20 mL of toluene was added to a cooled solution (−78°C) of 5.88 g (20 mmol) of **1b**. The solution was then warmed to −40°C and $HNMe_2$ formed allowed to evaporate through a bubble counter. The mixture was slowly warmed to 40°C and kept at that temperature for 60–90 min until the color changed to black. The mixture was then allowed to cool to ambient temperature and filtered. The filtrate was concentrated in vacuum, layered with 15 mL of Et_2O, and stored for 1–2 days at −30°C. The orange-brown precipitate formed was separated from the mother liquor by decantation and dried in vacuum to yield 4.2g mg (47 %) of **2b**[Cl] of mp 80°C (dec).

^{1}H NMR (C_6D_6): $\delta = 6.79$ (4H, *m*-H), 6.38 (2 H, C**H**), 2.29 (12 H, *o*-CH_3), 2.13 (6 H, *p*-CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 140.1$ (*p*-C), 134.8 (*i*-C), 134.0 (*o*-C), 128.2 (*m*-C), 124.8 (C-4/5), 19.5 (*o*-CH_3), 17.6 (*p*-CH_3). MS (EI, 16eV, 150°C): *m/e* (%) = 448(20) [M^+], 413(16) [M^+—Cl], 277(100) [M^+—Cl—Sb—CH_3]. Raman: $\bar{\nu} = 157$, 570, 973, 1163; 1205, 1266, 1559, 1862, 2905, 2971, 3048 cm^{-1}.

*2-Chloro-1,3-di-t-butyl-1,3,2-diazarsolene (**3a**[Cl])*

3.81 g (21 mmol) of $AsCl_3$ was added dropwise to a cooled (10°C) solution of 3.83 g (18 mmol) of **1a** · LiCl and 3.94 g (39 mmol) of NEt_3 in 100 mL of toluene. The mixture was then warmed to 60°C and stirred for 3 h at this temperature. After allowing to cool to ambient temperature, the mixture was filtered, concentrated to a volume of 50 mL, and layered with 30 mL of Et_2O. The yellow brown precipitate formed was collected by filtration and dried in vacuum to yield 2.80 g (56 %) of **3a**[Cl] of mp 155°C.

^{1}H NMR (C_6D_6): $\delta = 6.36$ (2 H, C**H**), 1.29 (18 H, C(C**H**$_3$)$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 118.0$ (C-4/5), 55.7 (**C**(CH$_3$)$_3$), 29.3 (C(**C**H$_3$)$_3$). MS (EI, 16 eV, 150°C): *m/e* (%) = 278(40) [M^+], 243(100) [M^+—Cl]. Raman: $\nu = 559$, 984, 1163; 1195, 1267, 1556, 2909, 2974, 3066 cm^{-1}. IR (KBr) : $\nu = 2955$(vs), 2850(m), 1595(w), 1546(w), 1497(s), 1488(s), 1313(m), 1210(vs), 1165(m), 1057(m), 1028(w), 704(s), 686(s), 487(m) cm^{-1}. IR (Nujol mull): $\nu = 3041$(w), 1556 (w, νC=C) cm^{-1}.

*2-Chloro-1,3-dimesityl-1,3,2-diazarsolene (**3b**[Cl])*

5.88 g (20 mmol) of **1b**, 3.99 g (22 mmol) of $AsCl_3$, and 2.42 g (24 mmol) of NEt_3 were reacted in 100 mL of toluene as described above for **3a**[Cl] to give 3.50 g (44 %) of **3b**[Cl] of mp 200°C.

^{1}H NMR (C_6D_6): $\delta = 6.72$ (4H, *m*-H), 6.01 (2 H, C**H**), 2.32 (12 H, *o*-CH_3), 2.08 (6 H, *p*-CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 136.0$ (*p*—C), 135.7 (*i*-C), 134.8 (*o*-C), 128.6 (*m*-C), 120.2 (C-4/5), 19.5 (*p*-CH_3), 17.7 (*o*-CH_3). MS (EI, 16 eV, 150°C): *m/e* (%) = 402 (20) [M^+], 367(16) [M^+—Cl], 277(100) [M^+—Cl—As—CH_3].

*1,3-Di-t-butyl-1,3,2-diazastibolenium Tetrachloroaluminate (**4a**[AlCl$_4$])*

A suspension of 210 mg (1.55 mmol) of $AlCl_3$ in 10 mL of Et_2O was added dropwise to a stirred solution of 500 mg (1.55 mmol) of **2a**[Cl] in 20 mL of Et_2O. Stirring was continued for 1 h. The yellow precipitate formed was then filtered off, washed with Et_2O, and recrystallized from MeCN/Et_2O to give 500 mg (73%) of **4a**[$AlCl_4$] as yellow crystals of mp 173°C (dec).

^{1}H NMR (CD_3CN): $\delta = 8.57$ (2 H, C**H**), 1.78 (18 H, C(C**H**$_3$)$_3$). $^{13}C\{^1H\}$ NMR (CD_3CN): $\delta = 137.9$ (C-4/5), 62.4 (**C**(CH$_3$)$_3$), 32.0 (C(**C**H$_3$)$_3$). ^{27}Al NMR (CD_3CN): $\delta = 105.2$. MS (EI, 16 eV, 150°C): *m/e* (%) = 278(40) [M^+], 243(100) [M^+—Cl]. Raman: $\bar{\nu} =$ 121, 130, 165, 188, 233, 287, 347, 391; 479, 563, 679, 796, 923, 951, 1038, 1136, 1225, 1442, 1472, 1509, 2910, 2982, 3104 cm^{-1}. IR (nujol mull): $\bar{\nu} =$ 491(s), 518(w), 678(w), 722(w), 1191(m), 1205(m), 1509(m), 3089(w), 3104(w) cm^{-1}. IR (polyethylene): $\bar{\nu} = 491$(s), 377(m), 182(m), 177(m) cm^{-1}.

*1,3-Di-t-butyl-1,3,2-diazastibolenium Tetrachlorogallate (**4a**[GaCl$_4$])*

330 mg (1 mmol) of **2a**[Cl] and 180 mg (1 mmol) of $GaCl_3$ were reacted as described above for **2a**[$AlCl_4$] to give 350 mg (70%) of yellow crystals of **2a**[$GaCl_4$], mp 190°C (dec). Analysis: Calcd. for $C_{10}H_{20}N_2SbGaCl_4$: C 23.95 H 4.02 N 5.59; found: C 23.97 H 4.04 N 5.47.

^{1}H NMR (CD_3CN): $\delta = 8.49$ (2 H, C**H**), 1.70 (18 H, C(C**H**$_3$)$_3$). $^{13}C\{^1H\}$ NMR (CD_3CN): $\delta = 136.2$ (C-4/5), 62.5 (**C**(CH$_3$)$_3$), 31.5 (C(**C**H$_3$)$_3$). MS (EI, 16 eV, 150°C): *m/e* (%) = 278(40) [M^+], 243(100) [M^+—Cl]. Raman: $\bar{\nu} = 123$, 150, 188, 233, 287, 344; 369; 375, 391, 563, 678, 795, 922, 950, 1036, 1135, 1224, 1444, 1471, 1508, 2909, 2981, 3103 cm^{-1}. IR (nujol mull): $\bar{\nu} =$ 518(w), 678(w), 722(w), 770(m), 1205(m), 1509(m), 3089(m), 3103 (m) cm^{-1}. IR (polyethylene): $\bar{\nu} = 478$, 430, 375, 286, 188, 150 cm^{-1}.

*1,3-Di-t-butyl-1,3,2-diazastibolenium Tetrachloroantimonate (**4a**[SbCl$_4$])*

650 mg (2 mmol) of **2a**[Cl] and 460 mg (2 mmol) of $SbCl_3$ were reacted as described above for **2a**[$AlCl_4$]

to give 560 mg (51%) of yellow crystals of **2a**[$GaCl_4$], mp 130°C (dec).

^{1}H NMR (CD_3CN): $\delta = 8.57$ (2 H, C**H**), 1.71 (18 H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (CD_3CN): $\delta = 136.9$ (C-4/5), 62.7 (**C**(CH_3)$_3$), 31.5 (C(**C**H$_3$)$_3$). MS (EI, 16 eV, 150°C): *m/e* (%) = 278(40) [M^+], 243(100) [M^+—Cl]. Raman: $\bar{\nu} = 187$, 235, 343, 292, 243, 564, 951, 1513, 2973, 3098 cm^{-1}. IR (nujol mull): $\bar{\nu} = 515$(w), 668(w), 722(w), 774(w), 1191(m), 1224(m), 1512(w), 3096(w) cm^{-1}. IR (polyethylene): $\bar{\nu} = 343$(m), 290(m), 241(w) cm^{-1}.

*1,3-Di-t-butyl-1,3,2-diazastibolenium Triflate (**4a**[OTf])*

780 mg (3.5 mmol) of Me_3SiOTf was added dropwise to a stirred solution of 1.14 g (3.5 mmol) of **2a**[Cl] in 20 mL of Et_2O. Stirring was continued for 1 h. The yellow precipitate formed was then filtered off, washed with Et_2O, and recrystallized from MeCN/Et_2O to give 1.10 g (72%) of **4a**[OTf] as yellow crystals of mp 180°C (dec).

^{1}H NMR (CD_2Cl_2): $\delta = 8.62$ (2 H, C**H**), 1.78 (18 H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 138.5$ (C-4/5), 63.4 (**C**(CH_3)$_3$), 33.3 (C(**C**H$_3$)$_3$). MS (EI, 16 eV, 150°C): *m/e* (%) = 278(40) [M^+], 243(100) [M^+—Cl]. Raman: $\bar{\nu} = 168$, 194, 290, 310, 346, 393, 569, 684, 754, 800, 954, 1025, 1139, 1220, 1476, 1512 cm^{-1}. IR (nujol mull): $\nu = 515$(m), 639(s), 1147(m), 1195(w), 1223(m), 1512(w), 3083(vw) cm^{-1}. IR (polyethylene): $\bar{\nu} = 193$(m), 208(m), 295(m), 346(m), 379(s), 448(w) cm^{-1}.

*1,3-Dimesityl-1,3,2-diazastibolenium Triflate (**4b**[OTF])*

2.25 g (5 mmol) of **2b**[Cl] and 1.11 g (5 mmol) of Me_3SiOTf were reacted as described above for **4a**[OTf] to give 2.00 g (71%) of yellow needles of **4b**[OTf], mp 185°C (dec).

^{1}H NMR (CD_3CN): $\delta = 8.41$ (2 H, C**H**), 7.17 (4H, *m*-H), 2.40 (12 H, *o*-CH_3), 2.20 (6 H, *p*-CH_3). ^{13}C{^{1}H} NMR (CD_3CN): $\delta = 142.7$ (*p*—C), 140.6 (*i*-C), 138.3 (*o*-C), 128.8 (*m*-C), 132.5 (C-4/5), 19.7 (*p*-CH_3), 16.4 (*o*-CH_3). MS (EI, 16 eV, 150°C): *m/e* (%) = 402 (20) [M^+], 367(16) [M^+—Cl], 277(100) [M^+—Cl—As—CH_3].

*1,3-Di-t-butyl-1,3,2-diazarsolenium Triflate (**5a**[OTf])*

970 mg (3.5 mmol) of **3a**[Cl] and 780 mg (3.5 mmol) of Me_3SiOTf were reacted in 30 mL of Et_2O/CH_2Cl_2 (2:1) as described above for **4a**[OTf] to give 1.00 g (73%) of crude **5a**[OTf] as a white powder of mp 160°C (dec) which was not purified further.

^{1}H NMR (CD_3CN): $\delta = 8.44$ (2 H, C**H**), 1.76 (18 H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (CD_3CN): $\delta = 134.6$ (C-4/5), 62.9 (**C**(CH_3)$_3$), 30.6 (C(**C**H$_3$)$_3$). MS (EI, 16 eV, 150°C): *m/e* (%) = 278(40) [M^+], 243(100) [M^+—Cl]. Raman: $\nu = 3134$, 3099, 2989, 2915, 1529, 1479, 1260, 1237, 1151, 1029, 986, 932, 809, 754, 719, 606, 415, 347, 248 cm^{-1}. IR (nujol mull): $\bar{\nu} = 515$(m), 637(s), 722(m); 1138(m), 1526(w), 3097(w) cm^{-1}.

*1,3-Dimesityl-1,3,2-diazarsolenium Triflate (**5b**[OTf])*

1.00 g (2.5 mmol) of **3b**[Cl] and 560 mg (2.5 mmol) of Me_3SiOTf were reacted in 30 mL of Et_2O/CH_2Cl_2 (2:1) as described above for **4a**[OTf] to give 1.20 g (93%) of colorless crystals of **5b**[OTf] of mp 185°C (dec).

^{1}H NMR (CD_2Cl_2): $\delta = 8.21$ (2 H, C**H**), 7.17 (4H, *m*-H), 2.43 (12 H, *o*-CH_3), 2.23 (6 H, *p*-CH_3). 13C{^{1}H} NMR (CD_2Cl_2): $\delta = 140.1$ (*p*-C), 139.5 (*o*-C), 135.9 (*i*-C), 133.1 (C-4/5), 129.3 (*m*-C), 19.8 (*p*-CH_3), 16.4 (*o*-CH_3). Raman: $\bar{\nu} = 165$, 224, 248, 311, 347, 415, 503, 571, 606, 719, 754, 809, 932, 986, 1029, 1054, 1151, 1214, 1226, 1237, 1260, 1450, 1479, 1529, 2731, 2796, 2915, 2989, 3099, 3134 cm^{-1}.

*Determination of K^{Diss} (As—Cl) of **3c**[Cl]*

Two stock solutions were prepared by dissolving 97.15 mg of **7a**[OTf] and 51.87 mg of **3b**[Cl] in CH_2Cl_2 and diluting the solutions to 2.76 mL and 1.78 mL, respectively. Three reaction mixtures were then prepared by mixing both stock solutions in ratios of 1:4, 2:3 and 3:2, respectively, and the averaged value of δ^{31}P of **6a**[Cl]/**7a**[OTf] determined in each solution. Using the values of $\delta^{31}P = 205.5$ (**7a**[OTf]), 170.5 (**11b**[Cl]) allowed to compute the molar fraction p_i(**6a**[Cl]) in each equilibrium mixture from the equation $\delta^{obsd} = \delta$(**6a**[Cl] p_i(**6a**[Cl]) + δ (**7a**[OTf])$\cdot$ (1–p_i(**6a**[Cl])). Using this value together with the known total concentrations of diazaphospholenium and diazaarsolenium compounds allowed then to compute the equilibrium constant K_1 of reaction. (1) (Scheme 3). K^{Diss}(As—Cl) was then obtained by computing K^{Diss}(As—Cl) = K_1/K^{Diss}(P—Cl) by using the previously published value for K^{Diss}(P—Cl) of **6a**[Cl] for each reaction mixture, and averaging.

*Crystal Structure Determinations of Compounds **2a**[Br], **3a**[Cl], and **5b**[OTf]*

The data were collected on a Nonius KappaCCD diffractometer at −150°C using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97 [28]). Empirical absorption corrections based on multiple reflections

TABLE 4 Crystallographic Data, Structure Solution, and Refinement of **2a**[Br], **3a**[Cl], and **5b**[OTf]

	2a*[Br]*	**3a***[Cl]*	**5b***[OTf]*
Formula	$C_{10}H_{20}BrN_2Sb$	$C_{10}H_{20}AsClN_2$	$C_{20}H_{24}AsN_2 \cdot CF_3O_3S \cdot \frac{1}{2}C_4H_{10}O$
M_r	369.94	278.65	553.46
Dimensions (mm)	0.50 × 0.30 × 0.10	0.50 × 0.25 × 0.15	0.70 × 0.60 × 0.50
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca* (no. 61)	*Pbca* (no. 61)	*C2/c* (no. 15)
a (Å)	11.7023(3)	11.6481(2)	25.0588(3)
b (Å)	10.9751(2)	12.0818(2)	15.8785(3)
c (Å)	21.2127(5)	18.7968(3)	17.2022(3)
β (°)			132.657(1)
V (Å^3)	2724.43(11)	2645.3(1)	5033.74(14)
Z	8	8	8
ρ (g cm^{-3})	1.804	1.399	1.461
μ (mm^{-1})	4.93	2.74	1.485
F(000)	1440	1152	2280
2 $\theta_{\max}$ (°)	55.0	55	55
	$-15 \le h \le 15$	$-15 \le h \le 15$	$-32 \le h \le 32$
	$-8 \le k \le 14$	$-15 \le k \le 15$	$-20 \le k \le 20$
	$-23 \le l \le 27$	$-24 \le l \le 24$	$-22 \le l \le 22$
No. of meads. data	12347	22019	32626
No. of unique data	3094	2978	5599
R_{int}	0.068	0.043	0.043
Refinement on	F^2	F^2	F^2
No. of parameters/Restraints	127/0	127/0	306/15
R [for $I > 2\sigma(I)$]	0.031	0.022	0.028
$wR2$ (all data)	0.070	0.060	0.067
Max./min. difference Peak (e Å^{-3})	−1.78/0.65	−0.64/0.29	−0.46/0.33

were applied. The nonhydrogen atoms were refined anisotropically, H atoms were refined using a riding model (fullmatrix least-squares refinement on F^2 (SHELXL-97 [29]). Crystals of **5b**[OTf] contained half a solvent molecule (Et_2O) per asymmetric unit. Details of data collection and refinement are given in Table 4. The data for **2a**[Cl], **4a**[OTf], and **4a**[SbCl4] have already been reported in a preliminary communication [19].

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-242440 (**2a**[Cl]) [19], CCDC 255333 (**2a**[Br]), CCDC 255334 (**3a**[Cl]), CCDC-242441 (**4a**[SbCl4]) [19], CCDC-242443 (**4a**[OTf]) [19], and CCDC 255335 (**5b**[OTf]), respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, UK.

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