SUPPORTING INFORMATION

Tris(2-mercapto-1-t-butylimidazolyl)hydroborato Gallium Derivatives: Synthesis of Di- and Trigallium Compounds in a Sulfur-Rich Coordination Environment

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EXPERIMENTAL SECTION

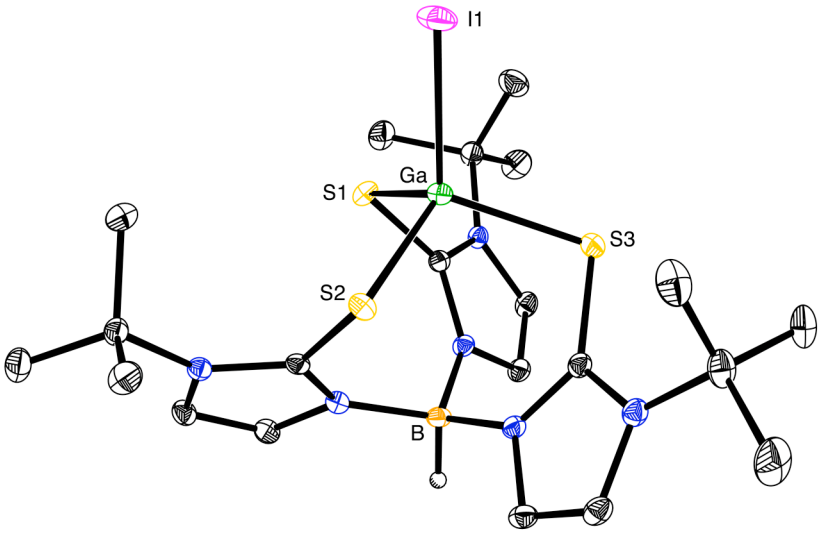
General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified.[1] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX and Bruker 400 DRX spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H; 7.26 for $CHCl_3$ and 1.94 for CHD_2CN).[2] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 77.16 for $CDCl_3$, 128.06 for C_6D_6[2] and 1.32 for the upfield signal of CD_3CN[3]). Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Mass spectra were obtained on a Micromass Quadrupole-Time-of-Flight mass spectrometer using fast atom bombardment (FAB). $[Tm^{But}]K$[4], $HGaCl_2$,[5] $[Tm^{But}]Tl$,[6] and "GaI"[7] were prepared by the literature methods. $GaCl_3$ (Strem & VWR), GaI_3 (Aldrich), and $GaCl_2$ (Strem) were obtained commercially and used as received.

Synthesis of {[Tm^{But}]GaI}I

A suspension of $[Tm^{But}]Tl$ (500 mg, 0.733 mmol) in THF (5 mL) was added to GaI_3 (363 mg, 0.806 mmol) resulting in the immediate deposition of a yellow precipitate. The mixture was stirred for 15 minutes, allowed to settle for an additional 15 minutes, and filtered. The filtrate was cooled to -35˚C for one day resulting in the precipitation of a white solid which was isolated by decanting the solution. The solid was dried *in vacuo* to give {$[Tm^{But}]GaI$}I as a white powder (450 mg, 77% yield). Colorless crystals of the composition {$[Tm^{But}]GaI$}I•C_6H_6 suitable for X-ray diffraction were obtained from vapor diffusion of Et_2O into a C_6H_6 solution. Analysis calcd. for {$[Tm^{But}]GaI$}I: C, 31.5%; H, 4.3%; N, 10.5%. Found: C, 31.7%; H, 4.0%; N, 10.4%. ^{1}H NMR ($CDCl_3$): 1.75 [s, 27 H of $HB\{C_3N_2H_2[C(C\underline{H}_3)_3]S\}_3$], 4.7 [br, $\underline{H}B\{C_3N_2H_2[C(CH_3)_3]S\}_3$], 7.30 [d, $^{3}J_{H\text{-}H}$=2 , 3 H of

$HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3]$, 7.43 [d, $^3J_{H\text{-}H}$=2, 3 H of $HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3]$. ^{13}C NMR ($CDCl_3$): 29.6 [q, $^1J_{C\text{-}H}$ = 128, 9 C, $HB\{C_3N_2H_2[C(\underline{C}H_3)_3]S\}_3]$, 61.7 [s, 3 C, $HB\{C_3N_2H_2[\underline{C}(CH_3)_3]CS\}_3]$, 121.1 [dd, $^1J_{C\text{-}H}$ = 200, $^3J_{C\text{-}H}$ = 12, 3 C of $HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3]$, 126.6 [d, $^1J_{C\text{-}H}$ = 200, $^3J_{C\text{-}H}$ = 7, 3 C of $HB\{\underline{C}_2N_2H_2[C(CH_3)_3]S\}_3]$, 145.6 [s, 3 C, $HB\{C_2N_2H_2[C(CH_3)_3]\underline{C}S\}_3]$. IR Data (KBr, cm^{-1}): 3437(br), 3122(w), 3085(w), 2975(m), 2931(w) 2870(w), 2462(br), 2300(w), 2228(w), 1719(w), 1655(w), 1618(w), 1559(s), 1479(m), 1427(s), 1401(w), 1372(s), 1361(s), 1326(m), 1260(m), 1232(w), 1193(vs), 1128(w), 1063(m), 1034(w), 984(w), 930(w), 907(w), 820(m), 751(vs), 689(s), 640(w), 587(m), 548(m), 494(w), 461(w), 442(w), 409(w). FAB-MS m/z = 673.0 $[M - I]^+$, M = $\{[Tm^{But}]GaI\}I$.

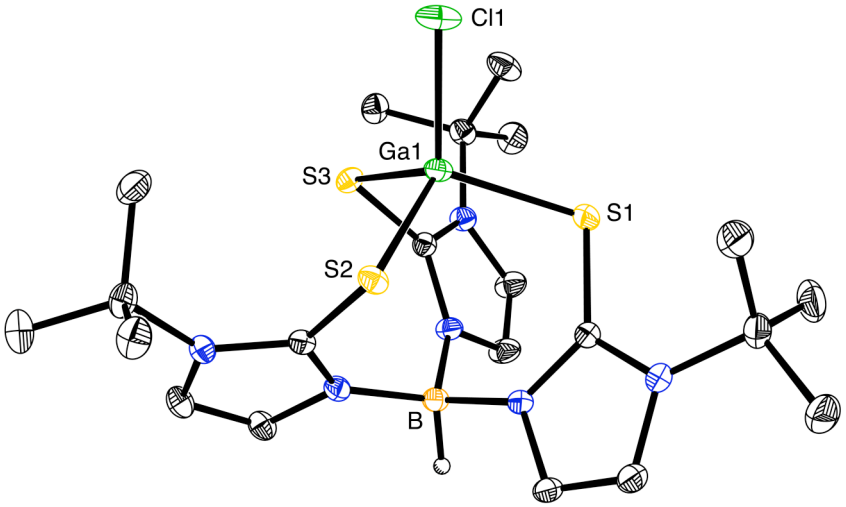


Molecular structure of $\{[Tm^{But}]GaI\}I$ (only the cation is shown for clarity)

Synthesis of $\{[Tm^{But}]GaCl\}[GaCl_4]$

A mixture of $GaCl_3$ (52 mg, 0.30 mmol) and $[Tm^{But}]Tl$ (100 mg, 0.15 mmol) was treated with CH_2Cl_2 (1.5 mL) and the suspension was stirred for 3 hours, thereby resulting in the formation of a white precipitate. The mixture was filtered and the filtrate was treated with pentane (1 mL) depositing a precipitate, and the volatile components were removed under reduced pressure leaving $\{[Tm^{But}]GaCl\}[GaCl_4]$ as a greasy, white solid

(55 mg, 47%). Colorless crystals of the composition {[Tm^{But}]GaCl}[GaCl$_4$]•2(CHCl$_3$) suitable for X-ray diffraction were obtained from a concentrated CHCl$_3$ solution. Analysis calcd. {[Tm^{But}]GaCl}[GaCl$_4$]: C, 31.8%; H, 4.3%; N, 10.6%. Found: C, 31.5%; H, 4.1%; N, 10.3%. ^{1}H NMR (CDCl$_3$): 1.77 [s, 27 H of HB{C$_3$N$_2$H$_2$[C(C<u>H</u>$_3$)$_3$]S}$_3$], 4.7 [br 1 H of <u>H</u>B{C$_3$N$_2$H$_2$[C(CH$_3$)$_3$]S}$_3$], 7.26 [d, $^3J_{H-H}$ = 2, 3 H of HB{C$_3$N$_2$<u>H</u>$_2$[C(CH$_3$)$_3$]S}$_3$], 7.36 [d, $^3J_{H-H}$ = 2, 3 H of HB{C$_3$N$_2$<u>H</u>$_2$[C(CH$_3$)$_3$]S}$_3$]. ^{13}C NMR (CDCl$_3$): 29.4 [q, $^1J_{C-H}$ = 128, 27 C, HB{C$_2$N$_2$H$_2$[C(<u>C</u>H$_3$)$_3$]CS}$_3$], 61.7 [3 C, HB{C$_2$N$_2$H$_2$[<u>C</u>(CH$_3$)$_3$]CS}$_3$], 120.9 [d, $^1J_{C-H}$ = 200, 3 C of HB{<u>C</u>$_2$N$_2$H$_2$[C(CH$_3$)$_3$]CS}$_3$], 126.6 [d, $^1J_{C-H}$ = 200, 3 C of HB{<u>C</u>$_2$N$_2$H$_2$[C(CH$_3$)$_3$]CS}$_3$], 144.9 [s, 3 C, HB{C$_2$N$_2$H$_2$[C(CH$_3$)$_3$]<u>C</u>S}$_3$]. IR Data (KBr, cm^{-1}): 3413 (br), 3183 (m), 3149 (m), 3101 (w), 2984 (vs), 2936 (m), 2887 (m), 2684 (w), 2468 (m), 2302 (w), 2238 (w), 1698 (br), 1562 (s), 1481 (s), 1459 (m), 1428 (vs), 1403 (s), 1363 (vs), 1325 (s), 1260 (m), 1233 (s), 1193 (vs), 1149 (s), 1132 (s), 1072 (m), 1032 (m) 983 (w), 930 (w), 819 (m) 742 (vs), 689 (s). FAB-MS: *m*/*z* = 582.7 [M – GaCl$_4$]$^+$, M = {[Tm^{But}]GaCl}[GaCl$_4$].



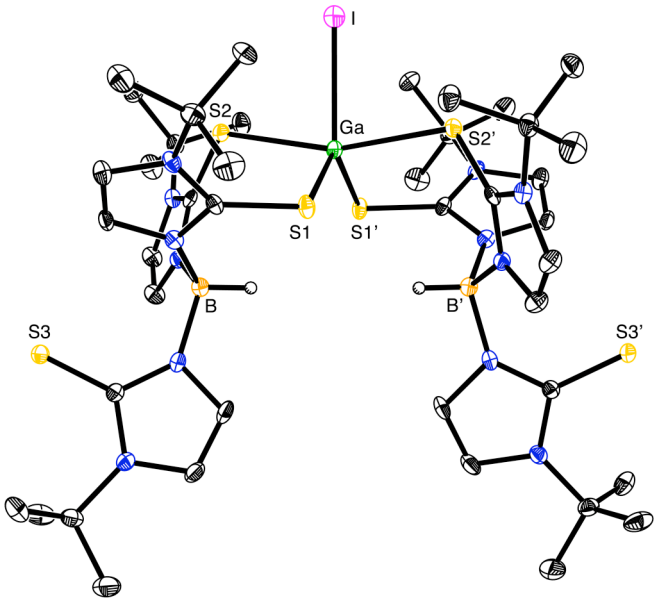
Molecular structure of {[Tm^{But}]GaCl}[GaCl$_4$] (only the cation is shown for clarity)

Synthesis of [κ^2-Tm^{But}]$_2$GaI

(a) A mixture of [Tm^{But}]Tl (50 mg, 0.073 mmol) and GaI$_3$ (17 mg, 0.038 mmol) was treated with C$_6$D$_6$ (0.7 ml) resulting in the immediate deposition of a yellow solid. The

mixture was mixed for a period of five minutes and filtered. The filtrate was transferred to an NMR tube, thereby demonstrating the formation of $[\kappa^2\text{-}Tm^{But}]_2GaI$ by ^1H NMR spectroscopy. Crystals of $[\kappa^2\text{-}Tm^{But}]_2GaI$ (*ca.* 10 mg) were deposited over a period of one day and were isolated by decantation. ^1H NMR (C_6D_6): 1.24 [s, 36 H of $[HB\{C_3N_2H_2[C(C\underline{H}_3)_3]S\}_3]_2$], 1.67 [s, 18 H of $[HB\{C_3N_2H_2[C(C\underline{H}_3)_3]S\}_3]_2$], 6.24 [s, 6 H of $[HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3]_2$], 6.80 [s, 2 H of $[HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3]_2$], 8.63 [s, 4 H of $[HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3]_2$], 2 H of $[\underline{H}B\{C_3N_2H_2[C(CH_3)_3]S\}_3]_2$ not observed. $^{13}C\{^1H\}$ NMR (C_6D_6): 28.3 [6 C of $[HB\{C_2N_2H_2[C(\underline{C}H_3)_3]CS\}_3]_2$], 29.6 [12 C of $[HB\{C_2N_2H_2[C(\underline{C}H_3)_3]CS\}_3]_2$], 58.5 [2 C of $[HB\{C_2N_2H_2[\underline{C}(CH_3)_3]CS\}_3]_2$], 60.4 [4 C of $[HB\{C_2N_2H_2[\underline{C}(CH_3)_3]CS\}_3]_2$], 115.1 [2 C of $[HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3]_2$], 118.4 [4 C of $[HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3]_2$], 123.9 [2 C of $[HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3]_2$], 126.3 [4 C of $[HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3]_2$], 6 C of $[HB\{C_2N_2H_2[C(CH_3)_3]\underline{C}S\}_3]_2$ not observed. IR Data (KBr, cm^{-1}): 3424 (br), 3144 (br), 3087 (br), 2977 (m), 2924 (m), 2467 (br), 1617 (w), 1559 (m), 1479 (m), 1427 (s), 1401 (m), 1359 (s), 1321 (m), 1260 (m), 1230 (m), 1193 (vs), 1171 (s), 1113 (m), 1062 (w), 1033 (w), 984 (w), 930 (w), 820 (w), 739 (m), 684 (m).

(b) A mixture of $[Tm^{But}]Tl$ (200 mg, 0.29 mmol) and GaI_3 (145 mg, 0.32 mmol) was treated with CH_2Cl_2 (2 mL) resulting in the immediate deposition of a yellow solid. The mixture was stirred for 30 minutes, allowed to settle for 15 minutes, and filtered. The volatile components were removed from the filtrate under reduced pressure to give a white solid that was treated with potassium (45 mg, 1.2 mmol) and C_6H_6 (2 mL) and stirred for 18 hours, with the intention of reducing $[Tm^{But}]GaI_2$ to $\{[Tm^{But}]GaI\}_2$. However, $[\kappa^2\text{-}Tm^{But}]_2GaI$ was obtained as a white solid (46 mg) after filtration and removing the volatile components *in vacuo*. Colorless crystals of composition $[\kappa^2\text{-}Tm^{But}]_2GaI\bullet 2(C_7H_8)$ suitable for X-ray diffraction were obtained from a concentrated toluene solution at -35°C solution.

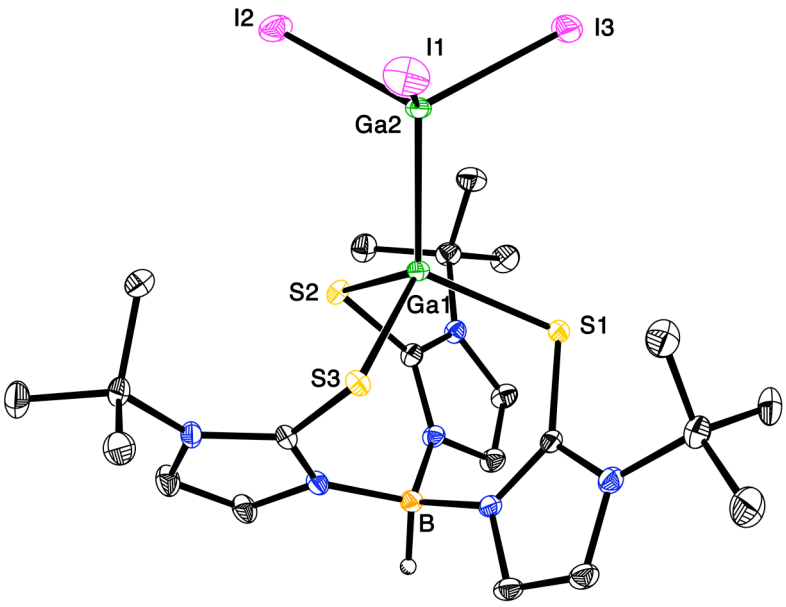


Molecular structure of [κ²-Tm^{But}]$_2$GaI (the molecule lies on a crystallographic two-fold axis)

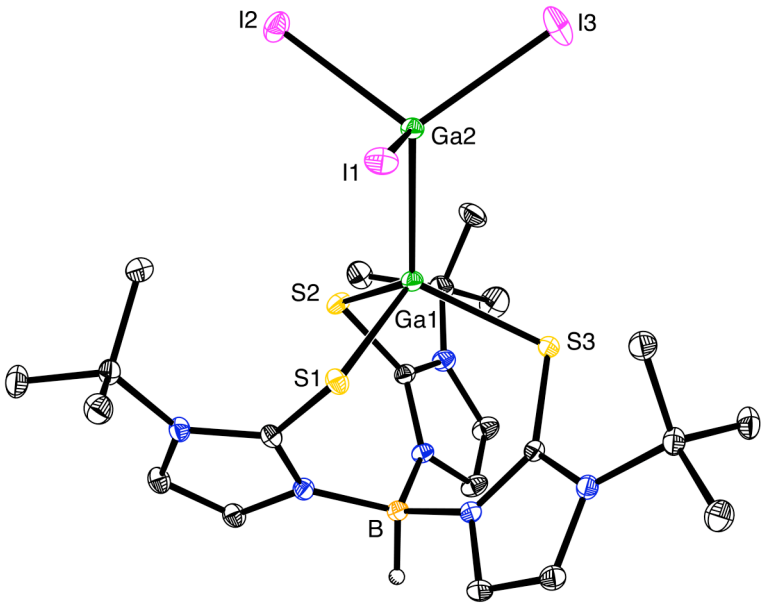
Synthesis of {[Tm^{But}]GaGaI$_3$

A solution of [Tm^{But}]Tl (25 mg, 0.037 mmol) in CD_3CN (0.7 mL) was cooled to -35˚C and treated with "GaI" (24 mg, 0.12 mmol) resulting in the immediate deposition of a dark brown solid in addition to some gallium metal. The mixture was mixed *via* a pipette for 5 minutes and filtered. The filtrate was monitored by ^{1}H NMR spectroscopy demonstrating the formation of [Tm^{But}]GaGaI$_3$. Colorless crystals of composition [Tm^{But}]GaGaI$_3$•2(CH_3CN) suitable for X–ray diffraction were deposited over a period of one day within the NMR tube. The mother liquor was decanted and the crystals were dried *in vacuo* giving [Tm^{But}]GaGaI$_3$ as a white solid (10 mg, 27%). Colorless crystals of composition [Tm^{But}]GaGaI$_3$•C_6H_6 suitable for X-ray diffraction were also isolated by the slow evaporation of a concentrated benzene/acetonitrile solution. Analysis calcd. [Tm^{But}]GaGaI$_3$•C_6H_6: C, 30.1%; H, 3.8%; N, 7.8%. Found: C, 30.3%; H, 3.6%; N, 7.7%. ^{1}H NMR (CD_3CN): 1.75 [s, 27 H of HB{$C_3N_2H_2$[C($C\underline{H}_3$)$_3$]S}$_3$], 7.13 [d, $^3J_{H\text{-}H}$ = 2 , 3 H of HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$], 7.36 [d, $^3J_{H\text{-}H}$ = 2, 3 H of HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$], 1 H of [$\underline{H}$B{$C_3N_2H_2$[C(CH_3)$_3$]S}$_3$] not observed. IR Data (KBr, cm^{-1}): 2989 (m), 2977 (vs), 2969 (vs), 2942 (m), 2925 (m), 2898 (m), 2867 (m), 2458 (br), 1700 (br), 1562 (s), 1479 (m), 1424 (vs), 1399 (m), 1366 (vs), 1317 (s), 1259 (m), 1230 (s) 1170 (vs), 1070 (s) 1030 (m), 982 (m),

927 (m), 843 (w), 818 (s), 758 (s), 731 (vs), 688 (vs). FAB-MS: m/z = 672.9 $[M - GaI_2]^+$, {M = $[Tm^{But}]GaGaI_3$}.



Molecular structure of $[Tm^{But}]GaGaI_3 \cdot 2(CH_3CN)$ (solvent not shown)

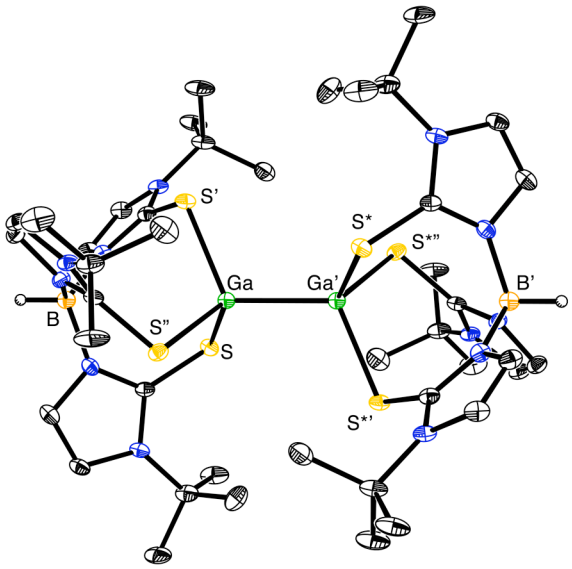


Molecular structure of $[Tm^{But}]GaGaI_3 \cdot C_6H_6$ (solvent not shown)

Synthesis of {$[Tm^{But}]GaGa[Tm^{But}]$}I_2

A mixture of "GaI" (41 mg, 0.21 mmol) and $[Tm^{But}]K$ (50 mg, 0.097 mmol) was treated with C_6H_6 (2 mL) and the suspension was stirred for 2.5 hours, thereby resulting in the

formation of a brown precipitate. The mixture was filtered and the precipitate was washed with benzene (2 × 1 mL) and then extracted into CH_3CN (2 mL). The volatile components from the extract were removed *in vacuo* leaving {[Tm^{But}]GaGa[Tm^{But}]}I_2 as a white solid (43 mg, 66%). Colorless crystals of composition {[Tm^{But}]GaGa[Tm^{But}]}I_2•6(CH_3CN) suitable for X-ray diffraction were obtained from a concentrated acetonitrile solution. Crystals suitable for elemental analysis were obtained from a concentrated CH_2Cl_2 solution. Analysis calcd. {[Tm^{But}]GaGa[Tm^{But}]}I_2 •2(CH_2Cl_2): C, 34.8%; H, 4.8%; N, 11.1%. Found: C, 34.9%; H, 4.9%; N, 10.3%. ^{1}H NMR (CD_3CN): 1.69 [br s, 36 H of [HB{$C_3N_2H_2$[C($C\underline{H}_3$)$_3$]S}$_3$]$_2$], 1.72 [br s, 18 H of [HB{$C_3N_2H_2$[C($C\underline{H}_3$)$_3$]S}$_3$]$_2$], 7.18 [d, $^3J_{H\text{-}H}$ = 2, 6 H of [HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$]$_2$], 7.38 [d, $^3J_{H\text{-}H}$ = 2, 2 H of [HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$]$_2$], 7.40 [d, $^3J_{H\text{-}H}$ = 2, 4 H of [HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$]$_2$], 2 H of [$\underline{H}$B{$C_3N_2H_2$[C(CH_3)$_3$]S}$_3$]$_2$ not observed. IR Data (KBr, cm^{-1}): 3167 (w), 3128 (w), 3049 (w), 2979 (s), 2931 (w), 2458(m), 1621 (w), 1562 (s), 1480 (m), 1427 (s), 1401 (m), 1362 (vs), 1321 (m), 1263 (m), 1229 (m), 1196 (vs), 1131 (m), 1074 (m), 1033 (m), 983 (w), 822 (m), 749 (s), 687 (m). FAB-MS: *m*/*z* = 1221.3 $[M - I]^+$, M = {[Tm^{But}]GaGa[Tm^{But}]}I_2.

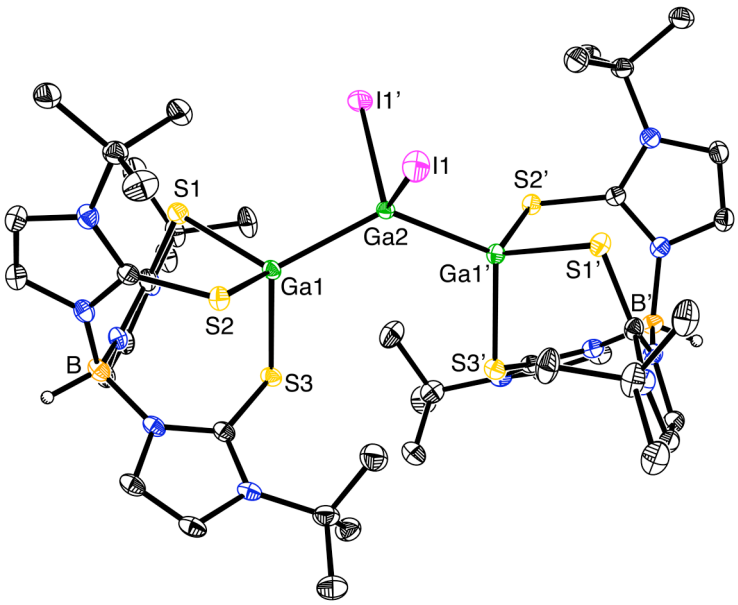


Molecular structure of {[Tm^{But}]GaGa[Tm^{But}]}I_2 (only the cation is shown; the molecule lies on a site with –3 crystallographic symmetry)

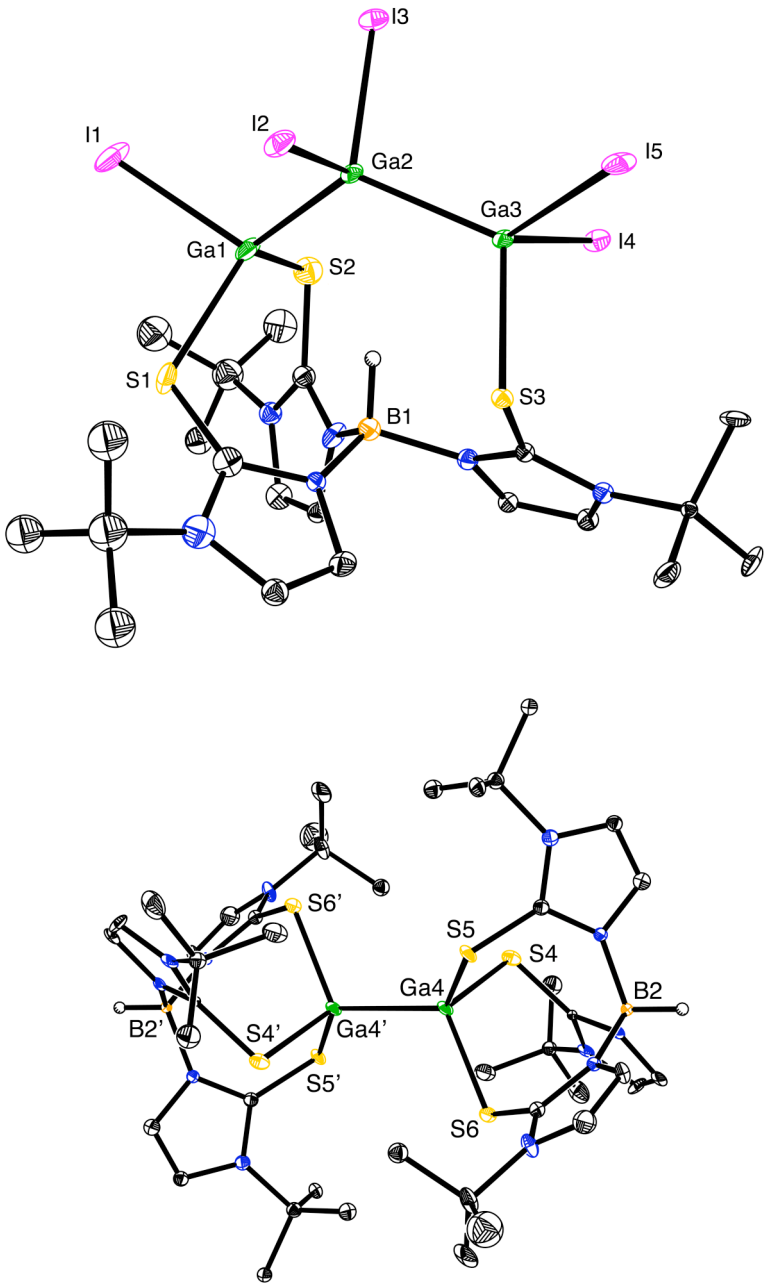
Synthesis of {[Tm^{But}]Ga(GaI$_2$)Ga[Tm^{But}]}I, and {[μ-κ^1,κ^2-Tm^{But}]GaI$_2$GaI$_2$GaI}$_2${[Tm^{But}]GaGa[Tm^{But}]}

(a) A mixture of [Tm^{But}]K (100 mg, 0.19 mmol) and "GaI" (114 mg, 0.58 mmol) was treated with cold (–35˚C) CH_3CN (2 mL). The resulting slurry was mixed *via* the use of a pipette for 1 minute and filtered. The filtrate was cooled to -35˚C and allowed to stand for two days resulting in the formation of colorless crystals of composition {[Tm^{But}]Ga(GaI$_2$)Ga[Tm^{But}]}I•2CH_3CN (55 mg, 35%). Analysis calcd. {[Tm^{But}]Ga(GaI$_2$)Ga[Tm^{But}]}I•2(CH_3CN): C, 34.0%; H, 4.6%; N, 12.1%. Found: C, 34.0%; H, 4.3%; N, 12.5%. ^{1}H NMR (CD_3CN): 1.75 [s, 54 H of [HB{$C_3N_2H_2$[C($C\underline{H}_3)_3$]S}$_3$]$_2$], 7.08 [d, $^3J_{H\text{-}H}$ = 2, 6 H of [HB{$C_3N_2\underline{H}_2$[C($CH_3)_3$]S}$_3$]$_2$], 7.32 [d, $^3J_{H\text{-}H}$ = 2, 6 H of [HB{$C_3N_2\underline{H}_2$[C($CH_3)_3$]S}$_3$]$_2$], 2 H of [$\underline{H}$B{$C_3N_2H_2$[C($CH_3)_3$]S}$_3$]$_2$ not observed. FAB-MS: *m*/*z* = 1417.1 [M]$^+$, M = [Tm^{But}]Ga(GaI$_2$)Ga[Tm^{But}].

(b) {[κ^1,κ^2-Tm^{But}]GaI$_2$GaI$_2$GaI}$_2${[Tm^{But}]GaGa[Tm^{But}]} was isolated by crystallization during the course of efforts to optimize the synthesis of {[Tm^{But}]Ga(GaI$_2$)Ga[Tm^{But}]}I by the use of acetonitrile as a solvent. A solution of [Tm^{But}]Tl (50 mg, 0.073 mmol) in CH_3CN (1 mL) was cooled to –35˚C and treated with "GaI" (43 mg, 0.22 mmol). The resulting slurry was mixed *via* the use of a pipette for 1 minute and filtered. The filtrate was cooled to -35˚C and allowed to stand for several days resulting in the formation of colorless crystals of composition {[κ^1,κ^2-Tm^{But}]GaI$_2$GaI$_2$GaI}$_2${[Tm^{But}]GaGa[Tm^{But}]} •8MeCN (*ca*. 5 mg).



Molecular structure of {[Tm^{But}]Ga(GaI$_2$)Ga[Tm^{But}]}I (only the cation is shown for clarity; the molecule lies on a crystallographic two-fold axis)



Molecular structure of {[μ-κ^1,κ^2-Tm^{But}]GaI$_2$GaI$_2$GaI}$_2${[Tm^{But}]GaGa[Tm^{But}]} (the cation lies on a crystallographic inversion center)

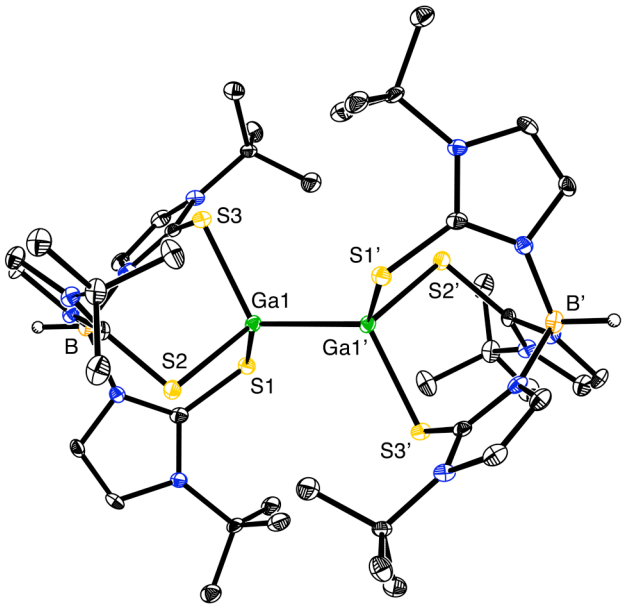
Conversion of {[Tm^{But}]Ga(GaI$_2$)Ga[Tm^{But}]}I to {[Tm^{But}]GaGa[Tm^{But}]}I$_2$ and [Tm^{But}]GaGaI$_3$

A solution of {[Tm^{But}]Ga(GaI$_2$)Ga[Tm^{But}]}I•(CH$_3$CN)$_2$ (5 mg) in CD$_3$CN (0.7 mL) was filtered and transferred to an NMR tube equipped with a J. Young valve. The solution was monitored by ^{1}H NMR demonstrating the complete conversion to

{[Tm^{But}]GaGa[Tm^{But}]}I_2 and [Tm^{But}]GaGaI_3 in a *ca*. 1:1 ratio over a period of six days at room temperature.

Synthesis of {[Tm^{But}]GaGa[Tm^{But}]}[$GaCl_4$]$_2$

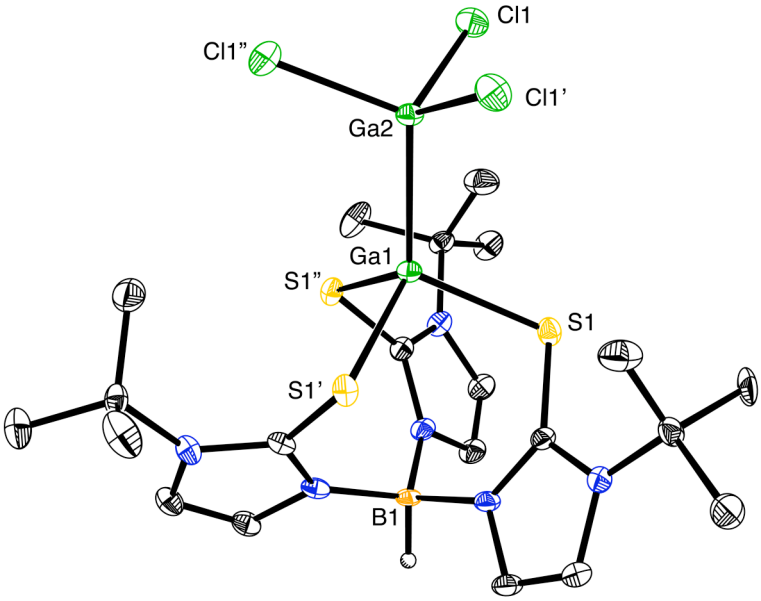
A mixture of $HGaCl_2$ (246 mg, 1.74 mmol) and [Tm^{But}]K (400 mg, 0.77 mmol) was treated with CH_3CN (4 mL) and the resulting white suspension was stirred for 3 hours. The mixture was filtered and the colorless filtrate was allowed to slowly evaporate at room temperature thereby depositing colorless crystals (296 mg, 50%) which were isolated and dried *in vacuo*. Colorless crystals of {[Tm^{But}]GaGa[Tm^{But}]}[$GaCl_4$]$_2$•2(Me_2CO) suitable for X-ray diffraction were obtained from acetone. Analysis calcd. {[Tm^{But}]GaGa[Tm^{But}]}[$GaCl_4$]$_2$•1.75(CH_3CN): C, 34.4%; H, 4.7%; N, 12.1%. Found: C, 34.6%; H, 4.7%; N, 11.5%. ^{1}H NMR (CD_3CN): 1.70 [br s, 36 H of [HB{$C_3N_2H_2$[C($C\underline{H}_3$)$_3$]S}$_3$]$_2$], 1.73 [br s, 18 H of [HB{$C_3N_2H_2$[C($C\underline{H}_3$)$_3$]S}$_3$]$_2$], 4.6 [br, 2H of [$\underline{H}$B{$C_3N_2H_2$[C(CH_3)$_3$]S}$_3$]$_2$], 7.18 [d, $^3J_{H\text{-}H}$ = 2, 6 H of [HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$]$_2$], 7.39 [d, $^3J_{H\text{-}H}$ = 2, 2 H of [HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$]$_2$], 7.40 [d, $^3J_{H\text{-}H}$ = 2, 4 H of [HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$]$_2$]. ^{13}C{^{1}H} NMR (CD_3CN): 29.5 [18 C of [HB{$C_2N_2H_2$[C($\underline{C}H_3$)$_3$]CS}$_3$]$_2$], 62.0 [6 C of [HB{ $C_2N_2H_2$[$\underline{C}$(CH_3)$_3$]CS}$_3$]$_2$], 121.1 [6 C of [HB{$\underline{C}_2N_2H_2$[C(CH_3)$_3$]CS}$_3$]$_2$], 126.3 [6 C of [HB{$\underline{C}_2N_2H_2$[C(CH_3)$_3$]CS}$_3$]$_2$], 148.6 [6 C [HB{$C_2N_2H_2$[C(CH_3)$_3$]$\underline{C}$S}$_3$]$_2$]. IR Data (KBr, cm^{-1}): 3382 (br), 3182 (m), 3148 (m), 3099 (w), 2982 (s), 2927 (s), 2681 (w), 2462 (m), 2359 (vw), 2301 (w), 2235 (w), 1674 (br), 1562 (s), 1481 (m), 1427 (vs), 1401 (m), 1375 (vs), 1363 (vs), 1322 (s), 1260 (m), 1232 (m), 1193 (vs), 1177 (vs), 1149 (w), 1131 (m), 1072 (m), 1032 (m), 982 (w), 929 (w), 819 (s), 739 (vs), 689 (s), 638 (w). FAB-MS: m/z = 1305.3 [M – $GaCl_4$]$^+$, M = {[Tm^{But}]GaGa[Tm^{But}]}[$GaCl_4$]$_2$.



Molecular structure of {[Tm^{But}]GaGa[Tm^{But}]}[GaCl$_4$]$_2$ (only the cation is shown for clarity; the molecule lies on a crystallographic inversion center)

Synthesis of {[Tm^{But}]GaGaCl$_3$

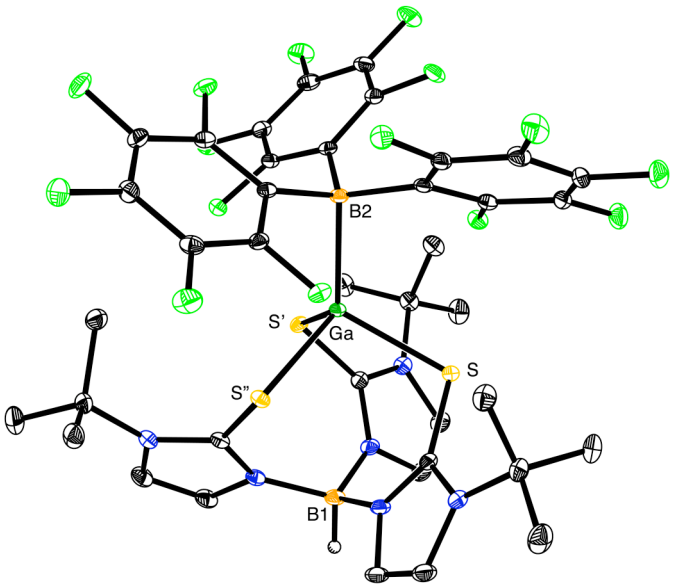
A mixture of [Tm^{But}]Tl (50 mg, 0.073 mmol) and Ga[GaCl$_4$] (21 mg, 0.075 mmol) was treated with CH_3CN (1.5 mL) resulting in the immediate deposition of a fluffy, white solid. The resulting slurry was mixed *via* the use of a pipette for 5 minutes and filtered. The filtrate was allowed to stand for three days at room temperature, thereby resulting in the formation of colorless crystals of [Tm^{But}]GaGaCl$_3$ (24 mg, 45%). ^{1}H NMR (CD_3CN): 1.74 [s, 27 H of HB{$C_3N_2H_2$[C($C\underline{H}_3$)$_3$]S}$_3$], 7.13 [d, $^3J_{H\text{-}H}$ = 2, 3 H of HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$], 7.35 [d, $^3J_{H\text{-}H}$=2, 3 H of HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$], 2 H of [$\underline{H}$B{$C_3N_2H_2$[C(CH_3)$_3$]S}$_3$]$_2$ not observed. FAB-MS: m/z = 583.0 [M – $GaCl_2$]$^+$, {M = [Tm^{But}]GaGaCl$_3$}.



Molecular structure of [Tm^{But}]GaGaCl$_3$ (the molecule lies on a crystallographic three-fold axis)

Synthesis of [Tm^{But}]GaB(C$_6$F$_5$)$_3$

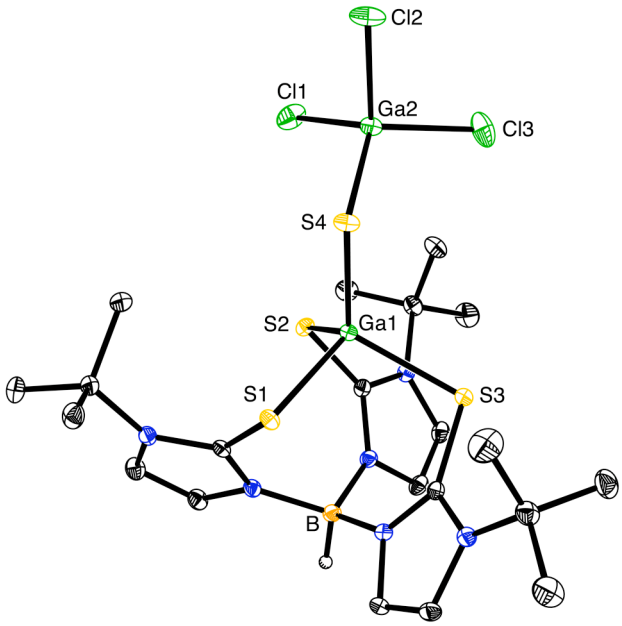
A mixture of [Tm^{But}]K (400 mg, 0.774 mmol), (HGaCl$_2$)$_2$ (246 mg, 0.87 mmol), and B(C$_6$F$_5$)$_3$ (396 mg, 0.773 mmol) was treated with CH$_3$CN (4 mL) and stirred for 3 hours. The solution was filtered and crystals of composition [Tm^{But}]GaB(C$_6$F$_5$)$_3$•(CH$_3$CN)$_3$ (*ca.* 20 mg) suitable for X-ray diffraction were isolated after letting the filtrate stand for several days.



Molecular structure of [Tm^{But}]GaB(C$_6$F$_5$)$_3$ (the molecule lies on a crystallographic three-fold axis)

Synthesis of [Tm^{But}]GaSGaCl$_3$

A mixture of [Tm^{But}]K (75 mg, 0.15 mmol), $HGaCl_2$ (41 mg, 0.29 mmol), and S_8 (37 mg, 0.15 mmol) was treated with CH_3CN (2 mL) and C_6H_6 (2 mL). The resulting slurry was stirred for 3 hours and the solution was filtered. Crystals of composition [Tm^{But}]GaSGaCl$_3$·C_6H_6 (*ca*. 5mg) were isolated after letting the filtrate stand for several days.



Molecular structure of [Tm^{But}]GaSGaCl$_3$

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).[8]

Table 1. Crystal, intensity collection and refinement data.

	{[Tm^{But}]GaI}I•C_6H_6	{[Tm^{But}]GaCl}[$GaCl_4$]•2($CHCl_3$)
lattice	Monoclinic	Triclinic
formula	$C_{27}H_{40}BGaI_2N_6S_3$	$C_{23}H_{36}BCl_{11}Ga_2N_6S_3$
formula weight	879.16	1032.96
space group	$P2_1/n$	$P\text{-}1$
a / Å	11.6794(5)	11.0927(5)
b / Å	16.3820(7)	14.4146(7)
c / Å	19.2080(8)	16.1852(8)
α / °	90.00	98.2300(10)
β / °	91.4430(10)	107.1550(10)
γ / °	90.00	112.1170(10)
V / Å^3	3673.9(3)	2194.38(18)
Z	4	2
temperature (K)	243(2)	273(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.589	1.563
μ (Mo Kα), mm^{-1}	2.626	2.066
θ max, deg.	26.73	26.37
no. of data collected	24641	14599
no. of data used	7759	8883
no. of parameters	395	347
R_{int}	0.0375	0.0150
R_1 [$I > 2\sigma(I)$]	0.0371	0.0421
wR_2 [$I > 2\sigma(I)$]	0.0758	0.1282
R_1 [all data]	0.0686	0.0509
wR_2 [all data]	0.0857	0.1342
GOF	1.015	1.102

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

	$[(Tm^{But})GaCl][GaCl_4]$ $\bullet 2(C_6H_6)$	$[(Tm^{But})GaCl][GaCl_4]$ $\bullet CH_3CN$
lattice	Triclinic	Monoclinic
formula	$C_{33}H_{46}BCl_5Ga_2N_6S_3$	$C_{23}H_{37}BCl_5Ga_2N_6S_3$
formula weight	950.44	835.28
space group	*P-1*	$P2_1/n$
a / Å	11.9637(12)	16.0697(7)
b / Å	13.0055(13)	17.5534(8)
c / Å	16.595(3)	26.6647(12)
α / °	99.187(2)	90.00
β / °	102.166(2)	95.1970(10)
γ / °	113.5400(10)	90.00
V / Å^3	2226.7(5)	7490.6(6)
Z	2	8
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.418	1.481
μ (Mo Kα), mm^{-1}	1.681	1.988
θ max, deg.	30.61	32.65
no. of data collected	36434	127603
no. of data used	13633	26197
no. of parameters	485	747
R_{int}	0.0467	0.0244
R_1 [$I > 2\sigma(I)$]	0.0389	0.0279
wR_2 [$I > 2\sigma(I)$]	0.0717	0.0672
R_1 [all data]	0.0720	0.0375
wR_2 [all data]	0.0807	0.0722
GOF	1.003	1.005

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

	$[\kappa^2\text{-}Tm^{But}]GaI\bullet 2(C_7H_8)$	$[Tm^{But}]GaGaI_3\bullet 2(CH_3CN)$
lattice	Monoclinic	Triclinic
formula	$C_{56}H_{84}B_2GaIN_{12}S_6$	$C_{25}H_{40}BGa_2I_3N_8S_3$
formula weight	1335.95	1079.78
space group	*C2/c*	*P-1*
a / Å	28.730(5)	11.0854(10)
b / Å	11.539(2)	11.1373(10)
c / Å	19.666(3)	16.5062(14)
α / °	90.00	76.4550(10)
β / °	102.550(3)	83.6380(10)
γ / °	90.00	80.9820(10)
V / Å^3	6363.8(19)	1950.9(3)
Z	4	2
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.394	1.838
μ (Mo Kα), mm^{-1}	1.161	3.943
θ max, deg.	25.03	32.73
no. of data collected	33678	33854
no. of data used	5626	13314
no. of parameters	356	401
R_{int}	0.0997	0.0225
R_1 [$I > 2\sigma(I)$]	0.0473	0.0297
wR_2 [$I > 2\sigma(I)$]	0.1059	0.0755
R_1 [all data]	0.0810	0.0360
wR_2 [all data]	0.1222	0.0779
GOF	1.030	1.009

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

	$[Tm^{But}]GaGaI_3 \bullet (C_6H_6)$	$[Tm^{But}]GaGaCl_3$
Lattice	Monoclinic	Rhombohedral
formula	$C_{27}H_{40}BGa_2I_3N_6S_3$	$C_{21}H_{34}BCl_3Ga_2N_6S_3$
formula weight	1075.78	723.32
space group	$P2_1/c$	$R\text{-}3$
a / Å	17.1401(10)	15.7834(8)
b / Å	11.9049(7)	15.7834(8)
c / Å	19.0672(11)	21.1015(11)
α / °	90.00	90.00
β / °	100.6150(10)	90.00
γ / °	90.00	120.00
V / Å^3	3824.1(4)	4552.4(4)
Z	4	6
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.869	1.583
μ (Mo Kα), mm^{-1}	4.021	2.269
θ max, deg.	32.75	32.71
no. of data collected	64566	22482
no. of data used	13386	3530
no. of parameters	382	220
R_{int}	0.0263	0.0849
R_1 [$I > 2\sigma(I)$]	0.0230	0.0400
wR_2 [$I > 2\sigma(I)$]	0.0541	0.0677
R_1 [all data]	0.0298	0.0941
wR_2 [all data]	0.0574	0.0747
GOF	1.032	1.047

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

	{[Tm^{But}]GaGa[Tm^{But}]}I_2 •6(CH_3CN)	{[Tm^{But}]GaGa[Tm^{But}]} $[GaCl_4]_2$•2(Me_2CO)
Lattice	Trigonal	Triclinic
formula	$C_{54}H_{86}B_2Ga_2I_2N_{18}S_6$	$C_{48}H_{80}B_2Cl_8Ga_4N_{12}O_2S_6$
formula weight	1594.63	1633.70
space group	*P-3*	*P-1*
a / Å	11.4967(17)	11.241(7)
b / Å	11.4967(17)	11.857(7)
c / Å	16.993(5)	15.252(9)
α / °	90.00	110.582(9)
β / °	90.00	107.533(9)
γ / °	120.00	94.069(9)
V / Å^3	1945.2(7)	1778.7(18)
Z	1	1
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.361	1.525
μ (Mo Kα), mm^{-1}	1.691	2.020
θ max, deg.	32.31	26.370
no. of data collected	31504	16090
no. of data used	4452	7261
no. of parameters	103	373
R_{int}	0.0506	0.0831
R_1 [$I > 2\sigma(I)$]	0.0653	0.0564
wR_2 [$I > 2\sigma(I)$]	0.1748	0.0870
R_1 [all data]	0.0747	0.1247
wR_2 [all data]	0.1792	0.1019
GOF	1.073	1.056

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

	{[Tm^{But}]Ga(GaI$_2$) Ga[Tm^{But}]I}•2(CH$_3$CN)	{[κ^1,κ^2-Tm^{But}]GaI$_2$GaI$_2$GaI} {[Tm^{But}]GaGa[Tm^{But}]}$_{0.5}$• 4(CH$_3$CN)
Lattice	Orthorhombic	Monoclinic
formula	$C_{46}H_{74}B_2Ga_3I_3N_{14}S_6$	$C_{50}H_{80}B_2Ga_4I_5N_{16}S_6$
formula weight	1627.03	2032.66
space group	*Pba2*	$P2_1/c$
a / Å	14.953(2)	30.236(4)
b / Å	20.106(3)	10.3955(13)
c / Å	11.2381(18)	27.107(3)
α / °	90.00	90.00
β / °	90.00	110.589(2)
γ / °	90.00	90.00
V / Å^3	3378.7(9)	7976.0(17)
Z	2	4
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.599	1.693
μ (Mo Kα), mm^{-1}	2.785	3.470
θ max, deg.	32.63	25.03
no. of data collected	56451	83123
no. of data used	11786	14088
no. of parameters	343	646
R_{int}	0.0458	0.1433
R_1 [$I > 2\sigma(I)$]	0.0378	0.1116
wR_2 [$I > 2\sigma(I)$]	0.0979	0.2935
R_1 [all data]	0.0537	0.1471
wR_2 [all data]	0.1061	0.3103
GOF	1.052	1.099
Abs. Struc. Para.	-0.011(10)	

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

	$[Tm^{But}]GaB(C_6F_5)_3 \cdot 3(CH_3CN)$	$[Tm^{But}]GaSGaS_3 \cdot C_6H_6$
Lattice	Trigonal	Monoclinic
formula	$C_{45}H_{43}B_2F_{15}GaN_9S_3$	$C_{27}H_{40}BCl_3Ga_2N_6S_4$
formula weight	1182.40	833.49
space group	*P-3*	$P2_1/c$
a/Å	16.5444(8)	15.8552(7)
b/Å	16.5444(8)	12.7781(5)
c/Å	11.2559(11)	18.4005(8)
α/°	90.00	90.00
β/°	90.00	100.1800(10)
γ/°	120.00	90.00
V/Å^3	2668.2(3)	3669.2(3)
Z	2	4
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.472	1.509
μ (Mo Kα), mm^{-1}	0.727	1.943
θ max, deg.	30.50	31.81
no. of data collected	42826	61896
no. of data used	5435	12471
no. of parameters	200	391
R_{int}	0.0647	0.0578
R_1 [$I > 2\sigma(I)$]	0.0354	0.0393
wR_2 [$I > 2\sigma(I)$]	0.0735	0.0845
R_1 [all data]	0.0518	0.0706
wR_2 [all data]	0.0767	0.0958
GOF	1.069	1.011

Computational Details

All calculations were carried out using DFT as implemented in the Jaguar 7.0 suite of *ab initio* quantum chemistry programs.[9] Geometry optimizations were performed with the B3LYP density functional[10] and LACVP** basis sets, *i.e.* 6-31G** (C, H, B, N, F, S, Cl) and LAV3P (Ga, In) basis sets.[11] Cartesian coordinates for geometry optimized structures are listed in Table 2. The energies of the optimized structures were reevaluated by additional single point calculations on each optimized geometry using cc-pVTZ(-f) correlation consistent triple-ζ (C, H, B, N, F, S, Cl) and LAV3P (Ga, In) basis sets.

Table 2. Cartesian Coordinated for Geometry Optimized Structures (energies in parentheses are for the higher basis set)

[Tm$^{Bu^t}$]Ga
-2370.90120951709 Hartrees
(-2371.34240733686 Hartrees)

atom	x	y	z
Ga1	0	0	2.278415787
B2	0	0	-1.918018238
C3	-1.278042236	1.897123816	-0.511159499
C4	-2.266295682	1.031543512	-2.312854366
C5	-3.11413675	1.951197923	-1.803759153
C6	-3.131050541	3.573928524	0.171304121
C7	-2.244226765	4.832735264	0.144208753
C8	-3.333835365	3.042348038	1.602412573
C9	-4.509266904	3.939458752	-0.408807403
C10	-1.0039363	-2.055378952	-0.511159499
C11	0.239804954	-2.478441389	-2.312854366
C12	-0.132718594	-3.672520498	-1.803759153
C13	-1.529587622	-4.498533571	0.171304121
C14	-3.063158126	-4.359925023	0.144208753
C15	-0.967833006	-4.408360138	1.602412573
C16	-1.157037904	-5.874869068	-0.408807403
C17	2.281978537	0.158255136	-0.511159499
C18	2.026490728	1.446897877	-2.312854366
C19	3.246855344	1.721322575	-1.803759153

C20	4.660638164	0.924605047	0.171304121
C21	5.307384891	-0.472810242	0.144208753
C22	4.301668371	1.366012099	1.602412573
C23	5.666304809	1.935410316	-0.408807403
H24	0	0	-3.126566024
H25	-2.367745315	0.396457508	-3.177630854
H26	-4.08313954	2.257420587	-2.151716825
H27	-2.133200984	5.200691847	-0.881444415
H28	-1.254410808	4.630647482	0.554174474
H29	-2.716352006	5.620269072	0.740650425
H30	-3.959750169	2.144434988	1.590641488
H31	-3.837748699	3.806850473	2.202891218
H32	-2.381951192	2.798910498	2.073708406
H33	-5.198983772	3.089855242	-0.403313142
H34	-4.439615525	4.338982443	-1.425529447
H35	-4.944919839	4.719710037	0.220863975
H36	0.840530384	-2.248756346	-3.177630854
H37	0.086586194	-4.664812862	-2.151716825
H38	-3.437330765	-4.447752167	-0.881444415
H39	-3.383052952	-3.401675368	0.554174474
H40	-3.50911979	-5.162564379	0.740650425
H41	0.122739908	-4.501461733	1.590641488
H42	-1.377954869	-5.227013103	2.202891218

H43	-1.232951998	-3.462285492	2.073708406
H44	-0.076401248	-6.047379641	-0.403313142
H45	-1.53786126	-6.014311049	-1.425529447
H46	-1.614928871	-6.642281219	0.220863975
H47	1.527214931	1.852298838	-3.177630854
H48	3.996553346	2.407392275	-2.151716825
H49	5.570531749	-0.75293968	-0.881444415
H50	4.63746376	-1.228972114	0.554174474
H51	6.225471796	-0.457704693	0.740650425
H52	3.83701026	2.357026745	1.590641488
H53	5.215703567	1.42016263	2.202891218
H54	3.61490319	0.663374994	2.073708406
H55	5.27538502	2.957524399	-0.403313142
H56	5.977476784	1.675328606	-1.425529447
H57	6.55984871	1.922571181	0.220863975
N58	-1.133165918	0.993086512	-1.520767634
N59	-2.505377477	2.501643365	-0.680528924
N60	-0.293455189	-1.477893727	-1.520767634
N61	-0.913797967	-3.420542224	-0.680528924
N62	1.426621107	0.484807215	-1.520767634
N63	3.419175444	0.918898858	-0.680528924
S64	-0.126486928	2.232120506	0.730573048
S65	-1.869829598	-1.225601146	0.730573048

S66	1.996316527	-1.00651936	0.730573048

[Tm^{But}]GaB(C_6F_5)$_3$
-4579.1487917336 Hartrees
(-4580.41214701828 Hartrees)

Atom	x	y	z
Ga1	0	0	-0.408185538
B2	0	0	-4.300581627
B3	0	0	1.819476087
C4	-1.424901996	1.770225654	-2.878499599
C5	-2.327195982	0.896320743	-4.712394889
C6	-3.225134362	1.769204028	-4.202225196
C7	-3.346971331	3.385561731	-2.22098378
C8	-2.504556449	4.672913287	-2.264384369
C9	-3.543417728	2.869923702	-0.785445808
C10	-4.730521165	3.684532571	-2.824801075
C11	-1.27826568	-0.930222764	2.217877994
C12	-1.252603087	-2.006978637	3.111651122
C13	-2.36726649	-2.790091222	3.413284235
C14	-3.594567657	-2.503857019	2.828662484
C15	-3.683785085	-1.432590599	1.945970192
C16	-2.544579965	-0.687153262	1.676552011
C17	-0.820609389	-2.119114153	-2.878499599
C18	0.387361458	-2.463571212	-4.712394889
C19	0.080391548	-3.677650302	-4.202225196

C20	-1.2584968	-4.591343064	-2.22098378
C21	-2.794583392	-4.505466153	-2.264384369
C22	-0.713717968	-4.50365162	-0.785445808
C23	-0.825638225	-5.939017787	-2.824801075
C24	2.245511384	0.348888499	-2.878499599
C25	1.939834525	1.567250469	-4.712394889
C26	3.144742814	1.908446274	-4.202225196
C27	4.60546813	1.205781333	-2.22098378
C28	5.299139841	-0.167447134	-2.264384369
C29	4.257135697	1.633727918	-0.785445808
C30	5.55615939	2.254485216	-2.824801075
C31	1.444729385	-0.641899169	2.217877994
C32	2.364396027	-0.081296776	3.111651122
C33	3.599923122	-0.655067307	3.413284235
C34	3.965687614	-1.861058397	2.828662484
C35	3.082552394	-2.473956166	1.945970192
C36	1.867382163	-1.86009426	1.676552011
C37	-0.166463705	1.572121933	2.217877994
C38	-1.111792941	2.088275412	3.111651122
C39	-1.232656632	3.445158529	3.413284235
C40	-0.371119957	4.364915415	2.828662484
C41	0.601232691	3.906546765	1.945970192
C42	0.677197801	2.547247522	1.676552011

F43	-0.119984545	-2.343377093	3.763766033
F44	-2.266124214	-3.812051311	4.277822225
F45	-4.67458354	-3.247181323	3.107583531
F46	-4.857392483	-1.134144235	1.364712644
F47	-2.701299502	0.33669733	0.79255574
F48	2.089416365	1.067778882	3.763766033
F49	4.434395383	-0.056495482	4.277822225
F50	5.149433286	-2.424717436	3.107583531
F51	3.410893961	-3.639553169	1.364712644
F52	1.05906131	-2.507742657	0.79255574
F53	-1.96943182	1.275598211	3.763766033
F54	-2.168271169	3.868546793	4.277822225
F55	-0.474849746	5.671898759	3.107583531
F56	1.446498522	4.773697404	1.364712644
F57	1.642238192	2.171045327	0.79255574
H58	0	0	-5.505537931
H59	-2.382726639	0.275309776	-5.591441151
H60	-4.200362104	2.038407238	-4.563067041
H61	-2.387162937	5.02358816	-3.295262555
H62	-1.516067105	4.524137314	-1.828642139
H63	-3.01527225	5.455115561	-1.694464017
H64	-4.105756569	1.932171622	-0.779800048
H65	-4.1115694	3.613898244	-0.218179608

H66	-2.595300813	2.703400763	-0.277694101
H67	-5.382636647	2.805739902	-2.819680096
H68	-4.666150348	4.081806992	-3.842802405
H69	-5.208093469	4.448494772	-2.206279418
H70	0.95293806	-2.201156687	-5.591441151
H71	0.334868601	-4.656823906	-4.563067041
H72	-3.156973496	-4.579137826	-3.295262555
H73	-3.159984291	-3.575021283	-1.828642139
H74	-3.216632532	-5.338860148	-1.694464017
H75	0.379568575	-4.521775301	-0.779800048
H76	-1.073942986	-5.367672672	-0.218179608
H77	-1.043563331	-3.599296816	-0.277694101
H78	0.261476293	-6.064370027	-2.819680096
H79	-1.201873374	-6.081908235	-3.842802405
H80	-1.248462747	-6.734588635	-2.206279418
H81	1.429788579	1.925846912	-5.591441151
H82	3.865493503	2.618416668	-4.563067041
H83	5.544136433	-0.444450334	-3.295262555
H84	4.676051396	-0.94911603	-1.828642139
H85	6.231904781	-0.116255413	-1.694464017
H86	3.726187993	2.589603679	-0.779800048
H87	5.185512386	1.753774428	-0.218179608
H88	3.638864144	0.895896053	-0.277694101

H89	5.121160355	3.258630125	-2.819680096
H90	5.868023722	2.000101244	-3.842802405
H91	6.456556216	2.286093863	-2.206279418
N92	-1.208702375	0.89906714	-3.899714548
N93	-2.666182565	2.324262452	-3.058920712
N94	-0.174263796	-1.496300533	-3.899714548
N95	-0.679779046	-3.471113058	-3.058920712
N96	1.382966171	0.597233393	-3.899714548
N97	3.345961611	1.146850606	-3.058920712
S98	-0.301365272	2.139302513	-1.606393302
S99	-1.702007687	-1.330641238	-1.606393302
S100	2.003372959	-0.808661275	-1.606393302

$B(C_6F_5)_3$
-2208.20580842365 Hartrees
(-2209.03200680080 Hartrees)

atom	x	y	z
F1	-4.667014074	0.973049528	-1.449470961
F2	1.540646197	-4.513576254	-1.446508355
F3	3.146295088	3.543858352	-1.491612816
F4	-2.044590845	1.51673557	-1.453569601
F5	2.29779394	1.000220678	-1.497058472
F6	-0.270507459	-2.536123493	-1.458345114
C7	-3.830220993	0.204585735	-0.745582401
C8	2.075263011	3.200508048	-0.769557168

C9	1.764575002	-3.405164599	-0.734238722
C10	-2.465637843	0.469484442	-0.725373391
F11	-5.630167149	-1.139233192	-0.01982969
F12	3.832941517	-4.267851583	0.008832604
C13	1.619696344	1.88712791	-0.749391621
C14	0.83853556	-2.36822751	-0.718736317
F15	1.830812432	5.426821087	-0.022826983
C16	2.939244017	-3.280623037	0.005369741
C17	-4.324786231	-0.876882189	-0.019167665
C18	1.402110731	4.166035004	-0.023348749
C19	0.490125513	1.479855781	-0.022490775
C20	-1.543318545	-0.317673559	-0.017102728
C21	1.036838925	-1.176765959	-0.004200316
C22	3.177396935	-2.121698186	0.741562575
C23	0.27933791	3.810577543	0.721787644
C24	-3.45138267	-1.683242072	0.708153164
B25	-0.007460002	-0.007409466	-0.01542383
C26	-0.159414725	2.491384109	0.701865469
C27	2.238251316	-1.097031085	0.717473528
C28	-2.090383281	-1.400003645	0.689861673
C29	4.299673812	-2.005957286	1.458017842
F30	-0.361363331	4.735149491	1.443722917
F31	-3.92755748	-2.715084362	1.411335421

F32	-1.238579241	2.202157978	1.44816506
F33	2.513575762	-0.008156267	1.454938344
F34	-1.296645946	-2.201589521	1.419102855

{[Tm$^{Bu^t}$]GaCl}$^+$

-2830.99699770126 Hartrees

(-2831.47958874028 Hartrees)

Atom	x	y	z
Ga1	-1.86085727	1.678193372	1.373358847
S2	-2.33857529	0.809565498	3.481352825
S3	0.175331086	2.767022992	1.599318505
S4	-3.474286283	3.327220545	1.03974304
Cl5	-1.859916194	0.192779457	-0.211655338
B6	-1.8704337	4.229916576	3.988661222
C7	-1.123514661	1.676162759	4.396448994
C8	0.048417354	3.27776916	5.37237056
C9	0.627156307	2.094426482	5.694777285
C10	0.244385273	-0.394667655	5.139547594
C11	0.585397543	-0.885893617	3.720185033
C12	1.485450836	-0.573538141	6.026783065
C13	-0.924183228	-1.173722604	5.769134941
C14	-0.502116786	4.379028212	1.684377645
C15	-1.537701648	6.19213522	2.408835664
C16	-1.031763309	6.472848996	1.181768301

C17	0.191287871	5.176236782	-0.681775745
C18	-0.631813122	4.119198233	-1.443116658
C19	1.679787861	4.805514031	-0.594193566
C20	0.058402583	6.518036782	-1.420416046
C21	-4.049744441	3.332095219	2.694834634
C22	-4.176171562	3.65962425	4.877437578
C23	-5.329258119	3.062635809	4.486394578
C24	-6.287142834	2.077807455	2.307168244
C25	-7.432223291	1.664479028	3.244368047
C26	-5.644250413	0.795089453	1.743693147
C27	-6.847064193	2.983482902	1.199303761
H28	-1.870905149	5.072897667	4.841650866
H29	0.317691667	4.282297357	5.656199526
H30	1.483067479	1.894912519	6.31331431
H31	-0.276011836	-0.865004193	3.054252054
H32	0.935552908	-1.920375028	3.780834099
H33	1.389357637	-0.283643343	3.285474395
H34	1.313889505	-0.24044977	7.054862597
H35	2.36440716	-0.064200015	5.620590454
H36	1.718662769	-1.640209324	6.065456576
H37	-1.827734991	-1.133422883	5.162131127
H38	-1.150741341	-0.791251403	6.769280245
H39	-0.633269454	-2.223611709	5.867813088

H40	-2.10047767	6.812764018	3.087731036
H41	-1.071476731	7.385786247	0.615931479
H42	-1.695995	4.373620121	-1.42945389
H43	-0.494502945	3.114637019	-1.045069534
H44	-0.303386076	4.104427501	-2.486541557
H45	2.086995937	4.756081538	-1.608217005
H46	1.840900518	3.837900609	-0.121198878
H47	2.238105057	5.5681444	-0.042565894
H48	-0.985017677	6.820304853	-1.551318974
H49	0.487465871	6.39560578	-2.41763254
H50	0.611039354	7.322414319	-0.925380524
H51	-3.858777429	3.983013529	5.855926153
H52	-6.191385004	2.789506827	5.066611715
H53	-7.943395322	2.525379026	3.685831368
H54	-7.094846875	0.993663515	4.039886107
H55	-8.169720889	1.119625052	2.650479737
H56	-4.894460831	1.000688877	0.981190454
H57	-6.426782168	0.189614564	1.277325186
H58	-5.195614563	0.201158923	2.545577717
H59	-7.302054159	3.882851031	1.625635098
H60	-7.623047771	2.437346221	0.655115892
H61	-6.080912747	3.280513812	0.483399659
N62	-1.042458512	3.022971151	4.562231334

N63	-0.105263261	1.089292914	5.082718343
N64	-1.218460183	4.883392763	2.720834262
N65	-0.38668234	5.334309052	0.72331685
N66	-3.370677211	3.820017228	3.764924927
N67	-5.250317417	2.851009727	3.118774552

{[Tm$^{Bu^t}$]GaI}$^+$

-2382.18877339570 Hartrees

(-2382.62899719170 Hartrees)

Atom	x	y	z
Ga1	3.509080181	2.271674424	-2.106578543
I2	3.795439252	-0.154775485	-1.327719345
S3	5.429909995	3.130196224	-3.118200375
S4	3.01414224	3.70027511	-0.327827692
S5	1.783856599	2.57866911	-3.645082466
B6	3.131050956	5.74762823	-3.137115364
H7	3.006652863	6.892741591	-3.472141036
N8	3.812815943	5.023699727	-4.347621976
N9	4.913716793	3.745433615	-5.773797231
N10	4.037315217	5.775315882	-1.858675914
N11	5.154001729	5.430858382	0.015326715
N12	1.682274764	5.231018406	-2.840738306
N13	-0.174590646	4.113854848	-2.413109135
C14	4.687858482	3.989988076	-4.451846641
C15	3.48904756	5.43130923	-5.628722037

C16	4.162501305	4.650009252	-6.507332165
C17	5.788275607	2.662013996	-6.393263629
C18	7.246560978	2.874755413	-5.952057815
C19	5.714532088	2.784727029	-7.924080225
C20	5.243830019	1.281053687	-5.985277188
C21	4.104148419	5.006264065	-0.741568517
C22	5.062895756	6.700614952	-1.793768959
C23	5.751411366	6.492762339	-0.645099662
C24	5.661788137	4.842175607	1.325851448
C25	4.56133984	4.957895922	2.394251609
C26	6.100463363	3.385779379	1.086393437
C27	6.88414189	5.651854633	1.787066181
C28	1.078737084	4.018350161	-2.938667432
C29	0.783169107	6.101330065	-2.252332611
C30	-0.357680705	5.419720167	-1.987215478
C31	-1.199361377	3.002034406	-2.21793196
C32	-2.453504433	3.598803258	-1.559049693
C33	-0.608709018	1.938930298	-1.27342377
C34	-1.589365828	2.42025748	-3.586908904
H35	2.81101416	6.250293948	-5.805660927
H36	4.172811183	4.67717195	-7.58146549
H37	7.599029065	3.869222025	-6.243250038
H38	7.877808825	2.133628191	-6.450575031

H39	7.376853585	2.755051944	-4.876392409
H40	6.092560923	3.746284287	-8.284376567
H41	4.702160747	2.624621061	-8.306737176
H42	6.349506558	2.005734143	-8.352352837
H43	5.813850694	0.508684095	-6.509431441
H44	4.193060285	1.179409514	-6.273797023
H45	5.338310666	1.097523395	-4.915583503
H46	5.210802096	7.434847096	-2.569069685
H47	6.599533742	7.020339604	-0.24867684
H48	3.678927713	4.367939432	2.147074712
H49	4.262792081	6.001805696	2.532166103
H50	4.954429622	4.590623472	3.346521944
H51	5.262978427	2.735301508	0.837486619
H52	6.561563229	3.001969446	2.000884465
H53	6.844740606	3.332934299	0.285711217
H54	6.641755022	6.70195738	1.976574425
H55	7.71460905	5.59220775	1.077270427
H56	7.232395796	5.224077766	2.730025956
H57	1.031445862	7.135450849	-2.076474616
H58	-1.275551439	5.763871093	-1.547107317
H59	-2.924199861	4.368455548	-2.178267587
H60	-2.247381034	4.006417182	-0.564967019
H61	-3.180753013	2.793149647	-1.434347057

H62	0.239789279	1.417619052	-1.7151307
H63	-1.379587307	1.194691178	-1.053971242
H64	-0.29781857	2.391959598	-0.326965692
H65	-1.993834044	3.200294033	-4.239431002
H66	-2.367547129	1.665785235	-3.440396585
H67	-0.748903336	1.940897318	-4.088353309

$[\kappa^2\text{-}Tm^{Bu^t}]_2GaI$

-4751.16230651586 Hartrees

(-4752.04166619027 Hartrees)

Atom	x	y	z
Ga1	0	0	-1.703219428
I2	0	0	-4.438688993
S3	5.602958538	-1.981605213	2.533177935
S4	-0.165618409	-2.04379667	-0.490486841
S5	-2.556030618	-0.020756469	-2.0126026
S6	2.556030618	0.020756469	-2.0126026
S7	-5.602958538	1.981605213	2.533177935
S8	0.165618409	2.04379667	-0.490486841
N9	1.852440927	-3.845951958	-1.122721381
N10	3.737081712	-2.086776152	4.579569822
N11	2.504039576	-2.242741542	0.244879052
N12	-4.358234633	-1.665846843	-0.688867971
N13	2.90355156	-1.385276531	2.648965268
N14	-3.464402141	-0.12445088	0.614698994

N15	3.464402141	0.12445088	0.614698994
N16	-2.90355156	1.385276531	2.648965268
N17	4.358234633	1.665846843	-0.688867971
N18	-3.737081712	2.086776152	4.579569822
N19	-2.504039576	2.242741542	0.244879052
N20	-1.852440927	3.845951958	-1.122721381
C21	1.914468443	-5.92063597	-2.484561667
C22	-0.110206765	-5.367713783	-1.132628137
C23	1.024206861	-4.768970797	-1.985271613
C24	5.199898772	-3.974202151	5.274799454
C25	0.490247974	-4.004097512	-3.20870567
C26	3.197582774	-4.040743731	-0.843570851
C27	-5.83531416	-3.51499443	-1.435546377
C28	-3.557800838	-3.260351965	-2.428276039
C29	3.595083955	-3.046891154	-0.012014056
C30	3.846263468	-2.741038976	6.971969255
C31	4.647403685	-2.590504322	5.665483038
C32	-4.773424675	-2.492410862	-1.879379567
C33	1.445597758	-2.725414403	-0.451727804
C34	5.777989501	-1.572498104	5.907851886
C35	4.0643795	-1.826171749	3.258119926
C36	-5.400639479	-1.574159039	-2.944432705
C37	-4.870592213	-1.836752287	0.590723256

C38	2.383665536	-1.816973117	4.769988404
C39	1.88352441	-1.39074038	3.592559636
C40	-4.310910599	-0.894957958	1.385101044
C41	-3.472627876	-0.614593573	-0.65234465
C42	3.472627876	0.614593573	-0.65234465
C43	4.310910599	0.894957958	1.385101044
C44	-5.777989501	1.572498104	5.907851886
C45	-1.88352441	1.39074038	3.592559636
C46	5.400639479	1.574159039	-2.944432705
C47	-2.383665536	1.816973117	4.769988404
C48	4.870592213	1.836752287	0.590723256
C49	-4.0643795	1.826171749	3.258119926
C50	-3.846263468	2.741038976	6.971969255
C51	-4.647403685	2.590504322	5.665483038
C52	4.773424675	2.492410862	-1.879379567
C53	-1.445597758	2.725414403	-0.451727804
C54	-3.595083955	3.046891154	-0.012014056
C55	3.557800838	3.260351965	-2.428276039
C56	5.83531416	3.51499443	-1.435546377
C57	-5.199898772	3.974202151	5.274799454
C58	-3.197582774	4.040743731	-0.843570851
C59	-0.490247974	4.004097512	-3.20870567
C60	-1.024206861	4.768970797	-1.985271613

C61	0.110206765	5.367713783	-1.132628137
C62	-1.914468443	5.92063597	-2.484561667
H63	1.296588435	-6.581950968	-3.097735454
H64	2.32215896	-6.518625155	-1.663471094
H65	-0.685607737	-6.071562254	-1.742551365
H66	0.297888963	-5.913362285	-0.275215832
H67	2.736297187	-5.564000172	-3.11262299
H68	4.380276913	-4.68845789	5.140998454
H69	5.849260375	-4.344439715	6.075262661
H70	-0.040857595	-4.703373417	-3.862804313
H71	3.76237879	-4.860080598	-1.248106099
H72	-0.788888145	-4.59693584	-0.76651243
H73	-6.126633453	-4.100726187	-2.311537694
H74	-5.450589161	-4.214258725	-0.686589392
H75	5.774930807	-3.920861167	4.349831909
H76	-3.87855804	-3.884933685	-3.268541541
H77	-3.137561308	-3.912236253	-1.655887004
H78	1.312220931	-3.560143511	-3.777376994
H79	3.032753544	-3.467528589	6.879398576
H80	-6.737853608	-3.033651282	-1.046367299
H81	4.526322399	-3.107698699	7.74586495
H82	-0.197208365	-3.208484021	-2.927988305
H83	4.549005773	-2.846067493	0.456159491

H84	-2.779679897	-2.581416618	-2.776323582
H85	-5.599365122	-2.587585407	0.832975245
H86	-5.750696074	-2.183739548	-3.783669177
H87	6.426252949	-1.93578921	6.712401978
H88	6.378339673	-1.429468181	5.008864521
H89	3.43644349	-1.78765861	7.320733293
H90	1.889771266	-1.947299957	5.715323714
H91	-6.259737983	-1.036909062	-2.529373601
H92	-4.681487726	-0.847702181	-3.323733897
H93	5.362863861	-0.606069597	6.214381984
H94	0.880527365	-1.097029306	3.329830538
H95	-4.472161064	-0.693404949	2.428521525
H96	1.410613404	-0.556499898	1.23683603
H97	-5.362863861	0.606069597	6.214381984
H98	4.472161064	0.693404949	2.428521525
H99	-1.410613404	0.556499898	1.23683603
H100	4.681487726	0.847702181	-3.323733897
H101	6.259737983	1.036909062	-2.529373601
H102	-0.880527365	1.097029306	3.329830538
H103	-6.378339673	1.429468181	5.008864521
H104	-3.43644349	1.78765861	7.320733293
H105	-6.426252949	1.93578921	6.712401978
H106	-1.889771266	1.947299957	5.715323714

H107	5.750696074	2.183739548	-3.783669177
H108	5.599365122	2.587585407	0.832975245
H109	-4.526322399	3.107698699	7.74586495
H110	2.779679897	2.581416618	-2.776323582
H111	6.737853608	3.033651282	-1.046367299
H112	-4.549005773	2.846067493	0.456159491
H113	-3.032753544	3.467528589	6.879398576
H114	0.197208365	3.208484021	-2.927988305
H115	-1.312220931	3.560143511	-3.777376994
H116	-5.774930807	3.920861167	4.349831909
H117	3.87855804	3.884933685	-3.268541541
H118	6.126633453	4.100726187	-2.311537694
H119	3.137561308	3.912236253	-1.655887004
H120	-5.849260375	4.344439715	6.075262661
H121	5.450589161	4.214258725	-0.686589392
H122	-4.380276913	4.68845789	5.140998454
H123	0.040857595	4.703373417	-3.862804313
H124	-3.76237879	4.860080598	-1.248106099
H125	0.788888145	4.59693584	-0.76651243
H126	-2.736297187	5.564000172	-3.11262299
H127	-0.297888963	5.913362285	-0.275215832
H128	0.685607737	6.071562254	-1.742551365
H129	-2.32215896	6.518625155	-1.663471094

H130	-1.296588435	6.581950968	-3.097735454
B131	2.520557946	-0.989951675	1.185879052
B132	-2.520557946	0.989951675	1.185879052

[Tm^{But}]GaSGaCl$_3$
-4152.00371287888 Hartrees
(-4152.61419200418 Hartrees)

atom	x	y	z
Ga1	2.301129303	9.693549041	14.54203302
Ga2	2.695879268	13.15081018	13.70436866
S3	3.648801513	8.035529428	15.63732679
S4	0.691559846	10.27404724	16.18462054
S5	0.992685161	8.378427346	13.04028671
S6	3.743144448	11.09553083	13.67454443
Cl7	1.964672074	13.55184627	15.78408746
Cl8	4.172140338	14.65979862	13.09147603
Cl9	0.947863406	13.09818165	12.31747811
B10	0.461358327	6.791276624	16.08030949
C11	2.71798307	7.822239975	17.09174049
C12	1.092882581	7.264269237	18.49240163
C13	2.087728047	7.816372152	19.22692831
C14	4.377331435	8.890182462	18.7708782
C15	5.595488385	8.021468299	18.41236407
C16	4.424938219	10.27324905	18.09497833
C17	4.349987896	9.090665812	20.29536988
C18	-0.651365855	9.218552435	15.82093609

C19	-1.919470996	7.426205295	15.49531183
C20	-2.709943542	8.514549032	15.34295078
C21	-2.454229537	11.06396043	15.47423952
C22	-1.742699854	11.81418418	14.33787025
C23	-2.255958936	11.75035309	16.83723316
C24	-3.960549557	11.01087319	15.16583866
C25	1.450988861	6.787799466	13.58584035
C26	1.666679333	4.959183254	14.82137218
C27	2.294573272	4.726580597	13.64478351
C28	2.797954615	6.04346412	11.4997181
C29	1.702440627	6.322180001	10.45649955
C30	3.514713384	4.736966976	11.11848583
C31	3.842619447	7.173161683	11.56576777
H32	-0.112803111	5.851813111	16.56683229
H33	0.139043188	6.866581821	18.79922871
H34	2.150517583	7.97635339	20.28752152
H35	5.53346839	7.044192987	18.90278286
H36	6.502833083	8.521639548	18.76402702
H37	5.686773142	7.873049518	17.33665942
H38	3.52684302	10.85282145	18.3282218
H39	4.525610996	10.20698452	17.01231486
H40	5.290069627	10.82286672	18.47832745
H41	4.316391375	8.142216957	20.84142451

H42	3.516653369	9.7237844	20.6146071
H43	5.273025549	9.600394689	20.58207316
H44	-2.156453872	6.377443198	15.4215144
H45	-3.757733632	8.573664932	15.11398859
H46	-1.848685167	11.27903898	13.38965919
H47	-0.684403588	11.96997409	14.53414265
H48	-2.199441803	12.80136533	14.22172842
H49	-2.752369537	11.18659136	17.63457865
H50	-2.703080253	12.74806744	16.79606221
H51	-1.201411898	11.87084607	17.08533265
H52	-4.169706853	10.55152249	14.19474438
H53	-4.325624304	12.03971172	15.12191041
H54	-4.531412144	10.49368569	15.9439943
H55	1.543048152	4.322425973	15.6821542
H56	2.806473447	3.846326191	13.3025545
H57	0.97005448	5.508347978	10.43686342
H58	2.164993648	6.387287452	9.467085502
H59	1.183743202	7.260718017	10.64941844
H60	2.8274534	3.88714779	11.05563752
H61	4.330109676	4.49456786	11.80664927
H62	3.9556283	4.874404982	10.12812717
H63	4.36096907	7.232558255	10.60379746
H64	4.5873941	6.964495081	12.34000902

H65	3.393533415	8.146157018	11.76273141
N66	1.480399392	7.269341955	17.16484621
N67	3.107048609	8.16861443	18.35412605
N68	-0.642373163	7.858345715	15.80132053
N69	-1.924713467	9.637523327	15.55022517
N70	1.144755395	6.238224335	14.78992815
N71	2.162726219	5.868338183	12.8678602

{[Tm$^{Bu^t}$]Ga(GaI$_2$)Ga[Tm$^{Bu^t}$]}$^+$
-4766.67393430275 Hartrees
(-4767.55105052252 Hartrees)

Atom	x	y	z
Ga1	-2.285200621	0.011999967	0.082754283
Ga2	2.285200621	-0.011999967	0.082754283
Ga3	0	0	1.210546491
I4	-0.050019563	2.205862654	2.776466932
I5	0.050019563	-2.205862654	2.776466932
S6	-2.434915827	0.398848204	-2.326696386
S7	2.434915827	-0.398848204	-2.326696386
S8	-3.594216685	-2.000103647	0.277611619
S9	-3.816905996	1.680675082	0.910345047
S10	3.594216685	2.000103647	0.277611619
S11	3.816905996	-1.680675082	0.910345047
B12	-5.780040553	0.063960148	-1.453694072
B13	5.780040553	-0.063960148	-1.453694072
N14	-3.459064789	-1.733270206	-3.793147118

N15	-4.927799738	-0.798095971	-2.440985011
N16	-5.340515506	1.559380666	-1.400323697
N17	-4.591743835	3.583794779	-0.949116054
N18	-5.955585706	-0.589385081	-0.050524543
N19	3.459064789	1.733270206	-3.793147118
N20	4.927799738	0.798095971	-2.440985011
N21	-5.862033084	-1.699409956	1.853968263
N22	5.340515506	-1.559380666	-1.400323697
N23	4.591743835	-3.583794779	-0.949116054
N24	5.955585706	0.589385081	-0.050524543
N25	5.862033084	1.699409956	1.853968263
C26	-2.50979138	-3.244023214	-5.521183703
C27	-4.659112832	-2.414997923	-3.934167958
C28	-5.555785911	-1.838374054	-3.102184492
C29	-1.829086079	-0.842889679	-5.442862169
C30	-5.795988308	2.414254435	-2.387839009
C31	-2.212222923	-2.061031493	-4.583279005
C32	-5.339998016	3.65818313	-2.115117096
C33	1.829086079	0.842889679	-5.442862169
C34	2.50979138	3.244023214	-5.521183703
C35	-3.638172199	-0.743675193	-2.862984391
C36	2.212222923	2.061031493	-4.583279005
C37	-4.216461764	6.030839791	-1.146076191

C38	-1.085793775	-2.476205636	-3.620021355
C39	-7.135917826	-0.36563763	0.634496869
C40	-4.59680801	2.283106108	-0.524200972
C41	4.659112832	2.414997923	-3.934167958
C42	1.085793775	2.476205636	-3.620021355
C43	-3.915234782	4.778468722	-0.3040636
C44	3.638172199	0.743675193	-2.862984391
C45	5.555785911	1.838374054	-3.102184492
C46	-4.491674728	4.988191133	1.107342434
C47	-5.176006939	-1.405307419	0.707899551
C48	-2.39266602	4.554714136	-0.282111739
C49	-7.082879577	-1.044767509	1.802665233
C50	5.795988308	-2.414254435	-2.387839009
C51	5.339998016	-3.65818313	-2.115117096
C52	4.216461764	-6.030839791	-1.146076191
C53	2.39266602	-4.554714136	-0.282111739
C54	3.915234782	-4.778468722	-0.3040636
C55	4.59680801	-2.283106108	-0.524200972
C56	-5.159269779	-3.995801245	2.522560082
C57	-5.417914322	-2.563470514	3.021530511
C58	-6.550020627	-2.606589032	4.062209894
C59	4.491674728	-4.988191133	1.107342434
C60	-4.172890648	-1.936608051	3.671521119

C61	5.176006939	1.405307419	0.707899551
C62	7.135917826	0.36563763	0.634496869
C63	7.082879577	1.044767509	1.802665233
C64	5.159269779	3.995801245	2.522560082
C65	5.417914322	2.563470514	3.021530511
C66	4.172890648	1.936608051	3.671521119
C67	6.550020627	2.606589032	4.062209894
H68	-3.294966103	-3.013804263	-6.247872312
H69	-2.648246804	-0.573673629	-6.11790509
H70	-4.784783184	-3.238914334	-4.611491311
H71	-6.419390707	2.062770481	-3.19391717
H72	-6.594280307	-2.070421313	-2.928672359
H73	-1.599377121	-3.463521387	-6.084766575
H74	-5.499551008	4.577824423	-2.646928488
H75	2.648246804	0.573673629	-6.11790509
H76	-0.956252968	-1.095290031	-6.052818628
H77	0.956252968	1.095290031	-6.052818628
H78	-2.780098246	-4.150966716	-4.972127173
H79	3.294966103	3.013804263	-6.247872312
H80	1.599377121	3.463521387	-6.084766575
H81	-6.8830243	0.079845041	-1.933678436
H82	-1.580157907	0.024313399	-4.830339594
H83	-5.2867692	6.254629442	-1.194367039

H84	1.580157907	-0.024313399	-4.830339594
H85	-3.816209308	5.955784367	-2.162021065
H86	2.780098246	4.150966716	-4.972127173
H87	-7.91711543	0.252168461	0.223288401
H88	0.213524247	2.785847646	-4.203889625
H89	4.784783184	3.238914334	-4.611491311
H90	-0.213524247	-2.785847646	-4.203889625
H91	-3.727957341	6.882335632	-0.666114063
H92	-1.401702306	-3.323149909	-3.002903693
H93	-0.786092563	-1.657912094	-2.966369579
H94	-5.576378523	5.131685579	1.064982999
H95	-2.019328326	4.358512044	-1.292788898
H96	0.786092563	1.657912094	-2.966369579
H97	6.419390707	-2.062770481	-3.19391717
H98	1.401702306	3.323149909	-3.002903693
H99	5.499551008	-4.577824423	-2.646928488
H100	3.816209308	-5.955784367	-2.162021065
H101	6.594280307	2.070421313	-2.928672359
H102	-7.814387632	-1.118731402	2.585333639
H103	-4.047125553	5.888150801	1.542702132
H104	-1.906931732	5.462387361	0.089002051
H105	2.019328326	-4.358512044	-1.292788898
H106	-4.270509839	4.150319362	1.768719532

H107	5.2867692	-6.254629442	-1.194367039
H108	-2.103626	3.731764239	0.371429868
H109	3.727957341	-6.882335632	-0.666114063
H110	6.8830243	-0.079845041	-1.933678436
H111	-6.056326735	-4.410168284	2.05040752
H112	1.906931732	-5.462387361	0.089002051
H113	-4.332602168	-4.039354452	1.813282264
H114	-7.470538083	-3.042300712	3.661094946
H115	2.103626	-3.731764239	0.371429868
H116	-6.767720704	-1.619761534	4.481639158
H117	-3.305802075	-1.950802755	3.011656316
H118	-4.903570523	-4.627868005	3.378110488
H119	5.576378523	-5.131685579	1.064982999
H120	-4.373531524	-0.904140163	3.974546944
H121	4.047125553	-5.888150801	1.542702132
H122	-6.220391791	-3.243098536	4.886827057
H123	7.91711543	-0.252168461	0.223288401
H124	4.270509839	-4.150319362	1.768719532
H125	-3.914309766	-2.508265101	4.567883197
H126	4.332602168	4.039354452	1.813282264
H127	3.305802075	1.950802755	3.011656316
H128	6.056326735	4.410168284	2.05040752
H129	7.814387632	1.118731402	2.585333639

H130	4.373531524	0.904140163	3.974546944
H131	4.903570523	4.627868005	3.378110488
H132	3.914309766	2.508265101	4.567883197
H133	7.470538083	3.042300712	3.661094946
H134	6.767720704	1.619761534	4.481639158
H135	6.220391791	3.243098536	4.886827057

{[κ^1,κ^2-Tm$^{Bu^t}$]GaI_2GaI_2GaI}$^-$
-2432.37072390506 Hartrees
(-2432.81391860458 Hartrees)

Atom	x	y	z
Ga1	3.670400332	-14.6833827	21.14131564
Ga2	1.543426093	-16.05305126	21.59861401
Ga3	-0.700605735	-14.84861795	21.40143249
I4	6.093253931	-15.72396801	20.45550751
I5	1.808109302	-16.8769283	24.18834301
I6	1.586278148	-18.18876802	19.9758123
I7	-1.26046443	-13.53339918	19.06719334
I8	-2.97164883	-16.11519714	22.1436765
S9	4.727626025	-13.25542383	22.90350936
S0	3.449449965	-12.9802914	19.27314643
S11	-0.851326782	-12.98075497	23.15821437
B12	1.954935513	-11.78201195	21.98533786
N13	2.441759921	-11.80370357	23.47422372
N14	3.624056748	-12.29607056	25.26923992
N15	3.039101359	-11.02107586	21.16565096

N6	4.604167228	-10.48990301	19.7053718
N17	0.59115107	-11.02153631	21.87828175
N18	-1.559316345	-10.53496872	22.01915847
C19	3.545283939	-12.46618001	23.90880108
C20	1.825821719	-11.21546312	24.55957401
C21	2.550240155	-11.50776447	25.6656987
C22	4.660632683	-12.85347552	26.21204114
C23	6.031618488	-12.23833245	25.87532634
C24	4.28810827	-12.45999031	27.65253331
C25	4.674980372	-14.38872155	26.11374957
C26	3.700735135	-11.46494812	20.06087726
C27	3.559354007	-9.790902549	21.52634569
C28	4.510198018	-9.451708969	20.62579273
C29	5.578308069	-10.51493982	18.55481956
C30	6.358554627	-9.188027	18.53075513
C31	6.578048455	-11.66859512	18.75209412
C32	4.799251508	-10.64198168	17.2329387
C33	-0.614582022	-11.48715088	22.31832995
C34	0.387988468	-9.798771478	21.26634719
C35	-0.927943778	-9.492892455	21.35622584
C36	-3.023449946	-10.53222068	22.39302094
C37	-3.139472502	-10.52103889	23.92832687
C38	-3.674445168	-9.251151909	21.84070122

C39	-3.736864914	-11.74615418	21.77588929
H40	1.829638267	-12.8892762	21.57907709
H41	0.906272749	-10.66437782	24.46396638
H42	2.371235595	-11.2421262	26.69091599
H43	6.350880086	-12.49943393	24.86569295
H44	6.778845841	-12.61604782	26.5806636
H45	5.99781745	-11.14667849	25.96398041
H46	5.044439093	-12.87864116	28.32162395
H47	3.31947368	-12.87081352	27.95246019
H48	4.282354177	-11.37505079	27.80210701
H49	4.987736751	-14.73119598	25.12818843
H50	3.681688353	-14.80075984	26.3110713
H51	5.373466667	-14.78535218	26.85785235
H52	3.219895476	-9.266583352	22.40553066
H53	5.122013202	-8.570001819	20.57251771
H54	5.702637996	-8.321243181	18.3971841
H55	7.043700632	-9.216199856	17.67941073
H56	6.96351694	-9.046183896	19.43182894
H57	6.085017176	-12.6402417	18.7675981
H58	7.123347569	-11.54629693	19.69298813
H59	7.30216893	-11.65876048	17.9306114
H60	4.237908153	-11.57517871	17.18524918
H61	5.505666352	-10.62088086	16.39688531

H62	4.102089222	-9.805477547	17.11414044
H63	1.185785682	-9.253749963	20.79197633
H64	-1.454903974	-8.633769333	20.98440099
H65	-4.19695916	-10.48817879	24.20943243
H66	-2.64643973	-9.636884632	24.34890269
H67	-2.696712921	-11.41787664	24.36349341
H68	-4.730921301	-9.264238975	22.12096929
H69	-3.625146108	-9.203784168	20.74847362
H70	-3.234664821	-8.340828629	22.26208581
H71	-4.809494016	-11.66428628	21.9813813
H72	-3.380221611	-12.68720893	22.19238782
H73	-3.586892802	-11.77640026	20.69373199

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.; Drezdzon, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2nd 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) (a) Tesmer, M.; Shu, M.; Vahrenkamp, H. *Inorg. Chem.* **2001**, *40*, 4022-4029.

(b) Singh, A. K.; Mehtab, S.; Singh, U. P.; Aggarwal, V. *Anal. Bioanal. Chem.* **2007**, *388*, 1867-1876.

(5) Nogai, S.; Schmidbaur, H. *Inorg. Chem.* **2002**, *41*, 4770-4774.

(6) Mihalcik, D. J.; White, J. L.; Tanski, J. M.; Zakharov, L. N.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2004**, 1626-1634.

(7) Green, M. L. H.; Mountford, P.; Smout, G. J.; Speel, S. R. *Polyhedron* **1990**, *9*, 2763-2765.

(8) (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.

(9) Jaguar 6.5, Schrödinger, LLC, Portland, Oregon.

(10) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

(b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100.

(c) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

(d) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200-1211.

(e) Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent -- Field for Molecules and Solids*; McGraw-Hill: New York, 1974.

(11) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270-283.

(b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284-298.

(c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310.