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Reactivity of TerN($SiMe_3$)$BiCl_2$—Synthesis of an Aminobismuthenium Cation and TerN($SiMe_3$)Bi(N_3)$_2$

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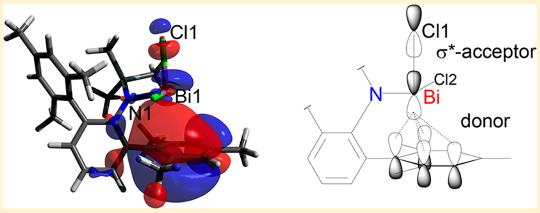
Supporting Information



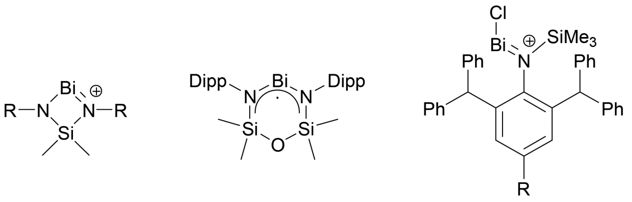
ABSTRACT: The reaction of TerN($SiMe_3$)$BiCl_2$ (**1**) (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl) with Lewis acids such as $GaCl_3$ and Ag[OTf] (OTf = OSO_2CF_3) was studied. While the reaction of **1** with $GaCl_3$ led to decomposition into bismuth black, $TerNH_2 \cdot GaCl_3$, and [$TerNH_3$][$GaCl_4$], the reactions of **1** with 1 and 2 equiv of Ag[OTf] resulted in methyl/triflate exchange reactions affording TerN($SiMe_2OTf$)Bi(Me)Cl (**2**) and TerN($SiMe_2OTf$)Bi(Me)OTf (**3**). To circumvent the methyl/triflate exchange, the diiodide compound TerN($SiMe_3$)BiI_2 (**5**) and the azide-substituted derivatives TerN($SiMe_3$)Bi(Cl)N_3 (**6**) and TerN($SiMe_3$)Bi(N_3)$_2$ (**7**) were prepared, although it was not possible to isolate pure **7** because of small impurities of **6**. All of the bismuth compounds (**1**−**7**) were characterized by single-crystal X-ray diffraction and NMR, IR, and Raman spectroscopy. According to quantum-chemical calculations, **3** can be regarded as a donor-stabilized aminobismuthenium cation with OTf^- as the counterion. As expected for bismuth compounds with aromatic scaffolds, Bi···π-arene interactions were observed. The influence of the substitution at the bismuth atom on the strength of this intramolecular interaction with the terphenyl moiety was studied by experimental (crystal structures) and theoretical methods. A correlation between the Lewis acidity (NBO charge) and the Bi···π-arene distance could be established.

INTRODUCTION

Nitrogen−bismuth compounds have been in the focus of main-group chemistry for more than three decades,[1−16] especially aminobismuthanes (bismuth amides), which were shown to be valuable starting materials in element organic chemistry.[17] Ever since the early works of Errington, Norman, and co-workers,[18,19] the number of structurally characterized amino-bismuthanes has grown steadily. Notably, derivatives featuring bulky substituents such as 2,4,6-tri-*tert*-butylphenyl (Mes*)[5,20] or 2,6-bis(2,4,6-trimethylphenyl)phenyl (Ter)[20−22] groups have been utilized to stabilize highly labile nitrogen−bismuth compounds but also Bi−E species (E = group 14−16 element).[2,9,23,24]

Lately there has been great interest in nitrogen−bismuth compounds containing silyl groups attached to the nitrogen atom, such as those depicted in Scheme 1. These compounds are versatile starting materials for the synthesis of low-valent (nitrogen−)bismuth compounds.[7,11,25−31]

Scheme 1. Examples of Low-Valent Nitrogen−Bismuth Compounds Exhibiting Silyl Amine Functionalities (R = *t*-Bu, Dipp = 2,6-Diisopropylphenyl)



In particular, *N*-(trimethylsilyl)aminobismuthanes with different sterically demanding groups at the nitrogen atom have been studied intensively. The Me_3Si group was introduced to increase the steric protection of the precursor, but at the same time, "Me_3Si^+", also known as "big proton", can easily be removed by strong nucleophiles such as X^- (X = halogen, OR) to afford, for instance, low-valent N−Bi cations.[11,20,25,28] However, on some occasions the elimination of the Me_3Si group was impossible,[28] contrary to results obtained with lighter congeners (RN($SiMe_3$)$PnCl_2$; Pn = P, As; R = Mes*).[32−34] In these cases, use of stannylated species rather than silylated species often represented a more favorable reaction pathway.[35]

Our quest for a salt bearing the bismadiazonium cation ($R-N\equiv Bi^+$), which could be used to generate an unknown cyclic tetrazabismuthole (RN_4Bi) in a [3 + 2] cycloaddition reaction with a covalent azide, led to our specific interest in the reactivity of *N*-(trimethylsilyl)aminodichlorobismuthanes of the type RN($SiMe_3$)$BiCl_2$. RN($SiMe_3$)$BiCl_2$ compounds seemed to be suitable precursors for the generation of $R-N\equiv Bi^+$ species because the lighter congeners of the tetrazapnictole series (RN_4Pn; Pn = P,[36] As,[34,37] Sb[38]) had already been successfully prepared by elimination of a trimethylsilyl group from RN($SiMe_3$)PnX_2 (X = Cl, OTf)

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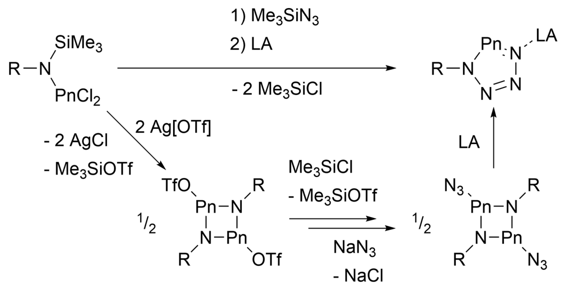
followed by Cl^- ion abstraction or isomerization by means of a strong Lewis acid (Scheme 2).

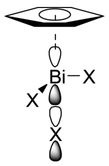
Scheme 2. General Approach for the Synthesis of Tetrazapnictoles (R = Ter, Mes*; Pn = P, As, Sb; LA = Lewis Acid)



Hence, TerN(SiMe$_3$)BiCl$_2$ (**1**), a molecule featuring both a bulky terphenyl group and an aminosilyl group, is a promising candidate for the preparation of low-valent Bi−N compounds, especially Ter−N≡Bi$^+$. Aside from their steric protection, terphenyls are also capable of stabilizing bismuth compounds by π-arene interactions with the bismuth center, a typical structural motif frequently found in bismuth compounds. This long-known phenomenon (also known as "Menshutkin" interactions or "Menshutkin-type" complexes) is not limited to bismuth but is also observed for antimony and arsenic compounds[39,40] and has been intensively investigated by experimental and theoretical studies.[41−43] Often, such interactions are intermolecular (e.g., with solvent molecules),[20,42] but some examples of intramolecular Menshutkin-type complexes are known in bismuth compounds bearing bulky arene substituents.[23,35,44,45] It has been demonstrated that such π-arene interactions have a significant stabilizing effect, for example, on highly reactive aminochlorobismuthenium cations.[28]

Bi···π-arene interactions have been the focus of numerous studies.[39,42,46−50] It was Hobza and co-workers who elucidated that the main contribution to these element···π-system interactions are dispersion interactions in addition to a small contribution from electron transfer.[41] This electron transfer can be discussed in terms of σ-hole bonding (Scheme 3). The Bi···π-arene interaction should be stronger when the Lewis acidity of the Bi atom increases. One possibility to extremely enhance the Lewis acidity is to generate a bismuthenium cation. It was previously shown that such bismuthenium cations can be stabilized by aromatic π systems.[28,51] Cationic Bi species were synthesized by abstracting a chloride ion utilizing Lewis acids or silver salts of weakly coordinating anions (WCAs). To that end, the behavior of **1** in the presence of GaCl$_3$ and Ag[OTf] was investigated. Moreover, the terphenyl compounds presented herein are interesting contributions not only for the development of N−Bi chemistry but also for the investigation of intramolecular Bi···π-arene interactions.

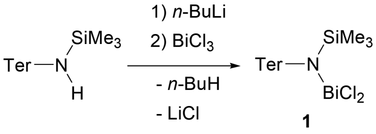
Scheme 3. A Bi···π-Arene Complex



RESULTS AND DISCUSSION

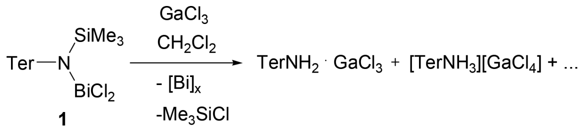
Synthesis. TerN(SiMe$_3$)BiCl$_2$ (**1**), a compound with a formally hidden N−Bi double bond, which can be generated by Me$_3$SiCl elimination, was synthesized according to a literature procedure by the reaction of in situ-generated TerN(SiMe$_3$)Li with BiCl$_3$ in Et$_2$O (Scheme 4).[20]

Scheme 4. Synthesis of TerN(SiMe$_3$)BiCl$_2$ (1)



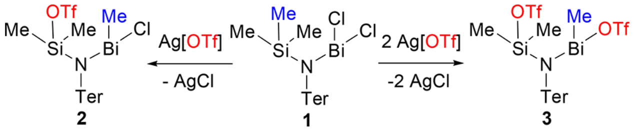
Addition of a Lewis acid such as GaCl$_3$ is one of the easiest ways to trigger Me$_3$SiCl elimination from silyl aminodichloropnictanes.[32,34,36,37] Indeed, upon addition of GaCl$_3$ at −80 °C (Scheme 5), Me$_3$SiCl elimination was observed, but unfortunately, the in situ-generated Ter−N═BiCl species decomposed readily into TerNH$_2$·GaCl$_3$ and [TerNH$_3$][GaCl$_4$] (both isolated as colorless, block-shaped crystals) and a violet-black oil of unknown composition (a complex mixture according to ^{1}H NMR spectroscopy). The decomposition took place very fast even at low temperatures. Hence, no intermediates could be identified. The origin of the protons could not be determined doubtlessly. However, it is possible that the decomposition of the Bi−N compound involved the formation of radical species, as was discussed previously in the synthesis of Mes*N(SiMe$_3$)BiCl$_2$.[20] Thus, the protons might be abstracted from the solvent (CH$_2$Cl$_2$).

Scheme 5. Reaction of 1 with GaCl$_3$



Since the elimination of Me$_3$SiCl in the presence of a Lewis acid was unsuccessful, the synthesis of TerN(SiMe$_3$)Bi(Cl)OTf was attempted. In this case, Me$_3$SiOTf elimination was expected to generate a species bearing a Bi−N double bond. It is known that the closely related antimony compound Mes*N(SiMe$_3$)Sb(OTf)$_2$ is intrinsically unstable toward Me$_3$SiOTf elimination.[52] To facilitate the synthesis of TerN(SiMe$_3$)Bi(Cl)OTf, **1** was treated with 1 equiv Ag[OTf] at low temperatures (−25 °C), resulting in an immediate color change from orange to red. Upon warming to ambient temperature, the suspension turned yellow. Upon warming to room temperature, the formed suspension turned yellow. Attempts to crystallize the reaction product from toluene failed, but X-ray-quality crystals could be grown from a saturated benzene solution in rather good yield (68%). The X-ray structure revealed the formation of a methyl/triflate exchange product (**2** in Scheme 6 and Figure 1). Strangely enough, when **1** was reacted with 2 equiv of Ag[OTf] in a similar fashion, Me$_3$SiOTf elimination could not be achieved either. The two chlorine atoms at the bismuth atom could be abstracted, though, leading to the formation of **3** (Scheme 6

Scheme 6. Reaction of 1 with Ag[OTf] and Formation of Methyl/Triflate Exchange Products 2 and 3



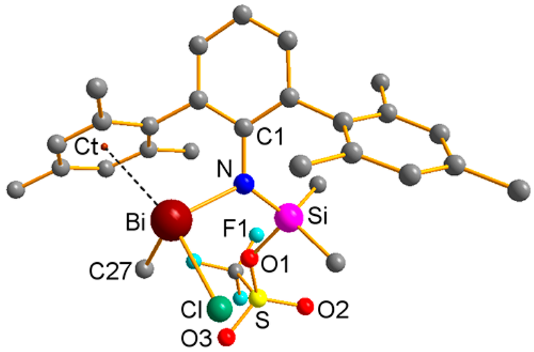


Figure 1. Ball-and-stick representation of the molecular structure of **2** in the crystal. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi–N 2.232(2), Bi–C27 2.231(2), Bi–Cl 2.5345(7), N–Si 1.705(2), O1–Si 1.771(2), O1–S 1.511(2); C27–Bi–Cl 89.91(8), C27–Bi–N 101.62(9), N–Bi–Cl 97.57(6), Si–N–Bi 125.0(1), S–O1–Si 134.7(1).

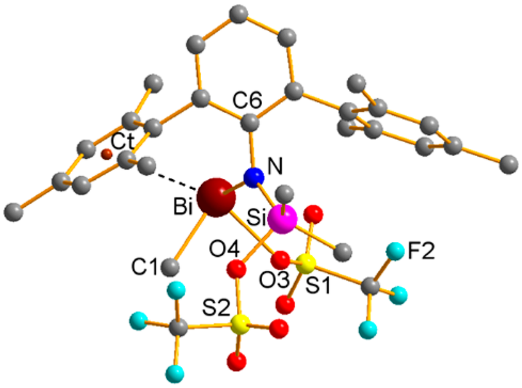


Figure 2. Ball-and-stick representation of the molecular structure of **3** in the crystal. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi–N 2.224(2), Bi–C1 2.219(2), O3–Bi 2.375(2), N–Si 1.709(2), O4–Si 1.751(2); C1–Bi–O3 83.05(6), C1–Bi–N 101.87(6), N–Bi–O3 93.38(5), Si–N–Bi 128.17(9), S1–O3–Bi 124.05(8), S2–O4–Si 130.7(1).

and Figure 2), which is also a product featuring methyl/triflate exchange, but with only one methyl group. Migration of a second methyl group was not observed, leaving one triflate attached to the bismuth center. Presumably, the first equivalent of Ag[OTf] results in abstraction of a chloride ion to afford a Bi^+ center, after which migration of the methyl group is favored over binding of the OTf^- ion directly to the positive bismuth center. Finally, after migration of the methyl group, the triflate gets attached to the positive Si center in accord with computed thermodynamic data favoring the exchange product **2** over the expected Bi–OTf species by 7.9 kcal/mol (see the Supporting Information (SI)). With the second equivalent of Ag[OTf], again chloride abstraction occurs in species **2**, but in this case formation of the bismuth–triflate bond is favored. Formally, three constitutional isomers of species **3** are possible: $TerN(SiMe_3)Bi(OTf)_2$, $TerN[SiMe_2(OTf)]Bi(Me)OTf$, and $TerN[SiMe(OTf)_2]BiMe_2$ but again the thermodynamic product is formed: $TerN[SiMe_2(OTf)]Bi(Me)OTf$ (**3**) is favored by 6.6 and 5.9 kcal/mol over $TerN(SiMe_3)Bi(OTf)_2$ and $TerN[SiMe(OTf)_2]BiMe_2$, respectively (see the Supporting Information).

The formation of **2** and **3** was not entirely unexpected since such methyl/triflate exchange reactions for the corresponding arsenic[53] and antimony[54] congeners were already known. To avoid the methyl/triflate exchange reaction, generation of $TerN(SiMe_3)Bi(OTf)_2$ by reacting $TerN(SiMe_3)Li$ with $Bi(OTf)_3$ was then attempted. Unfortunately, decomposition was observed. Bismuth black was identified as the major product besides $TerNH_2$ and a small amount of colorless crystals. Intriguingly, single-crystal diffraction of those colorless crystals revealed the formation of compound **4**, a C–C coupling product of two $TerNH_2$ moieties (see the Supporting Information). Since **4** was only formed in traces, analytical data are limited to structural (X-ray) and ^1H NMR data.

Transformation of the chloride derivative **1** into the iodide derivative prior to the triflate reaction was another approach to get a clean reaction with Ag[OTf] without methyl/triflate exchange. To that end, **1** was reacted with 2 equiv of Me_3SiI, which yielded the iodido species $TerN(SiMe_3)BiI_2$ (**5**) (Figure 3), as depicted in Scheme 7. The mixed halogenated species,

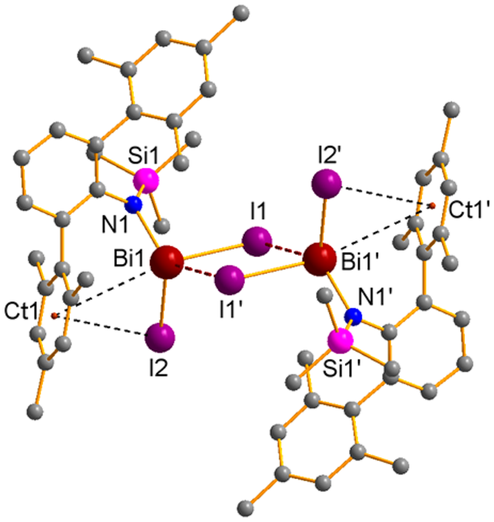
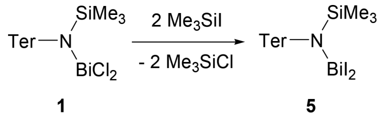


Figure 3. Ball-and-stick representation of the molecular structure of **5** in the crystal. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B1–N1 2.166(3), B1–I1 2.8992(3), Bi1–I2 2.8455(4), Bi1–I1′ 3.695(4), N1–Si1 1.762(3), C1–N1 1.431(5), B1–Ct1 3.7048(4), I1–Ct1 3.6643(4); N1–Bi1–I1 97.29(8), N1–Bi1–I2 110.07(8), I1–Bi1–I2 92.25(1), I1–Bi1–I1′ 80.573(9), C1–N1–Bi1 110.9(2), C1–N1–Si1 123.7(3), Si1–N1–Bi1 125.4(2). Symmetry code (′): −*x*, −*y*, 1 − *z*.

Scheme 7. Synthesis of 5



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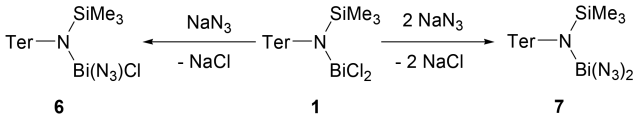
TerN($SiMe_3$)Bi(Cl)I, was not obtained, even in a reaction of **1** with only 1 equiv of Me_3SiI. In that case, always a 1:1 mixture of **1** and **5** was observed.

Compound **5** was unstable in CH_2Cl_2 or fluorobenzene solution at ambient temperature; however, it could be stored as a solid under an argon atmosphere in the dark at −35 °C for approximately 3 weeks. Longer storage resulted in the formation of a black solid and the free amine according to ^1H NMR spectroscopy. **5** was also sensitive toward light. Therefore, Raman spectra had to be collected at −80 °C. Because of the instability of **5**, especially in solution, it was impossible to carry out follow-up chemistry.

All of the above-discussed reactions aimed to generate a bismadiazonium salt that could be used in a [3 + 2] cycloaddition with an azide. Because of the obviously high reactivity and instability of the intermediates, e.g., with respect to methyl/triflate exchange, a new approach was chosen. Instead of generation of a bismadiazonium salt and subsequent addition of azide, the corresponding aminoazidobismuthanes were prepared. In this case, the N_3 functionality is already part of the molecule, which could give rise to an intramolecular [3 + 2] cycloaddition. Hence, in a second series of experiments we tried to generate tetrazabismutholes starting from substituted bismuth azides as illustrated in Scheme 2, a reaction which worked nicely for the antimony analogue. For this purpose, compound **1** was stirred with 1 or 2 equiv of NaN_3 in tetrahydrofuran (THF) to synthesize TerN($SiMe_3$)-Bi(Cl)N_3 (**6**) and TerN($SiMe_3$)Bi(N_3)$_2$ (**7**) (Scheme 8), respectively.

Scheme 8. Synthesis of the Azide-Substituted Compounds TerN(SiMe$_3$)Bi(Cl)N$_3$ (6) and TerN(SiMe$_3$)Bi(N$_3$)$_2$ (7)



The chloride/azide exchange reaction using NaN_3 (Scheme 8) yielded monoazide **6** (Figure 4) in a straightforward synthesis but turned out to be more complicated for the generation of diazide **7** (Figure 5). In the reaction of **1** with 2 equiv of NaN_3, **7** could be obtained only in a mixture with **6** (**6**:**7** ≈ 1:5). Even a reaction of **1** with a huge excess of NaN_3 led to such a mixture. Hence, complete conversion into **7** could not be achieved. In an attempt to obtain pure **7**, silver azide was used instead of sodium azide. However, this reaction always led to decomposition into bismuth black, $TerNH_2$, and TerN($SiMe_3$)H, as confirmed by ^1H NMR spectroscopy. To date it has not been possible to generate pure **7**. Nevertheless, we treated both azides with a Lewis acid in order to form a tetrazabismuthole as depicted in Scheme 2 for antimony. Unfortunately, reactions of **6** and **7** with a Lewis acid always resulted in decomposition to afford mainly bismuth black and $TerNH_2$.

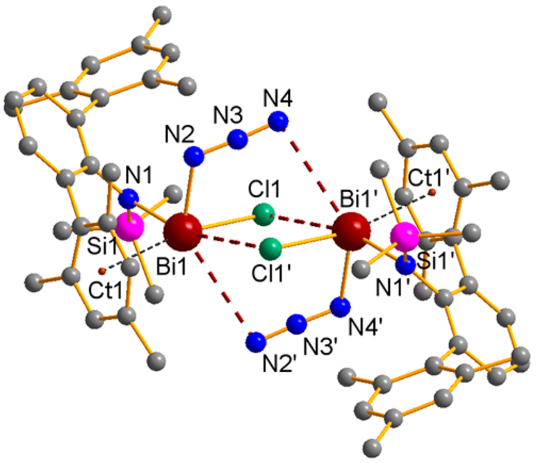


Figure 4. Ball-and-stick representation of the molecular structure of **6** in the crystal. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−Bi1 2.180(1), N2−Bi1 2.218(2), Cl1−Bi1 2.5642(3), N1−Si1 1.751(1), C1−N1 1.420(2), N2−N3 1.207(2), N3−N4 1.150(2); N1−Bi1−Cl1 95.02(3), N1−Bi1−N2 92.31(4), N2−Bi1−Cl1 89.89(3), C1−N1−Bi1 115.38(8), C1−N1−Si1 127.66(9), Si1−N1−Bi1 115.60(5), N3−N2−Bi1 116.1(1), N4−N3−N2 177.0(2), Cl1′−Bi1 3.3483(5), Cl1−Bi1−Cl1′ 83.07(2), Bi1−Cl1−Bi1′ 96.93(2). Symmetry code (′): 2 − *x*,1 − *y*, −*z*.

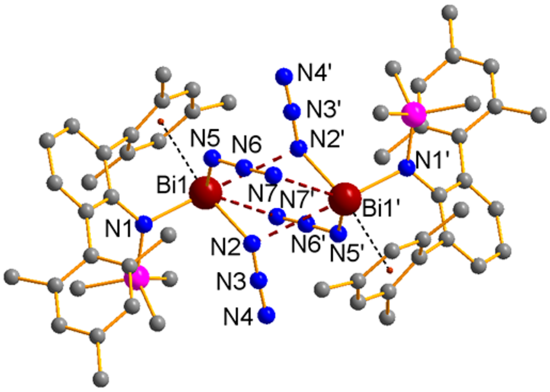


Figure 5. Ball-and-stick representation of the molecular structure of **7** in the crystal. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−Bi1 2.184(2), N2−Bi1 2.287(5), N5−Bi1 2.214(2), N1−Si1 1.753(2), C1−N1 1.420(2), N2−N3 1.227(3), N3−N4 1.152(3), N5−N6 1.214(2), N6−N7 1.146(2); N1−Bi1−N2 96.8(2), N1−Bi1−N5 92.26(5), N5−Bi1−N2 83.9(2), Si1−N1−Bi1 113.39(6), N3−N2−Bi1 122.7(4), N6−N5−Bi1 166.7(1), N4−N3−N2 175.6(3), N7−N6−N5 176.2(2). Symmetry code (′): 1 − *x*, −*y*, 1 − *z*.

Structure and Bonding. Compound **2**, TerN-[$SiMe_2$(OTf)]Bi(Cl)Me, crystallized in the orthorhombic space group $P2_12_12_1$ with four formula units in the unit cell as the benzene solvate **2**·$2C_6H_6$, while for **3**, TerN-[$SiMe_2$(OTf)]Bi(OTf)Me, a triclinic cell and space group $P\bar{1}$ with Z = 2 were found. Compound **3** crystallized as monobenzene solvate. The structures of **2** and **3** without the solvates are shown in Figures 1 and 2. For both compounds, no intermolecular interaction with the solvate molecules can be discussed, but the terphenyl substituent is arranged in such a fashion that one of the mesitylenes is in the proximity of the Bi center, allowing intramolecular *π*-arene interactions (vide infra), which can be best described as a [2 + 2 + 2] coordination mode. Both species feature an eclipsed, bent $R^1(R^2)$Bi−N−$SiMe_2$(OTf) frame (Bi−N−Si = 125.0(1) in **2** and 128.20(9)° in **3**) with trigonal-pyramidal Bi, trigonal-planar N, and strongly distorted tetrahedral Si centers (Table 1). Both the Bi−N and Si−O distances are in the typical range of strongly polarized Bi−N and Si−O bonds.[55] However, the Bi−OTf bond in compound **3** (Bi1−O3, 2.375(2) Å; Figure 2) is significantly longer than expected for a strongly polarized Bi−O single bond (the sum of the covalent radii is $\sum r_{cov}$(Bi−

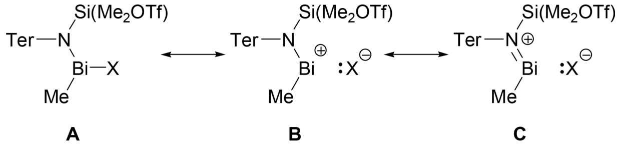
Table 1. Selected Parameters for the Description of the Bi−X Interaction in Compounds 2 and 3[a]

parameter	2	3
X−Bi/$\sum r_{cov}$[X−Bi] [%]	101	111
$\sum\angle$(Bi) [deg]	289.1	278.3
$\angle$(X−Bi−N) [deg]	97.57(6)	93.38(5)
Q_{CT} X → RBiMe [e][b]	0.51	0.28
lone valence at Bi[c]	no	yes
$\rho(r)$ at the BCP [e]	0.065	0.062
$\nabla^2\rho(r)$ at the BCP	0.143	0.236
$D_{298,hom}$ [kcal/mol][d]	+75	+78
$D_{298,het}$ [kcal/mol][d]	+152	+107

[a] **2**, X = Cl; **3**, X = OTf. [b] Based on NBO charges. [c] From NBO analysis. [d] Computed dissociation free energies for the homolytic (hom) and heterolytic (het) dissociation processes.

O) = 2.14 Å)[55] because of the weakly coordinating character of the OTf group. Additionally, the Bi−O3 bond is located opposite to the π-arene system; the same holds true for the Cl atom attached to Bi in compound **2**. Hence, the elongation of the Bi−O bond might also be discussed in terms of a hyperconjugative effect.[46,56] Because of the strong ionic bonding between the triflate and the formal Bi$^+$ compound, **3** can be regarded as an aminobismuthenium cation stabilized by a triflate anion. According to natural bond orbital (NBO) analysis, the triflate group carries an overall charge of −0.72e, which corresponds to a charge transfer of 0.28e onto the TerN[SiMe$_2$(OTf)]Bi(Me)$^+$ fragment, in accord with a highly polarized Bi−O bond or even an ion pair description. Further NBO analysis data support the latter idea by describing the bismuth atom with an empty valence 6p orbital, that is, as bismuthenium cation, as depicted in Scheme 9 by Lewis representation **B**. Interestingly, stabilization of the Bi$^+$ fragment bearing an electron sextet by hyperconjugation (n(O) → p(Bi), 96 kcal/mol; formula **A**) is much more pronounced than stabilization by formation of a Bi−N double bond (10 kcal/mol; formula **C**). The natural localized molecular orbital (NLMO) picture, which displays all of the delocalization effects, also features stabilization of the bismuthenium cation by donation of electron density of the adjacent lone pairs of the O atom into the formal empty p orbital located on the bismuth atom. Additionally, the computed electron localization function (ELF) supports the ionic description, since the localized electron density of O3 is roughly spherical and not directed toward Bi1 (Figure 6).

Scheme 9. Major Lewis Representations of the Bi−X Interaction According to NBO Analysis



A topological analysis of the electron density along the O3−Bi1 axis revealed only one valence-shell charge concentration (VSCC) in the Laplacian (Figure 7), also suggesting a mainly ionic interaction between O3 and Bi1,[57] which is in agreement with the NBO and ELF results (vide supra). Also, the calculated electron density at the bond critical point (BCP) is quite low ($\rho(r)$ = 0.062e) and the Laplacian is positive ($\nabla^2\rho(r)$ = 0.236), which is also an indicator of ionic bonding.[57−63]

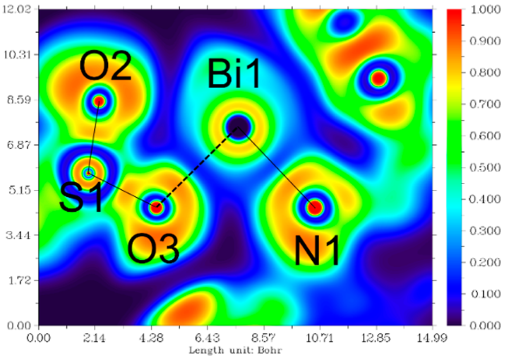


Figure 6. Two-dimensional cross section through the N1−Bi1−O3 plane of the electron localization function (ELF) of **3**.

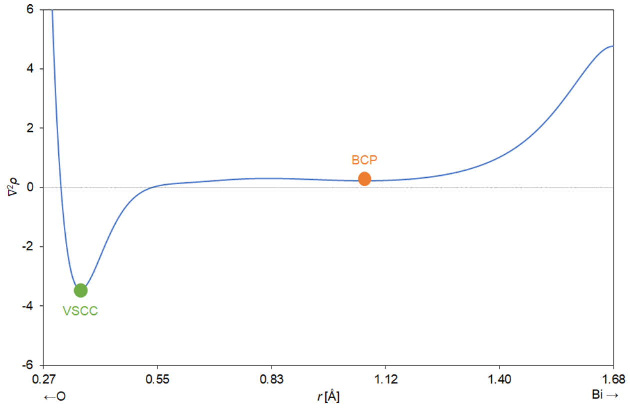


Figure 7. Plot of the Laplacian along the O3−Bi1 axis and position of the bond critical point (BCP) and valence-shell charge concentration (VSCC).

Table 1 summarizes some essential parameters of the Bi−X interaction in **2** (X = Cl) and **3** (X = OTf) to compare the chloride with the triflate substituent. When all of the bond indicators are taken into account, triflate derivative **3** can be regarded as a donor-stabilized bismuthenium cation while compound **2** is best described as chlorobismuthane with a highly polarized Bi−Cl bond.

Compound **5** was crystallized from the reaction mixture without further purification (Figure 3) in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. In the crystal, compound **5** forms centrosymmetric dimers with formal Bi$_2$I$_2$ rings as a result of long-range Bi···I intermolecular coordination (Bi1′−I1 = Bi1−I1′ = 3.6950(4) Å; cf. $\sum r_{vdW}$(Bi···I) = 4.4 Å).[64] Moreover, within compound **5** two slightly different Bi−I1 and Bi−I2 distances (Bi1−I1 = 2.8992(3) Å; Bi1−I2 = 2.8455(4) Å) are observed that are close to the sum of the covalent radii ($\sum r_{cov}$(I−Bi) = 2.84 Å).[55] The Bi−N distance (2.166(3) Å) is in the range of a polarized Bi−N single bond ($\sum r_{cov}$(N−Bi) = 2.22 Å)[55] and comparable to those found in species **2** (2.232(2) Å) and **3** (2.224(2) Å).[20] The angular sum at the bismuth atom ($\sum\angle$(Bi1) = 299.6°) is significantly larger than in **1** (282.0°) and other aminodichlorbismuthanes.[20] This might be due to the very large iodine atoms, in accord with Bent's rule.[65,66] Again the Bi center is stabilized by η^2 coordination (vide infra) with one mesitylene ring, as depicted in Figure 3. Moreover, the iodine atom is also close to the arene, leading to I···C$_{arene}$ π interactions.

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Both azido compounds **6** and **7** crystallized from a saturated benzene solution at room temperature as benzene solvates (Figures 4 and 5; see Table S2). There are no intermolecular interactions between the bismuth atoms and benzene solvate molecules in the crystal structure, but again, in both cases the Bi center is stabilized by coordination to one mesitylene ring of the terphenyl substituent (vide infra). Compound **6** crystallized in the triclinic space group $P\bar{1}$ with two molecules in the unit cell, while the mixture of **6** and **7** crystallized in the monoclinic space group $P2_1/n$ with four molecules per unit cell, both featuring centrosymmetric dimers in the solid state. We do want to stress that it was impossible to crystallize pure diazide **7**. The structural parameters of **6** and **7** are similar, and therefore, **6** can easily cocrystallize with **7**. The amino nitrogen–bismuth distance in **7** (Bi1–N1 = 2.184(2) Å) is the same as in **6** (2.180(1) Å) within the standard deviation and in the expected range for a polarized Bi–N single bond ($\sum r_{\mathrm{cov}}$(N–Bi) = 2.22 Å),[55] The same holds true for the distance of Bi1 to the nonbridging azido nitrogen (2.218(2) Å in **6** vs 2.214(2) Å in **7**). However, in **7** the distance to the bridging azido nitrogen (Bi1–N2 = 2.287(5) Å) is significantly longer, as it bridges both monomers in a $\mu_{1,1}$ fashion (cf. $Bi(N_3)_3$, d_{av}(Bi–N) = 2.316 Å).[67] The distance between Bi1 and N2′ of the adjacent molecule (B1···N2′ = 3.120(5) Å) lies well within the sum of the van der Waals radii ($\sum r_{\mathrm{vdW}}$(Bi···N) = 3.9 Å).[64] Interestingly, the Nγ of the azide group covalently bound to the bismuth atom in both species lies in the proximity to the adjacent Bi1′ atom (3.411(2) in **6** and 3.281(2) Å in **7**; cf. $\sum r_{\mathrm{vdW}}$(Bi···N) = 3.9 Å), and therefore, these azides can also be considered as bridging groups but in a $\mu_{1,3}$ mode (Figures 4 and 5).

All of the azide groups in **6** and **7** are in a trans-bent arrangement with N–N–N angles smaller than 180° (175–177°), and therefore, a small covalent contribution to the bismuth azide bonds can be discussed, in agreement with NBO analysis (see the Supporting Information), which features highly polarized Bi–N bonds (in the Bi–N NBO, ca. 83% of the electron density is localized at nitrogen and 17% at the bismuth center). In the case of compound **6**, the chlorine atom bridges the two monomeric units instead of the azide group, with a Bi1–Cl1 distance of 2.5642(3) Å, which is significantly longer than the sum of the covalent radii ($\sum r_{\mathrm{cov}}$(Bi–Cl) = 2.50 Å[55]) (Figure 4), while the second, much longer Bi1–Cl1′ distance of 3.3483(4) Å lies well within the sum of the van der Waals radii ($\sum r_{\mathrm{vdW}}$(Bi–Cl) = 4.1 Å).[64]

Bismuth-arene Interactions. All of the studied compounds feature a Bi–X bond (X = Cl, I, N, O) that is nearly perpendicular to one *o*-mesitylene ring system. As indicated by NBO analysis, the π system of the aromatic ring interacts with the antibonding orbital of the Bi–X bond (as shown in Figure 8 for species **1** as an example). Since this work led to several structurally characterized compounds featuring intramolecular Menshutkin-type interactions,[20,39,45,68–74] the influence of the substituents at the bismuth atom on the interaction could be studied in detail. Table 2 lists the minimum, maximum, average, and centroid (Ct) distances of the closest mesitylene ring system to the bismuth atom. Since it is rather difficult to give correct connectivities (hapticities) of asymmetrically coordinated mesitylenes to the bismuth center, we have used the criterion d(Bi···C$_{\mathrm{mesitylene}}$) < 4.2 Å (cf. $\sum r_{\mathrm{vdW}}$(Bi···C) = 4.0 Å), resulting in a formal hapticity value of 6 for all of the considered species except **5** (Figure 3), for which competition between iodine and bismuth for the arene interaction leads to hapticities of 4 for Bi and 3 for iodine (cf. $\sum r_{\mathrm{vdW}}$(I···C) = 3.8 Å) (Table 3).[64] Interestingly, the I–Ct distance is even smaller (3.66 Å compared with 3.70 Å for Bi–Ct). A closer look at the distances for all species revealed often either a [2 + 2 + 2] or [3 + 3] coordination mode of the mesitylene with the Bi center.

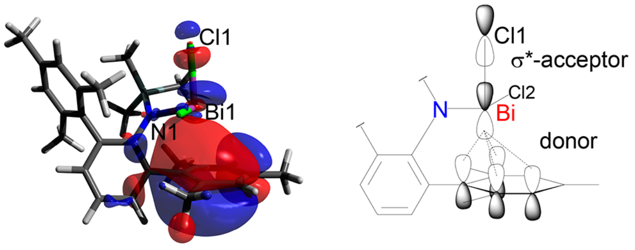

Figure 8. Bi···π-arene interaction in **1** in the NLMO picture (left) and in a simplified orbital picture (right).

Table 2. Bi···Mesitylene Distances (Minimum, Maximum, Average, Centroid, in Å) in Compounds 1–3 and 5–7

	d_{min}	d_{max}	d_{av}	d_{Ct}	cm[b]	η
1[a]	2.940(4)	3.637(4)	3.33	3.03	2 + 2 + 2	6
2	2.994(3)	4.206(3)	3.63	3.38	2 + 2 + 2	6
3	2.871(2)	4.089(2)	3.51	3.26	2 + 2 + 2	6
5	3.119(4)	4.668(5)	3.92	3.71	2 + 2	4
6	2.842(2)	3.444(2)	3.20	2.88	3 + 3	6
7	2.878(2)	3.468(2)	3.23	2.91	3 + 3	6

[a]Structural data were taken from ref 5. [b]cm = coordination mode.

The interaction of the mesitylene ring system with the Bi atom is also manifested in the NLMO picture (Figure 8). For example, the π system of the arene in **1** donates electron density into one of the antibonding σ^*(Bi–Cl) orbitals.

We tried to find a correlation between the substituents of the bismuth atom and the strength of the Bi···π-arene interaction. To compare the studied bismuth compounds, the bismuth partial charge was plotted as a function of the Bi···C$_{\mathrm{Mes}}$(min) distance.[75] The partial charges at the bismuth atoms (Table 4 and Figure 9) were computed at the PBE0/def2svp level of theory[76–78] including the D3(BJ) empirical dispersion.[48] In general, the Bi···C$_{\mathrm{Mes}}$(min) distance correlates well with the NBO charge at the Bi center: the shorter the Bi···mesitylene contact, the larger the calculated positive NBO charge at Bi (Figure 9). The only exception was found for the diazido compound **7**. Although this compound exhibits the largest NBO charge at Bi, the Bi···C$_{\mathrm{Mes}}$(min) distance is slightly longer than in **3** and **6**.

■ CONCLUSION

Even though the presented compounds turned out to be unsuited for the generation of a tetrazabismuthole, we could synthesize interesting derivatives of TerN(SiMe$_3$)BiCl$_2$ (**1**) via different routes, which allowed the study of the reactivity of aminobismuthanes.

Reactions with Ag[OTf] led to a methyl/triflate exchange reaction, indicating an extremely Lewis acidic transient species whose nature could not be established. In fact, a highly Lewis acidic, anion-stabilized aminobismuthenium salt, **3**, could be synthesized by substituting the remaining chloride in the methyl/triflate exchange product **2** by a second triflate using a second equivalent of Ag[OTf]. When TerN(SiMe$_3$)Li and Bi(OTf)$_3$ were utilized to synthesize TerN(SiMe$_3$)Bi(OTf)$_2$, small amounts of a C–C coupling product were observed.

Table 3. Bi/I···Mesitylene Distances in Compound **5** [Å]

	C1	C2	C3	C4	C5	C6
Bi	3.119(3)	3.277(4)	3.832(3)	4.070(4)	4.534(4)	4.668(5)
I	3.683(4)	3.762(4)	3.858(5)	4.009(4)	4.050(4)	4.148(4)

Table 4. Summary of NBO Analysis Data (Q_{Bi} and Q_{mes} in *e*, Localization of the Bi−N Bond and Bi Lone Pair in %)

	Q_{Bi}	$\sum Q_{mes}$[c]	Bi−N[d]	Bi−LP[e]
1[a]	+1.50	0.04	18	95
2[b]	+1.43	0.03	18	88
3[b]	+1.64	0.07	16	89
5[a]	+1.16	0.05	19	95
6[a]	+1.64	0.06	17	95
7[a]	+1.73	0.05	16	95

[a] Calculated as the dimer. [b] Calculated as monomers as found in the crystal. [c] Sum of the natural charges (NBO-based) at the coordinating Mes group (in *e*). [d] Localization of the Bi−N σ bond at Bi (in %). [e] 6s character of the lone pair (LP) at Bi (in %).

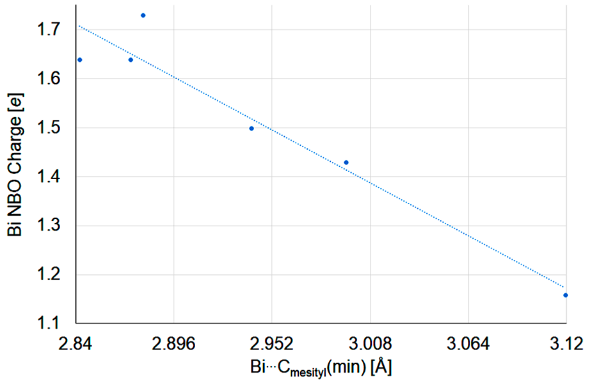

Figure 9. Correlation between the NBO charge at Bi1 and the closest Bi···mesitylene contact.

It was also shown that exchange of the chlorine atoms in **1** by other halogens (e.g., iodine) and pseudohalogens (e.g., azide) was possible. Pseudohalogens can be introduced using the respective sodium salts, but full conversion into the doubly substituted pseudohalogen derivative turned out to be difficult.

All of the compounds were structurally characterized and displayed either monomeric molecular species or centrosymmetric dimers when a halogen or pseudohalogen was present. All of the species featured classic bismuth···arene interactions stabilizing the bismuth compounds. Additionally, for the iodine species **5** a competition between Bi and I for arene interactions was found since the iodine also interacts with arenes. Moreover, a simple correlation between the positive charge at the bismuth and the shortest Bi···C_{Mes} distance was established in accord with previous studies and the description of the Bi···π-arene interaction as a Lewis acid−base pair.

■ EXPERIMENTAL SECTION

General Considerations. All of the manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Detailed information regarding experimental procedures and a full set of analytical data (including IR and Raman spectroscopy, melting points, etc.) can be found in the Supporting Information.

Caution! *Silver azide (AgN_3) is explosive and sensitive toward shock, heat, and electrical discharge. All manipulations with AgN_3 should be carried out wearing appropriate protective clothing.*

Synthesis of TerN(SiMe$_2$OTf)Bi(Me)Cl (2). To a stirred solution of TerN(SiMe$_3$)BiCl$_2$ (0.200 g, 0.28 mmol) in toluene (2 mL) was added a solution of Ag[OTf] (0.072 g, 0.28 mmol) in toluene (1 mL) dropwise at −25 °C. Upon warming to room temperature, the reaction mixture was stirred for 1.5 h and filtered (F4). The solvent was removed in vacuo, and the resulting yellow solid was recrystallized from benzene at room temperature. Washing with *n*-hexane (0.2 mL) and drying in vacuo for 3 h afforded **2**·$^1/_2C_6H_6$ (0.152 g, 0.19 mmol, 68.4% yield) as pale-yellow to colorless crystals.

Crystals obtained by recrystallization from benzene were suitable for single-crystal diffraction. **2** crystallized with two molecules of benzene. Drying in vacuo led to partial loss of solvent molecules (only half a molecule of benzene per molecule of **2** was found in the NMR spectra and CHN analysis).

Mp: 110 °C (decomp.). **CHN** calcd (found) in %: C 44.69 (44.61), H 4.48 (4.24), N 1.68 (1.65), S 3.85 (4.33). **^{1}H NMR** (298.2 K, CD$_2$Cl$_2$, 300.13 MHz, δ): −0.19 (broad, 3H, Si(C*H*$_3$)(CH$_3$)OTf), 0.18 (broad, 3H, Si(CH$_3$)(C*H*$_3$)OTf), 1.19 (s, 3H, Bi(C*H*$_3$)), 2.25 (broad, 12H, *o*-C*H*$_3$ from Mes), 2.35 (broad, 6H, *p*-C*H*$_3$ from Mes), 6.99−7.07 (broad (three resonances), 7H, arom. C*H*), 7.36 (s, 3H, $^1/_2C_6H_6$). **^{19}F{^{1}H} NMR** (298.2 K, CD$_2$Cl$_2$, 282.38 MHz, δ): −76.80 (s).

Synthesis of TerN(SiMe$_2$OTf)Bi(Me)OTf (3). At −40 °C, a solution of Ag[OTf] (0.154 g, 0.60 mmol) in toluene (1 mL) was added to a stirred solution of TerN(SiMe$_3$)BiCl$_2$ (0.200 g, 0.29 mmol) in toluene (2 mL). The reaction mixture was warmed to room temperature and stirred for 2.5 h. Upon filtration (F4), the solvent was removed in vacuo, and the resulting yellow solid was recrystallized from benzene at room temperature. The crystals were washed with *n*-hexane (0.2 mL) and dried in vacuo for 3 h, affording **3**·$^1/_2C_6H_6$ (0.178 g, 0.20 mmol, 70.0% yield) as a yellow solid.

Crystals obtained by recrystallization from benzene were suitable for single-crystal diffraction. **3** crystallized with one molecule of benzene. Drying in vacuo led to partial loss of solvent molecules (only half a molecule of benzene per molecule of **3** was found in the NMR spectra and CHN analysis).

Mp: 80 °C. **CHN** calcd (found) in %: C 40.59 (40.70), H 3.94 (3.77), N 1.48 (1.62), S 6.77 (6.80). **^{1}H NMR** (298.2 K, C$_6$D$_6$, 300.13 MHz, δ): 0.19 (broad, 6H, Si(C*H*$_3$)$_2$OTf), 1.47 (broad, 3H, Bi(C*H*$_3$)OTf), 2.07 (broad, 6H, Ter-C*H*$_3$), 2.13 (broad, 6H, Ter-C*H*$_3$), 2.24 (broad, 6H, Ter-C*H*$_3$), 6.64−6.99 (broad, 7H, Arom. C*H*), 7.16 (s, 3H, $^1/_2C_6H_6$). **^{19}F{^{1}H} NMR** (298.2 K, C$_6$D$_6$, 282.38 MHz, δ): −77.43 (s, C*F*$_3$), −76.32 (s, C*F*$_3$).

Synthesis of TerN(SiMe$_3$)BiI$_2$ (5). To a stirred solution of TerN(SiMe$_3$)BiCl$_2$ (0.188 g, 0.16 mmol) in CH$_2$Cl$_2$ (3 mL) is added Me$_3$SiI (0.065 g, 0.32 mmol, neat) dropwise at −40 °C. The dark red solution is stirred 15 min at this temperature and concentrated at −40 °C afterward. Storage at −80 °C for 8 h results in the deposition of red crystals of **5**. Removal of the supernatant by syringe, washing with *n*-hexane (0.1 mL) at −40 °C and drying in vacuo at room temperature for 2 h yields 0.044 g (0.05 mmol, 31.9%) **5**.

Mp.: 151 °C (Decomp.). **CHN** calc. (found) in %: C 37.56 (37.18), H 3.97 (3.65), N 1.62 (1.58). **^{1}H NMR** (298.2 K, CD$_2$Cl$_2$, 300.13 MHz): − 0.08 (s, 9H, Si(C*H*$_3$)$_3$), 2.14 (s, 6H, C*H*$_3$), 2.23 (s, 6H, C*H*$_3$), 2.36 (s, 6H, C*H*$_3$), 6.98−7.05 (m, 7H, arom. C*H*.

Synthesis of TerN(SiMe$_3$)Bi(Cl)N$_3$ (6). TerN(SiMe$_3$)BiCl$_2$ (0.362 g, 0.50 mmol) and NaN$_3$ (0.033 g, 0.50 mmol) were mixed together as solids and suspended in THF (4 mL) afterward. The reaction mixture was stirred for 17 h at room temperature. Upon removal of the solvent in vacuo, the resulting residue was extracted

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with benzene (3 mL) and filtered (F4). Concentration and storage at room temperature for 2 h led to the deposition of orange crystals (needles). The supernatant was removed by syringe and discarded. Washing with *n*-hexane (0.2 mL) and drying in vacuo for 3 h afforded **6**$\cdot{}^1/_{12}C_6H_6$ (0.196 g, 0.29 mmol, 57.1% yield) as an orange solid.

Crystals of **6** obtained from benzene were suitable for single-crystal diffraction. **6** crystallized with 1 equiv of benzene. Drying in vacuo led to partial loss of solvent molecules (only $^1/_{12}$ of a molecule of benzene per molecule of **6** was found in the NMR spectra and CHN analysis).

Mp: 175 °C (decomp.; red melt and gas evolution). **CHN** calcd (found) in %: C 47.62 (47.58), H 5.01 (4.72), N 8.08 (7.65). **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz, δ): −0.19 (broad, 9H, Si(CH_3)$_3$), 2.22 (broad, 12H, *o*-CH_3), 2.37 (broad, 6H, *p*-CH_3), 6.94−7.15 (broad, 7H, arom. C*H*), 7.36 (s, 0.5H, $^1/_{12}C_6H_6$). **^{29}Si INEPT NMR** (298.2 K, CD_2Cl_2, 59.63 MHz, δ): 10.9 (m).

Reaction of TerN(SiMe$_3$)BiCl$_2$ (1) with an Excess of NaN$_3$. TerN($SiMe_3$)$BiCl_2$ (0.200 g, 0.29 mmol) and NaN_3 (0.039 g, 0.60 mmol) were mixed together as solids and suspended in THF (4 mL). The reaction mixture was stirred for 23 h at room temperature, and the solvent was removed in vacuo afterward. The residue was extracted with benzene (4 mL) and filtered (F4). Concentration and storage at room temperature for 3 h led to the deposition of orange crystals containing 83% **7** and 17% **6**. Addition of more NaN_3 (0.020 g, 0.31 mmol), stirring in THF (4 mL) over 18 h, and workup as described above led to orange crystals containing 88% **7** and 12% **6**. It was not possible to synthesize pure **7** with this method. Spectra of the mixed compound are given in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00318.

> Synthesis of starting materials and compounds, description of additional experiments, NMR, IR, and Raman spectra, details of the X-ray structures and ORTEP depictions, and computational details (PDF)
>
> Cartesian coordinates (XYZ)

Accession Codes

CCDC 1841999−1842005 and 1854602 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Lyhs, B.; Schulz, S.; Westphal, U.; Bläser, D.; Boese, R.; Bolte, M. Heteroleptic Amidinate Complexes of Heavy Group 15 Elements - Synthesis, X-Ray Crystal Structures and Theoretical Calculations. *Eur. J. Inorg. Chem.* **2009**, *2009*, 2247−2253.

(2) von Hänisch, C.; Stahl, S. Synthese und Charakterisierung von Binären Molekülverbindungen der Gruppe 15 Elemente Mit P_2As_2-, PSb_2-, PBi_2-, PBi_3- und P_2Bi_4-Gerüst. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2230−2235.

(3) Chitsaz, S.; Harms, K.; Neumüller, B.; Dehnicke, K. Phosphaniminato-Komplexe von Bismut(III). Die Kristallstrukturen von $[BiF_2(NPEt_3)(HNPEt_3)]_2$ und $[Bi_2I(NPPh_3)_4]I_3$. *Z. Anorg. Allg. Chem.* **1999**, *625* (6), 939−944.

(4) Raston, C. L.; Skelton, B. W.; Tolhurst, V.-A.; White, A. H. Bis-Amido- Complexes of Heavier Group 15 Metal Chlorides with the Sterically Hindered, N-Functionalised Amido Ligand, $[\{2\text{-}(6\text{-}Me)\text{-}C_5H_3N\}NSiMe_3]^-$. *Polyhedron* **1998**, *17* (5−6), 935−942.

(5) Burford, N.; Macdonald, C. L. B.; Robertson, K. N.; Cameron, T. S. Synthesis and Structures of $Sb[N(H)C_6H_2(t)Bu_3]_3$ and $Bi[N(H)C_6H_2(t)Bu_3]_3$: Implications for the Steric Limits of Supermesityl Substitution. *Inorg. Chem.* **1996**, *35* (13), 4013−4016.

(6) Wirringa, U.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. Synthesis and Structure of a Cyclic Bismuth Amide. *Inorg. Chem.* **1994**, *33* (21), 4607−4608.

(7) Veith, M.; Bertsch, B.; Huch, V. Zur Element-Stickstoff-Doppelbindung in Kationen Cyclischer Bis(Amino)-Phospha-, Arsa-, -Stiba- Und -Bismutane. *Z. Anorg. Allg. Chem.* **1988**, *559* (1), 73−88.

(8) Briand, G. G.; Chivers, T.; Parvez, M. The Relative Stabilities of PhE(NH-t-Bu)$_2$ and PhE(μ-N-t-Bu)$_2$EPh (E = As, Sb, and Bi): X-Ray Structures of $\{Li_2[PhAs(N\text{-}t\text{-}Bu)_2]\}_2$ and PhE(μ-N-t-Bu)$_2$EPh (E = Sb, Bi). *Can. J. Chem.* **2003**, *81* (2), 169−174.

(9) Balakrishna, M. S.; Eisler, D. J.; Chivers, T. Chemistry of Pnictogen(III)-Nitrogen Ring Systems. *Chem. Soc. Rev.* **2007**, *36* (4), 650−664.

(10) Konu, J.; Balakrishna, M. S.; Chivers, T.; Swaddle, T. W. New Bonding Modes for Boraamidinate Ligands in Heavy Group 15 Complexes: Fluxional Behavior of the 1:2 Complexes, LiM[PhB-(NtBu)$_2$]$_2$ (M = As, Sb, Bi). *Inorg. Chem.* **2007**, *46* (7), 2627−2636.

(11) Evans, W. J.; Rego, D. B.; Ziller, J. W. Synthesis and Structure of the Cyclic Amido Bismuth Imide, $\{[(Me_3Si)_2N]Bi[\mu\text{-}N(SiMe_3)]\}_2$, via Loss of $SiMe_3$ from a $[N(SiMe_3)_2]^{1-}$ Ligand. *Inorg. Chim. Acta* **2007**, *360* (4), 1349−1353.

(12) Burford, N.; Edelstein, E.; Landry, J. C.; Ferguson, M. J.; McDonald, R. Identification of New N-Sb Topologies: Understanding the Sequential Dehydrochloride Coupling of Primary Amines and Trichloropnictines. *Chem. Commun.* **2005**, 5074−5076.

(13) Burford, N.; Cameron, T. S.; Macdonald, C. L. B.; Robertson, K. N.; Schurko, R.; Walsh, D.; McDonald, R.; Wasylishen, R. E. Dissociation of 2,4-Bis(2,4,6-Tri-Tert-Butylphenyl)-Cyclo-1,3-Dipnicta-2,4-Diazanes (Pnict = P, As, Sb) Imposed by Substituent Steric Strain: A Cyclobutane/Olefin Analogy. *Inorg. Chem.* **2005**, *44* (22), 8058−8064.

(14) Burford, N.; Landry, J. C.; Ferguson, M. J.; McDonald, R. Synthesis of Cyclo-2,4,6-Triarsa-1,3,5-Triazanes from Cyclo-2,4-Diarsa-1,3-Diazanes Demonstrating the General Influence of Substituent Steric Strain on the Relative Stability of Pnictazane Oligomers. *Inorg. Chem.* **2005**, *44* (16), 5897−5902.

(15) Burford, N.; Cameron, T. S.; Lam, K.-C.; LeBlanc, D. J.; Macdonald, C. L. B.; Phillips, A. D.; Rheingold, A. L.; Stark, L.; Walsh, D. Synthesis and Characterization of an Homologous Series of Bis(Amido)Diazadipnictetidines (Pnict = P, As, Sb, Bi). *Can. J. Chem.* **2001**, *79* (3), 342−348.

(16) Raston, C. L.; Skelton, B. W.; Tolhurst, V.-A.; White, A. H. Geminal Arsa(III)Amide and Trisubstituted Antimony and Bismuth Amides from the Sterically Hindered, N-Functionalised Amido Ligand $[\{2\text{-}(6\text{-}Me)C_5H_3N\}NSiMe_3]^-$. *J. Chem. Soc. Dalt. Trans.* **2000**, *2* (8), 1279−1285.

(17) Suzuki, H.; Matano, Y. *Organobismuth Chemistry*; Elsevier: Amsterdam, 2001.

(18) Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C.; Wishart, N. Synthesis and X-Ray Crystal Structure of a Homoleptic Bismuth Amide. *Polyhedron* **1989**, *8* (12), 1579−1580.

(19) Clegg, W.; Compton, N. A.; Errington, R. J.; Fisher, G. A.; Green, M. E.; Hockless, D. C. R.; Norman, N. C. X-Ray Crystal Structure of [Bi(NMe$_2$)$_3$]. *Inorg. Chem.* **1991**, *30*, 4680−4682.

(20) Hering-Junghans, C.; Schulz, A.; Thomas, M.; Villinger, A. Synthesis of Mono-, Di-, and Triaminobismuthanes and Observation of C−C Coupling of Aromatic Systems with Bismuth(III) Chloride. *Dalton Trans.* **2016**, *45* (14), 6053−6059.

(21) Michalik, D.; Schulz, A.; Villinger, A. Dichlorocyclodibismadiazane. *Angew. Chem., Int. Ed.* **2010**, *49* (41), 7575−7577.

(22) Lehmann, M.; Schulz, A.; Villinger, A. Cyclic Distiba- and Dibismadiazenium Cations. *Angew. Chem., Int. Ed.* **2012**, *51* (32), 8087−8091.

(23) Breunig, H. J.; Haddad, N.; Lork, E.; Mehring, M.; Mügge, C.; Nolde, C.; Rat, C.; Schürmann, M. Novel Sterically Congested Monoorganobismuth(III) Compounds: Synthesis, Structure, and Bismuth−Arene π Interaction in ArBiXY (X, Y = Br, I, OH). *Organometallics* **2009**, *28* (4), 1202−1211.

(24) Sasamori, T.; Tokitoh, N. Doubly Bonded Systems between Heavier Group 15 Elements. *Dalton Trans.* **2008**, 1395−1408.

(25) Dange, D.; Davey, A.; Abdalla, J. A. B.; Aldridge, S.; Jones, C. Utilisation of a Lithium Boryl as a Reducing Agent in Low Oxidation State Group 15 Chemistry: Synthesis and Characterisation of an Amido-Distibene and a Boryl-Dibismuthene. *Chem. Commun.* **2015**, *51* (33), 7128−7131.

(26) Schwamm, R. J.; Harmer, J. R.; Lein, M.; Fitchett, C. M.; Granville, S.; Coles, M. P. Isolation and Characterization of a Bismuth(II) Radical. *Angew. Chem., Int. Ed.* **2015**, *54* (36), 10630−10633.

(27) Schwamm, R. J.; Day, B. M.; Coles, M. P.; Fitchett, C. M. Low-Coordinate Bismuth Cations. *Inorg. Chem.* **2014**, *53* (7), 3778−3787.

(28) Hering-Junghans, C.; Thomas, M.; Villinger, A.; Schulz, A. Synthesis of Elusive Chloropnictenium Ions. *Chem. - Eur. J.* **2015**, *21* (18), 6713−6717.

(29) Day, B. M.; Coles, M. P. Assigning Hapticity to Cyclopentadienyl Derivatives of Antimony and Bismuth. *Organometallics* **2013**, *32* (15), 4270−4278.

(30) Schwamm, R. J.; Coles, M. P.; Fitchett, C. M. Group 1 Complexes of an (Amido-Amino)Silane and Their Use in the Synthesis of the Bi(III) Amide, Bi(Me$_2$Si{NAr}{N(H)Ar})Cl$_2$ (Ar = 2,6-Pr$_2$C$_6$H$_3$. *Organometallics* **2015**, *34* (11), 2500−2507.

(31) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. Bulky Alkyls, Amides, and Aryloxides of Main Group 5 Elements. Part 1. Persistent Phosphinyl and Arsinyl Radicals MRR′ and Their Chloro-Precursors MRR′Cl and Related Compounds. *J. Chem. Soc., Dalton Trans.* **1980**, 2428−2433.

(32) Mayer, P.; Schulz, A.; Villinger, A. GaCl$_3$-Assisted [3 + 2] Cycloaddition: A Route to New Binary PN-Heterocycles. *J. Organomet. Chem.* **2007**, *692* (13), 2839−2842.

(33) Baumann, W.; Schulz, A.; Villinger, A. A Blue Homoleptic Bismuth − Nitrogen Cation. *Angew. Chem., Int. Ed.* **2008**, *47* (49), 9530−9532.

(34) Kuprat, M.; Schulz, A.; Villinger, A. Arsa-Diazonium Salts with an Arsenic-Nitrogen Triple Bond. *Angew. Chem., Int. Ed.* **2013**, *52* (28), 7126−7130.

(35) Schulz, A.; Thomas, M.; Villinger, A. Synthesis of Aminobismuthanes via Me$_3$SnCl Elimination. *Z. Anorg. Allg. Chem.* **2017**, *643*, 1406−1414.

(36) Villinger, A.; Mayer, P.; Schulz, A. GaCl$_3$-Assisted [2 + 3] Cycloaddition: A Route to Tetrazaphospholes. *Chem. Commun.* **2006**, 1236−1238.

(37) Schulz, A.; Villinger, A. Tetrazarsoles - A New Class of Binary Arsenic-Nitrogen Heterocycles. *Angew. Chem., Int. Ed.* **2008**, *47* (3), 603−606.

(38) Lehmann, M.; Schulz, A.; Villinger, A. An Unusual Isomerization to Tetraazastiboles. *Angew. Chem., Int. Ed.* **2011**, *50* (22), 5221−5224.

(39) Schmidbaur, H.; Schier, A. π-Complexation of Post-Transition Metals by Neutral Aromatic Hydrocarbons: The Road from Observations in the 19th Century to New Aspects of Supramolecular Chemistry. *Organometallics* **2008**, *27* (11), 2361−2395.

(40) Silvestru, C.; Breunig, H. J.; Althaus, H. Structural Chemistry of Bismuth Compounds I. Organobismuth Derivatives. *Chem. Rev.* **1999**, *99* (11), 3277−3327.

(41) Lo, R.; Svec, P.; Ruzickova, Z.; Ruzicka, A.; Hobza, P. On the Nature of the Stabilisation of the E - Pi Pnictogen Bond in the SbCl$_3$ - Toluene Complex. *Chem. Commun.* **2016**, *52* (17), 3500−3503.

(42) Auer, A. A.; Mansfeld, D.; Nolde, C.; Schneider, W.; Schürmann, M.; Mehring, M. Bismuth - Arene π -Interaction : A Combined Experimental and Theoretical Approach. *Organometallics* **2009**, *28* (24), 5405−5411.

(43) Schier, A.; Wallis, J. M.; Müller, G.; Schmidbaur, H. [C$_6$H$_3$(CH$_3$)$_3$][BiCl$_3$] and [C$_6$(CH$_3$)$_6$[BiCl$_3$], Arene Complexes of Bismuth with Half-Sandwich and "Inverted" Sandwich Structures. *Angew. Chem., Int. Ed. Engl.* **1986**, *25* (8), 757−759.

(44) Avtomonov, E. V.; Li, X.-W.; Lorberth, J. Synthesis and Crystal Structure of Dimeric 2,4,6-Triphenylphenylbismutdichloride. *J. Organomet. Chem.* **1997**, *530* (1−2), 71−74.

(45) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. Homologous Series of Heavier Element Dipnictenes 2,6-Ar$_2$H$_3$C$_6$E = EC$_6$H$_3$-2,6-Ar$_2$ (E = P, As, Sb, Bi; Ar = Mes = C$_6$H$_2$-2,4,6-Me$_3$; or Trip = C$_6$H$_2$-2,4,6-IPr$_3$) Stabilized by *m*-Terphenyl Ligands. *J. Am. Chem. Soc.* **1999**, *121* (14), 3357−3367.

(46) Norman, N. C. Coordination Chemistry of Antimony and Bismuth: Lewis Acidity, σ^*-Orbitals and Coordination Geometry. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *87* (1−4), 167−176.

(47) Preda, A. M.; Schneider, W. B.; Schaarschmidt, D.; Lang, H.; Mertens, L.; Auer, A. A.; Mehring, M. The Role of Dispersion Type Metal···π Interaction in the Enantiotropic Phase Transition of Two Polymorphs of Tris-(Thienyl)Bismuthine. *Dalton Trans.* **2017**, *46* (39), 13492−13501.

(48) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32* (7), 1456−1465.

(49) Echeverria, J.; Aullon, G.; Danovich, D.; Shaik, S.; Alvarez, S. Dihydrogen Contacts in Alkanes Are Subtle but Not Faint. *Nat. Chem.* **2011**, *3*, 323−330.

(50) Echeverría, J.; Cirera, J.; Alvarez, S. Mercurophilic Interactions: A Theoretical Study on the Importance of Ligands. *Phys. Chem. Chem. Phys.* **2017**, *19* (18), 11645−11654.

(51) Frank, B. W.; Weber, J.; Fuchs, E. [CH$_3$C$_6$H$_5$BiCl$_2$][AlCl$_4$] and [(CH$_3$)$_6$C$_6$BiCl$_2$][AlCl$_4$] - Compounds Containing η_6-Arene-Complexed BiCl$_2^+$ Units. *Angew. Chem., Int. Ed. Engl.* **1987**, *26* (1), 74−75.

(52) Lehmann, M.; Schulz, A.; Villinger, A. Synthesis and Characterization of 1,3-Dihalogeno-2,4-Bis(2,4,6-Tri-Tert-Butylphenyl)-Cyclo-1,3-Distiba-2,4-Diazanes, [X-Sb(μ-NR)]$_2$ (X = F, Cl, Br, and I). *Eur. J. Inorg. Chem.* **2010**, *2010* (35), 5501−5508.

(53) Michalik, D.; Schulz, A.; Villinger, A. Lewis-Acid-Assisted Methyl Exchange Reactions in Silylated Aminodichloroarsanes. *Inorg. Chem.* **2008**, *47* (24), 11798−11806.

(54) Hering, C.; Lehmann, M.; Schulz, A.; Villinger, A. Chlorine/Methyl Exchange Reactions in Silylated Aminostibanes: A New Route to Stibinostibonium Cations. *Inorg. Chem.* **2012**, *51* (15), 8212−8224.

(55) Pyykkö, P.; Atsumi, M. Molecular Double-Bond Covalent Radii for Elements Li−E112. *Chem. - Eur. J.* **2009**, *15* (46), 12770−12779.

(56) Wang, C.; Guan, L.; Danovich, D.; Shaik, S.; Mo, Y. The Origins of the Directionality of Noncovalent Intermolecular Interactions. *J. Comput. Chem.* **2016**, *37* (1), 34−45.

(57) Fugel, M.; Beckmann, J.; Jayatilaka, D.; Gibbs, G. V.; Grabowsky, S. A Variety of Bond Analysis Methods, One Answer? An Investigation of the Element-Oxygen Bond of Hydroxides HnXOH. *Chem. - Eur. J.* **2018**, *24* (23), 6248−6261.

(58) Zhang, L.; Ying, F.; Wu, W.; Hiberty, P. C.; Shaik, S. Topology of Electron Charge Density for Chemical Bonds from Valence Bond Theory: A Probe of Bonding Types. *Chem. - Eur. J.* **2009**, *15* (12), 2979−2989.

DOI: 10.1021/acs.organomet.8b00318

(59) Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. Charge-Shift Bonding and Its Manifestations in Chemistry. *Nat. Chem.* **2009**, *1* (6), 443−449.

(60) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. Reports on Progress in Physics Charge Density of Molecules and Crystals. *Rep. Prog. Phys.* **1981**, *44*, 893−948.

(61) Frenking, G.; Esterhuysen, C.; Kovacs, A. Reply to "Comment on the Comparative Use of the Electron Density and Its Laplacian". *Chem. - Eur. J.* **2006**, *12* (30), 7773−7774.

(62) Nakanishi, W.; Hayashi, S.; Narahara, K. Atoms-in-Molecules Dual Parameter Analysis of Weak to Strong Interactions: Behaviors of Electronic Energy Densities versus Laplacian of Electron Densities at Bond Critical Points. *J. Phys. Chem. A* **2008**, *112* (51), 13593−13599.

(63) Popelier, P. On the Full Topology of the Laplacian of the Electron Density. *Coord. Chem. Rev.* **2000**, *197* (1), 169−189.

(64) Batsanov, S. S. Van Der Waals Radii of Elements. *Inorg. Mater.* **2001**, *37* (9), 871−885.

(65) Bent, H. A. An Appraisal of Valence-Bond Structures and Hybridization in Compounds of the First-Row Elements. *Chem. Rev.* **1961**, *61* (3), 275−311.

(66) Huheey, J. E. Bent's Rule: Energetics, Electronegativity, and the Structures of Nonmetal Fluorides. *Inorg. Chem.* **1981**, *20* (11), 4033−4035.

(67) Rosenstengel, K.; Schulz, A.; Villinger, A. Solid State Structure of $Bi(N_3)_3$, $Bi(N_3)_3$*Solvate and the Structural Dynamics in the $[Bi(N_3)_6]_3$- Anion. *Inorg. Chem.* **2013**, *52* (10), 6110−6126.

(68) Hinz, A.; Schulz, A.; Villinger, A.; Wolter, J.-M. Cyclo-Pnicta-Triazanes: Biradicaloids or Zwitterions? *J. Am. Chem. Soc.* **2015**, *137* (11), 3975−3980.

(69) Partyka, D. V.; Washington, M.; Updegraff, J. B.; Chen, X.; Incarvito, C. D.; Rheingold, A.; Protasiewicz, J. Surveying the {AuCl} Adducts of Bulky Phosphines Bearing the 2,6-Dimesitylphenyl Group. *J. Organomet. Chem.* **2009**, *694* (9−10), 1441−1446.

(70) Wehmschulte, R. J.; Khan, M. A.; Hossain, S. I. Reaction of *m*-Terphenyldichlorophosphanes with Sodium Azide: Synthesis and Characterization of Stable Azidocyclophosphazenes. *Inorg. Chem.* **2001**, *40* (12), 2756−2762.

(71) Hinz, A.; Rothe, J.; Schulz, A.; Villinger, A. Reduction of Dichloro(Diaza-Phospha)Stibanes − Isolation of a Donor-Stabilized Distibenium Dication. *Dalton Trans.* **2016**, *45* (14), 6044−6052.

(72) Mallow, O.; Khanfar, M. A.; Malischewski, M.; Finke, P.; Hesse, M.; Lork, E.; Augenstein, T.; Breher, F.; Harmer, J. R.; Vasilieva, N. V.; Zibarev, A.; Bogomyakov, A. S.; Seppelt, K.; Beckmann, J. Diaryldichalcogenide Radical Cations. *Chem. Sci.* **2015**, *6* (1), 497−504.

(73) Hering-Junghans, C.; Schulz, A.; Villinger, A. A Neutral Low-Coordinate Heterocyclic Bismuth-Tin Species. *Chem. Commun.* **2015**, *51* (72), 13834−13837.

(74) Burford, N.; Clyburne, J. A. C.; Wiles, J. A.; Cameron, T. S.; Robertson, K. N. Tethered Diarenes as Four-Site Donors to $SbCl_3$. *Organometallics* **1996**, *15* (1), 361−364.

(75) Glendening, E. D.; Landis, C. R.; Weinhold, F. NBO 6. 0: Natural Bond Orbital Analysis Program. *J. Comput. Chem.* **2013**, *34* (16), 1429−1437.

(76) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0Model. *J. Chem. Phys.* **1999**, *110* (13), 6158−6170.

(77) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297−3305.

(78) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8* (9), 1057−1065.

DOI: 10.1021/acs.organomet.8b00318