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COMMUNICATION

A Neutral Low-Coordinate Heterocyclic Bismuth-Tin Species†

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Abstract. The reaction of a distannadiazane bearing bulky ^RAr*-groups (^RAr* = C₆H₂{C(H)Ph₂}₂R-2,6,4; R = *i*Pr, *t*Bu) with ECl₃ (E = Sb, Bi) was studied resulting in the isolation of previously unknown *N,N*-bis(dichloropnictino)amines (**3**) and a novel heterocyclic carbenoid bismuth species (**4**) bearing a Bi^(III) and a Sn^(IV) center. The structure and bonding was investigated by means of X-ray structure elucidations and DFT calculations.

Pnictogen-nitrogen heterocycles of the type [XE(μ-NR)]₂ (E = P, As, Sb, Bi; species **I** in Figure 1) are valuable starting materials for preparative E-N chemistry.¹ Usually, [ClE(μ-NR)]₂ (E = P, As) is prepared from RN(ECl₂)H in a base-assisted (e.g. NEt₃) cyclization,² however, for the heavier analogous this strategy works poorly. For example, [ClBi(μ-NTer)]₂ (Ter = terphenyl = 2,6-bis-(2,4,6-trimethylphenyl)phenyl) was initially obtained in moderate yields of 45 % besides large amounts of ClBi(N(H)Ter)₂.³ In analogy to Veith's synthesis of the [Me₂SiE(μ-N*t*Bu)]⁺ (**II** in Figure 1),⁴ our group succeeded in establishing a straightforward route towards [ClE(μ-NTer)]₂ (E = Sb, Bi), based on the trans-metalation of the respective tin precursor.⁵ Now highly reactive *cyclo*-1,3-dipnicta-2,4-diazanium salts of the type [E(ClE)(μ-NTer)]⁺ (E = P, As,⁶ Sb, Bi;⁵ **III** in Figure 1) can be obtained by chloride abstraction from [ClE(μ-NTer)]₂ by means of Lewis acids such as GaCl₃. A new area of research was opened with the isolation of thermally stable biradicaloids of the type [E(μ-NTer)]₂ (E = P, As; **IV** in Figure 1) which can easily be accessed by reduction of [ClE(μ-NTer)]₂ with activated magnesium chips.⁷

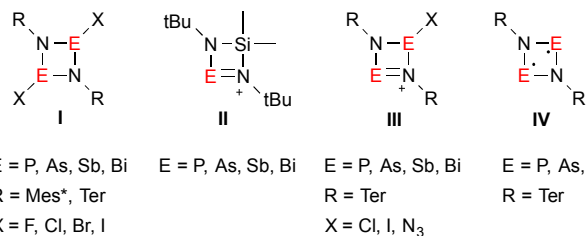
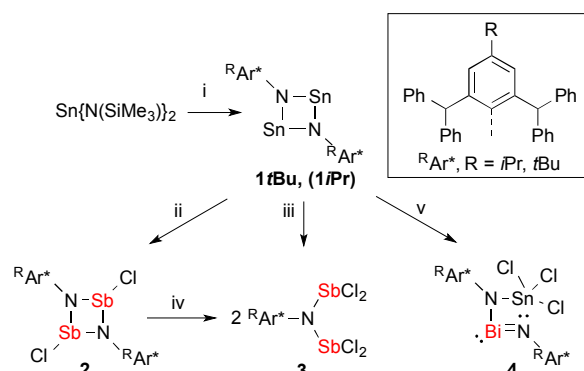


Figure 1. Selected known four-membered E-N heterocycles.⁴⁻⁷

Just recently, we described the synthesis of stable acyclic chloropnictenium ion salts, with an exceedingly bulky ^RAr*-group (Ar* = C₆H₂{C(H)Ph₂}₂R-2,6,4; R = Me, ^tBu) attached to the nitrogen atom.⁸ This sterically demanding moiety offers two flanking phenyl groups for arene-interactions with the low-coordinate reactive site of the molecules. Jones and co-workers realized new bonding situations with the aid of the ^RAr*-moiety,⁹ such as mono-coordinate Ge or Sn cations,¹⁰ singly bonded distannyne and Ge and Sn hydride complexes,^{11,12} that showed magnificent activity as a catalyst in hydroboration reactions.¹³ Just recently, the first example of an amido-distibene in [^tPrAr*N(SiⁱPr₃)Sb]₂ was reported.¹⁴ Herein we describe the synthesis of an unprecedented distannadiazane [Sn(μ-N^RAr*)]₂ with a planar N₂Sn₂-core and its trans-metalation with ECl₃ (E = Sb, Bi), resulting in the isolation of the first *N,N*-bis(dichlorostibino)amine and an elusive four-membered ring system with a N₂Bi^(III)Sn^(IV) unit.



Scheme 1. Preparation of **1R-4**: (i) 2 ^RAr*NH₂, -2 HN(SiMe₃)₂, (ii) 2 SbCl₃, -2 SnCl₂, (iii) 4 SbCl₃, -2 SnCl₂, (iv) 2 SbCl₃, (v) BiCl₃, -Sn.

In analogy to a procedure described by Power et al., leading to the first isolable distannadiazane [Sn(μ-NTer)]₂,¹⁵ the exceedingly bulky amine ^tBuAr*NH₂ and Sn{N(SiMe₃)₂}₂ were combined in a Schlenk-flask without solvent and heated to 160 °C over a period of 45 min,

affording a deep red solid. $\text{HN}(\text{SiMe}_3)_2$ and excess $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$ were removed *in vacuo* and the crude product was recrystallized from $\text{C}_6\text{H}_5\text{F}$ to obtain red crystals of $[\text{Sn}(\mu\text{-N}^{\text{tBu}}\text{Ar}^*)]_2$ (**1R**, $\text{R} = \text{tBu}$) in moderate yields (64 %). The synthesis of **1Me** and **1Pr** suffered from low solubility of the products in common organic solvents, however, minimal amounts of X-ray quality crystals of **1Pr** were obtained from C_6H_6 . In the ^{13}C and ^1H NMR spectrum **1Pr** and **1Bu** can be easily identified by the signals of the *para*-substituent of the inner phenyl group and their diagnostic ^{119}Sn NMR shifts (**1Pr** 783.1 ppm, **1Bu** 789.2 ppm; cf. $[\text{Sn}(\mu\text{-Nter})]_2$ 738.9 ppm). **1Pr** and **1Bu** crystallize as solvates of C_6H_6 or $\text{C}_6\text{H}_5\text{F}$ (see Figures S1 and S4 in the ESI), respectively, in the triclinic space group *P*-1 with one molecule in the asymmetric unit, which lies on a crystallographically imposed centre of inversion. In contrast to $[\text{Sn}(\mu\text{-Nter})]_2$, in which the Sn_2N_2 ring is characterized by a folding about the $\text{Sn}\cdots\text{Sn}$ Axis of 148° , the Sn_2N_2 -core is planar with slightly different $\text{N1}\text{---}\text{Sn1}$ and $\text{N1}'\text{---}\text{Sn1}'$ distances (**1Pr** 2.076(2), 2.086(2); **1Bu** 2.075(2), 2.090(2) Å; cf. $[\text{Sn}(\mu\text{-Nter})]_2$ 2.09, 2.11 Å), a transannular $\text{Sn1}\cdots\text{Sn1}'$ separation of 3.2304(4) (**1Pr**) and 3.2318(3) Å (**1Bu**) and rather acute angles at the tin center (**1Pr** 78.27(7), **1Bu** 78.22(6)°, cf. $[\text{Sn}(\mu\text{-Nter})]_2$ 77.6°).¹⁵ The nitrogen atoms are in a planar environment as expected for a formal sp^2 -hybridized center with a p-type lone pair (LP) of electrons. Hence, the planarity of the core is imposed by the increasing bulkiness of the tBuAr^* -moieties, as a bend core would result in pyramidalization about the N atoms to fit both R^{Ar^*} -groups in. Just recently, the bonding in $[\text{E}(\mu\text{-Nter})]_2$ ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$) was studied in detail by Ziegler et al., who analysed the interaction of the monomeric units $\text{E}(\mu\text{-Nter})$ in the dimeric structure, with the result that the dimer is kept together by two σ - and π -bonds.¹⁶

Combining red **1Bu** with two equivalents of SbCl_3 in CH_2Cl_2 resulted in an immediate decolourisation, accompanied by a colourless precipitate (Scheme 1, reaction ii), which was removed by filtration and from the filtrate X-ray quality crystals of *trans*- $[\text{ClSb}(\mu\text{-Nter})]_2$ (**2**) were grown overnight at room temperature. This metathesis route gives **2** reproducibly in good yields, while using the elimination of SnCl_2 as driving force, dates back to the seminal work of Veith,¹⁷ who established this route to prepare $[\text{Me}_2\text{SiECl}(\mu\text{-NtBu})_2]$ ring systems (vide supra, Figure 1 species II).¹⁸

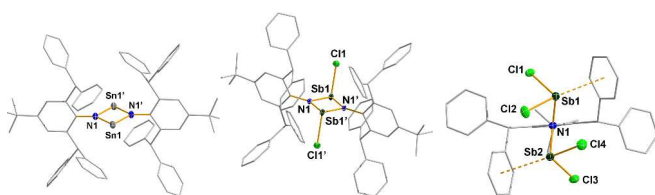


Figure 2. Molecular structures of **1Bu** (left), **2** (middle) and **3** (right). Thermal ellipsoids drawn at 50% probability and -100°C . tBuAr^* substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) of **1**: $\text{Sn1}\text{---}\text{N1}$ 2.0752(16), 2.0897(16); $\text{N1}\text{---}\text{Sn1}\text{---}\text{N1}'$ 78.22(6); **2**: $\text{Sb1}\text{---}\text{N1}$ 2.033(2), $\text{Sb1}\text{---}\text{N1}'$ 2.034(2), $\text{Sb1}\text{---}\text{Cl1}$ 2.4327(7), Sb1Sb1 3.1749(3), $\text{N1}\text{---}\text{C1}$ 1.430(3) Å, $\Sigma(\angle\text{Sb})$ 273.05; $\Sigma(\angle\text{N})$ 359.83, $\text{C1}\text{---}\text{C2}\text{---}\text{N1}\text{---}\text{Sb1}$ 77.6(2); **3**: $\text{Sb1}\text{---}\text{N1}$ 2.030(2), $\text{Sb1}\text{---}\text{Cl1}$ 2.3709(7), $\text{Sb1}\text{---}\text{Cl2}$ 2.4338(7), $\text{Sb2}\text{---}\text{N1}$ 2.039(2), $\text{Sb2}\text{---}\text{Cl3}$ 2.3731(7), $\text{Sb2}\text{---}\text{Cl4}$ 2.4199(7), $\text{N1}\text{---}\text{C1}$ 1.434(3), $\Sigma(\angle\text{Sb1})$ 280.08, $\Sigma(\angle\text{Sb2})$ 281.47, $\text{Sb1}\text{---}\text{N1}\text{---}\text{C1}\text{---}\text{C6}$ 80.0(2).

Pale yellow crystals of **2** are moisture-sensitive, but indefinitely stable in an inert gas atmosphere and can be heated above 270°C

without decomposition. **2** crystallizes solvent-free in the triclinic space group *P*-1 with one molecule in the unit cell and displays a *trans*-substituted centrosymmetric dimer with a planar Sb_2N_2 core protected by two bulky tBuAr^* groups (similar to the molecular structures of $[\text{XSb}(\mu\text{-NMe}^*)]_2$ $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$; *trans*- $[\text{ClSb}(\mu\text{-NtBu})]_2$).^{19,20} As expected the Sb atoms are trigonal pyramidal coordinated, with an s-type LP located on Sb and a trigonal planar coordination environment about the N atom. Additionally, one rather weak dipolar interaction between Sb and a flanking phenyl group ($\text{Sb}\cdots\text{C}_{\text{Cl}} = 3.29$ Å, $\text{C}_{\text{Cl}} =$ centroid) is detected (Figure 2, left).²¹ The formation of **2** can be reproduced, however, if an excess of SbCl_3 is used, a new product $\text{tBuAr}^*\text{N}(\text{SbCl}_2)_2$ (**3**) was isolated. Consequently, we reasoned that **3** was accessible directly from **1Bu** (reaction iii in Scheme 1) when combined with four equiv. of SbCl_3 , which yielded pure **3**. Moreover, treatment of **2** with two additional equiv. of SbCl_3 also afforded (reaction iv in Scheme 1) **3** in good yields (78 %). **3** is thermally stable and melts without decomposition at 236°C and also shows distinct ^1H NMR shifts for the *p*- tBu , the CHPh_2 and the inner phenyl H atoms. Furthermore, **3** belongs to the family of *N,N*-bis(dichlorophenyl)amines, which are well documented for phosphorus ($\text{RN}(\text{PCl}_2)_2$, $\text{R} = \text{Dipp}, \text{Trip}, \text{Ph}$).² Compound **3** was found to be monoclinic ($P2_1/n$) with one molecule of **3** and two disordered $\text{C}_6\text{H}_5\text{F}$ solvent molecules in the asymmetric unit. The $\text{Sb}\text{---}\text{N}$ distances of 2.030(2) and 2.039(2) Å are shorter than the sum of the covalent radii for Sb and N (cf. $\Sigma r_{\text{cov}}(\text{N}\text{---}\text{Sb}) = 2.11$ Å)²² representing highly polarized $\text{Sb}\text{---}\text{N}$ single bonds. The trigonal planar N atom lies between both pyramidal SbCl_2 units, which adopt a *trans* configuration with respect to the SbCl_2 moieties (Figure 2 right). Interestingly, two intramolecular $\text{Sb}\cdots\text{Cl}$ contacts ($\text{Sb1}\cdots\text{Cl4}$, $\text{Sb2}\cdots\text{Cl2}$ ca. 3.35 Å; cf. $\Sigma r_{\text{vdw}}(\text{N}\text{---}\text{Sb}) = 3.81$ Å),²³ stabilizing this *trans* configuration, but no intermolecular contacts are observed.

In addition, the reaction of **1Bu** with two equiv. of BiCl_3 was studied in CH_2Cl_2 , resulting in a black reaction mixture (reaction v in Scheme 1). After multiple filtrations a clear orange solution was obtained. Recrystallization yielded small amounts of orange crystals that were identified as the hitherto unknown $[\text{BiSnCl}_3(\mu\text{-N}^{\text{tBu}}\text{Ar}^*)]_2$ (**4**). The black residue could not be conclusively identified and we assume that elemental tin is formed in a complex redox process that might also involve the formation of elemental bismuth (vide infra). It has been shown before that the $\text{Sn}(\text{II})$ center in $[\text{Me}_2\text{Si}(\mu\text{-NtBu})_2]$ acts as a chloride acceptor in the coupling of phosphalkenes²⁴ and in the reaction with chlorophosphanes.²⁵

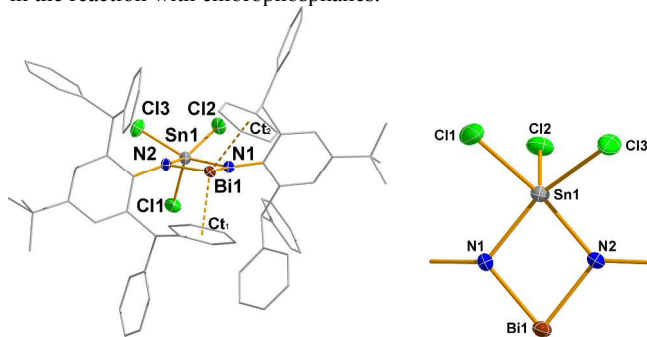


Figure 3. Molecular structures of **4**. Thermal ellipsoids drawn at 50% probability and -100°C . tBuAr^* substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) of **4**: $\text{Sn1}\text{---}\text{N1}$ 2.094(3), $\text{Sn1}\text{---}\text{N2}$ 2.107(3), $\text{Sn1}\text{---}\text{Cl1}$ 2.353(1), $\text{Sn1}\text{---}\text{Cl3}$ 2.387(1), $\text{Sn1}\text{---}\text{Cl2}$ 2.403(1), $\text{Sn1}\cdots\text{Bi1}$ 3.2631(4), $\text{Bi1}\text{---}\text{N1}$ 2.106(3), $\text{Bi1}\text{---}\text{N2}$ 2.108(3), $\text{N1}\text{---}\text{C37}$ 1.425(5), $\text{N2}\text{---}\text{C1}$ 1.426(5), $\text{N1}\text{---}\text{Sn1}\text{---}\text{N2}$ 78.41(12), $\text{N1}\text{---}\text{Bi1}\text{---}\text{N2}$ 78.10(12), $\Sigma(\angle\text{N1})$ 358.0, $\Sigma(\angle\text{N2})$ 353.4, $\text{Bi1}\text{---}\text{C}_{\text{Cl1}}$ 2.891, $\text{Bi1}\text{---}\text{C}_{\text{Cl2}}$ 2.978 Å.

Revision of the reaction conditions prompted us to repeat the experiment in C_6H_5F with one equivalent of $BiCl_3$ (with respect to **1tBu**), to exclude a chloride-shift from CH_2Cl_2 . This again resulted after filtration over a celite-padded frit and concentration of the filtrate in the deposition of orange crystals of **4** as a C_6H_5F solvate. Only small amounts of pure **4** could be isolated, therefore we cannot provide a comprehensive characterization. Nevertheless, the ^{119}Sn NMR spectrum of these isolated crystals revealed a signal at 115.5 ppm (Figure S13), which is in the expected range for a hypercoordinate $N_2Sn^{(IV)}Cl_3$ moiety (cf. $Me_3SnCl_2^-$: 47.7, $Me_2SnCl_3^-$: 128 ppm, $MeSnCl_4^-$: 274 ppm).²⁶ It should be noted that ^{119}Sn NMR data strongly depend on substitution, coordination number and solvent giving rise to large chemical shift differences (cf. $[SnCl_3\{\kappa^2-DippN(H)C_2H_4N(Dipp)\}]$ -303 ppm).²⁷ According to MO and NBO analyses (truncated model $[BiSnCl_3(\mu-NPh)_2]$, **4** can either be described as zwitterionic bismallyl species (Lewis representation A/C in Figure 4), as a bismuthenium species (E) or as an iminobismutane (B and D), and therefore represents the first neutral compound with a 4e-3c double bond delocalized along N-Bi-N (Figure 4). In addition, an s-type lone pair (93%, see Figures S14-15) is located at the Bi center. Lewis representations A/C represent the best Lewis structures according to NBO analysis. Along with structures of type E/F, which also possess a rather larger weight, since the π bonds are dominantly located at the N atoms (81%), this situation resembles that of N-heterocyclic carbenes (NHC)²⁸, which are stabilized by intramolecular π -donor- π -acceptor interactions (population of the $p_z(Bi) = 0.47e$) to stabilize the dicoordinate carbene C atom. It should be noted that also Bi-N s bonds (78%) are highly polar, as well as the Sn-Cl or Sn-N bonds (N, Cl: ca. 80%). The computed large positive charges at the Bi and Sn centers are very similar with +1.67 and 1.77e supporting the picture of highly polarized Bi-N and Sn-Y (Y = Cl, N) bonds.

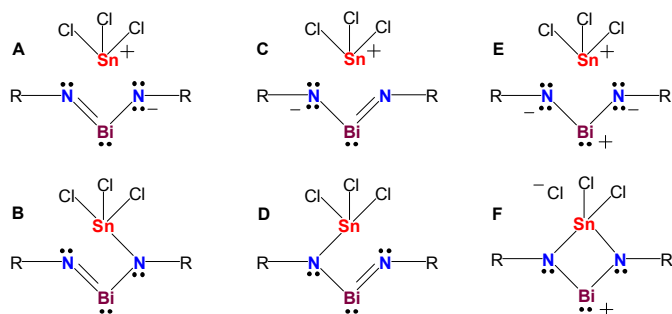


Figure 4. Selected Lewis representations of **4**.

4 crystallizes as CH_2Cl_2 solvate ($4 \cdot (CH_2Cl_2)_2$) in the triclinic space group $P-1$ with two molecules of **4** and four CH_2Cl_2 molecules (disordered on their positions) in the cell. Moreover, from C_6H_5F species **4** crystallizes as a solvate of fluorobenzene solvate ($4 \cdot C_6H_5F$) in the orthorhombic space group $Pna2_1$ (the discussion is led for $4 \cdot CH_2Cl_2$). The most prominent structural feature is the planar 4-membered Sn-N-Bi-N heterocycle featuring two different heavy main group metals (deviation from planarity $< 2.3^\circ$, Figure 3). Both Bi-N bond lengths are rather short with 2.106(3) and 2.108(3) Å (cf. $\Sigma r_{cov}(N-Bi) = 2.22$, $(N=Bi) = 2.01$ Å;²² $[Me_2SiBi(\mu-NtBu)_2]^+$ 2.08 Å, $[Bi(Ibi)(\mu-NTer)_2]^+$ 2.13 Å, $[Me_2SiBi(\mu-NDipp)_2]$ 2.12 Å, $Dipp = 2,6-iPrC_6H_3$)^{4,5,29} clearly displaying some Bi-N double bond character in accord with our computation (Figure 4). Interestingly, both Sn-N bond lengths (2.094(3) and 2.107(3) Å, cf. $\Sigma r_{cov}(N-Sn) = 2.11$, $(N=Sn) = 1.90$ Å) are in the similar range like the Bi-N distances, however, describing typical highly polarized $Sn^{(IV)}$ -N single bonds. Both the N-Bi-N angle and N-Sn-N angles are

rather acute with ca. 78° (cf. $[Me_2SiBi(\mu-NtBu)_2]^+$ 72.9, $[Bi(Ibi)(\mu-NTer)_2]^+$ 77.4, $[Me_2SiBi(\mu-NDipp)_2]^+$ 73.7),^{4,5,29} while the two Bi-N-Sn angles are much larger with 101 - 102° . A closer look at the secondary interactions revealed that the Sn-N-Bi-N heterocycle is well protected inside the pocket formed by the two $^{tBu}Ar^*$ -phenyl substituents. However, the dicoordinate bismuth is stabilized by strong secondary interactions (Menshutkin type π complexes)²¹ with two phenyl groups as indicated by very short Bi...centroid distances (2.891/2.978 Å; cf. $[^{Me}Ar^*N(SiMe_3)BiCl][Al(OR^F)_4]^+$ 2.86/2.94 Å)⁸ which are well within the range of van-der-Waals radii ($\Sigma r_{vdW}(C \cdots Bi) = 3.77$ Å).²³

In conclusion, we succeeded in the preparation of the first N,N'-bis(dichlorostibino)amine and an unusual heterocycle containing $Sn^{(IV)}$ and a dicoordinate Bi-center, which is protected by arene-interactions to flanking phenyl groups of the bulky Ar^* moiety. These species might be useful starting materials for the preparation of pnictadiazonium salts of Sb and Bi. In comparison to stable N-heterocyclic carbenes,²⁸ the dicoordinated Bi species **4** can be regarded as a heavy atom analog of NHCs.

Notes and references

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† Electronic supplementary information (ESI) available: Experimental and computational details and information on X-ray structure elucidation. CCDC 1403993-1403998. For ESI and crystallographic data in CIF or other electronic format see DOI: XXXX

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