

## Probing the Lewis acidity of heavier pnictogen trichlorides

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**Abstract.** Lewis acidity of  $\text{SbCl}_3$  and  $\text{BiCl}_3$  has been investigated in the solid as well as in solution state. Two  $\beta$ -ketoimine ligands,  $[\text{O}=\text{C}(\text{Me})]\text{CH}[\text{C}(\text{Me})\text{NHAr}]$  (**L1**, Ar=2,6-diisopropylphenyl) and  $[(\text{CH}_2)_2\{-\text{N}(\text{H})\text{C}(\text{Me})\text{CHC}(\text{Me})=\text{O}\}_2]$  (**L2**) are used to prepare the complexes  $[(\text{L1})(\text{THF})\text{SbCl}_3]_2$  (**1**),  $[(\text{L1})(\text{THF})\text{BiCl}_3]_2$  (**2**),  $[(\text{L2})\text{SbCl}_3]_2$  (**3**) and  $[(\text{L2})_3(\text{BiCl}_3)_2]$  (**4**), which are characterized by multinuclear NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction experiments. Solid-state structural analysis of **1–4** and solution studies on  $\text{SbCl}_3$  and  $\text{BiCl}_3$  using the Gutmann-Beckett method reveal the higher Lewis acidity of  $\text{BiCl}_3$  compared to  $\text{SbCl}_3$ .

**Keywords.** Pnictogen elements; Lewis acidity;  $\beta$ -ketoiminato ligands; Gutmann-Beckett method.

### 1. Introduction

Salts of heavier pnictogens (Pn), antimony and bismuth in +3 oxidation state are employed as Lewis acids in organic synthesis.<sup>1</sup> Common examples of these salts include chlorides, carboxylates and trifluoromethanesulfonate. A qualitative model for the origin of Lewis acidity in Sb(III) and Bi(III) compounds was proposed by Norman in 1994.<sup>2</sup> According to this model, a polarized Pn–X bond has a corresponding low lying antibonding  $\sigma^*$ -orbital that can accept a pair of electrons. The Pn–X bonds constitute the primary bonds, while the interaction between antibonding orbitals and Lewis bases constitute the secondary bonding. The energy levels of the antibonding orbitals and hence, Lewis acidity of  $\text{PnX}_3$  is dependent on the extent of polarization in primary bonds. We have recently used this model to explain the Lewis acidity in cationic bismuth complexes.<sup>3–5</sup> The cationic  $[(\text{Me}_2\text{NC}_6\text{H}_4)(\text{Mesityl})\text{Bi}]^+$  bears one  $\sigma^*$ -orbital and the dicationic tri-coordinate  $[\text{tris}(2,5\text{-dimethylpyrazolylborate})\text{bismuth(III)}]^{2+}$  bears two  $\pi^*$ - and one  $\sigma^*$ -orbitals. These anti-bonding orbitals exhibit remarkable Lewis acidity and can be employed for olefin hydrosilylation.<sup>4</sup> While there are few reports where Lewis acidity in Sb(III) and Bi(III) compounds has been explored, Lewis acidity of simple salts like  $\text{SbCl}_3$  and  $\text{BiCl}_3$  is not well-quantified.<sup>6</sup> In this work, we

have attempted to compare the Lewis acidity of  $\text{SbCl}_3$  and  $\text{BiCl}_3$  by the solid-state structure as well as solution studies.  $\beta$ -Ketoimine adducts of these salts have been prepared and structure elucidation done by single-crystal X-ray diffraction studies are used to study the Lewis acidity in the solid-state. Lewis acidity of  $\text{SbCl}_3$  and  $\text{BiCl}_3$  have been probed in solution by performing the Gutmann-Beckett test.<sup>7</sup>

### 2. Experimental

*General methods:* All manipulations were performed in a nitrogen/argon atmosphere using standard Schlenk and glovebox techniques. The solvents used for the synthesis and NMR experiments were dried, distilled, and degassed prior to use by standard methods. The distilled solvents were stored over appropriate drying agents.  $[\text{O}=\text{C}(\text{Me})]\text{CH}[\text{C}(\text{Me})\text{NHAr}]$ <sup>8</sup> and  $[(\text{CH}_2)_2\{-\text{N}(\text{H})\text{C}(\text{Me})\text{CHC}(\text{Me})=\text{O}\}_2]$ <sup>9</sup> were prepared according to the literature procedures. Anhydrous  $\text{SbCl}_3$  and  $\text{BiCl}_3$  were purchased from Sigma-Aldrich and used as such without any further purification. NMR measurements were performed with a Bruker 500 MHz spectrometer. Elemental analysis was performed with an Elemental Vario Micro Cube. Single-crystal X-ray diffraction experiments were performed on a Bruker Kappa Apex-II CCD diffractometer using  $\text{Mo-}K\alpha$  source ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods with SIR-92 and SHELX-2014.<sup>10</sup>

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Crystallographic data and structure refinement results are summarized in Table 1.

**Synthesis of 1:** THF (20 mL) was condensed on to a mixture of ([O=C(Me)]CH[C(Me)NHAry]) (1 mmol, 0.260 g) and SbCl<sub>3</sub> (1 mmol, 0.228 g) at −196 °C. The reaction mixture was stirred at room temperature for 12 h. Addition of excess *n*-pentane to the reaction mixture and storage of the resultant solution at −30 °C afforded crystalline precipitate of **1** (0.45 g, 92%); <sup>1</sup>H NMR (500 MHz, THF-D<sub>8</sub>): δ 1.11 (d, <sup>3</sup>J<sub>H-H</sub> = 5 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), δ 1.21 (d, <sup>3</sup>J<sub>H-H</sub> = 5 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), δ 1.60 (s, 3 H, CH<sub>3</sub>C(NH)), δ 2.00 (s, 3 H, CH<sub>3</sub>C(O)), δ 3.00–3.08 (m, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), δ 5.20 (s, 1 H, CH<sub>3</sub>C(NH)CH), δ 7.18–7.30 (m, 3 H, C<sub>6</sub>H<sub>3</sub>), δ 12.19 (s, 1 H, NH) ppm; <sup>13</sup>C NMR (126 MHz, THF-D<sub>8</sub>): δ 19.31 (CH<sub>3</sub>), δ 23.03 (CH(CH<sub>3</sub>)<sub>2</sub>), δ 25.03 (CH(CH<sub>3</sub>)<sub>2</sub>), δ 29.04 (CH<sub>3</sub>), δ 29.56 (CH(CH<sub>3</sub>)<sub>2</sub>), δ 96.18 ((CNH)CH(CO)), δ 124.43 (*m*-CH<sub>N-aryl</sub>), δ 129.16 (*p*-CH<sub>N-aryl</sub>), δ 134.98 (*o*-CH<sub>N-aryl</sub>), δ 147.34 (C<sub>N-aryl</sub>), δ 163.25 (C(NH)(CH<sub>3</sub>)), δ 195.77 (CO(CH<sub>3</sub>)) ppm; Elemental analysis (%) for C<sub>17</sub>H<sub>25</sub>-NOBiCl<sub>3</sub>: Calculated: C 68.64, H 8.13, N 4.71, Found: C 68.62, H 8.14, N 4.71

**Synthesis of 2:** THF (20 mL) was condensed on to a mixture of ([O=C(Me)]CH[C(Me)NHAry]) (1 mmol, 0.260 g) and BiCl<sub>3</sub> (1 mmol, 0.315 g) at −196 °C. The reaction mixture was stirred at room temperature. After 12 h it was filtered and concentrated. The

concentrated THF solution stored at −30 °C gave crystals of **2** (0.52 g, 90%). <sup>1</sup>H NMR (500 MHz, THF-D<sub>8</sub>): δ 1.11 (d, <sup>3</sup>J<sub>H-H</sub> = 10 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), δ 1.21 (d, <sup>3</sup>J<sub>H-H</sub> = 10 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), δ 1.60 (s, 3 H, CH<sub>3</sub>C(NH)), δ 2.00 (s, 3 H, CH<sub>3</sub>C(O)), δ 3.00–3.08 (m, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), δ 5.20 (s, 1 H, CH<sub>3</sub>C(NH)CH), δ 7.18–7.30 (m, 3 H, C<sub>6</sub>H<sub>3</sub>), δ 12.18 (s, 1H, NH) ppm; <sup>13</sup>C NMR (126 MHz, THF-D<sub>8</sub>): δ 19.31 (CH<sub>3</sub>), δ 23.03 (CH(CH<sub>3</sub>)<sub>2</sub>), δ 25.02 (CH(CH<sub>3</sub>)<sub>2</sub>), δ 29.07 (CH<sub>3</sub>), δ 29.56 (CH(CH<sub>3</sub>)<sub>2</sub>), δ 96.20 ((CNH)CH(CO)), δ 124.44 (*m*-CH<sub>N-aryl</sub>), δ 129.16 (*p*-CH<sub>N-aryl</sub>), δ 134.98 (*o*-CH<sub>N-aryl</sub>), δ 147.36 (C<sub>N-aryl</sub>), δ 163.32 (C(NH)(CH<sub>3</sub>)), δ 195.78 (CO(CH<sub>3</sub>)) ppm; Elemental analysis (%) for C<sub>17</sub>H<sub>25</sub>-NOBiCl<sub>3</sub>: Calculated: C 35.53, H 4.38, N 2.44, Found: C 35.52, H 4.39, N 2.46.

**Synthesis of 3:** THF (20 mL) was condensed on to a mixture of ([O=C(Me)]CH[C(Me)NHAry]) (1 mmol, 0.224 g) and SbCl<sub>3</sub> (1 mmol, 0.228 g) at −196 °C. The reaction mixture was stirred at room temperature for 12 h. The turbid reaction mixture was filtered and layered with *n*-pentane resulting in crystals of **3** (0.41 g, 90%). <sup>1</sup>H NMR (500 MHz, THF-D<sub>8</sub>): δ 1.87 (s, 6 H, CH<sub>3</sub>CN), δ 1.89 (s, 6 H, CH<sub>3</sub>CO), δ 3.42 (s(br), 4 H, CH<sub>2</sub>), δ 4.91 (s, 2 H, CH), δ 10.93 (s, 2 H, NH) ppm; <sup>13</sup>C NMR (126 MHz, THF-D<sub>8</sub>): δ 18.78 (CH<sub>3</sub>), δ 28.84 (CH<sub>3</sub>), δ 44.44 ((CH<sub>2</sub>)), δ 96.17 (CH), δ 163.65 (CH<sub>3</sub>CN), δ 194.64 (CH<sub>3</sub>CO) ppm;

**Table 1.** Crystallographic data, details of data collection, and structure refinement parameters for compounds **1–4**.

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>21</sub> H <sub>33</sub> Cl <sub>3</sub> NO <sub>2</sub> Sb	C <sub>21</sub> H <sub>33</sub> Cl <sub>3</sub> NO <sub>2</sub> Bi	C <sub>12</sub> H <sub>20</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>2</sub> Sb	C <sub>36</sub> H <sub>60</sub> Bi <sub>2</sub> Cl <sub>6</sub> N <sub>6</sub> O <sub>6</sub>
Formula weight [g mol <sup>−1</sup> ]	559.58	1291.61	1291.61	1303.56
Temperature [K]	150(2)	296(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P2 <sub>1</sub> /c	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
<i>a</i> [Å]	10.259	10.3167(7)	8.0941(3)	9.2239(11)
<i>b</i> [Å]	16.204	15.4216(11)	9.5066(3)	9.3247(12)
<i>c</i> [Å]	15.480	25.3050(18)	12.2441(5)	16.723(2)
α [°]	90	88.924(2)	103.073(2)	97.800(6)
β [°]	104.92	86.809(2)	95.752(2)	92.674(6)
γ [°]	90	71.979(2)	108.129(2)	107.100(5)
Volume [Å <sup>3</sup> ]	2486.5	3822.6(5)	857.24(6)	1356.4(3)
Z	4	3	2	1
Calculated density [mg m <sup>−3</sup> ]	1.495	1.683	1.753	1.596
θ range [°]	2.409 to 24.997	0.806 to 25.000	2.508 to 24.997	2.526 to 25.000
Reflections collected	33101	96181	12496	20130
Independent reflections ( <i>R</i> <sub>int</sub> )	4377 (0.0352)	13452 (0.1056)	3019 (0.0246)	4763 (0.0300)
Data/restraints/parameters	4377/0/259	13452/67/803	3019/0/185	4763/2/253
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.058	1.040	1.047	1.052
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0275, 0.0628	0.0459, 0.0811	0.0175, 0.0393	0.0205, 0.0475
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0375, 0.0703	0.0848, 0.0946	0.0205, 0.0405	0.0234, 0.0483
Largest diff. peak, hole [eÅ <sup>−3</sup> ]	0.788, −0.418	1.256, −1.777	0.374, −0.382	1.101, −1.112

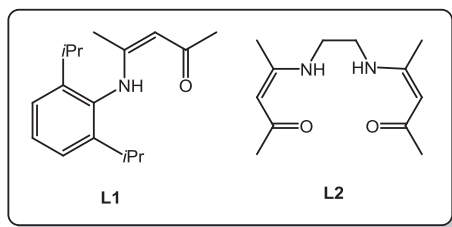
Elemental analysis (%) for  $C_{24}H_{40}N_4O_4Sb_2O$ : Calculated: C 31.86, H 4.46, N 6.19, Found: C 31.88, H 4.45, N 6.21.

Synthesis of **4**: THF (20 mL) was condensed on to a mixture of  $[(CH_2)_2\{N(H)C(Me)CHC(Me)=O\}_2]$  (3 mmol, 0.672 g) and  $BiCl_3$  (2 mmol, 0.630 g) at  $-196^\circ C$ . The reaction mixture was stirred at room temperature for 12 h. The resultant turbid reaction mixture was filtered and layered with *n*-pentane resulting in crystals of **4** (0.07 g, 76%).  $^1H$  NMR (500 MHz, THF- $D_8$ ):  $\delta$  1.87 (s, 6 H,  $CH_3CN$ ),  $\delta$  1.89 (s, 6 H,  $CH_3CO$ ),  $\delta$  3.42 (s(br), 4 H,  $CH_2$ ),  $\delta$  4.91 (s, 2 H,  $CH$ ),  $\delta$  10.93 (s, 2 H,  $NH$ ) ppm;  $^{13}C$  NMR (126 MHz, THF- $D_8$ ):  $\delta$  18.75 ( $CH_3$ ),  $\delta$  28.91 ( $CH_3$ ),  $\delta$  44.44 ( $CH_2$ ),  $\delta$  96.15 ( $CH$ ),  $\delta$  163.57 ( $CH_3CN$ ),  $\delta$  194.70 ( $CH_3CO$ ) ppm; Elemental analysis (%) for  $C_{35}H_{58}N_6O_6Bi_2Cl_6$ : Calculated: C 32.80, H 4.53, N 6.52, Found: C 32.79, H 4.56, N 6.54.

### 3. Results and Discussion

Based on our recent experience with  $\beta$ -ketoimine ligands in pnictogen coordination chemistry,<sup>11</sup> we set out to employ this ligand system to prepare adducts of  $SbCl_3$  and  $BiCl_3$ . Two  $\beta$ -ketoimine ligands, mono-functional  $[O=C(Me)]CH[C(Me)NHAr]$  (**L1**) where Ar is 2,6-diisopropylphenyl and the bi-functional  $[(CH_2)_2\{N(H)C(Me)CHC(Me)=O\}_2]$  (**L2**) were chosen in this study (Figure 1).

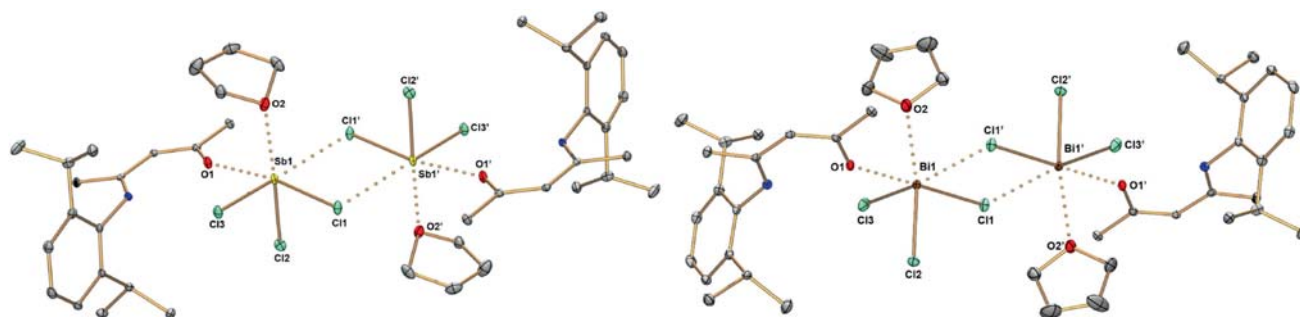
The reaction between equimolar quantities of  $PnCl_3$  ( $Pn = Sb, Bi$ ) and **L1** and subsequent crystallization of the reaction mixture from THF resulted in the isolation of analytically pure  $[(L1)(THF)SbCl_3]_2$  (**1**) and  $[(L1)(THF)BiCl_3]_2$  (**2**). Compounds **1** and **2** were characterized by single-crystal X-ray diffraction experiments, NMR spectroscopy and elemental analysis. **1** crystallizes in the monoclinic crystal system with  $P2_1/c$  space group while **2** crystallizes in the triclinic crystal system with space group  $P\bar{1}$ . Solid-state structures of **1** and **2** provided in Figure 2 reveal that the pnictogen atoms in **1** and **2** possess a coordination number of six.



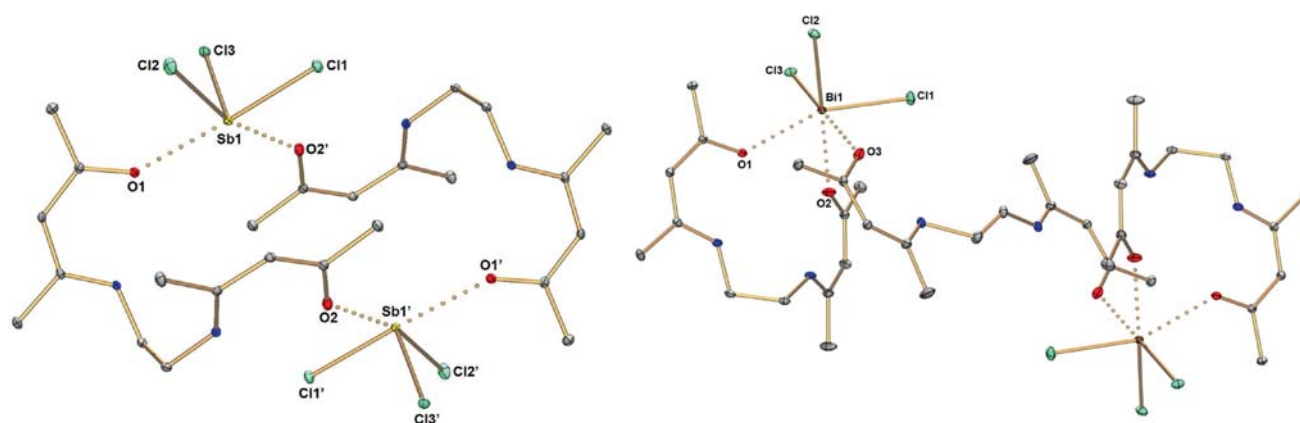
**Figure 1.**  $\beta$ -Ketoimine ligands used in the current study.

Analysis of bond lengths in **1** and **2** provide an insight into the bonding and Lewis acidity of  $PnCl_3$ . The average  $Sb-Cl$  and  $Bi-Cl$  ( $Pn-Cl1$ ,  $Pn-Cl2$  and  $Pn-Cl3$ ) distances in **1** and **2** are observed to be 2.408 and 2.565 Å, respectively. These values are close to the corresponding sum of the covalent radii of  $Pn$  and  $Cl$  atoms,  $\sum r_{cov}(Sb \& Cl) = 2.41$  Å and  $\sum r_{cov}(Bi \& Cl) = 2.50$  Å.<sup>12</sup> Thus, the three  $Pn-Cl$  interactions constitute the primary bonds. The three polarized  $Pn-Cl$  primary bonds concurrently give rise to three Lewis acidic interactions at sites *trans* to the  $Pn-Cl$  bonds. These secondary interactions to the pnictogen atoms occur *via* the coordination of O-atoms of **L1** and one THF molecule and a chloride bridging with the neighbouring monomeric units. The average  $Bi-O$  distance (2.472 Å) is shorter than the average  $Sb-O$  distance (2.586 Å). Similarly, the bridging  $Pn-Cl1'$  bond lengths,  $Bi-Cl1'$  distance (3.056 Å) is shorter than  $Sb-Cl1'$  distance (3.323 Å). Higher Lewis acidity of  $BiCl_3$  draws the O- and Cl-atoms closer to the bismuth center in the secondary coordination site in **2** as compared to **1**.

To strengthen our inference on the higher Lewis acidity of  $BiCl_3$  over  $SbCl_3$ , we further proceeded to synthesize the **L2** adducts of  $PnCl_3$ . We observed different ratios of  $Pn$  and **L2** in respective adducts. When  $PnCl_3$  was treated with **L2**, we isolated  $[L2SbCl_3]_2$  (**3**) and  $[(L2)_3(BiCl_3)_2]$  (**4**). NMR spectroscopy and elemental analysis of the crystallized samples of **3** and **4**, initially confirmed their identity and purity. Solid-state structures of **3** and **4** were elucidated using single-crystal X-ray diffraction experiments. Both **3** and **4** crystallize in the triclinic crystal system with  $P\bar{1}$  space group. Their solid-state structures are represented in Figure 3. An initial glance at the structure of **3** reveals that  $Sb$  exhibits a coordination number of five and a distorted square pyramidal arrangement of donor atoms. The three  $Sb-Cl$  bonds form the primary bonds with an average distance of 2.4135 Å. Only two secondary interactions are observed in **3**.  $O1$  and  $O2'$  coordinate to the  $Sb$  atom at the secondary bonding sites *trans* to  $Cl1$  and  $Cl2$  respectively with an average distance of 2.502 Å. The secondary coordination site *trans* to  $Cl3$  remains vacant, indicating that the energy of this orbital is too high for donor molecules to coordinate. In contrast to the structural features of **3**, compound **4** possessing  $Bi$  atom exhibiting a coordination number of six with a slightly distorted octahedral geometry. The three primary  $Bi-Cl$  bonds exhibit an average distance of 2.590 Å. Contrary to the observation in **3**, three secondary interactions are observed at the bismuth center



**Figure 2.** Solid state structures of **1** (left) and **2** (right). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] in **1**: Sb1–O1 2.411(2), Sb1–O2 2.761(3), Sb1–C11 2.4720(9), Sb1–C12 2.384(1), Sb1–C13 2.3681(8), O1–Sb1–C11 99.80(6), O1–Sb1–C13 80.23(6), C13–Sb1–C11 91.28(3), C12–Sb1–O2 175.21(6). Selected bond lengths [Å] and angles [°] in **2**: Bi1–O1 2.383(7), Bi1–O2 2.562(8), Bi1–C11 2.677(2), Bi1···C11 3.056(3), Bi1–C12 2.523(2), Bi1–C13 2.496(3), C11–Bi1–O1 103.0(1), O1–Bi1–C13 83.0(2), C13–Bi1–C11 91.07(8), C12–Bi1–O2 169.0(2).



**Figure 3.** Solid state structures of **3** (top) and **4** (bottom). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] in **3**: Sb1–O1 2.584(2), Sb1–O2 2.420(2), Sb1–C11 2.4310(7), Sb1–C12 2.4549(7), Sb1–C13 2.3546(6), O1–Sb1–C12 90.67(4), O1–Sb1–O2 102.95(6), C12–Sb1–C11 88.96(2), C13–Sb1–O1 84.22(4), C13–Sb1–O2 82.77(4). Selected bond lengths [Å] and angles [°] in **4**: Bi1–O1 2.551(3), Bi1–O2 2.476(3), Bi1–O3 2.453(4), Bi1–C11 2.580(1), Bi1–C12 2.599(1), Bi1–C13 2.593(1), C12–Bi1–O1 100.86(7), O1–Bi1–O2 72.8(1), C12–Bi1–C11 96.82(4), C11–Bi1–O2 87.57(9), C13–Bi1–O3 172.6(1).

*trans* to C11, C12 and C13. The three O-atoms bind to the bismuth center with an average Bi–O distance of 2.493 Å. The higher coordination number at Bi in **4** as compared to Sb in **3** is strong evidence for the higher Lewis acidity exhibited by BiCl<sub>3</sub> as compared to SbCl<sub>3</sub>.

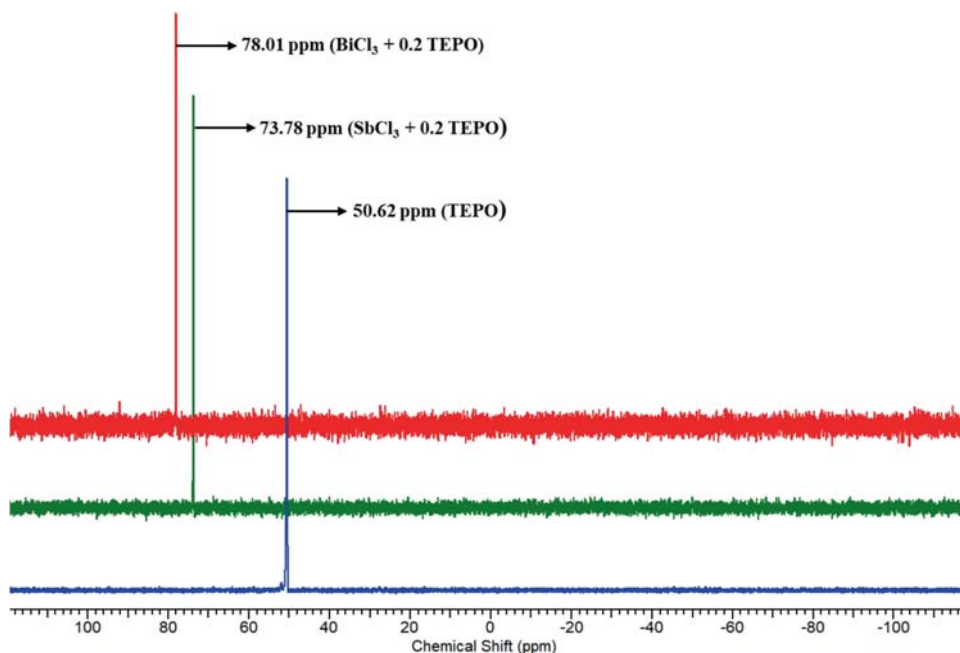
Having evidenced higher Lewis acidity in BiCl<sub>3</sub> in comparison to SbCl<sub>3</sub> in the solid-state, we went on to probe the Lewis acidity of the heavier pnictogen chloride in solution. We used a modified Gutmann-Beckett method to quantify the Lewis acidity of SbCl<sub>3</sub> and BiCl<sub>3</sub> in solution.<sup>13</sup> This method has been traditionally applied to electron-deficient boron compounds,<sup>14</sup> it has been recently applied in the Lewis acid chemistry of heavier main group elements.<sup>3,4,15</sup> In this test, triethyl phosphine oxide (TEPO) is used as a basic probe to quantify the Lewis acids using <sup>31</sup>P NMR spectroscopy. A solution of TEPO in CD<sub>2</sub>Cl<sub>2</sub>

shows a single sharp peak at  $\delta$  50.6 ppm in the <sup>31</sup>P NMR spectrum. When this solution was treated with eight equivalents of SbCl<sub>3</sub>, the peak shifted to  $\delta$  73.8 ppm, indicating a de-shielded phosphorus signal as a result of binding of TEPO to the Lewis acidic SbCl<sub>3</sub> (Figure 4). Treating the free TEPO solution in CD<sub>2</sub>Cl<sub>2</sub> with eight equivalents of BiCl<sub>3</sub> shifted the free TEPO signal in the <sup>31</sup>P NMR to  $\delta$  78.0 ppm. From this observation, it is clear that BiCl<sub>3</sub> de-shields the <sup>31</sup>P NMR signal more than SbCl<sub>3</sub> thus proving that the former is more Lewis acidic than the latter.

#### 4. Conclusions

$\beta$ -Ketoimine adducts of SbCl<sub>3</sub> and BiCl<sub>3</sub> were successfully synthesized and well-characterized. Solid-state structural analysis indicates that the secondary





**Figure 4.**  $^{31}\text{P}$  NMR spectra of TEPO, ( $\text{SbCl}_3 + 0.2 \text{ TEPO}$ ) and ( $\text{BiCl}_3 + 0.2 \text{ TEPO}$ ) recorded in  $\text{CD}_2\text{Cl}_2$ .

bonding is stronger in  $\text{BiCl}_3$  in comparison to  $\text{SbCl}_3$ . Gutmann-Beckett test reveals that  $\text{BiCl}_3$  de-shields the phosphorus signal of triethylphosphine oxide in  $^{31}\text{P}$  NMR spectrum more than  $\text{SbCl}_3$ . The solid-state and solution studies conclude that  $\text{BiCl}_3$  is more Lewis acidic than  $\text{SbCl}_3$ .

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