Ruthenium-Catalyzed Homo and Cross Metathesis Reactions of Alkenylpolyboranes: New Routes to Functional *o*-Carborane and Decaborane Derivatives

Xiaolan Wei, Patrick J. Carroll, and Larry G. Sneddon*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Received October 4, 2005

Both 1-(CH_2=$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**1**) and 6-[CH_2=$CH(CH_2)_4$]-$B_{10}H_{13}$ (**2**) undergo homometathesis and cross metathesis reactions in the presence of the Cl_2Ru(=CHPh)(PCy_3)L, L = PCy_3 (**I**) or H_2IMes (**II**), Grubbs catalysts. According to the Grubbs classification, **1** is a type-II olefin for **I** and a type-I olefin for **II** and **2** is a type-I olefin for both the **I** and **II** catalysts. Homometathesis of **1** produces the olefin-bridged compound 1,1′-(CH_2CH=$CHCH_2$)-(1,2-$C_2B_{10}H_{11}$)$_2$ (**3**), while the cross metathesis reactions of **1** with a variety of olefins are efficient, high-yield routes to functional *o*-carborane 1-R-1,2-$C_2B_{10}H_{11}$ derivatives, including R = $C_6H_5CH_2CH$=$CHCH_2$− (**4**), C_6H_5CH=$CHCH_2$− (**5**), $CH_3C(O)OCH_2CH$=$CHCH_2$− (**6**), $HOCH_2CH$=$CHCH_2$− (**7**), $ClCH_2CH$=$CHCH_2$− (**8**), $C_6H_5CH_2OCH_2CH$=$CHCH_2$− (**9**), $CH_3(CH_2)_3CH$=$CHCH_2$− (**10**), $CF_3C(O)OCH_2CH$=$CHCH_2$− (**11**), $CH_3C(O)(CH_2)_2CH$=$CHCH_2$− (**12**), *t*-$C_4H_9OC(O)NHCH_2CH$=$CHCH_2$− (**13**), $NC(CH_2)_3CH$=$CHCH_2$− (**14**), and {[$(CH_3)_4C_2O_2$]BCH_2CH=$CHCH_2$}− (**15**). Deboronation of 1,1′-(CH_2CH=$CHCH_2$)-(1,2-$C_2B_{10}H_{11}$)$_2$ (**3**) with CsF affords the olefin-bridged bis(dicarbollide) salt $2Cs^+$•[7,7′-(CH_2CH=$CHCH_2$)-7,8-($C_2B_9H_{11}$)$_2$]$^{2-}$ (**16**). Similar reactions of 1-[$CH_3(CH_2)_3CH$=$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (**10**) with CsF and tetrabutylammonium fluoride generate the Cs^+ (**17**) and $[N(C_4H_9)_4]^+$ (**18**) [7-$CH_3(CH_2)_3CH$=$CHCH_2$-7,8-$C_2B_9H_{11}$]$^-$ salts, respectively. Homometathesis of **2** affords 6,6′-[$(CH_2)_4CH$=$CH(CH_2)_4$]-($B_{10}H_{13}$)$_2$ (**19**), and its cross metathesis reactions with functional olefins yield a range of functionalized decaborane derivatives 6-R-$B_{10}H_{13}$ (R = $C_6H_5CH_2$-CH=$CH(CH_2)_4$− (**20**), $CH_3C(O)OCH_2CH$=$CH(CH_2)_4$− (**21**), $C_6H_5CH_2OCH_2CH$=$CH(CH_2)_4$− (**22**), $ClCH_2CH$=$CH(CH_2)_4$− (**23**), $CH_3(CH_2)_3CH$=$CH(CH_2)_4$− (**24**), $CF_3C(O)OCH_2CH$=$CH(CH_2)_4$− (**25**), C_6H_5CH=$CH(CH_2)_4$− (**26**), $CH_3C(O)(CH_2)_2CH$=$CH(CH_2)_4$− (**27**), $CH_3CH_2OCH_2CH$=$CH(CH_2)_4$− (**28**), and $CH_3OC(O)CH$=$CH(CH_2)_4$− (**29**)). Cross metathesis of **1** with **2** produces 1-[1-(1,2-$C_2B_{10}H_{11}$)]-CH_2-CH=$CH(CH_2)_4$-7-(6-$B_{10}H_{13}$) (**30**), having *o*-carborane and decaborane cages linked by an alkenyl bridge.

Introduction

Metal carbene catalyzed olefin metathesis reactions,[1] employing either the early transition metal based "Schrock-type" M(NAr)(=CHR)(OR′)$_2$L, M = Mo, W, catalysts[2] or the late transition metal based "Grubbs-type" Cl_2Ru(=CHPh)(PCy_3)L, L = PCy_3 (**I**) and H_2IMes (**II**), catalysts,[3] provide facile, high-yield routes to functional molecules and polymers. We previously reported the use of Grubbs ruthenium carbene complexes to catalyze the ring-opening metathesis polymerization (ROMP) reactions of alkenylpolyboranes, including 6-norbornenyldecaborane and 6-cyclooctenyldecaborane, to afford the corresponding polyborane polymers.[4] In this paper, we describe the first use of these ruthenium carbene complexes to catalyze the homo and cross metathesis reactions of alkenylpolyboranes and demonstrate that these reactions provide efficient routes to a wide range of functionalized alkenyl-*o*-carborane and alkenyldecaborane derivatives.

Experimental Section

General Synthetic Procedures and Materials. 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.[5] 1-(CH_2=$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**1**)[6a] and 6-[CH_2=$CH(CH_2)_4$]-$B_{10}H_{13}$ (**2**)[6b,c] were prepared according to literature methods. Allylbenzene, styrene, 1-hexene, methylacrylate, 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaboronate (allylpinacolborane), and allyl chloride (Aldrich) were distilled prior to use. *tert*-Butyl-*N*-allyl-

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10.1021/om050851l CCC: $33.50
Publication on Web 12/14/2005

carbamate (Aldrich) was recrystallized from cold hexanes prior to use. 2-Butene-1,4-diol, 1,4-*cis*-dibenzoxy-2-butene, cesium fluoride, tetrabutylammonium fluoride (1 M solution in THF), *trans*-stilbene, diacetoxybutene, $Cl_2Ru(=CHPh)(PCy_3)L$, L = PCy_3 (**I**) and H_2-IMes (**II**) (Aldrich), 5-hexen-2-one, allyltrifluoroacetate (Acros), and ACS grade ethanol (Pharmaco) were used as received. Allylethyl ether (Acros) and 5-cyano-1-pentene (Lancaster Synthesis) were distilled prior to use. The 1-(CH_2=CH)-1,2-$C_2B_{10}H_{11}$ (KatChem) was sublimed prior to use. The 1,4-diphenyl-2-butene was prepared according to literature methods.[7] CH_2Cl_2 and THF were purified by passage through an alumina column prior to use. HPLC or ACS grade hexanes, benzene, ethyl acetate, and silica gel with mesh sizes of 230−400 (Fisher) were used as received. $CDCl_3$ (D, 99.8%) and CD_3OD (D, 99%) (Cambridge Isotope Laboratory) were used as received. Thin-layer chromatography (TLC) analyses were conducted on 0.5 mm silica gel F-254 plates (Merck-5744) and stained with a basic $KMnO_4$ solution to visualize the carborane derivatives.

Physical Measurements. ^{1}H NMR at 500.4 MHz, ^{13}C NMR at 125.8 MHz, and ^{11}B NMR spectra at 160.1 MHz were obtained on a Bruker AMX 500 spectrometer. ^{11}B NMR spectra at 128.4 MHz were obtained on a Bruker DMX 400 spectrometer. All ^{11}B NMR chemical shifts are referenced to external $BF_3{\cdot}O(C_2H_5)_2$ (0.00 ppm) with a negative sign indicating an upfield shift. All ^{1}H 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. Low-resolution mass spectra (LRMS) using electrospray ionization (ESI) techniques were recorded on an Agilent LC-MS platform. Infrared spectra were recorded on a Perkin-Elmer 1430 IR spectrometer using NaCl plates or on a Perkin-Elmer 2000 FT-IR spectrometer using KBr pellets or NaCl plates. Elemental analyses were performed at Robertson Microlit Laboratories, Madison, NJ. Melting points were obtained on a standard melting point apparatus and are uncorrected.

1,1′-(CH_2CH=CHCH_2)-(1,2-$C_2B_{10}H_{11}$)$_2$ (3). In a drybox, a two-neck round-bottom flask equipped with a septum, stirbar, and vacuum adapter was charged with 16.6 mg (0.02 mmol) of **II**. The flask was sealed, taken out of the box, and slightly evacuated. Then, 0.5 mL of CH_2Cl_2 and 0.17 g (0.91 mmol) of **1** in 2 mL of CH_2Cl_2 were added through the septum. The reaction mixture was submerged in a 45 °C oil bath and stirred for 48 h. Column chromatography with hexanes and benzene eluents afforded 0.12 g (0.36 mmol, 79%) of **3** as a white solid. For **3**: mp = 278−280 °C. NCI-HRMS (*m*/*e*): calcd for $^{12}C_8{}^{11}B_{20}{}^1H_{28}$ 344.4052, found 344.4051. Anal. Calcd: C, 28.22; H, 8.29. Found: C, 28.45; H, 8.24. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): −3.8 (d, 2B, *J* 148), −7.1 (d, 2B, *J* 142), −10.8 (d, 4B, *J* 150), −13.5 (d, 4B, *J* 173), −14.7 (d, 8B, *J* 182). ^{1}H NMR (500.4 MHz, C_6D_6, ppm, *J* = Hz): 5.47 (t of t, 2H, J_1 4.3, J_2 1.8, =CH), 3.54 (s, br, 2H, cage C−H), 2.97 (d, 4H, *J* 4.1, =CH−CH_2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 129.5, 73.0, 60.3, 40.6. FT-IR (KBr pellet, cm^{-1}): 3064 (s), 2924 (w), 2854 (w), 2590 (vs), 1618 (w), 1434 (m), 1355 (w), 1292 (w), 1212 (m), 1153 (m), 1123 (w), 1080 (w), 1051 (w), 1017 (m), 983 (m), 937 (w), 821 (w), 724 (m), 677 (w), 640 (w), 555 (w), 504 (w).

1-($C_6H_5CH_2$CH=CHCH_2)-1,2-$C_2B_{10}H_{11}$ (4). As described for **3**, 0.38 g (1.8 mmol) of **1**, 1.5 g (7.2 mmol) of 1,4-diphenyl-2-butene,[7] and 8 mg (0.01 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 24 h. Column chromatography with hexanes eluted 1,4-diphenyl-2-butene. Subsequent elution with benzene afforded 0.33 g (1.2 mmol, 62%) of **4** as a light yellow oil, which slowly crystallized into a white solid at 0 °C. For **4**: mp < room temperature. NCI-HRMS (*m*/*e*): calcd for $^{12}C_{12}{}^{11}B_{10}{}^1H_{22}$ 276.2652, found 276.2652. Anal. Calcd: C, 52.52; H, 8.08. Found: C, 52.73; H, 8.07. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): −4.4 (d, 1B, *J* 148), −7.7 (d, 1B, *J* 147), −11.1 (d, 2B, *J* 150), −13.0 (d, 2B, *J* 150), −14.6 (d, 2B, *J* 145), −15.0 (d, 2B, *J* 153). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 7.41−7.23 (m, 5H, C_6H_5), 5.78 (d of t of t, 1H, J_1 15.1, J_2 8.3, J_3 1.1, =CH), 5.46 (d of t of t, 1H, J_1 15.2, J_2 7.6, J_3 1.5, =CH), 3.59 (s, br, 1H, cage C−H), 3.46 (d, 2H, *J* 6.8, =CH−CH_2), 2.98 (d, 2H, *J* 7.5, =CH−CH_2). IR (NaCl plate, cm^{-1}): 3060 (s), 2920 (w), 2600 (vs), 2320 (w), 1900 (br, w), 1450 (m), 1270 (w), 1255 (s), 1205 (w), 1110 (m), 1050 (m), 1010 (s), 970 (s), 930 (w), 755 (w), 720 (s), 690 (w).

1-(C_6H_5CH=CHCH_2)-1,2-$C_2B_{10}H_{11}$ (5). As described for **3**, 0.27 g (1.5 mmol) of **1**, 0.52 g (2.9 mmol) of *trans*-stilbene, and 10 mg (0.01 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 48 h. The solvent was evaporated and the residue extracted three times with cold hexanes. Column chromatography of the extract with a 5:1 hexanes/ethyl acetate eluent afforded 0.32 g (1.2 mmol, 81% yield) of **5** as a white solid. For **5**: mp = 90−91 °C. NCI-HRMS (*m*/*e*): calcd for $^{12}C_{11}{}^{11}B_{10}{}^1H_{20}$ 262.2496, found 262.2500. Anal. Calcd: C, 50.74; H, 7.74. Found: C, 50.46; H, 8.01. ^{11}B NMR: (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): −4.1 (d, 1B, *J* 150), −7.5 (d, 1B, *J* 149), −10.9 (d, 2B, *J* 151), −12.9 (d, 2B, *J* 156), −14.8 (d, 4B, *J* 160). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 7.32−7.20 (m, 5H, C_6H_5), 6.37 (d, 1H, *J* 15.7, =CH), 5.98 (m, 1H, =CH), 3.55 (s, br, 1H, cage C−H), 3.05 (d, 2H, *J* 7.7, =CHCH_2). IR (NaCl plate, cm^{-1}): 3080 (m), 3040 (m), 2550 (vs), 1600 (w), 1490 (m), 1455 (s), 1075 (m), 965 (s), 765 (s), 730 (w), 695 (s).

1-[CH_3C(O)OCH_2CH=CHCH_2]-1,2-$C_2B_{10}H_{11}$ (6). As described for **3**, 0.17 g (0.92 mmol) of **1**, 0.60 mL (3.8 mmol) of *cis*-1,4-diacetoxy-2-butene, and 15 mg (0.02 mmol) of **II** were refluxed in 2 mL of CH_2Cl_2 for 24 h. Column chromatography with a 3:1 hexanes/ethyl acetate eluent afforded the crude product. Vacuum distillation afforded 0.19 g (0.66 mmol, 84% yield) of **6** as a light colorless oil, which crystallized as a white solid at 0 °C. For **6**: mp = 23−24 °C. NCI-HRMS (*m*/*e*): calcd for $^{12}C_8{}^{11}B_{10}{}^{16}O_2{}^1H_{20}$ 258.2394, found 258.2402. Anal. Calcd: C, 37.48; H, 7.86. Found: C, 37.68; H, 7.81. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): −4.3 (d, 1B, *J* 149), −7.6 (d, 1B, *J* 149), −11.1 (d, 2B, *J* 150), −13.1 (d, 2B, *J* 167), −15.0 (d, 4B, *J* 158). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 5.64 (m, 2H, =CH), 4.56 (d, 2H, *J* 4.2, =CH−CH_2), 3.60 (s, br, 1H, cage C−H), 2.97 (d, 2H, *J* 6.0, =CH−CH_2), 2.08 (s, 3H, CH_3). IR (NaCl plate, cm^{-1}): 3420 (br, m), 3030 (m), 2920 (m), 2560 (vs), 1710 (vs), 1430 (m), 1365 (s), 1345 (s), 1215 (vs), 1105 (m), 1040 (m), 1005 (s), 955 (s), 825 (w), 705 (s).

1-(HOCH_2CH=CHCH_2)-1,2-$C_2B_{10}H_{11}$ (7). As described for **3**, 0.26 g (1.4 mmol) of **1**, 0.72 mL (8.8 mmol) of 2-butene-1,4-diol, and 19 mg (0.02 mmol) of **II** were refluxed in a cosolvent of 3 mL of CH_2Cl_2 and 1.5 mL of THF for 16 h. Column chromotography with benzene eluent afforded 0.23 g (1.1 mmol, 76% yield) of **7** as a colorless oil. For **7**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_6{}^{11}B_{10}{}^{16}O_1{}^1H_{18}$ 216.2288, found 216.2294. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): −4.5 (d, 1B, *J* 148), −7.8 (d, 1B, *J* 148), −11.3 (d, 2B, *J* 150), −13.2 (d, 2B, *J* 166), −15.2 (d, 4B, *J* 157). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 5.75 (m, 1H, =CH), 5.59 (m, 1H, =CH), 4.16 (d, 2H, *J* 6.0, =CH−CH_2), 3.61 (s, br, 1H, cage C−H), 2.89 (d, 2H, *J* 7.4, =CH−CH_2), 1.81 (s, 1H, OH). IR (NaCl plate, cm^{-1}): 3580 (w), 3450 (s, br), 3020 (s), 2905 (m), 2840 (w), 2540 (vs), 1745 (m), 1685 (s), 1415 (s), 1355 (m), 1290 (w), 1210 (w), 1080 (s), 1045 (m), 980 (s), 955 (s), 870 (w), 775 (w), 705 (s).

1-(ClCH_2CH=CHCH_2)-1,2-$C_2B_{10}H_{11}$ (8). As described for **3**, 0.20 g (1.1 mmol) of **1**, 1.2 mL (11.4 mmol) of *cis*-1,4-dichloro-2-butene, and 21 mg (0.02 mmol) of **II** were refluxed in 2 mL of CH_2Cl_2 for 15 h. Column chromatography with benzene eluent afforded 0.26 g (0.92 mmol, 87% yield) of **8** as a light yellow oil. For **8**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_6{}^{11}B_{10}{}^{35}Cl_1{}^1H_{17}$ 234.1949,

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found 234.1955. Anal. Calcd: C, 30.96; H, 7.36. Found: C, 31.44; H, 6.80. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): −4.3 (d, 1B, J 148), −7.6 (d, 1B, J 150), −11.1 (d, 2B, J 150), −13.3 (d, 2B, J ∼180), −15.0 (d, 4B, J 158). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.73 (m, 2H, =CH), 4.02 (d, 2H, J 5.9, =CH−CH_2), 3.57 (s, br, 1H, cage C−H), 2.98 (d, 2H, J 6.8, =CH−CH_2). IR (NaCl plate, cm^{-1}): 3015 (s), 2920 (m), 2570 (vs), 2285 (w), 1415 (s), 1325 (w), 1265 (w), 1235 (s), 1190 (w), 1140 (w), 1100 (w), 1040 (m), 995 (m), 980 (w), 945 (s), 760 (w), 745 (w), 705 (s), 670 (w).

1-($C_6H_5CH_2OCH_2CH$=$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (9). As described for **3**, 0.17 g (0.92 mmol) of **1**, 1.0 mL (3.9 mmol) of *cis*-1,4-dibenzoxy-2-butene, and 15 mg (0.02 mmol) of **II** were refluxed in 2 mL of CH_2Cl_2 for 15 h. Column chromatography with 3:1 and 1:1 hexanes/benzene eluents afforded 0.22 g (0.73 mmol, 79% yield) of **9** as a colorless oil. For **9**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_{13}{}^{11}B_{10}{}^{16}O_1{}^1H_{24}$ 306.2758, found 306.2759. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): −1.3 (d, 1B, J 152), −4.7 (d, 1B, J 146), −8.3 (d, 2B, J 149), −10.2 (d, 2B, J 170), −12.0 (d, 4B, J 156). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 7.40−7.33 (m, 5H, C_6H_5), 5.67 (m, 2H, =CH), 4.54 (s, 2H, CH_2−C_6H_5), 4.02 (d, 2H, J 5.0, =CH−CH_2), 3.56 (s, br, 1H, cage C−H), 2.97 (d, 2H, J 7.0, =CH−CH_2). IR (NaCl plate, cm^{-1}): 3125 (s), 3095 (s), 2980 (m), 2925 (s), 2680 (vs), 1490 (w), 1460 (m), 1440 (w), 1365 (m), 1205 (w), 1110 (m), 1085 (m), 980 (m), 795 (w), 745 (m), 720 (s), 680 (w).

1-[$CH_3(CH_2)_3CH$=$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (10). As described for **3**, 0.33 g (1.8 mmol) of **1**, 3 mL of 1-hexene, and 10 mg (0.01 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 14 h. Column chromatography with hexanes eluent afforded 0.38 g (1.6 mmol, 88% yield) of **10** as a colorless viscous oil. For **10**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_9{}^{11}B_{10}{}^1H_{24}$ 242.2809, found 242.2809. Anal. Calcd: C, 44.97; H, 10.06. Found: C, 44.60; H, 9.55. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): −4.4 (d, 1B, J 148), −7.8 (d, 1B, J 148), −11.1 (d, 2B, J 151), −12.9 (d, 2B, J 165), −15.0 (d, 4B, J 158). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.55 (m, 1H, =CH), 5.30 (m, 1H, =CH), 3.55 (s, br, 1H, cage C−H), 2.89 (d, 2H, J 7.4, =CH−CH_2), 2.06 (d, 2H, J 6.8, =CH−CH_2), 1.34 (m, 4H, 2CH_2), 0.91 (t, 3H, J 7.2, CH_3). IR (NaCl plate, cm^{-1}): 3080 (s), 2950 (s), 2915 (s), 2580 (vs), 1705 (w), 1660 (w), 1450 (m), 1430 (s), 1375 (w), 1290 (w), 1200 (w), 1110 (w), 1060 (m), 1010 (m), 960 (s), 930 (w), 715 (s).

1-[$CF_3C(O)OCH_2CH$=$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (11). As described for **3**, 0.24 g (1.3 mmol) of **1**, 1.0 mL (7.7 mmol) of allyltrifluoroacetate, and 28 mg (0.03 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 5 h. Column chromatography with a 1:1 hexanes/benzene eluent afforded 0.31 g (1.2 mmol, 77% yield) of **11** as a colorless oil. For **11**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_8{}^{11}B_{10}{}^{19}F_3{}^{16}O_2{}^1H_{17}$ 312.2111, found 312.2109. Anal. Calcd: C, 30.96; H, 5.52. Found: C, 31.41; H, 5.90. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): −1.3 (d, 1B, J 151), −4.6 (d, 1B, J 150), −8.3 (d, 2B, J 150), −10.5 (d, 2B, J 174), −11.7 (d, 4B, J 159). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.80 (m, 1H, =CH), 5.72 (m, 1H, =CH), 4.83 (d, 2H, J 6.0, =CH−CH_2), 3.56 (s, br, 1H, cage C−H), 3.01 (d, 2H, J 7.3, =CH−CH_2). IR (NaCl plate, cm^{-1}): 3035 (m), 2915 (w), 2550 (vs), 1760 (vs), 1530 (w), 1435 (m), 1410 (w), 1375 (m), 1325 (s), 1205 (vs), 1150 (vs), 1045 (w), 995 (m), 950 (s), 930 (w), 905 (m), 845 (w), 815 (w), 755 (m), 705 (s).

1-[$CH_3C(O)(CH_2)_2CH$=$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (12). As described for **3**, 0.23 g (1.2 mmol) of **1**, 1.2 mL (10 mmol) of 5-hexen-2-one, and 27 mg (0.03 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 18 h. Column chromatography with 1:1 hexanes/benzene and CH_2Cl_2 eluents afforded 0.22 g (0.87 mmol, 69% yield) of **12** as a light yellow oil, which slowly crystallized upon standing. For **12**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_9{}^{11}B_{10}{}^{16}O_1{}^1H_{22}$ 256.2601, found 256.2591. Anal. Calcd: C, 42.50; H, 8.72. Found: C, 43.31; H, 8.64. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): −4.5 (d, 1B, J 150), −7.8 (d, 1B, J 147), −11.2 (d, 2B, J 151), −13.1 (d, 2B, J 168), −15.0 (d, 4B, J 158). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.54 (m, 1H, =CH), 5.35 (m, 1H, =CH), 3.62 (s, br, 1H, cage C−H), 2.88 (d, 2H, J 7.5, =CH−CH_2), 2.54 (t, 2H, J 7.0, =CHCH_2CH_2), 2.32 (m, 2H, =CH−CH_2), 2.11 (s, 3H, CH_3). IR (NaCl plate, cm^{-1}): 3030 (s), 2895 (m), 2550 (vs), 1685 (vs), 1410 (m), 1390 (m), 1340 (s), 1290 (w), 1205 (w), 1165 (w), 1140 (s), 1045 (m), 995 (s), 955 (s), 760 (w), 705 (s).

1-[*t*-$C_4H_9OC(O)NHCH_2CH$=$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (13). As described for **3**, 0.15 g (0.82 mmol) of **1**, 0.70 g (4.5 mmol) of *tert*-butyl-*N*-allylcarbamate, and 27 mg (0.03 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 48 h. Column chromatography with benzene and 1:1 benzene/CH_2Cl_2 eluents followed by recrystallization from hexanes afforded 0.18 g (0.57 mmol, 70% yield) of **13** as a white solid. For **13**: mp = 108−110 °C. NCI-HRMS (*m*/*e*): calcd for $^{12}C_{11}{}^{11}B_{10}{}^{14}N_1{}^{16}O_2{}^1H_{27}$ 315.2972, found 315.2969. Anal. Calcd: C, 42.15; H, 8.68; N, 4.47. Found: C, 41.63; H, 8.35; N, 4.29. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): −4.7 (d, 1B, J 147), −7.8 (d, 1B, J 147), −11.1 (d, 2B, J 150), −13.0 (d, 2B, J 163), −15.1 (d, 4B, J 165). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.53 (m, 2H, =CH), 4.72 (s, br, 1H, NH), 3.81 (s, br, 1H, cage C−H), 3.70 (t, 2H, J 5.2, =CH−CH_2), 2.94 (d, 2H, J 7.1, =CH−CH_2), 1.46 (s, 9H, BOC−CH_3). FT-IR (KBr pellet, cm^{-1}): 3345 (s), 3060 (m), 2982 (m), 2925 (w), 2582 (vs), 1753 (s), 1687 (vs), 1543 (s), 1536 (m), 1509 (m), 1441 (w), 1408 (m), 1390 (w), 1294 (m), 1259 (w), 1162 (s), 1053 (m), 1021 (w), 977 (s), 866 (w), 788 (w), 724 (w), 597 (w).

1-[$NC(CH_2)_3CH$=$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (14). As described for **3**, 0.23 g (1.2 mmol) of **1**, 2.0 g (21 mmol) of 5-cyano-1-pentene, and 27 mg (0.03 mmol) of **II** were refluxed in 2 mL of CH_2Cl_2 for 14 h. Column chromatography with benzene and 1:1 benzene/CH_2Cl_2 eluents afforded 0.21 g (0.8 mmol, 66% yield) of **14** as a yellow oil. For **14**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_9{}^{11}B_{10}{}^{14}N_1{}^1H_{21}$ 253.2605, found 253.2611. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): −4.4 (d, 1B, J 148), −7.8 (d, 1B, J 148), −11.3 (d, 2B, J 150), −13.3 (d, 2B, J 176), −15.1 (d, 4B, J 158). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.48 (m, 2H, =CH), 3.58 (s, br, 1H, cage C−H), 2.92 (d, 2H, J 7.0, =CH−CH_2), 2.37 (t, 2H, J 7.0, CH_2CN), 2.27 (q, 2H, J 7.0, =CH−CH_2), 1.78 (p, 2H, J 7.2, CH_2). IR (NaCl plate, cm^{-1}): 3030 (s), 2905 (s), 2850 (m), 2815 (m), 2530 (vs), 2220 (m), 1710 (w), 1695 (w), 1650 (w), 1620 (w), 1430 (m), 1410 (s), 1340 (w), 1270 (w), 1245 (w), 1190 (w), 1100 (w), 995 (m), 950 (s), 770 (w), 705 (s).

1-{[$(CH_3)_4C_2O_2$]BCH_2CH=$CHCH_2$}-1,2-$C_2B_{10}H_{11}$ (15). As described for **3**, 0.27 g (1.5 mmol) of **1**, 1.0 mL (5.3 mmol) of 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaboronate, and 20 mg (0.02 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 14 h. Column chromatography with benzene eluent afforded 0.26 g (0.80 mmol, 55% yield) of **15** as a colorless oil, which slowly crystallized upon standing. For **15**: a white solid, mp = 53−54 °C. NCI-HRMS (*m*/*e*): calcd for $^{12}C_{12}{}^{11}B_{11}{}^{16}O_2{}^1H_{29}$ 326.3191, found 326.3181. Anal. Calcd: C, 44.45; H, 9.01. Found: C, 44.24; H, 9.06. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): 32.3 (s, 1B), −3.3 (d, 1B, J 119) −6.4 (d, 1B, J 147), −9.7 (d, 2B, J 146), −11.3 (d, 2B, J 172), −13.7 (d, 4B, J 156). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.61 (m, 1H, =CH), 5.28 (m, 1H, =CH), 4.00 (s, br, 1H, cage C−H), 2.88 (d, 2H, J 7.6, =CH−CH_2), 1.70 (d, 2H, J 7.5, =CH−CH_2), 1.25 (s, 12H, −CH_3). IR (NaCl plate, cm^{-1}): 3000 (s), 2930 (s), 2550 (vs), 1640 (w), 1610 (w), 1445 (m), 1415 (m), 1360 (vs), 1245 (m), 1190 (m), 1140 (m), 1115 (vs), 1085 (m), 1055 (m), 995 (m), 945 (s), 855 (m), 820 (s), 765 (w), 700 (m), 650 (w).

2Cs^+·[7,7′-(CH_2CH=$CHCH_2$)-(7,8-$C_2B_9H_{11}$)$_2$]$^{2-}$ (16). Following the procedure described by Do,[8a] 0.21 g (0.62 mmol) of **3** and 0.62 g of CsF (4.3 mmol) were dissolved in 20 mL of anhydrous ethanol. After three cycles of freeze−pump−thaw, the mixture was

refluxed in vacuo until ^{11}B NMR analysis showed complete consumption of **3** (48 h). The solvent was vacuum evaporated and the residue rinsed three times with cold deionized water and then dried in vacuo. Recrystallization from ethanol afforded 0.25 g (0.36 mmol, 58% yield) of **16** as a white solid. For **16**: mp > 300 °C. ESI-LRMS: (*m*/*e*) calcd for $^{12}C_8{}^{11}B_{18}{}^{1}H_{28}$ 161, found 161. ^{11}B NMR (160.1 MHz, CD_3OD, ppm, J = Hz): −11.0 (d, 4B, *J* 132), −13.6 (d, 2B, *J* 153), −17.2 (d, 2B, *J* 143), −18.5 (d, 4B, *J* 171), −21.9 (d, 2B, *J* 145), −33.5 (d, 2B, *J* 135), −37.2 (d, 2B, *J* 142). ^1H NMR (500.4 MHz, CD_3OD, ppm, J = Hz): 5.16 (m, 2H, =C*H*), 2.21 (m, 4H, =CH−CH_2), 2.06 (s, br, 2H, cage C−H), −2.68 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 3370 (br, s), 2900 (s), 2480 (vs), 1640 (s), 1420 (w), 1180 (m), 1050 (m), 1010 (s), 970 (m).

Cs^+[7-$CH_3(CH_2)_3CH$=$CHCH_2$-7,8-$C_2B_9H_{11}$]$^-$ (17). As described for **16**, 0.30 g (1.2 mmol) of **10** was reacted with 0.38 g (2.5 mmol) of CsF in 20 mL of anhydrous ethanol for 48 h under reflux in vacuo.[8a] The ethanol was evaporated, and the residue was rinsed three times with cold deionized water and dried in vacuo. Recrystallization from cold ethanol/water afforded 0.40 g (1.1 mmol, 88% yield) of **17** as a white solid. For **17**: mp > 300 °C. ESI-LRMS (*m*/*e*): calcd for $^{12}C_9{}^{11}B_9{}^{1}H_{24}$ 231, found 231. Anal. Calcd: C, 29.82; H, 6.67. Found: C, 29.80; H, 6.54. ^{11}B NMR (160.1 MHz, CD_3OD, ppm, J = Hz): −12.8 (d, 2B, *J* 130), −15.4 (d, 1B, *J* 153), −18.9 (d, 1B, *J* 146), −20.2 (d, 2B, *J* ∼134), −23.7 (d, 1B, *J* 150), −35.2 (d, 1B, *J* ∼134), −38.9 (d, 1B, *J* 128). ^1H NMR (500.4 MHz, CD_3OD, ppm, J = Hz): 5.44 (m, 1H, =CH), 5.24 (m, 1H, =CH), 2.04 (d, 2H, *J* 7.3, =CH−CH_2), 1.95 (d, 2H, *J* 6.6, =CH−CH_2), 1.60 (s, 1H, cage C−H), 1.32 (m, 4H, 2CH_2), 0.88 (t, 3H, *J* 7.0, CH_3), −2.82 (s, br, 1H, BHB). FT-IR (KBr pellet, cm^{-1}): 3399 (br, s), 2592 (m), 2932 (m), 2860 (w), 2528 (vs), 2288 (w), 2044 (w), 1701 (w), 1654 (w), 1420 (vs), 1300 (s), 1072 (s), 925 (m), 782 (w), 721 (m).

[$N(C_4H_9)_4$]$^+$[7-$CH_3(CH_2)_3CH$=$CHCH_2$-7,8-$C_2B_9H_{11}$]$^-$ (18). Following the procedure reported by Wade,[8b] 0.20 g (0.83 mmol) of **10** dissolved in 5 mL of THF was added to 3.3 mL of a 1 M tetrabutylammonium fluoride THF solution (3.3 mmol). The reaction mixture was stirred at room temperature overnight. Deionized water (10 mL) was added and the mixture then extracted three times with 20 mL of CH_2Cl_2. The organic layer was separated, filtered through silica gel, and then dried with $MgSO_4$. The bulk of the volatiles were removed via Rotovap, and the product was further dried on the high-vacuum line to afford 0.33 g (0.70 mmol, 84% yield) of **18** as a waxy white solid. For **18**: mp = 96−97 °C. ESI-LRMS (*m*/*e*): calcd for $^{12}C_9{}^{11}B_9{}^{1}H_{24}$ 231, found 231. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): −13.1 (d, 2B, *J* 133), −16.0 (d, 1B, *J* 146), −20.1 (s, br, 3B), −24.3 (d, 1B, *J* 140), −35.7 (d, 1B, *J* ∼134), −39.4 (d, 1B, *J* 140). ^1H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.50 (m, 1H, =CH), 5.29 (m, 1H, =CH), 3.18 (t, 36H, *J* 8.6, CH_3), 2.40 (d, 2H, *J* 6.0, =CH−CH_2), 2.21 (d, 2H, *J* 7.1, =CH−CH_2), 1.96 (m, 4H, 2CH_2), 1.86 (s, 1H, cage C−H), 1.03 (t, 3H, *J* 7.3, CH_3), −2.61 (s, br, 1H, BHB). FT-IR (KBr pellet, cm^{-1}): 3364 (s), 2963 (s), 2876 (s), 2521 (vs), 1420 (vs), 1304 (s), 1212 (w), 1134 (w), 1029 (m), 969 (w), 914 (m), 777 (m), 739 (m), 706 (w), 669 (w), 549 (w), 514 (w), 482 (w), 460 (w).

6,6′-[$(CH_2)_4CH$=$CH(CH_2)_4$]-($B_{10}H_{13}$)$_2$ (19). As described for **3**, 0.25 g (1.2 mmol) of **2** and 8 mg (0.01 mmol) of **I** were stirred in 2 mL of CH_2Cl_2 at room temperature for 24 h. Column chromatography with hexanes and benzene eluents afforded 0.14 g (0.36 mmol, 61% yield) of **19** as a light yellow solid. Alternatively, 0.40 g (2.0 mmol) of **2** and 8 mg of **II** (0.01 mmol) were refluxed in 2 mL of CH_2Cl_2 for 36 h. Column chromatography with hexanes and benzene eluents afforded 0.29 g (0.76 mmol, 78% yield) of **19**. For **19**: mp = 53−54 °C. NCI-HRMS (*m*/*e*) calcd for $^{12}C_{10}{}^{11}B_{20}{}^{1}H_{44}$ 384.5304, found 384.5316. Anal. Calcd: C, 31.55; H, 11.65. Found: C, 31.63; H, 11.86. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): 24.2 (s, 2, B6), 8.5 (d, 4, B1,3, *J* 166), 6.8 (d, 2, B9, *J* 145), −0.8 (d, 4, B5,7, *J* 153), −4.6 (d, 4, B8,10, *J* 154), −35.7 (d, 2, B2, *J* 154), −40.5 (d, 2, B4, *J* 153). ^1H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.42 (t, 2H, *J* 5.1, =CH), 2.04 (d, 4H, *J* 5.5, =CH−CH_2), 1.59 (m, 4H, CH_2), 1.47 (m, 4H, CH_2), 1.38 (m, 4H, CH_2), −1.71 (s, br, 4H, BHB), −2.02 (s, br, 4H, BHB). IR (NaCl plate, cm^{-1}): 2940 (s), 2870 (m), 2590 (vs), 1920 (br, w), 1550 (w), 1535 (w), 1500 (s), 1440 (m), 1410 (m), 1095 (m), 1000 (s), 960 (m), 935 (w), 920 (w), 860 (w), 845 (m), 815 (m), 700 (br, m).

6-[$C_6H_5CH_2CH$=$CH(CH_2)_4$]-$B_{10}H_{13}$ (20). As described for **3**, 0.38 g (1.8 mmol) of **2**, 1.5 g (7.2 mmol) of 1,4-diphenyl-2-butene,[7] and 8 mg (0.01 mmol) of **II** were refluxed in 2 mL of CH_2Cl_2, for 48 h. Column chromatography with 2% ethyl acetate in hexanes separated the excess 1,4-diphenyl-2-butene, while elution with benzene afforded 0.34 g (1.2 mmol, 62% yield) of **20** as a yellow oil, which slowly crystallized into a light yellow solid upon standing. For **20**: mp = 160−163 °C. NCI-HRMS (*m*/*e*): calcd for $^{12}C_{13}{}^{11}B_{10}{}^{1}H_{29}$ (M−H) 295.3200, found 295.3206. Anal. Calc: C, 53.02; H, 10.27. Found: C, 52.60; H, 9.62. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): 23.9 (s, 1, B6), 8.4 (d, 2, B1,3, *J* 147), 6.7 (d, 1, B9, *J* 165), −0.9 (d, 2, B5,7, *J* 153), −4.7 (d, 2, B8,10, *J* 152), −35.9 (d, 1, B2, *J* 154), −40.6 (d, 1, B4, *J* 154). ^1H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 7.37−7.21 (m, 5H, C_6H_5), 5.62 (m, 1H, =CH), 5.54 (m, 1H, =CH), 3.37 (d, 2H, *J* 6.5, =CH−CH_2), 2.10 (q, 2H, *J* 7.0, =CH−CH_2), 1.62 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), −1.70 (s, br, 2H, BHB), −2.01 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 3220 (w), 3060 (w), 3020 (m), 2905 (s), 2575 (vs), 1955 (w), 1905 (w), 1605 (w), 1555 (m), 1495 (vs), 1450 (s), 1415 (vs), 1340 (s), 1095 (s), 1000 (s), 965 (s), 940 (w), 920 (w), 890 (w), 840 (w), 815 (m), 735 (s), 700 (s).

6-[$CH_3C(O)OCH_2CH$=$CH(CH_2)_4$]-$B_{10}H_{13}$ (21). As described for **3**, 0.41 g (2.0 mmol) of **2**, 1.5 mL (9.4 mmol) of *cis*-1,4-diacetoxy-2-butene, and 8 mg (0.01 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 48 h. Column chromatography with a 4:1 hexanes/benzene eluent afforded 0.34 g (1.2 mmol, 61%) of **21** as a light yellow solid. For **21**: mp = 162−164 °C. NCI-HRMS (*m*/*e*): calcd for $^{12}C_9{}^{11}B_{10}{}^{16}O_2{}^{1}H_{28}$ 278.3020, found 278.3010. Anal. Calcd: C, 39.11; H, 10.21. Found: C, 38.60; H, 9.98. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): 24.0 (s, 1, B6), 8.1 (d, 2, B1,3, *J* 146), 6.8 (d, 1, B9, *J* ∼129), −1.1 (d, 2, B5,7, *J* 165), −4.8 (d, 2, B8,10, *J* 152), −35.8 (d, 1, B2, *J* 158), −40.6 (d, 1, B4, *J* 154). ^1H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 5.78 (m, 1H, =CH), 5.59 (m, 1H, =CH), 4.52 (d, 2H, *J* 6.4, =CH−CH_2), 2.14 (m, 2H, CH_2), 2.10 (s, 3H, CH_3), 1.58 (m, 2H, CH_2), 1.49 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), −1.71 (s, br, 2H, BHB), −2.01 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 2920 (s), 2865 (w), 2565 (vs), 1500 (m), 1475 (m), 1375 (m), 1285 (s), 1190 (w), 1020 (m), 1000 (m), 955 (m).

6-[$C_6H_5CH_2OCH_2CH$=$CH(CH_2)_4$]-$B_{10}H_{13}$ (22). As described for **3**, 0.27 g (1.3 mmol) of **2**, 1.5 mL (5.8 mmol) of 1,4-*cis*-dibenzoxy-2-butene, and 23 mg (0.02 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 20 h. Column chromatography with a 1:1 benzene/hexanes eluent afforded 0.45 g (1.0 mmol, 76% yield) of **22** as a viscous yellow oil. For **22**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_{14}{}^{11}B_{10}{}^{16}O_1{}^{1}H_{32}$ 326.3384, found 326.3401. Anal. Calcd: C, 51.82; H, 9.94. Found: C, 52.44; H, 9.52. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, J = Hz): 27.1 (s, 1, B6), 10.9 (d, 2, B1,3, *J* 149), 9.6 (d, 1, B9, *J* ∼126), 1.8 (d, 2, B5,7, *J* 161), −2.1 (d, 2, B8,10, *J* 148), −32.7 (d, 1, B2, *J* 157), −37.5 (d, 1, B4, *J* 157). ^1H NMR (500.4 MHz, $CDCl_3$, ppm, J = Hz): 7.39−7.36 (m, 5H, C_6H_5), 5.73 (m, 1H, =CH), 5.63 (m, 1H, =CH), 4.53 (s, 2H, CH_2−C_6H_5), 4.00 (d, 2H, *J* 6.2, =CH−CH_2), 2.11 (q, 2H, *J* 7.0, =CH−CH_2), 1.61 (m, 2H, CH_2), 1.52 (t, 2H, *J* 6.2, CH_2), 1.40 (m, 2H, CH_2),

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−1.71 (s, br, 2H, BHB), −2.01 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 3085 (w), 3205 (m), 3005 (s), 2895 (vs), 2810 (vs), 2550 (vs), 1940 (w), 1880 (w), 1785 (w), 1655 (w), 1530 (m), 1480 (s), 1420 (s), 1395 (m), 1340 (m), 1295 (w), 1245 (w), 1185 (w), 1075 (s), 1040 (m), 985 (s), 950 (s), 915 (m), 820 (w), 795 (w), 725 (m), 715 (m), 680 (m), 655 (m).

6-[ClCH$_2$CH═CH(CH$_2$)$_4$]-B$_{10}$H$_{13}$ (23). As described for **3**, 0.40 g (2.0 mmol) of **2**, 2.0 mL (24.5 mmol) of allyl chloride, and 8 mg (0.01 mmol) of **II** were refluxed in 2 mL of CH_2Cl_2 for 14 h. Column chromatography with a 1:1 benzene/hexanes eluent afforded 0.33 g (1.3 mmol, 67% yield) of **23** as a viscous light yellow oil. For **23**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_7{}^{11}B_{10}{}^{35}Cl_1{}^1H_{25}$ 254.2575, found 254.2552. Anal. Calcd: C, 33.25; H, 9.97. Found: C, 33.24; H, 9.76. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): 23.8 (s, 1, B6), 8.5 (d, 2, B1,3, *J* 147), 6.8 (d, 1, B9, *J* 164), −0.9 (d, 2, B5,7, *J* 154), −4.6 (d, 2, B8,10, *J* 152), −35.8 (d, 1, B2, *J* 154), −40.5 (d, 1, B4, *J* 154). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 5.79 (m, 1H, ═CH), 5.65 (m, 1H, ═CH), 4.05 (d, 2H, *J* 7.1, ═CH−C*H*$_2$), 2.12 (q, 2H, *J* 7.1, ═CH−C*H*$_2$), 1.57 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), −1.72 (s, br, 2H, BHB), −2.03 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 2895 (s), 2815 (m), 2515 (vs), 1880 (w), 1695 (s), 1645 (w), 1545 (m), 1515 (m), 1475 (s), 1415 (s), 1350 (w), 1225 (s), 1075 (m), 1020 (w), 980 (s), 940 (s), 910 (w), 895 (w), 840 (w), 815 (w), 790 (m), 705 (m), 665 (m).

6-[CH$_3$(CH$_2$)$_3$CH═CH(CH$_2$)$_4$]-B$_{10}$H$_{13}$ (24). As described for **3**, 0.26 g (1.3 mmol) of **2**, 2.0 mL of 1-hexene, and 10 mg (0.01 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 overnight. Column chromatography with hexanes eluent afforded the crude product, which was then vacuum distilled (85 °C, 7 mmHg) to afford 0.33 g (1.3 mmol, 78% yield) of **24** as a colorless oil. For **24**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_{10}{}^{10}B_{10}{}^1H_{32}$ 262.3434, found 262.3440. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): 24.0 (s, 1, B6), 8.4 (d, 2, B1,3, *J* 147), 6.7 (d, 1, B9, *J* 164), −0.9 (d, 2, B5,7, *J* 157), −4.7 (d, 2, B8,10, *J* 153), −35.8 (d, 1, B2, *J* 154), −40.6 (d, 1, B4, *J* 153). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 5.41 (m, 2H, ═CH), 2.02 (m, 4H, 2CH_2), 1.56 (m, 2H, CH_2), 1.42 (m, 4H, 2CH_2), 1.37 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 0.96 (t, 3H, *J* 5.7, CH_3), −1.72 (s, br, 2H, BHB), −2.02 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 2915 (s), 2900 (vs), 2815 (s), 2540 (vs), 2305 (w), 1900 (w), 1795 (m), 1580 (w), 1485 (m), 1445 (m), 1425 (m), 1360 (w), 1345 (w), 1080 (m), 990 (s), 950 (s), 795 (m), 705 (m).

6-[CF$_3$C(O)OCH$_2$CH═CH(CH$_2$)$_4$]-B$_{10}$H$_{13}$ (25). As described for **3**, 0.33 g (1.6 mmol) of **2**, 1.2 mL (9.2 mmol) of allyltrifluoroacetate, and 31 mg (0.03 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 18 h. Column chromatography with a 4:1 benzene/hexanes eluent afforded 0.42 g (1.3 mmol, 79% yield) of **25** as a colorless oil. For **25**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_9{}^{11}B_{10}{}^{37}O_2{}^{19}F_3{}^1H_{25}$ 332.2737, found 332.2727. Anal. Calcd: C, 32.72; H, 7.63. Found: C, 33.01; H, 7.66. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): 27.3 (s, 1, B6), 11.1 (d, 2, B1,3, *J* 149), 9.9 (d, 1, B9, *J* 148), 1.9 (d, 2, B5,7, *J* 156), −1.8 (d, 2, B8,10, *J* 151), −32.7 (d, 1, B2, *J* 158), −37.5 (d, 1, B4, *J* 157). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 5.92 (m, 1H, ═CH), 5.63 (m, 1H, ═CH), 4.80 (d, 2H, *J* 6.7, ═CH−C*H*$_2$), 2.16 (m, 2H, ═CH−C*H*$_2$), 1.57 (m, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), −1.73 (s, br, 2H, BHB), −2.01 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 2905 (vs), 2860 (s), 2560 (vs), 1950 (br, w), 1775 (s), 1665 (w), 1550 (w), 1495 (m), 1445 (w), 1395 (w), 1340 (m), 1215 (m), 1145 (s), 1090 (m), 995 (m), 965 (m), 910 (w), 855 (w), 835 (w), 810 (w), 775 (w), 725 (m).

6-[C$_6$H$_5$CH═CH(CH$_2$)$_4$]-B$_{10}$H$_{13}$ (26). As described for **3**, 0.23 g (1.1 mmol) of **2**, 0.6 mL of inhibitor-free styrene, and 8 mg (0.01 mmol) of **II** were stirred in 2 mL of CH_2Cl_2 at 30 °C for 60 h. Column chromatography with a 5:1 hexanes/ethyl acetate eluent afforded 0.29 g (1.0 mmol, 92% yield) of **26** as a yellow oil, which was then recrystallized from cold CH_2Cl_2. For **26**: a white solid, mp < room temperature. NCI-HRMS (*m*/*e*): calcd for $^{12}C_{12}{}^{11}B_{10}{}^1H_{28}$ 282.3122, found 282.3111. Anal. Calcd: C, 51.39; H, 10.06. Found: C, 50.60; H, 11.01. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): 23.8 (s, 1, B6), 8.5 (d, 2, B1,3, *J* 147), 6.8 (d, 1, B9, *J* 142), −0.8 (d, 2, B5,7, *J* 151), −4.6 (d, 2, B8,10, *J* 152), −35.8 (s, 1, B2, *J* 154), −40.5 (d, 1, B4, *J* 154). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 7.38−7.20 (m, 5H, C_6H_5), 6.41 (d, 1H, *J* 15.9, ═CH), 6.23 (m, 1H, ═CH), 2.27 (m, 2H, ═CH−C*H*$_2$), 2.04 (m, 2H, CH_2), 1.58 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), −1.71 (s, br, 2H, BHB), −2.03 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 3015 (m), 2920 (s), 2860 (m), 2595 (vs), 1930 (w), 1725 (w), 1650 (w), 1605 (w), 1550 (m), 1500 (s), 1450 (m), 1435 (m), 1415 (m), 1315 (m), 1100 (s), 1005 (s), 965 (s), 920 (w), 865 (w), 845 (w), 815 (m), 720 (w), 700 (m).

6-[CH$_3$C(O)(CH$_2$)$_2$CH═CH(CH$_2$)$_4$]-B$_{10}$H$_{13}$ (27). As described for **3**, 0.19 g (1.0 mmol) of **2**, 1.0 mL (8.6 mmol) of 5-hexen-2-one, and 16 mg (0.02 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 20 h. Column chromatography with benzene eluent afforded 0.15 g (0.6 mmol, 57% yield) of **27** as a yellow oil. For **27**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_{10}{}^{11}B_{10}{}^{16}O_1{}^1H_{30}$ 276.3227, found 276.3221. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): 27.1 (s, 1, B6), 11.1 (d, 2, B1,3, *J* 148), 9.5 (d, 1, B9, *J* ∼152), 2.0 (d, 2, B5,7, *J* 155), −2.0 (d, 2, B8,10, *J* 154), −32.8 (d, 1, B2, *J* 150), −37.6 (d, 1, B4, *J* 160). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 5.41 (m, 2H, ═CH), 2.49 (t, 2H, *J* 8.2, ═CH−C*H*$_2$), 2.30 (m, 2H, ═CH−C*H*$_2$), 2.16 (s, 3H, CH_3), 2.03 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 1.36 (m 2H, CH_2), −1.68 (s, br, 2H, BHB), −1.97 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 2915 (vs), 2875 (s), 2570 (vs), 1910 (w), 1695 (vs), 1555 (m), 1505 (s), 1440 (s), 1410 (s), 1355 (s), 1260 (w), 1240 (w), 1160 (m), 1095 (m), 1005 (s), 965 (s), 935 (w), 920 (w), 865 (w), 840 (w), 820 (w), 725 (m), 710 (w), 690 (w).

6-[CH$_3$CH$_2$OCH$_2$CH═CH(CH$_2$)$_4$]-B$_{10}$H$_{13}$ (28). As described for **3**, 0.21 g (1.1 mmol) of **2**, 2.0 mL (17.6 mmol) of allylethyl ether, and 17 mg (0.02 mmol) of **II** were heated at 30 °C in 1 mL of CH_2Cl_2 for 30 h. Column chromatography with a 1:1 benzene/CH_2Cl_2 eluent afforded 0.19 g (0.73 mmol, 70% yield) of **28** as a yellow oil. For **28**: NCI-HRMS (*m*/*e*): calcd for $^{12}C_9{}^{11}B_{10}{}^{16}O_1{}^1H_{29}$ (M−H) 263.3149, found 263.3157. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): 24.0 (s, 1, B6), 8.4 (d, 2, B1,3, *J* 146), 6.7 (d, 1, B9, *J* 161), −0.9 (d, 2, B5,7, *J* 156), −4.7 (d, 2, B8,10, *J* 148), −35.8 (d, 1, B2, *J* 154), −40.6 (d, 1, B4, *J* 153). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 5.62 (m, 1H, ═CH), 5.51 (m, 1H, ═CH), 3.85 (d, 2H, *J* 6.1, ═CH−C*H*$_2$), 3.42 (m, 2H, ═CH−C*H*$_2$), 2.03 (q, 2H, *J* 7.0, CH_2), 1.50 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.31 (m, 2H, CH_2), 1.15 (t, 3H, *J* 6.9, CH_3), −1.80 (s, br, 2H, BHB), −2.10 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 2950 (m), 2905 (s), 2815 (s), 2540 (vs), 1900 (br, w), 1655 (w), 1540 (w), 1485 (m), 1425 (m), 1355 (w), 1335 (w), 1245 (w), 1075 (vs), 980 (s), 945 (m), 915 (w), 895 (w), 865 (w), 840 (w), 820 (w), 795 (w), 705 (m), 690 (w), 670 (w).

6-[CH$_3$OC(O)CH═CH(CH$_2$)$_4$]-B$_{10}$H$_{13}$ (29). As described for **3**, 0.32 g (1.6 mmol) of **2**, 0.6 mL of inhibitor-free methylacrylate, and 10 mg (0.01 mmol) of **II** were refluxed in 3 mL of CH_2Cl_2 for 48 h. Column chromatography with a 1:1 hexanes/benzene eluent followed by drying in vacuo at 60 °C gave 0.38 g (1.4 mmol, 91% yield) of **29** as a white solid. For **29**: mp = 98−100 °C. NCI-HRMS (*m*/*e*): calcd for $^{12}C_8{}^{10}B_{10}{}^{16}O_2{}^1H_{26}$ 264.2863, found 264.2855. Anal. Calcd: C, 36.62; H, 9.99. Found: C, 36.47; H, 9.77. ^{11}B NMR (160.1 MHz, $CDCl_3$, ppm, *J* = Hz): 23.8 (s, 1, B6), 8.4 (d, 2, B1,3, *J* 148), 7.0 (d, 1, B9, *J* 156), −0.9 (d, 2, B5,7, *J* 156), −4.6 (d, 2, B8,10, *J* 148), −35.8 (d, 1, B2, *J* 154), −40.4 (d, 1, B4, *J* 153). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 6.88 (d of t, 1H, J_1 15.6, J_2 6.9, ═CH), 5.75 (d, 1H, *J* 15.6, ═CH), 3.65 (s, 3H, CH_3), 2.17 (m, 2H, ═CH−C*H*$_2$), 1.49 (m, 4H, 2CH_2), 1.34 (m, 2H, CH_2), −1.74 (s, br, 2H, BHB), −2.07 (s, br, 2H, BHB). IR (NaCl plate, cm^{-1}): 3020 (w), 2930 (s), 2885 (m), 2540 (vs),

1940 (w), 1700 (vs), 1660 (m), 1560 (w), 1505 (m), 1435 (s), 1315 (m), 1285 (s), 1205 (s), 1185 (m), 1160 (w), 1100 (m), 1040 (w), 1005 (s), 975 (m), 920 (w), 910 (w), 855 (w), 845 (w), 815 (w), 740 (m).

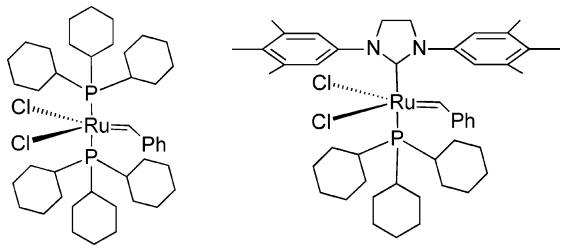
1-[1-(1,2-$C_2B_{10}H_{11}$)]-$CH_2CH{=}CH(CH_2)_4$-7-(6-$B_{10}H_{13}$) (30). As described for **3**, 0.72 g (3.9 mmol) of **1**, 0.20 g (1.0 mmol) of **2**, and 36 mg (0.04 mmol) of **II** were refluxed in 5 mL of CH_2Cl_2 for 18 h. Column chromatography with benzene eluent, followed by solvent evaporation afforded the crude product, which was then extracted with hexanes and further purified on silica gel using a 4:1 hexanes/benzene eluent. Recrystallization from toluene afforded 0.28 g (0.8 mmol, 71% yield) of **30** as a white solid. For **30**: mp = 68−69 °C. NCI-HRMS (*m*/*e*): calcd for $^{12}C_9{}^{10}B_{20}{}^{1}H_{35}$ (M−H) 363.4600, found 363.4600. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm, *J* = Hz): 24.2 (s, 1B), 8.7 (d, 2B, *J* 145), 7.1 (d, 1B, *J* 163), −0.6 (d, 2B, *J* 147), −4.3 (d, 3B, *J* 146), −7.6 (d, 1B, *J* 146), −11.0 (d, 2B, *J* 152), −12.9 (d, 2B, *J* 180), −14.6 (d, 4B, *J* 155), −35.6 (d, 1B, *J* 153), −40.2 (d, 1B, *J* 154). ^{1}H NMR (500.4 MHz, $CDCl_3$, ppm, *J* = Hz): 5.55 (m, 1H, =CH), 5.34 (m, 1H, =CH), 3.56 (s, br, 1H, cage-CH), 2.91 (d, 2H, *J* 7.4, =CH−C*H*$_2$), 2.11 (m, 2H, =CH−C*H*$_2$), 1.57 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.37 (m, 2H, CH_2), −1.72 (s, br, 2H, BHB), −2.01 (s, br, 2H, BHB). FT-IR (KBr pellet, cm^{-1}): 3217 (w), 3068 (m), 2925 (s), 2854 (m), 2575 (vs), 1902 (br, w), 1701 (w), 1633 (w), 1559 (w), 1501 (s), 1429 (m), 1265 (m), 1203 (w), 1098 (br, w), 1042 (w), 1017 (m), 1006 (s), 973 (m), 932 (w), 919 (w), 882 (w), 860 (w), 837 (w), 811 (m), 722 (m), 704 (w), 685 (w), 669 (w), 642 (w), 605 (w).

Crystallographic Data for Compounds 3, 5, 13, 15, and 30. Single crystals were grown from a 1:1 acetone/heptane solution of **3** (Upenn # 3213) at room temperature, from a CH_2Cl_2 solution of **5** (Upenn # 3224) at −20°C, from a hexanes solution of **13** (Upenn # 3248) at room temperature, from a hexanes solution of **15** (Upenn # 3247) at −20 °C, and from a toluene solution of **30** (Upenn # 3253) at room temperature.

Collection and Reduction of the Data. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation at a temperature of 143 K. Indexing was performed from a series of four 0.5° oscillation images with exposure of 30 s per frame for **3** and a series of twelve 0.5° rotation images with exposures of 30 s for **5**, **13**, **15**, and **30** with a crystal-to-detector distance of 36 mm for all crystals. Oscillation images were processed using CrystalClear,[9] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed to the CrystalStructure[10] program package for further processing and structure solution on a Dell Pentium III computer. The intensity data were corrected for Lorentz and polarization effects. Absorption corrections were made for **3**, **13**, **15**, and **30** using REQAB.[11]

Solution and Refinement of the Structures. The structures were solved by direct methods (SIR97).[12] Refinements were by full-matrix least squares based on F^2 using SHELXL-97.[13] All reflections were used during refinement (F^2's that were experimentally negative were replaced by F^2 = 0). Non-hydrogen atoms were refined anisotropically, cage hydrogen atoms were refined isotropically, and chain hydrogen atoms were included as constant contributions to the structure factors and were not refined. Disorder was found in the structures of **3**, **5**, and **15** and were refined accordingly. For **3**, disorder was observed with the C14−C14* double bond assuming two different orientations in a 4:1 ratio. For **5**, the two independent molecules of the asymmetric unit adopt different conformations with the phenyl rings in different orientations. The double bonds also adopted two different orientations in each of the independent molecules, which according to least-squares refinement had relative populations of 0.778:0.222 for molecule 1 and 0.510:0.490 for molecule 2. In **15**, one of the two independent molecules in the asymmetric unit had the C=C bond disordered in two orientations with relative populations of 0.70 and 0.30. In the second molecule, the pinacolborane group was disordered by a rotation of approximately 75° about the C−B bond with relative populations of 0.60 and 0.40.

(9) *CrystalClear*; Rigaku Corporation, 1999.
(10) *CrystalStructure*, Crystal Structure Analysis Package; Rigaku Corporation, 2002.
(11) *REQAB*: Jacobsen, R. A. Private communication, 1994.
(12) *SIR97*: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Moliterni, A.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.
(13) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Germany, 1997.



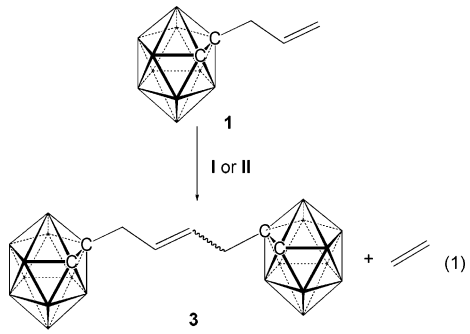
I **II**

Figure 1. Structures of the Grubbs "first-generation" $Cl_2Ru(=CHPh)(PCy_3)_2$ (**I**) and "second-generation" $Cl_2Ru(=CHPh)(PCy_3)(H_2IMes)$ (**II**) catalysts.

Results and Discussion

Because of their high reactivity, stability, and functional group tolerance,[3,14] the Grubbs ruthenium complexes, $Cl_2Ru(=CHPh)(PCy_3)L$, L = PCy_3 (**I**) and H_2IMes (**II**) (Figure 1), were employed as catalysts for the metathesis reactions of the two alkenylpolyboranes 1-($CH_2{=}CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**1**) and 6-[$CH_2{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (**2**).

Homometathesis of 1-($CH_2{=}CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (1). In a typical reaction (eq 1), **1** was heated in CH_2Cl_2 solution under gentle reflux in vacuo in the presence of **II**. Evolution of ethylene gas was immediately observed, and a white precipitate of **3** formed toward the end of the reaction. The reaction was determined to be complete (48 h when using 2 mol % of **II**) when the terminal olefinic resonances of **1** disappeared in the ^{1}H NMR spectrum.



for **I**: 10% conversion
for **II**: 79% yield, *E*/*Z* = 17:1

3 was separated from the catalyst residue via column chromatography using step elution with hexanes and benzene. Recrystallization from acetone/heptane cosolvent gave air-stable white crystals in 79% yield. **3** is soluble in polar solvents including CH_2Cl_2, $CHCl_3$, THF, and acetone, while being partially soluble in benzene and toluene and completely insoluble in hexanes.

The ^{11}B NMR spectrum of **3** was nearly identical to that of **1**, showing the five-line doublet pattern in 1:1:2:2:4 ratios

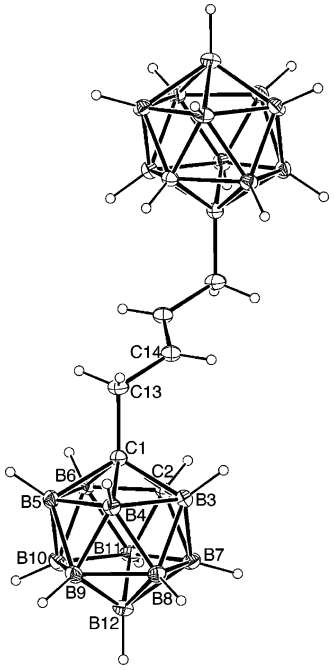


Figure 2. ORTEP representation of the structure of 1,1′-(CH_2-CH═$CHCH_2$)−(1,2-$C_2B_{10}H_{11}$)$_2$ (**3**). Selected bond distances (Å) and angles (deg): C1−C2, 1.648(2); C1−B3, 1.724(2); C1−B4, 1.705(2); C1−B5, 1.706(2); C1−B6, 1.727(2); C1−C13, 1.528(2); C13−C14, 1.496(2); C14−C14*, 1.321(4); C13−C1−C2, 120.14(9); C13−C1−B3, 118.00(10); C13−C1−B4, 120.68(9); C13−C1−B5, 119.93(10); C13−C1−B6, 116.67(9); C1−C13−C14, 114.65(11); C13−C14−C14*, 123.3(3).

characteristic of mono-C-substituted *o*-carborane derivatives.[15] In its ^{1}H NMR spectrum, the terminal olefinic resonances at 5.17 and 5.65 ppm in the spectrum of **1** were replaced by a single olefinic intensity-two triplet centered at 5.34 ppm. This resonance was coupled to the intensity-four doublet methylene resonance at 2.98 ppm. The broad intensity-one carborane C−H peak was found at 3.38 ppm. The ^{13}C NMR spectrum of **3** showed a single intensity-two peak at 129.5 ppm, rather than the two peaks (120.5 and 132.8 ppm) found[6a] in the spectrum of **1**. The close proximity of the bulky *o*-carborane cage to the double bond would be expected to favor a *trans*-product,[16] and, as determined by ^{1}H NMR integration, the *trans*- and *cis*-isomers of **3** were produced in a 17:1 ratio. The IR spectrum of **3** showed, like the spectra of **4**−**30**, a strong B−H absorption near 2590 cm^{-1} and the C═C stretch near 1618 cm^{-1}.

An X-ray crystallographic determination of *trans*-**3** confirmed a structure composed of two mono-C-substituted *o*-carborane cages linked by a −CH_2CH═$CHCH_2$− chain (Figure 2), with a crystallographic inversion center passing through the midpoint of the double bond. The C14−C14* (1.321(4) Å) bond length and the C13−C14−C14* (123.3(3)°) bond angle confirm the C14−C14* double bond and the sp^2 hybridization of C14.

The olefin-linked *o*-carborane compounds 1,1′-(CH═CH)-2,2′-R,R′-(1,2-$C_2B_{10}H_{10}$)$_2$ (R, R′ = Ph, *n*-Bu, *p*-MeC_6H_4; R = Ph, R′ = *p*-MeC_6H_4) have previously been synthesized in yields of 45−80% via the reactions of ene-diynes with decaborane.[17] The homometathesis route used for the synthesis of **3** provides a more convenient high-yield route to these types of high boron content materials.

1 showed different reactivities with the **I** and **II** catalysts. With 5 mol % of **I**, only ∼10% conversion of **1** was observed by ^{1}H NMR after 24 h, but nearly complete reaction was observed when **1** was refluxed with 5 mol % of **II** in CH_2Cl_2 for the same reaction period.

Grubbs has classified olefins into four different categories based on both their ability to undergo homometathesis and the ability of their homodimers to undergo secondary metathesis in the presence of metathesis catalysts.[18] Electron-rich and sterically unhindered olefins are type-I olefins. They undergo self-metathesis readily, and their homodimers are active for cross metatheses. Examples of type-I olefins for the **II** catalyst include terminal olefins such as 1-alkenes, allylbenzene, allylsilane, allyl esters, and allyl ethers. Electron-deficient olefins, including acrylates and sterically hindered olefins such as vinyl boronates and vinyl dioxolanes, are type-II olefins. They undergo homometathesis reactions at reduced rates, but participate in cross metathesis reactions with more active type-I olefins. Type-III olefins do not self-metathesize, but can still participate in cross metathesis. Type-IV olefins, including highly electron-deficient and sterically bulky olefins, do not undergo metathesis.

On the basis of its homometathesis and cross metathesis (vide infra) reactivities, **1**, like styrene, would be classified as a type-I olefin for **II** and a type-II olefin for **I**.[18] The reduced reactivity with **I** is probably a result of the influence of the bulky *o*-carborane weakening the metal−olefin bonding interaction. Consistent with this observation, it was found that 1-(CH_2═CH)-1,2-$C_2B_{10}H_{11}$, which has an even larger steric hindrance because of the carborane being directly attached to the vinyl group, did not homometathesize with either of the **I** or **II** catalysts.

Cross Metathesis Reactions of 1-(CH_2═$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (1). The synthetic utility of cross metathesis reactions can be limited by the unwanted homometathesis reactions of the individual olefinic partners. However, the reaction of a type-I olefin and a different type-I olefin homodimer has been shown to preferably form the cross metathesis product when an excess of the homodimer is used to suppress the homodimerization of the free olefin partner.[7,18] Accordingly, where they were available, type-I olefin dimers were favored as cross metathesis partners in our studies in order to enhance the selectivity for cross metathesis. That is, the **II**-catalyzed cross metathesis of the type-I olefin **1** with an excess of a type-**I** olefin homodimer should produce the cross metathesis product with high selectivity since the formation of **3** (the homodimer of **1**) would be greatly suppressed. Indeed, reaction of **1** with an excess of 1,4-diphenyl-2-butene (the homodimer of the type-I olefin allylbenzene) catalyzed by **II** afforded 1-($C_6H_5CH_2$CH═$CHCH_2$)-1,2-$C_2B_{10}H_{11}$

(14) For some examples of the applications and advantages of ruthenium-catalyzed cross metathesis reactions, see: (a) Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 1751−1753. (b) Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783−3784. (c) Choi, T.-L.; Chatterjee, A. K.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2004**, *40*, 1277−1279. (d) Chatterjee, A. K.; Choi, T.-L.; Grubbs, R. H. *Synlett* **2001**, 1034−1037. (e) Choi, T.-L.; Lee, C. W.; Chatterjee, A. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 10417−10418. (f) Goldberg, S. D.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 807−810. (g) Chatterjee, A. K.; Sanders, D. P.; Grubbs, R. H. *Org. Lett.* **2002**, *4*, 1939−1942. (h) Toste, F. D.; Chatterjee, A. K.; Grubbs, R. H. *Pure Appl. Chem.* **2002**, *74*, 7−10. (i) Chatterjee, A. K.; Toste, F. D.; Choi, T.-L.; Grubbs, R. H. *Adv. Synth. Catal.* **2002**, *344*, 634−637. (j) Chatterjee, A. K.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3171−3174.

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(16) (a) Ulman, M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2484−2489. (b) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749−750.

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(18) Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360−11370.

Table 1. Crystallography Data Collection and Structural Refinement Information

	3	**5**	**13**	**15**	**30**
empirical formula	$C_8B_{20}H_{28}$	$C_{11}B_{10}H_{20}$	$C_{11}B_{10}H_{27}NO_2$	$C_{12}B_{11}H_{29}O_2$	$C_9B_{20}H_{36}$
fw	340.50	260.37	313.44	324.26	360.58
cryst class	monoclinic	triclinic	orthorhombic	triclinic	orthorhombic
space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P2_12_12_1$ (#19)	$P\bar{1}$ (#2)	$Pna2_1$ (#33)
Z	2	4	4	4	4
a, Å	6.6668(7)	11.0159(11)	8.5581(5)	11.3607(10)	16.981(2)
b, Å	13.4716(13)	12.366(2)	10.3974(8)	12.2813(11)	19.783(2)
c, Å	11.5792(11)	12.610(2)	20.577(2)	14.8379(13)	6.9346(6)
α, deg		113.458(2)		95.676(2)	
β, deg	91.366(9)	94.507(2)		99.914(2)	
γ, deg		100.690(2)		100.532(2)	
V, Å^3	1039.7(2)	1526.2(3)	1831.0(2)	1986.7(3)	2340.2(4)
μ, cm^{-1}	0.46	0.54	0.64	0.59	0.44
cryst size, mm	0.35 × 0.27 × 0.10	0.38 × 0.27 × 0.15	0.32 × 0.30 × 0.18	0.22 × 0.20 × 0.06	0.42 × 0.18 × 0.08
D_{calc}, g/cm^3	1.088	1.133	1.137	1.084	1.023
F(000)	352	544	664	688	760
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
2θ angle, deg	6.04−50.66	5.28−50.68	5.16−50.68	5.08−50.68	5.22−50.08
temp, K	143	233	143	143	143
hkl collected	$-6 \le h \le 8$, $-14 \le k \le 15$, $-11 \le l \le 13$	$-11 \le h \le 13$, $-13 \le k \le 14$, $-14 \le l \le 14$	$-10 \le h \le 10$, $-12 \le k \le 11$, $-23 \le l \le 24$	$-13 \le h \le 12$, $-13 \le k \le 14$, $-17 \le l \le 15$	$-20 \le h \le 20$, $-23 \le k \le 18$, $-8 \le l \le 7$
no. of reflns measd	5970	12 440	15 693	17 501	10 257
no. of unique reflns	1801 (R_{int} = 0.0171)	5353 (R_{int} = 0.0589)	3136 (R_{int} = 0.0293)	7171 (R_{int} = 0.02111)	3472 (R_{int} = 0.0419)
no. of obsd reflns ($F > 4\sigma$)	1632	4501	3013	5546	2263
no. of reflns used in refinement	1801	5353	3136	7171	3472
no. of params	180	520	326	524	263
R^a indices ($F > 4\sigma$)	$R_1 = 0.0464$ $wR_2 = 0.1242$	$R_1 = 0.0525$ $wR_2 = 0.1312$	$R_1 = 0.0464$ $wR_2 = 0.1476$	$R_1 = 0.0835$ $wR_2 = 0.2200$	$R_1 = 0.0766$ $wR_1 = 0.1956$
R^a indices (all data)	$R_1 = 0.0505$ $wR_2 = 0.1286$	$R_1 = 0.0638$ $wR_2 = 0.1401$	$R_1 = 0.0500$ $wR_2 = 0.1602$	$R_1 = 0.1033$ $wR_2 = 0.2397$	$R_1 = 0.0945$ $wR_2 = 0.2179$
GOF^b	1.061	1.059	1.167	1.099	0.985
final diff peaks, e/Å^3	+0.196, −0.242	+0.239, −0.245	+0.372, −0.400	+1.010, −0.842	+0.332, −0.207

^{a} $R_1 = ||F_o| - |F_c||/|F_o|$; $wR_2 = \{w(F_o^2 - F_c^2)^2/w(F_o^2)^2\}^{1/2}$. ^{b} GOF = $\{w(F_o^2 - F_c^2)^2/n - p)\}^{1/2}$ where n = no. of reflections; p = no. of parameters refined.

(**4**) in ∼60% yield (Table 2, entry 1) with the excess 1,4-diphenyl-2-butene then easily recovered after the reaction by column chromatography. As shown in Scheme 1 and Table 2 (entries 2−6), the same protocol (**1** + excess type-I olefin dimer) was used for the **II**-catalyzed cross metathesis reactions of **1** with the olefin homodimers *trans*-stilbene, *cis*-1,4-diacetoxy-2-butene, 2-butene-1,4-diol, 1,4-dichloro-2-butene, and *cis*-1,4-dibenzoxyl-2-butene to give the cross metathesis products 1-(C_6H_5CH═$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**5**), 1-[$CH_3C(O)OCH_2$-CH═$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (**6**), 1-($HOCH_2CH$═$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**7**), 1-($ClCH_2CH$═$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**8**), and 1-($C_6H_5CH_2OCH_2CH$═$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**9**), in yields of 76−87%.

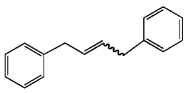
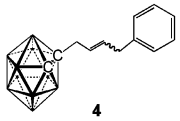
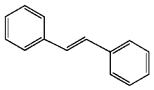
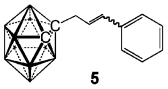
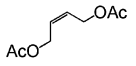
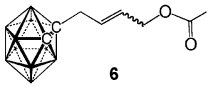
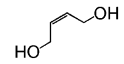
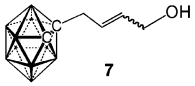
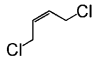
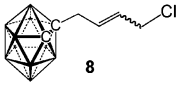
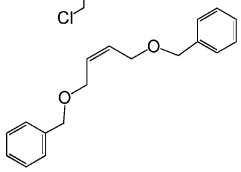
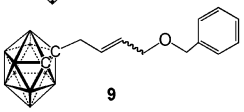
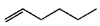
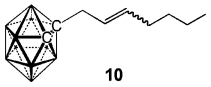
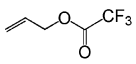
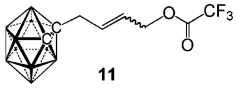
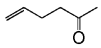
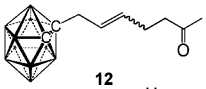
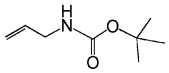
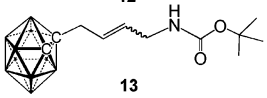
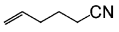
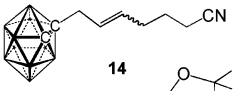
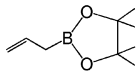
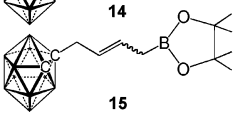
In cases where a homodimer was not readily available, the cross metathesis reactions of **1** with another type-I olefin partner were employed. For reactions involving two individual type-I olefinic partners, it has also been previously shown that a large excess of one olefin partner can be used to suppress the homometathesis of the other partner and favor the cross metathesis product.[7,18] Thus, the **II**-catalyzed reaction of the type-I olefin **1** with a large excess of another type-I olefin should favor cross metathesis, and, indeed, the **II**-catalyzed cross metathesis reaction of **1** with a large excess of 1-hexene afforded 1-[$CH_3(CH_2)_3CH$═$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (**10**) (Table 2, entry 7) in excellent yield (88%). The other product of the reaction, 5-decene (the homodimer of 1-hexene), was easily separated from **10** via column chromatography. A similar method (**1** + excess type-I olefin) was used for the **II**-catalyzed reactions of **1** with the terminal olefins (Table 2, entries 8−12) allyltrifluoroacetate, 5-hexen-2-one, *tert*-butyl-*N*-allylcarbamate, 5-cyano-1-pentene, and 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaboronate to give 1-[$CF_3C(O)OCH_2CH$═$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (**11**), 1-[$CH_3C(O)(CH_2)_2CH$═$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (**12**), 1-[*t*-C_4H_9-$OC(O)NHCH_2CH$═$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (**13**), 1-[$NC(CH_2)_3$-CH═$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (**14**), and 1-{[$(CH_3)_4C_2O_2$]BCH_2-CH═$CHCH_2$}-1,2-$C_2B_{10}H_{11}$ (**15**) in 55−88% yields.

I was found to have poor activity for the cross metathesis reactions of **1**. For example, when **1** was treated with the type-I dimer 1,4-diphenyl-2-butene, in the presence of 5 mol % of **I**, only low conversion of **1** occurred (<20% as determined by ^{1}H NMR). Thus, all the cross metathesis reactions employed **II** as the catalyst and were performed by heating a mixture of **1**, excess metathesis partner, and **II** in CH_2Cl_2 solution under gentle reflux in vacuo. The reactions were monitored using TLC and ^{1}H NMR. They were considered complete when the limiting reagent **1** was completely consumed. The products were then separated from the catalyst residue via step elution using column chromatography on silica gel and further purified by recrystallization or vacuum distillation.

Compounds **4**−**14** are air and water stable. The pinacolborane group of **15** slowly hydrolyzes in air so it must be stored under an inert atmosphere. All compounds showed good solubility in polar solvents including THF, methylene chloride, chloroform, and ethyl acetate. The less polar products **4**, **5**, and **14** were also soluble in hexanes, benzene, and toluene.

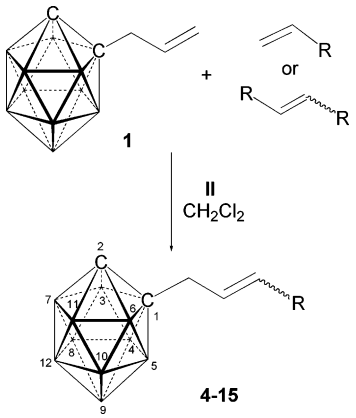
The ^{11}B NMR spectra of **4**−**15** are nearly identical to that of **3**, showing five doublets in 1:1:2:2:4 ratios. Their ^{1}H NMR spectra showed resonances characteristic of their internal olefinic protons and organic fragments, as well as broad B−H resonances between 1 and 3 ppm, and a broad intensity-one *o*-carborane C−H singlet. Integration of the olefinic proton resonances arising from the *cis*- and *trans*-conformations of the double bond again showed that the *trans*-products were favored.

Table 2. Cross Metathesis Reactions of 1 with Functional Olefins Catalyzed by II

entry	CM partner[a]	product	yield	E/Z[b]
1		 **4**	62%	15:1
2		 **5**	81%	>20:1
3		 **6**	84%	15:1
4		 **7**	76%	14:1
5		 **8**	87%	9:1
6		 **9**	79%	7:1
7		 **10**	88%	7:1
8		 **11**	77%	>20:1
9		 **12**	69%	>20:1
10		 **13**	70%	>20:1
11		 **14**	66%	3:1
12		 **15**	55%	8:1

[a] See Experimental Section for reactant ratios and workup procedures. [b] Determined by integration of ^{1}H NMR.

Scheme 1. Cross Metathesis Reactions of 1-(CH_2=$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (1) with Functional Olefins Catalyzed by II



As summarized in Table 1 and Figures 3−5, the structures of the *trans*-isomers of 1-(C_6H_5CH=$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**5**)

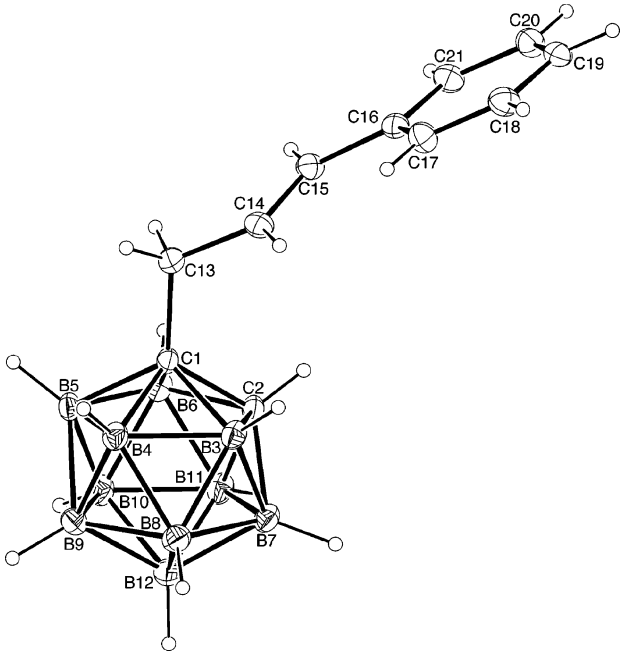


Figure 3. ORTEP representation of the structure of 1-(C_6H_5CH=$CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**5**). Selected bond distances (Å) and angles (deg): C1−C2, 1.645(2); C1−B3, 1.729(2); C1−B4, 1.703(2); C1−B5, 1.710(2); C1−B6, 1.733(2); C1−C13, 1.529(2); C13−C14, 1.494(3); C14−C15, 1.323(3); C15−C16, 1.488(2); C13−C1−C2, 119.69(12); C13−C1−B3, 119.26(13); C13−C1−B4, 122.07(13); C13−C1−B5, 119.55(12); C13−C1−B6, 115.62(14); C1−C13−C14, 116.7(2); C13−C14−C15, 124.9(2); C14−C15−C16, 126.7-(2); C15−C16−C17, 120.81(14); C15−C16−C21, 119.14(14).

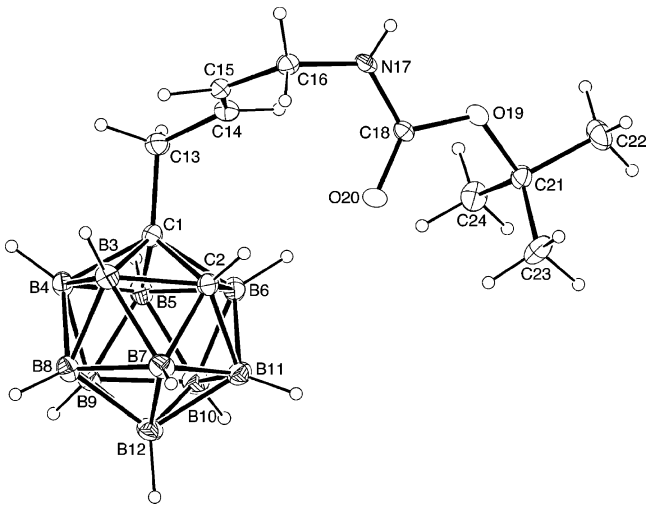
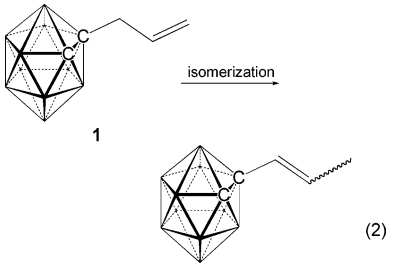


Figure 4. ORTEP representation of the structure of 1-[*t*-C_4H_9OC-(O)$NHCH_2CH$=$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (**13**). Selected bond distances (Å) and angles (deg): C1−C2, 1.658(3); C1−B3, 1.722(3); C1−B4, 1.713(3); C1−B5, 1.712(3); C1−B6, 1.726(3); C1−C13, 1.514(3); C13−C14, 1.501(3); C14−C15, 1.322(3); C15−C16, 1.504(3); C16−N17, 1.448(3); N17−C18, 1.341(3); C18−O19, 1.347(2); C18−O20, 1.223(3); O19−C21, 1.482(2); C21−C22, 1.522(3); C21−C23, 1.518(3); C21−C24, 1.517(3); C13−C1−C2, 118.8(2); C13−C1−B3, 116.7(2); C13−C1−B4, 121.2(2); C13−C1−B5, 121.7(2); C13−C1−B6, 117.4(2); C1−C13−C14, 113.6-(2); C13−C14−C15, 122.3(2); C14−C15−C16, 126.1(2); C15−C16−N17, 115.0(2); C16−N17−C18, 121.6(2); O19−C18−O20, 125.2(2); C18−O19−C21, 119.7(2); O19−C21−C22, 102.4(2); O19−C21−C23, 111.5(2); O19−C21−C24, 108.6(2).

(Figure 3), 1-[*t*-$C_4H_9OC(O)NHCH_2CH$=$CHCH_2$]-1,2-$C_2B_{10}H_{11}$ (**13**) (Figure 4), and 1-{[$(CH_3)_4C_2O_2$]BCH_2CH=$CHCH_2$}-1,2-

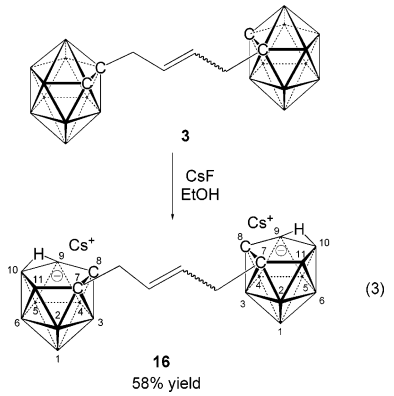
$C_2B_{10}H_{11}$ (**15**) (Figure 5) were confirmed by single-crystal X-ray determinations. The C14−C15 bond lengths (1.323(3) Å (**5**), 1.322(3) Å (**13**), and 1.324(4) Å (**15**)) and the ∼120° bond angles of C13−C14−C15 and C14−C15−C16 in each structure confirm a C14−C15 double bond. In **13**, the C16−N17−C18−O19 unit adopts the *trans*-conformation about the N17−C18 bond, which has been found in similar structures. The N17−C18 (1.341(3) Å) and C18−O19 (1.347(2) Å) bonds are significantly shorter than the respective C16−N17 (1.448(3) Å) and O19−C21 (1.482(2) Å) single bonds, suggesting, as was observed in the structure of BOC-glycine (*t*-$C_4H_9OC(O)NHCH_2$-COOH),[19] that the C18−O20 double bond imposes some double-bond character on the adjacent N17−C18 and C18−O19 bonds.

In the reactions with allylbenzene and BOC-$NHCH_2CH$═CH_2, olefin isomerization occurred to convert some of the starting olefins into their Ph-CH═CHMe and BOC-NHCH═$CHCH_3$ isomers. Likewise, the isomerization of **1** to form 1-(CH_3CH═CH)-1,2-$C_2B_{10}H_{11}$ was observed in these reactions (eq 2). It has been previously reported that ruthenium carbene complexes rearrange in CH_2Cl_2 solution to generate binuclear species responsible for olefin isomerizations.[20]



(2)

Deboronation of 3 and 10: Formation of Dicarbollide Salts 16, 17, and 18. Employing the method reported by Do,[8a] when **3** was reacted with a large excess of CsF in dry ethanol under reflux in vacuo for 48 h, deboronation of each of the *o*-carborane cages occurred to afford $2Cs^+ \cdot [7,7'\text{-}(CH_2CH$═$CHCH_2)\text{-}7,8\text{-}(C_2B_9H_{11})_2]^{2-}$ (**16**) in moderate yield (eq 3). Following recrystallization from ethanol and water, **16** was obtained as a white solid that was soluble in hot water and mixtures of water and ethanol.



(3)

The two cages in **16** are symmetry related, with each cage having C_1 symmetry, but owing to accidental overlap of several

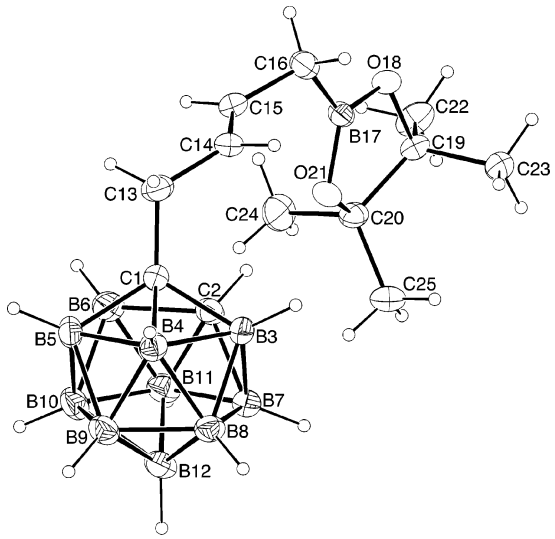
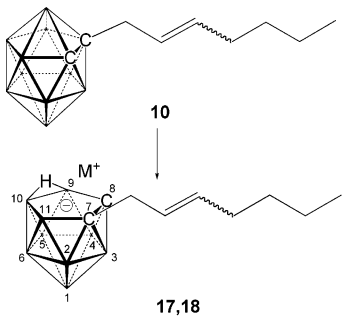


Figure 5. ORTEP representation of 1-{[$(CH_3)_4C_2O_2$]BCH_2CH═$CHCH_2$}-1,2-$C_2B_{10}H_{11}$ (**15**). Selected bond distances (Å) and angles (deg): C1−C2, 1.650(4); C1−B3, 1.716(4); C1−B4, 1.701(4); C1−B5, 1.707(4); C1−B6, 1.725(4); C1−C13, 1.533(3); C13−C14, 1.482(3); C14−C15, 1.324(4); C15−C16, 1.487(4); C16−B17, 1.572(4); B17−O18, 1.360(3); B17−O21, 1.370(3); O18−C19, 1.464(3); C19−C20, 1.566(4); C20−O21, 1.461(3); C19−C22, 1.520(4); C19−C23, 1.514(4); C20−C24, 1.522(4); C20−C25, 1.516(4); C13−C1−C2, 118.9(2); C13−C1−B3, 117.2(2); C13−C1−B4, 121.2(2); C13−C1−B5, 121.0(2); C13−C1−B6, 116.9-(2); C1−C13−C14, 115.3(2); C13−C14−C15, 124.7(3); C14−C15−C16, 127.1(4); C15−C16−B17, 118.2(2); C16−B17−O18, 124.2(2); C16−B17−O21, 122.2(2); O18−B17−O21, 113.5(2); B17−O18−C19, 107.8(2); O18−C19−C20, 102.0(2); C19−C20−O21, 102.6(2); C22−C19−C23, 110.0(2); C24−C20−C25, 110.8-(2).

resonances, **16** showed only seven doublets in ratios of 2:1:1:2:1:1:1 in its ^{11}B NMR spectrum. The two high-field peaks at −33.5 and −37.2 ppm are characteristic of the dicarbollide B10 and B1 borons, while the doublet at −33.5 ppm has fine splitting characteristic of bridge-hydrogen coupling leading to its assignment to the B10 boron.[15] The **16** ^1H NMR spectrum showed, in addition to the resonances arising from the $-CH_2CH$═$CHCH_2-$ chain and the cage C−H, a broad upfield singlet at −2.68 ppm that can be assigned to the bridging hydrogen attached at the B9 and B10 edge.

Compound **10**, 1-[$CH_3(CH_2)_3CH$═$CHCH_2$]-1,2-$C_2B_{10}H_{11}$, was likewise converted to the dicarbollide salts Cs^+ (**17**) and $N(C_4H_9)_4^+$ (**18**) 7-[$CH_3(CH_2)_3CH$═$CHCH_2$]-7,8-$C_2B_9H_{11}^-$ in good yields (88% for **17** and 75% for **18**) by treatment with CsF in refluxing ethanol and tetrabutylammonium fluoride (TBAF) in THF at room temperature, respectively (eq 4).[8]



(4)

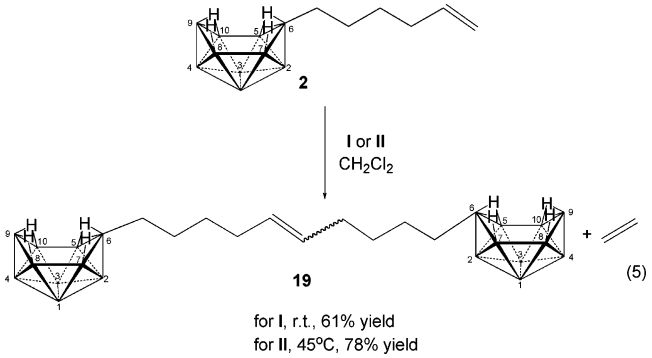
(19) (a) Wade, L. G., Jr. *Organic Chemistry*, 5th ed.; Prentice Hall: New Jersey, 2003. (b) Semertzidis, M.; Matsoukas, J.; Nastopoulos, V.; Voliotis, S.; Leban, I. *Acta Crystallogr.* **1989**, *C45*, 1474−1475.

(20) (a) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202−7207. (b) Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414−7415.

The cesium salt **17** was soluble in alcohol and in water at elevated temperatures. The TBA salt **18** was not soluble in water, but was very soluble in organic solvents including CH_2Cl_2, THF, and methanol.

The ^{11}B NMR spectra of **17** and **18** were similar to that of **16**. Their ^1H NMR spectra showed, in addition to the peaks assigned to the alkenyl chains and the tetrabutylammonium group of **18**, the cage C−H singlet and a broad upfield singlet (at −2.82 ppm for **17** and at −2.61 ppm for **18**) for the bridging hydrogen.

Homometathesis of 6-[CH_2═$CH(CH_2)_4$]-$B_{10}H_{13}$ (2). As shown in eq 5, when 6-[CH_2═$CH(CH_2)_4$]-$B_{10}H_{13}$ (**2**) was reacted with **I** and **II**, the homodimer 6,6′-[$(CH_2)_4CH$═$CH(CH_2)_4$]-$(B_{10}H_{13})_2$ (**19**) was obtained in 61% and 78% yields, respectively. Thus, according to the Grubbs classification, **2** is a type-I olefin for both the **I** and **II** catalysts. The terminal double bond in **2** is not in close proximity to the bulky decaborane cage, and catalyst access for both the **I** and **II** catalysts is thus apparently not sterically hindered.



The metathesis reactions were performed in CH_2Cl_2 in vacuo at room temperature for **I** and under gentle reflux for **II**. Ethylene gas was formed within 5 min, and the reaction was determined to be complete when the ^1H NMR spectrum showed complete consumption of **2**. The waxy, light yellow solid of **19** was then purified from the metal residue by column chromatography with stepwise elution of hexanes and benzene followed by precipitation from hexanes at −78 °C.

Compound **19** is stable under an inert atmosphere, but slowly hydrolyzes in air over days. It is soluble in benzene, toluene, methylene chloride, and chloroform, but is soluble in hexanes only at elevated temperatures.

The two decaborane clusters in **19** are symmetry related, so its ^{11}B NMR spectrum showed the downfield singlet and five doublets in a 1:2:1:2:2:2 ratio that are characteristic of 6-R-$B_{10}H_{13}$ derivatives.[15] The ^1H NMR spectrum showed the vinyl and methylene resonances of the olefinic intercage bridge, the overlapped terminal B−H resonances, and two broad, intensity-four resonances (at −1.71 and −2.01 ppm) arising from the decaborane bridging hydrogens.

Compounds with two decaborane clusters linked by saturated linear and cyclic hydrocarbon bridges have been previously synthesized by the metal-catalyzed hydroboration of dienes,[6b,c] but **19** is the first example of a compound bearing two decaborane clusters linked by an unsaturated carbon chain.

Cross Metathesis Reactions of 6-[CH_2═$CH(CH_2)_4$]-$B_{10}H_{13}$ (2). Although **2** is a type-I olefin for both the **I** and **II** catalysts, **II** was used in the cross metathesis reactions of **2** to take advantage of its higher catalytic activity. The reactions (Scheme 2) were performed and worked up in the manner described for the cross metathesis reactions of **1**, again using an excess of the olefinic homodimer (where available) or excess olefin

Scheme 2. Cross Metathesis Reactions of 6-[CH_2═$CH(CH_2)_4$]-$B_{10}H_{13}$ (2) with Functional Olefins Catalyzed by II

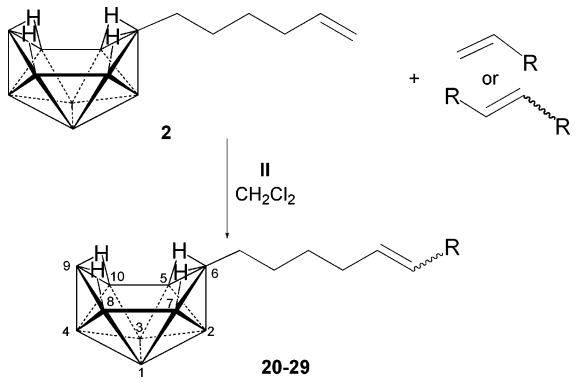
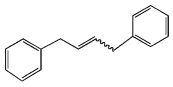
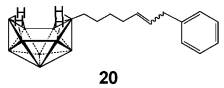
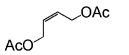
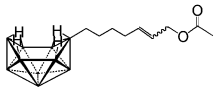
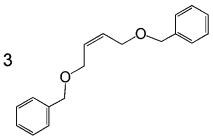
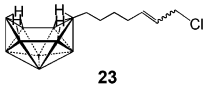
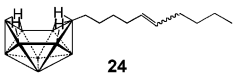
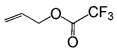
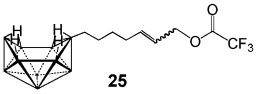
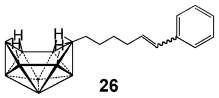
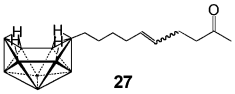
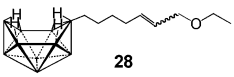
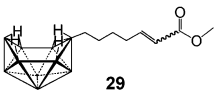


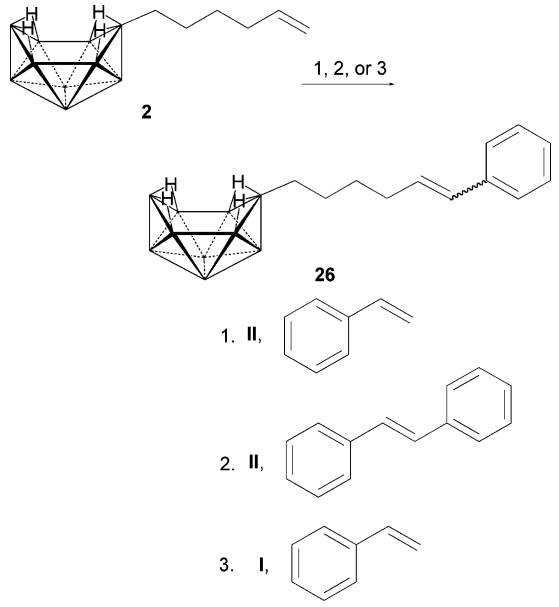
Table 3. Cross Metathesis Reactions of 2 with Functional Olefins Catalyzed by II

entry	CM partner[a]	product	yield	E/Z[b]
1		 **20**	62%	3:1
2		 **21**	61%	14:1
3		**22**	76%	15:1
4		 **23**	67%	5:1
5		 **24**	78%	5:1
6		 **25**	79%	10:1
7		 **26**	92%	>20:1
8		 **27**	57%	>20:1
9		 **28**	70%	3:1
10		 **29**	91%	10:1

[a] See Experimental Section for reactant ratios and workup procedures. [b] Determined by integration of ^1H NMR.

partner to favor the formation of the cross metathesis product. As can be seen in Table 3, when **2** was treated with an excess of the olefinic homodimers 1,4-dipenyl-2-butene, *cis*-1,4-diacetoxy-2-butene, and *cis*-1,4-dibenzoxyl-2-butene in the presence of **II**, 6-[$C_6H_5CH_2CH$═$CH(CH_2)_4$]-$B_{10}H_{13}$ (**20**), 6-[$CH_3C(O)OCH_2CH$═$CH(CH_2)_4$]-$B_{10}H_{13}$ (**21**), and 6-[C_6H_5-CH_2OCH_2CH═$CH(CH_2)_4$]-$B_{10}H_{13}$ (**22**) were formed in 61−76% yields, respectively, while reaction of **2** with an excess of the terminal olefins allyl chloride, 1-hexene, allyltrifluoroacetate,

Scheme 3. Different Approaches for the Preparation of 6-[$C_6H_5CH{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (26)



styrene, 5-hexen-2-one, allylethyl ether, and methylacrylate gave 6-[$ClCH_2CH{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (**23**), 6-[$CH_3(CH_2)_3CH{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (**24**), 6-[$CF_3C(O)OCH_2CH{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (**25**), 6-[$C_6H_5CH{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (**26**), 6-[$CH_3C(O)(CH_2)_2CH{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (**27**), 6-[$CH_3CH_2OCH_2CH{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (**28**), and 6-[$CH_3OC(O)CH{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (**29**) in 57−92% yields, respectively.

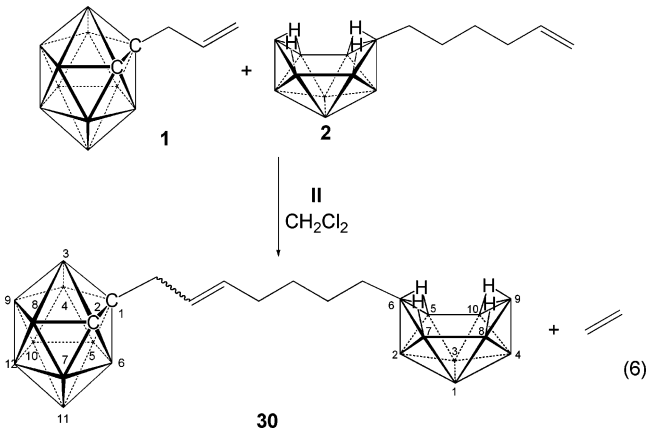
As shown in Scheme 3, three different methods can be employed to synthesize **26**: (1) reaction of **2** with excess styrene catalyzed by **II**, which afforded **26** along with *trans*- and *cis*-stilbene (the styrene homodimer); (2) reaction of **2** with excess *trans*-stilbene catalyzed by **II**; and (3) reaction of **2** with excess styrene catalyzed by **I**. In principle, method (3) should be the most selective since, according to the Grubbs model, styrene behaves as a type-II olefin for **I** and homometathesizes slowly. Using this method, **26** was, in fact, obtained selectively with no formation of either *trans*- or *cis*-stilbene; however, the reaction was too slow to be synthetically useful. Method (1) proved to be best since it employed an inexpensive starting material, provided high reactivity and selectivity, and allowed easy product separation by recrystallization.

Some olefins that were active for the cross metathesis reactions of **1** failed to react with **2**. 5-Cyano-1-pentene was completely unreactive, while 2-butene-1,4-diol degraded the decaborane cage by direct reaction. For the reactions of **2** with the BOC-protected allylamine BOC-$NHCH_2CH{=}CH_2$ and allylpinacolborane, olefin isomerization rather than cross metathesis was favored. Olefin isomerization to form benzylpropene $CH_3CH{=}CHC_6H_5$ also occurred in the reactions of **2** with allylbenzene and lowered the yield of the cross metathesis product **20**. Thus, since it avoids olefin isomerization, the reaction of **2** and 1,4-diphenyl-2-butene catalyzed by **II** is the most useful method for the synthesis of **20**.

Compounds **20**−**29** were stable under an inert atmosphere, but slowly hydrolyzed upon standing in air over days. All compounds were soluble in polar solvents, including methylene chloride, chloroform, and ethyl acetate. Compounds **20**, **22**, **24**, **26**, and **28** were also soluble in the less polar solvents hexanes, toluene, and benzene.

The ^{11}B NMR spectra of **20**−**29** again showed patterns characteristic of 6-substituted decaboranes.[15] Their ^{1}H NMR spectra showed the resonances of the olefinic bridge, the substituents attached by cross metathesis, and two broad upfield peaks assigned to the two sets of intensity-two decaborane bridging hydrogens. In cases where the olefinic peaks for the *trans*- and *cis*-isomers were resolved, integration again showed that the *trans*-conformation was favored.

Cross Metathesis of 1-($CH_2{=}CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (1) with 6-[$CH_2{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (2). The cross metathesis reaction of **1** and **2** afforded 1-[1-(1,2-$C_2B_{10}H_{11}$)]-$CH_2CH{=}CH(CH_2)_4$-7-(6-$B_{10}H_{13}$) (**30**), with the *o*-carborane and decaborane clusters linked via an olefinic bridge (eq 6).



(6)

The **I**-catalyzed cross metathesis of the type-II olefin **1** with the type-I olefin **2** should in principle afford **30** selectively, but the reaction was too slow to be practical. Both **1** and **2** are type-I olefins with **II**, and the **II**-catalyzed reaction of **1** and **2** in a 1:4 ratio produced both **30** and **19** (the homodimer of **2**), but it was not possible to separate these products by either column chromatography or recrystallization. The most convenient methods for the synthesis of **30** were by either the **II**-catalyzed reaction of an excess of **1** with **2** or the reaction of excess **3** (the homodimer of **1**) with **2**. Both of these methods gave product mixtures containing **30** and **3** that could then be readily separated by recrystallization from cold hexanes.

The ^{11}B NMR spectrum of **30** showed patterns characteristic of both clusters, i.e., the five-doublets for the *o*-carborane cluster and the one singlet and six doublets for the decaborane cluster, in a 1:1 ratio. The **30** ^{1}H NMR spectrum showed the resonances of the olefinic bridge, overlapping broad terminal B−H resonances in the 1−3 ppm region, the *o*-carborane CH resonance at 3.56 ppm, and two broad upfield singlets at −1.72 and −2.01 ppm assigned to the two sets of decaborane bridging hydrogens. According to the integration of the olefinic resonances in the ^{1}H NMR spectrum, the *trans* double-bond conformation was favored (5.5 *trans*/*cis* ratio).

As shown in Figure 6, a single-crystal X-ray crystallographic study confirmed that **30** has a structure composed of decaborane and *o*-carborane clusters linked by a seven-carbon chain with the C13−C14−C15 (121.1(4)°) and C14−C15−C16 (125.6(5)°) bond angles and C14−C15 (1.333(6) Å) bond length confirming a double bond between C14 and 15.

Conclusions

The results described above have clearly demonstrated that alkenylpolyborane ruthenium-catalyzed olefin metathesis reactions provide access to a variety of important polyborane compounds. Both 1-($CH_2{=}CHCH_2$)-1,2-$C_2B_{10}H_{11}$ (**1**) and 6-[$CH_2{=}CH(CH_2)_4$]-$B_{10}H_{13}$ (**2**) underwent homometathesis, as well as cross metathesis reactions with each other, to produce

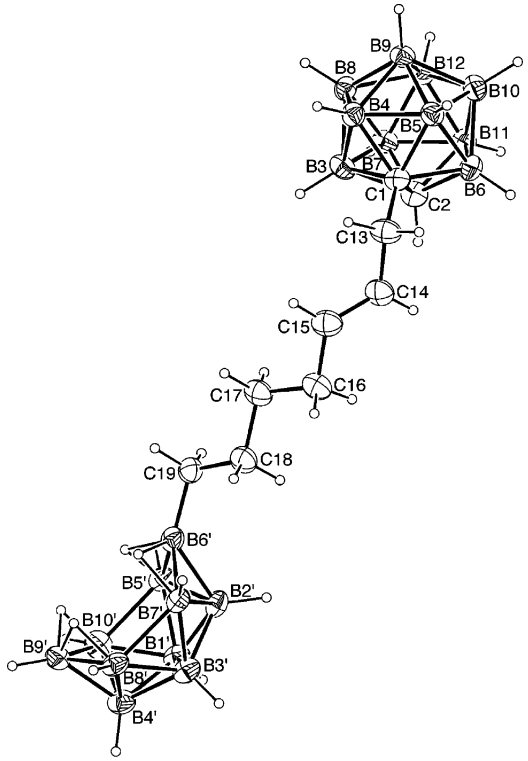


Figure 6. ORTEP representation of the structure of 1-[1-(1,2-$C_2B_{10}H_{11}$)]-$CH_2CH{=}CH(CH_2)_4$-7-(6-$B_{10}H_{13}$) (**30**). Selected bond distances (Å) and angles (deg): C1−C2, 1.640(5); C1−B3, 1.741(7); C1−B4, 1.712(5); C1−B5, 1.703(6); C1−B6, 1.701(6); C1−C13, 1.529(5); C13−C14, 1.464(6); C14−C15, 1.333(6); C15−C16, 1.473(6); C16−C17, 1.535(6); C17−C18, 1.519(6); C18−C19, 1.527(6); C19−B6′, 1.571(6); B2′−B6′, 1.742(6); B5′−B6′, 1.795(7); B6′−B7′, 1.813(6); B8′−B9′, 1.770(7); B4′−B9′, 1.726(7); B9′−B10′, 1.787(8); C13−C1−C2, 120.8(3); C13−C1−B3, 117.5(4); C13−C1−B4, 119.5(3); C13−C1−B5, 119.4(3); C13−C1−B6, 117.7(4); C1−C13−C14, 115.6(4); C13−C14−C15, 121.1(4); C14−C15−C16, 125.6(5); C15−C16−C17, 112.4(4); C16−C17−C18, 110.3(4); C17−C18−C19, 113.8(4); C18−C19−B6′, 114.4(4).

olefin-bridged compounds **3**, **19**, and **30** containing two polyborane clusters. The high boron content of these compounds suggests potential applications both as single-source precursors to boron-based ceramic materials and as high-boron platforms for medical (boron neutron capture therapy)[21] applications. As will be presented in a subsequent paper, the **3** and **19** carborane and decaborane homodimers can also be employed in ruthenium-catalyzed cross metatheses reactions with other olefin partners to provide high-yield access to an even wider array of functionalized polyboranes, including amino acid derivatives.

The ruthenium-catalyzed cross metathesis reactions of **1** provide mild, high-yield routes to alkenyl *o*-carborane derivatives containing phenyl (**4**, **5**), acetate (**6**, **11**), alcohol (**7**), halide (**8**), ether (**9**), alkenyl (**10**), ketone (**12**), protected-amine (**13**), cyanide (**14**), and pinacolborane (**15**) functionalities. Metal-catalyzed Suzuki-coupling reactions[22] involving the pinacolborane group of **15** should make this derivative especially useful for the syntheses of an even wider array of functional carboranes. Likewise, as illustrated by the syntheses of **16**, **17**, and **18**, a range of new water-soluble, functionalized dicarbollide salts that may also have applications for boron neutron capture therapy[21] should now be possible via deboronation reactions.

The corresponding ruthenium-catalyzed cross metathesis reactions of **2** have also provided the first routes to functional decaborane derivatives, including phenyl (**20**, **26**), acetate (**21**), ether (**22**, **28**), chloride (**23**), alkenyl (**24**), trifluoroacetate (**25**), ketone (**27**), and enoic ester (**29**) functionalized compounds. The high yields and selectivies of these reactions suggest that ruthenium-catalyzed cross metathesis reactions may prove useful for the functionalization of even more reactive polyboranes. We are presently exploring these possibilities.

Acknowledgment. We thank the National Science Foundation and the U.S. Department of Energy, Office of Basic Energy Sciences, for the support of this project.

Supporting Information Available: CIF files for **3**, **5**, **13**, **15**, and **30**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050851L

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