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Iridium and Ruthenium Catalyzed Syntheses, Hydroborations, and Metathesis Reactions of Alkenyl-Decaboranes

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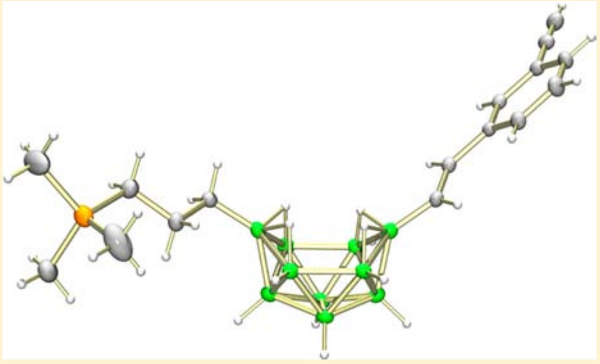
Supporting Information

ABSTRACT: The selective syntheses of new classes of 6,9-dialkenyl- and 6-alkenyl-decaboranes and 6-alkyl-9-alkenyl-decaboranes have been achieved via iridium and ruthenium catalyzed decaborane and 6-alkyl-decaborane alkyne-hydroborations. Reactions employing $[Cp^*IrCl_2]_2$ and $[RuCl_2(p\text{-cymene})]_2$ precatalysts gave β-E-alkenyl-decaboranes, while the corresponding reactions with $[RuI_2(p\text{-cymene})]_2$ gave the α-alkenyl-decaborane isomers, with the differences in product selectivity suggesting quite different mechanistic steps for the catalysts. The alkenyl-decaboranes were easily converted to other useful derivatives, including coupled-cage and functionally substituted compounds, via iridium-catalyzed hydroborations and ruthenium-catalyzed homo and cross olefin-metathesis reactions.



INTRODUCTION

We have previously demonstrated that transition metal complexes can be employed to catalyze polyborane hydroborations of both acetylenes and olefins to yield their alkenyl- or alkyl-substituted derivatives.[1,2] For decaborane, we found that platinum-catalyzed decaborane-olefin hydroborations employing H_2PtCl_6 and $PtBr_2$ precatalysts produce 6,9-dialkyl-decaboranes,[2b] while corresponding titanium-catalyzed reactions employing $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ selectively form monosubstituted 6-alkyl-decaboranes.[2d,e] Metal-catalyzed decaborane alkyne-hydroborations could provide high yield routes to synthetically useful alkenyl-decaborane derivatives; however, only recently have we been successful in finding catalysts for such reactions.[1j] In this paper, we report that $[Cp^*IrCl_2]_2$ and $[RuX_2(p\text{-cymene})]_2$ (X = Cl or I) complexes can be employed to catalyze the hydroboration reactions of terminal alkynes with both decaborane and 6-alkyl-decaboranes to give, depending upon the catalyst, catalyst loadings and reaction times, either the β-E or α-olefin isomers of the 6,9-dialkenyl or 6-alkenyl-decaboranes and 6-alkyl-9-alkenyl-decaboranes, respectively. Furthermore, we demonstrate that these alkenyl-decaboranes can be readily converted to other useful derivatives, including coupled-cage and functionally substituted compounds, with the aid of either iridium-catalyzed hydroboration or ruthenium-catalyzed homo and cross olefin-metathesis reactions.

EXPERIMENTAL SECTION

Unless otherwise noted, all reactions and manipulations were performed in dry glassware under nitrogen or argon atmospheres using the high-vacuum or inert-atmosphere techniques described by Shriver and Drezdzon.[3]

Materials. $[Cp^*IrCl_2]_2$, $[RuX_2(p\text{-cymene})]_2$ (X = Cl or I), $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, $[RuI_2(p\text{-cymene})]_2$ and Grubbs' II catalyst (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(phenylmethylene)(tricyclohexylphosphine)ruthenium) were used as received (Strem). The 1-octyne, 4-octyne, phenylacetylene, trimethylsilylacetylene, allyltrimethylsilane, 1-pentene, 6-bromo-1-hexene, allylchloride (Aldrich), 5-chloro-1-pentyne, 4-bromo-1-butyne, 1,3-diethynylbenzene, 1-penten-4-yne (GFS Chemicals), and 3-cyclohexylpropyne (Alfa-Aesar) were dried over CaH_2 and vacuum transferred prior to use. Decaborane (Callery) was freshly sublimed before use. Acetylene gas was obtained from Airgas and was purified by passage through a sulfuric acid bubbler, Drierite and KOH-pellets before use. The 6-$\{(CH_3)_3Si(CH_2)_3\}$-$B_{10}H_{13}$ and 6-$\{CH_3(CH_2)_4\}$-$B_{10}H_{13}$ were prepared according to the literature method.[2d,e] Reaction solvents (Fisher) were dried using standard procedures. Other solvents (Fisher) were used as received unless otherwise noted. Prior to use, silica gel (Fisher) was saturated with acetic acid vapors[4] for 12 h in an evacuated desiccator at room temperature, followed by vacuum drying at 120 °C for 5 h. The high pressure reaction vessel (88 mL, catalog no. 110207 0003, Andrew's Glass Company) used for the acetylene reactions was fitted with a stainless steel needle Swagelok valve (part no. SS-ORM2).

Physical Measurements. ^1H NMR spectra at 400.1 and 500 MHz and ^{11}B NMR spectra at 128.4 and 160.5 MHz were obtained on Bruker DMX 400 and DRX 500 spectrometers, respectively. All ^{11}B NMR chemical shifts are referenced to external $BF_3\cdot OEt_2$ (0.00 ppm) with a negative sign indicating an upfield shift. All ^1H NMR chemical shifts were measured relative to residual protons in the lock solvents and are referenced to Me_4Si (0.00 ppm). High and low-resolution mass spectra (HRMS and LRMS) using negative chemical ionization (NCI) techniques were recorded on a Micromass Autospec Spectrometer. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer using KBr salt plates. Elemental analyses were performed at Robertson Microlit Laboratories, Madison,

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NJ, or at the Microanalytical Facility at UC Berkeley, California. Melting points were obtained on a standard melting point apparatus and are uncorrected.

Control Experiments. ^{11}B NMR analyses of the following decaborane-alkyne mixtures showed no reaction. **1-Octyne**. A 100 mL round bottomed flask equipped with a high-vacuum Teflon stopcock was charged with 1-octyne (0.8 mL, 5.42 mmol) and decaborane (0.06 g, 0.49 mmol) and then stirred in an oil bath at 45 °C for 8 h. **Trimethylsilylacetylene**. Trimethylsilylacetylene (0.21 mL, 1.49 mmol), decaborane (0.06 g, 0.49 mmol), 45 °C, 3 h. **Acetylene**. A 88 mL high-pressure reaction vessel was charged with decaborane (0.12 g, 0.98 mmol), acetylene (~250 mL, ~3.11 atm, ~10.5 mmol) and ~4 mL of dry toluene and then stirred in an oil bath at 45 °C for 3 h.

Decaborane Alkyne-Hydroboration Reactions with $[Cp^*IrCl_2]_2$. *1-Octyne.* A 100 mL round bottomed flask equipped with a high-vacuum Teflon stopcock was charged under an inert atmosphere with $[Cp^*IrCl_2]_2$ (0.136 g, 0.17 mmol), 1-octyne (0.44 mL, 2.98 mmol), decaborane (0.120 g, 0.98 mmol) and ~2 mL of dry toluene. After the reaction was stirred in an oil bath at 45 °C for 3 h, ^{11}B NMR analysis showed complete conversion to **1**, and the reaction was stopped and exposed to air. The reaction mixture was flash-filtered through a short silica gel column. Separation by silica gel column chromatography with hexanes as eluent gave 0.277 g (0.81 mmol, 83%) of **1**.

6,9-(E-$CH_3(CH_2)_5CH{=}CH)_2$-$B_{10}H_{12}$ (1). Oil. Exact mass $^{12}C_{16}{}^{1}H_{42}{}^{11}B_{10}$: *m/z* calcd, 344.4217; measd, 344.4202. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 19.4 (s, 2, B6,9), 7.0 (d, 2, B1,3, *J* 138), −4.5 (d, 4, B5,7,8,10, *J* 154), −35.7 (d, 2, B2,4, *J* 151). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 6.35 (td, 2, =CH, *J* 18, 6), 5.92 (d, 2, =CH, *J* 18), 2.14 (m, 4, CH_2), 1.37 (m, 16, CH_2), 0.97 (t, 6, CH_3, *J* 7), −1.28 (br, s, 4, BHB). IR (KBr plates, cm^{-1}): 2958 (s), 2926 (vs), 2855 (s), 2571 (vs), 1629 (s), 1521 (w), 1466 (s), 1397 (m), 1379 (m), 1313 (w), 1261(s), 1197 (w), 1151 (m), 1128 (s), 1104 (s), 1017 (s), 994 (s), 960 (m), 903 (w), 866 (w), 800 (s), 759 (w), 723 (m), 706 (m), 682 (m), 664 (w), 637 (w).

Trimethylsilylacetylene. $[Cp^*IrCl_2]_2$ (0.012 g, 0.015 mmol), trimethylsilylacetylene (0.21 mL, 1.49 mmol), decaborane (0.06 g, 0.49 mmol), 45 °C, 3 h. Silica gel chromatography with hexanes. Recrystallized from *n*-heptane. Yield: 90% (0.140 g, 0.44 mmol) of **2**.

6,9-(E-$(CH_3)_3SiCH{=}CH)_2$-$B_{10}H_{12}$ (2). Solid. mp 185 °C. Anal. Calcd for $C_{10}H_{34}B_{10}Si_2$: C, 37.69; H, 10.75. Found: C, 37.86; H, 10.48. Exact mass $^{12}C_{10}{}^{1}H_{34}{}^{11}B_{10}{}^{28}Si_2$: *m/z* calcd, 320.3129; measd, 320.3140. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 19.8 (s, 2, B6,9), 8.0 (d, 2, B1,3, *J* 172), −3.6 (d, 4, B5,7,8,10, *J* 138), −35.2 (d, 2, B2,4, *J* 161). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 6.87 (d, 2, =CH, *J* 21), 6.68 (d, 2, =CH, *J* 21), 0.11 (s, 18, $(CH_3)_3Si$), −1.37 (br, 4, BHB). IR (KBr plates, cm^{-1}): 3055 (m), 2987 (m), 2959 (s), 2899 (m), 2686 (w), 2576 (vs), 2560 (vs), 2306 (w), 1972 (w), 1917 (w), 1888 (w), 1582 (w), 1505 (w), 1471 (m), 1417 (m), 1265 (s), 1249 (vs), 1202 (s), 1144 (w), 1111 (m), 1002 (s), 958 (w), 897 (m), 868 (s), 836 (vs), 797 (m), 736 (s), 704 (s).

Phenylacetylene. $[Cp^*IrCl_2]_2$ (0.120 g, 0.15 mmol), phenylacetylene (0.17 mL, 1.55 mmol), decaborane (0.066 g, 0.54 mmol), 45 °C, 3 h. Silica gel chromatography with hexanes. Yield: 87% (0.155 g, 0.47 mmol) of **3**.

6,9-(E-$(C_6H_5{-}CH{=}CH)_2$-$B_{10}H_{12}$ (3). Oil. Exact mass $^{12}C_{16}{}^{1}H_{26}{}^{11}B_{10}$: *m/z* calcd, 328.2965; measd, 328.3272. ^{11}B NMR (CD_2Cl_2, ppm, *J* = Hz): 20.6 (s, 2, B6,9), 7.1 (d, 2, B1,3, *J* 149), −4.0 (d, 4, B5,7,8,10, *J* 149), −35.2 (d, 2, B2,4, *J* 137). ^{1}H NMR (CD_2Cl_2, ppm, *J* = Hz): 7.59−7.32 (m, 10, -C_6H_5), 7.21 (d, 2, =CH, *J* 17), 6.76 (d, 2, =CH, *J* 19), −0.76 (br, 4, BHB). IR (KBr plates, cm^{-1}): 3025 (w), 2925 (w), 2569 (s), 1948 (w), 1887 (w), 1715 (w), 1614 (m), 1575 (w), 1494 (m), 1447 (m), 1393 (m), 1335 (m), 1277 (w), 1116 (m), 1073 (w), 977 (m), 899 (w), 837 (w), 747 (s), 689 (s).

4-Bromo-1-butyne. $[Cp^*IrCl_2]_2$ (0.154 g, 0.193 mmol), 4-bromo-1-butyne (0.14 mL, 1.49 mmol), decaborane (0.06 g, 0.49 mmol), 45 °C, 3 h. Silica gel chromatography with hexanes. Recrystallized from *n*-pentane. Yield: 39% (0.073 g, 0.19 mmol) of **4**.

6,9-(E-$Br(CH_2)_2CH{=}CH)_2$-$B_{10}H_{12}$ (4). Solid. Decomposed without melting. Exact mass $^{12}C_8{}^{1}H_{24}{}^{11}B_{10}{}^{79}Br_2$: *m/z* calcd, 388.1175; measd, 388.1164. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 19.8 (s, 2, B6,9), 8.0 (d, 2, B1,3, *J* 141), −3.4 (d, 4, B5,7,8,10, *J* 149), −35.2 (d, 2, B2,4, *J* 156). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 5.98 (td, 2, =CH, *J* 18, 8), 5.71 (d, 2, =CH, *J* 17), 2.91 (t, 4, CH_2Br, *J* 7), 2.25 (m, 4, CH_2), −1.52 (br, 4, BHB). IR (KBr plates, cm^{-1}): 3203 (w), 3004 (w), 2963 (m), 2925 (w), 2853 (w), 2569 (vs), 1973 (w), 1919 (w), 1887 (w), 1718 (w), 1631 (s), 1527 (m), 1477 (m), 1433 (s), 1418 (s), 1335 (m), 1265 (s), 1254 (s), 1209 (s), 1152 (m), 1123 (s), 1074 (m), 1062 (m), 1041 (m), 995 (s), 982 (s), 906 (m), 838 (m), 706 (m), 681 (m), 640 (m).

5-Chloro-1-pentyne. $[Cp^*IrCl_2]_2$ (0.110 g, 0.14 mmol), 4-chloro-1-pentyne (0.16 mL, 1.51 mmol), decaborane (0.06 g, 0.49 mmol), 45 °C, 3 h. Chromatography with hexanes. Yield: 37% (0.058 g, 0.18 mmol) of **5**.

6,9-(E-$Cl(CH_2)_3CH{=}CH)_2$-$B_{10}H_{12}$ (5). Oil. Exact mass $^{12}C_{10}{}^{1}H_{28}{}^{11}B_{10}{}^{35}Cl_2$: *m/z* calcd, 328.2499; measd, 328.2492. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 20.1 (s, 2, B6,9), 7.8 (d, 2, B1,3, *J* 146), −3.6 (d, 4, B5,7,8,10, *J* 149), −35.2 (d, 2, B2,4, *J* 149). ^{1}H NMR (C_6D_6, ppm *J* = Hz): 6.06 (td, 2, =CH, *J* 18, 7), 5.76 (d, 2, =CH, *J* 17), 3.11 (t, 4, CH_2Cl, *J* 7), 2.01 (m, 4, CH_2), 1.49 (m, 4, CH_2), −1.43 (br, 4, BHB). IR (KBr plates, cm^{-1}): 2959 (m), 2933 (m), 2864 (w), 2571 (m), 1717 (m), 1638 (m), 1441 (m), 1365 (m), 1288 (m), 1124 (m), 1074 (m), 996 (m), 799 (m), 724 (m), 651 (m).

Acetylene. A 88 mL high-pressure reaction vessel equipped with a Swagelok needle valve was charged under an inert atmosphere with $[Cp^*IrCl_2]_2$ (0.160 g, 0.20 mmol), decaborane (0.234 g, 1.91 mmol), and ~4 mL of dry toluene. A 500 mL flask equipped with a high-vacuum Teflon stopcock was filled with purified acetylene at room temperature (~6.22 atm, ~20.1 mmol). The acetylene was then vacuum transferred to the liquid-nitrogen cooled high-pressure reaction vessel. After the reaction mixture was stirred in an oil bath at 45 °C for 3 h, it was recharged under inert atmosphere with additional $[Cp^*IrCl_2]_2$ (0.158 g, 0.20 mmol) and acetylene (~20.1 mmol). After another 3 h stirring at 45 °C, another charge of $[Cp^*IrCl_2]_2$ (0.160 g, 0.20 mmol) and acetylene (~20.1 mmol) was added, and the reaction continued for 3 h more at 45 °C. The reaction was then stopped and the reaction mixture exposed to air. The ^{11}B NMR spectrum of the mixture showed complete conversion to **6**. The reaction mixture was then flash-filtered through a short silica gel column. Separation by silica gel column chromatography with *n*-pentane as eluent gave 0.041 g (0.24 mmol, 13%) of **6**.

6,9-($CH_2{=}CH)_2$-$B_{10}H_{12}$ (6). Exact mass $^{12}C_4{}^{1}H_{18}{}^{11}B_{10}$: *m/z* calcd, 176.2339; measd, 176.2321. ^{11}B NMR (C_6D_6, ppm *J* = Hz): 19.8 (s, 2, B6,9), 8.3 (d, 2, B1,3, *J* 142), −3.1 (d, 4, B5,7,8,10, *J* 160), −35.2 (d, B2,4, *J* 160). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 6.09 (m, 2H, =CH), 5.67 (m, 4H, =CH), −1.59 (br, 4, BHB). IR (KBr plates, cm^{-1}): 3069 (w), 2965 (m), 2937 (m), 2878 (w), 2573 (vs), 1964 (w), 1910 (w), 1708 (w), 1608 (w), 1527 (m), 1478 (m), 1413 (s), 1285 (w), 1260 (w), 1141 (w), 1112 (m), 994 (vs), 955 (s), 900 (m), 831 (m), 770 (w), 722 (m), 706 (m), 681 (m).

Decaborane Alkyne-Hydroboration Reactions with $[RuCl_2(p\text{-}cymene)]_2$. *1-Octyne.* $[RuCl_2(p\text{-}cymene)]_2$ (0.129 g, 0.21 mmol), 1-octyne (0.88 mL, 5.97 mmol), decaborane (0.242 g, 1.98 mmol), 45 °C, 3 h. Silica gel chromatography with hexanes. Unreacted decaborane (0.033 g, 0.27 mmol) removed by sublimation. Yield: 8% (0.047 g, 0.14 mmol) of **1** and 42% (0.166 g, 0.71 mmol) of **7**.

6-(E-$CH_3(CH_2)_5CH{=}CH)$-$B_{10}H_{13}$ (7). Oil. Exact mass $^{12}C_8{}^{1}H_{28}{}^{11}B_{10}$: *m/z* calcd, 234.3122; measd, 234.3138. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 21.9 (s, 1, B6), 9.3 (br, 2, B1,3), 8.0 (br, 1, B9), 0.4 (d, 2, B8,10, *J* 133), −5.5 (d, 2, B5,7, *J* 144), −32.9 (d, 1, B2, *J* 153), −38.7 (d, 1, B4, *J* 146). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 6.27 (td, 1, =CH, *J* 18, 6), 5.84 (d, 1, =CH, *J* 18), 2.04 (m, 2, CH_2), 1.30 (m, 8, CH_2), 0.91 (t, 3, CH_3, *J* 6), −1.60 (br, s, 2, BHB), −2.56 (br, s, 2, BHB). IR (KBr plates, cm^{-1}): 2956 (m), 2926 (s), 2855 (m), 2576 (s), 1628 (m), 1557 (w), 1498 (m), 1465 (m), 1276 (m), 1260 (m), 1129 (m), 1002 (s), 812 (w), 750 (s), 685 (w).

Decaborane Alkyne-Hydroboration Reactions with $[RuI_2(p\text{-}cymene)]_2$. *1-Octyne.* $[RuI_2(p\text{-}cymene)]_2$ (0.100 g, 0.10 mmol), 1-

octyne (0.88 mL, 5.97 mmol), decaborane (0.241 g, 1.97 mmol), 45 °C, 24 h. Silica gel chromatography with hexanes. Yield: 95% (0.639 g, 1.87 mmol) of **8**.

*6,9-$[H_2C{=}C\{(CH_2)_5CH_3\}]_2$-$B_{10}H_{12}$ (**8**).* Oil. Exact mass $^{12}C_{16}{}^{1}H_{42}{}^{11}B_{10}$: *m/z* calcd, 344.4217; measd, 344.4228. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 21.2 (s, 2, B6,9), 8.2 (d, 2, B1,3, *J* 146), −3.9 (d, 4, B5,7,8,10, *J* 137), −35.5 (d, 2, B2,4, *J* 155). ^1H NMR (C_6D_6, ppm, *J* = Hz): 5.44 (s, 2, $=CH_2$), 5.42 (s, 2, $=CH_2$), 2.27 (t, 4, CH_2, *J* 8), 1.53 (m, 4, CH_2), 1.31 (m, 12, CH_2), 0.92 (t, 6, CH_3, *J* 7), −1.19 (br, s, 4, BHB). IR (KBr plates, cm^{-1}): 3061 (w), 2957 (s), 2927 (vs), 2856 (s), 2575 (vs), 1609 (w), 1523 (w), 1466 (s), 1410 (m), 1379 (m), 1241 (w), 1210 (w), 1101 (w), 1054 (w), 996 (s), 958 (m), 924 (s), 884 (m), 826 (m), 723 (m), 708 (m), 681 (m).

In a separate experiment: $[RuI_2(p\text{-cymene})]_2$ (0.027 g, 0.03 mmol), 1-octyne (0.15 mL, 1.02 mmol), decaborane (0.241 g, 1.97 mmol), 45 °C, 24 h. Unreacted decaborane was removed by sublimation (0.049 g, 0.40 mmol) followed by silica gel column chromatography with hexanes. Yield: 31% (0.112 g, 0.48 mmol) of **9** and 16% (0.084 g, 0.25 mmol) of **8**.

*6-$[H_2C{=}C\{(CH_2)_5CH_3\}]$-$B_{10}H_{13}$ (**9**).* Oil. Exact mass $^{12}C_8{}^{1}H_{28}{}^{11}B_{10}$: *m/z* calcd, 234.3121; measd, 234.3093. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 20.6 (s, 1, B6), 8.4 (br, 2, B1,3), 7.1 (br, 1, B9), −1.3 (d, 2, B8,10, *J* 151), −6.3 (d, 2, B5,7, *J* 151), −34.9 (d, 1, B2, *J* 151), −39.9 (d, 1, B4, *J* 151). ^1H NMR (C_6D_6, ppm, *J* = Hz): 5.43 (s, 1, $=CH_2$), 5.42 (s, 1, $=CH_2$), 2.27 (t, 2, CH_2, *J* 8), 1.53 (m, 2, CH_2), 1.31 (m, 6, CH_2), 0.91 (t, 3, CH_3, *J* 7), −1.53 (s, 2, BHB), −2.60 (s, 2, BHB). IR (KBr plates, cm^{-1}): 3062 (w), 2957 (m), 2928 (s), 2856 (m), 2579 (vs), 1608 (w), 1553 (w), 1498 (m), 1457 (m), 1409 (m), 1377 (w), 1101 (m), 1053 (m), 1002 (s), 958 (m), 929 (m), 861 (m), 834 (m), 810 (m), 722 (m), 706 (m), 687 (m).

3-Cyclohexylpropyne. $[RuI_2(p\text{-cymene})_2]_2$ (0.100 g, 0.10 mmol), 3-cyclohexylpropyne (0.87 mL, 6.02 mmol), decaborane (0.241 g, 1.97 mmol), 45 °C, 21 h. Silica gel chromatography with hexanes. Recrystallized from *n*-heptane. Yield: 55% (0.395 g, 1.08 mmol) of **10**.

*6,9-$[H_2C{=}C\{CH_2(C_6H_{11})\}]_2$-$B_{10}H_{12}$ (**10**).* Solid. mp 78−80 °C. Anal. Calcd for $C_{18}H_{42}B_{10}$: C, 58.97; H, 11.55. Found: C, 58.82; H, 11.66. Exact mass $^{12}C_{18}{}^{1}H_{42}{}^{11}B_{10}$: *m/z* calcd, 368.4217; measd, 368.4237. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 21.1 (s, 2, B6,9), 8.2 (d, 2, B1,3, *J* 145), −3.8 (d, 4, B5,7,8,10, *J* 137), −35.4 (d, 2, B2,4, *J* 154). ^1H NMR (C_6D_6, ppm, *J* = Hz): 5.47 (s, 2, $=CH_2$), 5.36 (s, 2, $=CH_2$), 2.17 (d, 4, CH_2, *J* 7), 1.77 (m, 4, CH_2), 1.67 (m, 8, CH_2), 1.21 (m, 6, CH_2), 0.86 ppm (m, 4, CH_2), −1.16 (br, 4, BHB). IR (KBr plates, cm^{-1}): 3059 (w), 2922 (vs), 2851 (s), 2663 (w), 2570 (s), 1705 (w), 1607 (w), 1480 (w), 1448 (m), 1397 (m), 1328 (m), 1262 (m), 1216 (m), 1095 (m), 1019 (m), 997 (m), 964 (w), 925 (w), 891 (w), 843 (w), 822 (w), 805 (w), 736 (w), 708 (w).

4-Bromo-1-butyne. $[RuI_2(p\text{-cymene})_2]_2$ (0.137 g, 0.14 mmol), 4-bromo-1-butyne (0.14 mL, 1.49 mmol), decaborane (0.06 g, 0.49 mmol), 45 °C, 24 h. Silica gel chromatography with hexanes. Yield: 67% (0.130 g, 0.33 mmol) of **11**.

*6,9-$[H_2C{=}C(CH_2)_2Br]_2$-$B_{10}H_{12}$ (**11**).* Oil. Exact mass $^{12}C_8{}^{1}H_{24}{}^{11}B_{10}{}^{79}Br_2$: *m/z* calcd, 388.1175; measd, 388.1172. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 20.6 (s, 2, B6,9), 7.8 (d, 2, B1,3, *J* 150), −3.5 (d, 4, B5,7,8,10, *J* 154), −34.8 (d, 2, B2,4, *J* 156). ^1H NMR (C_6D_6, ppm, *J* = Hz): 5.50 (s, 2, $=CH_2$), 5.23 (s, 2, $=CH_2$), 3.07 (t, 4, CH_2Br, *J* 7), 2.46 (t, 4, CH_2, *J* 7), −1.19 (br, 4, BHB). IR (KBr plates, cm^{-1}): 3008 (w), 2963 (m), 2569 (vs), 1716 (m), 1609 (w), 1523 (w), 1477 (m), 1431 (m), 1416 (m), 1325 (w), 1305 (w), 1288 (m), 1261 (m), 1210 (m), 1121 (w), 1055 (w), 995 (s), 958 (w), 934 (m), 830 (w), 707 (w), 682 (m).

5-Chloro-1-pentyne. $[RuI_2(p\text{-cymene})_2]_2$ (0.20 g, 0.20 mmol), 5-chloro-1-pentyne (0.16 mL, 1.51 mmol), decaborane (0.064 g, 0.52 mmol), 45 °C, 24 h. Silica gel chromatography with hexanes. Yield: 90% (0.154 g, 0.47 mmol) of **12**.

*6,9-$[H_2C{=}C(CH_2)_3Cl]_2$-$B_{10}H_{12}$ (**12**).* Oil. Exact mass $^{12}C_{10}{}^{1}H_{28}{}^{11}B_{10}{}^{35}Cl_2$: *m/z* calcd, 328.2499; measd. 328.2483. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 21.4 (s, 2, B6,9), 8.8 (d, 2, B1,3, *J* 151), −3.4 (d, 4, B5,7,8,10, *J* 151), −35.0 (d, 2, B2,4, *J* 157). ^1H NMR (C_6D_6, ppm): 5.39 (s, 2, $=CH_2$), 5.30 (s, 2, $=CH_2$), 3.16 (t, 4, CH_2Cl, *J* 6), 2.26 (t, 4, CH_2, *J* 8), 1.70 (m, 4, CH_2), −1.34 (br, 4, BHB). IR (KBr plates, cm^{-1}): 3063 (w), 2994 (w), 2957 (m), 2938 (m), 2865 (w), 2573 (vs), 1911 (w, br), 1706 (w), 1630 (w), 1608 (w), 1527 (w), 1472 (w), 1442 (s), 1414 (m), 1354 (w), 1305 (w), 1292 (m), 1258 (w), 1196 (w), 1150 (w), 1138 (w), 1124 (w), 1107 (w), 1060 (w), 996 (s), 959 (w), 930 (m), 888 (w), 826 (w), 775 (w), 724 (m), 709 (w), 682 (m), 651 (m).

6-Alkyl-decaborane Alkyne-Hydroboration Reactions with $[Cp^*IrCl_2]_2$. *6-$\{(CH_3)_3Si(CH_2)_3\}$-$B_{10}H_{13}$ and phenylacetylene.* $[Cp^*IrCl_2]_2$ (0.034 g, 0.04 mmol), phenylacetylene (0.07 mL, 0.64 mmol), 6-$\{(CH_3)_3Si(CH_2)_3\}$-$B_{10}H_{13}$ (0.102 g, 0.43 mmol), 45 °C, 3 h. Silica gel chromatography with hexanes. Recrystallized from *n*-pentane. Yield: 77% (0.113 g, 0.33 mmol) of **13**.

*6-$\{(CH_3)_3Si(CH_2)_3\}$-9-(E-$C_6H_5CH{=}CH$)-$B_{10}H_{12}$ (**13**).* Solid. mp 102−104 °C. Anal. Calcd. for $C_{14}H_{34}B_{10}Si_1$: C, 49.66; H, 10.12. Found: C, 49.71; H, 10.31. Exact mass $^{12}C_{14}{}^{1}H_{34}{}^{11}B_{10}{}^{28}Si_1$: *m/z* calcd, 340.3360; measd, 340.3373. ^{11}B NMR (CD_2Cl_2, ppm, *J* = Hz): 24.2 (s, 1, B6), 20.3 (s, 1, B9), 7.5 (d, 2, B1,3, *J* 144), −2.3 (d, 2, B5,7 or 8,10, *J* 151), −4.4 (d, 2, B5,7 or 8,10, *J* 170), −35.7 (d, 1, B2 or B4, *J* 137), −36.7 (d, 1, B2 or B4, *J* 119). ^1H NMR (CD_2Cl_2, ppm, *J* = Hz): 7.49−7.30 (m, 5, -C_6H_5), 7.17 (d, 2, $=CH$, *J* 18), 6.71 (d, 2, $=CH$, *J* 8.8), 1.59 (m, 2, CH_2), 1.45 (m, 2, CH_2), 0.62 (t, 2, CH_2), 0.01 (s, 9, CH_3), −0.89 (br, 2, BHB), −1.41 (br, 2, BHB). IR (KBr plates, cm^{-1}): 3408 (m, br), 2952 (w), 2922 (w), 2570 (s), 1615 (m), 1576 (w), 1524 (w), 1495 (w), 1449 (w), 1408 (m), 1336 (w), 1248 (m), 1162 (w), 1116 (m), 998 (s), 976 (m), 906 (w), 861 (s), 836 (vs), 745 (m), 689 (s).

6-$\{(CH_3)_3Si(CH_2)_3\}$-$B_{10}H_{13}$ and 1,3-diethynylbenzene. $[Cp^*IrCl_2]_2$ (0.075 g, 0.094 mmol), 1,3-diethynylbenzene (0.2 mL, 1.50 mmol), 6-$\{(CH_3)_3Si(CH_2)_3\}$-$B_{10}H_{13}$ (0.126 g, 0.53 mmol), 45 °C, 3 h. Silica gel chromatography with hexanes. Recrystallized from *n*-pentane. Yield: 32% (0.06 g, 0.17 mmol) of **14**.

*6-$\{(CH_3)_3Si(CH_2)_3\}$-9-\{E-3-$HC{\equiv}C{-}C_6H_4$-1-$CH{=}CH$\}-$B_{10}H_{12}$ (**14**).* Solid. mp 100−104 °C. Anal. Calcd. for $C_{16}H_{34}B_{10}Si_1$: C, 52.99; H, 9.45. Found: C, 53.19; H, 9.09. Exact mass $^{12}C_{16}{}^{1}H_{34}{}^{11}B_{10}{}^{28}Si_1$: *m/z* calcd, 364.3360; measd, 364.3340. ^{11}B NMR (CD_2Cl_2, ppm, *J* = Hz): 24.9 (s, 1, B6), 20.7 (s, 1, B9), 8.2 (d, 2, B1,3, *J* 145), −1.9 (d, 2, B5,7 or B8,10, *J* 181), −3.2 (d, 2, B5,7 or B8,10, *J* 168), −35.3 (d, 1, B2 or B4, *J* 161), −35.8 (d, 1, B2 or B4, *J* 150). ^1H NMR (CD_2Cl_2, ppm, *J* = Hz): 7.50 (m, 1, -C_6H_4), 7.47 (m, 1, -C_6H_4), 7.44 (m, 1, -C_6H_4), 7.35 (m, 1, (C_6H_4), 7.13 (d, 1, $=CH$, *J* 18), 6.74 (d, 1, $=CH$, *J* 18), 3.16 (s, 1, CH), 1.61 (m, 2, CH_2), 0.88 (t, 2, CH_2, *J* 7), 0.64 (t, 2, CH_2, *J* 8), 0.00 (s, 9, CH_2), −0.93 (br, 2, BHB), −1.40 (br, 2, BHB). IR (KBr plates, cm^{-1}): 3295 (w), 3197 (w), 2953 (w), 2568 (m), 1704 (w), 1616 (w), 1596 (w), 1574 (w), 1476 (m), 1412 (m), 1275 (w), 1249 (w), 1260 (w), 1191 (w), 1168 (w), 1116 (w), 997 (w), 861 (w), 835 (w), 791 (w), 764 (m), 750 (m), 704 (w), 693 (w).

6-$\{(CH_3)_3Si(CH_2)_3\}$-$B_{10}H_{13}$ and 1-Penten-4-yne. $[Cp^*IrCl_2]_2$ (0.048 g, 0.052 mmol), 1-penten-4-yne (1 mL, ∼1 mmol), 6-$\{(CH_3)_3Si(CH_2)_3\}$-$B_{10}H_{13}$ (0.121 g, 0.52 mmol), 45 °C, 3 h. Silica gel chromatography with hexanes. Yield: 67% (0.105 g, 0.35 mmol) of **15**.

*6-$\{(CH_3)_3Si(CH_2)_3\}$-9-\{E-$H_2C{=}CHCH_2{-}CH{=}CH$\}-$B_{10}H_{12}$ (**15**).* Oil. Exact mass $^{12}C_{11}{}^{1}H_{34}{}^{11}B_{10}{}^{28}Si_1$: *m/z* calcd, 304.3360; measd, 304.3356. ^{11}B NMR (CD_2Cl_2, ppm, *J* = Hz): 23.6 (s, 1, B6), 20.4 (s, 1, B9), 8.4 (d, 2, B1,3, *J* 146), −2.1 (d, 2, B5,7 or B8,10, *J* 176), −3.6 (d, 2, B5,7 or B8,10, *J* 214), −35.3 (d, 2, B2 or B4, *J* 138), −35.3 (d, 2, B2 or B4, *J* 138), −36.4 (d, 2, B2 or B4, *J* 138). ^1H NMR (C_6D_6, ppm, *J* = Hz): 6.25 (td, 1, $=CH$, *J* 6), 5.82 (d, 1, $=CH$, *J* 18), 5.72 (m, 1, $=CH$), 5.03 (m, 2, $=CH$), 2.69 (m, 2, CH_2), 1.63 (m, 2, CH_2), 0.87 (m, 2, CH_2), 0.63 (t, 2, CH_2, *J* 7), 0.05 (s, 9, CH_3), −1.46 (br, 2, BHB), −1.85 (br, 2, BHB). IR (KBr plates, cm^{-1}): 2953 (m), 2922 (m), 2569 (vs), 1975 (w), 1918 (w), 1715 (w), 1627 (m), 1525 (w), 1480 (m), 1453 (m), 1412 (m), 1337 (m), 1291 (m), 1248 (s), 1163 (m), 1126 (m), 1094 (m), 1024 (m), 998 (s), 962 (m), 913 (m), 861 (s), 835 (vs), 757 (m), 723 (m), 706 (m), 691 (m), 665 (m).

6-$\{(CH_3)_3Si(CH_2)_3\}$-$B_{10}H_{13}$ and acetylene. A 88 mL high pressure reaction vessel equipped with a Swagelok needle valve was charged under an inert atmosphere with $[Cp^*IrCl_2]_2$ (0.159 g, 0.2 mmol), 6-$\{(CH_3)_3Si(CH_2)_3\}$-$B_{10}H_{13}$ (0.470 g, 1.99 mmol) and ∼4 mL of dry toluene. A 500 mL flask equipped with a high-vacuum Teflon stopcock was filled with purified acetylene at room temperature (∼6.22 atm, ∼20.1 mmol), and the acetylene then transferred to the high-pressure reaction vessel. After the reaction was stirred in an oil bath at 45 °C for 3 h, the reaction was stopped and exposed to air. ^{11}B NMR analysis showed complete conversion to **16**. The reaction mixture was flash-filtered through a short silica gel column. Separation by silica gel column chromatography with hexanes as eluent gave 0.319 g (1.22 mmol, 61%) of **16**.

6-{$(CH_3)_3Si(CH_2)_3$}-9-{CH_2═CH}-$B_{10}H_{12}$ ***(16)***. Solid. Exact mass $^{12}C_8{}^1H_{30}{}^{11}B_{10}{}^{14}Si_1$: *m/z* calcd, 264.3047; measd, 264.3047. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 24.5 (s, 1, B6), 19.6 (s, 1, B9), 7.9 (d, 2, B1,3, *J* 146), −2.3 (d, 2, B5,7 or B8,10, *J* 122), −3.4 (d, 2, B5,7 or B8,10, *J* 163), −36.3 (d, 2, B2,4, *J* 150). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 6.13 (m, 1, ═CH), 5.70 (m, 2, ═CH), 1.61 (m, 2, CH_2), 1.20 (m, 2, CH_2), 0.62 (m, 2, CH_2), 0.05 (s, 9, CH_3), −1.54 (br, 2, BHB), −1.90 (br, 2, BHB). IR (KBr plates, cm^{-1}): 3068 (w), 2954 (m), 2922 (m), 2892 (w), 2573 (vs), 1971 (w), 1913 (w), 1814 (w), 1710 (w), 1608 (w), 1527 (w), 1480 (m), 1413 (m), 1339 (w), 1288 (w), 1248 (s), 1164 (m), 1113 (m), 1025 (w), 997 (s), 957 (m), 902 (w), 861 (s), 835 (vs), 758 (w), 723 (m), 706 (m), 690 (m).

6-{$CH_3(CH_2)_4$}-$B_{10}H_{13}$ and Acetylene. $[Cp^*IrCl_2]_2$ (0.10 g, 0.13 mmol), acetylene (500 mL, 6.22 atm, 20.1 mmol), 6-{$CH_3(CH_2)_4$}-$B_{10}H_{13}$ (0.289 g, 1.5 mmol), 45 °C, 3 h. Yield: 69% (0.227 g, 1.04 mmol) of **17**.

6-{$CH_3(CH_2)_4$}-9-{CH_2═CH}-$B_{10}H_{12}$ ***(17)***. Oil. Exact mass $^{12}C_7{}^1H_{26}{}^{11}B_{10}$: *m/z* calcd, 220.2965; measd, 220.2968. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 24.4 (s, 1, B6), 19.5 (s, 1, B9), 8.7 (d, 2, B1,3, *J* 146), −2.1 (d, 4, B5,7 or B8,10, *J* 136), −3.1 (d, 4, B5,7 or B8,10, *J* 118), −35.9 (d, 2, B2,4, *J* 164). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 6.13 (m, 1, ═CH), 5.70 (m, 2, ═CH), 1.28 (m, 8, CH_2), 0.89 (m, 3, CH_3), −1.53 (br, 2, BHB), −1.95 (br, 2, BHB). IR (KBr plates, cm^{-1}): 3069 (w), 2959 (m), 2927 (s), 2859 (m), 2572 (vs), 1971 (w), 1916 (w), 1713 (m), 1608 (w), 1525 (m), 1479 (m), 1466 (m), 1412 (m), 1285 (m), 1221 (w), 1102 (m), 1076 (w), 996 (s), 953 (m), 903 (w), 835 (w), 802 (w), 777 (w), 722 (m), 706 (m), 681 (m).

NMR Studies of Catalyzed Decaborane Alkyne-Hydroboration Reactions. *$[RuCl_2(p\text{-cymene})]_2$.* A round bottomed flask was charged with $[RuCl_2(p\text{-cymene})]_2$ (0.153 g, 0.25 mmol) and decaborane (0.03 g, 0.25 mmol) in $CDCl_3$. The ^{1}H NMR spectrum of the mixture taken after 5 min showed the growth of a peak at −7 ppm. Next, 0.1 mL (0.68 mmol) of 1-octyne was added to the reaction, and the mixture stirred at 45 °C. After 15 min, ^{1}H NMR analysis showed a new peak at −10 ppm in addition to the peak at −7 ppm. After 3 h, the ^{1}H NMR spectrum of the reaction mixture showed only the peak at −10 ppm. ^{11}B NMR analysis indicated that the reaction had proceeded normally.

$[Cp^*IrCl_2]_2$. A round bottomed flask was charged with $[Cp^*IrCl_2]_2$ (0.200 g, 0.25 mmol) and decaborane (0.03 g, 0.25 mmol) in $CDCl_3$. The ^{1}H NMR spectrum of the mixture after 5 min, contained no peaks in the −5 to −10 ppm range. 1-Octyne (0.11 mL, 0.75 mmol) was then added, and the mixture stirred at 45 °C. After 30 min, ^{1}H NMR analysis showed a peak near −7 ppm. ^{11}B NMR analysis indicated the reaction to be complete at this point.

$[RuI_2(p\text{-cymene})]_2$. A round bottomed flask was charged with $[RuI_2(p\text{-cymene})]_2$ (0.245 g, 0.25 mmol) and decaborane (0.03 g, 0.25 mmol) in $CDCl_3$. The ^{1}H NMR spectrum of the mixture after 5 min showed no peaks in the −5 to −10 ppm range. 1-Octyne (0.1 mL, 0.68 mmol) was then added, and the mixture stirred at 45 °C. Over the next 24 h, ^{1}H NMR analysis showed no peaks appearing in the −5 to −10 ppm range. ^{11}B NMR analysis indicated that the reaction had proceeded normally and was complete at the end of 24 h.

Iridium-Catalyzed 6-Alkenyl-decaborane Hydroboration Reactions. ***16*** *and 6-{$(CH_3)_3Si(CH_2)_3$}-$B_{10}H_{13}$.* $[Cp^*IrCl_2]_2$ (0.05 g, 0.06 mmol), **16** (0.138 g, 0.53 mmol), 6-{$(CH_3)_3Si(CH_2)_3$}$B_{10}H_{13}$ (0.126 g, 0.53 mmol), toluene, 45 °C, 10 h. Silica gel chromatography with hexanes. Recrystallized from toluene. Yield: 15% (0.04 g, 0.08 mmol) of **18**.

6,6′-{$(CH_3)_3Si(CH_2)_3$}$_2$-9,9′-$(CH_2)_2$-$(B_{10}H_{12})_2$ ***(18)***. Solid. Decomposed without melting. Anal. Calcd. for $C_{14}H_{58}B_{20}Si_2$: C, 33.70; H, 11.72. Found: C, 33.82; H, 11.55. Exact mass $^{12}C_{14}{}^1H_{58}{}^{11}B_{20}{}^{14}Si_2$: *m/z* calcd, 502.5938; measd, 502.5956. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 24.1 (s, 2, B6,6′,9,9′), 9.1 (d, 2, B1,1′,3,3′, *J* 141), −2.2 (d, 4, B5,5′,7,7′,8,8′,10,10′, *J* 154), −36.6 (d, 2, B2,2′,4,4′, *J* 152). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 1.67 (m, 4, CH_2), 1.43 (s, 4, CH_2), 1.34 (m, 4, CH_2), 0.64 (m, 4, CH_2), 0.06 (s, 18, CH_3). IR (KBr plates, cm^{-1}): 2952 (w), 2920 (m), 2895 (w), 2884 (w), 2576 (vs), 2564 (s), 2549 (s), 2518 (s), 1518 (w), 1479 (m), 1450 (w), 1417 (w), 1338 (w), 1248 (m), 1211 (w), 1165 (w), 1126 (w), 1092 (w), 1078 (w), 1056 (w), 1025 (w), 999 (w), 982 (w), 960 (m), 935 (w), 922 (w), 905 (w), 863 (m), 832 (s), 784 (w), 758 (w), 730 (w), 709 (w), 688 (w), 669 (w).

17 *and 6-{$CH_3(CH_2)_4$}-$B_{10}H_{13}$.* $[Cp^*IrCl_2]_2$ (0.035 g, 0.04 mmol), **17** (0.10 g, 0.46 mmol), 6-{$H_3C(CH_2)_4$}-$B_{10}H_{13}$ (0.10 g, 0.52 mmol), 45 °C, 10 h. Silica gel chromatography with hexanes. Recrystallized from toluene. Yield: 22% (0.04 g, 0.10 mmol) of **19**.

6,6′-{$CH_3(CH_2)_4$}$_2$-9,9′-$(CH_2)_2$-$(B_{10}H_{12})_2$ ***(19)***. Solid. mp 148−149 °C. Anal. Calcd for $C_{12}H_{50}B_{20}$: C, 35.09; H, 12.27. Found: C, 34.85; H, 12.39. Exact mass $^{12}C_{12}{}^1H_{50}{}^{11}B_{20}$: *m/z* calcd, 414.5774; measd, 414.5766. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 24.0 (s, 4, B6,6′,9,9′), 8.7 (d, 4, B1,1′,3,3′, *J* 141), −2.5 (d, 8, B5,5′,7,7′,8,8′,10,10′, *J* 102), −36.9 (d, 4, B2,2′,4,4′, *J* 151). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 1.45 (s, 4, CH_2), 1.30 (m, 16, CH_2), 0.93 (m, 6, CH_3), −1.85 (br, 8, BHB). IR (KBr plates, cm^{-1}): 2954 (m), 2927 (s), 2870 (w), 2859 (w), 2566 (vs), 2512 (s), 1518 (w), 1481 (w), 1465 (w), 1457 (w), 1210 (w), 1123 (w), 1096 (m), 1050 (w), 997 (m), 960 (w), 937 (w), 905 (w), 894 (w), 834 (w), 806 (w), 764 (w), 721 (w), 706 (w).

Ruthenium-Catalyzed 6-Alkenyl-decaborane Metathesis Reactions. ***16*** *Homometathesis.* In a drybox, a two-neck round-bottom flask equipped with a septum, stirbar, and vacuum adapter was charged with Grubbs' II catalyst (0.02 g, 0.02 mmol). The flask was sealed, taken out of the box, and slightly evacuated. A solution of **16** (0.187 g, 0.71 mmol) in ∼2 mL of dry toluene was then added through the septum. The reaction mixture was submerged in a 45 °C oil bath and stirred for 48 h. Column chromatography with hexanes afforded 0.167 g (0.34 mmol, 48%) of **20** as a white solid.

6,6′-{$(CH_3)_3Si(CH_2)_3$}$_2$-9,9′-(CH═CH)-{$B_{10}H_{12}$}$_2$ ***(20)***. Solid. Decomposed without melting. Anal. Calcd for $C_{14}H_{56}B_{20}Si_2$: C, 33.83; H, 11.36. Found: C, 34.44; H, 10.88. Exact mass $^{12}C_{14}{}^1H_{56}{}^{11}B_{20}{}^{14}Si_2$: *m/z* calcd, 500.5782; measd, 500.5955. ^{11}B NMR (C_6D_6, ppm, *J* = Hz): 23.3 (s, 2, B6,6′), 18.3 (s, 2, B9,9′), 7.7 (d, 4, B1,1′,3,3′, *J* 140), −3.5 (br, 8, B5,5′,7,7′,8,8′,10,10′), 36.7 (d, 2, B2,2′,4,4′, *J* 140). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 6.75 (s, 2, ═CH), 1.68 (m, 4, CH_2), 1.33 (m, 4, CH_2), 0.66 (m, 4, CH_2), 0.08 (s, 18, CH_3), −1.50 (br, 2, BHB), −1.77 (br, 2, BHB). IR (KBr plates, cm^{-1}): 3210 (m, br), 2952 (m), 2921 (m), 2884 (w), 2794 (w), 2568 (vs), 2521 (s), 1517 (m), 1476 (s), 1451 (m), 1416 (m), 1338 (w), 1292 (w), 1248 (s), 1165 (w), 1147 (w), 1127 (w), 1106 (w), 1077 (w), 1057 (w), 1024 (w), 989 (m), 959 (m), 936 (w), 905 (m), 863 (s), 832 (s), 757 (w), 710 (m), 692 (w), 678 (w).

16 *and 1-Pentene.* In a drybox, a two-neck round-bottom flask equipped with a septum, stirbar, and vacuum adapter was charged with Grubbs' II catalyst (0.04 g, 0.05 mmol). The flask was sealed, taken out of the box, and slightly evacuated. A solution of 1-pentene (1.14 mL, 10.42 mmol), **16** (0.275 g, 1.05 mmol) in ∼2 mL of dry toluene was then added through the septum. The reaction mixture was submerged in a 45 °C oil bath and stirred for 48 h. Column chromatography with hexanes afforded 0.163 g (0.54 mmol, 51%) of **21**.

6-{$(CH_3)_3Si(CH_2)_3$}-9-{$CH_3(CH_2)_2CH$═CH}-$B_{10}H_{12}$ ***(21)***. Oil. Exact mass $^{12}C_{11}{}^1H_{36}{}^{11}B_{10}{}^{14}Si_1$: *m/z* calcd, 306.3517; measd, 306.3510. ^{11}B NMR (C_6D_6, ppm): 22.9 (s, 1, B6), 20.1 (s, 1, B9), 7.8 (d, 2, B1,3, *J* 140), −2.6 (d, 2, B5,7 or B8,10, *J* 158), −4.1 (d, 2, B5,7 or B8,10, *J* 246), −35.7 (d, 1, B2 or B4, *J* 157), −36.9 (d, 1, B2 or B4, *J* 154). ^{1}H NMR (C_6D_6, ppm, *J* = Hz): 6.26 (td, 1, ═CH, *J* 18, 6), 5.84 (d, 1, ═CH, *J* 18), 2.00 (m, 2, CH_2), 1.62 (m, 2, CH_2), 1.29 (m, 4, CH_2), 0.88 (m, 3, CH_2), 0.63 (t, 2, CH_2, *J* 8), 0.05 (s, 9, CH_3), −1.31 (br, 2, BHB), −1.83 (br, 2, BHB). IR (KBr plates, cm^{-1}): 2957 (s), 2925 (s), 2874 (m), 2571 (vs), 1975 (w), 1925 (w), 1713 (m), 1630 (m), 1525 (w), 1481 (m), 1464 (m), 1412 (m), 1338 (w), 1278 (m), 1248 (s), 1163 (w), 1128 (m), 1095 (w), 1074 (w), 1025 (w), 998 (s), 981 (m), 961 (m), 935 (w), 906 (w), 861 (s), 835 (vs), 757 (w), 739 (w), 724 (w), 704 (m), 690 (m), 669 (w).

Table 1. Crystallographic Data Collection and Structure Refinement Information

	2	4	10	14
empirical formula	$C_{10}H_{34}B_{10}Si_2$	$C_8B_{10}H_{24}Br_2$	$C_{18}B_{10}H_{42}$	$C_{16}B_{10}H_{34}Si$
formula weight	318.65	388.19	366.62	362.62
crystal class	orthorhombic	triclinic	triclinic	monoclinic
space group	*Pnma* (#62)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	*Cc* (#9)
Z	4	2	4	8
a, Å	10.449(2)	5.7403(3)	10.992(2)	69.954(3)
b, Å	31.394(5)	11.1992(6)	12.957(2)	6.4085(3)
c, Å	6.6452(14)	14.4436(8)	17.301(3)	10.4893(5)
α, deg		104.692(3)	97.650(6)	
β, deg		94.928(3)	96.083(5)	94.193(3)
γ, deg		90.028(3)	90.370(4)	
V, Å^3	2179.9(8)	894.61(8)	2427.8(7)	4689.8(4)
D_{calc}, g/cm^3	0.971	1.441	1.003	1.027
μ, mm^{-1}	0.151	4.510	0.049	0.099
λ, Å (Mo-K$_\alpha$)	0.71073	0.71073	0.71073	0.71073
crystal size, mm	0.44 × 0.35 × 0.18	0.45 × 0.10 × 0.02	0.40 × 0.35 × 0.06	0.35 × 0.20 × 0.005
F(000)	688	384	800	1552
2θ angle, deg	5.20−50.10	3.76−55.04	5.12−50.02	2.34−50.82
temperature, K	143(1)	143(1)	143(1)	143(1)
hkl collected	$-11 \leq h \leq 12$	$-7 \leq h \leq 7$	$-13 \leq h \leq 10$	$-84 \leq h \leq 84$
	$-37 \leq k \leq 34$	$-14 \leq k \leq 14$	$-15 \leq k \leq 14$	$-7 \leq k \leq 7$
	$-7 \leq l \leq 7$	$-18 \leq l \leq 18$	$-20 \leq l \leq 20$	$-12 \leq l \leq 12$
no. meas reflns	17956	19922	18403	28284
no. unique reflns	1925	4067	8434	8532
	(R_{int} = 0.0602)	(R_{int} = 0.0372)	(R_{int} = 0.0187)	(R_{int} = 0.0672)
no. parameters	133	191	842	590
R^a indices (all data)	R_1 = 0.0619	R_1 = 0.0620	R_1 = 0.0558	R_1 = 0.1084
	wR_2 = 0.1476	wR_2 = 0.1184	wR_2 = 0.1208	wR_2 = 0.1134
R^a indices ($F > 2\sigma$)	R_1 = 0.0581	R_1 = 0.0461	R_1 = 0.0448	R_1 = 0.0554
	wR_2 = 0.1450	wR_2 = 0.1113	wR_2 = 0.1101	wR_2 = 0.0963
GOF^b	1.089	1.066	1.045	0.995
final difference peaks, e/Å^3	0.259, −0.224	1.175, −0.567	0.158, −0.157	0.164, −0.169

	18	19	20
empiricalformula	$C_{14}B_{20}H_{58}Si_2$	$C_{12}B_{20}H_{50}$	$C_{14}B_{20}H_{56}Si_2$
formula weight	498.98	410.72	496.97
crystal class	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (#15)	$P2_1/c$ (#14)	*P*2/*c* (#13)
Z	4	2	2
a, Å	52.156(5)	16.787(2)	25.509(2)
b, Å	6.4205(6)	5.7385(9)	6.5166(7)
c, Å	10.4066(10)	15.027(2)	10.4197(11)
α, deg			
β, deg	99.024(3)	105.944(8)	94.253(4)
γ, deg			
V, Å^3	3441.7(6)	1391.9(3)	1727.3(3)
D_{calc}, g/cm^3	0.963	0.980	0.956
μ, mm^{-1}	0.110	0.043	0.110
λ, Å (Mo-K$_\alpha$)	0.71073	0.71073	0.71073
crystal size, mm	0.42 × 0.12 × 0.04	0.48 × 0.09 × 0.03	0.38 × 0.28 × 0.06
F(000)	1080	444	536
2θ angle, deg	3.16−50.28	5.04−50.24	3.20−50.16
temperature, K	143(1)	143(1)	143(1)
hkl collected	$-62 \leq h \leq 61$	$-19 \leq h \leq 20$	$-30 \leq h \leq 30$
	$-7 \leq k \leq 7$	$-6 \leq k \leq 6$	$-7 \leq k \leq 7$
	$-10 \leq l \leq 12$	$-17 \leq l \leq 17$	$-12 \leq l \leq 12$
no. meas reflns	28200	21290	26902
no. unique reflns	3073	2470	3063
	(R_{int} = 0.0541)	(R_{int} = 0.0692)	(R_{int} = 0.0372)
no. parameters	215	195	215
R^a indices (all data)	R_1 = 0.0721	R_1 = 0.0846	R_1 = 0.0939

Table 1. continued

	18	19	20
	wR_2 = 0.1682	wR_2 = 0.1971	wR_2 = 0.2211
R^a indices ($F > 2\sigma$)	R_1 = 0.0649	R_1 = 0.0671	R_1 = 0.0902
	wR_2 = 0.1647	wR_2 = 0.1760	wR_2 = 0.2190
GOF^b	1.252	1.077	1.159
final difference peaks, e/Å^3	0.471, −0.238	0.407, −0.297	1.062, −0.355

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. $^b\mathrm{GOF} = \{\sum w(F_o^2 - F_c^2)^2/(n - p)\}^{1/2}$.

16 and 6-Bromohexene. Grubbs' II catalyst (0.03 g, 0.04 mmol), **16** (0.175 g, 0.67 mmol), 6-bromohexene (0.9 mL, 6.73 mmol), toluene, 45 °C, 48 h. Silica gel chromatography with hexanes. Yield: 48% (0.127 g, 0.32 mmol) of **22**.

*6-{$(CH_3)_3Si(CH_2)_3$}-9-{$Br(CH_2)_4CH{=}CH$}-$B_{10}H_{12}$ (**22**).* Oil. Exact mass $^{12}C_{12}{}^1H_{37}{}^{11}B_{10}Br_1{}^{14}Si_1$: m/z calcd, 398.2778; measd, 398.2759. ^{11}B NMR (CD_2Cl_2, ppm, 160.5 MHz, J = Hz): 23.5 (s, 1, B6), 19.9 (s, 1, B9), 7.0 (d, 2, B1,3, J 143), −2.7 (d, 2, B5,7 or B8,10, J 142), −5.0 (d, 2, B5,7 or B8,10, J 159), −36.3 (d, 1, B2 or B4, J 148), −37.2 (d, 1, B2 or B4, J 140). ^{1}H NMR (CD_2Cl_2, ppm, 500 MHz): 6.34 (td, 1, =CH, J 18, 7), 5.96 (d, 1, =CH, J 18), 3.43 (t, 2, CH_2, J 7), 2.22 (m, 2, CH_2), 1.51 (m, 8, CH_2), 0.62 (t, 2, CH_2, J 9), 0.01 (s, 9, CH_3), −1.06 (br, 2, BHB), −1.45 (br, 2, BHB). IR (KBr plates, cm^{-1}): 3227 (w, br), 3004 (m), 2958 (vs), 2934 (vs), 2856 (s), 2569 (s), 1978 (w), 1927 (w), 1725 (m), 1668 (w), 1630 (w), 1600 (w), 1580 (w), 1454 (s), 1437 (s), 1359 (w), 1337 (w), 1278 (s), 1249 (vs), 1200 (w), 1163 (w), 1125 (w), 1074 (w), 1028 (w), 997 (m), 968 (vs), 861 (m), 836 (s), 738 (m), 706 (w), 692 (w), 646 (m), 562 (m).

16 and Allyltrimethylsilane. Grubbs' II catalyst (0.04 g, 0.05 mmol), **16** (0.267 g, 1.02 mmol), allyltrimethylsilane (1.66 mL, 10.44 mmol), toluene, 45 °C, 48 h. Silica gel chromatography with hexanes. Yield: 47% (0.167 g, 0.48 mmol) of **23**.

*6-{$(CH_3)_3Si(CH_2)_3$}-9-{$(CH_3)_3SiCH_2CH{=}CH$}-$B_{10}H_{12}$ (**23**).* Oily Solid. Exact mass $^{12}C_{12}{}^1H_{40}{}^{11}B_{10}{}^{14}Si_2$: m/z calcd, 350.3599; measd, 350.3589. ^{11}B NMR (C_6D_6, ppm, J = Hz): 23.4 (s, 1, B9), 21.6 (s, 1, B6), 8.2 (d, 2, B1,3, J 143), −1.7 (d, 2, B5,7 or B8,10, J 125), −4.4 (d, 2, B5,7 or B8,10, J 125), −35.1 (d, 1, B2 or B4, J 183), −36.5 (d, 1, B2 or B4, J 179). ^{1}H NMR (C_6D_6, ppm, J = Hz): 6.33 (td, 1, =CH, J 17, 8), 5.76 (d, 1, =CH, J 17), 1.58 (m, 4, CH_2), 1.18 (m, 2, CH_2), 0.59 (m, 2, CH_2), 0.04 (s, 18, CH_3), −1.27 (br, 2, BHB), −1.86 (br, 2, BHB). IR (KBr plates, cm^{-1}): 3213 (vs, br), 2954 (m), 2923 (w), 2890 (w), 2570 (s), 2258 (w), 1615 (m), 1453 (vs), 1417 (vs), 1277 (w), 1248 (s), 1198 (m), 1163 (w), 1123 (w), 1097 (w), 1023 (w), 998 (m), 961 (w), 934 (w), 905 (w), 856 (s), 836 (s), 762 (s), 750 (s), 726 (m), 704 (m), 692 (m), 548 (w).

Computational Studies. DFT/GIAO calculations using the Gaussian 03 package[5] were carried out as previously described.[6] The geometries were fully optimized at the B3LYP/6-311G* level within the specified symmetry constraints (using the standard basis sets included). A vibrational frequency analysis was carried out on each optimized geometry at the B3LYP/6-311G* level with a true minimum found for each structure (i.e., possessing no imaginary frequencies). The NMR chemical shifts were calculated at the B3LYP/6-311G* level using the GIAO option within Gaussian 03. ^{11}B NMR GIAO chemical shifts are referenced to $BF_3{\cdot}OEt_2$.

Crystallographic Data. All crystals were grown by slow evaporation from n-pentane, n-heptane, or toluene.

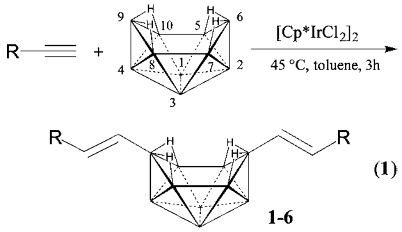
Collection and Reduction of the Data. Crystallographic data and structure refinement information are summarized in Table 1. The X-ray intensity data for 6,9-(E-$(CH_3)_3SiCH{=}CH)_2$-$B_{10}H_{12}$ (**2**, UPenn 3360) and 6,9-[$H_2C{=}C\{CH_2(C_6H_{11})\}$]$_2$-$B_{10}H_{12}$ (**10**, UPenn 3342) were collected on a Rigaku Mercury CCD and the data for 6,9-(E-$Br(CH_2)_2CH{=}CH)_2$-$B_{10}H_{12}$ (**4**, UPenn 3420), 6-{$(CH_3)_3Si(CH_2)_3$}-9-{3-HC≡C−C_6H_4-1-CH=CH}-$B_{10}H_{12}$ (**14**, UPenn 3422), 6,6′-{$(CH_3)_3Si(CH_2)_3$}$_2$-9,9′-$(CH_2)_2$-$(B_{10}H_{12})_2$ (**18**, UPenn 3391), 6,6′-$(CH_3(CH_2)_4\}_2$-9,9′-$(CH_2)_2$-$(B_{10}H_{12})_2$ (**19**, UPenn 3378) and 6,6′-{$(CH_3)_3Si(CH_2)_3$}$_2$-9,9′-(CH=CH)-$(B_{10}H_{12})_2$ (**20**, UPenn 3376) were collected on a Bruker APEXII CCD. Rotation frames for **2** and **10** were integrated using CrystalClear,[7] producing a list of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed to the CrystalStructure[8] program package for further processing and structure solution. Rotation frames for **4**, **14**, and **18**−**20** were integrated using SAINT,[9] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values that were then passed to the SHELXTL[10] program package for further processing and structure solution. Intensity data were corrected for Lorentz and polarization effects and for absorption.

Solution and Refinement of the Structures. The structures were solved by direct methods (SIR97[11] for **2** and **10** and SHELXS-97[12] for **4**, **14**, and **11**−**20**). Refinement was by full-matrix least-squares based on F^2 using SHELXL-97. All reflections were used during refinement (values of F^2 that were experimentally negative were replaced with F^2 = 0).

■ RESULTS AND DISCUSSION

Complexes such as $IrCl(CO)(PPh_3)_2$ and $RhH(CO)(PPh_3)_3$, which we previously found[1] to be active for inducing alkyne-hydroborations by polyboranes and borazine, proved to be unsuitable precatalysts for use with decaborane owing to the competing reactions of their dissociated phosphine ligands with decaborane to form 6,9-$(Ph_3P)_2B_{10}H_{12}$ adducts.[13] Thus, a potential decaborane alkyne-hydroboration precatalyst cannot contain dissociable, strongly basic ligands. As described below, we explored the use of two types of complexes that appeared to meet this requirement: $[Cp^*IrCl_2]_2$, which we had previously shown[1f] to catalyze alkyne-hydroborations with both smaller polyboranes and the o- and m-$C_2B_{10}H_{12}$ carboranes, and the $[RuX_2(p\text{-cymene})]_2$ arene-complexes, which Chang reported[14] will catalyze the hydrosilylation of terminal alkynes when X = Cl.

Iridium Catalyzed Decaborane Alkyne-Hydroborations. The $[Cp^*IrCl_2]_2$ complex was found to be an effective precatalyst for decaborane alkyne-hydroboration of the terminal alkynes, 1-octyne, trimethylsilylacetylene, phenylacetylene, 4-bromo-1-butyne, 5-chloro-1-pentyne and acetylene (eq 1). In a typical reaction, decaborane (0.98 mmol) was reacted with excess 1-octyne (2.98 mmol) and $[Cp^*IrCl_2]_2$ (0.17 mmol) in toluene for 3 h at 45 °C to give an 83% isolated yield (0.81 mmol) of 6,9-dioctenyl-decaborane (**1**).



(1)

The best reaction in terms of both lowest catalyst loading and highest yield was observed with trimethylsilylacetylene, where reactions with only 4 mol % $[Cp^*IrCl_2]_2$ gave a 90% isolated yield (~29 turnovers per Ir) of 6,9-(E-$Me_3SiCH{=}CH)_2$-$B_{10}H_{12}$ (**2**) in 3 h at 45 °C. Reactions with phenylacetylene likewise gave excellent yields of **3** (87%), but required higher catalyst loadings (28 mol % $[Cp^*IrCl_2]_2$) to reach completion. Lower yields were obtained for the reactions with 4-bromo-1-butyne (**4**, 39%) and 5-chloro-1-pentyne (**5**, 37%).

The parent 6,9-divinyl-decaborane (**6**) was obtained from decaborane and acetylene in the presence of $[Cp^*IrCl_2]_2$ by carrying out the reaction in a high pressure reactor vessel; however, the complete conversion of 2 mmol of decaborane to **6** at 45 °C could only be achieved by the addition of greater than a stoichiometric amount of iridium and by employing three 3-h reaction cycles, where each cycle involved adding both additional iridium complex and acetylene. The slow rate and poor yield (13%) of the reaction may be attributed to both catalyst decomposition, which was evidenced by the formation of colloidal metal particles during the reaction, and the limited solubility of acetylene in toluene.

In agreement with their density functional theory (DFT) optimized geometries and GIAO calculated NMR shifts (Supporting Information, Figures S1 and S2), the ^{11}B NMR spectra of **1**−**6** each consisted of four peaks in 2:4:2:2 ratios, with the alkenyl-substituted B6,9 resonance appearing as a singlet near 19 ppm (see Figure 1**A** for the spectrum of **1**). Consistent with their predicted C_{2v} cage-symmetries, the ^{1}H NMR spectra of **1**−**6** each showed only one bridge-hydrogen resonance near −1.3 ppm (see Supporting Information, Figure S3 for the spectrum of **1**). The olefinic-hydrogens of **1**−**5** appeared as ABX_2 multiplets with doublet coupling constants (J ∼ 18−21 Hz) between the two protons characteristic of β-E olefins.[15]

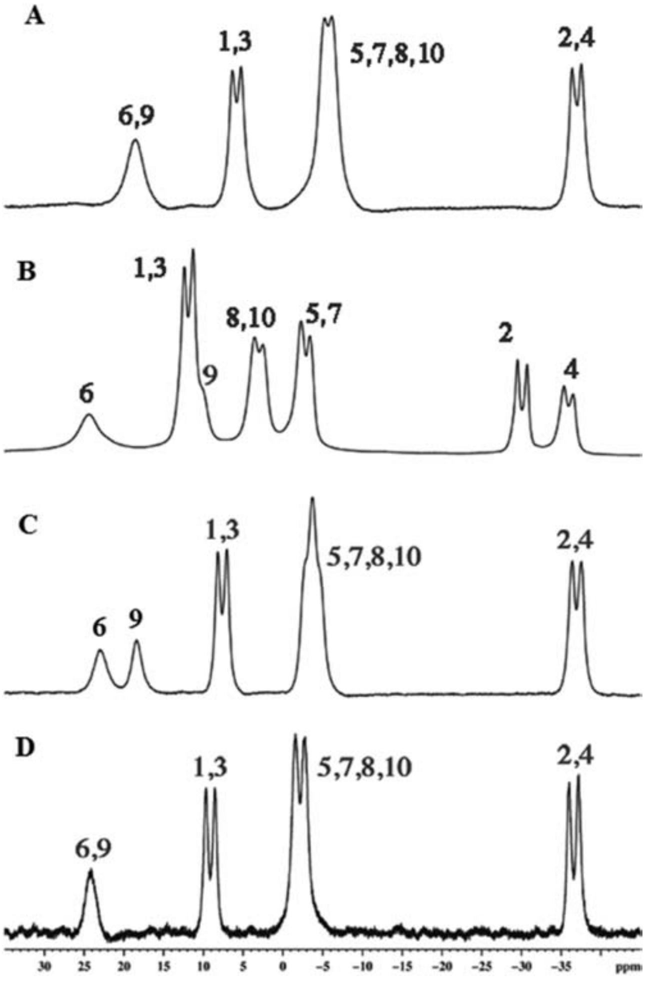


Figure 1. ^{11}B NMR spectra for **1** (**A**), **7** (**B**), **16** (**C**), and **18** (**D**).

The crystallographically determined structures of 6,9-(E-$Me_3SiCH{=}CH)_2$-$B_{10}H_{12}$ **2** (Figure 2, top) and 6,9-(E-$Br(CH_2)_2CH{=}CH)_2$-$B_{10}H_{12}$ **4** (Figure 2, middle) confirmed this conclusion. In these compounds, the $(CH_3)_3Si$- and $Br(CH_2)_2$- groups are positioned *trans* to the decaborane-cage, with both compounds showing the expected C═C bond lengths (**2**, C1═C2, 1.307(3) Å; **4**, C1═C2, 1.304(5) Å, C5═C6, 1.311(6) Å) and bond angles (**2**, B6−C1═C2, 125.6(2)°, C1═C2−Si1, 127.71(19)°; **4**, B6−C1═C2, 125.8(3)°, C1═C2−C3, 124.8(3)°, B9−C5═C6, 126.6(4)°, C5═C6−C7, 124.2(5)°) for their olefinic substituents.

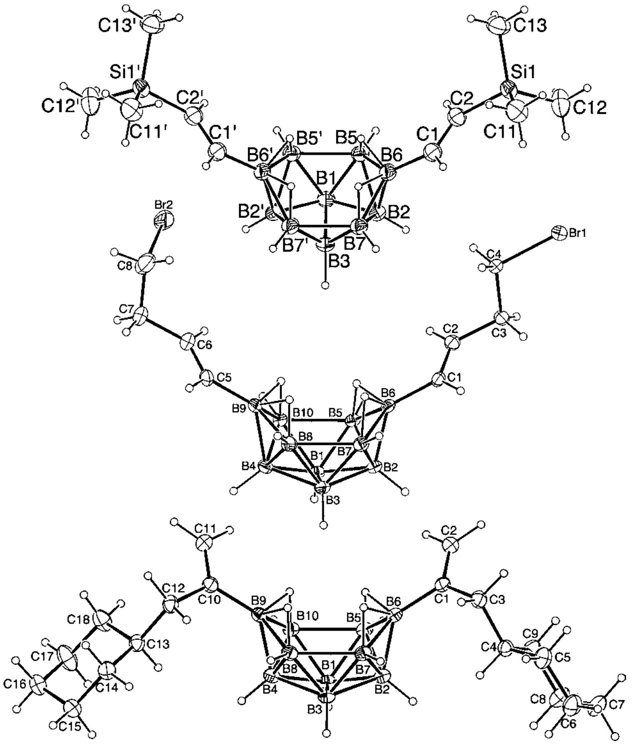
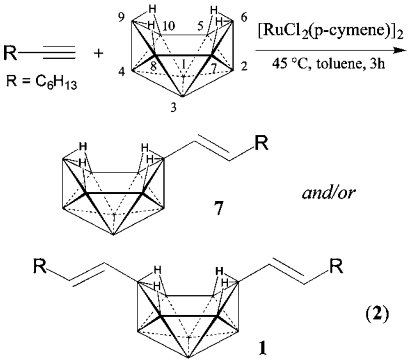


Figure 2. ORTEP drawings of the crystallographically determined structures of **2** (top), **4** (middle) and **10** (bottom). Selected bond lengths (Å) and angles (deg): (**2**) C1═C2, 1.307(3); B6−C1, 1.557(3); C2−Si1, 1.867(2), B6−B5, 1.803(3); B6−B7, 1.799(3); B6−B2, 1.738(3); B6−C1═C2, 125.6(2); C1═C2−Si1, 127.71(19), C1−B6−B2, 133.86(18); (**4**) C1═C2, 1.304(5); C5═C6, 1.311(6), B6−C1, 1.550(5), B9−C5, 1.549(5), C2−C3, 1.507(5), C6−C7, 1.505(5), B6−B5, 1.807(5), B6−B7, 1.808(6), B9−B8, 1.806(6), B9−B10, 1.807(6), B6−B2, 1.733(5), B9−B4, 1.733(5), B6−C1═C2, 125.8(3), C1═C2−C3, 124.8(3), B9−C5═C6, 126.6(4), C5═C6−C7, 124.2(5), C1−B6−B2, 130.2(3), C5−B9−B4, 130.5(3); (**10**) C1═C2, 1.329(2); B6−C1, 1.563(2); C10═C11, 1.328(2); B9−C10, 1.568(2); B5−B6, 1.802(2); B6−B7, 1.806(2); B8−B9, 1.816(2); B9−B10; 1.803(2); C2═C1−C3, 120.91(13); C2═C1−B6, 119.65(13); C3−C1−B6, 119.42(11); C11═C10−C12, 121.28(13); C11═C10−B9, 120.09(13); C12−C10−B9, 118.62(12), C1−B6−B2, 134.14(11), C10−B9−B4, 133.38(11).

The B6−C1 (**2**, 1.557(3) Å, **4**, 1.550(5) Å) and B9−C5 (**4**, 1.549(5) Å) bond lengths are shorter than the B−C lengths (∼1.57 Å) observed in 6-alkyl-decaboranes and 6,9-dialkyl-decaboranes,[2b,e,16] suggesting interaction of their olefinic π-systems with π-acidic orbitals on B6 and B9 that are oriented perpendicular to the olefinic plane. We had previously noted[1i] similar differences in the corresponding B−C bond lengths in the structures of the 7-alkyl-*arachno*-$C_2B_7H_{12}$ and 7-alkenyl-*arachno*-$C_2B_7H_{12}$ carboranes as evidence of olefin-cage π-bonding. Likewise, π-interactions involving partial donation of the amino-nitrogen lone pair to the cage B9-boron in the 6-ClC_6H_4-9-(RR′N)-*nido*-6-NB_9H_{10} azaboranes has previously been proposed.[17] The remainder of the intracage distances and angles in **2** and **4** are similar to those previously reported for 6,9-dialkyl-decaboranes.[2b,e,16]

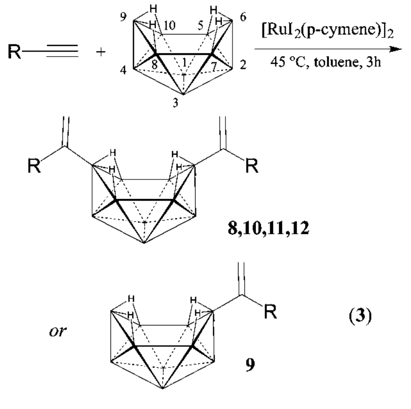
Ruthenium Catalyzed Decaborane Alkyne-Hydroborations. The ruthenium complex [Ru(p-cymene)Cl_2]$_2$ also catalyzed decaborane alkyne-hydroborations, but with slower rates than the [Cp*$IrCl_2$]$_2$ complex (eq 2).



(2)

For example, a 3 h reaction of decaborane (1.98 mmol) with excess 1-octyne (5.97 mmol) and [$RuCl_2$(p-cymene)]$_2$ (0.21 mmol) at 45 °C gave a 42% yield (0.71 mmol) of 6-(E-$CH_3(CH_2)_5CH{=}CH$)-$B_{10}H_{13}$ (**7**) along with an 8% yield (0.14 mmol) of 6,9-(E-$CH_3(CH_2)_5CH{=}CH$)$_2$-$B_{10}H_{12}$ (**1**). It was necessary to use a 40 mol % catalyst loading to achieve complete conversion to **1**. Consistent with its expected C_s cage-symmetry, the ^{11}B NMR spectrum (Figure 1**B**) of the monosubstituted derivative **7** exhibited seven resonances in 1:2:1:2:2:1:1 ratios, with the singlet resonance arising from the alkenyl-substituted B6-boron occurring near 21.9 ppm, in excellent agreement with the DFT/GIAO calculated shifts (Supporting Information, Figure S4). In its ^1H NMR spectrum (Supporting Information, Figure S5), **7** had two sets of bridge-hydrogen resonances, and the olefinic-hydrogen resonances again exhibited characteristic β-E coupling constants.

The [RuI_2(p-cymene)]$_2$ complex proved to be even more active for alkyne-hydroborations than either [$RuCl_2$(p-cymene)]$_2$ or [Cp*$IrCl_2$]$_2$ (eq 3). For example, the 3-h 45 °C reaction of decaborane (1.97 mmol) with excess 1-octyne (5.97 mmol) in the presence of 0.10 mmol of [RuI_2(p-cymene)]$_2$ produced a 95% isolated yield (1.87 mmol) of 6,9-dioctenyl-decaborane **8**. This yield corresponds to ~19 catalyst turnovers per Ru, compared to the >5 catalyst turnovers observed for comparable reactions with [$RuCl_2$(p-cymene)]$_2$ and [Cp*$IrCl_2$]$_2$, respectively. When a lower (1.5 mol %) catalyst loading and a 1:2 alkyne:decaborane ratio were used, 6-octenyl-decaborane **9** was obtained as the major product.

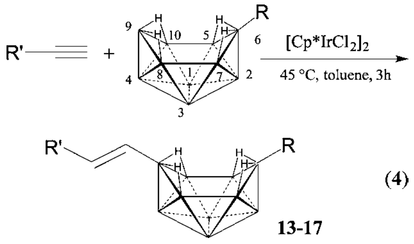


(3)

The ^{11}B NMR spectra of **8** and **9** were nearly identical to those of **1** and **7**, respectively; however, the olefinic-hydrogen patterns observed in their ^1H NMR spectra were quite different than those of **1** and **7**. Thus, as shown in the ^1H NMR spectrum of **9** in Supporting Information, Figure S6 the two olefinic-hydrogens appeared as two overlapping singlets near 5.44 ppm suggesting the formation of α-olefin isomers.

Reactions of decaborane with 3-cyclohexylpropyne, 4-bromo-1-butyne and 5-chloro-1-pentyne in the presence of [RuI_2(p-cymene)]$_2$ produced the corresponding 6,9-alkenyl-derivatives **10**, **11**, and **12** in 55%, 67%, and 90% isolated yields, respectively, with the ^1H NMR spectrum of each compound (see Supporting Information, Figure S7 for the spectrum of **10**) again indicating α-isomer formation. The crystallographic determination of 6,9-[$H_2C{=}C\{CH_2(C_6H_{11})\}$]$_2$-$B_{10}H_{12}$ (**10**) shown in Figure 2**C** confirmed this conclusion with both the -$CH_2(C_6H_{11})$ and -$B_{10}H_{12}$ groups attached to the β-carbon. The C1=C2 and C10=C11 bond lengths (1.329(2) and 1.328(2) Å) and the bond angles around C1, C2, C10, and C11 (see Figure 2 caption) are all consistent with olefinic values. As in **2** and **4**, the B6−C1 (1.563(2) Å) length was again found to be shorter than the corresponding B−C lengths in 6-alkyl and 6,9-dialkyl-decaboranes.[2b,e,16]

Iridium Catalyzed 6-Alkyl-Decaborane Alkyne-Hydroborations. The 6-alkyl-decaboranes, 6-{$(CH_3)_3Si(CH_2)_3$}-$B_{10}H_{13}$ and 6-{$CH_3(CH_2)_4$}-$B_{10}H_{13}$, which were synthesized via the titanium catalyzed hydroboration reactions of the corresponding olefins with decaborane,[2d,e] were also found to hydroborate alkynes in the presence of [Cp*$IrCl_2$]$_2$ (eq 4). The reactions of 6-{$(CH_3)_3Si(CH_2)_3$}-$B_{10}H_{13}$ in toluene with phenylacetylene, 1,3-diethynylbenzene and 1-penten-4-yne in the presence of [Cp*$IrCl_2$]$_2$ produced 6-{$(CH_3)_3Si(CH_2)_3$}-9-(E-$C_6H_5CH{=}CH$)-$B_{10}H_{12}$ (**13**), 6-{$(CH_3)_3Si(CH_2)_3$}-9-{E-3-$HC{\equiv}C{-}C_6H_4$-1-$CH{=}CH$}-$B_{10}H_{12}$ (**14**) and 6-{$(CH_3)_3Si(CH_2)_3$}-9-{E-$H_2C{=}CHCH_2{-}CH{=}CH$}-$B_{10}H_{12}$ (**15**) in 77%, 32% and 67% yields, while the reactions of 6-{$(CH_3)_3Si(CH_2)_3$}-$B_{10}H_{13}$ and 6-{$CH_3(CH_2)_4$}-$B_{10}H_{13}$ with acetylene in toluene at 45 °C for 3 h produced 6-{$(CH_3)_3Si(CH_2)_3$}-9-{$CH_2{=}CH$}-$B_{10}H_{12}$ (**16**) and 6-{$CH_3(CH_2)_4$}-9-{$CH_2{=}CH$}-$B_{10}H_{12}$ (**17**) in 61% and 69% yields, respectively.



(4)

As can be seen in the spectrum of **16** given in Figure 1**C**, the ^{11}B NMR spectra of **13**−**17** each showed only five peaks owing to overlap of the resonances of B1 with B3, B5,7 with B8,10, and B2 with B4. In agreement with the DFT/GIAO calculations (Supporting Information, Figure S8), the singlet

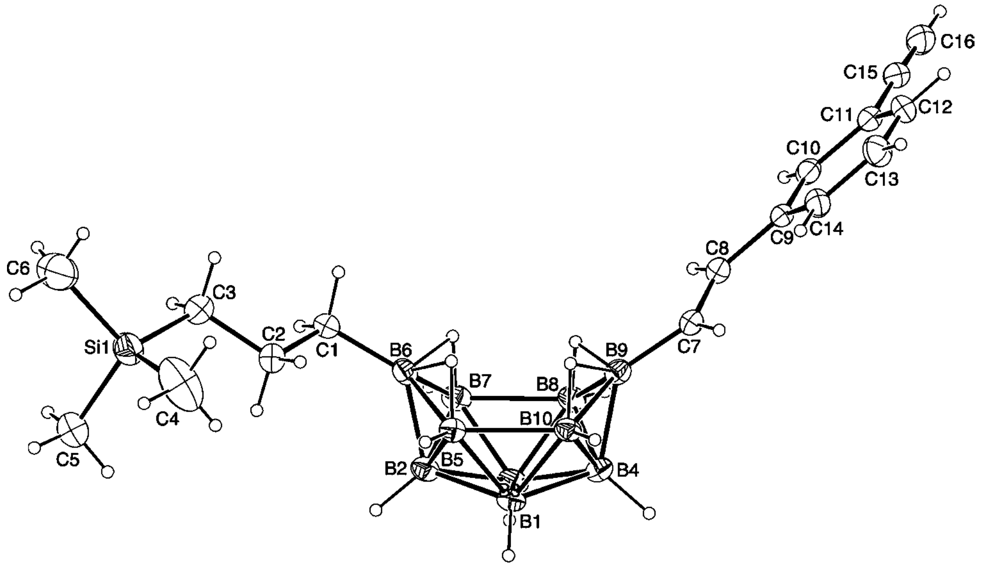


Figure 3. ORTEP drawing of the crystallographically determined structure of **14**. Selected bond lengths (Å) and angles (deg): B9−C7, 1.540(5); C7═C8, 1.317(4); B6−C1, 1.569(5); C1−C2, 1.523(5); B9−B8, 1.810(6), B9−B10, 1.809(6), B9−B4, 1.738(5), B6−C1, 1.570(5), B6−B5, 1.812(6), B6−B7, 1.803(6), B6−B2, 1.739(6), B9−C7═C8, 124.9(3); C7═C8−C9, 128.1(3); B6−C1−C2, 114.6(3); C1−C2−C3, 114.2(3), B10−B9−B8, 103.9(3); B5−B6−B7, 102.9(3), B10−B9−C7, 127.0(3), B8−B9−C7, 128.3(3), C7−B9−B4, 135.1(3), C1−B6−B2, 132.4(3).

resonance for the alkyl-substituted B6 was found in its characteristic position downfield (24.5 ppm) from that of the alkenyl-substituted B9 singlet (19.6 ppm). The ^{1}H NMR spectra of **16** and **17** each showed multiplet vinyl-resonances (near 6.1 and 5.7 ppm) in the same 1:2 ratio as **6**, along with two broad, closely spaced bridge hydrogen resonances, again reflecting their C_s cage-symmetries. The ^{1}H NMR spectra of **13−15** each exhibited olefinic-hydrogen resonances with characteristic β-E-olefin patterns and coupling constants.

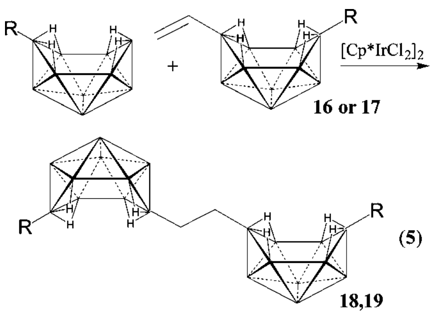
The crystallographically determined structure of **14** shown in Figure 3 confirmed 6-alkyl and 9-alkenyl substitutions with the alkenyl-group adopting the β-E structure and a C7═C8 distance of 1.317(4) Å. As noted above for **2**, **4** and **10**, the cage to alkenyl-carbon distance (B9−C7, 1.540(5) Å) in **14** is shorter than the cage to alkyl-carbon distance (B6−C1, 1.570(5) Å) again consistent with olefin π donation into an orbital on B6.

Possible Reaction Pathways for the Iridium and Ruthenium Catalyzed Alkyne-Hydroborations. Consistent with either Chalk-Harrod (CH)[18] or modified Chalk-Harrod (mCH)[19] mechanisms, Chang proposed[15] that the formation of vinylsilane products in the alkyne-hydrosilylation reactions with $[RuCl_2(p\text{-cymene}]_2$ involve initial silane oxidative-addition to form a metal-hydride complex. Similar to the observations made by Chang for the alkyne-hydrosilylation reactions, a metal-hydride resonance near −7 ppm immediately appeared in the ^{1}H NMR spectrum (Supporting Information, Figure S10) of the reaction of a stoichiometric amount of decaborane with $[RuCl_2(p\text{-cymene})]_2$. Addition of three equivalents of 1-octyne to this reaction then produced a new resonance in the metal-hydride region near −10 ppm. After ^{11}B NMR analysis indicated the decaborane octyne-hydroboration reaction was complete, only the −10 ppm resonance remained (Supporting Information, Figure S11). Likewise, while no metal-hydride peaks were initially observed by ^{1}H NMR when a stoichiometric amount of the $[Cp^*IrCl_2]_2$ and decaborane were reacted, a peak near −7 ppm appeared 30 min after the addition of three equivalents of 1-octyne. Given the experimental observations of metal-hydride resonances in the reactions of decaborane with both $[RuCl_2(p\text{-cymene})]_2$ and $[Cp^*IrCl_2]_2$, initial decaborane oxidative-addition can reasonably be proposed for the reactions with these complexes to yield, following either a hydride (CH) or decaboranyl (mCH) insertion step and final reductive-elimination, their β-E-alkenyl-decaborane products. Tuttle et al. recently reported[20] that both $[RuX_2(p\text{-cymene})]_2$ (X = Cl and I) also catalyze olefin-hydrosilylations and they used DFT calculations to explore CH, mCH and σ-bond metathesis mechanistic pathways for these reactions. They concluded that a hydride Chalk-Harrod (hCH) mechanism was favored that, while still proceeding by initial silane oxidative-addition to form a Ru(IV)-hydride complex, required a second reductive-elimination step to form a catalytically active Ru(II) species, $RuHX(p\text{-cymene})$. It is possible that such a Ru(II)-H species could also be involved in the decaborane reactions with $[RuCl_2(p\text{-cymene})]_2$.

In contrast to the reactions with $[Cp^*IrCl_2]_2$ and $[RuCl_2(p\text{-cymene})]_2$, no metal-hydride resonances were observed by ^{1}H NMR when $[RuI_2(p\text{-cymene})]_2$ was reacted with a stoichiometric amount of decaborane. Furthermore, also unlike with $[Cp^*IrCl_2]_2$ and $[RuCl_2(p\text{-cymene})]_2$, the reactions with $[RuI_2(p\text{-cymene})]_2$ yielded α-isomeric products. Both of these observations suggest that the reactions with $[RuI_2(p\text{-cymene})]_2$ occur by a different pathway. Trost[21] has previously observed α-vinylsilane formation with a proposed mechanism not involving metal-hydride species in alkyne-hydrosilylation reactions employing the $[CpRu(NCMe)_3]^+PF_6^-$ and $[Cp^*Ru(NCMe)_3]^+PF_6$ cationic complexes. A reaction sequence for the decaborane alkyne-hydroboration reactions based on Trost's proposed pathway for alkyne-hydrosilylations is shown in Supporting Information, Figure S12. Initially, I^- ions could dissociate from $[RuI_2(p\text{-cymene})]_2$ to form the 14-electron cationic $[RuI(p\text{-cymene})]^+$ complex, which is the isoelectronic analog of the $[CpRu(NCMe)]^+$ cation that is proposed to be active for hydrosilylations. Following coordination of the alkyne, the $[RuI(p\text{-cymene})(\eta^2\text{-RC}{\equiv}\text{CH})]^+$ complex could then, in a process analogous to that proposed for [CpRu-

$(NCMe)(\eta^2\text{-}RC{\equiv}CH)]^+$, undergo oxidative-addition by a process involving concerted B−H addition across the Ru-CH bond with, as proposed for the corresponding hydrosilylation reactions, initial H addition to the CH carbon being favored over decaboranyl addition. This addition could yield either metalla-cycloalkene or vinylruthenium intermediates that could then undergo reductive-elimination to produce the *α*-isomeric product. If this mechanism is operable for the reactions with $[RuI_2(p\text{-cymene})]_2$, then the difference in the mechanistic pathways for the $[RuI_2(p\text{-cymene})]_2$ and $[RuCl_2(p\text{-cymene})]_2$ complexes could simply arise from the weaker Ru−I versus Ru−Cl bond that would enable the more facile dissociation of the I^- ion to produce the required $[RuI(p\text{-cymene})]^+$ cation. Clearly more extensive mechanistic and computational studies will be required to clarify these differences.

Iridium Catalyzed Hydroborations of the 6-Alkyl-9-Vinyl-Decaboranes. While $[Cp^*IrCl_2]_2$ proved to be inactive for inducing the hydroboration of simple olefins, such as 1-pentene, by either decaborane or the 6-alkyl-decaboranes, it was found to catalyze the hydroboration of 6-alkyl-9-vinyl-decaboranes by 6-alkyl-decaboranes to yield linked-cage products (eq 5).

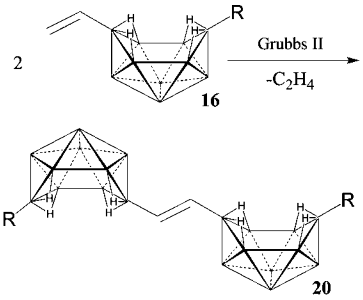


(5)

Hydroboration of **16** by $6\text{-}\{(CH_3)_3Si(CH_2)_3\}\text{-}B_{10}H_{13}$ in the presence of $[Cp^*IrCl_2]_2$ produced $6,6'\text{-}\{(CH_3)_3Si(CH_2)_3\}_2\text{-}9,9'\text{-}(CH_2)_2\text{-}(B_{10}H_{12})_2$ (**18**) in a 15% isolated yield, while hydroboration of **17** by $6\text{-}\{CH_3(CH_2)_4\}\text{-}B_{10}H_{13}$ formed $6,6'\text{-}\{CH_3(CH_2)_4\}_2\text{-}9,9'\text{-}(CH_2)_2\text{-}(B_{10}H_{12})_2$ (**19**) in a ~20% isolated yield. Owing to the different groups at their B6 and B9 borons, **18** and **19** have C_s symmetries, but their ^{11}B NMR spectra each showed only four peaks instead of the expected seven resonances owing to the small shielding differences of the terminal-alkyl and bridging $\text{-}C_2H_4\text{-}$ groups. Likewise, their ^1H NMR spectra each showed only one broad bridge-hydrogen resonance, instead of the two resonances found in the spectra of the 6-alkyl-decaboranes.

The crystallographically determined structures of **18** (top) and **19** (middle) shown in Figure 4 confirmed the formation of $\text{-}C_2H_4\text{-}$ linked coupled-cage compounds with the C11−C11′ distance (1.536(5) Å) and C11′−C11−B9, 113.7(3)° and C11′−C11−B9, 112.82(17)° angles consistent with a saturated linking fragment. In both compounds, the alkyl-carbon to cage-boron bonds (B9−C11, 1.575(4) Å (**18**) and B9−C12, 1.572 (5) Å (**19**)) are again in the expected ranges for B6 and B9 substituted alkyl-decaboranes.[2b,e,16]

Ruthenium Catalyzed Metathesis Reactions of 16. We have previously shown that Grubb's catalysts are highly effective for inducing metathesis reactions of polyboranes containing pendant olefin substituents, including homo- and cross-metathesis, RCM, ADMET and ROMP transformations.[22] In all of the previously reported examples, an olefinic carbon was not directly bonded to the cage (e.g., $6\text{-}(CH_2{=}CH(CH_2)_4)\text{-}B_{10}H_{13})^{19b}$), but separated by at least one saturated carbon that insulated any possible olefin-cage *π*-interactions. As discussed earlier, when an olefinic carbon is directly bonded to a cage-boron, such as in **16**, *π* donation to an acidic cage-boron orbital could reduce olefin *π* electron density and thereby reduce its metathesis reactivity. Nevertheless, it was found that **16** readily underwent both homo- and cross-metathesis reactions in the presence of Grubbs' II catalyst (eq 6).

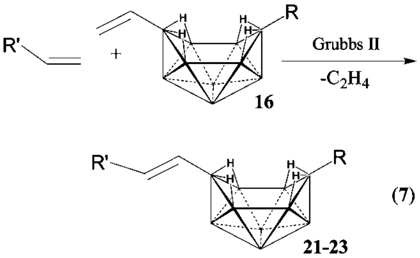


(6)

Homometathesis to form $6,6'\text{-}\{(CH_3)_3Si(CH_2)_3\}_2\text{-}9,9'\text{-}(CH{=}CH)\text{-}\{B_{10}H_{12}\}_2$ **20** in a 48% isolated yield **16** was achieved by heating a toluene solution of **16** at 45 °C for 48 h in the presence of 2.8 mol % of Grubbs' II catalyst. The ^{11}B NMR spectrum of **20** is nearly identical to that of **16**, with the singlets for the substituted B6 and B9 borons again occurring in the characteristic ranges for borons substituted with alkyl (B6, 23.3 ppm) and olefinic (B9, 18.3 ppm) substituents. The two equivalent olefinic-hydrogens appear in the ^1H NMR spectrum as a singlet at 6.75 ppm and, consistent with C_s cage-symmetry, the bridge-hydrogens appear as two broad upfield resonances.

The crystallographically determined structure of **20** shown in Figure 4 (bottom) confirmed that it is the first example of a coupled-decaborane compound linked by an unsaturated group. The decaborane cages are located in the *trans* positions with the bond lengths and angles of the linking group characteristic of olefinic carbons. The B9−C11 distance (1.558 (4) Å) is again in the range found for the other alkenyl B−C bonds; however, the olefinic C11=C11′ distance (1.338(7) Å) in **20** is longer than those found in the monocage *β*-E-alkenyldecaborane derivatives **2**, **4**, and **14**, which range from only 1.304(5) to 1.317(4) Å. This difference is consistent with an increased olefin *π* cage-donation resulting from the interaction of the *π* system with the two cages in **20**.

As depicted in eq 7, **16** underwent cross metathesis with 1-pentene, 6-bromo-1-hexene and allyltrimethylsilane in the presence of Grubbs' II catalyst to form the $6\text{-}\{(CH_3)_3Si(CH_2)_3\}\text{-}9\text{-}\{RCH{=}CH\}\text{-}B_{10}H_{12}$ derivatives **21**−**23** in 51%, 48% and 47% isolated yields, respectively.



(7)

The ^{11}B NMR spectra of **21**−**23** were nearly identical to that of **16** with the two singlet resonances appearing in their

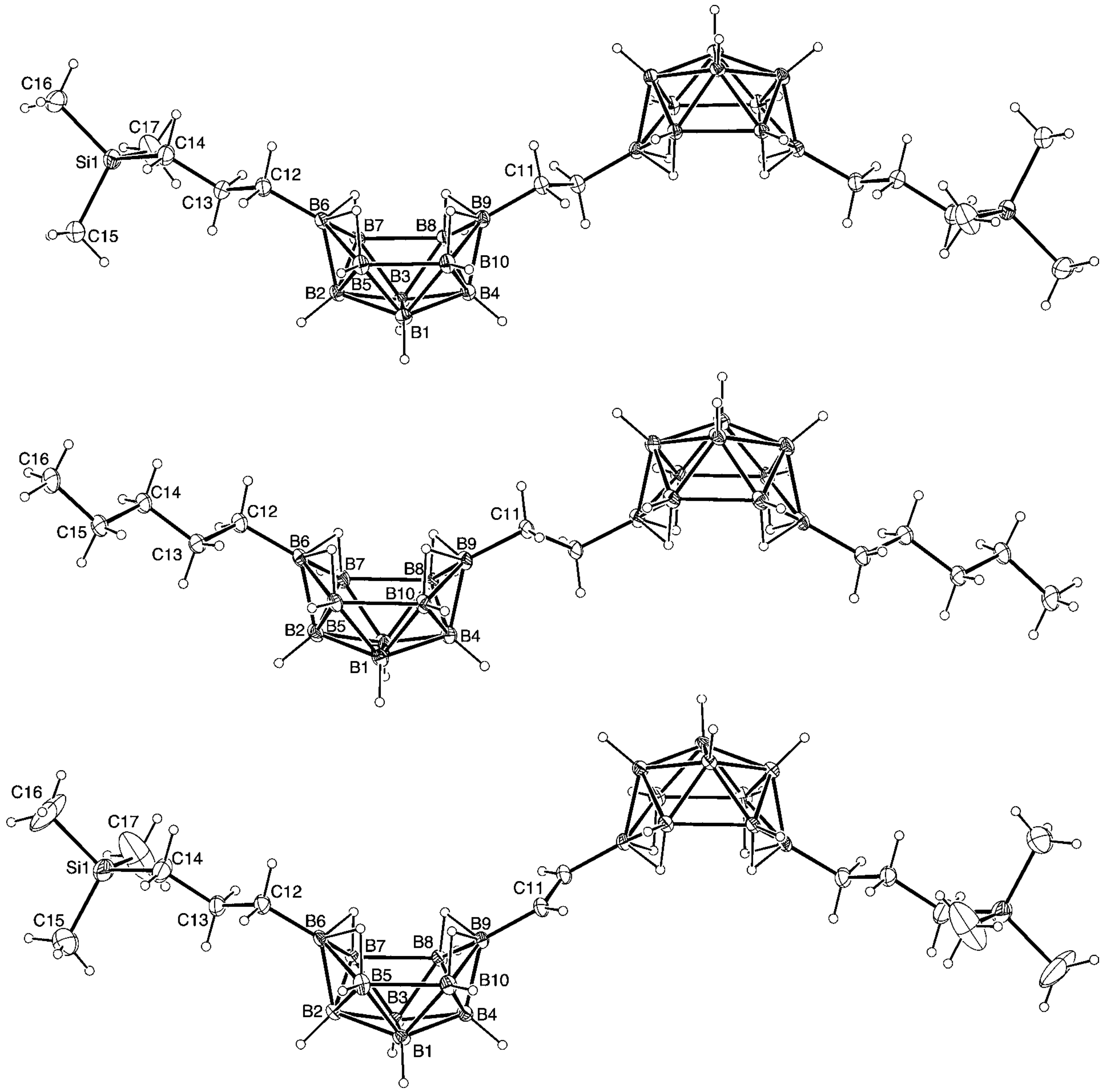


Figure 4. Crystallographically determined structures of **18** (top), **19** (middle), and **20** (bottom). Selected bond lengths (Å) and angles (deg): (**18**) C11−C11′, 1.536(5); B9−C11, 1.575(4); B6−C12, 1.575(4), B9−B4, 1.737(4); C11′−C11−B9, 113.8(3); B6−C12−C13, 114.1(2), C11−B9−B4, 130.9(2). (**19**) B9−C11, 1.573(2); B6−C12, 1.573(3); C11−C11′, 1.539(3), B9−B4, 1.731(3); C11−C11−B9, 112.81(17); C13−C12−B6, 114.17(15), C11−B9−B4, 129.95(15). (**20**) B9−C11, 1.558(4); B6−C12, 1.568(5); C11═C11′, 1.338(7), B9−B4, 1.733(5); C11′═C11−B9, 125.0(4); B6−C12−C13, 114.9(3), C11−B9−B4, 130.8(3).

characteristic downfield, (B6, ~23 ppm) and upfield (B9, ~20−21 ppm) positions. The olefinic protons in their ^{1}H NMR spectra each appeared as a triplet of doublets and a doublet with coupling constants characteristic of a *trans* product. Cross-metathesis reactions with olefins, such as allylchloride or allylethylether, which were previously found[22] to undergo cross-metathesis reactions with 6-(CH_2═$CH(CH_2)_4$)-$B_{10}H_{13}$, were unsuccessful, perhaps as a result of a decreased electron density of the vinyl group in **16** compared to 6-(CH_2═$CH(CH_2)_4$)-$B_{10}H_{13}$.

■ CONCLUSIONS

The iridium and ruthenium catalyzed decaborane and 6-alkyl-decaborane alkyne-hydroboration reactions reported herein now provide the first synthetic routes to both the *β*-E- and the *α*-olefin isomers of the previously unknown 6-alkenyl-, 6,9-dialkenyl-, and 6-alkyl-9-alkenyl-decaboranes in which the olefin group is directly bonded to a cage boron. That these compounds can be readily converted, with the aid of either iridium-catalyzed hydroboration or ruthenium-catalyzed homo- and cross- metathesis reactions to high-boron content linked-cage compounds and/or functionalized decaboranes, demonstrates that these alkenyl-decaboranes are valuable new starting materials for the construction of more complex polyboranes and carboranes including, for example, high boron-content functionalized polyboranes for use in boron neutron capture therapy and new polymeric materials for optical, electronic, and/or structural applications.[23]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures of DFT optimized-geometries with GIAO calculated chemical shifts, tables of Cartesian-coordinates, selected NMR spectra, figures illustrating possible mechanistic pathways and crystallographic data for the structural determinations of **2**, **4**, **10**, **14**, and **18–20** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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