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Bi–N Heterocycles

Dichlorocyclodibismadiazane**

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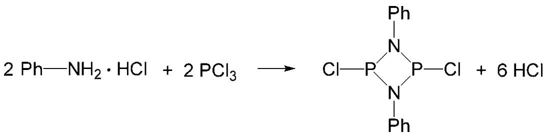
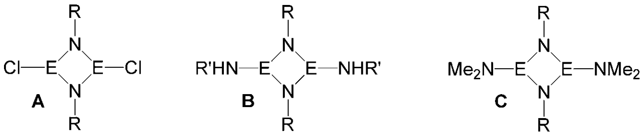
Four-membered pnictogen–nitrogen heterocycles of the type $[ClE(\mu\text{-}NR)]_2$ (E = element of Group 15) are known as 1,3-dichlorocyclo-1,3-dipnicta(III)-2,4-diazanes.[1] Especially the phosphorus species play a major role in preparative phosphorus–nitrogen chemistry, for example, in the preparation of macrocycles, polymers, main-group complexes, and ring-transformation reactions or the generation of cyclic binary PN cations.[2–4]

As early as 1894 Michaelis and Schroeter discovered the first cyclo-1,3-diphospha(III)-2,4-diazane when they treated aniline hydrochloride with an excess of PCl_3 for two days under reflux [Eq. (1)].[5] However, they thought they had isolated the monomeric species, $C_6H_5{-}N{=}P{-}Cl$. Today we know that the dimer represents the stable form of phenyl substituted 1,3-dichlorocyclo-1,3-diphospha(III)-2,4-diazane.[2a,3,6,7]



(1)

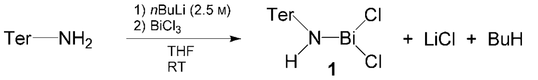
The chemistry of the heavier pnictogen analogues (As, Sb, Bi) of this classic inorganic E_2N_2 ring system has only slowly been developed in the last 50 years.[8–10] The simplest cyclodipnicta(III)diazanes are the dichloro derivatives, $[ClE(\mu\text{-}NR)]_2$, (**A**, Scheme 1) and are only known for E = P, As, and Sb, while bis(organoamino) derivatives **B** and bis(dimethylamino) derivatives **C** are observed for the whole series E = P–Bi.[1] The slow progress, especially in the chemistry of Bi_2N_2 ring systems compared to that of P_2N_2 rings can be attributed to the lability of Bi–N bonds. Hence, Chivers et al. pointed out, that "*The discovery of a suitable synthesis of dichloro derivatives of type* **A** *for bismuth would be a significant step forward*".[1] Herein, we report the synthesis and full characterization of the first dichlorocyclodibismadiazane.



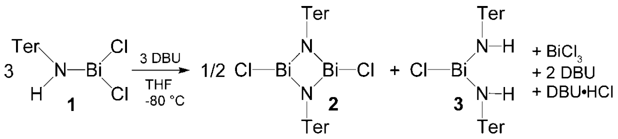
Scheme 1. Known cyclodipnicta(III)diazanes (**A**: E = P, As, Sb; **B** and **C**: E = P, As, Sb, Bi; R, R′ = aryl, alkyl).[1]

A typical route to cyclodipnictadiazanes is the facile HCl elimination, between primary amines and trichloropnictanes to give aminopnictanes. However, the isolation of the amination products is complicated because of the coincident formation of monoaminodichloro-, diaminochloro-, and trisaminopnictanes,[11] as well as the possibility for formation of the iminopnictanes. It is known, that the formation of a specific aminopnictane, iminopnictane or its dimer, the cyclodipnictadiazane, can be influenced by the presence of specific substituents (depending on the steric strain) on the amine and by the use of lithium amides rather than amines.[1] In this context, it was of interest to study the effect of a bulky group, such as the terphenyl group (Ter = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$)[12] on the reaction products.

To obtain 1,3-dichloro-2,4-di(*m*-terphenyl)cyclo-1,3-dibisma-2,4-diazane, [TerN–BiCl]$_2$, in a two-step reaction, first the dichloro(*m*-terphenylamino)bismutane (**1**) had to be prepared in the reaction of terphenylaniline, $TerNH_2$, with *n*-BuLi in the presence of $BiCl_3$ [Eq. (2)] at ambient temperatures. This reaction gave **1** as a red, crystalline solid in over 80 % yield (m.p. 189 °C (decomp)). The second step included a complex reaction of **1** in THF with DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene) at low temperatures (−80 °C) resulting in the formation of the terphenyl-substituted 1,3-dichlorocyclo-1,3-dibisma-2,4-diazane (**2**) and chlorobis(*m*-terphenylamino)bismuthane (**3**) along with $BiCl_3$ and DBU·HCl [Eq. (3)].



(2)



(3)

The major problem was how to isolate **2** and **3** from this reaction mixture. Extraction with benzene followed by fractional crystallization from benzene and dichloromethane resulted in the deposition of yellow (**3**) and red (**2**) crystals,

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respectively. This procedure was repeated several times, finally yielding pure **2** as a red, crystalline solid (yield 45%) as well as **3** as an orange, crystalline solid (yield 76%).

Analogous reactions involving LiN(H)Mes* (Mes* = 2,4,6-tri-*tert*-butylphenyl), give the amino(imino)pnictane Mes*−N=E−N(H)Mes* (E = P, As)[13] and the trisaminopnictane $E[(N(H)Mes^*]_3$ (E = Sb, Bi).[14] A slightly less-bulky group, such as Dipp (Dipp = 2,6-diisopropylphenyl) gives, in the reaction of ECl_3 with LiN(H)Dipp, the corresponding 1,3-diaminocyclo-1,3-dipnicta-2,4-diazanes, for all heavy pnictogens (E = P, As, Sb, and Bi; species **C** in Scheme 1).[15,11]

Compounds **1**, **2**, and **3** are astonishingly thermally stable (T_{decomp} **1**: 189, **2**: 205, **3**: 220 °C). They are moisture sensitive but stable as solids under argon atmosphere over a long period and in benzene at ambient temperature. All three compounds can be prepared in bulk and are stable when stored in a sealed tube. This together with the very good solubility in common organic solvents makes all three bismuth compounds good precursors for further synthesis.

The solid-state structures of all the bismuth compounds are shown in Figure 1. Crystallographic details are given in the Supporting Information. X-ray quality crystals of **1**–**3** were selected in a Fomblin YR-1800 (Alfa Aesar) at ambient temperatures and all samples were cooled to 173(2) K during the measurement.

Compounds **1** and **3** crystallize in the monoclinic space groups $P2_1/n$ and *P*n, respectively, with four formula units per cell. Both molecular structures consist of strongly distorted trigonal-planar nitrogen centers (angle sum at N: **1**: 351.4°, **3**: 360.0°) attached to a trigonal-pyramidal Bi center with the angles at Bi close to 90° (e.g. **1**: 86.19(9), 92.23(9), 90.22(5)°). The Bi−N bond lengths are 2.123(3) in **1**, 2.027(3) and 2.186(3) Å in **3** (cf. d_{cov}(Bi−N) 2.2 Å).[16] The Bi−Cl bond lengths with 2.536(2) and 2.539(2) in **1**, and 2.503(3) Å in **3** are in the expected range for a typical Bi−Cl single bond (cf. d_{cov}(Bi−Cl) 2.49 Å).[16]

While in **3** no significant intermolecular interactions are observed, in **1** strong symmetric intermolecular interactions (Bi···Cl1′ 3.370(2) Å, compared with the sum of the van der Waals radii Bi–Cl of 4.2 Å)[16] lead to the formation of a centrosymmetric $[TerN(H){-}BiCl_2]_2$ dimer (Figure 1 top right). It can be assumed that these Bi···Cl contacts are responsible for the generation of $BiCl_3$ and the bisamino compound **3** in the reaction to give **2** [Eq. (3)], dramatically decreasing the yield of **2**. Moreover, in **1**, numerous intramolecular Bi···C_{aryl} interactions are observed leading to strongly distorted terphenyl groups with one phenyl ring from each group moved close to the Bi center. The two shortest Bi···C_{aryl} contacts (Bi···C7 2.941(4) and Bi···C12 3.053(4) Å, sum of the van der Waals radii Bi–C 4.1 Å)[16] are indicated in Figure 1. Six further Bi···C_{aryl} contacts with Bi···C distances under 4.1 Å are detected (C8–C11: 3.22–3.53 Å, C1–C2: 3.16–3.51 Å). Similar intramolecular Bi···C_{aryl} interactions are also found in **3**.

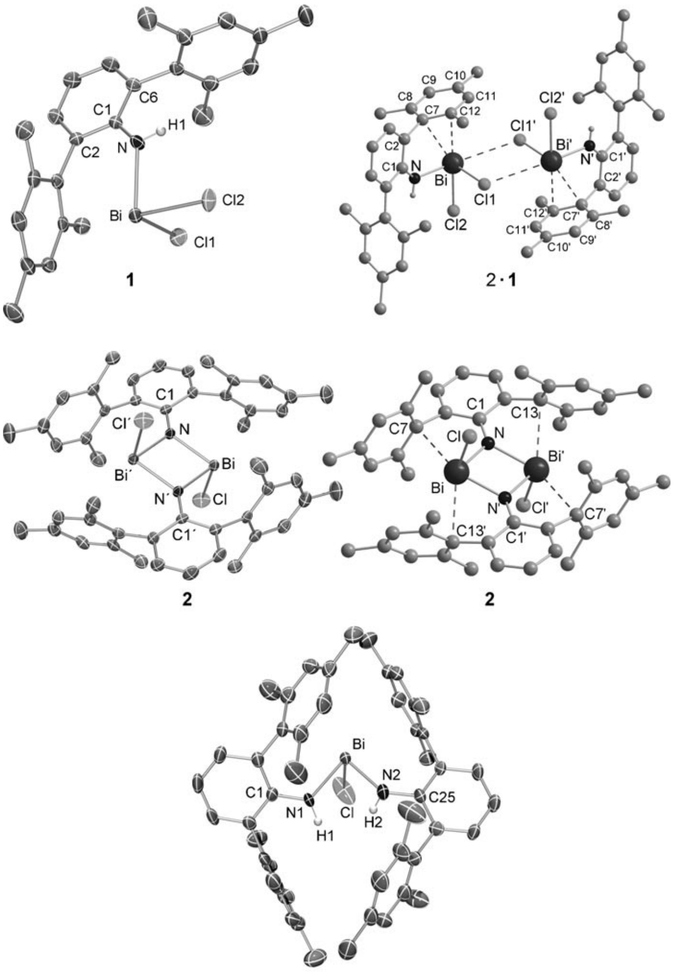

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Figure 1. ORTEP drawing of the molecular structures of **1–3**. Thermal ellipsoids set at 50% probability at 173 K. Also shown are the molecular structure of **1** showing intermolecular Bi···Cl and intramolecular Bi···C interactions. Symmetry code (′): 2−*x*,−*y*,−*z*) and of the molecular structure of **2** showing intramolecular Bi···C interactions. Selected bond lengths [Å], angles [°]: **1**: Bi–N 2.123(3), Bi–Cl2 2.536(2), Bi–Cl1 2.539(2), N–C1 1.387(4), N–H1 0.79(3); N-Bi-Cl2 86.19(9), N-Bi-Cl1 92.23(9), Cl2-Bi-Cl1 90.22(5), C1-N-Bi 126.9(2), C1-N-H1 112(3). **2**: Bi–N 2.151(2), Bi–Ni 2.169(3), Bi–Cl 2.537(2), Bi···Bi′ 3.389(2), N–C1 1.393(3); N-Bi-N′ 76.7(1), N-Bi-Cl 96.10(9), Ni-Bi-Cl 92.93(7), Cl-Bi-Bi′ 95.75(6), C1-N-Bi 130.3(2), C1-N-Bi′ 124.9(2), Bi-*N*-Bi′ 103.4(1); symmetry code (′): (−*x*,1−*y*,−*z*). **3**: Bi1–N2 2.027(3), Bi1–N1 2.186(3), Bi1–Cl1 2.503(3), N1–C1 1.389(4), N2–C25 1.390(4); N2-Bi1-N1 82.4(1), N2-Bi1-Cl1 95.7(2), N1-Bi1-Cl1 91.32(1), C1-N1-Bi1 122.9(2), C25-N2-Bi1 137.9(3).

Compound **2** crystallizes in the orthorhombic space group *Pbca* with four formula units per cell. The asymmetric unit consists of a TerN-Bi-Cl fragment, which lies on a twofold crystallographic axis. The centrosymmetric dimer is generated by applying the symmetry operation (−*x*, 1−*y*, −*z*; (Figure 1 middle). The molecule adopts a *trans* configuration with respect to the two exocyclic chlorine atoms on the N_2Bi_2 ring. This ring is sandwiched between the two bulky terphenyl groups. To date, only two structural studies with the Bi_2N_2 ring motif have been reported, which indicates the difficulty in preparing such bismuth heterocycles. Both $[DippN(H)Bi(\mu\text{-}NDipp)]_2$[7b,15] and $[PhBi(\mu\text{-}N\mathit{t}Bu)]_2$[17] also exist as *trans* isomers with planar Bi_2N_2 rings but in contrast to **2** are stabilized by an amino and phenyl group, respectively, attached to the Bi atoms. As expected, both nitrogen atoms of the Bi_2N_2 ring in **2** are in a trigonal planar coordination environment and the tricoordinate bismuth centers are trigonal pyramidal. In accord with that, the sum of the bond angles at the nitrogen atoms is very close to 360° (358.6°), and therefore a formal sp^2-hybridisation can be assumed. The molecular structure of **2** has a rhomboid N_2Bi_2 core with two slightly different Bi–N distances (2.151(2), 2.169(3) Å), that are in the typical range for Bi–N single bonds (cf. d_{cov}(Bi-N) 2.2 Å,[16] 2.158(4), and 2.174(5) Å in [DippN(H)Bi(μ-NDipp)]$_2$). Furthermore, a Bi···Bi′ contact is observed with a Bi···Bi′ distance of 3.389(2) Å, which is considerably shorter than the sum of the van der Waals radii of 4.8 Å[16] (3.355 Å in [DippN(H)Bi(μ-NDipp)]$_2$). Both chlorine atoms are almost perpendicular to the N_2Bi_2 core with a N-Bi-Cl angle of 96.10(9)° and N′-Bi-Cl angle 92.93 (7)°. A difference of approximately 27° is found between the N-Bi-N′ and Bi-N-Bi′ angles in accord with those found for example, in [DippN(H)Bi(μ-NDipp)]$_2$ (78.5° and 101.5°).

As discussed for compounds **1** and **3**, stabilizing intramolecular Bi···C_{aryl} interactions are also found in **2** with distances between 3.0 and 4.1 Å, and the shortest contacts are for C7 (3.020(3) Å) and C13 (3.024(3) Å, Figure 1 right middle).

Inspection of the conformational space at the B3LYP level of theory[18] displayed two different structures for the $Bi_2N_2Cl_2$ core: a *cis* and a *trans* arrangement of the Cl substituents. In agreement with the experiment, our calculations revealed that the *trans* form represents the most stable isomer ($\Delta E^{tot}(cis-trans) = +4.7\ \text{kcal mol}^{-1}$, $\Delta G^{298}(cis-trans) = 4.0\ \text{kcal mol}^{-1}$). Calculations of the whole series $[\text{TerN}-\text{ECl}]_2$ (E = N, P, As, Sb, Bi) show that the *cis/trans* energy gap increases down the group N(−0.57) < P(1.68) < As(3.54) < Sb(3.74) < Bi(4.7 kcal mol^{-1}). MO and NBO[19] calculations indicated highly polarized Bi−N and Bi−Cl bonds. The calculated natural atomic orbital population (NAO) net charges are $q(\text{Bi}) = +1.68$, -1.20 (N), and $-0.59\ e$ (Cl).

The UV/Vis spectrum of the red dichloromethane solution of **2** shows (besides strong $\pi \rightarrow \pi^*$ transition below 350 nm) a weak electronic transition at 461 nm, which could be tentatively assigned on the basis of TD-B3LYP calculation (448 nm);[18] this weak $\pi_{aryl} + n_N \rightarrow \sigma^*_{(Bi-Cl)}$ HOMO–LUMO electronic transition in **2** (Figure 2) give rise to the red color. The HOMO is a delocalized π_{aryl} molecular orbital with a large coefficient at the nitrogen atoms, while the LUMO is an antibonding Bi−Cl bond.

In conclusion, we present herein the first example of a dichlorocyclodibismadiazane, which may serve as nitrogen–bismuth precursor to the, as yet unknown, polybismazanes or cyclodibismadiazenium cations.

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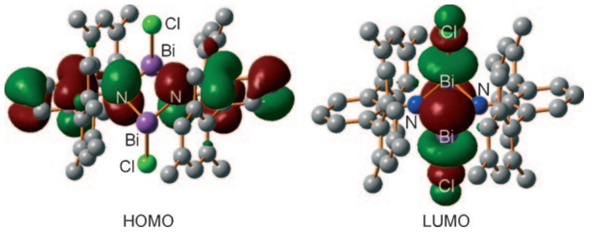

Figure 2. HOMO and LUMO in **2**.[18]

Keywords: bismuth · dichlorocyclodibismadiazane · heterocycles · nitrogen · structure elucidation

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