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Synthesis and unprecedented oxidation of a cationic Sb-analogue of an Arduengo's carbene†

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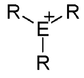
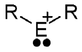
2-Chloro-1,3,2-diazastibolenes react with Lewis acids either *via* Sb–Cl cleavage to yield stable Sb-analogues of an N-heterocyclic carbene, or *via* an unprecedented oxidative fragmentation to give a diazadiene–$SbCl_3$ complex.

Carbenium (**I**, E = C),[1] nitrenium (**II**, E = N)[2] and phosphenium ions (**II**, E = P)[3] have received persistent interest due to their unique bonding situation and reactivity. The access to analogues with heavier group 14 and 15 elements was long obstructed by a growing tendency of species with progressively larger and softer Lewis-acidic centres to form adducts with Lewis bases,[4] and only over the last decades did examples of genuine cations **I** with E = Si,[5] Ge,[6] Sn[7] and **II** with E = As,[8] Sb,[9] Bi[9] become known.


I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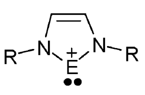
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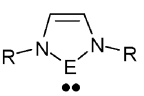

IV

The stability of known type **II** cations relies commonly on mesomeric interaction with π-donor substituents.[3,8,9] A highly efficient π-stabilisation is present in the diazaphospholenium and diazaarsolenium ions **III** (E = P, As)[10–13] that are isoelectronic analogues of *N*-heterocyclic carbenes **IV** (E = C). Having recently prepared the first stable stannylene **IV** (E = Sn),[14] we report now on the synthesis and properties of the novel Sb-centered cations **III** (E = Sb).

By analogy to the synthesis of the stannylenes **IV**,[14] the α-aminoaldimines **1a,b** reacted with $ClSb(NMe_2)_2$ to afford the 1,3,2-diazastibolenes **2a,b**; alternatively, **2a** was accessible by reacting **1a** with $SbCl_3$ in the presence of NEt_3 as acid scavenger.

Both products were isolated in 40–60% yield as orange-red, air and moisture sensitive solids and were characterised by analytical and spectroscopic data and a single-crystal X-ray diffraction study of **2a**.‡ §

Conversion of **2a,b** into the salts **3a,b**[X]‡ was achieved by Lewis-acid induced Sb–Cl cleavage, using $AlCl_3$, $GaCl_3$, $SbCl_3$, or $Me_3SiOSO_2CF_3$ as chloride acceptor. The presence of contact ion pairs in solution and the solid state was proven by the similarity of the ^1H and ^{13}C NMR spectra of salts with different anions, the detection of a sharp ^{27}Al NMR signal attributable to free $AlCl_4^-$, and single-crystal X-ray diffraction studies of **3a**[$SbCl_4$] and **3a**[SO_3CF_3].§

Crystals of **2a** consist of molecules (Fig. 1) that are connected by intermolecular Sb···Cl contacts (3.86 Å) slightly shorter than the sum of van der Waals radii (4.00 Å). The Sb–N distances in the planar five-membered rings are similar to those in *cyclo*-[$Me_2Si(NtBu)_2SbCl$] (**4**, 1.995(5) Å[15]). The C=C and C–N bonds match those in the homologous diazaphospholene *cyclo*-[$(CH)_2(NtBu)_2PCl$] (**5**, C=C 1.349, C–N 1.391 Å[13]) and range between double and single bonds; all features together suggest that the bonding in **2a** is as in **5**[13] characterised by sizeable $\pi(C_2N_2) \rightarrow \sigma^*(E\text{–}X)$-hyperconjugation. The Sb–Cl bond in **2a** is by 7% longer than in **4** (2.472(3) Å[15]) but still shorter than the P–Cl bond in **5** (2.692 Å[13]). This effect is quite surprising in the light of the increase in atomic radii from P to Sb but may be explained if one assumes that the cation **3a** is a stronger chloride acceptor – and thus a stronger Lewis acid – than the homologous diazaphospholenium ion. The validity of this hypothesis was independently underlined by the observed reaction of **3a**[$AlCl_4$] with **5** which proceeded *via* quantitative transfer of a chloride to give **2a** and the appropriate diazaphospholenium cation.

Crystalline **3a**[$SbCl_4$] (Fig. 2) contains anions that form, as in [NPr_4][$SbCl_4$],[16] centrosymmetric chloride-bridged dimers with distorted square-pyramidal coordination at the Sb-atoms, and cations whose dicoordinate Sb-atoms display weak contacts (3.43–3.94 Å) to Cl-atoms of adjacent anions that are clearly longer than in *cyclo*-[$Me_2Si(NtBu)_2Sb$][$AlCl_4$] (**6**, Sb···Cl 3.03, 3.07 Å[9]). The five-membered rings in the cations are planar and their structural features indistinguishable in both **3a**[SO_3CF_3] and **3a**[$SbCl_4$]. The Sb–N bonds are slightly longer than in **2a** or **6** (Sb–N 1.994, 1.998 Å[9]), and the C=C bond is longer and the C–N bonds are shorter than in **2a**. The equalisation of single and double bonds is more pronounced than in the appropriate diazaarsolenium ion[10] and all trends reproduce similar findings in the diazaphospholene system,[11,13] thus suggesting a higher degree of π-conjugation in the five-membered ring than in **2a**.

Whereas treatment of *P*-chloro-diazaphospholenes with $SbCl_5$ is

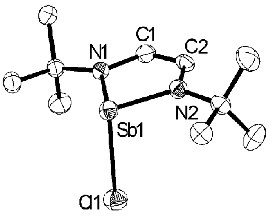
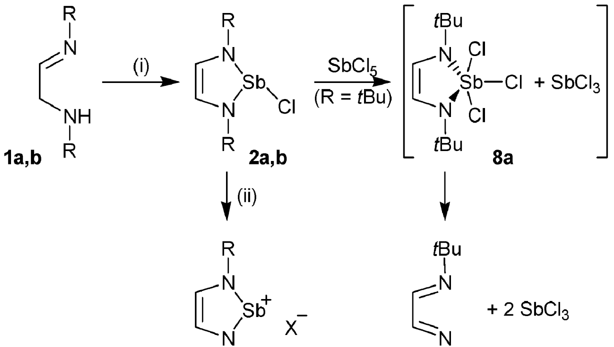


Fig. 1 ORTEP style drawing of **2a** with thermal ellipsoids at the 50% probability level; H-atoms omitted for clarity. Selected bond lengths [Å]: Cl1–Sb1 2.646(2), Sb1–N1 1.998(4), Sb1–N2 2.000(4), N1–C1 1.407(6), N2–C2 1.391(6), C1–C2 1.346(6).



Scheme 1 R = *t*Bu (**1a–3a**), Mes (**1b–3b**); X = $AlCl_4^-$, $GaCl_4^-$, $SbCl_4^-$, $SO_3CF_3^-$; (i) 1 equiv. $ClSb(NMe_2)_2$ or $SbCl_3$/2 NEt_3; (ii) 1 equiv. $AlCl_3$, $GaCl_3$, $SbCl_3$, or $Me_3SiOSO_2CF_3$.

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† Electronic supplementary information (ESI) available: experimental procedures and characterisations of all compounds described in this paper and theoretical data of [(**7c**)($SbCl_3$)$_2$] and **5c**[$SbCl_6$]. See http://www.rsc.org/suppdata/cc/b4/b409657f/

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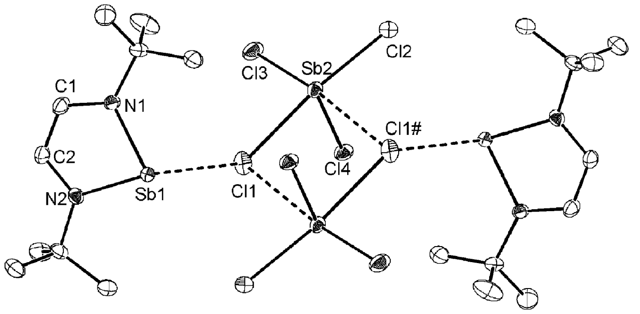

Fig. 2 ORTEP style drawing of **3a**[$SbCl_4$] with thermal ellipsoids at the 50% probability level; H-atoms omitted for clarity. Selected bond lengths [Å]: Sb1–N1 2.025(2), Sb1–N2 2.023(2), N1–C1 1.356(3), N2–C2 1.353(3), C1–C2 1.364(4), Sb2–Cl1 2.699(1), Sb2–Cl1# 3.054(1), Sb2–Cl2 2.517(1), Sb2–Cl3 2.421(1), Sb(2)–Cl(4) 2.362(1), Sb1–Cl1 3.433(1).

known as viable access to phosphenium hexachloroantimonates,[12] the corresponding reaction of **2a** afforded, quite surprisingly, not the salt **3a**[$SbCl_6$] but proceeded *via* fragmentation of the heterocycle to give $SbCl_3$ and the diazadiene **7a**. The products were isolated as a crystalline adduct of composition [(**7a**)($SbCl_3$)$_2$] that was was identified by a single-crystal X-ray diffraction study, but dissociated according to ^{1}H NMR studies into its constituents in solution.

The crystal structure of [(**7a**)($SbCl_3$)$_2$] (Fig. 3) features two pyramidal $SbCl_3$-units with bond lengths of 2.38–2.40 Å. The Sb1-atom is chelated by the diazadiene nitrogen atoms to form a planar five-membered SbN_2C_2-ring. The Sb–N bonds are by some 0.4 Å longer than in **2a** or **3a** and the C–C and C–N bond lengths represent normal single and double bonds, as expected for a diazadiene. Both Sb-atoms exhibit secondary contacts with distances between 3.04 and 3.57 Å to Cl-atoms of adjacent $SbCl_3$-units. Neglecting one weak interaction each (Sb–Cl > 3.50 Å, see thin lines in Fig. 3), both Sb-atoms attain a coordination number of six (Sb1: 5 + 1; Sb2: 3 + 3) and a distorted octahedral coordination geometry. If one adopts this view, the adduct [(**7a**)($SbCl_3$)$_2$] is formally described as a valence isomer of an ion pair **3a**[$SbCl_6$], with conversion between both forms being feasible by simple shifts of electrons and bridging chlorides between Sb-atoms. Computational studies (at the b3lyp/6-31g* level) on the model compounds [(**7c**)($SbCl_3$)$_2$] and **3c**[$SbCl_6$] (see Scheme 1, R = Me) revealed that both species are local minima on the energy hypersurface but that [(**7c**)($SbCl_3$)$_2$] is – in the gas phase – by 34.4 kcal mol^{-1} more stable than the ion pair **3c**[$SbCl_6$].

In line with these results, the outcome of the reaction of **2a** with $SbCl_5$ is rationalised by assuming that the initial step involves oxidative chlorination of **2a** rather than Lewis-acid induced Sb–Cl cleavage, to give a hypothetical intermediate **8a** which then decays *via* cheletropic fragmentation to the diazadiene **7a** and $SbCl_3$. This proposition was supported by the trapping of $SbCl_3$ by unreacted **2a** to give **3a**[$SbCl_4$]. The salt precipitated as isolable side-product from ethereal reaction mixtures but was as well converted into **7a** and $SbCl_3$ when the reaction proceeded.

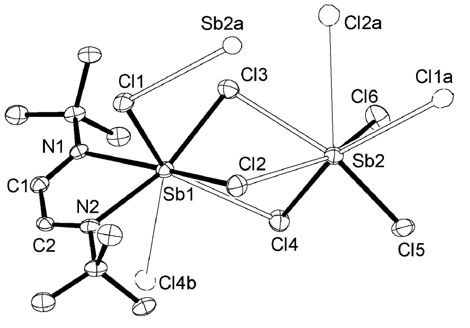

Fig. 3 ORTEP style drawing of [(**7a**)($SbCl_3$)$_2$] with thermal ellipsoids at the 50% probability level; H-atoms omitted for clarity; Sb2a, Cl1a, Cl2a, and Cl4b denote atoms of neighboring molecular units. Selected bond lengths [Å]: Sb1–N1 2.460(2), Sb1–N2 2.418(2), N1–C1 1.278(3), C2–N2 1.277(3), C1–C2 1.472(3), Sb1–Cl1 2.384(1), Sb1–Cl2 2.546(1), Sb1–Cl3 2.596(1), Sb1–Cl4 3.363(1), Cl1–Sb2a 3.334(1), Sb2–Cl2 3.196(1), Sb2–Cl3 3.041(1), Sb2–Cl4 2.406(1), Sb2–Cl5 2.412(1), Sb2–Cl6 2.380(1).

Oxidative fragmentation was as well observed upon air oxidation of **3a**[$AlCl_4$], and upon treatment of **2a** with PCl_5 to yield **7a**, $SbCl_3$, and PCl_3. This last reaction was completed by ring metathesis of PCl_3 with a second molecule of **2a** to give the salt [$(CH)_2(N$*t*$Bu)_2P$][$SbCl_4$] as isolable final product. The observed reactivity of **2a** towards $SbCl_5$ and PCl_5 is in marked contrast to that of diazaphospholenes which react under identical conditions exclusively *via* chloride abstraction and formation of diazaphospholenium salts[12] that are stable in dry oxygen.

In conclusion, it has been shown that the mesomeric stabilisation in the molecular framework of **III** is sufficient to allow the first synthesis of cationic Sb-analogues of *N*-heterocyclic imidazoyl carbenes, and that these species are distinguished from their lighter homologues by increased Lewis-acidity and a significantly higher lability to undergo unprecedented oxidation reactions under cheletropic ring fragmentation.

Notes and references

‡ Selected spectral data: **2a**: ^{1}H NMR (C_6D_6): δ = 6.6 (2H, CH), 1.25 (18H, tBu); MS (EI, 16 eV, 150 °C): *m*/*e* (%) = 324 (85) (M^+), 289 (85) ($M^+ - Cl$). **2b**: ^{1}H NMR (C_6D_6): δ = 6.79 (4H, *m*-H), 6.38 (2H, CH), 2.29 (12H, *o*-Me), 2.13 (6H, *p*-Me); MS (EI): *m*/*z* (%) = 448 (20) (M^+), 413 (16) ($M^+ - Cl$), 277 (100) ($M^+ -$ SbCl, Me). **3a**[$SbCl_4$]: ^{1}H NMR (CD_3CN): δ = 8.57 (2H, CH), 1.71 (18H, tBu). **3b**[SO_3CF_3]: ^{1}H NMR (CD_3CN): δ = 8.41 (2H, CH), 7.17 (4H, *m*-H), 2.40 (12H, *o*-Me), 2.20 (6H, *p*-Me).

§ Crystal data at 123 K: **2a**: $C_{10}H_{20}ClN_2Sb$, FW = 325.5, orthorhombic, *Pbca*, a = 11.5242(5) Å, b = 10.9946(4) Å, c = 21.0980(9) Å, V = 2673.2(2) Å^3, Z = 8; 13862 reflxns. collected (2344 unique), R_1 = 0.038 ($I > 2\sigma(I)$), wR_2 = 0.091. **3a**[$SbCl_4$]: $C_{10}H_{20}Cl_4N_2Sb_2$, FW = 553.6, monoclinic, $P2_1/n$, a = 10.1078(1) Å, b = 19.5200(2) Å, c = 10.2340(1) Å, β = 114.408(1)°, V = 1838.8(1) Å^3, Z = 4; 16986 reflxns. collected (3213 unique), R_1 = 0.018 ($I > 2\sigma(I)$), wR_2 = 0.042. **3a**[SO_3CF_3]·CH_2Cl_2, $C_{12}H_{22}Cl_2F_3N_2O_3SSb$, FW = 524.0, monoclinic, $P2_1/c$, a = 11.0192(1) Å, b = 10.3184(1) Å, c = 18.6936(2) Å, β = 104.138(1)°, V = 2061.1(1) Å^3, Z = 4; 32263 reflxns. collected (3603 unique), R_1 = 0.023 ($I > 2\sigma(I)$), wR_2 = 0.061. [(**7a**)($SbCl_3$)$_2$]: $C_{10}H_{20}Cl_6N_2Sb_2$, FW = 624.5, monoclinic, $C2/c$, a = 12.0617(1) Å, b = 17.4255(2) Å, c = 19.3913(2) Å, β = 102.081(1)°, V = 3985.4(1) Å^3, Z = 8; 34881 reflxns. collected (3512 unique), R_1 = 0.018 ($I > 2\sigma(I)$), wR_2 = 0.041. CCDC reference numbers: CCDC-242440 (**2a**), CCDC-242441 (**3a**[$SbCl_4$]), CCDC-242443 (**3a**[SO_3CF_3]), CCDC-242442 ([(**7a**)($SbCl_3$)$_2$]). See http://www.rsc.org/suppdata/cc/b4/b409657f/ for crystallographic data in .cif or other electronic format.

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