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A neutral low-coordinate heterocyclic bismuth-tin species†

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The reaction of 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 Fig. 1) are valuable starting materials for preparative E–N chemistry.¹ Usually, [CIE(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 analogs 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 [Me₂SiE(μ-N^tBu)]⁺ (II in Fig. 1),⁴ our group succeeded in establishing a straightforward route towards the synthesis of [CIE(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(CIE)(μ-NTer)]⁺ (E = P, As,⁶ Sb, Bi;⁷ III in Fig. 1) can be obtained by chloride abstraction from [CIE(μ-NTer)]₂ by means of Lewis acids such as GaCl₃. A new area of research opened up with the isolation of thermally stable biradicaloids of the type [E(μ-NTer)]₂ (E = P, As; IV in Fig. 1) which can easily be accessed by reduction of [CIE(μ-NTer)]₂ with activated magnesium chips.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, *t*Bu) 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 [IPrAr*N(SiPr₃)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.

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. HN(SiMe₃)₂ and excess Sn{N(SiMe₃)₂}₂ were removed *in vacuo* and the crude product was recrystallized from C₆H₅F to obtain red crystals of [Sn(μ-N^tBuAr*)]₂ (**1R**, R = *t*Bu) in moderate yields (64%). The synthesis of **1Me** and **1iPr** suffered from low solubility of the products in common organic solvents, however, minimal amounts of X-ray quality crystals of **1iPr** were obtained from C₆H₆. In the ¹³C and ¹H NMR spectrum **1iPr** and **1tBu** can be easily identified by the signals of the *para*-substituent of the inner phenyl group and their diagnostic ¹¹⁹Sn NMR shifts

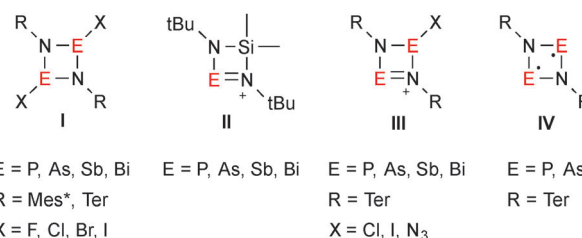


Fig. 1 Selected known four-membered E–N heterocycles.^{4–7}

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(**1iPr** 783.1 ppm, **1tBu** 789.2 ppm; cf. $[\text{Sn}(\mu\text{-Nter})]_2$ 738.9 ppm). **1iPr** and **1tBu** crystallize as solvates of C_6H_6 or $\text{C}_6\text{H}_5\text{F}$ (see Fig. S1 and S4 in the ESI[†]), respectively, in the triclinic space group $P\bar{1}$ 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 N1-Sn1 and N1'-Sn1' distances (**1iPr** 2.076(2), 2.086(2); **1tBu** 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) (**1iPr**) and 3.2318(3) Å (**1tBu**) and rather acute angles at the tin center (**1iPr** 78.27(7), **1tBu** 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 $t\text{BuAr}^*$ -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 **1tBu** 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 $\text{trans}[\text{ClSb}(\mu\text{-Nter})]_2$ (**2**) were grown overnight at room temperature. This metathesis route gives **2** reproducibly in good yields, while using the elimination of SnCl_2 as the driving force, which 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*, Fig. 1 species II).¹⁸

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 $P\bar{1}$ 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 $t\text{BuAr}^*$ groups similar to the molecular structures of $[\text{XSb}(\mu\text{-NMes}^*)]_2$ $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$; $\text{trans}[\text{ClSb}(\mu\text{-NtBu})]_2$.^{19,20} As expected the Sb atoms are trigonal

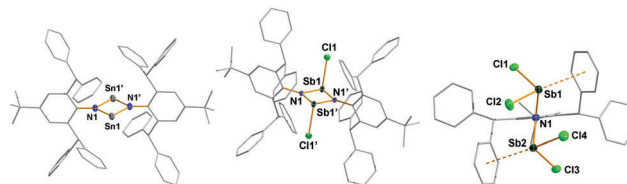
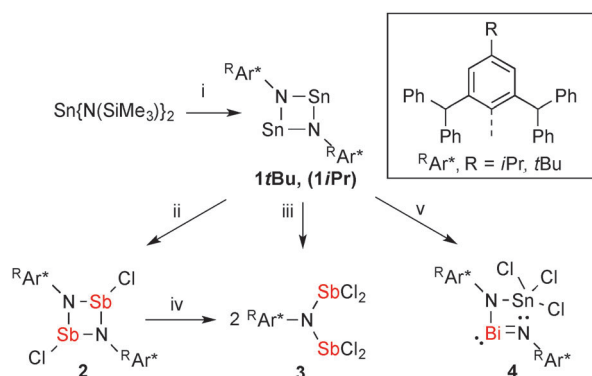


Fig. 2 Molecular structures of **1tBu** (left), **2** (middle) and **3** (right). Thermal ellipsoids drawn at 50% probability and -100°C . $t\text{BuAr}^*$ substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) of **1tBu**: Sn1-N1 2.0752(16), 2.0897(16); N1-Sn1-N1' 78.22(6); **2**: Sb1-N1 2.033(2), Sb1-N1' 2.034(2), Sb1-Cl1 2.4327(7), Sb1Sb1 3.1749(3), N1-C1 1.430(3) Å, $\sum(\angle\text{Sb})$ 273.05; $\sum(\angle\text{N})$ 359.83, Cl1-C2-N1-Sb1 77.6(2); **3**: Sb1-N1 2.030(2), Sb1-Cl1 2.3709(7), Sb1-Cl2 2.4338(7), Sb2-N1 2.039(2), Sb2-Cl3 2.3731(7), Sb2-Cl4 2.4199(7), N1-C1 1.434(3), $\sum(\angle\text{Sb1})$ 280.08, $\sum(\angle\text{Sb2})$ 281.47, Sb1-N1-C1-C6 80.0(2).

pyramidally 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 ($\text{Sb}\cdots\text{C}_{\text{Ct}} = 3.29$ Å, $\text{C}_{\text{Ct}} = \text{centroid}$) is detected (Fig. 2, left).²¹ The formation of **2** can be reproduced, however, if an excess of SbCl_3 is used, a new product $t\text{BuAr}^*\text{N}(\text{SbCl}_2)_2$ (**3**) was isolated. Consequently, we reasoned that **3** was accessible directly from **1tBu** (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*- $t\text{Bu}$, the CHPh_2 and the inner phenyl H atoms. Furthermore, **3** belongs to the family of *N,N*-bis(dichloropnictino)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 Sb-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. $\sum r_{\text{cov}}(\text{N-Sb}) = 2.11$ Å)²² representing highly polarized Sb-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 (Fig. 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. $\sum r_{\text{vdW}}(\text{N-Sb}) = 3.81$ Å),²³ stabilizing this *trans* configuration, but no intermolecular contacts are observed.

In addition, the reaction of **1tBu** 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 $[\text{BiSnCl}_3(\mu\text{-N}^t\text{BuAr}^*)]_2$ (**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 $[\text{Me}_2\text{SiSn}(\mu\text{-NtBu})]_2$ acts as a chloride acceptor in the coupling of phosphalkenes²⁴ and in the reaction with chlorophosphanes.²⁵

Revision of the reaction conditions prompted us to repeat the experiment in $\text{C}_6\text{H}_5\text{F}$ with one equivalent of BiCl_3



Scheme 1 Preparation of **1R-4**: (i) 2 $\text{R}^*\text{Ar}^*\text{NH}_2$, $-2 \text{HN}(\text{SiMe}_3)_2$, (ii) 2 SbCl_3 , -2SnCl_2 , (iii) 4 SbCl_3 , -2SnCl_2 , (iv) 2 SbCl_3 , and (v) BiCl_3 , $-\text{Sn}$.

(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 $\text{C}_6\text{H}_5\text{F}$ 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 (Fig. S13, ESI[†]), which is in the expected range for a hypercoordinate $\text{N}_2\text{Sn}^{(\text{IV})}\text{Cl}_3$ moiety (cf. $\text{Me}_3\text{SnCl}_2^-$: 47.7, $\text{Me}_2\text{SnCl}_3^-$: 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. $[\text{SnCl}_3\{\kappa^2\text{-DippN}(\text{H})\text{C}_2\text{H}_4\text{N}(\text{Dipp})\}]^-$ –303 ppm).²⁷ According to MO and NBO analyses of the truncated model $[\text{BiSnCl}_3(\mu\text{-NPh})_2]$, **4** can either be described as zwitterionic bismallyl species (Lewis representation A/C in Fig. 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 (Fig. 4). In addition, an s-type lone pair (93%, see Fig. S14 and S15, ESI[†]) 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 large 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 $p_z(\text{Bi}) = 0.47\text{e}$) to stabilize the dicoordinate carbene C atom. It should be noted that also Bi–N σ 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 values of +1.67 and 1.77e supporting the picture of highly polarized Bi–N and Sn–Y (Y = Cl, N) bonds.

4 crystallizes as CH_2Cl_2 solvate ($(\text{4} \cdot (\text{CH}_2\text{Cl}_2)_2)$) in the triclinic space group $P\bar{1}$ with two molecules of **4** and four CH_2Cl_2 molecules (disordered on their positions) in the cell. Moreover, from $\text{C}_6\text{H}_5\text{F}$ species **4** crystallizes as a solvate of fluorobenzene solvate ($\text{4} \cdot \text{C}_6\text{H}_5\text{F}$) in the orthorhombic space group $Pna2_1$ (the discussion is led for $\text{4} \cdot \text{CH}_2\text{Cl}_2$). 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 $< 2.3^\circ$, Fig. 3). Both Bi–N bond lengths are rather short with 2.106(3) and 2.108(3) Å (cf. $\sum r_{\text{cov}}(\text{N–Bi}) = 2.22$, $(\text{N}=\text{Bi}) = 2.01$ Å;²² $[\text{Me}_2\text{SiBi}(\mu\text{-NtBu})_2]^+$ 2.08 Å, $[\text{Bi}(\text{IBi})(\mu\text{-Nter})_2]^+$ 2.13 Å, and $[\text{Me}_2\text{SiBi}(\mu\text{-NDipp})_2]$ 2.12 Å, where Dipp = 2,6-*i*PrC₆H₃)^{4,5,29} clearly displaying some Bi–N double bond character in accord with our computation (Fig. 4). Interestingly, both Sn–N bond lengths (2.094(3) and 2.107(3) Å, cf. $\sum r_{\text{cov}}(\text{N–Sn}) = 2.11$, $(\text{N}=\text{Sn}) = 1.90$ Å) are in the similar range like the Bi–N distances, however, describing typical highly polarized $\text{Sn}^{(\text{IV})}\text{–N}$ single bonds. Both the N–Bi–N angle and N–Sn–N angles are rather acute with ca. 78° (cf. $[\text{Me}_2\text{SiBi}(\mu\text{-NtBu})_2]^+$ 72.9° , $[\text{Bi}(\text{IBi})(\mu\text{-Nter})_2]^+$ 77.4° , and $[\text{Me}_2\text{SiBi}(\mu\text{-NDipp})_2]^+$ 73.7°)^{4,5,29} while the two Bi–N–Sn angles are much larger with $101\text{--}102^\circ$. 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 $^t\text{BuAr}^*$ -phenyl substituents. However, the dicoordinate bismuth is stabilized by strong secondary interactions (Menshutkin type π complexes)²¹

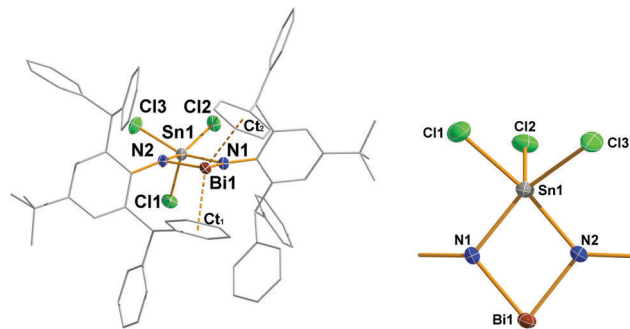


Fig. 3 Molecular structures of **4**. Thermal ellipsoids drawn at 50% probability and -100°C . $^t\text{BuAr}^*$ substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) of **4**: Sn1–N1 2.094(3), Sn1–N2 2.107(3), Sn1–Cl1 2.353(1), Sn1–Cl3 2.387(1), Sn1–Cl2 2.403(1), Sn1...Bi1 3.2631(4), Bi1–N1 2.106(3), Bi1–N2 2.108(3), N1–C37 1.425(5), N2–C1 1.426(5), N1–Sn1–N2 $78.41(12)$, N1–Bi1–N2 $78.10(12)$, $\sum(\angle \text{N1})$ 358.0, $\sum(\angle \text{N2})$ 353.4, Bi1–C_{ct1} 2.891, Bi1–C_{ct2} 2.978 Å.

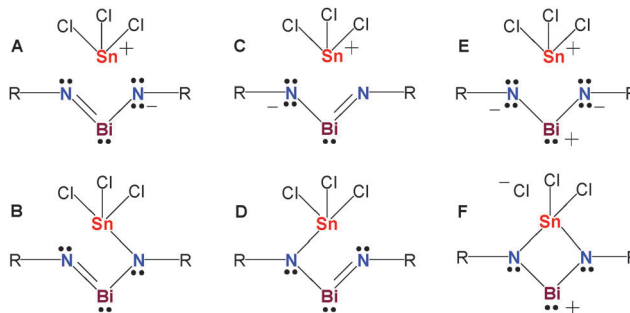


Fig. 4 Selected Lewis representations of **4**.

with two phenyl groups as indicated by very short Bi...centroid distances (2.891/2.978 Å; cf. $[\text{MeAr}^*\text{N}(\text{SiMe}_3)\text{BiCl}][\text{Al}(\text{OR}^F)_4]^+$ 2.86/2.94 Å)⁸ which are well within the range of van-der-Waals radii ($\sum r_{\text{vdw}}(\text{C} \cdots \text{Bi}) = 3.77$ Å).²³

In conclusion, we succeeded in the preparation of the first N,N' -bis(dichlorostibinino)amine and an unusual heterocycle containing $\text{Sn}^{(\text{IV})}$ 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.

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