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Cationic Bismuth Amides: Accessibility, Structure, and Reactivity

Hannah Dengel^[a] and Crispin Lichtenberg*^[a]

Abstract: The synthetic access to cationic bismuth compounds based on simple, monodentate, synthetically useful amido ligands, $[Bi(NR_2)_2(L)_n]^+$, has been investigated (R = Me, Pr, Ph; L = neutral ligand). With [BPh₄]⁻ as a counteranion, the formation of contact ion pairs and subsequent phenyl transfer from B to Bi is observed. An intermediate of this reaction, [Bi(NMe₂)₂(HNMe₂)(BPh₄)] (1), could be isolated and fully characterized. The use of fluorinated tetrarylborates as counteranions leads to more stable cationic bismuth amides. The solvent-separated ion pairs $[Bi_2(\mu_2 NMe_{2}_{2}(NMe_{2}_{2}(thf)_{6}]^{2+}$ (4) and $[Bi(N/Pr_{2})_{2}(thf)_{3}]^{+}$ (5) were fully characterized with $[B(3,5-C_6H_3(CF_3)_2)_4]^-$ anions balancing the positive charge. The coordination chemistry, aggregation in solution, and spectroscopic features of these compounds were investigated. Compounds 4 and 5 show an increased reactivity towards diisopropylcarbodiimide compared to their neutral parent compounds. These reactions result in formation of the first cationic bismuth guanidinates. Characterization techniques include ¹H, ¹¹B, ¹³C, ¹⁵N, ¹⁹F and ³¹P (VT-)NMR and IR spectroscopy, single crystal X-ray diffraction analysis, and DFT calculations.

Introduction

Well-defined, cationic bismuth species have recently been subjects of intense research efforts. They show an increased Lewis acidity and electrophilicity compared to their neutral parent compounds while maintaining a high functional group tolerance. This makes them attractive targets for applications in stoichiometric group transfer reactions and catalysis. Catalytic transformations that have been realized to date include the allylation of aldehydes,^[1] diastereoselective aldol condensations,^[2] diastereoselective Mannich reactions,^[3] and the polymerization of activated olefins.^[4]

Neutral bismuth amide compounds have been investigated in some detail.^[5] They are valuable and easily accessible precursors for atomic layer deposition,^[5e] for nanoparticle synthesis,^[6] and for the preparation of clusters^[7] or bismuth compounds featuring more complex ligand scaffolds.^[8] Furthermore, their reactivity towards substrates such as CH acidic compounds,^[9] silanes,^[9] heterocumulenes,^[5a,9,10] alkenes, alkynes, aldehydes, and ketones^[11] has been studied.

However, the considerable number of literature-known bismuth cations featuring Bi–C bonds contrasts with the small number of cationic bismuth amides that do not contain

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Scheme 1. Examples of literature-known cationic bismuth amides.

supporting Bi-C bonds.^[12,13] Early work in the field aimed at the synthesis of low-coordinate bismuth cations stabilized by a dianionic, bidentate silyldiamido ligand (Scheme 1, A).[14a] This work has recently been extended by variation of the substitution pattern of the silyldiamido ligand.[14b] Moreover, different synthetic routes to access type A compounds were evaluated and halide abstraction by a Lewis acid was determined to be the only reliable method thus far.^[14b] Using a different ligand scaffold a cationic bismuth compound bearing one chloro and one silylamido ligand has been presented as an isolable complex en route to the synthesis of a potential bismadiazonium ion (Scheme 1, B).^[15] The literature-known cationic bismuth amides are based on bidentate or bulky ligands that confer stability to these species by chelation effects, steric protection or secondary metal-ligand interactions.^[12-15] We became interested in cationic bismuth species based on simple, monodentate amides. Such compounds represent attractive synthetic targets, because these "synthetically useful" amido groups can potentially be transferred to electrophilic substrates or act as initiating groups in catalytic transformations such as polymerization or hydroamination reactions

Herein, we report the synthesis, isolation, characterization, and reactivity of the first examples of cationic bismuth compounds featuring simple, synthetically useful amido ligands.

Results and Discussion

Cationic Bi amides with [BPh4]⁻ counterions

In order to generate a cationic bismuth amide, Bi(NMe₂)₃ was treated with the Brønsted acid [HNEt₃][BPh₄] at ambient temperature in THF (Scheme 2). A yellow crystalline product could be isolated after immediately subjecting the reaction mixture to solvent diffusion crystallization at -30 °C.

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Scheme 2. Formation and degradation pathway of isolable contact ion pair $[Bi(NR_2)_2(HNMe_2)(BPh_4)]$ (1).

Single crystal X-ray diffraction analysis (orthorhombic space group $Pna2_1$, Z = 4) revealed the identity of this compound as the contact ion pair [Bi(NMe₂)₂(HNMe₂)(BPh₄)] (1) (Figure 1). The bismuth atom shows bonding interactions with two amido groups, one amino group, and the π -electrons of two phenyl groups. This results in a distorted trigonal bipyramidal coordination geometry around Bi with the amine and one phenyl group in the axial positions (N3-Bi1-ct1, 166.0(3)°). The distance between Bi1 and the centroid of the axial phenyl substituent, ct1, amounts to 3.33 Å (Bi1-CPh1, 3.48-3.71 Å), which is slightly larger than the corresponding distance reported for an inverted sandwich complex featuring a Bi-toluene-Bi unit (Bi-ct^{toluene}, 3.26 Å).^[16] The Bi1-ct2 distance (3.52 Å) is larger, but the corresponding Bi-CPh distances are still below the sum of the van der Waals radii of these elements (4.00 Å).^[17] Thus, weak Bi1- π (Ph2) bonding interactions are assigned, which is



Figure 1. Molecular structure of $[Bi(NMe_2)_2(HNMe_2)(BPh_4)]$ (1) in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms (except for H3) are omitted for clarity. Centroids of phenyl rings are indicated by "ct". Selected bond lengths (Å) and angles (°): Bi1–N1, 2.050(14); Bi1–N2, 2.118(14); Bi1–N3, 2.419(10); Bi–ct1, 3.326(15); Bi–ct2, 3.520(12); N1–Bi1–N2, 93.0(6); N1–Bi1–N3, 88.6(6); N2–Bi1–N3, 89.0(6); N1–Bi–t1, 148.9(4); N2–Bi–ct1, 116.4(4); N3–Bi–ct1, 166.0(3); N1–Bi–ct2, 105.3(5); N2–Bi–ct2, 91.3(5); N3–Bi–ct2, 82.4(3); ct1–Bi–ct2, 84.9(3); Σ C–N1–C/Bi, 360; Σ C–N2–C/Bi, 350; Σ C–N3–C/Bi, 325.

supported by DFT calculations.^[18] The Bi–N^{amido} bond lengths amount to 2.05-2.12 Å. The difference in Bi–N^{amido} distances goes along with a stronger pyramidalization of the nitrogen atom N2 that is associated with the longer bond (sum of angles: 350° (N2) vs. 360° (N1)). Despite the higher coordination number (CN = 5), the Bi–N bonds in compound **1** are on average 0.10 Å shorter than those in the neutral parent compound Bi(NMe₂)₃ (CN = 3; avg. Bi–N, 2.19 Å).^[5b] This was ascribed to the cationic charge of the [Bi(NMe₂)₂(HNMe₂)]⁺ group and the relatively weak Bi– π (Ph) bonding (*vide supra*). Compound **1** is the first example of a monodentate amine interacting with a bismuth center. The Bi1–N3 bond length of 2.42 Å is similar to those found in [Bi(cyclen)(H₂O)(CIO₄)₃] (2.38-2.41 Å).^[19]

The ¹H NMR spectrum of **1** in a mixture of $C_6D_6/THF-d_8$ (1000:1)^[20] shows three signals with relative intensities of 12:6:1 in the non-aromatic region. This confirms the presence of two amido groups (δ = 3.42 (s, 12H) ppm) and one amine (δ = 1.91 (d, 6H), 5.06 (br s, 1H) ppm).^[21] The [BPh₄]⁻ anion shows two sets of resonances with relative intensities of 3:1, each of which is characteristic for phenyl groups. This indicates interactions between the bismuth atom and one phenyl substituent, i.e. compound **1** also forms a contact ion pair in solution. This coordination behavior was also observed at low temperatures of -40 °C in a toluene-*d*₈/THF-*d*₈ solvent mixture.^[49] ¹H NMR spectra of **1** in pure THF-*d*₈ show only one set of resonances for the [BPh₄]⁻ anion, suggesting that a solvent-separated ion pair can also be formed under these conditions.^[22,23]

When stored at -30 °C as a solid, compound 1 is stable for a period of months. A reasonable solution NMR characterization can be performed, when data acquisition is started immediately after dissolving the compound. However, 1 shows first signs of decomposition in solution at room temperature after ca. 10 min. as determined by ¹H NMR spectroscopy. The decomposition pathway of 1 was investigated by ¹¹B NMR spectroscopy in THF. The intensity of the sharp resonance at -6.7 ppm that is associated with the $[BPh_4]^-$ anion gradually decreases while a new, broad resonance at 0.6 ppm gradually increases in intensity and becomes the dominating species after ca. 19 h. This is in agreement with formation of an amine-borane, [BPh₃(NHMe₂)] (2). Indeed, 2 could be isolated in 81% yield from a solution of in situ generated compound 1 that had been kept at ambient temperature for 2 d and was fully characterized (Supp. Inf.).

Whereas a stable cationic aryl bismuth species with a $[BPh_4]^-$ counteranion has been described,^[24] Ph/RCO₂ exchange between $[BPh_4]^-$ and Bi(RCO₂)₃ has been reported as a method for the preparation of aryl bismuth compounds.^[25] In an attempt to synthesize a cationic bismuth amide with a $[BPh_4]^-$ counterion Ph/Cl exchange between Bi((NAryl)₂SiMe₂)Cl and Na[BPh₄] has been reported.^[14b] Our results on the isolation of **1** and its decomposition to **2** show that cationic bismuth amides with $[BPh_4]^-$ counterions are isolable, indeed, but represent intermediates en route to B–C bond activation products.

In order to evaluate the effect of the substituents at nitrogen on the stability of $[Bi(NR_2)_2(L)_n(BPh_4)]$, reactions between $Bi(NR_2)_3$ and $[HNEt_3][BPh_4]$ were performed and monitored by NMR spectroscopy (R = ^{*i*}Pr, Ph; Scheme 3, Supp. Inf.).



Scheme 3. Reaction of [HNEt₃][BPh₄] with Bi(NR₂)₃ (R = Pr, Ph).

It might have been anticipated that an increase of the steric bulk around the nitrogen atoms leads to an increased stability of the cationic species. However, rapid, quantitative consumption of the starting materials with formation of [BPh₃(thf)] was observed in both cases (for details see Supp. Inf.). The ¹H NMR spectra recorded after 10 min reaction time revealed [BPh₃(thf)] and BiPh(NR₂)₂ as the main products. These compounds result from transfer of a phenyl group from [BPh₄]⁻ to [Bi(NR₂)₂]⁺. With increasing reaction times, Ph/NR₂ exchange between boron and bismuth species was also observed. The first exchange gives compounds BPh₂(NR₂)/BiPh₂(NR₂) and was observed for R = ^{*i*}Pr, Ph. Detection of compounds BPh(N'Pr₂)₂ and BiPh₃ indicated even a second Ph/NR₂ exchange in the case of R = ^{*i*}Pr, ^[50]

Work-up of the reaction between $Bi(N'Pr_2)_3$ and $[HNEt_3][BPh_4]$ after short reaction times confirmed $[BPh_3(thf)]$ as the main product with an isolated yield of 51%. Furthermore, a few black crystals could be isolated from the bulk product by manual separation. Using single crystal X-ray diffraction analysis, this sample could be identified as the originally targeted cationic bismuth species, which had formed as a solid in trace amounts. Compound $[Bi(N'Pr_2)_2(BPh_4)]$ (3) crystallizes in the orthorhombic space group *Pccn* with *Z* = 4. As expected, 3 also forms a contact ion pair in the solid state. In contrast to its methyl-substituted derivative 1, however, there is no neutral amine ligand present in compound 3. The metal center in 3 is coordinated by two amido ligands and two phenyl groups of the



Figure 2. Molecular structure of $[Bi(NPr_2)_2(BPh_4)]$ (3) in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Centroids of phenyl rings are indicated by "ct". Selected bond lengths (Å) and angles (°): Bi1–N1, 2.101(3); Bi1–ct, 3.228(5); N1–Bi1–N1', 95.71(18); N1–Bi1–ct, 115.94(12); N1–Bi1–ct', 121.01(12); ct–Bi1–ct', 89.57(12); C7–B1–C7', 101.88(19); C13–B1–C13', 103.95(19); ΣC–N1–C/Bi, 360.

 $[BPh_4]^{-} \text{ unit, each of which are crystallographically equivalent.} This results in an unusual (distorted) tetrahedral coordination geometry around Bi1 (N/ct–Bi1–N/ct, 89.6°-121.0°). The Bi–N^{amido} bonds (2.10 Å) are intermediate between those found in 1 (2.05-2.12 Å). The nitrogen atoms show trigonal planar coordination geometries (<math display="inline">\Sigma C-N1-C/ct, 360^{\circ}$). The Bi1–ct distances of 3.23 Å are intermediate between those found in [BiCl₂(C₆Me₆)(AlCl₄)] (2.72 Å)^[26,27] and an inverted sandwich compound with a Bi-toluene-Bi unit (3.26 Å),^[16a] and clearly shorter than those of compound 1 (Bi-ct, 3.33-3.52 Å).^[16b] This is ascribed to the lower coordination number of the bismuth atom in **3**.

Cationic Bi amides with [B(3,5-C₆H₃(CF₃)₂)₄]⁻ counterions.

In order to generate more stable cationic bismuth species based on simple, synthetically useful amido ligands, the effect of a fluorinated borate counteranion was investigated. The bismuth amides Bi(NR₂)₃ (R = Me, [/]Pr) were reacted with the strong Brønsted acid [H(OEt₂)₂][A] ([A]⁻ = [B(3,5-C₆H₃(CF₃)₂)₄]⁻) (Scheme 4).^[28] In the case of the methyl-substituted ligand, a dinuclear, dicationic species, $[Bi_2(\mu_2-NMe_2)_2(NMe_2)_2(thf)_6]^{2+}$ 2[A]⁻ (4), was obtained as a yellow solid, whereas use of sterically more demanding *iso*propyl substituents gave a mononuclear cationic species, $[Bi(N'Pr_2)_2(thf)_3]^+$ [A]⁻ (5), as an orange solid. Both compounds are insoluble in hydrocarbons, but soluble in polar solvents such as THF. In contrast to compounds 1 and 3, no B–C bond activation was detected for compounds 4 and 5 due to their tetraarylborate counterions acting as true weakly coordinating anions.

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Scheme 4. Reaction of $Bi(NR_2)_3$ with $[H(OEt_2)_2]^+[A]^-$ (R = Me, ${}^{i}Pr$; $[A]^- = [B(3,5-C_6H_3(CF_3)_2)_4]^-$).

The molecular structures of **4** and **5** in the solid state were determined by single crystal X-ray diffraction analyses. Both compounds crystallized as solvent-separated ion pairs in the monoclinic space group $P2_1/c$ with Z = 4 (Figures 3, 4). The bismuth-containing part of compound **4** is a dication consisting of two crystallographically equivalent monomeric subunits. The two metal centers are linked by two amido groups in bridging coordination modes, resulting in an essentially planar Bi₂N₂ unit. This aggregation behavior was ascribed to the low steric demand of the methyl substituents at nitrogen. The coordination sphere of each bismuth atom is saturated by interaction with one terminal amido ligand and three THF ligands, which leads to distorted octahedral coordination geometry are due to the bridging coordination mode of two amido groups and



Figure 3. Molecular structure of the dicationic of $[Bi_2(\mu_2-NMe_2)_2(NMe_2)_2(thf)_6]^{2+}$ 2 $[B(3,5-C_6H_3(CF_3)_2)_4]^-$ (4) in the solid state. Hydrogen atoms and two latticebound THF molecules per formula unit are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level; carbon atoms of THF ligands are shown as wireframe. Selected bond lengths (Å) and angles (°): Bi1–N1, 2.335(3); Bi1–N1', 2.337(3); Bi1–N2, 2.120(3); Bi1–O1, 2.701(3); Bi1–O2, 2.711(3); Bi1–O3, 3.342(3); N1–Bi1–N1', 77.59(12); N2–Bi1–O3, 162.12(13); O1–Bi1–O2, 114.87(10); Bi1–N1–Bi1', 102.41(12); CC–N2–C/Bi, 354.



Figure 4. Molecular structure of the cation of $[Bi(N^iPr_2)_2(thf)_3]$ $[B(3,5-C_6H_3(CF_3)_2)_4]$ (5) in the solid state. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level; carbon atoms of THF ligands are shown as wireframe. Selected bond lengths (Å) and angles (°): Bi1–N1, 2.091(7); Bi1–N2, 2.112(7); Bi1–O1, 2.654(6); Bi1–O2, 2.572(6); Bi1–O3, 3.185(8); N1–Bi1–N2, 98.7(3); N1–Bi1–O1, 92.7(3); N2–Bi1–O3, 144.7(3); O1–Bi1–O2, 169.41(19); ΣC –N1–C/Bi, 360; ΣC –N2–C/Bi, 354.

to the weak bonding of one THF ligand (vide infra). In contrast to other cationic bismuth compounds with monodentate ligands, the bismuth-centered lone pair in 4 is not stereochemically active.[4,29] The two crystallographically distinct Bi-N distances that involve the bridging amido groups are identical within limits of error (Bi1-N1/N1', 2.34 Å) and elongated compared to terminal Bi1-N2 bonds (2.12 Å). A shortening of the terminal $Bi1_{\mathbb{T}}N2$ bond compared to the average Bi-N bond length in neutral Bi(NMe₂)₃ (2.19 Å)^[5b] was ascribed to the cationic character of 4. The THF ligands in 4 occupy facial sites of the coordination polyhedra. They differ with respect to the ligand that is located in *trans* position relative to the O^{THF} atom, which is either a bridging amido group in the case of O1/2 or a terminal amido group in case of O3. Accordingly, the substantial elongation of the Bi1-O3 distance (3.34 Å; sum of van der Waals radii: 3.82 Å) compared to the Bi1-O1/2 distances (2.70-2.71 Å) is due to a thermodynamic trans effect.

The higher steric bulk of the *iso*propyl substituents in **5** leads to formation of a mononuclear compound in the solid state. The bismuth center in **5** shows a coordination number of five and an additional stereochemically active lone pair. A T_5 value of 0.41 indicates a distorted square pyramidal coordination geometry.^[51] The amido groups occupy the apical (N1) or an equatorial position, respectively. However, despite their different coordination environments, the Bi–N bond lengths are identical within limits of error with an average value of 2.10 Å. The Bi–O1/2 distances in **5** are 0.05-0.14 Å shorter than the Bi1–O1/2 distances in **4**. This is due to the lower coordination number of the bismuth center and the absence of strong donors *trans* to these THF ligands in **5**. The third THF ligand in compound **5** is located *trans* to the equatorial amido ligand and experiences a pronounced thermodynamic *trans* effect (Bi1–O3, 3.19 Å).

NMR spectroscopic analysis of **4** in THF– d_8 indicates formation of solvent-separated ion pairs in solution. The ¹H NMR

spectrum at room temperature shows one resonance for the (NMe₂)⁻ groups. Upon cooling the sample, this signal gradually broadens and coalescence is observed at ca. -10 °C. Two wellseparated, sharp singlets of equal intensity and with similar chemical shifts are detected at a temperature of $-60 \degree C$ ($\delta = 4.43$, 4.53 ppm). These were ascribed to (NMe₂)⁻ groups in bridging and terminal coordination modes of [Bi₂(µ₂-NMe₂)₂(NMe₂)₂(thf)₆]²⁺. The exchange rate at -10 °C is approximated as $k \approx 70$ s⁻¹. Thus, the dimeric arrangement of **4** also represents a ground state in solution, with exchange phenomena taking place at room temperature.

NMR spectroscopic data of compound **5** is in agreement with a mononuclear $[Bi(N'Pr_2)_2(thf)_3]^+$ unit as the cationic part of a solvent-separated ion pair. The ¹H NMR spectrum shows a characteristic septet for the *CH*Me₂ groups at 6.03 ppm, which corresponds to a downfield shift by 1.56 ppm compared to the neutral starting material.^[5e] The appearance of only one set of signals for the *iso*propyl groups in the ¹H and ¹³C NMR spectra rules out the rigid square pyramidal coordination geometry that was observed in the solid state. In agreement with this, the THF ligands in compound **5** are substitutionally labile as shown by ¹H NMR spectroscopy in THF-*d*₈. This is further supported by substitution of the THF ligand in **5** by two equivalents of the stronger donor OPPh₃ to give $[Bi(N'Pr_2)_2(OPPh_3)_2][A]$ (**6**), which was characterized spectroscopically.

¹⁵N NMR spectroscopy

In addition to standard NMR spectroscopic characterization, ¹⁵N NMR spectroscopy can be a valuable tool for the investigation of nitrogen containing compounds. However, such studies on bismuth complexes are extremely rare.^[30] We performed ¹⁵N solution NMR spectroscopic experiments on a small series of closely related amido bismuth complexes that differ with respect to the overall complex charge or the donor strength of additional neutral ligands bound to Bi (Scheme 5 and Supp. Inf.).^[31]

Compound Bi(N'Pr₂)₃ shows a ¹⁵N NMR chemical shift of – 268 ppm. This corresponds to a downfield shift of ca. 40 ppm or ca. 16-23 ppm compared to HN'Pr₂ or amine adducts of LiN'Pr₂, respectively.^[32,33] Upon exchange of one anionic (N'Pr₂)⁻ ligand in Bi(N'Pr₂)₃ for two equivalents of OPPh₃ as a strong, neutral σ -donor to give [Bi(N'Pr₂)₂(OPPh₃)₂]⁺, a downfield shift of almost



100 ppm is observed ($\delta = -172$ ppm). Exchange of OPPh₃ ligands for weaker THF ligands results in a downfield shift of an additional 20 ppm ([Bi(N[/]Pr₂)₂(thf)_n]⁺: $\delta = -152$ ppm). The ¹⁵N NMR downfield shift upon going from neutral to cationic bismuth complexes of up to 116 ppm is significantly larger than the downfield shift of ca. 10-26 ppm observed upon protonation of tertiary alkylamines.^[34] Overall, this brief NMR spectroscopic case study reveals that in a series of (di*iso*propyl)amido bismuth compounds, the ¹⁵N NMR chemical shift shows a strong response to the charge of the bismuth complex. More subtle modifications of the electronic situation at nitrogen (induced by different neutral donors bound to Bi) are also reflected.

DFT calculations

DFT calculations were performed on compounds **1**, **3**, **4**, **5** and related species in order to gain further insights into some of their ground state properties and reactivity. Bonding parameters of the experimentally observed compounds were reproduced satisfactorily (Supp. Inf.).

(i) The experimental results on contact ion pairs $[Bi(NR_2)_2(L)_n(BPh_4)]$ showed that such compounds are isolable intermediates in a B-C bond activation of the [BPh₄]⁻ counterion. Somewhat counterintuitively, smaller substituents at nitrogen increase the stability of these species. The computational results suggest that B-C bond activation proceeds in all cases through a transition state with a phenyl group in a bridging coordination mode, [Bi(NR₂)₂(µ₂-Ph)(BPh₃)] (Supp. Inf.). For compound 3, such a transition state is directly accessible. For compound 1, however, the neutral amine HNMe2 must leave the coordination sphere of Bi before an energetically accessible transition state can be realized. This could take place by dissociation of HNMe₂ either directly from the contact ion pair 1 or from the cation [Bi(NMe₂)₂(HNMe₂)(solv)_n]⁺ after formation of a solventseparated ion pair. Thus, the ability to coordinate an additional neutral donor ligand makes compound 1 more stable than compound 3.

(ii) In order to gain further insights into the aggregation behavior of cationic bismuth amides, thermodynamic parameters of dissociation/association reactions were determined. The formation of a solvent-separated ion pair according to the reaction shown in Table 1 was calculated to be slightly exothermic and endergonic with [BPh₄]⁻ as the counteranion [A]⁻ (entry 1). This is in agreement with the experimentally observed

| Table 1. Calculated thermodynamic parameters for formation of contact vs.solvent-separated ion pairs of species related to 1 and 4; L = HNMe ₂ . $[Bi(NMe_2)_2(A)(L)] + 2$ THF $\longrightarrow [Bi(NMe_2)_2(L)(thf)_2]^+ [A]^-$ | | | | |
|---|--|--|---|--|
| Entry | Borate "A" | ∆ <i>H^{rel}</i> [kcal⋅mol ⁻¹] | ∆G ^{rel} [kcal⋅mol ⁻¹] | |
| 1 | BPh₄ | -3.9 | +6.6 | |
| 2 | B(3,5-C ₆ H ₃ (CF ₃) ₂) ₄ | -14.8 | -11.9 | |

Scheme 5. ¹⁵N NMR chemical shifts for neutral and cationic di*iso*propylamido bismuth complexes in solution.

behavior of **1** in THF. Exchanging the $[BPh_4]^-$ anion for $[B(3,5-C_6H_3(CF_3)_2)_4]^-$ in this reaction makes the formation of a solventseparated ion pair exothermic and exergonic (entry 2). This was also indicated by experimental observations. Similar results were obtained for *iso*propyl substituted analogs (Supp. Inf.).

(iii) The thermodynamic parameters for the formation of dinuclear dicationic amido-bismuth species were determined for the amido ligands $(NR_2)^-$ with R = Me, *i*Pr. The reaction shown in Table 2 is energetically favorable for R = Me (entry 1), but disfavored for R = *i*Pr (entry 2). This further supports the interpretation of NMR spectroscopic results regarding the aggregation behavior of compounds **4** and **5** in THF-*d*₈ solution.

| Table 2. Calculated thermodynamic parameters for the dimerization of amido-bismuth cations (species related to compounds 4 and 5). | | | | | |
|--|-----|---|---|--|--|
| 2 $[Bi(NR_2)_2(thf)_3]^+ \longrightarrow [Bi_2(\mu - NR_2)_2(NR_2)_2(thf)_6]^{2+}$ | | | | | |
| Entry | R | ΔH ^{rel} [kcal⋅mol ⁻¹] | ∆G ^{rel} [kcal·mol ⁻¹] | | |
| 1 | Ме | -21.7 | -6.3 | | |
| 2 | /Pr | +14.3 | +32.2 | | |

(iv) A frontier orbital analysis of the synthetically relevant species $[Bi_2(\mu_2\text{-}NMe_2)_2(NMe_2)_2(thf)_6]^{2+}$ (4cat) and $[Bi(N'Pr_2)_2(thf)_3]^+$ (5cat) revealed strong contributions of metal-centered p-type orbitals to the LUMOs in both cases (Figure 5). In both compounds, substitutionally labile THF ligands have to be replaced by potential substrate molecules in order to realize a sufficient orbital interaction with the LUMO and thus allow for pre-coordination/activation of the substrate. As expected, the HOMOs of the cationic bismuth species are mostly nitrogen centered (Supp. Inf.).



Figure 5. LUMOs of cationic species $[Bi_2(\mu_2\text{-}NMe_2)_2(NMe_2)_2-(thf)_6]^{2+}$ and $[Bi(N'Pr_2)(thf)_3]^+$ at iso values of 0.04.

(v) An NBO analysis of Bi(NMe₂)₃, Bi(N[/]Pr₂)₃, [Bi₂(μ_2 -NMe₂)₂(NMe₂)₂(thf)₆]²⁺ and [Bi(N[/]Pr₂)₂(thf)₃]⁺ confirmed more positive natural charges for the bismuth atoms in the cationic complexes (**4cat**: +1.91e; **5cat**: +1.83e) compared to the neutral parent compounds (Bi(NMe₂)₃: +1.67e; Bi(N[/]Pr₂)₃: +1.67e). The Bi–N bonds in the cationic species are strongly polarized

towards nitrogen (localization at N: 85-88% (**4cat**) and 83-84% (**5cat**). Somewhat counterintuitive, the polarization of the Bi–N bonds towards nitrogen is slightly less pronounced in the neutral compounds (localization at N: 80-82% (Bi(NMe₂)₃) and 81-82% (Bi(N/Pr₂)₃).

Reactivity of cationic bismuth amides

As described above, the bismuth amide cations $[Bi(NR_2)_2]^+$ react with their $[BPh_4]^-$ counteranions, leading to B–C bond activation (R = Me, 'Pr, Ph). To compare the reactivity of these cationic species with that of their neutral parent compounds, the bismuth amides $Bi(NR_2)_3$ were reacted with stoichiometric amounts of Na[BPh_4] in THF at room temperature. In all cases, however, the $[BPh_4]^-$ anion remained intact within reaction times of ≥ 24 h as detected by ¹¹B NMR spectroscopy. This is a first example of the increased reactivity of cationic bismuth amides compared to their neutral counterparts.

The bismuth amides **4** and **5** with fluorinated tetraarylborate anions show an increased stability, making them more suitable for reactivity studies with external electrophiles. Carbodiimides are attractive substrates for reactions with bismuth amides, as they would yield the corresponding guanidinates. Lanthanoid guanidinates have been investigated as homogeneous catalysts in the polymerization of olefins and cyclic esters or as precursors for atomic layer deposition (ALD) and chemical vapor deposition (CVD).^[35] Bismuth compounds based on bicyclic guanidinates have also been reported as precursors for ALD and CVD.^[36] However, there is so far only a single example of the synthesis of a bismuth guanidinate from a carbodiimide;^[9] in this case, the bismuth amide starting material contained one reactive dimethylamido group. We chose di*iso*propylcarbodiimide, ([/]PrN)₂C, as a model substrate (Scheme 6).



Reaction of the neutral methyl-substituted bismuth amide, Bi(NMe₂)₃, with three equivalents of (ⁱPrN)₂C (one equivalent per amido group) gave the targeted insertion product 7 with \geq 95% selectivity as indicated by NMR spectroscopy. However, extended reaction times of 11 h were necessary to obtain full conversion. For the isopropyl-substituted neutral bismuth amide, Bi(NⁱPr₂)₃, no reaction with (ⁱPrN)₂C was observed in 24 h at room temperature. This was ascribed to the steric bulk of the (N/Pr2)- groups and an inability to activate the substrate by precoordination. In contrast, the cationic bismuth amides 4 and 5 reacted with two equivalents of di isopropylcarbodiimide, accompanied by an immediate color change, to give the insertion products 8 and 9. This corresponds to a substantial increase in reactivity for the cationic bismuth amide species compared to their neutral parent compounds. Full conversion of 4 was observed within reaction times of \leq 10 min. In the case of 5, insertion of the first equivalent of carbodiimide is fast (≤ 10 min), but the second insertion proceeds more slowly (full

conversion after 12 h). Compounds **7**, **8**, and **9** were isolated as pale yellow (**7**) or colorless solids (**8**, **9**) in yields of 75-96%. The cationic complexes **8** and **9** are obtained free of THF, when dried *in vacuo* for prolonged periods of time, but contain two equivalents of THF per metal center, when dried in a stream of argon. Compound **9** was analyzed by single crystal X-ray diffraction (Figure 6; monoclinic space group $P2_1$ with Z = 2). The bismuth atom is found in a distorted octahedral coordination geometry. The distortion is due to the small bite angle of the angles around Bi from those expected for an ideal octahedral coordination geometry. Values of 58°-111° and 136°-168° were observed for ligands in *cis*- and *trans* positions, respectively.



Figure 6. Molecular structure of the cation of $[Bi((PrN)_2CN'Pr_2)_2(thf)_2]^+$ $[B(3,5-C_6H_3(CF_3)_2)_4]^-$ ([9-2 thf]) in the solid state. Hydrogen atoms and one latticebound THF molecule are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level; carbon atoms of THF ligands are shown as wireframe. The asymmetric unit contains two formula units of [9-2 thf], one of which is shown. Selected bond lengths (Å) and angles (°): Bi1–N1, 2.218(6); Bi1–N2, 2.351(8); Bi1–N4, 2.213(7); Bi1–N5, 2.388(7); Bi1–O1, 2.981(7); Bi1– O2, 2.998(9); C1–N1, 1.342(11); C1–N2, 1.360(12); C1–N3, 1.368(11); C14– N4, 1.387(11); C14–N5, 1.311(12); C14–N6, 1.381(11); N1–Bi1–N2, 58.2(3); N2–Bi1–N5, 136.0(3); N4–Bi1–O2, 168.2(3); N5–Bi1–O2, 110.6(3).

The THF ligands in **9** adopt a *cis* configuration. The Bi–O distances of 2.99-3.00 Å are slightly shorter than the Bi1–O3 distance in compound **5**. This suggests weak Bi-O^{THF} bonding and is in agreement with the possibility to remove the THF ligands under reduced pressure. Each of the guanidinate ligands shows one short and one long bond to the Bi center (Bi1–N1/4, 2.21-2.22 Å; Bi1–N2/5, 2.35-2.39 Å). This was ascribed to a thermodynamic *trans* effect, as the N atoms in *trans* position to the weaker O^{THF} donor atom show shorter Bi–N bonds than those in *trans* position to another N atom. The bonds of the central carbon atom C1/14 to the nitrogen atoms N1-6 measure 1.31-1.39 Å, which is between values expected for C–N single and double bonds suggesting electron delocalization within the guanidinate ligands. This behavior was also observed in the only other bismuth compound containing a guanidinate ligand.^[9]

The *iso*propyl substituents of compounds **8** and **9** generate broad ¹H NMR resonances at ambient temperature in THF- d_8 solution, indicating dynamic coordination behavior. At -40 °C, low temperature limiting spectra were obtained with all

*iso*propyl groups of each guanidinate ligand being magnetically inequivalent. For compound **9**, this is in agreement with the solid state structure being essentially maintained in solution. It is suggested that **8** shows an analogous structure in THF- d_8 solution.

Conclusions

Cationic bismuth compounds based on simple, synthetically useful, monodentate amido ligands were investigated. The use of [BPh₄]⁻ counteranions leads to contact ion pairs that readily undergo phenyl transfer from B to Bi at ambient temperature in solution (R = Me, i Pr, Ph). Contact ion pairs [Bi(NR₂)₂(L)_n(BPh₄)] are intermediates in this transformation (L = neutral ligand; n = 0 1). One of these compounds, [Bi(NMe₂)₂(HNMe₂)(BPh₄)] (1), could be isolated and fully characterized. The low steric bulk of the methyl substituents in 1 allows coordination of the additional neutral donor HNMe2, which decelerates its decomposition. A more effective stabilization of bismuth amide cations is achieved by use of the fluorinated counteranion $[B(3,5-C_6H_3(CF_3)_2)_4]^{-1}$ (abbreviated as [A]-), which does not undergo aryl transfer from The solvent-separated ion pairs $[Bi_2(\mu_2 -$ В to Bi. $NMe_2_2(NMe_2_2(thf)_6]^{2+} 2[A]^-$ (4) and $[Bi(N'Pr_2_2_2(thf)_3]^+ [A]^-$ (5) were isolated and fully characterized. The analysis of 5 and related compounds by ¹⁵N NMR spectroscopy revealed a strong response of the ¹⁵N NMR chemical shift on the formal charge at Bi. In a proof of principle study, compounds 4 and 5 were reacted with diisopropylcarbodiimide as an electrophile. In both cases, the cationic bismuth amides show a higher reactivity than their neutral parent compounds. These selective insertion reactions allowed for the synthesis and characterization of the first cationic bismuth guanidinates. It is anticipated that these results on the accessibility, characteristics, and reactivity of cationic bismuth amides will aid in the future design of stable complexes of this kind for possible applications in synthesis, catalysis, and materials science.

Experimental Section

General considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in inert atmosphere gloveboxes containing an atmosphere of purified argon. Solvents were degassed and purified according to standard laboratory procedures. NMR spectra were recorded on Bruker instruments operating at 300, 400, or 500 MHz with respect to ¹H. ¹H and ¹³C NMR chemical shifts are reported relative to SiMe₄ using the residual ¹H and ¹³C chemical shifts of the solvent as a secondary standard. ¹¹B and ¹⁹F NMR chemical shifts are reported relative to [BF3(OEt2)] and CFCl3, respectively, as external standards. ¹⁵N NMR chemical shifts are reported relative to CH3NO2 (90% in CDCl3) and were determined by two-dimensional ¹H-¹⁵N correlation NMR spectroscopic experiments (no ¹⁵N NMR resonances could be detected for compounds 1 and 4 using this technique). If not otherwise noted, NMR spectra were recorded at ambient temperature. Infrared spectra were collected on a Bruker FT-IR-Alpha spectrometer. Elemental analyses were performed on a Leco or a Carlo Erba instrument. Reproducibly satisfactory elemental analyses of 1 proved to be difficult to obtain, which was ascribed to the air and temperature sensitivity of the compound. Instead, the Bi content of ${\bf 1}$ was determined in a complexometric titration according to literature procedures using a solution of the disodium salt of ethylenediaminetetraacetic acid as a titrant and Xylenol Orange as an indicator. Single crystals suitable for X-ray diffraction were coated with polyisobutylene or perfluorinated polyether oil in a glovebox, transferred to a nylon loop and then transferred to the goniometer of a diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å). The structures were solved using direct methods (SHELXS) completed by Fourier synthesis and refined by full-matrix least-squares procedures. CCDC 1500494-1500499 contain the crystallographic information for this work.

DFT calculations. DFT calculations were performed with the Gaussian program^[37] using the 6-31G(d,p)^[38] (H, B, C, N, O, F), 6-311G(d,p) (Al, Cl), or the LanL2DZ^[39] (Bi) basis set and the B3LYP functional.^[40] A solvent model (smd,solvent=thf) was used for all calculations.^[41] The D3 version of Grimme's dispersion model with the original D3 damping function was applied.^[42] Frequency analyses of the reported structures showed no imaginary frequencies for ground states and one imaginary frequency for transition states. Thermodynamic parameters were calculated at a temperature of 298.15 K and a pressure of 1.00 atm. NBO analyses were performed using NBO 6.^[43] NMR shielding tensors were calculated using the gauge independent atomic orbitals method and ¹¹B NMR chemical shifts determined by comparison with BF₃(OEt₂).^[44]

Bi(NMe₂)₃. Bi(NMe₂)₃ was synthesized according to the literature.^[5b] Analytical data were in agreement with the literature. Additional data: ¹⁵N NMR (51 MHz, C₆D₆): δ = –318.5 (s, NMe₂) ppm.

Bi(**N**^{*i*}**Pr**₂)₃. Bi(**N**^{*i*}**Pr**₂)₃ was synthesized according to the literature.^[5e] Use of sublimed BiCl₃ as a starting material led to a slight increase in the isolated yield for reactions performed on the 6 mmol scale with respect to BiCl₃ (74% (this work) vs. 69% (ref. 5e). Analytical data were in agreement with the literature. Additional data: ¹⁵N NMR (51 MHz, C₆D₆): δ = –267.6 (s, N^{*i*}Pr₂) ppm.

[Bi(NMe₂)₂(HNMe₂)(BPh₄)] (1). [HNEt₃][BPh₄] (29 mg, 69 µmol) was added to a solution of Bi(NMe₂)₃ (24 mg, 70 µmol) in THF (1 mL). The reaction mixture was layered with pentane (5 mL) and cooled to -30 °C. After 14 h, a yellow solid was isolated by filtration and dried in a stream of argon. Yield: 42 mg, 63 µmol, 91%.

¹H NMR (400 MHz, C₆D₆/THF-*d*₈ (1000:1)): \bar{o} = 1.91 (br d, 6H, ³J_{HH} = 4.7 Hz, HN*Me*₂), 3.42 (br s, 12 H, Bi(N*Me*₂)₂), 5.06 (br s, 1H, *H*NMe₂), 7.13-

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7.16 (m, 3H, p-Ph¹ (partially overlapping with solvent resonance), 7.27 (dd, 6H, ³*J*_{HH} = 7.5 Hz, ³*J*_{HH} = 7.5 Hz, *m*-Ph¹), 7.34 (dd, 2H, ³*J*_{HH} = 7.4 Hz, ³J_{HH} = 7.4 Hz, *m*-Ph²), 7.48 (t, 1H, ³J_{HH} = 7.5 Hz, *p*-Ph², partially overlapping with resonance due to o-Ph¹), 7.52 (d, 6H, ${}^{3}J_{HH} = 7.5$ Hz, o-Ph¹, partially overlapping with resonance due to p-Ph²), 7.86 (d, 2H, ³J_{HH} = 7.4 Hz, o-Ph²) ppm. ¹³C NMR (101 MHz, C₆D₆/THF-d₈ (1000:1)): δ = 38.90 (s, HNMe₂), 43.62^[45] (br s, Bi(NMe₂)₂), 125.25 (s, p-Ph¹), 127.45 (s, m-Ph1), 130.89 (s, m-Ph2), 131.09^[45] (s, p-Ph2), 134.55 (s, o-Ph1), 136.74 (s, o-Ph²) ppm. Resonances for ipso-Ph carbon atoms could not be detected. ¹¹B NMR (128 MHz, C₆D₆): δ = 1.1 (br s) ppm. ¹¹B NMR (128 MHz, THF- d_8): \bar{o} = -6.7 (s) ppm. ATI IR (neat): \bar{v} = 3244 (w, NH), 3053 (w), 2990 (w), 2866 (w), 2777 (w), 1577 (w), 1478 (m), 1457 (w), 1427 (m), 1308 (w), 1265 (s), 1257 (m), 1239 (s), 1189 (w), 1178 (w), 1137 (s), 1097 (w), 1067 (w), 1050 (w), 1035 (w), 1020 (w), 1011 (s), 995 (w), 981 (m), 968 (w), 952 (w), 913 (s), 903 (m) cm⁻¹. Anal. calc. for C₃₀H₃₉BBiN₃ (661.45 g/mol): Bi, 31.6; found: Bi, 31.9.

[Me₂NHBPh₃] (2). [HNEt₃][BPh₄] (29 mg, 69 µmol) was added to a solution of Bi(NMe₂)₃ (24 mg, 70 µmol) in THF (1 mL). After 2 d, the reaction mixture was filtered. The filtrate was layered with hexanes (3 mL) and cooled to -30 °C. After 3 d, colorless crystals of **2** were isolated by filtration and dried *in vacuo*. Yield: 16 mg, 56 µmol, 81%.

¹H NMR (400 MHz, C₆D₆): δ = 1.63 (d, 6H, ³J_{HH} = 5.9 Hz, Me), 3.53 (br s, 1H, NH), 7.15-7.19 (m, 3H, *p*-Ph), 7.26-7.30 (m, 6H, *m*-Ph), 7.39-7.41 (m 6H, *o*-Ph) ppm. ¹³C NMR (101 MHz, C₆D₆): δ = 38.71 (s, Me), 125.46 (s, *p*-Ph), 127.57 (s, *m*-Ph), 134.37 (s, *o*-Ph), 150.50 (br s, *ipso*-Ph) ppm. ¹¹B NMR (128 MHz, C₆D₆): δ = 1.08 (s) ppm. ¹¹B NMR (128 MHz, THF-*d*₈): δ = 0.56 (s) ppm. ATI IR (neat): 0 = 3228 (w, NH), 3063 (w), 3018 (w) 3007 (w), 2994 (w), 2971 (w), 2949 (w), 1488 (w), 1470 (w), 1459 (w), 1429 (m), 1380 (m), 1338 (w), 1316 (w), 1290 (m), 1281 (w), 1271 (w), 1263 (w), 1246 (w), 1220 (w), 1188 (m), 1178 (m), 1151 (m), 1142 (w), 1131 (w), 1118 (w), 1102 (w), 1091 (m), 1074 (w), 1059 (w), 1044 (w), 1032 (m), 1012 (m), 1000 (m), 982 (w), 960 (w), 960 (w), 952(w), 924 (s), 914 (w), 905 (w) cm⁻¹. Anal. calc. for C₂₀H₂₂BN (287.21 g/mol): C, 83.64; H, 7.72; N, 4.88; found: C, 83.61; H, 7.78; N, 4.60.

Reaction of Bi(NⁱPr₂)₃ with [HNEt₃][BPh₄]. A (NMR scale): [HNEt₃][BPh₄] (12.4 mg, 29 µmol) was added to a solution of Bi(NⁱPr₂)₃ (15.0 mg, 29 µmol) in THF-*d*₈ (0.5 mL). The reaction mixture was analyzed by NMR spectroscopy. The following species were identified after 10 min: NEt₃, [BPh₃(thf)], HNⁱPr₂, BiPh(NⁱPr₂)₂ (for further details see Supp. Inf.).

BiPh(N[/]Pr₂)₂: ¹H NMR (400 MHz, THF-*d*₈) δ = 1.22 (d, 24H, ³J_{HH} = 6.6 Hz, CH*M*e₂), 4.45 (sept, 4H, ³J_{HH} = 6.6 Hz, C*H*Me₂), 7.23-7.27 (m, 1H, *p*-Ph), 7.54-7.57 (m, 2H, o-Ph), 7.30-7.33 (m, 2H, *m*-Ph) ppm.

B (lab scale): [HNEt₃][BPh₄] (34 mg, 81 µmol) was added to a solution of Bi(NⁱPr₂)₃ (41 mg, 80 µmol) in THF (0.4 mL). The reaction mixture was filtered. The filtrate was layered with hexanes (4 mL) and stored at – 30 °C for 2 days. A solid material was isolated by filtration and dried under a stream of Argon. It consisted of a colorless solid (identified as [BPh₃(thf)]) and trace amounts of black crystals, which were separated manually and identified as [Bi(NⁱPr₂)₂(BPh₄)] (**6**) using single crystal X-ray diffraction techniques.^[46] Yield of [BPh₃(thf)]: 13 mg, 41 µmol, 51%.

¹H NMR (400 MHz, THF-*d*₈): δ = 1.75-1.78 (m, 4H, β-THF), 3.59-3.63 (m, 4H, α-THF), 7.33-7.41 (m, 9H, *p*-Ph, *m*-Ph), 7.55 (d, 6H, ³*J*_{HH} = 6.8 Hz, α-Ph) ppm. ¹¹B NMR (128 MHz, THF-*d*₈): δ = 52.72 (br s) ppm. These and further NMR spectroscopic analyses were in agreement with those obtained for authentic sample. Unit cell (determined using single crystal X-ray diffraction analysis at T = 170 K): monoclinic space group *P*₂₁/c; a = 9.0589(6) Å; b = 12.7256(9) Å; c = 15.4884(10) Å; α = γ = 90°; β = 104.808(2)°; these values are in agreement with previously reported data.^[47]

Reaction of Bi(NPh₂)₃ with [HNEt₃][BPh₄]. [HNEt₃][BPh₄] (8.9 mg, 21 µmol) was added to a solution of Bi(NPh₂)₃ (15 mg, 21 µmol) in THF-*d*₈ (0.5 mL). The reaction mixture was analyzed by NMR spectroscopy. NEt₃ and [BPh₃(thf)] were unambiguously identified after 10 min (for further details see Supp. Inf.).

 $[\text{Bi}_2(\mu_2\text{-NMe}_2)_2(\text{NMe}_2)_2(\text{hf})_6][\text{B}(3,5\text{-}C_6\text{H}_3(\text{CF}_3)_2)_4)]_2$ (4). A solution of $[\text{H}(\text{OEt}_2)_2][\text{B}(3,5\text{-}C_6\text{H}_3(\text{CF}_3)_2)_4)]$ (68 mg, 67 µmol) in THF (0.5 mL) was added dropwise to a stirred solution of $[\text{Bi}(\text{NMe}_2)_3]$ (24 mg, 70 µmol) in THF (0.5 mL). The reaction mixture was layered with hexanes (4 mL) and cooled to -30 °C. After 16 h, a yellow solid was isolated by filtration, washed with hexanes (2 mL), and dried *in vacuo*. Yield: 82 mg, 30 µmol, 90%. The equivalents n of THF in the isolated compound has to be checked individually for every batch. Values ranging from n = 4 to n = 6 (vacuum dried) or up to n = 8 (dried in a stream of Argon) have been observed.

¹H NMR (300 MHz, THF-*d*₈, 26 °C, *c*(monomer) = 0.01 м): δ = 1.75-1.80 (m, n×4H, β-THF), 3.59-3.64 (m, n×4H, α-THF), 4.49 (s, 12H, NMe₂), 7.57 (s, 4H, p-(3,5-C₆H₃(CF₃)₂), 7.79 (s, 8H, o-(3,5-C₆H₃(CF₃)₂) ppm. ¹H NMR (300 MHz, THF-*d*₈, -60 °C, *c*(monomer) = 0.01 м): δ = 1.76-1.81 (m, n×4H, β-THF), 3.60-3.64 (m, n×4H, α-THF), 4.43 (s, 6H, μ₂-NMe₂), 4.53 (s, 6H, terminal NMe₂), 7.69 (s, 4H, p-(3,5-C₆H₃(CF₃)₂), 7.87 (s, 8H, o-(3,5-C₆H₃(CF₃)₂) ppm. ¹³C NMR (126 MHz, THF-d₈, 26 °C, c(monomer) = 0.01 m): \bar{o} = 26.55 (s, β -THF), 43.92 (s, NMe₂), 68.39 (s, α -THF), 118.35 (sept, ${}^{3}J_{CF}$ = 3.9 Hz, p-(3,5-C₆H₃(CF₃)₂)), 125.68 (quart, ${}^{1}J_{CF}$ = 272.2 Hz, CF₃), 130.19 (quartquart, ${}^{2}J_{CF}$ = 31.5 Hz, ${}^{4}J_{CF}$ = 2.9 Hz, m-(3,5- $C_6H_3(CF_3)_2)$, 135.76 (br s, o-(3,5- $C_6H_3(CF_3)_2)$), 162.97 (quart, ¹ J_{BC} = 59.8 Hz, ipso-(3,5-C₆H₃(CF₃)₂)) ppm. ¹³C NMR (75 MHz, THF-d₈, -60 °C, c(monomer) = 0.01 м): δ = 26.56 (s, β-THF), 43.30 (s, μ₂-NMe₂), 45.43 (s, terminal NMe₂), 68.40 (s, α-THF), 118.55 (br s, p-(3,5-C₆H₃(CF₃)₂)), 125.58 (quart, ¹J_{CF} = 272.3 Hz, CF₃), 130.09 (br quart, ²J_{CF} = 31.6 Hz, *m*- $(3,5-C_6H_3(CF_3)_2))$, 135.55 (br s, o- $(3,5-C_6H_3(CF_3)_2))$, 163.07 (quart, ¹J_{BC} = 48.2 Hz, ipso-(3,5-C₆H₃(CF₃)₂)) ppm. ¹¹B NMR (156 MHz, THF-d₈, 26 °C): δ = -6.7 (s) ppm. ¹⁹F NMR (376 MHz, THF-*d*₈, 26 °C): δ = -63.4 (s) ppm. Anal. calc. for C72H48B2Bi2F48N4 (OC4H8)5 (2681.24 g/mol): C, 41.2; H, 3.3; N, 2.1; found: C, 41.3; H, 3.2; N, 1.9.

[Bi(N[']Pr₂)₂(thf)₃][B(3,5-C₆H₃(CF₃)₂)₄)] (5). A solution of [H(OEt₂)₂][B(3,5-C₆H₃(CF₃)₂)₄] (54 mg, 53 µmol) in THF (0.5 mL) was added dropwise to a stirred solution of Bi(N[']Pr₂)₃ (30 mg, 59 µmol) in THF (0.5 mL). The solution was layered with hexanes (4 mL) and cooled to -30 °C. After 14 h, an orange crystalline material had formed, which was isolated by filtration, washed with hexanes (2 mL) and dried *in vacuo*. Yield: 72 mg, 48 µmol, 91%.

The amount of THF in the isolated compound has to be checked individually for every batch. Values ranging from n = 2 to n = 3 molecules of THF per formula unit have been observed, depending on the time the compound is exposed to reduced pressure.

¹H NMR (400 MHz, THF-*d*₈): δ = 1.41 (d, 24H, ³*J*_{HH} = 6.6 Hz, CH*Me*₂), 1.76-1.79 (m, 12H, β-THF), 3.60-3.63 (m, 12H, α-THF), 6.03 (sept, 4H, ³*J*_{HH} = 6.6 Hz, *CH*Me₂), 7.57 (s, 4H, *p*-(3,5-C₆H₃(CF₃)₂), 7.79 (s, 8H, *o*-(3,5-C₆H₃(CF₃)₂) ppm. ¹³C NMR (126 MHz, THF-*d*₈): δ = 26.54 (s, β-THF), 29.72 (s, CH*M*e₂), 53.98 (s, CHMe₂), 68.39 (s, α-THF), 118.35 (sept, ³*J*_{CF} = 3.9 Hz, *p*-(3,5-C₆H₃(CF₃)₂)), 125.69 (quart, ¹*J*_{CF} = 272.2 Hz, CF₃), 130.20 (quartquart, ²*J*_{CF} = 31.6 Hz, ⁴*J*_{CF} = 2.9 Hz, *m*-(3,5-C₆H₃(CF₃)₂)), 135.77 (br s, *o*-(3,5-C₆H₃(CF₃)₂)), 162.98 (quart, ¹*J*_{BC} = 50.0 Hz, *ipso*-(3,5-C₆H₃(CF₃)₂)) ppm. ¹¹B NMR (160 MHz, THF-*d*₈): δ = -6.6 (s, B(C₆H₃(CF₃)₂)) ppm. ¹⁹F NMR (471 MHz, THF-*d*₈): δ = -63.4 (s, CF₃) ppm. ¹⁵N NMR (51 MHz, THF-*d*₈): δ = -151.6 (s, N'Pr₂) ppm. Anal. calc. for C₄₄H₄₀B₁Bi₁F₂₄N₂ · (C₄H₈O)_{2.5} (1452.84 g/mol): C, 44.6; H, 4.2; N, 1.9; found: C, 44.6; H, 4.0; N, 1.9.

 $[Bi(N'Pr_2)_2(OPPh_3)_2][B(3,5-C_6H_3(CF_3)_2)_4)]$ (6). OPPh₃ (6.4 mg, 23 µmol) was added to a solution of 5 (17 mg, 11 µmol) in THF- d_8 (0.5 mL). The resulting orange solution was analyzed by NMR spectroscopy.

¹H NMR (400 MHz, THF-*d*₈): δ = 1.25 (d, 24H, ³*J*_{HH} = 6.6 Hz, CH*M*e₂), 5.75 (sept, 4H, ³*J*_{HH} = 6.6 Hz, C*HM*e₂), 7.52-7.56 (m, 12H, *m*-Ph), 7.57 (s, 4H, *p*-(3,5-C₆H₃(CF₃)₂), 7.64-7.70 (m, 18H, *o*,*p*-Ph), 7.79 (s, 8H, *o*-(3,5-C₆H₃(CF₃)₂) ppm. ¹³C NMR (126 MHz, THF-*d*₈): δ = 29.52 (s, CH*M*e₂), 53.12 (s, CHMe₂), 118.36 (sept, ³*J*_{CF} = 3.9 Hz, *p*-(3,5-C₆H₃(CF₃)₂)), 125.69 (quart, ¹*J*_{CF} = 272.3 Hz, CF₃), 130.02 (d, ³*J*_{CP} = 12.3 Hz, *m*-Ph), 130.20 (quartquart, ²*J*_{CF} = 31.8 Hz, ⁴*J*_{CF} = 2.7 Hz, *m*-(3,5-C₆H₃(CF₃)₂)), 133.35 (d, ²*J*_{CP} = 10.4 Hz, *o*-Ph), 134.06 (d, ⁴*J*_{CP} = 1.6 Hz, *p*-Ph), 135.77 (br s, *o*-(3,5-C₆H₃(CF₃)₂)), 162.99 (quart, ¹*J*_{BC} = 49.9 Hz, *ipso*-(3,5-C₆H₃(CF₃)₂)) ppm. Resonances for THF were also detected. A ¹³C resonance for the *ipso*-Ph atom could not be detected.^[48] 11^B NMR (160 MHz, THF-*d*₈): δ = -6.5 (s, B(C₆H₃(CF₃)₂)) ppm. ³¹P NMR (162 MHz, THF-*d*₈): δ = -171.8 (s, NPr₂) ppm.

Attempted reactions of Bi(NR₂)₃ with Na[BPh₄] (R = Me, Pr, Ph). For each reaction, one equivalent of Na[BPh₄] was added to a solution of Bi(NR₂)₃ in THF to give a yellow (R = Me, Pr) or orange (R = Ph) solution The reactions were monitored by ¹¹B NMR spectroscopy. No conversion of [BPh₄]⁻ could be detected after reaction times of >24 h. The experiments were performed on a 30 µmol scale.

[Bi((i PrN)₂CNMe₂)₃] (7). i PrN=C=NⁱPr (12 mg, 95 µmol) was added to a solution of Bi(NMe₂)₃ (10 mg, 29 µmol) in C₆D₆ (0.5 mL). Full conversion to Bi((NⁱPr)₂CNMe₂)₃ (7) with a selectivity of ≥95% was detected after 11 h. The reaction was repeated using toluene as a solvent and doubling the batch size (59 µmol of Bi(NMe₂)₃). After 14 h, all volatiles were removed under reduced pressure to give a yellow solid, which was dried *in vacuo*. Yield: 37 mg, 51 µmol, 86%.

¹H NMR (400 MHz, C₆D₆) δ = 1.37 (d, 36H, ³J_{HH} = 6.4 Hz, CH*M*e₂), 2.66 (s, 18H, NMe₂), 4.46 (br sept, 6H, ³J_{HH} = 6.4 Hz, C*H*Me₂) ppm. ¹³C NMR (126 MHz, C₆D₆): δ = 26.22 (br s, CH*M*e₂), 40.95 (s, NMe₂), 47.35 (s, CHMe₂), 165.56 (br s, (NⁱPr)₂CNMe₂) ppm. ¹⁵N NMR (41 MHz, THF-*d*₈): δ = -206.1 (s, (ⁱPrN)₂C(NMe₂)) ppm. A resonance for (ⁱPrN)₂C(*N*Me₂) was not detected. Anal. calc. for C₂₇H₆₀BiN₉ · (C₆H₁₄)_{0.05} (723.94 g/mol): C, 45.3; H, 8.5; N, 17.4; found: C, 45.7; H, 8.8; N, 17.3.

Reaction of Bi(NⁱPr₂)₃ with ⁱPrN=C=NⁱPr. ⁱPrN=C=NⁱPr (9.0 mg, 71 µmol) was added to a solution of Bi(NⁱPr₂)₃ (10 mg, 20 µmol) in C₆D₆ (0.5 mL). No conversion of the carbodiimide was detected by ¹H NMR spectroscopy after reaction times of up to 23 h.

[**Bi**((^{*i*}PrN)₂**CNMe**₂)₂][**B**(3,5-C₆H₃(**CF**₃)₂)₄)] (8). ^{*i*}PrN=C=N^{*i*}Pr (7.0 mg, 55 µmol) was added to a solution of **4** (35 mg, 25 µmol) in THF-*d*₈ (0.5 mL). The color of the reaction mixture changed immediately from intense yellow to pale yellow. Full conversion to the insertion product **8** was detected after 10 min by ¹H NMR spectroscopy. The reaction was repeated using non-deuterated THF as a solvent. After 4 h, the reaction mixture was layered with hexanes (4 mL) and cooled to -30 °C to give a colorless crystalline solid after 16 h. The solid was isolated by filtration, washed with hexanes (2 × 1 mL) and dried *in vacuo*. Yield: 34 mg, 24 µmol, 96%.

¹H NMR (400 MHz, THF- d_8) δ = 1.23 (d, 24H, ³J_{HH} = 6.4 Hz, CHMe₂), 2.95 (s, 12H, NMe2), 5.29 (br s, 4H, CHMe2), 7.57 (s, 4H, p-(3,5-C₆H₃(CF₃)₂), 7.79 (s, 8H, o-(3,5-C₆H₃(CF₃)₂) ppm. ¹H NMR (500 MHz, -40 °C) $\delta = 1.05$ ³Јнн THF-d₈. (d. 6H. 6.3 Hz. = (MeMeCHN)(ⁱPrN)C(NMe₂)), 1.22 ³**Ј**нн (d, 6H. 6.3 Hz. (PrN)(MeMeCHN)C(NMe2)), 1.26 6H, ³Јнн (d, 6.3 Hz. (MeMeCHN)(PrN)C(NMe2)), 1.36 (d, 6H, ³**Ј**НН 6.3 Hz, (ⁱPrN)(Me*Me*CHN)C(NMe₂)), 2.95 (s, 12H, NMe₂), 4.88 (br sept, 2H, ³J_{HH} (MeMeCHN)(ⁱPrN)C(NMe₂)), 5.69 6.3 Hz, (br 2H, s,

(PrN)(MeMeCHN)C(NMe2)), 7.66 (s, 4H, p-(3,5-C6H3(CF3)2), 7.85 (s, 8H, o-(3,5-C₆H₃(CF₃)₂) ppm. ¹³C NMR (101 MHz, THF-d₈): δ = 25.58 (br s, CHMe2, overlapping with solvent resonance), 40.64 (s, NMe2), 48.41 (br s, CHMe₂), 118.36 (sept, ${}^{3}J_{CF}$ = 3.9 Hz, p-(3,5-C₆H₃(CF₃)₂)), 125.69 (quart, ${}^{1}J_{CF}$ = 272.3 Hz, CF₃), 130.21 (quartquart, ${}^{2}J_{CF}$ = 31.6 Hz, ${}^{4}J_{CF}$ = 2.9 Hz, m-(3,5-C₆H₃(CF₃)₂)), 135.77 (br s, o-(3,5-C₆H₃(CF₃)₂)), 162.99 (quart, ¹J_{BC} = 49.8 Hz, *ipso*-(3,5-C₆H₃(CF₃)₂)), 171.04 (s, (NⁱPr)₂CNMe₂) ppm. ¹³C NMR (126 MHz, THF- d_8 , -40 °C): δ = 25.20 (s, (MeMeCHN)('PrN)C(NMe2)) 25.31 (s, ('PrN)(MeMeCHN)C(NMe2)), 25.34 (s, (MeMeCHN)(ⁱPrN)C(NMe₂)), 26.16 (s, (ⁱPrN)(MeMeCHN)C(NMe₂)), 40.51 (br s, NMe₂), 47.49 (s, (Me₂CHN)([/]PrN)C(NMe₂)), 49.05 (s, (ⁱPrN)(Me₂CHN)C(NMe₂)), 118.49 (br s, p-(3,5-C₆H₃(CF₃)₂)), 125.58 (quart, ${}^{1}J_{CF}$ = 272.3 Hz, CF₃), 130.10 (quartquart, ${}^{2}J_{CF}$ = 31.6 Hz, ${}^{4}J_{CF}$ = 2.9 Hz, m-(3,5-C₆H₃(CF₃)₂)), 135.59 (br s, o-(3,5-C₆H₃(CF₃)₂)), 163.03 (quart, ${}^{1}J_{BC} = 49.8 \text{ Hz}$, *ipso*-(3,5-C₆H₃(CF₃)₂)), 170.67 (s, (NⁱPr)₂CNMe₂) ppm. ¹¹B NMR (160 MHz, THF- d_8): $\delta = -6.6$ (s, B(3,5-C₆H₃(CF₃)₂)₄) ppm. ¹⁹F NMR (471 MHz, THF- d_8): δ = -63.4 (s, CF₃) ppm. ¹⁵N NMR (51 MHz, THF-d₈, -40 °C): δ = -312.8 (s, NMe₂), -227.3 (s, (Pr/N)(PrN)C(NMe₂)), -216.7 (s, (ⁱPrN)(ⁱPrM)C(NMe₂)) ppm. Anal. calc. for C₅₀H₅₂BBiF₂₄N₆ (1412.76 g/mol): C, 42.5; H, 3.7; N, 6.0; found: C, 42.5; H, 3.3; N, 5.9.

 $[Bi((PrN)_2CNPr_2)_2][B(3,5-C_6H_3(CF_3)_2)_4)]$ (9). PrN=C=NPr (6.0 mg, 48 μ mol) was added to a solution of 5 (30 mg, 20 μ mol) in THF-d₈ (0.5 mL). The color of the reaction mixture changed immediately from orange to pale yellow. Full conversion to the mono-insertion product was detected after 10 min by NMR spectroscopy. Full conversion to compound 9 was detected after 12 h by NMR spectroscopy. The reaction was repeated using non-deuterated THF as a solvent. After 14 h, the reaction mixture was filtered and lavered with hexanes (4 mL) and cooled to -30 °C. After 1 d, a colorless crystalline material had formed, which was isolated by filtration, washed with hexanes (2×1 mL) and dried in vacuo. Yield: 23 mg, 15 µmol, 75%.

Data for intermediate compound [Bi((/PrN)2C(N/Pr2))(N/Pr2)] [B(3,5-C₆H₃(CF₃)₂)₄)]: ¹H NMR (400 MHz, THF- d_8) δ = 1.22 (d, 6H, ³J_{HH} = 6.4 (*Me*MeC*H*N)₂C(N^{*i*}Pr₂)), 1.23 (d, 6H, ³J_{HH} 6.4 Hz, Hz, = ³**Ј**НН = 6.8 $(MeMeCHN)_2C(N'Pr_2)), 1.36$ (d, 12H, Hz. (PrN)2C(N(CHMe2)2)), 1.39 (d, 12H, ³J_{HH} = 6.6 Hz, N(CHMe2)2), 3.74 (sept, 2H, ${}^{3}J_{HH} = 6.8$ Hz, (${}^{\prime}PrN)_{2}C(N(CHMe_{2})_{2}))$, 5.36 (sept, 2H, ${}^{3}J_{HH} = 6.4$ Hz, (Me₂CHN)₂C(NⁱPr₂)), 5.98 (sept, 2H, ³J_{HH} = 6.6 Hz, N(CHMe₂)₂), 7.57 (s, 4H, p-(3,5-C₆H₃(CF₃)₂), 7.79 (s, 8H, o-(3,5-C₆H₃(CF₃)₂) ppm. ¹³C NMR (126 MHz, THF- d_8): δ = 23.36 (s, (^{*i*}PrN)₂C(N(CH*Me*₂)₂)), 25.16 (s, (MeMeCHN)₂C(NⁱPr₂)), 26.79 (s, (MeMeCHN)₂C(NⁱPr₂)), 29.35 (s, $(Me_2CHN)_2C(N'Pr_2)),$ N(CHMe₂)₂). 48.00 51.99 (s. (s. (ⁱPrN)₂C(N(CHMe₂)₂)), 53.43 (s, N(CHMe₂)₂), 118.35 (sept, ³J_{CF} = 3.9 Hz, p-(3,5-C₆H₃(CF₃)₂)), 125.69 (quart, ¹J_{CF} = 272.3 Hz, CF₃), 130.21 (quartquart, ²J_{CF} = 31.6 Hz, ⁴J_{CF} = 2.9 Hz, *m*-(3,5-C₆H₃(CF₃)₂)), 135.77 (br s, $o-(3,5-C_6H_3(CF_3)_2)$), 162.99 (quart, ${}^1J_{BC} = 49.9$ Hz, *ipso-*(3,5-C₆H₃(CF₃)₂)), 173.42 (s, (N[/]Pr)₂CNMe₂) ppm. Resonances for THF and excess <code>'PrN=C=N'Pr</code> were also detected. ¹¹B NMR (160 MHz, THF-d₈): δ = -6.6 (s, B(3,5-C₆H₃(CF₃)₂)₄) ppm. ¹⁹F NMR (471 MHz, THF- d_8): δ = -63.4 (s, CF₃) ppm. ¹⁵N NMR (41 MHz, THF-*d*₈): δ = -282.6 (s, (ⁱPrN)₂C(*N*ⁱPr₂)), -212.7 (s, (ⁱPr*N*)₂C(NⁱPr₂)), -169.6 (s, Bi(*N*ⁱPr₂) ppm. Data for compound 9: ¹H NMR (400 MHz, THF- d_8) δ = 1.30 (br s, 24H, CHMe2), 1.35 (br s, 24H, CHMe2), 3.71 (br s, 4H, (PrN)2C(N(CHMe2)2)), 4.95 (br s, 2H, (Me₂CHN)(PrN)C(NPr₂)), 5.71 (br s, 2H, $({}^{i}\!PrN)(Me_2C{\it H}\!N)_2C(N{}^{i}\!Pr_2)),\ 7.57\ (s,\ 4H,\ {\it p}\mbox{-}(3,5\mbox{-}C_6H_3(CF_3)_2),\ 7.78\ (s,\ 8H,\ {\it p}\mbox{-}(3,5\mbox{-}(3,5\mbox{-}C_6H_3(CF_3)_2),\ 7.78\ (s,\ 8H,\ {\it p}\mbox{-}(3,5\mbox{-}$ o-(3,5-C₆H₃(CF₃)₂) ppm. ¹H NMR (500 MHz, THF-d₈, -40 °C) δ = 1.16 (d, 6H, ³J_{HH} = 6.0 Hz, (*Me*MeCHN)(*PrN*)C(N*Pr*₂)), 1.23 (d, 6H, ³J_{HH} = 7.0 Hz, (PrN)2C(N(CHMeMe)Pr)), 1.27 (d, 6H, ³J_{HH} 6.3 Hz, = (PrN)(MeMeCHN)C(NPr2)), 1.31 (m, 12H, (MeMeCHN)(PrN)C(NPr(CHMeMe)) (overlapping)), 1.38 (d, 6H, $^{3}J_{HH} =$ (ⁱPrN)(MeMeCHN)C(NⁱPr₂)), 6.3 Hz, 1.45 (12H, (ⁱPrN)₂C(N(CHMeMe)(CHMeMe)) (overlapping)), 3.66 (br sept, 2H, ³J_{HH} = 7.0 Hz, (ⁱPrN)₂C(N(CHMe₂)ⁱPr)), 3.73 (br sept, 2H, ³J_{HH} = 6.6 Hz,

(ⁱPrN)₂C(NⁱPr(CHMe₂))), 4.77 (br sept, 2H, ³**Ј**нн = 6.0 (Me₂C*H*N)(^{*i*}PrN)C(N^{*i*}Pr₂)), 5.75 (br sept, ${}^{3}J_{\rm HH} = 6.3$ Hz, 2H. (ⁱPrN)(Me₂CHN)C(NⁱPr₂)), 7.66 (s, 4H, p-(3,5-C₆H₃(CF₃)₂), 7.85 (s, 8H, o-(ⁱPrN)₂C(N(CHMeMe)ⁱPr)), 27.80 (s, (s,

 $(3,5-C_6H_3(CF_3)_2)$ ppm. ¹³C NMR (126 MHz, THF-*d*₈, -40 °C): δ = 21.83 (s, (iPrN)2C(N(CHMeMe)iPr)), 22.02 (s, (iPrN)2C(NiPr(CHMeMe))), 24.73 (s, (ⁱPrN)₂C(N(CHMeMe)ⁱPr)), 25.22 (s, (ⁱPrN)(MeMeCHN)C(NⁱPr₂)), 25.28 (s, (ⁱPrN)(MeMeCHN)C(NⁱPr₂)), 25.97 (s, (ⁱPrN)₂C(NⁱPr(CHMeMe))), 26.33 (MeMeCHN)(ⁱPrN)C(NⁱPr₂)), 48.55 (s, (Me₂CHN)(ⁱPrN)C(NⁱPr₂)), 49.21 (s, (ⁱPrN)(Me₂CHN)C(NⁱPr₂)), 53.00 (s, (ⁱPrN)₂C(N(CHMe₂)ⁱPr), 53.72 (s, (PrN)2C(NPr(CHMe2)), 118.48 (br s, p-(3,5-C6H3(CF3)2)), 125.58 (quart, ${}^{1}J_{CF}$ = 272.3 Hz, CF₃), 130.09 (quartquart, ${}^{2}J_{CF}$ = 31.5 Hz, ${}^{4}J_{CF}$ = 2.7 Hz, m-(3,5-C₆H₃(CF₃)₂)), 135.58 (br s, o-(3,5-C₆H₃(CF₃)₂)), 163.03 (quart, ¹J_{BC} = 49.6 Hz, *ipso*-(3,5-C₆H₃(CF₃)₂)), 173.60 (s, (N/Pr)₂CN/Pr₂) ppm. ¹¹B NMR (156 MHz, THF- d_8 , 26 °C): δ = -6.6 (s) ppm. ¹⁹F NMR (376 MHz, THF-d₈, 26 °C): δ = -63.4 (s) ppm. ¹⁵N NMR (51 MHz, THF-d₈, -40 °C): δ = -285.3 (s, (PrN)2C(NPr2)), -216.7 (s, (PrN)(PrN)C(NPr2)), -205.1 (s, (<code>PrN)(PrN)C(NPr2)) ppm. Anal. calc. for C58H68BBiF24N6</code> · (OC4H8)0.5 (1561.03 g/mol): C, 46.2; H, 4.7; N, 5.4; found: C, 46.1; H, 4.4; N, 5.1.

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- [21] The presence of an NH functionality was confirmed by IR spectroscopy $(\bar{u} = 3244 \text{ cm}^{-1}).$
- [22] Near quantitative formation of [BPh₃(NHMe₂)] from 1 in THF solution indicates that 1 can also form a contact ion pair under these conditions, most likely in an equilibrium with a solvent-separated ion pair (*vide infra*).
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Layout 2:

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Diamido Bismuth Cations

- isolable species
- more reactive than ${\rm Bi}({\rm NR}_2)_3$
- anion-dependent stability

Hannah Dengel and Crispin Lichtenberg*

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Cationic Bismuth Amides: Accessibility, Structure, and Reactivity

Highly reactive. Cationic bismuth amides undergo facile B–C bond activation with their [BPh₄]⁻ counteranions. The cationic complexes can be stabilized by use of fluorinated tetra-arylborate counteranions. Compared to their neutral parent compounds, they show an increased reactivity towards di*iso*propylcarbodiimide, allowing direct access to cationic bismuth guanidinates.