Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Monovalent Indium in a Sulfur-Rich Coordination Environment: Synthesis, Structure and Reactivity of *Tris*(2-mercapto-1-t-butylimidazolyl)hydroborato Indium, $[Tm^{Bu^t}]In$

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EXPERIMENTAL SECTION

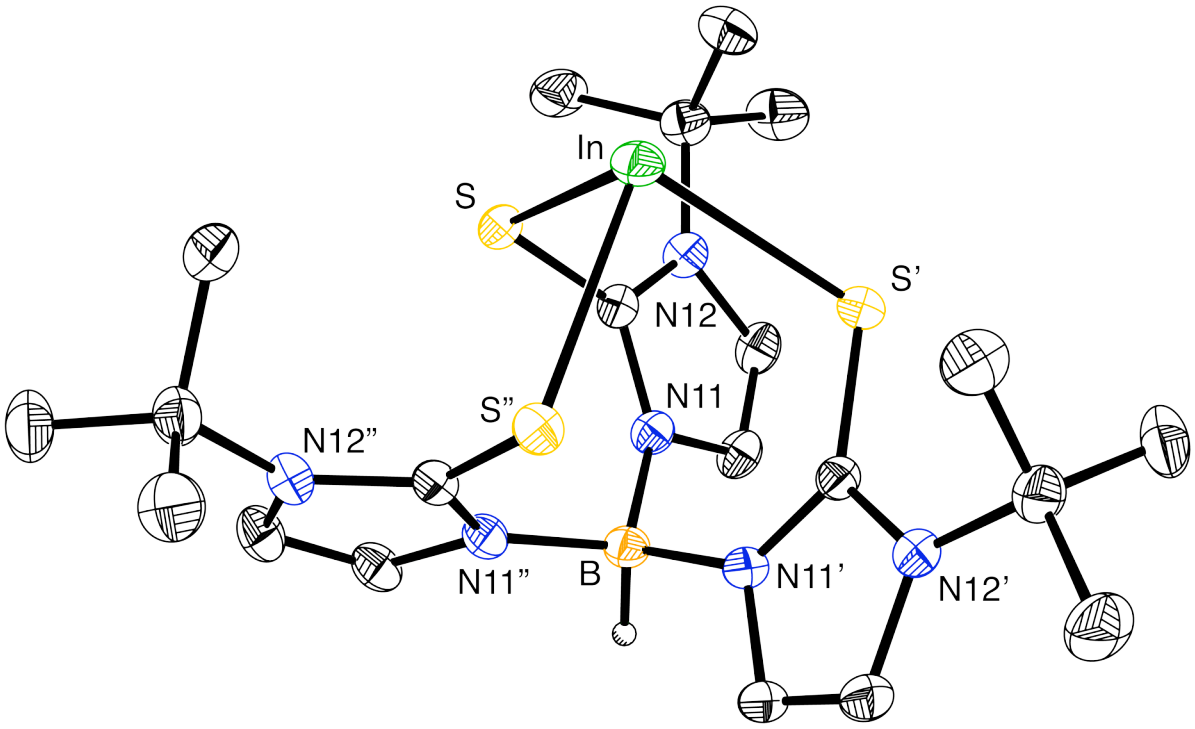
General Considerations

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 128.06 for C_6D_6[2] and 67.4 for the downfield signal of THF–d_8[3]). ^{19}F NMR spectra are reported in ppm relative to $CFCl_3$ ($\delta = 0$) and were referenced using external $PhCF_3$ in $CDCl_3$ ($\delta = -63.7$).[4] 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[5] and [Tm^{But}]Tl[6] were prepared by the literature methods. InCl (Strem), $InCl_3$ (Aldrich) and InI_3 (Ventron Division of Morton Thiokol) were obtained commercially and used as received.

Synthesis of [Tm^{But}]In

A mixture of InCl (340 mg, 2.26 mmol) and [Tm^{But}]K (1.00 g, 1.94 mmol) was treated with methanol (25 mL) at -78˚C and the suspension was stirred for 1.5 hours, thereby resulting in the formation of a dark olive green precipitate. The volatile components were removed at 0˚C to give a brown solid that was extracted into benzene (20 mL). The volatile components were removed from the golden filtrate by lyophilization giving [Tm^{But}]In as a pale yellow solid (395 mg, 34 % yield). Colorless crystals of composition [Tm^{But}]In•(C_6H_6) suitable for X-ray diffraction were obtained from vapor diffusion of pentane into a solution in benzene. Analysis calcd. [Tm^{But}]In(C_6H_6)$_{0.5}$: C, 45.7%; H, 5.9%;

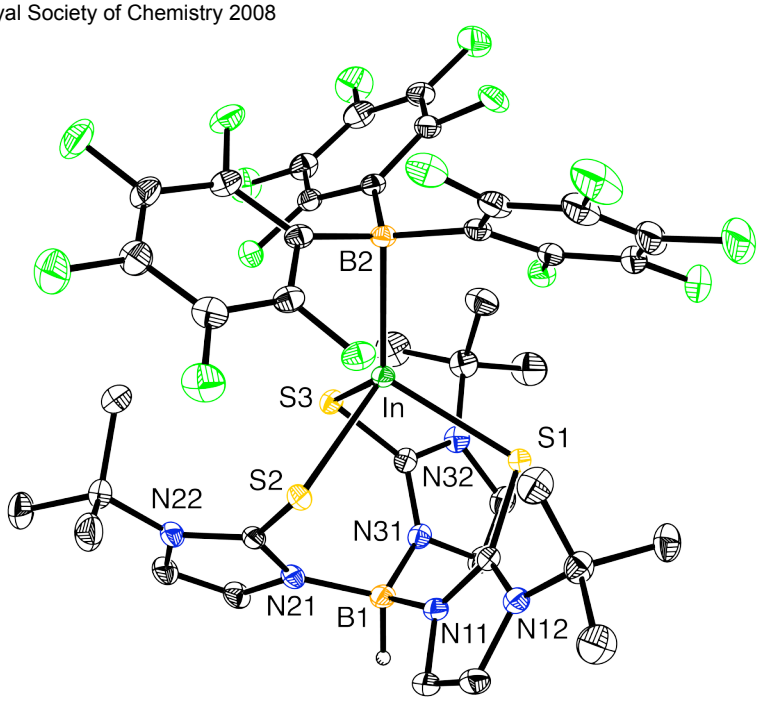
N, 13.3%. Found: C, 44.9%; H, 6.2%; N, 12.5%. ^{1}H NMR (C_6D_6): 1.58 [s, 27 H of $HB\{C_3N_2H_2[C(C\underline{H}_3)_3]S\}_3$], 6.45 [d, $^{3}J_{H\text{-}H}$ = 2, 3 H of $HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3$], 6.72 [d, $^{3}J_{H\text{-}H}$ = 2, 3 H of $HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3$]. $^{13}C\{^{1}H\}$ NMR (C_6D_6): 29.2 [9 C, $HB\{C_3N_2H_2[C(\underline{C}H_3)_3]S\}_3$], 58.9 [3 C, $HB\{C_3N_2H_2[\underline{C}(CH_3)_3]CS\}_3$], 116.1 [3 C of $HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3$], 121.7 [3 C of $HB\{\underline{C}_2N_2H_2[C(CH_3)_3]S\}_3$], 160.3 [3 C, $HB\{C_2N_2H_2[C(CH_3)_3]\underline{C}S\}_3$]. IR Data (KBr, cm^{-1}): 3420 (br), 3180 (w), 3145 (w), 3033 (w), 2978 (s), 2923 (m), 2435 (br), 1567 (m), 1479 (m), 1452 (w), 1420 (s), 1397 (s), 1356 (vs), 1300 (m), 1262 (m), 1224 (m), 1198 (vs), 1170 (s), 1109 (m), 1062 (w), 1027 (w), 928 (w), 821 (m), 754 (m), 722 (m), 681 (s), 589 (w), 553 (w), 494 (w), 464 (w). FAB-MS: *m*/*z* = 591.9 $[M]^{+}$, M = $[Tm^{But}]In$.



Molecular structure of [Tm^{But}]In

Synthesis of $[Tm^{But}]InB(C_6F_5)_3$

A mixture of $[Tm^{But}]In$ (50 mg, 0.084 mmol) and $B(C_6F_5)_3$ (44 mg, 0.086 mmol) was treated with toluene (1 mL) and the resulting yellow solution was placed at -35°C for a period of 5 days, thereby resulting in the deposition of pale yellow crystals. The crystals were washed with hexanes (2 × 0.5 mL) and dried *in vacuo* to give $[Tm^{But}]InB(C_6F_5)_3$ as a pale yellow solid (45 mg, 49% yield). Crystals suitable for elemental analysis were obtained from benzene. Analysis calcd. $[Tm^{But}]InB(C_6F_5)_3 \bullet (C_6H_6)$: C, 45.7%; H, 3.4%; N, 7.1%. Found: C, 45.5%; H, 3.1%; N, 7.1%. ^1H NMR (C_6D_6): 1.12 [s, 27 H of $HB\{C_3N_2H_2[C(C\underline{H}_3)_3]S\}_3$], 6.21 [d, $^3J_{H-H} = 2$, 3 H of $HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3$], 6.39 [d, $^3J_{H-H} = 2$, 3 H of $HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 28.2 [9 C, $HB\{C_3N_2H_2[C(\underline{C}H_3)_3]S\}_3$], 60.1 [3 C, $HB\{C_3N_2H_2[\underline{C}(CH_3)_3]CS\}_3$], 118.1 [3 C of $HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3$], 123.0 [3 C of $HB\{\underline{C}_2N_2H_2[C(CH_3)_3]S\}_3$], 153.8 [3 C of $HB\{C_2N_2H_2[C(CH_3)_3]\underline{C}S\}_3$], 18 C of $B(\underline{C}_6F_5)_3$ were not observed. $^{19}F\{^1H\}$ NMR (C_6D_6): -166.9 [m, 6 *m*-F of $B(C_6\underline{F}_5)_3$], -163.4 [t, $^3J_{F-F} = 20$, 3 *p*-F of $B(C_6\underline{F}_5)_3$], -130.4 [d, $^3J_{F-F} = 18$, 6 *o*-F of $B(C_6\underline{F}_5)_3$]. IR Data (KBr, cm^{-1}): 3448(br), 3192(w), 3152(w), 3091(w), 3071(w), 3036(w), 2982(m), 2930(w), 2668(w), 2422(br), 2299(w), 2234(w), 1963(w), 1819(w), 1642(m), 1601(w), 1566(m), 1512(vs), 1461(vs), 1422(s), 1400(m), 1361(vs), 1312(s), 1280(s), 1230(m), 1195(vs), 1177(vs), 1131(m), 1098(vs), 1033(m), 980(vs), 962(vs), 929(w), 821(m), 772(s), 730(s), 683(s), 659(s), 615(m), 588(m), 573(m), 552(m), 543(w), 519(w), 495(m), 459(w).

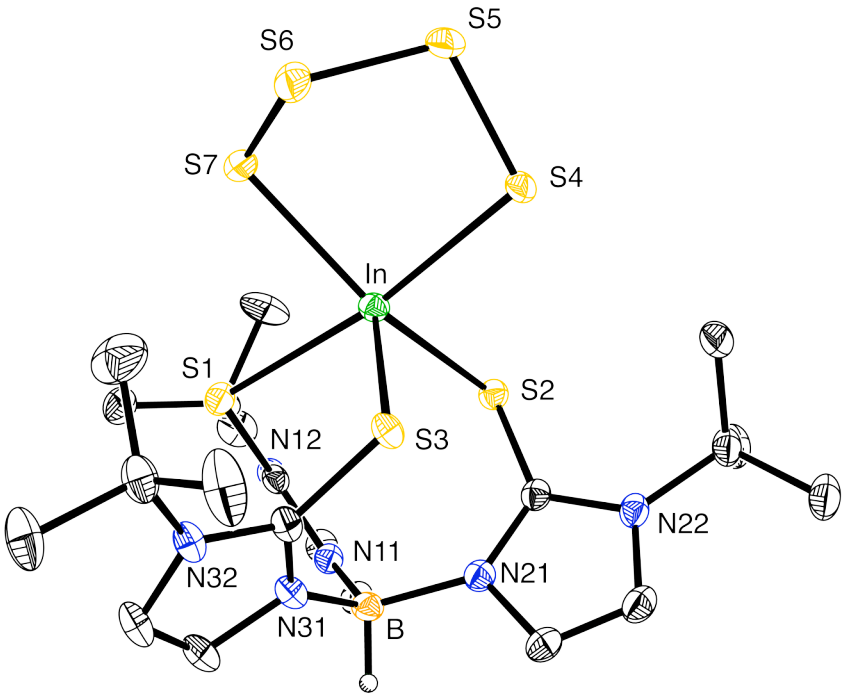


Molecular structure of [Tm^{But}]InB(C$_6$F$_5$)$_3$

Synthesis of [Tm^{But}]In(κ^2–S$_4$)

A mixture of [Tm^{But}]In (50 mg, 0.084 mmol) and S_8 (11 mg, 0.043 mmol) was treated with THF (2 mL). The resulting yellow solution was stirred for 1 day, after which the volatile components were removed *in vacuo*, thereby giving a yellow solid that was extracted into acetonitrile (2 × 1 mL). The volatile components were removed from the combined extract *in vacuo* to give [Tm^{But}]InS$_4$ as a pale yellow solid (27 mg, 45% yield). Colorless crystals of composition [Tm^{But}]InS$_4$ suitable for X-ray diffraction were obtained from benzene. Crystals suitable for elemental analysis were obtained from THF. Analysis calcd. [Tm^{But}]InS$_4$•0.5(THF): C, 36.5%; H, 5.1%; N, 11.1%. Found: C, 37.4%; H, 5.1%; N, 11.8%. ^{1}H NMR (CD_3CN): 1.71 [s, 27 H of HB{$C_3N_2H_2$[C($\underline{C}H_3$)$_3$]S}$_3$], 4.3 [br, 1 H of $\underline{H}$B{$C_3N_2H_2$[C(CH_3)$_3$]S}$_3$], 6.87 [d, $^3J_{H\text{-}H}$ = 2, 3 H of HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$], 7.23 [d, $^3J_{H\text{-}H}$ = 2, 3 H of HB{$C_3N_2\underline{H}_2$[C(CH_3)$_3$]S}$_3$]. ^{13}C{^{1}H} NMR (THF- d_8): 30.3 [9 C, HB{$C_3N_2H_2$[C($\underline{C}H_3$)$_3$]S}$_3$], 60.5 [3 C, HB{$C_3N_2H_2$[$\underline{C}$(CH_3)$_3$]CS}$_3$], 119.3 [3 C of HB{$\underline{C}_2N_2H_2$[C(CH_3)$_3$]CS}$_3$], 124.6 [3 C of HB{$\underline{C}_2N_2H_2$[C(CH_3)$_3$]S}$_3$], 154.2 [3 C of

$HB\{C_2N_2H_2[C(CH_3)_3]\underline{C}S\}_3]$. IR Data (KBr, cm^{-1}): 2976 (s), 2959 (s), 2885 (w), 2426 (m), 2299 (w), 2241 (w), 1567 (s), 1480 (m), 1421 (s), 1398 (s), 1359 (vs), 1308 (s), 1259 (m), 1230 (s), 1198 (vs), 1102 (m), 1073 (m), 1030 (w), 978 (w), 945 (w), 929 (w), 822 (s), 769 (s), 732 (vs), 685 (vs).

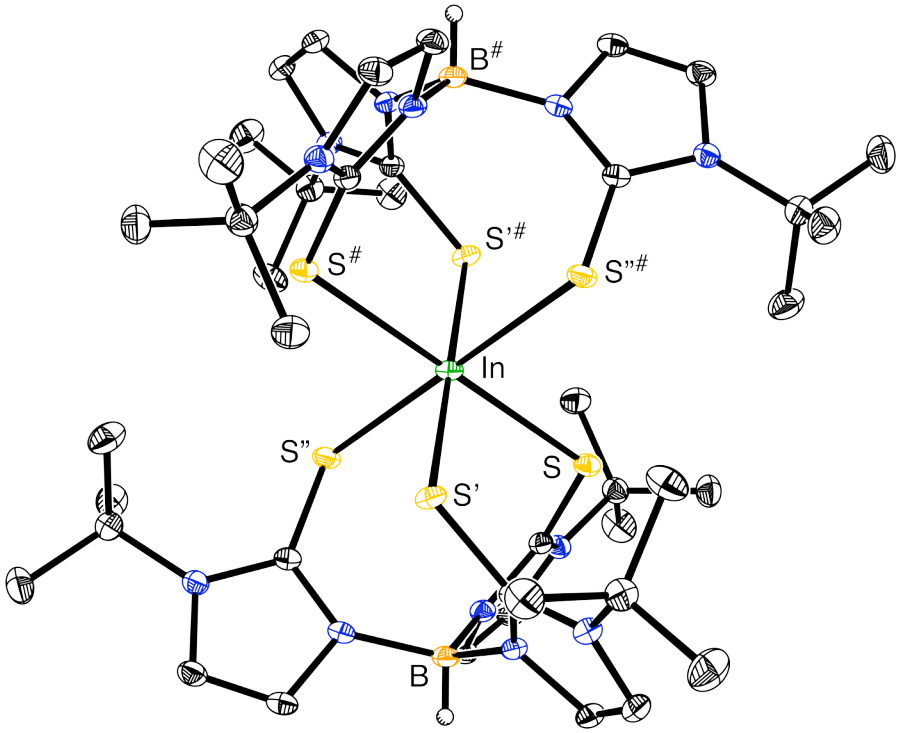


Molecular structure of [Tm^{But}]In(κ^2–S_4)

Synthesis of [(Tm^{But})$_2$In]I

A mixture of InI_3 (110 mg, 0.222 mmol) and [Tm^{But}]Tl (300 mg, 0.440 mmol) was treated with THF (3 mL), thereby resulting in the immediate deposition of a yellow precipitate. The mixture was stirred for one hour and the volatile components were removed *in vacuo*. The orange solid was extracted into CH_2Cl_2 (5 mL) and filtered. The volatile components were removed from the filtrate *in vacuo*, giving [(Tm^{But})$_2$In]I as a white solid (195 mg, 73% yield). Colorless crystals suitable for X-ray diffraction were obtained by vapor diffusion of Et_2O into a solution of [(Tm^{But})$_2$In]I in a mixture of benzene and CH_2Cl_2. Crystals suitable for elemental analysis were obtained from THF. Analysis calcd. [(Tm^{But})$_2$In]I•2(THF): C, 44.8%; H, 6.3%; N, 12.5%. Found: C, 45.0%; H, 5.8%; N,

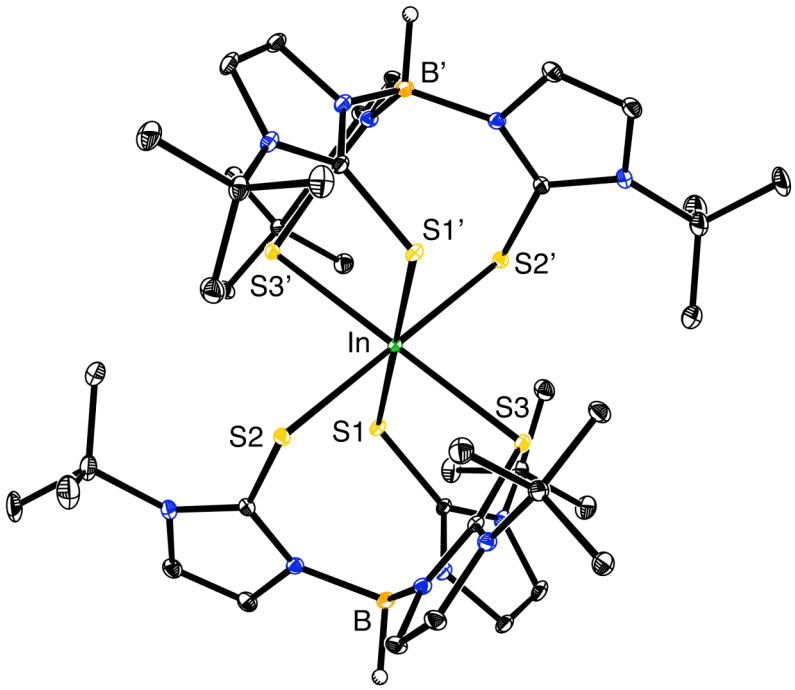
12.3%. ^{1}H NMR ($CDCl_3$): 1.74 [s, 54 H of $(HB\{C_3N_2H_2[C(C\underline{H}_3)_3]S\}_3)_2$], 4.4 [br, 2 H of $(\underline{H}B\{C_3N_2H_2[C(CH_3)_3]S\}_3)_2$], 6.82 [d, $^{3}J_{H\text{-}H}$ = 2, 6 H of $(HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3)_2$], 7.08 [d, $^{3}J_{H\text{-}H}$ = 2, 6 H of $(\underline{H}B\{C_3N_2H_2[C(CH_3)_3]S\}_3)_2$]. ^{13}C NMR ($CDCl_3$): 30.2 [q, $^{1}J_{C\text{-}H}$ = 128, 18 C, $(HB\{C_3N_2H_2[C(\underline{C}H_3)_3]S\}_3)_2$], 60.1 [s, 6 C, $(HB\{C_3N_2H_2[\underline{C}(CH_3)_3]CS\}_3)_2$], 118.4 [d, $^{1}J_{C\text{-}H}$ = 195, 6 C of $(HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3)_2$], 124.0 [d, $^{1}J_{C\text{-}H}$ = 196, 6 C of $(HB\{\underline{C}_2N_2H_2[C(CH_3)_3]S\}_3)_2$], 153.2 [s, 6 C, $(HB\{C_2N_2H_2[C(CH_3)_3]\underline{C}S\}_3)_2$]. IR Data (KBr, cm^{-1}): 3422 (br), 3141 (w), 3083 (w), 2977 (s), 2925 (m), 2421 (br), 2248 (w), 1567 (m), 1479 (m), 1458 (w), 1420 (vs), 1398 (m), 1356 (vs), 1309 (s), 1261 (m), 1228 (s), 1198 (vs), 1177 (vs), 1105 (w), 1073 (m), 1032 (w), 929 (w), 823 (m), 768 (m), 733 (s), 687 (s), 591 (m), 552 (m), 496 (m), 459 (m). FAB-MS: m/z = 1069.2 $[M]^+$, M = $[(Tm^{But})_2In]$.



Molecular structure of $[(Tm^{But})_2In]I$ (only the cation is shown)

Synthesis of $[(Tm^{But})_2In]Cl$

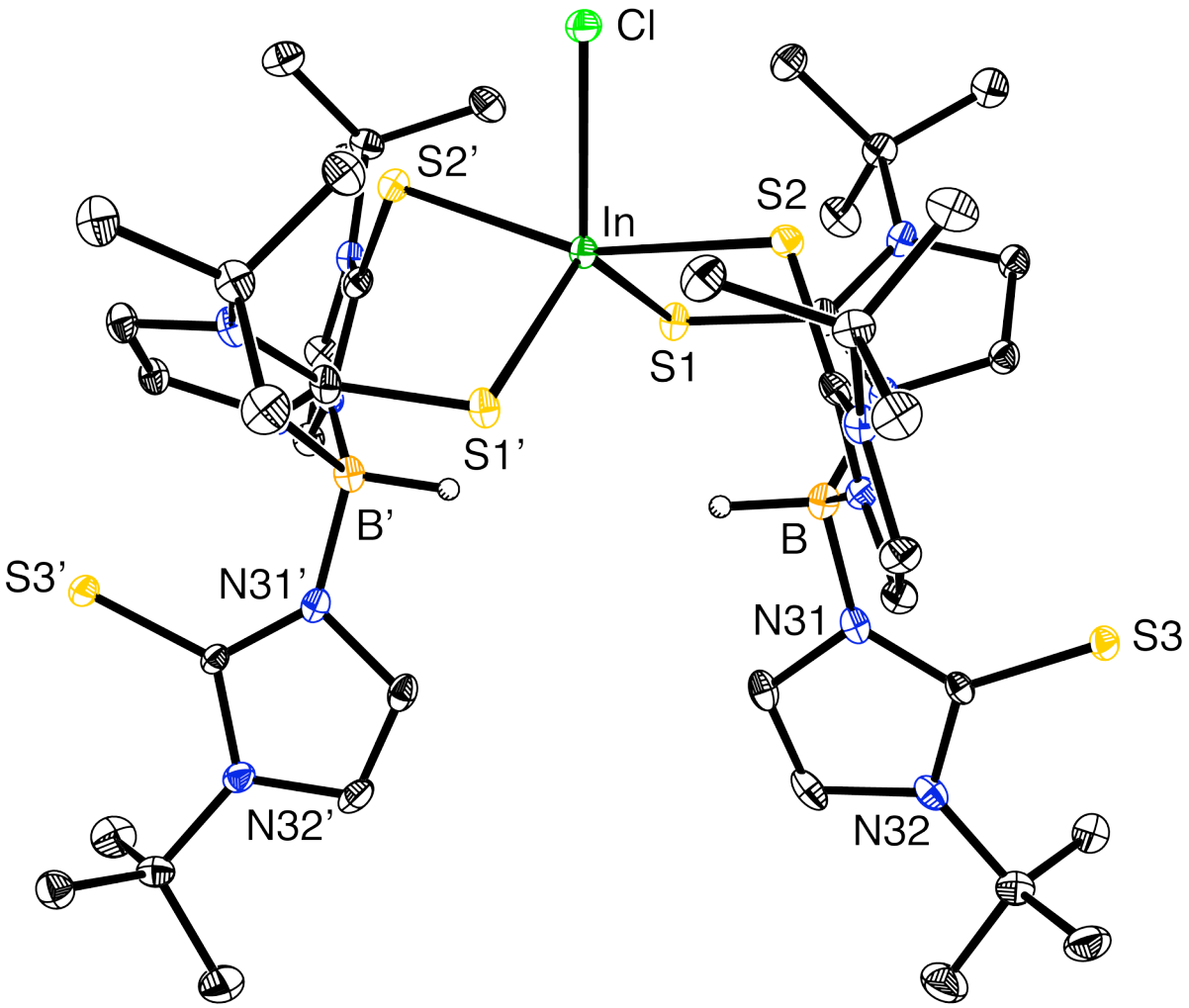
A solution of $InCl_3$ (21 mg, 0.095 mmol) in acetonitrile (2 mL) was added to a solution of $[Tm^{But}]K$ (100 mg, 0.19 mmol) in acetonitrile (1 mL) over a period of 30 minutes. The mixture was stirred for 3 hours and the volatile components were removed *in vacuo*. The white solid was washed with C_6H_6 (2 × 1 mL) and extracted into CH_3CN (2 × 1 mL). The volatile components of the extract were removed *in vacuo* giving $[(Tm^{But})_2In]Cl$ as a white solid (65 mg, 62% yield). Colorless crystals of the composition $[(Tm^{But})_2In]Cl$ suitable for X-ray diffraction were obtained from a concentrated solution in CH_3CN. Crystals suitable for elemental analysis were obtained from $CHCl_3$. Analysis calcd. $[(Tm^{But})_2In]Cl \cdot 2.25(CHCl_3)$: C, 38.7%; H, 5.2%; N, 12.2%. Found: C, 38.6%; H, 5.0%; N, 12.2%. ^{1}H NMR ($CDCl_3$): 1.74 [s, 54 H of $(HB\{C_3N_2H_2[C(C\underline{H}_3)_3]S\}_3)_2$], 4.4 [br, 2 H of $(\underline{H}B\{C_3N_2H_2[C(CH_3)_3]S\}_3)_2$], 6.82 [d, $^3J_{H\text{-}H}$ = 2, 6 H of $(HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3)_2$], 7.10 [d, $^3J_{H\text{-}H}$ = 2, 6 H of $(HB\{C_3N_2\underline{H}_2[C(CH_3)_3]S\}_3)_2$] ^{13}C NMR ($CDCl_3$): 29.9 [18 C, $(HB\{C_3N_2H_2[C(\underline{C}H_3)_3]S\}_3)_2$], 59.9 [6 C, $(HB\{C_3N_2H_2[\underline{C}(CH_3)_3]S\}_3)_2$], 118.2 [6 C of $(HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3)_2$], 123.7 [6 C of $(HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CS\}_3)_2$], 6 C of $(HB\{C_2N_2H_2[C(CH_3)_3]\underline{C}S\}_3)_2$ were not observed. IR Data (KBr, cm^{-1}): 3427 (br), 3171 (w), 3161 (w), 3142 (s), 3070 (vs), 2977 (vs), 2925 (s), 2660 (w), 2419 (s), 2298 (w), 2245 (m), 2181 (s), 1830 (w), 1765(w), 1681(w), 1644(w), 1569(vs), 1478(s), 1421(vs), 1398(vs), 1356(vs), 1310(vs), 1262 (s), 1228 (vs), 1198 (vs), 1137 (s), 1073 (s), 1031 (m), 974 (w), 927 (vs), 823 (s), 764 (vs), 731 (vs), 688 (vs). FAB-MS m/z = 1069.2 $[M]^+$, M = $[(Tm^{But})_2In]$.



Molecular structure of [(Tm^{But})$_2$In]Cl (only the cation is shown)

Synthesis of [κ^2–Tm^{But}]$_2$InCl

A solution of [Tm^{But}]In (25 mg, 0.042 mmol) in benzene (0.5 mL) was treated with pyridine-*N*-oxide (4 mg, 0.042 mmol) and heated at 80 °C for 3 days resulting in the formation of a white precipitate. The precipitate was isolated by filtration and crystallized from chloroform (0.5 mL).



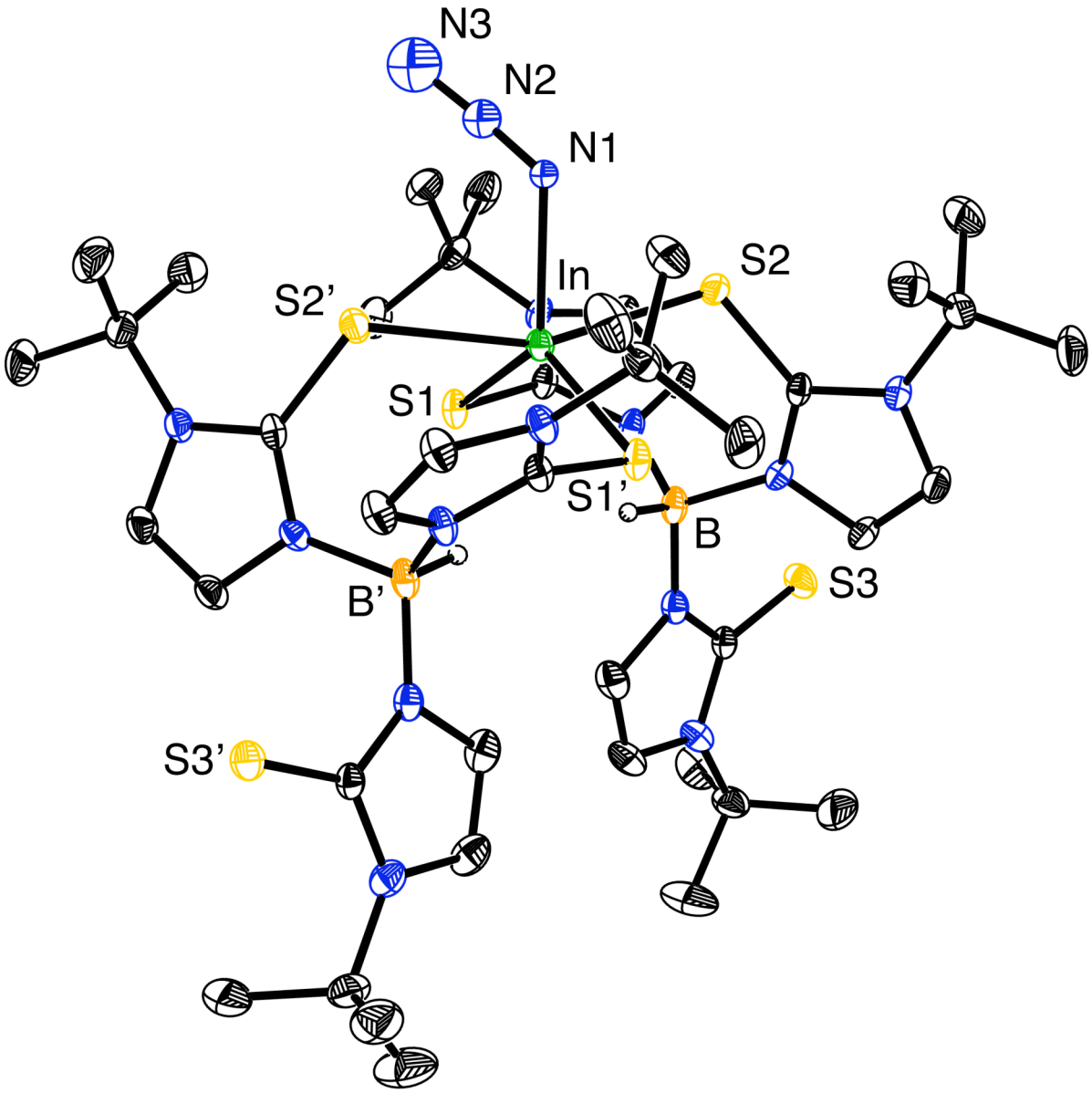
Molecular structure of [κ²–Tm^{But}]$_2$InCl

Synthesis of [κ²–Tm^{But}]$_2$InN$_3$

(a) [Tm^{But}]In (25 mg, 0.042 mmol) was treated with a cold (-35˚C) solution of Me_3SiN_3 (5 mg, 0.043 mmol) in chloroform (0.5 mL). The mixture was filtered and allowed to stand at room temperature for two weeks resulting in the formation of colorless crystals of [κ²-Tm^{But}]InN$_3$ (ca. 2 mg) which were isolated and structurally characterized by X–ray diffraction.

(b) [Tm^{But}]In (100 mg, 0.169 mmol) was treated with a solution of *p*–TolS(O)$_2$N$_3$ (34 mg, 0.172 mmol) in benzene (1 mL). The golden solution was filtered and allowed to stand

at room temperature for one week resulting in the formation of colorless crystals of [κ^2-Tm^{But}]InN_3 (ca. 10 mg) which were isolated and structurally characterized by X–ray diffraction.



Molecular structure of [κ^2–Tm^{But}]$_2InN_3$

(only one disordered configuration of the azide ligand is shown)

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).[7] For $[Tm^{But}]In$, $[Tm^{But}]InB(C_6F_5)_3$, and $\{[Tm^{But}]_2In\}[Cl]$, the B–H hydrogens were restrained to 1.05Å. The κ^2–S_4 ligand of $[Tm^{But}]In(\kappa^2–S_4)$ exhibits two fold disorder and were refined such that common In–S bond lengths of the disordered configurations were restrained to be the same. The N_3 ligand of $[\kappa^2–Tm^{But}]_2InN_3$ exhibits two fold disorder and were refined such that common bond lengths of the disordered configurations were restrained to be the same.

Table 1. Crystal, intensity collection and refinement data.

	$[Tm^{But}]In\cdot 0.5(C_6H_6)$	$[Tm^{But}]Tl\cdot 0.5(C_6H_6)$
lattice	Rhombohedral	Triclinic
formula	$C_{24}H_{37}BInN_6S_3$	$C_{24}H_{37}BN_6S_3Tl$
formula weight	631.41	720.96
space group	*R-3*	*P-1*
a / Å	13.5112(4)	14.6625(11)
b / Å	13.5112(4)	15.6152(12)
c / Å	28.6753(18)	15.6517(11)
α / °	90.00	69.9950(10)
β / °	90.00	67.7660(10)
γ / °	120.00	71.1020(10)
V / Å^3	4533.4(3)	3038.1(4)
Z	6	4
temperature (K)	273(2)	243(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.388	1.576
μ (Mo Kα), mm^{-1}	1.012	5.545
θ max, deg.	28.58	27.10
no. of data	2445	12871
no. of parameters	103	640
R_1	0.0313	0.0328
wR_2	0.1330	0.0741
GOF	1.028	1.065

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

	$[Tm^{But}]In{\rightarrow}B(C_6F_5)_3 \cdot 2(C_6H_6)$	$[Tm^{But}]In(\kappa^2\text{–}S_4)$
lattice	Triclinic	Monoclinic
formula	$C_{51}H_{46}B_2F_{15}InN_6S_3$	$C_{21}H_{34}BInN_6S_7$
formula weight	1260.56	720.59
space group	*P-1*	$P2_1/n$
a/Å	12.1353(6)	11.6446(6)
b/Å	12.5348(6)	16.4002(9)
c/Å	20.0186(10)	16.1622(9)
α/°	81.989(1)	90
β/°	77.827(1)	92.026(1)
γ/°	70.812(1)	90
V/Å^3	2803.2	3084.6(3)
Z	2	4
temperature (K)	243(2)	243(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.493	1.552
μ (Mo Kα), mm^{-1}	0.624	1.263
θ max, deg.	26.370	28.330
no. of data	11342	7135
no. of parameters	708	366
R_1	0.0286	0.0302
wR_2	0.0938	0.0899
GOF	1.063	1.026

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

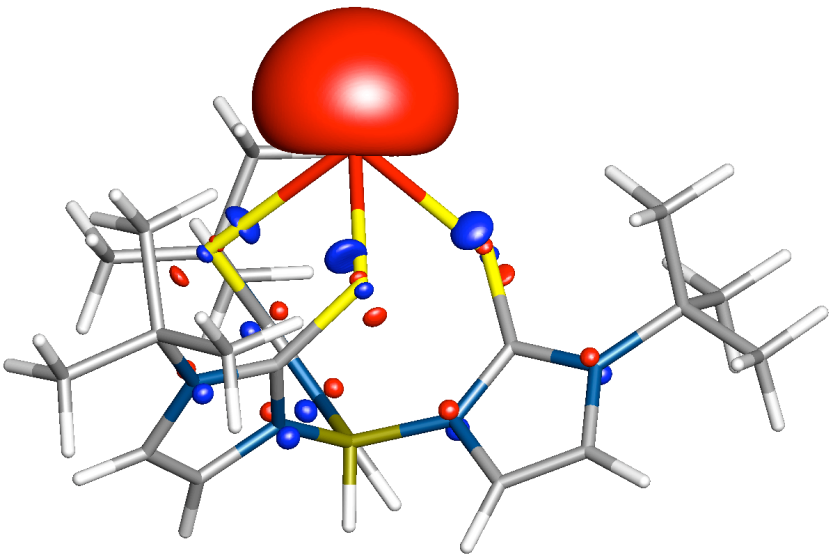
	$[\kappa^2\text{–}Tm^{But}]_2InCl\cdot 2(C_6H_6)$	$[\kappa^2\text{–}Tm^{But}]_2InN_3\cdot 2(C_6H_6)$
lattice	Monoclinic	Monoclinic
formula	$C_{54}H_{80}B_2ClInN_{12}S_6$	$C_{54}H_{80}B_2InN_{15}S_6$
formula weight	1261.55	1268.13
space group	*C2/c*	*C2/c*
a / Å	28.367(3)	28.0261(17)
b / Å	11.6180(14)	12.0762(8)
c / Å	19.433(2)	19.4918(12)
α / °	90.00	90.00
β / °	103.393(2)	101.905(2)
γ / °	90.00	90.00
V / Å^3	6230.5(13)	6455.1(7)
Z	4	4
temperature (K)	125(2)	243(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.345	1.305
μ (Mo Kα), mm^{-1}	0.669	0.607
θ max, deg.	30.60	28.27
no. of data	9575	7555
no. of parameters	379	355
R_1	0.0514	0.0594
wR_2	0.1159	0.0745
GOF	1.051	1.045

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

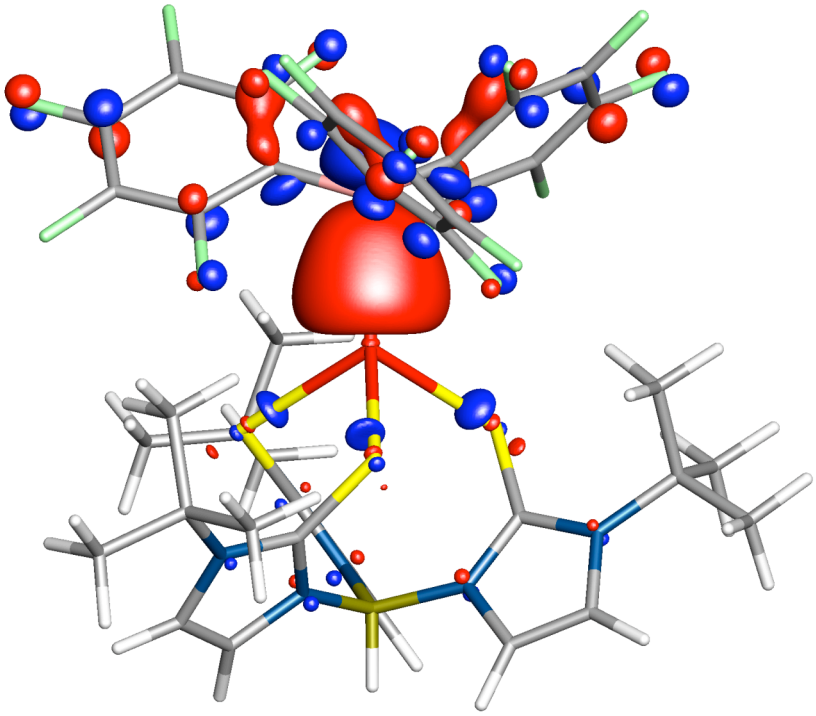
	$\{[Tm^{But}]_2In\}[Cl]\cdot 3(CH_3CN)$	$\{[Tm^{But}]_2In\}[I]\cdot(C_6H_6)$
lattice	Monoclinic	Trigonal
formula	$C_{48}H_{77}B_2ClInN_{15}S_6$	$C_{48}H_{74}B_2IInN_{12}S_6$
formula weight	1228.50	1274.89
space group	$P2_1/c$	$P\text{-}31c$
a/Å	15.5243(10)	11.8575(14)
b/Å	15.9024(10)	11.8575(14)
c/Å	25.6301(16)	26.003(6)
α/°	90	90
β/°	102.280(1)	90
γ/°	90	120
V/Å^3	6182.6(7)	3166.2(9)
Z	4	2
temperature (K)	125(2)	243(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.320	1.337
μ (Mo Kα), mm^{-1}	0.673	1.099
θ max, deg.	32.470	28.270
no. of data	21156	2518
no. of parameters	670	101
R_1	0.0365	0.0399
wR_2	0.1698	0.1037
GOF	1.056	1.012

Computational Details

All calculations were carried out using DFT as implemented in the Jaguar 7.0 suite of *ab initio* quantum chemistry programs.[8] Geometry optimizations were performed with the B3LYP density functional[9] and LACVP** basis sets, *i.e.* 6-31G** (C, H, B, N, F, S) and LAV3P (In) basis sets.[10] 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) and LAV3P (In) basis sets. Molecular orbital analyses were performed with the aid of Jimp 2,[11] which employs Fenske-Hall calculations[12] and visualization using MOPLOT.[13]



HOMO of [Tm$^{Bu^t}$]In



HOMO of $[Tm^{Bu^t}]InB(C_6F_5)_3$

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

[Tm$^{Bu^t}$]In
–2370.73465521007 Hartrees
(–2371.17590165816 Hartrees)

atom	x	y	z
H1	-5.308058171	1.010970376	-2.042480459
H2	3.529555113	4.091428033	-2.042480459
H3	1.778503057	-5.102398408	-2.042480459
In4	0	0	-2.236282594
H5	-3.538636975	1.029758025	-1.903637773
H6	2.661115097	2.549670503	-1.903637773
H7	0.877521878	-3.579428528	-1.903637773
C8	1.653132451	-4.192838659	-1.44590153
C9	-4.457671018	0.664764631	-1.44590153
C10	2.804538567	3.528074028	-1.44590153
H11	2.596221644	-3.637399429	-1.460967452
H12	-4.448191132	-0.429694183	-1.460967452
H13	1.851969487	4.067093613	-1.460967452
H14	5.40914897	3.157911772	-0.536051141
H15	-5.439406302	3.105504535	-0.536051141
H16	0.030257332	-6.263416307	-0.536051141
H17	2.44567628	-6.381279723	-0.073040289
H18	-6.749188489	1.072622074	-0.073040289

H19	4.303512209	5.308657649	-0.073040289
H20	4.551388157	1.617576504	-0.32664241
H21	-3.676556424	3.132829514	-0.32664241
H22	-0.874831733	-4.750406018	-0.32664241
C23	-0.051138966	-5.349724391	0.061821182
C24	4.658566709	2.630574552	0.061821182
C25	-4.607427743	2.71914984	0.061821182
C26	1.281279414	-4.580194482	-0.002352689
C27	-4.607204483	1.18047672	-0.002352689
C28	3.325925069	3.399717763	-0.002352689
S29	-1.379191426	1.824443082	-0.52725592
S30	2.26960977	0.28219327	-0.52725592
S31	-0.890418344	-2.106636352	-0.52725592
C32	3.556390304	4.816140939	0.554916178
C33	2.392705249	-5.487994818	0.554916178
C34	-5.949095553	0.67185388	0.554916178
H35	2.648017083	5.425636289	0.52443518
H36	-6.0227474	-0.419568081	0.52443518
H37	3.374730317	-5.006068208	0.52443518
H38	5.020011451	2.576537991	1.09431963
H39	-4.74135308	3.059188448	1.09431963
H40	-0.278658371	-5.635726439	1.09431963
H41	3.945700093	4.802039526	1.577803601

H42	-6.131538266	1.016056753	1.577803601
H43	2.185838173	-5.818096279	1.577803601
N44	-3.484052947	0.642558023	0.844163686
N45	1.185554903	-3.338557372	0.844163686
N46	2.298498045	2.695999349	0.844163686
C47	0.324284161	-2.273938593	0.685988092
C48	1.807146508	1.417807618	0.685988092
C49	-2.131430669	0.856130975	0.685988092
C50	-3.671741919	-0.177545554	1.952100887
C51	1.682112	3.268594555	1.952100887
C52	1.989629919	-3.091049001	1.952100887
N53	-1.49740387	0.180367262	1.685816859
N54	0.904904566	1.20660616	1.685816859
N55	0.592499304	-1.386973422	1.685816859
H56	-4.64264475	-0.491066434	2.288131056
H57	2.746598382	-3.775115077	2.288131056
H58	1.896046368	4.266181512	2.288131056
B59	0	0	2.083367
C60	0.834175443	2.349360468	2.462277044
C61	-2.45169357	-0.452263109	2.462277044
C62	1.617518126	-1.897097359	2.462277044
H63	0.180016409	2.406775648	3.316834881
H64	-2.174337056	-1.047489041	3.316834881

H65	1.994320648	-1.359286607	3.316834881
H66	0	0	3.292104611

$[Tm^{Bu^t}]In{\rightarrow}B(C_6F_5)_3$
–4578.973543465780 Hartrees
(–4580.23867095914 Hartrees)

atom	x	y	z
H1	2.53287774	0.808289165	-6.667780576
H2	4.144369979	0.565337104	-5.996352277
H3	2.931848432	-0.744046057	-5.935372508
C4	3.083977547	0.336326876	-5.850531834
H5	2.2737166	2.877336857	-5.35323168
H6	0.529468894	0.956399902	-5.313637754
F7	-4.023123696	2.886754226	-3.848919796
H8	4.633356031	-1.008314602	-4.501672056
F9	-2.550845637	5.094690247	-3.185608037
H10	3.851190559	2.638000761	-4.580067093
C11	2.536797991	0.8981861	-4.526375719
H12	0.889247413	-0.531078229	-4.41921981
C13	2.781497154	2.417488471	-4.499861356
C14	1.040944512	0.551693586	-4.434613242
C15	4.307783873	-0.664054932	-3.537779631
C16	-3.170958988	2.836257716	-2.813724344
C17	-2.430980752	3.963438046	-2.47742697

H18	2.395612067	2.871828486	-3.586885834
N19	3.282387578	0.257931759	-3.37567177
H20	0.579514054	0.97630542	-3.545119876
F21	-1.66772095	-3.196801523	-3.750433305
F22	-3.824903885	0.640793631	-2.443696995
C23	4.760705273	-0.990364998	-2.306289993
H24	5.546739234	-1.665817268	-2.010805591
C25	-3.037528407	1.668049854	-2.064300833
F26	-0.868112174	-0.968321933	-2.508963425
C27	-1.561755235	3.899483829	-1.394015517
F28	-0.829833978	4.971477056	-1.051462616
C29	-2.299178715	-2.804630336	-2.632443433
C30	3.114646137	0.47914834	-2.031961644
F31	-3.748982057	-4.676411494	-2.745815306
C32	-1.916579803	-1.649003508	-1.965147012
N33	4.027887068	-0.282938134	-1.370724082
H34	1.472416859	-4.94005708	-0.730591297
C35	-3.352435943	-3.557810137	-2.124477633
C36	-2.171102473	1.541624277	-0.971107344
C37	-1.464314295	2.712822285	-0.681125469
S38	1.555290978	-2.270864147	-0.758178467
S39	1.973584685	1.560564255	-1.29815364
H40	2.797992503	-5.942741973	-0.100861106

H41	1.112283499	-6.41435037	0.181541271
C42	1.792868626	-5.560614293	0.106655678
C43	-2.503006904	-1.169320731	-0.789538461
C44	-3.98426051	-3.130821973	-0.962576579
H45	5.580130857	-0.600988065	0.164243461
F46	-0.578152501	2.714370258	0.355310989
B47	-1.99176522	0.197377689	-0.076589531
B48	4.381194261	-0.474036243	0.138191322
In49	0.371185762	-0.055896534	0.040278864
C50	2.731218278	-2.567199904	0.48262442
C51	-3.562542281	-1.961904364	-0.330123369
H52	5.873036792	1.790425014	0.347808188
N53	3.82118162	-1.797279019	0.748198404
H54	-0.023708567	-3.613365848	0.972827842
F55	-5.009623372	-3.839775519	-0.466442251
F56	-3.902319339	2.213739119	1.104144091
C57	1.771857826	-4.781190271	1.433820403
N58	2.751444343	-3.631004341	1.348123985
C59	4.992886837	1.832922686	0.968480672
N60	4.090023219	0.786417416	1.013294296
H61	-0.311402997	-5.091679734	1.90149879
C62	0.369006091	-4.244893038	1.76729308
F63	-4.263400372	-1.611683481	0.767869124

C64	4.51987819	-2.380886529	1.789128405
C65	-2.443782188	0.356487113	1.475057104
H66	3.196346371	-6.167139995	2.3850528
C67	3.868647086	-3.505347751	2.162736687
H68	1.490838322	-6.549744023	2.611531391
C69	-3.330303606	1.331164804	1.948713648
C70	2.209942921	-5.728108171	2.565099323
C71	4.556703109	2.807392282	1.798123984
H72	5.426448098	-1.942603228	2.173371982
H73	1.218378556	3.967448465	1.881053059
H74	4.994597175	3.761599392	2.024569432
C75	3.089588453	1.122296757	1.872532671
H76	0.381353305	-3.665672351	2.694747037
H77	4.112627967	-4.216732369	2.929568072
S78	1.730129454	0.125841145	2.289962793
N79	3.370532394	2.369403688	2.370869011
F80	-1.102292865	-1.498440223	2.137982217
H81	0.591734575	2.542198911	2.723268169
C82	-1.982092627	-0.51044442	2.47021681
H83	2.205781321	-5.234945941	3.541909477
C84	1.172256034	3.454416149	2.845612963
H85	3.344932284	5.118784833	2.714402667
C86	-3.700667483	1.454162407	3.287223514

F87	-4.554607519	2.415094265	3.671207073
H88	0.647240358	4.103442851	3.553532547
C89	2.583449289	3.167929276	3.386856339
C90	3.293888993	4.512341638	3.623865808
C91	-2.321431653	-0.431710123	3.814318575
H92	4.301495345	4.386974616	4.032701878
C93	-3.196577989	0.566193826	4.230154908
H94	2.711619848	5.074173399	4.358427777
H95	2.037851859	1.433388819	4.608054591
C96	2.546895547	2.391626064	4.71533386
F97	-1.815961465	-1.298820285	4.70578042
H98	3.561796323	2.213273342	5.086220729
H99	2.009966524	2.983992985	5.46252826
F100	-3.545408422	0.669474163	5.519544765

[Tm$^{Bu^t}$]In(κ^2–S_4)
–3963.55052675350 Hartrees
(–3964.14759426603 Hartrees)

atom	x	y	z
S1	0.073553164	-0.67940328	-5.521058974
S2	1.829234422	-1.585313772	-4.85700298
S3	2.478632588	-0.300434581	-3.311287081

S4	-1.214635698	-0.81253117	-3.835198515
H5	-0.899945433	4.79905835	-3.018525764
H6	-0.202632103	3.238565008	-2.563849999
H7	-0.907702553	4.010814354	-2.259485506
H8	-1.911387316	3.576625919	-2.225555556
H9	-4.08643417	-3.660321872	-1.702774348
H10	-2.880798215	-2.366450834	-1.730439617
H11	0.968624855	5.983686254	-1.64144264
In12	0.331665026	-0.307336052	-1.941794109
H13	-1.411891312	6.518355142	-1.384448604
H14	4.968863195	-3.068641954	-1.036791959
C15	-3.318346413	-3.150275428	-1.113115388
H16	-2.538927499	-3.877713103	-0.865225632
H17	3.33639997	-2.417862343	-1.258605295
H18	1.634961623	4.428222445	-1.121953869
C19	-0.535611175	4.624051428	-0.897443303
C20	0.894394609	5.193146583	-0.888416066
H21	4.679015701	-1.3233431	-0.924993157
H22	-2.559798368	5.433041442	-0.602739709
C23	4.260546136	-2.306975079	-0.695052411
C24	-1.51852613	5.769176817	-0.596062485
H25	-5.844496467	-2.026263737	-0.721096963
S26	-2.132218063	0.057536225	-0.725980349

H27	-4.659424949	-0.709284354	-0.704942011
S28	1.256650929	1.820749063	-0.783534404
C29	-5.052541565	-1.550597643	-0.134364256
H30	-5.375642258	-4.192328555	0.312887373
H31	1.130407368	5.628739887	0.088176057
C32	-3.958628203	-2.590025636	0.169221189
H33	-1.303701514	6.263929113	0.356418181
S34	0.855616837	-2.139182102	-0.146179162
H35	4.181639151	-4.62407374	0.861033589
N36	-0.663713494	3.572121013	0.182731301
H37	2.52299649	-4.036669621	0.673043918
C38	0.010735959	2.382806967	0.286289073
C39	-4.597673573	-3.7561182	0.944434041
C40	4.046238516	-2.469262398	0.81720415
H41	6.069824185	-3.089051677	1.150116821
H42	-3.877574869	-4.548994651	1.168923862
C43	3.472670407	-3.85206303	1.175378904
H44	-5.494328151	-1.174128534	0.79448692
C45	-2.09104754	-0.881016636	0.722488098
N46	-2.889950791	-1.95616446	1.028932793
H47	5.875045117	-1.345294963	1.299825794
C48	5.403879934	-2.307210043	1.523786785
C49	1.774218162	-1.220993076	1.010649489

C50	-1.538104713	3.666090379	1.256060005
H51	-2.184543839	4.510294619	1.408330093
N52	3.099747715	-1.39830908	1.322388824
H53	-5.074777859	-3.427849803	1.873459961
H54	3.326150002	-3.943426026	2.256897103
N55	-0.427871305	1.751565763	1.405402483
N56	-1.264010337	-0.672505591	1.785572627
H57	5.329068919	-2.430408024	2.608912193
C58	-1.387189277	2.547679211	2.00222736
N59	1.299033912	-0.203564499	1.780721467
C60	-2.535653907	-2.417481885	2.290468128
B61	-0.136871791	0.359822274	2.053017594
C62	3.446325012	-0.455708304	2.280216699
H63	-3.019757735	-3.252723147	2.761684196
H64	4.43678653	-0.379242836	2.688779021
C65	-1.540279802	-1.626128923	2.749624089
C66	2.340134811	0.271868578	2.55617378
H67	-1.882255728	2.245960887	2.91065732
H68	-0.164419378	0.56026512	3.241826001
H69	2.199396698	1.085659347	3.248383721
H70	-1.005323188	-1.652743718	3.684890386

$[(Tm^{But})_2In]^+$
–4739.42022427666 Hartrees
(–4740.29201588321 Hartrees)

atom	x	y	z
H1	0.679549276	-3.947265925	-6.220034361
H2	2.102455262	-2.971900181	-5.819175686
H3	-2.496907939	3.737783947	-5.917467625
H4	-3.370069998	2.248285671	-5.564644966
C5	1.408596149	-3.726007421	-5.435696838
H6	1.96906446	-4.644810292	-5.246663549
C7	-3.071083611	3.215205704	-5.14817884
H8	-0.847628339	-2.36686655	-5.433342043
H9	-3.965143711	3.812920654	-4.946388923
H10	0.404818805	-1.186197784	-5.01864592
H11	-0.421014134	2.746372617	-5.126323918
C12	-0.197902078	-2.008426383	-4.628108428
H13	-1.222272269	1.242826928	-4.633698974
H14	-4.824376515	2.073037171	-3.872879235
H15	-1.270706334	5.007978243	-4.192336474
C16	0.662919768	-3.200424489	-4.190025124
C17	-0.93357225	2.243886569	-4.299676734
H18	-1.006138074	-4.577380294	-4.318411491
C19	-2.173295202	3.063448125	-3.907105169
H20	-0.82544112	-1.627690635	-3.82422469
C21	-0.246338262	-4.287876944	-3.585936079
C22	-1.798868305	4.468304589	-3.400145481

H23	2.670462083	-4.800598829	-3.253618704
H24	-2.697408439	5.038305599	-3.142034457
H25	0.314142727	-5.186347941	-3.310838646
C26	-4.272330831	1.954089677	-2.959146147
H27	-0.234569768	2.14163144	-3.471419749
N28	1.708902358	-2.861897054	-3.145151696
C29	2.65101949	-3.825117852	-2.801151378
N30	-2.945681615	2.34155257	-2.824695708
H31	4.171535077	4.897940795	-2.321506335
H32	5.258265218	2.942360171	-2.384437805
H33	-0.752745604	-3.908501943	-2.694029384
H34	-1.149973494	4.421038274	-2.524754464
H35	5.338367872	0.2142793	-2.445752259
C36	1.948019271	-1.744982507	-2.383245332
S37	1.078385318	-0.243446023	-2.380171436
C38	-4.672894883	1.449987093	-1.770833356
C39	3.465789368	-3.289933576	-1.867570044
H40	-5.631215436	1.059645403	-1.46951399
C41	4.709878547	2.227264697	-1.799959162
C42	4.749006891	0.87665795	-1.833092754
H43	1.803147047	4.262808696	-1.652208383
H44	-3.406665484	-3.557130044	-1.74154747
C45	4.43241006	4.959439874	-1.260522325

H46	4.322803529	-3.710859953	-1.367473195
N47	3.040050532	-1.998886802	-1.612367854
H48	5.502791482	4.766755177	-1.140400228
H49	4.248629487	5.987746841	-0.938882073
H50	-3.860814267	-5.231599401	-1.380436638
C51	-2.543126867	2.049496229	-1.543673154
H52	-5.054863617	-3.935203452	-1.198827411
C53	-3.996811681	-4.189001845	-1.076528831
H54	5.012045035	-1.48262846	-0.801350718
S55	-2.075946483	-1.353499638	-0.981406523
N56	-3.609826999	1.519099982	-0.887510714
N57	3.800090743	2.596168626	-0.818390536
N58	3.872980358	0.390378537	-0.878459539
C59	2.090412478	4.404576719	-0.606155934
H60	1.950855689	5.460545038	-0.352990533
C61	3.565850434	4.029024031	-0.393058374
B62	3.872417329	-1.145656336	-0.604749598
S63	-0.972942135	2.334492985	-0.861682252
C64	3.276292834	1.450565217	-0.269424911
H65	1.424024643	3.808874791	0.015373859
H66	-1.424024643	-3.808874791	-0.015373859
In67	0	0	0
C68	-3.276292834	-1.450565217	0.269424911

C69	-3.565850434	-4.029024031	0.393058374
H70	-1.950855689	-5.460545038	0.352990533
B71	-3.872417329	1.145656336	0.604749598
C72	-2.090412478	-4.404576719	0.606155934
H73	-5.012045035	1.48262846	0.801350718
S74	0.972942135	-2.334492985	0.861682252
N75	-3.800090743	-2.596168626	0.818390536
H76	-4.248629487	-5.987746841	0.938882073
C77	3.996811681	4.189001845	1.076528831
N78	-3.872980358	-0.390378537	0.878459539
H79	5.054863617	3.935203452	1.198827411
H80	-5.502791482	-4.766755177	1.140400228
N81	3.609826999	-1.519099982	0.887510714
H82	3.860814267	5.231599401	1.380436638
S83	2.075946483	1.353499638	0.981406523
C84	-4.43241006	-4.959439874	1.260522325
H85	-4.322803529	3.710859953	1.367473195
H86	3.406665484	3.557130044	1.74154747
C87	2.543126867	-2.049496229	1.543673154
H88	-1.803147047	-4.262808696	1.652208383
H89	5.631215436	-1.059645403	1.46951399
C90	-4.709878547	-2.227264697	1.799959162
N91	-3.040050532	1.998886802	1.612367854

C92	-4.749006891	-0.87665795	1.833092754
C93	-3.465789368	3.289933576	1.867570044
C94	4.672894883	-1.449987093	1.770833356
H95	-4.171535077	-4.897940795	2.321506335
H96	-5.258265218	-2.942360171	2.384437805
H97	-5.338367872	-0.2142793	2.445752259
H98	1.149973494	-4.421038274	2.524754464
C99	-1.948019271	1.744982507	2.383245332
H100	0.752745604	3.908501943	2.694029384
S101	-1.078385318	0.243446023	2.380171436
C102	-2.65101949	3.825117852	2.801151378
N103	2.945681615	-2.34155257	2.824695708
H104	2.697408439	-5.038305599	3.142034457
H105	-0.314142727	5.186347941	3.310838646
H106	-2.670462083	4.800598829	3.253618704
C107	4.272330831	-1.954089677	2.959146147
N108	-1.708902358	2.861897054	3.145151696
C109	1.798868305	-4.468304589	3.400145481
H110	0.234569768	-2.14163144	3.471419749
C111	0.246338262	4.287876944	3.585936079
H112	0.82544112	1.627690635	3.82422469
H113	1.270706334	-5.007978243	4.192336474
H114	1.006138074	4.577380294	4.318411491

H115	4.824376515	-2.073037171	3.872879235
C116	2.173295202	-3.063448125	3.907105169
C117	-0.662919768	3.200424489	4.190025124
C118	0.93357225	-2.243886569	4.299676734
C119	0.197902078	2.008426383	4.628108428
H120	1.222272269	-1.242826928	4.633698974
H121	3.965143711	-3.812920654	4.946388923
H122	0.421014134	-2.746372617	5.126323918
H123	-0.404818805	1.186197784	5.01864592
C124	3.071083611	-3.215205704	5.14817884
H125	-1.96906446	4.644810292	5.246663549
H126	0.847628339	2.36686655	5.433342043
C127	-1.408596149	3.726007421	5.435696838
H128	3.370069998	-2.248285671	5.564644966
H129	2.496907939	-3.737783947	5.917467625
H130	-2.102455262	2.971900181	5.819175686
H131	-0.679549276	3.947265925	6.220034361

$B(C_6F_5)_3$
-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

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