

# Platinum Stannaborate Complexes: Activated Isonitrile Insertion

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**Summary:** The stannaborate complexes  $\{(Ph_3P)(H_{11}B_{11}-Sn)Pt(tBuNC)[C(Ph)NHtBu]\}$  (**2**) and  $\{(dppe)(H_{11}B_{11}-Sn)Pt[C(Ph)NHtBu]\}$  (**4**) were obtained by insertion of *t*BuNC into the Pt–Ph bond of  $[Bu_3MeN][trans-(Ph_3P)_2Pt(Ph)(SnB_{11}H_{11})]$  and  $[Bu_3MeN][(dppe)Pt(Ph)(SnB_{11}H_{11})]$  at room temperature. The insertion products were characterized by elemental analysis, NMR spectroscopy, and X-ray crystal structure analysis.

## Introduction

About 2 years ago we started to investigate the coordination chemistry of the stanna-*closo*-dodecaborate cluster  $[SnB_{11}H_{11}]^{2-}$ .<sup>1</sup> It turns out that we found with this nearly icosahedral dianionic cluster a ligand of good accessibility and interesting coordination abilities. Thus, a variety of transition metal complexes with the heteroborate coordinated via a tin–metal bond have been published.<sup>2–5</sup> In comparison to the nucleophilic dianion  $[SnB_{11}H_{11}]^{2-}$  the isoelectronic *closo*-clusters  $[Sn(CR)_2B_4H_4]$  and  $[Sn(CR)_2B_9H_9]$  show no tendency to function as a Lewis base.<sup>6–8</sup> On the contrary, they react as Lewis acids and form adducts with bases such as the bipyridine ligand, which has been the subject of theoretical studies.<sup>9</sup>

Our starting work on the chemistry of the stanna-*closo*-dodecaborate cluster was focused on a strategy to synthesize zwitterions with the borate cluster as the negative pole in the molecule. These polar molecules exhibit a very high dipole moment and, although

provided with several alkyl substituents, low solubility even in polar solvents. Due to these preparative difficulties the chemistry of these zwitterions remains almost unexplored.

However, tin coordination chemistry is of special interest with respect to cocatalytical properties of the  $SnCl_3$  ligand.<sup>10</sup> One interesting feature is the activation of the CO insertion into the Pt–C bond by the  $SnCl_3$  ligand.<sup>11</sup> Since we prepared a series of stannaborate platinum complexes in high yield, we started to investigate the insertion chemistry of these complexes. In our first approach to this field we reacted several platinum complexes with *t*BuNC. Isonitriles are known to insert readily into the M–C bond of transition metal complexes and are ligands with better  $\sigma$ -donor and poorer  $\pi$ -acceptor abilities than CO.<sup>12</sup> In this publication we present the reaction between *t*BuNC and phenyl substituted stannaborate platinum complexes with either trans coordinated triphenylphosphines or chelating bis(diphenylphosphanyl)ethane (dppe) in the ligand sphere.

## Results and Discussion

Our investigations were stimulated from the surprising reaction of the platinumhydride  $[Bu_3MeN][trans-(Et_3P)_2PtH(SnB_{11}H_{11})]$  with *t*BuNC to give the five-coordinated complex  $[Bu_3MeN]_2[(Et_3P)_2Pt(SnB_{11}H_{11})_2(tBuNC)]$ .<sup>5</sup> In principle, isocyanides can react as Lewis bases under nucleophilic substitution or insertion into the respective M–H, M–C, or M–M bond.<sup>13–15</sup> Both complexes **1** and **3** react at room temperature under insertion of the isocyanide into the Pt–phenyl bond (Schemes 1 and 2).

The insertion chemistry of isocyanides was studied in many cases in order to get further insight into the mechanism of the CO insertion. Due to the possible

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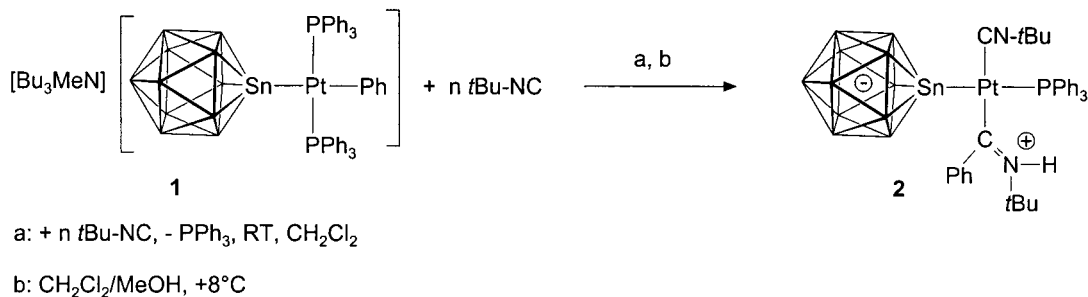
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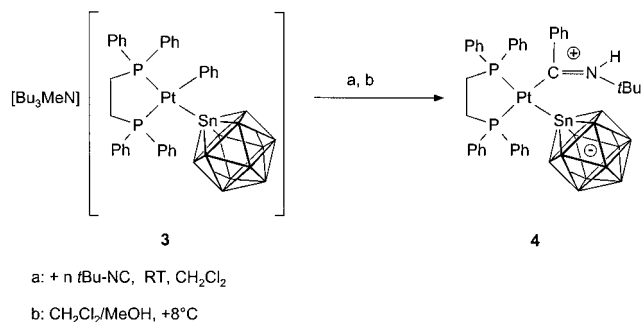
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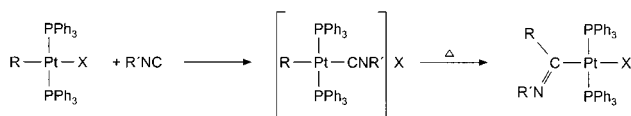
Scheme 1



Scheme 2



Scheme 3



isolation of reaction intermediates, the less reactive isocyanides were studied instead of CO itself. More than 20 years ago Treichel et al. investigated the reaction between isocyanides and platinum complexes [ $\text{trans}(\text{Ph}_3\text{P})_2\text{PtRX}$ ] ( $\text{RX} = \text{MeI}$ ,  $\text{PhCl}$ ,  $\text{PhBr}$ , and  $\text{PhI}$ ) and [ $\text{R}_2\text{PtL}_2$ ] ( $\text{R} = \text{Me}$ ,  $\text{Ph}$ ;  $\text{L} =$  several phosphines) in benzene. In the case of the halide complexes [ $\text{trans}(\text{Ph}_3\text{P})_2\text{PtRX}$ ] a substitution of the halide against the isocyanide was found to occur at room temperature. The insertion products however were obtained from these salts in good yield after refluxing the benzene suspensions for a short time (Scheme 3).<sup>13</sup> The dimethyl or diphenyl complexes [ $\text{R}_2\text{PtL}_2$ ] gave with the isocyanides at room temperature species [ $\text{R}_2\text{Pt}(\text{CNR}')\text{L}$ ] arising from ligand substitution. Isocyanide insertion was observed in reactions of [ $\text{R}_2\text{Pt}(\text{PEt}_3)_2$ ] or [ $\text{R}_2\text{Pt}(\text{PPhMe}_2)_2$ ] after refluxing the reaction mixture in benzene.<sup>14</sup>

Without heating the reaction mixtures  $t\text{BuNC}$  inserts into the  $\text{Pt}-\text{Ph}$  bond of the stannaborate complexes **1** and **3**. In our opinion, this increase in reactivity in comparison to the complexes [ $(\text{Ph}_3\text{P})_2\text{PtPhX}$ ] ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) and [ $\text{R}_2\text{PtL}_2$ ] investigated by Treichel et al. has to be attributed to the stannaborate ligand. During the course of our investigations we have not been able to detect species other than the products of the insertion. In this reaction the position of the cluster ligand with respect to the phenyl substituent seems not to be of any importance. In compound **1** it is in trans position, whereas in **3** in cis position. We think that the activation derives from the lability of the stannaborate ligand itself. It is known from the mechanistic studies of the  $\text{SnCl}_3$  activated CO insertion that the first step in this reaction procedure is also the substitution of the  $\text{SnCl}_3$

ligand against the CO molecule followed by migration into the  $\text{C}-\text{Pt}$  bond.<sup>10,11</sup> These findings are in agreement to the early observations of Treichel et al.

By accident, both reaction products were isolated and characterized as the protonated zwitterionic molecules from a methanol dichloromethane mixture. These polar molecules offer the advantage of crystallizing nearly quantitatively from the respective solvents. Both substances **2** and **4** are resistant toward moisture and air and were characterized by elemental analysis, IR spectroscopy, NMR spectroscopy, and single-crystal X-ray structure analysis.

From the IR and NMR spectroscopical investigations the geometry of the square planar coordinated transition metal complexes was unequivocally determined: The broad  $^1\text{H}$  NMR resonance at 11.52 ppm (complex **2**) and 11.60 ppm (complex **4**) are good indicators for the formation of the betain structures by protonation of the nitrogen atoms. In the case of complex **2** two types of isocyanide coordination are evident in the IR spectrum. Besides insertion of isocyanide a substitution of a triphenylphosphine by  $t\text{BuNC}$  was observed with a value of  $2219\text{ cm}^{-1}$  for the CN triple bond in  $\text{Pt}-\text{CN}t\text{Bu}$ . For the inserted isocyanide, an iminium cation results after protonation and a value of  $1516$  (complex **2**) or  $1570\text{ cm}^{-1}$  (complex **4**) for the CN double bond was detected in the infrared spectrum. These IR spectroscopical findings are in agreement with analogous isocyanide coordination in methyl and phenyl platinum complexes.<sup>14</sup> The remaining triphenylphosphine ligand in complex **2** is responsible for a single  $^{31}\text{P}$  resonance at 13.3 ppm. The coupling constants of  $^1J_{\text{Pt}-\text{P}}$  of 2944 Hz and  $^2J_{\text{P}-\text{Sn}117,119}$  of 1966 and 2058 Hz are in consistent with a trans orientation of the phosphine and stannaborate ligands at the platinum center.<sup>5</sup> The chelate complex **4** shows two signals at 42.5 and 48.1 ppm. On the basis of the coupling constants  $^1J_{\text{Pt}-\text{P}}$  and  $^2J_{\text{P}-\text{Sn}117,119}$  these signals can be attributed to the phosphorus atoms in cis (42.5 ppm) and trans (48.1 ppm) positions with respect to the stannaborate substituent.<sup>16</sup> These  $^{31}\text{P}$  NMR spectroscopical observations are in good agree-

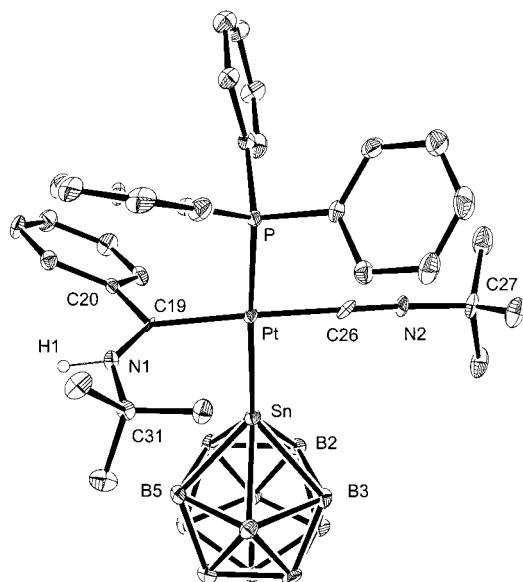
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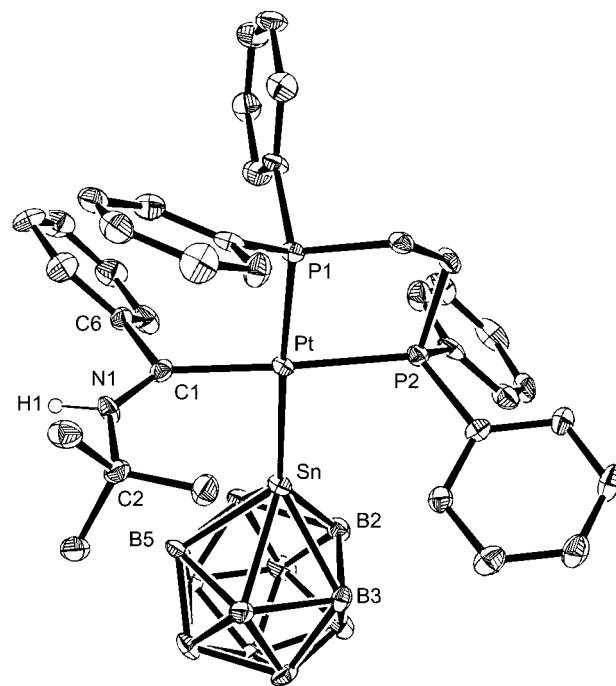
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**Figure 1.** Ortep drawing of the zwitterionic molecule **2**. Thermal ellipsoids are drawn at the 50% probability level. With the exception of the NH hydrogen atom other hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Pt–P1, 2.324(2); Pt–Sn, 2.595(1); Pt–C26, 1.967(9); Pt–C19, 2.021(7); Sn–B2, 2.320(9); Sn–B3, 2.315(11); Sn–B4, 2.304(10); Sn–B5, 2.315(10); Sn–B6, 2.297(10); N1–C19, 1.310(10); N1–C31, 1.527(11); N2–C26, 1.161(11); N2–C27, 1.472(11); C19–C20, 1.497(12); C19–N1–C31, 133.7(7); N1–C19–C20, 114.4(7); C20–C19–Pt, 116.4(5); N1–C19–Pt, 129.2(6); C26–Pt–P, 91.0(3); C19–Pt–P, 94.4(2); C26–Pt–Sn, 86.4(2); C19–Pt–Sn, 88.3(2); P–Pt–Sn, 177.3(1); C26–Pt–C19, 173.1(3); N2–C26–Pt, 179.4(8); C26–N2–C27, 176.7(9).

ment with the resonances in the  $^{31}\text{P}$  NMR spectrum detected for the starting material complex **3** (47.3, 48.2 ppm).<sup>3</sup>

To establish firmly the structures of complexes **2** and **4**, single crystals were grown from a mixture of dichloromethane and methanol. The zwitterion **2** crystallizes in the triclinic space group  $P\bar{1}$ , and **4** crystallizes in the monoclinic space group  $P2_1/c$  as yellow bars. The results of the X-ray crystal structure analysis confirm in both cases the nearly square planar coordination geometry at the platinum center. Pictures of the molecules are shown in Figure 1 and Figure 2. The bond lengths representing the coordination of the phosphine, isonitrile, and the stannaborate ligand are not of any particularity. The most interesting feature is represented with the inserted isonitrile fragment. The bond lengths Pt–C19 of 2.021(7) Å and Pt–C1 of 2.047(8) Å are only slightly shorter than a single bond between these elements. [*trans*-(Ph<sub>3</sub>P)<sub>2</sub>PtPh<sub>2</sub>Pt–C, 2.080(8) Å];<sup>21</sup> *trans*-(Ph<sub>3</sub>P)<sub>2</sub>Pt(SnB<sub>11</sub>H<sub>11</sub>)Ph Pt–C, 2.061(5) Å]. As expected after protonation of the nitrogen atom the C19–N1 [1.310(10) Å] and C1–N bond lengths [1.312(10) Å] are close to a double bond and can be compared with the C–N distances in (dmpe)Pt(Me)(MeOC=NC<sub>6</sub>H<sub>4</sub>Cl)



**Figure 2.** Ortep drawing of the zwitterionic molecule **4**. Thermal ellipsoids are drawn at the 50% probability level. With the exception of the NH hydrogen atom other hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Pt–P1, 2.300(2); Pt–P2, 2.306(2); Pt–C1, 2.047(8); Pt–Sn, 2.601(1); Sn–B2, 2.316(10); Sn–B3, 2.298(11); Sn–B4, 2.286(11); Sn–B5, 2.325(9); Sn–B6, 2.323(9); N1–C1, 1.312(10); N1–C2, 1.496(10); C1–C6, 1.517(11); C1–Pt–P1, 94.9(2); P1–Pt–P2, 84.5(1); P2–Pt–Sn, 92.4(1); C1–Pt–Sn, 88.1(2); C1–Pt–P2, 176.3(2); P1–Pt–Sn, 176.4(1); C1–N1–C2, 132.6(7); N1–C1–C6, 111.6(7); N1–C1–Pt, 132.4(6); C6–C1–Pt, 115.9(5).

[1.285(7) Å] and [*cis*-(*t*BuNC)(MeSiPh<sub>2</sub>)Pt(CH=N*t*Bu)]<sub>2</sub> [1.285(7) Å].<sup>22,23</sup>

This study shows that in the series of Pt(II) complexes [(Ph<sub>3</sub>P)<sub>2</sub>PtR<sub>2</sub>], [(Ph<sub>3</sub>P)<sub>2</sub>PtRX], and [(Ph<sub>3</sub>P)<sub>2</sub>PtR-(SnB<sub>11</sub>H<sub>11</sub>)]<sup>−</sup> the tin derivative exhibits the highest reactivity with respect to the insertion of isonitrile into the Pt–R bond. This might be due to the relatively high substitution lability of the heteroborate ligand. We are currently investigating the influence of the stannaborate ligand on the insertion chemistry of CO.

## Experimental Section

**General Procedures.** All manipulations were carried out under dry N<sub>2</sub> in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under N<sub>2</sub>. NMR Bruker AC 200 (<sup>1</sup>H: 200 MHz, int. TMS; <sup>13</sup>C{<sup>1</sup>H}: 50 MHz, int. TMS; <sup>11</sup>B{<sup>1</sup>H}: 64 MHz, ext. BF<sub>3</sub>·Et<sub>2</sub>O; <sup>31</sup>P{<sup>1</sup>H}: 81 MHz, ext. H<sub>3</sub>PO<sub>4</sub>). Elemental analysis: Institut fuer Anorganische Chemie der Universitaet zu Koeln, Heraeus C,H,N,O–Rapid elemental analyzer.

[Bu<sub>3</sub>MeN][*trans*-(Ph<sub>3</sub>P)<sub>2</sub>Pt(Ph)(SnB<sub>11</sub>H<sub>11</sub>)] and [Bu<sub>3</sub>MeN]-[(dppe)Pt(Ph)(SnB<sub>11</sub>H<sub>11</sub>)] were prepared according to the literature procedures.<sup>3</sup>

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{(Ph<sub>3</sub>P)(H<sub>11</sub>B<sub>11</sub>Sn)Pt(*t*BuNC)[C(Ph)NH*t*Bu]} (2). A round-bottom flask was charged with [Bu<sub>3</sub>MeN][*trans*-(Ph<sub>3</sub>P)<sub>2</sub>Pt(Ph)-(SnB<sub>11</sub>H<sub>11</sub>)] (1) (0.30 g, 0.24 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The resulting solution was stirred at room temperature, and *t*BuNC (0.1 mL, 0.88 mmol) was added via syringe. Isolation was carried out by slow diffusion of methanol into the reaction mixture at 8 °C to give pure 2 (0.20 g, 87% yield) as yellow crystals. <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ 1.04 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub> (C{C<sub>6</sub>H<sub>5</sub>}{NH-*t*Bu})), 1.54 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>(*t*BuNC)), 7.27–7.65 (m, br, 20H, C-*H* (P-C<sub>6</sub>H<sub>5</sub>, C-C<sub>6</sub>H<sub>5</sub>)), 11.52 (s, br, 1H, N-*H*). <sup>11</sup>B{<sup>1</sup>H} NMR (64 MHz, DMSO-*d*<sub>6</sub>): δ -8.0 (s, B12), -14.5 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ 28.2/28.4 (s, -C(CH<sub>3</sub>)<sub>3</sub>), 59.6/60.1 (s, -C(CH<sub>3</sub>)<sub>3</sub>), 126.8–133.5 (m, C-*H*, (P-C<sub>6</sub>H<sub>5</sub>, C-C<sub>6</sub>H<sub>5</sub>)), 142.2 (s, <sup>3</sup>J<sub>C-Sn</sub> = 35 Hz, C<sub>ipso</sub> (C-C<sub>6</sub>H<sub>5</sub>)), 211.2 (d, <sup>1</sup>J<sub>C-Pt</sub> = 885 Hz, C-C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, DMSO-*d*<sub>6</sub>): δ 3.3 (s, <sup>1</sup>J<sub>P-Pt</sub> = 2944 Hz, <sup>2</sup>J<sub>P-117Sn</sub> = 1966 Hz, <sup>2</sup>J<sub>P-119Sn</sub> = 2058 Hz, Ph<sub>3</sub>P (in *trans* position to SnB<sub>11</sub>H<sub>11</sub>)). FT-IR: ν(NC) = 2219, 1561 cm<sup>-1</sup>. Anal. Calcd for C<sub>34</sub>H<sub>50</sub>B<sub>11</sub>N<sub>2</sub>PtSn: C, 42.90; H, 5.30; N, 2.95. Found: C, 42.23; H, 5.38; N, 2.94.

{(dppe)(H<sub>11</sub>B<sub>11</sub>Sn)Pt[C(Ph)NH*t*Bu]} (4). A round-bottom flask was charged with [Bu<sub>3</sub>MeN][(dppe)Pt(Ph)(SnB<sub>11</sub>H<sub>11</sub>)] (3) (0.52 g, 0.46 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (40 mL). The resulting solution was stirred at room temperature, and *t*BuNC (0.2 mL, 1.76 mmol) was added via syringe. The color of the solution turned yellow. After 12 h of stirring at room temperature the product was isolated by slow diffusion of methanol into the reaction mixture to give pure 4 as yellow crystals (0.36 g, 78%). <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ 1.17 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>), 2.50–3.00 (m, br, 4H, P-CH<sub>2</sub>-CH<sub>2</sub>P), 5.53 (s, 2H, CH<sub>2</sub>Cl<sub>2</sub>), 6.90–7.80 (m, br, 21H, C-*H* (P-C<sub>6</sub>H<sub>5</sub>, C-C<sub>6</sub>H<sub>5</sub>)), 7.90–8.20 (m, 4H, C-*H* (P-C<sub>6</sub>H<sub>5</sub>)), 11.60 (s, br, 1H, N-*H*). <sup>11</sup>B{<sup>1</sup>H} NMR (64 MHz, DMSO-*d*<sub>6</sub>): δ -8.0 (s, B12), -14.4 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ 26.0–31.0 (m, br, P-CH<sub>2</sub>-CH<sub>2</sub>-P), 28.1 (s, -C(CH<sub>3</sub>)<sub>3</sub>), 54.5 (s, CH<sub>2</sub>Cl<sub>2</sub>), 60.1 (s, -C(CH<sub>3</sub>)<sub>3</sub>), 126.4–138.0 (m, C-*H*, (P-C<sub>6</sub>H<sub>5</sub>, C-C<sub>6</sub>H<sub>5</sub>)), 144.3 (s, <sup>3</sup>J<sub>C-Sn</sub> = 35 Hz, C<sub>ipso</sub> (C-C<sub>6</sub>H<sub>5</sub>)), 220.3 (d, <sup>2</sup>J<sub>C-P</sub> = 108 Hz, C-C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, DMSO-*d*<sub>6</sub>): δ 42.5 (d, <sup>1</sup>J<sub>P-Pt</sub> = 1915 Hz, <sup>2</sup>J<sub>P-Sn</sub> = 226 Hz, <sup>2</sup>J<sub>P-P</sub> = 8 Hz, Ph<sub>2</sub>P-CH<sub>2</sub>- (in *cis* position to SnB<sub>11</sub>H<sub>11</sub>)), 48.1 (d, <sup>1</sup>J<sub>P-Pt</sub> = 2977 Hz, <sup>2</sup>J<sub>P-Sn</sub> = 1972 Hz, <sup>2</sup>J<sub>P-P</sub> = 8 Hz, Ph<sub>2</sub>P-CH<sub>2</sub>- (in *trans* position to SnB<sub>11</sub>H<sub>11</sub>)). FT-IR ν(NC) = 1570 cm<sup>-1</sup>. Anal. Calcd for C<sub>37</sub>H<sub>50</sub>B<sub>11</sub>NP<sub>2</sub>PtSn + CH<sub>2</sub>Cl<sub>2</sub>: C, 41.94; H, 4.82; N, 1.29. Found: C, 42.28; H, 5.14; N, 1.51.

**X-ray Crystal Structure Analysis of 2·2CH<sub>2</sub>Cl<sub>2</sub>.** C<sub>36</sub>H<sub>54</sub>B<sub>11</sub>-Cl<sub>4</sub>N<sub>2</sub>PtSn; formula mass 1120.27 g mol<sup>-1</sup>, triclinic space group *P* $\bar{1}$ , *a* = 10.373(2) Å, *b* = 13.120(2) Å, *c* = 18.233(3) Å, α = 73.57(2)°, β = 80.90(2)°, γ = 78.08(2)°, *V* = 2315.5(6) Å<sup>3</sup>, *Z* = 2, ρ<sub>calc</sub> = 1.607 g cm<sup>-3</sup>, μ = 3.852 mm<sup>-1</sup>. Image plate diffractometer (IPDS, Stoe); Mo K<sub>α</sub> radiation (graphite mono-

chromator, λ = 0.710 73 Å); data collection at 170 K on a single crystal of dimensions 0.3 × 0.4 × 0.2 mm, 1.9 ≤ θ ≤ 24.2°; 6877 independent reflections measured, 4960 "observed" [*I* > 2σ(*I*)]; data corrections: Lorentz and polarization factors; structure solution by direct methods and difference Fourier synthesis, *F*<sup>2</sup> refinement;<sup>18–20</sup> anisotropic parameters for non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and refined with isotropic thermal parameters. Convergence was obtained for 507 variables with *wR*<sub>2</sub> = 0.121, *R*<sub>1</sub> = 0.066, GooF = 0.734; max residual density +1.70 (1.01 Å from Pt) e Å<sup>-3</sup>.

**X-ray Crystal Structure Analysis of 4·2CH<sub>2</sub>Cl<sub>2</sub>·CH<sub>3</sub>OH.** C<sub>40</sub>H<sub>58</sub>B<sub>11</sub>Cl<sub>4</sub>NOP<sub>2</sub>PtSn; formula mass 1205.30 g mol<sup>-1</sup>; monoclinic space group *P*2<sub>1</sub>/*c*, *a* = 11.857(2) Å, *b* = 19.463(2) Å, *c* = 22.521(3) Å, β = 91.86(2)°, *V* = 5194.3(14) Å<sup>3</sup>, *Z* = 4, ρ<sub>calc</sub> = 1.541 g cm<sup>-3</sup>, μ = 3.47 mm<sup>-1</sup>. Image plate diffractometer (IPDS, Stoe); Mo K<sub>α</sub> radiation (graphite monochromator, λ = 0.710 73 Å); data collection at 170 K on a single crystal of dimensions 0.2 × 0.3 × 0.2 mm, 1.9 ≤ θ ≤ 24.2°; 8044 independent reflections measured, 6238 "observed" [*I* > 2σ(*I*)]; data corrections: Lorentz and polarization factors; numerical absorption correction with programs X-RED and X-SHAPE (Stoe Darmstadt, 1994);<sup>17</sup> structure solution by direct methods and difference Fourier synthesis, *F*<sup>2</sup> refinement;<sup>18–20</sup> anisotropic parameters for non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and refined with isotropic thermal parameters. Convergence was obtained for 557 variables with *wR*<sub>2</sub> = 0.135, *R*<sub>1</sub> = 0.067, GooF = 0.963; max residual density +1.57 (2.80 Å from C82) e Å<sup>-3</sup>.

Further details on the crystal structure determinations are available on request from the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 166945 (2), 166944 (4). Copies of the data can be obtained free of charge from the Director, CCDC 12 Union Rd., Cambridge CB2 1EZ, U.K. (fax, + 44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://ccdc.cam.ac.uk).

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**Supporting Information Available:** Listings of all fractional atomic coordinates and equivalent isotropic displacement parameters, interatomic distances, angles, and anisotropic displacement parameters of 2 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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