

# An Anionic Aluminabenzene Bearing Aromatic and Ambiphilic Contributions

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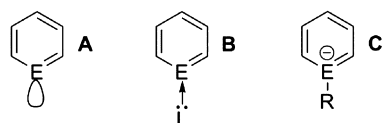
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**S** Supporting Information

**ABSTRACT:** The synthesis and structure of an anionic aluminabenzene, which is the first example of an aluminum-containing heterobenzene, are reported. The molecular structure of this aluminabenzene exhibits a planar six-membered ring, and the absence of any bond alternation between its unsaturated bonds is consistent with the structural criteria of aromaticity. Theoretical calculations and the NMR spectroscopic analysis of this anionic aluminabenzene furthermore suggest that, in addition to the aromatic conjugation of six  $\pi$ -electrons, an ambiphilic contribution from a Lewis acidic aluminum center and an anionic pentadienyl moiety are present. Due to this contribution, the aluminabenzene is able to react with Lewis bases such as 4-dimethylaminopyridine and electrophiles such as methyl iodide.

Benzene is one of the most fundamental organic molecules. Six-membered  $6\pi$  aromatic systems similar to benzene typically consist of carbon and nitrogen atoms. The incorporation of heavier main group elements from the third, fourth, or higher periods of the periodic table into such aromatic systems has recently attracted much attention, mostly because benzene rings containing heavy elements best describe the structural motif of “heavy aromaticity”.<sup>1</sup> Whereas the synthesis of a variety of benzene derivatives with elements from group 14 and 15, e.g., as sila-,<sup>2</sup> germa-,<sup>3</sup> phospho-,<sup>4</sup> arsa-,<sup>5</sup> stiba-,<sup>6,7</sup> and bismabenzene,<sup>7</sup> has been reported and allowed further insight into their aromaticity, reports on the isolation of analogues with group 13 elements still remain limited.<sup>8</sup> The incorporation of an electron-deficient group 13 element in these benzene derivatives with  $6\pi$  electrons results in the presence of an empty  $sp^2$  orbital (A, Chart 1), which should lead to considerable instability. It is therefore not surprising that so far, no example of a heterobenzene containing a group 13 element and a vacant  $sp^2$  orbital has been reported. However, several examples of corresponding Lewis base-coordinated compounds (B, Chart

**Chart 1. Heterobenzenes Containing a Group 13 Element**

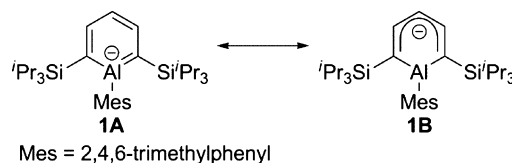


E = group 13 element, L = Lewis base, R = anionic ligand

1) and anionic complexes (C, Chart 1) have been synthesized and these show remarkable stability, once the vacant  $sp^2$  orbital is occupied. Although several boron-containing heterobenzene derivatives are known, only one example containing the heavier group 13 element gallium has been reported in the form of an anionic galabenzene, which was spectroscopically characterized in solution.<sup>9</sup> The corresponding aluminum analogue, aluminabenzene, still remains unknown despite several theoretical studies suggesting its aromaticity.<sup>10</sup> Examples of an aluminum–carbon double bond also remain elusive, even though it represents a fundamental class of chemical bonds. The synthetic difficulty to isolate aluminabenzenes may be attributed to the energetically unfavorable orbital overlapping between the 3p orbital of aluminum and the 2p orbital of carbon to form an unsaturated bond. The closest example to aluminum-containing aromatic compounds with unsaturated bonds between aluminum and carbon is a dianionic aluminacyclopentadiene, which was recently synthesized, characterized, and interpreted as an aluminum analogue of the cyclopentadienyl anion, in which the endocyclic Al–C bonds were found to be contracted in comparison to its precursor.<sup>11</sup>

Herein, we report the synthesis and characterization of the anionic aluminabenzene **1**, which represents the first isolated example of an aluminum-containing benzene ring (Chart 2). The

**Chart 2. Mesomeric Resonance Structures of 1**

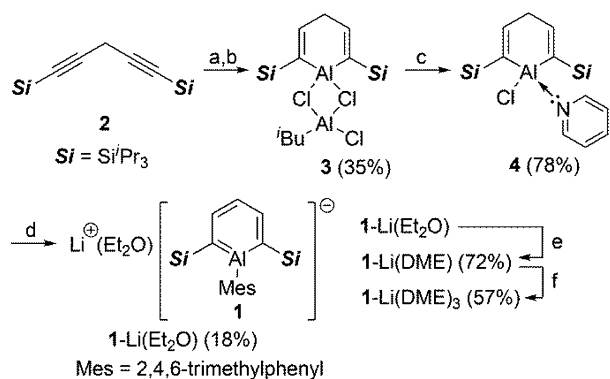


crystallographic analysis, as well as the theoretical and spectroscopic examinations, suggests for this compound a significant contribution of the ambiphilic resonance form **1B** in addition to the aromatic resonance form **1A**. This notion was supported by the ability of **1** to sequentially react with a Lewis base and an electrophile.

Aluminabenzene **1** was synthesized following the synthetic strategy outlined in Scheme 1. The reaction of bis-(triisopropylsilyl)diyne **2** with DIBAL-H, followed by addition of <sup>n</sup>Bu<sub>2</sub>SnCl<sub>2</sub>, resulted in the formation of chloro-bridged dinuclear aluminacyclohexadiene **3** in 32% yield (for a discussion

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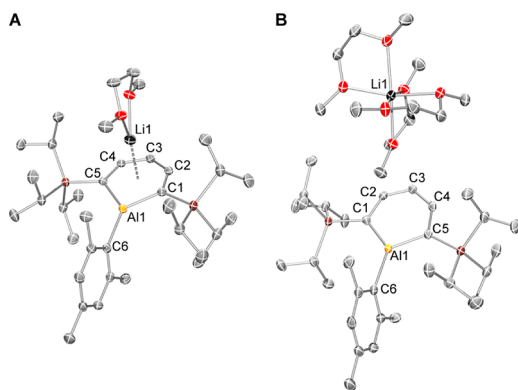
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Scheme 1. Synthesis of **1** and Recrystallization Conditions<sup>a</sup>

<sup>a</sup>Reaction conditions: (a) DIBAL-H, hexane; (b)  $t\text{Bu}_2\text{SnCl}_2$ , hexane; (c) pyridine; (d) MesLi,  $\text{Et}_2\text{O}$ ; (e) treatment with DME, then recrystallization from toluene at  $-35^\circ\text{C}$ ; (f) recrystallization from DME at  $-35^\circ\text{C}$ .

of the reaction mechanism, see the Supporting Information (SI)). Subsequent treatment of **3** with pyridine afforded pyridine-coordinated aluminacyclohexadiene **4** in 78% yield, which was used as a precursor for **1**. Although attempts to abstract a proton from **4** with bulky bases such as TMPLi to generate the corresponding neutral Lewis base-coordinated aluminabenzene (**B**, Chart 1) were unsuccessful, the reaction of **4** with mesityllithium in  $\text{Et}_2\text{O}$  at  $-35^\circ\text{C}$  gave the anionic aluminabenzene  $1\text{-Li}(\text{Et}_2\text{O})$ . Unfortunately, the attempted recrystallization of  $1\text{-Li}(\text{Et}_2\text{O})$  failed to produce single crystals suitable for X-ray crystallographic analysis, but the optimization of the recrystallization conditions showed that the  $\text{Et}_2\text{O}$  solvate molecule coordinating the lithium cation could be exchanged through the addition of other coordinating solvents such as 1,2-dimethoxyethane (DME). Depending on the conditions, recrystallization of  $1\text{-Li}(\text{Et}_2\text{O})$  in the presence of DME deposited two types of crystals,  $1\text{-Li}(\text{DME})$  or  $1\text{-Li}(\text{DME})_3$ , both of which were suitable for X-ray crystallographic analysis. Treatment of  $1\text{-Li}(\text{Et}_2\text{O})$  with DME and a subsequent recrystallization from toluene at  $-35^\circ\text{C}$  resulted in the deposition of single crystals of  $1\text{-Li}(\text{DME})$  in 72% yield. Recrystallization of  $1\text{-Li}(\text{DME})$  from DME at  $-35^\circ\text{C}$  afforded single crystals of  $1\text{-Li}(\text{DME})_3$  in 57% yield.

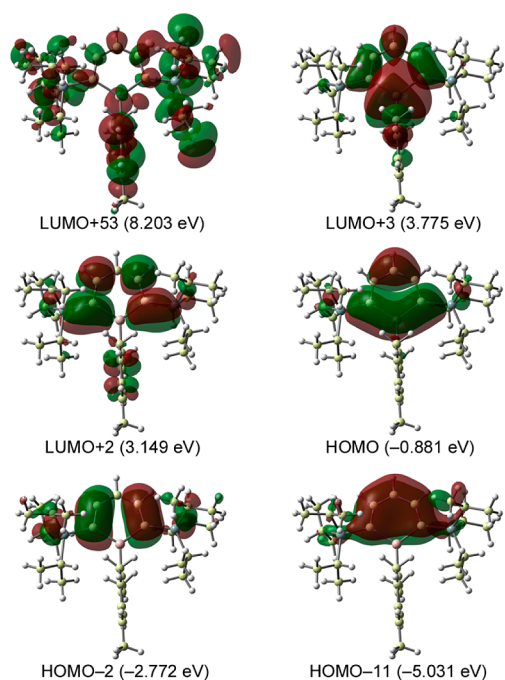
The molecular structures of  $1\text{-Li}(\text{DME})$  and  $1\text{-Li}(\text{DME})_3$  are shown in Figure 1. In  $1\text{-Li}(\text{DME})$ , an interaction between the



**Figure 1.** Molecular structures of  $1\text{-Li}(\text{DME})$  (A) and  $1\text{-Li}(\text{DME})_3$  (B) (50% thermal ellipsoid probability). Hydrogen atoms and solvate molecules are omitted for clarity and only selected atoms are labeled.

lithium cation and the aluminabenzene ring was observed [Al1–Li1 = 2.982(4) Å, C–Li1 = 2.290(4)–2.665(4) Å]. Due to the steric repulsion between the solvated cation  $[\text{Li}(\text{DME})]^+$  and the mesityl substituent, the aluminum atom is situated slightly above the C1–C5 plane, resulting in an angle of  $16.78(11)^\circ$  between the C1–C2–C3–C4–C5 least-squares plane and the Al1–C1–C5 plane (Figure S7). Due to the solvation by three molecules of DME, the lithium cation in  $1\text{-Li}(\text{DME})_3$  is completely separated from the anionic moiety (Al1–Li1 > 7 Å) in the solid state. The sum of the internal angles of the six-membered ring in the aluminabenzene is  $720^\circ$ , indicating a completely planar structure. The Al center in  $1\text{-Li}(\text{DME})_3$  exhibits a three-coordinated geometry and the planar structure is supported by the sum of angles ( $360^\circ$ ) around the Al center. The C–C bond lengths in the aluminabenzene rings are almost equal and in the range of 1.403(3)–1.420(3) and 1.403(3)–1.414(3) Å for  $1\text{-Li}(\text{DME})$  and  $1\text{-Li}(\text{DME})_3$ , respectively. The observed values are between typical carbon–carbon single and double bonds and comparable to those of benzene.<sup>12</sup> The endocyclic Al1–C1 and Al1–C5 distances are 1.930(2)/1.928(2) Å for  $1\text{-Li}(\text{DME})$  and 1.924(2)/1.922(2) Å for  $1\text{-Li}(\text{DME})_3$ . These are significantly shorter compared to the exocyclic Al1–C6 single bond lengths of 1.984(2) Å for  $1\text{-Li}(\text{DME})$ , and 2.010(2) Å for  $1\text{-Li}(\text{DME})_3$ . The observed metric parameters are also comparable to those of the previously reported dianionic aluminacyclopentadiene.<sup>11</sup> The combined structural analysis allows the conclusion that aluminabenzene **1** exhibits a planar structure and contains unsaturated bonds without bond alternation, which is in agreement with the structural criteria of aromaticity.

To elucidate the electronic structure of anionic aluminabenzene **1**, we conducted DFT calculations<sup>13</sup> at the B3LYP/6-31G(d) level, because there, the structural optimization for the real anionic aluminabenzene **1** was able to reproduce the experimentally observed structure of the anionic aluminabenzene moiety in  $1\text{-Li}(\text{DME})_3$ . The optimized structure is moreover comparable to the parent anionic aluminabenzene  $[\text{AlC}_5\text{H}_6]^-$ , which was previously calculated at the same level of theory and may also have a planar structure with a delocalized  $\pi$ -electron system,<sup>10a</sup> except for a slight expansion (0.9%) of the Al–C distances in **1** (1.924/1.926 Å) relative to the parent aluminabenzene (1.908 Å). This elongation can mostly likely be attributed to the repulsion between the sterically demanding mesityl and silyl groups. An examination of the frontier orbital situation showed that similar to benzene, six  $\pi$ -MOs are filled with six  $\pi$ -electrons in **1** (Figure 2). But in contrast to the HOMOs and LUMOs of benzene, which consist of two pairs of degenerate orbitals, the HOMO and LUMO of **1** are, owing to its unsymmetrical structure, not degenerate. The HOMO-11 of **1** expands mainly over the pentadienyl moiety, suggesting that the conjugation between the 3p atomic orbital of aluminum and the 2p atomic orbital of carbon is less effective in **1** relative to benzene. The bond order analysis based on the Wiberg bond index (WBI)<sup>14</sup> suggested an unsaturated character for the aluminabenzene ring of **1**, especially for the Al–C bonds. The bond order values for the C–C bonds were estimated to be 1.38–1.48, which fall between those of single and double bonds. Bond order values of 0.70 and 0.71 were obtained for the endocyclic Al–C bonds, which is approximately 1.4 times higher than that of the exocyclic Al–C(Mes) single bond (0.51). The calculated NPA charge<sup>15</sup> indicated a charge localization in **1**. Although the entire aluminabenzene ring carries a negative charge, the local charge on the Al atom is estimated to be positive (+1.5). In contrast to that, the charges on the five carbon atoms



**Figure 2.** Selected molecular orbitals of **1** calculated at the B3LYP/6-31G(d) level. The LUMO is localized on the mesityl group (SI).

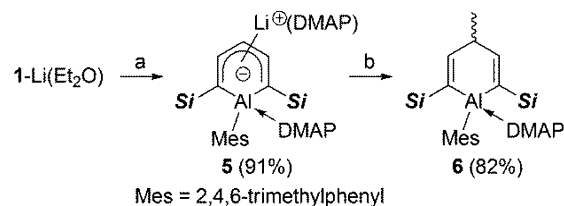
are calculated to be negative (*ortho*-C =  $-1.4$ , *meta*-C =  $-0.19$ , and *para*-C =  $-0.35$ ). Previously reported calculations for the parent anionic aluminabenzene  $[\text{AlC}_5\text{H}_6]^-$  revealed a similar trend for the charge separation (Al =  $+0.60$ , *ortho*-C =  $-0.65$ , *meta*-C =  $-0.08$ , *para*-C =  $-0.14$ ). Considering the NPA charge, the charge-localized character of the aluminabenzene ring in **1** can be interpreted as the result of a neutral Lewis acidic aluminum and an anionic pentadienyl moiety, consistent with resonance structure **1B**. The differences in the atomic charges between **1** and  $[\text{AlC}_5\text{H}_6]^-$  could then be feasibly attributed to substituent effects of the electronegative mesityl and the electropositive *ortho*-silyl groups. To further investigate the aromatic character of **1**, we carried out an analysis of the nuclear independent chemical shifts (NICS)<sup>16,17</sup> at the B3LYP/6-311+G(d,p) level, which provided NICS(0) and NICS(1) values of  $-1.53$  and  $-3.75$ , respectively. Even though these values are smaller than the reported NICS(0) and NICS(1) values for  $[\text{AlC}_5\text{H}_6]^-$  ( $-4.13/-5.63$ ), which were calculated at the same level,<sup>10d</sup> they still suggest an aromatic contribution to the structure of **1**. The lower NICS values of **1** might originate from a substantial contribution of the charge localized structure **1B**, which should have no aromatic ring current. Nevertheless, the contribution from the aromatic resonance structure **1A** should not be neglected, as the WBIs suggest an unsaturated bond character for the aluminabenzene ring.

The experimental NMR spectra of **1** are also consistent with the presence of a resonance hybrid with contributions from both aromatic **1A** and ambiphilic **1B**. In the <sup>1</sup>H NMR spectrum of **1**-Li(DME), the resonances for the *meta*- and *para*-protons attached to the aluminabenzene ring were observed at 8.16 (*meta*) and 5.98 (*para*) ppm, which is characteristic for aromatic compounds. In accordance with the <sup>1</sup>H NMR analysis, the signals for the corresponding *para*-, *ortho*-, and *meta*-carbon atoms in the <sup>13</sup>C NMR spectrum were also observed in the aromatic region (104.6, 121.0, and 151.7 ppm, respectively). However, the chemical shift differences ( $\Delta\delta$ ) for the hydrogen and carbon

atoms of the ring are pronounced:  $\Delta\delta_{\text{H}} = 2.18$  ppm between *para*- and *meta*-hydrogen atoms, as well as  $\Delta\delta_{\text{C}} = 46.1$  ppm between *para*- and *meta*-carbon atoms. The calculated NPA charges for aluminabenzene **1** suggested that atoms in *para*-position should carry more negative charge than those in *meta*-positions. Consequently, the hydrogen and carbon atoms in *para*-position may be magnetically shielded, resulting in an upfield shift relative to the atoms in *meta*-position. These chemical shift differences are similar to those observed for the 1,5-bis(trimethylsilyl)pentadienyl anion,<sup>18</sup> corroborating a considerable contribution from canonical form **1B**. For lithium cations coordinated by an anionic aromatic ring, the chemical shift of the <sup>7</sup>Li NMR can be used to probe for an evidence of the aromaticity, as the diatropic ring current magnetically shields the lithium cation.<sup>17,19,20</sup> According to the structural analysis, the lithium cation in **1**-Li(DME) is situated above the aluminabenzene ring, and should therefore be shielded by the aromatic ring current. Indeed, the <sup>7</sup>Li resonance of **1**-Li(DME) in C<sub>6</sub>D<sub>6</sub> was observed to be upfield shifted at  $-4.5$  ppm, which is comparable to other aromatic lithium salts<sup>19,20</sup> and demonstrates the aromaticity of aluminabenzene **1**. In contrast, the <sup>7</sup>Li resonance for a DME solution of **1**-Li(DME), where **1**-Li(DME)<sub>3</sub> may form in solution, was observed at  $-1.2$  ppm. The downfield shift of this resonance relative to that in C<sub>6</sub>D<sub>6</sub> can be explained by the increased distance between the lithium cation and the aluminabenzene as a result of the exhaustive solvation with DME.

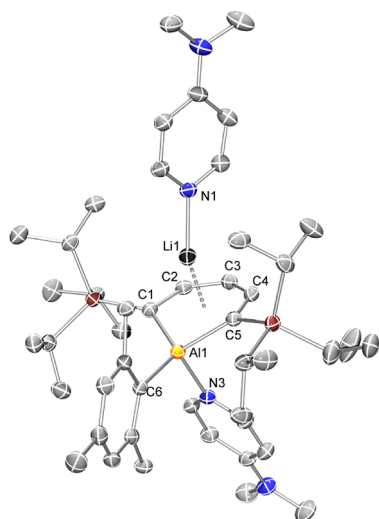
The reactivity of aluminabenzene **1** also manifested the contribution of the ambiphilic structure **1B** (Scheme 2).

#### Scheme 2. Reactions of **1**-Li(Et<sub>2</sub>O) with DMAP and MeI<sup>a</sup>



<sup>a</sup>Reaction conditions: (a) DMAP, toluene; (b) MeI, toluene.

Reaction of **1**-Li(Et<sub>2</sub>O) with the strong Lewis base 4-dimethylaminopyridine (DMAP) in toluene produced the Lewis acid–base complex **5** cleanly in 91% yield, which reflects the Lewis acidic nature of the Al center. On the other hand, methyl iodide did not react with **1**-Li(Et<sub>2</sub>O) in C<sub>6</sub>D<sub>6</sub>. However, Lewis complex **5** smoothly reacted with methyl iodide in toluene to give methylated compound **6** in 81% yield. This result may indicate that the nucleophilicity of the conjugated carbanion in **1B** is initially weak, but significantly increased in carbanion **5** due to the potentially induced dearomatization, resulting from the coordination of the Lewis base to the Al center. The molecular structure of **5** (Figure 3) was determined by X-ray crystallography and showed a tetrahedral coordination geometry for the Al center, which confirmed the aforementioned dearomatization. The observed C–C bond lengths of the aluminacycle [ $1.398(4)$ – $1.427(4)$  Å] are comparable to those in **1**-Li(DME) and **1**-Li(DME)<sub>3</sub>, but the Al–C bond lengths were found to be substantially increased [ $1.974(3)/1.987(3)$  Å]. This bond elongation indicates that the coordination of DMAP hampers the cyclic  $\pi$ -conjugation between the Al atom and the pentadienyl moiety. The NMR analysis of Lewis complex **5** further supported the notion of a dearomatization as a result of



**Figure 3.** Molecular structure of **5** (50% thermal ellipsoid probability). All hydrogen atoms and solvate molecules are omitted for clarity and only selected atoms are labeled.

the coordination of a Lewis base. Although the  $^1\text{H}$  NMR resonances for the protons of the aluminacycle in **5** (6.07 and 8.17 ppm) were, probably due to the anionic charge of the pentadienyl moiety, comparable to those of **1**, the  $^7\text{Li}$  NMR resonance for **5** ( $-1.8$  ppm) was observed to be 2.8 ppm downfield shifted relative to that of **1**-Li(DME) ( $-4.5$  ppm). The X-ray crystallographic analysis of **5** showed that the lithium cation is situated above the ring. The observed downfield shift of the  $^7\text{Li}$  NMR signal of **5** relative to **1** is also consistent with a dearomatization resulting from the coordination of DMAP to the Al center.

On the basis of these results, the structure of aluminabenzene **1** is best described as a resonance hybrid with contributions from both aromatic (**1A**) and the ambiphilic (**1B**) resonance structures. The substantial contribution of ambiphilic **1B** may arise from the relatively weak aluminum–carbon multiple bond in the aluminabenzene. Sequential reactions of **1** with DMAP and methyl iodide were able to demonstrate that **1** reacts as a Lewis pair, where Lewis acidic and basic centers coexist, which is consistent with resonance structure **1B**.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, crystallographic data, DFT calculations and a full citation of ref 13. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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