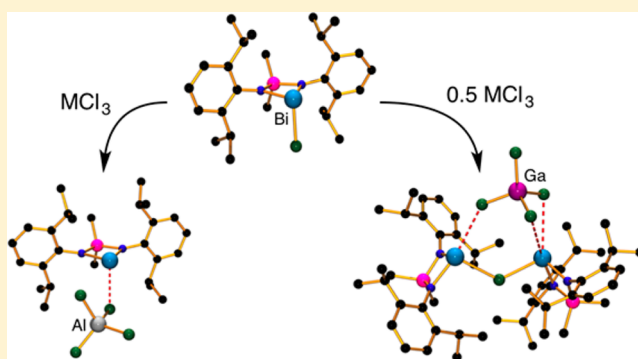


## Low-Coordinate Bismuth Cations

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## Supporting Information

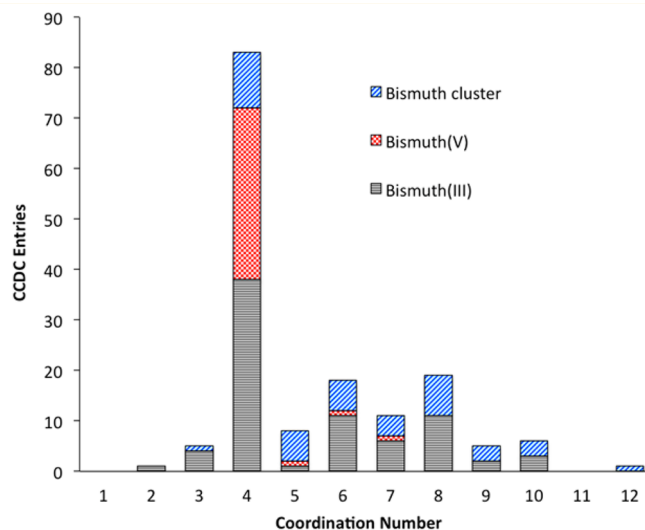
**ABSTRACT:** Chloride abstraction from the diamido-bismuth compound  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{Cl}$  (**1**, Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) using  $\text{MCl}_3$  (M = Al, Ga) is a facile route to cationic species. Stoichiometric reactions afford the tetrachlorometallate salts  $[\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)][\text{MCl}_4]$  (**2a**, M = Al; **3a**, M = Ga), whereas reaction with 0.5 equiv of the group 13 reagent gives the  $\mu$ -chlorido bridged cations  $[\{\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\}_2(\mu\text{-Cl})][\text{MCl}_4]$  (**2b**, M = Al; **3b**, M = Ga). The crystal structure of **2a** shows a formally two-coordinate bismuth cation, with a  $\text{Bi}\cdots\text{Cl}$  contact to the  $[\text{AlCl}_4]^-$  anion, whereas the structure of **3b** shows a total of three  $\text{Bi}\cdots\text{Cl}$  contacts to  $[\text{GaCl}_4]^-$ . Both species associate as {1:1}<sub>2</sub> dimers in the solid state through additional  $\text{Bi}\cdots\text{Cl}$  interactions. Attempted preparation of cationic complexes using either  $\text{NaBR}_4$  (R = Ph, Et) or  $[\text{HNEt}_3][\text{BPh}_4]$  were unsuccessful. Instead of forming the borate salts, the neutral compounds  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{R}$  (**4**, R = Et; **5**, R = Ph) were isolated as a result of aryl/alkyl transfer from boron to bismuth.



## 1. INTRODUCTION

Commercially available  $\text{BiX}_3$  compounds (X = halogen, triflate, nitrate) are used as Lewis acidic reagents to promote a range of organic transformations<sup>1</sup> and polymerization reactions.<sup>2</sup> More recently cationic bismuth compounds have been investigated,<sup>3,4</sup> developing the concept that an increased electrophilicity associated with the positively charged metal center will enhance the activity of the reagents. Due in part to the large radius of the element [Shannon ionic radii  $\text{Bi}^{3+}$ : 6-coordinate = 1.03 Å; 8-coordinate = 1.17 Å],<sup>5</sup> much of the research on cationic bismuth compounds has focused on the application of multidentate ligands able to provide additional interactions to support the metal center.<sup>6</sup> Prominent among these examples are the potentially tridentate systems based on either a dianionic (C,E,C) framework (E = N, O, S),<sup>4,7</sup> or the mono-anionic (E,C,E)-system.<sup>8,9</sup> Relatively little work has been directed toward the study of low-coordinate bismuth cations.

A survey of the Cambridge Structural Database<sup>10</sup> was conducted to examine the distribution of coordination numbers associated with crystallographically characterized cationic bismuth compounds. The results, displayed in Figure 1, were divided into three classes: bismuth(III), bismuth(V), and bismuth clusters (defined in this survey as species containing three or more Bi atoms). Most examples have been reported in which the bismuth is 4-coordinate (52.5%), with 6- and 8-coordinate bismuth each representing 12.0% of the total number of structures listed in the database. Both high- (>8-coordinate: 7.6%) and especially low- (<4-coordinate: 3.8%) coordinate species are poorly represented. For each coordination



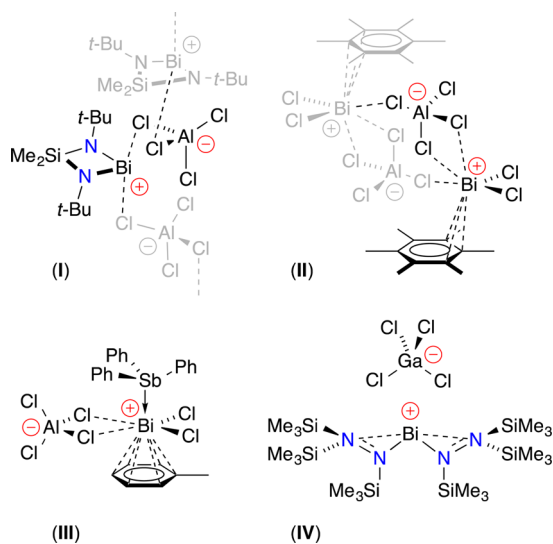
**Figure 1.** Graph showing the coordination number of structurally characterized bismuth cations (bismuth clusters defined as compounds containing three or more Bi atoms in the structure).

number there is a fairly even split between Bi(III) and higher nuclearity “cluster” compounds, with far fewer examples of Bi(V) cations. The exception is the 4-coordinate species, for which a large number of  $[\text{BiAr}_4]^+$  cations have been structurally determined.

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The only structurally characterized two-coordinated bismuth cation is supported by the bulky diamido-ligand  $[\text{Me}_2\text{Si}\{\text{N}t\text{-Bu}\}_2]^{2-}$  (I, Figure 2).<sup>11</sup> The salt is generated by chloride abstraction



**Figure 2.** Examples of structurally characterized bismuth cations containing tetrachlorometallate anions (see text for references).

from the neutral Bi(III) precursor  $\text{Bi}(\text{Me}_2\text{Si}\{\text{N}t\text{-Bu}\}_2)\text{Cl}$ , using  $\text{MCl}_3$  ( $\text{M} = \text{Al}, \text{Ga}, \text{and In}$ ), to afford the corresponding tetrachlorometallate species. This strategy for cation production has been applied to other bismuth systems.<sup>12–17</sup> The aluminum reagent  $\text{AlCl}_3$  dominates as the chloride abstraction agent, with relatively few reports on the use of  $\text{GaCl}_3$ ,<sup>11,15,17</sup> and only a single report of this reactivity being achieved with  $\text{InCl}_3$ ;<sup>11</sup> these trends presumably reflect the differing Lewis acidity of the group 13 reagents.

The solid-state structure of the tetrachloroaluminate salt I contains long-range  $\text{Bi}\cdots\text{Cl}$  interactions between the  $[\text{Bi}(\text{Me}_2\text{Si}\{\text{N}t\text{-Bu}\}_2)]^+$  cation and chlorides from two  $[\text{AlCl}_4]^-$  anions, generating a polymeric chain parallel to the *b*-axis of the unit cell. Such moderation of positive charge in bismuth salts through the formation of intermolecular  $\text{Bi}\cdots\text{Cl}$  contacts to the  $[\text{MCl}_4]^-$  counterions is relatively common, and may be augmented by additional associations in the solid state. For example, the reaction of  $\text{BiCl}_3$  and  $\text{AlCl}_3$  in the presence of hexamethyl benzene affords the  $\{1:1\}_2$  dimeric salt with an  $\eta^2$ -bonded aromatic ring (II),<sup>12</sup> whereas generating the  $[\text{BiCl}_2]^+$  cation in the presence of  $\text{SbPh}_3$ , using toluene as solvent, restricted the aggregation to the monobismuth species (III).<sup>16</sup> The only structurally characterized tetrachlorogallate salt of bismuth involves the  $N,N',N'$ -tris(trimethylsilyl)hydrazido ligand (IV).<sup>15</sup> In this example bismuth is involved in three-center four-electron bonding to the two ligands, precluding the formation of interion  $\text{Bi}\cdots\text{Cl}$  interactions with the  $[\text{GaCl}_4]^-$  anion.

In this Contribution we examine the scope and limitations of cation formation, using  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{Cl}$  (1,  $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ),<sup>18</sup> as a starting material. Compound 1 is stable under anaerobic conditions, and we have demonstrated that the chelating diamide ligand is a stable platform for further derivation of the  $\text{Bi}\text{--}\text{Cl}$  bond. While formation of cationic species is relatively straightforward using  $\text{MCl}_3$  ( $\text{M} = \text{Al}, \text{Ga}$ ), attempts at synthesizing salts containing borate anions  $[\text{BR}_4]^-$

were complicated by transfer of the R-group and formation of  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{R}$ .

## 2. EXPERIMENTAL SECTION

**2.1. General.** All manipulations were carried out under dry nitrogen using standard Schlenk-line and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agents and degassed prior to use. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300.1 ( $^1\text{H}$ ) and 75.4 ( $^{13}\text{C}$ ) MHz or a Varian VNMRs 500 MHz spectrometer at 500.1 ( $^1\text{H}$ ), 160.4 ( $^{11}\text{B}$ ), 125.4 ( $^{13}\text{C}$ ), and 99.3 ( $^{29}\text{Si}$ ) MHz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances.  $^{29}\text{Si}$  NMR chemical shifts were obtained from  $^1\text{H}\text{--}^{29}\text{Si}$  heteronuclear multiple-bond correlation (HMBC) spectra. Elemental analyses were performed by S. Boyer at London Metropolitan University.  $\text{BiCl}_3$  was freshly sublimed prior to the synthesis of  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{Cl}$  (1), which was made according to our previously published procedure.<sup>18</sup>  $[\text{HNET}_3][\text{BPh}_4]$  was synthesized from  $[\text{HNET}_3]\text{Cl}$  and  $\text{Na}[\text{BPh}_4]$  according to the procedure described by Evans and co-workers.<sup>9</sup> All other chemicals were purchased from commercial sources and used as received.

**2.2. Preparation of  $[\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)]_2[\text{AlCl}_4]$  (2a).** A solution of 1 (0.100 g, 0.15 mmol) in toluene (5 mL) was added dropwise to a stirred suspension of  $\text{AlCl}_3$  (0.019 g, 0.15 mmol) in toluene (5 mL). The resulting dark red solution was stirred for 4 h followed by concentration and storage at  $-30^\circ\text{C}$ . After 24 h, dark red crystals were obtained. Yield 0.105 g, 88%. Anal. Calcd. for  $\text{C}_{26}\text{H}_{40}\text{N}_2\text{AlBiCl}_4\text{Si}$  (786.47): C, 39.71; H, 5.13; N, 3.56%. Found: C, 39.85; H, 5.01; N, 3.68%.  $^1\text{H}$  NMR:  $\delta$  7.26 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 4H, *m-CH*), 6.60 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 2H, *p-CH*), 3.49 (m br, 4H, *CHMe\_2*), 1.21 (br, 24H, *CHMe\_2*), 0.13 (s, 6H, *SiMe\_2*).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  \*, 148.5, 128.8, 122.5 ( $\text{C}_6\text{H}_3$ ), 28.2 (*CHMe\_2*), 27.0 (br, *CHMe\_2*), 10.4 (*SiMe*). \* *o-C* not observed.  $^{29}\text{Si}$  NMR:  $\delta$  38.0.

**2.3. Generation of  $\{[\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)]_2(\mu\text{-Cl})\}[\text{AlCl}_4]$  (2b).** *Method 1—NMR Scale.* A solution of 2a (0.020 g, 0.026 mmol) in  $\text{C}_6\text{D}_6$  (0.5 mL) was added to 1 (0.085 g, 0.013 mmol). The  $^1\text{H}$  NMR spectrum indicated complete consumption of starting materials after 10 min at room temperature.

*Method 2—Preparative Scale.* A solution of 1 (0.040 g, 0.061 mmol) in toluene (2 mL) was added to a stirring suspension of  $\text{AlCl}_3$  (0.004 g, 0.031 mmol) in toluene (2 mL). The resulting suspension was stirred for 4 h followed by the removal of volatiles.  $^1\text{H}$  NMR analysis of the crude product revealed formation of 2b.  $^1\text{H}$  NMR:  $\delta$  7.24 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 4H, *m-CH*), 6.74 (t,  $^3J_{\text{HH}} = 7.8$  Hz, 2H, *p-CH*), 3.86 (br sept, 4H, *CHMe\_2*), 1.25 (d,  $^3J_{\text{HH}} = 6.6$  Hz, 24H, *CHMe\_2*), 0.20 (s, 6H, *SiMe\_2*).

**2.4. Generation of  $[\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)]_2[\text{GaCl}_4]$  (3a).** *Method 1—NMR Scale.* A solution of 2b (0.020 g, 0.026 mmol) in  $\text{C}_6\text{D}_6$  (0.5 mL) was added to 1 (0.009 g, 0.013 mmol). The  $^1\text{H}$  NMR spectrum indicated complete consumption of starting materials after 10 min at room temperature.

*Method 2—Preparative Scale.* A solution of 1 (0.040 g, 0.061 mmol) in toluene (2 mL) was added to a solution of  $\text{GaCl}_3$  (0.011 g, 0.061 mmol) in toluene (2 mL). Removal of the volatiles followed by  $^1\text{H}$  NMR analysis of the crude products revealed formation of 3a.  $^1\text{H}$  NMR:  $\delta$  7.28 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 4H, *m-CH*), 6.58 (t,  $^3J_{\text{HH}} = 7.8$  Hz, 2H, *p-CH*), 3.51 (sept,  $^3J_{\text{HH}} = 6.7$  Hz, 4H, *CHMe\_2*), 1.24 (br, 24H, *CHMe\_2*), 0.13 (s, 6H, *SiMe\_2*).

**2.5. Preparation of  $\{[\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)]_2(\mu\text{-Cl})\}[\text{GaCl}_4]$  (3b).** A solution of 1 (0.100 g, 0.15 mmol) in toluene (4 mL) was added dropwise to a stirring suspension of  $\text{GaCl}_3$  (0.013 g, 0.075 mmol) in toluene (4 mL). The resulting dark red solution was stirred for 2 h followed by concentration of the solution and storage at  $-30^\circ\text{C}$ . After 24 h, small dark red crystals of 3b were obtained. Yield 0.047 g, 40%. Anal. Calcd. for  $\text{C}_{52}\text{H}_{80}\text{N}_4\text{Bi}_2\text{Cl}_5\text{GaSi}_2$  (1482.34): C, 42.13; H, 5.44; N, 3.78%. Found: C, 41.97; H, 5.31; N, 3.90%.  $^1\text{H}$  NMR:  $\delta$  7.25 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 4H, *m-CH*), 6.74 (t,  $^3J_{\text{HH}} = 7.8$  Hz, 2H, *p-CH*), 3.90 (sept,  $^3J_{\text{HH}} = 6.8$  Hz, 4H, *CHMe\_2*), 1.27 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 24H, *CHMe\_2*), 0.21 (s, 6H, *SiMe\_2*).  $^{29}\text{Si}$  NMR:  $\delta$  31.2.  $^{13}\text{C}\{^1\text{H}\}$  NMR data

could not be obtained due to decomposition of **3b** in solution over extended periods of time.

**2.6. Preparation of Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)Ph (4).** *Method 1—Preparative Scale from Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)Cl + NaBPh<sub>4</sub>.* A solution of **1** (0.100 g, 0.15 mmol) in toluene (5 mL) was added dropwise to a stirring suspension of NaBPh<sub>4</sub> (0.051 g, 0.15 mmol) in toluene (5 mL). The resulting solution was stirred for 72 h at 90 °C, followed by removal of the volatiles. Extraction into hexane and filtering through Celite resulted in a clear yellow solution. The solution was concentrated and stored at –30 °C. After 24 h, a number of white crystals of BPh<sub>3</sub> were deposited. Further concentration and storage at –30 °C yielded a second crop of crystals, identified as a mixture of BPh<sub>3</sub> and **4**. Yield 0.070 g, 67%.

*Method 2—NMR Scale from Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)Et + [HNEt<sub>3</sub>][BPh<sub>4</sub>].* A solution of **5** (0.020 g, 0.031 mmol) in C<sub>6</sub>D<sub>6</sub> was added to [HNEt<sub>3</sub>][BPh<sub>4</sub>] (0.013 g, 0.031 mmol). The <sup>1</sup>H NMR spectrum revealed complete formation of **4** and BPh<sub>3</sub> after 0.5 h at room temperature.

Anal. Calcd. for C<sub>32</sub>H<sub>45</sub>N<sub>2</sub>BiSi (694.78): C, 55.32; H, 6.53; N, 4.03%. Found: C, 55.48; H, 6.64; N, 3.95%. <sup>1</sup>H NMR: δ 8.48 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, *o*-C<sub>6</sub>H<sub>5</sub>), 7.57 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1H, *p*-C<sub>6</sub>H<sub>5</sub>), 6.95 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, *m*-C<sub>6</sub>H<sub>5</sub>), 4.30 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 4H, CHMe<sub>2</sub>), 1.28 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 24H, CHMe<sub>2</sub>), 0.63, 0.15 (s, SiMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 148.0 (br, C<sub>6</sub>H<sub>5</sub>), 147.2 (C<sub>6</sub>H<sub>5</sub>), 140.9 (C<sub>6</sub>H<sub>5</sub>), 136.2 (C<sub>6</sub>H<sub>5</sub>), 131.6 (C<sub>6</sub>H<sub>5</sub>), 129.4 (C<sub>6</sub>H<sub>5</sub>), 128.4 (C<sub>6</sub>H<sub>5</sub>), 124.5 (C<sub>6</sub>H<sub>5</sub>), 27.8 (br, CHMe<sub>2</sub>), 25.1 (br, CHMe<sub>2</sub>), 17.5, 4.8 (SiMe). <sup>29</sup>Si NMR: δ 19.5.

**2.7. Preparation of Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)Et (5).** A solution of **1** (0.100 g, 0.15 mmol) in toluene (5 mL) was added dropwise to a stirring suspension of NaBEt<sub>4</sub> (0.023 g, 0.15 mmol) in toluene (5 mL). The resulting solution was stirred for 24 h at room temperature, followed by removal of the volatiles and extraction into hexane. The resulting suspension was filtered through Celite and concentrated, followed by storage at –30 °C. After 24 h, clear yellow crystals were formed. Yield 0.061 g, 63%. Anal. Calcd. for C<sub>28</sub>H<sub>45</sub>N<sub>2</sub>BiSi (646.73): C, 52.00; H, 7.01; N, 4.33%. Found: C, 51.91; H, 7.12; N, 4.24%. <sup>1</sup>H NMR: δ 7.19 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 4H, *m*-CH), 6.99 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, *p*-CH), 4.28 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 4H, CHMe<sub>2</sub>), 2.47 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 2.04 (q, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.31 (br, 24H, CHMe<sub>2</sub>), 0.42 (s, 3H, SiMe<sub>2</sub>), 0.04 (s, 3H, SiMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 147.9, 141.4, 124.2, 123.5 (C<sub>6</sub>H<sub>5</sub>), 27.7 (CHMe<sub>2</sub>), 25.9, 25.4 (CHMe<sub>2</sub>), 15.6 (SiMe), 8.7 (CH<sub>2</sub>CH<sub>3</sub>), 5.2 (SiMe). BiCH<sub>2</sub>CH<sub>3</sub> was not observed. <sup>29</sup>Si NMR: δ 17.8.

**2.8. Crystal Structure Data.** Crystals were covered in inert oil, and suitable single crystals were selected under a microscope and mounted on an Enraf Nonius Kappa CCD diffractometer (**2a**) or an Agilent SuperNova diffractometer fitted with an Atlas detector (**3b**, **4**, **5**). Data was collected at 173(2) K (**2a**) or 120.01(10) K (**3b**, **4**, **5**) using Mo K $\alpha$  radiation at 0.71073 Å (**2a**, **4**, **5**) or Cu K $\alpha$  radiation at 1.5418 Å (**3b**). The structures were refined with SHELXL-97.<sup>19</sup> Additional features of note are listed below:

$\{[Bi(Me_2Si\{NAr\}_2)]_2(\mu-Cl)\}[GaCl_4]$  (**3b**). The compound crystallizes with a molecule of hexane in the unit cell.

$Bi(Me_2Si\{NAr\}_2)Ph$  (**4**). The toluene solvate was located on an inversion center and was refined at half-occupancy; hydrogen atoms were not included in this model.

$Bi(Me_2Si\{NAr\}_2)Et$  (**5**). The data solves in both the R3 and R $\bar{3}$  space groups; the latter model (in which the molecule is located on an inversion center) is presented. The disorder was modeled as alternative positions of the BiEt/SiMe<sub>2</sub> groups, with a single position for the NAr groups. There are large solvent channels in the crystal structure containing a poorly resolved and unidentified solvent; this was not modeled in the solution.

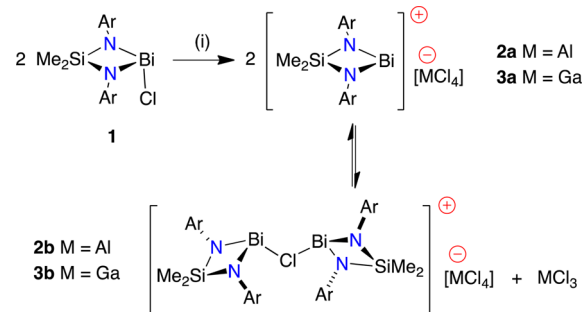
### 3. RESULTS AND DISCUSSION

**3.1. Reaction of Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)Cl with MCl<sub>3</sub> (M = Al, Ga, In).** NMR spectroscopy is a convenient tool for the detection of changes to the Bi environment in relation to the chelating diamide ligand. The C<sub>1</sub> symmetry imposed by the pyramidal geometry of the bismuth atom in Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)

Cl (**1**) is most clearly evident from inequivalent SiMe<sub>2</sub> resonances at  $\delta_H$  0.60 and 0.07 ppm.<sup>18</sup> Formation of a planar 2-coordinate Bi cation would, however, generate a single set of ligand resonances in the NMR spectrum, predicted for a C<sub>2h</sub> ligand environment.

The reaction between Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)Cl and one equiv of AlCl<sub>3</sub> in toluene proceeds with an immediate color change from yellow to deep red. Concentration and cooling of the resultant solution to –30 °C afforded deep red crystals of the tetrachloroaluminate salt, [Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)]<sup>+</sup>[AlCl<sub>4</sub>]<sup>–</sup> (**2a**, Scheme 1). The <sup>1</sup>H NMR spectrum shows a single sharp

**Scheme 1. Synthetic Routes to Bismuth Cations 2 and 3<sup>a</sup>**

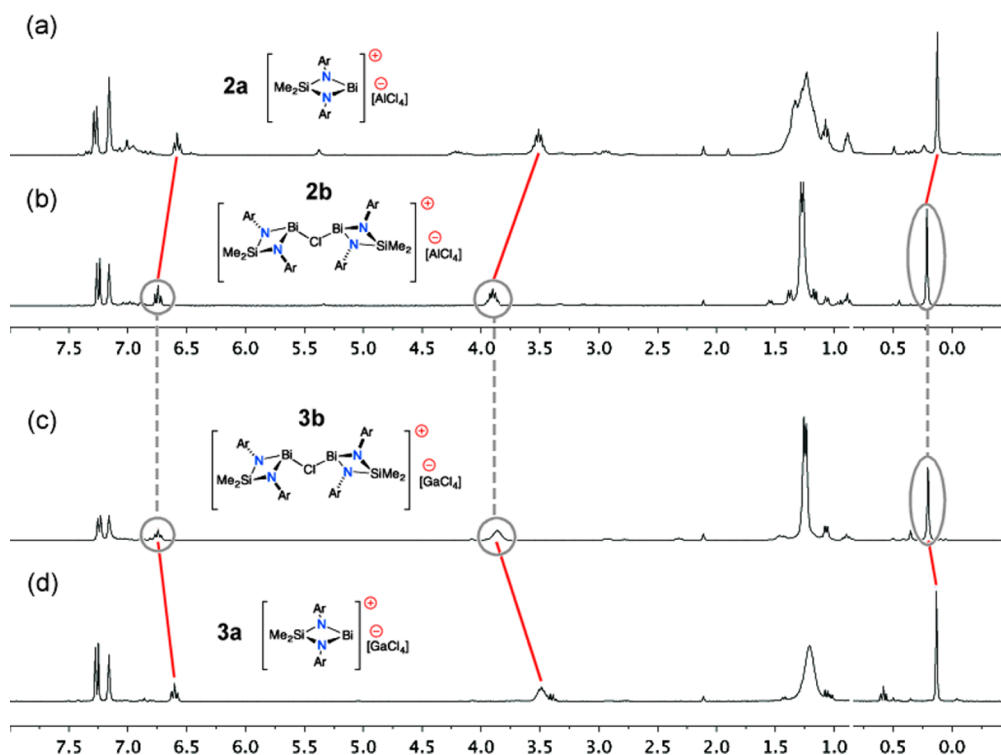


<sup>a</sup>(i) 2MCl<sub>3</sub> (2 M = Al; 3 M = Ga).

peak for the SiMe<sub>2</sub> protons at  $\delta_H$  0.13 ppm and broad resonances at  $\delta_H$  3.49 and 1.21 ppm for the *iso*-propyl methine and methyl protons, respectively (Figure 3a). These data are consistent with the formation of [Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)]<sup>+</sup>, although we recognize that a number of alternative structures involving cation⋯anion interactions in the solution state also fit these data (Supporting Information, Figure S1). There is a notable low-field shift of the <sup>29</sup>Si NMR resonance upon generation of the cation, from  $\delta_{Si}$  = 29.7 ppm in **1** to  $\delta_{Si}$  = 38.0 in **2a** ( $\Delta\delta_{Si}$  = +8.3 ppm). This indicates that changes to the environment at the bismuth center influence spectroscopic properties of the remote silicon atom, which therefore serves as a convenient handle to probe the electronic state of the metal in solution.

The analogous NMR scale reaction between **1** and GaCl<sub>3</sub> (1 equiv) in C<sub>6</sub>D<sub>6</sub> proceeded in a similar manner, with an immediate color change on mixing to afford a deep red solution. The <sup>1</sup>H NMR spectrum was similar to that observed for isolated **2a**, with SiMe<sub>2</sub>, CHMe<sub>2</sub>, and CHMe<sub>2</sub> resonances at  $\delta_H$  3.51, 1.24, and 0.13 ppm, respectively, and are assigned to the tetrachlorogallate analogue of **2a**, [Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)]<sup>+</sup>[GaCl<sub>4</sub>]<sup>–</sup>, **3a** (Figure 3d). Attempted isolation of **3a** at –30 °C, however, gave two visually distinct species that cocrystallized as pale yellow and deep red solids. The lighter-colored solid was <sup>1</sup>H NMR silent and had a melting point of 78–79 °C, consistent with GaCl<sub>3</sub> (mp 77.9 ± 0.2 °C).<sup>20</sup> Mechanical separation enabled full characterization of the red crystals, including single-crystal X-ray diffraction analysis, which identified the crystals as the dibismuth cation  $\{[Bi(Me_2Si\{NAr\}_2)]_2(\mu-Cl)\}[GaCl_4]$  (**3b**).

The <sup>1</sup>H NMR spectrum of an isolated sample of **3b** is also consistent with a C<sub>2h</sub> symmetric structure in solution, with selected peaks shifted notably downfield from the corresponding resonances for the [Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)]<sup>+</sup> cation in **3a** (Figure 3c). These chemical shift differences are most prominent for the *p*-C<sub>6</sub>H<sub>5</sub> ( $\delta_H$  6.74 ppm), CHMe<sub>2</sub> ( $\delta_H$  3.90 ppm), and SiMe<sub>2</sub> ( $\delta_H$  0.21 ppm) resonances in **3b**, with  $\Delta\delta_H$  values of



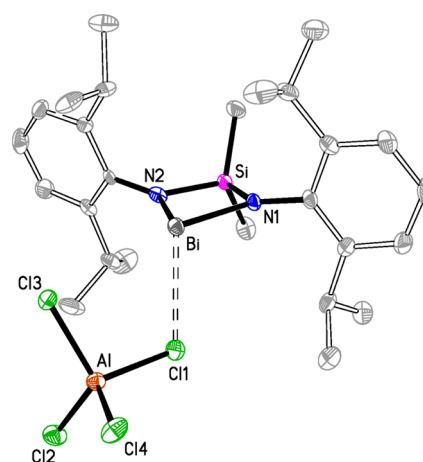
**Figure 3.**  $^1\text{H}$  NMR spectra of cationic Bi compounds **2a**, **2b**, **3a**, and **3b**. (a) **2a** from isolated  $[\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)][\text{AlCl}_4]$ ; (b) **2b** from  $[\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)][\text{AlCl}_4]$  + 1 equiv of  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{Cl}$  (**1**); (c) **3b** from isolated  $[\{\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\}_2(\mu\text{-Cl})][\text{GaCl}_4]$ ; (d) **3a** from  $[\{\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\}_2(\mu\text{-Cl})][\text{GaCl}_4]$  + 1 equiv of  $\text{GaCl}_3$ .

0.16, 0.39, and 0.08 ppm, respectively. As for **2a**, the  $^{29}\text{Si}$  NMR resonance is shifted to low field ( $\delta_{\text{Si}} = 31.2$  ppm), although the magnitude of the shift is much less than it is in the monobismuth cation ( $\Delta\delta_{\text{Si}} = +1.5$ ). These data show that the bimetallic  $[\{\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\}_2(\mu\text{-Cl})]^+$  cation is not retained as a rigid unit in solution.

Addition of 1 equiv of  $\text{GaCl}_3$  to an NMR sample of **3b** in  $\text{C}_6\text{D}_6$  resulted in complete conversion to **3a**. In light of these results, the aluminum system was re-examined to determine whether similar interconversion between **2a** and the tetrachloroaluminate analogue of **3b** is possible. Addition of one equiv of **1** to a solution of **2a** gave a  $^1\text{H}$  NMR spectrum consistent with  $[\{\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\}_2(\mu\text{-Cl})][\text{AlCl}_4]$  (**2b**, Figure 3b), with a maximum  $\Delta\delta$  of 0.04 ppm ( $\text{CHMe}_2$ ) compared with the spectrum obtained from **3b**.

Veith reported that  $\text{Bi}(\text{Me}_2\text{Si}\{\text{N}t\text{-Bu}\}_2)\text{Cl}$  also underwent chloride abstraction to afford the cation formed when reacted with  $\text{InCl}_3$ .<sup>11</sup> However no color change was observed when  $\text{InCl}_3$  was added to a solution of **1**, and NMR analysis indicated that no reaction had occurred. Attempts to promote cation formation by heating the mixture to 80 °C afforded an intractable mixture of species by  $^1\text{H}$  NMR, and no clean product could be isolated. No detailed analysis of changes to the electronic structure upon replacing the nitrogen substituents from *t*-Bu in Veith's compound to 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> in **1** have been performed to explain this lack of reactivity. However, differences in the steric profile of the ligands are evident from the solid-state structures of the chlorides, where  $\text{Bi}(\text{Me}_2\text{Si}\{\text{N}t\text{-Bu}\}_2)\text{Cl}$  forms a one-dimensional (1-D) chain linked by  $\text{Bi}\cdots\text{Cl}$  interactions and **1** is trimeric with  $\text{Bi}\cdots\text{aryl}$   $\pi$ -bonding interactions.

The molecular structure of the tetrachloroaluminate salt  $[\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)][\text{AlCl}_4]$  **2a** is shown in Figure 4, with crystal structure and refinement data collected in Table 1; selected



**Figure 4.** Thermal ellipsoid plot (30% probability, H-atoms omitted) of  $[\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)][\text{AlCl}_4]$  (**2a**).

bond lengths and angles, along with those of the previously reported structure of compound **1** are presented in Table 2. The compound crystallizes as the {1:1} salt with the closest  $\text{Bi}\cdots\text{Cl}$  contact of 2.953(3) Å, considerably longer than the terminal  $\text{Bi}-\text{Cl}$  bonds in **1** [2.556(1) Å and 2.4857(16) Å]. The  $\text{Bi}-\text{N}$  distances in **2a** are within  $3\sigma$  of those in the neutral compound, albeit with a trend toward shorter bonds. The bismuth atom in **2a** deviates slightly from the  $\text{N}_2\text{Si}$  least-squares plane (0.09(1) Å), which contrasts with the *endo* conformation<sup>21</sup> of **1** in which displacements of 0.294(6) and 0.229(8) Å of the bismuth from this plane are observed. This shift contributes to the larger ligand bite angle of 73.7(3)° in **2a** compared with values of 70.74(16)° and 71.78(11)° observed in **1**.

**Table 1. Crystal Structure and Refinement Data for [Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)][AlCl<sub>4</sub>] (2a), [{Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)<sub>2</sub>(μ-Cl)][GaCl<sub>4</sub>] (3b), Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)Ph (4), and Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)Et (5)**

|  | 2a  | 3b·C <sub>6</sub> H <sub>14</sub>  | 2(4)·C <sub>7</sub> (H <sub>8</sub> )  | 5   |
|--|---|--|--|---|
| empirical formula  | C <sub>26</sub> H <sub>40</sub> AlBiCl <sub>4</sub> N <sub>2</sub> Si | C <sub>38</sub> H <sub>94</sub> Bi <sub>2</sub> Cl <sub>5</sub> GaN <sub>4</sub> Si <sub>2</sub> | C <sub>135</sub> H <sub>180</sub> Bi <sub>4</sub> N <sub>8</sub> Si <sub>4</sub> | C <sub>28</sub> H <sub>45</sub> BiN <sub>2</sub> Si |
| M <sub>r</sub>   | 786.45  | 1568.48  | 2863.15  | 646.73  |
| T [K]  | 173(2)  | 120.01(10)   | 120.02(10)   | 120.0   |
| crystal size [mm]  | 0.08 × 0.08 × 0.01  | 0.10 × 0.08 × 0.02   | 0.35 × 0.16 × 0.05   | 0.21 × 0.15 × 0.14                                  |
| crystal system   | orthorhombic  | triclinic  | triclinic  | trigonal  |
| space group  | <i>Pbcn</i> (No.60)   | <i>P</i> $\bar{1}$ (No.2)  | <i>P</i> $\bar{1}$ (No.2)  | <i>R</i> $\bar{3}$ (No.148)                         |
| <i>a</i> [Å]   | 24.9726(10)   | 12.8472(5)   | 12.9068(2)   | 28.7503(11)   |
| <i>b</i> [Å]   | 16.6486(4)  | 17.0713(7)   | 15.6323(4)   | 28.7503(11)   |
| <i>c</i> [Å]   | 16.1717(6)  | 17.4081(7)   | 17.3240(5)   | 9.8541(5)   |
| $\alpha$ [deg]   | 90  | 117.739(4)   | 108.940(2)   | 90  |
| $\beta$ [deg]  | 90  | 92.142(3)  | 93.6783(18)  | 90  |
| $\gamma$ [deg]   | 90  | 90.447(3)  | 100.2794(18)   | 120   |
| <i>V</i> [Å <sup>3</sup> ]                                   | 6723.5(4)   | 3375.4(3)  | 3224.91(14)  | 7053.9(6)   |
| <i>Z</i>   | 8   | 2  | 1  | 9   |
| <i>D</i> <sub>calc.</sub> [mg m <sup>-3</sup> ]              | 1.55  | 1.54   | 1.47   | 1.37  |
| absorption coefficient [mm <sup>-1</sup> ]                   | 5.64  | 12.97  | 5.53   | 5.67  |
| 2 $\theta$ range for data collection [deg]                   | 7.02 to 54.16   | 2.87 to 74.00  | 5.32 to 60.0   | 5.66 to 66.22                                       |
| reflections collected  | 26421   | 26092  | 66037  | 16452   |
| independent reflections                                      | 7374 [R <sub>int</sub> 0.161]   | 13265 [R <sub>int</sub> 0.034]   | 18799 [R <sub>int</sub> 0.035]   | 5348 [R <sub>int</sub> 0.072]                       |
| reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )          | 4578  | 11200  | 15967  | 4288  |
| data/restraints/parameters                                   | 7374/0/316  | 13265/36/671   | 18799/0/714  | 5348/114/179  |
| final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | <i>R</i> 1 = 0.077, <i>wR</i> <sub>2</sub> = 0.163                    | <i>R</i> 1 = 0.031, <i>wR</i> <sub>2</sub> = 0.073   | <i>R</i> 1 = 0.024, <i>wR</i> <sub>2</sub> = 0.053                               | <i>R</i> 1 = 0.129, <i>wR</i> <sub>2</sub> = 0.272  |
| final <i>R</i> indices (all data)                            | <i>R</i> 1 = 0.131 <i>wR</i> <sub>2</sub> = 0.189                     | <i>R</i> 1 = 0.040, <i>wR</i> <sub>2</sub> = 0.080   | <i>R</i> 1 = 0.033, <i>wR</i> <sub>2</sub> = 0.056                               | <i>R</i> 1 = 0.151 <i>wR</i> <sub>2</sub> = 0.280   |
| GOF on <i>F</i> <sup>2</sup>                                 | 1.018   | 1.036  | 1.036  | 1.323   |
| largest diff. peak/hole [e Å <sup>-3</sup> ]                 | 3.64 and -3.18 <sup>a</sup>   | 1.66 and -2.15   | 1.82 and -0.97   | 1.88 and -3.13                                      |

<sup>a</sup>Close to Bi.

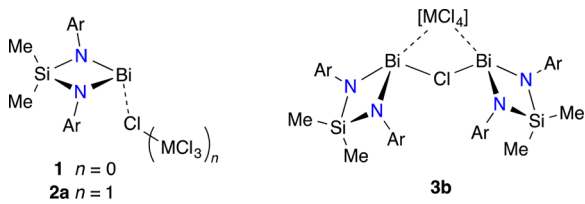
There is a relatively large range of Al–Cl bond lengths in the tetrachloroaluminate anion ( $\Delta_{\text{AlCl}} = 0.08$  Å), reflecting differing degrees of Bi···Cl interaction. The longest Al–Cl bond (2.172(4) Å) involves chloride Cl1, which is most closely associated with the bismuth. The shortest bond (Al–Cl2, 2.091(5) Å) is at the low end of the range noted for a series of noncoordinated [AlCl<sub>4</sub>]<sup>−</sup> anions within the structurally characterized compounds [M(crown)<sub>*n*</sub>(THF)<sub>*m*</sub>][AlCl<sub>4</sub>] (M = Li/Na, crown = 12-c-4, *n* = 2, *m* = 0; M = Na/K, crown = 18-c-6, *n* = 1, *m* = 2; M = K, crown = 15-c-5, *n* = 2, *m* = 0; range of Al–Cl bond lengths = 2.102(2)–2.1469(9) Å),<sup>22</sup> consistent with a terminal chloride ligand. The remaining Al–Cl bonds are intermediate between these two values and involve chlorides that are engaged in intermolecular Bi···Cl interactions to another cation, resulting in an overall {1:1}<sub>2</sub> molecular structure (Figure 5). The bonding mode of the [AlCl<sub>4</sub>]<sup>−</sup> anion in hexa- $\mu$ -chlorido-1:3 $\kappa^4$ Cl,1:4 $\kappa^2$ Cl,2:3 $\kappa^2$ Cl,2:4 $\kappa^4$ Cl-dichlorido-1 $\kappa$ Cl,2 $\kappa$ Cl-[*N,N'*-dimethylsilanediy]bis(2,6-dipropylphenylamido-3 $\kappa$ N)][*N,N'*-dimethylsilanediy]bis(2,6-dipropylphenylamido-4 $\kappa$ N)]dialuminumdibismuth ([2a]<sub>2</sub>) is unusual, but has been previously observed in polymeric tin<sup>23</sup> and samarium<sup>24</sup> complexes.

The bismuth component of the tetrachlorogallate salt 3b consists of a  $\mu$ -chlorido-bridged monocation in which each pyramidal Bi atom retains a bidentate diamido-ligand. The interplanar angle between the SiN<sub>2</sub>Bi metallacycles is 144.03(11)° with a *trans*–*trans* arrangement of the ligands with respect to Si···Bi–Cl–Bi···Si. This unit is supported by three Bi···Cl interactions to the [GaCl<sub>4</sub>]<sup>−</sup> anion (Figure 6). The Bi–Cl1 bond lengths within the cation are inequivalent (2.7888(12) and 2.6902(12) Å to Bi1 and Bi2, respectively;  $\Delta_{\text{BiCl}} = 0.10$  Å), suggesting a localization of positive charge on Bi2. Both of the

Bi–Cl distances are longer than the terminal chloride bonds in 1 and shorter than the closest Bi···Cl ion-contact in 2a, suggesting an intermediate bonding type with delocalization across the Bi–Cl–Bi moiety. The asymmetry is in good agreement with the only other structurally characterized mono chloride-bridged cation, [{*t*-BuN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Bi]<sub>2</sub>(μ-Cl)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>],<sup>7</sup> for which  $\Delta_{\text{BiCl}} = 0.11$  Å. As noted for 2a, there is no significant decrease in Bi–N bond lengths upon generation of the cation, and the Bi atoms are essentially coplanar with the chelating diamide (deviation from the N<sub>2</sub>Si least-squares plane = 0.088(8) and 0.050(7) Å for Bi1 and Bi2, respectively), generating relatively large ligand bite angles of 72.08(15)° and 72.21(15)°.

The interior Bi···Cl distances in the asymmetric unit of 3b span the range of 3.3168(2)–3.5618(2) Å and are considerably shorter than they are in the crystal structure of IV in which no bismuth-to-tetrachlorogallate contacts are described.<sup>15</sup> Two of the interactions in 3b involve Bi2, also consistent with this being the more positive metal. The Ga–Cl bond lengths (range from 2.1622(14) Å to 2.1878(14) Å) span those reported for IV and the series of [M(crown)<sub>*n*</sub>(THF)<sub>*m*</sub>][GaCl<sub>4</sub>] compounds (M = Li/Na, crown = 12-c-4, *n* = 2, *m* = 0; M = Na, crown = 18-c-6, *n* = 1, *m* = 0; M = K, crown = 18-c-6, *n* = 1, *m* = 2).<sup>25</sup> The difference in the Ga–Cl bond lengths within the anion ( $\Delta_{\text{GaCl}} = 0.03$  Å) is considerably smaller than the corresponding difference in the Al–Cl distances of 2a, consistent with all four chlorides being involved in Bi···Cl interactions. Indeed, examination of the unit cell of 3b confirms that Cl4 is associating with a second cation (Cl4···Bi1' 3.3277(1) Å) to generate the {1:1}<sub>2</sub> aggregate bis[μ-chlorido-[*N,N'*-dimethylsilanediy]bis(2,6-dipropylphenylamido-1 $\kappa$ N)]-[*N,N'*-dimethylsilanediy]bis(2,6-dipropylphenylamido-2 $\kappa$ N)]dibismuth(1+)}deca- $\mu$ -chlorido-1:3 $\kappa^4$ Cl,1:4 $\kappa^2$ Cl,1:5 $\kappa^2$ Cl,

Table 2. Selected Bond Lengths (Å) for 2a and 3b, Presented with Those of 1 for Comparison



|         | 1 <sup>a</sup> | 2a <sup>b</sup> | 3b <sup>c</sup> |
|---------|----------------|-----------------|-----------------|
| Bi–N    | 2.132(3)       | 2.118(8)        | 2.121(4)        |
|         | 2.144(3)       | 2.120(8)        | 2.131(3)        |
|         | 2.181(3)       |                 | 2.143(3)        |
| Bi–Cl   | 2.4857(16)     |                 | 2.6902(12)      |
|         | 2.5560(10)     |                 | 2.7888(12)      |
|         |                | 2.953(3)        | 3.3168(14)      |
| Bi...Cl |                |                 | 3.3277(13)      |
|         |                |                 | 3.5373(16)      |
|         |                |                 | 3.5618(14)      |
| Si–N    | 1.733(3)       | 1.763(9)        | 1.734(4)        |
|         | 1.735(3)       | 1.765(8)        | 1.736(4)        |
|         | 1.736(3)       |                 | 1.748(4)        |
|         |                |                 | 1.752(4)        |
| M–Cl    |                | 2.091(5)        | 2.1622(14)      |
|         |                | 2.134(4)        | 2.1689(15)      |
|         |                | 2.152(4)        | 2.1770(13)      |
|         |                | 2.172(4)        | 2.1878(14)      |
| N–Bi–N  | 70.74(16)      | 73.7(3)         | 72.08(15)       |
|         | 71.78(11)      |                 | 72.21(15)       |
| N–Si–N  | 92.58(15)      | 92.1(4)         | 92.67(17)       |
|         | 93.3(2)        |                 |                 |
| Bi–N–Si | 97.17(14)      | 97.1(3)         | 97.00(17)       |
|         | 97.54(13)      | 97.0(3)         | 97.64(18)       |
|         | 97.71(14)      |                 | 97.88(18)       |
|         |                |                 | 98.16(17)       |
| N–Bi–Cl | 96.34(9)       | 94.2(2)         | 94.28(11)       |
|         | 96.37(9)       | 98.1(2)         | 97.56(11)       |
|         | 97.89(9)       |                 | 97.76(10)       |
|         |                |                 | 101.12(11)      |

<sup>a</sup>1.5 molecules in the unit cell. <sup>b</sup>M = Al. <sup>c</sup>M = Ga.

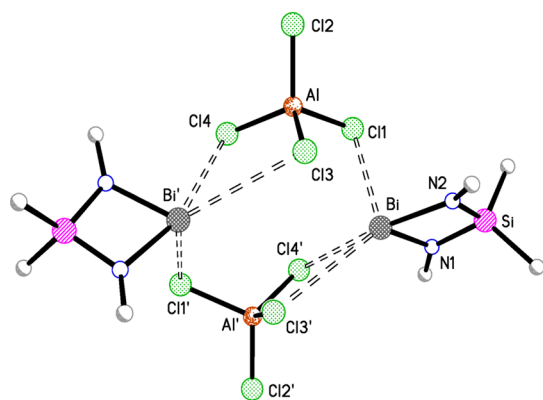


Figure 5. Molecular structure of [2a]<sub>2</sub>, showing the bridging [AlCl<sub>4</sub>]<sup>−</sup> anions (′ = 1 − x, y, 1/2 − z; aryl groups reduced to show only *ipso*-carbon atoms).

1:6κ<sup>2</sup>Cl,2:4κ<sup>2</sup>Cl,2:5κ<sup>2</sup>Cl,2:6κ<sup>4</sup>Cl,3:4κ<sup>2</sup>Cl,5:6κ<sup>2</sup>Cl-[N,N′-dimethylsilanediybis(2,6-dipropan-2-ylphenylamido-3κN)]-

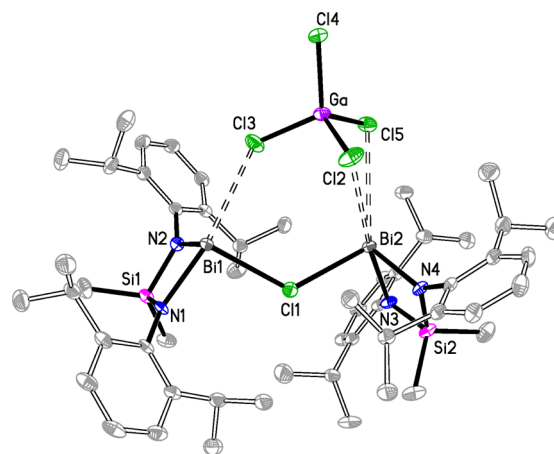


Figure 6. Thermal ellipsoid plot (30% probability, H-atoms and hexane solvate omitted) of [{Bi(Me<sub>2</sub>Si{NAr}<sub>2</sub>)<sub>2</sub>}]<sub>2</sub>(μ-Cl)[GaCl<sub>4</sub>] (3b).

[N,N′-dimethylsilanediybis(2,6-dipropan-2-ylphenylamido-4κN)][N,N′-dimethylsilanediybis(2,6-dipropan-2-ylphenylamido-5κN)][N,N′-dimethylsilanediybis(2,6-dipropan-2-ylphenylamido-6κN)]digalliumtetrabismuthate(2-) in the solid state ([3b]<sub>2</sub>, Figure 7). This is the only structurally characterized

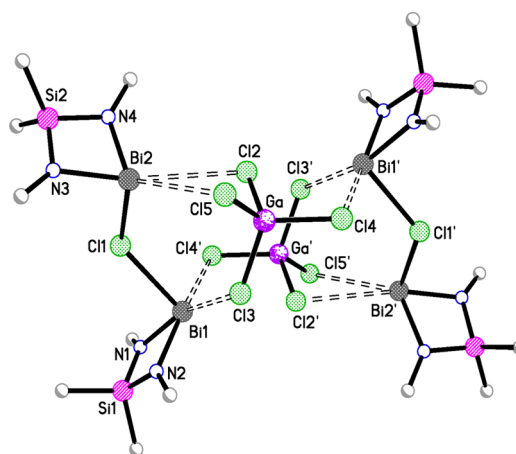


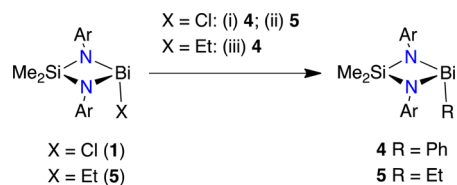
Figure 7. Molecular structure of [3b]<sub>2</sub>, showing the bridging [GaCl<sub>4</sub>]<sup>−</sup> anions (′ = −x, −y, −z; aryl groups reduced to show only *ipso*-carbon atoms).

example of the tetrachlorogallate anion interacting through all four chloride ligands.

**3.2. Reaction with M[BR<sub>4</sub>] (M = Na, R = Ph, Et; M = HNEt<sub>3</sub>, R = Ph).** Evans and co-workers have shown that the bis(aryl) bismuth chloride compound BiAr′<sub>2</sub>Cl (Ar′ = 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) is converted to the tetraphenylborate salt upon reaction with NaBPh<sub>4</sub> (Scheme 2). The cation is also generated from the protonolysis reaction of the allyl compound BiAr′<sub>2</sub>(CH<sub>2</sub>CH=CH<sub>2</sub>) with [HNEt<sub>3</sub>][BPh<sub>4</sub>].<sup>9</sup> Monitoring a mixture of 1 and NaBPh<sub>4</sub> by <sup>1</sup>H NMR spectroscopy indicated that the reaction did not proceed at room temperature. Heating the reaction to 90 °C for 3 d, however, afforded a mixture of yellow 4 and colorless crystals upon workup. Physical separation allowed pure samples of 4 to be prepared for analysis by NMR spectroscopy, elemental analysis, and X-ray diffraction.

<sup>1</sup>H NMR data for 4 indicate a C<sub>1</sub> symmetry structure, with SiMe<sub>2</sub> resonances at δ<sub>H</sub> 0.63 and 0.15 ppm. Integration of the aromatic region of the spectrum is consistent with the presence

**Scheme 2.** Reaction of  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{X}$  ( $1$   $\text{X} = \text{Cl}$ ,  $5$   $\text{X} = \text{Et}$ ) with  $[\text{A}][\text{BR}_4]$  ( $\text{A} = \text{Na}$ ,  $\text{R} = \text{Ph}$ ,  $\text{Et}$ ;  $\text{A} = \text{HNEt}_3$ ,  $\text{R} = \text{Ph}$ )<sup>a</sup>



<sup>a</sup>(i)  $\text{NaBPh}_4$ ; (ii)  $\text{NaBEt}_4$ ; (iii)  $[\text{HNEt}_3][\text{BPh}_4]$ .

of a single phenyl group, with the peaks assigned to the *ortho*-protons at low field ( $\delta_{\text{H}} = 8.48$  ppm,  $\text{C}_6\text{D}_6$ ). This chemical shift is significantly different from that observed for the  $[\text{BPh}_4]^-$  anion (e.g.,  $[\text{Bi}(\text{Ar}')_2][\text{BPh}_4]$ ;  $\delta_{\text{H}} = 6.99$  ppm,  $\text{CD}_3\text{CN}$ <sup>9</sup>) and  $\text{BiPh}_3$  ( $\delta_{\text{H}} = 7.73$  ppm,  $\text{C}_6\text{D}_6$ ). These data are consistent with formation of the phenyl compound  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{Ph}$ , confirmed by elemental analysis and an X-ray crystal structure determination (*vide infra*). The colorless crystals that formed during the reaction were identified as  $\text{BPh}_3$  by <sup>11</sup>B NMR spectroscopy ( $\delta_{\text{B}} = 68$  ppm<sup>26</sup>) and by comparison of their unit cell with published data.<sup>27</sup>

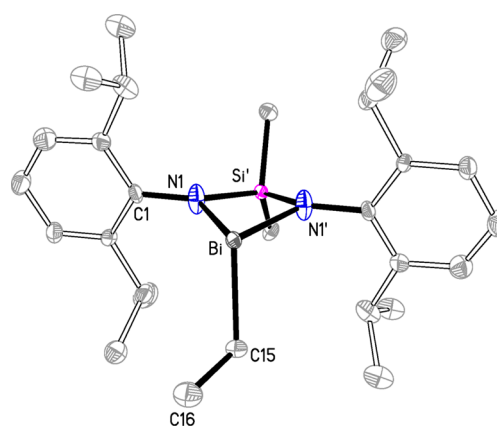
Aryl transfer reactions from  $[\text{BAR}_4]^-$  anions are well documented,<sup>28</sup> and the reaction of  $\text{Na}[\text{BAR}_4']$  ( $\text{Ar}' = \text{Ph}$ , *p*-tolyl, 4-F-C<sub>6</sub>H<sub>4</sub>) with bismuth(III) carboxylates has been reported recently as a convenient route to  $\text{BiAr}_3'$  species.<sup>29</sup> To probe this mode of reactivity further we examined the reaction of **1** with  $\text{Na}[\text{BEt}_4]$ , where the tetraethylborate anion is known to behave as an alkyl transfer reagent.<sup>30</sup> In this case the reaction proceeded at room temperature, affording pale yellow crystals on workup. <sup>1</sup>H NMR data was consistent with the bismuth ethyl compound  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{Et}$  (**5**) showing a C<sub>1</sub> symmetry ( $\text{SiMe}_2$ :  $\delta_{\text{H}} = 0.42$  and  $0.04$  ppm). The resonances for methyl and methylene groups of the ethyl ligand appear as a triplet and quartet at  $\delta_{\text{H}} = 2.47$  and  $2.04$  ppm, respectively. The <sup>29</sup>Si NMR resonances for **4** ( $\delta_{\text{Si}} = 19.5$  ppm) and **5** ( $\delta_{\text{Si}} = 17.8$  ppm) are shifted to higher field compared with **1** ( $\Delta\delta_{\text{Si}} = -10.2$  ppm and  $-11.9$  ppm, respectively), reflecting the relatively electron-rich metallacycle upon exchanging the bismuth substituent from chloride to aryl/alkyl groups.

The structures of **4** and **5** were determined by single-crystal X-ray diffraction experiments (Tables 1 and 3; Figures 8 and 9).

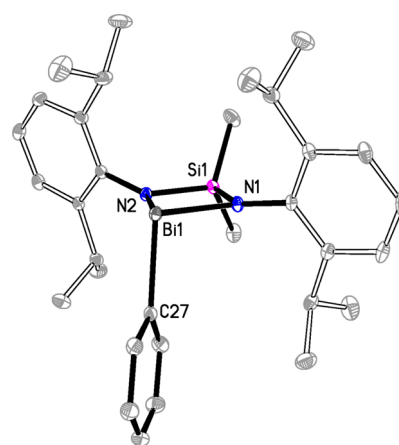
**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **4**

|            |           |            |            |
|------------|-----------|------------|------------|
| Bi1–N1     | 2.168(2)  | Bi2–N3     | 2.1790(19) |
| Bi1–N2     | 2.177(2)  | Bi2–N4     | 2.172(2)   |
| Bi1–C27    | 2.253(3)  | Bi2–C58    | 2.252(3)   |
| Si1–N1     | 1.713(2)  | Si2–N3     | 1.721(2)   |
| Si1–N2     | 1.726(2)  | Si2–N4     | 1.731(2)   |
| N1–Bi1–N2  | 70.50(7)  | N3–Bi2–N4  | 70.86(7)   |
| N1–Bi1–C27 | 98.02(9)  | N3–Bi2–C58 | 100.32(8)  |
| N2–Bi1–C27 | 100.50(9) | N4–Bi2–C58 | 97.44(9)   |
| Bi1–N1–Si1 | 98.21(9)  | Bi2–N3–Si2 | 97.63(9)   |
| Bi1–N2–Si1 | 97.49(9)  | Bi2–N4–Si2 | 97.59(9)   |
| N1–Si1–N2  | 93.65(10) | N3–Si2–N4  | 93.90(10)  |

Unfortunately the data solution for compound **5** was complicated by molecular disorder that was modeled in the  $R\bar{3}$  space group as being about an inversion center (Supporting Information, Figure S2). This disorder is most likely caused by the small size of the ethyl substituent compared to other X-groups in the  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{X}$  compounds, resulting in a



**Figure 8.** Thermal ellipsoid plot (30% probability) of  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{Et}$ , **5** ( $' = 1 - x, 1 - y, -z$ ; H-atoms omitted).

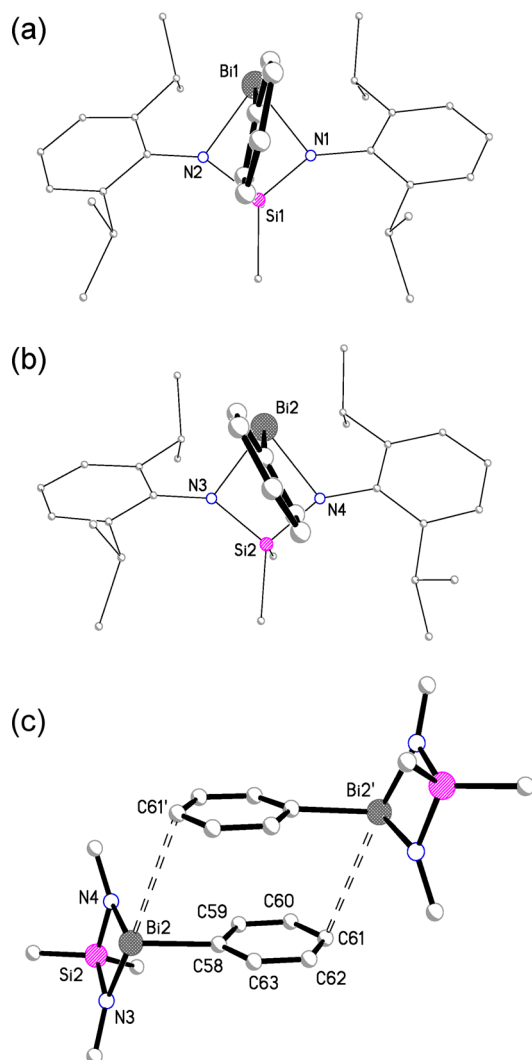


**Figure 9.** Thermal ellipsoid plot (30% probability) of one of the independent molecules of  $\text{Bi}(\text{Me}_2\text{Si}\{\text{NAr}\}_2)\text{Ph}$ , **4** (H-atoms and toluene solvate omitted).

small energy difference between the two orientations of the metallacycle with respect to the aryl substituents. As a result the solution of the data is not of sufficient quality for a meaningful discussion of bond lengths and angles; it does, however, confirm the connectivity of **5** as a rare example of a monomeric bismuth-ethyl compound (Figure 8).<sup>31</sup>

Compound **4** crystallizes as the toluene solvate, with two independent molecules in the unit cell that differ primarily with respect to the orientation of the phenyl substituent (Figure 9). Each molecule is monomeric with a pyramidal geometry of the Bi atom and an essentially planar metallacycle (deviation of Bi from mean  $\text{SiN}_2$  plane: Bi1 0.121(4) Å, Bi2 0.037(4) Å). The Bi–N bond lengths in **4** are longer than in the other structures examined during this study, resulting in a smaller average bite angle of 70.68(7)° for the diamide ligand. The Bi–C bond length (2.253(3) Å) is unexceptional and is within the range noted for  $\text{BiPh}_3$  (2.237(7) to 2.273(8) Å).<sup>32</sup>

Comparing the two molecules within the unit cell we note that phenyl groups are rotated in opposite directions along the Bi–C<sub>ipso</sub> bond relative to the plane bisecting the metallacycle through the silicon, bismuth, and C<sub>ipso</sub> atoms (molecule Bi1 = +14.85(7)°; molecule Bi2 = –29.56(11)°, where +ve = clockwise direction—Figure 10a,b). This twisted orientation brings the portion of the phenyl group located below the metallacycle into close proximity with one of the *i*-Pr groups of the aryl substituents. The resulting steric conflict is alleviated by the nitrogen



**Figure 10.** Schematic representations of the two molecules of **4**, showing (a) the different rotation of the phenyl ligand relative to the Si $\cdots$ Bi–C $_{ipso}$  vector, (b) the displacement of one of the aryl groups out of the plane of the metallacycle, and (c) the dimerization of molecule Bi2 ( $' = 2 - x, -y, 1 - z$ ).

aryl-substituent being located above the BiNSiN-plane, illustrated by the different angles that the N–C $_{ipso}$  bonds adopt with respect to this plane (molecule Bi1: N1–C1 = 5.9°, N2–C13 = 15.3°; molecule Bi2: N3–C34 = 9.3°, N4–C46 = 21.2°; see Supporting Information, Figure S3).

The twisting of the phenyl ligand is more pronounced in molecule Bi2. Examination of the packing shows that this molecule is involved in intermolecular interactions with a symmetry generated equivalent positioned about an inversion center (Figure 10c). The *para*-carbon atom of the phenyl substituent (C61) is located at 3.629(3) Å from Bi2' ( $' = 2 - x, -y, 1 - z$ ), within the range of distances previously attributed to a bonding interaction within the series of compounds [BiCl $_3$ ·(C $_6$ H $_{6-n}$ Me $_n$ )] (Bi $\cdots$ C distances 3.168(7) to 3.751(8) Å).<sup>33</sup> However, the large ring slippage of 2.57 Å from the centroid of the C $_6$ -ring suggests that it is the  $\pi$ – $\pi$  interactions between the two phenyl rings that dominate (centroid–centroid distance 3.827(3) Å, plane-to-plane shift 1.295(5) Å), although the role of crystal packing forces should not be dismissed.

## 4. DISCUSSION

The paucity of low-coordinate bismuth cations is illustrated by the facts that **2a** is only the second formally two-coordinate Bi $^+$  center to be structurally characterized and that **2a** is a derivative of the first example.<sup>11</sup> This is perhaps not surprising given the large radius of the element and the focus on multidentate ligands in this area of chemistry. As a consequence, additional interion (and other intermolecular) interactions become important in the condensed (solid) state, as shown by the Bi $\cdots$ Cl contacts present in the structures of **2a** and **3b**.

Previous work has quantified the bond order (BO) of Bi $\cdots$ Cl interactions (eq 1),<sup>34</sup> using values of  $r_0 = 2.423$  Å<sup>35</sup> and  $B = 0.39$ .<sup>36</sup> We recently used this equation to show that the intermolecular Bi $\cdots$ Cl BO between associated molecules in the trimeric unit of **1** was 0.14<sup>18</sup> and that this was significantly less than that calculated for a similar Bi $\cdots$ Cl interaction in the *Nt*-Bu analogue (BO = 0.20).<sup>37</sup> Table 4 summarizes a series of BOs for some bismuth chloride compounds and the corresponding cations, generated by halide abstraction using MCl $_3$  (M = Al, Ga).

$$\text{BO} = \exp\left[\frac{(r_0 - r)}{B}\right] \quad (\text{eq 1})$$

According to eq 1, the terminal bismuth chloride bonds in **1** have BOs of 0.85 and 0.71, reflecting the relatively long Bi–Cl distances. The smaller BO (weaker bond) corresponds to the chloride involved in bridging interactions to another molecule, showing the sensitivity of this measurement to small changes in the environment of the bond. Given that these Bi–Cl BOs are significantly less than unity, it is perhaps not surprising that chloride abstraction and generation of bismuth cations is a relatively facile process.

Conversion of **1** to the cation and association of the formally positive bismuth metal and the tetrachloroaluminate anion gives a BO of 0.26 for the primary Bi $\cdots$ Cl interaction, suggesting a strongly associated ion pair in the solid state with a reduction of  $\sim 0.5$  on generation of the cation ( $\Delta\text{BO} = -0.59$  and  $-0.45$ ). Unfortunately, it is not possible to make a direct comparison with the  $\Delta\text{BO}$  in the corresponding *Nt*-Bu cation (**I**, Figure 2), as the primary Bi–Cl bond in the neutral compound (BO = 0.43) is already weakened by intermolecular interactions along a 1-D chain in the crystal structure (*vide supra*). Nevertheless a reduction is observed upon generation of the cation, with the principal Bi $\cdots$ [Cl–AlCl $_3$ ] BO of 0.19 in this case approximately equal to the weaker Bi–Cl $\cdots$ Bi bridging bond along the chain. The calculated BO values for the Bi $\cdots$ [Cl–AlCl $_3$ ] interactions of the associated dimer in **2** (Figure 5) are 0.11 and 0.04 for Cl4 and Cl3, respectively. These values indicate weak, nonsymmetrical bonding to the second bismuth cation with values lower than the major interion interactions in **I**.

Comparing these BOs with the corresponding values for other ligand systems shows that the  $\Delta\text{BO}$ s upon cation generation are highly dependent on the ligand. For example, the bulky cyclopentadienyl derivative [Bi(Cp $''$ )Cl $_2$ ] $_2$  has BO values of 0.75 for the terminal Bi–Cl bonds, with the BOs of the nonsymmetrical bridging  $\mu$ -chlorides being 0.53 and 0.19 (average from two crystal modifications). Formation of the cation retains the dimeric unit, with only minor modifications to the Bi( $\mu$ -Cl)Bi BOs (0.57 and 0.20), and the closest contact to the [AlCl $_4$ ] $^-$  corresponding to a BO of 0.06.



Table 4. Bond Orders (BOs) for Bi–Cl Bonds and Bi⋯Cl Interactions, Calculated Using eq 1

| compound  | Bi–Cl<br>bond order (BO)  | [Bi]⋯[Cl–MCl <sub>3</sub> ]<br>bond order (BO) | reference |
|---|---|--|-----------|
| [Bi(Me <sub>2</sub> Si{NAr} <sub>2</sub> )Cl] <sub>3</sub> <sup>a</sup> (1)                 | 0.85<br>0.71<br>0.14 (μ <sup>-</sup> )                                  |  | 18        |
| [Bi(Me <sub>2</sub> Si{NAr} <sub>2</sub> )] [AlCl <sub>4</sub> ] (2a)                       |   | 0.26<br>0.11<br>0.04                           | this work |
| [Bi(Me <sub>2</sub> Si{Nt-Bu} <sub>2</sub> )Cl] <sub>∞</sub>                                | 0.43 (μ <sup>-</sup> )<br>0.20 (μ <sup>-</sup> )                        |  | 37        |
| [Bi(Me <sub>2</sub> Si{Nt-Bu} <sub>2</sub> )] [AlCl <sub>4</sub> ] (I)                      |   | 0.19<br>0.17<br>0.03<br>0.02                   | 11        |
| [Bi(Cp <sup>''</sup> )Cl] <sub>2</sub> <sup>a</sup>   | 0.75/0.74<br>0.48/0.57 (μ <sup>-</sup> )<br>0.22/0.16 (μ <sup>-</sup> ) |  | 14, 38    |
| [Bi(Cp <sup>''</sup> )Cl] [AlCl <sub>4</sub> ]  | 0.57 (μ <sup>-</sup> )<br>0.20 (μ <sup>-</sup> )                        | 0.06<br>0.06                                   | 14        |
| Bi(N{SiMe <sub>3</sub> }N{SiMe <sub>3</sub> } <sub>2</sub> ) <sub>2</sub> Cl                | 0.77  |  | 15        |
| [Bi(N{SiMe <sub>3</sub> }N{SiMe <sub>3</sub> } <sub>2</sub> )] [GaCl <sub>4</sub> ] (IV)    |   | 0.03<br>0.03                                   | 15        |
| [{Bi(Me <sub>2</sub> Si{NAr} <sub>2</sub> )} <sub>2</sub> (μ-Cl)] [GaCl <sub>4</sub> ] (3b) | 0.50 (μ <sup>-</sup> )<br>0.39 (μ <sup>-</sup> )                        | 0.10<br>0.10<br>0.06<br>0.05                   | this work |

<sup>a</sup>Two different crystal modifications; Cp<sup>''</sup> = [1,2,3,4-*i*Pr<sub>4</sub>C<sub>5</sub>H]<sup>-</sup>.

The tetrachlorogallate salt **3b** has a nonsymmetrically bridging chloride in the cationic unit, with BOs of 0.50 and 0.39. Despite being aligned well within the dimeric unit (Figure 7), the interior BOs for Bi⋯[Cl–GaCl<sub>3</sub>] are only 0.10 to 0.05, indicating a weak interaction. These are only slightly more than the calculated BOs of 0.03 in [Bi(N{SiMe<sub>3</sub>}N{SiMe<sub>3</sub>}<sub>2</sub>)] [GaCl<sub>4</sub>] (IV).

In summary, the BOs associated with terminal Bi–Cl bonds in neutral species are significantly less than those expected for a single bond, being typically in the range of 0.7–0.8. In contrast the intermolecular BOs calculated for Bi–Cl⋯Bi bridges during the formation of μ,μ-dichlorobridged dimers can be as much as ~0.55 and during the association of neutral molecules can be up to ~0.43. Surprisingly, formation of “contact” ion pairs does not give such large values of BO between the Bi<sup>+</sup> center and the tetrachloroaluminate anion, despite the electrostatic attraction between the ions. This may be due to a delocalization of the positive charge into the ancillary ligands at Bi (as noted for the *N,N',N'*-tris(trimethylsilyl)hyradzido salt IV) and the relative exposure of the (long) terminal Bi–Cl bonds compared with the much shorter Al–Cl bonds.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Alternative solution-state structures for a C<sub>2h</sub> ligand environment; additional projections of the crystal structures of **4** and **5**; crystallographic information files (CIF format) for **2a** (CCDC 990963), **3b** (CCDC 990964), **4** (CCDC 990965), and **5** (CCDC 990966). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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