

**SUPPORTING INFORMATION**

***Bis(2-mercapto-1-R-imidazolyl)hydroborato* Complexes of Aluminum,  
Gallium, Indium and Thallium: Compounds Possessing Gallium–  
Gallium Bonds and a Trivalent Thallium Alkyl**

Kevin Yurkerwich, Fergal Coleman and Gerard Parkin,\*

*Department of Chemistry,  
Columbia University,  
New York, New York 10027, USA.  
E-mail: parkin@columbia.edu*

*Received xxxx xx, 2010.*

---

## EXPERIMENTAL SECTION

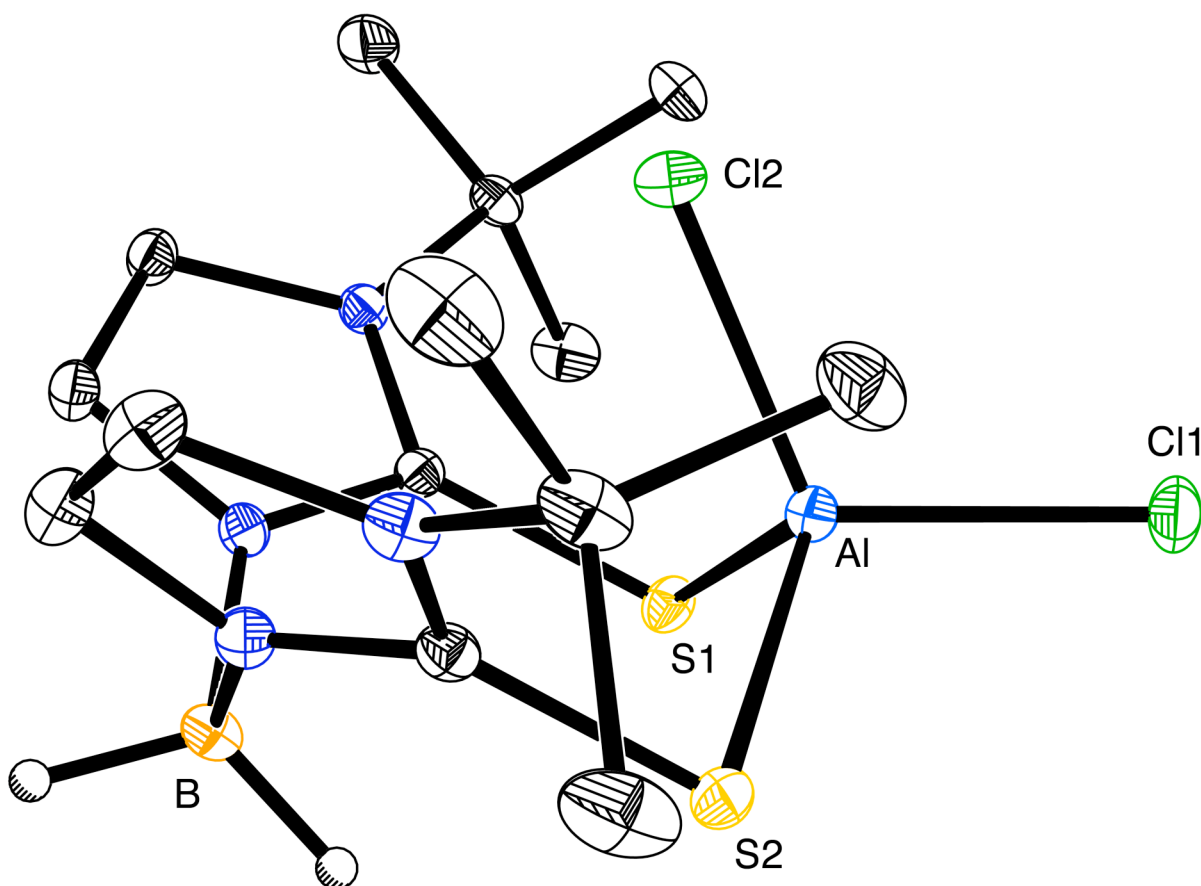
### General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified.<sup>1</sup> Solvents were purified and degassed by standard procedures. <sup>1</sup>H NMR spectra were measured on Bruker 300 DRX and Bruker 400 AVIII spectrometers. <sup>1</sup>H NMR chemical shifts are reported in ppm relative to SiMe<sub>4</sub> (δ = 0) and were referenced internally with respect to the protio solvent impurity (δ 7.26 for CHCl<sub>3</sub>, 1.94 for CHD<sub>2</sub>CN and 2.50 for *d*<sub>6</sub>-DMSO).<sup>2</sup> <sup>13</sup>C NMR chemical shifts are reported in ppm relative to SiMe<sub>4</sub> (δ = 0) and were referenced internally with respect to the solvent (δ 77.16 for CDCl<sub>3</sub> and 1.32 for the upfield signal of CD<sub>3</sub>CN<sup>3</sup>). Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometer and are reported in cm<sup>-1</sup>. Mass spectra were obtained on a Micromass Quadrupole-Time-of-Flight mass spectrometer using fast atom bombardment (FAB). Hmim<sup>Bu<sup>t</sup></sup>,<sup>4</sup> [Bm<sup>Me</sup>]<sup>Li</sup>,<sup>5</sup> [Bm<sup>Me</sup>]<sup>Tl</sup>,<sup>5</sup> [Bm<sup>Bu<sup>t</sup></sup>]<sup>Na</sup>,<sup>6</sup> [Bm<sup>Bu<sup>t</sup></sup>]<sup>Tl</sup>,<sup>7</sup> "GaI",<sup>8</sup> and Me<sub>2</sub>TlCl<sup>9</sup> were prepared by the literature methods. GaCl<sub>3</sub> (Strem & VWR), GaBr<sub>3</sub> (Aldrich), GaI<sub>3</sub> (Aldrich), InCl<sub>3</sub> (Aldrich), InBr<sub>3</sub> (Strem), InI<sub>3</sub> (Aldrich), and TlI (Aldrich) were obtained commercially and used as received.

### Synthesis of [Bm<sup>Bu<sup>t</sup></sup>]<sup>Al</sup>Cl<sub>2</sub>

A mixture of [Bm<sup>Bu<sup>t</sup></sup>]<sup>Na</sup> (100 mg, 0.29 mmol) and AlCl<sub>3</sub> (77 mg, 0.58 mmol) was treated with cold (-35°C) MeCN (1.5 mL). The mixture was mixed *via* pipette for 5 minutes and filtered. The filtrate was cooled to -35°C, thereby depositing yellow crystals of composition [Bm<sup>Bu<sup>t</sup></sup>]<sup>Al</sup>Cl<sub>2</sub> (84 mg, 69%) suitable for X-ray diffraction over a period of two days. Analysis calcd. for [Bm<sup>Bu<sup>t</sup></sup>]<sup>Al</sup>Cl<sub>2</sub>: C, 39.9%; H, 5.7%; N, 13.3%. Found: C, 38.8%; H, 5.3%; N, 12.8%. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 1.72 [s, 18 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]S<sub>2</sub>}], 3.6 [br, 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]S<sub>2</sub>}], 7.29 [d, <sup>3</sup>J<sub>H-H</sub>=2, 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]S<sub>2</sub>}], 7.31 [d, <sup>3</sup>J<sub>H-H</sub>=2, 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]S<sub>2</sub>)]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 29.4 [6 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>}], 61.3 [2 C of

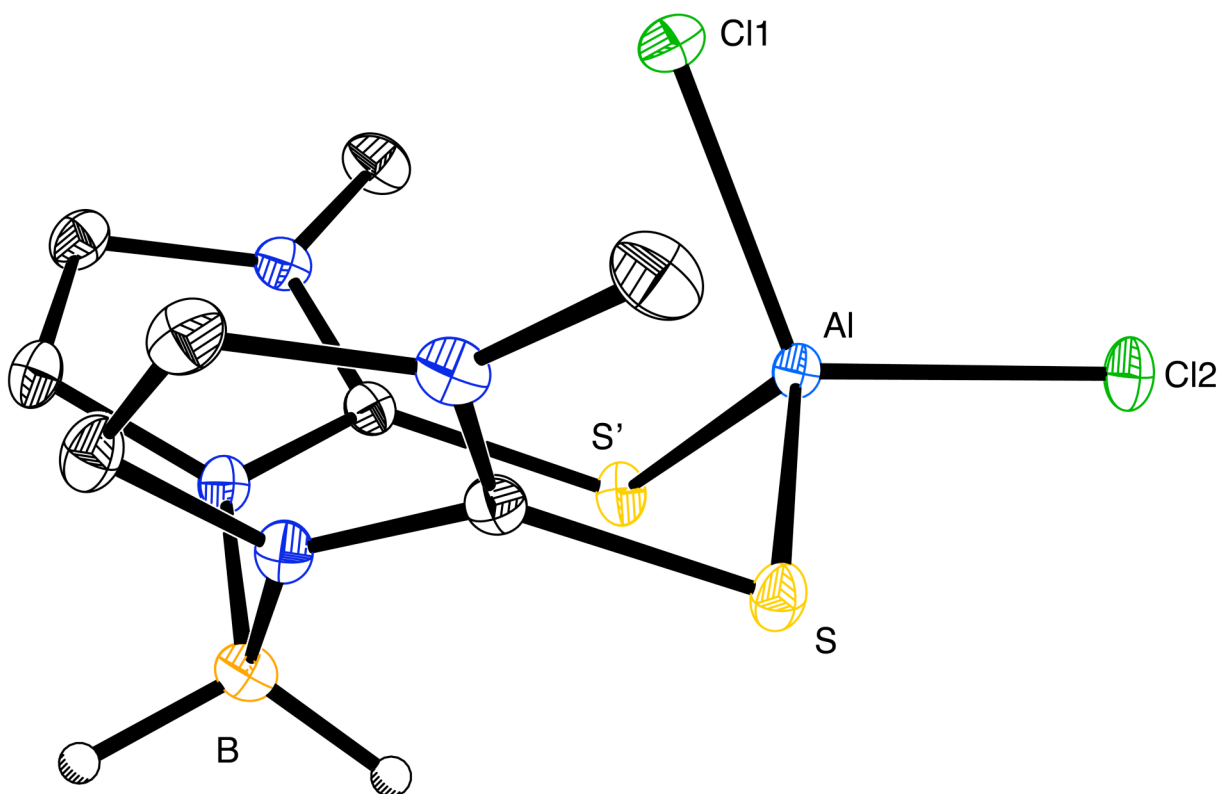
$\text{H}_2\text{B}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_2$ , 121.1 [2 C of  $\text{H}_2\text{B}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_2$ ], 126.0 [2 C of  $\text{H}_2\text{B}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_2$ ], 2 C of  $\text{H}_2\text{B}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_2$  not observed.



*Molecular structure of  $[\text{Bm}^{\text{But}}]\text{AlCl}_2$*

### Synthesis of $[\text{Bm}^{\text{Me}}]\text{AlCl}_2$

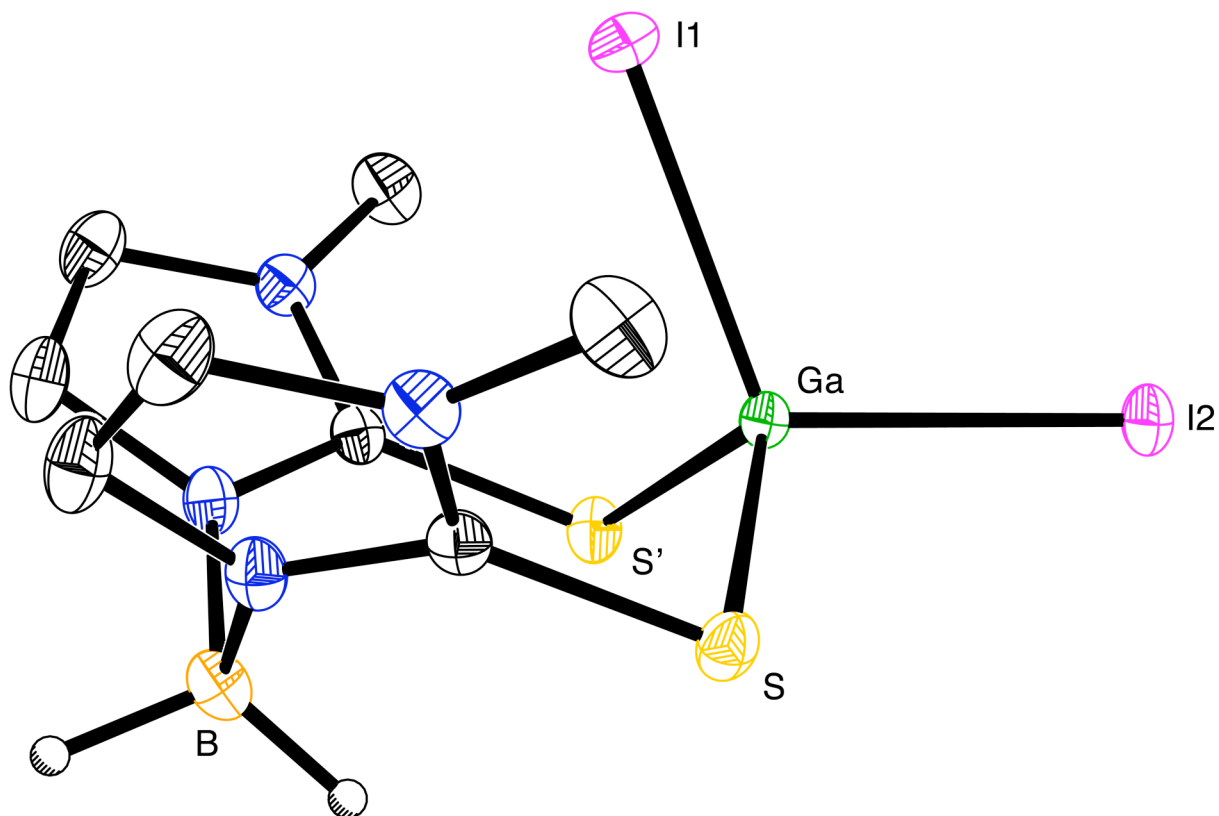
$[\text{Bm}^{\text{Me}}]\text{Li}$  (100 mg, 0.41 mmol) was treated with a solution of  $\text{AlCl}_3$  (55 mg, 0.41 mmol) in MeCN (1.5 mL). The mixture was stirred for 2.5 hours and filtered. Colorless crystals of composition  $[\text{Bm}^{\text{Me}}]\text{AlCl}_2$  (ca. 10 mg) were obtained after a period of one week at room temperature.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): 3.46 [s, 6 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{CH}_3]\text{S}\}_2$ ], 6.69 [d,  $^3J_{\text{H-H}} = 2$ , 2 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{CH}_3]\text{S}\}_2$ ], 6.79 [d,  $^3J_{\text{H-H}} = 2$ , 2 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{CH}_3]\text{S}\}_2$ ], 2 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{CH}_3]\text{S}\}_2$  not observed.



*Molecular structure of [Bm<sup>Me</sup>]AlCl<sub>2</sub>*

### Synthesis of [Bm<sup>Me</sup>]GaI<sub>2</sub>

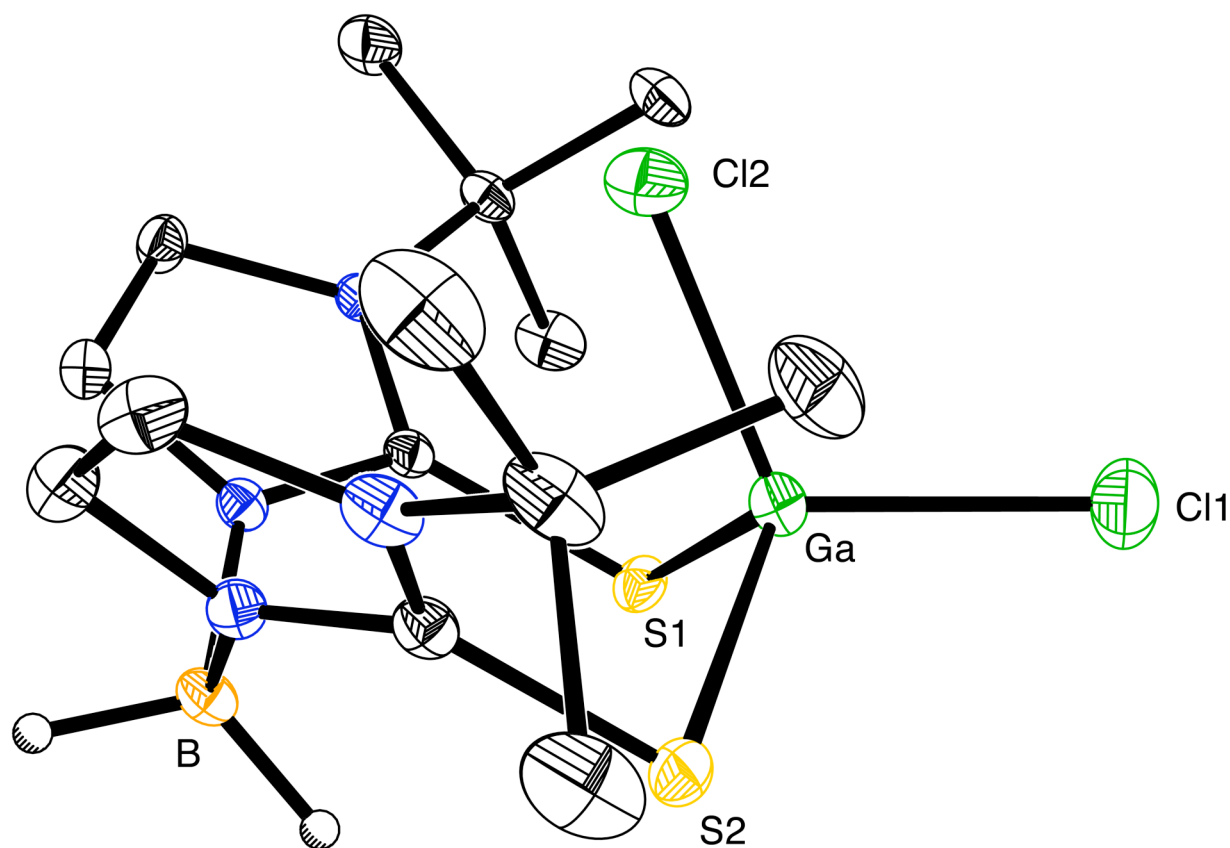
A suspension of [Bm<sup>Me</sup>]Tl (100 mg, 0.226 mmol) in THF (3 mL) was added dropwise to GaI<sub>3</sub> (103 mg, 0.229 mmol) resulting in the immediate deposition of an orange precipitate. The mixture was stirred for 15 minutes, allowed to settle for an additional 15 minutes, and filtered. The insoluble components were extracted with THF (1.5 mL) and the extract was combined with the reaction filtrate. The volatile components were removed *in vacuo* to give [Bm<sup>Me</sup>]GaI<sub>2</sub> as a white powder (105 mg, 82% yield). Colorless crystals of the composition [Bm<sup>Me</sup>]GaI<sub>2</sub> suitable for X-ray diffraction were obtained from a concentrated methylene chloride solution. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 3.64 [s, 6 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)S<sub>2</sub>}], 7.15 [d, <sup>3</sup>J<sub>H-H</sub> = 2, 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)S<sub>2</sub>}], 7.34 [d, <sup>3</sup>J<sub>H-H</sub> = 2, 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)S<sub>2</sub>}], and 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)S<sub>2</sub>} not observed.



Molecular structure of  $[Bm^{Me}]GaI_2$

### Synthesis of $[Bm^{Bu^t}]GaCl_2$

A mixture of  $[Bm^{Bu^t}]Na$  (100 mg, 0.29 mmol) and  $HGaCl_2$  (82 mg, 0.58 mmol) was treated with cold ( $-35^\circ C$ ) MeCN (1.0 mL). The mixture was mixed *via* pipette for 5 minutes and filtered. The filtrate was cooled to  $-35^\circ C$ , thereby depositing colorless crystals of composition  $[Bm^{Bu^t}]GaCl_2$  (73 mg, 54%) suitable for X-ray diffraction over a period of three days. Analysis calcd. for  $[Bm^{Bu^t}]GaCl_2$ : C, 36.2%; H, 5.2%; N, 12.1%. Found: C, 35.3%; H, 5.1%; N, 11.6%.  $^1H$  NMR ( $CD_3CN$ ): 1.73 [s, 18 H of  $H_2B\{C_3N_2H_2[C(\underline{CH}_3)_3S]_2\}$ ], 3.6 [br, 2 H of  $\underline{H}_2B\{C_3N_2H_2[C(CH_3)_3S]_2\}$ ], 7.32 [d,  $^3J_{H-H} = 2$ , 2 H of  $H_2B\{C_3N_2H_2[C(\underline{CH}_3)_3S]_2\}$ ], 7.34 [d,  $^3J_{H-H} = 2$ , 2 H of  $H_2B\{C_3N_2H_2[C(\underline{CH}_3)_3S]_2\}$ ].  $^{13}C\{^1H\}$  NMR ( $CD_3CN$ ): 29.6 [6 C of  $H_2B\{C_2N_2H_2[C(\underline{CH}_3)_3CS]_2\}$ ], 61.6 [2 C of  $H_2B\{C_2N_2H_2[C(\underline{CH}_3)_3CS]_2\}$ ], 121.1 [2 C of  $H_2B\{C_2N_2H_2[C(\underline{CH}_3)_3CS]_2\}$ ], 126.5 [2 C of  $H_2B\{C_2N_2H_2[C(\underline{CH}_3)_3CS]_2\}$ ], 2 C of  $H_2B\{C_2N_2H_2[C(\underline{CH}_3)_3CS]_2\}$  not observed. FAB-MS  $m/z$  = 429.2  $[M - Cl]^+$ ; 463.2  $[M - 1]^+$ ,  $M = [Bm^{Bu^t}]GaCl_2$ .



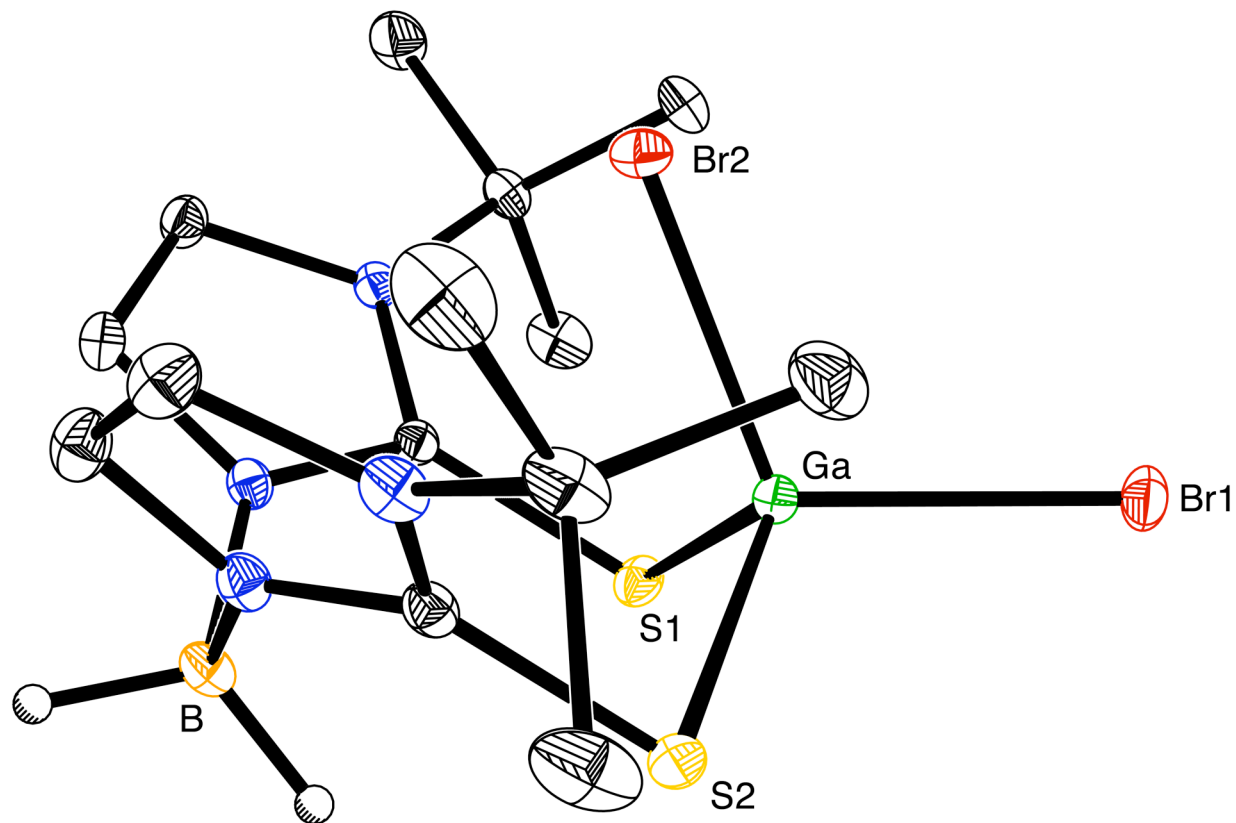
Molecular structure of  $[Bm^{But}]GaCl_2$

### Synthesis of $[Bm^{But}]GaBr_2$

A mixture of  $[Bm^{But}]Na$  (100 mg, 0.289 mmol) and  $GaBr_3$  (179 mg, 0.578 mmol) was treated with cold ( $-35^\circ C$ ) MeCN (1.5 mL). The mixture was mixed *via* pipette for 5 minutes and filtered. The filtrate was cooled to  $-35^\circ C$ , thereby depositing colorless crystals of composition  $[Bm^{But}]GaBr_2$  (121 mg, 76%) suitable for X-ray diffraction over a period of three days. Analysis calcd. for  $[Bm^{But}]GaBr_2$ : C, 30.4%; H, 4.4%; N, 10.1%.

Found: C, 29.1%; H, 4.2%; N, 9.6%.  $^1H$  NMR ( $CD_3CN$ ): 1.73 [s, 18 H of  $H_2B\{C_3N_2H_2[C(CH_3)_3]S\}_2$ ], 3.6 [br, 2 H of  $H_2B\{C_3N_2H_2[C(CH_3)_3]S\}_2$ ], 7.32 [d,  $^3J_{H-H} = 2$ , 2 H of  $H_2B\{C_3N_2H_2[C(CH_3)_3]S\}_2$ ], 7.35 [d,  $^3J_{H-H} = 2$ , 2 H of  $H_2B\{C_3N_2H_2[C(CH_3)_3]S\}_2$ ].  $^{13}C\{^1H\}$  NMR ( $CD_3CN$ ): 29.8 [6 C of  $H_2B\{C_2N_2H_2[C(CH_3)_3]CS\}_2$ ], 61.6 [2 C of  $H_2B\{C_2N_2H_2[C(CH_3)_3]CS\}_2$ ], 121.1 [2 C of  $H_2B\{C_2N_2H_2[C(CH_3)_3]CS\}_2$ ], 126.6 [2 C of

$\text{H}_2\text{B}\{\underline{\text{C}}_2\text{N}_2\text{H}_2[\underline{\text{C}}(\text{CH}_3)_3]\underline{\text{C}}\text{S}\}_2$ , 2 C of  $\text{H}_2\text{B}\{\underline{\text{C}}_2\text{N}_2\text{H}_2[\underline{\text{C}}(\text{CH}_3)_3]\underline{\text{C}}\text{S}\}_2$  not observed. FAB-MS  $m/z$   
= 473.2  $[\text{M} - \text{Br}]^+$ ; 551.2  $[\text{M} - 1]^+$ ,  $\text{M} = [\text{Bm}^{\text{But}}]\text{GaBr}_2$ .

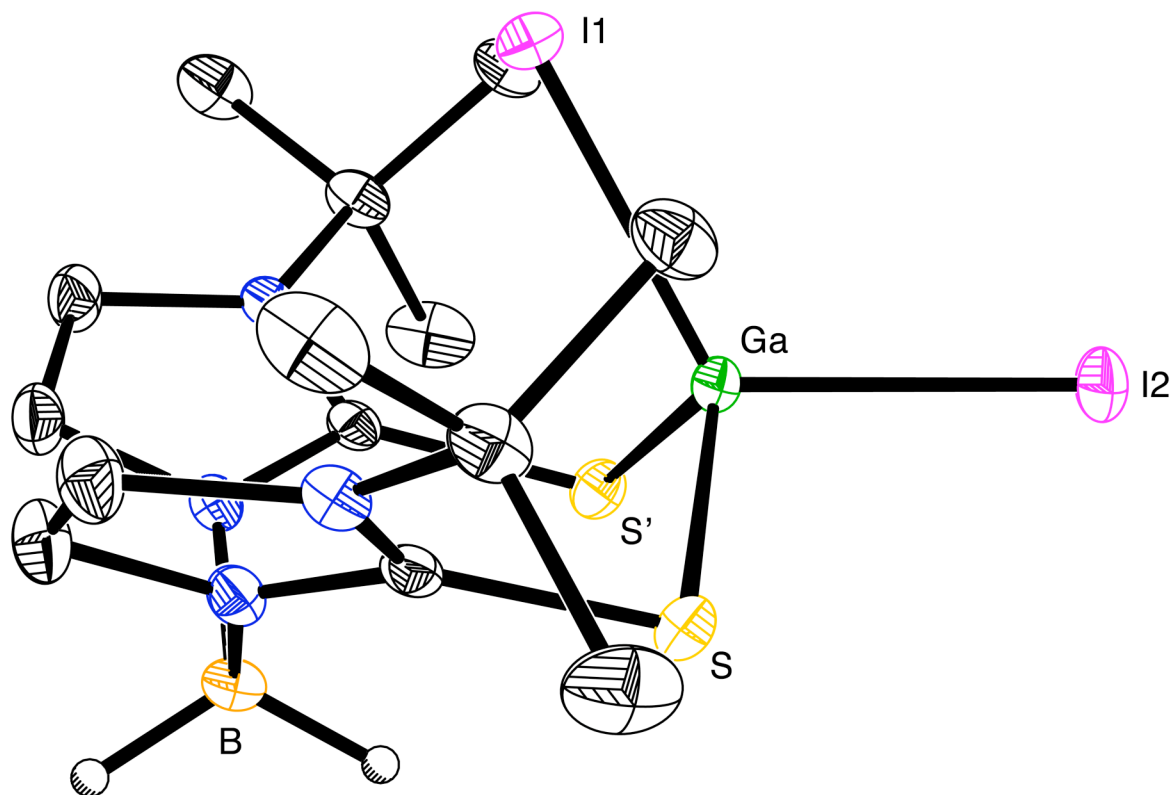


Molecular structure of  $[\text{Bm}^{\text{But}}]\text{GaBr}_2$

### Synthesis of $[\text{Bm}^{\text{But}}]\text{GaI}_2$

A mixture of  $[\text{Bm}^{\text{But}}]\text{Na}$  (50 mg, 0.14 mmol) and  $\text{GaI}_3$  (130 mg, 0.29 mmol) was treated with cold ( $-35^\circ\text{C}$ ) MeCN (1.0 mL). The mixture was mixed *via* pipette for 5 minutes and filtered. The filtrate was cooled to  $-35^\circ\text{C}$ , thereby depositing colorless crystals of composition  $[\text{Bm}^{\text{But}}]\text{GaI}_2$  (32 mg, 36%) suitable for X-ray diffraction over a period of three days. Analysis calcd. for  $[\text{Bm}^{\text{But}}]\text{GaI}_2$ : C, 26.0%; H, 3.7%; N, 8.7%. Found: C, 25.0%; H, 3.5%; N, 8.3%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): 1.74 [s, 18 H of  $\text{H}_2\text{B}\{\underline{\text{C}}_3\text{N}_2\text{H}_2[\underline{\text{C}}(\underline{\text{C}}\text{H}_3)_3]\underline{\text{S}}\}$ ], 7.32 [d,  $^3J_{\text{H-H}} = 2$ , 2 H of  $\text{H}_2\text{B}\{\underline{\text{C}}_3\text{N}_2\text{H}_2[\underline{\text{C}}(\text{CH}_3)_3]\underline{\text{S}}\}_2$ ], 7.36 [d,  $^3J_{\text{H-H}} = 2$ , 2 H of  $\text{H}_2\text{B}\{\underline{\text{C}}_3\text{N}_2\text{H}_2[\underline{\text{C}}(\text{CH}_3)_3]\underline{\text{S}}\}_2$ ], 2 H of  $\underline{\text{H}}_2\text{B}\{\underline{\text{C}}_3\text{N}_2\text{H}_2[\underline{\text{C}}(\text{CH}_3)_3]\underline{\text{S}}\}_2$  not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ): 30.1 [6 C of  $\text{H}_2\text{B}\{\underline{\text{C}}_2\text{N}_2\text{H}_2[\underline{\text{C}}(\underline{\text{C}}\text{H}_3)_3]\underline{\text{C}}\text{S}\}_2$ ], 61.7 [2 C of  $\text{H}_2\text{B}\{\underline{\text{C}}_3\text{N}_2\text{H}_2[\underline{\text{C}}(\text{CH}_3)_3]\underline{\text{S}}\}_2$ ], 121.1 [2 C of  $\text{H}_2\text{B}\{\underline{\text{C}}_2\text{N}_2\text{H}_2[\underline{\text{C}}(\text{CH}_3)_3]\underline{\text{C}}\text{S}\}_2$ ], 126.7 [2 C of

$\text{H}_2\text{B}[\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}]_2$ , 2 C of  $\text{H}_2\text{B}[\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}]_2$  not observed. FAB-MS  
 $m/z = 519.2 [\text{M} - \text{I}]^+$ ,  $\text{M} = [\text{Bm}^{\text{Bu}^t}]\text{GaI}_2$ .



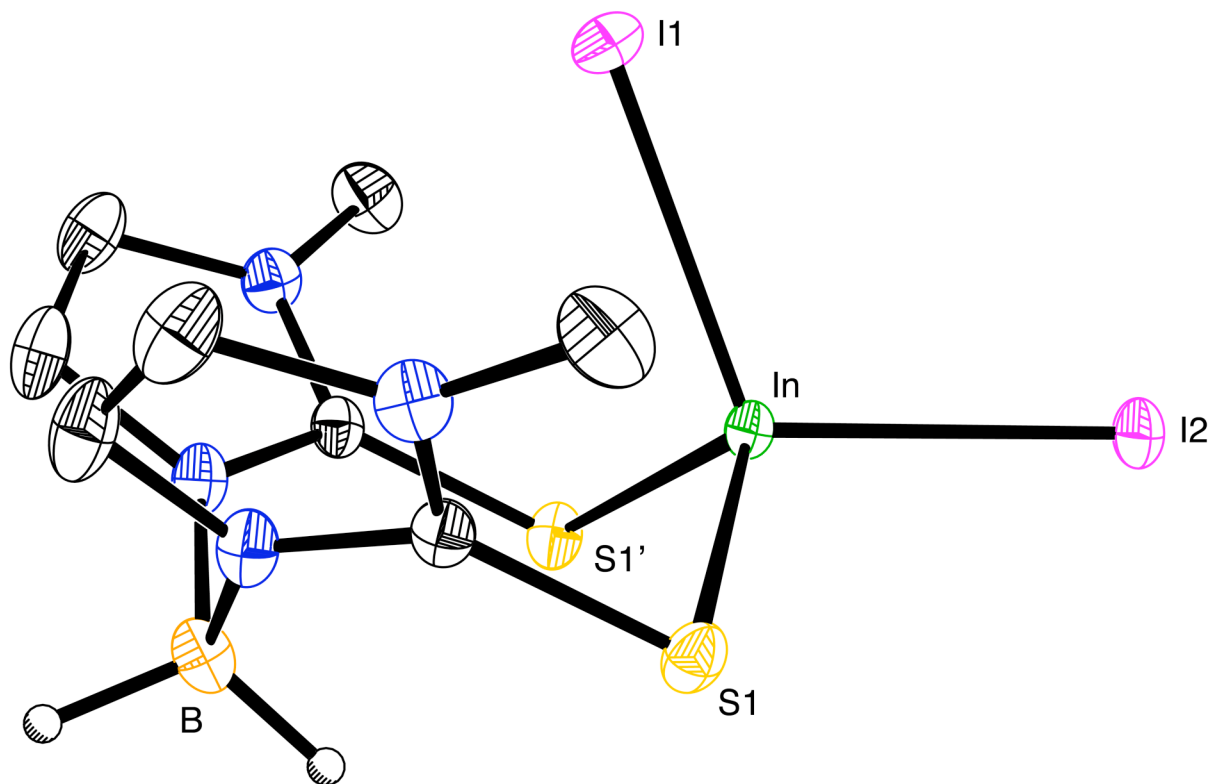
*Molecular structure of  $[\text{Bm}^{\text{Bu}^t}]\text{GaI}_2$*

### Synthesis of $[\text{Bm}^{\text{Me}}]\text{InI}_2$

A suspension of  $[\text{Bm}^{\text{Me}}]\text{I}$  (100 mg, 0.226 mmol) in THF (3 mL) was added dropwise to  $\text{InI}_3$  (113 mg, 0.228 mmol) resulting in the immediate deposition of an orange precipitate. The mixture was stirred for 15 minutes, allowed to settle for an additional 15 minutes, and filtered. The insoluble components were washed with THF (1.5 mL) and the extract was combined with the reaction filtrate. The volatile components were removed from the filtrate *in vacuo* to give  $[\text{Bm}^{\text{Me}}]\text{InI}_2$  as a white powder (116 mg, 85% yield). Colorless crystals of the composition  $[\text{Bm}^{\text{Me}}]\text{InI}_2$  suitable for X-ray diffraction were obtained from a concentrated solution in dichloromethane. Analysis calcd.  $[\text{Bm}^{\text{Me}}]\text{InI}_2$ : C, 15.8%; H, 2.0%; N, 9.2%. Found: C, 15.7%; H, 1.8%; N, 8.9%.  $^1\text{H}$  NMR



(CD<sub>3</sub>CN): 3.63 [s, 6 H of HB{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)S<sub>2</sub>}<sub>2</sub>], 7.14 [d, <sup>3</sup>J<sub>H-H</sub> = 2, 2 H of HB{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)S<sub>2</sub>}<sub>2</sub>], 7.26 [br d, <sup>3</sup>J<sub>H-H</sub> = 2, 2 H of HB{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)S<sub>2</sub>}<sub>2</sub>], and 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)S<sub>2</sub>}<sub>2</sub> not observed. IR Data (KBr, cm<sup>-1</sup>): 3156 (s), 3132 (s), 3084 (w), 2942 (m), 2713 (w), 2481 (s), 2411 (s), 2360 (w), 2285 (w), 2231 (w), 1585 (w), 1553 (s), 1466 (s), 1401 (w), 1378 (m), 1341 (m), 1304 (m), 1261 (w), 1190 (s), 1171 (s), 1120 (vs), 1089 (w), 1040 (w), 1014 (w), 1003(w), 802 (w), 747 (w), 733 (s), 721 (s), 716 (s), 701 (w), 678 (m), 644 (w), 618 (w), 591 (w), 498 (m), 448 (m), 433 (w), 417 (w).

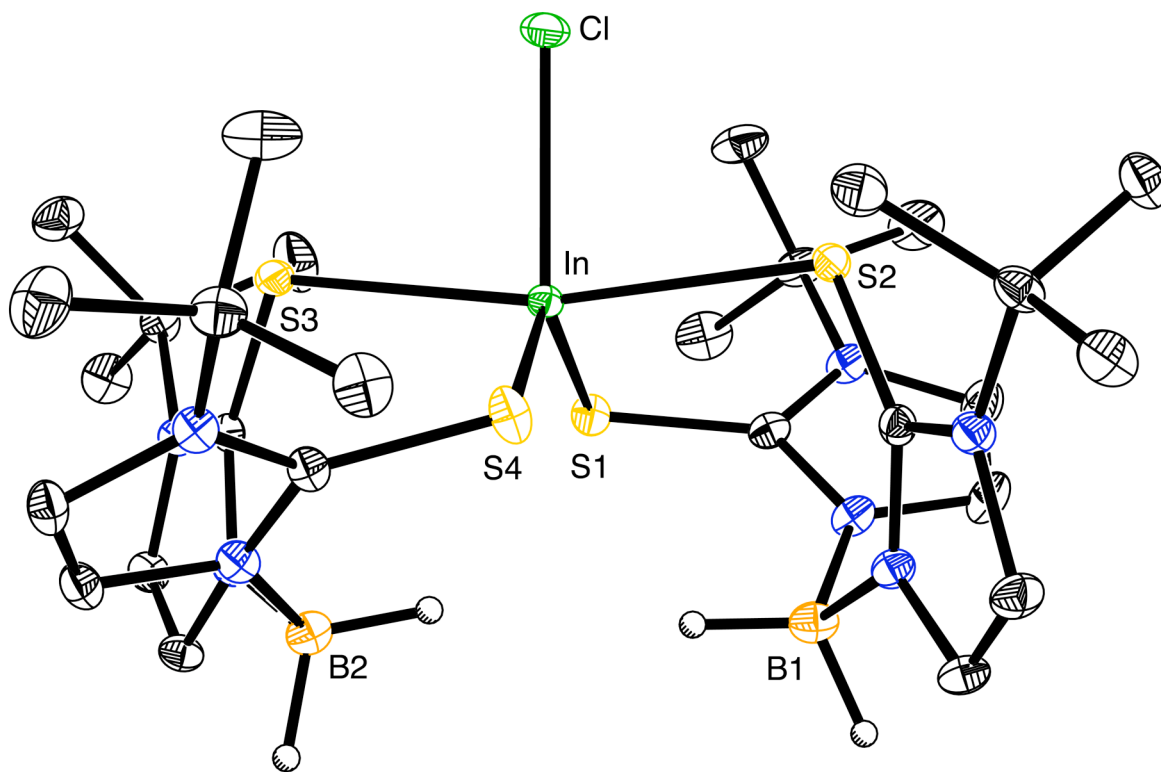


Molecular structure of [Bm<sup>Me</sup>]InI<sub>2</sub>

### Synthesis of [Bm<sup>Bu<sup>t</sup></sup>]<sub>2</sub>InCl

A suspension of [Bm<sup>Bu<sup>t</sup></sup>]Na (50 mg, 0.14 mmol) in CD<sub>3</sub>CN (0.7 mL) was added to InCl<sub>3</sub> (16 mg, 0.072 mmol) the mixture was mixed *via* pipette for 5 minutes. The mixture was monitored by <sup>1</sup>H NMR and filtered after two hours. Colorless crystals of composition [Bm<sup>Bu<sup>t</sup></sup>]<sub>2</sub>InCl·2(CH<sub>3</sub>CN) (20 mg, 32%) suitable for X-ray diffraction were deposited over a period of two days at room temperature. Analysis calcd. for [Bm<sup>Bu<sup>t</sup></sup>]<sub>2</sub>InCl: C, 42.2%;

H, 6.1%; N, 14.1%. Found: C, 42.2%; H, 6.1%; N, 13.9%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): 1.70 [s, 36 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{S}_2\}$ ], 3.6 [br, 4 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{S}_2\}$ ], 6.97 [d,  $^3J_{\text{H-H}} = 2$ , 4 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{S}_2\}$ ], 7.15 [d,  $^3J_{\text{H-H}} = 2$ , 4 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{S}_2\}$ ]. FAB-MS  $m/z = 761.3$  [ $\text{M} - \text{Cl}$ ] $^+$ ,  $\text{M} = [\text{Bm}^{\text{But}}]_2\text{InCl}$ .

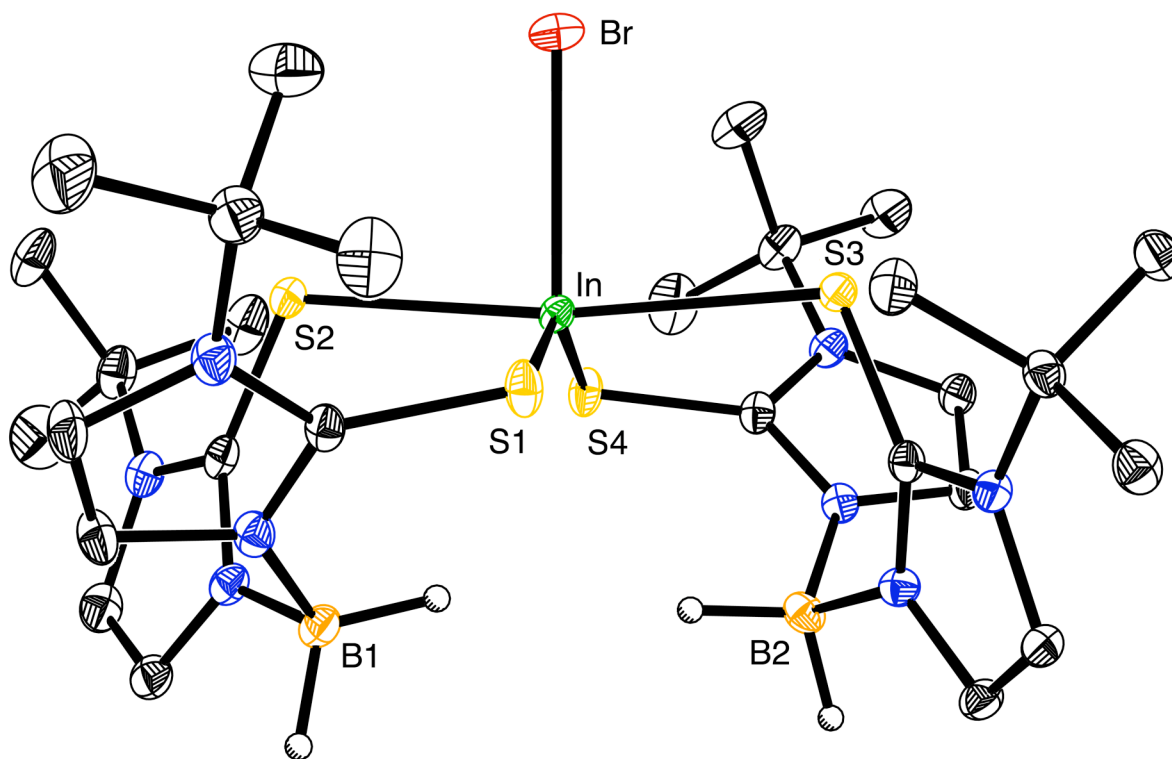


*Molecular structure of  $[\text{Bm}^{\text{But}}]_2\text{InCl}$*

### Synthesis of $[\text{Bm}^{\text{But}}]_2\text{InBr}$

A mixture of  $[\text{Bm}^{\text{But}}]\text{Na}$  (100 mg, 0.29 mmol) and  $\text{InBr}_3$  (51 mg, 0.15 mmol) was treated with cold ( $-35^\circ\text{C}$ ) MeCN (1.5 mL). The mixture was mixed *via* pipette for 5 minutes and filtered. The filtrate was cooled to  $-35^\circ\text{C}$ , thereby depositing colorless crystals of composition  $[\text{Bm}^{\text{But}}]_2\text{InBr}$  (38 mg, 31%) suitable for X-ray diffraction over a period of three days. Analysis calcd. for  $[\text{Bm}^{\text{But}}]_2\text{InBr}$ : C, 40.0%; H, 5.8%; N, 13.3%. Found: C, 39.7%; H, 5.6%; N, 13.1%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): 1.70 [s, 36 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{S}_2\}$ ], 3.7 [br, 4 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{S}_2\}$ ], 6.98 [d,  $^3J_{\text{H-H}} = 2$ , 4 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{S}_2\}$ ], 7.15 [d,  $^3J_{\text{H-H}} = 2$ , 4 H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{S}_2\}$ ].  $^{13}\text{C}\{^1\text{H}\}$

NMR (CD<sub>3</sub>CN): 29.5 [12 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>]<sub>2</sub>], 60.2 [4 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>]<sub>2</sub>], 124.4 [4 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>]<sub>2</sub>], 4 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>] obscured by solvent, and 4 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>] not observed. FAB-MS m/z = 760.9 [M - Br]<sup>+</sup>, M = [Bm<sup>Bu<sup>t</sup></sup>]<sub>2</sub>InBr.



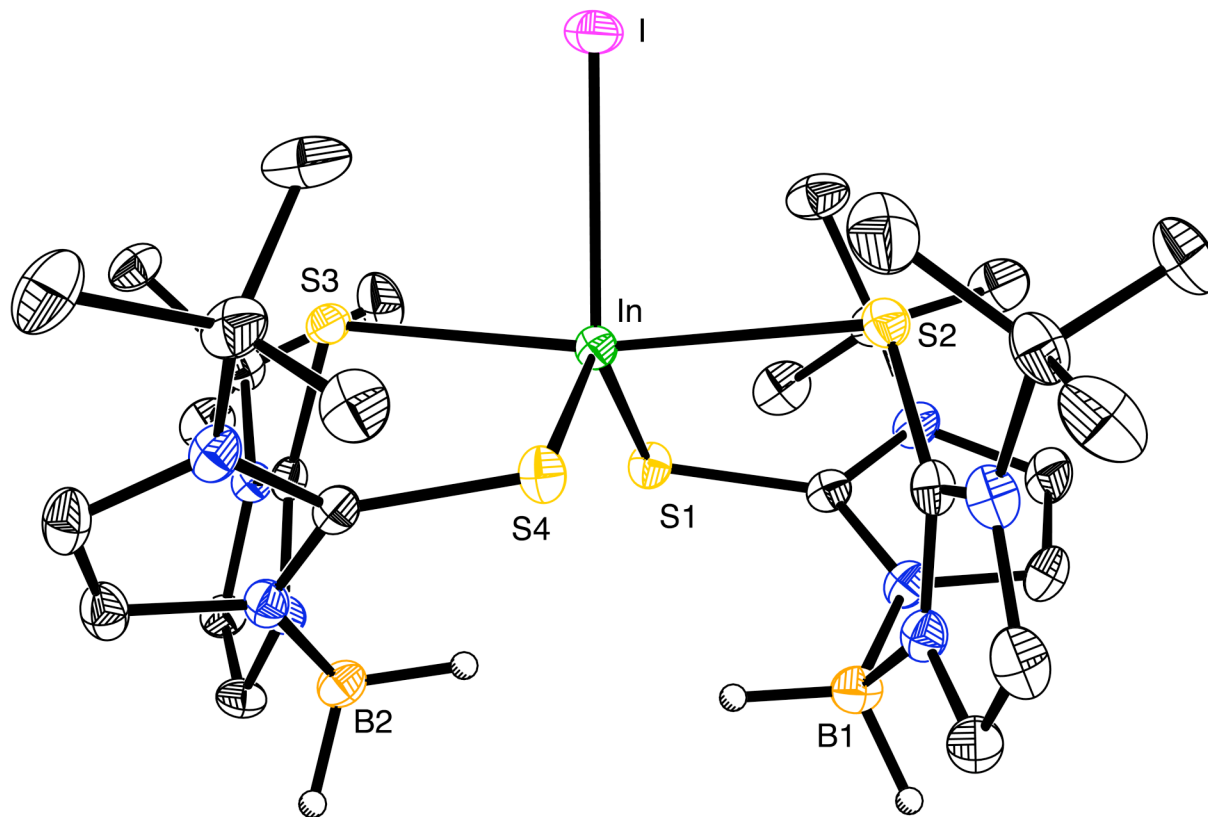
Molecular structure of [Bm<sup>Bu<sup>t</sup></sup>]<sub>2</sub>InBr

### Synthesis of [Bm<sup>Bu<sup>t</sup></sup>]<sub>2</sub>InI

(i) A mixture of [Bm<sup>Bu<sup>t</sup></sup>]Na (100 mg, 0.29 mmol) and InI<sub>3</sub> (72 mg, 0.15 mmol) was treated with cold (-35°C) MeCN (1.5 mL). The mixture was mixed *via* pipette for 5 minutes and filtered. The filtrate was cooled to -35°C, thereby depositing colorless crystals of composition [Bm<sup>Bu<sup>t</sup></sup>]<sub>2</sub>InI (36 mg, 28%) suitable for X-ray diffraction over a period of three days.

(ii) A mixture of [Bm<sup>Bu<sup>t</sup></sup>]Na (100 mg, 0.289 mmol) and InI (209 mg, 0.866 mmol) was treated with CD<sub>3</sub>CN (0.7 mL), mixed *via* pipette for 5 minutes, and filtered. The mixture was monitored by <sup>1</sup>H NMR spectroscopy and filtered after two hours. Pale yellow crystals of composition [Bm<sup>Bu<sup>t</sup></sup>]<sub>2</sub>InI·2(CH<sub>3</sub>CN) (47 mg, 33%) suitable for X-ray diffraction

were deposited over a period of two days at room temperature. Analysis calcd. for  $[\text{Bm}^{\text{Bu}^t}]_2\text{InI} \cdot 1.5(\text{CH}_3\text{CN})$ : C, 39.2%; H, 5.6%; N, 14.0%. Found: C, 39.5%; H, 5.5%; N, 13.6%.  $^1\text{H NMR}$  ( $d_6$ -DMSO): 1.70 [s, 36 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3\text{S}]_2\}$ ], 3.7 [br, 4 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3\text{S}]_2\}$ ], 6.99 [br d,  $^3J_{\text{H-H}} = 1$ , 4 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3\text{S}]_2\}$ ], 7.17 [br d,  $^3J_{\text{H-H}} = 1$ , 4 H of  $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3\text{S}]_2\}$ ]. FAB-MS  $m/z = 761.0$   $[\text{M} - \text{I}]^+$ ,  $\text{M} = [\text{Bm}^{\text{Bu}^t}]_2\text{InI}$ .

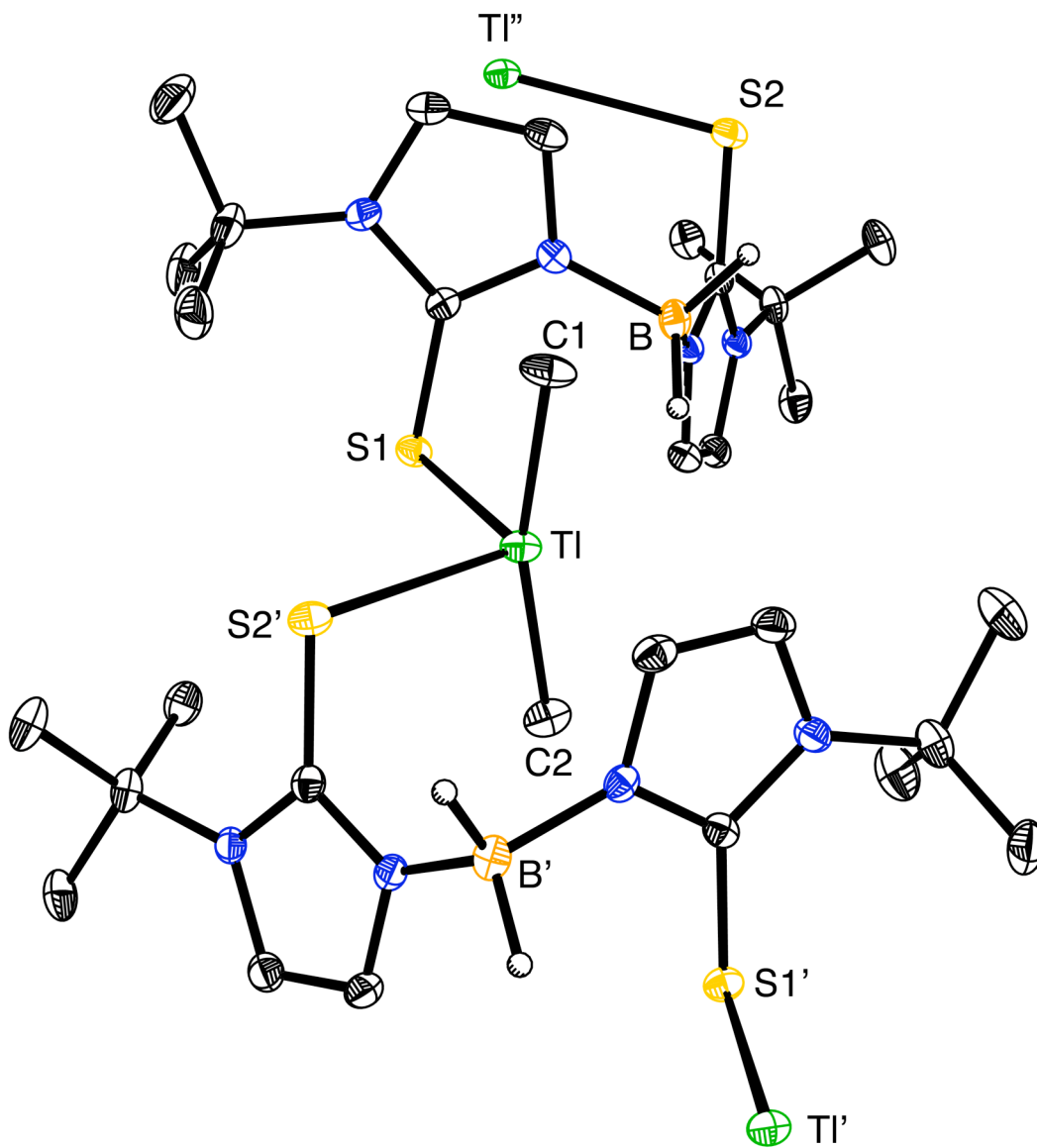


*Molecular structure of  $[\text{Bm}^{\text{Bu}^t}]_2\text{InI}$*

### Synthesis of $[\text{Bm}^{\text{Bu}^t}]\text{TlMe}_2$

A mixture of  $[\text{Bm}^{\text{Bu}^t}]\text{Tl}$  (178 mg, 0.337 mmol) and  $\text{Me}_2\text{TlCl}$  (100 mg, 0.371 mmol) was treated with MeCN (1.5 mL) resulting in the immediate deposition of a bright yellow solid. The resulting mixture was mixed *via* pipette for 5 minutes and filtered. The filtrate was cooled to  $-35^\circ\text{C}$ , thereby depositing colorless crystals of composition  $[\text{Bm}^{\text{Bu}^t}]\text{TlMe}_2 \cdot \text{CH}_3\text{CN}$  (63 mg, 31%) over a period of one week. Analysis calcd. for  $[\text{Bm}^{\text{Bu}^t}]\text{TlMe}_2$ : C, 34.5%; H, 5.4%; N, 10.0%. Found: C, 34.2%; H, 4.2%; N, 10.3%.  $^1\text{H}$

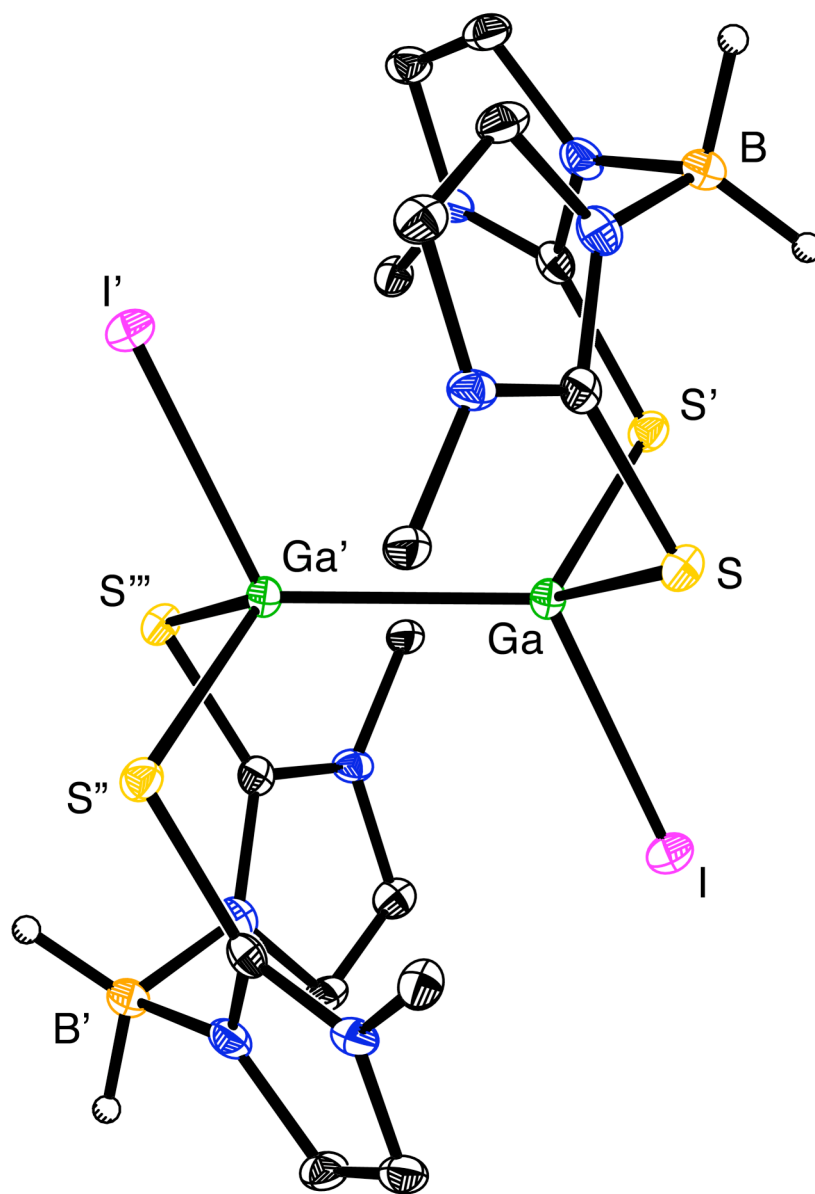
NMR (CDCl<sub>3</sub>): 0.6 [br d, <sup>3</sup>J<sub>H-H</sub> = 357, 6 H of TlMe<sub>2</sub>], 1.75 [s, 18 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]S<sub>2</sub>}, 3.6 [br, 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]S<sub>2</sub>}, 6.89 [d, <sup>3</sup>J<sub>H-H</sub> = 2, 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]S<sub>2</sub>}, 6.97 [d, <sup>3</sup>J<sub>H-H</sub> = 2, 2 H of H<sub>2</sub>B{C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]S<sub>2</sub>}.  
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 29.1 [6 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>}, 59.0 [2 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>}, 115.7 [2 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>}, 123.5 [2 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>}, 155.1 [2 C of H<sub>2</sub>B{C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>[C(CH<sub>3</sub>)<sub>3</sub>]CS<sub>2</sub>}, 2 C of TlMe<sub>2</sub> not observed. FAB-MS m/z = 543.2 [M - CH<sub>3</sub>]<sup>+</sup>, M = [Bm<sup>Bu<sup>t</sup></sup>]Tl(CH<sub>3</sub>)<sub>2</sub>.



Molecular structure of [Bm<sup>Bu<sup>t</sup></sup>]<sub>2</sub>TlMe<sub>2</sub>

### Synthesis of $[\text{Bm}^{\text{Me}}]\text{Ga}(\text{I})\text{Ga}(\text{I})[\text{Bm}^{\text{Me}}]$

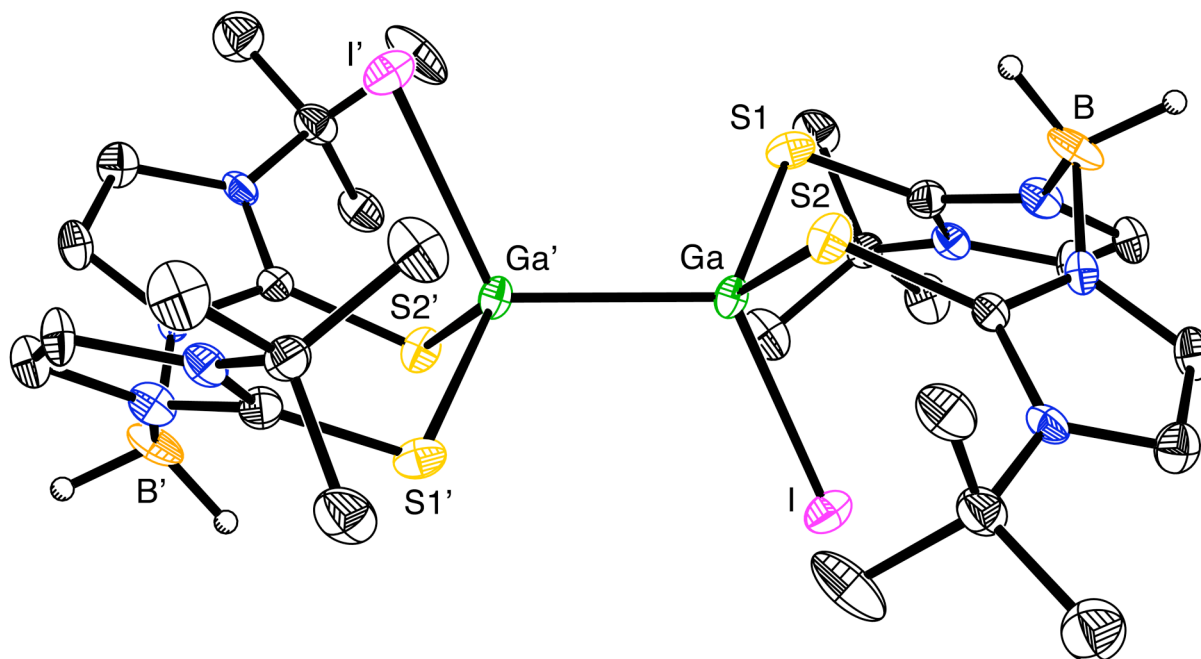
A mixture of  $[\text{Bm}^{\text{Me}}]\text{Li}$  (100 mg, 0.406 mmol) and "GaI" (160 mg, 0.813 mmol) was treated with  $\text{C}_6\text{H}_6$  (2.5 mL). The mixture was stirred for three hours and filtered. The insoluble material was extracted into a mixture of MeCN (1.0 mL) and  $\text{CH}_2\text{Cl}_2$  (1.0 mL), from which colorless crystals of composition  $[\text{Bm}^{\text{Me}}]\text{Ga}(\text{I})\text{Ga}(\text{I})[\text{Bm}^{\text{Me}}]$  (ca. 10 mg) were obtained after a period of several weeks at room temperature.



*Molecular structure of  $[\text{Bm}^{\text{Me}}]\text{Ga}(\text{I})\text{Ga}(\text{I})[\text{Bm}^{\text{Me}}]$*

### Synthesis of $[\text{Bm}^{\text{Bu}^t}]\text{Ga}(\text{I})\text{Ga}(\text{I})[\text{Bm}^{\text{Bu}^t}]$

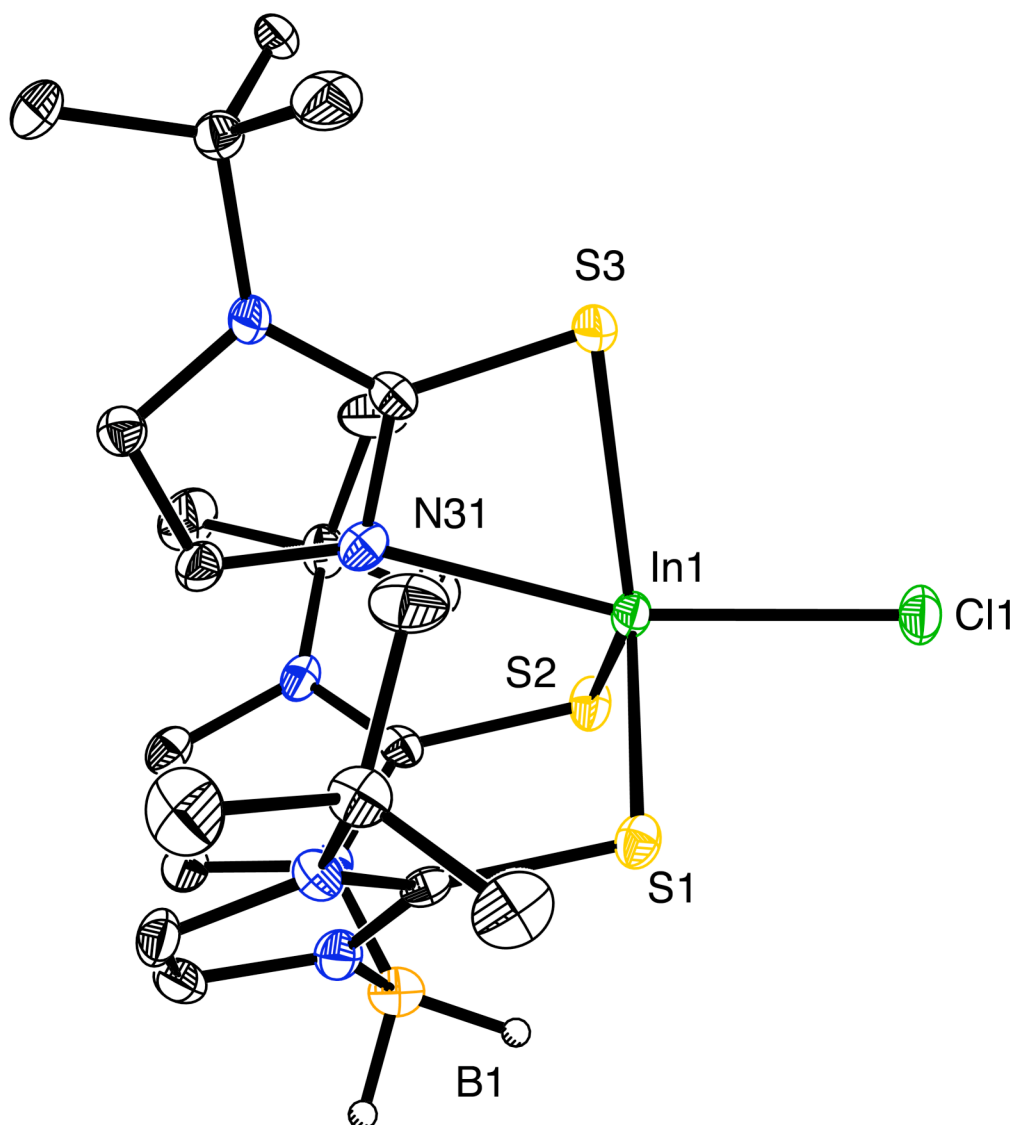
A mixture of  $[\text{Bm}^{\text{Bu}^t}]\text{Na}$  (100 mg, 0.289 mmol) and "GaI" (170 mg, 0.866 mmol) was treated with cold ( $-35^\circ\text{C}$ ) MeCN (1.5 mL). The resulting mixture was mixed *via* pipette and filtered. The filtrate was cooled to  $-35^\circ\text{C}$ , thereby depositing colorless crystals of  $[\text{Bm}^{\text{Bu}^t}]\text{Ga}(\text{I})\text{Ga}(\text{I})[\text{Bm}^{\text{Bu}^t}]$  and  $[\text{Bm}^{\text{Bu}^t}]\text{GaI}_2$  (*ca.* 10 mg, 1:1) over a period of several days.



*Molecular structure of  $[\text{Bm}^{\text{Bu}^t}]\text{Ga}(\text{I})\text{Ga}(\text{I})[\text{Bm}^{\text{Bu}^t}]$*

### Synthesis of $[\text{Bm}^{\text{Bu}^t}]\text{In}(\text{mim}^{\text{Bu}^t})\text{Cl}$

A mixture of  $[\text{Bm}^{\text{Bu}^t}]\text{Na}$  (*ca.* 100 mg) and InCl (130 mg, 0.866 mmol) was treated with MeCN (2.5 mL). The resulting mixture was mixed *via* pipette for 5 minutes and filtered. Colorless crystals of composition  $[\text{Bm}^{\text{Bu}^t}]\text{In}(\text{mim}^{\text{Bu}^t})\text{Cl}$  (*ca.* 10 mg) were deposited over a period of four days at room temperature.



*Molecular structure of [Bm<sup>But</sup>]In(mim<sup>But</sup>)Cl*

### X-ray structure determinations

X-ray diffraction data were collected on either a Bruker Apex II diffractometer or a Bruker P4 diffractometer equipped with a SMART CCD detector. Crystal data, data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on  $F^2$  with SHELXTL (Version 6.1).<sup>10</sup>



**Table 1.** Crystal, intensity collection and refinement data.

	<b>[Bm<sup>Me</sup>]<sub>2</sub>AlCl<sub>2</sub></b>	<b>[Bm<sup>Bu<sup>t</sup>]<sub>2</sub>AlCl<sub>2</sub></sup></b>
lattice	Orthorhombic	Orthorhombic
formula	C <sub>8</sub> H <sub>12</sub> AlBCl <sub>2</sub> N <sub>4</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>24</sub> AlBCl <sub>2</sub> N <sub>4</sub> S <sub>2</sub>
formula weight	337.03	421.18
space group	<i>Pnma</i>	<i>Pbca</i>
<i>a</i> /Å	8.3215(5)	11.4813(6)
<i>b</i> /Å	13.0872(9)	12.4010(6)
<i>c</i> /Å	13.3622(9)	28.5197(14)
$\alpha$ /°	90	90
$\beta$ /°	90	90
$\gamma$ /°	90	90
<i>V</i> /Å <sup>3</sup>	1455.21(17)	4060.6(4)
<i>Z</i>	4	8
temperature (K)	125(2)	125(2)
radiation ( $\lambda$ , Å)	0.71073	0.71073
$\rho$ (calcd.), g cm <sup>-3</sup>	1.538	1.378
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	0.779	0.573
$\theta$ max, deg.	28.28	32.74
no. of data collected	19240	66807
no. of data used	1884	7281
no. of parameters	92	223
$R_1$ [ $I > 2\sigma(I)$ ]	0.0216	0.0277
$wR_2$ [ $I > 2\sigma(I)$ ]	0.0648	0.0702
$R_1$ [all data]	0.0227	0.0335
$wR_2$ [all data]	0.0661	0.0736
GOF	1.076	1.052
$R_{int}$	0.0188	0.0266

**Table 1 (continued)** Crystal, intensity collection and refinement data.

	<b>[Bm<sup>Bu<sup>t</sup></sup>]GaCl<sub>2</sub></b>	<b>[Bm<sup>Bu<sup>t</sup></sup>]GaBr<sub>2</sub></b>
lattice	Orthorhombic	Orthorhombic
formula	C <sub>14</sub> H <sub>24</sub> BGaCl <sub>2</sub> N <sub>4</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>24</sub> BGaBr <sub>2</sub> N <sub>4</sub> S <sub>2</sub>
formula weight	463.92	552.84
space group	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> /Å	11.4551(5)	11.5227(5)
<i>b</i> /Å	12.3855(5)	12.6478(5)
<i>c</i> /Å	28.4550(12)	28.7910(12)
$\alpha$ /°	90	90
$\beta$ /°	90	90
$\gamma$ /°	90	90
<i>V</i> /Å <sup>3</sup>	4037.1(3)	4195.9(3)
<i>Z</i>	8	8
temperature (K)	125(2)	125(2)
radiation ( $\lambda$ , Å)	0.71073	0.71073
$\rho$ (calcd.), g cm <sup>-3</sup>	1.527	1.750
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	1.839	5.324
$\theta$ max, deg.	28.28	31.51
no. of data collected	52776	67705
no. of data used	5016	6981
no. of parameters	223	223
$R_1$ [ $I > 2\sigma(I)$ ]	0.0388	0.0262
$wR_2$ [ $I > 2\sigma(I)$ ]	0.1133	0.0551
$R_1$ [all data]	0.0477	0.0375
$wR_2$ [all data]	0.1202	0.0592
GOF	1.066	1.064
$R_{int}$	0.0320	0.0453

**Table 1 (continued)** Crystal, intensity collection and refinement data.

	[Bm <sup>Me</sup> ] <sub>2</sub> Gal <sub>2</sub>	[Bm <sup>Bu<sup>t</sup></sup> ] <sub>2</sub> Gal <sub>2</sub>
lattice	Orthorhombic	Orthorhombic
formula	C <sub>8</sub> H <sub>12</sub> BGal <sub>2</sub> N <sub>4</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>24</sub> BGal <sub>2</sub> N <sub>4</sub> S <sub>2</sub>
formula weight	562.67	646.82
space group	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> /Å	8.8213(3)	13.6133(16)
<i>b</i> /Å	13.2681(5)	14.6412(18)
<i>c</i> /Å	14.3161(5)	11.4378(14)
$\alpha$ /°	90	90
$\beta$ /°	90	90
$\gamma$ /°	90	90
<i>V</i> /Å <sup>3</sup>	1675.58(10)	2279.7(5)
<i>Z</i>	4	4
temperature (K)	243(2)	125(2)
radiation ( $\lambda$ , Å)	0.71073	0.71073
$\rho$ (calcd.), g cm <sup>-3</sup>	2.230	1.885
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	5.564	4.103
$\theta$ max, deg.	27.10	30.48
no. of data collected	11074	35083
no. of data used	1935	3593
no. of parameters	93	119
$R_1$ [ $I > 2\sigma(I)$ ]	0.0170	0.0287
$wR_2$ [ $I > 2\sigma(I)$ ]	0.0397	0.0518
$R_1$ [all data]	0.0195	0.0523
$wR_2$ [all data]	0.0405	0.0582
GOF	1.140	1.000
$R_{int}$	0.0222	0.0764

**Table 1 (continued)** Crystal, intensity collection and refinement data.

	<b>[Bm<sup>Me</sup>]InI<sub>2</sub></b>	<b>[Bm<sup>Bu</sup>]In(mim<sup>Bu</sup>)Cl</b>
lattice	Orthorhombic	Monoclinic
formula	C <sub>8</sub> H <sub>12</sub> BI <sub>2</sub> InN <sub>4</sub> S <sub>2</sub>	C <sub>21</sub> H <sub>35</sub> BClInN <sub>6</sub> S <sub>3</sub>
formula weight	607.77	628.81
space group	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> /Å	8.9426(7)	24.951(3)
<i>b</i> /Å	13.3473(11)	12.0422(16)
<i>c</i> /Å	14.5746(12)	19.097(3)
$\alpha$ /°	90	90
$\beta$ /°	90	97.109(2)
$\gamma$ /°	90	90
<i>V</i> /Å <sup>3</sup>	1739.6(2)	5693.8(13)
<i>Z</i>	4	8
temperature (K)	243(2)	200(2)
radiation ( $\lambda$ , Å)	0.71073	0.71073
$\rho$ (calcd.), g cm <sup>-3</sup>	2.321	1.467
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	5.136	1.165
$\theta$ max, deg.	27.10	25.03
no. of data collected	11492	58883
no. of data used	2003	10017
no. of parameters	93	608
$R_1$ [ $I > 2\sigma(I)$ ]	0.0169	0.0986
$wR_2$ [ $I > 2\sigma(I)$ ]	0.0409	0.3102
$R_1$ [all data]	0.0198	0.1090
$wR_2$ [all data]	0.0420	0.3161
GOF	1.066	1.181
$R_{int}$	0.0279	0.0553

**Table 1 (continued)** Crystal, intensity collection and refinement data.

	$[\text{Bm}^{\text{Bu}^t}]_2\text{InCl}\cdot 2(\text{CH}_3\text{CN})$	$[\text{Bm}^{\text{Bu}^t}]_2\text{InBr}\cdot 1.5(\text{CH}_3\text{CN})$
lattice	Triclinic	Monoclinic
formula	$\text{C}_{32}\text{H}_{54}\text{B}_2\text{ClInN}_{10}\text{S}_4$	$\text{C}_{31}\text{H}_{52.5}\text{B}_2\text{BrInN}_{9.5}\text{S}_4$
formula weight	878.98	923.44
space group	$P-1$	$P2_1/c$
$a/\text{\AA}$	10.3310(7)	21.2905(17)
$b/\text{\AA}$	11.3612(8)	11.3455(9)
$c/\text{\AA}$	18.9319(13)	18.8012(15)
$\alpha/^\circ$	102.7120(10)	90
$\beta/^\circ$	91.8870(10)	112.6590(10)
$\gamma/^\circ$	90.7230(10)	90
$V/\text{\AA}^3$	2166.0(3)	4190.9(6)
$Z$	2	4
temperature (K)	125(2)	125(2)
radiation ( $\lambda$ , $\text{\AA}$ )	0.71073	0.71073
$\rho$ (calcd.), $\text{g cm}^{-3}$	1.348	1.431
$\mu$ (Mo $K\alpha$ ), $\text{mm}^{-1}$	0.835	1.751
$\theta$ max, deg.	28.28	28.28
no. of data collected	30397	56199
no. of data used	10733	10403
no. of parameters	464	448
$R_1 [I > 2\sigma(I)]$	0.0261	0.0358
$wR_2 [I > 2\sigma(I)]$	0.0598	0.0948
$R_1$ [all data]	0.0323	0.0463
$wR_2$ [all data]	0.0626	0.1004
GOF	1.034	1.094
$R_{\text{int}}$	0.0284	0.0309

**Table 1 (continued)** Crystal, intensity collection and refinement data.

	$[\text{Bm}^{\text{Bu}^t}]_2\text{InI}\cdot 2(\text{CH}_3\text{CN})$	$[\text{Bm}^{\text{Bu}^t}]\text{TlMe}_2\cdot \text{CH}_3\text{CN}$
lattice	Triclinic	Orthorhombic
formula	$\text{C}_{32}\text{H}_{54}\text{B}_2\text{InN}_{10}\text{S}_4$	$\text{C}_{18}\text{H}_{33}\text{BN}_5\text{S}_2\text{Tl}$
formula weight	970.43	598.79
space group	<i>P</i> -1	<i>Pbca</i>
<i>a</i> /Å	10.4479(11)	14.2742(6)
<i>b</i> /Å	11.2540(12)	13.6250(8)
<i>c</i> /Å	19.202(2)	25.4330(11)
$\alpha$ /°	100.971(2)	90
$\beta$ /°	91.700(2)	90
$\gamma$ /°	90.610(2)	90
<i>V</i> /Å <sup>3</sup>	2215.2(4)	4946.4(4)
<i>Z</i>	2	8
temperature (K)	125(2)	125(2)
radiation ( $\lambda$ , Å)	0.71073	0.71073
$\rho$ (calcd.), g cm <sup>-3</sup>	1.455	1.608
$\mu$ (Mo $K\alpha$ ), mm <sup>-1</sup>	1.453	6.711
$\theta$ max, deg.	28.28	32.44
no. of data collected	30576	81600
no. of data used	10947	8825
no. of parameters	464	251
$R_1$ [ $I > 2\sigma(I)$ ]	0.0453	0.0271
$wR_2$ [ $I > 2\sigma(I)$ ]	0.1156	0.0495
$R_1$ [all data]	0.0602	0.0560
$wR_2$ [all data]	0.1258	0.0574
GOF	1.056	1.061
$R_{\text{int}}$	0.0394	0.0522

**Table 1 (continued)** Crystal, intensity collection and refinement data.

	<b>[Bm<sup>Me</sup>](GaI)(GaI)[Bm<sup>Me</sup>]</b>	<b>[Bm<sup>Bu<sup>t</sup></sup>](GaI)(GaI)[Bm<sup>Bu<sup>t</sup></sup>]</b>
lattice	Monoclinic	Monoclinic
formula	C <sub>16</sub> H <sub>24</sub> B <sub>2</sub> Ga <sub>2</sub> I <sub>2</sub> N <sub>8</sub> S <sub>4</sub>	C <sub>28</sub> H <sub>48</sub> B <sub>2</sub> Ga <sub>2</sub> I <sub>2</sub> N <sub>8</sub> S <sub>4</sub>
formula weight	871.53	1039.84
space group	<i>C2/m</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> /Å	12.149(3)	9.873(9)
<i>b</i> /Å	11.964(3)	18.840(17)
<i>c</i> /Å	11.163(3)	12.499(12)
$\alpha$ /°	90	90
$\beta$ /°	121.214(4)	110.952(14)
$\gamma$ /°	90	90
<i>V</i> /Å <sup>3</sup>	1387.7(7)	2171(3)
<i>Z</i>	2	2
temperature (K)	125(2)	125(2)
radiation ( $\lambda$ , Å)	0.71073	0.71073
$\rho$ (calcd.), g cm <sup>-3</sup>	2.086	1.591
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	4.491	2.884
$\theta$ max, deg.	28.28	25.03
no. of data collected	9629	14470
no. of data used	1805	3828
no. of parameters	86	214
$R_1$ [ $I > 2\sigma(I)$ ]	0.0428	0.0615
$wR_2$ [ $I > 2\sigma(I)$ ]	0.0845	0.1196
$R_1$ [all data]	0.0869	0.1226
$wR_2$ [all data]	0.0987	0.1408
GOF	1.016	1.036
$R_{int}$	0.1086	0.1535

## References

- (1) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic Chemistry*, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23.  
(b) Burger, B.J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98.  
(c) Shriver, D. F.; Drezdson, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2<sup>nd</sup> Edition; Wiley-Interscience: New York, 1986.
- (2) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. J. *Org. Chem.* **1997**, *62*, 7512-7515.
- (3) "CIL NMR Solvent Data Chart", Cambridge Isotope Laboratories, Inc., Andover, MA 01810-5413, USA.
- (4) Cassidy, C. S.; Reinhardt, L. A.; Cleland, W. W.; Frey, P. A. *J. Chem. Soc., Perkin Trans. 2* **1999**, 635-641.
- (5) Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. J. *Chem. Soc., Dalton Trans.* **2000**, 891-897.
- (6) Alvarez, H. M.; Tran, T. B.; Richter, M. A.; Alyounes, D. M.; Rabinovich, D.; Tanski, J. M.; Krawiec, M. *Inorg. Chem.* **2003**, *42*, 2149-2156.
- (7) Alvarez, H. M.; Gillespie, P. A.; Gause, C. D.; Rheingold, A. L.; Golen, J. A.; Rabinovich, D. *Polyhedron* **2004**, *23*, 617-622.
- (8) Green, M. L. H.; Mountford, P.; Smout, G. J.; Speel, S. R. *Polyhedron* **1990**, *9*, 2763-2765.
- (9) Markó, I.E.; Southern, J. M. *J. Org. Chem.* **1990**, *55*, 3368-3370.
- (10) (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.  
(b) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.