

## Supporting Information

### An Isolable Anionic Gallabenzene: Synthesis and Characterization

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## 1. Experimental Procedures

### General methods

All manipulations of air- and/or moisture-sensitive compounds were performed in a KOREA KIYON glove box under inert atmosphere of argon. Anhydrous hexane, toluene, and diethylether (Et<sub>2</sub>O) were dried by passage through a GrassContour solvent purification system. Anhydrous 1,2-dimethoxyethane (DME) was purchased from Kanto Chemical Co., Ltd. Deuterated benzene (C<sub>6</sub>D<sub>6</sub>) were distilled from sodium/benzophenone prior to use. Mesityllithium was prepared according to the literature procedure.<sup>S1</sup> Aluminacyclohexadiene **2** was prepared according to the literature procedure.<sup>S2</sup> Other chemicals were used as received. The nuclear magnetic resonance (NMR) measurements were carried out by a JEOL ECA-500 spectrometer (500 MHz for <sup>1</sup>H, 126 MHz for <sup>13</sup>C, and 194 MHz for <sup>7</sup>Li) or a Varian Mercury 400 spectrometer (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C). Chemical shifts ( $\delta$ ) are given by definition as dimensionless numbers and relative to <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of the residual C<sub>6</sub>D<sub>5</sub>H for <sup>1</sup>H ( $\delta$  = 7.16) and C<sub>6</sub>D<sub>6</sub> itself for <sup>13</sup>C ( $\delta$  = 128.0). The <sup>7</sup>Li NMR spectra were referenced using an external standard of 1 M LiCl aqueous solution. The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. Melting points were measured on a MPA100 Optimelt Automated Melting Point System and are uncorrected.

### Synthesis of gallacyclohexadiene **3**

To a toluene solution (60 mL) of aluminacyclohexadiene **2** (1.00 g, 1.92 mmol), GaCl<sub>3</sub> (338 mg, 1.92 mmol) was added. After stirring at room temperature for 3 h, pyridine (292  $\mu$ L, 3.62 mmol) was added dropwise to a mixture. After stirring for 30 min, a resulting mixture was filtered, and concentrated under reduced pressure. The repetitious recrystallization from toluene to give gallacyclohexadiene **3** as colorless crystals (833 mg, 1.48 mmol, 77%): mp (in a sealed tube) 186–188 °C (dec.); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz)  $\delta$ : 0.69-1.65 (m, 32H), 1.39-1.52(m, 6H), 2.87-3.66 (d, 2H), 6.41 (m, 2H), 6.69 (m, 1H), 7.41 (t,  $J$  = 4 Hz, 2H), 8.63 (m, 2H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.4 MHz)  $\delta$ : 12.0 (CH), 19.4 (CH<sub>3</sub>), 39.7 (CH<sub>2</sub>), 125.1 (CH), 140.0 (CH), 144.5 (4°), 147.4 (CH), 156.7 (CH); Anal. calcd. for C<sub>28</sub>H<sub>51</sub>ClGaNSi<sub>2</sub>: C, 59.73; H, 9.13; N, 2.49. Found C, 59.67; H, 9.00; N, 2.38.

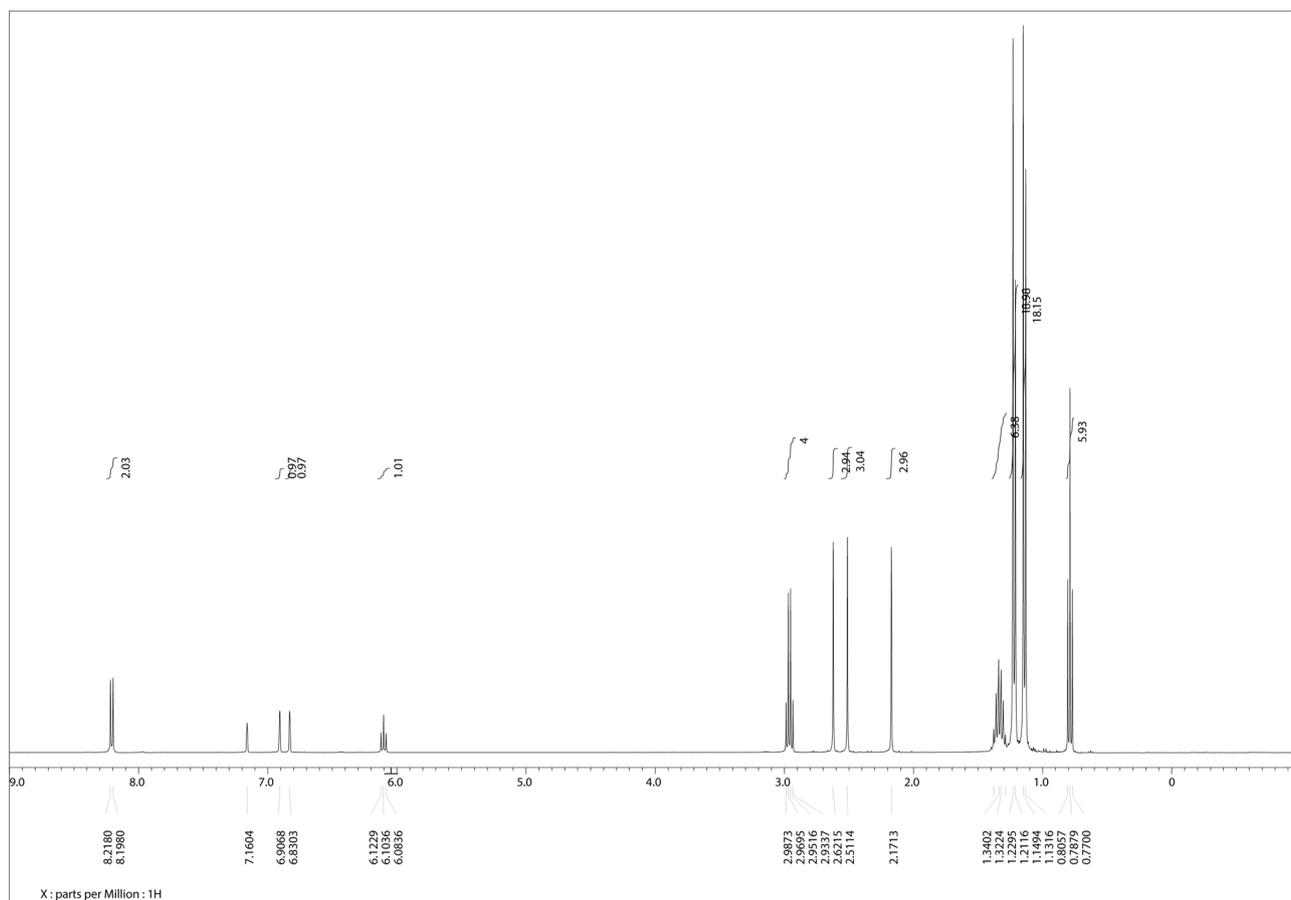
### Synthesis of gallabenzene **1Ga-Li(solv)** (solv: Et<sub>2</sub>O, DME, and DME<sub>3</sub>)

Mesityllithium (296.6 mg, 2.352 mmol) was added to a Et<sub>2</sub>O suspension (7.1 mL) of gallacyclohexadiene **3** (400 mg, 0.711 mmol) at –35 °C. A mixture was stirred for 3 h at –35 °C, then warmed to room temperature and stirred for 4 h. A resulting mixture was filtered, and concentrated under reduced pressure. The resulting brown oil was recrystallized from Et<sub>2</sub>O to give gallabenzene **1Ga-Li(Et<sub>2</sub>O)** as pale yellow crystals (296 mg, 0.457 mmol, 64%): mp (in a sealed tube) 198–200 °C (dec.); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz)  $\delta$ : 0.79 (t,  $J$  = 7 Hz, 6H), 1.14 (d,  $J$  = 7 Hz, 18H), 1.22 (d,  $J$  = 7 Hz, 18H), 1.27-1.40 (m, 6H), 2.17 (s, 3H), 2.51 (s, 3H), 2.62 (s, 3H), 2.96 (q,  $J$  = 7 Hz, 4H), 6.10 (t,  $J$  = 8 Hz, 1H), 6.83 (s, 1H), 6.91 (s, 1H), 8.21 (d,  $J$  = 8 Hz, 2H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz)  $\delta$ : 14.7 (CH), 16.3 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 21.8 (CH<sub>3</sub>), 23.1 (CH<sub>3</sub>), 29.2 (CH<sub>3</sub>), 30.4 (CH<sub>3</sub>), 67.2 (CH<sub>2</sub>), 104.0 (CH), 126.7 (CH), 127.3 (CH), 130.3 (4°), 136.9 (4°), 141.2 (4°), 143.4 (4°), 148.3 (CH), 148.7 (4°); <sup>7</sup>Li NMR(C<sub>6</sub>D<sub>6</sub>, 194 MHz)  $\delta$ :

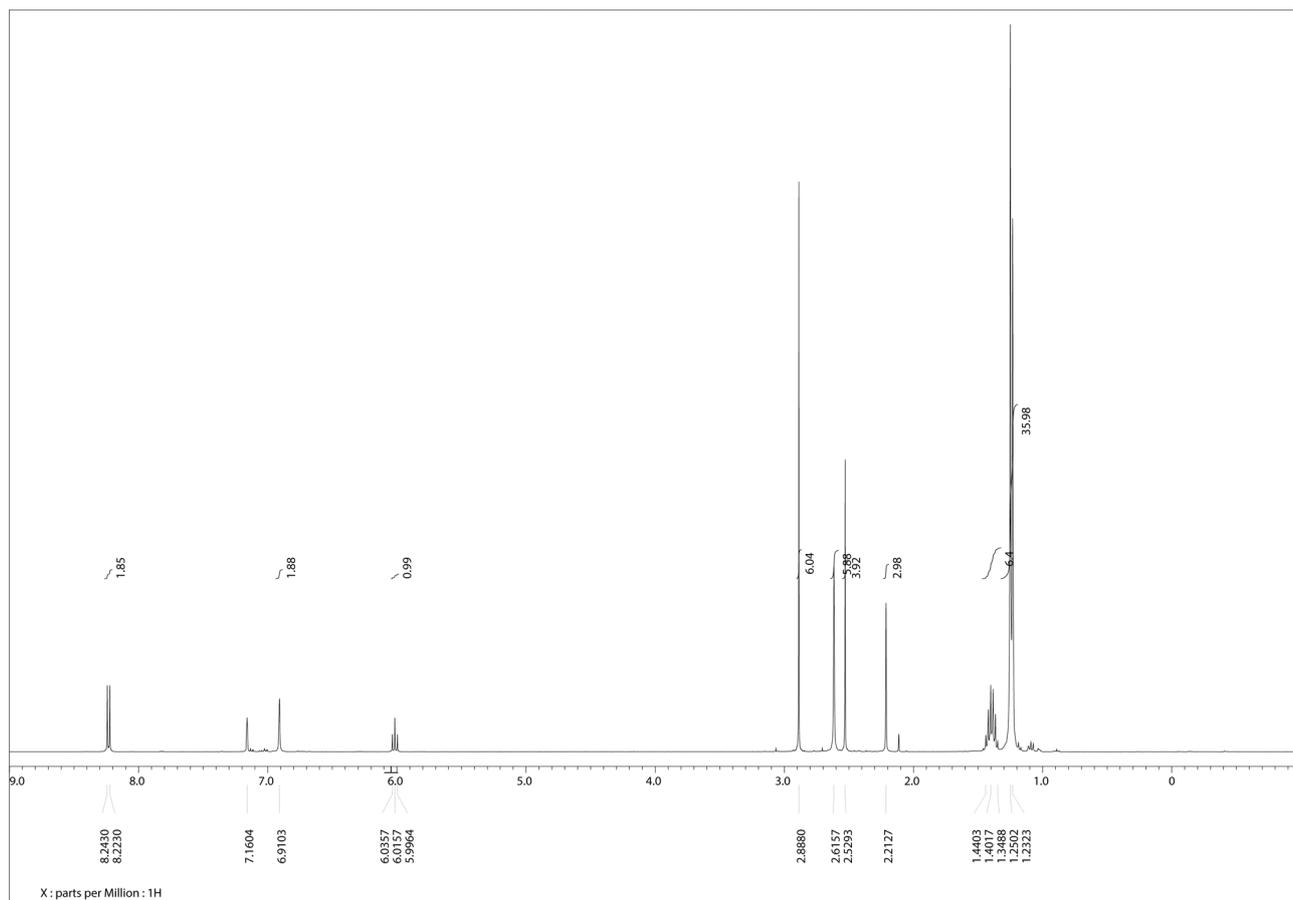
–5.2. UV-vis (hexane)  $\lambda_{\max}$  ( $\epsilon$ ): 361 nm (18100). The purity of **1Ga**-Li(Et<sub>2</sub>O) was confirmed by the <sup>1</sup>H NMR spectroscopy (Figure S1).

To a toluene (4.5 mL) solution of **1Ga**-Li(Et<sub>2</sub>O) (159 mg, 0.245 mmol), DME (24.3  $\mu$ L, 0.269 mmol) was added. After the concentration under vacuum, the resulting solid was recrystallized from toluene to give **1**-Li(DME) as pale-yellow crystals (137.9 mg, 0.208 mol, 85%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz)  $\delta$ : 1.24 (d,  $J$  = 7 Hz, 32H), 1.34-1.45 (m, 6H), 2.21 (s, 3H), 2.53 (s, 4H), 2.62 (s, 6H), 2.89 (s, 6H), 6.02 (t,  $J$  = 8 Hz, 1H), 6.91 (s, 2H), 8.23 (d,  $J$  = 8 Hz, 2H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz)  $\delta$ : 13.1 (CH), 20.0 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>), 59.7 (CH<sub>3</sub>), 69.6 (CH<sub>2</sub>), 103.0 (CH), 126.9 (CH), 129.5 (4°), 136.6 (4°), 142.6 (4°), 148.2 (CH), 150.6 (4°); <sup>7</sup>Li NMR(C<sub>6</sub>D<sub>6</sub>, 194 MHz)  $\delta$ : –4.8. The purity of **1Ga**-Li(DME) was confirmed by the <sup>1</sup>H NMR spectroscopy (Figure S2).

Crystalline **1Ga**-Li(DME) (54.1 mg, 0.0815 mmol) was recrystallized from DME at –35 °C to give aluminabenzene **1Ga**-Li(DME)<sub>3</sub> as pale-yellow crystals (59.8 mg, 0.0709 mmol, 87%): The NMR spectra of **1Ga**-(DME)<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> are identical to those of **1Ga**-(DME). This result suggests that DME molecules coordinated to lithium cation would eliminate easily to give a mixture of **1Ga**-(DME) and free DME molecules. Anal. calcd. for C<sub>44</sub>H<sub>86</sub>GaLiO<sub>6</sub>Si<sub>2</sub>: C, 62.62; H, 10.27. Found C, 62.32; H, 10.67.



**Figure S1.** <sup>1</sup>H NMR spectrum of **1Ga**-Li(Et<sub>2</sub>O) (400 MHz, C<sub>6</sub>D<sub>6</sub>).



**Figure S2.**  $^1\text{H}$  NMR spectrum of **1Ga-Li(DME)** (400 MHz,  $\text{C}_6\text{D}_6$ ).

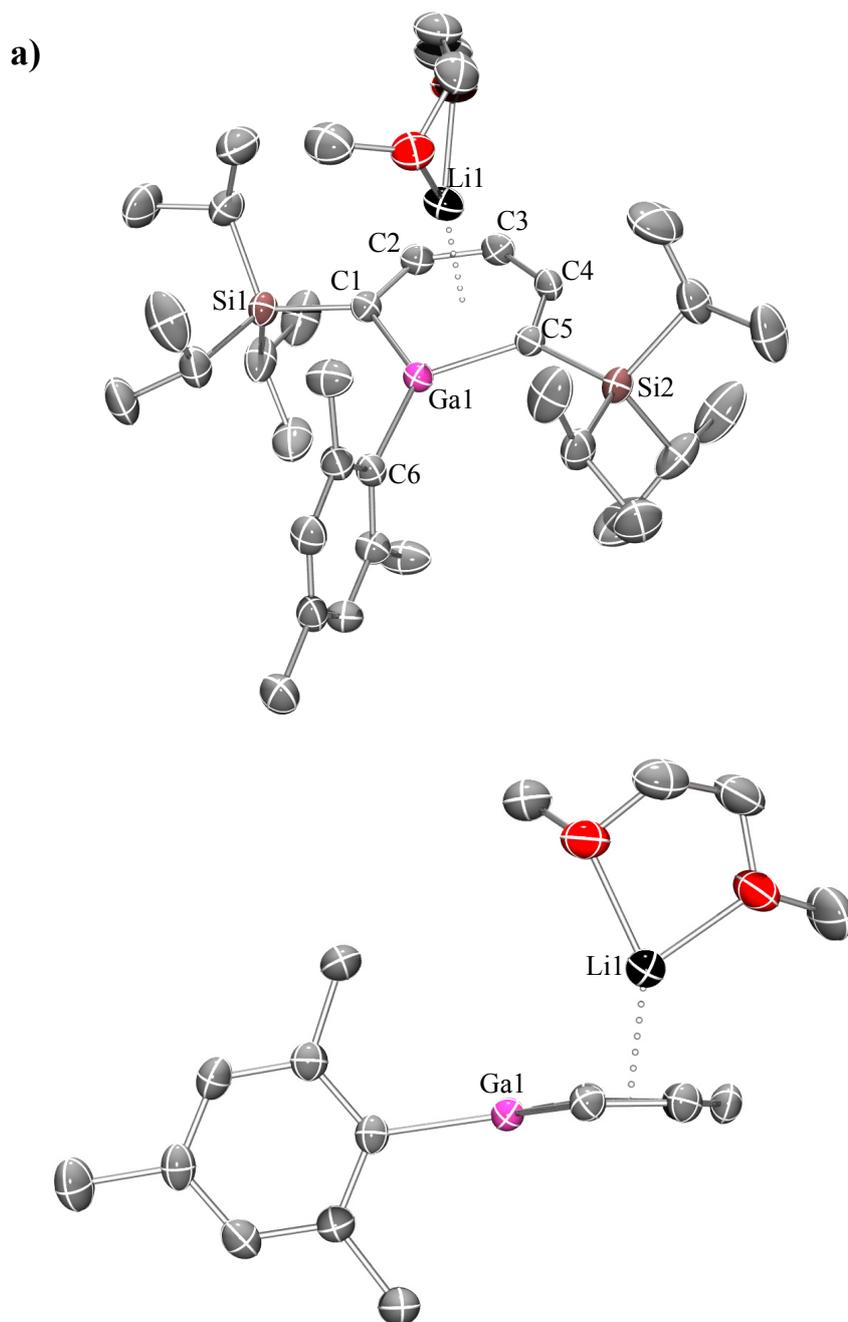
## 2. X-ray Crystallographic Analysis

Crystallographic data for **1Ga**-Li(DME), **1Ga**-Li(DME)<sub>3</sub>, and **3** are summarized in table S1. The crystal was coated with oil (Immersion Oil, type B: Code 1248, Cargille Laboratories, Inc.) and put on a MicroMount™ (MiTeGen, LLC), and then mounted on diffractometer. Diffraction data were collected on a Saturn CCD detectors using MoK $\alpha$  radiation. The Bragg spots were integrated using the CrystalClear program package<sup>S3</sup>. Absorption corrections were applied. All the following procedure for analysis, Yadokari-XG 2009 was used as a graphical interface.<sup>S4</sup> The structures were solved by a direct method with programs of SIR2004<sup>S5</sup> and refined by a full-matrix least squares method with the program of SHELXL-2013.<sup>S6</sup> Anisotropic temperature factors were applied to all non-hydrogen atoms. The hydrogen atoms were put at calculated positions, and refined applying riding models. The detailed crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 1058886 (**1Ga**-Li(DME)), CCDC 1058887 (**1Ga**-Li(DME)<sub>3</sub>), CCDC 1058888 (**3**). A copy of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/products/csd/request>.

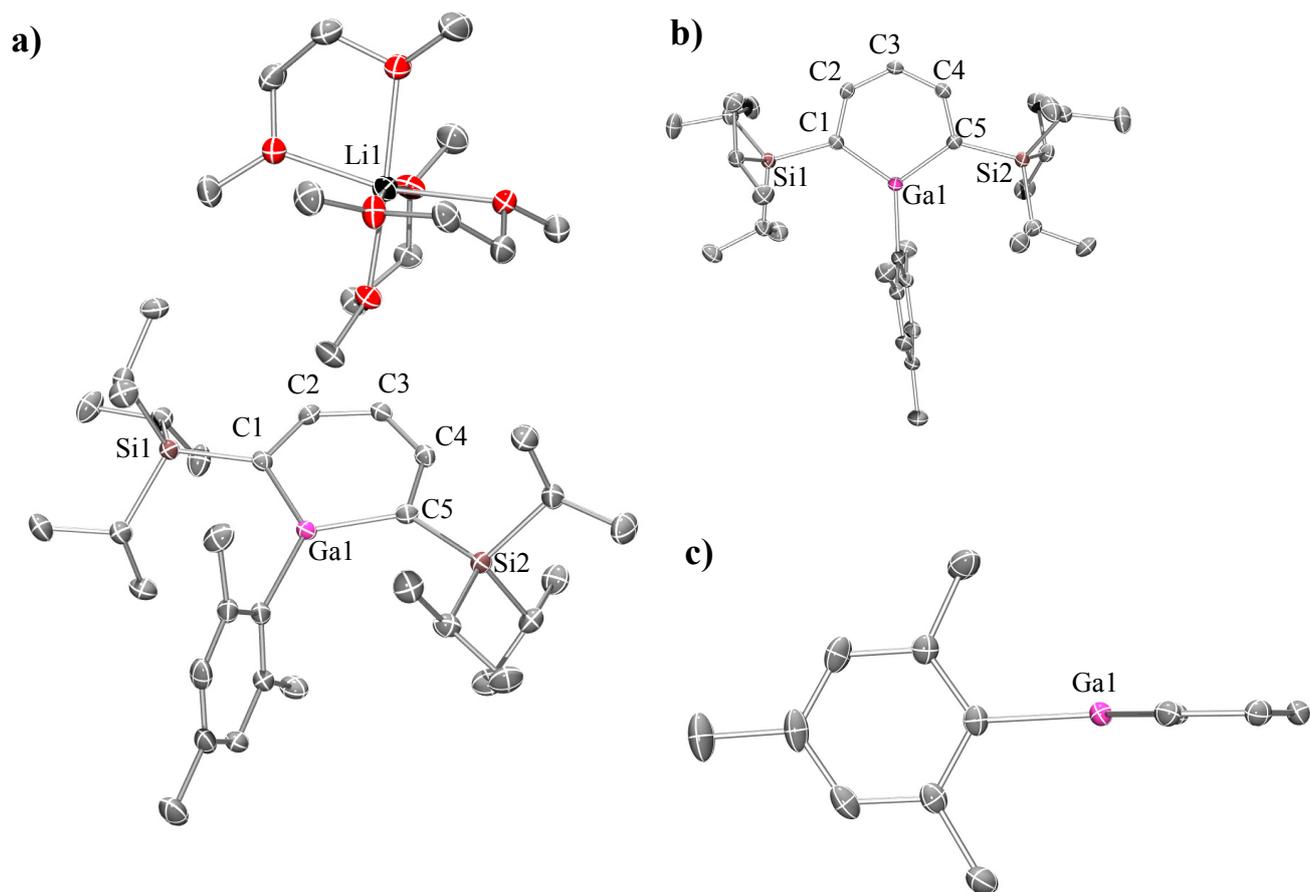
**Table S1.** Crystallographic data for **1Ga-Li(DME)**, **1Ga-Li(DME)<sub>3</sub>**, and **3**.

	<b>1Ga-Li(DME)</b>	<b>1Ga-Li(DME)<sub>3</sub></b>	<b>3</b>
formula	C <sub>36</sub> H <sub>66</sub> GaLiO <sub>2</sub> Si <sub>2</sub>	C <sub>44</sub> H <sub>86</sub> GaLiO <sub>6</sub> Si <sub>2</sub>	C <sub>28</sub> H <sub>51</sub> ClGaNSi <sub>2</sub>
<i>M</i>	663.72	843.96	563.04
<i>T</i> / K	173	93	93
color	pale-yellow	pale-yellow	colorless
size, mm	0.20 x 0.03 x 0.03	0.21 x 0.06 x 0.02	0.17 x 0.17 x 0.04
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)
<i>a</i> / Å	8.7398(16)	13.000(2)	14.1431(16)
<i>b</i> / Å	29.690(5)	28.938(5)	13.6702(14)
<i>c</i> / Å	15.217(3)	13.964(2)	17.1961(19)
$\alpha$ / °	90	90	90
$\beta$ / °	101.070(4)	108.411(2)	112.4196(13)
$\gamma$ / °	90	90	90
<i>V</i> / Å <sup>3</sup>	3875.1(12)	4984.3(14)	3073.4(6)
<i>Z</i>	4	4	4
<i>D<sub>x</sub></i> / g cm <sup>-3</sup>	1.138	1.125	1.217
$\mu$ / mm <sup>-1</sup>	0.799	0.640	1.077
<i>F</i> (000)	1440	1840	1208
$\theta$ range / °	3.04 to 27.48	3.08 to 27.50	3.12 to 27.47
reflections collected	31909	40799	24833
unique reflections	8863	11386	7001
refined parameters	396	508	310
GOF on <i>F</i> <sup>2</sup>	1.080	1.085	1.082
<i>R</i> 1 [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0633	0.0610	0.0351
w <i>R</i> 2 (all data) <sup>b</sup>	0.1598	0.1605	0.0838
$\Delta\rho_{\min, \max}$ / e Å <sup>-3</sup>	-0.782, 0.819	-1.138, 0.929	-0.650, 0.335

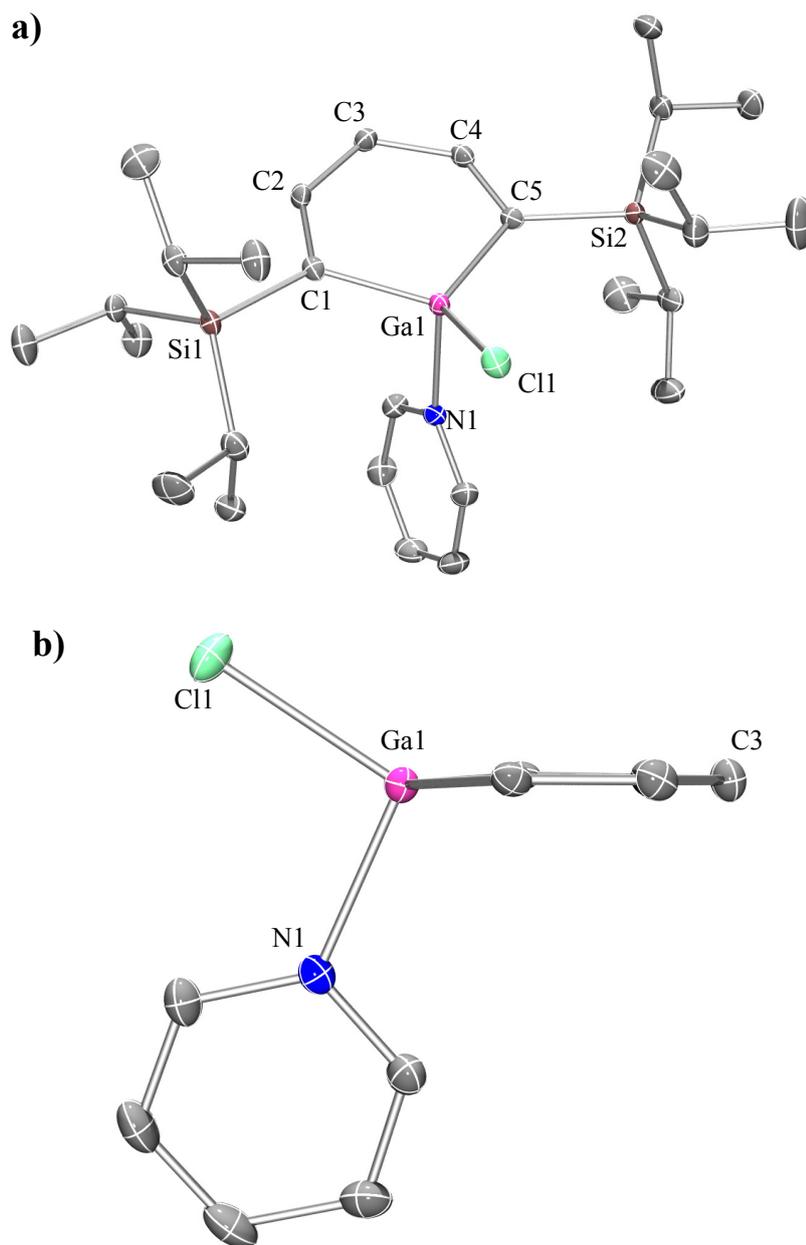
<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , <sup>b</sup>  $wR2 = [\sum \{w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}]^{1/2}$



**Figure S3.** a) Molecular structure of **1Ga-Li(DME)** (50% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity. b) Side view of **1Ga-Li(DME)**. Hydrogen atoms and triisopropylsilyl groups are omitted for clarity. Selected bond distances (Å) and angles (°) for **1Ga-Li(DME)**: Ga1–C1 = 1.939(3), Ga1–C5 = 1.941(3), Ga1–C6 = 1.985(3), C1–C2 = 1.402(4), C2–C3 = 1.403(5), C3–C4 = 1.408(5), C4–C5 = 1.396(4), Ga1–Li1 = 2.931(6), C1–Li1 = 2.562(7), C2–Li1 = 2.338(7), C3–Li1 = 2.301(7), C4–Li1 = 2.442(7), C5–Li1 = 2.702(7), C1–Ga1–C5 = 105.63(14), Ga1–C1–C2 = 114.5(2), C1–C2–C3 = 128.8(3), C2–C3–C4 = 126.6(3), C3–C4–C5 = 128.6(3), C4–C5–Ga1 = 114.9(2), C1–Ga1–C6 = 128.75(13), C5–Ga1–C6 = 125.62(13).



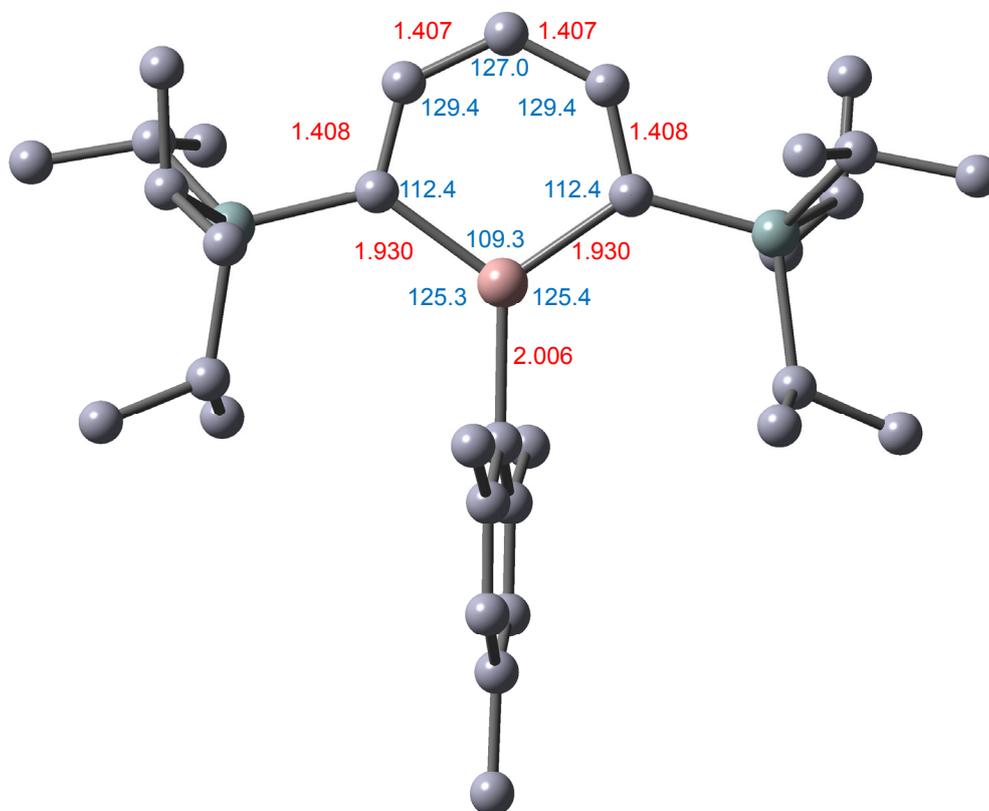
**Figure S4.** a) Molecular Structure of **1Ga-Li(DME)<sub>3</sub>** (50% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity. b) Top view of **1Ga-Li(DME)<sub>3</sub>**. Hydrogen atoms and Li(DME)<sub>3</sub> moiety are omitted for clarity. c) Side view of **1Ga-Li(DME)<sub>3</sub>**. Triisopropyl silyl groups and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for **1Ga-Li(DME)<sub>3</sub>**: Ga1–C1 = 1.927(3), Ga1–C5 = 1.927(3), C1–C2 = 1.411(4), C2–C3 = 1.409(4), C3–C4 = 1.406(4), C4–C5 = 1.409(4), Ga1–C6 = 2.004(3), C1–Ga1–C5 = 108.72(11), Ga1–C1–C2 = 113.31(19), C1–C2–C3 = 128.5(2), C2–C3–C4 = 127.4(2), C3–C4–C5 = 129.0(2), C4–C5–Ga1 = 113.06(19), C1–Ga1–C6 = 127.87(11), C5–Ga1–C6 = 123.33(11).



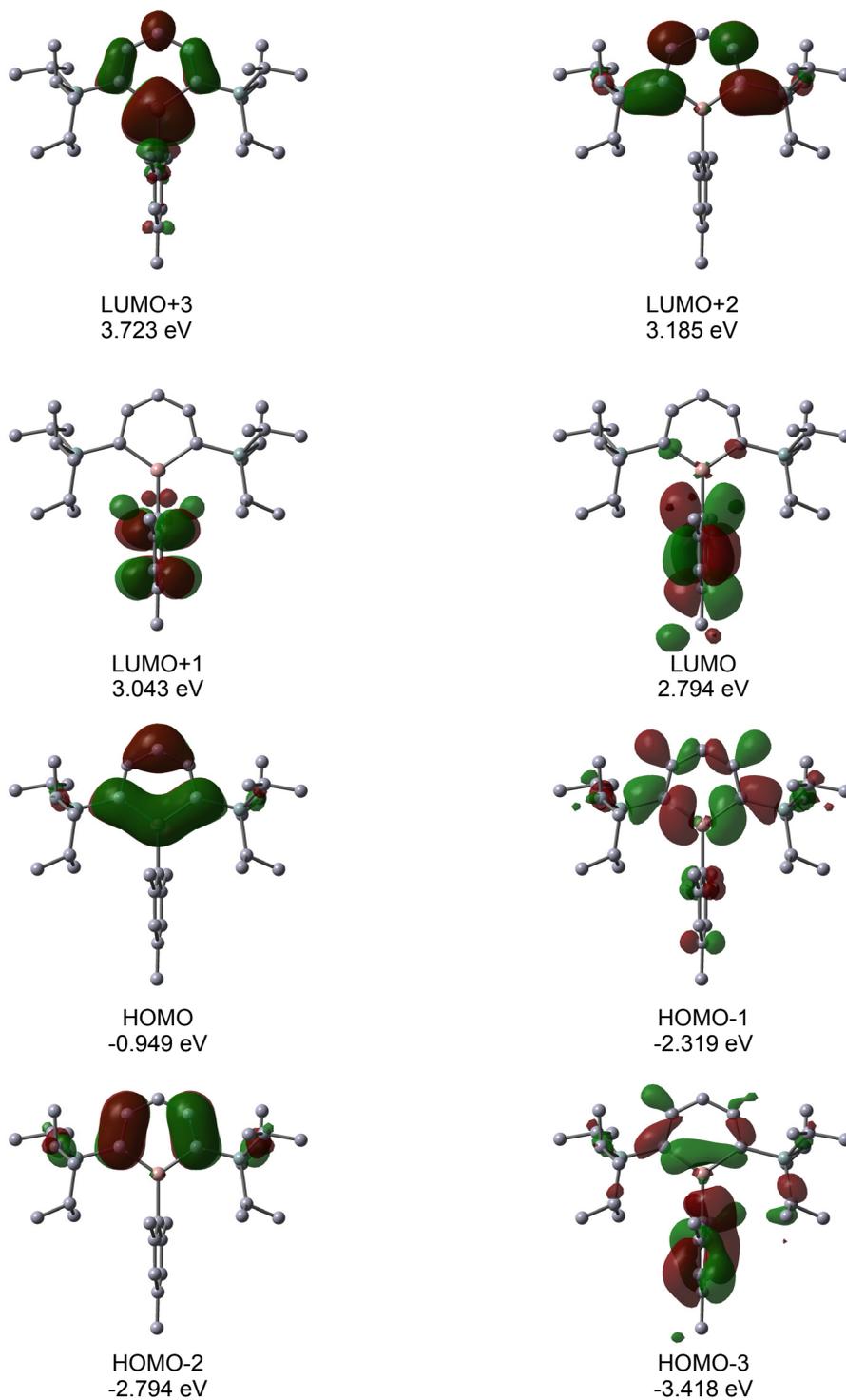
**Figure S5.** a) Molecular structure of **3** (50% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity. b) Side view of **3**. Triisopropylsilyl groups and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for **3**: Ga1–C1 = 1.9574(18), Ga1–C5 = 1.9649(17), C1–C2 = 1.345(2), C2–C3 = 1.504(2), C3–C4 = 1.512(2), C4–C5 = 1.350(2), Ga1–Cl1 = 2.2218(5), Ga1–N1 = 2.0624(15), C1–Ga1–C5 = 111.17(7), Ga1–C1–C2 = 112.53(13), C1–C2–C3 = 130.18(16), C2–C3–C4 = 123.47(15), C3–C4–C5 = 131.19(16), C4–C5–Ga1 = 111.25(13), C1–Ga1–Cl1 = 116.42(5), C5–Ga1–Cl1 = 116.70(5), C1–Ga1–N1 = 101.81(7), C5–Ga1–N1 = 108.74(6), N1–Ga1–Cl1 = 99.88(4).

### 3. Theoretical Calculations

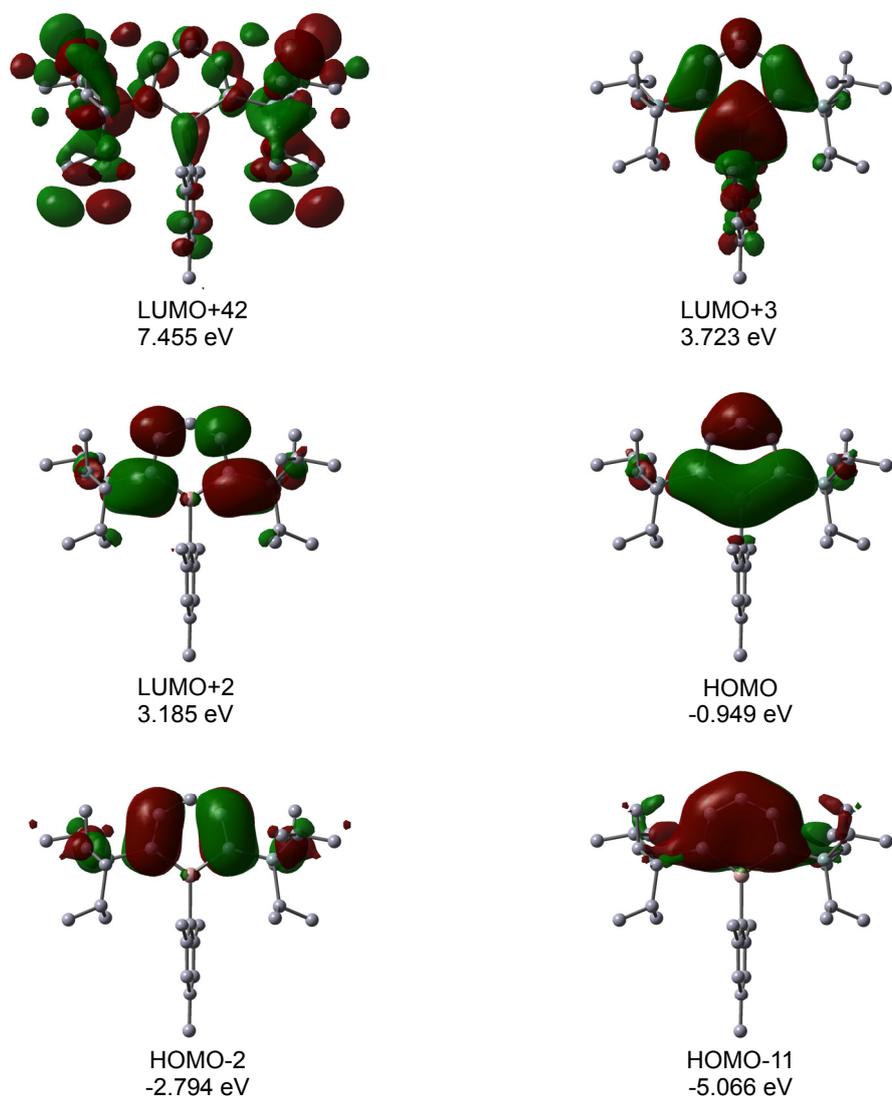
The geometry optimization of **1Ga** was performed at the B3LYP/6-31G(d)<sup>S7-S9</sup> level of theory by using Gaussian 09 program package.<sup>S10</sup> The optimized structures, selected structural parameters, and selected molecular orbitals of **1Ga** is shown in Figure S6-S8. The Wiberg bond index (WBI)<sup>S11</sup> and natural population analysis (NPA)<sup>S12</sup> charge distribution were calculated by natural bond orbital (NBO) method (Figure S9).<sup>S12</sup> The NICS<sup>S13</sup> calculation was performed using gauge-independent atomic orbital (GIAO) method<sup>S14</sup> at the B3LYP/6-311+G(2d,p)<sup>S7, S15</sup> level of theory (Figure S10).



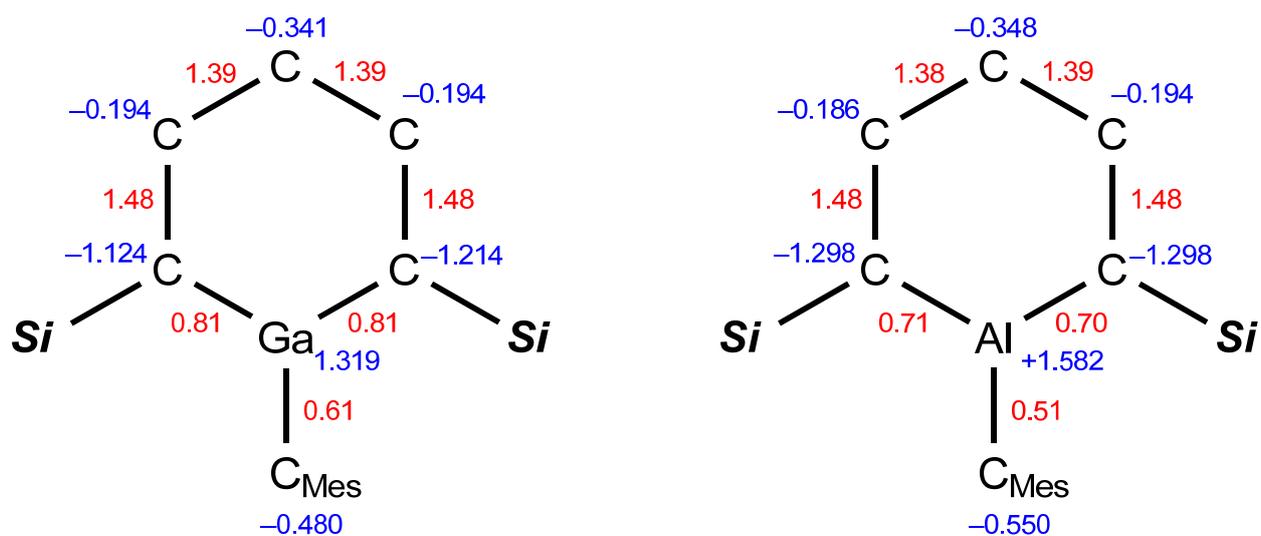
**Figure S6.** Optimized structure and selected bond distances (Å, Red) and angles (°, Blue) of **1Ga** at the B3LYP/6-31G(d) level of theory. Hydrogen atoms are omitted for clarity.



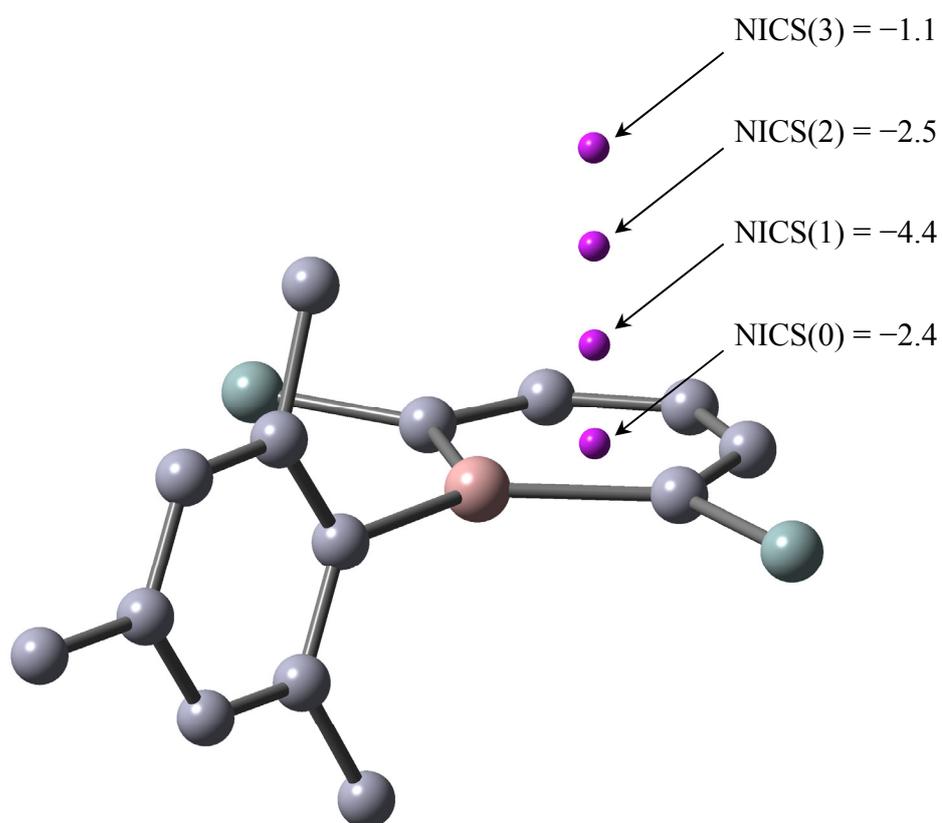
**Figure S7.** Frontier molecular orbitals of **1Ga** calculated at the B3LYP/6-31G(d) level of theory. Hydrogen atoms are omitted for clarity.



**Figure S8.** Selected  $\pi$  orbitals of **1Ga** calculated at the B3LYP/6-31G(d) level of theory. Hydrogen atoms are omitted for clarity.



**Figure S9.** Wiberg bond indices (WBI) (Red) and natural population analysis charge distributions (Blue) of **1Ga** (left) and **1Al** (right).<sup>S2</sup>



**Figure S10.** Calculated NICS values of **1Ga**. Hydrogen atoms and isopropyl groups are omitted for clarity.

## 4. References

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