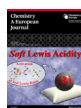


**Lewis Acids** | *Very Important Paper*
**VIP** **Molecular Bismuth Cations: Assessment of Soft Lewis Acidity**

 Jacqueline Ramler and Crispin Lichtenberg\*<sup>[a]</sup>


**Abstract:** Three-coordinate cationic bismuth compounds [Bi(diaryl)(EPM<sub>3</sub>)]<sup>+</sup>[SbF<sub>6</sub>]<sup>-</sup> have been isolated and fully characterized (diaryl = [(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>H<sub>2</sub>]<sup>2+</sup>, E = S, Se). They represent rare examples of molecular complexes with Bi⋯EPR<sub>3</sub> interactions (R = monoanionic substituent). The <sup>31</sup>P NMR chemical shift of EPM<sub>3</sub> has been found to be sensitive to the formation of LA⋯EPM<sub>3</sub> 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 orga-

nobismuth 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.<sup>[1]</sup> 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),<sup>[1b,2]</sup> addition reactions (such as hydroamination, hydrosilylation, and carbo/amino-bismuthation),<sup>[1a-c,3]</sup> addition-elimination sequences (such as aldol and Mannich reactions),<sup>[1a-c,4]</sup> electrophilic aromatic substitution reactions (such as Friedel Crafts alkylations and acylations),<sup>[1a-c,2b,5]</sup> S<sub>N</sub>i type reactions (such as dehydro-halogenation reactions),<sup>[1c,6]</sup> CH activation (such as the metalation of (C<sub>5</sub>H<sub>5</sub>)<sup>-</sup>, (C<sub>5</sub>H<sub>4</sub>Me)<sup>-</sup>, (NAr<sub>2</sub>)<sup>-</sup>),<sup>[7]</sup> and small-molecule activation (such as carbon monoxide insertion).<sup>[8]</sup> The utilization of bismuth Lewis acids can lead to selectivities and activities that are difficult or impossible to obtain with other reagents.<sup>[1b,2a,3a,9]</sup> In other cases bismuth compounds show advantages in terms of affordability, stability towards air and moisture, or functional group tolerance.<sup>[1,7d,e]</sup> In addition, prospects for catalyst recyclability have been demonstrated.<sup>[4b,10]</sup>

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.<sup>[11]</sup>

We have recently suggested a scheme for the classification of bismuth Lewis acids.<sup>[12]</sup> Distinctions are made between three types of compounds: class A) R<sub>2</sub>Bi-X with an electronegative ligand X; class B) R<sub>2</sub>Bi⋯X' with ligands X' such as (O<sub>3</sub>SCF<sub>3</sub>)<sup>-</sup> or (AlCl<sub>4</sub>)<sup>-</sup>, which lead to a weak Bi⋯X' interaction; and class C) cationic species [R<sub>2</sub>Bi(L)<sub>n</sub>][WCA] without any directional bonding interactions between bismuth and the weakly coordinating counteranion (WCA), for which [SbF<sub>6</sub>]<sup>-</sup> or [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> are typical examples. While σ\*(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.<sup>[13–17]</sup> 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.<sup>[1,3–5,7d,e,13–15]</sup>

In contrast to the frequent application of bismuth Lewis acids in synthesis and catalysis, efforts to quantify bismuth-

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based Lewis acidity have only scarcely been reported.<sup>[3b,12,18]</sup> More specifically, there are no detailed studies available that deal with the quantification of the hard or soft character of bismuth Lewis acids.

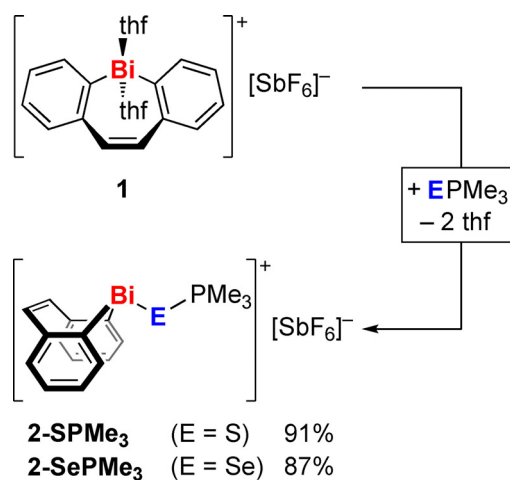
Here we report Lewis acid/base pair formation between well-defined bismuth compounds and soft Lewis bases  $\text{EPMe}_3$  ( $\text{E}=\text{S}, \text{Se}$ ) and suggest an operationally simple method to establish trends in the softness of Lewis acidity.

## Results and Discussion

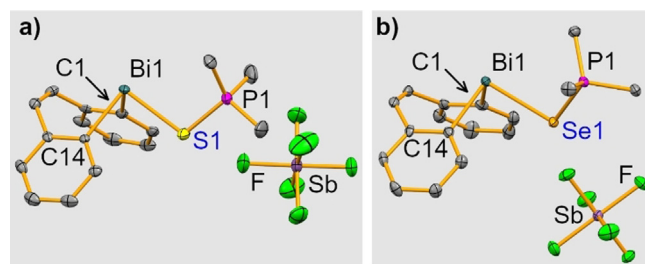
Cationic bismuth compounds show an enhanced Lewis acidity when compared with their neutral parent compounds. Cationic diaryl bismuth compounds are the most prominent subgroup of this family of compounds. They usually bind two equivalents of a Lewis base through their empty bismuth-centered  $6p$ -orbital. We aimed at diaryl bismuth cations that preferentially bind one equivalent of a donor in order to allow direct comparison 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).<sup>[12]</sup> 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  $\text{EPMe}_3$  ( $\text{E}=\text{S}, \text{Se}$ ; Scheme 1). Indeed, compounds **2-SPMe<sub>3</sub>** and **2-SePMe<sub>3</sub>** could be isolated in excellent yields of 87–91% as pale yellow solids. Adducts of bismuth compounds and phosphane sulfides or selenides are extremely rare: compounds  $[\text{Bi}(\text{SC}_6\text{F}_5)_3(\text{SPPH}_3)]$  and  $[\text{BiX}_3(\text{SeP}(4\text{-F-C}_6\text{H}_4)_3)]$  ( $\text{X}=\text{Cl}, \text{Br}$ ) have been reported.<sup>[19]</sup> NMR spectroscopic data is not available for the former compound and only  $^{31}\text{P}$  NMR chemical shifts (with-

out  $^1J_{\text{PSe}}$  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,  $\text{SeP}(4\text{-F-C}_6\text{H}_4)_3$ .<sup>[20]</sup> For compounds **2-SPMe<sub>3</sub>** and **2-SePMe<sub>3</sub>**, 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*-carbon atoms (**2-SPMe<sub>3</sub>**: 176.9 ppm; **2-SePMe<sub>3</sub>**: 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),<sup>[12]</sup> suggesting considerable  $\text{Bi}\cdots\text{S/Se}$  bonding interactions in solution. This is further supported by large down-field shifts of the  $^{31}\text{P}$  and  $^{77}\text{Se}$  NMR spectroscopic resonances of these compounds when compared to the free phosphane chalcogenides ( $^{31}\text{P}$  NMR: **2-SPMe<sub>3</sub>**: 44.2 ppm; **2-SePMe<sub>3</sub>**: 21.1 ppm;  $\text{SPMe}_3$ : 29.2 ppm;  $\text{SePMe}_3$ : 7.8 ppm;  $^{77}\text{Se}$  NMR: **2-SePMe<sub>3</sub>**:  $-44.2$  ppm;  $\text{SePMe}_3$ :  $-234.9$  ppm).<sup>[21]</sup> A significant decrease of the  $^1J_{\text{PSe}}$  coupling constant from 689 Hz in free  $\text{SePMe}_3$ <sup>[21]</sup> to 488 Hz in the bismuth complex **2-SePMe<sub>3</sub>** indicates weakening of the  $\text{P}\cdots\text{Se}$  bond<sup>[22,23]</sup> and is—to the best of our knowledge—the largest decrease reported for metal complexes of  $\text{SePMe}_3$ .<sup>[24,25]</sup>

Single-crystal X-ray analyses were carried out for compounds **2-SPMe<sub>3</sub>** and **2-SePMe<sub>3</sub>**, 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., without strong directional bonding interactions between cation and anion). The bismepine ligands adopt bent conformations with angles of  $88.7^\circ$  and  $76.5^\circ$  between the mean planes of the benzo groups, as recently reported for bismepines with three-coordinate bismuth atoms.<sup>[12]</sup> The bismuth atoms are found in pyramidal coordination geometries with bond angles around Bi1 ranging from  $85.1\text{--}90.6^\circ$  and  $87.8\text{--}92.1^\circ$  for **2-SPMe<sub>3</sub>** and **2-SePMe<sub>3</sub>**, respectively. A coordination number of three is extremely unusual for diorganobismuth cations, which commonly adopt coordination numbers of four with the empty  $6p$ -orbital of bismuth being involved in bonding interactions with two ligands.<sup>[3d,4,10,12,18,26–28]</sup> The  $\text{Bi1}\text{--S1/Se1}$



**Scheme 1.** Reaction of cationic bismepine **1** with soft donors  $\text{EPMe}_3$  to give compounds **2-EPMe<sub>3</sub>** through thf elimination ( $\text{E}=\text{S}, \text{Se}$ ).



**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)  $\text{E}=\text{S}$ : **2-SPMe<sub>3</sub>**; b)  $\text{E}=\text{Se}$ : **2-SePMe<sub>3</sub>**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and a lattice-bound  $\text{CH}_2\text{Cl}_2$  molecule in the structure of **2-SPMe<sub>3</sub>** are omitted for clarity. Selected bond lengths (Å) and bond angles ( $^\circ$ ): **2-SPMe<sub>3</sub>**:  $\text{Bi1}\text{--C1}$ , 2.248(6);  $\text{Bi1}\text{--C14}$ , 2.246(5);  $\text{Bi1}\text{--S1}$ , 2.6105(16);  $\text{P1}\text{--S1}$ , 2.026(2);  $\text{C1}\text{--Bi1}\text{--C14}$ , 85.1(2);  $\text{C1}\text{--Bi1}\text{--S1}$ , 90.59(15);  $\text{C14}\text{--Bi1}\text{--S1}$ , 88.81(14);  $\text{Bi1}\text{--S1}\text{--P1}$ , 106.12(8). **2-SePMe<sub>3</sub>**:  $\text{Bi1}\text{--C1}$ , 2.237(4);  $\text{Bi1}\text{--C14}$ , 2.240(4);  $\text{Bi1}\text{--Se1}$ , 2.7222(4);  $\text{P1}\text{--Se1}$ , 2.1889(11);  $\text{C1}\text{--Bi1}\text{--C14}$ , 87.77(13);  $\text{C1}\text{--Bi1}\text{--Se1}$ , 91.24(10);  $\text{C14}\text{--Bi1}\text{--Se1}$ , 92.08(10);  $\text{Bi1}\text{--Se1}\text{--P1}$ , 100.31(3).

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).<sup>[29]</sup> They are much shorter than the corresponding bonds in the literature-known adducts [Bi(SC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(SPPPh<sub>3</sub>)] (Bi–SPPPh<sub>3</sub>, 3.01 Å) and [BiX<sub>3</sub>(SeP(4-F-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)] (X = Cl, Br; Bi–Se, 3.35–3.37 Å).<sup>[19]</sup> In fact, they are in the range of values reported for regular covalent Bi–S/Se bonds in compounds of type Bi(aryl)<sub>2</sub>(EPH) (E = S: 2.54–2.63 Å; E = Se: 2.70–2.73 Å).<sup>[30–32]</sup> In agreement with these findings, the P1–S1/Se1 bonds in **2-SPMe<sub>3</sub>** (2.03 Å) and **2-SePMe<sub>3</sub>** (2.19 Å) are significantly elongated as compared to those in SPMe<sub>3</sub> (1.97 Å, Supporting Information) and SePMe<sub>3</sub> (2.12 Å, Supporting Information).<sup>[33]</sup> This effect is more pronounced in **2-SPMe<sub>3</sub>** than in literature-known metal complexes with terminal SPMe<sub>3</sub> ligands that have been crystallographically characterized (M = Cr, Fe, Cu, In).<sup>[34]</sup> **2-SePMe<sub>3</sub>** is the first complex of the SePMe<sub>3</sub> ligand that has been crystallographically characterized so that no direct comparison is possible.

The spectroscopic and structural analyses of **2-EPMe<sub>3</sub>** revealed considerable bonding interactions between the Lewis acidic bismuth atoms in these compounds and the soft Lewis bases EPMe<sub>3</sub> (E = S, Se). With its large, diffuse, and polarizable atomic orbitals, bismuth can indeed be expected to generate a soft Lewis acidity in its molecular complexes. Differences in the hardness/softness of Lewis acids have previously been discussed for small series of compounds such as B(C<sub>6</sub>F<sub>5</sub>)<sub>n</sub>(OC<sub>6</sub>F<sub>5</sub>)<sub>3–n</sub> (n = 0–3), where the choice of the method for quantification can strongly affect the outcome of the measurement (e.g., OPET<sub>3</sub> as a donor in the Gutmann–Beckett (GB)<sup>[35–37]</sup> method vs. crotonaldehyde as a donor in Childs<sup>[38]</sup> method).<sup>[39]</sup> To the best of our knowledge, however, attempts to assess the softness of a broader range of bismuth Lewis acids have not been reported to date. We suggest here a modification of the GB method in order to compare the softness of Lewis acids in an operationally simple approach. In the original GB method, a sample containing OPET<sub>3</sub> and a (potential) Lewis acid is analyzed by <sup>31</sup>P NMR spectroscopy. An acceptor number (AN) can be calculated according to Equation (1):

$$\text{AN (OPET}_3) = 2.21 \times (\delta(^{31}\text{P NMR})_{\text{Sample}}/\text{ppm} - 41.0) \quad (1)$$

where AN = 0 corresponds to OPET<sub>3</sub> in hexane and AN = 100 corresponds to OPET<sub>3</sub>·SbCl<sub>5</sub> in dichloroethane.<sup>[35a]</sup> We have exchanged the hard, oxygen-based donor in the original GB method for the softer donors SPMe<sub>3</sub> and SePMe<sub>3</sub>.<sup>[40]</sup> In analogy with the original GB method, acceptor numbers AN (SPMe<sub>3</sub>) and AN (SePMe<sub>3</sub>) may be determined according to Equations (2) and (3):

$$\text{AN (SPMe}_3) = 6.41 \times (\delta(^{31}\text{P NMR})_{\text{Sample}}/\text{ppm} - 29.2) \quad (2)$$

$$\text{AN (SePMe}_3) = 5.71 \times (\delta(^{31}\text{P NMR})_{\text{Sample}}/\text{ppm} - 7.8) \quad (3)$$

where AN = 0 corresponds to EPMe<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> and AN = 100 corresponds to EPMe<sub>3</sub> with one equiv Gal<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> (E = S, Se). Gal<sub>3</sub> was chosen as a reference point out of a range of potential candidates, because it is a simple, readily available, strong and soft Lewis acid that reacts with EPMe<sub>3</sub> in simple and pre-

dictable Lewis pair formations in a 1:1 ratio (SbCl<sub>5</sub>, SbF<sub>5</sub>, and Bi(OTf)<sub>3</sub>, for instance, had to be ruled out due to side reactions; see Supporting Information).

With SPMe<sub>3</sub> as a Lewis base, aryl bismuth compounds and halobismepines showed no or only minor interactions according to acceptor numbers of AN (SPMe<sub>3</sub>) = 0–12 (Table 1, entries 2–6). BiCl<sub>3</sub>, BiBr<sub>3</sub>, and BiI<sub>3</sub> showed moderate to minor interactions with AN (SPMe<sub>3</sub>) = 26, 17, and 13, respectively (entries 7–9). For compounds of type BiR<sub>2</sub>X and BiX<sub>3</sub>, the acceptor numbers increase with increasing electronegativity of the halide X. Stronger interactions were detected for the bismepine triflate Bi(diaryl)(OTf) (**3**) and Bi(OTf)<sub>3</sub> (AN (SPMe<sub>3</sub>) = 44–52; entries 10, 11; diaryl = [(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>H<sub>2</sub>]<sup>2–</sup>).<sup>[41]</sup> Very high acceptor numbers of AN (SPMe<sub>3</sub>) = 85–96 were obtained for the bismepine cation **1**, its corresponding SPMe<sub>3</sub> adduct **2-SPMe<sub>3</sub>**, and the diphenyl bismuth cation [BiPh<sub>2</sub>(thf)<sub>2</sub>][SbF<sub>6</sub>] (**4**), all of which bear [SbF<sub>6</sub>]<sup>–</sup> counteranions (entries 12–14). The slightly lower acceptor number of **4** is ascribed to the freely accessible bismuth-centered empty 6p-orbital in the complex fragment [BiPh<sub>2</sub>]<sup>+</sup>, which allows binding of two equivalents of a Lewis base<sup>[42]</sup> rather than only one as in **2-SPMe<sub>3</sub>**. This is further supported by a single-crystal X-ray analysis of [BiPh<sub>2</sub>(SPMe<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>], obtained from reaction of **4** with one equiv SPMe<sub>3</sub> (Supporting Information).

**Table 1.** Investigations of potential Lewis acids with the modified Gutmann–Beckett method, using SPMe<sub>3</sub> as a donor.

Entry	Compound	δ <sup>31</sup> P [ppm] <sup>[a]</sup>	AN (SPMe <sub>3</sub> ) <sup>[b]</sup>
1	SPMe <sub>3</sub>	29.2	0 (by definition)
2	BiPh <sub>3</sub>	30.2	6
3	Bi <sub>2</sub> (diaryl) <sub>3</sub> <sup>[a]</sup>	29.2	0
4	Bi(diaryl)Cl <sup>[a]</sup>	31.0	12
5	Bi(diaryl)Br <sup>[a]</sup>	30.3	7
6	Bi(diaryl)I <sup>[a]</sup>	29.2	0
7	BiCl <sub>3</sub>	33.2	26
8	BiBr <sub>3</sub>	31.8	17
9	BiI <sub>3</sub>	31.2	13
10	Bi(OTf) <sub>3</sub>	37.3	52
11	Bi(diaryl)(OTf) ( <b>3</b> ) <sup>[c,d]</sup>	36.1	44
<b>12</b>	<b>1</b>	<b>44.0</b>	<b>95</b>
<b>13</b>	<b>2-SPMe<sub>3</sub></b>	<b>44.2</b> <sup>[e]</sup>	<b>96</b>
14	[BiPh <sub>2</sub> (thf) <sub>2</sub> ][SbF <sub>6</sub> ] ( <b>4</b> )	42.5	85
15	Me <sub>3</sub> SiOTf	29.3	1
16	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	35.8	42
17	AlCl <sub>3</sub>	41.3	78
18	Gal <sub>3</sub>	44.8	100 (by definition)
19	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (thf)	29.4	1
20	AlCl <sub>3</sub> (thf)	29.7	3
21	Gal <sub>3</sub> (thf)	43.4	91
22	Gal <sub>3</sub> (py) <sup>[f]</sup>	30.2	6
23	2-SPMe <sub>3</sub> + py <sup>[f]</sup>	40.8	74
24	2-SPMe <sub>3</sub> + 2 py <sup>[f]</sup>	35.8	42

[a] If not otherwise noted, CD<sub>2</sub>Cl<sub>2</sub> solutions of equimolar amounts of the potential Lewis acid and SPMe<sub>3</sub> were investigated at 23 °C (for details see experimental part). [b] determined according to equation 2 (see text). [c] diaryl = [(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>H<sub>2</sub>]<sup>2–</sup> as in compound **1**; that is, [Bi(diaryl)]<sup>+</sup> corresponds to a cationic dibenzobismepine complex fragment.<sup>[12]</sup> [d] small amounts of THF were added to fully solubilize **3** (CD<sub>2</sub>Cl<sub>2</sub>/THF = 25:1, v/v). [e] obtained from NMR spectroscopic analysis of isolated **2-SPMe<sub>3</sub>** in CD<sub>2</sub>Cl<sub>2</sub>. [f] py = pyridine.

In order to allow a discussion of Bi-SPMe<sub>3</sub> interactions in the broader context of Lewis acidity, Me<sub>3</sub>SiOTf, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, and AlCl<sub>3</sub> 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 Me<sub>3</sub>SiOTf an extraordinarily high acceptor number towards OPET<sub>3</sub> of AN (OPET<sub>3</sub>)=116 was determined (Supporting Information). In contrast, an acceptor number of only AN (SPMe<sub>3</sub>)=1 was found for the softer donor SPMe<sub>3</sub> (entry 15), demonstrating that the exceptional Lewis acidity of cationic bismuth species towards soft donors is not only due to their ionic character, but also to the shape, energy, and accessibility of their LUMO. Acceptor numbers AN (SPMe<sub>3</sub>) of 42 and 78 were obtained for the boron and the aluminum compound, respectively (entries 16, 17), which are significantly lower than those of the cationic bismuth species **1**, **2-SPMe<sub>3</sub>**, and **4** (entries 12–14). It should be noted that compound **1** contains two equivalents of thf and that the addition of 1 equiv SPMe<sub>3</sub> to a solution of **1** gave an acceptor number which is virtually identical to that of isolated **2-SPMe<sub>3</sub>** (entries 12, 13). In other words, the softer donor SPMe<sub>3</sub> 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(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and AlCl<sub>3</sub> for either thf or SPMe<sub>3</sub>, samples containing one equivalent of the Lewis acid, one equivalent of thf, and one equivalent of SPMe<sub>3</sub> were investigated. Acceptor numbers AN (SPMe<sub>3</sub>) of **1** and **3** were obtained (entries 19, 20), demonstrating that the softer donor SPMe<sub>3</sub> cannot compete with the harder donor thf for the relatively hard binding sites in B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and AlCl<sub>3</sub>.

The preference to bind a soft donor SPMe<sub>3</sub> or a hard donor such as pyridine was also compared for compound **2-SPMe<sub>3</sub>** and Gal<sub>3</sub>. While Gal<sub>3</sub> 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-SPMe<sub>3</sub>** 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 (SPMe<sub>3</sub>) <10 were obtained for compound **2-SPMe<sub>3</sub>** (for titration experiments see Supporting Information).

With SePMe<sub>3</sub> as a Lewis base, the trends were similar to those observed for SPMe<sub>3</sub>. Aryl bismuth compounds, halobismepines, and in this case even all bismuth halides BiX<sub>3</sub> (X=Cl–I) showed acceptor numbers suggesting weak or even negligible Lewis acid/base interactions (AN (SePMe<sub>3</sub>)=0–14; Table 2, entries 2–9). For the bismuth triflates Bi(OTf)<sub>3</sub> and **3**, acceptor numbers of AN (SePMe<sub>3</sub>)=46 and 61 demonstrate significant Bi...SePMe<sub>3</sub> bonding (entries 10, 11).<sup>[41]</sup> For Bi(OTf)<sub>3</sub>, extended reaction times led to the appearance of an additional resonance in the <sup>31</sup>P NMR spectrum, which is not due to a simple 1:1 adduct and is tentatively ascribed to the formation of [Bi(SePMe<sub>3</sub>)<sub>6</sub>][OTf]<sub>3</sub> (Supporting Information). High acceptor numbers of 65–76 were obtained for cationic bismuth compounds **1**, **2-SePMe<sub>3</sub>**, and **4**, indicating considerable interactions with SePMe<sub>3</sub> (entries 12–14).<sup>[43]</sup>

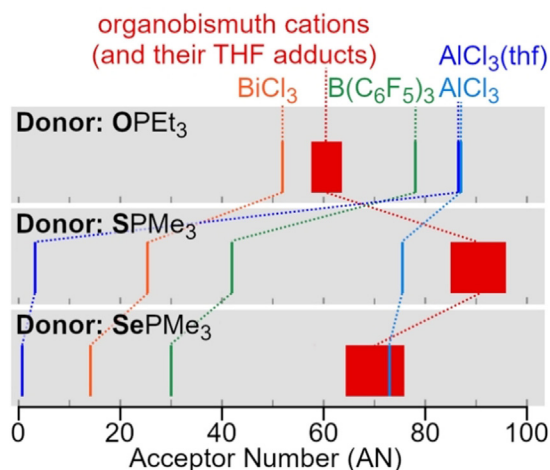
**Table 2.** Investigations of potential Lewis acids with the modified Gutmann–Beckett method, using SePMe<sub>3</sub> as a donor.

Entry	Compound	δ <sup>31</sup> P [ppm] <sup>[a]</sup>	AN (SePMe <sub>3</sub> ) <sup>[b]</sup>
1	SePMe <sub>3</sub>	7.8	0 (by definition)
2	BiPh <sub>3</sub>	8.9	6
3	Bi <sub>2</sub> (diaryl) <sub>3</sub> <sup>[c]</sup>	7.8	0
4	Bi(diaryl)Cl <sup>[c]</sup>	9.0	7
5	Bi(diaryl)Br <sup>[c]</sup>	8.4	3
6	Bi(diaryl)I <sup>[c]</sup>	8.0	1
7	BiCl <sub>3</sub>	10.3	14
8	BiBr <sub>3</sub>	9.7	11
9	BiI <sub>3</sub>	9.5	10
10	Bi(OTf) <sub>3</sub>	15.8 <sup>[d]</sup>	46
11	Bi(diaryl)(OTf) ( <b>3</b> ) <sup>[d,e]</sup>	18.5	61
12	<b>1</b>	19.2 <sup>[f]</sup>	65
13	<b>2-SePMe<sub>3</sub></b>	21.1 <sup>[f]</sup>	76
14	[BiPh <sub>2</sub> (thf) <sub>2</sub> ][SbF <sub>6</sub> ] <sup>(4)</sup>	20.5	73
15	Me <sub>3</sub> SiOTf	7.9	1
16	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	13.0	30
17	AlCl <sub>3</sub>	20.5	73
18	Gal <sub>3</sub>	25.3	100 (by definition)
19	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (thf)	7.9	1
20	AlCl <sub>3</sub> (thf)	8.0	1
21	Gal <sub>3</sub> (thf)	24.2	94
22	Gal <sub>3</sub> (py) <sup>[g]</sup>	9.0	7
23	2-SePMe <sub>3</sub> + py <sup>[g]</sup>	16.5	50
24	2-SePMe <sub>3</sub> + 2 py <sup>[g]</sup>	15.3	43

[a] If not otherwise noted, CD<sub>2</sub>Cl<sub>2</sub> solutions of equimolar amounts of the potential Lewis acid and SPMe<sub>3</sub> were investigated at 23 °C (for details see experimental part). [b] determined according to equation 3 (see text). [c] diaryl=[(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>H<sub>2</sub>]<sup>2-</sup> as in compound **1**; that is, [Bi(diaryl)]<sup>+</sup> corresponds to a cationic dibenzobismepine complex fragment.<sup>[12]</sup> [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** (CD<sub>2</sub>Cl<sub>2</sub>/THF=25:1, v/v). [f] obtained from NMR spectroscopic analysis of isolated **2-SePMe<sub>3</sub>** in CD<sub>2</sub>Cl<sub>2</sub>. [g] py=pyridine.

Analysis of Me<sub>3</sub>SiOTf, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, and AlCl<sub>3</sub> 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 SePMe<sub>3</sub> (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...SePMe<sub>3</sub> interactions, as judged from acceptor numbers of only 1 in both cases (entries 19, 20). Similar results were obtained for competition experiments with Gal<sub>3</sub> and **2-SePMe<sub>3</sub>** as Lewis acids and pyridine and SePMe<sub>3</sub> as Lewis bases. Gal<sub>3</sub> showed a minor acceptor number of 7 in the presence of pyridine, while acceptor numbers of 50 and 43 indicate significant Bi...SePMe<sub>3</sub> interactions for **2-SPMe<sub>3</sub>** 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 (SePMe<sub>3</sub>) to an insignificant value of 2 for compound **2-SePMe<sub>3</sub>** (for titration experiments see Supporting Information).

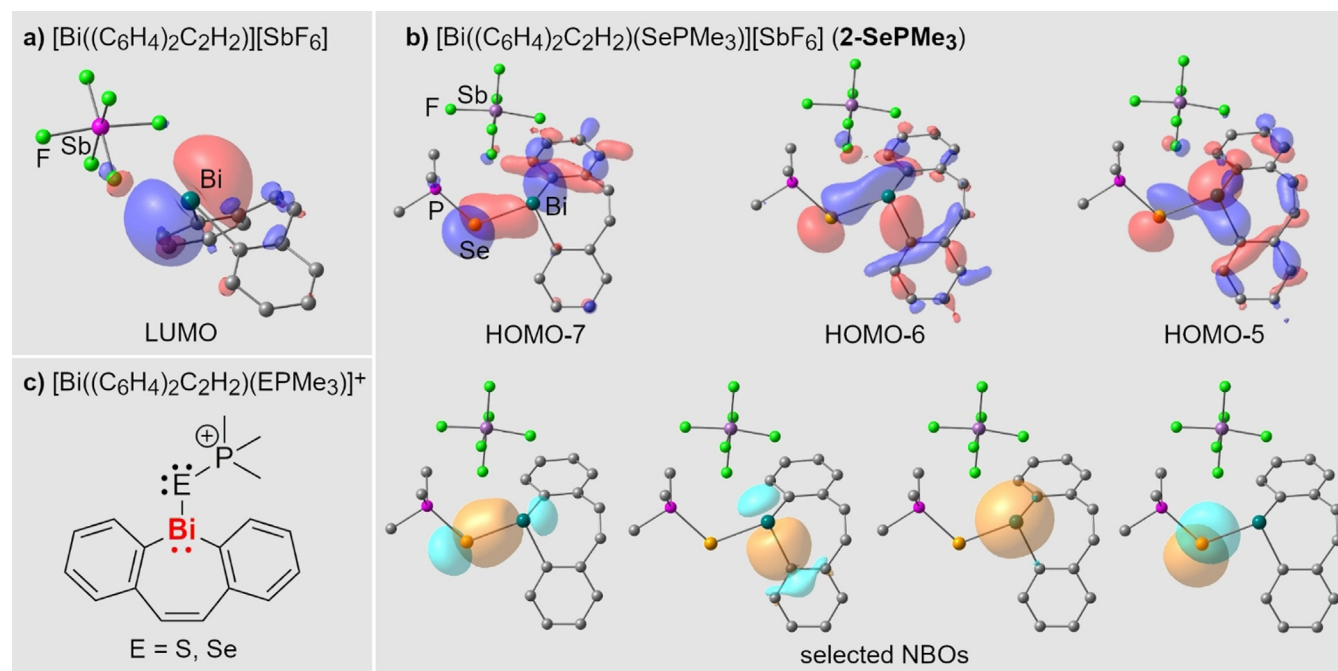
Major findings from our studies of bismuth-centered Lewis acidity based on the GB method (previous work<sup>[12]</sup> and Supporting Information) and modified versions thereof (this work) are summarized in Figure 2. As a trend it is apparent that bismuth Lewis acids of class A<sup>[12]</sup> with a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



**Figure 2.** Comparison of acceptor numbers for selected Lewis acids obtained from the Gutmann–Beckett method (top, previous results<sup>[12]</sup> and this work) and modified versions (middle and bottom, this work). “Organobismuth cations” refers to class C compounds (cf. introduction and ref. [12]) without strong directional cation–anion interactions.

strong and hard donor  $\text{OPEt}_3$ , but only relatively low Lewis acidities towards weaker and softer donors  $\text{SPMe}_3$  and  $\text{SePMe}_3$ . In contrast, bismuth Lewis acids of class C<sup>[12]</sup> 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  $\text{Me}_3\text{SiOTf}$ ,  $\text{B}(\text{C}_6\text{F}_5)_3$ , and  $\text{AlCl}_3$ ) cationic bismuth compounds of class C maintain an extraordinary Lewis acidity towards the soft donors  $\text{SPMe}_3$  and  $\text{SePMe}_3$  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-EPMe<sub>3</sub>** 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  $[\text{Bi}((\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_2)] [\text{SbF}_6]$ . 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-SePMe<sub>3</sub>**. The LUMO of  $[\text{Bi}((\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_2)] [\text{SbF}_6]$  is best described as an empty bismuth 6p-orbital with only minor contributions from other atomic orbitals (Figure 3a). 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-SPMe<sub>3</sub>** and **2-SePMe<sub>3</sub>**. Theoretical analysis of **2-SPMe<sub>3</sub>** and **2-SePMe<sub>3</sub>** 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%).<sup>[44]</sup> The molecular orbitals with significant Bi–S/Se bonding contributions are the HOMO–5 (only for **2-SePMe<sub>3</sub>**) as well as the HOMO–6 and HOMO–7 (for **2-SPMe<sub>3</sub>** and **2-SePMe<sub>3</sub>**), 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 3b and Supporting Information). In agreement with these results, natural resonance theory (NRT) revealed exclusively resonance structures featuring  $\text{R}_2\text{Bi}(\text{S/Se})\text{-P}^+\text{Me}_3$  structural motifs (with mesomeric effects



**Figure 3.** a) LUMO of  $[\text{Bi}((\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_2)] [\text{SbF}_6]$  with its conformation fixed to that found in the optimized structure of **2-SePMe<sub>3</sub>**. b) Selected molecular orbitals (top) and NBOs (bottom) of **2-SePMe<sub>3</sub>** with isovalues of 0.04. c) Resonance structure of the **2-EPMe<sub>3</sub>** according to NRT (E = S, Se;  $[\text{SbF}_6]^-$  omitted for clarity; only one (out of many) resonance structures of the bismepine core is depicted (see text)).

being relevant only within the bismepine core and the  $(\text{SbF}_6)^-$  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  $\text{EPMe}_3$  and Lewis acids based on bismuth and group 13 elements (B–Ga) were determined ( $\text{E}=\text{O}, \text{S}, \text{Se}$ ; Table 3 ( $\Delta G$  values) and Supporting Information ( $\Delta H$  values and additional examples)). Starting from coordinatively unsaturated Lewis acids, the adduct formations are strongly exergonic ( $\Delta G=-20$  to  $-45 \text{ kcal mol}^{-1}$ ) for all compounds but  $\text{B}(\text{C}_6\text{F}_5)_3$ , which shows a mildly exergonic reaction with  $\text{OPMe}_3$  and endergonic reactions with  $\text{S/SePMe}_3$  (entries 1–6, for  $\Delta H$  values see Supporting Information).<sup>[45]</sup> Most importantly, reactions of all the group 13 compounds become less exergonic (or even endergonic) upon changing the Lewis base from  $\text{OPMe}_3$  to  $\text{S/SePMe}_3$  (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  $\text{EPMe}_3$  to displace one or two thf ligands from the coordination sphere of coordinatively saturated Lewis acids (from a thermodynamic point of view), reactions with compounds  $[\text{LA}]-(\text{thf})_n$  were investigated ( $[\text{LA}]$ =Lewis acid;  $n=1-2$ ). With the exception of  $\text{B}(\text{C}_6\text{F}_5)_3$  (entry 7), exergonic reactions are observed for the group 13 compounds with  $\text{OPMe}_3$  ( $\Delta G=-10$  to  $-11 \text{ kcal mol}^{-1}$ ,  $n=1$ ; entries 8–11), while those with bismuth compounds are clearly exergonic for  $n=1$  and marginally endergonic for  $n=2$  ( $\Delta G=-12.4$  and  $+0.3 \text{ kcal mol}^{-1}$ ; entries 12,13). Ligand substitutions with  $\text{S/SePMe}_3$  at the hard aluminum center are endergonic by 8 to 9  $\text{kcal mol}^{-1}$  (entry 8). For the softer gallium compounds, substitution of thf by  $\text{S/SePMe}_3$  is

only slightly endergonic ( $\Delta G=+3$  to  $+5 \text{ kcal mol}^{-1}$ ,  $n=1$ ; entries 9–11). For the bismuth cations, these reactions are clearly exergonic for  $n=1$  ( $\Delta G=-17$  to  $-19 \text{ kcal mol}^{-1}$ , entry 12) and still slightly exergonic for  $n=2$  ( $\Delta G=-5$  to  $-6 \text{ kcal mol}^{-1}$ , entry 13). These trends are in good agreement with experimental results obtained from the modified GB method.<sup>[45]</sup>

## Conclusions

The ability of bismuth(III) compounds to form Lewis acid/base adducts with the soft donors  $\text{EPMe}_3$  has been investigated ( $\text{E}=\text{S}, \text{Se}$ ). Cationic bismuth compounds  $[\text{BiR}_2(\text{EPMe}_3)][\text{SbF}_6]$  featuring rare  $\text{Bi}\cdots\text{EPR}_3$  interactions were isolated and fully characterized. The bismuth atoms in these compounds show coordination numbers of three, which is extremely unusual for cationic bismuth species without directional  $\text{Bi}\cdots$ counteranion interactions. Detailed experimental and theoretical analyses revealed significant  $\text{Bi}\cdots\text{EPR}_3$  bonding with strong covalent contributions that persists in the solid state and in solution. The  $^{31}\text{P}$  NMR chemical shift of  $\text{EPMe}_3$  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  $\text{EPMe}_3$  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  $\text{BiR}_3$ ,  $\text{BiR}_2\text{X}$ ,  $\text{BiX}_3$ , and  $[\text{BiR}_2]^+$  with this approach, delivering experimental evidence for their soft Lewis acidity. Especially cationic bismuth species  $[\text{BiR}_2]^+$  that interact with the donor through an empty p-orbital (not through a  $\sigma^*$ -orbital) are potent soft Lewis acids. In contrast to well-established, relatively hard Lewis acids such as  $\text{Me}_3\text{SiOTf}$ ,  $\text{B}(\text{C}_6\text{F}_5)_3$ , and  $\text{AlCl}_3$  and the softer Lewis acid  $\text{GaI}_3$ , 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  $^1\text{H}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported relative to  $\text{SiMe}_4$  using the residual  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of the solvent as a secondary standard.  $^{31}\text{P}$  and  $^{77}\text{Se}$  NMR chemical shifts are reported relative to  $\text{H}_3\text{PO}_4$  (85% aqueous solution) and  $\text{SeMe}_2$  (plus 5%  $\text{C}_6\text{D}_6$ ) 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 ( $\lambda=0.71073 \text{ \AA}$ ). The structures were solved using intrin-

**Table 3.** Calculated free reaction enthalpy of Lewis pair formation with varying Lewis acids and donors  $\text{EPMe}_3$  ( $\text{E}=\text{O}, \text{S}, \text{Se}$ ) in the presence of 0–2 equivalents of thf.

Entry	[LA]	$n$	$\Delta G$ [kcal mol <sup>-1</sup> ]		
			$\text{E}=\text{O}$	$\text{E}=\text{S}$	$\text{E}=\text{Se}$
1	$\text{B}(\text{C}_6\text{F}_5)_3$	0	-0.7	+16.7	+18.3
2	$\text{AlCl}_3$	0	-41.8	-23.0	-22.0
3	$\text{GaCl}_3$	0	-39.6	-25.0	-24.4
4	$\text{GaBr}_3$	0	-37.7	-24.3	-23.8
5	$\text{GaI}_3$	0	-32.7	-19.5	-19.6
6	$[\text{Bi}(\text{diaryl})][\text{SbF}_6]^{[\text{a}]}$	0	-38.6	-43.6	-44.8
7	$\text{B}(\text{C}_6\text{F}_5)_3$	1	+8.8	+26.3	+27.9
8	$\text{AlCl}_3$	1	-10.8	+8.1	+9.1
9	$\text{GaCl}_3$	1	-10.4	+4.2	+4.8
10	$\text{GaBr}_3$	1	-10.9	+2.5	+3.0
11	$\text{GaI}_3$	1	-10.3	+2.9	+2.8
12	$[\text{Bi}(\text{diaryl})][\text{SbF}_6]^{[\text{a}]}$	1	-12.4	-17.4	-18.6
13	$[\text{Bi}(\text{diaryl})][\text{SbF}_6]^{[\text{a}]}$	2	+0.3	-4.7	-5.9

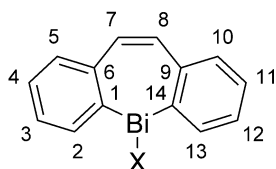
[a] diaryl =  $[(\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_2]^{2-}$ ; that is,  $[\text{LA}] = [\text{Bi}(\text{diaryl})][\text{SbF}_6]$  with two thf ligands ( $n=2$ ) corresponds to compound 1.

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](http://www.ccdc.cam.ac.uk/structures).

DFT calculations were performed with the Gaussian program<sup>[46]</sup> using the 6-31G(d,p)<sup>[47]</sup> [H, C, N, O, F], 6-311G(d,p)<sup>[48]</sup> [Al, P, S], and the LANL2DZ<sup>[49]</sup> [Ga, In, Se, Sb, Bi, Br, I] basis set and the B3LYP functional.<sup>[50]</sup> The D3 version of Grimme's dispersion model with the original D3 damping function was applied.<sup>[51]</sup> 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.<sup>[52]</sup>

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



**[Bi((C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>H<sub>2</sub>)(SPMe<sub>3</sub>)] [SbF<sub>6</sub>] (2-SPMe<sub>3</sub>):** To a solution of [Bi((C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>H<sub>2</sub>)(thf)<sub>2</sub>][SbF<sub>6</sub>] (1) (30.0 mg, 39.1 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.7 mL) was added SPMe<sub>3</sub> (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, 35.6 μmol, 91%. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 2.21 (d, 9H, <sup>2</sup>J<sub>PH</sub> = 13.3 Hz, PMe<sub>3</sub>), 7.09 (s, 2H, H-7, H-8), 7.43 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, C<sub>6</sub>H<sub>4</sub>), 7.71 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 8.41 (m, 2H, C<sub>6</sub>H<sub>4</sub>) ppm. <sup>1</sup>H NMR (500 MHz, [D<sub>8</sub>]THF): δ = 1.94 (d, 12H, <sup>2</sup>J<sub>PH</sub> = 13.7 Hz, PMe<sub>3</sub>), 6.75 (s, 2H, H-7, H-8), 7.40 (ddd, 2H, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, H-4, H-11) 7.59 (ddd, 2H, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, H-3, C-12), 7.84 (dd, 2H, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, H-5, H-10), 8.18 (dd, 2H, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, H-2, H-13) ppm. <sup>13</sup>C NMR (126 MHz, [D<sub>8</sub>]THF): δ = 19.15 (d, <sup>1</sup>J<sub>CP</sub> = 53.8 Hz, PMe<sub>3</sub>), 129.76 (s, H-4, H-11), 130.15 (s, C-3, C-12), 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 <sup>13</sup>C, <sup>1</sup>H HMBC experiments) ppm. <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 44.2 (s) ppm. <sup>31</sup>P NMR (202 MHz, [D<sub>8</sub>]THF): δ = 41.4 (s) ppm.

**Elemental analysis:** Anal. calc. for: [C<sub>17</sub>H<sub>19</sub>BiPSSbF<sub>6</sub>] (731.10 g mol<sup>-1</sup>): C 27.93, H 2.62, S 4.39; found: C 28.19, H 2.58, S 4.36.

**[Bi((C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>H<sub>2</sub>)(SePMe<sub>3</sub>)] [SbF<sub>6</sub>] (2-SePMe<sub>3</sub>):** To a solution of [Bi((C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>H<sub>2</sub>)(thf)<sub>2</sub>][SbF<sub>6</sub>] (1) (20.0 mg, 26.1 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added SePMe<sub>3</sub> (4.2 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: 18.0 mg, 23.1 μmol, 87%. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 2.23 (d, 9H, <sup>2</sup>J<sub>PH</sub> = 13.4 Hz, PMe<sub>3</sub>), 7.01 (s, 2H, H-7, H-8), 7.43 (ddd, 2H, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, H-4, H-11) 7.63 (ddd, 2H, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, H-3, C-12), 7.72 (dd, 2H,

<sup>4</sup>J<sub>HH</sub> = 1.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, H-5, H-10), 8.43 (dd, 2H, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, H-2, H-13) ppm. <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 19.48 (d, <sup>1</sup>J<sub>CP</sub> = 47.8 Hz, PMe<sub>3</sub>), 129.61 (s, H-4, H-11), 132.24 (s, C-3, C-12), 133.49 (s, C-7, C-8), 133.81 (s, C-5, C-10), 136.77 (s, C-2, C-13), 143.49 (s, C-6, C-9), 162.89 (br, C-1, C-14) ppm. <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 21.1 (s, <sup>1</sup>J<sub>PSe</sub> = 488.2 Hz) ppm. <sup>31</sup>P NMR (202 MHz, THF): δ = 19.1 (s) ppm. <sup>77</sup>Se NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = −44.2 (br, detected via <sup>1</sup>H, <sup>77</sup>Se HMBC experiments) ppm.

**Elemental analysis:** Anal. calc. for: [C<sub>17</sub>H<sub>19</sub>BiPSeSbF<sub>6</sub>] (778.01 g mol<sup>-1</sup>): C 26.24, H 2.46; found: C 25.88, H 2.48.

**[BiPh<sub>2</sub>(thf)<sub>2</sub>][SbF<sub>6</sub>] (4):** To a solution of diphenylbismuth chloride (50.0 mg, 0.13 mmol) in THF (1 mL) was added a solution of AgSbF<sub>6</sub> (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%. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.82 (m, 4H, β-thf), 3.70 (m, 4H, α-thf), 7.56–7.69 (m, 2H, *p*-C<sub>6</sub>H<sub>5</sub>), 8.02 (dd, 4H, <sup>3</sup>J<sub>HH</sub> = 6.6, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, *o*-C<sub>6</sub>H<sub>5</sub>), 8.47 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, *m*-C<sub>6</sub>H<sub>5</sub>) ppm. <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 26.03 (s, β-thf), 71.12 (s, α-thf), 130.86 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 133.63 (s, *o*-C<sub>6</sub>H<sub>5</sub>), 137.64 (s, *m*-C<sub>6</sub>H<sub>5</sub>) 198.46 (s, *ipso*-C<sub>6</sub>H<sub>5</sub>) ppm.

**Elemental analysis:** Anal. calc. for: [C<sub>12</sub>H<sub>10</sub>BiSbF<sub>6</sub>](OC<sub>4</sub>H<sub>8</sub>)<sub>2</sub> (743.16 g mol<sup>-1</sup>): C 32.32, H 3.53; found: C 32.42, H 3.64.

### General procedure for modified Gutmann–Beckett method

If not otherwise noted, equimolar amounts of the potential Lewis acid and the Lewis base EPMe<sub>3</sub> 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 <sup>31</sup>P NMR chemical shifts: i) the use of CD<sub>2</sub>Cl<sub>2</sub> as the solvent, so that locking and shimming was possible; ii) the use of CH<sub>2</sub>Cl<sub>2</sub> as the solvent along with a capillary containing deuterated acetone, so that locking and shimming was possible; iii) the use of CH<sub>2</sub>Cl<sub>2</sub> as the solvent along with a capillary containing an 85% aqueous solution of H<sub>3</sub>PO<sub>4</sub> 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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- [40] Compounds B(C<sub>6</sub>F<sub>5</sub>)<sub>n</sub>(OC<sub>6</sub>F<sub>5</sub>)<sub>3-n</sub> (n=0–3) have previously been reacted with SPEt<sub>3</sub>, where only for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> a significant interaction could be determined by <sup>31</sup>P NMR spectroscopy: see ref. [39].
- [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<sub>3</sub>) and AN(SePMe<sub>3</sub>).
- [42] It should be noted that entropic effects, which are relevant in reactions “[LA](thf)<sub>n</sub>+EPMe<sub>3</sub>→[LA](EPMe<sub>3</sub>)+nthf” for n=0 and n=2, but not for n=1, may be overestimated by DFT methods. For ΔH values of these reactions see Supporting Information.
- [43] Even solutions of compound **2-SPMe<sub>3</sub>** in THF gave an acceptor number of AN(SePMe<sub>3</sub>)=65.
- [44] NBO analyses indicate that olefin → Bi donor/acceptor interactions are present in **2-SPMe<sub>3</sub>** and **2-SePMe<sub>3</sub>** and realized through π(C=C) → σ\*(Bi-S/Se) interactions. The corresponding deletion energies amount to 2.9 kcal mol<sup>-1</sup> for **2-SPMe<sub>3</sub>** and 3.1 kcal mol<sup>-1</sup> for **2-SePMe<sub>3</sub>**, which is in the range of those reported for the corresponding halobismepines (E<sub>del</sub>=2.6–2.9 kcal mol<sup>-1</sup>; ref. [12]).
- [45] It should be noted that entropic effects, which are relevant in reactions “[LA](thf)<sub>n</sub>+EPMe<sub>3</sub>→[LA](EPMe<sub>3</sub>)+nthf” for n=0 and n=2, but not for n=1, may be overestimated by DFT methods. For ΔH values of these reactions see Supporting Information.
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