

Contribution from the Department of Chemistry,  
University of Michigan, Ann Arbor, Michigan 48109**Crystal and Molecular Structures and Syntheses of 9,9-(PPh<sub>3</sub>)<sub>2</sub>-6,9-SPtB<sub>8</sub>H<sub>10</sub> and 8-OEt-9,9-(PPh<sub>3</sub>)<sub>2</sub>-6,9-SPtB<sub>8</sub>H<sub>9</sub>. Related Platinathiadecaboranes**

T. K. HILTY, D. A. THOMPSON, W. M. BUTLER, and R. W. RUDOLPH\*

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Platinathiaboranes were prepared by the reaction of L<sub>4</sub>Pt (L = PMe<sub>2</sub>Ph, PEt<sub>3</sub>, and PPh<sub>3</sub>) with 1-SB<sub>9</sub>H<sub>9</sub> in ethanol. X-ray crystallographic characterization left an ambiguity regarding the formulation of the thiaaborane ligand as SB<sub>8</sub>H<sub>9</sub> or SB<sub>8</sub>H<sub>10</sub>. Mass spectrometry and <sup>1</sup>H NMR characterization showed that the complexes had the general formulation L<sub>2</sub>Pt(SB<sub>8</sub>H<sub>10</sub>). Therefore, the framework electron count corresponds with the nido skeletal structure found crystallographically, and the structure is not "unexpected" as found for other d<sup>8</sup> and d<sup>9</sup> metallaeteroboranes. In addition to the three 9,9-L<sub>2</sub>-6,9-SPtB<sub>8</sub>H<sub>10</sub> molecules, 8-OEt-9,9-(PPh<sub>3</sub>)<sub>2</sub>-6,9-SPtB<sub>8</sub>H<sub>9</sub> was characterized, and the relationship of these four platinathiadecaboranes to the previously reported L<sub>2</sub>M(SB<sub>8</sub>H<sub>9</sub>) (M = Pd, Pt) is discussed. It appears that the synthetic method is a degradative insertion. Even treatment of SB<sub>11</sub>H<sub>11</sub> with L<sub>4</sub>Pt in ethanol leads to the kinetically stable L<sub>2</sub>Pt(SB<sub>8</sub>H<sub>10</sub>) molecule. The reactants behave differently in benzene or cyclohexane, and the nature of these products is discussed. The crystals of 9,9-(PPh<sub>3</sub>)<sub>2</sub>-6,9-SPtB<sub>8</sub>H<sub>10</sub>, I, and 8-OEt-9,9-(PPh<sub>3</sub>)<sub>2</sub>-6,9-SPtB<sub>8</sub>H<sub>9</sub>, II, both form in the monoclinic space group P2<sub>1</sub>/n with *a* = 11.522 (5) Å, *b* = 20.005 (5) Å, *c* = 16.398 (4) Å, β = 95.74(3)°, and *Z* = 4 for I and *a* = 13.336 (4) Å, *b* = 21.034 (5) Å, *c* = 14.545 (3) Å, β = 103.04 (2)°, and *Z* = 4 for II. The conventional *R* index converged at 0.043 and 0.051 for I and II, respectively, with full matrix refinement including the scale factor, positional and anisotropic thermal parameters for all nonhydrogen atoms, and fixed phenyl hydrogen positions.

**Introduction**

The first platinathiaborane, (Et<sub>3</sub>P)<sub>2</sub>PtSB<sub>10</sub>H<sub>10</sub>, was reported by Muetterties,<sup>1</sup> who proposed a structure consisting of an icosahedron with a platinum atom at a vertex adjacent to the sulfur atom. The proposal was made in analogy of SB<sub>10</sub>H<sub>10</sub><sup>2-</sup> to dicarbollide, C<sub>2</sub>B<sub>9</sub>H<sub>11</sub><sup>2-</sup>,<sup>2</sup> and its reactions with transition metals. The crystal structure of (Et<sub>3</sub>P)<sub>2</sub>Pt(H)SB<sub>9</sub>H<sub>10</sub><sup>3</sup> gave the first definitive structural data for a platinathiaborane. This complex has a platinum atom completing an 11-atom nido cage<sup>4</sup> and bonded to a sulfur atom. These platinathiaboranes, which were synthesized from the platinum(II) reagents *cis*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> and *trans*-(Et<sub>3</sub>P)<sub>2</sub>PtHCl, respectively, contain endopolyhedral platinum atoms.

Ugo et al. observed that the zerovalent complexes (Ph<sub>3</sub>P)<sub>*n*</sub>Pt, *n* = 3 or 4, react with HCl to give [(Ph<sub>3</sub>P)<sub>3</sub>PtH]Cl, (Ph<sub>3</sub>P)<sub>2</sub>PtHCl, and perhaps (Ph<sub>3</sub>P)<sub>2</sub>PtH<sub>2</sub>Cl<sub>2</sub>.<sup>5</sup> Previous oxidative-addition reactions using *closo* carboranes<sup>6</sup> and thiaboranes<sup>7</sup> with low-valent iridium species were shown to produce complexes containing exopolyhedral metal atoms. In view of the oxidative-addition reactions observed by Ugo<sup>5</sup> and the analogous reactions of iridium with *closo* heteroboranes, it was anticipated that new exopolyhedral platinum *closo* thiaborane products could be produced.

The reactions of *closo*-1-SB<sub>9</sub>H<sub>9</sub> or 1-SB<sub>11</sub>H<sub>11</sub> and L<sub>4</sub>Pt (L = Me<sub>2</sub>PhP, Et<sub>3</sub>P, and Ph<sub>3</sub>P) in alcohol give complexes of the formula L<sub>2</sub>PtSB<sub>8</sub>H<sub>10</sub>. When L<sub>2</sub>Pt(C<sub>2</sub>H<sub>4</sub>) is used instead of L<sub>4</sub>Pt, L<sub>2</sub>Pt(SB<sub>8</sub>H<sub>9</sub>)(OEt) results.<sup>8</sup> The characterization of these platinathiaboranes including the X-ray structures of (PPh<sub>3</sub>)<sub>2</sub>Pt(SB<sub>8</sub>H<sub>10</sub>), I, and (PPh<sub>3</sub>)<sub>2</sub>Pt(SB<sub>8</sub>H<sub>9</sub>)(OEt), II, is reported here in detail. Contrary to expectation, these clusters contain endopolyhedral platinum; however, the reaction may proceed through an exopolyhedral intermediate. The observed structures are also discussed in relationship to those found for other platinaheteroboranes.

**Experimental Section**

**General Methods.** Infrared spectra were determined on a Perkin-Elmer 457 as either KBr disks or Nujol mulls on KBr plates. The <sup>11</sup>B NMR spectra were obtained on a JEOL JNM-PS-100 with a EC-100 data system operating at 32.1 MHz or on a Bruker 270 operating at 86.3 MHz (University of Wisconsin). Proton NMR spectra were obtained on a Varian T-60 and a JEOL JNM-PS-100. Chemical shifts are reported relative to external (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O·BF<sub>3</sub> and internal Si(CH<sub>3</sub>)<sub>4</sub> for <sup>11</sup>B and <sup>1</sup>H NMR, respectively. The mass spectra were obtained on an Associated Electronic Industries MS-902. Melting

points were determined in sealed tubes and are uncorrected.

**Materials.** 1-SB<sub>9</sub>H<sub>9</sub> was prepared by vacuum pyrolysis of 6-SB<sub>9</sub>H<sub>11</sub>.<sup>9</sup> SB<sub>11</sub>H<sub>11</sub> was obtained from the pyrolysis of 7-SB<sub>10</sub>H<sub>12</sub><sup>9</sup> or the method of Hermanek.<sup>10</sup> All solvents were dried prior to use and distilled in vacuo or transferred by syringe under a nitrogen atmosphere. Reactions were all carried out under a nitrogen or argon atmosphere. The PMe<sub>2</sub>Ph and PEt<sub>3</sub> were purchased from Strem Chemical Co. The K<sub>2</sub>PtCl<sub>4</sub> was purchased from ROC/RIC or Alfa Ventron. Triphenylphosphine was recrystallized from benzene/ethanol prior to use. Platinum complexes (PMe<sub>2</sub>Ph)<sub>4</sub>Pt,<sup>11</sup> (PEt<sub>3</sub>)<sub>3</sub>Pt,<sup>11,12</sup> and (PPh<sub>3</sub>)<sub>4</sub>Pt<sup>13</sup> were synthesized by literature procedures and confirmed by analyses (Spang Microanalytical Laboratory), melting point, IR, or NMR.

**Synthesis of (PMe<sub>2</sub>Ph)<sub>2</sub>Pt(SB<sub>8</sub>H<sub>10</sub>), III.** To 30 mL of dry ethanol in a 100-mL three-necked flask was added 1.262 g (1.69 mmol) of (PMe<sub>2</sub>Ph)<sub>4</sub>Pt. One equivalent (233 mg, 1.69 mmol) of 1-SB<sub>9</sub>H<sub>9</sub> was added to the solution, and the mixture was refluxed for 4 h during which time the solution turned from yellow to pale pink to pale yellow containing white crystals of product. After the flask was cooled, the precipitate was filtered in the glovebox and washed with ethanol, giving 647 mg of white product (63%). The crude product was recrystallized from 20 mL of methylene chloride and 50 mL of ethanol, giving 440 mg (43%) of off-white crystalline material. The product was dried for 24 h in vacuo to remove solvent; mp 173–176 °C dec. Anal. Calcd: Pt, 32.5; C, 32.0; H, 5.4; B, 14.4; S, 5.3. Found: Pt, 32.7; C, 32.0; H, 5.4; B, 13.7; S, 6.3.

**Synthesis of (PPh<sub>3</sub>)<sub>2</sub>Pt(SB<sub>8</sub>H<sub>10</sub>), I.** The procedure used was the same as that described above, except 40 mg (0.290 mmol) of 1-SB<sub>9</sub>H<sub>9</sub> was added to 367 mg (0.295 mmol) of (PPh<sub>3</sub>)<sub>4</sub>Pt in ethanol. Refluxing of the solution for 18 h gave a 185-mg amount of (74%) white solid and slightly yellow filtrate. The solid (PPh<sub>3</sub>)<sub>2</sub>Pt(SB<sub>8</sub>H<sub>10</sub>) was recrystallized from methylene chloride/ethanol. During the reaction a brown precipitate was noted after 2–3 h of refluxing. This color dissipated on continued refluxing; mp 206–208 °C dec.

**Synthesis of (PEt<sub>3</sub>)<sub>2</sub>Pt(SB<sub>8</sub>H<sub>10</sub>), IV.** To approximately 1 mmol of (PEt<sub>3</sub>)<sub>3</sub>Pt in ethanol was added 130 mg (0.942 mmol) of 1-SB<sub>9</sub>H<sub>9</sub>, and the mixture was refluxed under nitrogen for 28 h. When the colorless solution was cooled to room temperature, white crystals precipitated from solution. The mixture was taken into the glovebox and filtered under nitrogen and washed with 7 mL of ethanol to give 192 mg (36%) of crude white product. The sample was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> and filtered, and addition of 15 mL of ethanol gave a white crystalline product, mp 173–175 °C dec. Anal. Calcd: C, 26.0; H, 7.1. Found: C, 27.4; H, 7.0.

**Synthesis of (PPh<sub>3</sub>)<sub>2</sub>Pt(SB<sub>8</sub>H<sub>9</sub>)(OEt), II.** To approximately 0.1 mmol of (PPh<sub>3</sub>)<sub>2</sub>Pt(C<sub>2</sub>H<sub>4</sub>) in 15 mL of EtOH was added 28 mg (0.2 mmol) of 1-SB<sub>9</sub>H<sub>9</sub>, and the mixture was stirred at 25 °C under nitrogen for 3 h. An off-white solid product (63 mg) was recovered by filtration. The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/EtOH.

Table I. Summary of Crystal Data and Intensity Collection

	9,9-(PPh <sub>3</sub> ) <sub>2</sub> -6,9-SPtB <sub>8</sub> H <sub>10</sub> (I)	8-OEt-9,9-(PPh <sub>3</sub> ) <sub>2</sub> -6,9-SPtB <sub>8</sub> H <sub>9</sub> (II)
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	11.522 (5)	13.336 (4)
<i>b</i> , Å	20.005 (5)	21.034 (5)
<i>c</i> , Å	16.398 (4)	14.545 (3)
$\beta$ , deg	95.74 (3)	103.04 (2)
<i>V</i> , Å <sup>3</sup>	3760 (2)	3974 (2)
mol wt	848.31	892.36
<i>Z</i>	4	4
<i>d</i> <sub>obsd</sub> , g/cm <sup>3</sup>	1.49 (1)	1.48 (1)
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.498	1.491
cryst dimens, mm	0.258 × 0.142 × 0.132	0.062 × 0.174 × 0.154
cryst shape	parallelepiped	diamond
radiation, Å	$\lambda$ (Mo K $\alpha$ ) 0.710 69 monochromatized from a graphite crystal	
takeoff angle, deg	4.0	4.0
linear abs coeff ( $\mu$ ), cm <sup>-1</sup> (Mo K $\alpha$ )	40.88	38.75
scan speed, deg/min	variable (2.0–15.0), determined as function of peak intensity	
scan range (2 $\theta$ ), deg	Mo K $\alpha_1$ – 0.8 to Mo K $\alpha_2$ + 0.8	Mo K $\alpha_1$ – 0.7 to Mo K $\alpha_2$ + 0.7
ratio of bkgd scan time to peak scan time	0.8	0.7
std rflns	(404), (174), (292)	(002), (040), (200)
deviation of stds during data collection	<5%	<5%
2 $\theta$ limit, deg	45	45
rflns collected	5430	5968
rflns with $F^2 > 3\sigma(F^2)$	3211	2964
<i>R</i> factor	0.043	0.051
<i>R</i> <sub>w</sub> factor	0.049	0.056

The crystallographic characterization of II is given in the text. The <sup>1</sup>H NMR of II in CDCl<sub>3</sub> shows the ethoxide group as two quartets of relative intensity 1 at 3.07 and 2.22 ppm and a triplet of relative intensity 3 at 0.30 ppm downfield from Si(CH<sub>3</sub>)<sub>4</sub> ( $J_{\text{HH}} = 7.5$  Hz).

**Reaction of (PMe<sub>2</sub>Ph)<sub>4</sub>Pt with 1-SB<sub>9</sub>H<sub>9</sub> in Cyclohexane.** To about 35 mL of dry cyclohexane (distilled in vacuo from sodium/benzophenone) was added 140 mg (0.187 mmol) of (PMe<sub>2</sub>Ph)<sub>4</sub>Pt. To the stirred solution under nitrogen was added 26 mg (0.188 mmol) of 1-SB<sub>9</sub>H<sub>9</sub>. The very slightly soluble P<sub>4</sub>Pt precipitate became more flocculent. After being stirred at 25 °C for 4 days, the solution was colorless with a yellow precipitate. The solid was filtered in a glovebox under nitrogen by using a fritted glass funnel. Washing with dry cyclohexane gave 93 mg (81%) of yellow product formulated as (PMe<sub>2</sub>Ph)<sub>2</sub>Pt(SB<sub>9</sub>H<sub>9</sub>).

**Crystal Description and Data Collection.** The crystals of I and II were obtained by recrystallization in a drybox from a solution of methylene chloride and ethanol at room temperature. They exist as air stable, clear, shiny parallelepipeds. Data collections were substantially identical for both I and II. The procedure is described in detail for I. The essential information is described in Table I for both I and II.

The monoclinic unit cell was determined to have a space group symmetry of *P*2<sub>1</sub>/*c* from space group extinctions observed on precession photographs. This space group is unique; however, the nonstandard setting of *P*2<sub>1</sub>/*n* was chosen to give a  $\beta$  angle closer to 90°. Initially, the unit cell parameters were obtained from precession photographs. A more accurate determination of the unit cell parameters was obtained from a least-squares fit of 15 reflections whose angular settings were refined.

The crystal density,  $d_{\text{obsd}} = 1.49$  (1) g/cm<sup>3</sup>, was determined from floatation in heptane and carbon tetrachloride. The density calculated from the unit cell volume and its contents is  $d_{\text{calcd}} = 1.498$  g/cm<sup>3</sup>. There are four molecules in the unit cell, corresponding to one molecule in each asymmetric unit of the space group.

A Syntex P1 computer-controlled four-circle diffractometer, equipped with a graphite monochromator, scintillation counter, and pulse-height discriminator, was employed for data collection. The diffractometer was programmed to operate in a  $\theta$ -2 $\theta$  variable-speed scan mode, in which the speed of the scan was dependent on a peak height preview of the reflection intensity. High-intensity reflections were collected at 15°/min, low-intensity reflections at 2°/min, and medium-intensity reflections at speeds intermediate of the two extremes. The scan range also varied according to the scattering angle of a reflection. The scan range extended from 0.8° less than the Bragg setting angles for Mo K $\alpha_1$  to 0.8° greater than the setting angle for Mo K $\alpha_2$ . The ratio of the background scan time to the peak scan time was 0.8.

A total of 5430 symmetry unique reflections were collected by using Mo K $\alpha$  radiation. This corresponds to one-fourth of the reciprocal lattice sphere ( $h \geq 0, k \geq 0, \pm l$ ) to a 2 $\theta$  value of 45°. The intensity and its standard deviation were calculated from the diffractometer data by using the background-peak-background method, which can be summarized in the formulas

$$I = \left[ \sum_{i=1}^n I_i - (B_1 + B_2)(t_s/t_b) \right] \text{SR}$$

$$\sigma_I = \left[ \sum_{i=1}^n I_i + (B_1 + B_2)(t_s/t_b)^2 \right]^{1/2} \text{SR}$$

where  $n$  equals the number of intervals into which the scan is divided,  $I_i$  is the accumulated count for the  $i$ th interval,  $B_1 + B_2$  is the sum of the background counts, the ratio  $t_s/t_b$  is that of the time spent measuring the scan and the background, and SR is the angular scan rate in degrees per minute.

After the calculations just described were performed on the 5430 reflections collected, 3211 were found to have intensities equal to or greater than 3 times their standard deviation. Only these reflections were used in the structure determination. In addition, three standard reflections (404, 174, 292) were collected after every 100 reflections. Statistics on these three reflections showed fluctuations of only 5%. Lorentz and polarization corrections were applied to the reflection intensities and their standard deviations.

No absorption correction was made ( $\mu(\text{Mo K}\alpha) = 40.0$  cm<sup>-1</sup>). A summary of this information is given in Table I.

**Solution and Refinement of the Structures. Complex I.** The structure of 9,9-(PPh<sub>3</sub>)<sub>2</sub>-6,9-SPtB<sub>8</sub>H<sub>10</sub> was solved by heavy-atom techniques. A three-dimensional unsharpened Patterson synthesis<sup>14</sup> clearly revealed the atomic coordinates of the platinum atom in an asymmetric unit. Refinement of the scale factor produced the residuals

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_w = \left[ \frac{\sum w_i ||F_o| - |F_c||^2}{\sum w_i |F_o|^2} \right]^{1/2}$$

of 0.297 and 0.355, respectively. The observed and calculated structure factors are given by  $F_o$  and  $F_c$ , respectively. The weights,  $w_i$ , were taken as  $1/\sigma^2(F_o)$ , and the function minimized in the least-squares refinement was  $\sum w_i (|F_o| - |F_c|)^2$ . The average deviation in an observation of unit weight is defined as  $[\sum w_i (|F_o| - |F_c|)^2 / (m - n)]^{1/2}$  where  $m$  is the number of reflections and  $n$  is the number of refined

**Table II.** Refined Nonhydrogen Positional Parameters for  $(\text{Ph}_3\text{P})_2\text{PtSB}_8\text{H}_{10}^a$ 

	<i>x</i>	<i>y</i>	<i>z</i>
Pt	0.3597 (0)	0.5837 (0)	0.2766 (0)
P1	0.3358 (3)	0.4698 (2)	0.2939 (2)
P2	0.1669 (3)	0.6103 (2)	0.2349 (2)
C110	0.4676 (11)	0.4205 (7)	0.3215 (8)
C111	0.5133 (13)	0.4179 (8)	0.4028 (9)
C112	0.6168 (16)	0.3831 (9)	0.4246 (12)
C113	0.6781 (16)	0.3531 (9)	0.3676 (14)
C114	0.6293 (17)	0.3539 (8)	0.2884 (13)
C115	0.5251 (13)	0.3870 (7)	0.2635 (9)
C120	0.2511 (12)	0.4499 (7)	0.3786 (8)
C121	0.2252 (13)	0.3834 (8)	0.3991 (9)
C122	0.1638 (15)	0.3700 (9)	0.4651 (10)
C123	0.1348 (15)	0.4216 (10)	0.5136 (9)
C124	0.1607 (14)	0.4857 (8)	0.4965 (9)
C125	0.2256 (13)	0.4997 (8)	0.4291 (8)
C130	0.2696 (13)	0.4314 (6)	0.1998 (8)
C131	0.3108 (14)	0.4551 (7)	0.1279 (9)
C132	0.2706 (15)	0.4317 (7)	0.0524 (9)
C133	0.1810 (17)	0.3825 (9)	0.0474 (9)
C134	0.1423 (15)	0.3578 (8)	0.1179 (10)
C135	0.1841 (13)	0.3826 (7)	0.1936 (9)
C210	0.1063 (12)	0.6650 (6)	0.3094 (8)
C211	-0.0131 (12)	0.6799 (6)	0.3021 (8)
C212	-0.0576 (13)	0.7227 (7)	0.3578 (9)
C213	0.0147 (15)	0.7515 (8)	0.4195 (9)
C214	0.1300 (14)	0.7367 (7)	0.4288 (8)
C215	0.1786 (12)	0.6924 (7)	0.3733 (7)
C220	0.0544 (10)	0.5480 (6)	0.2154 (7)
C221	0.0070 (12)	0.5162 (7)	0.2798 (9)
C222	-0.0793 (13)	0.4652 (7)	0.2684 (9)
C223	-0.1133 (13)	0.4471 (7)	0.1876 (9)
C224	-0.0714 (14)	0.4768 (8)	0.1250 (9)
C225	0.0135 (12)	0.5267 (7)	0.1358 (8)
C230	0.1569 (12)	0.6549 (7)	0.1370 (8)
C231	0.2208 (12)	0.6300 (7)	0.0759 (8)
C232	0.2165 (14)	0.6618 (8)	-0.0001 (8)
C233	0.1494 (16)	0.7151 (9)	-0.0147 (10)
C234	0.0881 (15)	0.7419 (8)	0.0440 (11)
C235	0.0896 (13)	0.7120 (7)	0.1208 (8)
S	0.5691 (5)	0.6302 (3)	0.1134 (3)
B1	0.6388 (12)	0.6480 (10)	0.3005 (14)
B2	0.6472 (20)	0.6836 (10)	0.1994 (15)
B3	0.5479 (15)	0.7168 (9)	0.2648 (11)
B4	0.4953 (16)	0.6532 (9)	0.3254 (10)
B5	0.6403 (17)	0.5884 (10)	0.2146 (16)
B7	0.4899 (16)	0.7032 (9)	0.1600 (10)
B8	0.4011 (13)	0.6897 (8)	0.2459 (10)
B10	0.5520 (15)	0.5724 (11)	0.3005 (16)

<sup>a</sup> Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables.

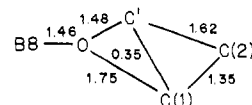
parameters. Atomic scattering factors for nonhydrogen atoms were calculated by using the analytical expressions of Cromer and Waber.<sup>15</sup> Anomalous dispersion corrections,  $\Delta f'$  and  $\Delta f''$ , were included for the platinum atom.<sup>16</sup> The hydrogen scattering factors were obtained from the calculation of Stewart, Davidson, and Simpson.<sup>17</sup> A difference Fourier synthesis revealed the location of the phosphorus atoms and two carbon atoms. One cycle of refinement resulted in the residuals  $R = 0.21$  and  $R_w = 0.28$ . A second difference Fourier electron-density map revealed the location of all the remaining nonhydrogen atoms. Two cycles of full-matrix least-squares refinement of the scale factor, positional parameters of all nonhydrogen atoms, and the isotropic temperature factor of only the platinum, phosphorus, and sulfur atoms led to convergence with  $R = 0.063$  and  $R_w = 0.071$ . Two cycles of least-squares refinement varying the scale factor and positional and isotropic thermal parameters of all nonhydrogen atoms led to further convergence of  $R = 0.057$  and  $R_w = 0.064$ . Fixed hydrogen atom contributions to the structure factors from the triphenylphosphine hydrogens were included in subsequent refinements. Hydrogen atom coordinates were calculated<sup>14</sup> by assuming carbon-hydrogen bond distances of 0.95 Å in idealized trigonal-planar geometry. Fixed isotropic temperature factors were assigned to the hydrogen atoms on the basis of the isotropic temperature factor of the carbon atom to which they were bonded. The positional and

isotropic parameters were included in the scattering-factor contribution but were not refined further. Another full-matrix least-squares cycle, including the phenyl hydrogens and anisotropic temperature refinement, resulted in the residuals  $R = 0.043$  and  $R_w = 0.049$ . A difference Fourier synthesis was calculated in an attempt to locate the 10 cage hydrogens. Location of these hydrogens was difficult due to the residuals of the dominant platinum atom.

The two highest peaks in the final difference map were located 1.04 and 1.18 Å from the platinum atom (fractional coordinates of 0.35, 0.57, 0.22 and 0.35, 0.57, 0.34, respectively). The corresponding electron densities of the peaks were 2.8 (3) and 1.6 (3)  $e \text{ \AA}^{-3}$ . All other peaks had densities less than 0.95  $e \text{ \AA}^{-3}$ . The standard deviation in an observation of unit weight was 1.36.

Final positional parameters are given in Table II for the nonhydrogen atoms. Final thermal parameters are given in Table III. Fixed positional and isotropic parameters for the phenyl hydrogen contribution and the structure factor amplitudes for  $F_o$  and  $F_c$  are available as supplementary material.

**Complex II.** The structure of 8-OEt-9,9-( $\text{Ph}_3\text{P}$ )<sub>2</sub>-6,9-SPtB<sub>8</sub>H<sub>9</sub> was solved by the straightforward application of the heavy-atom technique. A three-dimensional unsharpened Patterson<sup>14</sup> synthesis was calculated from the 2964 reflections having intensities greater than 3 standard deviations. The location of the platinum atom was unambiguously determined from this map. A single difference Fourier synthesis at this point was sufficient to locate all remaining nonhydrogen atoms of the molecule occupying general positions in an asymmetric unit. Refinement of all *x*, *y*, and *z* parameters using a full-matrix least-squares program led to  $R = 0.104$  and  $R_w = 0.113$ . Three additional cycles of least-squares refinement including all positional parameters and isotropic temperature parameters led to residuals of  $R = 0.071$  and  $R_w = 0.079$ . The isotropic temperature factors of the ethoxide atoms were noted to have rather high values ( $O = 8.6$ ,  $C(1) = 15.2$ ,  $C(2) = 14.6$ ). In addition, the bond distances associated with the ethoxide group were unusual ( $O-C(1) = 1.62$ ,  $C(1)-C(2) = 1.43$  Å). A difference map was calculated in order to examine the possibility of disorder of the ethoxide group. At this point, no peak was located which made chemical sense. The majority of peaks were located about the platinum atom. It was decided to continue refinement with  $C(1)$  in its current location. Before anisotropic refinement, the data were corrected for absorption effects. The average absorption correction was 1.362 with a minimum correction of 1.267 and a maximum correction of 1.704. Four cycles of full-matrix least-squares refinement, including all positional parameters, the anisotropic temperature parameters of all nonhydrogen atoms except the ethoxide group which was kept isotropic, and the scaling factor, led to  $R = 0.058$  and  $R_w = 0.064$ . Inclusion of the phenyl hydrogens in fixed positions led to a further reduction to  $R = 0.051$  and  $R_w = 0.056$ . Of the 445 parameters refined, only one had a shift greater than 1 standard deviation. The bond distances of the ethoxide group were worse than before with  $O-C(1) = 1.74$  Å and  $C(1)-C(2) = 1.36$  Å. Calculation of a difference map showed the most intense peak to be located 0.3 Å from  $C(1)$ . The electron density of this peak is 1.32  $e/\text{Å}^3$ , a significant value and indicative of disorder of  $C(1)$ . The bond distances of  $O$  and  $C(2)$  to  $C'$  made more chemical sense than those to  $C(1)$ :



The nature of this disorder was examined. One trial involved the complete removal of  $C(1)$  and included  $C'$  as the correct carbon atom. The result of this refinement was that  $C'$  moved back to the position of  $C(1)$  in one cycle of refinement. Another attempt involved our varying the occupancy factors of  $C'$  and  $C(1)$  while holding their positions constant. This resulted in a 93:7 electron distribution between the two sites, with the majority residing on  $C'$ . Although the model produced no significant decrease in the residuals, it gave chemically reasonable distances and angles, and, therefore, it was the model accepted. The parameters for both models are included in the tables.

The final difference map showed the most intense peak to be located near the platinum atom with an electron density of 1.07  $e/\text{Å}^3$ . In the area of the disordered  $C(1)$  and  $C'$  one peak of 0.42  $e/\text{Å}^3$  was located near  $C(1)$ . The standard deviation in an observation of unit weight was 1.36.

Final positional parameters are given in Table IV for the nonhydrogen atoms. Table V contains the final thermal parameters of

Table III. Final Thermal Parameters for  $(\text{Ph}_3\text{P})_2\text{PtSB}_8\text{H}_{10}$ <sup>a</sup>

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$	$B, \text{Å}^2$
Pt	3.3 (0)	2.9 (0)	3.0 (0)	-0.2 (0)	0.1 (0)	0.3 (0)	3.1 (0)
P1	3.7 (2)	2.6 (2)	3.3 (2)	-0.1 (1)	0.3 (1)	0.2 (1)	3.2 (1)
P2	3.1 (2)	3.0 (2)	2.6 (2)	-0.1 (1)	0.2 (1)	-0.2 (1)	2.9 (1)
C110	3.8 (6)	3.3 (6)	4.5 (7)	-0.4 (7)	-0.3 (6)	0.6 (7)	3.8 (2)
C111	5.2 (8)	4.6 (7)	6.1 (8)	-0.2 (8)	-0.4 (7)	1.2 (8)	5.2 (3)
C112	5.6 (10)	5.8 (9)	8.6 (12)	-0.6 (8)	-2.0 (9)	2.7 (9)	6.1 (4)
C113	4.9 (10)	5.1 (9)	11.4 (14)	0.2 (8)	-1.1 (10)	1.5 (9)	6.5 (5)
C114	6.1 (11)	5.0 (9)	9.8 (14)	0.1 (8)	0.9 (10)	-0.1 (9)	6.7 (5)
C115	3.9 (7)	4.9 (8)	6.1 (9)	1.0 (6)	0.1 (7)	0.2 (7)	4.8 (3)
C120	4.0 (7)	3.2 (7)	3.6 (7)	0.3 (6)	0.7 (6)	0.5 (6)	3.5 (3)
C121	5.5 (9)	4.7 (8)	4.6 (8)	-0.3 (7)	0.5 (7)	0.6 (7)	4.9 (4)
C122	7.0 (10)	7.2 (11)	5.5 (8)	-0.5 (8)	2.9 (7)	1.8 (8)	5.7 (4)
C123	8.8 (11)	7.3 (10)	4.7 (8)	-0.5 (10)	3.7 (8)	1.6 (9)	5.5 (3)
C124	7.6 (10)	5.6 (10)	4.4 (8)	0.3 (8)	2.2 (7)	-0.0 (7)	5.5 (4)
C125	6.6 (9)	4.8 (9)	2.9 (6)	-0.6 (7)	-0.3 (6)	0.6 (6)	4.5 (3)
C130	5.5 (8)	3.0 (7)	3.5 (7)	1.3 (6)	1.1 (6)	0.5 (5)	3.6 (4)
C131	6.5 (9)	4.3 (8)	4.3 (7)	0.6 (7)	0.8 (7)	-0.1 (6)	4.9 (3)
C132	8.5 (10)	3.8 (8)	4.2 (8)	1.6 (7)	0.9 (8)	-0.2 (6)	4.9 (5)
C133	10.5 (12)	6.4 (9)	3.2 (7)	2.3 (10)	-2.0 (8)	-1.4 (7)	5.5 (4)
C134	7.9 (11)	6.0 (10)	4.2 (8)	0.6 (8)	-1.4 (8)	-1.9 (7)	5.4 (4)
C135	5.7 (8)	3.6 (7)	5.0 (8)	0.2 (7)	0.1 (7)	0.1 (6)	4.7 (3)
C210	3.7 (7)	3.2 (6)	2.7 (6)	-0.8 (6)	-0.1 (6)	-0.3 (5)	3.1 (3)
C211	4.6 (8)	4.1 (7)	3.1 (7)	0.1 (6)	0.6 (6)	-0.2 (5)	3.9 (3)
C212	5.1 (8)	4.9 (8)	4.5 (7)	-0.4 (7)	2.0 (7)	-0.8 (6)	4.5 (3)
C213	6.3 (9)	4.9 (8)	5.8 (8)	-0.6 (8)	3.5 (7)	-2.1 (7)	4.6 (3)
C214	6.6 (9)	4.6 (8)	4.0 (7)	-1.9 (7)	1.4 (7)	-2.1 (6)	4.3 (3)
C215	4.2 (8)	5.3 (8)	2.9 (6)	-1.0 (6)	0.9 (6)	-1.6 (6)	3.7 (3)
C220	2.8 (6)	2.5 (5)	2.7 (6)	0.5 (5)	0.6 (5)	0.5 (5)	2.6 (2)
C221	4.8 (8)	5.3 (8)	3.7 (8)	0.8 (7)	0.5 (6)	-0.2 (7)	4.5 (3)
C222	5.5 (8)	4.3 (8)	7.0 (10)	-2.0 (7)	1.4 (7)	-0.0 (7)	5.1 (4)
C223	4.6 (8)	4.0 (7)	4.7 (8)	-0.4 (6)	-0.9 (7)	-0.7 (6)	4.3 (3)
C224	6.5 (9)	4.9 (8)	3.3 (7)	-1.2 (7)	-0.8 (7)	-0.7 (6)	4.5 (3)
C225	4.3 (7)	3.9 (7)	3.6 (7)	-0.0 (6)	-0.1 (6)	-0.9 (6)	3.9 (3)
C230	4.7 (8)	2.8 (6)	4.4 (7)	-0.4 (6)	-0.0 (6)	0.2 (6)	3.9 (3)
C231	4.7 (8)	4.1 (8)	4.2 (7)	-0.1 (6)	0.6 (6)	-0.9 (6)	4.2 (3)
C232	7.3 (9)	4.6 (8)	3.0 (7)	-1.6 (8)	-0.4 (7)	-0.2 (6)	4.5 (3)
C233	8.8 (11)	5.6 (9)	3.9 (8)	-1.7 (9)	0.8 (8)	0.4 (7)	5.6 (4)
C234	7.8 (11)	4.3 (8)	6.8 (11)	0.4 (8)	-1.1 (9)	1.6 (8)	5.9 (4)
C235	5.3 (8)	4.2 (8)	4.0 (8)	0.0 (7)	-0.2 (6)	-0.9 (6)	4.4 (3)
S	9.3 (4)	8.6 (3)	7.8 (3)	-0.3 (3)	4.8 (3)	-1.5 (3)	7.4 (1)
B1	3.3 (10)	5.4 (11)	10.3 (15)	-0.6 (8)	-1.7 (10)	2.2 (11)	5.4 (5)
B2	6.0 (12)	4.8 (10)	10.1 (18)	-0.7 (10)	-0.3 (12)	0.3 (10)	6.6 (5)
B3	3.8 (9)	4.3 (10)	5.7 (10)	-1.0 (8)	1.2 (7)	0.2 (8)	4.3 (4)
B4	5.4 (10)	5.3 (10)	3.7 (8)	-2.5 (9)	-0.1 (7)	0.1 (7)	4.4 (4)
B5	3.6 (8)	4.9 (9)	14.3 (17)	0.4 (11)	2.6 (10)	-0.7 (15)	6.0 (7)
B7	5.4 (10)	4.6 (9)	4.0 (9)	-0.5 (8)	0.5 (8)	0.7 (7)	4.6 (4)
B8	3.2 (8)	3.3 (8)	4.1 (8)	-1.7 (6)	0.6 (7)	-0.5 (6)	3.1 (3)
B10	2.3 (8)	5.7 (13)	13.6 (19)	-0.5 (8)	-1.2 (10)	4.0 (12)	5.2 (6)

<sup>a</sup> The anisotropic thermal parameters have units of  $\text{Å}^2$ . They enter the expression for the structure factor in the form  $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*b^* + 2B_{23}klb^*c^*)]$ . The isotropic values,  $B$ , are given in the last column.

the nonhydrogen atoms of the molecule. The positional and isotropic thermal parameters of the phenyl hydrogens and the structure factor amplitudes for  $F_o$  and  $F_c$  are available as supplementary material.

## Discussion

**Structure and Bonding.** Recent reports indicated that certain metallaheteroboranes formed from the more electron-rich transition elements have "exceptional" structures (Table VI). Crystallographic studies of 3-( $\text{Et}_2\text{NCS}_2$ )-3,1,2- $\text{AuC}_2\text{B}_9\text{H}_{11}$ <sup>18</sup> and 8,8-( $\text{Me}_3\text{P}$ )<sub>2</sub>-7,8,10- $\text{CPtCB}_8\text{H}_{10}$ ,<sup>19</sup> for instance, demonstrated they contain open (nido) structures in lieu of the more symmetric closo structures anticipated from framework electron counting rules. No mention in either of these reports was made regarding an examination for the presence of bridging hydrogens which if present would explain the observed structures according to the counting rules.<sup>4,20,21</sup> Admittedly, both compounds were synthesized under conditions not likely to introduce bridging hydrogens.

If only X-ray crystallography had been used for characterization of the platinathiorboranes discussed here, they might have been termed *closo*- $\text{L}_2\text{Pt}(\text{SB}_8\text{H}_8)$  molecules with "exceptional" nido structures. Thus, it became imperative to

clearly determine the presence of the bridging hydrogens. The mass spectrum of the triethylphosphine derivative supported their presence, but unequivocal substantiation from the crystal structure determination was not forthcoming. Several peaks were located in correct geometric positions for terminal and bridging hydrogens; however, residuals of greater intensity than that of many of the hydrogens were unexplainable. Explanation regarding their absence in the structures was derived from the dominant scattering of the heavy platinum atom creating residual peaks in the electron density maps with intensities approximately equal in magnitude to those of the hydrogen atoms.

The bond distances and bond angles for I and II are given in Tables VII and VIII, respectively. Figures 1-4 illustrate the molecular structures and unit cell packing. Supporting evidence for the bridging hydrogens was obtained by examining bond distances in the structures, specifically those on the open face, and comparing them with other structures. For instance, the average B-B bond distance between B7, B8 and B5, B10 in 9,9-( $\text{Ph}_3\text{P}$ )<sub>2</sub>-9,6- $\text{Pt}(\text{SB}_8\text{H}_{10})$  and 8-OEt-9,9-( $\text{Ph}_3\text{P}$ )<sub>2</sub>-9,6- $\text{Pt}(\text{SB}_8\text{H}_9)$  is 1.844 (28) Å. The other ten-vertex boranes containing bridging hydrogens in the same place show the

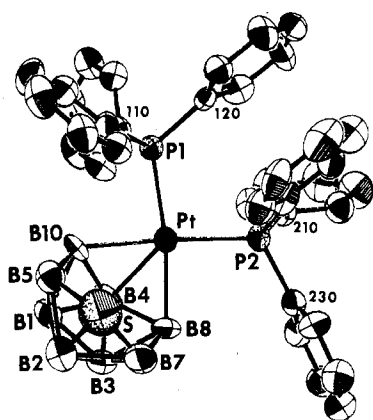


Figure 1. Perspective view of I showing the atomic numbering scheme. The hydrogens are omitted for clarity.

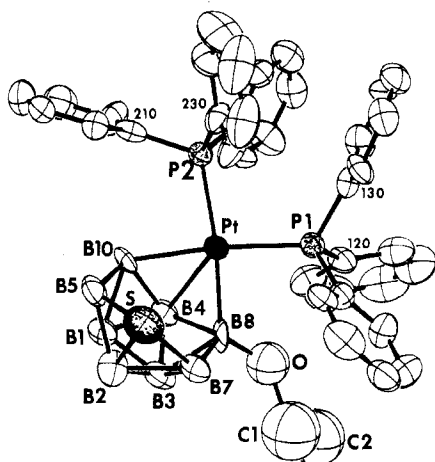


Figure 2. Single molecule of II showing the atomic numbering scheme. The hydrogens are omitted for clarity.

following bond distances (Å): 1.88 (1) in  $B_{10}H_{12}(SM_e)_2$ <sup>22</sup> and 1.87 (1) in 6,6-( $Et_3P$ )<sub>2</sub>-5,9-Me<sub>2</sub>-6,5,9-NiC<sub>2</sub>B<sub>7</sub>H<sub>9</sub>.<sup>23</sup> Structures containing no bridging hydrogens in these positions exhibit significantly longer distances (Å): 1.973 (4) in  $B_{10}H_{14}$ <sup>24</sup> and 2.037 (7) in 5-THF-6-(CO)<sub>3</sub>-6-MnB<sub>9</sub>H<sub>12</sub>.<sup>25</sup>

Although these data are certainly indicative of the extra hydrogens, the best evidence was provided by <sup>1</sup>H NMR. All four platinumthiaboranes prepared, ( $Ph_3P$ )<sub>2</sub>Pt(SBH<sub>10</sub>) (I), ( $Ph_3P$ )<sub>2</sub>Pt(SB<sub>8</sub>H<sub>9</sub>(OEt)) (II), ( $PhMe_2P$ )<sub>2</sub>Pt(SB<sub>8</sub>H<sub>10</sub>) (III), and ( $Et_3P$ )<sub>2</sub>Pt(SB<sub>8</sub>H<sub>10</sub>) (IV), showed a broad peak at  $\tau$  11–12.<sup>8</sup> A <sup>1</sup>H[<sup>11</sup>B] spectrum for the triphenylphosphine compound (I) was obtained and demonstrated that the peak at  $\tau$  11.4 was due to bridging hydrogens since it was sharpened but not shifted on decoupling. The remainder of the spectrum was consistent with the phosphine ligands and unresolved terminal B–H signals. However, due to the broad terminal B–H signals present, no intensity information could be obtained.

The bond distances present in the two structures I and II compare favorably with other compounds. The  $\eta^3$  bonding observed for the platinum atom has bond lengths to boron in the range 2.17–2.24 (2) Å for both I and II. Other compounds show Pt–B distances such as: 2.13–2.38 (4) Å in ( $Me_2PhP$ )<sub>2</sub>PtB<sub>3</sub>H<sub>7</sub>,<sup>26</sup> a compound also containing  $\eta^3$  bonding; 2.20–2.25 (2) Å in ( $Et_3P$ )<sub>2</sub>Pt(H)(SB<sub>9</sub>H<sub>10</sub>),<sup>3</sup> and a range of 2.16–2.34 Å in a variety of platinumcarboranes, ( $Et_3P$ )<sub>2</sub>Pt-(B<sub>7</sub>H<sub>7</sub>C<sub>2</sub>Me<sub>2</sub>),<sup>27</sup> the  $\alpha$  and  $\beta$  forms of ( $Me_3P$ )<sub>2</sub>Pt-(Me<sub>2</sub>C<sub>2</sub>B<sub>6</sub>H<sub>6</sub>)<sup>28</sup> and ( $Me_3P$ )<sub>2</sub>Pt(C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>).<sup>28</sup> Bond distances for each compound are reported in Table VI.

The platinum–phosphorus distances are 2.316 and 2.320 Å for I and 2.317 and 2.330 Å for the ethoxide-substituted structure II. Other representative structures given in Table

Table IV. Refined Nonhydrogen Positional Parameters for ( $Ph_3P$ )<sub>2</sub>Pt[SB<sub>8</sub>H<sub>9</sub>(OEt)]

atom	x	y	z
Pt	0.3235 (1)	0.6144 (0)	0.3411 (0)
P1	0.2720 (4)	0.5583 (2)	0.2001 (3)
P2	0.1811 (4)	0.5937 (2)	0.4028 (3)
C110	0.2976 (13)	0.6008 (13)	0.0990 (11)
C111	0.2649 (14)	0.6623 (9)	0.0842 (13)
C112	0.2868 (19)	0.6991 (10)	0.0062 (18)
C113	0.3389 (19)	0.6721 (13)	-0.0503 (16)
C114	0.3703 (18)	0.6085 (14)	-0.0379 (15)
C115	0.3470 (17)	0.5741 (10)	0.0365 (14)
C120	0.3389 (14)	0.4829 (8)	0.2028 (14)
C121	0.4252 (18)	0.4712 (11)	0.2777 (15)
C122	0.4811 (19)	0.4132 (15)	0.2815 (20)
C123	0.4442 (26)	0.3695 (12)	0.2088 (26)
C124	0.3623 (22)	0.3825 (12)	0.1385 (20)
C125	0.3077 (16)	0.4370 (10)	0.1346 (15)
C130	0.1377 (14)	0.5351 (8)	0.1578 (12)
C131	0.1001 (17)	0.4784 (9)	0.1880 (13)
C132	-0.0046 (16)	0.4623 (10)	0.1639 (15)
C133	-0.0728 (15)	0.5046 (11)	0.1073 (15)
C134	-0.0361 (17)	0.5608 (10)	0.0788 (14)
C135	0.0677 (15)	0.5762 (9)	0.1023 (13)
C210	0.1855 (12)	0.6202 (11)	0.5232 (12)
C211	0.1538 (15)	0.6830 (10)	0.5345 (14)
C212	0.1589 (16)	0.7049 (13)	0.6246 (19)
C213	0.1918 (18)	0.6666 (13)	0.7055 (17)
C214	0.2172 (16)	0.6049 (12)	0.6886 (14)
C215	0.2142 (15)	0.5818 (10)	0.5988 (13)
C220	0.1635 (13)	0.5096 (8)	0.4110 (12)
C221	0.2505 (14)	0.4720 (8)	0.4303 (13)
C222	0.2459 (17)	0.4077 (10)	0.4371 (15)
C223	0.1516 (20)	0.3771 (10)	0.4208 (14)
C224	0.0631 (16)	0.4136 (11)	0.4013 (14)
C225	0.0696 (14)	0.4794 (9)	0.3978 (12)
C230	0.0653 (14)	0.6305 (8)	0.3384 (12)
C231	-0.0308 (16)	0.6246 (10)	0.3667 (14)
C232	-0.1149 (18)	0.6562 (14)	0.3195 (21)
C233	-0.1069 (25)	0.6978 (14)	0.2464 (20)
C234	-0.0182 (26)	0.7053 (12)	0.2207 (17)
C235	0.0696 (16)	0.6727 (10)	0.2678 (14)
S	0.3737 (5)	0.7922 (3)	0.3115 (5)
B1	0.5098 (18)	0.7138 (10)	0.4691 (16)
B2	0.5076 (19)	0.7735 (12)	0.3870 (16)
B3	0.5494 (17)	0.6973 (11)	0.3642 (16)
B4	0.4817 (15)	0.6389 (10)	0.4155 (15)
B5	0.3918 (17)	0.7620 (11)	0.4430 (15)
B7	0.4609 (17)	0.7327 (9)	0.2603 (16)
B8	0.4560 (18)	0.6468 (11)	0.2913 (16)
B10	0.3854 (17)	0.6756 (10)	0.4668 (15)
O	0.5033 (13)	0.6033 (8)	0.2335 (11)
C(1) <sup>a</sup>	0.6035 (39)	0.6064 (25)	0.1717 (32)
C <sup>b</sup>	0.5920 (35)	0.6150 (25)	0.1920 (32)
C(2)	0.6433 (34)	0.5537 (21)	0.1665 (28)

<sup>a</sup> Occupancy 0.07. <sup>b</sup> Occupancy 0.93.

VI show a range of 2.23–2.45 Å. The spread of Pt–P distances is large, and differences are usually attributed to variations in  $d\pi$ – $p\pi$  bonding. Strong platinum to boron bonding is suggested since the observed Pt–P bond distances are in the upper end of the observed range.

The boron–boron lengths are also as expected, except for B2–B7 in the ethoxide-substituted structure II which is slightly longer (2.00 Å). The perturbations caused by the ethoxide group are minor, with only atom B7 being shifted away from B2, B3, and the sulfur atom and the platinum atom being shifted toward the substituted B8. Otherwise, the bond distances in the two cages are identical within experimental error.

The boron–sulfur distances appear to be insensitive to structural changes. For example, the distances in structure I range from 1.92 to 1.96 Å while, in II, the range is from 1.91 to 1.98 Å. In ( $Et_3P$ )<sub>2</sub>Pt(H)(SB<sub>9</sub>H<sub>10</sub>),<sup>3</sup> the reported B–S average is 2.02 (5) Å. Pure thiaborane structures having no

Table V. Final Thermal Parameters for  $(\text{Ph}_3\text{P})_2\text{Pt}[\text{SB}_8\text{H}_7](\text{OEt})^a$ 

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$	$B, \text{\AA}^3$
Pt	2.8 (0)	3.4 (0)	2.9 (0)	-0.4 (0)	0.4 (0)	-0.0 (0)	3.0 (0)
P1	3.3 (2)	2.9 (2)	3.2 (2)	-0.3 (2)	0.7 (2)	-0.2 (2)	3.1 (1)
P2	2.7 (2)	3.6 (3)	3.0 (2)	-0.1 (2)	0.5 (2)	-0.1 (2)	3.1 (1)
C110	3.8 (9)	3.3 (12)	3.0 (8)	-0.9 (7)	0.4 (7)	-0.0 (7)	3.3 (5)
C111	3.1 (9)	4.5 (11)	4.6 (11)	-1.0 (9)	-0.1 (8)	0.0 (9)	4.0 (5)
C112	6.5 (14)	4.7 (13)	6.4 (15)	-0.2 (11)	-0.3 (12)	2.3 (11)	5.5 (7)
C113	6.1 (14)	7.1 (16)	5.2 (14)	-3.3 (13)	1.1 (11)	-0.5 (12)	5.6 (7)
C114	7.3 (14)	7.6 (16)	5.0 (12)	-0.9 (15)	2.8 (10)	-0.1 (13)	6.1 (3)
C115	6.1 (13)	6.6 (13)	3.8 (11)	-0.1 (11)	1.4 (10)	-0.6 (10)	5.3 (5)
C120	2.7 (9)	3.5 (10)	5.4 (11)	0.3 (8)	0.7 (8)	-0.6 (9)	3.7 (5)
C121	5.5 (13)	5.8 (13)	6.3 (13)	1.4 (11)	2.1 (11)	0.7 (10)	5.6 (6)
C122	5.0 (14)	8.9 (19)	10.8 (19)	3.7 (14)	1.2 (14)	4.4 (15)	6.5 (7)
C123	8.6 (20)	4.5 (16)	13.2 (24)	2.6 (14)	4.8 (18)	2.6 (14)	7.0 (10)
C124	8.9 (17)	4.4 (13)	12.0 (20)	1.8 (15)	4.8 (15)	-1.1 (15)	6.8 (4)
C125	5.0 (12)	4.3 (12)	7.2 (13)	0.6 (10)	2.5 (10)	0.4 (10)	5.1 (5)
C130	4.9 (11)	3.6 (9)	3.0 (8)	0.4 (8)	0.9 (9)	-0.7 (8)	3.7 (3)
C131	6.4 (13)	2.3 (10)	4.8 (11)	-0.4 (9)	0.9 (10)	0.4 (8)	4.1 (6)
C132	3.4 (11)	6.3 (13)	5.7 (12)	-1.7 (10)	2.2 (9)	-2.2 (10)	4.3 (5)
C133	3.3 (11)	6.0 (13)	5.3 (12)	0.1 (10)	0.1 (9)	-1.0 (10)	4.8 (5)
C134	5.0 (13)	4.1 (11)	5.0 (11)	1.1 (10)	-0.2 (10)	-0.5 (9)	4.7 (5)
C135	2.8 (9)	4.7 (11)	4.3 (10)	-0.5 (8)	-0.7 (8)	-0.8 (8)	3.8 (4)
C210	2.2 (7)	4.4 (10)	5.1 (10)	-0.7 (9)	0.5 (7)	0.5 (10)	3.6 (4)
C211	4.9 (11)	5.8 (13)	4.0 (11)	-1.5 (10)	1.5 (9)	-1.1 (9)	4.6 (6)
C212	4.0 (12)	10.4 (19)	7.2 (15)	-2.9 (12)	2.3 (12)	-5.0 (14)	5.4 (6)
C213	5.8 (14)	9.1 (9)	4.8 (13)	-1.0 (13)	0.7 (11)	-2.7 (13)	6.0 (6)
C214	5.9 (12)	7.9 (16)	4.3 (11)	-0.9 (12)	0.3 (9)	0.7 (11)	5.9 (6)
C215	5.0 (11)	8.2 (14)	2.7 (9)	1.4 (10)	0.6 (8)	0.2 (10)	4.7 (5)
C220	2.7 (9)	3.7 (9)	3.8 (9)	0.2 (8)	0.7 (7)	0.2 (7)	3.4 (4)
C221	2.9 (9)	2.0 (9)	6.0 (11)	-0.0 (8)	1.0 (8)	0.3 (8)	3.3 (5)
C222	5.7 (13)	3.6 (13)	7.8 (14)	-0.2 (9)	0.4 (11)	0.8 (9)	5.5 (7)
C223	8.8 (16)	3.5 (12)	4.9 (11)	-1.0 (12)	0.7 (11)	0.8 (9)	5.3 (5)
C224	4.8 (12)	5.5 (13)	5.1 (11)	-0.2 (10)	0.1 (9)	0.7 (9)	5.2 (6)
C225	3.8 (10)	4.2 (11)	4.2 (10)	0.7 (8)	1.2 (8)	0.1 (8)	3.9 (5)
C230	3.9 (9)	4.4 (12)	3.3 (9)	1.3 (8)	0.9 (7)	-0.5 (8)	3.6 (5)
C231	4.4 (11)	6.6 (14)	6.1 (12)	0.6 (11)	0.2 (9)	0.3 (11)	5.7 (5)
C232	4.3 (13)	9.5 (18)	10.4 (19)	1.4 (13)	-2.0 (13)	0.5 (15)	7.2 (7)
C233	10.5 (22)	8.5 (18)	6.1 (17)	6.6 (17)	-1.4 (16)	-1.0 (13)	6.6 (8)
C234	10.7 (21)	5.8 (14)	4.9 (13)	3.2 (15)	0.4 (15)	-0.3 (10)	6.4 (6)
C235	6.3 (13)	4.8 (12)	3.6 (10)	2.5 (10)	1.6 (9)	-0.1 (9)	4.2 (5)
S	5.6 (4)	6.2 (4)	7.4 (4)	0.2 (3)	0.6 (3)	0.7 (3)	6.5 (2)
B1	4.5 (12)	2.5 (10)	4.9 (13)	-0.6 (9)	1.1 (10)	0.3 (9)	3.7 (6)
B2	4.7 (13)	5.3 (14)	4.5 (12)	1.3 (11)	0.0 (11)	-0.2 (11)	4.8 (6)
B3	3.5 (12)	5.7 (14)	4.3 (12)	-1.4 (10)	-0.2 (10)	0.6 (10)	4.3 (6)
B4	2.0 (9)	5.7 (14)	3.9 (10)	-0.2 (8)	-0.4 (8)	-0.6 (9)	3.5 (6)
B5	3.3 (11)	5.0 (13)	4.4 (12)	-0.6 (10)	-0.4 (9)	-1.5 (10)	4.0 (6)
B7	3.7 (11)	2.2 (10)	5.3 (13)	-0.1 (9)	0.8 (10)	0.3 (9)	3.5 (6)
B8	4.7 (12)	4.7 (12)	5.2 (13)	-0.1 (10)	1.3 (10)	-4.3 (10)	2.8 (5)
B10	4.5 (12)	3.3 (11)	4.5 (12)	-2.7 (10)	0.9 (10)	-1.6 (9)	3.1 (5)
O							9.4 (5)
C(1)							10.0 (13)
C'							10.0 (13)
C(2)							9.2 (11)

<sup>a</sup> The anisotropic thermal parameters have units of  $\text{\AA}^2$ . They enter the expression for the structure factor in the form  $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*b^* + 2B_{23}klb^*c^*)]$ . The isotropic values,  $B$ , are given in the last column.

Table VI. Selected Compounds Illustrating the Range of Bond Distances ( $\text{\AA}$ )

	Pt-B	Pt-P	B-B	B-S	ref
$(\text{Et}_3\text{P})_2\text{Pt}(\text{Me}_2\text{C}_2\text{B}_7\text{H}_7)$	2.16-2.34	2.322	1.74-2.02		27
$(\text{Me}_3\text{P})_2\text{Pt}(\text{Me}_2\text{C}_2\text{B}_6\text{H}_6)\text{-}\alpha$	2.19-2.22	2.307	1.81-1.98		28
$(\text{Me}_3\text{P})_2\text{Pt}(\text{Me}_2\text{C}_2\text{B}_6\text{H}_6)\text{-}\beta$	2.19-2.24	2.311-2.314	1.78-2.00		28
$(\text{Me}_3\text{P})_2\text{Pt}(\text{C}_2\text{B}_5\text{H}_5)$	2.16-2.17	2.45	1.84-2.24		28
$(\text{Me}_2\text{PhP})_2\text{Pt}(\text{B}_3\text{H}_7)$	2.13-2.38	2.301-2.311	1.85-1.92		26
$(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\text{B}_9\text{H}_{10}\text{S}$	2.20-2.25	2.36-2.39	1.81	2.02	3
<i>trans</i> - $(\text{C}_2\text{H}_5)_3\text{P}_2\text{Pt}_2\text{Cl}_4$		2.230			29
$2,2'$ - $(1\text{-SB}_9\text{H}_8)_2$			1.69-1.94	1.92-1.93	30
$\text{B}_9\text{H}_{12}\text{S}^-$				1.89	31
$\text{B}_{10}\text{H}_{12}(\text{SMe}_2)_2$				1.92	22
$(\text{Ph}_3\text{P})_2\text{Pt}(\text{SB}_9\text{H}_{10})$	2.18-2.24	2.316-2.320	1.75-1.92	1.92-1.96	this work
$(\text{Ph}_3\text{P})_2\text{PtB}_8\text{H}_7\text{S}(\text{OEt})$	2.17-2.24	2.317-2.330	1.73-2.01	1.91-1.98	this work

heteroatoms other than sulfur are  $2,2'$ - $(1\text{-SB}_9\text{H}_8)_2$ ,<sup>30</sup> having B-S distances of 1.918 (3)-1.930 (3)  $\text{\AA}$ , and  $\text{SB}_9\text{H}_{12}$ ,<sup>31</sup> with an average distance of 1.89 (3)  $\text{\AA}$ . Even the exopolyhedral B-S distance of 1.92 (1)  $\text{\AA}$  observed in  $\text{B}_{10}\text{H}_{12}(\text{SMe}_2)_2$ <sup>22</sup> falls

within the range of 1.89 to 2.02  $\text{\AA}$ .

It is difficult to avoid comparing the  $\eta^3$  bonding observed in structures I and II with the  $\pi$ -allyl geometries. Similar bonding was also observed in  $(\text{Me}_2\text{PhP})_2\text{PtB}_3\text{H}_7$ ,<sup>26</sup> however,

Table VII

Intramolecular Distances (Å) for $(\text{Ph}_3\text{P})_2\text{PtSB}_3\text{H}_{10}$							
Pt-P1	2.316 (4)	C120-C121	1.411 (18)	C214-C215	1.425 (18)	S-B5	1.963 (25)
Pt-P2	2.320 (3)	C121-C122	1.377 (19)	C215-C210	1.384 (17)	B1-B2	1.817 (31)
Pt-B4	2.184 (16)	C122-C123	1.364 (21)	C220-C221	1.390 (17)	B1-B3	1.793 (26)
Pt-B8	2.242 (15)	C123-C124	1.352 (21)	C221-C222	1.424 (18)	B1-B4	1.745 (26)
Pt-B10	2.222 (17)	C124-C125	1.421 (19)	C222-C223	1.391 (19)	B1-B5	1.847 (31)
P1-C110	1.828 (13)	C125-C120	1.346 (18)	C223-C224	1.320 (18)	B1-B10	1.813 (26)
P1-C120	1.820 (13)	C130-C131	1.396 (18)	C224-C225	1.396 (18)	B2-B3	1.773 (29)
P1-C130	1.820 (14)	C131-C132	1.361 (19)	C225-C220	1.408 (16)	B2-B5	1.924 (29)
P2-C210	1.829 (14)	C132-C133	1.423 (22)	C230-C231	1.393 (18)	B2-B7	1.903 (28)
P2-C220	1.804 (12)	C133-C134	1.373 (22)	C231-C232	1.395 (18)	B3-B4	1.759 (23)
P2-C230	1.831 (14)	C134-C135	1.378 (19)	C232-C233	1.325 (21)	B3-B7	1.801 (23)
C110-C111	1.384 (17)	C135-C130	1.384 (18)	C233-C234	1.360 (21)	B3-B8	1.774 (21)
C111-C112	1.396 (21)	C210-C211	1.402 (18)	C234-C235	1.394 (19)	B4-B8	1.768 (23)
C112-C113	1.365 (24)	C211-C212	1.388 (17)	C235-C230	1.390 (18)	B4-B10	1.806 (29)
C113-C114	1.362 (24)	C212-C213	1.371 (19)	S-B2	1.920 (22)	B5-B10	1.846 (32)
C114-C115	1.395 (21)	C213-C214	1.354 (19)	S-B7	1.921 (19)	B7-B8	1.843 (23)
C115-C110	1.387 (18)						

Intramolecular Bond Angles (deg) for $(\text{Ph}_3\text{P})_2\text{PtSB}_3\text{H}_{10}$							
(a) Angles Involving Platinum							
P1-Pt-P2	98.0 (1)	Pt-P1-C130	110.8 (4)	P2-Pt-B4	126.2 (6)	Pt-P2-C230	110.2 (5)
P1-Pt-B4	132.2 (5)	Pt-B4-B8	68.2 (7)	P2-Pt-B8	86.3 (4)	Pt-B4-B1	122.4 (12)
P1-Pt-B8	171.4 (4)	Pt-B4-B10	66.9 (8)	P2-Pt-B10	169.6 (5)	Pt-B4-B3	121.9 (10)
P1-Pt-B10	90.4 (5)	Pt-B8-B3	118.1 (10)	B4-Pt-B10	48.4 (8)	Pt-B10-B1	117.1 (12)
B4-Pt-B8	47.1 (6)	Pt-B8-B4	64.7 (7)	B8-Pt-B10	84.5 (6)	Pt-B10-B4	64.7 (8)
Pt-P1-C110	117.0 (5)	Pt-B8-B7	117.2 (10)	Pt-P2-C210	111.0 (5)	Pt-B10-B5	117.7 (13)
Pt-P1-C120	112.8 (5)			Pt-P2-C220	122.9 (4)		
(b) Angles Involving Phosphorus							
C110-P1-C120	100.9 (6)	P1-C120-C121	122.0 (11)	C210-P2-C220	102.5 (6)	P2-C220-C221	120.7 (10)
C110-P1-C130	104.5 (6)	P1-C120-C125	118.3 (11)	C210-P2-C230	107.4 (6)	P2-C220-C225	122.8 (10)
C120-P1-C130	110.1 (7)	P1-C130-C131	115.1 (11)	C220-P2-C230	101.5 (6)	P2-C230-C231	117.7 (11)
P1-C110-C111	119.1 (12)	P1-C130-C135	126.4 (11)	P2-C210-C211	120.5 (10)	P2-C230-C235	123.5 (12)
P1-C110-C115	122.2 (11)			P2-C210-C215	120.1 (11)		
(c) Angles Involving Phenyl Rings							
C111-C110-C115	118.7 (13)	C122-C123-C124	121.7 (14)	C211-C210-C215	119.4 (13)	C222-C223-C224	122.3 (14)
C110-C111-C112	119.9 (16)	C123-C124-C125	119.4 (15)	C210-C211-C212	120.0 (13)	C223-C224-C225	121.9 (13)
C111-C112-C113	122.1 (17)	C124-C125-C120	119.7 (14)	C211-C212-C213	120.5 (14)	C224-C225-C220	119.9 (13)
C112-C113-C114	117.0 (18)	C131-C130-C135	118.5 (13)	C212-C213-C214	120.5 (13)	C231-C230-C235	118.8 (13)
C113-C114-C115	123.3 (18)	C130-C131-C132	122.5 (15)	C213-C214-C215	120.5 (13)	C230-C231-C232	120.3 (14)
C114-C115-C110	118.9 (15)	C131-C132-C133	118.1 (14)	C214-C215-C210	119.0 (13)	C231-C232-C233	119.7 (15)
C121-C120-C125	119.1 (13)	C132-C133-C134	119.6 (14)	C221-C220-C225	116.4 (12)	C232-C233-C234	121.6 (16)
C120-C121-C122	120.5 (15)	C133-C134-C135	121.1 (17)	C220-C221-C222	123.4 (13)	C233-C234-C235	120.7 (16)
C121-C122-C123	119.0 (16)	C134-C135-C130	120.2 (15)	C221-C222-C223	115.9 (14)	C234-C235-C230	118.8 (14)
(d) Angles Involving Thiaborane Cage							
B2-S-B7	59.3 (8)	B1-B3-B2	61.3 (12)	S-B2-B1	112.8 (12)	B1-B3-B7	110.2 (14)
B2-S-B5	59.4 (9)	B1-B3-B4	58.9 (11)	S-B2-B3	111.7 (13)	B1-B3-B8	109.8 (12)
B5-S-B7	99.4 (8)	B2-B3-B7	64.3 (11)	S-B5-B1	109.6 (12)	B2-B3-B4	110.5 (14)
S-B2-B5	61.4 (10)	B4-B3-B8	60.1 (9)	S-B5-B10	120.2 (12)	B2-B3-B8	116.2 (13)
S-B2-B7	60.3 (9)	B7-B3-B8	62.1 (9)	S-B7-B3	110.4 (11)	B4-B3-B7	108.3 (12)
S-B5-B2	59.2 (10)	B1-B4-B3	61.5 (10)	S-B7-B8	120.9 (11)	B1-B4-B8	112.3 (13)
S-B7-B2	60.3 (9)	B1-B4-B10	61.4 (11)	B2-B1-B4	109.1 (14)	B3-B4-B10	111.5 (13)
B2-B1-B3	58.8 (10)	B3-B4-B8	60.4 (9)	B2-B1-B10	114.0 (15)	B8-B4-B10	114.3 (12)
B2-B1-B5	63.3 (13)	B1-B5-B2	57.6 (12)	B3-B1-B5	107.2 (14)	B2-B5-B10	107.6 (15)
B3-B1-B4	59.6 (10)	B1-B5-B10	58.8 (12)	B4-B1-B5	107.4 (13)	B2-B7-B8	107.0 (12)
B4-B1-B10	61.0 (11)	B2-B7-B3	57.1 (10)	B3-B1-B10	109.6 (12)	B4-B8-B7	106.1 (11)
B5-B1-B10	60.6 (13)	B3-B7-B8	58.2 (8)	B1-B2-B7	104.8 (14)	B4-B10-B5	104.9 (13)
B1-B2-B3	59.9 (12)	B3-B8-B4	59.5 (9)	B3-B2-B5	104.8 (14)	B1-B10-B4	57.7 (11)
B1-B2-B5	59.1 (12)	B3-B8-B7	59.7 (9)	B5-B2-B7	101.4 (13)	B1-B10-B5	60.6 (11)
B3-B2-B7	58.5 (10)						

because of the disorder associated with the  $\text{B}_3\text{H}_7^{2-}$  ligand, structures I and II give the clearest definition of  $\eta^3$  bonding. A large amount of structural work has been performed on  $\pi$ -allyl metal complexes.<sup>29,32-34</sup> One Pt- $\pi$ -allyl structure determined is  $(\text{acac})_2\text{Pt}_2(\text{C}_3\text{H}_5)_2$  (acac = acetylacetonate), in which the allyl groups bridge the two platinum atoms. One allyl carbon is  $\sigma$  bonded to Pt1, and the other two allyl carbon atoms are  $\pi$  bonded to Pt2. The dihedral angles between the allyl plane and the metal-ligand plane in the  $\pi$ -allyl complexes are in the 111–127° range, entirely consistent with the 117.2° angle observed for I. Most  $\pi$ -allyl compounds have symmetrically coordinated  $\pi$ -allyl ligands based on C-C and M-C distances. The symmetric geometry is indicated by two equivalent outer M-C bond distances with a central M-C

distance equal to or slightly less than the outer distance. Asymmetrical metal-allyl geometries are found for  $[(\text{C}_3\text{H}_5)_2\text{RhCl}]_2^{35}$  and  $[(\text{C}_5\text{H}_9)\text{PdCl}]_2^{36}$ .

The disordered structure of  $(\text{Me}_2\text{PhP})_2\text{PtB}_3\text{H}_7^{26}$  showed an asymmetric bonding pattern having a short B-B bond in the ligand plane associated with one long Pt-B bond and two shorter Pt-B distances associated with a longer B-B bond length. Muettterties et al. reported two possible causes for the  $\text{B}_3\text{H}_7^{2-}$  occurring in an asymmetric pattern,<sup>26</sup> i.e., the effect of crystal packing forces or maximum metal to ligand overlap with an asymmetric  $\text{B}_3\text{H}_7$ . Structure I clearly shows that the symmetric bonding exists between the platinum and the thiaborane ligand,  $\text{SB}_3\text{H}_{10}^{2-}$ . The two equivalent outer Pt-B distances of 2.222 and 2.242 Å are identical considering the

Table VIII

Intramolecular Distances (Å) for $(\text{Ph}_3\text{P})_2\text{Pt}[\text{SB}_8\text{H}_9(\text{OEt})]$							
Pt-P1	2.317 (5)	C120-C121	1.381 (22)	C215-C210	1.358 (24)	B1-B3	1.759 (32)
Pt-P2	2.330 (5)	C121-C122	1.358 (23)	C220-C221	1.416 (25)	B1-B4	1.759 (28)
Pt-B4	2.204 (19)	C122-C123	1.385 (28)	C221-C222	1.424 (30)	B1-B5	1.839 (31)
Pt-B8	2.166 (24)	C123-C124	1.382 (28)	C222-C223	1.405 (34)	B1-B10	1.836 (29)
Pt-B10	2.237 (19)	C124-C125	1.389 (24)	C223-C224	1.345 (34)	B2-B3	1.754 (32)
P1-C110	1.826 (19)	C125-C120	1.378 (22)	C224-C225	1.352 (29)	B2-B5	1.917 (35)
P1-C120	1.790 (17)	C130-C131	1.436 (25)	C225-C220	1.379 (24)	B2-B7	2.001 (31)
P1-C130	1.793 (18)	C131-C132	1.350 (28)	C230-C231	1.402 (23)	B3-B4	1.785 (30)
P2-C210	1.818 (17)	C132-C133	1.401 (36)	C231-C232	1.402 (26)	B3-B7	1.850 (29)
P2-C220	1.817 (18)	C133-C134	1.327 (37)	C232-C233	1.399 (26)	B3-B8	1.791 (29)
P2-C230	1.824 (19)	C134-C135	1.397 (30)	C233-C234	1.378 (27)	B4-B8	1.769 (30)
C110-C111	1.407 (26)	C135-C130	1.369 (24)	C234-C235	1.388 (26)	B4-B10	1.797 (30)
C111-C112	1.377 (25)	C210-C211	1.368 (24)	C235-C230	1.389 (23)	B5-B10	1.857 (30)
C112-C113	1.412 (30)	C211-C212	1.456 (27)	S-B2	1.914 (24)	B7-B8	1.865 (31)
C113-C114	1.378 (30)	C212-C213	1.319 (29)	S-B7	1.966 (23)	B8-O	1.476 (24)
C114-C115	1.385 (26)	C213-C214	1.402 (32)	S-B5	1.977 (23)	O-C(1)	1.771 (48)
C115-C110	1.349 (24)	C214-C215	1.394 (26)	B1-B2	1.730 (31)	C(1)-C(2)	1.332 (53)
Intramolecular Bond Angles (deg) for $(\text{Ph}_3\text{P})_2\text{Pt}[\text{SB}_8\text{H}_9(\text{OEt})]$							
(a) Angles Involving Platinum							
P1-Pt-P2	98.1 (2)	Pt-P2-C230	113.7 (7)	P1-Pt-B4	127.6 (6)	Pt-P1-C130	120.3 (6)
P2-Pt-B4	129.1 (6)	Pt-B4-B8	65.0 (10)	P1-Pt-B8	88.1 (5)	Pt-B4-B1	120.8 (13)
P2-Pt-B8	172.1 (6)	Pt-B4-B10	67.1 (9)	P1-Pt-B10	172.6 (6)	Pt-B4-B3	118.3 (12)
P2-Pt-B10	88.6 (6)	Pt-B8-B3	120.0 (13)	B4-Pt-B10	47.7 (8)	Pt-B10-B1	115.6 (13)
B4-Pt-B8	47.8 (8)	Pt-B8-B4	67.2 (10)	B8-Pt-B10	85.0 (7)	Pt-B10-B4	65.2 (9)
Pt-P2-C210	117.5 (5)	Pt-B8-B7	117.5 (13)	Pt-P1-C110	113.1 (5)	Pt-B10-B5	115.8 (12)
Pt-P2-C220	110.1 (6)	Pt-B8-O	118.7 (15)	Pt-P1-C120	112.1 (7)		
(b) Angles Involving Phosphorus							
C210-P2-C220	102.4 (9)	P2-C220-C221	117.5 (14)	C110-P1-C120	105.4 (9)	P1-C120-C121	118.6 (15)
C210-P2-C230	101.9 (8)	P2-C220-C225	125.2 (14)	C110-P1-C130	102.0 (8)	P1-C120-C125	121.9 (15)
C220-P2-C230	110.5 (8)	P2-C230-C231	122.1 (15)	C120-P1-C130	102.3 (8)	P1-C130-C131	121.0 (15)
P2-C210-C211	117.0 (15)	P2-C230-C235	119.6 (16)	P1-C110-C111	118.7 (15)	P1-C130-C135	120.6 (14)
P2-C210-C215	122.7 (18)			P1-C110-C115	123.1 (15)		
(c) Angles Involving Phenyl Rings							
C211-C210-C215	120.3 (19)	C222-C223-C224	118.5 (20)	C111-C110-C115	118.1 (17)	C122-C123-C124	121.7 (24)
C210-C211-C212	118.3 (21)	C223-C224-C225	120.2 (19)	C110-C111-C112	120.9 (19)	C123-C124-C125	122.7 (26)
C211-C212-C213	122.8 (24)	C224-C225-C220	121.1 (17)	C111-C112-C113	118.8 (22)	C124-C125-C120	119.4 (22)
C212-C213-C214	115.6 (21)	C231-C230-C235	117.6 (18)	C112-C113-C114	121.1 (23)	C131-C130-C135	118.1 (18)
C213-C214-C215	122.9 (20)	C230-C231-C232	120.2 (22)	C113-C114-C115	118.8 (21)	C130-C131-C132	122.2 (19)
C214-C215-C210	120.1 (20)	C231-C232-C233	119.8 (26)	C114-C115-C110	122.2 (21)	C131-C132-C133	118.2 (19)
C221-C220-C225	117.3 (16)	C232-C233-C234	120.9 (25)	C121-C120-C125	119.5 (18)	C132-C133-C134	119.6 (19)
C220-C221-C222	122.4 (18)	C233-C234-C235	120.4 (26)	C120-C121-C122	120.4 (21)	C133-C134-C135	121.9 (19)
C221-C222-C223	120.4 (20)	C234-C235-C230	120.9 (22)	C121-C122-C123	116.1 (22)	C134-C15-C130	120.0 (19)
(d) Angles Involving Thiaborane Cage and Ethoxide Group							
B2-S-B7	62.1 (9)	B1-B3-B4	59.5 (12)	S-B2-B1	114.4 (16)	B2-B3-B4	109.7 (18)
B2-S-B5	59.0 (10)	B2-B3-B7	67.4 (13)	S-B2-B3	112.0 (14)	B2-B3-B8	116.5 (17)
B5-S-B7	102.0 (9)	B4-B3-B8	59.3 (12)	S-B5-B1	106.8 (14)	B4-B3-B7	109.1 (14)
S-B2-B5	62.2 (10)	B7-B3-B8	61.6 (12)	S-B5-B10	119.6 (13)	B1-B4-B8	109.9 (16)
S-B2-B7	60.2 (9)	B1-B4-B3	59.5 (13)	S-B7-B3	105.6 (14)	B3-B4-B10	110.8 (16)
S-B5-B2	58.8 (10)	B1-B4-B10	62.2 (12)	S-B7-B8	118.0 (14)	B8-B4-B10	113.1 (15)
S-B7-B2	57.7 (9)	B3-B4-B8	60.5 (12)	B2-B1-B4	112.1 (16)	B2-B5-B10	106.1 (15)
B2-B1-B3	60.3 (13)	B1-B5-B2	54.8 (11)	B2-B1-B10	115.5 (17)	B2-B7-B8	102.4 (14)
B2-B1-B5	64.9 (13)	B1-B5-B10	59.6 (12)	B3-B1-B5	109.9 (15)	B4-B8-B7	109.2 (14)
B3-B1-B4	61.0 (12)	B2-B7-B3	54.0 (11)	B4-B1-B5	108.4 (15)	B4-B10-B5	106.0 (15)
B4-B1-B10	59.9 (11)	B3-B7-B8	57.6 (11)	B3-B1-B10	110.2 (15)	B1-B10-B4	57.9 (11)
B5-B1-B10	60.7 (12)	B3-B8-B4	60.2 (12)	B1-B2-B7	106.1 (15)	B1-B10-B5	59.7 (11)
B1-B2-B3	60.6 (13)	B3-B8-B7	60.8 (12)	B3-B2-B5	106.6 (17)	B3-B8-O	112.0 (17)
B1-B2-B5	60.3 (13)	B4-B8-O	121.0 (19)	B5-B2-B7	102.9 (15)	B7-B8-O	114.8 (18)
B3-B2-B7	58.6 (11)	B8-O-C(1)	137.2 (24)	B1-B3-B7	111.6 (17)	O-C(1)-C(2)	110.3 (40)
B1-B3-B2	59.0 (13)			B1-B3-B8	109.0 (16)	O-C'-C(2)	113.2 (40)

error associated with them, and the central distance of 2.184 Å is slightly shorter than the outer bond lengths. The B-B distances are also statistically identical, 1.797 and 1.769 (30) Å.

**Other Characterization.** The infrared and NMR spectra of I-IV are given in Tables IX and X, respectively. Although the  $^1\text{H}$  NMR of III in the methyl region was typical of reported  $\text{X}_6\text{AA}'\text{X}'_6$  spectra<sup>37</sup> with additional coupling to  $^{195}\text{Pt}$ , no analysis was attempted. The  $^{11}\text{B}$  NMR spectra of I-IV are consistent with the X-ray structure, those of I, III, and IV are almost identical, and that of I is shown in Figure 5. The peaks with shoulders at +36.8 and -21.6 ppm are due to Pt-bound borons as discussed previously.<sup>8</sup> As expected, the

$^{11}\text{B}$  spectrum of II is more complex than those of I, III, and IV since the ethoxide is substituted off the effective mirror plane formed by atoms 2, 4, 6, and 9 in the complex.

We have found that  $\text{L}_2\text{Pt}(\text{SB}_8\text{H}_9)$  complexes also form when  $\text{SB}_{11}\text{H}_{11}$ <sup>38</sup> is substituted for  $\text{SB}_9\text{H}_9$  as a starting material. Other experiments show that thiaboranes are degraded by ethanol. It appears that our synthetic method is a degradative insertion reaction where the Pt moiety is able to form a kinetically stable coordination complex after the thiaborane has been degraded to an  $\text{SB}_8$  framework. The range of metal-lathiaboranes which are susceptible to degradation by alcohol is not defined. However, since the previously reported  $\text{L}_2\text{M}(\text{SB}_9\text{H}_9)$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) complexes<sup>39</sup> were recrystallized



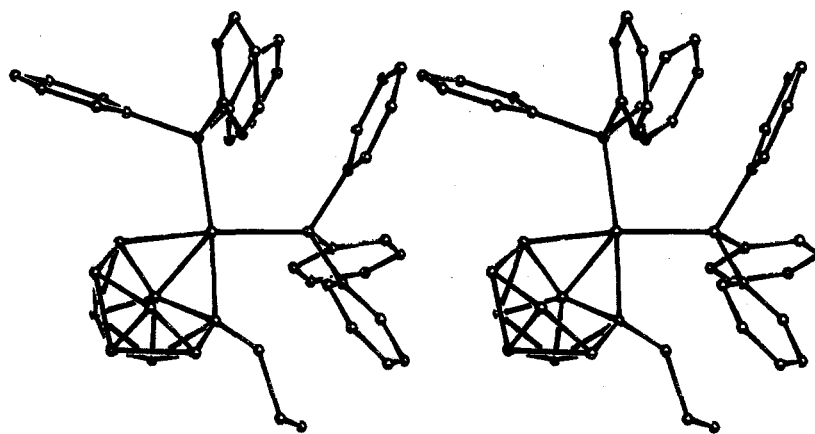


Figure 3. Stereoview of the molecule  $(\text{Ph}_3\text{P})_2\text{PtB}_8\text{H}_9\text{S}(\text{OEt})$ .

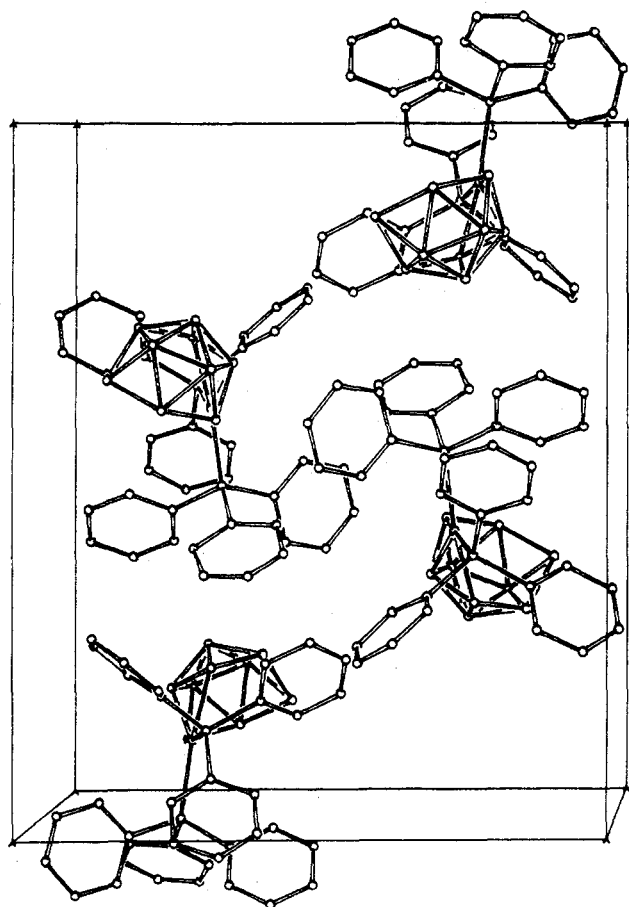


Figure 4. Crystal packing of four molecules of  $(\text{Ph}_3\text{P})_2\text{PtB}_8\text{H}_9\text{S}$  in the unit cell.

from solutions containing ethanol and display  $^{11}\text{B}$  NMR spectra strikingly similar to those which we find for the  $\text{L}_2\text{Pt}(\text{SB}_8\text{H}_{10})$  complexes (Figure 5), they should be reinvestigated.

In contrast to alcohol, in aprotic solvents such as benzene and cyclohexane the interaction of  $\text{SB}_8\text{H}_9$  with  $\text{L}_4\text{Pt}$  reagents is distinctly different. Although highly pure products have not yet been obtained, preliminary results are consistent with Pt bound in an expolyhedral manner and with no cage degradation. The room-temperature reaction gives a product which is probably similar to  $[(\text{PPh}_3)_2\text{Cu}]_2\text{B}_{10}\text{H}_{10}$ , the crystal structure of which<sup>41</sup> shows that two B-H groups of the  $\text{B}_{10}$ -cage bridge to a single copper. Similar Pt-H-B bonding is suggested for  $\text{SB}_8\text{H}_9$ , but no clear evidence has been obtained. At reflux a new product is obtained which shows a

Table IX. Infrared Spectra

$[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Pt}(\text{SB}_8\text{H}_{10})$   
2956 vs, 2923 vs, 2862 s, 2518 vs, 2453 s, 1450 s, 1423 s, 1405 sh, 1377 m, 1242 m, 1204 m, 1151 m, 1042 vs, 1012 vs, 990 m, 948 m, 922 w, 911 s, 880 m, 869 w, 798 m, 778m, 765 vs, 745 sh, 712 vs, 663 w, 631 m, 582 m, 539 w, 494 w, 461 m, 423 m

$[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)]_2\text{Pt}(\text{SB}_8\text{H}_{10})$   
3061 w, 3040 m, 2962 w, 2900 m, 2503 vs, 1949 w, 1890 w, 1803 w, 1486 m, 1436 s, 1421 m, 1411 sh, 1310 m, 1297 w, 1284 m, 1103 vs, 1032 vs, 1009 vs, 975 w, 942 vs, 903 vs, 882 sh, 863 m, 841 m, 832 m, 793 s, 740 vs, 726 s, 708 s, 687 s, 581 s, 540 m, 480 s, 462 m, 436 s, 407 m, 363 m, 356 m

$[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Pt}(\text{SB}_8\text{H}_{10})$   
3049 m, 2540 vs, 2452 m, 1952 w, 1890 w, 1810 w, 1479 s, 1438 vs, 1311 w, 1230 m, br, 1183 w, 1158 m, 1093 vs, 1029 m, 1013 s, 998 m, 943 w, 910 w, 876 w, 864 w, 798 m, 749 m, 738 s, 689 vs, 632 w, 610 w, 570 w, 521 vs, 508 vs, 495 sh, 450 w, 430 w

$[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Pt}[\text{SB}_8\text{H}_9(\text{OC}_2\text{H}_5)]$   
3049 m, 2969 w, 2540 vs, 2050 w, 1958 w, 1890 w, 1815 w, 1588 w, 1572 w, 1482 s, 1438 vs, 1311 w, 1185 m, br, 1160 m, 1093 s, 1027 m, 998 m, 912 w, 840 w, 800 w, 740 s, 689 vs, 609 w, 620 vs, 508 vs, 491 sh, 450 w, 478 w

Table X

(a)  $^{11}\text{B}$  NMR Data<sup>a</sup>  
 $(\text{PPh}_3)_2\text{Pt}(\text{SB}_8\text{H}_{10})$ :<sup>b</sup> -38 (1), -4.6 (1), 6.7 (2), 17 (2), 25.5 (2)  
 $(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{SB}_8\text{H}_{10})$ :<sup>c</sup> -36.8 (1), -3.73 (1), 5.14 (2), 21.6 (2), 27.0 (2)  
 $(\text{PEt}_3)_2\text{Pt}(\text{SB}_8\text{H}_{10})$ :<sup>b</sup> -38 (1), -4.2 (1), 5.1 (2), 21.5 (2), 26 (2)  
 $(\text{PPh}_3)_2\text{Pt}[\text{SB}_8\text{H}_9(\text{OEt})]$ :<sup>b</sup> -36 (1), -7.7 (2), 5.5 (2), 13.3 (1), 23 (1), 26 (1)

(b)  $^1\text{H}$  NMR Data<sup>d</sup>  
 $(\text{PPh}_3)_2\text{Pt}(\text{SB}_8\text{H}_{10})$ :<sup>e</sup> 2.25 (Ph)  
 $(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{SB}_8\text{H}_{10})$ :<sup>e</sup> 2.65 (Ph), 8.31 (Me)  
 $(\text{PEt}_3)_2\text{Pt}(\text{SB}_8\text{H}_{10})$ :<sup>e</sup> 7.97 ( $\text{CH}_2$ ), 8.94 (Me)  
 $(\text{PPh}_3)_2\text{Pt}[\text{SB}_8\text{H}_9(\text{OEt})]$ :<sup>e</sup> 2.86 (Ph), 6.94 (CH), 7.80 (CH), 9.70 (Me)

<sup>a</sup> Spectra obtained in  $\text{CDCl}_3$ . Chemical shift of proton-decoupled peak reported followed by relative intensity by parentheses. <sup>b</sup> Run at 32.1 MHz. <sup>c</sup> Run at 86.6 MHz. <sup>d</sup> Obtained in  $\text{CDCl}_3$  at 100 MHz. Reported as center of resonance ( $\tau$ ) followed by assignment in parentheses. <sup>e</sup> Bridge-hydrogen signal also seen at  $\tau$  11-12. See text.

strong  $\nu(\text{Pt-H})$  at  $1963\text{ cm}^{-1}$  and a  $^1\text{H}$  NMR with a hydride signal at  $\tau$  18 (satellites,  $J_{195\text{Pt-H}} = 708\text{ Hz}$ ). This product probably results from oxidative addition of a B-H site to the platinum to give a species analogous to the expolyhedral iridium thioaranes we previously characterized.<sup>7</sup> Stone has

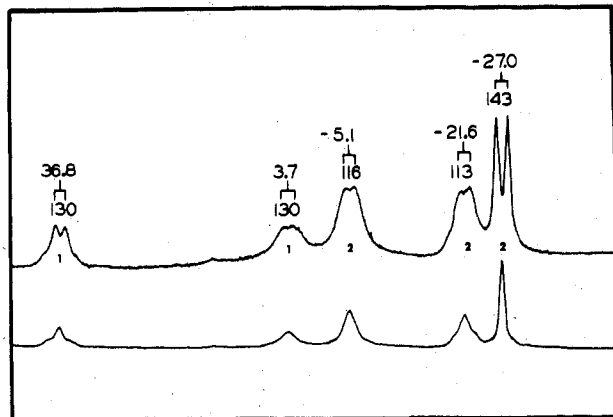


Figure 5. 86.6-MHz  $^{11}\text{B}$  NMR spectra of  $(\text{PhMe}_2\text{P})_2\text{PtB}_8\text{H}_{10}\text{S}$ .

recently proposed<sup>23</sup> a similar hydride intermediate for certain platinacarbaboranes.

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**Registry No.** I, 64560-46-9; II, 64560-47-0; III, 64560-44-7; IV, 64560-45-8;  $(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{SB}_9\text{H}_9)$ , 71009-97-7;  $(\text{PMe}_2\text{Ph})_4\text{Pt}$ , 33361-89-6;  $(\text{PPh}_3)_4\text{Pt}$ , 14221-02-4;  $(\text{PEt}_3)_3\text{Pt}$ , 39045-37-9;  $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ , 12120-15-9;  $1\text{-SB}_9\text{H}_9$ , 41646-56-4.

**Supplementary Material Available:** Structure factor tables, phenyl hydrogen positions, and isotropic thermal parameters (27 pages). Ordering information is given on any current masthead page.

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