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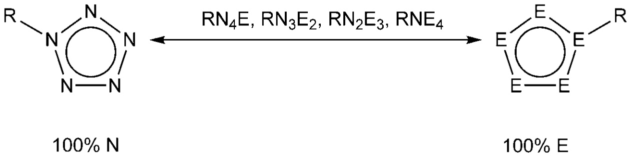
Sb–N Chemistry

An Unusual Isomerization to Tetraazastiboles**

Mathias Lehmann, Axel Schulz, and Alexander Villinger**

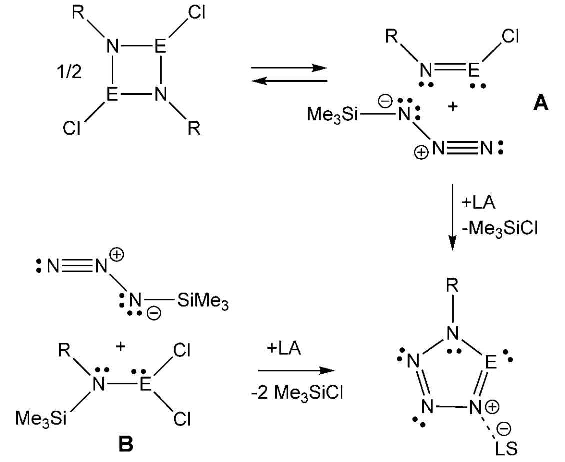
Dedicated to Professor Peter Klüfers on the occasion of his 60th birthday

Pentazoles are aromatic molecules consisting of a five-membered nitrogen-atom ring (Scheme 1), one of which is bonded to a hydrogen atom (HN_5) or an organic substituent (RN_5; R is usually an aryl group). They form a class of highly endothermic and explosive compounds. The existence of an all-nitrogen aromatic azole ring, RN_5 ($R = C_6H_5$), was considered by Clusius and Hurzeler[1] and shown by Huisgen and Ugi[2] in the reaction of phenyldiazonium chloride, $[C_6H_5N_2]^+Cl^-$, and lithium azide, LiN_3, leading to the intermediate formation of acyclic phenyldiazonium azide (65 %) and phenyl pentazole (35 %), in which the pentazole ring is strongly stabilized by conjugation with the phenyl ring.



Scheme 1. Five-membered aromatic heterocycles consisting exclusively of Group 15 atoms (E).

Substitution of one nitrogen atom in pentazoles by a heavier element of Group 15 leads to isovalent tetraazapnictoles (Scheme 1), RN_4E (E = P, As, Sb, Bi), which also have electronic structures that are related to those of aromatic hydrocarbons with $(4n+2)\pi$ electrons.[3] Only recently, two examples of tetraazapnictoles (E = P, R = Mes* = 2,4,6-tri-*tert*-butylphenyl or *m*-Ter = 2,6-bis(2,4,6-trimethylphenyl)-phenyl;[4a,5] E = As,[6] R = Mes*) have been isolated and fully characterized. Two different synthetic routes to tetraazapnictoles have been described:[4,6] 1) The reaction of iminopnictanes with trimethylsilylazide (Scheme 2, route A) gives, in the presence of a Lewis acid such as $GaCl_3$, the corresponding tetraazapnictole RN_4E (E = P, As) stabilized as $GaCl_3$ adducts; 2) utilization of Me_3Si-substituted aminodichloropnictanes, which can be regarded as "disguised" kinetically stabilized iminopnictanes, gives the desired RN_4E in high yields when added to Me_3SiN_3 (Scheme 2, route B). This reaction only occurs when a Lewis acid is added, as it induces Me_3SiCl elimination and thus the release of the reactive iminopnictane.[7,8]



Scheme 2. Synthetic routes to tetraazapnictoles, RN_4E (LA = Lewis acid, E = Group 15 element, R = bulky substituent).

Substitution of two nitrogen atoms in pentazoles by heavier Group 15 elements leads to triazadipnictoles, RN_3E_2, of which only the triazadiphosphole[4b,9,10] was reported (E = P, $R = N(SiMe_3)_2$, Mes*). All other classes of heterocycles consisting only of Group 15 atoms, namely RN_2E_3, RNE_4, and RE_5, remain unknown. To the best of our knowledge, analogous Group 15 heterocycles involving Sb and Bi have not been reported. Following our interest in Group 15 element nitrogen compounds with a high nitrogen content,[4–11] we describe herein the synthesis, isolation, and full characterization of a tetraazastibole, RN_4Sb (R = Mes*), stabilized as $B(C_6F_5)_3$ adduct.

As illustrated in Scheme 2, both synthetic procedures (method A and B) were studied to isolate the tetraazastibole Mes*N_4Sb. At first we started with an investigation of the equilibrium between cyclic distibadiazane and its monomer, the iminostibane (Scheme 2), by means of ^{1}H NMR spectroscopy. However, in contrast to the situation found for E = P, As, only the dimer was detected. In agreement with these experimental data, quantum chemical calculations show that the heavier the pnictogen, the more stable the dimer is: $\Delta_{298}H(\text{monomer}\rightarrow\text{dimer})$: $+49.7$ (P) $< +14.4$ (As) < -95.4 (Sb) $< -121.5\ \text{kJ}\,\text{mol}^{-1}$ (Bi).[8,12] As the monomer is needed for the cyclization step, no cycloaddition occurred when Me_3SiN_3 was added in the presence of $GaCl_3$ (Scheme 2 and Scheme 3). In a next series of experiments, route B was followed, which included the synthesis of the Me_3Si-substituted aminodichlorostibane Mes*$N(SiMe_3)SbCl_2$.[13] How-

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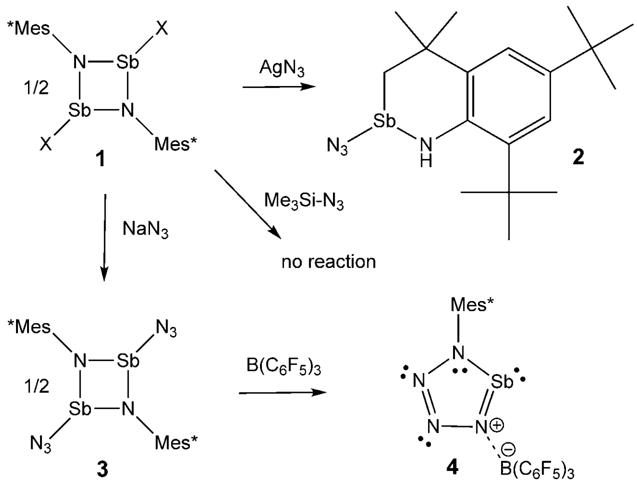

Scheme 3. Synthesis of **2**, **3**, and tetraazastibole **4** (**1**-X; X = Cl, I).

ever, this route also failed to yield RN_4Sb when $GaCl_3$ is added, as only a methyl–azide exchange reaction was observed, leading to a complex reaction mixture from which $Mes^*N(SiMe_2N_3)SbCl_2$ could be isolated.[14,15]

In a new approach, we tried to synthesize $[N_3Sb(\mu\text{-}NMes^*)_2SbN_3]$ to see whether route A (Scheme 2) would be suitable for the generation of RN_4Sb directly starting with the azide species. As it was impossible to prepare $[N_3Sb(\mu\text{-}NMes^*)_2SbN_3]$ from Me_3SiN_3 (route A, Scheme 2 and Scheme 3), 1,3-diiodo-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-*cyclo*-1,3-distiba-2,4-diazane (**1**-I) was treated with neat, carefully dried AgN_3, surprisingly yielding 2-azido-6,8-di-*tert*-butyl-4,4-dimethyl-1,2,3,4-tetrahydro-1-aza-2-stibanaphthalene (**2**; Scheme 3, Figure 1). Presumably, the diazide **3** that initially forms can also exist as the monomer, and insertion of the Sb–N moiety into the C–H bond of the adjacent *tert*-butyl groups occurs (79 % yield).[16] Compound **2** is a pale yellow crystalline solid that is thermally stable up to 188 °C.

The synthesis of diazide **3** was finally achieved in the reaction of a solution of **1**-Cl in tetrahydrofuran (THF) and NaN_3. The resulting yellow suspension was stirred for 24 h at ambient temperatures. After removal of the solvent and extraction with toluene, yellow crystals of **3** were obtained at 5 °C (yield 90 %). The novel diazide **3** is neither heat nor shock sensitive and decomposes above 190 °C.

At this stage we wondered what happens when a Lewis acid is added to diazide **3**. As we knew from the reaction with silver azide that monomerization might occur, which is triggered by the action of a Lewis acid, such as Ag^+ ions, we decided to use the bulky Lewis acid $B(C_6F_5)_3$.[17] Furthermore, if the tetraazastibole is formed, the Lewis acid should be capable of forming an RN_4Sb adduct. For RN_4E ($E = P$; $R = Mes^*$, *m*-Ter and $E = As$; $R = Mes^*$), it was shown[4,6,11c] that this adduct formation is essential for kinetic stabilization of RN_4E heterocycles, otherwise they quickly decompose, releasing N_2. Indeed, upon adding $B(C_6F_5)_3$ to a solution of diazide **3** in CH_2Cl_2, 1-(2,4,6-tri-*tert*-butylphenyl)-1,2,3,4,5-tetraazastibole as the tris(pentafluorophenyl)borane adduct (**4**) is formed. Optimization of the reaction conditions with the help of ^1H and ^{19}F NMR spectroscopy led to a synthetic procedure that includes a stepwise addition of $B(C_6F_5)_3$. The best yield (39 %) was obtained when only 0.5 equiv of $B(C_6F_5)_3$ was added over a period of five minutes at 0 °C. The resulting dark violet solution was stirred for 36 h at ambient temperature. The second half-equivalent of $B(C_6F_5)_3$ was added over a period of five minutes at 0 °C and the mixture was stirred again for 36 h. After concentration, the solution was stored at ambient temperatures for several hours, resulting in the deposition of orange crystals of **4**. Tetraazastibole **4** was fully characterized by NMR, infrared, and Raman spectroscopy, elemental analysis, and single-crystal structure elucidation.[15] Pure dry **4** is thermally stable at temperatures of up to 160 °C (above which it decomposes), is neither heat- nor shock-sensitive, and decomposes only very slowly, releasing N_2 gas even at ambient temperatures.

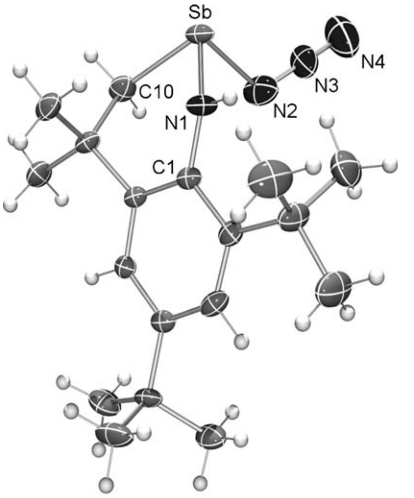

Figure 1. ORTEP drawing of the crystal structure of **2**. Ellipsoids are set at 50 % probability at 173 K. Selected bond lengths [Å] and angles [°]: Sb1–N1 2.040(4), Sb1–C10 2.140(4), Sb1–N2 2.143(4), N1–C1 1.400(5), N2–N3 1.201(6), N3–N4 1.134(6); N1-Sb1-C10 89.5(2), N1-Sb1-N2 95.8(2), C10-Sb1-N2 87.6(2), C1-N1-Sb1 123.8(3), N4-N3-N2 174.0(6).

Monoazide **2** crystallizes in the monoclinic space group $P2_1/c$ with eight formula units per cell (two independent molecules), while diazide **3** crystallizes in the triclinic space group $P\bar{1}$ with one formula unit per cell. The Sb atom (Figure 1 and Figure 2) adopts a trigonal pyramidal geometry in **2** and **3** with Sb–N bond lengths of between 2.04–2.14 Å (**2** Sb1–N1 2.040(4) and Sb1–N2 2.143(4), **3** Sb–N2 2.110(2), cf. $\Sigma r_{cov}(Sb\text{–}N) = 2.11$ Å),[18] in accord with Sb–N single bonds. As depicted in Figure 2, the Sb_2N_2 ring is planar in **3** ($\measuredangle$N1'-Sb-N1-Sb' = 0.0°) and almost square (*d*(Sb–N1') = 2.037(1), Sb–N1 2.056(1) Å), with both azide groups in *trans* configuration.[19] In contrast to $[N_3Sb(\mu\text{-}N\mathit{t}Bu)_2SbN_3]$, where both azide substituents adopt an *endo* conformation,[20] an *exo* conformation is observed in **3**. As shown on numerous occasions,[21,22] covalently bound azide groups, such as Sb–NNN, have a *trans*-bent configuration (regarding the Sb atom in **2** and **3**), with a N-N-N angle of 174.0(4)° in **2** and 175.6(2)° in **3**.

X-ray elucidation of crystals from the reaction sequence illustrated in Scheme 3 revealed the novel $B(C_6F_5)_3$-stabilized

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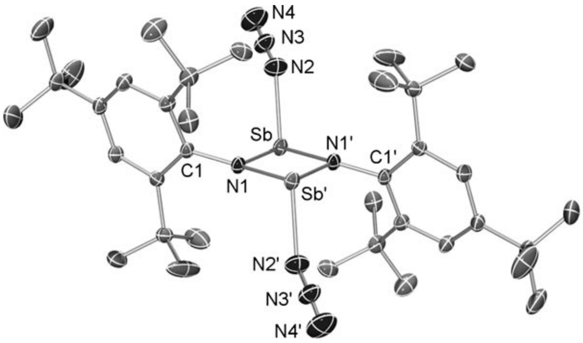

Figure 2. ORTEP drawing of the crystal structure of **3**. Ellipsoids are set at 50% probability at 173 K. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sb–N1′ 2.037(1), Sb–N1 2.056(1), Sb–N2 2.110(2), Sb⋯Sb′ 3.1575(2), N1–C1 1.442(2), N2–N3 1.215(2), N3–N4 1.134(2); N1′-Sb-N1 79.01(6), N1′-Sb-N2 96.48(6), N1-Sb-N2 99.25(6), C1-N1-Sb′ 116.35(9), C1-N1-Sb 139.4(1), Sb′-N1-Sb 100.99(6), N3-N2-Sb 119.1(1), N4-N3-N2 175.6(2), N1′-Sb-N1-Sb′ 0.0; symmetry code: (i) $-x+2$, $-y+1$, $-z+1$.

1-(2,4,6-tri-*tert*-butylphenyl)tetraazastibole. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with four units per cell. As depicted in Figure 3, the SbN_4 ring is planar (∡N4-Sb-N1-N2 0.5(1)°), as is the case in pentazoles,[23] triazadiphospholes,[9] tetraazaphospholes,[4,5] and tetraazaarsoles.[4] It is interesting to compare pnictoles (containing dicoordinated pnictogens) with pyrrole (HNC_4H_4) and Group 15 analogues of pyrrole (containing tricoordinated pnictogens). While pyrrole is planar and can be referred to as an aromatic system, heavier Group 15 analogues of pyrrole are pyramidal and are therefore non-aromatic.[24]

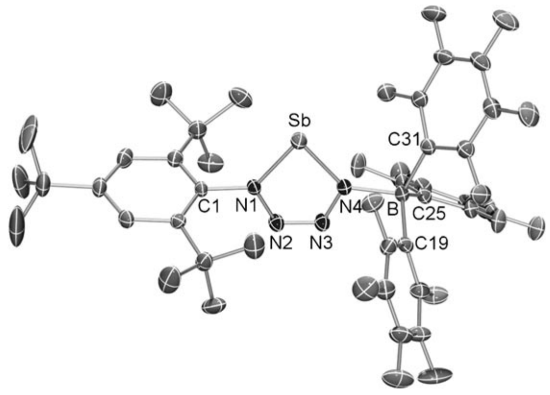

Figure 3. ORTEP drawing of the crystal structure of **4**. Ellipsoids are set at 50% probability at 173 K. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sb–N4 1.976(2), Sb–N1 2.000(2), N1–N2 1.352(2), N1–C1 1.447(3), N2–N3 1.272(3), N3–N4 1.357(3), N4–B 1.598(3); N4-Sb-N1 77.01(7), N2-N1-C1 117.0(2), N2-N1-Sb 115.3(1), C1-N1-Sb 127.4(1), N3-N2-N1 115.4(2), N2-N3-N4 117.3(2), N3-N4-B 113.3(2), N3-N4-Sb 115.0(1), B-N4-Sb 131.0(1), N4-Sb-N1-N2 0.5(1).

Table 1: Selected structural data (bond lengths in Å, angles in °) and decomposition temperatures (°C) of tetraazapnictoles.

N_4E[a]	E = N[23b]	E = P[4]	E = As[6]	E = Sb
E–N1	1.322(2)	1.631(4)	1.805(2)	2.000(2)
N1–N2	1.322(2)	1.355(5)	1.349(2)	1.352(2)
N2–N3	1.307(2)	1.286(5)	1.286(3)	1.272(3)
N3–N4	1.338(2)	1.374(5)	1.366(3)	1.357(3)
N4–E	1.307(2)	1.664(3)	1.784(2)	1.975(2)
N1-E-N4	105.4(1)	88.2(2)	82.8(1)	77.01(7)
$T_{decomp.}$	−5	145	190	160

[a] Connectivity: N1-E-N4, R-N1-N2-N3-N4·LA, with LA = $GaCl_3$ for P, As; $B(C_6F_5)_3$ for Sb, no LA for N; R = Mes* for P–Sb and phenyl for N.

The most prominent structural features are summarized in Table 1. The major difference arises from the decreasing N-E-N angle with an increase in the pnictogen: 105.4 (N) < 88.2 (P) < 82.8 (As) < 77.0° (Sb). The SbN_4 ring is slightly distorted, with two longer N–N bonds (d(N1–N2) = 1.352(2) and d(N3–N4) = 1.357(3) Å) and one short N–N distance (d(N2-N3) = 1.272(3)). These N–N distances of 1.27–1.36 Å are substantially shorter than the sum of the covalent radii (d_{cov}(N–N) = 1.48 and d_{cov}(N=N) = 1.20),[18] which indicates partial double-bond character for all of the N–N bonds, with the N2–N3 bond being close to having a bond order of two. Although **4** seems to be predisposed to the release of molecular nitrogen, no fast decomposition was observed. Obviously, the bare SbN_4 ring is kinetically protected between the large aryl and large $B(C_6F_5)_3$ unit.

Partial double-bond character can also be assumed for the two Sb–N bonds (d(Sb–N1) = 2.000(2) and d(Sb–N4) = 1.975(2) Å) of the SbN_4 ring (compare with *cyclo*-[$(CH)_2$-$(NMe)_2Sb]^+[SbCl_4]^-$ 2.025(2) and 2.023(2) Å),[25] which lie in the range between a single and a double bond (d_{cov}(N–Sb) = 2.11 and d_{cov}(N=Sb) = 1.91 Å).[18] Only little is known about compounds with dicoordinated Sb atoms containing a Sb–N double bond.[26,27] The first fully characterized compound with a partial Sb–N double bond (1.99(2) and 2.00(2) Å) is the four-membered cationic heterocycle $[Me_2Si(NtBu)_2Sb]^+$ with $[AlCl_4]^-$ as counterion, prepared by Veith et al. in 1988.[26a]

The B–N bond length of 1.598(3) Å is in the typical range found for other $B(C_6F_5)_3$ adducts,[28] cf. 1.616(3) Å in $CH_3CN{\cdot}B(C_6F_5)_3$).[29] The short Sb–N and N–N bonds, together with the planarity, indicate the presence of a strongly delocalized 6π-electron system, which is supported by NBO calculations (NBO = natural bond orbital analysis).[30,31] As expected, according to NBO analysis, the Sb–N bonds within the SbN_4 ring are strongly polarized, with a partial charge of +1.49 at Sb, −0.57 and −0.71e at N1 and N4, respectively, while the bonds between the adjacent nitrogen atoms of the ring are almost ideally covalent (q(N2) = −0.04, q(N3) = −0.01e). For comparison, the adduct-free Mes*N_4Sb species was calculated, with an electron-rich Sb–N heterocycle (q(Sb) = +1.15, q(N1) = −0.53, q(N2) = −0.08, q(N3) = −0.07, q(N4) = −0.67e). The computed charge transfer within the Lewis base/acid adduct **4** is rather large with 0.41e (compare with 0.14e in Mes*$N_4As{\cdot}GaCl_3$ and 0.15e in Mes*$N_4P{\cdot}GaCl_3$). A closer look at the charges reveals that upon $B(C_6F_5)_3$ complexation, the positive charge at the Sb atom increases considerably, while the charges at the N atoms do not change much (Δq: Sb 0.34, N1 −0.04, N2 0.04, N3 0.06, N4 −0.04e). Therefore, the charge transfer can mainly be attributed to the Sb atom, and it amounts to 89%.

In summary, all of the considered species **2**, **3**, and **4** can be regarded as constitutional isomers with respect to the

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Mes*N$_4$Sb formula unit. Thus, the conversion of diazide **3** into tetraazastibole **4** is an unusual isomerization triggered by the action of the Lewis acid $B(C_6F_5)_3$. Furthermore, the Lewis acid is needed for adduct formation at the end of the reaction sequence, so that the N$_4$Sb ring is kinetically protected between the large aryl and large $B(C_6F_5)_3$ unit. Therefore, **4** represents a $B(C_6F_5)_3$-stabilized tetraazastibole, which can formally be regarded as the [3+2] cycloaddition product of [Mes*NSb]$^+$ and N_3^- ions. The first tetraazastibole **4** resembles aromatic hydrocarbons that have $(4n+2)$ π electrons and therefore formally obey the Hückel rule.

Experimental Section

Caution! Covalent azides/tetraazapnictoles are potentially hazardous and can decompose explosively under various conditions! Appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing) should be taken, particularly when dealing with large quantities. Experimental details are found in the Supporting Information.[15]

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