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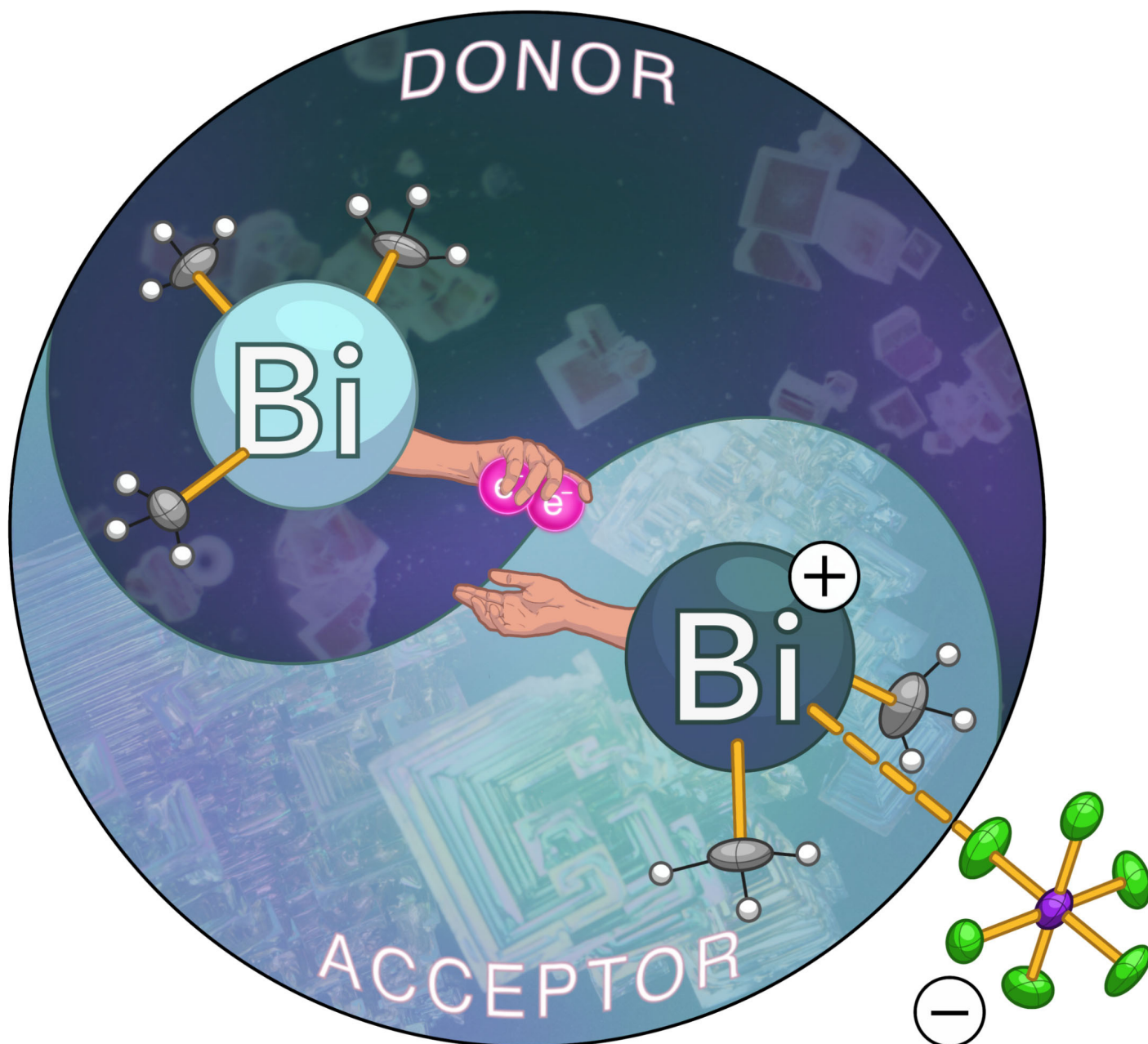
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The Dimethylbismuth Cation: Entry Into Dative Bi–Bi Bonding and Unconventional Methyl Exchange

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Abstract: The isolation of simple, fundamentally important, and highly reactive organometallic compounds remains among the most challenging tasks in synthetic chemistry. The detailed characterization of such compounds is key to the discovery of novel bonding scenarios and reactivity. The dimethylbismuth cation, $[\text{BiMe}_2(\text{SbF}_6)]$ (**1**), has been isolated and characterized. Its reaction with BiMe_3 gives access to an unprecedented dative bond, a $\text{Bi} \rightarrow \text{Bi}$ donor-acceptor interaction. The exchange of methyl groups (arguably the simplest hydrocarbon moiety) between different metal atoms is among the most principal types of reactions in organometallic chemistry. The reaction of **1** with BiMe_3 enables an $S_{\text{E}}2(\text{back})$ -type methyl exchange, which is, for the first time, investigated in detail for isolable, (pseudo-)homoleptic main-group compounds.

Contributions towards a detailed and profound understanding of bonding interactions between heavier p-block elements E have revived the field of main group chemistry in the last decades.^[1] E–E bonding interactions tend to become weaker with an increasing principal quantum number of E, because the relevant atomic orbitals become larger and more diffuse. In this respect, the investigation of species with bonding interactions between bismuth (the heaviest element without significant radioactivity) is especially challenging. While the first species with a Bi–Bi single bond, $\text{Me}_2\text{Bi–BiMe}_2$ (**A**), was generated as early as 1935,^[2] its isolation and detailed re-investigation was achieved only about 50 years later (Figure 1a).^[3,4] Following these pioneering contributions, different types of compounds featuring Bi–Bi multiple bonds have been reported more recently. These include dibismuthenes such as the pivotal $\text{TbtBi}=\text{BiTbt}$ (**B**) ($\text{Tbt} = 2,4,6\text{-[CH}(\text{SiMe}_3)_2\text{]}_3\text{-C}_6\text{H}_2$),^[5] Bi_2 units in the coordination sphere of transition metals (as in $\text{Bi}_2(\text{W}(\text{CO})_5)_3$ (**C**)),^[6] $[\text{K}(\text{222-crypt})]_2\text{-[Bi}_2\text{]}$ containing naked $[\text{Bi}_2]^{2-}$ anions (**D**),^[7] and free Bi_2 (**E**), which has been generated and analyzed in the gas phase and in noble gas matrices (Figure 1a).^[8]

In contrast, compounds featuring unidirectional $\text{Bi} \rightarrow \text{Bi}$ donor-acceptor interactions have not been reported to date. Unsupported $\text{E} \rightarrow \text{E}$ bonding has recently been documented,

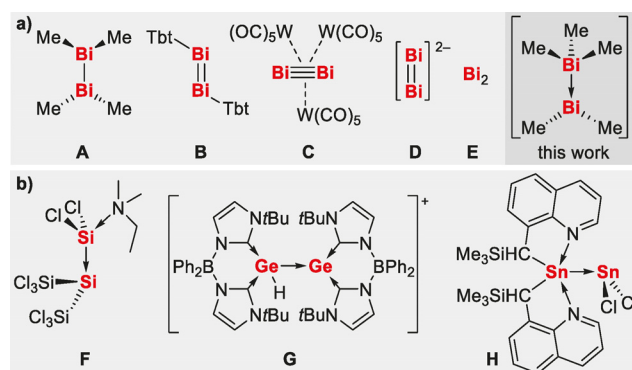


Figure 1. Compounds with a) different types of bismuth-bismuth bonding and b) unidirectional $\text{E} \rightarrow \text{E}$ donor-acceptor bonding.

for instance, in the low-valent silicon(II), germanium(II), and tin(II) compounds **F–H**, in which the central atoms bear one lone pair and one empty p-orbital (Figure 1b).^[9,10] In the chemistry of group 15 compounds, unidirectional $\text{E} \rightarrow \text{E}$ bonding can be realized by combining a cationic complex fragment $[\text{PnR}_2]^+$, which contains one empty p-orbital at Pn, with a trivalent species PnR_3 , which bears one lone pair at Pn ($\text{Pn} = \text{P–Bi}$).^[4e,11,12] In fact, $\text{E} \rightarrow \text{E}$ bonding has been achieved for all group 15 elements but bismuth.^[11e] So why is the generation of $\text{E} \rightarrow \text{E}$ dative bonding especially challenging in the case of the heaviest congener? On the one hand, the accessibility of (e.g. nitrogen- and aryl-substituted) bismuth cations is well-documented,^[13,14] and they have recently been established as potent soft Lewis-acids.^[15] On the other hand, $[\text{BiR}_2]^+$ cations without extreme steric stabilization or considerable $\text{Bi} \cdots \text{anion}$ bonding remain elusive.^[14] In addition, compounds of type BiR_3 are poor donors due to the inert pair effect and relativistic effects.^[16] Further complications may arise from ligand scrambling,^[17] when targeting species of type $[\text{R}_3\text{Bi} \rightarrow \text{BiR}_2]^+$. Herein, we report the first example of a mononuclear alkylbismuth cation, $[\text{BiMe}_2(\text{SbF}_6)]$, and its reactivity towards BiMe_3 , revealing unprecedented donor-acceptor interactions and unconventional methyl exchange.

Reaction of BiMe_2Cl with AgSbF_6 in dichloromethane (DCM) gave $[\text{BiMe}_2(\text{SbF}_6)]$ (**1**), which was isolated as a yellow, light-sensitive crystalline material in 75% yield (Figure 2a). Solution NMR spectroscopy in CD_2Cl_2 revealed one singlet in the ^1H ($\delta = 2.28$ ppm) and the ^{13}C NMR spectrum ($\delta = 64.4$ ppm), respectively. Compared to the neutral parent compound BiMe_3 , these resonances experience a dramatic increase in chemical shifts of $\Delta\delta = +1.17$ ppm (^1H) and $\Delta\delta = +71.2$ ppm (^{13}C), which reflects the electron-deficient nature of **1**.^[18] The light-sensitivity of **1** prompted us to perform UV/vis spectroscopic analyses. In DCM solution, a broad absorption band with its maximum at 321 nm was observed, which stretches well into the visible region of $\lambda > 400$ nm (Supp. Inf.). In good agreement with these data, CAM-B3LYP-based calculations revealed a first electronically excited state (S_1) with dominant contributions by a $\text{HOMO} \rightarrow \text{LUMO}$ transition (72%) at $\lambda_{\text{calc}} = 333$ nm. The HOMO is associated with the occupied in-plane bismuth p-orbital, which is partially delocalized into the Bi–C σ bonds, while the LUMO is represented by an empty bismuth-

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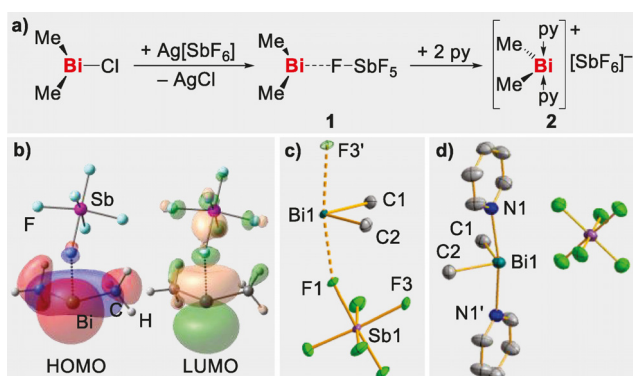


Figure 2. a) Synthesis of **1** and **2**. b) Frontier orbitals (Kohn–Sham) of **1** at isovalues of 0.04, as determined by DFT calculations. c) Molecular structure of $[\text{BiMe}_2(\text{SbF}_6)]$ (**1**) in the solid state, F3' exceeds one formula unit and is shown as a transparent ellipsoid.^[31] Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi1–C1, 2.215(5); Bi1–C2, 2.223(5); Bi1–F1, 2.451(3); Bi1–F3', 2.452(3); C1–Bi1–C2, 93.0(2); F1–Bi1–F3', 169.73(11). d) Molecular structure of $[\text{BiMe}_2(\text{py})_2][\text{SbF}_6]$ (**2**) in the solid state.^[31] Displacement ellipsoids are shown at the 50% probability level. Bi1–C1, 2.235(12); Bi1–C2, 2.223(12); Bi1–N1, 2.519(7); C1–Bi1–C2, 92.3(5); N1–Bi1–N1', 169.1(3).

centered p-orbital (Figure 2b). Geometry optimization of the S_1 state leads to a separation of the BiMe_2^+ and the SbF_6^- moieties, as a consequence of populating the bismuth p-orbital oriented along the Bi–F axis. In congruency with these findings, coordination of pyridine to $[\text{BiMe}_2]^+$ blocks this transition, leading to the colorless compound $[\text{BiMe}_2(\text{py})_2][\text{SbF}_6]$ (**2**), which was isolated in 84% yield and fully characterized (Figure 2a, py = pyridine).

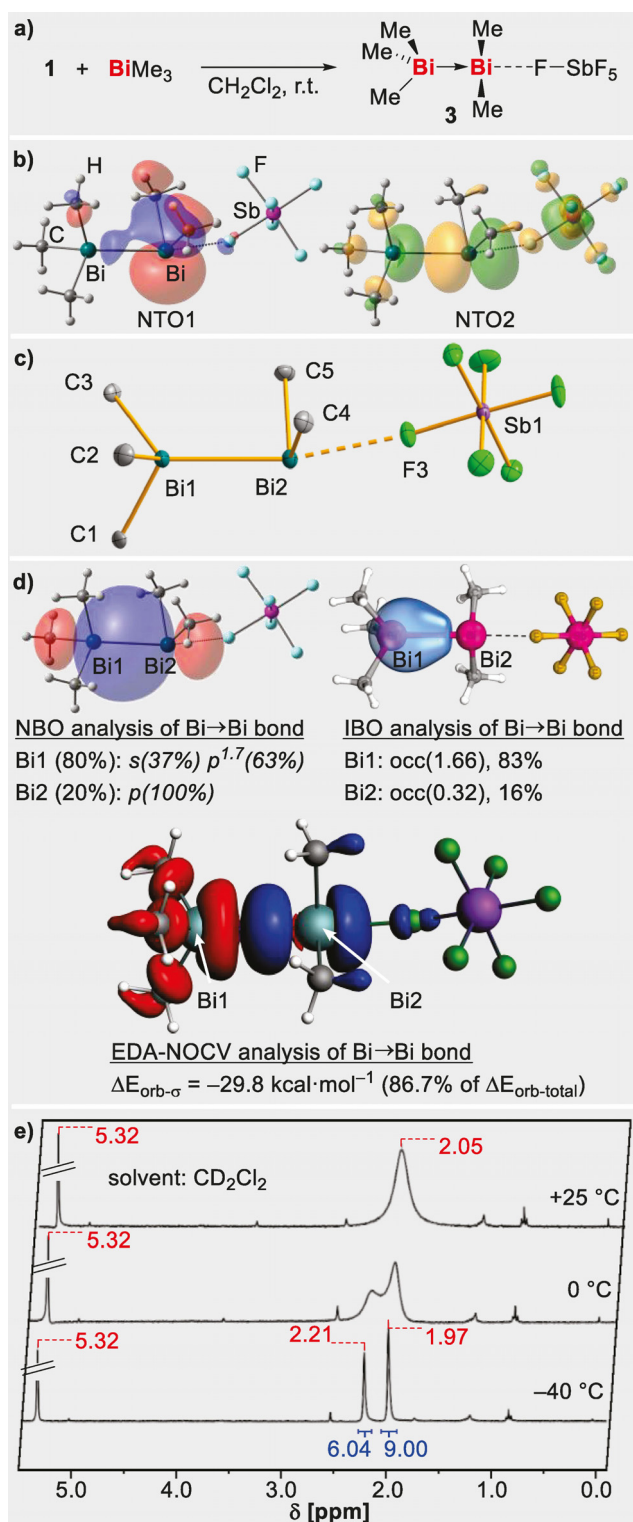
Single-crystal X-ray diffraction analysis of **1** revealed the formation of a contact ion pair in the solid state with Bi⋯F distances of 2.45 Å—interactions that are strong enough to sufficiently stabilize **1**, but weak enough to maintain a high reactivity towards Lewis bases (Figure 2c, orthorhombic space group $Pbca$ with $Z=8$). Each $[\text{BiMe}_2]^+$ unit interacts with two fluorine atoms of neighboring $[\text{SbF}_6]^-$ moieties, leading to a one-dimensional coordination polymer along the crystallographic b-axis in the solid state (Supp. Inf.). The bismuth atom adopts a bisphenoidal coordination geometry with the fluorine atoms in axial (F–Bi–F, 169.7°) and the carbon atoms in equatorial positions (C–Bi–C, 93.0°). The Bi–C bonds (2.22 Å) are on average and within one standard deviation shorter than those in neutral BiMe_3 (2.23–2.29 Å; average: 2.26 Å) or in the trinuclear complex $[(\text{BiMe}_2)_3(\text{Tm}^{\text{tBu}})_2]^+$ (2.24–2.27 Å; average: 2.25 Å; Tm^{tBu} = hydrotris(2-mercapto-1-tert-butylimidazolyl)borate),^[19] and similar to those in **2** (2.22–2.24 Å; average: 2.23 Å; Figure 2d). Compounds **1** and **2** are the first examples of well-defined mononuclear cationic bismuth alkyl complexes.

The soft Lewis acidic nature of compound **1**, the absence of neutral donor ligands, and its lack of extreme steric protection prompted us to investigate its behavior towards the potential soft Lewis base BiMe_3 , thereby targeting the formation of the hitherto unknown Bi→Bi donor/acceptor bond. Reaction of **1** with BiMe_3 in DCM gave pale yellow solutions, from which light yellow crystals of the composition

$[\text{BiMe}_2(\text{BiMe}_3)(\text{SbF}_6)]$ (**3**) were isolated in 88% yield (Figure 3a). UV/vis spectroscopy in DCM solution revealed a broad absorption band peaking at 302 nm and reaching slightly into the visible region of $\lambda > 400$ nm (Supp. Inf.). Based on TD-DFT calculations and the natural transition orbital (NTO) analysis using CAM-B3LYP, the $S_0 \rightarrow S_1$ excitation ($\lambda_{\text{calc}} = 289$ nm) was ascribed to an $n(\text{Bi}2) \rightarrow \sigma^*(\text{Bi}1-\text{Bi}2)$ transition with additional $\sigma(\text{Bi}2-\text{Me}) \rightarrow \sigma^*(\text{Bi}1-\text{Bi}2)$ contributions (Figure 3b and Supp. Inf.). In line with these results, geometry optimization of the S_1 state leads to dissociation of the Bi–Bi bond as a consequence of populating the $\sigma^*(\text{Bi}1-\text{Bi}2)$ orbital.

Single-crystal X-ray diffraction analysis of compound **3** unambiguously confirmed the formation of an adduct between BiMe_3 and $[\text{BiMe}_2(\text{SbF}_6)]$ (Figure 3c, monoclinic space group $P2_1/c$, $Z=4$). The Bi→Bi bond length amounts to the remarkably small value of only 3.00 Å. This is well within the range of Bi–Bi bond lengths that have been reported for dibismuthanes with unsupported, covalent Bi–Bi single bonds, such as Bi_2Et_4 , Bi_2Ph_4 , and Bi_2Mes_4 (2.98–3.09 Å).^[20,21] All Bi–C bond lengths are in the range of 2.21–2.24 Å, ranging between those reported for the single components of this compound (i.e. **1** and BiMe_3). Both bismuth atoms in **3** show a coordination number of four. Bi1 shows a distorted tetrahedral coordination geometry. This is unusual for four-coordinate bismuth(III) compounds,^[22] in which the bismuth center commonly acts as a Lewis acid resulting in bisphenoidal coordination geometries. BiMe_3 in particular has so far only been coordinated as a donor to transition metal complex fragments in $[\text{M}(\text{CO})_5(\text{BiMe}_3)]$ ($\text{M} = \text{Cr}, \text{W}$).^[16c] The angle sums C–Bi–C in these compounds (297.0–298.7°) are larger than in non-coordinate BiMe_3 (276.6°), but even larger in compound **3** (302.4°), suggesting a remarkably large degree of hybridization between 6s and 6p bismuth atomic orbitals in the BiMe_3 unit of **3**. The Bi2 atom in **3** shows the expected bisphenoidal coordination geometry with $[\text{SbF}_6]^-$ (Bi–F, 2.809 Å) and BiMe_3 in the axial positions. In line with these results, natural bond orbital (NBO) analyses of **3** (Figure 3d) reveal an unusually large hybridization between the 6s and 6p orbitals in Bi1 to give a hybrid orbital with 37% s- and 63% p-character (atom labeling is as in Figure 3).^[23] This occupied hybrid orbital of Bi1 and a vacant (“non-hybridized”) p-orbital of Bi2 form the Bi→Bi donor-acceptor interaction, which is strongly polarized towards Bi1 (localization at Bi1: 79%). A Wiberg bond index (WBI) of 0.52 is associated with this Bi→Bi interaction, which is reasonably large compared to the WBIs of 0.24 that were found for the dative N→Bi interactions in **2** (a WBI of 0.95 is obtained for the regular Bi–Bi single bond in $\text{Me}_2\text{Bi}-\text{BiMe}_2$).

The description of the Bi–Bi interaction in **3** as a Bi→Bi dative bond is further corroborated by the intrinsic bond orbital (IBO) analysis and the energy decomposition analysis combined with the natural orbitals for chemical valence (EDA-NOCV) method, the latter excluding the electron-sharing bond scenario due to its larger (i.e. more negative) orbital interaction (ΔE_{orb}) component in comparison to that obtained for a Bi→Bi dative bond (Figure 3d and Supp. Inf.). Furthermore, inspection of the NOCV deformation densities reveals that ΔE_{orb} is dominated by σ donation from Bi1 to Bi2



($\Delta E_{orb-\sigma} = -29.9 \text{ kcal}\cdot\text{mol}^{-1}$, 87% of ΔE_{orb}), and accounts for ca. 50% of all stabilizing contributions between the BiMe_3 and $[\text{BiMe}_2][\text{SbF}_6]$ fragments in **3**.

^1H NMR spectroscopic analysis of **3** in CD_2Cl_2 at 25°C gave one broad resonance (FWHM = 42 Hz) for all five methyl groups of the compound (Figure 3e (top)). A coalescence temperature of 16°C was determined, and splitting

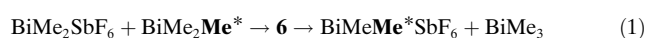
Figure 3. a) Synthesis of $[\text{BiMe}_2(\text{BiMe}_3)(\text{SbF}_6)]$ (**3**). b) Natural transition orbitals of the $S_0 \rightarrow S_1$ excitation of **3** at isovalues of 0.04, as determined by (TD-)DFT calculations. c) Molecular structure of **3** in the solid state.^[31] Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Bi1–C1, 2.219(18); Bi1–C2, 2.21(2); Bi1–C3, 2.223(18); Bi2–C4, 2.24(2); Bi2–C5, 2.24(2); Bi1–Bi2, 3.0005(11); Bi2...F3, 2.809; C1–Bi1–C2, 97.7(7); C2–Bi1–C3, 103.1(8); C1–Bi1–C3, 101.6(7); C4–Bi2–C5, 94.2(8). d) investigation of Bi→Bi bond in **3** with NBO, IBO and EDA-NOCV (charge flows from red to blue) analyses (for details see Supp. Inf.); e) ^1H VT-NMR spectra of **3** in CD_2Cl_2 ; red (blue) numbers indicate chemical shift (integrals) of the respective signals.

of the broad resonance into two sharp signals with an intensity ratio of 2:3 was observed at -40°C with chemical shifts of $\delta = 1.97$ (9H) and 2.21 (6H) ppm. In line with the ^1H NMR data, the ^{13}C NMR spectrum at -40°C shows two resonances at $\delta = 26.1$ ppm (BiMe_3) and 73.5 ppm (BiMe_2). That is, the ^{13}C NMR chemical shifts in **3** experience a considerable to strong shift to higher frequencies in the case of the BiMe_2 group ($\Delta\delta = 9.1$ ppm) and the BiMe_3 moiety ($\Delta\delta = 32.9$ ppm), respectively. These findings demonstrate that at low temperature in solution, **3** shows a quasi-static bonding situation as indicated by the Lewis formula in Figure 3a with a Bi→Bi bonding interaction. At ambient temperature in solution, however, all methyl groups of compound **3** exchange rapidly on the time scale of the NMR spectroscopic experiment. The VT NMR spectroscopic data were subjected to line-shape analysis, revealing activation parameters of $\Delta H^\ddagger = 8.5 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -16.7 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $\Delta G^\ddagger(298 \text{ K}) = 13.5 \text{ kcal}\cdot\text{mol}^{-1}$, and $k(298 \text{ K}) = 1010 \text{ s}^{-1}$ (Supp. Inf.). These results may be compared to bonding situations in lighter group 15 homologs of compound **3**. $[\text{Me}_3\text{P}-\text{PMe}_2][\text{OTf}]$ and related species are stable in solution, where they show a static bonding situation without exchange reactions at room temperature.^[11a,b] Compounds such as $[\text{PhMe}_2\text{As}-\text{AsPhMe}][\text{OTf}]$ are stable in solution, but the exchange of AsPhMe_2 ligands (without exchange of the hydrocarbon ligands) takes place at room temperature in solution.^[11d] $[\text{Me}_3\text{Sb}-\text{SbMe}_2][\text{SbMe}_2\text{Br}_2]$ has been structurally characterized in the solid state, but decomposes into mixtures of mononuclear starting materials in solution, so that characteristic spectroscopic features in solution have not been reported.^[11c] Similarly, the structure of $[(\text{Me}_2\text{Sb})_3][\text{SbMe}_2\text{Br}_2]$ has been reported not to be preserved in solution.^[24] Compound $[\text{Me}_3\text{Sb}-\text{SbMe}_2][\text{GaCl}_4]$ was obtained in very small amounts and not as a pure substance, which complicated its detailed spectroscopic characterization.^[25] Thus, the heaviest congener of this series, $[\text{BiMe}_2(\text{BiMe}_3)(\text{SbF}_6)]$ (**3**), shows a remarkable combination of being sufficiently stable in solution due to the pronounced and soft Lewis acidity of cationic bismuth species^[14,15] such as $[\text{BiMe}_2]^+$ and a dynamic bonding situation due to rapid and reversible Bi–C bond cleavage/formation in solution.

Methyl exchange reactions in organometallic main group species have been reported in some detail for compounds such as $(\text{AlMe}_3)_2$, for its Lewis base adducts, and for its mixtures with other organometallic compounds such as GaMe_3 , InMe_3 , ZnMe_2 , and LiMe .^[26] Intra- as well as

intermolecular exchange mechanisms have been discussed, sometimes controversially, as in the case of $(\text{AlMe}_3)_2$.^[26] We performed DFT calculations in order to elucidate the mechanism of methyl exchange in compound **3** (Figure 4). A reaction pathway with an sp^3 -hybridized methyl group bridging two cationic bismuth centers (reminiscent of methyl exchange discussed for compounds such as Al_2Me_6) was first considered (Figure 4). Surprisingly, a local minimum structure **4** with a three-membered Bi_2C ring as a key structural motif was located on the potential energy surface (PES). According to the IBO analysis, the $\text{Bi}-(\mu_2\text{-sp}^3\text{-CH}_3)\text{-Bi}$ motif can be described as a three-center-two-electron bond with Bi-C ($2\times$) and Bi-Bi bonding interactions (Supp. Inf.). However, the free energy, ΔG , for the reaction $\mathbf{3} \rightarrow \mathbf{4}$ is $+20.7 \text{ kcal mol}^{-1}$. This value does not yet include an (expectedly small) kinetic barrier and is thus unlikely to solely account for the experimentally observed process. Alternatively, $\text{Bi} \rightarrow \text{Bi}$ bond dissociation was considered as the initiating step of the methyl exchange reaction. This bond scission proceeds barrierless to give the starting materials **1** and BiMe_3 in a slightly endergonic reaction ($\Delta G = +1.9 \text{ kcal mol}^{-1}$). While an electrophilic attack of **1** at the bismuth-centered lone pair of BiMe_3 regenerates the adduct **3**, an electrophilic attack of **1** at the methyl group of BiMe_3 was also considered. It proceeds via a van der Waals intermediate **5** located $6.9 \text{ kcal mol}^{-1}$ above **3**, with the corresponding transition state (**TS1**) lying $14.2 \text{ kcal mol}^{-1}$ above **3**. These results are in excellent agreement with the experimentally determined value of $\Delta G^\ddagger(298 \text{ K}) = 13.5 \text{ kcal mol}^{-1}$, and the associative character of the reaction $\mathbf{1} + \text{BiMe}_3 \rightarrow \mathbf{5} \rightarrow \text{TS1}$ is in congruency with the negative activation entropy delineated from line-shape analyses ($\Delta S^\ddagger = -16.7 \text{ cal mol}^{-1} \text{ K}^{-1}$). Remarkably, the resulting compound **6** was identified as a local minimum on the PES. It shows an sp^2 -hybridized

methyl group with a coordination number of five, which is best described as a methyl anion according to its natural charge of -1.20 , bridging two bismuth atoms in a (quasi-)linear $\text{Bi}-(\mu_2\text{-sp}^2\text{-CH}_3)\text{-Bi}$ structural motif. Accordingly, NBO and IBO calculations on **6** indicate a $\text{Bi}-(\mu_2\text{-sp}^2\text{-CH}_3)\text{-Bi}$ three-center-two-electron bond and a lone pair at each bismuth center, which leads to a closed-shell singlet system with a calculated HOMO-LUMO gap of 4.28 eV (Supp. Inf.). The reaction $\mathbf{3} \rightarrow \mathbf{6}$ is endergonic by only $7.1 \text{ kcal mol}^{-1}$. Our findings suggest that the exchange of methyl groups between the two bismuth atoms in **1** proceeds via a species featuring an unusual methyl anion with an sp^2 -hybridized carbon atom bridging two Bi centers. These findings are in agreement with the previously calculated low inversion barrier of the methyl anion ($1.50 \text{ kcal mol}^{-1}$)^[27] and demonstrate its practical relevance in methyl anion exchange reactions of organometallic p-block species. The methyl exchange reaction [Eq. (1)]:



corresponds to a bimolecular electrophilic substitution reaction ($\text{S}_{\text{E}2}$ (back)), that is, the electrophilic analog of the well-known nucleophilic $\text{S}_{\text{N}2}$ substitution reaction in organic chemistry. Methyl exchange along this pathway has rarely been discussed to date, but has been suggested or shown for heterobimetallic systems of late transition metal compounds^[28] and for hypothetical systems such as $[\text{Li}_2\text{Me}]^+$.^[29] To the best of the authors' knowledge, the relevance of backside $\text{S}_{\text{E}2}$ -type methyl exchange is now for the first time demonstrated for a simple, isolable, (pseudo-)homoleptic, and homometallic compound. The isolation of compounds featuring $\text{Al}-(\mu_2\text{-sp}^2\text{-CH}_3)\text{-Al}$ structural motifs suggests that this may well be a more general phenomenon.^[30]

In order to shed some light on the role of the pnictogen atom in $\text{S}_{\text{E}2}$ type methyl exchange reactions, model compounds $[\text{Pn}_2\text{Me}_5]^+$ (**7-Pn**) were studied by DFT calculations ($\text{Pn} = \text{N-Bi}$). These investigations show that such transformations are most favorable for the heaviest congener bismuth, underlining its unique combination of soft Lewis acidity and relatively weak Pn-Me bonding that allows for reversible Bi-C bond cleavage (Supp. Inf.).

In summary, $[\text{BiMe}_2(\text{SbF}_6)]$ (**1**) has been synthesized, isolated, and fully characterized and represents the first example of a mononuclear dialkyl bismuth cation. Reaction of **1** with BiMe_3 gives $[\text{BiMe}_2(\text{BiMe}_3)(\text{SbF}_6)]$ (**3**) featuring the unprecedented structural motif of a $\text{Bi}^{\text{III}} \rightarrow \text{Bi}^{\text{III}}$ donor-acceptor interaction. Methyl exchange in **3** is rapid at room temperature in solution and is suggested to proceed via an initial $\text{Bi} \rightarrow \text{Bi}$ bond dissociation followed by formation of an intermediate with a trigonal planar (sp^2 -hybridized) methyl anion. This corresponds to an $\text{S}_{\text{E}2}$ (back) mechanism, which has been described for heterobimetallic late transition metal complexes, but rarely been considered or even been pinpointed as a concept for methyl exchange in main group chemistry to date and may be more common than previously anticipated. These findings highlight the unusual properties of cationic bismuth species as Lewis acids with the ability to

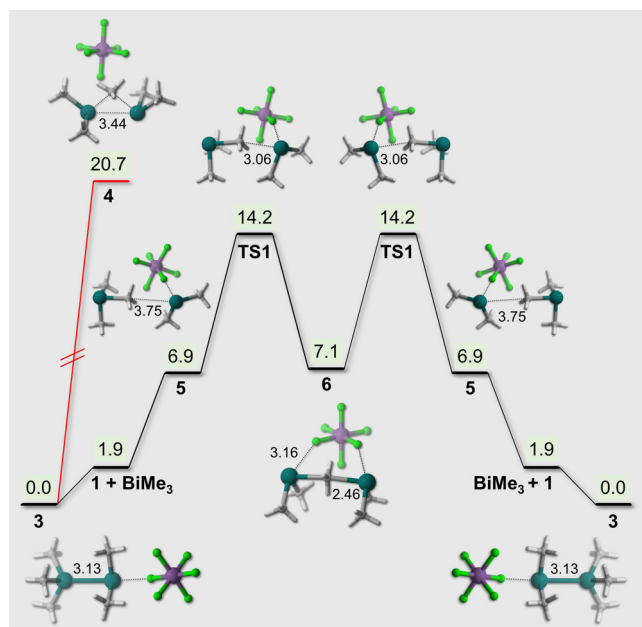


Figure 4. Free energy (ΔG) profile of the proposed methyl exchange reaction mechanism of **3**. Disfavored reaction pathway is shown in red. Selected calculated interatomic distances are given in Å.

undergo reversible Bi–C bond cleavage, which we aim to exploit in future synthetic and catalytic applications.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: bismuth · cationic species · electrophilic substitution · Lewis acidity · methyl exchange

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