General Procedure for the Preparation of Amino Acid Ester Isocyanates 1 from Amino Acid Ester Hydrochlorides. A 250-mL, three-necked, round-bottomed flask, fitted with two rubber septa, a nitrogen inlet adapter, and a magnetic stirring bar, was charged with 0.0300 mol of amino acid ester hydrochloride, 100 mL of CH_2Cl_2, and 9.8 mL (0.121 mol) of pyridine. The resulting suspension or solution was cooled in an ice bath for 15 min. A solution of phosgene (1.93 M in toluene, 20.0 mL, 0.0386 mol) [CAUTION: USE HOOD] was added by syringe over 20–30 s, and the resulting light yellow solution was stirred at 0 °C for 2 h. The reaction mixture was extracted two times with 300 mL of cold 0.5 M aqueous HCl and ca. 200 mL of crushed ice. Each aqueous layer was re-extracted with 100 mL of CH_2Cl_2. The combined organic phases were extracted with a mixture of 300 mL of cold saturated aqueous NaCl solution and ca. 200 mL of crused ice, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to afford the crude isocyanate as a light brown oil. (During workup, the isocyanate is only exposed to water for a total of 5–10 min.) The product was purified by Kugelrohr distillation under reduced pressure.

Ethyl (*S*)-2-Isocyanatopropanoate (1a). Reaction of 4.61 g (0.0300 mol) of L-alanine methyl ester hydrochloride followed by Kugelrohr distillation (25 °C, 0.2 mmHg) yielded 3.10 g (72%) of **1a** as a colorless liquid: $[\alpha]^{22}_D$ −24.1° (neat); IR (film) 2270, 2243, 1743, 1215 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.27 (q, *J* = 7.1 Hz, 2 H), 4.07 (q, *J* = 7.1 Hz, 1 H), 1.50 (d, *J* = 7.1 Hz, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 126.7, 62.4, 52.8, 20.3, 14.1. Anal. Calcd for $C_6H_9NO_3$: C, 50.35; H, 6.34; N, 9.79. Found: C, 50.08; H, 6.36; N, 9.69.

Methyl (*S*)-2-Isocyanato-3-methylbutanoate (1b). Reaction of 5.20 g (0.0310 mol) of L-valine methyl ester hydrochloride followed by Kugelrohr distillation (75 °C, 0.04 mmHg) yielded 4.22 g (87%) of **1b** as a colorless liquid: $[\alpha]^{19}_D$ −21.1° (neat); IR (film) 2258, 1743, 1219 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.95 (d, *J* = 3.7 Hz, 1 H), 3.82 (s, 3 H), 2.27–2.22 (m, 1 H), 1.03 (d, *J* = 6.8 Hz, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 126.9, 63.2, 52.9, 31.8, 19.6, 16.5. Anal. Calcd for $C_7H_{10}NO_3$: C, 53.49; H, 7.05; N, 8.91. Found: C, 53.38; H, 7.14, N, 8.79.

Methyl (*S*)-2-Isocyanato-4-methylpentanoate (1c). Reaction of 5.31 g (0.0293 mol) of L-leucine methyl ester hydrochloride followed by Kugelrohr distillation (90 °C, 0.06 mmHg) yielded 4.65 g (93%) of **1c** as a colorless liquid: $[\alpha]^{21}_D$ −36.1° (neat); IR (film) 2260, 1745, 1213 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.04 (dd, *J* = 8.8, 5.6 Hz, 1 H), 3.81 (s, 3 H), 1.90–1.78 (m, 1 H), 1.68–1.60 (m, 2 H), 0.94 (t, *J* = 6.6 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 126.3, 55.8, 53.0, 42.7, 24.9, 22.8, 21.0. Anal. Calcd for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.23; H, 7.64; N, 8.19.

Methyl (2*S*,3*S*)-2-Isocyanato-3-methylpentanoate (1d). Reaction of 5.28 g (0.0291 mol) of L-isoleucine methyl ester hydrochloride followed by Kugelrohr distillation (85 °C, 3.3 mmHg) yielded 4.48 g (90%) of **1d** as a colorless liquid: $[\alpha]^{19}_D$ −4.3° (neat); IR (film) 2266, 1745, 1217, cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.97 (d, *J* = 3.9 Hz, 1 H), 3.81 (s, 3 H), 2.02–1.92 (m, 1 H), 1.42–1.22 (m, 2 H), 1.00 (d, *J* = 6.8 Hz, 3 H), 0.90 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 126.7, 62.7, 52.9, 38.4, 24.2, 16.3, 11.4. Anal. Calcd for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.24; H, 7.69; N, 8.25.

Methyl (*S*)-2-Isocyanato-3-phenylpropanoate (1e). Reaction of 6.47 g (0.0300 mol) of L-phenylalanine methyl ester hydrochloride followed by Kugelrohr distillation (130 °C, 0.1 mmHg) yielded 5.76 g (94%) of **1e** as a colorless oil, which crystallized upon refrigeration: $[\alpha]^{21}_D$ +71.9° (neat); IR (film) 2258, 1745, 1221 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.23 (m, 3 H), 7.20–7.17 (m, 2 H), 4.26 (dd, *J* = 7.7, 4.6 Hz, 1 H), 3.79 (s, 3 H), 3.15 (dd, ABX pattern, *J* = 13.8, 4.6 Hz, 1 H), 3.01 (dd, ABX pattern, *J* = 13.8, 7.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 135.5, 129.2, 128.6, 127.4, 126.8, 58.5, 53.1, 39.9. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.11; H, 5.28; N, 6.85.

Methyl (*S*)-2-Isocyanato-4-(methylthio)butanoate (1f). Reaction of 5.99 g (0.0300 mol) of L-methionine methyl ester hydrochloride followed by Kugelrohr distillation (145 °C, 0.8 mmHg) yielded 5.42 g (95%) of **1f** as a colorless liquid: $[\alpha]^{21}_D$ −52.5° (neat); IR (film) 2252, 1745, 1223 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.29 (dd, *J* = 8.6, 4.2 Hz, 1 H), 3.83 (s, 3 H), 2.65–2.57 (m, 2 H), 2.18–1.94 (m, 2 H), 2.11 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 126.8, 55.9, 53.3, 32.8, 30.0, 15.3. Anal. Calcd for $C_7H_{11}NO_3S$: C, 44.43; H, 5.86; N, 7.40. Found: C, 44.42; H, 5.88; N, 7.33.

Methyl (*S*)-2-Isocyanato-3-(1,1-dimethylethoxy)-propanoate (1g). Reaction of 6.35 g (0.0300 mol) of *O*-*tert*-butyl-L-serine methyl ester hydrochloride followed by Kugelrohr distillation (70 °C, 0.15 mmHg) yielded 5.58 g (92%) of **1g** as a colorless liquid: $[\alpha]^{22}_D$ +17.0° (neat); IR (film) 2238, 1753, 1214 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (appar t, *J* = 4.2 Hz, 1 H), 3.81 (s, 3 H), 3.71 (dd, ABX pattern, *J* = 9.3, 4.6 Hz, 1 H), 3.67 (dd, ABX pattern, *J* = 9.0, 3.5 Hz, 1 H), 1.20 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 129.2, 73.9, 62.8, 58.1, 52.9, 27.2. Anal. Calcd for $C_9H_{15}NO_4$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.61; H, 7.65; N, 6.96.

Diethyl (*S*)-2-Isocyanatopentanedioate (1h). Reaction of 7.19 g (0.0300 mol) of L-glutamic acid diethyl ester hydrochloride followed by Kugelrohr distillation (108 °C, 0.15 mmHg) yielded 6.46 g (94%) of **1h** as a colorless liquid: $[\alpha]^{23}_D$ −43.9 (neat); IR (film) 2252, 1740, 1213 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.28 (q, *J* = 7.1 Hz, 2 H), 4.19–4.11 (m, 3 H), 2.49–2.43 (m, 2 H), 2.29–2.18 (m, 1 H), 2.07–1.97 (m, 1 H), 1.33 (t, *J* = 7.1 Hz, 3 H), 1.27 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 170.8, 127.0, 62.6, 60.6, 56.5, 30.0, 28.8, 14.0. Anal. Calcd for $C_{10}H_{15}NO_5$: C, 52.40; H, 6.60; N, 6.11. Found: C, 52.51; H, 6.67; N, 6.15.

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Transmetalation of Disubstituted Alkenyl Groups from Zirconium to Boron Compounds

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The hydrozirconation reaction, developed by Schwartz and co-workers,[1,2] has been used for the preparation of organozirconium compounds. A major drawback of these types of organozirconiums is their inability to undergo general carbon–carbon bond forming reactions. To overcome this limitation, transmetalation of organic groups from zirconium to other metals, which have an established ability to form carbon–carbon bonds, was explored.[3,4]

One of the most widely studied and versatile class of intermediates known to the organic chemist is the organoboranes.[5,6] Although many structurally different types of organoboranes can easily be prepared, there are some limitations to the types of groups that can be placed on boron. By combining the versatility of organoboranes with the unique reactivity and selectivity of the hydro-

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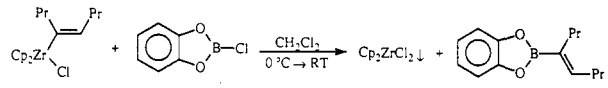
zirconation reaction, a potentially useful route for the synthetic organic chemist to prepare organic products can be attained.

In principle, organic groups would be expected to migrate from zirconium to a more electronegative metal, such as boron. Surprisingly, the transmetalation of alkenyl and alkyl groups from zirconium to boron was not actively investigated until recently. Caulton reported the first migration of an alkyl group, transferring methyl groups from the related dimethylzirconocene, Cp_2ZrMe_2, to boron, forming a mixture of methylboranes.[7] We have systematically explored migration of alkyl groups to a variety of trihaloboranes and organohaloboranes.[8] More recently, other research groups have reported the migration of alkenyl groups from zirconium to boron compounds. Fagan and co-workers published a novel synthesis of boroles using zirconium metallocycles.[9] Fryzuk used the selective hydrozirconation of 1,3-enynes followed by transmetalation to diphenylbromoborane to form 1,3-dienyldiphenylboranes.[10] We have been exploring the migration of organic groups from transition metals to boron. Recently we reported the migration of 1-alkenyl groups from zirconium to a variety of boranes.[11] The transmetalation proceeded readily with the chloro- and bromoboranes to give high yields of the 1-alkenylboranes with complete retention of the regio- and stereochemistry.

Although the hydroboration of symmetrical internal alkynes cleanly forms disubstituted vinylboranes in high yields, unsymmetrical internal alkynes yield mixtures of vinylboranes. The hydrozirconation of these same alkynes with a slight excess of the zirconium hydride[12] give higher regioselectivities as compared to those of the most selective hydroborating agents: 9-BBN, $HBBr_2{\cdot}SMe_2$, and Mes_2BH.[13-17] In both of these reactions there is an increase in the regioselectivity with increasing steric bulk of the alkyl groups, placing the zirconium or boron preferentially on the least hindered carbon.

Results and Discussion

In this study, we investigated the selective hydrozirconation of disubstituted alkynes followed by migration to chloro- and bromoboranes. We used the 4-octenyl-, 2-hexenyl-, and the (4-methyl-2-pentenyl)zirconocene chlorides as representative disubstituted alkenyl systems. In our initial studies we used the symmetrical 4-octenyl group to examine migrations from zirconium to boron. The 4-octenylzirconocene chloride was prepared via hydrozirconation of 4-octyne in methylene chloride. This complex, 5 mmol, was then transmetalated with 1 equiv of *B*-chlorocatecholborane in methylene chloride at 0 °C forming an off-white precipitate (Cp_2ZrCl_2) within 0.25 h. The reaction mixture was analyzed by ^{11}B NMR and showed the appearance of a new signal at +32 ppm along with a small shoulder seen at 28.5 ppm. To distinguish between the expected product and starting material, a small amount of methanol was added to the reaction mixture, converting the unreacted *B*-chlorocatecholborane (+28.5 ppm) into *B*-methoxycatecholborane (ca. +22 ppm). If an excess of methanol is added, the *B*-methoxycatecholborane is transesterified into trimethoxyborane (+18.4 ppm). The yield was 80% *B*-4-octenylcatecholborane on the basis of relative peak area by ^{11}B NMR.



The transmetalation of this same disubstituted alkenylzirconocene complex, 5 mmol, with 1 equiv of boron trichloride resulted in the immediate precipitation of Cp_2ZrCl_2. The ^{11}B NMR spectrum showed the formation of a single product as observed at +54.2 ppm, which is consistent with the migration of the vinyl group. Since trivinylboranes and vinylchloroboranes have similar chemical shifts, ca. +55 ppm, the reaction mixture was methanolyzed with an excess of methanol, forming readily distinguishable derivatives. In this example a new major peak was observed at +28.8 ppm which corresponds to the expected 4-octenyldimethoxyborane (75%); the only other boron-containing product was trimethoxyborane as seen at +18.5 ppm (25%). These initial transmetalation reactions behaved very similarly to those reported with the 1-alkenylzirconium system.[11]

The hydrozirconation of internal unsymmetrical alkynes in a ≤1:1 ratio gives similar low regioelectivities as do most boranes.[2] However, if a slight excess of the zirconium hydride is then added, there is a dramatic shift in the regiochemistries. This shift has been attributed to a second hydrozirconation of the vinylzirconium mixture, forming a bimetallic complex as an intermediate. Unlike the regiochemistry observed in the hydroboration reaction, the two zirconium metals are bonded to both former acetylenic carbons due to steric effects.[12] This complex readily dehydrozirconates, eliminating the more sterically hindered zirconium as $Cp_2ZrH(Cl)$. Since these reactions proceed by cis-addition and cis-elimination, the stereochemistry of the vinylzirconium group is retained. The excess Schwartz's reagent catalyzes the isomeriztion primarily due to steric effects, placing the zirconium at the least hindered position. We found that the hydrozirconation of the unsymmetrical internal alkynes in benzene, with 3–5 mol % excess $Cp_2ZrH(Cl)$,[18] worked as well as the method reported by Schwartz.[12] The hydrozirconation was initially carried out at 0 °C and allowed to come to room temperature overnight. The regioselectivity of the organozirconium can be determined from the ^1H NMR spectrum by comparing the integrals of the two types of methyl protons.[12] The regioselectivities of the vinylboranes were determined after the migration the alkenyl groups from zirconium to boron trichloride, as described above, followed by oxidation with $NaOH/H_2O_2$ to form the corresponding ketones. The ratios of the isomeric ketones were determined using capillary GC, showing somewhat better regioselectivities than previously reported values. In the 2-hexenyl system, we found 97:3 ratio of the 2-hexanone to 3-hexanone. The regioselectivity of the 4-methyl-2-pentenyl system gave ≥99.7% selectivity to 4-methyl-2-pentanone and no 2-methyl-3-pentanone was observed. It is unknown whether the differences in re-

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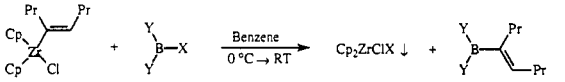
Table I. Migration of 4-Octenyl Group from Zirconium to Chloroboranes



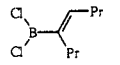
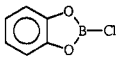
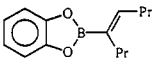
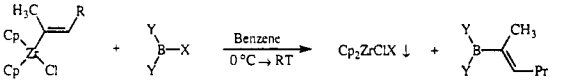
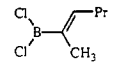
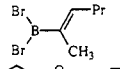
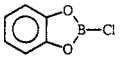
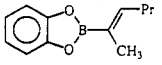
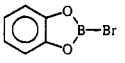
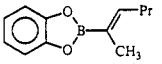
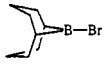
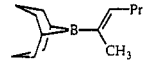
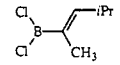
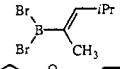
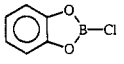
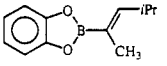
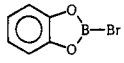
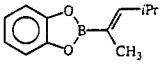
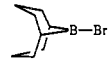
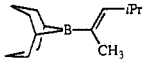
borane	chem shift	product	chem shift	chem shift after methanolysis	yield, %
BCl_3	46.0		54.2	28.8	75
	28.5		32.0	32.4	80

Table II. Migration of Disubstituted Alkenyl Groups from Zirconium to Haloboranes



borane	chem shift	product	chem shift	chem shift after methanolysis	yield, %
BCl_3	46.0		54.2	28.8	83
BBr_3	38.5		54.2	28.1	54
	28.5		32.0	32.4	80
	26.9		31.4	31.3	63
	6.8[a]			0.6[a]	71
BCl_3	46.0		54.3	28.2	67
BBr_3	38.5		54.9	27.9	37
	28.5		31.6	31.5	76
	26.9		31.5	31.7	79
	6.8[a]			0.1[a]	84

[a] Material was analyzed as the pyridine complex.

gioselectivity are due to the slight change in reaction conditions or steric effects in the migration of the alkenyl group to the boron. The stereochemistry of these vinylboranes was established from the NOESY spectrum. There was a strong cross peak between the two allylic positions which agree with the *Z* stereochemistry of the vinylborane. No other isomers were detected, within the limits of detection, ca. 5%, in either proton or carbon spectra, suggesting isomeric purity ≥95 mol %. These disubstituted alkenylzirconium complexes were reacted with the same series of haloboranes as examined in the transmetalation of the 1-alkenyl groups.[11] The migration of the disubstituted alkenyl groups is slightly slower than that of the 1-alkenyl groups and with a slight reduction in corresponding yields. However, the more sterically hindered *B*-chlorothexylalkylborane and *B*-chlorodiisopinocampheylborane did not undergo transmetalation to form the alkenylboranes. The vinyldihaloboranes can be prepared from boron trichloride or tribromide. However, tribromoborane does not selectively give the desired vinyldibromoboranes. In addition to the expected vinylbromoboranes, ca. +55 ppm, small amounts of boron materials were observed at +64 and +26.5 ppm. Apparently these products are formed from the reaction of HBr liberated in the hydrolysis of the bromoborane, yielding an alkyldibromoborane and vinylboronic or α-bromoboronic acids. Methanolysis of the reaction mixture showed only moderate amounts of the vinyldimethoxyborane (37–54%), 12–15% of the alkylboronic ester, and 31–51% of trimethoxyborane. There was no indication of divinyl- or trivinylboranes formed in these reactions. These results are summarized in Tables I and II.

In this study, we have demonstrated that disubstituted alkenyl groups readily migrate from zirconium to a variety of boron compounds. Hydrozirconation of unsymmetrical alkynes using 3–5 mol % excess of $Cp_2ZrH(Cl)$ forms the disubstituted alkenylzirconiums with high regioselectivity. The transmetalation of these alkenylzirconiums to different boranes gives alkenylboranes in higher regioselectivity than can be readily attained by hydroboration. This regioselective organometallic route to disubstituted alkenylboranes offers a number of advantages over hydroboration. The regioselectivities are better or as good as the most selective hydroborating agents, readily allowing the preparation of a diverse variety of vinylorganoboranes and avoiding formation of small amounts of dihydroborated products.[13] More importantly to the synthetic organic chemist, these alkenylboranes can be further

transformed into a variety organic substrates, using carbon–carbon bond forming reactions that have been established with organoborane chemistry.

Experimental Section

General Comments. All glassware was dried at 130 °C for at least 4 h, assembled hot, and cooled under a stream of nitrogen. All reactions were carried out under a static pressure of nitrogen. $Cp_2ZrH(Cl)$, Schwartz's reagent, was prepared as previously reported by Buchwald.[18] The boranes and acetylenes are available from commercial sources (Aldrich, Wiley). Solvents used were ACS grade and were dried prior to use. Manipulation of borane reagents was done under a nitrogen atmosphere by using hypodermic needles or double-ended needles and solids were handled in a glove bag.[19] The ^1H, ^{11}B, and ^{13}C NMR spectra were recorded with a Chemagnetics 200-MHz spectrometer at 199.4229, 63.9837, and 50.1500 MHz, respectively. The 2D NMR spectra were recorded on a General Electric QE-300 NMR at University of California, Riverside. Chemical shifts values are given in parts per million (δ) relative to Me_4Si for ^1H and ^{13}C spectra and relative to $BF_3{\cdot}OEt_2$ in ^{11}B NMR. Capillary gas chromatographic analysis were performed on a Hewlett-Packard 5890 using a HP 3390A digital integrator on a 30-m SPB-1 capillary column using decane as an internal standard. All yields reported as isolated materials have purities greater than 95% based on ^{11}B, ^1H, and ^{13}C NMR spectroscopy. The major impurities are attributed to benzene, pentane, or methylene chloride. Microanalysis was performed by Desert Analytics, Tuscon, AZ. Samples were sent sealed in nitrogen-filled vials.

Preparation of Dicyclopentadienyl-(*E*)-4-octenylzirconium Chloride. To a 50-mL flask with a septum-covered sidearm, equipped with a magnetic stirring bar and adapter, was added 20 mmol of Schwartz's reagent, $Cp_2ZrH(Cl)$ (5.16 g), suspended in 15 mL of methylene chloride. The mixture was cooled to 0 °C and 22 mmol of 4-octyne (2.20 g, 2.90 mL) was slowly added followed by an additional 2.1 mL of methylene chloride to give an approximate 1 M solution. After 15–30 min, the solid disappeared to give a clear yellow solution: ^1H NMR ($CDCl_3$) δ 6.08 (s, 10 H), 5.88 (t, 1 H, J = 6 Hz), 2.51 (t, 2 H), 1.93 (q, 2 H), 1.37 (m, 4 H), 1.00 (t, 3 H), 0.86 (t, 3 H).

Preparation of Dicyclopentadienyl-(*E*)-2-hexenylzirconium Chloride.[12] To a 50-mL flask with a septum-covered sidearm, equipped with a magnetic stirring bar and adapter, was added 6.5 mmol (3% excess) of Schwartz's reagent, $Cp_2ZrH(Cl)$ (1.68 g), suspended in 11.6 mL of benzene. The mixture was cooled to 0 °C and 6.32 mmol of 2-hexyne (0.518 g, 0.7 mL) was slowly added to give an approximate 0.5 M solution. The mixture was allowed to react overnight to give a dark orange solution. For NMR purposes, the liquid was decanted from the excess Schwartz's reagent, and the benzene was removed under vacuum and replaced with $CDCl_3$: ^1H NMR ($CDCl_3$) δ 6.10 (s, 10 H), 5.71 (t, 1 H), 1.91 (s, 3 H), 1.50 (q, 2 H), 1.31 (m, 2 H), 0.86 (t, 3 H).

Preparation of Dicyclopentadienyl-(*E*)-(4-methyl-2-pentenyl)zirconium Chloride.[12] To a 50-mL flask with a septum-covered sidearm, equipped with a magnetic stirring bar and adapter, was added 13.43 mmol (3% excess) of Schwartz's reagent, $Cp_2ZrH(Cl)$ (3.46 g), suspended in 24.6 mL of benzene. The mixture was cooled to 0 °C and 13.0 mmol of 4-methyl-2-pentyne (1.071 g, 1.5 mL) was slowly added to give an approximate 0.5 M solution. The mixture was allowed to react overnight to give a red solution. For NMR purposes, the liquid was decanted from the excess Schwartz's reagent, and the benzene was removed under vacuum and replaced with $CDCl_3$: ^1H NMR ($CDCl_3$) δ 6.11 (s, 10 H), 5.56 (d, 1 H), 2.43 (m, 1 H), 1.95 (d, 3 H), 0.87 (d, 6 H).

General Procedure for the Transmetalation from Zirconium to Boron. The disubstituted alkenylzirconium complexes were prepared as described above and used as needed. The borane solutions were cooled to 0 °C and a stoichiometric amount of the zirconium complex was added. Most of the reactions were observed to form an off-white precipitate within 15–30 min. Because some of the vinylboranes may have essentially the same chemical shifts as the starting borane, these reactions were analyzed by ^{11}B NMR before and after the addition of excess methanol to the NMR tube to distinguish between starting material and product. Yields were based on relative peak areas in the ^{11}B NMR. This method appears to give satisfactory results for boron-containing materials with similar peak widths.[11,20,21] These values were also in agreement with the results from the oxidation of the vinyldichloroborane to the ketone as analyzed by GC using an internal standard. Products were isolated by first separating the solids from the reaction mixture and the solvent was removed under reduced pressure. The residue was extracted with 4 × 10 mL of pentane followed by removal of the pentane from the combined extracts to yield the pure product, as indicated by NMR. Results of these reactions are summarized in Tables I and II.

Preparation of (*Z*)-4-Octenyldichloroborane. The preparation of the dichloroborane was carried out as described in the general transmetalation procedure by adding 5 mmol of the dicyclopentadienyl-(*E*)-4-octenylzirconium chloride solution to boron trichloride in methylene chloride (5 mmol, 5 mL). The boron NMR spectroscopic data is in agreement with expected and previously reported values:[22] ^{11}B NMR (CH_2Cl_2) +54.2 ppm, methanolysis converts product to the (*Z*)-4-octenyldimethoxyborane +28.8 ppm with 75% conversion.

Preparation of (*Z*)-2-Hexenyldichloroborane. The product was prepared by adding 5 mmol of the dicyclopentadienyl-(*E*)-2-hexenylzirconium chloride solution to boron trichloride in methylene chloride (5 mmol, 5 mL). The boron NMR spectroscopic data is in agreement with expected and previously reported values:[22] ^{11}B NMR (CH_2Cl_2) +53.7 ppm, after methanolysis +28.1 ppm, 83% conversion of starting material. In a separate reaction, 5 mmol of the 2-hexenyldichloroborane was oxidized by the addition of 10 mmol of NaOH (3.30 mL, 3.0M) followed by 5 mmol of 30% H_2O_2. Analysis by GC indicated 97:3 ratio of 2-hexanone to 3-hexanone with a 78% yield of the two isomeric ketones.

Preparation of (*Z*)-(4-Methyl-2-pentenyl)dichloroborane. The preparation was conducted as in the general procedure by adding 5 mmol of the dicyclopentadienyl-(*E*)-(4-methyl-2-pentenyl)zirconium chloride solution to boron trichloride in methylene chloride (5 mmol, 5 mL). The boron NMR spectroscopic data are in agreement with expected and previously reported values:[22] ^{11}B NMR (CH_2Cl_2) +54.3 ppm, after methanolysis +28.2 ppm, 67% yield. Analysis by GC of the oxidation products of a similar reaction indicated >99.7% regioselectivity of the 4-methyl-2-pentanone with 64% yield of the two isomeric ketones.

Preparation of (*Z*)-2-Hexenyldibromoborane.[15] As in the general procedure, 5 mmol of the dicyclopentadienyl-2-hexenylzirconium chloride solution was added to boron tribromide in methylene chloride (5 mmol, 5 mL). The boron NMR spectroscopic data is in agreement with expected values: ^{11}B NMR (CH_2Cl_2) +54.2 ppm, after methanolysis +28.1 ppm with 54% conversion. The other material present was trimethoxyborane (31%) and a boronic ester (15%).

Preparation of (*Z*)-(4-Methyl-2-pentenyl)dibromoborane.[15] The alkenyldibromoborane was prepared by the addition of 5 mmol of the dicyclopentadienyl-(*E*)-(4-methyl-2-pentenyl)zirconium chloride solution to boron tribromide in methylene chloride (5 mmol, 5 mL) at 0 °C. The boron NMR spectroscopic data is in agreement with expected values: ^{11}B NMR (CH_2Cl_2) +54.9 ppm, after methanolysis +27.9 ppm, 37% conversion, trimethoxyborane (51%) and a boronic ester (12%).

Preparation of 2(*Z*)-4-Octenyl-1,3,2-dioxaborazole.[23] The preparation was conducted as in the general procedure by adding 5 mmol of the dicyclopentadienyl-(*E*)-4-octenylzirconium chloride solution to 5 mmol of *B*-chlorocatecholborane (0.769 g) in 5 mL of methylene chloride: ^{11}B NMR (CH_2Cl_2) +32.0 ppm, after methanolysis +32.4 ppm with 80% of the starting material converted to product, the remainder being trimethoxyborane. In a

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similar reaction, methanolysis was not done but the solids were separated from the supernate and were washed with 4 × 10 mL of pentane to remove any remaining boron species from the zirconium. These washings were combined with the supernate and the solvents were removed under reduced pressure rendering an oil which was distilled using short path distillation to afford 2(*Z*)-4-octenyl-1,3,2-dioxaborazole. Isolated yield: 1.51 g (66%) 2(*Z*)-4-octenyl-1,3,2-dioxaborazole, bp 90–100 °C (0.1 mmHg). Spectroscopic data are in agreement with expected values: ^{1}H NMR ($CDCl_3$) δ 7.11 (m, 4 H), 6.76 (t, 1 H, *J* = 7.3 H), 2.40–2.05 (m, 4 H), 1.50 (m, 4 H), 0.90 (m, 6 H); ^{13}C ($CDCl_3$) δ 149.7, 148.63, 122.30, 112.20, 30.90, 30.47, 23.27, 22.30, 14.02, 13.70; IR (neat) 3063, 2961, 2932, 2873, 1626, 1479, 1414, 1387, 1335, 980, 808, 747 cm^{-1}; EI mass spectrum *m*/*z* (relative intensity) 230 (M^+, 37), 174 (28), 160 (17), 159 (26), 146 (15), 145 (11), 120 (18), 67 (25), 65 (42), 41 (100).

Preparation of 2(*Z*)-2-Hexenyl-1,3,2-dioxaborazole.[24] The preparation was conducted as in the general procedure by adding 5 mmol of the dicyclopentadienyl-2-hexenylzirconium chloride solution to 5 mmol of *B*-bromocatecholborane (0.994 g) in methylene chloride. The same experiment was also conducted using 5 mmol of *B*-chlorocatecholborane (0.769 g) in 5 mL of methylene chloride: ^{11}B NMR (CH_2Cl_2) +31.4 ppm (Br) +31.4 ppm (Cl), after methanolysis +31.3 ppm (Br), +31.7 ppm (Cl) with 63% and 66% conversion of the bromo and chlorocatecholborane, respectively. The remaining material was the methanolyzed starting material. In a similar reaction, methanolysis was not done but the solids were separated from the supernate and were washed with 4 × 10 mL of pentane to remove any remaining boron species from the zirconium. These washings were combined with the supernate and the solvents were removed under reduced pressure rendering an oil which was distilled using short path distillation to afford 2(*Z*)-2-hexenyl-1,3,2-dioxaborazole. Isolated yield: 1.213 g (69%) of 2(*Z*)-2-hexenyl-1,3,2-dioxaborazole, bp 90–100 °C (0.1 mmHg). Spectroscopic data are in agreement with expected values: ^{1}H NMR ($CDCl_3$) δ 7.09 (m, 4 H), 6.75 (tq, 1 H, *J* = 7.3 Hz, *J* = 1.8 Hz), 2.21 (q, 2 H, *J* = 7.1 Hz), 1.88 (s, 3 H), 1.49 (sext, 2 H, *J* = 7.1 Hz), 0.95 (t, 3 H, *J* = 7.3 H); ^{13}C ($CDCl_3$) δ 149.75, 148.57, 122.30, 112.14, 30.95, 21.92, 13.81, 13.38; IR (neat) 3063, 2960, 2932, 2872, 1631, 1475, 1416, 1389, 1331, 956, 814, 741 cm^{-1}; EI mass spectrum *m*/*z* (relative intensity) 202 (M^+, 16), 173 (16), 160 (45), 159 (21), 146 (10), 145 (17), 120 (34), 67 (17), 65 (47), 39 (100).

Preparation of 2(*Z*)-(4-Methyl-2-pentenyl)-1,3,2-dioxaborazole. Following the general procedure for transmetalation, 5 mmol of the dicyclopentadienyl(4-methyl-2-pentenyl)zirconium chloride solution was added to 5 mmol of *B*-bromocatecholborane (0.994 g) in methylene chloride at 0 °C. The same experiment was also conducted using 5 mmol of *B*-chlorocatecholborane (0.769 g) in 5 mL of methylene chloride: ^{11}B NMR (CH_2Cl_2) +31.5 ppm (Br) +31.6 ppm (Cl), after methanolysis +31.7 ppm (Br) 79% conversion, +31.7 ppm (Cl) 76% conversion of starting material. The remaining material was the methanolyzed starting material. In a similar reaction, methanolysis was not done but the solids were separated from the supernate and were washed with 4 × 10 mL of pentane to remove any remaining boron species from the zirconium. These washings were combined with the supernate and the solvents were removed under reduced pressure, rendering an oil which was distilled using short path distillation to afford 2(*Z*)-(4-methyl-2-pentenyl)-1,3,2-dioxaborazole. Isolated yield: 1.006 g (68%) of 2(*Z*)-(4-methyl-2-pentenyl)-1,3,2-dioxaborazole, bp 85–90 °C (0.1 mmHg). Spectroscopic data are in agreement with expected values: ^{1}H NMR ($CDCl_3$) δ 7.08 (m, 4 H), 6.57 (dq, 1 H, *J* = 7.3 Hz, *J* = 1.7 Hz), 2.88–2.70 (m, 1 H), 1.89 (d, 3 H, *J* = 1.7 Hz), 1.03 (d, 6 H, *J* = 6.6 Hz); ^{13}C ($CDCl_3$) δ 156.63, 148.57, 122.30, 112.14, 27.78, 21.98, 13.17; IR (neat) 3064, 2961, 2932, 2873, 1626, 1479, 1418, 1387, 1348, 958, 808, 747 cm^{-1}; EI mass spectrum *m*/*z* (relative intensity) 202 (M^+, 38), 187 (36), 186 (10), 159 (48), 158 (20), 146 (10), 145 (17), 120 (21), 69 (60), 65 (47), 41 (100). Anal. Calcd for $C_{12}H_{15}BO_2$: C, 71.33; H, 7.48. Found: C, 71.28; H, 7.38.

Preparation of (*Z*)-2-Hexenyl-9-BBN.[13] The product was prepared by the addition of 5 mmol of the dicyclopentadienyl-2-hexenylzirconium chloride solution to *B*-bromo-9-BBN in methylene chloride (5 mmol, 5 mL). Because vinyl-9-BBN derivatives are reactive with methanol, the product was analyzed as the pyridine adduct by the addition of 5 mmol of pyridine. Spectroscopic data are in agreement with expected values: ^{11}B NMR (CH_2Cl_2) 0.6 ppm, 71% conversion of starting material with the rest being the pyridine adduct of *B*-bromo-9-BBN.

Preparation of (*Z*)-(4-Methyl-2-pentenyl)-9-BBN.[13] A total of 5 mmol of dicyclopentadienyl-(4-methyl-2-pentenyl)zirconium chloride solution was added to *B*-bromo-9-BBN in methylene chloride (5 mmol, 5 mL). As before, the product was analyzed as the pyridine adduct after addition of 5 mmol of pyridine. Spectroscopic data are in agreement with expected values: ^{11}B NMR (CH_2Cl_2) +0.1 ppm, 84% yield with the other material being the pyridine adduct of *B*-bromo-9-BBN.

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Supplementary Material Available: The ^{1}H–^{1}H NOSEY and COSY NMR data for 2-hexenyl-, 4-octenyl-, and (4-methyl-2-pentenyl)-1,3,2-dioxaboroazoles and ^{1}H–^{13}C HETCOR NMR data for (4-methyl-2-pentenyl)-1,3,2-dioxaboroazole (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Enantiomerically Pure 2,2′-Oxybis[*N*-(1-phenylethyl)acetamide]. An Especially Effective Chiral Solvating Agent for Determinations of Enantiomer Compositions by NMR Spectroscopy

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The imposition of a nonracemic influence on an enantiomeric condition changes the latter to diasteromeric states which may display discernably different properties. Thus, determination of the enantiomeric composition of a sample by allowing it to interact with a chiral shift reagent or a chiral solvating agent and measuring the ratio of the resultant diastereomeric NMR signals[1,2] is an application of this principle which should be widely applicable because of its simplicity. In actual practice, however, the method frequently fails because the diastereomeric signals are either insufficiently separated or they are obscured. The solution to these technical problems lies in development of a broad array of chiral solvating agents to cover a sufficiently wide range of applications, and our recent work on the strong solute–solute interactions of chiral carboxamides[3] suggested the possibility of using a solution of an enantiomerically pure carboxamide as a chiral environment into which partially resolved chiral samples may be placed for NMR determinations of their enantiomer compositions. This approach has succeeded, and we describe here the preparation, properties, and use

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