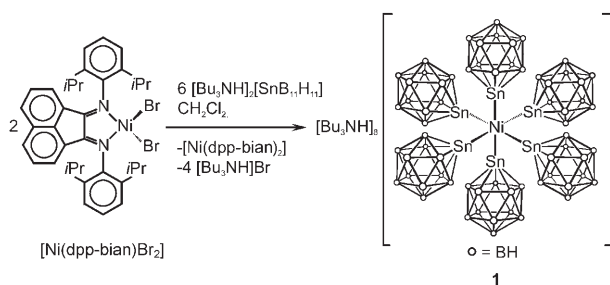


Octahedral Coordination Compounds of the Ni, Pd, Pt Triad**

Marius Kirchmann, Klaus Eichele, Falko M. Schappacher, Rainer Pöttgen, and Lars Wesemann*

Coordination compounds of the nickel triad with tin are well-established, and in the case of the ligands $[\text{SnCl}_3]^-$, $[\text{SnPh}_3]^-$, $\text{Sn}(\text{NtBu})_2\text{SiMe}_2$, $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$, $\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2$, and $[\text{SnB}_{11}\text{H}_{11}]^{2-}$, a variety of complexes has been characterized, predominantly with the transition metal in the formal oxidation state II.^[1,2] We present herein a homoleptic series of octahedrally tin-coordinated complexes $[\text{M}(\text{SnB}_{11}\text{H}_{11})_6]^{8-}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) with the metal in the formal oxidation state IV. Our investigations of the coordination chemistry of stanna-*closo*-dodecaborate have revealed that this borate serves as a versatile ligand in coordination chemistry.^[2] In its reaction with platinum electrophiles, we found complexes which are active catalysts in hydroformylation reactions; with the coinage metals, cluster formation is the dominant reaction; and with ruthenium complex fragments, ambident coordination modes together with dynamic behavior of the heteroborate were characterized.^[3–10]

To synthesize a diazabutadiene nickel complex with stanna-*closo*-dodecaborate as ligand, we treated the nickel halide $[\text{Ni}(\text{dpp-bian})\text{Br}_2]$ with three equivalents $[\text{SnB}_{11}\text{H}_{11}]^{2-}$ (Scheme 1).^[11] The octahedral nickel complex **1** was isolated



Scheme 1. Synthesis of $[\text{Bu}_3\text{NH}]_6[\text{Ni}(\text{SnB}_{11}\text{H}_{11})_6]$ (**1**).

from this reaction mixture as purple crystals and was characterized by elemental analysis, mass spectrometry, X-ray crystal structure analysis (Figure 1), heteronuclear

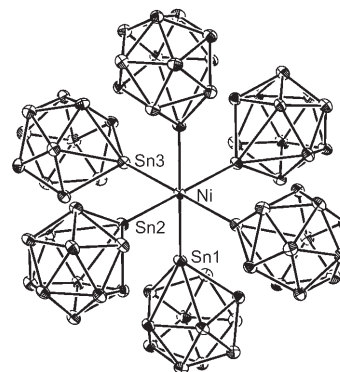


Figure 1. Molecular structure of the anion of $[\text{Bu}_3\text{NH}]_6[\text{Ni}(\text{SnB}_{11}\text{H}_{11})_6]$ (**1**); H atoms and cations have been omitted for clarity; ellipsoids are set at 30% probability. Selected bond lengths [Å] and angles [°]: Ni–Sn1 2.5475(4), Ni–Sn2 2.5343(4), Ni–Sn3 2.5274(4); Sn1–Ni–Sn2 90.12(1), Sn1–Ni–Sn3 90.96(1), Sn2–Ni–Sn3 89.14(1).

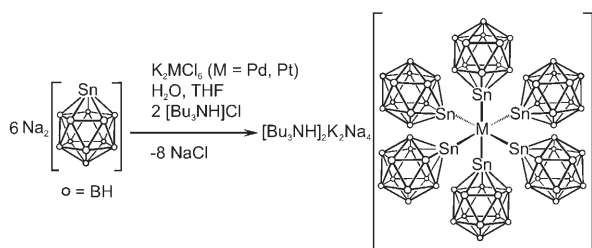
NMR spectroscopy (Figures 3 and 4) and ^{119}Sn Mössbauer spectroscopy (Figure 6).

The octaanionic complex $[\text{Ni}(\text{SnB}_{11}\text{H}_{11})_6]^{8-}$ with nickel in the formal oxidation state IV is the product of an oxidation reaction, raising the question of the corresponding reduction product. It has been reported that $[\text{Ni}(\text{dab})\text{Br}_2]$ ($\text{dab} = 1,4$ -diazabutadiene or α -diimine) can readily be reduced in the presence of additional dab, resulting in the formation of $[\text{Ni}(\text{dab})_2]$ ^[12–14] with nickel in its common oxidation state II and anionic radical dab ligands.^[15–18] To our knowledge, the reduction product $[\text{Ni}(\text{dpp-bian})_2]$ has not been reported to date, and we were not able to identify the dark violet compound in the remaining reaction mixture (Scheme 1). To investigate whether a reduction of $[\text{Ni}(\text{dab})\text{Br}_2]$ is possible with our stannaborate $[\text{SnB}_{11}\text{H}_{11}]^{2-}$, we carried out the reaction of $[\text{Ni}(4\text{-MePh-dab})\text{Br}_2]$ ($4\text{-MePh-dab} = 1,4$ -bis(4-methylphenyl)-1,4-diaza-1,3-butadiene) with $[\text{Bu}_3\text{NH}]_2-[\text{SnB}_{11}\text{H}_{11}]$. Although the yield of **1** was strongly reduced to about 5%, $[\text{Ni}(4\text{-MePh-dab})_2]$ could be isolated and identified by ^1H and ^{13}C NMR spectroscopy.^[12] This result, as well as the reaction stoichiometry of 1:3, supports the suggested oxidation of the nickel(II) starting material to nickel(IV) coupled with a reduction of $[\text{Ni}(\text{dpp-bian})\text{Br}_2]$ (Scheme 1).^[19] Hence, the yield of **1** can be corrected to 64% with respect to the nickel(II) starting material. At the end of the workup procedure of **1**, dark red crystals of $[\text{Bu}_3\text{NH}]_6[\text{Ni}(\text{SnB}_{11}\text{H}_{11})_4]$ (**2**) were isolated and, owing to the small amount, only characterized by single crystal structure analysis. This complex completes the series of the square-planar hexaanions $[\text{M}(\text{SnB}_{11}\text{H}_{11})_4]^{6-}$ ($\text{M} = \text{Pd}, \text{Pt}$), and the square-planar coordination mode of **2** is further convincing evidence for the substantial ligand strength of the tin ligand stanna-*closo*-dodecaborate.^[3]

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The homologous complexes of **1** with hexacoordinate palladium and platinum $[M(\text{SnB}_{11}\text{H}_{11})_6]^{8-}$ ($M = \text{Pd}$ (**3**), Pt (**4**)) were synthesized by substitution reactions starting with the respective hexachloride complexes and the sodium salt $\text{Na}_2[\text{SnB}_{11}\text{H}_{11}]$ in a mixture of water and THF (Scheme 2).



Scheme 2. Synthesis of $[\text{Bu}_3\text{NH}]_2\text{K}_2\text{Na}_4[\text{M}(\text{SnB}_{11}\text{H}_{11})_6]$; $M = \text{Pd}$ (**3**), Pt (**4**).

The unusual combination of cations was found accidentally to give large crystals of **3** and **4** when diethyl ether was slowly diffused into a THF solution. The complexes **3** and **4** were characterized by elemental analyses, X-ray crystal structure analyses, and heteronuclear NMR spectroscopy.^[20] It is noteworthy that the octahedral complexes **1**, **3**, and **4** all show remarkable stability towards moisture and air.

The structure refinement for **1** in space group $P2_1/c$ reveals that the nickel center is almost ideally octahedrally coordinated by six stannaborate ligands, whereby the nickel atom lies on a center of symmetry. In addition, there are four $[\text{Bu}_3\text{NH}]^+$ counterions and three partially disordered toluene molecules included in the asymmetric unit, which confirms the eight-fold negative charge of the anion. The structure of the octaanion of **1** is depicted in Figure 1. The Ni–Sn bond lengths are between 2.5211(6) and 2.5403(7) Å, which is in good agreement with the Ni–Sn separation in the five-coordinate nickel–tin complex $[\text{Ni}(\text{np}_3)(\text{SnPh}_3)][\text{BPh}_4]$ ($\text{np}_3 = \text{tris}(2\text{-(diphenylphosphino)ethyl)amine}$)^[1,21] and somewhat longer than the Ni–Sn bonds of the compounds $[\text{Ni}(\text{Sn}(\text{NBu}_2)_2\text{SiMe}_2)_4\text{Br}_2]$ (2.459(4)–2.460(4) Å)^[1] and $[\text{Bu}_4\text{N}][\text{Ni}(\text{PPh}_3)\text{Cp}(\text{SnB}_{11}\text{H}_{11})]$ (2.412(1) Å; Cp = cyclopentadienyl).^[22] The Ni–Sn distances are comparable with those in the intermetallic stannides Ni_3Sn_4 (2.54–2.77 Å) and AuNiSn_2 (2.64 Å).^[23,24] Compound **2** crystallizes in space group $P\bar{1}$. The molecular structure of the anion is shown in Figure 2 and reveals an almost ideal square-planar coordination. As in compound **1**, the nickel atom lies on a center of symmetry. Furthermore, besides the three partly disordered $[\text{Bu}_3\text{NH}]^+$ counterions, one spatially disordered benzene molecule is included in the asymmetric unit. In contrast to compound **1**, the Ni–Sn bonds (2.4761(4) and 2.4706(5) Å) are shorter but are also in good accordance with known Ni–Sn distances.^[1,21,22]

Examination of the crystal structure solutions of **3** and **4** revealed that both compounds crystallize in the same space group $P2_1/n$ with almost identical unit cell constants and angles. The metals display nearly ideal octahedral coordination by six tin ligands and lie on a center of symmetry. The metal–tin separations of **3** (2.6122(5)–2.6144(5) Å) and **4**

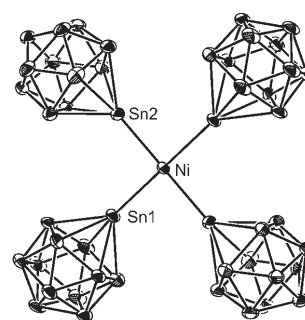


Figure 2. Molecular structure of the anion of $[\text{Bu}_3\text{NH}]_6[\text{Ni}(\text{SnB}_{11}\text{H}_{11})_4]$ (**2**); H atoms and cations have been omitted for clarity; ellipsoids are set at 30% probability. Selected bond lengths [Å] and angles [°]: Ni–Sn1 2.4761(4), Ni–Sn2 2.4706(5); Sn1–Ni–Sn2 89.81(2).

(2.6162(5)–2.6186(5) Å) fall within the range of known palladium–tin and platinum–tin distances.^[1,3,4] In addition, the cationic part of both compounds consists of four cations ($[\text{Bu}_3\text{NH}]$, K, 2Na) per asymmetric unit. The Pd–Sn and Pt–Sn distances observed in the two coordination compounds are considerably shorter than those observed in intermetallic stannides, for example, 2.78–2.84 Å in PdSn_2 , PdSn_3 , and PdSn_4 ,^[25] 2.77–2.80 Å in CaPdSn_2 ,^[26] 2.64–2.92 Å in $\text{Ca}_2\text{Pt}_3\text{Sn}_5$,^[26] and 2.64–2.85 Å in $\text{Yb}_2\text{Pt}_3\text{Sn}_5$.^[27]

To examine the composition of **1**, **3**, and **4** in solution, the respective salts were dissolved in dichloromethane or THF, and ^{11}B , ^{119}Sn , and ^{195}Pt NMR spectroscopy experiments were carried out (Table 1, Figures 3–5). The signal around $\delta =$

Table 1. $^{11}\text{B}\{^1\text{H}\}$, $^{119}\text{Sn}\{^1\text{H}\}$, and ^{195}Pt NMR spectroscopic data for **1**, **3**, and **4**.

	$^{11}\text{B}\{^1\text{H}\}$ [ppm]	$^{119}\text{Sn}\{^1\text{H}\}$ [ppm]	$^2J(^{119}\text{Sn}-^{117}\text{Sn})$ <i>cis</i> [Hz]	$^2J(^{119}\text{Sn}-^{117}\text{Sn})$ <i>trans</i> [Hz]
1 ^[a]	−15.9	−319	1931	13 489
3 ^[b]	−15.2	−284	1135	19 700
4 ^[c]	−15.6	−470	1050	15 287

[a] In CD_2Cl_2 . [b] In $[\text{D}_8]\text{THF}$. [c] In $[\text{D}_8]\text{THF}$ at 5 °C; ^{195}Pt NMR: $\delta = -7724$ ($J(^{195}\text{Pt}-^{119}\text{Sn}) = 7900$ Hz, $J(^{195}\text{Pt}-^{117}\text{Sn}) = 7550$ Hz).

−15 ppm in the ^{11}B NMR spectrum, as well as the resonances in the ^{119}Sn NMR spectra of **1**, **3**, and **4**, are an unambiguous indicator for coordination of the tin ligand (for comparison, signals of the uncoordinated cluster: ^{11}B NMR: $\delta = -6, -11, -12$ ppm; ^{119}Sn NMR: $\delta = -550$ ppm).^[2] The ^{119}Sn NMR resonances exhibit ^{117}Sn satellites corresponding to small *cis* coupling constants (1931, 1135, 1050 Hz) and large *trans* coupling constants (13 489, 19 700, 15 287 Hz; Figure 3). The ^{119}Sn NMR spectrum of $[\text{Ni}(\text{SnB}_{11}\text{H}_{11})_6]^{8-}$ in solution is in good accordance with the solid-state ^{119}Sn VACP/MAS NMR spectrum showing a signal at −329 ppm (Figure 4).

Furthermore, the presence of platinum in compound **4** gives rise to ^{195}Pt satellites with $J(^{195}\text{Pt}-^{119}\text{Sn}) = 7900$ Hz in the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **4**. Since no resonances of uncoordinated stannaborate are visible in the ^{11}B and ^{119}Sn spectra of **1**, **3**, and **4**, all six ligands remain mainly coordinated in solution. The examination of the ^{195}Pt spec-

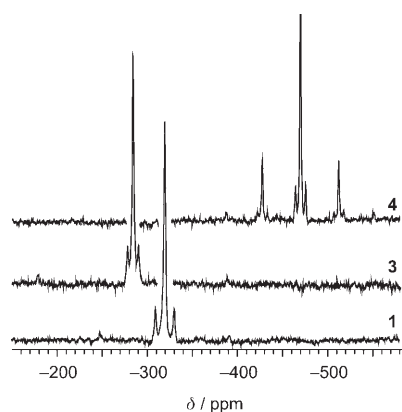


Figure 3. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra of **1**, **3**, and **4**.

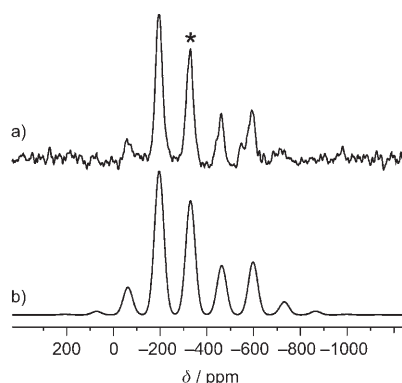


Figure 4. a) Experimental^[20] and b) simulated VACP-MAS ^{119}Sn NMR spectrum of **1** (VACP/MAS = variable amplitude cross polarization magic angle spinning). The isotropic chemical shift δ_{iso} is marked by an asterisk. The chemical shift anisotropy has been determined by an analysis of the spinning sideband intensities.^[31,32] The value of the span Ω (612 ppm) as well as the positive sign of the skew κ (0.98) are in good agreement with the reported results for $\eta^1(\text{Sn})$ coordinated stanna-*closo*-dodecaborate.^[33]

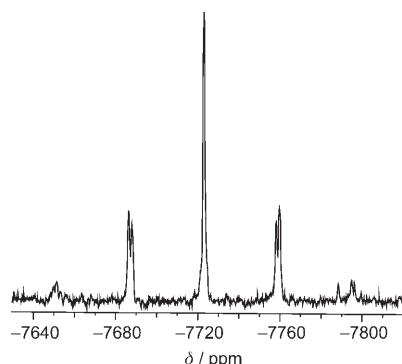


Figure 5. ^{195}Pt NMR spectrum of **4**.

trum of **4** met with difficulties, owing to the fact that the reported platinum(IV) chemical shift window is very large ($\delta \approx 15\,000$ ppm), and the resonance for **4** could not be found within this range.^[28–30] Extending the window towards lower frequencies, however, reveals a signal at -7724 ppm flanked

by ^{117}Sn and ^{119}Sn satellites with $^1J(^{195}\text{Pt}-^{119}\text{Sn}) = 7900$ Hz and $^1J(^{195}\text{Pt}-^{117}\text{Sn}) = 7550$ Hz (Figure 5). With the ^{195}Pt resonance at $\delta = -7724$ ppm, we have found the first example of a coordination compound exhibiting a ^{195}Pt NMR signal in such an upfield chemical shift area. Thus, the stannaborate $[\text{SnB}_{11}\text{H}_{11}]^{2-}$ is a very strong shielding ligand.

The ^{119}Sn Mössbauer spectrum of compound **1** recorded at 77 K is presented in Figure 6 together with a transmission integral fit. The spectrum was reproduced well with a single

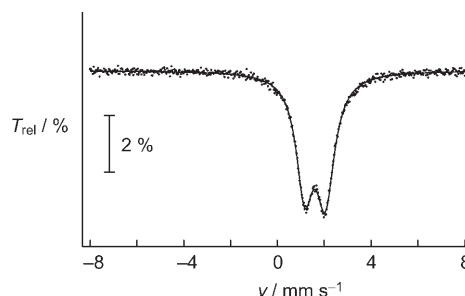


Figure 6. Experimental (dots) and simulated ^{119}Sn Mössbauer spectrum (line) of **1**, recorded at 77 K.^[20]

tin signal at an isomer shift of $\delta = 1.60(1)$ mm s^{-1} and an experimental line width of $\Gamma = 0.88(1)$ mm s^{-1} subjected to quadrupole splitting of $\Delta E_Q = 0.89(1)$ mm s^{-1} . The isomer shift lies between the tin(II) specific isomer shift of $[\text{SnB}_{11}\text{H}_{11}]^{2-}$ ($\delta = 2.46$ mm s^{-1}) and the isomer shift of the tin(IV) compound $[\text{MeSnB}_{11}\text{H}_{11}]^-$ ($\delta = 1.18$ mm s^{-1}) and is therefore a good indicator for the strong electron-donating effect of $[\text{SnB}_{11}\text{H}_{11}]^{2-}$ in **1**.^[7,34,35] Good agreement could be found with $[\text{Pt}(\text{SnB}_{11}\text{H}_{11})_4]^{6-}$ ($\delta = 1.66$ mm s^{-1}).^[3]

The metal–tin stretching vibrations of **1**, **3**, and **4** could be found at 224, 194, and 168 cm^{-1} , respectively, which is in analogy with the reported Pd–Sn and Pt–Sn stretching vibrations.^[3] Elemental analyses of **3** and **4** have been carried out for the tributylmethylammonium salts.

To conclude, the first homoleptic series of octahedrally coordinated tin complexes of Ni, Pd, and Pt in the formal oxidation state IV was presented. Furthermore, the tetra-coordinated nickel derivative completes the series of square-planar complexes and is another example for the outstanding ligand strength of stanna-*closo*-dodecaborate.

Experimental Section

All manipulations were carried out under argon atmosphere in Schlenk glassware.

1: A solution of $[\text{Ni}(\text{dpp-bian})\text{Br}_2]$ (120 mg, 0.16 mmol) was added to a solution of $[\text{Bu}_3\text{NH}]_2[\text{SnB}_{11}\text{H}_{11}]$ (311 mg, 0.5 mmol) in dichloromethane (20 mL). The color of the solution changed from brown to dark green to dark violet. The solvent was evaporated in vacuum and the residue was extracted with toluene (100 mL). After slow diffusion of hexane into the toluene solution, large dark crystals could be isolated (155 mg, 64% yield). Elemental analysis (%) calcd for $\text{C}_{96}\text{H}_{290}\text{B}_{66}\text{N}_8\text{NiSn}_6$ (3041.89 g mol^{-1}): C 37.91, H 9.61, N 3.68; found: C 37.95, H 9.16, N 3.78. FIR (ATR): $\tilde{\nu} = 224$ cm^{-1} , $\nu_{\text{Ni-Sn}}$. ESI-MS (negative ion mode): $m/z = 2855.6$ $[\text{Bu}_3\text{NH}]_7[\text{Ni}(\text{SnB}_{11}\text{H}_{11})_6]^-$.

$^{11}\text{B}\{^1\text{H}\}$ NMR (80.25 MHz, CD_2Cl_2): $\delta = -15.9$ ppm (11 B, B2–B12). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (93.25 MHz, CD_2Cl_2): $\delta = -319$ ppm, *cis* $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 1931$ Hz, *trans* $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 13489$ Hz.

2: The residue of **1** was further extracted with benzene (50 mL), resulting in a dark red solution. Slow diffusion of hexane into this solution yielded dark red crystals of **2** (5 mg, 1% yield).

3: A solution of $[\text{Na}]_2[\text{SnB}_{11}\text{H}_{11}]$ (176 mg, 0.6 mmol) in THF (5 mL) was added to a solution of K_2PtCl_6 (40 mg, 0.1 mmol) in H_2O (2 mL), resulting in a dark red solution. The solvents were evaporated in vacuum, and the red solid was redissolved in THF. After the addition of $[\text{Bu}_3\text{NH}]\text{Cl}$ (44 mg, 0.2 mmol), slow diffusion of Et_2O into the red solution resulted in the formation of **3** as dark red crystals (133 mg, 63% yield). Elemental analysis (%) for $[\text{Bu}_3\text{NMe}]_6[\text{Pt}(\text{SnB}_{11}\text{H}_{11})_6]$, calcd for $\text{C}_{104}\text{H}_{306}\text{B}_{66}\text{N}_8\text{PtSn}_6$ (3201.83 g mol $^{-1}$): C 39.01, H 9.63, N 3.50; found: C 39.75, H 9.20, N 2.94. FIR (ATR): $\tilde{\nu} = 194$ cm $^{-1}$, $\nu_{\text{Pt-Sn}}$. $^{11}\text{B}\{^1\text{H}\}$ NMR (80.25 MHz, $[\text{D}_8]\text{THF}$): $\delta = -15.2$ (11 B, B2–B12). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (93.25 MHz, $[\text{D}_8]\text{THF}$): $\delta = -284$ ppm, *cis* $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 1135$ Hz, *trans* $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 19700$ Hz.

4: A solution of $\text{Na}_2[\text{SnB}_{11}\text{H}_{11}]$ (176 mg, 0.6 mmol) in THF (5 mL) was added to a solution of K_2PtCl_6 (49 mg, 0.1 mmol) in H_2O (2 mL), resulting in an orange solution. The solvents were evaporated in vacuum, and the orange solid was redissolved in THF. After the addition of $[\text{Bu}_3\text{NH}]\text{Cl}$ (44 mg, 0.2 mmol), slow diffusion of Et_2O into the orange solution resulted in the formation of **4** as orange crystals (140 mg, 65% yield). Elemental analysis (%) for $[\text{Bu}_3\text{NMe}]_6[\text{Pt}(\text{SnB}_{11}\text{H}_{11})_6]$, calcd for $\text{C}_{104}\text{H}_{306}\text{B}_{66}\text{N}_8\text{PtSn}_6$ (3290.49 g mol $^{-1}$): C 37.96, H 9.37, N 3.41; found: C 38.22, H 8.66, N 2.93. FIR (ATR): $\tilde{\nu} = 168$ cm $^{-1}$, $\nu_{\text{Pt-Sn}}$. $^{11}\text{B}\{^1\text{H}\}$ NMR (80.25 MHz, $[\text{D}_8]\text{THF}$): $\delta = -15.6$ ppm (11 B, B2–B12). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (93.25 MHz, $[\text{D}_8]\text{THF}$): $\delta = -470$ ppm, $^1J(^{195}\text{Pt}-^{119}\text{Sn}) = 7900$ Hz, *cis* $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 1050$ Hz, *trans* $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 15278$ Hz. ^{195}Pt NMR (106.68 MHz, $[\text{D}_8]\text{THF}$, 5°C): $\delta = -7724$ ppm $^1J(^{195}\text{Pt}-^{119}\text{Sn}) = 7900$ Hz, $^1J(^{195}\text{Pt}-^{117}\text{Sn}) = 7550$ Hz.

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