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Transition Metal Promoted Reactions of Boron Hydrides. 13.[1] Platinum Catalyzed Synthesis of 6,9-Dialkyldecaboranes

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Both chloroplatinic acid and platinum bromide have been found to catalyze the reactions of decaborane(14) with terminal olefins, including ethylene, propylene, 1-butene, and 1-pentene, to give the corresponding 6,9-$R_2B_{10}H_{12}$ derivatives in high yields. Chemical studies of 6,9-$(n\text{-}C_5H_{11})_2B_{10}H_{12}$ (I) show that, in contrast to decaborane(14), I does not react to form dibase adducts with the Lewis bases Et_3N, Ph_3P, Et_2S, or MeCN. However, I undergoes many other reactions, including deprotonation to 6,9-$(n\text{-}C_5H_{11})_2B_{10}H_{11}^-$, reduction to *arachno*-6,9-$(n\text{-}C_5H_{11})_2B_{10}H_{12}^{2-}$, and degradation to *arachno*-4-$(n\text{-}C_5H_{11})B_9H_{13}^-$, analogous to those observed for decaborane(14) when more forcing conditions are employed. Reaction of 6,9-$(n\text{-}C_5H_{11})_2B_{10}H_{12}$ with trimethylphosphine also results in cage degradation to produce a compound which, based on its NMR data, is proposed to have an *arachno*-4-$(n\text{-}C_5H_{11})$-6,8-$(Me_3P)_2B_9H_{10}$ cage framework structure. Reaction of 6,9-$(n\text{-}C_5H_{11})_2B_{10}H_{11}^-$ with (COD)$PtCl_2$ was found to produce the platinaborane *commo*-Pt-[*nido*-7-Pt-8,11-$(n\text{-}C_5H_{11})_2B_{10}H_{10}]_2^{2-}$ in good yields. A single-crystal X-ray determination confirmed that the compound has a geometry analogous to that previously confirmed for $[B_{10}H_{12}]_2M^{2-}$ (M = Ni, Pd, Pt) in which the platinum atom occupies a common vertex in two 11-vertex *nido*-platinaborane clusters.

We have previously demonstrated that transition metal reagents can catalyze a variety of reactions involving the polyhedral boranes or borazine, including acetylene additions and insertions, olefin additions and substitutions, and dehydrocoupling reactions.[2] Although metal catalysis has now been employed to activate the reactions of a range of boron compounds,[3] we have not previously been successful in using these techniques to effect the reactions of the most important polyhedral borane, decaborane(14). In this paper we report the first example of such a transition metal catalyzed reaction, involving the use of platinum catalysts to effect the high-yield reactions of decaborane(14) with terminal olefins to form the corresponding alkylated 6,9-$R_2B_{10}H_{12}$ derivatives.

Experimental Section

All manipulations were carried out by using standard high vacuum or inert-atmosphere techniques as described by Shriver.[4]

Materials. Ethylene (grade 2.5) was obtained from Airco. Platinum bromide, propylene, 1-butene and 1-pentene were purchased from Aldrich. Chloroplatinic acid hexahydrate (39.05% Pt) was obtained from Johnson Matthey Inc. Hexane was obtained from EM Science and was used without further purification.

Gas-liquid chromatography was conducted on a Varian Aerograph Series 1400 gas chromatograph equipped with a 7 ft × 0.25 in. 10% SE-30 on a chromosorb W(100/120-mesh) column.

Physical Measurements. Boron-11 NMR spectra at 64.2 MHz and proton NMR spectra at 200 MHz were obtained on a Bruker AF-200 spectrometer. Boron-11 NMR spectra at 160.5 MHz and proton NMR at 500 MHz were obtained on a Bruker AM 500 spectrometer. All boron-11 chemical shifts are referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield chemical shift. Chemical shifts for ^1H NMR spectra (ppm) were measured relative to the lock solvent and referenced to TMS. Low- and high-resolution mass spectra were obtained on a VG-7070H mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1430 infrared spectrophotometer. Elemental analyses were performed at Robertson Microlit Laboratories. All yields are calculated based on starting decaborane or dipentyldecaborane.

Crystallographic Data for VII. Single crystals were grown by slow evaporation under nitrogen of a THF solution. The cell constants were determined from a least-squares fit of the setting angles for 25 accurately centered reflections.

Collection and Reduction of the Data. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Cu Kα radiation. Three standard reflections measured every 3500 s of X-ray exposure showed no intensity decay. The intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied.

Solution and Refinement of the Structure. The structure was solved by standard heavy atom Patterson techniques followed by weighted Fourier syntheses. All cage hydrogens were located. Refinement was by full-matrix least squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically. The cage hydrogen atoms were isotropically refined. The positions of the pentyl and PPN hydrogens were calculated and included as constant contributions to the structure factors without refinement.

Chloroplatinic Acid Reactions. 1-Pentene. A 54-mg sample (0.104 mmol) of $H_2PtCl_6 \cdot 6H_2O$ was loaded with 0.24 g (2.0 mmol) of decaborane(14) into a 25-mL two-neck round-bottom flask, fitted with a vacuum stopcock and a rubber septum. The flask was evacuated, and 5 mL of 1-pentene was vacuum distilled into the flask. The reaction mixture was then brought to room temperature and its composition monitored by GLC throughout the reaction period. After 31 h all $B_{10}H_{14}$ was consumed. The pentene was then vacuum evaporated, and the residue was dissolved in hexane and filtered through a short plug of silica gel. Subsequent evaporation of the hexane left 0.481 g of a white material, which was shown by GLC analysis to be a mixture of 87% 6,9-dipentyldecaborane I and 13% 5,6,9-tripentyldecaborane. This product distribution corresponds to a total of ~36 catalyst turnovers and an ~80% yield of 6,9-dipentyldecaborane. Preparative GLC was used to further purify samples of I for spectroscopic studies. For I: mp 64 °C; R_v = 10.1 ($B_{10}H_{14}$ = 1). ^{11}B NMR (64.2 MHz, ppm C_6D_6): 25.1 (s, 2, B6,9), 9.0 (d, 2, J = 139 Hz, B1,3), –1.7 (d, 4, J = 147 Hz, B5,7,8,10), –36.0 (d, 2, J = 152 Hz, B2,4). $^1H\{^{11}B\}$ NMR (200 MHz, C_6D_6): 3.99 (s, 2, HB1,3), 3.00 (s, 4, HB5,7,8,10), 1.48 (m, 2, CH), 1.28 (m, 4, CH), 1.11 (m, 2, CH), 0.91 (t, 3, J = 7 Hz, CH) –1.92 (s, 4, BHB). Exact mass for $^{12}C_{10}{}^1H_{34}{}^{11}B_{10}$: calcd, 264.3591; found, 264.362; IR (KBr pellet, cm^{-1}): 2955 (s), 2920 (vs), 2850 (s), 2570 (vs), 2515 (s), 1975 (w), 1925 (w), 1520 (w), 1480 (w), 1465 (w), 1410 (m), 1375 (w), 1345 (m), 1285 (m), 1260 (m), 1225 (s), 1180 (w), 1130 (w), 1100 (vs), 1050 (w), 1000 (vs), 965 (m), 945 (m), 905 (s), 840 (m), 800 (w), 720 (w), 705 (s), 675 (m), 610 (w).

In a separate experiment, 0.04 mmol of chloroplatinic acid was reacted with 4.0 mmol of decaborane (1% Pt/$B_{10}H_{14}$ ratio), in 7 mL of 1-pentene.

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(1) Part 12: Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 6201–6209.

(2) For a review of metal-catalyzed reactions of polyhedral boranes, see: Sneddon, L. G. *Pure Appl. Chem.* **1987**, *59*, 837–846 and references therein.

(3) Burgress, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179–1191.

(4) Shriver, D. F.; Drezdzon, M. A. *Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

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After 4 days of reaction with stirring at room temperature, the concentration of $B_{10}H_{14}$ appeared to remain constant and the color of the solution had darkened. GLC analysis gave an estimated composition of this mixture as 0.38 mmol of $B_{10}H_{14}$ and 1.0 mmol of monopentyl-, 2.25 mmol of 6,9-dipentyl-, and 0.39 mmol of tripentyldecaborane. This product distribution corresponds to a total of 167 turnovers.

1-Butene. An 88-mL Fischer & Porter pressure vessel (Part No. 100-205-0003) was charged with 44.3 mg (0.089 mmol) of chloroplatinic acid and 0.25 g (2.0 mmol) of decaborane. The flask was evacuated and excess 1-butene was vacuum transferred to the flask. The mixture was stirred for 28 h at room temperature. The olefin was evaporated and the residue sublimed at 70–80 °C for ~3 h. The sublimed material (0.437 g) was shown by GLC to consist of 2% $B_{10}H_{14}$, 8% monobutyldecaborane, 81% 6,9-dibutyldecaborane (II), and 8% tributyldecaborane. This product distribution corresponds to 42 catalyst turnovers and an estimated 75% yield of 6,9-dibutyldecaborane (II). Preparative GLC was used to further purify samples of II for spectroscopic studies. For II: mp = 32 °C; R_v = 6.1 ($B_{10}H_{14}$ = 1). ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 25.3 (s, 2, B6,9), 9.0 (d, 2, J = 141 Hz, B1,3), –1.8 (d, 4, J = 143 Hz, B5,7,8,10), –36.1 (d, 2, J = 151 Hz, B2,4). ^1H NMR (200 MHz, C_6D_6): 1.39 (m, 4, CH), 1.09 (m, 2, CH), 0.90 (t, 3, J = 7 Hz, CH). Exact mass for $^{12}C_8{}^1H_{30}{}^{11}B_{10}$: calcd, 236.3278; found, 236.327. IR (KBr pellet, cm^{-1}): 2950 (vs), 2920 (vs), 2860 (s), 2570 (vs), 1975 (w), 1925 (w), 1525 (w), 1480 (w), 1460 (m), 1410 (s), 1375 (m), 1340 (m), 1310 (m), 1230 (s), 1190 (w), 1120 (w), 1100 (s), 1040 (w), 995 (vs), 960 (m), 930 (w), 900 (s), 840 (s), 810 (w), 780 (w), 720 (m), 705 (m), 680 (m), 605 (w).

Propylene. Excess propylene was vacuum transferred to an 88-mL Fischer & Porter reaction flask containing 45 mg (0.09 mmol) of $H_2PtCl_6{\cdot}6H_2O$ and 0.25 g (2.0 mmol) of $B_{10}H_{14}$. The mixture was stirred for 26 h at room temperature and then worked up as in the previous reaction. The sublimed material weighed 0.356 g and according to GLC analysis had the following composition: 5% $B_{10}H_{14}$, 21% monopropyldecaborane, 65% 6,9-dipropyldecaborane (III), and 9% tripropyldecaborane. This product distribution corresponds to ~35 catalyst turnovers and an estimated 56% yield of 6,9-dipropyldecaborane. Preparative GLC was used to further purify samples of III for spectroscopic studies. For III: mp = 44 °C; R_v = 3.1 ($B_{10}H_{14}$ = 1). ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 24.6 (s, 2, B6,9), 8.7 (d, 2, J = 145 Hz, B1,3), –1.9 (d, 4, J = 156 Hz, B5,7,8,10), –36.4 (d, 2, J = 153 Hz, B2,4). ^1H NMR (200 MHz, C_6D_6): 1.48 (m, 2, CH), 1.05 (m, 2, CH), 0.93 (t, 3, J = 7 Hz, CH). Exact mass for $^{12}C_6{}^1H_{26}{}^{11}B_{10}$: calcd, 208.2965; found, 208.298; Anal. Calcd: C, 34.95; H, 12.62. Found: 34.84; H, 11.39. IR (KBr pellet, cm^{-1}): 2960 (s), 2920 (s), 2890 (w), 2870 (m), 2580 (vs), 2560 (vs), 2520 (s), 1975 (w), 1920 (w), 1525 (w), 1480 (w), 1460 (m), 1410 (m), 1375 (w), 1340 (m), 1250 (m), 1130 (m), 1100 (vs), 1055 (w), 1030 (w), 1000 (vs), 960 (m), 930 (w), 910 (s), 885 (w), 840 (m), 800 (w), 705 (m), 680 (m).

Ethylene. A 62-mg (0.12-mmol) sample of chloroplatinic acid and 0.25 g (2.0 mmol) of decaborane were loaded in an 88 mL Fischer & Porter vessel, which was then evacuated. Toluene (~3 mL) and ~30 mmol of ethylene were then vacuum distilled into the flask. The reaction was stirred for 20 h at room temperature, and then the ethylene was evaporated and the residue washed through silica gel with an excess of hexane. Evaporation of the hexane left 0.343 g of material. GLC analysis showed that the material consisted of 2% decaborane, 5% monoethyldecaborane, 73% 6,9-diethyldecaborane (IV), 16% triethyldecaborane, and 4% tetraethyldecaborane. This product distribution corresponds to ~33 catalyst turnovers and a ~70% yield (1.4 mmol) of 6,9-diethyldecaborane. Preparative GLC was used to further purify samples of IV for spectroscopic studies. For IV: mp = 54 °C; R_v = 1.71 ($B_{10}H_{14}$ = 1). ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 25.7 (s, 2, B6,9), 9.3 (d, 2, J = 143 Hz, B1,3), –1.4 (d, 4, J = 153 Hz, B5,7,8,10), –36.0 (d, 2, J = 156 Hz, B2,4). ^1H NMR (200 MHz, C_6D_6): 3.2 (q, HB1,3, J = ~150 Hz), 2.78 (q, HB5,7,8,10, J = ~158 Hz), 1.37 (m, 2, CH), 1.17 (t, 3, J = 7 Hz, CH), ~0.20 (q, HB2,4, J = 150 Hz), –1.57 (s, 4, BHB). Exact mass for $^{12}C_4{}^1H_{22}{}^{11}B_{10}$: calcd, 180.2652; found, 180.2656. IR (KBr pellet, cm^{-1}): 2960 (s), 2930 (w), 2900 (w), 2870 (w), 2570 (vs), 2550 (s), 1975 (w), 1925 (w), 1525 (w), 1480 (m), 1455 (w), 1415 (m), 1375 (m), 1280 (w), 1260 (w), 1120 (w), 1095 (s), 1035 (s), 1000 (s), 985 (m), 970 (w), 950 (m), 895 (vs), 835 (s), 780 (m), 750 (m), 725 (m), 705 (s), 675 (w).

Platinum Bromide Reactions. 1-Pentene. A 0.17-g sample of decaborane (1.39 mmol) was added to 25 mg of platinum bromide (0.07 mmol) along with 3 mL of 1-pentene. The mixture was stirred for 2 days, then separated as described above. A white solid, 0.304 g, was obtained after 3 h of sublimation at 70 °C, which was shown by GLC analysis to consist of 84% I and 16% tripentyldecaborane. This product distribution corresponds to 34 catalyst turnovers and a 70% yield of I based on starting decaborane.

A similar reaction was run in the presence of an excess of mercury. A 30-mg (0.08-mmol) sample of platinum bromide was reacted with 0.10 g (0.82 mmol) of decaborane in 20 mL of pentene in the presence of 0.1 g (0.5 mmol) of mercury. The reaction mixture was stirred at room temperature for 4 days. A ^{11}B NMR spectrum of the resulting dark suspension showed only $B_{10}H_{14}$.

Larger scale reactions were carried out as follows: In a 100-mL flask equipped with a vacuum stopcock, 2.0 g of decaborane (16.4 mmol) and 0.33 g (0.93 mmol) of platinum bromide were added to 50 mL of 1-pentene. The reaction was run for 5 h at 50 °C and monitored by TLC. Pentene was evaporated and the mixture extracted with approximately 100 mL of pentane. The pentane solution was stirred with 100 mL of an aqueous solution containing 2 g of KOH, until a TLC of the pentane layer showed that none of the monopentyl derivative was present. The pentane layer was separated and the water layer extracted with another 50 mL of pentane. The two pentane portions were dried over $MgSO_4$ and cooled at –78 °C until the product precipitated. Filtration gave 2.51 g of a white solid. Concentration of the pentane solution to 30 mL followed by cooling and filtration gave another 0.523 g of white product. The total yield (3.03 g, 11.6 mmol) of I was 71%. The boron-11 NMR spectrum showed the presence of only trace amounts of trialkyldecaborane.

1-Butene. A 0.17-g sample of decaborane (1.4 mmol) was loaded with 25 mg of platinum bromide (0.07 mmol) in a Fischer & Porter reaction vessel. The flask was evacuated, and ~50 mmol of 1-butene was vacuum transferred into the flask. The mixture was then stirred for 48 h at room temperature. The butene was evaporated, and the crude product was extracted with 50 mL of methylene chloride. Evaporation of the methylene chloride left a residue which was sublimed at 70 °C for 3 h. The cold finger was washed with methylene chloride, which was then evaporated to give 0.315 g of an oily substance. GLC analysis showed that it contained 86% II and 14% tributyldecaborane. This product distribution corresponds to 40 turnovers and an 82% yield of II based on starting decaborane.

Propylene. Decaborane 0.34 g (2.8 mmol), 50 mg of $PtBr_2$ (0.14 mmol), and ~60 mmol of propylene were loaded in a Fischer & Porter pressure reactor. The mixture was stirred at room temperature for 46 h and separated as described above. Sublimation at 70 °C yielded 0.532 g of crude product which was shown by GLC to consist of 73% III, 14% tripropyldecaborane, and 13% tetrapropyldecaborane, corresponding to 40 catalyst turnovers and an ~67% yield of III.

Reactions of 6,9-(n-C_5H_{11})$_2B_{10}H_{12}$. 6,9-(n-C_5H_{11})$_2B_{10}H_{11}^-$ (I^-). A 100-mL flask was charged with 0.18 g (0.69 mmol) of I, an excess of NaH, and 30 mL of THF. The solution was brought to room temperature and stirred until the bubbling subsided (1 h). An excess of $NMe_4^+Cl^-$ was added and the mixture stirred for 4 h. The solvent was removed and the resulting $NMe_4^+(C_5H_{11})_2B_{10}H_{11}^-$, $(NMe_4^+)I^-$, was recrystallized from ether and heptane. Filtration gave a white solid 0.175 g (0.52 mmol) in 76% yield. For I^- data are as follows. ^{11}B NMR (64.2 MHz, ppm, CD_3CN): 19.2 (s, 2), 0.6 (d, 1, J = 103 Hz), –6.8 (d, 5, J = 111 Hz), –35.0 (d, 2, J = 135 Hz). ^1H NMR (500 MHz, CD_3CN): 3.08 (s, NMe_4), 1.46 (m, CH), 1.27 (m, CH), 0.86 (m, CH), –2.41 (s, 1, BHB), –3.09 (s, 2, BHB). (IR cm^{-1} KBr): 3015 (w), 2960 (w), 2920 (m), 2840 (w), 2500 (vs), 1460 (s), 1420 (w), 1320 (w), 1290 (w), 1220 (w), 1090 (w), 1025 (w), 955 (s), 780 (w), 720 (w).

6,9-(n-C_5H_{11})$_2B_{10}H_{12}^{2-}$ (I^{2-}). A 0.13-g (0.5-mmol) sample of I was added through a sidearm addition funnel to a sodium ammonia solution (1 g of Na in 5 mL of NH_3) maintained at –78 °C. The mixture was stirred for 30 min, after which the ammonia was evaporated and the residue was extracted with 50 mL of THF. The extract was filtered and the filtrate concentrated to ~1 mL. Addition of 10 mL of a 0.5 M aqueous solution of tetramethylammonium hydroxide resulted in the formation of an off-white precipitate which was filtered and washed with ether and pentane to give 93 mg (0.23 mmol, 46% yield) of $(NMe_4^+)_2$-(6,9-(n-C_5H_{11})$_2B_{10}H_{12}^{2-}$), $(NMe_4^+)_2I^{2-}$. For I^{2-} data are as follows. ^{11}B NMR (160 MHz, ppm, CD_3CN): –8.4 (d, 2, B2,4, J = 118 Hz), –20.7 (d, 4, B5,7,8,10, J = 108 Hz), –24.3 (d, 2, B6,9, J = 97 Hz), –41.6 (d, 2, B1,3, J = 128 Hz). $^1H\{^{11}B\}$ NMR (200 MHz, CD_3CN): 3.10 (s, NMe_4), 1.23 (m, CH), 0.85 (m, CH), 0.31 (m, CH), –0.75 (s, BH), –1.56 (s, BH), –4.94 (s, BHB). ^{11}B–^{11}B 2D NMR, crosspeaks: B1,3–B2,4; B1,3–B5,7,8,10; B2,4–B5,7,8,10; B2,4–B6,9; B6,9–B5,7,8,10.

***arachno*-4-(n-C_5H_{11})$B_9H_{13}^-$ (V).** A THF solution of $Li^+(n\text{-}C_5H_{11})_2B_{10}H_{11}^-$ was made by reaction of 54 mg (0.21 mmol) of I with an equimolar amount of MeLi. The THF was vacuum evaporated, and 30 mL of water containing an excess of KOH (90 mg) was cannulated in. The mixture was stirred for 3 h at 60 °C, and then the solution was cooled and shaken with 30 mL of CH_2Cl_2 containing 0.2 g (0.3 mmol) of (PPN)Cl. The organic layer was removed and the aqueous phase washed with another 10 mL of CH_2Cl_2. The methylene chloride was removed and the residue recrystallized from THF/hexane to give 108 mg of product (0.15 mmol) corresponding to a 71% yield. For V data are as follows. ^{11}B NMR (160.5 MHz, ppm, CD_3CN): 8.8 (s, 1), 5.2 (d, 2, J = 144 Hz), –7.2 (d, 2, J = 135 Hz), –19.1 (d, 2, J = 114 Hz), –26.9 (d, 1, J = 145 Hz), –41.9 (d, 1, J = 139 Hz). ^1H NMR (200 MHz, CD_3CN): 7.56 (m, phenyl, PPN), 1.38 (m, CH), 1.28 (m, CH), 1.13 (m, CH), 0.97 (m, CH), 0.86 (m, CH), –1.28 (s, 4, BHB). IR (cm^{-1}): 3050 (w), 2940 (w), 2910 (m), 2840 (w), 2500 (vs), 2450 (m), 2410 (m), 1580 (w), 1470 (m), 1435 (s), 1380 (w), 1230 (vs), 1180 (m), 1125 (vs), 1020 (w), 1000 (m), 810 (m), 750 (m), 725 (s), 695 (s), 620 (w), 550 (m), 530 (s), 495 (s), 400 (m).

***arachno*-4-(*n*-C_5H_{11})-6,8-(Me_3P)$_2B_9H_{10}$ (VI).** A 0.12-g sample (0.45 mmol) of I was dissolved in 5 mL of toluene in a 50-mL reaction flask. A 1.8 mL sample of 1 M trimethylphosphine in toluene was added. The mixture was stirred at 70 °C for 15 min. The volatile compounds were then vacuum evaporated, and the residue was extracted with 100 mL of dry pentane. The extract was concentrated to 5 mL and filtered, leaving 96 mg (0.29 mmol) for a 64% yield. For VI data are as follows. ^{11}B NMR (160.5 MHz, ppm, C_6D_6): –2.73 (broad, 3), –9.5 (d, 1, J = 116 Hz), –11.9 (d, 2, J = 127 Hz), –43.5 (dd, 2, $J_{BP} \sim 94$ Hz, $J_{BH} \sim 115$ Hz), –52.2 (d, 1, J = 138 Hz). ^{31}P NMR (80 MHz, ppm, C_6D_6): –5.96 (q, $J_{PB} = \sim 95$ Hz). $^1H\{^{11}B\}$ NMR (200 MHz, C_6D_6): 3.25 (s, BH), 2.44 (br, BH), 1.95 (m, CH), 1.55 (m, CH); 0.94 (m, CH), 0.84 (d, PMe, $^2J_{HP}$ = 11 Hz), –0.58 (s, BH), –1.5 (s, BHB). Exact mass for $P_2C_{11}B_9H_{37}$: calcd, 331.3286; found, 331.3322.

(PPN^+)$_2$-*commo*-Pt-[*nido*-7-Pt-8,11-(*n*-C_5H_{11})$_2B_{10}H_{10}$]$_2^{2-}$ (VII). A 0.21-g (0.8-mmol) sample of 6,9-dipentyldecaborane was dissolved in 20 mL of THF. Excess NaH was added through a sidearm addition funnel at –78 °C. The solution was stirred at room temperature until bubbling stopped (2 h). The filtered THF solution of Na^+(*n*-C_5H_{11})$_2B_{10}H_{11}^-$ was cannulated into 30 mL of a CH_3CN solution containing 0.17 g (0.45 mmol) of (COD)$PtCl_2$ and 0.17 g (0.8 mmol) of proton sponge. The mixture was stirred overnight. An excess of TMA chloride was added and this mixture stirred for 6 h. The solvents were removed and the product extracted with methylene chloride. Recrystallization from CH_2Cl_2/toluene gave 169 mg (0.2 mmol) of a golden yellow compound, corresponding to a 45% yield based on starting (COD)$PtCl_2$. The TMA cation was exchanged for PPN cation, by stirring a solution of (NMe_4^+)$_2$ *commo*-Pt-[*nido*-7-Pt-8,11-(*n*-C_5H_{11})$_2B_{10}H_{10}$]$_2^{2-}$ and (PPN)Cl in CH_2Cl_2 overnight. For VII data are as follows. Anal. Calcd for $PtP_4N_2C_{92}B_{20}H_{124}$: C, 61.6; N, 1.56; H, 6.97. Found: C, 62.73; N, 1.65; H, 6.26. ^{11}B NMR (160.5 MHz, ppm, CD_3CN): 20.6 (s), 7.1 (d, J = 115 Hz), –5.8 (d, $J = \sim 120$ Hz), –24.4 (d, J = 115 Hz). ^1H NMR (200 MHz, C_6D_6): 7.51 (m, phenyl, PPN), 1.79 (m, CH), 1.28 (m, CH), 0.87 (m, CH), –1.82 (s, BHB). IR (KBr, cm^{-1}): 2960 (w), 2910 (m), 2860 (w), 2500 (vs), 1460 (s), 1280 (vs), 1120 (vs), 1005 (m), 990 (m), 750 (m), 730 (s), 700 (s), 550 (s), 540 (s), 505 (s), 400 (w).

Reactions of 6,9-Dipentyldecaborane with Lewis Bases. 6,9-(*n*-C_5H_{11})$_2B_{10}H_{12}$ and Et_3N. A 0.2-g (0.76-mmol) sample of I was dissolved in 25 mL of xylene to which 0.5 mL of dry triethylamine was added. The solution was stirred at 130 °C of 12 h. A ^{11}B NMR spectrum taken at this time showed no reaction.

6,9-(*n*-C_5H_{11})$_2B_{10}H_{12}$ and (C_6H_5)$_3$P. A 0.1-g (0.38-mmol) sample of I, was added to 20 mL of xylenes containing 0.5 g (1.9 mmol) of triphenylphosphine. The mixture was stirred at 110 °C for 7 h. A ^{11}B NMR spectrum taken at this time showed no reaction.

6,9-(*n*-C_5H_{11})$_2B_{10}H_{12}$ and (C_2H_5)$_2$S. A 70-mg (0.26-mmol) sample of I was stirred at reflux temperature in 25 mL of diethyl sulfide. After 18 h the solution was clear, and its ^{11}B NMR spectrum showed only I.

6,9-(*n*-C_5H_{11})$_2B_{10}H_{12}$ and CH_3CN. A 70-mg (0.26-mmol) sample of I was refluxed for 18 h in 20 mL of acetonitrile. The solution remained clear, and its ^{11}B NMR spectrum showed only I.

Results and Discussion

Synthesis of the 6,9-(*n*-C_5H_{11})$_2B_{10}H_{12}$. Prior to the work described in this paper, there was no high-yield, selective route for direct decaborane(14) alkylation directed at the electropositive B6,9 boron sites. Pyrolytic alkylations involving ethylene–diborane,[5] or $B_{10}H_{14}$–EtBr mixtures[6] are nonselective giving low yield mixtures of two or more of the mono-, di-, tri-, and tetraalkyldecaboranes. Other methods for the direct alkylation of decaborane(14) have employed Friedel–Crafts conditions,[7] and in accord with the predicted[8] electron charge densities in decaborane(14) of 2,4 > 1,3 > 5,7,8,10 > 6,9, it has been found that the B2,4 and B1,3 borons are the preferred sites in such electrophilic alkylations.

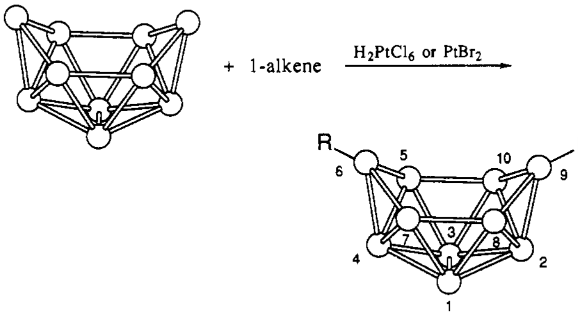
Table I. Summary of the Platinum Catalyzed Reactions

catalyst	mol % Pt[a]	olefin	time	temp, °C	% yield of 6,9-$R_2B_{10}H_{12}$	tot. turnovers
H_2PtCl_6	5.2	1-pentene	31 h	23	80	36
H_2PtCl_6	2.5	1-pentene	24 h	30	63	61
H_2PtCl_6	1.0	1-pentene	4 d	23	55	167
H_2PtCl_6	4.5	1-butene	28 h	23	75	42
H_2PtCl_6	4.5	propylene	26 h	23	56	35
H_2PtCl_6	6	ethylene[b]	20 h	23	70	33
H_2PtCl_6	6	*cis*-2-butene	48 h	40	0	0
H_2PtCl_6	6	1-pentyne	2 d	30	0	0
$PtBr_2$	5.0	1-pentene	2 d	23	70	34
$PtBr_2$	4.7	1-pentene	5 h	23	71	25[c]
$PtBr_2$	5.0	1-butene	2 d	23	82	40
$PtBr_2$	5.0	propylene	46 h	23	67	40

[a] Compared to decarborane. [b] Toluene solvent. [c] Calculated based only on 6,9-$R_2B_{10}H_{12}$ product.

Alkylations at the boron 6- or 5-positions have been possible by the reaction of the $B_{10}H_{13}^-$ ion with either alkyl Grignards,[9] alkyl sulfates,[9a,10] or benzyl halides,[10a,11] or by the reaction of decaborane with alkyllithium compounds followed by acidification.[12,13] Gaines has also recently reported[13] a new procedure for the formation of 6-alkylated decaboranes starting with (SMe_2)$_2$-$B_{10}H_{12}$.

In our studies, both chloroplatinic acid and platinum bromide were found to catalyze the hydroboration reactions of terminal olefins with decaborane(14) to achieve high yields of 6,9-$R_2B_{10}H_{12}$ products. The activities of the two catalysts are comparable as summarized in Table I. Both catalysts were also found to be inactive for the reactions of decaborane(14) with either internal olefins or alkynes.



(1)

A typical reaction involved stirring a 0.05:1 mole ratio of chloroplatinic acid/decaborane(14) in liquid 1-pentene at room temperature for 48 h. At that time, analytical GLC showed that

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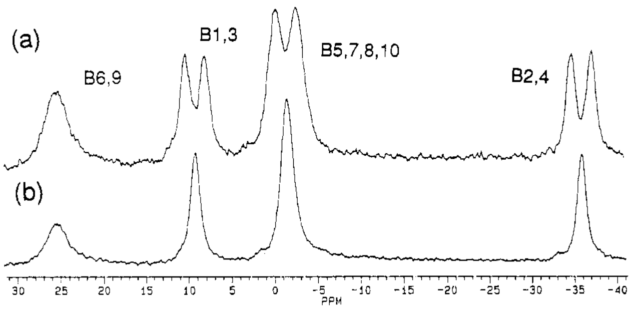

Figure 1. ^{11}B NMR spectra of 6,9-dipentyldecaborane (I): (a) proton coupled; (b) proton decoupled.

the reaction mixture was composed of mainly 6,9-dipentyldecaborane, along with a small amount of the tripentyl derivative. In all cases, once the concentration of a dialkyl product started to increase, the formation of trialkyl or, in the case of small olefins, tetraalkyl derivatives was observed. Separation of the 6,9-dialkyldecaboranes from the mono- and trisubstituted byproducts for spectroscopic characterizations was then achieved by preparative GLC.

In large-scale reactions, 6,9-dipentyldecaborane of good purity was obtained by stopping the reaction before completion to minimize the formation of tripentyldecaborane; however, under these conditions appreciable amounts of monopentyldecaborane and unreacted decaborane(14) would still be present in the reaction mixture. As discussed below, it was found that the dialkyldecaboranes, unlike both decaborane and the monoalkyldecaboranes, do not readily react with hydroxide; therefore, isolation of 6,9-dipentyldecaborane could be readily achieved by stirring the crude product with an aqueous KOH solution, followed by extraction with pentane and recrystallization at -78 °C. This procedure produced a white solid, which was shown by NMR to be >95% 6,9-dipentyldecaborane.

Reactions with other terminal olefins likewise gave the corresponding dialkylated decaborane derivatives, with the spectroscopic data for each compound in accord with the proposed 6,9-substitution. Thus, their ^{11}B NMR spectra, as shown for I in Figure 1, like that of decaborane(14),[14] consists of four resonances in a ratio of 2:2:4:2, consistent with the presence of a molecular mirror plane. For each compound, the signal due to the 6,9-borons appears at low field (~25 ppm) as a singlet in the proton-coupled spectrum, supporting alkyl-substitutions at these borons. The ^1H NMR spectra of all compounds show resonances arising from the alkyl groups in the 1 to 2 ppm region and single resonances, corresponding to the equivalent bridging hydrogens, in the ~-1.5 to -2.0 ppm range. In the boron-decoupled ^1H NMR spectrum, the singlet resonance for the 6,9-BH protons, which is observed[15] at 4.0 ppm in decaborane(14), is absent.

The mechanism of the platinum-catalyzed decaborane/olefin-addition reactions was not studied; however, chloroplatinic acid $H_2PtCl_6{\cdot}H_2O$ is one of the most commonly used catalysts for olefin hydrosilations and the mechanism of the decaborane reactions is presumed to be related to those proposed for the analogous hydrosilations.[16] As found in hydrosilations, an induction period was observed (~6 h at room temperature) in the chloroplatinic acid catalyzed decaborane/olefin-addition reactions suggesting the formation of a catalytic Pt^{II} species by reduction of H_2PtCl_6. Such a nucleophilic platinum(II) species should then attack at the most positive boron sites (i.e. B6,9) of the cage, and indeed, the high selectivity of the decaborane alkylation supports a process involving oxidative-addition of the 6,9BH units to the platinum. Thus, a sequence, such as depicted in Figure 2, involving oxidative-addition, olefin-insertion, and reductive-elimination steps would appear reasonable. A similar sequence can be proposed for platinum bromide catalyzed reactions.

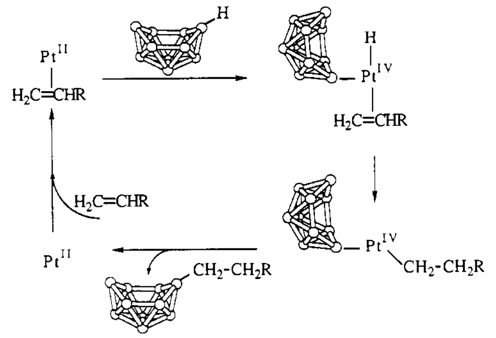

Figure 2. Possible mechanism for the platinum-catalyzed decaborane/olefin-addition reactions.

Although the above reaction sequence is possible, it should also be noted that recent studies have suggested that hydrosilations catalyzed by chloroplatinic acid are, in fact, heterogeneous reactions.[17] When a mercury test was applied to the decaborane/chloroplatinic acid system, no reaction was observed, suggesting a heterogeneous reaction; however, as Whitesides has cautioned, the mercury test cannot be considered conclusive.[18]

Chemical Studies of 6,9-Dipentyldecaborane. Moderate Lewis bases react with $B_{10}H_{14}$ to form the bisadducts *arachno*-6,9-$L_2B_{10}H_{12}$.[19] In I the hydrogens on the 6 and 9 boron atoms in decaborane(14) are replaced by the bulky pentyl groups and, therefore, a decrease in the reactivity of the cage is expected when these boron sites are involved in the reaction. Accordingly, it was found that I would not react with the Lewis bases dimethyl sulfide, acetonitrile, triphenylphosphine, or triethylamine to form dibase adducts. This lack of reactivity could be due to both the steric effects of the alkyl groups inhibiting reaction at the B6,9 positions and the electronic effect of the electron releasing alkyls, which increase the electron density on the B6 and B9 positions and thus decrease their susceptibility to nucleophilic attacks.

The presence of the electron releasing alkyl groups on the 6- and 9-positions would also be expected to destabilize any negative charge on the cage. Consistent with this expectation, the deprotonation of I with sodium hydride or methyllithium took place at a slower rate and required a higher temperature to initiate reaction, than the analogous reactions with the parent decaborane.

$$6,9\text{-}(n\text{-}C_5H_{11})_2B_{10}H_{12} + NaH \xrightarrow{THF} \underset{I^-}{Na^+6,9\text{-}(n\text{-}C_5H_{11})_2B_{10}H_{11}^-} \quad (2)$$

The PPN$^+$ salt of I^- has a ^{11}B NMR spectrum reminiscent of that of the parent $B_{10}H_{13}^-$,[20] consisting of four resonances in a 2:1:5:2 ratio. One of the intensity 2 resonances, corresponding to the alkylated 6,9-borons, appears as a singlet at 19.2 ppm. The observed ratios in both $B_{10}H_{13}^-$ and $6,9\text{-}(n\text{-}C_5H_{11})_2B_{10}H_{11}^-$ suggest a molecular mirror plane, but this is inconsistent with the solid-

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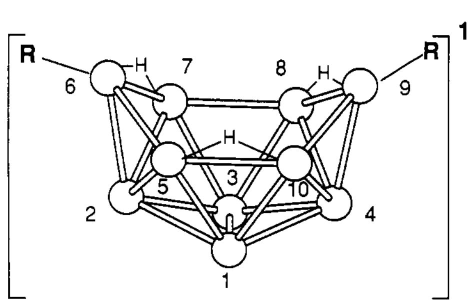

Figure 3. Proposed averaged solution structure for 6,9-(n-C_5H_{11})$_2$$B_{10}H_{11}^-$ (I^-). Terminal hydrogens are not shown.

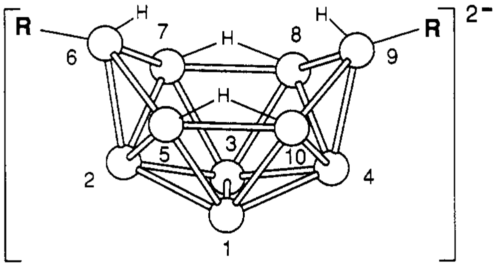

Figure 4. Proposed structure for 6,9-(n-C_5H_{11})$_2$$B_{10}H_{11}^{2-}$ (I^{2-}). Terminal hydrogens are not shown.

state structure determined for $B_{10}H_{13}^-$.[21] To account for this inconsistency it has been proposed that $B_{10}H_{13}^-$ is fluxional in solution with one bridging hydrogen tautomerizing across the B6–5, B5–10 and B10–9 edges. Such fluxionality must also be present in 6,9-(n-C_5H_{11})$_2$$B_{10}H_{11}^-$, so that, on the NMR time scale, a spectrum consistent with the average structure shown in Figure 3 is observed. Supporting this conclusion, the 500 MHz proton NMR shows two singlets, of intensities 1 and 2, respectively, at -2.41 and -3.09 ppm arising from the three bridging hydrogens.

When reacted with a sodium/ammonia solution, I was reduced to the *arachno*-(n-C_5H_{11})$_2$$B_{10}H_{12}^{2-}$ (I^{2-}) dianion. I^{2-} was found to be thermally and oxidatively unstable and, when it was allowed to stand in THF solvent, hydride abstraction to form $R_2B_{10}H_{11}^-$ (I^-) was observed.

$$6,9\text{-}(n\text{-}C_5H_{11})_2B_{10}H_{12} + Na/NH_3 \rightarrow \underset{I^{2-}}{arachno\text{-}6,9\text{-}(n\text{-}C_5H_{11})_2B_{10}H_{12}^{2-}} \quad (3)$$

The ^{11}B NMR spectrum of I^{2-} is similar[22] to that of the parent $(Na^+)_2B_{10}H_{14}^{2-}$, except that the resonance for the 6,9-borons, which appears as a triplet at -34 ppm in $B_{10}H_{14}^{2-}$, is shifted downfield to -24.3 ppm and appears as a doublet in I^{2-}. The proton NMR spectrum of I^{2-} exhibits a high field signal (-4.94 ppm) arising from the hydrogens bridging the B7–B8 and B5–B10 edges. The boron-decoupled proton NMR shows another singlet at a relatively high field (-1.56 ppm), arising from the endo-hydrogens on the B6 and B9 positions. A structure consistent with these data is shown in Figure 4.

The reaction of decaborane(14) with hydroxide ion results[23] in initial deprotonation, followed by degradation[24] to the *arachno*-$B_9H_{14}^-$ anion. In contrast, I was not deprotonated by hydroxide. Degradation of I to yield *arachno*-4-(n-C_5H_{11})$B_9H_{13}^-$ was achieved by first deprotonation with sodium hydride, then reaction of I^- with a KOH solution at elevated temperatures.

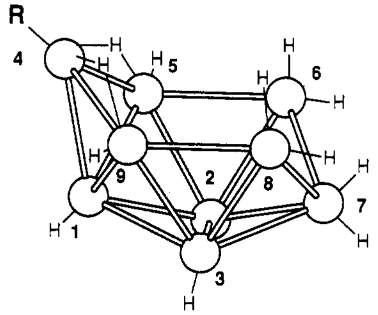

Figure 5. Proposed structure for 4-(n-C_5H_{11})$B_9H_{13}^-$ (V).

Table II. Summary of Structure Determination of $(PPN^+)_2$-*commo*-Pt-[*nido*-7-Pt-8,11-(n-C_5H_{11})$_2$$B_{10}H_{10}$]$_2^{2-}$ (VII)

formula	$PtB_{20}C_{92}H_{124}P_4N_2$
fw	1793.23
cryst class	monoclinic
space group	$P2_1/c$ (No. 14)
Z	2
cell const	
a, Å	15.284(3)
b, Å	18.834(2)
c, Å	17.791(2)
β, deg	110.43(1)
V, Å^3	4799(2)
μ, cm^{-1}	37.10
transm (min,, max, avg, %)	82.48, 99.92, 91.26
D_{calc}, g/cm^3	1.241
F(000)	1856
radiation	Cu Kα (λ = 1.541 84 Å)
θ range, deg	2.0–50.0
scan mode	ω–2θ
h,k,l collcd	±15,–18,+17
no. of reflcns measd	5319
no. of unique reflcns	5112
no. of reflcns used in refinement	3013 ($F^2 > 3.0\sigma$)
no. of params	578
data/param ratio	5.2
R_1	0.049
R_2	0.058
GOF	1.643

$$6,9\text{-}(n\text{-}C_5H_{11})_2B_{10}H_{11}^- + OH^- + 2H_2O \xrightarrow{60\ ^\circ C,\ 3h} \underset{V}{arachno\text{-}4\text{-}(n\text{-}C_5H_{11})B_9H_{13}^-} + (C_5H_{11}O)B(OH)_2 + {}^1/_2H_2 \quad (4)$$

Although an X-ray crystallographic study[25] has shown that *arachno*-$B_9H_{14}^-$ has only C_s symmetry in the solid state, its ^{11}B NMR spectrum[25a] consists of only three equal intensity doublet resonances, indicating a C_{3v} cage symmetry in solution. In contrast, the ^{11}B NMR spectrum of *arachno*-4-(n-C_5H_{11})$B_9H_{13}^-$ exhibits six signals in a 1:2:2:2:1:1 ratio, with a singlet of intensity 1 at 8.8 ppm. Thus, the degradation of I with hydroxide results in the removal of one of the pentyl-substituted 6,9-borons to yield a monoalkylated B9 framework. A possible structure for V based on the established solid-state structure of *arachno*-$B_9H_{14}^-$ is shown in Figure 5. The fact that no triplet resonances are observed in the ^{11}B NMR spectrum suggests that discrete -BH_2 units are not present in solution. Consistent with this expectation, the proton NMR spectrum also shows, in addition to the alkyl resonances, a broad peak at -1.28 ppm that appears to arise, as in *arachno*-$B_9H_{14}^-$,[25a] from both the bridging and endo B6,7,8 hydrogens. Thus, even though V has a lower cage symmetry

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Table III. Refined Positional Parameters for $(PPN^+)_2$-*commo*-Pt-[*nido*-7-Pt-8,11-(n-$C_5H_{11})_2B_{10}H_{10}]_2{}^{2-}$ (VII)

atom	x	y	z	B_{eq},[a] Å^2
Pt7	0.5000	0.0000	0.5000	6.36(1)
B1	0.2745(8)	0.0616(5)	0.4430(8)	7.7(4)
B2	0.3614(7)	0.0169(6)	0.5178(6)	6.3(3)
B3	0.3573(8)	0.0156(5)	0.4129(6)	6.1(3)
B4	0.3150(9)	0.0988(7)	0.3730(8)	8.2(4)
B5	0.3071(8)	0.1503(6)	0.4516(9)	8.4(4)
B6	0.3274(8)	0.1022(6)	0.5385(8)	7.7(4)
B8	0.4305(8)	0.0763(6)	0.3868(7)	7.1(3)
B9	0.3981(8)	0.1653(7)	0.4168(8)	8.4(4)
B10	0.4085(9)	0.1632(6)	0.5276(8)	7.9(4)
B11	0.4469(9)	0.0782(7)	0.5792(8)	8.3(4)
C1	0.502(1)	0.0868(7)	0.6718(7)	13.3(5)
C2	0.456(1)	0.105(1)	0.7244(9)	19.5(8)
C3	0.524(1)	0.108(1)	0.823(1)	18.0(6)
C4	0.465(1)	0.096(2)	0.859(1)	33(1)
C5	0.524(1)	0.101(1)	0.940(1)	24.8(9)
C6	0.4660(8)	0.0827(6)	0.3163(7)	11.2(4)
C7	0.514(1)	0.139(1)	0.2978(8)	17.5(6)
C8	0.546(1)	0.148(1)	0.2319(8)	17.5(6)
C9	0.604(1)	0.185(2)	0.224(1)	34(1)
C10	0.621(1)	0.188(2)	0.158(1)	39(2)
P1	0.9202(2)	0.0099(1)	0.1629(1)	5.42(6)
P2	0.9445(2)	0.1670(1)	0.1760(1)	5.15(6)
N	0.9166(4)	0.0901(3)	0.1391(4)	5.1(2)
C11	0.8259(6)	−0.0357(5)	0.0912(5)	5.6(2)
C12	0.7887(7)	−0.0120(5)	0.0137(6)	7.6(3)
C13	0.7161(8)	−0.0468(6)	−0.0428(7)	9.5(4)
C14	0.6842(7)	−0.1071(7)	−0.0238(8)	11.1(4)
C15	0.7172(7)	−0.1342(5)	0.0503(7)	9.3(3)
C16	0.7902(6)	−0.0995(5)	0.1104(6)	7.7(3)
C17	0.9098(6)	−0.0067(4)	0.2591(5)	6.2(2)
C18	0.9812(7)	−0.0328(6)	0.3238(6)	8.2(3)
C19	0.9688(8)	−0.0431(6)	0.3947(6)	9.8(4)
C20	0.8866(9)	−0.0290(7)	0.4031(6)	10.8(4)
C21	0.8120(8)	−0.0032(6)	0.3387(6)	9.7(3)
C22	0.8244(7)	0.0085(5)	0.2674(6)	8.1(3)
C23	1.0255(6)	−0.0325(4)	0.1618(5)	5.3(2)
C24	1.1106(6)	−0.0018(5)	0.2032(6)	6.8(3)
C25	1.1930(7)	−0.0342(6)	0.2031(6)	7.8(3)
C26	1.1905(6)	−0.0940(6)	0.1618(6)	8.6(3)
C27	1.1061(7)	−0.1241(5)	0.1199(7)	9.4(3)
C28	1.0244(7)	−0.0932(5)	0.1192(6)	7.6(3)
C29	0.8540(6)	0.2275(4)	0.1195(5)	5.6(2)
C30	0.8558(7)	0.2968(5)	0.1422(7)	9.0(4)
C31	0.7889(8)	0.3452(5)	0.0965(8)	10.9(4)
C32	0.7229(8)	0.3225(5)	0.0317(7)	10.2(4)
C33	0.7199(8)	0.2547(6)	0.0075(7)	10.0(4)
C34	0.7865(7)	0.2062(5)	0.0524(6)	7.7(3)
C35	0.9559(5)	0.1748(4)	0.2785(5)	5.4(2)
C36	1.0416(6)	0.1645(5)	0.3395(6)	7.6(3)
C37	1.0475(7)	0.1673(6)	0.4176(6)	9.3(4)
C38	0.9717(8)	0.1784(5)	0.4378(6)	8.5(3)
C39	0.8874(7)	0.1857(6)	0.3800(6)	9.0(3)
C40	0.8796(6)	0.1845(5)	0.3006(5)	7.4(3)
C41	1.0492(6)	0.1975(4)	0.1630(5)	5.3(2)
C42	1.0764(6)	0.1668(5)	0.1056(5)	7.2(3)
C43	1.1522(7)	0.1927(6)	0.0888(6)	9.4(3)
C44	1.2025(7)	0.2482(5)	0.1313(7)	9.6(3)
C45	1.1760(7)	0.2780(6)	0.1875(7)	10.8(4)
C46	1.1009(7)	0.2537(5)	0.2039(6)	9.4(3)
H1	0.211(4)	0.043(4)	0.439(3)	6(2)*
H2	0.329(5)	−0.039(4)	0.549(4)	7(2)*
H3	0.331(4)	−0.032(3)	0.371(3)	5(2)*
H4	0.274(4)	0.107(3)	0.319(3)	6(2)*
H5	0.256(4)	0.195(3)	0.432(3)	6(2)*
H6	0.299(5)	0.118(4)	0.584(4)	9(2)*
H9	0.413(5)	0.220(4)	0.374(4)	9(2)*
H10	0.426(4)	0.216(3)	0.559(3)	5(2)*
H89	0.465(5)	0.130(4)	0.433(4)	7(2)*
H1011	0.486(5)	0.115(4)	0.559(4)	9(2)*

[a] $B_{eq} = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}\,ac\cos\beta + \beta_{23}bc\cos\alpha]$.

than *arachno*-$B_9H_{14}{}^-$, in solution there appears to be a similar tautomerization of the endo- and bridging hydrogens about the surface of the open face leading to only one average resonance.

Table IV. Selected Bond Distances (Å) in $(PPN^+)_2$-*commo*-Pt-[*nido*-7-Pt-8,11-(n-$C_5H_{11})_2B_{10}H_{10}]_2{}^{2-}$ (VII)

Pt7–B2	2.271(11)	B9–B10	1.921(20)
Pt7–B3	2.210(10)	B9–H9	1.356(81)
Pt7–B8	2.400(11)	B9–H89	1.170(69)
Pt7–B11	2.370(14)	B10–B11	1.836(17)
B1–B2	1.734(14)	B10–H10	1.132(61)
B1–B3	1.764(18)	B10–H1011	1.437(74)
B1–B4	1.723(21)	B11–C1	1.573(17)
B1–B5	1.735(16)	B11–H1011	1.055(86)
B1–B6	1.780(17)	C1–C2	1.387(25)
B1–H1	1.006(67)	C2–C3	1.694(20)
B2–B3	1.846(17)	C3–C4	1.300(30)
B2–B6	1.768(16)	C4–C5	1.408(27)
B2–B11	1.800(15)	C6–C7	1.394(22)
B2–H2	1.370(79)	C7–C8	1.426(25)
B3–B4	1.748(16)	C8–C9	1.165(33)
B3–B8	1.771(17)	C9–C10	1.293(35)
B3–H3	1.140(61)	B4–B5	1.741(20)
B4–B8	1.747(18)	B6–B10	1.749(18)
B4–B9	1.760(17)	B6–B11	1.772(17)
B4–H4	0.951(52)	B6–H6	1.085(83)
B5–B6	1.725(19)	B8–B9	1.878(17)
B5–B9	1.731(22)	B8–C6	1.534(20)
B5–B10	1.681(15)	B8–H89	1.293(67)
B5–H5	1.123(61)		

Although I was unreactive toward the other Lewis bases discussed above, it was found that reaction of excess trimethylphosphine with I at 70 °C resulted in cage degradation and the formation of a white product containing two coordinated trimethylphosphines. While *arachno*-L·B_9H_{13} (L = SMe_2, PR_3, MeCN etc.)[26] adducts are known, VI appears to be the first example of a dibase adduct of the nonaborane framework.

$$6,9\text{-}(n\text{-}C_5H_{11})_2B_{10}H_{12} + PMe_3 \xrightarrow[70\ ^\circ C,\ 10\ min.]{toluene,\ PMe_3} arachno\text{-}4\text{-}(n\text{-}C_5H_{11})\text{-}6,8\text{-}(Me_3P)_2B_9H_{10} \quad (5)$$

VI

Exact mass measurements support the composition (n-C_5H_{11})-$(PMe_3)_2B_9H_{10}$. A cluster of this formula should contain 24 skeletal electrons and fall in the nine-vertex (n + 3) arachno cluster class. VI is thus isoelectronic with *arachno*-$B_9H_{14}{}^-$, *arachno*-L·B_9H_{13}, and *arachno*-$C_2B_7H_{13}$[27] and should adopt a cage geometry similar to these compounds, based on a 11-vertex polyhedron missing two vertices. Such a structure for VI that is consistent with the spectral data discussed below is shown in Figure 6.

The proton-decoupled ^{11}B NMR spectrum of VI consists of five signals in a 3:1:2:2:1 ratio with the intensity 3 peak appearing to be an overlap of two resonances of relative 1:2 intensities. The intensity 2 peak at −43.5 ppm appears as a doublet in the proton-decoupled NMR spectrum owing to the coupling of the B6,8 borons to the coordinated phosphorus atoms. The phosphorus-31 NMR spectrum consists of a single quartet, indicating that the two phosphorus atoms are chemically equivalent and that they are each coupled to only one boron atom. The magnitude of the boron–phosphorus coupling observed in both the ^{11}B and ^{31}P NMR spectra (J_{BP} = ~95 Hz) is consistent with other such couplings observed in phosphine-substituted polyhedral boranes.[28] Although the ^{11}B–^{11}B 2-D NMR is too overlapped to allow complete assignment, the resonances at −9.5(1) and −11.9(2) ppm clearly show doublet structure in their crosspeaks with the B6,8 resonance indicative of $^2J_{BBP}$ couplings[28] and, therefore, suggest the assignment of these peaks to the B7 and B5,9 cage positions, respectively. The overlapping resonances of intensity

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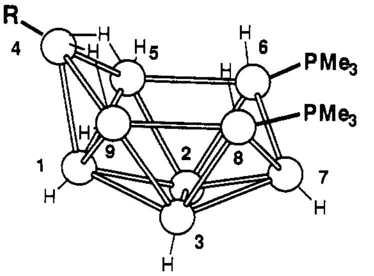

Figure 6. Proposed structure for *arachno*-4-(n-C_5H_{11})-6,8-$(PMe_3)_2B_9H_{10}$ (VI).

3 at low field (-2.73 ppm) would then be assigned to the B4 singlet and the B2,3 doublet. The highest field doublet must then be due to the B1 boron, and indeed, this assignment is consistent with the spectrum observed for the isoelectronic cluster *arachno*-$C_2B_7H_{13}$, where the B1 resonance is found at -50 ppm. The proton NMR shows, in addition to the signals of the alkyl groups, a doublet attributed to the phosphine methyl groups.

Preliminary investigation of the metallaborane chemistry of the dialkyldecaboranes showed that the presence of the alkyl groups at the B6,9 positions does not inhibit the formation of metallaboranes analogous to those formed from the parent decaborane.[29] Thus, the reaction of 6,9-(n-C_5H_{11})$_2B_{10}H_{11}^-$ with (1,5-cyclooctadiene)platinum dichloride resulted in the formation of *commo*-Pt[*nido*-7-Pt-8,11-(n-C_5H_{11})$_2B_{10}H_{10}$]$_2^{2-}$ (VII).

$$6,9\text{-}(n\text{-}C_5H_{11})_2B_{10}H_{12} + (COD)PtCl_2 \xrightarrow{THF} commo\text{-}Pt\text{-}[nido\text{-}7\text{-}Pt\text{-}8,11\text{-}(n\text{-}C_5H_{11})_2B_{10}H_{10}]_2^{2-} \quad (6)$$

VII

The ^{11}B NMR spectrum of the product is broad, consisting of a singlet and three doublet resonances, and provides little structural information. However, a single-crystal X-ray study confirmed the structure depicted in the ORTEP drawing in Figure 7. VII is composed of two decaborane cages each bound in a η^4 fashion to the platinum, with the platinum being a common vertex in two 11-vertex cages. Consistent with the nido electron count of each cage, the cage frameworks are based on an icosahedron missing one vertex. The platinum sits on a crystallographic center of symmetry, and the two cages are symmetry related. Structural data are given in Tables II-IV.

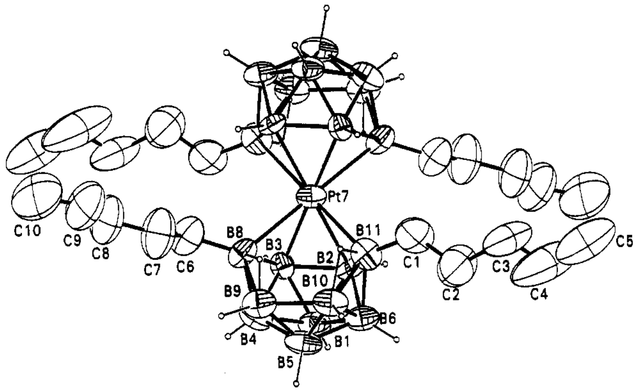

Figure 7. ORTEP drawing of the platinaborane cage structure of $(PPN^+)_2$-*commo*-Pt-[*nido*-7-Pt-8,11-(n-C_5H_{11})$_2B_{10}H_{10}$]$_2^{2-}$ (VII).

The corresponding decaborane complexes $[B_{10}H_{12}]_2M^{2-}$ (M = Ni, Pd, Pt) have previously been synthesized and structures analogous to that observed for VII have been determined.[30-32] The bond distances within the cages and the bond angles around the platinum atoms in VII and $[B_{10}H_{12}]_2Pt^{2-}$ [32] are similar. The observed Pt7-B8 (2.400(11) Å) and Pt7-B11 (2.370(14) Å) distances on the open face, as well as the Pt7-B2 (2.271(11) Å), Pt7-B3 (2.210(10) Å), and the Pt7 to B2-B3-B8-B11 plane centroid distance (1.649 Å) are slightly elongated compared to those in $[B_{10}H_{12}]_2Pt^{2-}$, but are in the range of comparable distances observed in other platinaboranes.[33] There is no bonding interaction between the platinum atom and B9 or B10. The bridging hydrogens on the open face were located on the B8-B9 and B10-B11 edges, and accordingly, these edges have somewhat shorter bond distances, 1.878(17) and 1.836(17) Å, than the unbridged B9-B10 edge, 1.921(10 Å. The remaining B-B distances within the cage are in the normal range of other metallaundecaboranes.[33]

The pentyl groups are attached to the boron atoms adjacent to the platinum and are oriented in such a fashion that the two chains on the opposite cages are aligned in the same direction. This arrangement leads to a selective orientation of the pentyl groups in the crystal, such that they are pointing along the crystallographic *c*-axis. This observation suggests that dialkyldecaborane ligands may find use for the construction of metallaborane complexes with selective alignments in the solid state.

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Supplementary Material Available: Tables of anisotropic temperature factors, bond distances, bond angles, calculated hydrogen positions, and least-squares planes (16 pages). Ordering information is given on any current masthead page.

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