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Transition-Metal-Promoted Reactions of Boron Hydrides. 17.[1] Titanium-Catalyzed Decaborane−Olefin Hydroborations

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Abstract: The titanium-catalyzed hydroboration reactions of decaborane with a variety of terminal olefins have been found to result in the exclusive, high-yield formation of monosubstituted decaborane 6-R-$B_{10}H_{13}$ products, arising from anti-Markovnikov addition of the cage B6−H to the olefin. The titanium-catalyzed reactions are slow, often less than one turnover per hour; however, their high selectivities and yields coupled with the fact that they are simple, one-pot reactions give them significant advantages over the previously reported routes to 6-R-$B_{10}H_{13}$ compounds. The catalyst also has extended activity with reactions carried out for as long as 13 days, showing little decrease in reactivity, thereby allowing for the production of large amounts of 6-R-$B_{10}H_{13}$. The titanium-catalyzed reactions of decaborane with the nonconjugated diolefins, 1,5-hexadiene and diallylsilane, were found to give, depending upon reaction conditions and stoichiometries, high yields of either alkenyl-substituted 6-($CH_2{=}CH(CH_2)_4$)-$B_{10}H_{13}$ (**4**) and 6-($CH_2{=}CHCH_2SiMe_2(CH_2)_3$)-$B_{10}H_{13}$ (**5**) or linked-cage 6,6′-$(CH_2)_6$-$(B_{10}H_{13})_2$ (**6**) and Me_2Si(6-$(CH_2)_3$-$B_{10}H_{13})_2$ (**7**) compounds, respectively. The unique tetra-cage product, Si(6-$(CH_2)_3$-$B_{10}H_{13})_4$ (**8**), was obtained by the catalyzed reaction of 4 equiv of decaborane with tetraallylsilane. Sequential use of the titanium catalyst and previously reported platinum catalysts ($PtBr_2$ or $H_2PtCl_6{\cdot}6H_2O$ with an initiator) provides an efficient pathway to asymmetrically substituted 6-R-9-R′-$B_{10}H_{12}$ species. The structures of compounds **5**, **6**, and **8**, as well as a platinum derivative, $(PSH^+)_2$-*commo*-Pt-[*nido*-7-Pt-8-(*n*-C_8H_{17})$B_{10}H_{11}]_2^{2-}$, of 6-(*n*-octyl)decaborane have been established by single-crystal crystallographic determinations.

The development of new, systematic ways to functionalize polyboranes, such as decaborane $B_{10}H_{14}$, with organic substituents has been of great recent interest because of the emerging uses[2] of a variety of organo-polyboranes in such diverse applications as boron neutron capture agents, noncoordinating anions, extractants for radioactive wastes, and inorganic polymer components. We have previously shown that late transition metal complexes can be used to catalyze the reactions of certain polyboranes with olefins and acetylenes to provide excellent routes to alkyl- or alkenyl-substituted products.[1] For example, either chloroplatinic acid or platinum(II) bromide can be used to catalytically hydroborate terminal olefins with decaborane to yield 6,9-$R_2B_{10}H_{12}$ derivatives in high yield.[3]

Early transition metal complexes have also recently been found to catalyze olefin and acetylene hydroborations with monoboranes, such as catecholborane (HBCat) or pinacolborane.[4] For example, He and Hartwig reported[4a] that $Cp_2Ti(CO)_2$ catalyzes the hydroboration reactions of HBCat with acetylenes, while Cp_2TiMe_2 is an effective catalyst for reactions of HBCat with olefins. These reports suggested that early-metal metallocene complexes might also be useful for catalyzing reactions involving polyboranes, with the possibility that new types of activities and selectivities might be observed. We report here our discovery of titanium-catalyzed decaborane−olefin hydroboration reactions that, in contrast to the previous platinum-catalyzed decaborane−olefin hydroborations, provide excellent routes to both monoalkyl and monoalkenyl decaboranes, as well as new types of decaborane linked-cage compounds.[5]

Experimental Section

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver and Drezdzon.[6]

Materials. $Cp_2Ti(CO)_2$ was purchased from Strem and used as received. Cp_2TiMe_2 was prepared according to the literature procedure.[7]

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(1) For previous papers in this series, see: Kadlecek, D.; Carrol, P. J.; Sneddon L. G. *J. Am. Chem. Soc.* **2000**, *122*, 10868−10877 and references therein.

(2) Plesek, J. *Chem. Rev.* **1992**, *92*, 269−278.

(3) Mazighi, K.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1993**, *32*, 1963−1969.

(4) For examples, see: (a) He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 1696−1702. (b) Hartwig, J. F.; Muhoro, C. N.; He, X.; Eisenstein, O.; Bosque, R.; Maseras, F. *J. Am. Chem. Soc.* **1996**, *118*, 10936−10937. (c) Hartwig, J. F.; Waltz, K. M.; Muhoro, C. N.; He, X.; Eisenstein, O.; Bosque, R.; Maseras, F. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: London, 1997; pp 491−502. (d) Muhoro, C. N.; Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1510−1512. (e) Muhoro, C. N.; He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 5033−5046. (f) Hartwig, J. F.; Muhoro, C. N. *Organometallics* **2000**, *19*, 30−38. (g) Motry, D. H.; Smith, M. R., III. *J. Am. Chem. Soc.* **1995**, *117*, 6615−6616. (h) Motry, D. H.; Brazil, A. G.; Smith, M. R., III. *J. Am. Chem. Soc.* **1997**, *119*, 2743−2744. (i) Lantero, D. R.; Ward, D. L.; Smith, M. R., III. *J. Am. Chem. Soc.* **1997**, *119*, 9699−9708. (j) Lantero, D. R.; Miller, S. L.; Ch, J.-Y.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1999**, *18*, 235−247. (k) Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 3127−3128. (l) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118*, 909−910. (m) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal. A: Chem.* **1995**, *95*, 121−128. (n) Erker, G.; Noe, R.; Wingbermühle, D.; Petersen, J. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1213−1215. (o) Binger, P.; Sandmeyer, F.; Krüger, C.; Kuhnigk, J.; Goddard, R.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 197−198.

(5) Part of this work was previously communicated, see: Pender, M.; Wideman, T.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1998**, *120*, 9108−9109.

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

(7) Erskine, G. J.; Wilson, D. A.; McCowan, J. D. *J. Organomet. Chem.* **1976**, *114*, 119−125.

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Table 1. Summary of Reaction Conditions and Results

reaction	olefin	decaborane (g, mmol)	$Cp_2Ti(CO)_2$ (g, mmol)/mol %	time (h)/ temp (°C)	% conversion/ TON[c]	product (g, mmol)/ isolated yield (%)
1a	1-hexene (25 mL)	0.516, 4.22	(0.049, 0.21)/5.0	21/90	100/20	**1** (0.82, 4.0)/94
1b	1-hexene (13 mL)	1.00, 2.18	(0.244, 1.03)/12.6	24/80	100/8	**1** (1.52, 7.37)/89.7
1c[a]	1-hexene	0.051, 0.42	(0.0049, 0.021)/5.0	14/70	0/0	no reaction
1d[a]	1-hexene	0.054, 0.44	(0.0010, 0.0043)/0.97	15/75	10/10	**1** not isolated
2a	1-octene (20 mL)	2.34, 19.2	(0.10, 0.43)/2.3	64/90	100/45	**2** (3.92, 16.8)/88
2b[a]	1-octene	0.052, 0.42	(0.0022, 0.0093)/2.2	16/90	40/18	**2** not isolated
3a	AllylTMS (20 mL)	0.24, 2.0	(0.039, 0.17)/8.5	16/83	95/11	**3** (0.37, 1.6)/79
3b	AllylTMS (2.9 mL)[b]	0.24, 2.0	(0.023, 0.098)/4.9	48/90	100/20	**3** (0.42, 1.8)/88
4a	1,5-hexadiene (16 mL)	0.19, 1.6	(0.021, 0.090)/5.6	24/90	100/18	**4** (0.28, 1.4)/88
4b	1,5-hexadiene (75 mL)	5.15, 42.1	(0.4695, 2.006)/4.76	21/90	100/21	**4** (7.94, 38.9)/92.3
5	$Allyl_2SiMe_2$ (18 mL)	1.50, 12.3	(0.1316, 0.5622)/4.57	36/83	100/22	**5** (2.96, 11.3) 91.9
6	1,5-hexadiene (1.38 g)[b]	4.13, 33.8	(0.380, 1.62)/4.79	144/90	100/21	**6** (5.08, 15.6) 92.0
7	$Allyl_2SiMe_2$ (0.63 g)[b]	1.10, 9.0	(0.160, 0.685)/7.61	288/88	100/13	**7** (1.48, 3.85) 85.5
8	$Allyl_4Si$ (0.10 g)[b]	0.25, 2.1	(0.039, 0.17)/8.1	192/90	90/11	**8** (0.19, 1.1) 54

[a] NMR scale reaction. [b] Toluene or benzene used as solvent. [c] TON = turnover number, as determined by 64.2 MHz ^{11}B NMR.

Platinum(II) bromide and $H_2PtCl_6{\cdot}6H_2O$ were purchased from Aldrich and used as received. All olefins were purchased from Aldrich, Sigma, or Gelest and were dried over CaH_2 and vacuum transferred prior to use. Decaborane was freshly sublimed before use. Reaction solvents were obtained from Fischer and dried using standard procedures. Other solvents were also obtained from Fischer and used as received unless noted otherwise.

Physical Measurements. ^1H NMR spectra at 200.1 MHz and ^{11}B NMR spectra at 64.2 MHz were obtained on a Bruker AF-200 Fourier transform spectrometer. The ^{11}B NMR chemical shifts are relative to external $BF_3{\cdot}Et_2O$ (0.00 ppm), with a negative sign indicating an upfield shift. Chemical shifts for ^1H NMR spectra are based on 7.16 ppm for C_6D_6 (relative to Me_4Si at 0.00 ppm). Gas chromatography/mass spectrometry was performed on a Hewlett-Packard 5890A gas chromatograph (equipped with a cross-linked methylsilicone column) interfaced to a Hewlett-Packard 5970 mass-selective detector. Infrared spectra were recorded on a Perkin-Elmer 1430 infrared spectrophotometer. Elemental analyses were performed at the University of Pennsylvania microanalysis facility. High-resolution mass spectra were recorded on a VG-ZAB-E high-resolution mass spectrometer using negative ionization techniques.

Table 1 contains a summary of the conditions and results of the reactions of decaborane with olefins in the presence of catalytic amounts of $Cp_2Ti(CO)_2$. Detailed descriptions of typical reactions and the spectroscopic data for the products of all reactions are presented below.

Reactions with Monoolefins. 6-(*n*-C_6H_{13})-$B_{10}H_{13}$, 1. In a typical reaction, a 50 mL round-bottom flask equipped with a high-vacuum Teflon stopcock was charged under an inert atmosphere with 0.049 g (0.21 mmol) of $Cp_2Ti(CO)_2$, 0.516 g (4.22 mmol) of decaborane, and 25 mL of 1-hexene. The flask was cooled to −196 °C and evacuated. The reaction flask was sealed and brought to room temperature, and the body of the flask was completely submerged in a 90 °C oil bath. After 21 h, ^{11}B NMR analysis showed no unreacted decaborane. The reaction was stopped and exposed to air. The reaction mixture was then eluted down a silica gel column with 500 mL of hexanes. The bulk of the volatiles was removed by rotary evaporation. Volatiles were further removed on the high-vacuum line overnight. GC/MS analysis of the remaining yellow oil, 0.82 g (4.0 mmol, 94% yield), showed 6-(*n*-C_6H_{13})-$B_{10}H_{13}$ as the only product. Anal. Calcd for $C_6H_{26}B_{10}$: C, 34.92; H, 12.70. Found C, 35.09; H, 11.26. Exact mass $^{12}C_6{}^1H_{26}{}^{11}B_{10}$: *m/z* calcd, 208.2965; measd, 208.2973. ^{11}B NMR (64.2 MHz, C_6D_6): 25.9 (s, 1, B6), 10.9 (d, 2, B1,3), 9.2 (d, 1, B9), 1.0 (d, 2, B5,7), −2.5 (d, 2, B8,10), −33.4 (d, 1, B2), −38.0 ppm (d, 1, B4). ^1H NMR (200.1 MHz, C_6D_6): 1.48 (m, 2, CH_2), 1.30 (m, 6, CH_2), 1.10 (m, 2, CH_2), 0.92 (t, 3, CH_3), −2.45 ppm (s, 4, BHB). IR (NaCl plates, cm^{-1}): 2920 (vs), 2900 (vs), 2830 (vs), 2540 (vs), 1970 (w), 1930 (b,w), 1890 (b,m), 1540 (m), 1520 (m), 1490 (vs), 1445 (b,s), 1410 (s,sh), 1370 (m), 1340 (w), 1200 (w), 1085 (s), 990 (vs), 950 (s), 925 (m), 910 (m), 875 (m), 850 (m), 830 (m), 800 (m), 760 (w), 710 (s), 700 (m), 680 (m).

6-(*n*-C_8H_{17})-$B_{10}H_{13}$, 2. Oil. Anal. Calcd for $C_8H_{30}B_{10}$: C, 40.99; H, 12.90. Found: C, 41.20; H, 13.40. Exact mass $^{12}C_8{}^1H_{30}{}^{11}B_{10}$: *m/z* calcd, 236.3278; measd, 236.3277. ^{11}B NMR (64.2 MHz, C_6D_6): 25.5 (s, 1, B6), 9.9 (d, 2, B1,3), 8.3 (d, 1, B9), 0.7 (d, 2, B5,7), −3.2 (d, 2, B8, 10), −34.2 (d, 1, B2), −39.1 ppm (d, 1, B4). ^1H NMR (200.1 MHz, C_6D_6): 1.44 (m, 2, CH_2), 1.18 (m, 12, CH_2), 0.79 (t, 3, CH_3), −1.9 ppm (s, 4, BHB). IR (NaCl plates, cm^{-1}): 2900 (vs), 2830 (vs), 2550 (vs), 1970 (w), 1940 (b,w), 1895 (b,m), 1550 (s), 1530 (s), 1495 (s), 1455 (b,vs), 1405 (s), 1375 (m), 1345 (w), 1305 (b,w), 1090 (s), 995 (vs), 955 (s), 930 (m), 910 (m), 900 (m), 880 (w), 855 (m), 830 (m), 805 (s), 715 (s), 700 (s), 680 (s).

6-($Me_3Si(CH_2)_3$)-$B_{10}H_{13}$, 3. mp 36.5−38.0 °C. Anal. Calcd for $C_6H_{27}B_{10}Si$: C, 30.48; H, 11.93. Found: C, 30.50; H, 12.47. ^{11}B NMR (64.2 MHz, C_6D_6): 25.4 (s, 1, B6), 11.0 (d, 2, B1,3), 9.2 (d, 1, B9), 1.0 (d, 2, B5,7), −2.5 (d, 2, B8,10), −33.4 (d, 1, B2), −37.9 ppm (d, 1, B4). ^1H NMR (200.1 MHz, C_6D_6): 1.61 (m, 2, CH_2), 1.19 (m, 2, CH_2), 0.60 (m, 2, CH_2), 0.05 (s, 9, CH_3), −2.4 ppm (s, 4, BHB). IR (NaCl plates, CCl_4, cm^{-1}): 2960 (w), 2930 (m), 2540 (s), 2480 (m, sh), 1250 (m), 1160 (w), 1100 (w), 990 (m).

6-($CH_2{=}CH(CH_2)_4$)-$B_{10}H_{13}$, 4. Oil. Exact mass $^{12}C_6{}^1H_{24}{}^{11}B_{10}$: *m/z* calcd, 206.2808; measd, 206.2840. ^{11}B NMR (64.2 MHz, C_6D_6): 25.9 (s, 1, B6), 10.1 (d, 2, B1,3), 8.5 (d, 1, B9), 0.8 (d, 2, B5,7), −2.9 (d, 2, B8,10), −34.2 (d, 1, B2), −38.9 ppm (d, 1, B4). ^1H NMR (200.1 MHz, C_6D_6): 5.66 (m, 1, $=CH-$), 4.95 (m, 2, $CH_2=$), 1.97 (m, 2, CH_2), 1.40 (m, 4, CH_2), 1.11 (m, 2, CH_2), −1.89 ppm (s, 4, BHB). IR (NaCl plates, cm^{-1}): 3070 (m), 2960 (m), 2910 (vs), 2840 (s), 2560 (vs), 1975 (b,w), 1945 (b,w), 1895 (b,m), 1635 (s), 1550 (s), 1530 (s), 1490 (vs), 1430 (b,s), 1410 (s), 1350 (w), 1255 (w), 1090 (s), 995 (vs), 950 (s), 905 (vs), 875 (m), 850 (m), 830 (m), 805 (s), 715 (s), 700 (s), 685 (s), 630 (m), 620 (m).

6-($CH_2{=}CHCH_2SiMe_2(CH_2)_3$)-$B_{10}H_{13}$, 5. Oil. Anal. Calcd for $C_8H_{30}B_{10}Si$: C, 36.60; H, 11.52. Found: C, 36.88; H, 11.92. ^{11}B NMR (64.2 MHz, C_6D_6): 24.7 (s, 1, B6), 10.3 (d, 2, B1,3), 8.5 (d, 1, B9), 0.3 (d, 2, B5,7), −3.2 (d, 2, B8,10), −34.2 (d, 1, B2), −38.7 ppm (d, 1, B4). ^1H NMR (200.1 MHz, C_6D_6): 5.80 (m, 1, $=CH-$), 4.96 (m, 2, $CH_2=$), 1.56 (m, 4, CH_2), 1.18 (m, 2, CH_2), 0.62 (m, 2, CH_2), 0.03 (s, 6, CH_3), −2.3 ppm (s, 4, BHB). IR (NaCl plates, cm^{-1}): 3050 (w), 2930 (m), 2900 (s), 2860 (m), 2550 (vs), 1970 (b,w), 1930 (b,w), 1890 (b,w), 1620 (m), 1545 (w), 1490 (s), 1405 (m), 1330 (w), 1240 (s), 1185 (w), 1145 (m), 1085 (w), 1020 (w), 995 (s), 950 (w), 920 (m), 880 (m), 820 (vs), 720 (w), 690 (m), 630 (m).

6-(*n*-C_8H_{17})-$B_{10}H_{13}$, 2. In a separate experiment designed to determine the robustness of the $Cp_2Ti(CO)_2$ catalyst, a 500 mL round-bottom flask, equipped with a high-vacuum Teflon stopcock, was charged under an inert atmosphere with 0.056 g (0.24 mmol) of $Cp_2Ti(CO)_2$, 39.0 mL (249 mmol) of 1-octene, and 1.33 g (10.9 mmol) of decaborane. The flask was cooled to −196 °C and evacuated. The reaction flask was then brought to room temperature, and the body of the flask was completely submerged in an 85 °C oil bath. After ~45 min, the reaction mixture had changed from reddish brown to dark green. A total of 7.11 g (58.2 mmol) of decaborane was added in increments over the course of 12 days (see Table 2). After 307 h, all decaborane had been consumed. When the reaction mixture was exposed to the air, the solution changed from green to orange, and a precipitate formed. The mixture was eluted down a silica gel column with toluene until no

Table 2. Summary of 13 Day Titanium-Catalyzed Reaction of Decaborane with 1-Octene

time (h)	total turnovers	$B_{10}H_{14}$ mmol added
0	0	10.9
43	34	11.6
96	71	16.2
139	97	9.2
187	140	10.3
307	244	0

product was visible by TLC in the fractions. The bulk of the volatiles was removed via rotary evaporation. Volatiles were further removed on a high-vacuum line overnight. GC/MS analysis of the remaining brown oil, 12.36 g (52.7 mmol, 90.5% yield), showed 6-(*n*-C_8H_{17})-$B_{10}H_{13}$ to be the only product.

Reactions of 6-(*n*-C_8H_{17})-$B_{10}H_{13}$ with Lewis Bases. A 2.0 mL aliquot of a 0.020 M solution of 6-(*n*-octyl)decaborane in toluene was stirred with 5.0 mL of dimethyl sulfide overnight at 90 °C. A ^{11}B NMR spectrum taken at this time showed no reaction. This reaction was repeated with equal quantities of diethyl sulfide and acetonitrile, but no reaction was observed by ^{11}B NMR analysis. As was previously observed for reactions with 6,9-R_2-$B_{10}H_{12}$,[3] the reaction of 6-(*n*-octyl)decaborane with triethylamine resulted in deprotonation to form the monoanion, i.e., 6-(*n*-C_8H_{17})-$B_{10}H_{12}^-$.

Multicage Syntheses. 6,6′-(CH_2)$_6$-($B_{10}H_{13}$)$_2$, 6. A 500 mL round-bottom flask, equipped with a high-vacuum Teflon stopcock, was charged under an inert atmosphere with 0.380 g (1.62 mmol) of $Cp_2Ti(CO)_2$, 4.13 g (33.8 mmol) of decaborane, 1.38 g (16.9 mmol) of 1,5-hexadiene, and 25 mL of toluene freshly vacuum distilled from Na/benzophenone. The flask was evacuated while being cooled at −196 °C. The flask was then sealed and brought to room temperature, and then the body of the flask was submerged in a 90 °C oil bath. After ∼6 days, ^{11}B NMR analysis showed that all decaborane had been consumed. The reaction mixture was exposed to air and eluted down a silica gel column with toluene. The bulk of the volatiles was removed by rotary evaporation. Volatiles were further removed on the high-vacuum line overnight. GC/MS analysis of the remaining peach-colored solid, 5.08 g (15.6 mmol, 92.0% yield), showed 6,6′-(CH_2)$_6$-($B_{10}H_{13}$)$_2$ to be the only product. Crystals were grown from a 1:1 heptane and benzene solution at −10 °C. mp 95.5−96.5 °C. Anal. Calcd for $C_6H_{38}B_{20}$: C, 22.07; H, 11.73. Found: C, 21.44; H, 11.86. Exact mass $^{12}C_6{}^1H_{38}{}^{11}B_{20}$: *m/z* calcd, 330.4835; measd, 330.4849. ^{11}B NMR (64.2 MHz, C_6D_6): 25.4 (s, 1, B6), 9.9 (d, 2, B1,3), 8.2 (d, 1, B9), 0.4 (d, 2, B5,7), −3.2 (d, 2, B8,10), −34.3 (d, 1, B2), −39.0 ppm (d, 1, B4). ^{1}H NMR (200.1 MHz, C_6D_6): 1.56 (m, 4, CH_2), 1.40 (m, 4, CH_2), 1.15 (m, 4, CH_2), −2.4 ppm (s, 8, BHB). IR (NaCl plates, CCl_4, cm^{-1}): 2940 (m), 2910 (m), 2860 (w), 2560 (s), 1355 (b,m), 1260 (m), 1095 (m), 1020 (m), 760 (m).

(CH_3)$_2$Si(6-(CH_2)$_3$-$B_{10}H_{13}$)$_2$, 7. A 100 mL round-bottom flask, equipped with a high-vacuum Teflon stopcock, was charged under an inert atmosphere with 0.160 g (0.685 mmol) of $Cp_2Ti(CO)_2$, 1.10 g (9.00 mmol) of decaborane, 0.63 g (4.5 mmol) of diallyldimethylsilane, and 10 mL of toluene freshly vacuum distilled from Na/benzophenone. The flask was evacuated while being cooled at −196 °C and then sealed. After initially warming to room temperature, the body of the flask was submerged in an 88 °C oil bath. After 12 days, ^{11}B NMR analysis showed that the reaction was complete. The reaction mixture was exposed to air and eluted down a silica gel column with 200 mL of toluene. The bulk of the volatiles was removed by rotary evaporation. Volatiles were further removed on the high-vacuum line overnight to yield 1.48 g (3.85 mmol, 85% yield) of a peach-colored solid. mp 109.0−110.5 °C. Exact mass $^{12}C_8{}^1H_{44}{}^{11}B_{20}{}^{28}Si$: *m/z* calcd, 388.5073; measd, 388.5088. ^{11}B NMR (64.2 MHz, C_6D_6): 24.6 (s, 1, B6), 10.4 (d, 2, B1,3), 8.7 (d, 1, B9), 0.4 (d, 2, B5,7), −3.1 (d, 2, B8,10), −34.1 (d, 1, B2), −38.6 ppm (d, 1, B4). ^{1}H NMR (200.1 MHz, C_6D_6): 1.68 (m, 4, CH_2), 1.24 (m, 4, CH_2), 0.72 (m, 4, CH_2), 0.12 (s, 6, CH_3), −2.5 ppm (s, 8, BHB). IR (NaCl plates, cm^{-1}): 2940 (m), 2900 (m), 2880 (sh,w), 2560 (s), 1490 (m), 1420 (b,w), 1240 (m), 1210 (b,w), 1150 (w), 1085 (w), 1000 (m), 940 (w), 690 (w).

Si(6-(CH_2)$_3$-$B_{10}H_{13}$)$_4$, 8. A 50 mL round-bottom flask, equipped with a high-vacuum Teflon stopcock, was charged under an inert atmosphere with 0.039 g (0.17 mmol) of $Cp_2Ti(CO)_2$, 0.10 g (0.52 mmol) of tetraallylsilane, 0.25 g (2.1 mmol) of decaborane, and 10 mL of toluene freshly vacuum distilled from Na/benzophenone. The reaction flask was evacuated at −196 °C and then sealed. After initially warming to room temperature, the body of the flask was submerged in a 90 °C oil bath. After 8 days, the reaction mixture was cooled to room temperature, exposed to air, and eluted down a silica gel column with 300 mL of hexanes followed by 300 mL of toluene. Following the removal of volatiles, 0.19 g of product remained, corresponding to a 54% isolated yield. Crystals were grown from a 3:1 mixture of benzene and heptane at −10 °C. mp 139−140.5 °C. Anal. Calcd for $C_{12}H_{76}B_{40}Si$: C, 21.16; H, 11.25. Found C, 22.53; H, 11.98. LRMS (electrospray) for $^{28}Si^{12}C_{12}{}^1H_{76}{}^{11}B_{38}$ (P-2H): *m/z* calcd, 686; measd, 686. ^{11}B NMR (64.2 MHz, C_6D_6): 25.8 (s, 1, B6), 11.2 (d, 3, B1,3 and B9), 1.3 (d, 2, B5,7), −2.2 (d, 2, B8,10), −33.3 (d, 1, B2), −37.6 ppm (d, 1, B4). ^{1}H NMR (200.1 MHz, C_6D_6): 1.92 (m, 8, CH_2), 1.32 (m, 8, CH_2), 0.99 (m, 8, CH_2), −2.1 (s, 8, BHB), −2.5 ppm (s, 8, BHB). IR (NaCl, CCl_4, plates, cm^{-1}): 2920 (w), 2900 (m), 2880 (w), 2560 (s), 1490 (m), 1420 (b,w), 1240 (m), 1210 (w), 1140 (w), 1000 (w), 970 (sh,w), 670 (w).

Syntheses of 6-(*n*-C_8H_{17})-9-(C_6H_5-(CH_2)$_3$)-$B_{10}H_{12}$, 9. $PtBr_2$-Catalyzed Reaction. A 100 mL reaction tube equipped with a high-vacuum Teflon stopcock was charged under an inert atmosphere with 0.024 g (0.066 mmol, 3.5 mol %) of $PtBr_2$, 0.43 g (1.9 mmol) of 6-(*n*-octyl)decaborane, and 3.13 g (26.5 mmol) of allylbenzene. The reaction flask was cooled to −196 °C, evacuated, and then warmed to room temperature. The body of the reaction tube was then submerged in a 60 °C oil bath. After 4 h, ^{11}B NMR analysis showed that all of the 6-(*n*-octyl)decaborane had been consumed. The reaction mixture was eluted through a silica gel plug and then through activated carbon with a 1:1 mixture of benzene and hexanes. The bulk of the volatiles was removed by rotary evaporation. Volatiles were further removed on the high-vacuum line overnight. GC/MS analysis of the remaining light brown oil, 0.64 g (1.8 mmol, 97% yield, 29 turnovers), showed 6-(*n*-C_8H_{17})-9-(C_6H_5-(CH_2)$_3$)-$B_{10}H_{12}$ (**9**) as the only product. Exact mass $^{12}C_{17}{}^1H_{40}{}^{11}B_{10}$: *m/z* calcd, 354.4061; measd, 354.4075. ^{11}B NMR (64.2 MHz, C_6D_6): 23.9 (s, 2, B6,9), 8.4 (d, 2, B1,3), −2.4 (d, 4, B5,7,8,10), −36.8 ppm (d, 2, B2,4). ^{1}H NMR (200.1 MHz, C_6D_6): 7.11 (m, 5, Ph), 2.61 (t, 2, CH_2), 1.83 (m, 2, CH_2), 1.44 (m, 4, CH_2), 1.19 (m, 12, CH_2), 0.80 (t, 3, CH_3), −1.8 ppm (s, 4, BHB). IR (NaCl plates, cm^{-1}): 3050 (w), 3010 (m), 2910 (vs), 2840 (s), 2550 (vs), 1920 (vb,w), 1600 (w), 1520 (m), 1500 (s), 1490 (s), 1450 (s), 1410 (s), 1350 (w), 1260 (w), 1095 (s), 1080 (m), 1030 (w), 995 (s), 960 (w), 900 (w), 840 (w), 810 (b,w), 745 (s), 730 (m), 700 (s).

$H_2PtCl_6 \cdot 6H_2O$-Catalyzed Reaction. A 100 mL reaction tube equipped with a high-vacuum Teflon stopcock was charged under an inert atmosphere with 0.0121 g (0.023 mmol) of $H_2PtCl_6 \cdot 6H_2O$, 4.0 mL of allylbenzene, and 0.15 g (0.64 mmol) of 6-(*n*-octyl)decaborane. The tube was cooled to −196 °C and evacuated on a high-vacuum line. The flask was warmed to room temperature and then immersed in a 65 °C oil bath and stirred for 22 h. Analysis by ^{11}B NMR showed the formation of 6-(*n*-C_8H_{17})-9-(C_6H_5-(CH_2)$_3$)-$B_{10}H_{12}$ (**9**) to be less than 50% complete (14 turnovers).

$H_2PtCl_6 \cdot 6H_2O$ Catalyst with Decaborane Initiator. A 100 mL reaction tube equipped with a high-vacuum Teflon stopcock was charged under an inert atmosphere with 0.0268 g (0.052 mmol) of $H_2PtCl_6 \cdot 6H_2O$, 3.23 g of allylbenzene, 0.31 g (1.3 mmol) of 6-(*n*-octyl)decaborane, and 0.0094 g (0.070 mmol) of decaborane. The reaction tube was cooled to −196 °C and evacuated on a high-vacuum line. The tube was warmed to room temperature and then immersed and stirred in a 65 °C oil bath. Analysis by ^{11}B NMR showed the reaction to be complete after 14 h. TLC analysis indicated that, in addition to the major product 6-(*n*-C_8H_{17})-9-(C_6H_5-(CH_2)$_3$)-$B_{10}H_{12}$ (**9**), small amounts of 6,9-(C_6H_5-(CH_2)$_3$)-2-$B_{10}H_{12}$ were also produced, with the latter compound resulting from the platinum-catalyzed reaction of allylbenzene with the $B_{10}H_{14}$ initiaitor. After separation by flash filtering through a silica gel column, 0.41 g of a mixture was obtained, which corresponds (assuming the ratio of products is equal to the ratio of starting decaborane and 6-(*n*-octyl)decaborane) to an isolated yield of 83% (25 turnovers).

$H_2PtCl_6 \cdot 6H_2O$ Catalyst with Triethylsilane Initiator. A 100 mL reaction tube equipped with a high-vacuum Teflon stopcock was

Table 3. Crystallographic Data Collection and Structure Refinement Information

	5	**6**	**8**	**10**
formula	$C_8B_{10}H_{30}Si$	$C_6B_{20}H_{38}$	$C_{12}B_{40}H_{76}Si$	$PtC_{44}B_{20}H_{98}N_4O_2$
formula weight	262.51	326.56	681.22	1126.55
crystal class	monoclinic	triclinic	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
Z	8	2	4	4
cell constants				
a	13.5697(3) Å	10.0173(9) Å	12.1547(1) Å	14.1449(5) Å
b	14.9807(5) Å	14.2662(10) Å	30.8009(2) Å	16.7051(5) Å
c	17.6395(3) Å	8.1422(6) Å	12.7664(1) Å	25.5823(12) Å
α		94.144(4)°		
β	94.442(2)°	104.290(3)°	102.918(1) Å^3	95.5610(10)°
γ		82.144(6)°		
V	3575.1(2) Å^3	1116.1(2) Å^3	4658.47(6) Å^3	6016.4(4) Å^3
μ	1.09 cm^{-1}	0.40 cm^{-1}	0.65 cm^{-1}	23.70 cm^{-1}
crystal size, mm	0.30 × 0.28 × 0.20	0.34 × 0.20 × 0.08	0.45 × 0.18 × 0.15	0.32 × 0.20 × 0.03
D_{calc}	0.975 g/cm^3	0.972 g/cm^3	0.971 g/cm^3	1.244 g/cm^3
F(000)	1136	348	1448	2336
radiation	Mo Kα $\lambda = 0.71069$ Å	Mo Kα $\lambda = 0.71069$ Å	Mo Kα $\lambda = 0.71069$ Å	Mo Kα $\lambda = 0.71069$ Å
2θ range	5.44−50.7°	5.16−50.70°	5.14−50.7°	4.88−50.7°
temperature, K	180	200	200	200
hkl collected	$-16 \leq h \leq 16$; $-18 \leq k \leq 18$; $-21 \leq l \leq 20$	$-12 \leq h \leq 12$; $-17 \leq k \leq 17$; $-9 \leq l \leq 9$	$-14 \leq h \leq 14$; $-36 \leq k \leq 36$; $-15 \leq l \leq 15$	$-16 \leq h \leq 16$; $-17 \leq k \leq 20$; $-29 \leq l \leq 30$
no. reflections measured	12 056	8368	32 624	39 097
no. unique reflections	3226 ($R_{int} = 0.0330$)	3697 ($R_{int} = 0.0324$)	8432 ($R_{int} = 0.0395$)	10 576 ($R_{int} = 0.0832$)
no. observed reflections	3002 ($F > 4\sigma$)	3178 ($F > 4\sigma$)	7340 ($F > 4\sigma$)	9170 ($F > 4\sigma$)
no. reflections used in refinement	3226	3697	8432	10 576
no. parameters	292	388	478	650
R indices ($F > 4\sigma$)^a	$R_1 = 0.0496$ w$R_2 = 0.1131$	$R_1 = 0.0665$ w$R_2 = 0.1518$	$R_1 = 0.0895$ w$R_2 = 0.1982$	$R_1 = 0.0987$ wR_2=0.1782
R indices (all data)^a	$R_1 = 0.0538$ w$R_2 = 0.1155$	$R_1 = 0.0776$ w$R_2 = 0.1590$	$R_1 = 0.1039$ w$R_2 = 0.2067$	$R_1 = 0.1153$ w$R_2 = 0.1850$
GOF	1.150	1.161	1.172	1.283
final difference peaks, e/Å^3	+0.124, −0.288	+0.168, −0.146	+0.299, −0.262	+3.119, −1.585

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

charged under an inert atmosphere with 0.0217 g (0.042 mmol) of $H_2PtCl_6 \cdot 6H_2O$, 8.0 mL of allylbenzene, 0.25 g (1.1 mmol) of 6-(*n*-octyl)-decaborane, and 0.04 g of a 17% solution of triethylsilane in allylbenzene (0.059 mmol Et_3SiH). The reaction tube was cooled to −196 °C and evacuated on a high-vacuum line. The reaction flask was warmed to room temperature and immersed in a 65 °C oil bath. After the solution was stirred for 7 h, ^{11}B NMR analysis showed complete reaction to form 6-(*n*-C_8H_{17})-9-(C_6H_5-$(CH_2)_3$)-$B_{10}H_{12}$ (**9**). Following separation of products by column chromatography (silica gel, hexanes: toluene 3:1), 0.59 g of product was obtained, which corresponds to an isolated yield of 90% (26 turnovers).

(PSH^+)$_2$-*commo*-Pt-[*nido*-7-Pt-8-(*n*-C_8H_{17})-$B_{10}H_{11}$]$_2^{2-}$, 10. A two-neck round-bottom flask equipped with a vacuum adapter, stir bar, and septum was charged with 0.39 g (1.7 mmol) of 6-(*n*-octyl)decaborane and evacuated on the high-vacuum line. On the Schlenk line, 15 mL of dry THF was syringed into the flask, which was then cooled to −78 °C. An excess (∼1.5-fold) of NaH was added under a positive pressure of nitrogen. This mixture was allowed to stir for 1.5 h while warming to room temperature. The mixture was then filtered and the filtrate transferred to a 100 mL Schlenk tube. To this tube was added, with rapid stirring, 25 mL of a CH_3CN solution containing 0.36 g (1.7 mmol) of proton sponge (PS) and 0.32 g (0.85 mmol) of (COD)$PtCl_2$. This mixture was stirred for 16 h. Solvent was removed, and the remaining crude product was then recrystallized from CH_2Cl_2 to yield 0.37 g of a brown/yellow solid, which corresponds to a 40% yield based on starting Pt. Crystals were grown from a pentane and methylene chloride solution (1:1) at −10 °C. Anal. Calcd for $C_{44}H_{94}B_{20}N_4Pt$: C, 48.46; H, 8.69; N, 5.14. Found: C, 48.35; H, 8.67; N, 4.62. LRMS (electrospray) for $^{12}C_{30}{}^{1}H_{74}{}^{11}B_{20}{}^{14}N_2{}^{196}Pt$ (P−PSH^+): *m/z* calcd, 880; measd, 880. ^{11}B NMR (64.2 MHz, C_6D_6): 7.6 (s), −2.9 (broad), −23.3 (d), −27.9 ppm (d). ^{1}H NMR (200.1 MHz, C_6D_6): 19.16 (s, 2, NHN), 8.03 (m, 4, naphth), 7.74 (m, 8, naphth), 3.20 (s, 24, CH_3), 1.72 (m, 4, CH_2), 1.57 (m, 24, CH_2), 0.87 (m, 6, CH_3), −1.7 (s, 2, BHB), −2.2 ppm (s, 2, BHB). IR (NaCl plates, CCl_4, cm^{-1}): 3020 (s), 2940 (m), 2650 (s), 2620 (vs), 2460 (w), 1620 (w), 1590 (w), 1580 (m), 1560 (w), 1540 (w), 1500 (m), 1430 (w), 1395 (w), 1290 (w), 1240 (w), 1195 (w), 1170 (w), 1110 (w), 1090 (w), 1050 (w), 1020 (m), 860 (vs), 840 (vs), 830 (vs), 710 (w), 700 (w), 680 (m).

Crystallographic Data for Compounds 5, 6, 8, and 10. Single crystals of 6-(CH_2=$CHCH_2SiMe_2(CH_2)_3$)-$B_{10}H_{13}$ (**5**, UPenn 3164), 6,6′-$(CH_2)_6$-$(B_{10}H_{13})_2$ (**6**, UPenn 3133), Si(6-$(CH_2)_3$-$B_{10}H_{13}$)$_4$ (**8**, UPenn 3175), and (PSH^+)$_2$-*commo*-Pt-[*nido*-7-Pt-8-(*n*-C_8H_{17})-$B_{10}H_{11}$]$_2^{2-}$ (**10**, UPenn 3138) were grown as described above. Suitably sized crystals were mounted and transferred to the diffractometer.

Collection and Reduction of the Data. As described in Table 3, X-ray intensity data for **5**, **6**, **8**, and **10** were collected on a Rigaku R-AXIS IIc area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Indexing was performed on a series of oscillation images. A hemisphere of data was collected using 8°, 10°, 5°, and 4° oscillation angles for **5**, **6**, **8**, and **10**, respectively, with a crystal-to-detector distance of 82 mm. Oscillation images for each compound were processed using bioteX,[8] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed on to the teXsan[9] program package for further processing and structure solution on a Silicon Graphics Indigo R4000 computer. The intensity data were corrected for Lorentz and polarization effects, but not for absorption.

Solution and Refinement of the Structures. Each structure was solved by direct methods (SIR92).[10] Refinement was by full-matrix least-squares based on F^2 using SHELXL-93.[11] All reflections were used during refinement (F^2's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme for **5** was $w = 1/[\sigma^2(F_o^2) + 0.0456P^2 + 2.9033P]$; for **6**, $w = 1/[\sigma^2(F_o^2) + 0.0571P^2 + 0.4865P]$;

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(8) *BioteX*: A suite of Programs for the collection, Reduction and Interpretation of Imaging Plate Data; Molecular Structure Corp.: The Woodlands, TX, 1995.

(9) *teXsan*: Crystal Structure Analysis Package; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.

(10) *SIR92*: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidoro, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

for **8**, $w = 1/[\sigma^2(F_o^2) + 0.0692P^2 + 3.2471P]$; and for **10**, $w = 1/[\sigma^2(F_o^2) + 0.0198P^2 + 81.0910P]$, where $P = (F_o^2 + 2F_c^2)/3$.

For all compounds, non-hydrogen atoms were refined anisotropically. For **5** and **6**, hydrogen atoms were refined isotropically. For **8**, hydrogen atoms were included as constant contributions to the structure factors and were not refined. For **10**, hydrogen atoms were refined according to a "riding" model except for the cage hydrogens, H9, H10, H11, H89, H1011, H9′, H10′, H11′, H89′, and H1011′, which were included as constant contributions to the structure factors and were not refined.

Crystal and refinement data, refined positional parameters, and bond distances and angles are presented in Tables S1−16 (Supporting Information).

Results

Reactions with Monoolefins. As summarized in Table 1, decaborane was found to react (eq 1) with simple terminal olefins, such as 1-hexene, 1-octene, and allyltrimethylsilane, in the presence of catalytic amounts of $Cp_2Ti(CO)_2$ to yield monoalkyldecaboranes of the formula $6\text{-}RCH_2CH_2\text{-}B_{10}H_{13}$.

$$B_{10}H_{14} + RCH{=}CH_2 \xrightarrow{Cp_2Ti(CO)_2} 6\text{-}RCH_2CH_2\text{-}B_{10}H_{13} \quad (1)$$

The reactions were monitored by ^{11}B NMR and stopped when the initial starting decaborane was consumed. For each reaction, an initial induction period of at least 1 h was observed that was accompanied by a characteristic color change of the reaction mixture from dark red to dark green. Generally, the reactions were complete in 24 h at 90 °C when using ∼5 mol % catalyst and an excess of olefin. Quantitative conversion of decaborane to the $6\text{-}R\text{-}B_{10}H_{13}$ products was observed in the ^{11}B NMR spectra of the reaction solutions. Separation of the catalyst by flash filtration of the reaction solution through a silica gel plug, followed by removal of volatiles under vacuum, afforded typical isolated yields of ∼90%.

The titanium-catalyzed reactions are slow (typically less than one turnover per h), but the catalyst was found to be very long-lived. For example, as shown in Table 2, ^{11}B NMR analysis of an experiment where ∼10−12 mmol samples of decaborane were added every 2 days (total decaborane added: 7.11 g, 58.2 mmol) to a reaction mixture containing only 0.24 mmol of $Cp_2Ti(CO)_2$ (0.41 mol %) and an excess of 1-octene (39.0 mL, 249 mmol) showed no significant decrease in the rate of formation of 6-(*n*-octyl)decaborane over 13 days (244 total catalyst turnovers). Workup of the reaction as described above gave the oily, liquid product in a 90.5% isolated yield (12.4 g).

Even when the reactions were carried out for extended times, the titanium-catalyzed reactions proved to be highly selective in yielding only monosubstituted decaborane products, $6\text{-}R\text{-}B_{10}H_{13}$ resulting from anti-Markovnikov addition to the olefin. For example, GC/MS analysis of the 13 day reaction described above confirmed 6-(*n*-octyl)decaborane as the sole product. The titanium catalyst was found to be inactive for olefins containing halide, oxygen, nitrile, or N−H groups, due to deactivation of the catalyst by a process most reasonably involving the direct reaction of these species at the electrophilic titanium center.

The compositions of all products were established by elemental analysis and/or exact mass determinations. Both the C_s symmetry pattern and the downfield singlet at ∼26 ppm observed in ^{11}B NMR spectra of all products are consistent with the attachment of an alkyl group to the 6-position of the decaborane framework, and these spectra are in agreement with previous studies of the structures and NMR properties of $6\text{-}R\text{-}B_{10}H_{13}$ compounds.[12] Their ^1H NMR spectra all show the characteristic cage and substituent resonances that are consistent with anti-Markovnikov addition of the olefin at the 6-boron position.

Compounds **1**, **2**, and **3** were not characterized crystallographically; however, the structure of **2** was confirmed by an X-ray structural characterization of its platinum derivative, **10**. Mazighi et al.[3] earlier showed that the *commo*-Pt-[*nido*-7-Pt-$8,11\text{-}(n\text{-}C_5H_{11})_2\text{-}B_{10}H_{10}]_2^{2-}$ complex is formed upon reacting 2 equiv of $6,9\text{-}R_2\text{-}B_{10}H_{11}^-$ with $PtCl_2(COD)$. As shown in eqs 2 and 3, when $6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{13}$ was reacted in a similar manner, the proton sponge (PS) salt, $(PSH^+)_2$-*commo*-Pt-[*nido*-7-Pt-8-$(n\text{-}C_8H_{17})\text{-}B_{10}H_{11}]^{2-}$ (**10**) was obtained in a 40% isolated yield.

$$6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{13} + NaH \rightarrow Na^+[6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{12}]^- + H_2 \quad (2)$$

$$2Na^+[6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{12}]^- + 2PS + PtCl_2(COD) \rightarrow \underset{\mathbf{10}}{(PSH^+)_2\text{-}commo\text{-}Pt\text{-}[nido\text{-}7\text{-}Pt\text{-}8\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{11}]_2^{2-}} + 2NaCl + COD \quad (3)$$

An X-ray structural study confirmed the structure shown in the ORTEP representation in Figure 1. The platinum acts as a common vertex in two 11-vertex cages, with each cage bound in an η^4 fashion to the formal Pt^{2+} center. In agreement with their *nido* (26 skeletal electrons) electron counts, each PtB_{10} cage has an open-cage structure based on an icosahedron missing one vertex. The alkyl groups of the two cages are oriented on opposite sides of the platinum. The Pt−B8 bond length in **10** (2.34(2) Å) is similar to the Pt−B8 and Pt−B11 bond lengths in *commo*-Pt-[*nido*-7-Pt-$8,11\text{-}(n\text{-}C_5H_{11})_2\text{-}B_{10}H_{10}]_2^{2-}$ (2.400(11) and 2.370(14) Å), while the Pt−B11 length in **10** (2.275(12) Å) is significantly shorter and similar to those observed for Pt−B8 and Pt−B11 (2.273(3) and 2.295(3) Å) in the parent *commo*-Pt-[*nido*-7-Pt−$B_{10}H_{12}]_2^{2-}$ complex.[13]

Reactions with Polyenes: 1,5-Hexadiene and Diallylsilane. The titanium-catalyzed reactions of decaborane with nonconjugated diolefins, such as 1,5-hexadiene and diallylsilane, gave, depending upon reaction conditions and stoichiometries, high yields of either alkenyl-substituted or linked-cage products.

When 1,5-hexadiene or diallylsilane was used in excess, the alkenyl-substituted products $6\text{-}(CH_2{=}CH(CH_2)_4)\text{-}B_{10}H_{13}$ (**4**) and $6\text{-}(CH_2{=}CHCH_2SiMe_2(CH_2)_3)\text{-}B_{10}H_{13}$ (**5**) were produced, respectively, in excellent (∼90%) isolated yields (eqs 4 and 5). As shown in Table 1, both reactions were carried out with conditions similar to those described above.

$$B_{10}H_{14} + \text{xs } H_2C{=}CH\text{-}(CH_2)_2\text{-}CH{=}CH_2 \xrightarrow{Cp_2Ti(CO)_2} \underset{\mathbf{4}}{6\text{-}(H_2C{=}CH\text{-}(CH_2)_4)\text{-}B_{10}H_{13}} \quad (4)$$

$$B_{10}H_{14} + \text{xs } Me_2Si(CH_2CH{=}CH_2)_2 \xrightarrow{Cp_2Ti(CO)_2} \underset{\mathbf{5}}{6\text{-}(CH_2{=}CHCH_2SiMe_2(CH_2)_3)\text{-}B_{10}H_{13}} \quad (5)$$

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[11] Sheldrick, G. M. *SHELXL-93*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1993.

[12] (a) Gaines, D. F.; Bridges, A. N. *Organometallics* **1993**, *12*, 2015−2016. (b) Bridges, A. N.; Powell, D. R.; Dopke, J. A.; Desper, J. M.; Gaines, D. F. *Inorg. Chem.* **1998**, *37*, 503−509.

[13] (a) Klanberg, F.; Wegner, P. A.; Parshall, G. W.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 2072−2077. (b) MacGregor, S. A.; Yellowlees, L. J.; Welch, A. J. *Acta Crystallogr.* **1990**, *C46*, 1399−1405.

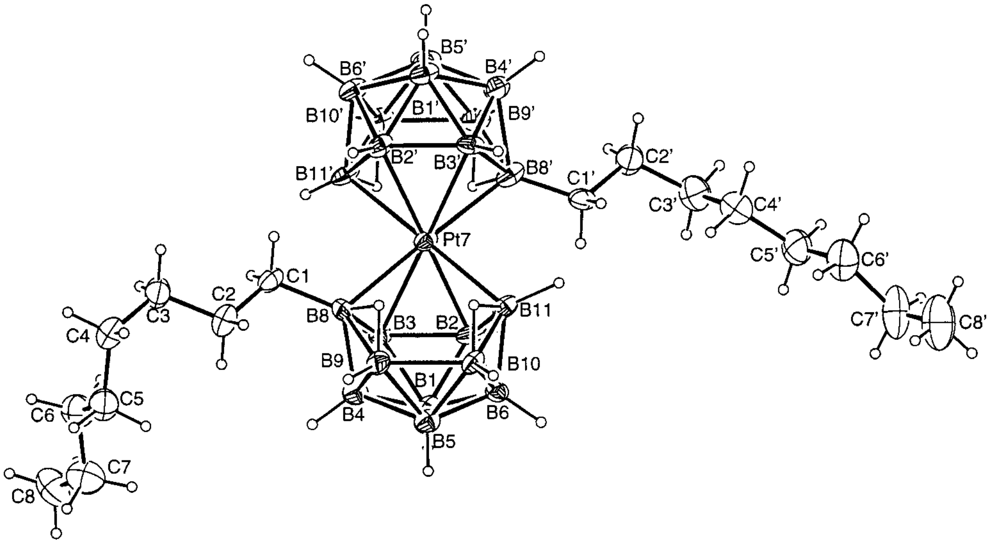

Figure 1. ORTEP drawing of the structure of the anion of compound $(PSH^+)_2$-*commo*-Pt-[*nido*-7-Pt-8-(*n*-C_8H_{17})$B_{10}H_{11}$]$_2^{2-}$ (**10**). Selected bond lengths (Å) and angles (°): Pt7−B2, 2.218(12); Pt7−B3, 2.242(12); Pt7−B8, 2.387(13); Pt7−B11, 2.275(12); Pt7−B8′, 2.34(2); Pt7−B11′, 2.287(13); B8−B3, 1.79(2); B3−B2, 1.85(2); B2−B11, 1.78(2); B8−B9, 1.81(2); B9−B10, 1.95(2); B10−B11, 1.86(2); C1−B8, 1.60(2); C1−B8−Pt7, 118.4(9); B8−Pt7−B8′, 178.3(5); B2−Pt7−B2′, 179.2(5).

The ^{11}B NMR spectra observed for **4** and **5** are similar to those of the monoalkyldecaboranes **1**, **2**, and **3**, with a characteristic singlet at a shift near 25 ppm corresponding to the substituted B6 boron. Their ^1H NMR spectra likewise show the resonances for the cage and $-CH_2-$ (and $(CH_3)_2Si$ for **5**) protons, but they also exhibit multiplet resonances centered near 4.9 and 5.7 ppm that are characteristic of a vinyl group. Supporting this interpretation, both compounds exhibit C═C stretching bands, 1635 (**4**) and 1620 cm^{-1} (**5**), in their infrared spectra.

As shown in the ORTEP drawing in Figure 2, the structure of **5** was confirmed by means of a single-crystal X-ray crystallographic determination. As can be seen in the figure, hydroboration of only one of the allyl groups of diallylsilane by the decaborane B6−H unit has occurred to yield a compound in which the decaborane cage is substituted at the 6-boron position by the $CH_2{=}CHCH_2SiMe_2(CH_2)_3-$ group. The presence of the terminal double bond is confirmed by the planar nature of the $H_2C(16){=}C(15)H-$ unit and the C15−C16 bond length of 1.320(3) Å. All other bond lengths and angles in this compound are comparable to those reported for 6-Thx-$B_{10}H_{13}$ (Thx = CMe_2CHMe_2).[12]

By both changing the reaction stoichiometry and carrying out the reactions for longer times, complete hydroboration of 1,5-hexadiene and diallylsilane could easily be achieved to produce the linked cage compounds, 6,6′-$(CH_2)_6$-$(B_{10}H_{13})_2$ (**6**) and $Me_2Si(6\text{-}(CH_2)_3\text{-}B_{10}H_{13})_2$ (**7**), respectively (eqs 6 and 7).

$$2B_{10}H_{14} + H_2C{=}CH\text{-}(CH_2)_2\text{-}CH{=}CH_2 \xrightarrow{Cp_2Ti(CO)_2} \underset{\mathbf{6}}{6,6'\text{-}(CH_2)_6\text{-}(B_{10}H_{13})_2} \quad (6)$$

$$2B_{10}H_{14} + Me_2Si(CH_2CH{=}CH_2)_2 \xrightarrow{Cp_2Ti(CO)_2} \underset{\mathbf{7}}{Me_2Si(6\text{-}(CH_2)_3\text{-}B_{10}H_{13})_2} \quad (7)$$

The reaction of a 2:1 ratio of decaborane to 1,5-hexadiene in the presence 4.8 mol % $Cp_2Ti(CO)_2$ at 90 °C was complete in 6 days (21 total turnovers) and afforded **6** in 92% isolated yield.

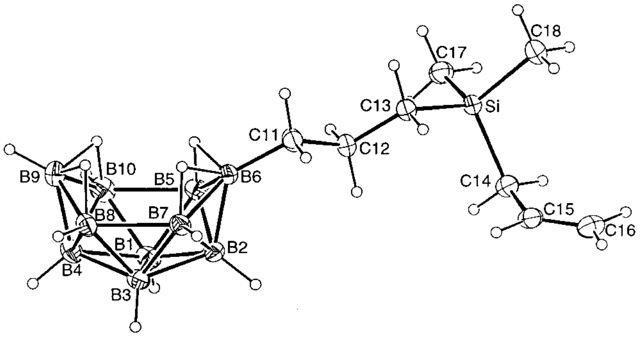

Figure 2. ORTEP drawing of the structure of 6-($CH_2{=}CHCH_2SiMe_2$-$(CH_2)_3$)-$B_{10}H_{13}$ (**5**). Selected bond lengths (Å) and angles (°): C15−C16, 1.320(3); C14−C15, 1.484(3); Si−C14, 1.890(2); B6−C11, 1.577(3); B5−B6, 1.803(3); B5−B10, 1.981(3); B9−B10, 1.784(4); B7−B8, 1.969(3); B6−B7, 1.798(3); C14−C15−C16, 126.0(2); C13−Si−C14, 110.74(9); C14−Si−C18, 109.33(10); C14−Si−C17, 108.12.

Likewise, the synthesis of **7** was achieved in an 85% isolated yield by reacting a 2:1 ratio of decaborane to diallyldimethylsilane for 12 days at 88 °C using 7.6 mol % $Cp_2Ti(CO)_2$ (13 total turnovers).

The ^{11}B NMR spectra observed for **6** and **7** are nearly identical to those of **4** and **5**, but the ^1H NMR spectra for **6** and **7** do not contain the vinyl proton resonances found in the later compounds. Likewise, their IR spectra do not have bands in the 1600 cm^{-1} region.

The structure of 6,6′-$(CH_2)_6$-$(B_{10}H_{13})_2$ was established by a single-crystal X-ray determination as shown in the ORTEP diagram in Figure 3. Both of the two independent molecules in the unit cell are shown in the figure. The structures differ only in the conformation of the linking alkyl group. Anti-Markovnikov addition at the 6-vertex of decaborane is again confirmed. All bond lengths and angles are in the normal ranges and comparable to those found in **5** and 6-Thx-$B_{10}H_{13}$.[12]

Reaction with $Si(CH_2CH{=}CH_2)_4$: Synthesis of $Si(6\text{-}(CH_2)_3\text{-}B_{10}H_{13})_4$. The unique, tetracage product, $Si(6\text{-}(CH_2)_3\text{-}B_{10}H_{13})_4$ (**8**) was obtained by the reaction of 4 equiv of decaborane with tetraallylsilane for 8 days at 90 °C in the

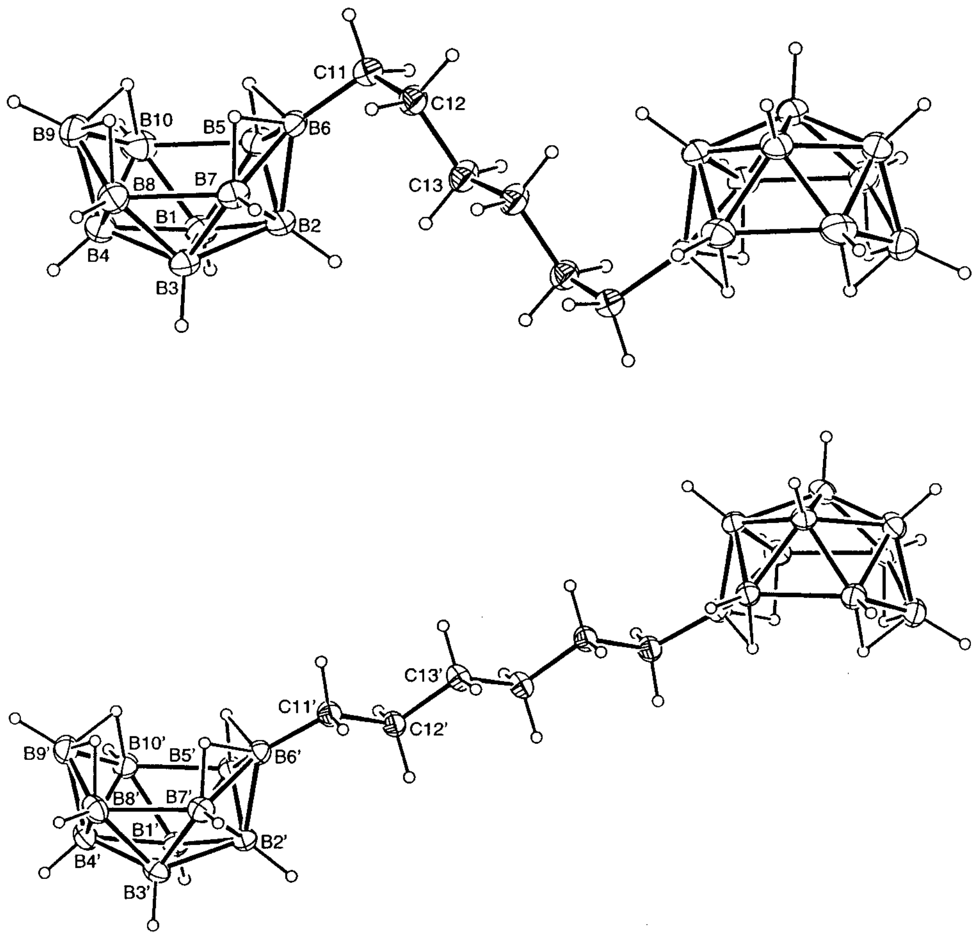

Figure 3. ORTEP drawing of the structure of 6,6′-$(CH_2)_6$-$(B_{10}H_{13})_2$ (**6**). Selected bond lengths (Å): B6−C11, 1.570(3); B5−B6, 1.802(4); B5−B10, 1.985(4); B9−B10, 1.781(5); B7−B8, 1.992(4); B6−B7, 1.794(4).

presence of 8.1 mol % $Cp_2Ti(CO)_2$ (12 total turnovers) (eq 8).

$$4B_{10}H_{14} + Si(CH_2CH{=}CH_2)_4 \xrightarrow{Cp_2Ti(CO)_2} \underset{\mathbf{8}}{Si(6\text{-}(CH_2)_3\text{-}B_{10}H_{13})_4} \quad (8)$$

The reaction progress was monitored by ^{11}B and ^{1}H NMR. Since the reaction involves the successive hydroboration of the four allyl groups, intermediate species were observed during the course of the reaction, but the reaction was not stopped until complete hydroboration was achieved. The final solid product was isolated by eluting the reaction mixture down a silica gel column with hexanes followed by toluene and was obtained in a 54% isolated yield. The ^{11}B and ^{1}H NMR and IR spectra observed for **8** are similar to those observed for 6,6′-$(CH_2)_6$-$(B_{10}H_{13})_2$.

The structure shown in the ORTEP representation (Figure 4) was confirmed by means of a single-crystal X-ray determination. As can be seen in the figure, complete hydroboration of tetraallylsilane was achieved to produce a tetradecaboranyl silane. The C−Si−C angles around the silicon center are approximately tetrahedral, ranging from 105° to 114°, but the four cages are not, in fact, tetrahedrally oriented. Instead, the four linking $-(CH_2)_3-$ chains adopt configurations in the solid state that allow the four cages to be nearly coplanar. This is clearly shown by the fact that the four angles B6A−Si−B6B (96.33(5)°), B6B−Si−B6C (65.43(5)°), B6C−Si−B6D (127.3-(5)°), and B6D−Si−B6A (77.31°(5)) sum to 366.37°, which is remarkably close to the 360° value expected for a planar structure. All other bond lengths and angles in **8** are comparable to those found in **5**, **6**, and 6-Thx-$B_{10}H_{13}$.[12]

Synthesis of an Asymmetrically Substituted Dialkyldecaborane. As discussed earlier, Mazighi and co-workers have shown that chloroplatinic acid and platinum bromide are effective catalysts for the hydroboration of olefins with decaborane to form products of the formula 6,9-R_2-$B_{10}H_{12}$.[3] The fact that the titanium and platinum catalysts give high yields of mono- and dialkyldecaboranes, respectively, suggested that these catalysts could be used in tandem to provide a route to asymmetrically substituted dialkyldecaboranes. Thus, following the synthesis of a 6-R-$B_{10}H_{13}$ compound with the titanocene-catalyzed reaction, a different substituent could be introduced at B(9) by reacting the monoalkyldecaborane with a second olefin in the presence of a platinum catalyst. With this aim in mind, the chloroplatinic acid-catalyzed reaction of 6-(n-C_8H_{17})-$B_{10}H_{13}$ (**2**), which was obtained from the $Cp_2Ti(CO)_2$-catalyzed reaction of decaborane with octene, with allylbenzene was examined. However, the first attempt to synthesize the expected 6-(n-C_8H_{17})-9-(C_6H_5-$(CH_2)_3$)-$B_{10}H_{12}$ product showed the platinum-catalyzed reaction to be surprisingly slow. Thus, after reaction for 22 h at 65 °C with 3.7 mol % catalyst, less than 50% conversion was observed (eq 9).

$$6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{13} + CH_2{=}CHCH_2\text{-}C_6H_5 \xrightarrow[22\text{ h, }65\text{ °C}]{3.7\text{ mol \% }H_2PtCl_6\cdot 6H_2O} \underset{\mathbf{9}}{6\text{-}(n\text{-}C_8H_{17})\text{-}9\text{-}(C_6H_5\text{-}(CH_2)_3)\text{-}B_{10}H_{12}} \ (<50\%\text{ conv}) \quad (9)$$

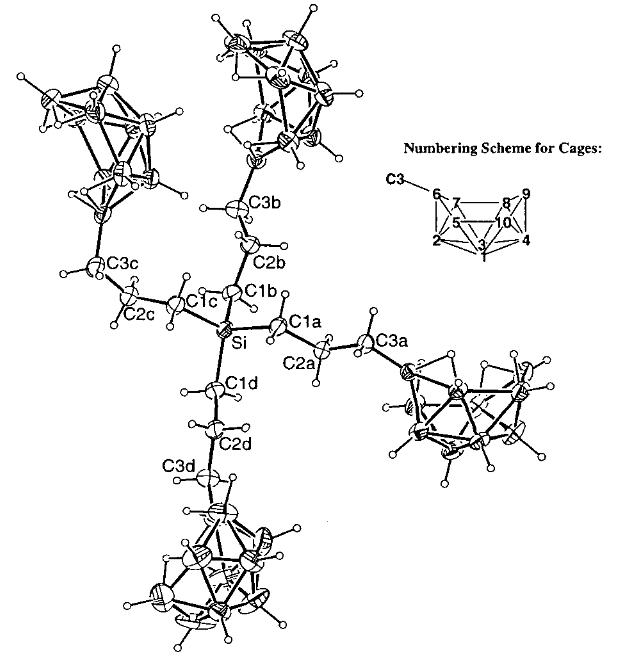

Figure 4. ORTEP drawing of the structure of $Si(6\text{-}(CH_2)_3\text{-}B_{10}H_{13})_4$ (**8**). Selected bond lengths (Å) and angles (°): Si−C1a, 1.883(3); C3a−B6a, 1.565(4); B5a−B6a, 1.806(4); B5a−B10a, 1.980(5); B9a−B10a, 1.780(5); B7a−B8a, 1.976(5); B6a−B7a, 1.794(5); C1a−Si−C1b, 111.34(13); C1a−Si−C1c, 105.29(13); C1a−Si−C1d, 110.04(13); C1b−Si−C1c, 109.02(12); C1b−Si−C1d, 107.00(13); C1c−Si−C1d, 114.22(14).

Such a result does not seem reasonable since, under similar conditions, a reaction of decaborane with excess olefin and chloroplatinic acid would have gone to completion to form the $6,9\text{-}R_2\text{-}B_{10}H_{12}$ product.

The initial steps in both the chloroplatinic acid-catalyzed hydrosilylation[14] and hydroboration[1,3] of olefins are thought to be similar and to involve the initial reduction of chloroplatinic acid (Pt^{IV}) to a catalytically active Pt^{II} species. Consistent with this step, an induction period is observed in both the chloroplatinic acid-catalyzed hydrosilylations[14] and polyborane hydroborations,[1,3] during which time the active Pt^{II} species is generated. The sluggish reaction of $6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{13}$ and allylbenzene with $H_2PtCl_6{\cdot}6H_2O$ suggested that the initial reduction step was slow. That is, in contrast to $B_{10}H_{14}$, the $6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{13}$ reactant apparently does not effectively reduce Pt^{IV} to the catalyically active Pt^{II} species. Supporting this idea, it was found that when a small amount of decaborane was added as an initiator to reactions with $6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{13}$, the induction period was greatly reduced, and excellent conversions to the $6\text{-}(n\text{-}C_8H_{17})\text{-}9\text{-}(C_6H_5\text{-}(CH_2)_3)\text{-}B_{10}H_{12}$ product **9** were observed (eq 10).

$$6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{13} + CH_2{=}CHCH_2\text{-}C_6H_5 \xrightarrow[14\text{ h, }65\ ^\circ C]{4.0\text{ mol \% } H_2PtCl_6{\cdot}6H_2O//B_{10}H_{14}\text{ init}} \underset{\mathbf{9}}{6\text{-}(n\text{-}C_8H_{17})\text{-}9\text{-}(C_6H_5\text{-}(CH_2)_3)\text{-}B_{10}H_{12}}\ (100\%\text{ conv}) \quad (10)$$

Likewise, when a small amount of Et_3SiH, which is known to reduce Pt^{IV} to Pt^{II} in chloroplatinic acid-catalyzed hydrosilylations,[14] was added to a similar reaction, the reaction was found to go to completion in only 7 h, with product **9** then obtained in 90% isolated yields (eq 11).

$$6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{13} + CH_2{=}CHCH_2\text{-}C_6H_5 \xrightarrow[7\text{ h, }65\ ^\circ C]{3.8\text{ mol \% } H_2PtCl_6{\cdot}6H_2O/Et_3SiH\text{ init}} \underset{\mathbf{9}}{6\text{-}(n\text{-}C_8H_{17})\text{-}9\text{-}(C_6H_5\text{-}(CH_2)_3)\text{-}B_{10}H_{12}}\ (100\%\text{ conv}) \quad (11)$$

Best results were obtained when a Pt^{II} source, 3.5 mol % $PtBr_2$, was used as the catalyst. No initiator was needed, and the reaction went to completion in only 4 h at 60 °C (28 total turnovers) (eq 12).

$$6\text{-}(n\text{-}C_8H_{17})\text{-}B_{10}H_{13} + CH_2{=}CHCH_2\text{-}C_6H_5 \xrightarrow[4\text{ h, }60\ ^\circ C]{3.5\text{ mol \% }PtBr_2} \underset{\mathbf{9}}{6\text{-}(n\text{-}C_8H_{17})\text{-}9\text{-}(C_6H_5\text{-}(CH_2)_3)\text{-}B_{10}H_{12}}\ (100\%\text{ conv}) \quad (12)$$

Workup of the reaction by simply filtering the reaction mixture through a silica gel column and activated carbon, followed by evaporation of volatiles, gave the final product in 97% isolated yield.

Discussion

The titanium-catalyzed decaborane−olefin hydroboration reactions provide a new route for the controlled, high-yield functionalization of decaborane that is complementary to the previously established platinum systems. Whereas $PtBr_2$ and $H_2PtCl_6{\cdot}6H_2O$ yield predominately dialkyldecaboranes,[3] the reactions employing dicarbonyltitanocene afford exclusively monosubstituted decaboranes. The titanium-catalyzed reactions are slow, often less than one turnover per hour (see Table 1); however, their high selectivities and yields coupled with the fact that they are simple, one-pot reactions give them significant advantages over the previously reported routes to $6\text{-}R\text{-}B_{10}H_{13}$ compounds.[12] The robustness of the catalyst also allows its use for the complete hydroboration of polyenes, as illustrated by the synthesis of the unique tetracage compound, $Si(6\text{-}(CH_2)_3\text{-}B_{10}H_{13})_4$ (**8**), and, as a result, may now enable efficient routes to dendritic materials based on the polyboranes.

Recent studies by a number of workers have clearly shown that the mechanistic steps involved in the early-metal-catalyzed hydroboration reactions of olefins with monoboranes[4] are distinct from those observed for late-transition-metal-catalyzed hydroboration reactions.[15] Thus, although both the platinum and titanium complexes catalyze decaborane−olefin hydroborations, they most probably do so by significantly different mechanistic steps.

A possible catalytic cycle for the reaction of decaborane with alkenes, based on Hartwig's proposed mechanism[4f] for the Cp_2TiMe_2- and $Cp_2Ti(CO)_2$-catalyzed hydroborations of alkenes and alkynes with catecholborane, is illustrated in Figure 5. Thermally induced loss of CO from $Cp_2Ti(CO)_2$ (**A**) would produce the initial coordinately unsaturated monocarbonyl complex $Cp_2Ti(CO)$ (**B**). With coordinately unsaturated late transition metals, boranes can react via oxidative addition of a BH group, but such a process is less likely with an early metal. In the case of the catecholborane reactions with Cp_2TiMe_2, the borane instead binds to the titanium to form a catalytically active σ-complex $Cp_2Ti\text{-}(\sigma\text{-}(H\text{-}BCat))_2$.[4b,e,f] Since, even in the absence of olefin, decaborane was observed to react with $Cp_2Ti(CO)_2$ to form an initial, highly reactive (and as yet uncharacterized) complex, the formation of either $Cp_2Ti\text{-}\sigma\text{-}(H\text{-}B_{10}H_{13})CO$ (**C**) or, with loss

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(14) Speir, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407−448.

(15) For recent reviews on metal-catalyzed hydroboration reactions, see: (a) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957−5026. (b) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179−1191.

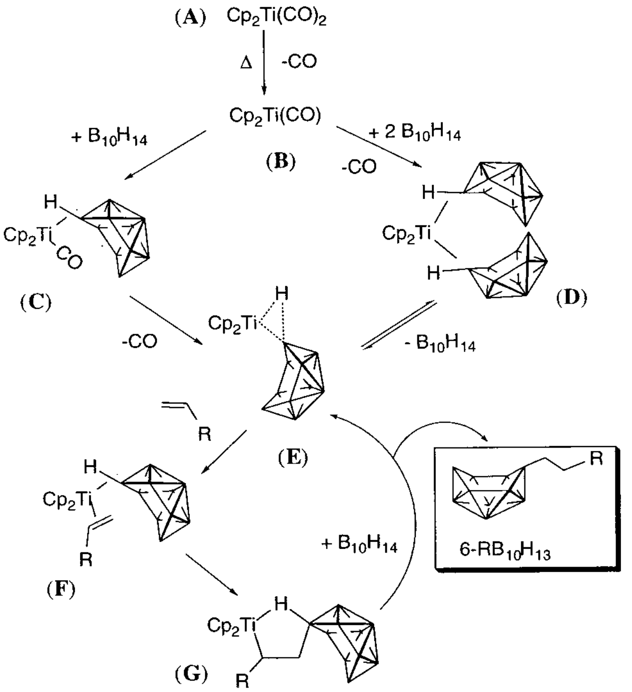

Figure 5. Possible reaction mechanism for titanium-catalyzed decaborane−olefin hydroborations.

of an additional CO, the Cp$_2$Ti-(σ-(H-B$_{10}$H$_{13}$))$_2$ (**D**) complex is reasonable. Dissociation of CO from **C**, or B$_{10}$H$_{14}$ from **D**, would generate the same coordinately unsaturated 16 e$^-$ complex **E**, which could then bind olefin to form the 18 e$^-$ complex **F**. Rearrangement of this formal Ti(II) complex to the Ti(IV) metallacyclopentane structure **G** could occur in a manner similar to that proposed for the catecholborane complex. Reductive elimination would yield the final 6-R-B$_{10}$H$_{13}$ product, with the remaining metal fragment then reacting with another equivalent of decaborane to regenerate **E** and continue the cycle.

The question then arises: Why do the platinum-catalyzed decaborane−olefin reactions yield 6,9-dialkyldecaboranes, while the titanium reactions yield exclusively, even under forcing conditions, monosubstituted 6-R-B$_{10}$H$_{13}$ products? Given the separation and opposite orientation of the 6 and 9 BH groups, sterics would seem to be an unimportant factor in these differences. Therefore, the answer to the question may lie in the differences in the modes of decaborane activation by late-metal and early-metal centers. Platinum(II) can activate boranes (or silanes) via an oxidative-addition step,[14] and for this process, it is unlikely that there is any significant difference in reactivity of the 9 B−H positions of B$_{10}$H$_{14}$ and 6-R-B$_{10}$H$_{13}$. As a result, dialkyl products, 6,9-R$_2$-B$_{10}$H$_{12}$, are produced in the platinum-catalyzed reactions. Under more forcing conditions, even higher alkylated products resulting from reactions at the other BH positions are obtained.[3] On the other hand, as discussed above, instead of undergoing oxidative addition, catecholborane is activated at the titanium center by forming the Cp$_2$Ti−(σ-(H-BCat))$_2$ σ-complex. Extended Hückel calculations[4b,e] on model compounds have provided evidence that the HBCat fragment, indeed, functions as a σ-donor from the B−H bond to the titanium LUMO d(x^2−y^2) orbital, but also that there is significant back-donation of electron density from the titanium HOMO d(xy) orbital to the vacant LUMO p-orbital centered on the boron that provides significant stabilization.[16] Thus, the stability of the Cp$_2$Ti(σ-H-BCat)$_2$ complex results from the fact that the catecholborane can function not only as a σ-donor but also as an acceptor.

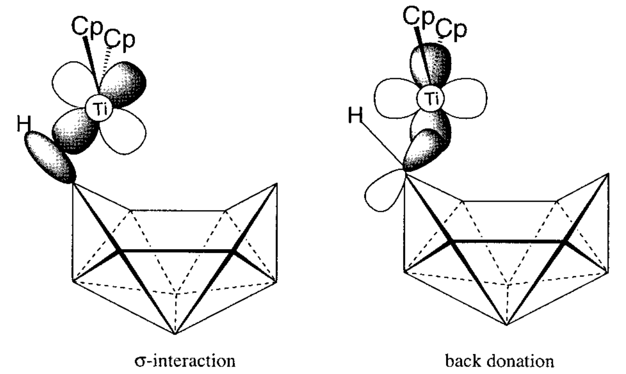

Figure 6. Possible synergistic bonding interactions between decaborane and the Cp$_2$Ti fragment.

As depicted in Figure 6, bonding interactions similar to those proposed for Cp$_2$Ti(σ-H-BCat)$_2$ can be envisioned in a decaborane σ-complexes such as **C** and **D**. Thus, both a σ-donation from the B−H bond to the titanium and back-donation from the titanium to an acceptor orbital centered on the B6(9) boron could be synergistic bonding components. Titanium-to-boron back-bonding at these sites is consistent with the fact that the decaborane 6 and 9 borons are known to be Lewis acidic. For example, as shown in eq 13, decaborane readily reacts with bases, such as dimethyl sulfide or acetonitrile, to form adducts at these positions.[17]

$$\mathrm{B_{10}H_{14} + 2SMe_2 \xrightarrow{\Delta} 6,9\text{-}B_{10}H_{12}(SMe_2)_2 + H_2} \qquad (13)$$

Since similar interactions are possible at both the 6 and 9 positions, the question then becomes: Why do the titanium-catalyzed reactions stop after substitution at the 6-position? That is, why does substitution at the 6-position affect reaction at the 9-position? Given again the separation of the 6 and 9 borons, an influence on the electronic properties of the B9 boron by a substituent introduced at the 6 boron might seem surprising. However, “antipodal” effects, in which a substituent on one side of a cluster strongly influences the chemical shift and/or chemical properties of a group on the opposite side of the cage, are well established[18] and are a consequence of the delocalized nature of cluster bonding. Consistent with the presence of such an antipodal effect in 6-R-B$_{10}$H$_{13}$, it was found (eq 14) in a series of experiments that 6-(n-octyl)-B$_{10}$H$_{13}$ was completely unreactive toward bases such as dimethyl sulfide or acetonitrile under conditions in which decaborane readily reacts to form 6,9-B$_{10}$H$_{12}$L$_2$ adducts. Thus, attachment of an alkyl group at the 6 boron results in a decrease in the Lewis acidity at the B9 site.

$$6\text{-}(n\text{-}\mathrm{C_8H_{17}})\text{-}\mathrm{B_{10}H_{13}} + \text{xs } \mathrm{SMe_2} \xrightarrow{\Delta} \text{No Reaction} \qquad (14)$$

This lower Lewis acidity of the B9 position of 6-R-B$_{10}$H$_{13}$ would thus be unfavorable for the formation of a Cp$_2$Ti(9-(σ-H-B$_{10}$H$_{12}$R)) complex, since the stabilization obtained from back-donation to the B9 boron would be decreased. Since such

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[16] Back-donation of the Ti d(xy) orbital into the B−H σ* orbital might also be possible, but the calculations reported[4e] by Hartwig et al. indicate that, at least for the Cp$_2$Ti(σ-H-BCat)$_2$ complex, the vacant boron p-orbital is significantly lower in energy.

[17] (a) Knoth, W. H.; Muetteries, E. L. *J. Inorg. Nucl. Chem.* **1961**, *20*, 66−72. (b) Cragg, R. H.; Fortuin, M. S.; Greenwood, N. N. *J. Chem. Soc. A* **1970**, 1817−1821. (c) Pace, R. J.; Williams, J.; Williams, R. L. *J. Chem. Soc.* **1961**, 2196−2204. (d) Hawthorne, M. F.; Pilling, R. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1967**, *89*, 1067−1074.

[18] See, for example: Hermánek, S. *Chem. Rev.* **1992**, *92*, 325−362 and references therein.

a complex is the intermediate in the proposed reaction scheme in Figure 5 that is required for the hydroboration of an olefin by the B9−H unit, reaction does not occur, and, as a result, monoalkyldecaboranes are the only product of the reaction.

Hartwig showed that with catecholborane, $Cp_2Ti(CO)_2$ was actually a better catalyst for the hydroboration of alkynes than alkenes.[4a] Unfortunately, we found no activity for the reactions of decaborane with alkynes. This is most likely due to the fact that the decaborane reactions require higher temperatures (>70 °C) than the catecholborane reactions (room temperature). Alkynes readily react at room temperature with $Cp_2Ti(CO)_2$ to form $Cp_2Ti(CO)(\eta^2\text{-}R_2C_2)$ complexes,[19] and such species are thought to be important initial intermediates in the catalyzed catecholborane alkyne reactions.[4a,f] However, above 30 °C and in the presence of excess alkyne, these complexes are known to decompose to $Cp_2Ti(C_4R_4)$ metallacycles.[18] Thus, the instability of required $Cp_2Ti(CO)(\eta^2\text{-}R_2C_2)$ intermediates at the temperatures required for the decaborane reactions prevents decaborane−alkyne hydroboration.

Cp_2TiMe_2 had also been found to be a better catalyst than $Cp_2Ti(CO)_2$ for the hydroboration of olefins with catecholborane.[4a] However, in our studies of the Cp_2TiMe_2-catalyzed reactions of decaborane with alkenes, little reaction was observed at room temperature. At higher temperatures, the formation of 6-R-$B_{10}H_{13}$ products was observed, but no temperature was found which would give complete conversion before catalyst decomposition.

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Supporting Information Available: Tables listing refined positional and thermal parameters, bond distances, and bond angles for compounds, **5**, **6**, **8**, and **10** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] (a) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *Dalton Trans.* **1978**, 1398−1403. (b) Fachinetti, G.; Floriani, C *J. Chem. Soc., Chem. Commun.* **1974**, 66−67.