Main-Group Chemistry

DOI: 10.1002/anie.201203267

Cyclic Distiba- and Dibismadiazenium Cations**

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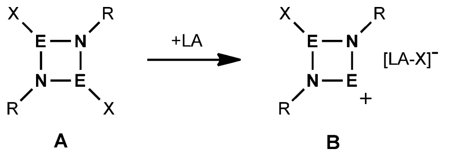
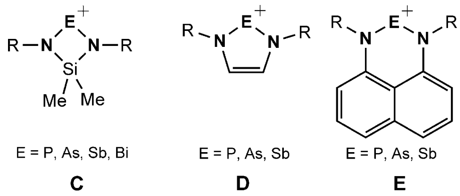
Four-membered pnictogen-nitrogen heterocycles of the type $[XE(\mu\text{-NR})]_2$ (E = element of Group 15, X = halogen) are known as 1,3-dihalogeno-*cyclo*-1,3-dipnicta(III)-2,4-diazanes (Scheme 1, species **A**). The phosphorus species in particular play a major role in preparative phosphorus–nitrogen chemistry, for example in the preparation of macrocycles, polymers, main-group complexes, and ring transformation reactions or the generation of cyclic binary PN cations.[1] In recent years, new examples for *cyclo*-1,3-dipnicta(III)-2,4-diazanes were prepared by introduction of bulky R substituents and characterized, with the focus on kinetic stabilization.[2–6] Only recently, the synthesis of salts bearing the highly reactive *cyclo*-1,3-dipnicta(III)-2,4-diazenium cations $[ClE(\mu\text{-NTer})_2E]^+$ (E = P and As; Ter = terphenyl = 2,6-bis(2,4,6-trimethylphenyl)phenyl; Scheme 1, species **B**) was reported.[7,8] The generation of such cations was achieved by halide abstraction upon addition of strong Lewis acids, such as $GaCl_3$.[9] Utilization of the bulky terphenyl group leads to the formation of separated ion pairs in the crystal with large interionic distances.



Scheme 1. Reaction of *cyclo*-dipnicta(III)diazanes with a Lewis acid (LA), yielding *cyclo*-dipnicta(III)diazenium salts (R = bulky substituent, X = halogen, pseudohalogen).

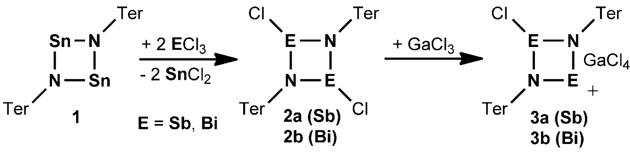
For the heavier Group 15 elements antimony and bismuth, the analogous *cyclo*-1,3-dipnicta(III)-2,4-diazenium cations are unknown, and examples with dicoordinated N-E^+-N centers in heterocycles are rare (Scheme 2). Veith et al. prepared a series of pnictogen cations with a $[Me_2SiE(\mu\text{-N}t\text{Bu})_2]^+$ ring (species **C**).[10] Owing to the relatively low steric demand of the *tert*-butyl groups attached to the N atoms in these systems, strong intermolecular interactions are present in these Sb- and Bi-containing cyclic cations. Moreover, five- and six-membered cationic heterocycles containing Sb atoms are known (species **D** and **E**).[11,12]



Scheme 2. Examples for cyclic nitrogen–pnictogen cations.

Herein we present on the synthesis and full characterization of heavy Group 15 element-containing *cyclo*-dipnictadiazenium cations $[XE(\mu\text{-NTer})_2E]^+$ and $[E_2(\mu\text{-NTer})_2]^{2+}$ (E = Sb, Bi; X = Cl, I) starting from a new facile synthesis of terphenyl-substituted 1,3-dichloro-*cyclo*-1,3-dipnicta-2,4-diazanes $[ClE(\mu\text{-NR})]_2$.

The synthesis of 1,3-dichloro-*cyclo*-1,3-dipnicta-2,4-diazanes (**B**) by facile HCl elimination reactions starting from primary amines and element(III) chlorides or aminopnictanes has been studied in detail for more than one century, and especially in the case of Sb and Bi, side reactions lead to complex product mixtures, thus dramatically decreasing the yield.[3,6,13,14] To be able to carry out follow-up chemistry, it was vital to develop a straightforward high-yield synthetic route to $[ClE(\mu\text{-NR})]_2$ species (E = Sb, Bi). Inspired by Veith's synthesis[10] of $[Me_2SiE(\mu\text{-N}t\text{Bu})_2]^+$ by transmetalation reaction utilizing the corresponding stannane as starting material, we prepared first the cyclic distannadiazane $[Sn(\mu\text{-NTer})]_2$ (**1**), a compound which was only recently reported by Power et al.[15] Therefore, distannadiazane **1** was treated with pnictogen(III) chlorides ECl_3 (E = Sb, Bi), and indeed the corresponding *cyclo*-1,3-dipnicta-2,4-diazanes $[ClE(\mu\text{-NTer})]_2$ (E = Sb (**2a**), Bi (**2b**)) were formed in good yields (Sb: 79 %, Bi: 68 %), as illustrated in Scheme 3. This new procedure allows the preparation of pure **2a** and **2b** in large quantities,[16] and almost no side reactions are observed.



Scheme 3. Two-step synthesis of *cyclo*-dipnictadiazenium cations [ClE-(μ-NTer)2E]$^+$: 1) transmetallation and 2) chloride abstraction.

Slow addition of $GaCl_3$ to a yellow solution of **2a** in CH_2Cl_2 at −78 °C led to the immediate formation of the *cyclo*-distibadiazenium cation $[ClSb(\mu\text{-NTer})_2Sb]^+$, which was indi-

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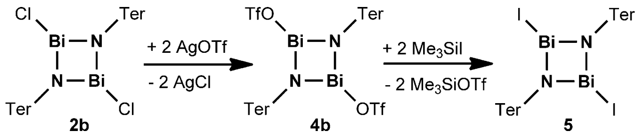
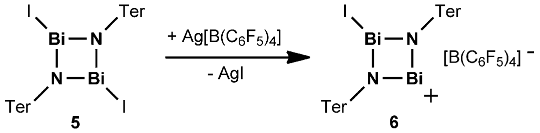
[**] Financial support by the DFG is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203267.

cated by a color change from yellow to dark green (Scheme 3). After filtration and concentration, the solution was stored at −25 °C, resulting in the deposition of violet crystals (black appearance, 60 % yield) which were unequivocally characterized (X-ray, elemental analysis, NMR, IR, Raman spectroscopy) as [ClSb(μ-NTer)$_2$Sb][GaCl$_4$] (**3a**; Figure 1, left). Interestingly, upon addition of GaCl$_3$, neither monomerization nor any transformation to trimeric or oligomeric species was observed.[17] The same procedure was also applied to the analogous Bi species **2b**. However, after initial formation of a dark-brown solution, indicating, according to ^{1}H and ^{13}C NMR studies, the presence of the [ClBi(μ-NTer)$_2$Bi]$^+$ ion (Scheme 3), the isolation as [GaCl$_4$]$^-$ salt (**3b**) from this mixture was impossible owing to rapid decomposition upon crystallization conditions (high concentration). Utilization of other chloride-abstracting reagents, such as SbCl$_5$ and Ag[SbF$_6$], gave the same result. Obviously, the anions [GaCl$_4$]$^-$, [SbCl$_6$]$^-$, and [SbF$_6$]$^-$ were involved in the decomposition process and were not innocent. Therefore, we decided to use the chemically robust weakly coordinating anion [B(C$_6$F$_5$)$_4$]$^-$ as counterion for the [ClBi(μ-NTer)$_2$Bi]$^+$ ion to avoid decomposition triggered by cation–anion interactions. As the reaction of [ClBi(μ-NR)]$_2$ (**2b**) with Ag[B(C$_6$F$_5$)$_4$] was surprisingly slow and immediate decomposition was observed, a chlorine/iodine exchange was attempted to yield [IBi(μ-NTer)]$_2$. It is known that element triflate compounds are good starting materials for a triflate–iodine substitution, which is easily achieved by addition of Me$_3$SiI, inducing the elimination of Me$_3$Si−OTf.[5] Thus, at first [ClBi(μ-NTer)]$_2$ (**2b**) was transformed to the hitherto unknown compound [(TfO)Bi(μ-NTer)]$_2$ (**4b**) in the reaction of **2b** with two equivalents of AgOTf (Scheme 4).[16] It should be noted that this route also worked well for the Sb species, yielding the desired triflate species [(TfO)Sb(μ-NTer)]$_2$ (**4a**) in good yields (Sb: 65 %, Bi: 88 %) as pure crystalline solids. In the next step, **4b** was reacted with an excess of Me$_3$SiI, which resulted in the formation of [IBi(μ-NTer)]$_2$ (**5**).[16] Compound **5** could also be obtained when **2b** was treated with two equivalents of NaI, but a complete conversion, separation from side products, and NaCl by extraction was very difficult to achieve and was time-consuming. Thus an overall yield of only 20 % was obtained, while with the triflate substitution route pure crystalline **5** was isolated in an overall yield of more than 60 %.Compound **5** (Scheme 5) is stable as a dimer in toluene at ambient temperature, as shown by ^{1}H and ^{13}C NMR studies. However, after adding a solution of [Ag(toluene)$_3$][B(C$_6$F$_5$)$_4$] in toluene at −78 °C, the initially deep-red solution turned violet and a black precipitate formed. The black suspension was stirred for 30 min at −78 °C and then allowed to warm up to ambient temperature over 30 min. After filtration, the black residue was dissolved in CH$_2$Cl$_2$ and the dark violet solution (black in appearance) was again filtered, concentrated, and stored at −25 °C for several hours. This process resulted in the deposition of black crystals (yield 46 %), which were identified by single-crystal X-ray studies (Figure 1, right) as the *cyclo*-dibismadiazenium tetrakis(pentafluorophenyl)borate dichloromethane solvate [IBi(μ-NTer)$_2$Bi][B(C$_6$F$_5$)$_4$]·3 CH$_2$Cl$_2$ (**6**·3 CH$_2$Cl$_2$).



Scheme 4. Synthesis of iodine species **5** by Cl/OTf/I exchange.



Scheme 5. Synthesis of *cyclo*-dibisma(III)diazenium cation **6**.

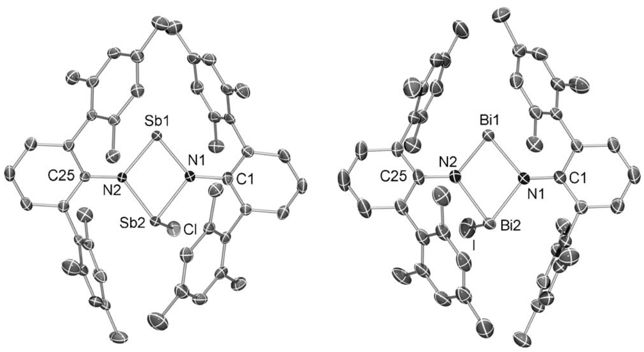


Figure 1. ORTEP representation of the molecular structure of the cations in **3a** (left) and **6**·3 CH$_2$Cl$_2$ (right). Ellipsoids are set at 50 % probability (at 173 K); hydrogen atoms, anions, and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: **3a**: Sb1–N1 1.996(2), Sb1–N2 2.024(2), Sb2–N2 2.071(2), Sb2–N1 2.115(2), Sb2–Cl 2.3646(8), Sb1···Sb2 3.2100(3), N1–C1 1.405(3), N2–C25 1.399(3); N1-Sb1-N2 78.84(9), N2-Sb2-N1 75.16(9), N2-Sb2-Cl 99.30(7), N1-Sb2-Cl 87.87(6), C1-N1-Sb1 131.4(2), C1-N1-Sb2 123.9(2), Sb1-N1-Sb2 102.7(1), C25-N2-Sb1 127.6(2), C25-N2-Sb2 124.9(2), Sb1-N2-Sb2 103.2(1); **6**·3 CH$_2$Cl$_2$: Bi1–N2 2.114(3), Bi1–N1 2.155(3), Bi2–N1 2.196(3), Bi2–N2 2.241(3), Bi2–I 2.8580(4), Bi1···Bi2 3.4155(3), N1–C1 1.402(4), N2–C25 1.402(4); N1-Bi2-N2 74.0(2), N1-Bi2-I1 100.11(9), N2-Bi2-I 89.34(9), N2-Bi1-N1 77.4(2), C1-N1-Bi1 127.9(2), C1-N1-Bi2 126.9(2), Bi1-N1-Bi2 103.4(2), C25-N2-Bi1 130.0(3), C25-N2-Bi2 125.3(2), C1-N1-Bi1 127.9(2), Bi1-N2-Bi2 103.3(2).

Both salts **3a** and **6**·3 CH$_2$Cl$_2$ bearing the *cyclo*-dipnictadiazenium ions are air- and moisture-sensitive but stable in argon over a long period as solids.[16] The black appearance of **3a** and **6**·3 CH$_2$Cl$_2$ vanishes rapidly when traces of H$_2$O or oxygen are present. Compounds **3a** and **6**·3 CH$_2$Cl$_2$ are easily prepared in bulk and are stable for long periods when stored in a sealed tube and kept at −30 °C in the dark. Compound **3a** is thermally stable up to 295 °C, whereas **6**·3 CH$_2$Cl$_2$ can be heated up to 191 °C. Decomposition starts at these temperatures. X-ray studies of crystals from the reaction sequences illustrated in Scheme 3 (Sb) and Scheme 5 (Bi) reveal that salts **3a** and **6**·3 CH$_2$Cl$_2$ with a *cyclo*-1,3-dipnicta-2,4-diazenium cation that is kinetically protected in the pocket formed by the terphenyl groups (Figure 1). Compound **3a** crystallizes without solvent in the monoclinic space group $P2_1/c$ with four formula units per cell, whereas **6**·3 CH_2Cl_2 crystallizes in the triclinic space group $P\bar{1}$ with two units per cell. All three CH_2Cl_2 molecules are disordered. In both compounds, ion pairs are crystallized with no significant cation–anion interactions (closest distances in **3a**: $d(\mathrm{Sb1\cdots Cl_{anion}}) = 6.000$; **6**·3 CH_2Cl_2: $d(\mathrm{Bi1\cdots F_{anion}}) = 6.16$ Å), showing the excellent steric protection by the two terphenyl groups. As depicted in Figure 1, the Sb_2N_2 ring in **3a** is almost planar, with a deviation from planarity ∡(N1-Sb1-N2-Sb2) = −2.46°, in accord with the values found for the P (−2.3°)[7] and As species (−1.4°),[8] while in **6**·3 CH_2Cl_2 a significantly puckered Bi_2N_2 ring (∡(N-Bi1-N-Bi2) = −10.8(1)°) is observed. The transannular E···E distances of 3.2100(3) Å (Sb) and 3.4155(3) Å (Bi) are only slightly longer than the sum of the covalent radii (Sb: 2.80, Bi: 3.02 Å)[18] but significantly shorter than the sum of the van der Waals radii (Sb: 4.4, Bi: 4.8 Å).[19] Thus strong van der Waals interactions across the ring can be assumed. In both species the four-membered heterocycle is slightly distorted with two longer E–N bonds (**3a**: d(Sb2–N2) = 2.071(2), d(Sb2–N1) = 2.115(2); **6**·3 CH_2Cl_2: d(Bi2–N1) = 2.196(3), d(Bi2–N2) = 2.241(3) Å) and two considerably shorter E–N bonds (**3a**: d(Sb1–N1) = 1.996(2), d(Sb1–N2) = 2.024(2); **6**·3 CH_2Cl_2: d(Bi1–N2) = 2.114(3), d(Bi1–N1) = 2.155(3) Å; cf. d(Sb–N) = 1.99(2)–2.00(2) Å in $[\mathrm{Me_2Si(\mu\text{-}N}t\mathrm{Bu)_2Sb][AlCl_4]}$)[10] and d(Bi-N) = 2.08(1)/2.09(1) Å in $[\mathrm{Me_2Si(\mu\text{-}N}t\mathrm{Bu)_2Bi][AlCl_4]}$).[10] The two shorter E–N bonds of between 2.00–2.02 (**3a**) and 2.11–2.16 (**6**·3 CH_2Cl_2) are substantially shorter than the sum of the covalent radii for a single bond (d_{cov}(N–Sb) = 2.11 vs. d_{cov}(N=Sb) = 1.93 and d_{cov}(N–Bi) = 2.22 vs. d_{cov}(N=Bi) = 2.01),[18] which indicates partial double-bond character for these E–N bonds along the N1-E1-N2 unit (Figure 1, Scheme 6). For comparison, the Sb–N distances of 2.051(2)–2.063(2) Å[16b] in $[\mathrm{ClSb(\mu\text{-}NTer)}]_2$ (**2a**) and 2.167(2)–2.173(2) Å[16b] in $[\mathrm{IBi(\mu\text{-}NTer)}]_2$ (**5**) represent typical single bonds for Sb–N and Bi–N compounds, respectively. Interestingly, the two short Bi–N bond lengths in **6**·3 CH_2Cl_2 differ by about 0.41 Å, which can be attributed to considerable van der Waals interaction between one Cl atom of one CH_2Cl_2 solvent molecule and Bi1 (d(Bi1···Cl) = 3.261(4) Å; cf. $\Sigma r_{\mathrm{vdW}} = 4.2$ Å). This can be explained by a larger electrostatic repulsion of the Cl atom, located above the Bi1–N1 bond, with the negatively charged N1 atom compared to N2 (d(N1···Cl) = 3.608(5) vs. d(N2···Cl) = 4.592(5) Å). It should be noted that the E–N bonds are highly ionic, which also leads to bond shortening. With respect to the Bi–N distances and bond situation, it is of interest to include $[\mathrm{(TfO)Bi(\mu\text{-}NTer)}]_2$ (**4b**) into the discussion (Figure 2). Bistriflate **4b** crystallizes free of solvent from toluene in the monoclinic space group $P2_1/n$ with two formula units. (Crystallization from CH_2Cl_2 and benzene gives the solvate **4b**·CH_2Cl_2 and **4b**·benzene; see the Supporting Information).[16b] The main structural motif in all three structures is the centrosymmetric dimer with a planar Bi_2N_2 ring (in contrast to **6**·3 CH_2Cl_2), only two short Bi–N distances (d(Bi1–N1) = 2.144(3), d(Bi1–N1′) = 2.164(4) Å), and two bridging triflate anions (using O1 and O3). Astonishingly, the Bi–O distances are rather long at 2.513(3) and 2.566(4) Å (cf. d_{cov}(Bi–O) = 2.14 Å) displaying the transition to separated ions.[20] For comparison, the formation of solid complexes $\mathrm{BiCl_3}\cdot n\,\mathrm{DMSO}$ (n = 1–4) was studied in detail,[21] and the structure of $\mathrm{BiCl_3\cdot 2\,DMSO}$ reported with even shorter Bi–O distances of 2.345(9) and 2.387(10) Å.[22] Thus, $[\mathrm{(TfO)Bi(\mu\text{-}NTer)}]_2$ (**4b**) might be regarded as a salt containing a donor-stabilized dication $[\mathrm{Bi_2(\mu\text{-}NTer)_2}]^{2+}$, which is also indicated by the black appearance of its crystals[8] and MO/NBO analysis data.

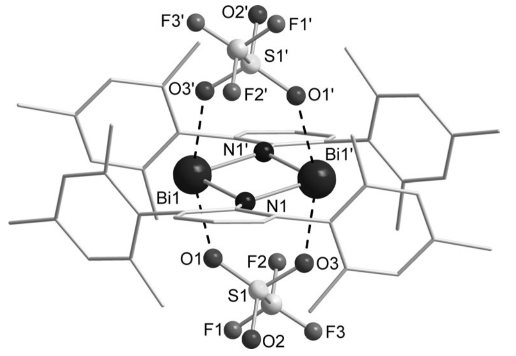
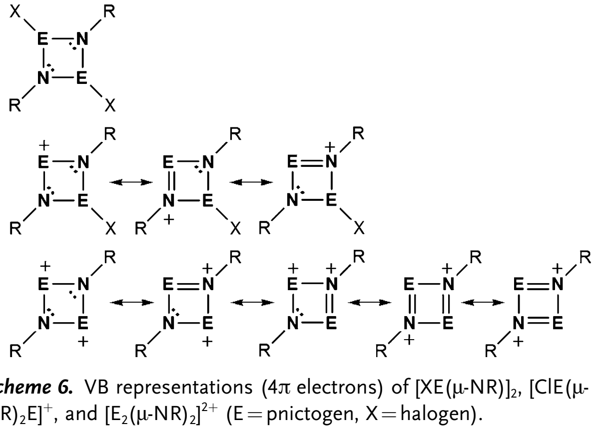


Figure 2. Ball-and-stick representation of the $(TfO)_2Bi_2N_2$ core for the molecular structure of **4b** in the crystal. The terphenyl substituent is shown as a wireframe model. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi1–N1 2.144(3), Bi1–N1′ 2.164(4), Bi1–O1 2.513(3), Bi1–O3′ 2.566(4), Bi1···Bi1′ 3.3188(4); N1-Bi1-N1′ 79.2(2), N1-Bi1-O1 82.7(2), N1′-Bi1-O1 83.5(2), N1-Bi1-O3′ 81.7(2), N1-Bi1-O3′ 81.4(2), O1-Bi1-O3′ 160.1(1).



Scheme 6. VB representations (4π electrons) of $[\mathrm{XE(\mu\text{-}NR)}]_2$, $[\mathrm{ClE(\mu\text{-}NR)_2E}]^+$, and $[\mathrm{E_2(\mu\text{-}NR)_2}]^{2+}$ (E = pnictogen, X = halogen).

A similar situation is found for $[\mathrm{(TfO)Sb(\mu\text{-}NTer)}]_2$ (**4a**) but with significantly different Sb–O distances (2.302(2) and 2.662(1) Å; cf. d_{cov}(Sb–O) = 2.03 Å).[16b] For the lighter arsenic analogue, only one OTf group can be introduced, indicating a lack of space inside the terphenyl pocket owing to the shorter As–N (1.819(2), 1.830(2) Å) and As–OTf (2.159(2) Å, cf. d_{cov}(As–O) = 1.84) bond distances.[8]

Computations were carried out for the neutral chlorine species $[\mathrm{ClE(\mu\text{-}NTer)}]_2$ (E = P, As, Sb, Bi) as well as for the corresponding cations $[\mathrm{ClE(\mu\text{-}NTer)_2E}]^+$ to gain deeper insight into charge distribution and bonding in these molecules. MO/NBO analyses show highly polarized N–E bonds with partial π bonds for the dicoordinated pnictogen centers in the cations.[23,24] VB representations of the neutral, mono-, and dicationic species are shown in Scheme 6. From NBO analysis, it can be determined that ionic bonding plays an essential role as displayed by the first Lewis representation in the resonance representation of the mono- and dications. From the experimental and theoretical data it can be concluded that cation formation in $[\mathrm{XE}(\mu\text{-NR})]_2$ is favored by bulky substituents, preventing the anion from interacting with the positively charged E centers, and by delocalization of the lone pair (occupying a p atomic orbital) located on both N atoms into the σ^*(E–X) bonds (hyperconjugation), leading to partial E–N π bonds, as indicated by NBO analysis. The NBO partial charges (Table 1) reveal that a considerable charge transfer ($\mathrm{P/P^+}$: 0.36/0.72, $\mathrm{As/As^+}$: 0.35/0.68, $\mathrm{Sb/Sb^+}$: 0.25/0.61, and $\mathrm{Bi/Bi^+}$: 0.20/0.56 e) from the two terphenyl groups into the heterocycle occurs, which increases upon cation formation. Compared to the neutral compounds, the positive charge at the dicoordinated pnictogen centers does not change much or even slightly decreases in the cations, indicating a considerable π-electron transfer from the N atoms, which occurs along with the increased charge transfer of the terphenyl groups. For comparison, the partial charges were also calculated for the triflate species **4b** to study the amount of $[\mathrm{Bi_2}(\mu\text{-NTer})_2]^{2+}$ character. In agreement with the structure discussion, the positive charge at the Bi center increases from +1.67 in the monocation to 1.92 e in **4b**, and an overall charge for the $\mathrm{Bi_2N_2}$ core of 1.24 e was calculated (cf. 1.02 e for the monocation, Table 1). The charge transfer from the two triflate groups amounts to 0.25 e per $\mathrm{OTf^-}$ ion, leading to a $[\mathrm{Bi_2}(\mu\text{-NTer})_2]^{1.5+}$ unit displaying a considerable dicationic character.

Table 1: NBO partial charge [*e*] for optimized structures of *cyclo*-dipnictadiazanes of the type $[\mathrm{ClE}(\mu\text{-NTer})]_2$ (E = P, As, Sb, Bi) and the corresponding cations $[\mathrm{ClE}(\mu\text{-NTer})_2\mathrm{E}]^+$.[16,23]

	P	P+	As	As+	Sb	Sb+	Bi	Bi+
E1[a]	1.30	1.26	1.43	1.45	1.62	1.59	1.69	1.58
E2	1.30	1.36	1.43	1.40	1.63	1.60	1.69	1.75
N1	−1.10	−1.04	−1.13	−1.09	−1.20	−1.16	−1.19	−1.15
N2	−1.08	−1.05	−1.15	−1.10	−1.22	−1.19	−1.22	−1.16
Cl1	−0.39	−0.25	−0.45	−0.34	−0.53	−0.46	−0.59	−0.54
Cl2	−0.39	–	−0.45	–	−0.53	–	−0.59	–
$\mathrm{Ter_2}$	0.36	0.72	0.35	0.68	0.25	0.61	0.20	0.56

[a] E1 represents the dicoordinated pnictogen atom in the cations.

In conclusion, we have presented a new facile synthetic route to terphenyl-substituted *cyclo*-dipnictadiazanes $[\mathrm{ClE}(\mu\text{-NR})]_2$ (E = Sb, Bi) by utilizing transmetallation reactions. Substitution of chloride by triflate yields the highly ionic species $[(\mathrm{TfO})\mathrm{E}(\mu\text{-NR})]_2$ (E = Sb, Bi), which can be described as a salt bearing a novel donor-stabilized dication $[\mathrm{E_2}(\mu\text{-NTer})_2]^{2+}$. The first monocations of the type $[\mathrm{ClE}(\mu\text{-NTer})_2\mathrm{E}]^+$ and $[\mathrm{IBi}(\mu\text{-NTerBi})]^+$ were obtained by halide abstraction with weakly coordinating anions ($[\mathrm{GaCl_4}]^-$ and $[\mathrm{B(C_6F_5)_4}]^-$) as counterions. A considerable degree of E–N π bonding, which stabilizes the strongly Lewis acidic E^{n+} centers (n = 1, 2), is computed for these cations.

Received: April 27, 2012
Revised: May 23, 2012

Keywords: antimony · bismuth · cations · dipnictadiazanes · structure determination

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