Diamidonaphthalene-supported pnictogenium cations: Synthesis of an N-heterocyclic stibenium cation by a novel protonation route†

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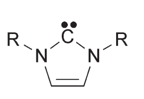
A 1,8-bis(alkylamido)naphthalene framework has been applied to the construction of N-heterocyclic arsenium and stibenium cations; a novel synthetic route, involving protonation of an ancillary amido ligand, was used to generate the base-stabilized stibenium cation.

Electron deficient, coordinatively unsaturated species exhibit fundamentally fascinating structural and electronic features as well as provide for novel applications as synthetic reagents. Heteroatom-stabilized carbenes (**1**) and their analogues represent important and now widely exploited examples within this class of compounds.[1] Isoelectronic, cationic, dicoordinate pnictogen (group 15) compounds (**2–6**) have, since the discovery of the first stable phosphenium ions some 40 years ago,[2] remained a focal point of research. These phosphenium,[3–5] arsenium,[6–8] and stibenium[9–11] ions are six-electron, unsaturated species containing lone pairs of electrons and vacant p-orbitals, and accordingly display amphoteric properties as Lewis bases and acids. This report presents the synthesis and characterization of pnictogenium cations captured in a novel electronic and steric environment provided by *N*,*N*′-disubstituted-1,8-diamidonaphthalene ligation.[12]



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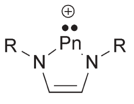
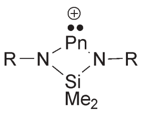


2 Pn = P, As, Sb



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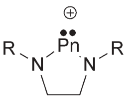

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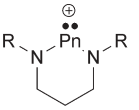

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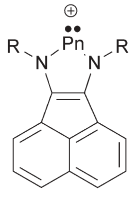
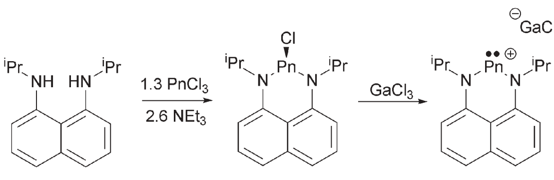


6 Pn = P, As

The diamidochloropnictines **7** serve as precursors for pnictogenium cation synthesis, and are available from the dehydrohalide coupling reactions of 1,8-bis(isopropylamino)naphthalene with the appropriate pnictogen trichloride (eqn 1). Triethylamine was an efficient base in these reactions, and the soluble yellow diamidochloroarsine $\mathrm{ClAs(^iPrN)_2C_{10}H_6}$ (**7As**) and orange diamidochlorostibine $\mathrm{ClSb(^iPrN)_2C_{10}H_6}$ (**7Sb**) were readily separated from solid $\mathrm{Et_3NHCl}$ in good yields after stirring for four days in toluene at room temperature. The static, pyramidal structures for the Pn centres in compounds **7** were clearly indicated by the appearance of two distinct doublets for the ^{i}Pr methyl groups in the ^{1}H NMR spectra of these compounds. The structures of **7As** and **7Sb** were further confirmed by single-crystal X-ray analyses.‡ Selected bond lengths and angles for these two species are listed in Table 1.



7 Pn = As, Sb **8 Pn = As** (1)

The addition of $\mathrm{GaCl_3}$ to a toluene solution of $\mathrm{ClAs(^iPrN)_2C_{10}H_6}$ **7As** resulted in the immediate precipitation of a blue solid, which was characterized through spectroscopic and crystallographic means as the arsenium salt $\mathrm{[As(^iPrN)_2C_{10}H_6][GaCl_4]}$ **8** (Fig. 1).‡ The cation and anion are well separated in the solid state structure of **8**, with the closest As–Cl contact being 3.49(1) Å. The N-heterocyclic arsenium cation in **8** displays a unique architecture where the dicoordinate arsenic centre sits in a six-membered ring with a π-conjugated carbon backbone. Structural features that accompany the formation of the arsenium cation are a contraction of the As–N bonds (**7As** As–N(1) = 1.810(2) Å; As–N(2) = 1.812(2) Å; **8** As–N(1) = 1.762(7) Å, As–N(2) = 1.757(7) Å), an opening of the N–As–N angle (**7As** 95.61(9)°; **8** 101.4(3)°), and the formation of a more planar heterocyclic framework (Table 1). All of these changes are consistent with increased As–N π-bonding in the coordinatively unsaturated cation. In addition, the As–N bond lengths of **8** are directly comparable to the reported average As–N bond lengths of cyclic diaminoarsenium species such as $\mathrm{[H_2C_2(N^tBu)_2As]Cl}$ (**2As**, R = ^{t}Bu, av. = 1.811(9) Å),[4] $\mathrm{[H_4C_2(NMe)_2As]AlCl_4}$ (**4As**, R = Me, av. = 1.859(8) Å),[6] and $\mathrm{[(CH_2)_3(NMe)_2As]GaCl_4}$ (**5As**, R = Me, av. = 1.68(3) Å).[7]

Unexpectedly, the addition of either $\mathrm{GaCl_3}$ or $\mathrm{AlCl_3}$ to toluene solutions of the diamidochlorostibine **7Sb** resulted in the precipitation of metallic antimony from the reaction, even at low temperatures. Furthermore, trimethylsilyl triflate did not react with **7Sb** at room temperature, and heating **7Sb** with $\mathrm{Me_3SiOTf}$ (OTf = triflate) in toluene also resulted in the precipitation of metallic antimony. Attempts to prepare the targeted stibenium cation with the silver salts AgOTf or $\mathrm{AgBF_4}$ were also unsuccessful. A new

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† Electronic supplementary information (ESI) available: Experimental and spectroscopic data for compounds **7As**, **7Sb**, **8**, **9**, and **10**. See DOI: 10.1039/b617434e

Table 1 Selected bond lengths (Å) and angles (°) in diamidonaphthalene-supported pnictines and pnictogenium cations

Compound	Number	Pn–N(1)	Pn–N(2)	Pn–X^{a}	N(1)–Pn–N(2)	Bend angle^{b}
ClAs(^{i}PrN)$_2$C$_{10}$H$_6$	**7As**	1.810(2)	1.812(2)	2.2820(8)	95.61(9)	31.9
ClSb(^{i}PrN)$_2$C$_{10}$H$_6$	**7Sb**	2.021(5)	2.017(4)	2.392(2)	86.5(2)	39.6
[As(^{i}PrN)$_2$C$_{10}$H$_6$]GaCl$_4$	**8**	1.762(7)	1.757(7)	3.49(1)	101.4(3)	3.9
(Me$_2$N)Sb(^{i}PrN)$_2$C$_{10}$H$_6$	**9**	2.022(3)	2.028(4)	2.056(4)	86.2(2)	42.0
[Sb(^{i}PrN)$_2$C$_{10}$H$_6$·NHMe$_2$]OSO$_2$CF$_3$	**10**	1.997(4)	2.000(4)	2.323(4)	93.0(2)	26.0

^{a} Length of third bond to pnictogen atom or closest cation–anion contact. ^{b} Angle between naphthalene plane and N–Pn–N plane.

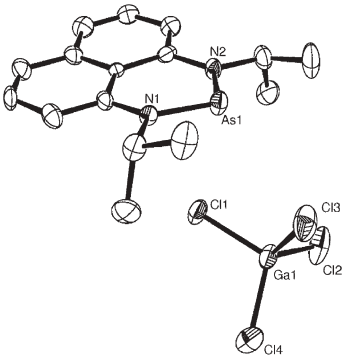
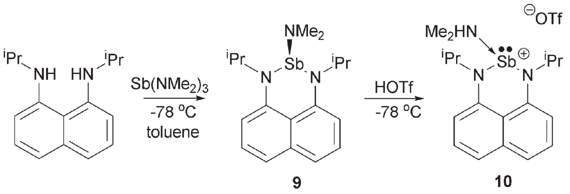


Fig. 1 Thermal ellipsoid plot showing the molecular structure and partial atom-numbering scheme of [As(^{i}PrN)$_2$C$_{10}$H$_6$]GaCl$_4$ **8**. Hydrogen atoms have been omitted for clarity.

synthetic strategy, which did not involve abstraction of a halide from antimony, was developed (eqn 2).



(2)

The transamination reaction between Sb(NMe$_2$)$_3$ and 1,8-bis(isopropylamino)naphthalene was carried out in toluene with the reagents initially combined at −78 °C, and then slowly allowed to warm to room temperature. During this process, the initial purple solution gradually turned orange in colour and evolution of NHMe$_2$ gas was apparent. The new heteroleptic trisamidostibene, (Me$_2$N)Sb(^{i}PrN)$_2$C$_{10}$H$_6$ **9** was isolated in good yield as a yellow crystalline solid. Like the chloro analogue, the ^{1}H NMR spectrum of **9** exhibited two signals for the ^{i}Pr methyl groups consistent with the proposed pyramidal Sb centre. This was further confirmed in the solid state structure of **9** as shown in Fig. 2.‡ Compound **9** exhibits nearly identical metrical parameters to those observed in the structure of **7Sb**, with the exception of the Sb–NMe$_2$ bond (Sb–N(3) = 2.056(4) Å) (Table 1).

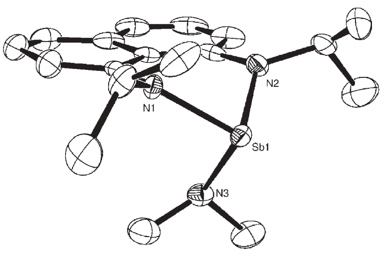


Fig. 2 Thermal ellipsoid plot showing the molecular structure and partial atom-numbering scheme of (Me$_2$N)Sb(^{i}PrN)$_2$C$_{10}$H$_6$ **9**. Hydrogen atoms have been omitted for clarity.

We anticipated that addition of triflic acid (HOTf) to **9** would protonate the dimethylamido group, liberate NHMe$_2$, and generate a stibenium triflate salt; however, no gas evolution was observed in the reaction of **9** with HOTf.[13] A ^{1}H NMR spectrum of the yellow crystalline product **10** indicated the presence of NHMe$_2$ which we proposed to be coordinated to the stibenium centre. In contrast to our observations for **7** and **9**, the ^{i}Pr substituents of **10** gave only a single resonance for the methyl groups in both the ^{1}H and ^{13}C NMR spectra of this compound. The identity of **10** was further confirmed by X-ray crystallography (Fig. 3).‡[14] The NHMe$_2$ ligand could not be removed by prolonged exposure of solid samples of **10** to vacuum at room temperature.

The structural changes that are observed with formation of the dimethylamine-stabilized stibenium cation **10** from **9** are summarized in Table 1 and support our protonation approach to stibenium cation generation. Specifically, protonation of the dimethylamido nitrogen leads to a substantial increase in the Sb–N(3) bond length to 2.323(4) Å. Concomitant with this is a slight decrease in the Sb–N(naphthalene) bond lengths (Sb–N(1) = 1.997(4) Å, Sb–N(2) = 2.000(4) Å) to values that are directly comparable to those in the two previously reported examples of N-heterocyclic stibenium cations: [H$_2$C$_2$(N^{t}Bu)$_2$Sb]SbCl$_4$ (**2Sb**, R = ^{t}Bu, av. Sb–N = 2.024(2) Å)[9] and [Me$_2$Si(N^{t}Bu)$_2$Sb]AlCl$_4$ (**3Sb**, R = ^{t}Bu, av. Sb–N = 2.00(2) Å).[11] The Sb–N(3) bond length in **10** is significantly shorter than that observed in the NHMe$_2$ adduct of the neutral diamidochlorostibine [SbCl(μ-N^{t}Bu)]$_2$ (Sb–N = 2.524(3) Å),[15] supporting the existence of a more electron-deficient cationic Sb centre in [Sb(^{i}PrN)$_2$C$_{10}$H$_6$·NHMe$_2$]OSO$_2$CF$_3$.

Consistent with the NMR observations, and as anticipated, the Sb(^{i}PrN)$_2$C$_{10}$H$_6$ framework adopts a more planar geometry

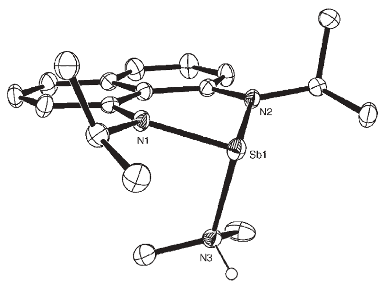


Fig. 3 Thermal ellipsoid plot showing the molecular structure and partial atom-numbering scheme of [Sb(^{i}PrN)$_2$C$_{10}$H$_6$·NHMe$_2$]OSO$_2$CF$_3$ **10** (only one of the two independent cations in the unit cell is shown). Hydrogen atoms and the triflate anion have been omitted for clarity.

compared to **7Sb** or **9**. As well, the N(1)–Sb–N(2) angle observed in **10** (93.0(2)°) has increased by several degrees from that observed in the trisamidostibine **9** (86.2(2)°) and **7Sb** (86.5(2)°). This observation parallels the change in the N–As–N angle that was observed with the conversion of arsine **7As** to the arsenium cation **8**. It should be noted that the base-stabilized stibenium cation in **10** is well-separated from the triflate anion, the closest Sb–O contact being 2.823(9) Å in length.

In conclusion, the library of known N-heterocyclic arsenium and stibenium cations has been expanded to include examples supported by a 1,8-bis(alkylamido)naphthalene framework. These differ from the previously reported cations **2–6** in that the dicoordinate pnictogen atom is included in a six-membered ring forming part of an extended π-conjugated framework. In fact, compounds **7Sb**, **9**, and **10** represent the first examples of antimony atoms enclosed in a six-membered N-heterocyclic ring. Circumventing the usual halide abstraction route, the base-stabilized stibenium cation in **10** has been generated using a novel synthetic route involving protonation of an amido substituent. This reaction should be generally applicable to the synthesis of other low-coordinate pnictogen compounds.

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Notes and references

‡ Crystallographic measurements were made at 213 K using a Bruker AXS SMART 1 k CCD diffractometer (Mo-Kα, $\lambda = 0.71073$ Å).

Crystal Data: $ClAs(^{i}PrN)_2C_{10}H_6$ (**7As**): $C_{16}H_{20}N_2ClAs$, $M = 350.71$, monoclinic, space group $P2_1/n$, $a = 8.8383(19)$, $b = 16.434(3)$, $c = 11.551(2)$ Å, $\beta = 106.825(3)°$, $V = 1606.0(6)$ Å^3, $Z = 4$, μ(Mo-Kα) = 2.275 mm^{-1}, $D_{calc} = 1.450$ g·cm^{-3}, 9898 measured reflections (3256 unique), 181 refined parameters, $R1$(F) [2656 reflections with $I > 2\sigma(I)$] = 0.0309, $wR2(F^2)$ [all data] = 0.0711.

$ClSb(^{i}PrN)_2C_{10}H_6$ (**7Sb**): $C_{37.6}H_{46.4}N_4Cl_2Sb_2$ (two independent molecules of $C_{16}H_{20}N_2ClSb$ and 0.8 of a disordered toluene solvate), $M = 868.79$, monoclinic, space group $P2_1/n$, $a = 15.669(4)$, $b = 11.931(3)$, $c = 21.118(5)$ Å, $\beta = 92.125(4)°$, $V = 3945.3(15)$ Å^3, $Z = 4$, μ(Mo-Kα) = 1.535 mm^{-1}, $D_{calc} = 1.463$ g·cm^{-3}, 18116 measured reflections (7934 unique), 381 refined parameters, $R1$(F) [5939 reflections with $I > 2\sigma(I)$] = 0.0456, $wR2(F^2)$ [all data] = 0.1356.

$[As(^{i}PrN)_2C_{10}H_6]GaCl_4$ (**8**): $C_{16}H_{20}N_2Cl_4GaAs\cdot(C_7H_8)_{0.25}$, $M = 549.81$, monoclinic, space group $P2_1/n$, $a = 7.233(2)$, $b = 17.341(6)$, $c = 19.580(7)$ Å, $\beta = 99.501(6)°$, $V = 2418.3(14)$ Å^3, $Z = 4$, μ(Mo-Kα) = 2.942 mm^{-1}, $D_{calc} = 1.510$ g·cm^{-3}, 13716 measured reflections (2915 unique), 233 refined parameters, $R1$(F) [1858 reflections with $I > 2\sigma(I)$] = 0.0605, $wR2(F^2)$ [all data] = 0.1550.

$(NMe_2)Sb(^{i}PrN)_2C_{10}H_6$ (**9**): $C_{18}H_{26}N_3Sb$, $M = 406.17$, orthorhombic, space group $Pna2_1$, $a = 14.606(3)$, $b = 9.7332(17)$, $c = 12.753(2)$ Å, $V = 1813.0(5)$ Å^3, $Z = 4$, μ(Mo-Kα) = 1.523 mm^{-1}, $D_{calc} = 1.488$ g·cm^{-3}, 12716 measured reflections (3066 unique), 199 refined parameters, $R1$(F) [2578 reflections with $I > 2\sigma(I)$] = 0.0240, $wR2(F^2)$ [all data] = 0.0643.

$[Sb(^{i}PrN)_2C_{10}H_6\cdot NHMe_2]OSO_2CF_3$ (**10**): $C_{38}H_{54}N_6O_6F_6S_2Sb_2$ (two independent units of $C_{17}H_{27}N_3O_3F_3SSb$), $M = 1112.49$, triclinic, space group $P\bar{1}$, $a = 8.5648(13)$, $b = 9.7606(15)$, $c = 27.018(4)$ Å, $\alpha = 81.973(2)$, $\beta = 89.580(2)$, $\gamma = 81.727(2)°$, $V = 2213.0(6)$ Å^3, $Z = 2$, μ(Mo-Kα) = 1.391 mm^{-1}, $D_{calc} = 1.670$ g·cm^{-3}, 20501 measured reflections (7522 unique), 541 refined parameters, $R1$(F) [5704 reflections with $I > 2\sigma(I)$] = 0.0379, $wR2(F^2)$ [all data] = 0.0963.

CCDC 629186–629190. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617434e

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