

Anionic Indabenzene: Synthesis and Characterization

 Taichi Nakamura,^a Katsunori Suzuki,^{*b} and Makoto Yamashita^{*b}

 Received 00th January 20xx,
 Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

An anionic indabenzene was synthesized by the transmetalation of an aluminacyclohexadiene with bulky silyl substituents, and fully characterized by multinuclear NMR spectroscopy and X-ray crystallography. The observed structural features are consistent with the formal criteria of aromaticity. Additionally, the results of DFT calculations suggested contributions from an ambiphilic resonance structure, similar to the corresponding aluminum and gallium derivatives.

Aromaticity is arguably one of the most attractive properties of organic π -conjugated molecules. The replacement of a carbon atom in benzene, as the prototypical carbon-based aromatic molecule, with a heteroatom such as nitrogen or oxygen generates the corresponding heterobenzenes, i.e. pyridines and pyrylium salts, which exhibit properties that are slightly different from those of benzene. The replacement of carbon atoms in benzene with heteroatoms from beyond the third row of the periodic system of elements (PSE) induces properties that are even more distinct from those of benzene.¹ For example, in comparison with the properties of benzene, those of sila-, germa-, phospho-, arsa-, stibabenzene are characterized by higher reactivity and narrower HOMO-LUMO gaps.² Stiba- and bismabenzene derivatives represent the very limited examples for heterobenzenes that contain an element from the fifth or sixth row of the PSE, respectively.^{3,4} Yet, in contrast to the well-documented chemistry of heterobenzenes involving elements from group 14 or 15, the chemistry of heterobenzenes containing elements from group 13 remains mostly limited to that of borabenzene,⁵ except for the spectroscopic observation of a gallabenzene analogue.⁶ We have recently reported the synthesis of an anionic aluminabenzene (**1-Al**), which

represents the first example of an aluminium-containing heterobenzene (Figure 1A).^{7a} More importantly, aluminacyclohexadiene **2-L** could be used as a synthetic intermediate to synthesize, isolate, and structurally characterize the anionic gallabenzene **1-Ga**.^{7b} These anionic heterobenzenes that contain elements from group 13 do not exhibit a purely aromatic character derived from the conjugated ring system with six π -electrons, but also contributions from ambiphilic resonance structures that consist of a negatively charged pentadienyl moiety and a neutral Lewis-acidic group-13 element (Figure 1B). Although alumina- and gallabenzene derivatives have been synthesized and characterized, their heavier analogues, i.e., inda- and thallabenzene, have remained elusive, probably due to the high reactivity of unsaturated In-C and Tl-C unsaturated bonds. Herein, we report the synthesis of the first anionic indabenzene (**1-In**) that contains unsaturated In-C bonds.

Initially, we attempted a transmetalation of **2-NEt₃**, which was synthesized from a previously reported alumina-cyclohexadiene derivative,^{7a} with InCl₃ in order to obtain the corresponding indacyclohexadiene according to the synthetic method for the anionic gallabenzene **1-Ga**.^{7b} Unfortunately, this reaction did not proceed, probably due to the poor solubility of InCl₃. However, upon changing to InCl₃-NEt₃ as a more soluble precursor, the transmetalation proceeded under complete consumption of **2-NEt₃**. Still, we were unable to isolate the targeted indacyclohexadiene. We assumed that NEt₃ would

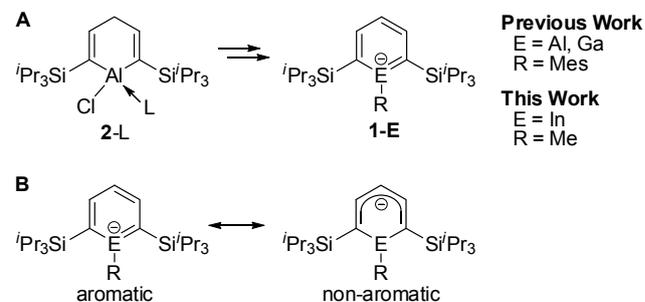


Fig. 1 (A) Synthesis of heterobenzenes from aluminacyclohexadiene **2-L** and (B) resonance contributions in anionic alumina-, galla-, and indabenzene **1-E**.

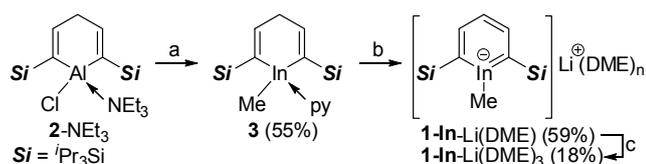
^a Department of Applied Chemistry, Graduate School of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo, 112-8551 Japan

^b Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

† Electronic Supplementary Information (ESI) available: Experimental procedure, X-ray crystallographic analysis and theoretical calculations. See DOI: 10.1039/x0xx00000x

inhibit the cyclization to form the indacyclohexadiene, and therefore, we treated the resulting reaction mixture with a Lewis acid to capture NEt_3 . After the optimization of the reaction conditions, methyl-substituted indacyclohexadiene **3** was isolated by the reaction of **2**- NEt_3 with $\text{InCl}_3\text{-NEt}_3$, followed by consecutive treatment with AlMe_3 and pyridine (Scheme 1).⁸ The structure of **3** was determined by NMR spectroscopic analysis and X-ray crystallography (Fig. S6). NMR signals assignable to the methyl group attached on In atom were observed at 0.40 ppm for ^1H and -7.5 ppm for ^{13}C , being similar to those of the previously reported Lewis acid-base complex between trialkylindium and pyridine derivative, (4-dimethylaminopyridine)- InMe_3 complex (0.19 ppm for ^1H , -7.6 ppm for ^{13}C in C_6D_6).⁹ In the crystal state, the indium atom adapted tetrahedral geometry due to the coordination of pyridine. The In-C atomic distances were 2.143(3)-2.175(2) Å, being comparable to the covalent In-C bond length (2.16 Å).¹⁰ After deprotonation at the 4-position with lithium tetramethylpiperide (LiTMP), recrystallization of the reaction mixture from toluene after the addition of 1 equivalent of DME afforded anionic indabenzene **1-In-Li(DME)** as a contact-ion pair with Li(DME) in 59% yield. The structure of **1-In-Li(DME)** was confirmed by multinuclear NMR spectroscopy, high-resolution mass spectrometry, and X-ray crystallography (Fig. 2A). Even though **1-In-Li(DME)** is air- and moisture-sensitive, it is stable at room temperature under an atmosphere of argon.

According to the structural analysis of **1-In-Li(DME)** (Fig. 2A), the indabenzene ring is slightly bent away from the lithium cation, which is coordinated to the indabenzene ligand with an In-Li distance of 2.965(7) Å. This distance is longer than the sum of the covalent radii (2.73 Å).¹⁰ In addition to **1-In-Li(DME)**, a cation-separated anionic indabenzene [**1-In**] $[\text{Li}(\text{DME})_3]$ was obtained from the recrystallization of **1-In-Li(DME)** in DME (Scheme 1). In the crystal structure of [**1-In**] $[\text{Li}(\text{DME})_3]$ (Fig. 2B), an interatomic $\text{Li}\cdots\text{In}$ distance of >7 Å was observed, which indicates the absence of any interactions between the lithium cation and the indabenzene ring. The internal bond angles of the indabenzene ($\sim 720^\circ$) and the angle sum around the indium atom ($\sim 360^\circ$) in [**1-In**] $[\text{Li}(\text{DME})_3]$ suggest the presence of a planar indabenzene ring in [**1-In**] $[\text{Li}(\text{DME})_3]$. The C-C bond lengths in the indabenzene ring [1.389(6)-1.413(6) Å] are similar to those of previously reported anionic alumina- and gallabenzenes,⁷ as well as comparable to those in benzene.¹¹ The endocyclic In-C1 [2.109(4) Å] and In1-C5 bonds [2.117(4) Å] are shorter than the exocyclic In1-C6 single bond [2.165(4) Å],¹¹ and fall into the range of the shortest hitherto reported In-C bond



Scheme 1 Synthesis of **1-In-Li(DME)** and [**1-In**] $[\text{Li}(\text{DME})_3]$ from **2-NEt₃**.^a

^aReaction conditions: (a) 1) $\text{InCl}_3\text{-NEt}_3$, 2) AlMe_3 , 3) pyridine, toluene; (b) 1) LiTMP, 2) DME, toluene; (c) recrystallization from DME at -35°C .

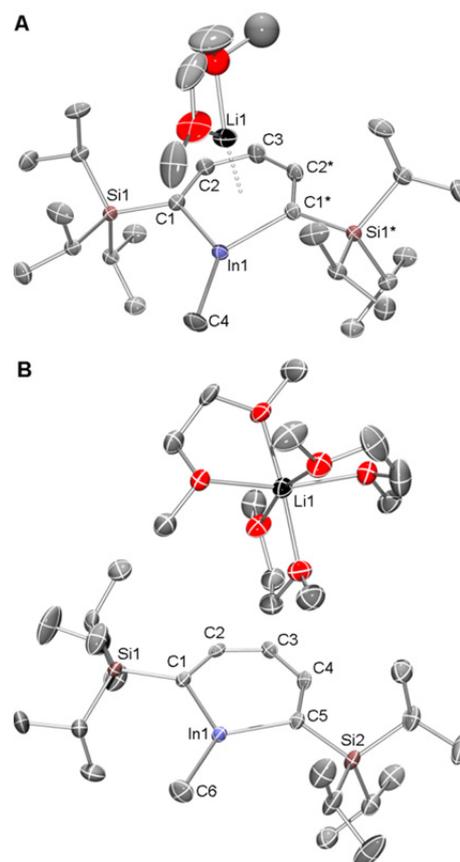


Fig. 2 (A) Crystal structure of **1-In-Li(DME)** with thermal ellipsoids set at 50% probability; hydrogen atoms, as well as benzene solvate and disordered DME molecules are omitted for clarity. The O and C atoms in DME were refined isotropically due to the disorder (cf. ESI). (B) Crystal structure of [**1-In**] $[\text{Li}(\text{DME})_3]$ with thermal ellipsoids set at 50% probability; hydrogen atoms omitted for clarity.

distances in planar triaryl/alkyl indium compounds [In-C: 2.111(14)-2.200(3) Å; av. 2.175 Å].¹³⁻¹⁵ This result suggests an unsaturated character for the endocyclic In-C bond in [**1-In**] $[\text{Li}(\text{DME})_3]$. In the indabenzene ring, tangible bond alternation was not observed. These structural features are comparable to those of previously reported benzene derivatives that contain group-13 elements.⁷

The ^1H , ^{13}C , and ^7Li NMR spectra of **1-In-Li(DME)** in C_6D_6 revealed resonances for the protons attached to the indabenzene ring at 5.88 ppm (*para*) and 8.57 ppm (*meta*). The ^{13}C NMR spectrum showed three signals in the aromatic region at 102.0 ppm, 141.0 ppm, and 148.6 ppm, which were assigned to the *para*-, *ortho*-, and *meta*-carbon atoms of the indabenzene ring, respectively. These chemical shifts are similar to those of previously reported **1-Al** and **1-Ga**.⁷ The resonances assignable to In-Me group of **1-In-Li(DME)** were observed at 0.67 ppm for ^1H and -2.9 ppm for ^{13}C , being similar to those of the precursor **3**. These values were also comparable to those of a boron analogue, methyl-substituted boratabenzene, $\text{Li}[\text{MeBC}_5\text{H}_5]$ (0.67 ppm for ^1H , 4.4 ppm for ^{13}C).¹⁶ The ^7Li NMR spectra of **1-In-Li(DME)** and [**1-In**] $[\text{Li}(\text{DME})_3]$ support the existence of an aromatic ring current. For **1-In-Li(DME)**, a signal for the Li cation on the indabenzene ring was observed at -4.41 ppm, which is shifted to higher field relative to the liberated Li cation of [**1-In**] $[\text{Li}(\text{DME})_3]$ in DME (-1.17 ppm).

This high-field shift can be rationalized in terms of the magnetic shielding effect arising from the aromatic ring current in the indabenzene ring.

To gain further insight into the electronic structure of the anionic indabenzene, DFT calculations at the B3LYP/[LanL2DZ (In) and 6-31G(d) (Si, C, H) levels of theory were carried out on cation-free **1-In** and reference compound InPh₃. The thus obtained optimized structure was comparable to those observed by the X-ray diffraction analyses. The calculated molecular orbitals (MOs) of **1-In** are similar to those of benzene (Figure 3). The HOMO is delocalized around 6 π framework, which consists of the 5p orbital of indium and the 2p orbitals of the carbon atoms. For the HOMO-9, the orbital coefficient is localized on the pentadienyl moiety, suggesting an ineffective orbital overlap between the 5p orbital of indium and the 2p orbitals of the carbon moiety. A bond order analysis based on the Wiberg bond indexes (WBI)¹⁷ corroborated the unsaturated character of the indabenzene ring. The values of the endocyclic In–C bonds (0.728/0.729) in **1-In** are higher than that of the exocyclic In–C bond (0.579) in the same molecule and those of the calculated In–C bonds (0.594) in InPh₃.¹⁸ A charge-distribution analysis based on a natural population analysis (NPA) of **1-In** suggested a contribution from a resonance structure with ambiphilic character. Although the net charge on the indabenzene ring is negative, the calculated charge distribution on the indium atom is positive (+1.48). In contrast, those on the five carbon atoms in the ring are negative (–0.36 to –1.23). These results suggest a resonance structure for **1-In** that is characterized by an ambiphilic character, i.e., one that contains a neutral indium atom and an anionic pentadienyl moiety. However, the cationic charge on the indium atom in **1-In** was smaller than that of InPh₃ (1.67),¹⁸ which suggests a delocalization of the anionic charge over the indabenzene ring.

According to the results of the WBI and NPA charge-distribution analyses, the electronic structure of the indabenzene should be best represented by a hybrid between a 6 π aromatic system and the corresponding ambiphilic resonance structure. The nuclear independent chemical shifts (NICS)¹⁹ of the indabenzene ring in **1-In** were calculated at the B3LYP/[ATZP (In)^{20,21} and 6-311+G(2d,p) (Si, C, H) levels of theory. The calculated NICS(1) (–4.6) and NICS(1)_{zz} values (–10.6) are negative,²² and thus corroborate the existence of a diatropic ring current derived from the aromatic character of **1-In**, which is similar to the case of **1-Al** and **1-Ga**.⁷

In summary, an anionic indabenzene was synthesized and characterized as the first example for a cyclic 6 π aromatic system that contains an In atom. Based on the structural analysis, NMR chemical shifts, and the results of the DFT calculations, this anionic indabenzene should, despite the presence of an element from the fifth row of the PSE, exhibit contributions from aromatic and ambiphilic resonance structures.

This work was supported by Grants-in-Aid for Scientific Research from the JSPS (KAKENHI grants 17H01191 and 17K19128), the Asahi Glass Foundation, and CREST 14529307 from the JST. T.N. is grateful to the JSPS for a

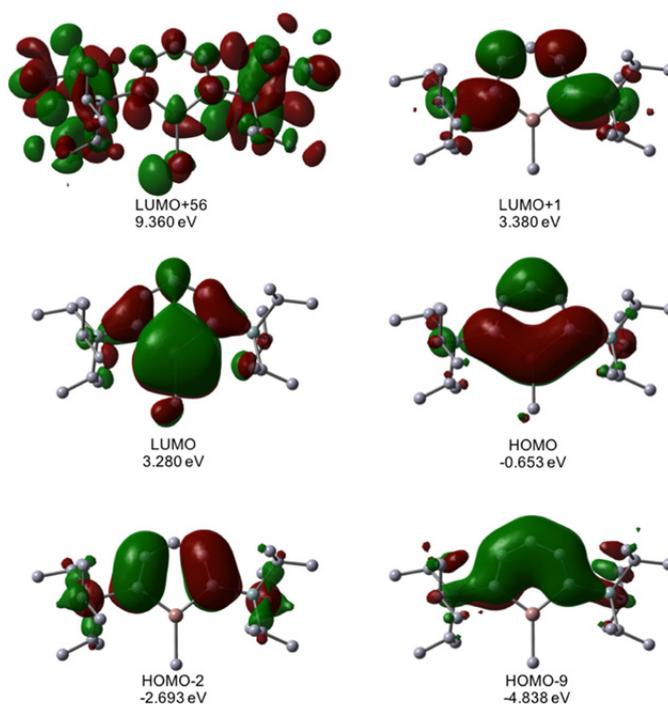


Fig. 3 Selected molecular orbitals for **1-In**; hydrogen atoms omitted for clarity.

Research Fellowship for Young Scientists (16J09602). We thank Prof. T. Hiyama (Chuo University) for providing us with access to an X-ray diffractometer. We also thank Prof. H. Shinokubo (Nagoya University) for his assistance with ESI-MS measurements.

Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

- (a) V. Y. Lee and A. Sekiguchi, In *Organometallic Compounds of Low-Coordinate Si, Ge, Sn, and Pb: From Phantom Species to Stable Compounds*; John Wiley & Sons, Ltd.: Chichester, 2010. (b) N. Tokitoh, *Acc. Chem. Res.* **2004**, *37*, 86. (c) N. Tokitoh, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 429. (d) A. J., III. Ashe, *Acc. Chem. Res.* **1978**, *11*, 153. (e) A. J., III. Ashe, *Top. Curr. Chem.* **1982**, *105*, 125.
- (a) K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, *Angew. Chem., Int. Ed.* **2000**, *39*, 634. (b) K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, *J. Am. Chem. Soc.* **2000**, *122*, 5648. (c) N. Nakata, N. Takeda, N. Tokitoh, *J. Am. Chem. Soc.* **2002**, *124*, 6914. (d) G. Markl, *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 846. (e) A. J., III. Ashe, *J. Am. Chem. Soc.* **1971**, *93*, 3293. (f) A. J., III; Ashe, T. R. Diephouse, M. Y. El-Sheikh, *J. Am. Chem. Soc.* **1982**, *104*, 5693.
- A stannaphthalene has been reported as an example for a naphthalene derivative that contains a tin atom; see: Y. Mizuhata, T. Sasamori, N. Takeda, and N. Tokitoh, *J. Am. Chem. Soc.* **2006**, *128*, 1050.
- T. Ishii, K. Suzuki, T. Nakamura, and M. Yamashita, *J. Am. Chem. Soc.* **2016**, *138*, 12787.
- G. C. Fu, *Adv. Organomet. Chem.* **2001**, *47*, 101. (b) M. J. D. Bosdet and W. E. Piers, *Can. J. Chem.* **2008**, *86*, 8.
- A. J., III Ashe, S. Al-Ahmad, and J. W. Kampf, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1357.

- 7 (a) T. Nakamura, K. Suzuki, and M. Yamashita, *J. Am. Chem. Soc.* **2014**, *136*, 9276. (b) T. Nakamura, K. Suzuki, and M. Yamashita, *Organometallics* **2015**, *34*, 1806.
- 8 For the proposed reaction sequence, see: ESI.
- 9 F. Thomas, T. Bauer, S. Schulz, M. Nieger, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2018.
- 10 J. Emsley, *The Elements*, 3rd ed.; Oxford University Press: New York, 1998.
- 11 V. J. Minkin, M. N. Glukhovtsev, Y. B. Simkin, In *Aromaticity and Antiaromaticity; Electronic and Structural Aspects*; Wiley: New York, 1994.
- 12 Considering the difference in length between CH₃-C(aryl) and C(aryl)-C(aryl) bonds (0.019 Å; see: F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.), the In-C1 and In-C5 bonds should be significantly shorter than the exocyclic In1-C6 single bond.
- 13 For the In-C bond lengths of eleven compounds that contain planar triaryl-substituted indium atoms, which have previously been reported in the Cambridge Structural Database (version 5.38; Oct. 2017), see: F. H. Allen, *Acta Crystallogr. Sect. B: Struct. Sci.* **2002**, *58*, 380.
- 14 The shortest In-C bond length of 2.06(4) Å reported in the CSD (CCDC 1275733) was excluded, as this distance was subsequently corrected to 2.16(4) Å by the author; see: (a) E. L. Amma, R. E. Rundle, *J. Am. Chem. Soc.* **1958**, *80*, 4141. (b) R. G. Vranka, E. L. Amma, *J. Am. Chem. Soc.* **1967**, *89*, 3121.
- 15 For the shortest previously reported In-C bond length (2.111(14) Å), see: J. F. Malone, W. S. McDonald, *J. Chem. Soc. A*, **1970**, 3362. For the longest previously reported In-C bond length (2.200(3) Å), see: B. Quillian, Y. Wang, P. Wei, A. Handy, G. H. Robinson, *J. Orgmet. Chem.* **2006**, *691*, 3765.
- 16 G. E. Herberich, B. Schmidt, U. Englert, *Organometallics* **1995**, *14*, 471.
- 17 O. V. Sizova, L. V. Skripnikov, A. Y. Sokolov, *THEOCHEM* **2008**, *870*, 1.
- 18 Based on our calculations at the same level of theory; for further details, see: ESI).
- 19 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, and P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.
- 20 L. S. C. Martins, F. A. L. de Souza, G. A. Ceolin, F. E. Jorge, R. C. Berrêdo, C. T. Campos, *Comput. Theor. Chem.* **2013**, *1013*, 62.
- 21 The ADZP all electron basis set was purchased from the EMSL Basis Set Library; see: (a) D. Feller, *J. Comp. Chem.* **1996**, *17*, 1571. (b) K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.* **2007**, *47*, 1045.
- 22 Although the NICS(0) value was negative, the calculated NICS(0)_{zz} was slightly positive, probably due to the deshielding effect of the indium atom.