Molecular Bismuth Cations: Assessment of Soft Lewis Acidity

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Abstract: Three-coordinate cationic bismuth compounds (Bi(diaryl)(EPMe3))[SbF6] have been isolated and fully characterized (diaryl = [(C6H4)2C2H2]2, E = S, Se). They represent rare examples of molecular complexes with Bi–EPMe3 interactions (R = monoanionic substituent). The 19P NMR chemical shift of EPMe3 has been found to be sensitive to the formation of LA–EPMe3 Lewis acid/base interactions (LA = Lewis acid). This corresponds to a modification of the Gutmann–Beckett method and reveals information about the hardness/softness of the Lewis acid under investigation. A series of organobismuth compounds, bismuth halides, and cationic bismuth species have been investigated with this approach and compared to traditional group 13 and cationic group 14 Lewis acids. Especially cationic bismuth species have been shown to be potent soft Lewis acids that may prefer Lewis pair formation with a soft (S/Se-based) rather than a hard (O/N-based) donor. Analytical techniques applied in this work include (heteronuclear) NMR spectroscopy, single-crystal X-ray diffraction analysis, and DFT calculations.

Introduction

Bismuth(III) compounds are frequently applied as Lewis acids in stoichiometric and catalytic organic and organometallic transformations.[1] Various types of reactions have been realized with this strategy. The long (and non-exhaustive) list of examples includes pericyclic reactions (such as Diels–Alder reactions),[1b, 2] addition reactions (such as hydrosilylation, hydroamination, and carbo/amino-bismuthation),[1a–c, 3] addition–elimination sequences (such as aldol and Mannich reactions),[1a–c, 4] and small-molecule activation (such as carbon monoxide insertion).[5] The utilization of bismuth Lewis acids can lead to selectivities and activities that are difficult or impossible to obtain with other reagents.[1b, 2a, 3a, 9] In other cases bismuth compounds show advantages in terms of affordability, stability towards air and moisture, or functional group tolerance.[1a, 3b, 4, 7d, e] In addition, prospects for catalyst recyclability have been demonstrated.[4b, 10]

While the abovementioned applications make use of Lewis acid/base interactions between bismuth compounds and organic substrates, the coordination of metal-centered Lewis bases to Lewis acidic bismuth components has also been reported. This has been exploited for the design of bismuth-containing Z-type (donor/acceptor) ligands, in which the bismuth atom is responsible for the electron-accepting character of the overall ligand.[11]

We have recently suggested a scheme for the classification of bismuth Lewis acids.[12] Distinctions are made between three types of compounds: class A) R2Bi–X with an electronegative ligand X; class B) R2Bi–X’ with ligands X’ such as (O3SFCF3)− or (AlCl4)−, which lead to a weak Bi–X’ interaction; and class C) cationic species [R2BiI4]−[WCA] without any directional bonding interactions between bismuth and the weakly coordinating counteranion (WCA), for which [SbF6]− or [B(C6F5)4]− are typical examples. While π*(Bi–X/X’)-orbitals are responsible for the Lewis acidic character of class A and B compounds, an empty bismuth-centered p-orbital will accept electron density from Lewis basic bonding partners in the case of class C complexes. For all three classes of bismuth Lewis acids, the orbitals involved in the formation of interactions with Lewis bases are large and diffuse, which is why they may be expected to be soft Lewis acids. This is supported by the fact that interactions with typical soft Lewis bases such as arene moieties, stibanes, and telluroethers have been reported.[13–17] It can be anticipated that the expectedly soft character of bismuth-based Lewis acidity is integral to some of the observed properties and reactivity patterns of bismuth species. Examples include their relatively high tolerance towards (hard) oxygen-based functional groups and their ability to efficiently coordinate and activate (soft) arene and olefin donor groups.[3–6, 7a, e, 13–15]

In contrast to the frequent application of bismuth Lewis acids in synthesis and catalysis, efforts to quantify bismuth-
based Lewis acidity have only scarcely been reported.\textsuperscript{3b,12,18} More specifically, there are no detailed studies available that deal with the quantification of the hard or soft character of bismuth Lewis acids.

Here we report Lewis acid/base pair formation between well-defined bismuth compounds and soft Lewis bases $\text{EPMe}_3$ (E = S, Se) and suggest an operationally simple method to establish trends in the softness of Lewis acidity.

## Results and Discussion

Cationic bismuth compounds show an enhanced Lewis acidity when compared with their neutral parent compounds. Cationic diaryl bismuth compounds are the most prominent subgroup of this family of compounds. They usually bind two equivalents of a Lewis base through their empty bismuth-centered 6p-orbital. We aimed at diaryl bismuth cations that preferentially bind one equivalent of a donor in order to allow direct comparison of a Lewis base through their empty bismuth-centered 6p-orbital with archetypical examples of Lewis acids based on group 13 elements. Recently reported cationic bismepines such as compound 1 appeared to be promising candidates, because the olefin bridge in the ligand backbone reduces the flexibility of the aryl groups and provides moderate steric shielding of the bismuth center (Scheme 1).\textsuperscript{12} While two equivalents of Lewis bases with a low steric profile (such as thf) interact with the bismuth atom in 1, sterically more demanding Lewis bases should make the generation of Lewis acid/base adducts with a 1:1 stoichiometry possible. In order to test for the potential of the Lewis acidic bismuth center in 1 to bind soft donors by substitution of the hard thf ligands, compound 1 was reacted with one equivalent of the phosphane chalcogenides $\text{EPMe}_3$ (E = S, Se; Scheme 1). Indeed, compounds $\text{2-SPMe}_3$ and $\text{2-SePMe}_3$ could be isolated in excellent yields of 87–91% as pale yellow solids. Adducts of bismuth compounds and phosphorus sulfides or selenides are extremely rare: compounds \[ \text{Bi}((\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_2)\text{Cl} \] ($\text{Bi}((\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_2)\text{Cl}$) have been reported.\textsuperscript{19} NMR spectroscopic data is not available for the former compound and only $^3\text{P}$ NMR chemical shifts (without $^1\text{J}_{\text{Ps}}$ coupling constants) are given for the latter two species, indicating a minor up-field shift of up to 3.7 ppm with respect to the free phosphane selenide, $\text{SeP}(\text{4-F-C}_6\text{H}_4)_3$.\textsuperscript{20} For compounds $\text{2-SPMe}_3$ and $\text{2-SePMe}_3$, the $^1\text{H}$ NMR spectra display resonances typical of a benzo group, plus a singlet in the olefinic region and a doublet for the methyl groups bound to phosphorus. In $^{13}\text{C}$ NMR spectra, the resonances of the ipso atoms (2-SPMe$_3$; 176.9 ppm; 2-SePMe$_3$; 162.9 ppm) are significantly up-field-shifted compared to 1 ($\delta = 193.9$ ppm) and close to those of the corresponding chlorobismepine $\text{Bi}((\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_2)\text{Cl}$ ($\delta = 172.9$ ppm),\textsuperscript{12} suggesting considerable Bi–S/Se bonding interactions in solution. This is further supported by large down-field shifts of the $^3\text{P}$ and $^{77}\text{Se}$ NMR spectroscopic resonances of these compounds when compared to the free phosphane chalcogenides ($^3\text{P}$ NMR: $\text{2-SePMe}_3$: 44.2 ppm; $\text{2-SePMe}_3$: 21.1 ppm; $\text{SPMe}_3$: 7.8 ppm; $^{77}\text{Se}$ NMR: $\text{2-SePMe}_3$: $-44.2$ ppm; $\text{2-SePMe}_3$: $-234.9$ ppm).\textsuperscript{21} A significant decrease of the $^1\text{J}_{\text{Ps}}$ coupling constant from 689 Hz in free $\text{SePMe}_3$\textsuperscript{21} to 488 Hz in the bismuth complex 2-SePMe$_3$ indicates weakening of the P–Se bond\textsuperscript{21,23} and is—to the best of our knowledge—the largest decrease reported for metal complexes of $\text{SePMe}_3$.\textsuperscript{24,26}

Single-crystal X-ray analyses were carried out for compounds $\text{2-SPMe}_3$ and $\text{2-SePMe}_3$, revealing an isostructural relationship (monoclinic space group P2$_1$/c with $Z = 4$ in both cases; Figure 1). The complexes crystallize as separated ion pairs (i.e., Figure 1). Molecular structures of $[\text{Bi}((\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_2)(\text{EPMe}_3)]^{+}[\text{SbF}_6]^{-}$ in the solid state: a) E = S: $\text{2-SPMe}_3$; b) E = Se: $\text{2-SePMe}_3$. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and a lattice-bound CH$_2$Cl$_2$ molecule in the structure of 2-SPMe$_3$ are omitted for clarity. Selected bond lengths (Å) and bond angles (°): $\text{2-SPMe}_3$: Bi1–C1, 2.248(5); Bi1–C14, 2.246(5); Bi1–S1, 2.6105(16); P1–S1, 2.026(2); C1–Bi1–C14, 85.12(2); C1–Bi1–S1, 90.59(15); C14–Bi1–S1, 88.81(14); Bi1–S1–P1, 106.12(8); $\text{2-SePMe}_3$: Bi1–C1, 2.237(4); Bi1–C14, 2.240(4); Bi1–Se1, 2.722(4); P1–Se1, 2.1889(11); C1–Bi1–C14, 87.77(13); C1–Bi1–Se1, 91.24(10); C14–Bi1–Se1, 92.08(10); Bi1–Se1–P1, 100.31(3). The Bi1–S1/Se1

![ Molecular structures of $[\text{Bi}((\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_2)(\text{EPMe}_3)]^{+}[\text{SbF}_6]^{-}$ in the solid state: a) E = S: $\text{2-SPMe}_3$; b) E = Se: $\text{2-SePMe}_3$. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and a lattice-bound CH$_2$Cl$_2$ molecule in the structure of 2-SPMe$_3$ are omitted for clarity. Selected bond lengths (Å) and bond angles (°): $\text{2-SPMe}_3$: Bi1–C1, 2.248(5); Bi1–C14, 2.246(5); Bi1–S1, 2.6105(16); P1–S1, 2.026(2); C1–Bi1–C14, 85.12(2); C1–Bi1–S1, 90.59(15); C14–Bi1–S1, 88.81(14); Bi1–S1–P1, 106.12(8); $\text{2-SePMe}_3$: Bi1–C1, 2.237(4); Bi1–C14, 2.240(4); Bi1–Se1, 2.722(4); P1–Se1, 2.1889(11); C1–Bi1–C14, 87.77(13); C1–Bi1–Se1, 91.24(10); C14–Bi1–Se1, 92.08(10); Bi1–Se1–P1, 100.31(3). ](image-url)
bond length of 2.61 Å and 2.72 Å are 31–33% below the sum of the van der Waals radii (S, 1.80 Å; Se, 1.90 Å; Bi, 2.07 Å). They are much shorter than the corresponding bonds in the literature-known adducts \([\text{Bi}(\text{SC}_{6}\text{F}_{5})_{3}(\text{SPh}_{3})] (\text{Bi-S/Se}) 3.01 \text{ Å})\) and \([\text{BiX}_{3}(\text{SeP(4-F-C}_{6}\text{H}_{4})_{3})] (\text{X} = \text{Cl}; \text{Br}; \text{Bi-Se}, 3.35–3.37 \text{ Å})\). In fact, they are in the range of values reported for regular covalent Bi−S/Se bonds in compounds of type Bi(aryl)\(_{2}\)(EPPh) \(E = 5\): 2.54–2.63 Å; \(E = \text{Se}: 2.70–2.73 \text{ Å}\).[30–32] In agreement with these findings, the P1–S1/S1 bonds in 2-SePMe\(_{3}\) (2.03 Å) and 2-SePMe\(_{3}\) (2.19 Å) are significantly elongated as compared to those in SPMe\(_{3}\) (1.97 Å, Supporting Information) and SePMe\(_{3}\) (2.12 Å, Supporting Information).[33] This effect is more pronounced in 2-SePMe\(_{3}\) than in literature-known metal complexes with terminal SPMe\(_{3}\) ligands that have been crystallographically characterized \((M = \text{Cr}, \text{Fe}, \text{Cu}, \text{In})\).[34] 2-SePMe\(_{3}\) is the first complex of the SePMe\(_{3}\) ligand that has been crystallographically characterized so that no direct comparison is possible.

The spectroscopic and structural analyses of 2-EPMe\(_{3}\) revealed considerable bonding interactions between the Lewis acidic bismuth atoms in these compounds and the soft Lewis bases EPMe\(_{3}\) \((E = \text{S}, \text{Se})\). With its large, diffuse, and polarizable S, Se bonds in compounds of type Bi(aryl)\(_{2}\)(EPPh) \((E = \text{S}, \text{Se})\), this is further supported by a single-crystal X-ray analysis of \([\text{BiPh}_{2}(\text{thf})_{2}][\text{SbF}_{6}]\) (4), which allows binding of two equivalents of a Lewis base[42] rather than only one as in 2-SePMe\(_{3}\). This is further supported by a single-crystal X-ray analysis of \([\text{BiPh}_{2}(\text{SePMe}_{3})_{2}][\text{SbF}_{6}]\), obtained from reaction of 4 with one equiv SPMe\(_{3}\), (Supporting Information).

Table 1. Investigations of potential Lewis acids with the modified Gutmann–Beckett method, using SPMe\(_{3}\) as a donor.

| Entry | Compound | \(\delta^{31}\text{P NMR} \text{ppm}\) | AN \((\text{SPMe}_{3})\) |
|-------|----------|-----------------|----------------|
| 1     | 4        | 44.0            | 95             |
| 2     | 2-SPMe\(_{3}\) | 44.2[c]        | 96             |
| 3     | 1        | 40.8            | 74             |
| 4     | 1        | 35.8            | 42             |
| 5     | 1        | 35.8            | 42             |
| 6     | 1        | 35.8            | 42             |
| 7     | 1        | 35.8            | 42             |
| 8     | 1        | 35.8            | 42             |
| 9     | 1        | 35.8            | 42             |
| 10    | 1        | 35.8            | 42             |
| 11    | 1        | 35.8            | 42             |
| 12    | 1        | 35.8            | 42             |
| 13    | 1        | 35.8            | 42             |
| 14    | 1        | 35.8            | 42             |
| 15    | 1        | 35.8            | 42             |
| 16    | 1        | 35.8            | 42             |
| 17    | 1        | 35.8            | 42             |
| 18    | 1        | 35.8            | 42             |
| 19    | 1        | 35.8            | 42             |
| 20    | 1        | 35.8            | 42             |
| 21    | 1        | 35.8            | 42             |
| 22    | 1        | 35.8            | 42             |
| 23    | 1        | 35.8            | 42             |
| 24    | 1        | 35.8            | 42             |

[a] if not otherwise noted, CD\(_{2}\)Cl\(_{2}\) solutions of equimolar amounts of the potential Lewis acid and SPMe\(_{3}\) were investigated at 23 °C (for details see experimental part). [b] determined according to equation 2 (see text). [c] dianion \([-\text{Bi}(\text{SPh}_{3})_{2}][\text{SbF}_{6}]\) as in compound 1; that is, \([\text{Bi}(\text{SPh}_{3})_{2}][\text{SbF}_{6}]\) corresponds to a cationic dibenzobismepine complex fragment.[36] [d] small amounts of THF were added to fully solubilize 3 \((\text{CD}_{2})\text{Cl}_{2}/\text{THF} = 25:1, \text{v/v})\.

[8] obtained from NMR spectroscopic analysis of isolated 2-SPMe\(_{3}\) in \((\text{CD}_{2})\text{Cl}_{2}\). [f] py = pyridine.
In order to allow a discussion of Bi-SPMe₃ interactions in the broader context of Lewis acidity, Me₃SiOTf, B(C₆F₅)₃, and AlCl₃ were chosen as typical examples of frequently applied, (relatively) hard Lewis acids and investigated with the modified GB method (for further examples see Supporting Information). It should be noted that for cationic Me₃SiOTf an extraordinarily broad Lewis acid/base interactions (AN (SePMe₃) = 7.8) was observed for compound 1 and 3 were obtained for the boron and the aluminum compound, respectively (entries 16, 17), which are significantly lower than those of the bismuth species 1, 2-SPMe₂, and 4 (entries 12–14). It should be noted that compound 1 contains two equivalents of thf and that the addition of 1 equiv SPMe₃ to a solution of 1 gave an acceptor number which is virtually identical to that of isolated 2-SPMe₂ (entries 12, 13). In other words, the softer donor SPMe₃ can efficiently displace two equivalents of the harder donor thf from the coordination sphere of the bismuth atom in 1. In order to evaluate the preference of the harder Lewis acids B(C₆F₅)₃ and AlCl₃ for either thf or SPMe₃, samples containing one equivalent of the Lewis acid, one equivalent of thf, and one equivalent of SPMe₃ were investigated. Acceptor numbers AN (SPMe₃) of 1 and 3 were obtained (entries 19, 20), demonstrating that the softer donor SPMe₃ cannot compete with the harder donor thf for the relatively hard binding sites in B(C₆F₅)₃ and AlCl₃.

The preference to bind a soft donor SPMe₃ or a hard donor such as pyridine was also compared for compound 2-SPMe₂ and Gal₃. While Gal₃ showed only a minor acceptor number of 6 in the presence of one equivalent of pyridine, significant acceptor numbers of 74 and 42 were obtained for compound 2-SPMe₂ in the presence of one and two equivalents of pyridine, respectively (entries 22–24). Only with a large (>20-fold) excess of pyridine, values of AN (SPMe₃) < 10 were observed for compound 2-SPMe₂ (for titration experiments see Supporting Information).

With SePMe₃ as a Lewis base, the trends were similar to those observed for SPMe₃. Aryl bismuth compounds, halobismepines, and in this case even all bismuth halides BiX₃ (X = Cl–I) showed acceptor numbers suggesting weak or even negligible Lewis acid/base interactions (AN (SePMe₃) = 0–14; Table 2, entries 2–9). For the bismuth triflates Bi(OTf)₃ and 3, acceptor numbers of AN (SePMe₃) = 46 and 61 demonstrate significant Bi–SePMe₃ bonding (entries 10, 11). For Bi(OTf)₃, extended reaction times led to the appearance of an additional resonance in the ³¹P NMR spectrum, which is not due to a simple 1:1 adduct and is tentatively ascribed to the formation of [Bi(SePMe₃)₃][OTf] (Supporting Information). High acceptor numbers of 65–76 were obtained for cationic bismuth compounds 1, 2-SePMe₃, and 4, indicating considerable interactions with SePMe₃ (entries 12–14).

Analysis of Me₃SiOTf, B(C₆F₅)₃, and AlCl₃ with the modified GB method revealed that the Si species shows a negligible acceptor number, while the B and the Al compound show moderate to high acceptor numbers towards the soft donor SePMe₃ (entries 15–17). But in contrast to the bismuth cation 1 (entries 12, 13), the presence of one equivalent of the hard donor thf leads to negligible B/Al–SePMe₃ interactions, as judged from acceptor numbers of only 1 in both cases (entries 19, 20). Similar results were obtained for competition experiments with Gal₃ and 2-SePMe₃ as Lewis acids and pyridine and SePMe₃ as Lewis bases. Gal₃ showed a minor acceptor number of 7 in the presence of pyridine, while acceptor numbers of 50 and 43 indicate significant Bi–SePMe₃ interactions for 2-SePMe₃ in the presence of one and two equivalents of pyridine, respectively (entries 22–24). A large (>20-fold) excess of pyridine was necessary to lower the acceptor number AN (SePMe₃) to an insignificant value of 2 for compound 2-SePMe₃ (for titration experiments see Supporting Information).

Major findings from our studies of bismuth-centered Lewis acidity based on the GB method (previous work[21] and Supporting Information) and modified versions thereof (this work) are summarized in Figure 2. As a trend it is apparent that bismuth Lewis acids of class A[12] with a n°(Bi-X) acceptor orbital (cf. introduction)[12] show moderate Lewis acidities towards the

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### Table 2. Investigations of potential Lewis acids with the modified Gutmann–Beckett method, using SePMe₃ as a donor.

| Entry | Compound | δ ¹³P (ppm)[a] | AN (SePMe₃)[b] |
|-------|----------|---------------|----------------|
| 1     | SePMe₃   | 7.8           | 0 (by definition) |
| 2     | BiPh₃    | 8.9           | 6              |
| 3     | Bi(dialky)Cl[c] | 7.8 | 0  |
| 4     | Bi(dialky)Br[d] | 9.0 | 7.7 |
| 5     | Bi(dialky)I[e] | 8.4 | 3.6 |
| 6     | Bi(dialky)[g] | 0.0 | 1  |
| 7     | BCl₃     | 10.3          | 14             |
| 8     | BiF₃     | 9.7           | 11             |
| 9     | Bi₂O    | 9.5           | 10             |
| 10    | Bi(OTf)₂ | 15.8[f]      | 46             |
| 11    | Bi(OTf)(OTf)[j] | 15.8[j] | 46 |
| 12    | 1       | 19.2          | 65             |
| 13    | 2-SePMe₃ | 21.1[k]      | 76             |
| 14    | [BiPh₃(thf)][Sbf₆] (4) | 20.5 | 73 |
| 15    | Me₃SiOTf | 7.8           | 1              |
| 16    | B(C₆F₅)₃ | 13.0          | 30             |
| 17    | AlCl₃    | 20.5          | 73             |
| 18    | Gal₃     | 25.3          | 100 (by definition) |
| 19    | B(C₆F₅)(thf) | 7.9 | 1  |
| 20    | AlCl₃(thf) | 8.0 | 1  |
| 21    | Gal₃(thf) | 24.2          | 94             |
| 22    | Gal₃(py)[l] | 9.0 | 7  |
| 23    | 2-SePMe₃ + py[k] | 16.5 | 50 |
| 24    | 2-SePMe₃ + 2 py[k] | 15.3 | 43 |

[a] If not otherwise noted, CDCl₃ solutions of equimolar amounts of the potential Lewis acid and SePMe₃ were investigated at 23 °C (for details see experimental part). [b] determined according to equation 3 (see text). [c] dialky = [(C₆H₄)(C(H)₂)₃] as in compound 1; that is, [Bi(dialky)]⁻ corresponds to a cationic dibenzobismepine complex fragment[12] [d] An additional resonance is detected after extended reaction times (for discussion see text and Supporting Information). [e] small amounts of THF were added to fully solubilize 3 (CDCl₃/THF = 25:1, v/v). [f] obtained from NMR spectroscopic analysis of isolated 2-SePMe₃ in CDCl₃. [g] py = pyridine.

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strong and hard donor OPEt₃, but only relatively low Lewis acidities towards weaker and softer donors SPMe₃ and SePMe₃. In contrast, bismuth Lewis acids of class C [12] with an empty 6p(Bi) acceptor orbital show a considerable Lewis acidity towards all three types of donors. It is especially remarkable that (in contrast to Me₃SiOTf, B(C₆F₅)₃, and AlCl₃) cationic bismuth compounds of class C maintain an extraordinary Lewis acidity towards the soft donors SPMe₃ and SePMe₃ even in the presence of a hard donor such as thf and pyridine.

DFT calculations and natural bond orbital (NBO) analyses were performed in order to characterize the Bi–S/Se interactions in compounds 2-EPMe₃ in more detail (E = S, Se; for details see experimental and Supporting Information). The bismuth Lewis acidic component in these complexes is the (so far non-isolable) low-valent bismepine cation [Bi((C₆H₄)₂C₂H₂)][SbF₆]. A frontier orbital analysis of this species was carried out, with its conformation fixed to that found in the optimized structure of the adduct 2-SePMe₃. The LUMO of [Bi((C₆H₄)₂C₂H₂)][SbF₆] is best described as an empty bismuth 6p-orbital with only minor contributions from other atomic orbitals (Figure 3 a). The bent conformation of the bismepine core results in steric protection of one lobe of the LUMO by the olefinic functional group of the ligand backbone. This should favor adduct formation in a 1:1 stoichiometry with donors that have at least a moderate steric load, as experimentally observed for 2-SPMe₃ and 2-SePMe₃. Theoretical analysis of 2-SPMe₃ and 2-SePMe₃ indicate that the Bi–S/Se interactions can be interpreted as regular covalent bonds, the NBOs of which are mainly composed of bismuth 6p atomic orbitals and 3/4p S/Se atomic orbitals and strongly polarized towards the chalcogen (S: 79.9%; Se: 78.0%). [44] The molecular orbitals with significant Bi–S/Se bonding contributions are the HOMO–5 (only for 2-SePMe₃) as well as the HOMO–6 and HOMO–7 (for 2-SPMe₃ and 2-SePMe₃), which are mainly composed through linear combinations of NBOs associated with Bi–S/Se (5–25%) and Bi–C bonds (8–29%) as well as Bi (10%) and S/Se lone pairs (7–32%) (Figure 3 b and Supporting Information). In agreement with these results, natural resonance theory (NRT) revealed exclusively resonance structures featuring R₂Bi-(S/Se)-P⁺Me₃ structural motifs (with mesomeric effects
being relevant only within the bismpine core and the (SbF₆⁻) anion; resonance structure of the cations shown in Figure 3c). According to NRT, the Bi–S/Se single bonds are generated through 40%/44% covalent and 60%/56% ionic contributions. This is in agreement with large Wiberg bond indices of 0.61 (Bi–S) and 0.65 (Bi–Se) for these bonds.

Thermodynamic parameters of adduct formations between EPMe₃ and Lewis acids based on bismuth and group 13 elements (B–Ga) were determined (E = O, S, Se; Table 3 ([G] values and Supporting Information ([H] values and additional examples)). Starting from coordinatively unsaturated Lewis acids, the adduct formations are strongly exergonic ([G] = −20 to −45 kcal mol⁻¹) for all compounds but B(C₆F₅)₃, which shows a mildly exergonic reaction with OPMe₃ and endergonic reactions with S/SePMes (entries 1–6, for [H] values see Supporting Information).[43] Most importantly, reactions of all the group 13 compounds become less exergonic (or even endergonic) upon changing the Lewis base from OPMe₃ to S/SePMes (entries 1–5). The opposite behavior is observed for the cationic bismuth species (entry 6), underlining its soft character according to the HSAB principle.

In order to evaluate trends in the ability of donors EPMe₃ to displace one or two thf ligands from the coordination sphere of coordinately saturated Lewis acids (from a thermodynamic point of view), reactions with compounds [LA]−(thf)ₙ⁻, were investigated ([LA]⁻ = Lewis acid; n = 1–2). With the exception of B(C₆F₅)₃ (entry 7), exergonic reactions are observed for the group 13 compounds with OPMe₃ ([G] = −10 to −11 kcal mol⁻¹, n = 1; entries 8–11), while those with bismuth compounds are clearly exergonic for n = 1 and marginally endergonic for n = 2 ([G] = −12.4 and +0.3 kcal mol⁻¹; entries 12,13). Ligand substitutions with S/SePMes at the hard aluminum center are endergonic by 8 to 9 kcal mol⁻¹ (entry 8). For the softer gallium compounds, substitution of thf by S/SePMes is marginally exergonic ([G] = +3 to +5 kcal mol⁻¹, n = 1; entries 9–11). For the bismuth cations, these reactions are clearly exergonic for n = 1 ([G] = −17 to −19 kcal mol⁻¹, entry 12) and still slightly exergonic for n = 2 ([G] = −5 to −6 kcal mol⁻¹, entry 13). These trends are in good agreement with experimental results obtained from the modified GB method.[43]

**Conclusions**

The ability of bismuth(III) compounds to form Lewis acid/base adducts with the soft donors EPMe₃ has been investigated (E = S, Se). Cationic bismuth compounds [BiR₂(EPMe₃)][SbF₆] featuring rare Bi–EPR₃ bonding with strong covalent contributions that persists in the solid state and in solution. The ¹⁹F NMR chemical shift of EPMe₃ in the presence of a compound “LA” may be used as an easily accessible experimental parameter to investigate the Lewis acidity of LA. In specific, we suggest the utilization of soft donors such as EPMe₃ in order to assess the hardness/softness of a Lewis acid. This is equivalent to an extension of the Gutmann–Beckett method. We have investigated bismuth compounds of type BiR₂, BiR₃X, BiX₃, and [BiR₃]⁺ with this approach, delivering experimental evidence for their Lewis acidity. Especially cationic bismuth species [BiR₃]⁺ that interact with the donor through an empty p-orbital (not through a σ-orbital) are potent soft Lewis acids. In contrast to well-established, relatively hard Lewis acids such as Me₅SiOTf, B(C₆F₅)₃, and AlCl₃ and the softer Lewis acid GaL₆, they can still efficiently activate soft donors in the presence of hard donors such as thf and pyridine (cf. Figure 2). Future research efforts will be directed towards the exploitation of these findings in the activation of substrates with soft donor functionalities for stoichiometric and catalytic transformations.

### Experimental Section

**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 400 or 500 MHz with respect to ¹H. ¹⁹F and ³¹C NMR chemical shifts are reported relative to SiMe₃ using the residual ¹H and ¹³C chemical shifts of the solvent as a secondary standard. ¹⁹F and ³¹C NMR chemical shifts are reported relative to H₂PO₄ (85% aqueous solution) and SeMe₆ (plus 5% C₆D₆) as external standards. NMR spectra were recorded at ambient temperature (typically 23°C), if not otherwise noted. Elemental analyses were performed on a Leco or a Carlo Erba instrument. 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 (λ = 0.71073 Å). The structures were solved using intrin-

**Table 3. Calculated free reaction enthalpy of Lewis pair formation with varying Lewis acids and donors EPMe₃ (E = O, S, Se) in the presence of 0–2 equivalents of thf.**

| Entry | [LA]⁻ | (thf)ₙ⁻ | + E=EPMe₃ | [LA]⁻–E=EPMe₃₁ | n | [G] (kcal mol⁻¹) |
|-------|-------|--------|----------|-----------------|---|-----------|
| 1     | B(C₆F₅)₃ | 0      | 0         | 0               | 0 | +16.7     |
| 2     | 1      | 0.7    | 1         | 1               | 0 | +18.3     |
| 3     | 1      | 1.0    | 0         | 0               | 0 | +20.0     |
| 4     | 0      | −37.7  | 0         | 0               | 0 | −23.3     |
| 5     | 0      | −32.7  | 0         | 0               | 0 | −19.5     |
| 6     | 0      | −38.6  | 0         | 0               | 0 | −44.8     |
| 7     | 0      | +8.8   | 0         | 0               | 0 | +27.9     |
| 8     | 1      | 10.8   | 1         | 1               | 1 | +9.1      |
| 9     | 0      | 10.4   | 0         | 0               | 0 | +4.8      |
| 10    | 0      | −10.9  | 0         | 0               | 0 | −2.5      |
| 11    | 0      | −10.3  | 0         | 0               | 0 | +2.9      |
| 12    | 0      | −12.4  | 1         | 1               | 1 | −18.6     |
| 13    | 0      | +0.3   | 2         | 2               | 2 | −5.9      |

[a] diaryl = [(C₆H₅)₂C₆H₄]⁺; that is, [LA]⁻ = [Bi(diaryl)][SbF₆]⁻ with two thf ligands (n = 2) corresponds to compound 1.
sic phasing methods (SHELXT) completed by Fourier synthesis and refined by full-matrix least-squares procedures. Deposition Numbers 1961401, 1961402, 1961405, 1961406, 1961407, and 1994719, 1994720, 1994721 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

DFT calculations were performed with the Gaussian program[46] using the 6-31G(d,p) [47] [H, C, N, O, F], 6–311G(d,p) [48] [Al, P, S], and the LANL2DZ[49] [Ga, In, Se, Sb, Bi, Br, I] basis set and the B3LYP functional.[50] The D3 version of Grimme’s dispersion model with the original D3 damping function was applied.[51] Frequency analyses of the reported structures showed no imaginary frequencies for ground states. 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.[52]

The following labeling Scheme has been used for the assignment of atoms to resonances detected in NMR spectroscopic experiments:

[BI([C6H4]C6H4)3PMe3][SbF6] (2-PMe3): To a solution of [BI([C6H4]C6H4)3(thf)][SbF6] (1) (30.0 mg, 39.1 μmol) in CH2Cl2 (0.7 mL) was added PMe3 (4.2 mg, 39.1 μmol) at ambient temperature. The light yellow solution was layered with n-pentane (0.7 mL) and stored at −30 °C. A pale yellow solid had precipitated after 1 d, was isolated by filtration, and dried in vacuo. Yield: 26.0 mg, 85 %. 1H NMR (400 MHz, CD2Cl2): δ = 2.23 (d, 9 H, JHH = 19.1 Hz, 3 *-C6H5), 129.61 (s, H-4, H-11), 132.24 (s, C-3, C-12), 133.49 (s, C-7, C-8), 135.91 (s, C-5, C-10), 136.77 (s, C-2, C-13), 143.49 (s, C-6, C-9), 152.35 (s, C-1, C-14) ppm. 13C NMR (100 MHz, CD2Cl2): δ = 44.2 (s) ppm. 13P NMR (100 MHz, CD2Cl2): δ = −1.8 ppm. 31P NMR (100 MHz, CD2Cl2): δ = −1.8 ppm.

[BI([C6H4]C6H4)3SePMe3][SbF6] (3-SePMe3): To a solution of [BI([C6H4]C6H4)3(thf)][SbF6] (1) (200.0 mg, 26.1 μmol) in CH2Cl2 (0.5 mL) was added SePMe3 (42.2 mg, 26.1 μmol) at ambient temperature. The light yellow solution was layered with n-pentane (0.7 mL) and stored at −30 °C. A pale yellow solid had precipitated after 1 d, was isolated by filtration, and dried in vacuo. Yield: 180.0 mg, 23.1 μmol, 87 %. 1H NMR (500 MHz, CD2Cl2): δ = 2.23 (d, 9 H, JHH = 13.4 Hz, 3 *-C6H5), 7.43 (s, 2 H, C-7, C-8), 8.18 (dd, 2 H, JHH = 1.3 Hz, JPH = 7.4 Hz, C-2, C-13) ppm. 13C NMR (100 MHz, CD2Cl2): δ = −1.8 ppm. 31P NMR (100 MHz, CD2Cl2): δ = −2.23 (d, 9 H, JHH = 13.4 Hz, 3 *-C6H5), 7.43 (s, 2 H, C-7, C-8), 8.18 (dd, 2 H, JHH = 1.3 Hz, JPH = 7.4 Hz, C-2, C-13) ppm. 13C NMR (100 MHz, CD2Cl2): δ = 71.12 (s, C-6, C-10), 129.61 (s, H-4, H-11), 132.95 (s, C-7, C-8), 135.91 (s, C-5, C-10), 136.95 (s, C-2, C-13), 146.21 (s, C-6, C-9), 176.86 (br, C-1, C-14, detected via 13C NMR) ppm. 13C NMR (100 MHz, CD2Cl2): δ = 44.2 (s) ppm. 13P NMR (100 MHz, CD2Cl2): δ = −1.8 ppm. 31P NMR (100 MHz, CD2Cl2): δ = −1.8 ppm.

[BI([C6H4]C6H4)3(thf)][SbF6] (4): To a solution of diphenylbismuth chloride (50.0 mg, 0.13 mmol) in THF (1 mL) was added a solution of AgSbF6 (43.1 mg, 0.13 mmol) in THF (0.5 mL). The colorless suspension was filtered. The filtrate was layered with n-pentane (1.5 mL) and stored at −30 °C. The product was obtained after 2 d by filtration, and dried in vacuo. Yield: 83 mg, 0.11 mmol, 86 %. 1H NMR (500 MHz, CD2Cl2): δ = 1.82 (m, 4 H, JHH = 3.7 Hz, 3 *-thf), 7.38 (m, 4 H, α-thf), 7.58–7.69 (m, 2 H, p-C6H4), 8.02 (dd, 4 H, JHH = 6.6 Hz, JPH = 6.6 Hz, o-C6H4), 8.47 (d, 4 H, JHH = 6.9 Hz, m-C6H4) ppm. 13C NMR (126 MHz, CD2Cl2): δ = 143.49 (s, 1 *-C6H5), 7.43 (d, 2 H, JHH = 1.1 Hz, JPH = 7.7 Hz, H-3, C-12), 7.63 (d, 2 H, JHH = 1.1 Hz, JPH = 7.7 Hz, H-2, C-13) ppm. 13C NMR (126 MHz, CD2Cl2): δ = 143.49 (s, 1 *-C6H5), 7.43 (d, 2 H, JHH = 1.1 Hz, JPH = 7.7 Hz, H-3, C-12), 7.63 (d, 2 H, JHH = 1.1 Hz, JPH = 7.7 Hz, H-2, C-13) ppm. 13C NMR (126 MHz, CD2Cl2): δ = 143.49 (s, 1 *-C6H5), 7.43 (d, 2 H, JHH = 1.1 Hz, JPH = 7.7 Hz, H-3, C-12), 7.63 (d, 2 H, JHH = 1.1 Hz, JPH = 7.7 Hz, H-2, C-13) ppm. 13C NMR (126 MHz, CD2Cl2): δ = 143.49 (s, 1 *-C6H5), 7.43 (d, 2 H, JHH = 1.1 Hz, JPH = 7.7 Hz, H-3, C-12), 7.63 (d, 2 H, JHH = 1.1 Hz, JPH = 7.7 Hz, H-2, C-13) ppm.

General procedure for modified Gutmann–Beckett method

If not otherwise noted, equimolar amounts of the potential Lewis acid and the Lewis base EPMe3 were dissolved in dichloromethane (E = S, Se). In competition experiments, the required amount of another Lewis base was added (the sequence of addition was not relevant; see Supporting Information). One of the following three different methods was used for the determination of accurate 31P NMR chemical shifts: i) the use of CD3Cl as the solvent, so that locking and shifting was possible; ii) the use of CH3Cl as the solvent along with a capillary containing deuterated acetone, so that locking and shifting was possible; iii) the use of CH2Cl2 as the solvent along with a capillary containing an 85 % aqueous solution of H3PO4 as a reference. The three methods gave identical results, when applied to identical samples. For details see Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: bismuth · bonding analysis · cationic species · HSAB principle · Lewis acids

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For bismuth(III) compounds, dispersion interactions through the lone

\[ \text{Bi} \rightarrow \text{Bi} \]  

are reported. For instance, the observation of an up-field rather than the expected down-field shift upon coordination of \( \text{SeF}(4\text{Cl}-\text{B}) \) to \( \text{BiCl}_3 \) and \( \text{BiBr}_3 \) is discussed in ref. [19].

The observation of a up-field shift rather than the expected down-field shift upon coordination of \( \text{SeF}(4\text{Cl}-\text{B}) \) to \( \text{BiCl}_3 \) and \( \text{BiBr}_3 \) is discussed in ref. [19].

It should be noted that no correlation between the magnitude of \( \Delta_{\text{BDD}} \) and the calculated homolytic P–Se bond dissociation energy could be found in a series of free phosphane selenides: S. R. Alvarado, I. A. Skert, H. J. Vela, Organometallics 2015, 34, 4023–4031.

The single-crystal X-ray analysis of \( \text{SePMe_3} \) was reported in the literature [ref. (21a)] and carried out at ambient temperature. We repeated the analysis at a temperature of 100 K for better comparison (Supporting Information).

The observation of an up-field rather than the expected down-field shift upon coordination of \( \text{SeF}(4\text{Cl}-\text{B}) \) to \( \text{BiCl}_3 \) and \( \text{BiBr}_3 \) is discussed in ref. [19].

Effects such as a lack of efficient Lewis pair formation between OPEt \( 3^- \) and \( \text{Bi} \) were found in a series of free phosphane selenides: S. R. Alvarado, I. A. Skert, H. J. Vela, Organometallics 2015, 34, 4023–4031.

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For bismuth(III) compounds, dispersion interactions through the lone pair at bismuth and the π electrons of arenes have been investigated, which is not in focus of this contribution and are therefore not discussed in detail (e.g.: I. Caraceli, I. Haiduc, J. Zuckerman-Schpector, E. R. Tieckel, Coord. Chem. Rev. 2013, 257, 2863–2879; also see ref. [13a–c]).

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[37] It should be noted that the Gutmann–Beckett method (and modifications thereof) provide an estimate of the Lewis acidity of the compound under investigation by assessing the polarizability of the $E=PR_3$ bond through $^{31}P$ NMR spectroscopic measurements ($E=O$ (original method); $S, Se$ (modifications)). Being based on NMR spectroscopy, effects such as magnetic anisotropy of the Lewis acid (or substituents $R$ in $EPR_3$) may influence the results (see ref. [36]).

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[41] Note that small amounts of THF had to be added in order to fully solubilize compound 3. The nature of the solvents used may have an impact of the acceptor numbers $AN(SPMe_3)$ and $AN(SePMe_3)$.

[42] It should be noted that entropic effects, which are relevant in reactions "$[LA](thf)_n + EPMe_3 \rightarrow [LA](EPMe_3)_n + n$ thf$"$ for $n=0$ and $n=2$, but not for $n=1$, may be overestimated by DFT methods. For $\Delta H$ values of these reactions see Supporting Information.

[43] Even solutions of compound 2-SePMe$_3$ in THF gave an acceptor number of $AN(SePMe_3)=65$.

[44] NBO analyses indicate that olefin $\rightarrow$ Bi donor/acceptor interactions are present in 2-SPMe$_3$ and 2-SePMe$_3$ and realized through $\pi(C=C) \rightarrow \sigma*(Bi-S/Se)$ interactions. The corresponding deletion energies amount to 2.9 kcal mol$^{-1}$ for 2-SPMe$_3$ and 3.1 kcal mol$^{-1}$ for 2-SePMe$_3$, which is in the range of those reported for the corresponding halobismepines ($\Delta_{dss}=2.6–2.9$ kcal mol$^{-1}$; ref. [12]).

[45] It should be noted that entropic effects, which are relevant in reactions "$[LA](thf)_n + EPMe_3 \rightarrow [LA](EPMe_3)_n + n$ thf$"$ for $n=0$ and $n=2$, but not for $n=1$, may be overestimated by DFT methods. For $\Delta H$ values of these reactions see Supporting Information.

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