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# A neutral low-coordinate heterocyclic bismuth-tin species†

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**The reaction of distannadiazane bearing bulky <sup>R</sup>Ar\*-groups (<sup>R</sup>Ar\* = C<sub>6</sub>H<sub>2</sub>{C(H)Ph<sub>2</sub>}<sub>2</sub>R-2,6,4; R = *i*Pr, *t*Bu) with ECl<sub>3</sub> (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<sup>(III)</sup> and a Sn<sup>(IV)</sup> 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)]<sub>2</sub> (E = P, As, Sb, Bi; species I in Fig. 1) are valuable starting materials for preparative E–N chemistry.<sup>1</sup> Usually, [CIE(μ-NR)]<sub>2</sub> (E = P, As) is prepared from RN(ECl<sub>2</sub>)H in a base-assisted (*e.g.* NEt<sub>3</sub>) cyclization,<sup>2</sup> however, for the heavier analogs this strategy works poorly. For example, [ClBi(μ-NTer)]<sub>2</sub> (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)<sub>2</sub>.<sup>3</sup> In analogy to Veith's synthesis of [Me<sub>2</sub>SiE(μ-N*t*Bu)<sub>2</sub>]<sup>+</sup> (II in Fig. 1),<sup>4</sup> our group succeeded in establishing a straightforward route towards the synthesis of [CIE(μ-NTer)]<sub>2</sub> (E = Sb, Bi), based on the *trans*-metalation of the respective tin precursor.<sup>5</sup> Now highly reactive *cyclo*-1,3-dipnicta-2,4-diazanium salts of the type [E(CIE)(μ-NTer)<sub>2</sub>]<sup>+</sup> (E = P, As,<sup>6</sup> Sb, Bi;<sup>5</sup> III in Fig. 1) can be obtained by chloride abstraction from [CIE(μ-NTer)]<sub>2</sub> by means of Lewis acids such as GaCl<sub>3</sub>. A new area of research opened up with the isolation of thermally stable biradicaloids of the type [E(μ-NTer)]<sub>2</sub> (E = P, As; IV in Fig. 1) which can easily be accessed by reduction of [CIE(μ-NTer)]<sub>2</sub> with activated magnesium chips.<sup>7</sup>

Just recently, we described the synthesis of stable acyclic chloropnictenium ion salts, with an exceedingly bulky <sup>R</sup>Ar\*-group (Ar\* = C<sub>6</sub>H<sub>2</sub>{C(H)Ph<sub>2</sub>}<sub>2</sub>R-2,6,4; R = Me, *t*Bu) attached to the nitrogen atom.<sup>8</sup>

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 <sup>R</sup>Ar\*-moiety,<sup>9</sup> such as mono-coordinate Ge or Sn cations,<sup>10</sup> singly bonded distannyne and Ge and Sn hydride complexes,<sup>11,12</sup> that showed magnificent activity as a catalyst in hydroboration reactions.<sup>13</sup> Just recently, the first example of an amido-distibene in [Pr<sup>Ar\*</sup>N(SiPr<sub>3</sub>)Sb]<sub>2</sub> was reported.<sup>14</sup> Herein we describe the synthesis of an unprecedented distannadiazane [Sn(μ-N<sup>R</sup>Ar\*)]<sub>2</sub> with a planar N<sub>2</sub>Sn<sub>2</sub>-core and its *trans*-metalation with ECl<sub>3</sub> (E = Sb, Bi), resulting in the isolation of the first *N,N*-bis(dichlorostibino)amine and an elusive four-membered ring system with a N<sub>2</sub>Bi<sup>(III)</sup>Sn<sup>(IV)</sup> unit.

In analogy to a procedure described by Power *et al.*, leading to the first isolable distannadiazane [Sn(μ-NTer)]<sub>2</sub>,<sup>15</sup> the exceedingly bulky amine <sup>t</sup>BuAr\*NH<sub>2</sub> and Sn{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> 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(SiMe<sub>3</sub>)<sub>2</sub> and excess Sn{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> were removed *in vacuo* and the crude product was recrystallized from C<sub>6</sub>H<sub>5</sub>F to obtain red crystals of [Sn(μ-N<sup>t</sup>BuAr\*)]<sub>2</sub> (**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 C<sub>6</sub>H<sub>6</sub>. In the <sup>13</sup>C and <sup>1</sup>H NMR spectrum **1iPr** and **1tBu** can be easily identified by the signals of the *para*-substituent of the inner phenyl group and their diagnostic <sup>119</sup>Sn NMR shifts

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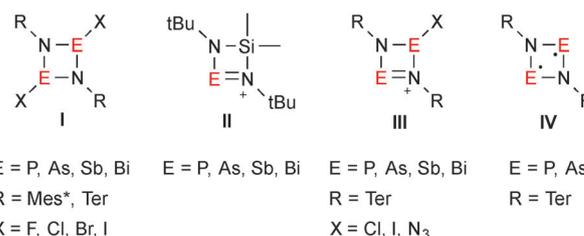


Fig. 1 Selected known four-membered E–N heterocycles.<sup>4–7</sup>



(**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  $\text{C}_6\text{H}_6$  or  $\text{C}_6\text{H}_5\text{F}$  (see Fig. S1 and S4 in the ESI<sup>†</sup>), 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  $\text{Sn}_2\text{N}_2$  ring is characterized by a folding about the  $\text{Sn}\cdots\text{Sn}$  axis of  $148^\circ$ , the  $\text{Sn}_2\text{N}_2$ -core is planar with slightly different  $\text{N1-Sn1}$  and  $\text{N1'-Sn1'}$  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**  $78.22(6)^\circ$ , cf.  $[\text{Sn}(\mu\text{-Nter})_2]$   $77.6^\circ$ ).<sup>15</sup> The nitrogen atoms are in a planar environment as expected for a formal  $\text{sp}^2$ -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  $\text{R}^*\text{Ar}^*$ -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  $\sigma$ - and  $\pi$ -bonds.<sup>16</sup>

Combining red **1tBu** with two equivalents of  $\text{SbCl}_3$  in  $\text{CH}_2\text{Cl}_2$  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  $\text{SnCl}_2$  as the driving force, which dates back to the seminal work of Veith,<sup>17</sup> who established this route to prepare  $[\text{Me}_2\text{SiEC}(\mu\text{-N}t\text{Bu})_2]$  ring systems (*vide supra*, Fig. 1 species II).<sup>18</sup>

Pale yellow crystals of **2** are moisture-sensitive, but indefinitely stable in an inert gas atmosphere and can be heated above  $270^\circ\text{C}$  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  $\text{Sb}_2\text{N}_2$  core protected by two bulky  $t\text{BuAr}^*$  groups similar to the molecular structures of  $[\text{XSb}(\mu\text{-NMes}^*)_2]$   $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ; *trans*- $[\text{ClSb}(\mu\text{-N}t\text{Bu})_2]$ .<sup>19,20</sup> As expected the Sb atoms are trigonal

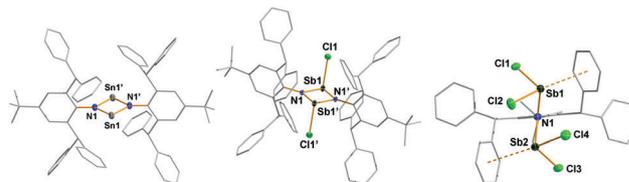
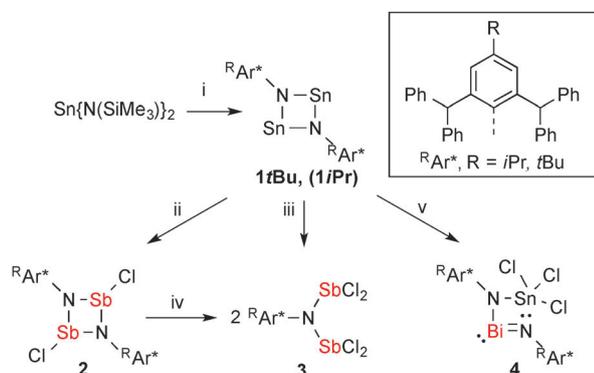


Fig. 2 Molecular structures of **1tBu** (left), **2** (middle) and **3** (right). Thermal ellipsoids drawn at 50% probability and  $-100^\circ\text{C}$ .  $t\text{BuAr}^*$  substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) of **1tBu**: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

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).<sup>21</sup> The formation of **2** can be reproduced, however, if an excess of  $\text{SbCl}_3$  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  $\text{SbCl}_3$ , which yielded pure **3**. Moreover, treatment of **2** with two additional equiv. of  $\text{SbCl}_3$  also afforded (reaction (iv) in Scheme 1) **3** in good yields (78%). **3** is thermally stable and melts without decomposition at  $236^\circ\text{C}$  and also shows distinct  $^1\text{H}$  NMR shifts for the *p*- $t\text{Bu}$ , the  $\text{CHPh}_2$  and the inner phenyl H atoms. Furthermore, **3** belongs to the family of *N,N*-bis(dichloro-pnictino)amines, which are well documented for phosphorus ( $\text{RN}(\text{PCl}_2)_2$ ,  $\text{R} = \text{Dipp}, \text{Trip}, \text{Ph}$ ).<sup>2</sup> 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)<sup>22</sup> representing highly polarized Sb-N single bonds. The trigonal planar N atom lies between both pyramidal  $\text{SbCl}_2$  units, which adopt a *trans* configuration with respect to the  $\text{SbCl}_2$  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),<sup>23</sup> stabilizing this *trans* configuration, but no intermolecular contacts are observed.

In addition, the reaction of **1tBu** with two equiv. of  $\text{BiCl}_3$  was studied in  $\text{CH}_2\text{Cl}_2$ , 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  $[\text{Me}_2\text{SiSn}(\mu\text{-N}t\text{Bu})_2]$  acts as a chloride acceptor in the coupling of phosphalkenes<sup>24</sup> and in the reaction with chlorophosphanes.<sup>25</sup>

Revision of the reaction conditions prompted us to repeat the experiment in  $\text{C}_6\text{H}_5\text{F}$  with one equivalent of  $\text{BiCl}_3$



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



(with respect to **1tBu**), to exclude a chloride-shift from  $\text{CH}_2\text{Cl}_2$ . 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  $^{119}\text{Sn}$  NMR spectrum of these isolated crystals revealed a signal at 115.5 ppm (Fig. S13, ESI<sup>†</sup>), 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,  $\text{MeSnCl}_4^-$ : 274 ppm).<sup>26</sup> It should be noted that  $^{119}\text{Sn}$  NMR data strongly depend on substitution, coordination number and solvent giving rise to large chemical shift differences (cf.  $[\text{SnCl}_3\{\text{k}^2\text{-DippN}(\text{H})\text{C}_2\text{H}_4\text{N}(\text{Dipp})\}]^-$  –303 ppm).<sup>27</sup> According to MO and NBO analyses of the truncated model  $[\text{BiSnCl}_3(\mu\text{-NPh})_2]$ , **4** can either be described as zwitterionic bismally 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<sup>†</sup>) 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  $\pi$  bonds are dominantly located at the N atoms (81%), this situation resembles that of N-heterocyclic carbenes (NHC),<sup>28</sup> which are stabilized by intramolecular  $\pi$ -donor– $\pi$ -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  $\sigma$  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  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$  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;<sup>22</sup>  $[\text{Me}_2\text{SiBi}(\mu\text{-NtBu})_2]^+$  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-*iPrC}\_6\text{H}\_3*)<sup>4,5,29</sup> 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  $\text{Sn}^{(\text{IV})}$ –N single bonds. Both the N–Bi–N angle and N–Sn–N angles are rather acute with ca.  $78^\circ$  (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),<sup>4,5,29</sup> 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 <sup>tBu</sup>Ar\*–phenyl substituents. However, the dicoordinate bismuth is stabilized by strong secondary interactions (Menshutkin type  $\pi$  complexes)<sup>21</sup>

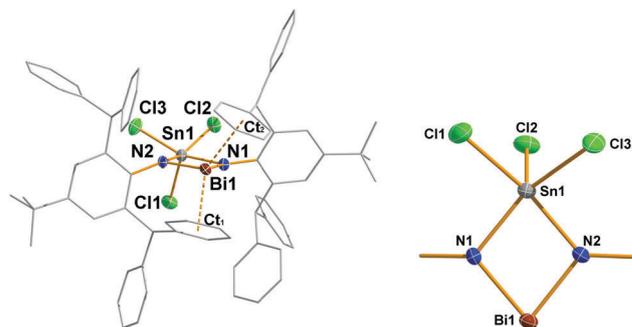


Fig. 3 Molecular structures of **4**. Thermal ellipsoids drawn at 50% probability and  $-100^\circ\text{C}$ . <sup>tBu</sup>Ar\* substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) of **4**: Sn1–N1 2.094(3), Sn1–N2 2.107(3), Sn1–Cl1 2.353(1), 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<sub>Cl1</sub> 2.891, Bi1–C<sub>Cl2</sub> 2.978 Å.

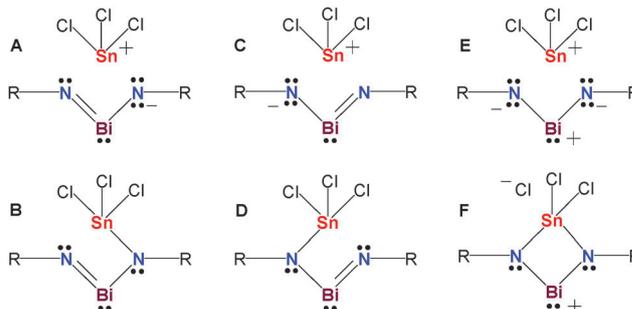


Fig. 4 Selected Lewis representations of **4**.

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)<sup>8</sup> which are well within the range of van-der-Waals radii ( $\sum r_{\text{vdw}}(\text{C} \cdots \text{Bi}) = 3.77$  Å).<sup>23</sup>

In conclusion, we succeeded in the preparation of the first *N,N'*-bis(dichlorostibino)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,<sup>28</sup> the dicoordinated Bi species **4** can be regarded as a heavy atom analog of NHCs.

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