Supporting Information

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

General considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in 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 $^1$H. $^1$H and $^{13}$C NMR chemical shifts are reported relative to SiMe$_4$ using the residual $^1$H and $^{13}$C chemical shifts of the solvent as a secondary standard. $^{19}$F NMR chemical shifts are reported relative to CFCl$_3$ as external standards. NMR spectra were recorded at ambient temperature (typically 23 °C), if not otherwise noted. UV-vis spectra were recorded with a UV5 Mettler Toledo UV-vis-Excellence spectrometer. Elemental analyses was obtained using a Leco, or a Carlo Erba instrument. Single crystals suitable for X-ray diffraction analysis were coated with polyisobutylene or perfluorinated polyether oil in a glovebox, transferred to a nylon loop and then to the goniometer of a diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å). The data obtained were integrated with SAINT and a semi-empirical absorption correction from equivalents with SADABS was applied. The structure was solved and refined using the Bruker SHELX 2014 software package. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropically on calculated positions by using a riding model with their $U_{iso}$ values constrained to 1.5 $U_{eq}$ of their pivot atoms for terminal sp$^3$ carbon atoms and 1.2 times for all other atoms. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 2080851-2080853. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

For comparison with compounds 1-3, NMR spectroscopic data in the solvent CD$_2$Cl$_2$ was collected for literature-known BiMe$_3$ and BiMe$_2$Cl.

BiMe$_3$:  
$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta = 1.11$ (s, 9H, CH$_3$) ppm.  
$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): $\delta = -6.82$ (br, CH$_3$) ppm.

BiMe$_2$Cl:  
$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta = 1.80$ (s, 6H, CH$_3$) ppm.  
$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): $\delta = 34.66$ (br, CH$_3$) ppm.

[BiMe$_2$(SbF$_6$)] (1). A solution of AgSbF$_6$ (0.22 g, 0.63 mmol) in methylene chloride (DCM) (3 mL) was added to a solution of BiMe$_2$Cl (0.17 g, 0.63 mmol) in DCM (2 mL). The precipitate was filtered off. All volatiles were removed from the yellow filtrate under reduced pressure to give a yellow powder, which was dried in vacuo. Yield: 0.22 g, 0.47 mmol, 75%.

Single crystals suitable for X-ray diffraction analysis of 1 were obtained by layering a solution of 1 in DCM with n-pentane and storage at −30 °C for 16 h.
$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta = 1.47$ (s, 6H, CH$_3$) ppm.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 2.28$ (s, 6H, CH$_3$) ppm.

$^{13}$C NMR (101 MHz, C$_6$D$_6$): $\delta = 66.72$ (br, CH$_3$) ppm.

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): $\delta = 64.38$ (br, CH$_3$) ppm.

$^{19}$F NMR (376 MHz, C$_6$D$_6$): $\delta = -123.02$ (s, SbF$_6$) ppm.

$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$): $\delta = -128.44$ (s, SbF$_6$) ppm.

**Elemental analysis:** Anal. calc. for: C$_2$H$_6$BiSbF$_6$ (474.84 g/mol): C 5.06, H 1.27, found: C 5.45, H 1.40.

**Light-sensitivity of 1.** In order to obtain compound 1 in high purity and good yield, the synthesis (especially the work-up) should be performed under exclusion of light. 1 was stored in the dark at –30 °C without notable degradation for at least one month. The follow-up reactions reported in this work proceed at rates that are so high that the exclusion of light was not necessary.

**Interactions of 1 with arenes.** The NMR spectra obtained in C$_6$D$_6$ are likely represent the benzene adduct in solution instead of the contact ion pair. This is indicated by a color change from yellow to colorless when dissolving 1 in benzene. Unfortunately, attempts to crystallize the benzene adduct only lead in the precipitation of the contact ion pair as yellow crystals. However, reaction of 1 (20.0 mg, 42.1 µmol) with two equivalents of hexamethyl benzene (12.8 mg, 78.8 µmol) in CD$_2$Cl$_2$ (0.5 mL) resulted in a highfield shift of the methyl protons of 1 in the $^1$H NMR spectrum obtained from the reaction solution ($\Delta \delta = 0.5$ ppm), which is in line with the results obtained for the pyridine adduct 2 (data for compound [BiMe$_2$(C$_6$Me$_6$)$_2$][SbF$_6$]: $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 1.81$ (s, 6H, BiMe$_2$), 2.26 (s, 36H, C$_6$Me$_6$) ppm.).

**Derivatives of 1 with more weakly coordinating anions.** Attempts to synthesize donor-solvent-free dimethylbismuth cations with counteranions that are more weakly coordinating than [SbF$_6$]$^-$ (e.g. [B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$^-$) were unsuccessful to date. Aryl transfer from B to Bi was observed as a side reaction, for instance.

[BiMe$_2$(py)$_2$][SbF$_6$] (2). [BiMe$_2$(SbF$_6$)] (1) (85.6 mg, 0.18 mmol) was dissolved in DCM (2 mL), and pyridine (28.5 mg, 0.36 mmol, 30 µl) was added. The colorless solution was layered with n-pentane (2 mL). After 1 d at –30 °C a colorless crystalline solid had precipitated, was isolated by filtration, and dried in vacuo. Yield: 97 mg, 0.15 mmol, 84%.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 1.79$ (s, 6H, CH$_3$), 7.60 (t, 4H, $^3$J$_{HH}$ = 6.92 Hz, H2/H6), 8.05 (t, 2H, $^3$J$_{HH}$ = 7.75 Hz, H4), 8.64 (d, 4H, $^3$J$_{HH}$ = 4.67 Hz, H3/H5) ppm.

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): $\delta = 33.86$ (CH$_3$), 126.86 (s, C2/C6), 140.58 (s, C4), 149.75 (s, C3/C5) ppm.

A signal for the [SbF$_6$]$^-$ anion in a $^{19}$F NMR experiment could not be detected due to signal broadening.

**Elemental analysis:** Anal. calc. for: C$_2$H$_6$BiF$_6$Sb(C$_5$H$_5$N)$_2$ (633.00 g/mol): C 22.77, H 2.55, N 4.43 found: C 22.96, H 2.32, N 4.77.
[BiMe₂(BiMe₃)(SbF₆)] (3). [BiMe₂(SbF₆)] (1) (20 mg, 42.2 µmol) was dissolved in DCM (2 mL) and a solution of BiMe₃ (11.2 mg, 42.2 µmol) in DCM (1 mL) was added. The light yellow solution was stored at −30 °C. After 1 d light yellow crystals were obtained, isolated by filtration, and dried in vacuo. Yield: 27 mg, 37.0 µmol, 88%.

1H NMR (500 MHz, 298.15 K, CD₂Cl₂): δ = 2.05 (br, 15H, CH₃) ppm.

19F NMR (470 MHz, 233.15 K, CD₂Cl₂): δ = −124.39 (SbF₆) ppm.

Elemental analysis: Anal. calc. for: C₅H₁₅Bi₂F₆Sb (728.89 g/mol): C 8.24, H 2.07, found: C 8.39, H 1.89.

Reaction of Bi₂Me₅SbF₆ with two equivalents of pyridine. Pyridine (3.3 µL, 41 µmol) was added to a light yellow solution of Bi₂Me₅SbF₆ (3) (15.0 mg, 20.6 µmol) in CD₂Cl₂ (0.5 mL). A 1H NMR spectroscopic analysis of the obtained colorless solution showed the quantitative formation of BiMe₃ and BiMe₂(py)₂SbF₆ (2).
Single Crystal X-ray Diffraction Analysis

The structure of compound 1 in the solid state, as determined by single-crystal X-ray diffraction analysis, is shown in Figure S1. While there are two shorter Bi⋯F contacts (Bi1⋯F1 and Bi1⋯F3 in Figure S1), the two remaining Bi⋯F interactions are associated with large Bi⋯F distances (Bi1⋯F5 and Bi1⋯F6 in Figure S1) and assumed to be very weak.

Figure S1. Top: Cutout of the solid-state structure of [BiMe₂(SbF₆)] (1), illustrating the coordination environment of Bi1 including weak intermolecular contacts. Bottom: Cutout of the solid-state structure of [BiMe₂(SbF₆)] (1), illustrating the arrangement as a one-dimensional coordination polymer in the solid state. Displacement ellipsoids are represented at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Bi1–C1, 2.215(5); Bi1–C2, 2.223(5); Bi1–F1, 2.451(3); Bi1–F3, 2.452(3); Bi1⋯F5, 3.272(3); Bi1⋯F6, 3.452(3); C1–Bi1–C2, 93.0(2); C1–Bi1–F1, 83.91(17); C2–Bi1–F1, 87.20(17); C1–Bi1–F3, 88.60(17); C2–Bi1–F3, 86.18(17); F1–Bi1–F3, 169.73(11); Sb1–F1–Bi1, 160.53(17).
Compound 1 is well-soluble in weakly coordinating solvents such as 1,2-difluorobenzene and dichloromethane. Furthermore, the $^1$H and $^{13}$C NMR spectra of 1 in dichloromethane-$d_2$ show no unusual signal broadening. These observations speak against oligo- or polymeric species of 1 dominating in solution, and we suggest that 1 is best described as a mononuclear solvent-stabilized contact ion pair in solution.

The structure of compound 2 in the solid state, as determined by single-crystal X-ray diffraction analysis, is shown in Figure S2. Since the coordination sphere of bismuth is saturated and no indications for aggregation in solution were obtained, it is suggested that compound 2 essentially maintains its solid state structure in solution.

![Figure S2. Molecular structure of [BiMe$_2$(py)$_2$][SbF$_6$] (2) in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and second, crystallographically independent [SbF$_6$]$^-$ anion which is present in the unit cell are omitted for clarity (the overall occupancy of each [SbF$_6$]$^-$ moiety is 0.5). Selected bond length (Å) and angles (°): Bi1–C7, 2.223(12); Bi1–C6, 2.235(12); Bi1–N1, 2.519(7); Bi1–N1’, 2.197(7); Bi1···F1, 3.483(7); C7–Bi1–C6, 92.3(5); C7–Bi1–N1, 86.35(16); C6–Bi1–N1, 86.08(16); C7–Bi1–N1, 86.35(16); C6–Bi1–N1, 86.08(16); N1–Bi1–N1’, 169.1(3).]
Compound 3 was analyzed by single-crystal X-ray diffraction analysis, and a cutout of its structure in the solid state (including neighboring [SbF₆]⁻ units) is shown in Figure S3. Compound 3 shows three relatively long Bi····F contacts in the solid state (Bi1/2····F1, Bi1/2····F2, and Bi1····F5 in Figure S3). These are expected to be weak and to persist only in the solid state. Furthermore, 3 shows one relatively short Bi····F contact in the solid state (Bi2····F3 in Figure S3). This contact is expected to persist in the low-temperature scenario of the structure of compound 3 in solution. However, it has to be emphasized that at temperatures significantly larger than −40 °C, compound 3 shows a dynamic behavior in solution (methyl exchange, additional local energetic minima accessible, reversible Bi→Bi bond dissociation possible, as outlined in the main part); i.e. at these temperatures, the solid state structure of 3 is not fully maintained in solution.

**Figure S3.** Cutout of the solid-state structure of [Bi₂Me₅(SbF₆)] (3) (including weak intermolecular interactions). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Three of the four [SbF₆]⁻ anions exceed one formula unit and belong to neighboring Bi₂Me₅SbF₆ units. Selected bond length (Å) and angles (°): C4–Bi2, 2.24(2); C5–Bi2, 2.24(2); C1–Bi1, 2.219(18); Bi1–C2, 2.21(2); Bi1–C3, 2.223(18); Bi1–Bi2, 3.0005(11); Bi2····F3, 2.809(12); Bi1····F1, 3.212; Bi1–F2, 3.177; Bi2····F1, 3.366; Bi2····F2, 3.275; Bi1····F5, 3.274; C2–Bi1–C1, 97.7(7); C2–Bi1–C3, 103.1(8); C1–Bi1–C3, 101.6(7); C2–Bi1–Bi2, 120.6 (6); C1–Bi1–Bi2, 113.9(5); C3–Bi1–Bi2, 116.8(5); C5–Bi2–C4, 94.2(8); C5–Bi2–Bi1, 90.3(5); C4–Bi2–Bi1, 91.8(5).

[BiMe₂(BiMe₃)(SbF₆)] (3) crystallizes in the monoclinic space group P2₁/c with Z = 4 as a two-component twin with the two components in a ratio of 99:1 that are related by a 180° rotation about the reciprocal [100] axis.
Variable Temperature NMR Spectroscopic Experiments

Variable temperature $^1$H NMR spectroscopic experiments on CD$_2$Cl$_2$ solutions of compound 3 were carried out in the temperature range of $-50$ °C to $+25$ °C. For line shape analyses the program TopSpin 4.0.4 of Bruker was used. At room temperature, 3 shows only one broad resonance, which splits into two resonances with the integral ratio 2:3 in the low-temperature scenario. The coalescence temperature is 16 °C.

Since the Bruker software *DNMR Lineshape Analysis* has limited capabilities when exchange reactions are considered, the following intermolecular exchange model was used (Figure S4). The activation parameters were obtained from the Eyring plot (Figure S5) and are summarized in Table S1.

An alternative approach, in which line shape analysis with intermolecular exchange reactions between two methyl groups and three equivalent methyl groups was examined, gave very similar results ($\Delta G^\ddagger (298 \text{ K}) = 13.3 \text{ kcal} \cdot \text{mol}^{-1}$).

![Figure S4. Exchange reactions which form the basis for the line shape analysis.](image)

![Figure S5. Eyring plot of the reaction rate for the methyl exchange in Bi$_2$Me$_5$SbF$_6$ (3) determined by line shape analysis.](image)

| Compound     | $\Delta G^\ddagger (298 \text{ K})$ [kcal · mol$^{-1}$] | $\Delta H^\ddagger$ [kcal · mol$^{-1}$] | $\Delta S^\ddagger$ [cal · mol$^{-1}$ · K$^{-1}$] | $k (298 \text{ K})$ [s$^{-1}$] |
|--------------|--------------------------------------------------------|----------------------------------------|-----------------------------------------------|-------------------------------|
| Bi$_2$Me$_5$SbF$_6$ | 13.5                                                   | 8.5                                    | $-16.7$                                       | 1010                          |
Figure S6. VT $^1$H NMR spectra of [Bi$_2$Me$_5$(SbF$_6$)] (3) in a temperature range of +25 °C to −50 °C. The coalescence temperature is 289.15 K (16 °C). Beginning decomposition of [Bi$_2$Me$_5$(SbF$_6$)] (3) can be observed during the VT $^1$H NMR spectroscopic measurements.

The $^{19}$F NMR spectrum of compound 3 at −40 °C showed one broad resonance, indicating that dynamic processes of the [SbF$_6$]$^-$ group were not resolved on the time scale of this experiment.
Figure S7. Experimental UV/vis spectrum of [BiMe₃(SbF₆)] (1) (0.68 mM) in DCM (black, absorption maximum at $\lambda_{\text{max}} = 321$ nm, $\varepsilon(\lambda_{\text{max}}) = 624$ L·mol⁻¹·cm⁻¹) and calculated transitions (blue).

Table S2. Details on lowest energy UV/vis transitions relevant to the experimental absorption spectrum of BiMe₃SbF₆ (1) as determined by TD-DFT calculations.

| Excitation  | $\lambda$ [nm] | f    | Main MO contributions type | %  |
|-------------|----------------|------|---------------------------|----|
| $S_0 \rightarrow S_1$ | 332.7       | 0.0333 | HOMO $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+1 | 72, 27 |
| $S_0 \rightarrow S_2$ | 268.0       | 0.0000 | HOMO-1 $\rightarrow$ LUMO, HOMO-1 $\rightarrow$ LUMO+1 | 27, 72 |
| $S_0 \rightarrow S_3$ | 236.2       | 0.0079 | HOMO $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+1 | 27, 71 |
Figure S8. Selected molecular orbitals of compound [BiMe$_2$(SbF$_6$)] (1) (isovalues = 0.03) with main contributions to transitions listed in Table S2.
**Figure S9.** Experimental UV/vis spectrum of [Bi₂Me₅(SbF₆)] (3) (0.41 mM) in DCM (black, absorption maximum at $\lambda_{\text{max}} = 302$ nm, $\varepsilon(\lambda_{\text{max}}) = 1308$ L·mol⁻¹·cm⁻¹) and calculated transition (blue).

**Table S3.** Details on lowest energy UV/vis transitions relevant to the experimental absorption spectrum of Bi₂Me₅SbF₆ (3) as determined by TD-DFT calculations.

| Excitation | $\lambda$ [nm] | $f$ | Main MO contributions type | % |
|------------|----------------|-----|----------------------------|----|
| $S_0 \rightarrow S_1$ | 288.8 | 0.2792 | HOMO → LUMO | 56 |
|             |             |     | HOMO → LUMO+1             | 21 |
|             |             |     | HOMO-1 → LUMO             | 14 |
|             |             |     | HOMO-1 → LUMO+1           | 6  |
Figure S10. Selected molecular orbitals of compound \([\text{Bi}_2\text{Me}_5(\text{SbF}_6)]\) (3) (isovalues = 0.03) with main contributions to transition \(S_0 \rightarrow S_1\) listed in Table S3.
DFT Calculations

DFT calculations were performed with the Gaussian 16, Revision B.01 program package[1] using the B3LYP[2] functional and the 6-311++G(d,p)[3] (H, C, F) and LanL2DZ/ECP[4] (Sb, Bi) basis sets. The D3 version of Grimme’s dispersion model with the original D3 damping function was applied.[5] Frequency analyses of the reported structures showed no imaginary frequencies for minimum energy structures and only one imaginary frequency for transition states. In order to assess the connectivity between the obtained transition states and the corresponding intermediates, further geometry optimizations along the imaginary modes and additional intrinsic reaction coordinate (IRC)[6] calculations were performed. Thermodynamic parameters were calculated at a temperature of 298.15 K and a pressure of 1.00 atm. NBO analyses were performed using the program version NBO 7.[7] To investigate the role of the pnictogen atom in the methyl exchange reactions, $[\text{Pn}_2\text{Me}_5]^+$ (7-Pn), their bond dissociation to PnMe$_3$ + PnMe$_2^+$, and the Me$_3$Pn–(µ$_2$-$sp^2$-CH$_3$)–PnMe$_2^+$ (8-Pn) systems were investigated using B3LYP-D3 and the 6-31G(d,p)[8] (H, C, N, P) and LANL2DZ/ECP (As, Sb, Bi) basis sets. All calculations, including geometry optimizations, were performed with the PCM[9] solvent model and dichloromethane ($\varepsilon = 8.93$) as solvent. A concentration correction of $\Delta G^{0\rightarrow*} = RT\ln(24.46) = 1.89$ kcal mol$^{-1}$ ($T = 298.15$ K) was added to the free energies of all calculated species to change the 1.00 atm gas phase values to the condensed phase standard state concentration of 1.00 mol·L$^{-1}$, which leads to a proper description of associative/dissociative steps.[10] Virtually identical results were obtained from calculations using other density functionals and quadruple-zeta basis sets. In order to investigate the vertical electronic transitions, TD-DFT calculations were performed using the CAM-B3LYP[11] functional at the B3LYP optimized geometries. For 3, the $S_0\rightarrow S_1$ vertical excitation was analyzed using the natural transition orbitals (NTO)[12] method. Finally, the bonding situation of selected systems was investigated using the intrinsic bond orbital (IBO)[13] and the energy decomposition analysis based on natural orbitals for chemical valence (EDA-NOCV)[14] methods. The EDA-NOCV calculations on 3 were done considering two distinct scenarios, where the Bi–Bi bond was described either as electron-sharing or donor-acceptor interaction. These investigations, which were performed using the ADF 2019 software,[15] were conducted at the B3LYP-D3/QZ4P level, with relativistic effects considered using the zeroth order regular approximation (ZORA) method.[16]
**Influence of Pn on methyl exchange reactions.** In order to investigate the role of the pnictogen atom in the methyl exchange reactions presented here, compounds \([\text{Pn}_2\text{Me}_5]^+\) (7-Pn) were investigated by DFT calculations and shortly discussed in the main part (Pn = N-Bi, Figure S11). The bond dissociation energies associated with the reactions 7-Pn \(\rightarrow\) PnMe\(_3\) + PnMe\(_2^+\) constantly decrease, when going down the group from N (\(\Delta G = 70.8\) kcal\(\cdot\)mol\(^{-1}\)) to Bi (\(\Delta G = 17.0\) kcal\(\cdot\)mol\(^{-1}\)). For Pn = N, a compound of type Me\(_2\)Pn–(\(\mu_2\)-sp\(^2\)-CH\(_3\))–PnMe\(_2^+\) (8-Pn) could not be located as an energy minimum on the PES and the migration of a proton from the bridging methyl group to a nitrogen atom was observed instead to give compound 9-N. Compound 8-P corresponds to a saddle point on the PES and is slightly higher in energy than the dissociated species PMe\(_3\) + PMe\(_2^+\).

![Figure S11](image)

**Figure S11.** Free energies (\(\Delta G\)) of reactions 7-Pn \(\rightarrow\) PnMe\(_3\) + PnMe\(_2^+\) and PnMe\(_3\) + PnMe\(_2^+\) \(\rightarrow\) 8-Pn (Pn = N-Bi). All \(\Delta G\) values (kcal\(\cdot\)mol\(^{-1}\)) are given with respect to the corresponding 7-Pn compounds. The structure of 9-N and the free energy of reaction 7-N \(\rightarrow\) 9-N is also shown. Calculated Pn–(sp\(^2\)-CH\(_3\)) bond lengths are given in Å.
Energies of Compounds Investigated by DFT Calculations

The energies of compounds investigated by DFT calculations are given in Table S4 (concentration corrections not added). Their Cartesian coordinates are given in a separate .xyz file.

Table S4. Energies of calculated species.

| Entry | Compound | $\Delta G$ [hartree] | Imaginary frequencies |
|-------|----------|----------------------|----------------------|
| 1     | BiMe$_2$SbF$_6$ (1) | –690.0794 | none |
| 2     | BiMe$_2$(py)$_2$SbF$_6$ (2) | –1186.7053 | none |
| 3     | BiMe$_3$ | –125.1482 | none |
| 4     | Bi$_2$Me$_5$SbF$_6$ (3) | –815.227712 | none |
| 5     | Bi$_2$Me$_5$SbF$_6$ (4) | –815.194804 | none |
| 6     | Bi$_2$Me$_5$SbF$_6$ (5) | –815.216688 | none |
| 7     | Bi$_2$Me$_5$SbF$_6$ (TS1) | –815.205027 | 1 |
| 8     | Bi$_2$Me$_5$SbF$_6$ (6) | –815.216337 | none |
| 9     | Bi$_2$Me$_4$ | –170.514824 | none |
| 10    | N$_2$Me$_5^+$ (7-N) | –308.714929 | none |
| 11    | P$_2$Me$_5^+$ (7-P) | –882.027852 | none |
| 12    | As$_2$Me$_5^+$ (7-As) | –211.53249 | none |
| 13    | Sb$_2$Me$_5^+$ (7-Sb) | –210.094591 | none |
| 14    | Bi$_2$Me$_5^+$ (7-Bi) | –210.172091 | none |
| 15    | Me$_2$Pn–(µ$_2$-sp$^2$-CH$_3$)–PnMe$_2^+$ (8-P) | –881.932491 | 1 |
| 16    | Me$_2$Pn–(µ$_2$-sp$^2$-CH$_3$)–PnMe$_2^+$ (8-As) | –211.475067 | none |
| 17    | Me$_2$Pn–(µ$_2$-sp$^2$-CH$_3$)–PnMe$_2^+$ (8-Sb) | –210.061389 | none |
| 18    | Me$_2$Pn–(µ$_2$-sp$^2$-CH$_3$)–PnMe$_2^+$ (8-Bi) | –210.160652 | none |
| 19    | N$_2$Me$_5^+$ (9-N) | –308.754084 | none |

Table S5. Free energy profile of the proposed methyl exchange reaction mechanism of 3 from distinct levels of theory.

| Reaction Step | B3LYP-D3(BJ)/6-311++G**(H, C, F)/LanL2DZ/ECP (Sb, Bi) | oB97XD/def2-QZVPP (H, C, F)/def2/ECP (Sb, Bi) | M062X-D3/def2-QZVPP (H, C, F)/def2/ECP (Sb, Bi) |
|---------------|------------------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 3             | 0.0                                                  | 0.0                                           | 0.0                                           |
| 1 + BiMe$_3$  | 1.9                                                  | 2.6                                           | –2.8                                         |
| 4             | 20.7                                                 | 19.7                                          | 16.2                                          |
| 5             | 6.9                                                  | 9.2                                           | 6.6                                           |
| TS1           | 14.2                                                 | 16.2                                          | 11.7                                          |
| 6             | 7.1                                                  | 9.8                                           | 6.8                                           |
NBO Calculations

Figure S12. NBO of 3 depicting the Bi→Bi bond.

Figure S13. NBO of 6 depicting the Bi–(μ₂-sp²-CH₃)–Bi three-center-two-electron bond.
IBO Calculations

Figure S14. IBOs depicting the (a) Bi→Bi bond of 3, (b) the three-center-two-electron bond of 4, and (c) the Bi–(μ₂-sp³-CH₃)–Bi three-center-two-electron bond of 6.
EDA-NOCV Calculations

Table S6. EDA-NOCV results (B3LYP-D3/QZ4P) for 3. The donor-acceptor and the electron-sharing bond scenarios for the fragments BiMe3 and 1 are considered. Energy terms are given in kcal mol\(^{-1}\). For \(\Delta E_{\text{disp}}\), \(\Delta E_{\text{elstat}}\), and \(\Delta E_{\text{orb}}\), the values in parentheses show the weight of each contribution with respect to the total attractive interaction. For \(\Delta E_{\text{orb-\sigma}}\) and \(\Delta E_{\text{orb-rest}}\), the values in parentheses show the weight of each contribution with respect to the total orbital interaction, \(\Delta E_{\text{orb}}\).

| Energy terms | BiMe3 + 1 | [BiMe3]\(^{+}\) + 1\(^{-}\) |
|--------------|-----------|------------------|
| \(\Delta E_{\text{int}}\) | \(-20.9\) | \(-137.1\) |
| \(\Delta E_{\text{Pauli}}\) | \(53.4\) | \(90.9\) |
| \(\Delta E_{\text{elstat}}\) | \(-35.9\) (48.4%) | \(-123.8\) |
| \(\Delta E_{\text{disp}}\) | \(-3.9\) (5.3%) | \(-3.9\) |
| \(\Delta E_{\text{orb}}\) | \(-34.4\) (46.4%) | \(-100.3\) |
| \(\Delta E_{\text{orb-\sigma}}\) | \(-29.8\) (86.7%) | - |
| \(\Delta E_{\text{orb-rest}}\) | \(-4.6\) (13.3%) | - |

Figure S15. (a) NOCV pair and (b) deformation density plot of the main bonding configuration that contributes to the total \(\Delta E_{\text{orb}}\) term in the EDA-NOCV description of 3 obtained at the B3LYP-D3/QZ4P level. The NOCV eigenvalues and the main orbital interaction energy \(\Delta E_{\text{orb-\sigma}}\) (in kcal\cdot mol\(^{-1}\)) are also shown. The percentage of \(\Delta E_{\text{orb-\sigma}}\) with respect to the total \(\Delta E_{\text{orb}}\) is shown in parenthesis. Isovalues: 0.0015 a.u. Charge flows from red to blue.
**Figure S16.** $^1$H and $^{19}$F NMR spectra of [BiMe$_2$(SbF$_6$)] (1) in C$_6$D$_6$. 
Figure S17. $^1$H NMR spectrum [BiMe$_2$(SbF$_6$)] (1) in CD$_2$Cl$_2$. 
Figure S18. $^{19}$F and $^{13}$C NMR spectra of [BiMe$_2$(SbF$_6$)] (1) in CD$_2$Cl$_2$. 
Figure S19. $^1$H and $^{13}$C NMR spectra of [BiMe$_2$(py)$_2$][SbF$_6$] (2) in CD$_2$Cl$_2$. 
Figure S20. $^1$H NMR spectrum of [BiMe$_2$(BiMe$_3$)(SbF$_6$)] (3) in CD$_2$Cl$_2$. 
Figure S21. $^{19}$F and $^{13}$C NMR spectra of [BiMe$_2$(BiMe$_3$)(SbF$_6$)] (3) in CD$_2$Cl$_2$ at a temperature of 233 K.
Figure S22. $^1$H NMR spectrum of [BiMe$_2$(C$_6$Me$_6$)$_2$][SbF$_6$] in CD$_2$Cl$_2$. 
A range of compounds with Pn→Pn bonding have been reported to the literature and have been discussed in the main part (Pn = pnictogen atom).\textsuperscript{[17]} In order to provide a visual summary, these compounds are depicted in Figure S23a. In addition to compounds with homonuclear Pn→Pn bonding, complexes with heteronuclear Pn→Pn’ bonding have also been reported.\textsuperscript{[17c]} Examples are shown in Figure S23b.\textsuperscript{[18]}

**Figure S23.** Examples of literature-known compounds with Pn→Pn (a) and Pn→Pn’ bonding (b) (Pn = pnictogen).
References

[1] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, M. W. Li, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian Inc., Wallingford CT, 2016.

[2] a) S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200–1211. b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785–789; c) A. D. Becke, J. Chem. Phys. 1993, 98, 5648–5652; d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623–11627.

[3] a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, J. Chem. Phys. 1980, 72, 650–654; b) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, J. Comput. Chem. 1983, 4, 294–301.

[4] W. R. Wadt, P. J. Hay, J. Chem. Phys. 1985, 82, 284–298.

[5] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.

[6] K. Ishida, K. Morokuma, A. Komornicki, J. Chem. Phys. 1977, 66, 2153–2156.

[7] a) F. Weinhold, C. R. Landis, E. D. Glendening, Int. Rev. Phys. Chem. 2016, 35, 399–440; b) E. D. Glendening, C. R. Landis, F. Weinhold, J. Comput. Chem. 2019, jcc.25873.

[8] a) M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Huhre, J. Am. Chem. Soc. 1982, 104, 2797–2803; b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. Chem. Phys. 1982, 77, 3654–3665.

[9] G. Scalmani, M. J. Frisch, J. Chem. Phys. 2010, 132, 114110.

[10] M. Sparta, C. Riqlinger, F. Neese, J. Chem. Theory Comput. 2014, 10, 1099–1108.

[11] T. Yanai, D. P. Tew, N. C. Handy, Chem. Phys. Lett. 2004, 393, 51–57.

[12] R. L. Martin, J. Chem. Phys. 2003, 118, 4775–4777.

[13] G. Knizia, J. Chem. Theory Comput. 2013, 9, 4834–4843.

[14] M. P. Mitoraj, A. Michalak, T. Ziegler, T., J. Chem. Theory Comput. 2009, 5, 962–975.

[15] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, Comput. Chem. 2001, 22, 931–967.

[16] a) E. van Lenthe, E. J. Baerends, J. G. Snijders, J. G., J. Chem. Phys. 1993, 99, 4597–4610; b) E. van Lenthe, E. J. Baerends, J. G. Snijders, J. Chem. Phys. 1994, 101, 9783–9792.

[17] J. J. Weigand, S. D. Riegel, N. Burford, A. Decken, J. Am. Chem. Soc. 2007, 129, 7969–7976; b) S. S. Chitnis, E. MacDonald, N. Burford, U. Werner-Zwanziger, R.
McDonald, *Chem. Commun.* 2012, 48, 7359-7361; c) H. Althaus, H. J. Breunig, E. Lork, *Chem. Commun.* 1999, 1971-1972; d) N. L. Kilah, M. L. Weir, S. B. Wild, *Dalton Trans.* 2008, 2480-2486; e) A. P. M. Robertson, P. A. Gray, N. Burford, *Angew. Chem. Int. Ed.* 2014, 53, 6050-6069; f) H. J. Breunig, M. Denker, E. Lork, *Angew. Chem. Int. Ed.* 1996, 35, 1005-1006; g) C. Hering, M. Lehmann, A. Schulz, A. Villinger, *Inorg. Chem.* 2012, 51, 8212-8224.

[18] E. Conrad, N. Burford, R. McDonald, M. J. Ferguson, *J. Am. Chem. Soc.* 2009, 131, 5066.

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