

An Isolable Bismabenzene: Synthesis, Structure, and Reactivity

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S Supporting Information

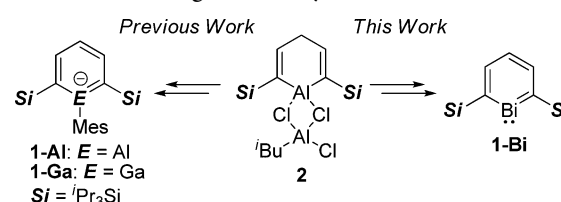
ABSTRACT: A stable bismabenzene was synthesized, isolated, and structurally characterized. The prospective aromaticity of this heavy benzene, bearing a sixth-row element, was examined by X-ray crystallography and NMR and UV–vis spectroscopy, as well as theoretical DFT calculations. Structural analysis of this bismabenzene revealed a planar ring containing unsaturated Bi–C and C–C bonds. As bond alternations could not be observed, these results are consistent with the formal criteria of aromaticity. Theoretical calculations also support the aromatic nature of this bismabenzene, which reacted with an alkyne to form the corresponding [4+2] cycloadduct, thus demonstrating a small yet tangible aromatic stabilization energy.

Aromaticity is one of the most fundamental concepts in organic chemistry. Generally, second-row p-block elements such as carbon and nitrogen can be easily incorporated in aromatic frameworks. Substitution of a carbon atom in benzene with a heavier element affords aromatic molecules that exhibit unique properties, which arise from the energetically high p-orbital of the heavy element. Since the first successful isolation of a phosphabenzene (phosphinine) by Markl,¹ various benzene derivatives containing heavy main-group elements have been investigated in order to better understand their aromaticity.² In addition to phosphabenzenes, benzenes containing third- and fourth-row elements of groups 13–15, such as galla-,³ sila-,⁴ germa-,⁵ and arsabenzenes,⁶ have been synthesized and characterized. In contrast, studies on benzene derivatives containing fifth-row elements are limited: only two reports on a stibabenzene and stannanaphthalene have been reported so far, by Ashe et al.⁷ and Tokitoh et al.,⁸ respectively. Reports on the successful isolation of heterobenzenes bearing sixth-row elements still remain elusive. Ashe et al. described the synthesis of a bismabenzene, which immediately dimerized on account of the highly reactive unsaturated C–Bi bonds.^{7b,9} This bismabenzene was spectroscopically characterized at low temperature, but structural information was not obtained. And even though Saito et al. recently proposed aromaticity for an isolated plumbole dianion,¹⁰ benzene derivatives containing a sixth-row main-group element have not yet been characterized. The synthetic difficulties encountered with the isolation of benzenes that contain heavy main-group elements is most likely due to the highly reactive unsaturated bonds between the carbon atoms and the heavy elements.

Recently, we reported the synthesis of the anionic alumina-benzene **1-Al** as the first example of an aluminum-containing

heterobenzene via aluminacyclohexadiene intermediate **2** (Scheme 1).¹¹ In addition to **1-Al**, we synthesized the isolable

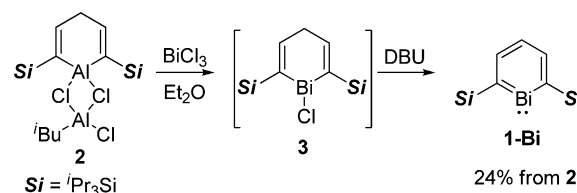
Scheme 1. Synthesis of Isolable Alumina-, Galla-, and Bismabenzenes Using Aluminacyclohexadiene 2



anionic gallabenzene **1-Ga**, which contains two bulky ⁱPr₃Si groups at the 2- and 6-positions, from the transmetalation of **2** with GaCl₃.¹² This result indicates that aluminacyclohexadiene **2** could be a versatile synthetic precursor with the potential to offer kinetic protection for a variety of heterobenzenes. Herein, we report the synthesis of bismabenzene **1-Bi** by transmetalation of **2**. Compound **1-Bi** represents the first example of an isolable heterobenzene containing a main-group element from the sixth row, which was exhaustively characterized by X-ray crystallography and NMR and UV–vis spectroscopy, as well as theoretical DFT calculations. The obtained results are consistent with the formal criteria for aromaticity. Moreover, **1-Bi** underwent a [4+2] cycloaddition with an electron-deficient alkyne, which demonstrates the presence of highly reactive unsaturated C–Bi bonds.

Bismabenzene **1-Bi** was synthesized by the reaction of **2**¹¹ with BiCl₃,¹³ followed by a treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 2). In the absence of DBU, bismacyclohexadiene **3** was identified as an intermediate.¹⁴ Isolated yellow crystals of **1-Bi** can be stored at room temperature for more than 3 months under an inert atmosphere. Characterization of **1-Bi** was accomplished by ¹H and ¹³C NMR spectroscopy, high-resolution mass

Scheme 2. Synthesis of Bismabenzene 1-Bi



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spectrometry, and elemental analysis. The molecular structure of **1-Bi** was unambiguously determined by X-ray crystallography (Figure 1).

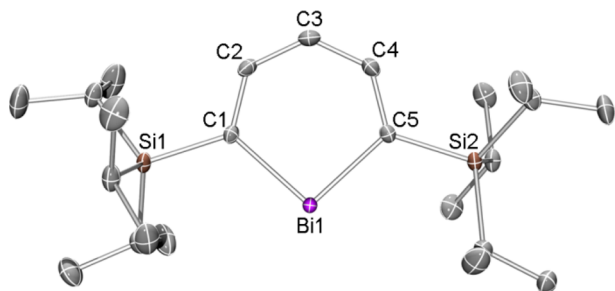


Figure 1. Molecular structure of **1-Bi** (thermal ellipsoids set at 50% probability; hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Bi1–C1 2.160(4), Bi1–C5 2.154(4), C1–C2 1.398(5), C2–C3 1.402(6), C3–C4 1.393(6), C4–C5 1.395(6), C1–Si1 1.873(4), C5–Si2 1.876(4), C1–Bi1–C5 95.32(14), Bi1–C1–C2 118.4(3), C1–C2–C3 129.2(4), C2–C3–C4 128.9(4), C3–C4–C5 129.5(4), C4–C5–Bi1 118.6(3), Bi1–C1–Si1 120.04(19), Si1–C1–C2 121.5(3), Bi1–C5–Si2 119.72(19), Si1–C1–C2 121.6(3).

In the crystalline state, the six-membered ring of **1-Bi** is planar, which is evident from the sum (720°) of the internal bond angles. The bond angles around C1 and C5 suggest that these atoms are sp^2 -hybridized. The Bi1–C1 and Bi1–C5 bond lengths [2.160(4) and 2.154(4) Å] are shorter than typical Bi–C single bonds [$Bi-C_{aromatic} = 2.26(3)$ Å, $Bi-C_{aliphatic} = 2.30(5)$ Å],¹⁵ indicating an unsaturated character of these Bi–C bonds. The C–C bond lengths within the ring are virtually identical [1.393(6)–1.402(6) Å] and comparable to those of benzene (1.39 Å).¹⁶ These results thus suggest not only an unsaturated character for the C–C bonds but also an absence of bond alternation within the bismabenzene ring. These structural features are in agreement with the formal criteria for aromaticity. The C1–Bi1–C5 angle [$95.32(14)^\circ$] is significantly smaller than the 120° angle expected for ideal sp^2 -hybridization. The fact that the bismuth atom does not engage in sp^2 -hybridization is consistent with the observed trend of decreasing C–E–C angles in group 15 heterobenzenes upon descending group 15 (E = P, As, Sb).^{2c,d}

The NMR spectra of **1-Bi** also reflect its intrinsic aromaticity. The 1H NMR resonances for the protons attached to the bismabenzene ring were observed in the low-field region, i.e., at 11.6 and 7.7 ppm for the *meta*- and *para*-protons, respectively. The ^{13}C NMR spectrum of **1-Bi** showed three signals at 222.5, 136.7, and 153.6 ppm, which were assigned to the *ortho*-, *meta*-, and *para*-carbon atoms of the ring. The low-field shift of these signals is indicative for the presence of an aromatic ring current in the bismabenzene ring. The *ortho*-carbon atoms and *meta*-protons resonated at unusually low field, which was attributed to the deshielding effects of the heavy element, previously proposed by Ashe et al.¹⁷

To gain further insight into the electronic structure of **1-Bi**, we performed DFT calculations using the ADF2016 program package.¹⁸ For the structural optimization, the all-electron Slater-type basis set TZ2P¹⁹ was used with the scalar zeroth-order regular approximation (ZORA) for the relativistic effect.^{20,21} The structural optimization of **1-Bi** was able to reproduce the planar ring structure determined by X-ray crystallography (Figure 2a); selected molecular orbitals (MOs)

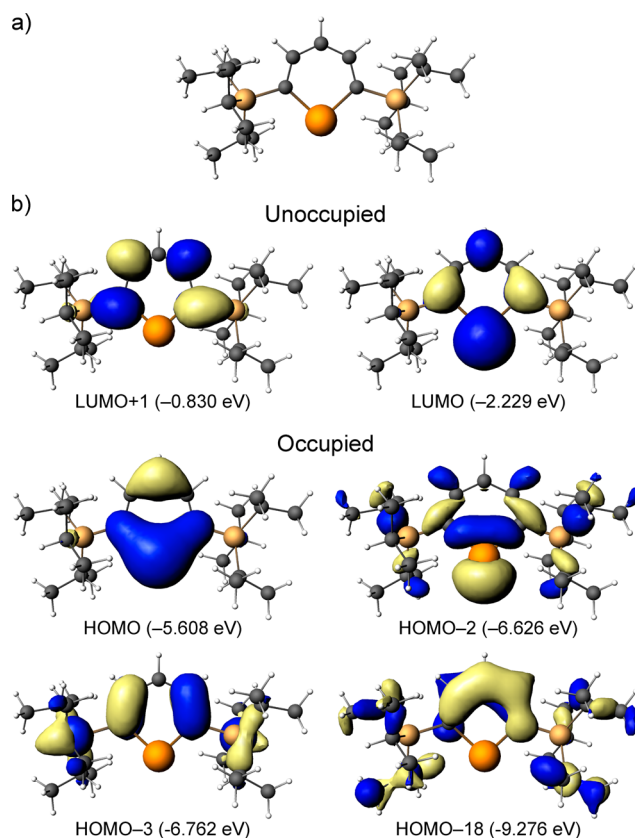


Figure 2. (a) Optimized structure of **1-Bi** at the BP/TZ2P level of theory. (b) Selected molecular orbitals of **1-Bi**, calculated at the B3LYP/[QZ4P for Bi,Si,C, TZ2P for H]/BP/TZ2P level of theory. The HOMO–1 is a σ -type orbital around the bismabenzene ring (for further details, see Supporting Information).

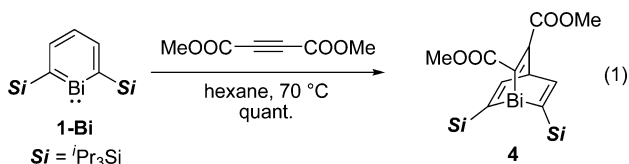
of **1-Bi** are shown in Figure 2b. The frontier MOs showed four π - and π^* -type orbitals (LUMO+1, LUMO, HOMO, and HOMO–3) distributed around the bismabenzene ring, similar to those of typical aromatic systems such as benzene and pyridine. In the case of pyridine and silyl-substituted pyridine, the HOMO consists predominantly of the lone-pair orbital on the nitrogen atom (Figures S9 and S10). In contrast, the HOMO of **1-Bi** is a π -type orbital around the bismabenzene ring, which is energetically higher than the lone-pair orbital on the bismuth atom (HOMO–2). The high HOMO level could be explained by the less effective π -overlap between the 6p-orbital on bismuth and the 2p-orbital on the carbon atoms. Consistent with such a diminished π -overlap, the LUMO of **1-Bi**, which consists of p-orbitals of the bismuth and five carbon atoms, was found to be energetically lower than that of pyridine. Due to the less effective π -overlap, the HOMO–18 of **1-Bi**, which corresponds to the bonding π -orbitals of benzene and pyridine, shows the delocalization of the π -electrons around five carbon atoms of the bismabenzene ring. To reveal the nature of the bonding in **1-Bi**, NBO analysis was performed,²² which afforded Wiberg bond indices²³ of 1.52 (C_{ortho} – C_{meta}), 1.39 (C_{meta} – C_{para}), and 1.18 (Bi–C) for the C–C and Bi–C bonds. These values are in accordance with the unsaturated character of the bismabenzene ring, and the NBO analysis also confirms the less effective orbital hybridization of the bismuth atom. The σ -bonds of ideally sp^2 -hybridized atoms should exhibit 33% s-character and 67% p-character. In contrast, the Bi–C σ -bonds in **1-Bi** consist predominantly of

contributions from the p-orbital of the bismuth atom (s, 8.9%; p, 91.0%). Conversely, the lone-pair orbital on the bismuth atom shows a predominant s-character (s, 82.9%; p, 17.1%). These results may be attributed to the diminished propensity toward hybridization between 6s- and 6p-orbitals.^{24,25} The high p-character of the Bi–C σ -bonds should be responsible for the decreased C–Bi–C bond angle observed in the solid-state structure.

To investigate the aromatic nature of **1-Bi**, NICS calculations were carried out.²⁶ The Slater-type quadruple- ζ all-electron basis set (QZ4P)¹⁹ was chosen for the bismuth, silicon, and carbon atoms, whereby the spin-orbit ZORA accounted for the relativistic effect of the bismuth atom. For **1-Bi**, negative NICS values were estimated [NICS(0) = –3.4; NICS(1) = –7.3]. Moreover, a substantially negative NICS_{zz} value (–18.3) was obtained at 1 Å above the ring center of **1-Bi**. These results may indicate the presence of a diatropic ring current derived from the aromatic bismabenzene ring. GIAO calculations on **1-Bi** were able to confirm the experimentally observed, unusually low-field-shifted NMR signals for the *ortho*-carbon and *meta*-hydrogen atoms (Figure S12).

The small HOMO–LUMO gap predicted by the DFT calculations is experimentally reflected in the UV–vis absorption spectrum of **1-Bi**. In hexane, **1-Bi** revealed an absorption band at 417 nm ($\epsilon = 4600 \text{ L mol}^{-1} \text{ cm}^{-1}$), which is responsible for the yellow color of **1-Bi** (Figure S5). TD-DFT calculations at the B3LYP/[QZ4P for Bi, Si, C, TZ2P for H] level of theory (Figure S13) predicted a π – π^* -type HOMO–LUMO transition in **1-Bi** at 382 nm (oscillator strength $f = 0.0568$), which is in agreement with the experimentally obtained value. The observed absorption wavelength was $\sim 100 \text{ nm}$ red-shifted relative to that of previously reported stibabenzene ($\lambda_{\text{max}} = 312 \text{ nm}$).⁷ This result is consistent with the less effective orbital overlap between 6p- and 2p-orbitals derived from the bismabenzene ring relative to the 5p–2p interaction in the stibabenzene.

We also investigated the reactivity of **1-Bi**. As the parent bismabenzene, which is not isolable due to facile dimerization, reacts with alkynes,⁹ we wanted to examine the reactivity of **1-Bi** toward unsaturated C–C bonds. The reaction of **1-Bi** with dimethyl acetylenedicarboxylate (DMAD) proceeded in a [4+2] fashion to afford bisma[2.2.2]bicyclooctadiene **4** as colorless crystals (eq 1). The structure of **4** was determined by



X-ray crystallography (Figure S5). It should be noted that **1-Bi** retains, in spite of the presence of dimerization-preventing bulky silyl groups at the 2- and 6-positions, high reactivity toward small molecules. This reactivity should be attributed to the presence of unsaturated bonds involving a sixth-row element.

In summary, bismabenzene **1-Bi** was synthesized, using aluminacyclohexadiene **2** as a synthetic precursor. This bismabenzene constitutes the first isolable example of a heterobenzene that contains a main-group element from the sixth row. The results of the structural characterization by X-ray crystallography and theoretical DFT calculations suggest tangible aromatic nature for **1-Bi**.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08714.

Experimental procedures, X-ray crystallographic analysis, UV–vis absorption spectrum, and theoretical calculations, including Figures S1–S13 and Tables S1–S4 (PDF)

X-ray crystallographic data for **1-Bi**, **3**, and **4** (CIF)

Molecular structure of **1-Bi** (XYZ)

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Notes

The authors declare no competing financial interest.

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