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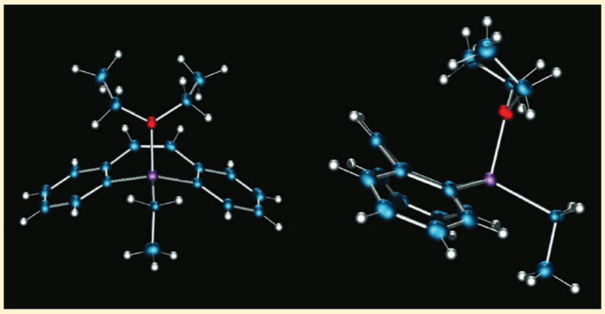
Aluminepin: Aluminum Analogues of Borepin and Gallepin

Kengo Yoshida,*[†,‡] Taniyuki Furuyama,[‡] Chao Wang,[†,‡] Atsuya Muranaka,[‡] Daisuke Hashizume,[‡] Shuji Yasuike,[‡] and Masanobu Uchiyama*[†,‡]

[†]Graduate School of Pharmaceutical Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[‡]RIKEN-ASI, 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan

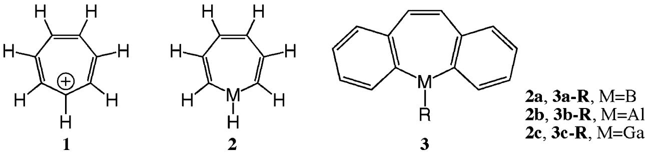
S *Supporting Information*

ABSTRACT: We report synthesis of dibenzoaluminepin as the first aluminepin, an aluminum analogue of borepin and gallepin. This compound contains one molecule of ethereal solvent on the Al atom, which adopts a tetrahedral geometry. The central 7-membered aluminepin ring has a boatlike conformation and was characterized by single-crystal X-ray diffraction, $^{1}H/^{13}C$ NMR, and DFT studies. In addition, NICS, NBO, and theoretical calculations provide insight into the nature of the bonding and aromaticity of aluminepins.



Tropylium cation (**1**) is a well-known nonbenzenoid aromatic compound (Chart 1).[1] Since Vol'pin first proposed borepin (**2a**, M = B), which is isoelectronic with **1**, as a neutral and Hückel 6π-aromatic tropylium analogue,[2] the aromatic character of borepins has been extensively investigated.[3] With regard to other heteropins incorporating group 13 metals, there is only one recent report on dibenzo[*b*,*f*]gallepin (**3c**, M = Ga),[4] which was isolated as a nonplanar 7-membered ring with a molecule of TMEDA coordinated to the Ga atom, while the corresponding aluminum-containing heteropin (aluminepin) has not been reported to date. Thus, it is of interest to investigate the generality and aromatic properties of heteropins incorporating group 13 metals. Here, we report the synthesis and spectroscopic/computational characterization of aluminepins.

Chart 1



DFT calculations[5] indicated that group 13 dibenzoheteropins (**3a-**, **b-**, and **-c-H**, M = B, Al, and Ga) meet the requirements of aromaticity (Figure 1); i.e., they have planar structures and the computed frontier π-orbitals at the B3LYP/6-311+G* level[6] show very similar features to those of phenanthrene (**4**). Incidentally, they have rather lower HOMO–LUMO energy gaps than that of the relevant aromatic hydrocarbon **4**. We confirmed that the planar geometry is the local minimum by starting with an artificial nonplanar geometry of **3**. Geometry optimization then resulted in smooth migration of the group 13 metal atom without any energy barrier to form the planar structure. The LUMO+1 orbital of **4** is energetically stabilized by a group 13 metal in proportion to its electronegativity (B: 2.04, Al: 1.61, Ga: 1.81).

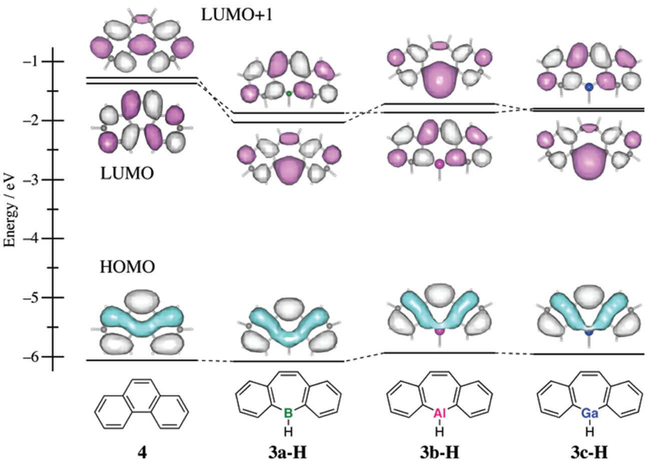


Figure 1. Energy levels of three Kohn–Sham orbitals and the contour plots for phenanthrene and group 13 dibenzoheteropins (B3LYP/6-311+G*).

In order to get the first aluminepin in hand and to investigate its chemical properties, we planned to synthesize dibenzo[*b*,*f*]aluminepin. An aluminum-containing 5-membered heterocycle (aluminole) has been reported,[7] but an attempt to generate a 7-membered heterocycle (aluminepin) by ring expansion of benzoaluminole was unsuccessful.[8] To develop a synthetic route to dibenzoaluminepin (**3-R**, M = Al), we therefore started

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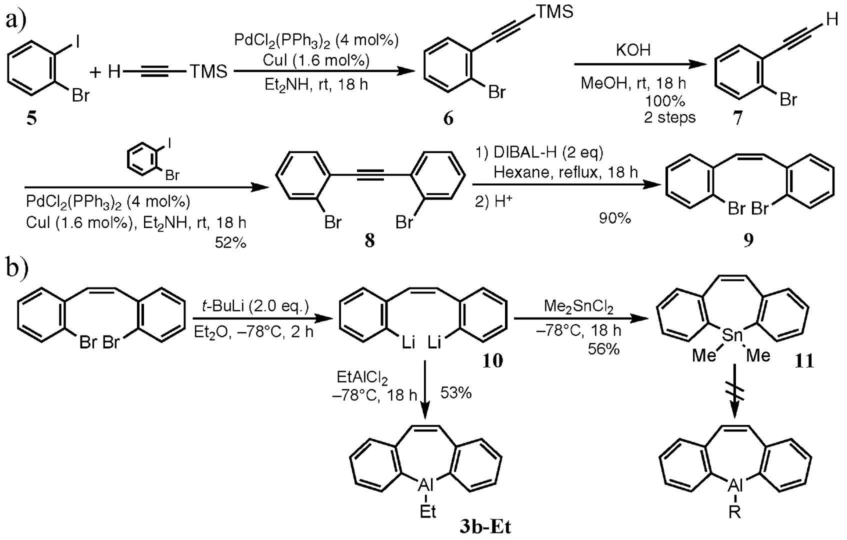
Scheme 1. (a) Synthesis of 2,2′-Dibromo-Z-stilbene. (b) Synthesis of Dibenzo[*b*,*f*]aluminepin



our investigation from two directions, via tin–aluminum and lithium–aluminum exchange reactions. 2,2′-Dibromo-Z-stilbene (**9**) was synthesized from 2-bromoiodobenzene in four steps by means of two Sonogashira coupling reactions and DIBAL-mediated partial *cis* reduction of the acetylene moiety as described by a member of our group[9] (Scheme 1). Most borepins have been synthesized by tin–boron exchange reaction of the appropriate stannepin with boron halides. Although tin–aluminum exchange reactions of **11** using various kinds of aluminum reagents were investigated, all attempts were unsuccessful and the reaction mixtures showed only complex NMR spectra. Next, we focused on direct alumination of **9** via a dilithio intermediate, as used to synthesize gallepin[4] and 5-,[10] 6-,[11] and 7-membered[9] heterocycles.

After extensive experimentation using **9**, we found that ethylaluminum dichloride reacted smoothly with the dilithio intermediate (**10**) at −78 °C to give an aluminepin. After the reaction, the solvents were removed under reduced pressure. The residue was extracted with pentane, and cooling in a freezer for 3 days afforded colorless crystals containing a molecule of diethyl ether as a ligand (Figure 2).[12] As judged from the bond length of Al(1)–O(1) (1.905 Å), as well as the sum of the bond angles around the Al atom (340.77°: C(1)–Al(1)–C(14) (109.89°), C(1)–Al(1)–C(15) (114.20°), and C(14)–Al(1)–C(15) (116.68°)), the Al atom adopts a tetrahedral geometry and the central 7-membered aluminepin ring has a boatlike conformation. All attempts to remove the diethyl ether coordinated to the aluminum atom failed. NMR experiments in solution also supported the presence of one molecule of diethyl ether per dibenzoaluminepin. The coordination of diethyl ether to dibenzoaluminepin could also be detected in ^{1}H and ^{13}C NMR spectra, since the signals of diethyl ether were clearly shifted. These observations are similar to those in the case of dibenzogallepin **3c**[4] but very different from those for borepins.

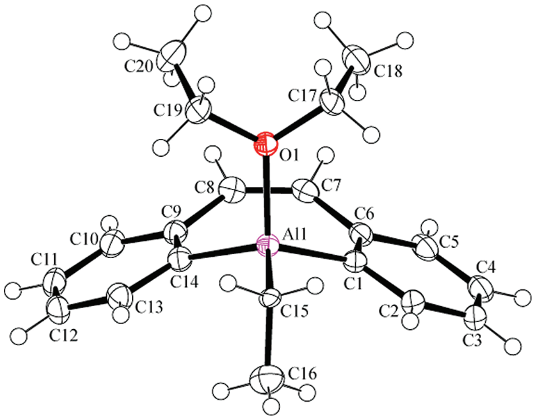


Figure 2. Molecular structure of dibanzoaluminepin (**3b-Et**) (thermal ellipsoids are shown at 50% probability levels).

To address the aromaticity and coordination properties of group 13 heteropins, we performed theoretical/computational studies of **2a–c** as model heteropins. Nucleus-independent chemical shifts (NICS)[13] for **2a–c** were first computed at the B3LYP/6-311+G* level to assess the aromatic character. The NICS(0) and NICS(1) values of **2a** (−3.55 and −6.88), **2b** (−0.80 and −3.08), and **2c** (−1.16 and −3.56) suggest that all group 13 heteropins show aromatic nature, i.e., aromatic 6π-electron structures (although their NICS values are small) (Figure 3). The aromatic character becomes weaker in the order of **2a**, **2c**, and **2b**.[14] Solvation reactions of the heteropins with a molecule of dimethyl ether were then examined. DFT calculations indicated that aluminepin **2b** and gallepin **2c** coordinate with Me_2O to form a solvation complex **12b** and **12c** with large exothermicity (−12.9 and −5.9 kcal/mol, respectively), whereas there is no stabilization energy gain in the case of borepin **2a**. Indeed, the planar structure of **2a** and its NICS values showed little change in the absence/presence of Me_2O. On the other hand, solvation of the group 13 atom of **2b** or **2c** with a Me_2O molecule resulted in a marked change of the geometry of the heteropin ring to generate a boatlike structure, decreasing the aromatic character. The origin of the coordinating effect was investigated by NBO analysis.[15] Second-order perturbation analysis of the aluminepin complex with Me_2O indicated a large stabilization energy (59.8 kcal/mol) between the lone pair of the O atom (donor NBO) and the vacant p* orbital of the Al atom (acceptor NBO). In the case of gallepin, the stabilization energy between O and Ga atoms is 40.8 kcal/mol, while the stabilization energy between **2a** and Me_2O is below the 0.5 kcal/mol default NBO threshold.

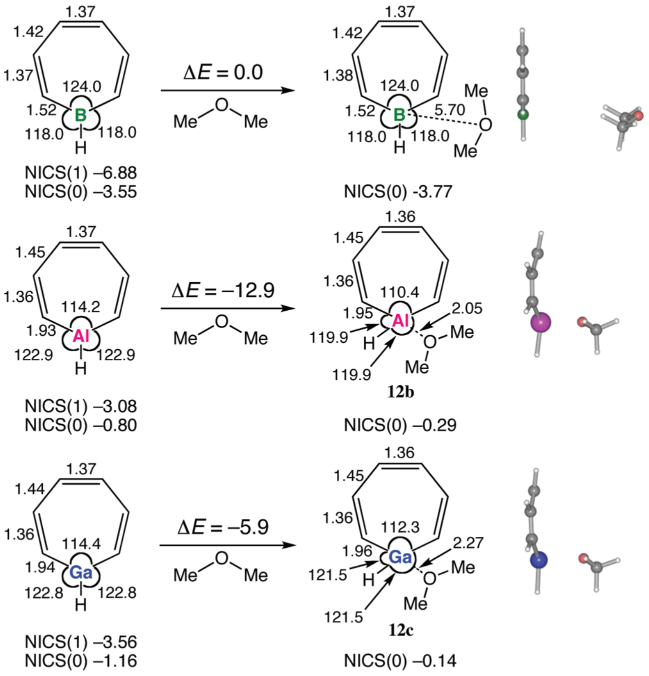


Figure 3. Optimized bond length (Å) and angles (deg) for group 13 heteropins with and without dimethyl ether. Relative energies Δ*E* are given in kcal/mol.

NBO analysis revealed that donation from the π-bond of the triene moiety of **2a** or **2b** to the vacant p* orbital of the group 13 atom, i.e., an indicator of aromatic interaction, corresponds to 23.8 or 8.7 kcal/mol, respectively (Supporting Information).

In summary, we have prepared the first isoelectronic aluminum analogue of the iconic tropylium cation and characterized it by means of X-ray, NMR, and theoretical studies. DFT calculations indicate that group 13 heteropins (M = B, Al, and Ga) all meet the requirements of aromaticity, but the electronic structures and physical properties of aluminepin synthesized here (also the gallepin synthesized by Robinson et al.)[4] are quite different from those of the well-known borepins. The present work underlines that the aromatic characters of group 13 heteropins are deeply related to electronegativity, Lewis acidity, and the nature of the vacant orbital of the central metal. Efforts to extend heteropin chemistry in order to develop new functional materials and to elucidate the physical properties of these compounds (including indinepins and solvent-free aluminepins/gallepins) by means of synthetic, theoretical, and spectroscopic studies are in progress.

■ EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all experiments were carried out under Ar atmosphere with anhydrous solvent. ^{t}BuLi was titrated prior to use.[16] NMR data were collected at room temperature. For **3b-Et**, the sample was run in a CH_2Cl_2 solution. ^{1}H NMR spectra were referenced to a solvent (CH_2Cl_2) signal (5.24 ppm). The capillary tube contained THF-d_8 used as the ^{13}C chemical shift reference and lock solvent. All spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal standard.

2-(Trimethylsilylethynyl)bromobenzene (6).[17] To a suspension of bis(triphenylphosphine)palladium dichloride (1.4 g, 2 mmol) and copper(I) iodide (156 mg, 0.8 mmol) in diethylamine (45 mL) in an ice bath were added dropwise 2-bromoiodobenzene (**5**) (6.4 mL, 50 mmol) and trimethylsilylacetylene (8.5 mL, 60 mmol) successively. The mixture was then stirred for 18 h at room temperature before being quenched with 2 N hydrochloric acid. The aqueous phase was extracted with ethyl acetate, and the combined organic layer was washed with sodium bicarbonate and brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was treated with a short silica gel column with hexane as an eluent to give **6** as pale brown liquid, which was directly used for next reaction.

2-Ethynylbromobenzene (7).[17] In an ice bath, the above obtained **6** (12.6 g, 50 mmol) was mixed with a solution of potassium hydroxide (13 g, 0.2 mol) in methanol (100 mL) and then stirred for 18 h at room temperature before being quenched with 2 N hydrochloric acid. The aqueous phase was extracted with hexane, and the combined organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane) to give **7** as a pale yellow oil (9.0 g, yield: 100% from **5**). ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$, $SiMe_4$), δ (ppm): 7.61−7.52 (2H), 7.30−7.18 (2H), 3.78 (1H).

2,2′-Dibromodiphenylacetylene (8).[17] To a suspension of bis(triphenylphosphine)palladium dichloride (0.55 g, 0.78 mmol) and copper(I) iodide (61 mg, 0.32 mmol) in diethylamine (45 mL) in an ice bath were added dropwise 2-bromoiodobenzene (9.4 mL, 73 mmol) and **7** (13.2 g, 73 mmol) successively. The mixture was stirred for 18 h at room temperature before being quenched with 2 N hydrochloric acid. The aqueous phase was extracted with ethyl acetate, and the combined organic layer was washed with sodium bicarbonate and brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane) to give **8** as a brown powder. (12.7 g, yield: 52%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, $SiMe_4$), δ (ppm): 7.63−7.60 (2H), 7.33−7.18 (6H).

2,2′-Dibromo-*Z*-stilbene (9).[18] A solution of DIBAL-H in hexane (1.03 M, 86.7 mL) was added dropwise to a suspension of **8** (12.7 g, 38 mmol) in hexane (30 mL) in ice bath. After that, the mixture was refluxed with stirring for 18 h and then quenched with water. The aqueous phase was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane) to give **9** as a white powder. (11.5 g, yield: 90%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, $SiMe_4$), δ (ppm): 7.56 (2H), 7.05−6.98 (6H), 6.78 (1H)

Dibenzostannepin (11). To a solution of **9** (1.69 g, 5 mmol) in diethyl ether (20 mL) was added *t*-BuLi (1.51 M in pentane, 6.6 mL, 10 mmol) at −78 °C. The mixture was stirred for an additional 2 h before a solution of dimethyltin dichloride (1.36 g, 6.0 mol) in diethyl ether (5 mL) was added dropwise at the same temperature. This mixture was stirred for for 18 h at room temperature and then quenched with water. The aqueous phase was extracted with diethyl ether and the combined organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane) to give **11** as pale yellow oil. (920 mg, 56%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, $SiMe_4$), δ (ppm): 7.47 (2H), 7.41−7.22 (6H), 6.90 (1H), 0.50 (6H). ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$, $SiMe_4$), δ (ppm): 143.4, 141.7, 134.7, 134.2, 129.0, 128.3, 127.0, −11.7.

Dibenzoaluminepin (3b-Et). To a solution of **9** (676 mg, 2 mmol) in diethyl ether (5 mL) was added *t*-BuLi (1.49 M in pentane, 2.7 mL, 4 mmol) at −78 °C. The mixture was stirred for an additional 2 h before a solution of ethylaluminum dichloride (1.0 M in pentane, 2 mL, 2 mmol) was added dropwise at the same temperature. This mixture was stirred for 18 h at room temperature before solvent was removed under reduced pressure. The residue was extracted with pentane, and the extracts was allowed to cool in a freezer for 3 days to afford **3b-Et**−diethyl ether complex as colorless crystals (250 mg, yield: 53%). ^{1}H NMR (400 MHz, 25 °C, CH_2Cl_2), δ (ppm): 7.69 (2H), 7.22−7.11 (6H), 6.68 (2H), 3.76 (4H), 1.23 (3H), 0.98 (6H), 0.40 (2H). ^{13}C NMR (100 MHz, 25 °C, CH_2Cl_2/THF-d_8), δ (ppm): 150.5, 145.7, 137.6, 134.4, 130.5, 128.1, 126.4, 68.1, 13.8, 10.1, −1.9.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of **11** and **3b-Et**, computational details, and X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: (+81)48-467-2879. Email: kengoyoshida@riken.jp (K.Y.); uchi_yama@riken.jp (M.U.).

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DFT calculations were performed using the RIKEN Integrated Cluster of Clusters (RICC).

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