Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Reactivity of the Ni→B Dative σ–Bond in the Nickel Boratrane Compounds [κ⁴–B(mim^{But})$_3$]NiX (X = Cl, OAc, NCS, N$_3$): Synthesis of a Series of *B*-Functionalized *Tris*(2-mercapto-1-t-butylimidazolyl)borato Complexes, [YTm^{But}]NiZ

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EXPERIMENTAL SECTION

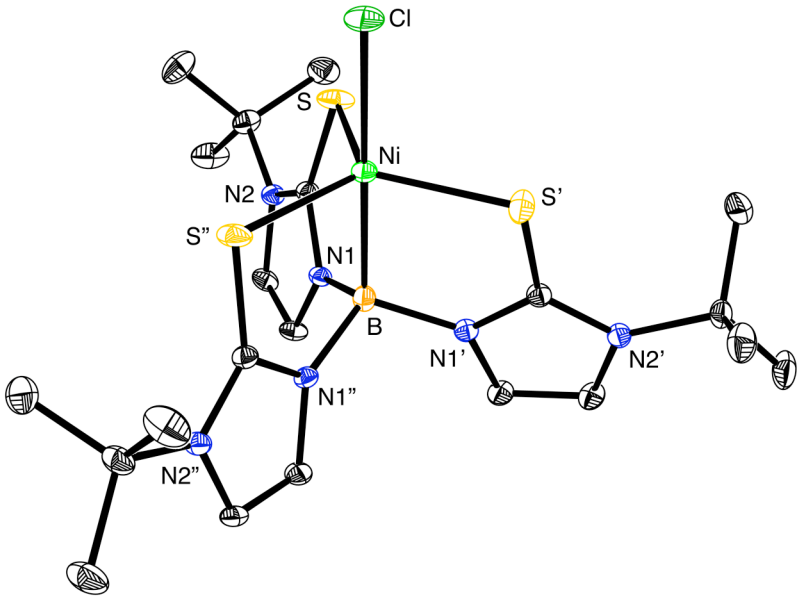
General Considerations

All manipulations were performed using a combination of dry 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 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; 1.94 for CD_2HN; 7.26 for $CHCl_3$).[2] ^{19}F NMR spectra are reported in ppm relative to $CFCl_3$ ($\delta = 0$) and were referenced using external $PhCF_3$ in $CDCl_3$ ($\delta = -63.7$).[3] ^{11}B NMR spectra are reported with reference to $BF_3(OEt_2)$ ($\delta = 0.0$).[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 was prepared by the literature method.[5]

Synthesis of [κ^4–B(mim^{But})$_3$]NiCl

A solution of [Tm^{But}]K (3.0 g, 5.8 mmol) in CH_3OH (30 mL) was treated with a solution of $NiCl_2 \cdot 6H_2O$ (1.4 g, 5.9 mmol) in CH_3OH (30 mL), resulting in a green solution with a green precipitate. The mixture was stirred for 15 minutes and then exposed to air and stirred for an additional 2 hours. The mixture was concentrated to ca. 10 mL and treated with Et_2O (30 mL), thereby depositing more material. The resulting precipitate was isolated by filtration and washed with acetone/H_2O (1:1, 30 mL), acetone (2 × 30 mL) and Et_2O (2 × 30 mL) and dried *in vacuo*, giving [κ^4-B(mim^{But})$_3$]NiCl as a green powder (1.9 g, 57%). Crystals suitable for X-ray diffraction were grown by slow evaporation of an acetonitrile solution. Anal. calcd. for $C_{21}H_{33}BClN_6NiS_3$: C, 44.2%; H, 5.8%; N, 14.7%. Found: C, 44.2%; H, 5.9%; N, 14.6%. ^{1}H NMR (CD_3CN): -0.15 [s, 27H, 3 Bu^t], 12.95 [s, 3H, 3 C<u>H</u> mim^{But}], 17.64 [s, 3H, 3 C<u>H</u> mim^{But}]. ^{1}H NMR (CD_3OD): 0.04 [s,

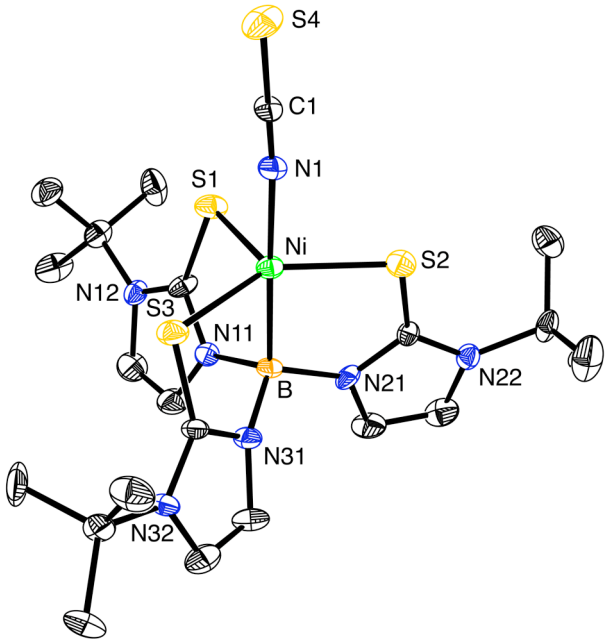
27H, 3 Bu^t], 11.86 [s, 3H, 3 C<u>H</u> mim$^{Bu^t}$], 17.64 [s, 3H, 3 C<u>H</u> mim$^{Bu^t}$]. IR Data (KBr pellet, cm^{-1}): 3178 (m), 3111 (m), 3070 (m), 2992 (m), 2971 (m), 2932 (w), 1561 (w), 1426 (s), 1392 (s), 1378 (s), 1369 (s), 1308 (m), 1262 (w), 1229 (w), 1189 (s), 1163 (s), 1138 (w), 1067 (m), 1028 (m), 820 (m), 803 (m), 784 (s), 735 (s), 696 (m). Mass spectrum: m/z = 534.4 {M–Cl}$^+$.



Molecular structure of [κ^4–B(mim$^{Bu^t}$)$_3$]NiCl (20% thermal parameters)

Synthesis of [κ^4–B(mim^{But})$_3$]NiNCS

A mixture of [κ^4-B(mim^{But})$_3$]NiCl (0.200 g, 0.35 mmol) and KSCN (0.034 g, 0.35 mmol) in CH_3CN (8 mL) was stirred at 70˚C for 1 day after which period the resulting green mixture was filtered. The green precipitate was extracted into CH_3CN (20 mL) and the two filtrates were combined. The volatile components were removed *in vacuo* to give [κ^4–B(mim^{But})$_3$]NiNCS as a green solid (0.046 g, 22%). Crystals suitable for X-ray diffraction were grown by slow evaporation of an acetonitrile solution. Anal. calcd. for $C_{22}H_{33}BN_7NiS_4$: C, 44.5%; H, 5.6%; N, 16.5%. Found: C, 43.6%; H, 5.5%; N, 15.7%. ^{1}H NMR (CD_3CN): 0.01 [s, 27H, 3 Bu^t], 12.75 [s, 3H, 3 CH mim^{But}], 17.31 [s, 3H, 3 CH mim^{But}]. IR Data (KBr pellet, cm^{-1}): 3166 (w), 3130 (w), 3076 (w), 2977 (m), 2935 (w), 2093 (s), 1559 (w), 1427 (m), 1393 (s), 1381 (m), 1370 (m), 1309 (w), 1231 (w), 1191 (s), 1159 (m), 1132 (w), 1067 (w), 1033 (w), 820 (w), 786 (m), 725 (m), 690 (m).

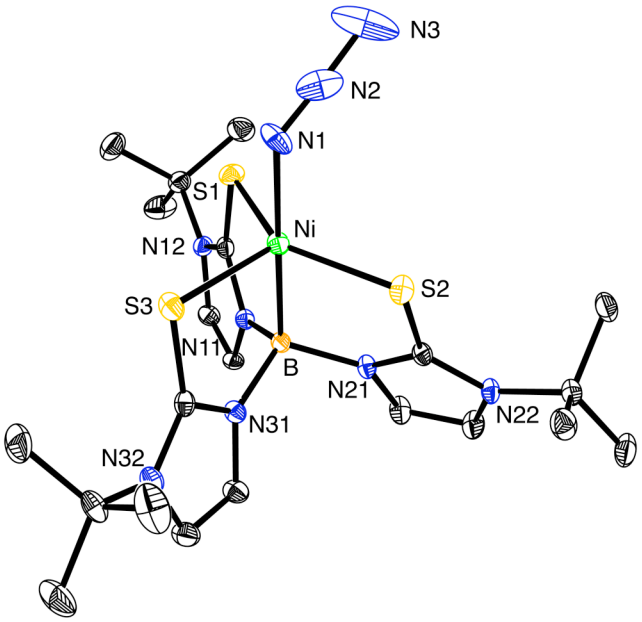


Molecular structure of [κ^4–B(mim^{But})$_3$]NiNCS (20% thermal parameters)

Synthesis of [κ^4–B(mim^{But})$_3$]NiN$_3$

A mixture of [κ^4-B(mim^{But})$_3$]NiCl (0.200 g, 0.35 mmol) and NaN_3 (0.023 g, 0.35 mmol) in CH_3CN (25 mL) was stirred at 70˚C for 1 day. After this period, the mixture was filtered, giving a green filtrate. The volatile components were removed from the filtrate

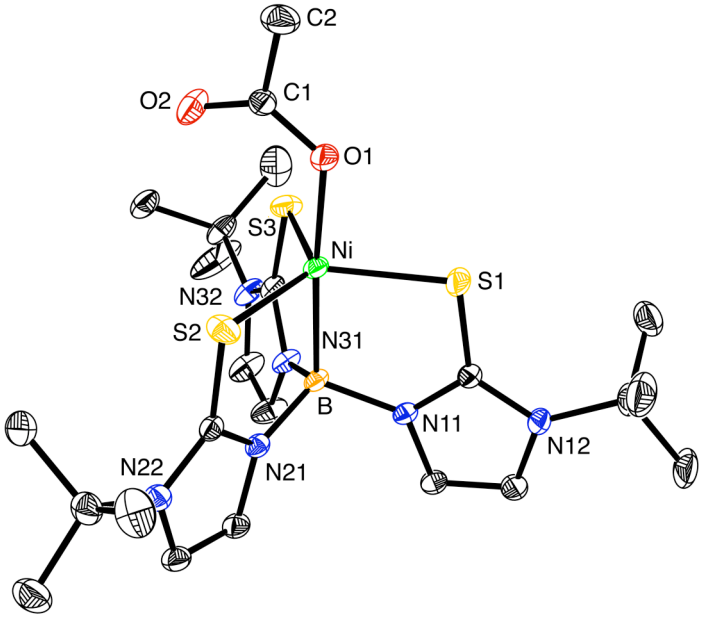
to give [κ^4–B(mim$^{Bu^t}$)$_3$]NiN_3 as a green solid (0.055 g, 27%). Crystals of composition [κ^4–B(mim$^{Bu^t}$)$_3$]NiN_3•2CH_3CN suitable for X-ray diffraction were grown by slow evaporation of an acetonitrile solution. Anal. calcd. for $C_{21}H_{33}BN_9NiS_3$: C, 43.7%; H, 5.8%; N, 21.8%. Found: C, 41.9%; H, 5.3%; N, 20.2%. ^{1}H NMR (CD_3CN): -0.01 [s, 27H, 3 Bu^t], 12.64 [s, 3H, 3 C<u>H</u> mim$^{Bu^t}$], 17.44 [s, 3H, 3 C<u>H</u> mim$^{Bu^t}$]. IR Data (KBr pellet, cm^{-1}): 3167 (w), 3119 (w), 3076 (w), 2976 (m), 2918 (w), 2145 (w), 2111 (w), 2038 (s), 1560 (w), 1427 (m), 1393 (s), 1370 (m), 1310 (w), 1232 (w), 1193 (s), 1162 (m), 1134 (w), 1070 (m), 1033 (w), 820 (w), 785 (m), 735 (w), 685 (w). Mass spectrum: m/z = 534.5 $\{M–N_3\}^+$.



Molecular structure of [κ^4–B(mim$^{Bu^t}$)$_3$]NiN_3 (20% thermal parameters)

Synthesis of [κ^4–B(mim^{But})$_3$]NiOAc

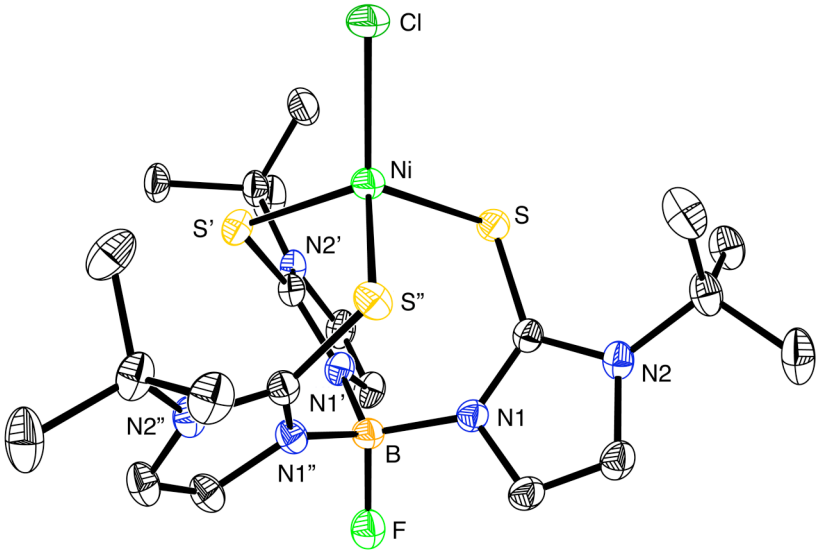
A mixture of [κ^4-B(mim^{But})$_3$]NiCl (0.200 g, 0.35 mmol) and TlOAc (0.100 g, 0.38 mmol) in CH_3OH (20 mL) was stirred at room temperature for 12 hours. After this period, the mixture was filtered to give a green filtrate. The volatile components were removed *in vacuo* from the filtrate to give a green residue, which was extracted with CH_2Cl_2 (20 mL). The volatile components were removed *in vacuo* from the CH_2Cl_2 extract to give [κ^4–B(mim^{But})$_3$]NiOAc as a green powder (0.019 g, 9%). Crystals of composition [κ^4–B(mim^{But})$_3$]NiOAc•CH_3CN suitable for X-ray diffraction were grown by slow evaporation of an acetonitrile/methanol (10:1) solution. ^{1}H NMR ($CDCl_3$): -0.03 [s, 27H, 3 Bu^t], 12.56 [s, 3H], 16.1 [s, br, 3H], 17.8 [s, 3H].



Molecular structure of [κ^4–B(mim^{But})$_3$]NiOAc (40% thermal parameters)

Synthesis of [FTm^{But}]NiCl

A suspension of [κ^4-B(mim^{But})$_3$]NiCl (0.100 g, 0.18 mmol) in benzene (3 mL) in an ampoule was treated with a solution of XeF_2 (0.040 g, 0.24 mmol) in benzene (7 mL). The resulting mixture was stirred for 12 hours at 100°C and then filtered. The volatile components were removed from the filtrate by lyophilization to give [FTm^{But}]NiCl as green powder, which was washed with pentane (2 × 10 mL) and dried *in vacuo* (0.056 g, 54%). Crystals of composition [FTm^{But}]NiCl•C_6H_6 suitable for X-ray diffraction were grown by slow evaporation of a benzene solution. Anal. calcd. for $C_{21}H_{33}BClFN_6NiS_3$•$(C_6H_6)_{0.2}$: C, 44.0%; H, 5.7%; N, 13.9%. Found: C, 44.0%; H, 5.7%; N, 12.7%. ^{1}H NMR (C_6D_6): -7.64 [s, 3H, 3 C<u>H</u> mim^{But}], 5.66 [s, 27H, 3 Bu^t], 9.60 [s, 3H, 3 C<u>H</u> mim^{But}]. ^{11}B NMR (C_6D_6): -64.0 [d, J_{B-F} = 36 Hz]. ^{19}F NMR (C_6D_6): -140 ~ -200 [br]. Mass spectrum: *m*/*z* = 553.2 {M–Cl}$^+$, 569.1 {M–F}$^+$, 588.1 {M}$^+$.

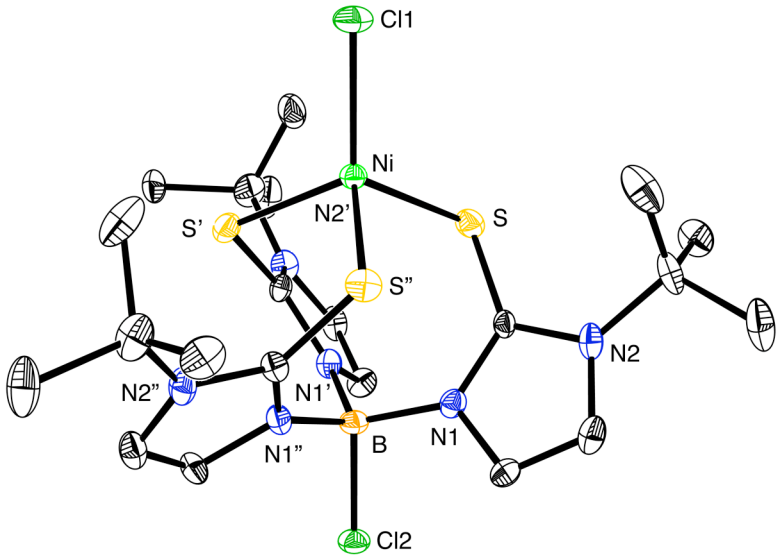


Molecular structure of [FTm^{But}]NiCl (40% thermal parameters)

Synthesis of [ClTm^{But}]NiCl

A mixture of [κ^4-B(mim^{But})$_3$]NiCl (0.100 g, 0.18 mmol) and $CHCl_3$ (0.10 mL, 1.2 mmol) in toluene (10 mL) was stirred in a glass ampoule at 120°C for 10 hours. After this period, the volatile components were removed *in vacuo* and the residue obtained was extracted into benzene (20 mL). The volatile components were removed from the extract by lyophilization to give [ClTm^{But}]NiCl as green powder (0.040 g, 37%). Crystals of

composition [ClTm^{But}]NiCl •C_6H_6 suitable for X-ray diffraction were grown by slow evaporation of a benzene solution. Anal. calcd. for $C_{21}H_{33}BCl_2N_6NiS_3$•$(C_6H_6)_{0.8}$: C, 46.3%; H, 5.7%; N, 12.6%. Found: C, 46.3%; H, 6.7%; N, 11.7%. ^{1}H NMR (C_6D_6): -8.91 [s, 3H, 3 C<u>H</u> mim^{But}], 5.93 [s, 27H, 3 Bu^t], 8.02 [s, 3H, 3 C<u>H</u> mim^{But}]. IR Data (KBr pellet, cm^{-1}): 3185 (w), 3156 (w), 2981 (m), 2921 (w), 1409 (m), 1368 (m), 1355 (s), 1294 (w), 1232 (w), 1186 (s), 1170 (s), 1075 (m), 1030 (w), 821 (w), 797 (m), 770 (m), 744 (w), 731 (w), 685 (w), 497 (m), 483 (m), 473 (m). Mass spectrum: m/z = 568.8 $\{M–Cl\}^+$, 605.7 $\{M\}^+$.

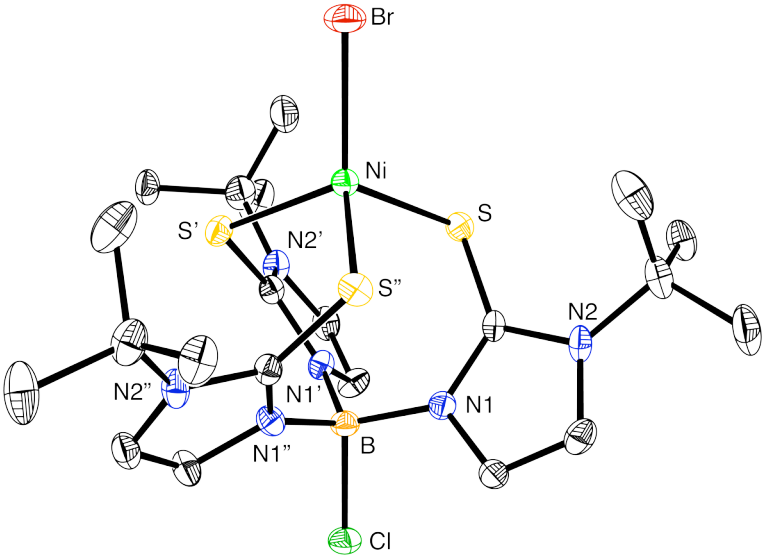


Molecular structure of [ClTm^{But}]NiCl (40% thermal parameters)

Synthesis of [ClTm^{But}]NiBr

A mixture of [κ^4-B(mim^{But})$_3$]NiCl (0.040 g, 0.07 mmol) and $CHBr_3$ (6 μL, 0.07 mmol) in benzene-d_6 (0.7 mL) was placed in a J-Young NMR tube and heated at 120°C for 2 days. The resulting mixture was filtered and the volatile components were removed from the filtrate by lyophilization to give [ClTm^{But}]NiBr as green powder (0.005 g, 10%). Crystals of composition [ClTm^{But}]NiBr •C_6H_6 suitable for X-ray diffraction were grown by slow evaporation of a benzene solution. Anal. calcd. for $C_{21}H_{33}BBrClN_6NiS_3$•$(C_6H_6)_{0.5}$: C, 41.8%; H, 5.2%; N, 12.2%. Found: C, 41.4%; H, 5.5%; N, 11.2%. ^{1}H NMR (C_6D_6): -7.27 [s, 3H, 3 C<u>H</u> mim^{But}], 4.08 [s, 27H, 3 Bu^t], 8.65 [s, 3H, 3 C<u>H</u> mim^{But}]. IR Data (KBr pellet, cm^{-1}): 3187 (w), 3160 (w), 2971 (m), 2928 (w), 1410 (w), 1356 (s), 1295 (w), 1188 (s), 1170 (s),

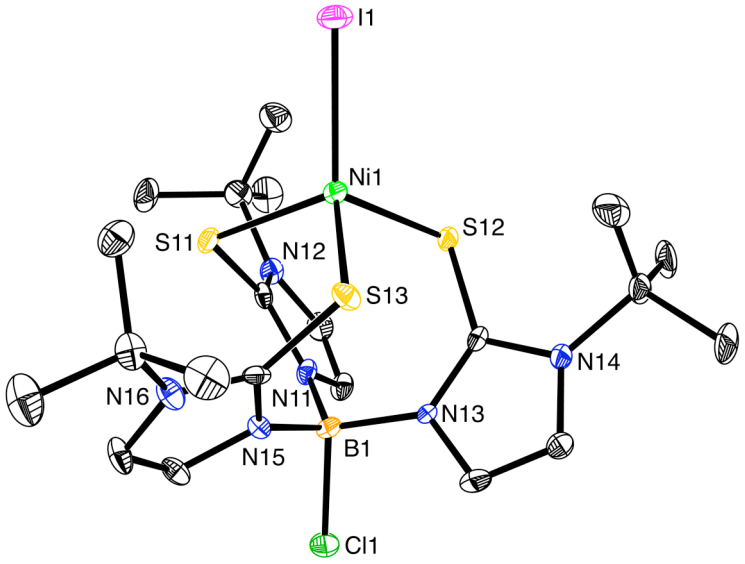
1077 (m), 820 (w), 798 (m), 768 (m), 732 (w), 685 (w), 669 (w), 481 (m), 474 (m). Mass spectrum: m/z = 569.0 $\{M–Br\}^+$, 650.0 $\{M\}^+$.



Molecular structure of [ClTm$^{Bu^t}$]NiBr (20% thermal parameters)

Synthesis of [ClTm^{But}]NiI

A suspension of [κ^4-B(mim^{But})$_3$]NiCl (0.140 g, 0.25 mmol) in benzene (5 mL) was treated with a solution of I_2 (0.031 g, 0.12 mmol) in benzene (5 mL). The mixture was stirred for 30 minutes and then filtered. The volatile components were removed from the filtrate by lyophilization to give [ClTm^{But}]NiI as an orange powder, which was washed with Et_2O (10 mL) and dried *in vacuo* (0.055 g, 33%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a benzene solution. Anal. calcd. for $C_{21}H_{33}BClIN_6NiS_3$: C, 36.2%; H, 4.8%; N, 12.1%. Found: C, 35.7%; H, 4.6%; N, 11.1%. ^{1}H NMR (C_6D_6): -4.76 [s, 3H, 3 C<u>H</u> mim^{But}], 1.50 [s, 27H, 3 Bu^t], 9.46 [s, 3H, 3 C<u>H</u> mim^{But}]. IR Data (KBr pellet, cm^{-1}): 3192 (w), 3182 (w), 3155 (w), 2976 (m), 2920 (m), 1571 (m), 1481 (w), 1410 (m), 1371 (m), 1355 (s), 1297 (m), 1229 (w), 1187 (s), 1169 (s), 1076 (m), 1031 (w), 980 (w), 821 (m), 796 (m), 768 (m), 731 (m), 727 (m), 684 (m). Mass spectrum: m/z = 569.1 {M–I}$^+$, 696.0 {M}$^+$.

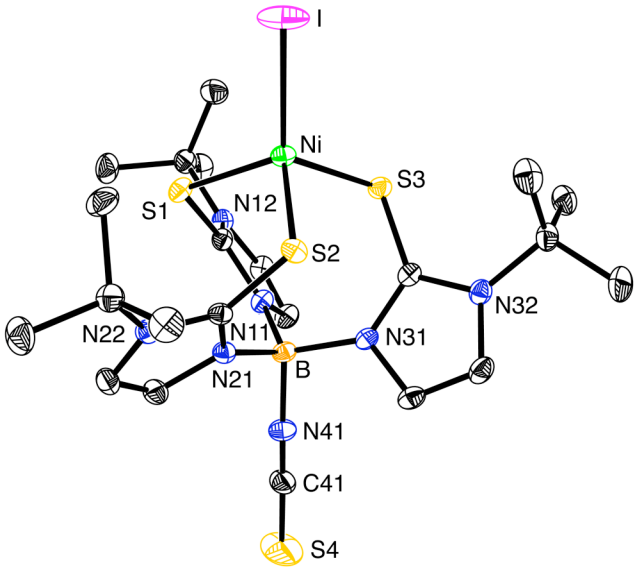


Molecular structure of [ClTm^{But}]NiI (20% thermal parameters)

Synthesis of [SCNTm^{But}]NiI

A suspension of [κ^4-B(mim^{But})$_3$]NiNCS (0.040 g, 0.067 mmol) in benzene (0.5 mL) was treated with a solution of I_2 (0.009 g, 0.035 mmol) in benzene (1 mL). The resulting mixture was stirred for 30 minutes at room temperature and then filtered. The volatile

components were removed from the filtrate by lyophilization to give [ClTm^{But}]NiI as yellow powder, which was washed with pentane (2 × 0.5 mL) and dried *in vacuo* (0.018 g, 37%). Crystals of composition [SCNTm^{But}]NiI •C_6H_6 suitable for X-ray diffraction were grown by slow evaporation of a benzene solution. Anal. calcd. for $C_{22}H_{33}BIN_7NiS_4$: C, 36.7%; H, 4.6%; N, 13.6%. Found: C, 37.4%; H, 4.0%; N, 13.7%. ^{1}H NMR (C_6D_6): -4.96 [s, 3H, 3 C<u>H</u> mim^{But}], 1.45 [s, 27H, 3 Bu^t], 10.40 [s, 3H, 3 C<u>H</u> mim^{But}]. IR Data (KBr pellet, cm^{-1}): 2978 (m), 2924 (w), 2088 (s), 1570 (w), 1481 (w), 1412 (m), 1357 (vs), 1298 (m), 1187 (s), 1169 (s), 1078 (m), 1032 (w), 821 (w), 806 (w), 773 (m), 730 (w), 686 (w). Mass spectrum: m/z = 592.5 $\{M–I\}^+$.

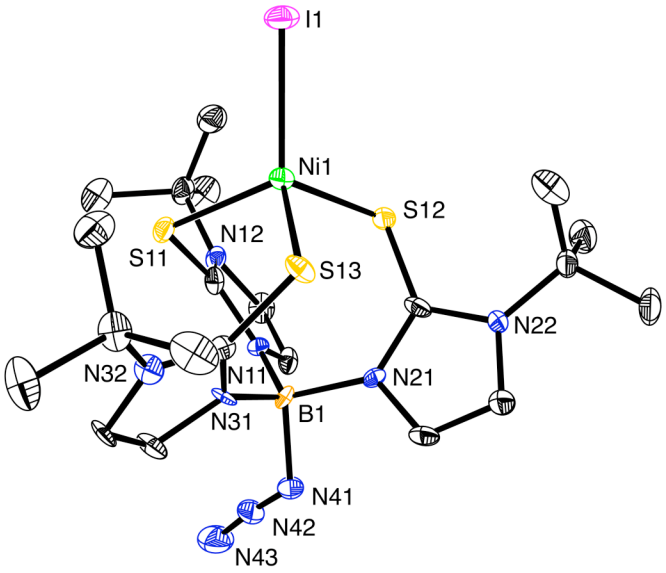


Molecular structure of [SCNTm^{But}]NiI (20% thermal parameters)

Synthesis of [N_3Tm^{But}]NiI

A suspension of [κ^4-B(mim^{But})$_3$]NiN_3 (0.040 g, 0.069 mmol) in benzene (0.5 mL) was treated with a solution of I_2 (0.010 g, 0.039 mmol) in benzene (1 mL). The resulting mixture was stirred for 30 minutes at room temperature and then filtered. The volatile components were removed from the filtrate by lyophilization to give [N_3Tm^{But}]NiI as an orange powder, which was washed with pentane (2 × 0.5 mL) and dried *in vacuo* (0.017 g, 35%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a benzene solution. ^{1}H NMR (C_6D_6): -4.85 [s, 3H, 3 C<u>H</u> mim^{But}], 1.45 [s, 27H, 3 Bu^t], 10.01

[s, 3H, 3 C<u>H</u> mim^{But}]. IR Data (KBr pellet, cm^{-1}): 2976 (m), 2920 (m), 2851 (w), 2128 (vs), 1568 (w), 1481 (w), 1457 (w), 1413 (m), 1398 (w), 1367 (s), 1356 (vs), 1295 (m), 1261 (w), 1230 (w), 1187 (s), 1168 (s), 1077 (m), 1032 (w), 984 (w), 872 (w), 829 (m), 797 (m), 723 (w), 689 (w). Mass spectrum: m/z = 576.6 {M–I}$^+$.



Molecular structure of [N_3Tm^{But}]NiI (20% thermal parameters)

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 and 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 (Versions 5.10 and 6.1).[6]

Computational Details

All calculations were carried out using DFT as implemented in the Jaguar 7.0 suite of *ab initio* quantum chemistry programs.[7] Geometry optimizations were performed with the B3LYP density functional[8] and LACVP** basis sets, *i.e.* 6-31G** (C, H, N, B, F, S and Cl) and LACVP (Ni) and LAV3P (Br and I) basis sets.[9] 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, N, B, F, S and Cl), LACV3P (Ni) and LAV3P (Br and I) basis sets.

Table 1. Crystal, intensity collection and refinement data.

	[κ⁴-B(mim$^{Bu^t}$)$_3$]NiCl	**[κ⁴-B(mim$^{Bu^t}$)$_3$]NiN$_3$·2CH$_3$CN**
lattice	rhombohedral	monoclinic
formula	$C_{21}H_{33}BClN_6NiS_3$	$C_{25}H_{39}BN_{11}NiS_3$
formula weight	570.68	659.37
space group	*R3c*	$P2_1/n$
a / Å	15.8290(6)	14.081(2)
b / Å	15.8290(6)	15.395(2)
c / Å	18.450(1)	16.195(2)
α / °	90	90
β / °	90	108.294(3)
γ / °	120	90
V / Å^3	4003.3(4)	3333.3(7)
Z	6	4
temperature (K)	243	243
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.420	1.314
μ (Mo Kα), mm^{-1}	1.084	0.804
θ max, deg.	28.28	26.37
no. of data	1568	6814
no. of parameters	101	382
R_1	0.0340	0.0561
wR_2	0.0765	0.1559
GOF	1.068	1.013

	[κ⁴-B(mim$^{Bu^t}$)$_3$]NiNCS	**[κ⁴-B(mim$^{Bu^t}$)$_3$]NiOAc·CH$_3$CN**
lattice	orthorhombic	monoclinic
formula	$C_{22}H_{33}BN_7NiS_4$	$C_{25}H_{39}BN_7NiO_2S_3$
formula weight	593.31	635.33
space group	*Pna2$_1$*	*P2$_1$/c*
a / Å	14.582(2)	10.4645(4)
b / Å	13.815(2)	14.1609(5)
c / Å	15.049(2)	20.7525(7)
α / °	90	90
β / °	90	91.7673(4)
γ / °	90	90
V / Å^3	3031.4(7)	3073.8(2)
Z	4	4
temperature (K)	243	115
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.300	1.373
μ (Mo Kα), mm^{-1}	0.939	0.870
θ max, deg.	28.31	28.22
no. of data	5421	7181
no. of parameters	327	348
R_1	0.0741	0.0448
wR_2	0.1564	0.1216
GOF	1.046	1.034

	[FTm^{But}]NiCl·C_6H_6	**[ClTm^{But}]NiCl·C_6H_6**
lattice	hexagonal	hexagonal
formula	$C_{27}H_{39}BClFN_6NiS_3$	$C_{27}H_{39}BCl_2N_6NiS_3$
formula weight	667.79	684.24
space group	$P6_3$	$P6_3$
a/Å	11.3970(3)	11.4569(3)
b/Å	11.3970(3)	11.4569(3)
c/Å	14.7256(8)	14.8181(8)
α/°	90	90
β/°	90	90
γ/°	120	120
V/Å^3	1656.5(1)	1684.5(1)
Z	2	2
temperature (K)	125	115
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.339	1.349
μ (Mo Kα), mm^{-1}	0.888	0.948
θ max, deg.	32.55	28.32
no. of data	3894	2683
no. of parameters	122	125
R_1	0.0294	0.0519
wR_2	0.0705	0.1353
GOF	1.028	1.052

	[ClTm^{But}]NiBr·C_6H_6	**[ClTm^{But}]NiI**
lattice	hexagonal	monoclinic
formula	$C_{27}H_{39}BBrClN_6NiS_3$	$C_{21}H_{33}BClIN_6NiS_3$
formula weight	728.70	697.58
space group	$P6_3$	$P2_1/c$
a/Å	11.5255(3)	14.165(1)
b/Å	11.5255(3)	20.585(2)
c/Å	15.193(1)	20.539(2)
α/°	90	90
β/°	90	92.282(2)
γ/°	120	90
V/Å^3	1747.8(1)	5984(1)
Z	2	8
temperature (K)	243	243
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.385	1.549
μ (Mo Kα), mm^{-1}	1.980	2.000
θ max, deg.	28.29	28.36
no. of data	2791	13803
no. of parameters	111	614
R_1	0.0572	0.0692
wR_2	0.1611	0.1858
GOF	1.046	1.011

	[SCNTm^{But}]NiI·C_6H_6	**[N_3Tm^{But}]NiI**
lattice	triclinic	monoclinic
formula	$C_{28}H_{39}BIN_7NiS_4$	$C_{21}H_{33}BIN_9NiS_3$
formula weight	798.32	704.16
space group	*P-1*	$P2_1/c$
a/Å	10.5227(4)	14.042(1)
b/Å	11.0009(5)	20.687(1)
c/Å	16.8869(7)	21.084(1)
α/°	77.080(1)	90
β/°	89.159(1)	92.870(2)
γ/°	70.941(1)	90
V/Å^3	1797.3(1)	6116.9(8)
Z	2	8
temperature (K)	243	243
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.475	1.529
μ (Mo Kα), mm^{-1}	1.660	1.876
θ max, deg.	28.31	24.18
no. of data	8122	9775
no. of parameters	379	650
R_1	0.0557	0.0628
wR_2	0.1451	0.0974
GOF	1.035	1.004

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

FTmNiCl
-2743.87644399768 Hartrees
(-2744.31487778504 Hartrees)

atom	x	y	z
Ni	0.0000000000	0.0000000000	1.8904189756
S	-1.7540053093	-1.2518366490	0.8307794547
Cl	0.0000000000	0.0000000000	4.1366351441
F	0.0000000000	0.0000000000	-3.3663623957
B	0.0000000000	0.0000000000	-1.9668190840
N	-1.4783414297	0.2279615436	-1.5342004970
N	-3.4481658556	0.3292069144	-0.5846107985
C	-2.2019514761	-0.2080663430	-0.4676161104
C	-2.2910508285	1.0447929358	-2.3116793175
H	-1.9230212345	1.4947879529	-3.2179076704
C	-3.5119177040	1.1073242226	-1.7291358730
H	-4.4124027402	1.6243463498	-2.0188942937
C	-4.5321367059	0.1391940892	0.3709252496
H	-4.1400184552	0.2325296192	1.3845564228
H	-5.2871972455	0.9054117983	0.1895901667
H	-4.9806597692	-0.8515018459	0.2586153314
S	1.9611249941	-0.8930948317	0.8307794547
N	0.5417502270	-1.3942620054	-1.5342004970

N	1.4389813769	-3.1508026846	-0.5846107985
C	1.2811664767	-1.8029127447	-0.4676161104
C	0.2407081901	-2.5065046868	-2.3116793175
H	-0.3330137233	-2.4127792175	-3.2179076704
C	0.7969879450	-3.5950720590	-1.7291358730
H	0.7994761667	-4.6334260396	-2.0188942937
C	2.1455227356	-3.9945425653	0.3709252496
H	1.8686326702	-3.7016259640	1.3845564228
H	1.8594890045	-5.0315530286	0.1895901667
H	3.2277521145	-3.8876269648	0.2586153314
S	-0.2071196848	2.1449314807	0.8307794547
N	0.9365912027	1.1663004618	-1.5342004970
N	2.0091844788	2.8215957702	-0.5846107985
C	0.9207849994	2.0109790877	-0.4676161104
C	2.0503426384	1.4617117509	-2.3116793175
H	2.2560349577	0.9179912646	-3.2179076704
C	2.7149297590	2.4877478364	-1.7291358730
H	3.6129265735	3.0090796899	-2.0188942937
C	2.3866139703	3.8553484761	0.3709252496
H	2.2713857850	3.4690963448	1.3845564228
H	3.4277082410	4.1261412303	0.1895901667
H	1.7529076547	4.7391288107	0.2586153314

ClTmNiF
-2743.81853746678 Hartrees
(-2744.26958648035 Hartrees)

atom	x	y	z
Ni	0.0000000036	0.0000000012	1.9067271993
S	-1.7016923913	-1.3183297752	0.7663729476
F	-0.0000000038	-0.0000000024	3.7013520617
Cl	-0.0000000044	-0.0000000047	-3.9090305897
B	0.0000000047	0.0000000059	-1.9901329604
N	-1.4700956199	0.2466315079	-1.5612208921
N	-3.4102879926	0.3250046011	-0.5427034205
C	-2.1723963347	-0.2381279954	-0.4925431751
C	-2.2889698612	1.1393161810	-2.2481563129
H	-1.9457802318	1.6473949659	-3.1323235444
C	-3.4887351688	1.1831957293	-1.6261501696
H	-4.3854533566	1.7358637104	-1.8555334796
C	-4.4708067518	0.0959645650	0.4297815188
H	-4.0605968431	0.1674966506	1.4381873854
H	-5.2389499055	0.8565488383	0.2824755362
H	-4.9080572591	-0.8973117315	0.2991997570
S	1.9922134708	-0.8125560925	0.7695055417
N	0.5233375679	-1.3967048613	-1.5602454329
N	1.4263153464	-3.1145554419	-0.5395501595
C	1.2931440537	-1.7611095193	-0.4901464550
C	0.1627758428	-2.5530725592	-2.2474358388

H	-0.4473861519	-2.5109816384	-3.1326902516
C	0.7252413332	-3.6131015473	-1.6241127772
H	0.6971938057	-4.6661239283	-1.8532532007
C	2.1547293794	-3.9172728440	0.4341379661
H	1.8859912633	-3.5978209520	1.4421007836
H	1.8816089904	-4.9631819667	0.2867977908
H	3.2335560222	-3.7979754585	0.3048734740
S	-0.2923683929	2.1324973876	0.7704758338
N	0.9473547331	1.1509057525	-1.5593556223
N	1.9827979342	2.7933662847	-0.5403021513
C	0.8777145819	2.0007223675	-0.4898270245
C	2.1292157198	1.4165821518	-2.2464708050
H	2.3981819706	0.8663094205	-3.1310703203
C	2.7651793340	2.4348589010	-1.6244940933
H	3.6907525683	2.9375372834	-1.8542482013
C	2.3133935042	3.8267781682	0.4322006218
H	2.1712317506	3.4353861679	1.4405858968
H	3.3556355345	4.1133926695	0.2844978027
H	1.6703443843	4.7010304435	0.3019283441

BrTmNiCl
-2657.16793734626 Hartrees
(-2657.57721243469 Hartrees)

atom	x	y	z
Ni	-0.0000000004	-0.0000000001	2.3439103774
S	-1.6670964560	-1.3637870274	1.2482262526
Cl	0.0000000002	0.0000000001	4.5829299985
Br	-0.0000000002	0.0000000000	-3.6448134556
B	0.0000000003	0.0000000001	-1.4715765327
N	-1.4697843200	0.2288141699	-1.0629944274
N	-3.3946469162	0.3057585671	-0.0118492958
C	-2.1623434883	-0.2688769781	0.0088388165
C	-2.2900650105	1.1454006424	-1.7175155366
H	-1.9549999623	1.6666131887	-2.5970874718
C	-3.4797185021	1.1859560109	-1.0772831542
H	-4.3745636100	1.7511408067	-1.2819995143
C	-4.4502552071	0.0752388147	0.9672451971
H	-3.9955110271	-0.1042305187	1.9417293568
H	-5.0851865169	0.9617669386	1.0066763275
H	-5.0522759907	-0.7953711810	0.6912538220
S	2.0137517809	-0.7613636608	1.2462949520
N	0.5375726922	-1.3878547297	-1.0642910797
N	1.4350357281	-3.0930920549	-0.0142949562
C	1.3146631655	-1.7387388121	0.0074379754

C	0.1557885365	-2.5564378377	-1.7201775842
H	-0.4629665357	-2.5267416856	-2.5998348277
C	0.7167074928	-3.6068027326	-1.0807716044
H	0.6763931915	-4.6642214424	-1.2864908537
C	2.1637790730	-3.8927372076	0.9631872348
H	2.1069668958	-3.4007401512	1.9343854160
H	1.7031791317	-4.8806006033	1.0152628918
H	3.2148213161	-3.9925753841	0.6768104716
S	-0.3484536774	2.1238963271	1.2479659389
N	0.9325701613	1.1592228413	-1.0635113858
N	1.9611177842	2.7875665122	-0.0114861379
C	0.8479064303	2.0067792014	0.0090866512
C	2.1355640657	1.4132863338	-1.7189404034
H	2.4190952537	0.8635810598	-2.5992665204
C	2.7650803158	2.4232150447	-1.0782321813
H	3.7011960982	2.9169172121	-1.2832862609
C	2.2899671656	3.8171793433	0.9671727321
H	1.8879888001	3.5231798578	1.9369417667
H	3.3759549414	3.9082754848	1.0229462648
H	1.8553280473	4.7789623005	0.6795094625

ClTmNiBr
-2657.18379752059 Hartrees
(-2657.58917118896 Hartrees)

atom	x	y	z
Ni	0.0000000014	0.0000000022	2.3522718957
S	-1.6860818935	-1.3322696995	1.2590924145
Br	-0.0000000010	-0.0000000005	4.7709839800
Cl	-0.0000000005	0.0000000028	-3.4212078677
B	0.0000000001	-0.0000000045	-1.5072986690
N	-1.4706070219	0.2371376019	-1.0714436069
N	-3.3959474604	0.3250910413	-0.0250007465
C	-2.1618058653	-0.2449893756	0.0048934700
C	-2.2939478032	1.1359659393	-1.7447608244
H	-1.9604449207	1.6437736691	-2.6328546006
C	-3.4844232926	1.1863411035	-1.1045994050
H	-4.3805976192	1.7456749181	-1.3193447297
C	-4.4361577419	0.1116661296	0.9746486773
H	-4.0302050267	0.2908514052	1.9718264646
H	-5.2501776730	0.8088897428	0.7716326231
H	-4.8100741705	-0.9135767826	0.9279185861
S	1.9951032600	-0.7970906326	1.2579110160
N	0.5311563019	-1.3930166565	-1.0742579946
N	1.4258503612	-3.1042749289	-0.0347998812
C	1.2957103771	-1.7511237177	0.0006269047

C	0.1701209435	-2.5544359084	-1.7524673503
H	-0.4365146881	-2.5187160958	-2.6404316004
C	0.7266866687	-3.6105561589	-1.1165754717
H	0.6953557829	-4.6656554778	-1.3353233239
C	2.1349300602	-3.8990358482	0.9613226603
H	1.7774775457	-3.6411850212	1.9598395999
H	1.9413251117	-4.9526600657	0.7555126470
H	3.2091229972	-3.7066109737	0.9135576682
S	-0.3093114231	2.1253218513	1.2602028507
N	0.9405018707	1.1557942653	-1.0721528926
N	1.9779823938	2.7807423118	-0.0270128577
C	0.8686737984	1.9948766504	0.0045179015
C	2.1285571138	1.4219281930	-1.7477620130
H	2.4004845284	0.8797827044	-2.6365607715
C	2.7666344125	2.4288318807	-1.1084623488
H	3.6978841798	2.9270454076	-1.3244727268
C	2.3127838266	3.7894596869	0.9716069837
H	2.2669693026	3.3488296440	1.9691230834
H	3.3227420937	4.1474094717	0.7671232974
H	1.6103806847	4.6247018122	0.9253082599

ITmNiCl
-2655.37540490418 Hartrees
(-2655.78355641257 Hartrees)

atom	x	y	z
Ni	0.0000000000	0.0000000000	2.6969781577
S	-1.6567010280	-1.3740963140	1.5905184486
Cl	0.0000000000	0.0000000000	4.9364811414
I	0.0000000000	0.0000000000	-3.5484162705
B	0.0000000000	0.0000000000	-1.1243614696
N	-1.4657619717	0.2334537140	-0.7173619147
N	-3.3754535780	0.3118098866	0.3628748682
C	-2.1497009842	-0.2732753282	0.3572478736
C	-2.2845711334	1.1736477402	-1.3398433885
H	-1.9588173698	1.7092582770	-2.2142820164
C	-3.4644012337	1.2158643122	-0.6814628552
H	-4.3555002522	1.7941537310	-0.8643513426
C	-4.3968045887	0.0923153086	1.3812886410
H	-3.9819494821	0.2971836020	2.3702952970
H	-5.2288558150	0.7676889395	1.1778464173
H	-4.7472695723	-0.9414762040	1.3561746309
S	2.0193251637	-0.7457089214	1.5956654744
N	0.5322383339	-1.3851421768	-0.7150570807
N	1.4207009018	-3.0767375984	0.3667882834
C	1.3128547861	-1.7227549854	0.3607591035

C	0.1297573577	-2.5652407737	-1.3371234012
H	-0.4961346114	-2.5523375055	-2.2121971266
C	0.6840395225	-3.6071637736	-0.6778849222
H	0.6305395481	-4.6681762558	-0.8604358213
C	2.1216513950	-3.8503835904	1.3859959369
H	1.7357626353	-3.5936678577	2.3746215417
H	1.9541428376	-4.9088984746	1.1827058814
H	3.1919238588	-3.6357305910	1.3615782681
S	-0.3616610427	2.1219844494	1.5953436515
N	0.9341092641	1.1534988696	-0.7157045004
N	1.9561418684	2.7680098297	0.3658370712
C	0.8370715969	1.9982675454	0.3601854823
C	2.1573498931	1.3941125387	-1.3380965663
H	2.4585317103	0.8452429743	-2.2131489542
C	2.7832602986	2.3948389018	-0.6791283948
H	3.7290521226	2.8785410301	-0.8620255332
C	2.2764768346	3.7616395784	1.3850269323
H	2.2472559497	3.2989721999	2.3735975013
H	3.2770059618	4.1454659045	1.1814146842
H	1.5557604274	4.5814699875	1.3609891312

ClTmNiI
-2655.40192077623 Hartrees
(-2655.80693194184 Hartrees)

atom	x	y	z
Ni	0.0000000017	0.0000000026	2.7092580964
S	-1.6799568193	-1.3340535949	1.6160409039
I	-0.0000000013	-0.0000000013	5.3012968836
Cl	-0.0000000011	0.0000000007	-3.0685082290
B	0.0000000008	-0.0000000019	-1.1555738221
N	-1.4719634510	0.2316576214	-0.7189239450
N	-3.3922955210	0.3230936950	0.3360423179
C	-2.1587731753	-0.2484999519	0.3610696926
C	-2.2964326547	1.1316088767	-1.3887899861
H	-1.9665435134	1.6365884826	-2.2799294891
C	-3.4837047217	1.1851461243	-0.7426643173
H	-4.3803206478	1.7448955163	-0.9545001273
C	-4.4250512906	0.1186792383	1.3455290661
H	-4.0263511291	0.3524120618	2.3345904400
H	-5.2609484358	0.7802490081	1.1139208291
H	-4.7651920365	-0.9189322460	1.3415342589
S	1.9950461766	-0.7887724579	1.6141521601
N	0.5345207097	-1.3904706728	-0.7196537795
N	1.4176635824	-3.0997331717	0.3327552916
C	1.2947949970	-1.7458484500	0.3593225563

C	0.1683551327	-2.5540880074	-1.3910498613
H	-0.4342081625	-2.5203344259	-2.2819575338
C	0.7168177387	-3.6092673614	-0.7464059948
H	0.6813249344	-4.6654247433	-0.9594195745
C	2.1125895440	-3.8922824197	1.3408283711
H	1.7115026868	-3.6652135710	2.3304906575
H	1.9582933761	-4.9468849337	1.1083377804
H	3.1810901994	-3.6671602698	1.3361111069
S	-0.3175985331	2.1208891553	1.6162662623
N	0.9352182077	1.1592288694	-0.7187830489
N	1.9717414863	2.7792538937	0.3349523080
C	0.8616963596	1.9944323699	0.3610053659
C	2.1259184411	1.4257210881	-1.3895868642
H	2.3988490497	0.8878318946	-2.2807342958
C	2.7640957120	2.4287001062	-0.7441985505
H	3.6958431091	2.9274690936	-0.9567959931
C	2.3095096632	3.7769007373	1.3439148215
H	2.3147126032	3.3149798702	2.3330876205
H	3.2991640648	4.1725081461	1.1112852584
H	1.5789151959	4.5884277228	1.3404536530

ITmNiNCS
-2686.20142772115 Hartrees
(-2686.63664906656 Hartrees)

atom	x	y	z
Ni	-0.1760734516	-0.1299257870	2.6975532459
S	-1.8249642414	-1.4528332226	1.5169437523
N	0.2574140424	0.1926180130	4.5411038455
C	0.7254446684	0.5465925139	5.5792742497
S	1.3365257785	1.0056252099	6.9972817555
I	0.0923238840	0.0474310220	-3.5140897304
B	-0.0462408426	-0.0293108333	-1.0950188922
N	-1.5336625834	0.1897879287	-0.7566284100
N	-3.4985801816	0.2307915079	0.2230438416
C	-2.2664497905	-0.3366634168	0.2758282754
C	-2.3329617192	1.1259545284	-1.4112162351
H	-1.9692911003	1.6764850390	-2.2609466439
C	-3.5455758883	1.1457146213	-0.8151236526
H	-4.4336712349	1.7147013283	-1.0375255524
C	-4.5727476746	-0.0220144128	1.1765270795
H	-4.2336393516	0.2104871513	2.1882548163
H	-5.4179992527	0.6147265143	0.9122335594
H	-4.8762354747	-1.0701883083	1.1414126304
S	1.8630796323	-0.8899725734	1.6773287208
N	0.4606069610	-1.4326687957	-0.7092064345

N	1.3225580936	-3.1674030570	0.3245591942
C	1.2073651464	-1.8146270824	0.3748093495
C	0.0788476054	-2.5858695015	-1.3917566091
H	-0.5208135182	-2.5367783919	-2.2837399954
C	0.6190419857	-3.6540395220	-0.7633027451
H	0.5768573693	-4.7060702576	-0.9944178015
C	2.0079897791	-3.9828995666	1.3211469126
H	1.5991577083	-3.7773546034	2.3124743779
H	1.8551026192	-5.0319431593	1.0644680579
H	3.0765754770	-3.7586984287	1.3308576904
S	-0.5615296738	2.0290584230	1.6447177162
N	0.8690592053	1.1034308155	-0.6003765226
N	1.8453921539	2.6672543663	0.5931327994
C	0.7162671175	1.9197357495	0.4917667361
C	2.1335677384	1.3397293731	-1.1354198474
H	2.4826133825	0.8107529509	-2.0050304921
C	2.7315787291	2.3095033304	-0.4071231494
H	3.6955083563	2.7801342506	-0.5137225444
C	2.1168786360	3.6215543043	1.6643010630
H	2.0143491723	3.1277271983	2.6325867938
H	3.1358258374	3.9900101443	1.5391872366
H	1.4149444856	4.4565436367	1.6197814169

SCNTmNiI
-2686.24649431386 Hartrees
(-2686.67601718693 Hartrees)

atom	x	y	z
I	0.0277377839	-2.2468524347	5.7177066203
Ni	1.6499165626	-0.4007743467	4.9022930615
S	3.3551619968	-0.9644807350	3.2998281447
S	2.9495787766	0.7113522004	6.5866732158
S	0.5793688449	1.4497042838	3.8023502765
S	6.4875097733	5.7051401687	2.4429079267
N	3.5070097073	1.7057589810	2.4289001754
N	2.8495688282	0.2482826397	0.9304865493
N	4.8043413775	1.6016109148	4.6678516754
N	5.5905419390	0.2476051229	6.2009178373
N	2.7335145534	3.1413139158	4.4426830577
N	0.8059250508	3.6654913933	5.3435941741
N	4.8353705665	3.6132685806	3.2444770550
B	3.9452534435	2.4852470682	3.7086323624
C	3.2499605993	0.3811553471	2.2245975407
C	3.2396133277	2.3875793074	1.2457283263
H	3.3662627486	3.4540723870	1.1682965348
C	2.8383530949	1.4887487175	0.3170596874
H	2.5535497452	1.6150877548	-0.7150089156
C	2.4438199309	-1.0063427953	0.3073612803
H	1.7429016925	-1.5275937198	0.9611499591

H	1.9652461993	-0.7745135193	-0.6451088874
H	3.3097997733	-1.6505439086	0.1362390615
C	4.4641722818	0.8835782421	5.7772262020
C	6.1527773454	1.3814399641	4.4046169690
H	6.6471639334	1.8440550290	3.5673346427
C	6.6420888434	0.5497565155	5.3535475892
H	7.6327597122	0.1525952093	5.5053617312
C	5.6575151925	-0.6585489490	7.3417822981
H	4.8391079418	-1.3779011646	7.2843201641
H	6.6157394551	-1.1787575372	7.3077220052
H	5.5728308564	-0.1052513681	8.2802235782
C	1.4226043793	2.7708665547	4.5238571206
C	2.9169464056	4.2663666466	5.2405712724
H	3.8796533281	4.7386991514	5.3383554247
C	1.7262582781	4.5955432654	5.7935571745
H	1.4507822483	5.4002885717	6.4559231663
C	-0.5996763710	3.6106063507	5.7294271830
H	-0.8527375481	2.5949752779	6.0375441887
H	-0.7526715150	4.3025499353	6.5587360978
H	-1.2416149156	3.8932812031	4.8915120074
C	5.5403391972	4.5061733792	2.9036026649

Table 3. "Snap" bond enthalpies for [YTm^{Me}]NiZ determined by DFT calculations on [YTm^{Me}]NiZ (S = 1), [YTm^{Me}]Ni (S = 1/2), [B(mim^{Me})$_3$]NiZ (S = 3/2) performed with the B3LYP functional and cc-pVTZ(-f)/LACV3P/LAV3P basis sets.

[YTm^{Me}]NiZ	***D*(B–Y)/kcal mol^{-1}**	***D*(Ni–Z)/kcal mol^{-1}**
[FTm^{Me}]NiCl	160.8 (Y = F)	76.5 (Z = Cl)
[ClTm^{Me}]NiF	108.8 (Y = Cl)	102.5 (Z = F)
[ClTm^{Me}]NiBr	112.8 (Y = Cl)	70.6 (Z = Br)
[ClTm^{Me}]NiI	108.1 (Y = Cl)	61.6 (Z = I)
[BrTm^{Me}]NiCl	93.0 (Y = Br)	83.0 (Z = Cl)
[ITm^{Me}]NiCl	76.6 (Y = I)	82.9 (Z = Cl)

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