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Migration of Groups from Zirconium to Boron: Aspects of Synthesis and Utility

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Abstract: *The hydrozirconation of alkenes or alkynes yields the dicyclopentadienyl alkyl- or alkenylzirconium chloride, respectively, in high yields and with high regioselectivity. The reaction of these organozirconium compounds with a boron halide results in the exchange of the halogen and organic group, forming the organoborane. We report here a systematic investigation of the transmetallation of organic groups from zirconium to a variety of boron compounds. The migration is facile to a variety of boron halides, yielding structurally different types of alkyl or alkenylboranes in good to high yields. Exploiting the unique reactivity and selectivity of the hydrozirconation reaction for the preparation of organoboranes expands the range of potential of both metals for synthesis.*

Introduction

Methods for the preparation of organozirconocene compounds have been developed since the early sixties. The majority of preparations involved alkylation of zirconocene dihalides with organolithium or -magnesium.[1] The first stable alkyl- and alkenylzirconium compounds were prepared by Wailes and Weigold, who inserted carbon-carbon multiple bonds into zirconium hydride bonds. This is now referred to as the hydrozirconation reaction.[2-5]

Hydrozirconation has been shown to be useful for preparing organozirconocene compounds.[6] Utilization of these organozirconium (IV) complexes for organic synthesis was pioneered by Schwartz.[7,8,9] Unfortunately, these bis(cyclopentadienyl) zirconium alkyl- and alkenyl chlorides have poor reactivity with carbon electrophiles. Thus, they do not generally undergo carbon-carbon bond forming reactions, necessitating the selective replacement of zirconium. This led to the development of transmetallation methods primarily by Schwartz and Negishi. Other metals with better carbon-carbon bond forming abilities replaced zirconium by transmetallation. These metals include aluminum,[10,11,12] copper,[13] palladium,[14,15] mercury,[16] tin,[17] nickel[18] and zinc.[19] Transmetallation transformed a relatively unknown process into a versatile and reliable synthetic method.

For more than twenty years, organozirconium compounds have developed into useful reagents and intermediates for organic synthesis.[7,20-22] More recently, Zr(II) metallacyclic compounds have been developed and studied by Buchwald[23] and Negishi[24]. Early examples of these metallacycle compounds, derived from reductive coupling of unsaturated organic substrates, were restricted to forming symmetrical compounds.[25,26] This limited the cross coupling reactions of two different organic substrates. Also, the cross-coupling of alkynes and heteroatom species proved to be difficult. An important breakthrough in this chemistry was the preparation of zirconium benzyne complexes by Erker.[27,28]

Buchwald utilized Erker's chemistry and developed substituted benzyne complexes of zirconium in situ. These zirconium complexes are then coupled with other substrates including nitriles and alkynes.[29] The metallacycles, which are formed with high regiochemistry, can be converted to organic substrates by treatment with an electrophilic agent. Depending on the electrophile, a variety of arylketones, benzthiophenes or benzthiazoles, can be prepared.[30] This chemistry has been further improved to include complexes of benzdiyne,[31] napthalyne,[32] cyclohexyne,[33] and acyclic alkynes.[34] The factors that control regio- and stereochemical results has been delineated. Clearly, improvements in the formation of these reactive zirconium complexes by reductive coupling has been a useful addition to organic synthesis.

Negishi studied in the stoichiometric and catalytic chemistry of Zr(II).[35] This utilizes zirconocene, "$ZrCp_2$", generated by treatment of zirconocene dichloride with 2 equiv of *n*-BuLi[36] or *t*-BuLi[37], followed by decomposition to zirconocene. Though it remains elusive, zirconocene is the 14 electron species that undergoes transformation to five-member zirconacycles. Coupling of unsaturated hydrocarbons has interesting selectivity.

These metallacycles, regardless of "pair"-selection types, form with a preference for alkyl substituents on alkenes or alkynes prefer to be β to the zirconium. Aryl, alkenyl or silyl substituents prefer to be α to the zirconium. The stereochemistry of the substituents favors a *trans* configuration. These zirconacycles can also contain oxygen and nitrogen moieties. Reaction with electrophiles gives organic substrates of high regiochemistry. Further development has led to highly chemoselective reactions of these zirconacycles giving selective functionalization of the organic products formed.[38]

One of the most widely studied and versatile intermediates known to the organic chemist are the organoboranes.[39,40] The variety of products that can be prepared via organoboranes is essentially only limited by the types of organic groups that can be placed on boron. The hydrozirconation reaction has a number of similarities to the hydroboration reaction. The zirconium hydride readily undergoes a *cis* addition across carbon-carbon multiple bonds, placing the zirconium at the least sterically hindered position. Hydroboration of symmetrical internal alkynes cleanly yields disubstituted vinylboranes, where unsymmetrical internal alkynes produce mixtures of vinylboranes due to lower regioselectivity in the addition of the borane. The hydrozirconation of these same alkynes has improved regioselectivity compared to the most selective hydroborating agents: 9-BBN, $HBBr_2{\cdot}SMe_2$ and Mes_2BH.[41-45] It is evident that a large difference in the steric bulk about the carbon-carbon triple bond places zirconium or boron on the least hindered carbon. These regioselectivities are summarized in Table 1.

Table 1. Comparison of the Regioselectivity from Hydrozirconation and Hydroboration of Internal Alkynes

Alkyne	Hydrozirconation[a]	Hydroboration[b]	Reagent
2-pentyne	89:11	78:22	9-BBN
2-hexyne	91:9	78:22, 90:10	9-BBN, Mes_2BH
5-methyl-2-hexyne	>95:<5	72:28	9-BBN
4-methyl-2-pentyne	>98:<2	96:4	9-BBN, BBr_2H
4,4-dimethyl-2-pentyne	>98:2	>99	9-BBN, BBr_2H

[a] see ref. 6

[b] see ref. mentioned above

Alkylboranes isomerize similarly to alkylzirconiums but generally at temperatures greater than 150 °C.[46,47] The alkylzirconiums isomerize at room temperature or lower. This facile isomerization is more selective than that of the alkylboranes. The isomerization, placing the zirconium at the terminal end of an alkyl chain, occurs rapidly at room temperature provided that the isomerization is not blocked by a tertiary or quaternary carbon.[11,48-50] The reaction of electrophiles with organozirconiums is similar to that of the organoboranes, though with some differences. The importance of combining of the unique reactivity and selectivity of the hydrozirconation reaction with the versatility of organoboranes as a potentially powerful method for preparation of new organoboranes. Early examples of transmetallation of organic groups from zirconium showed they proceeded to more electronegative metals. Thus, one would expect that organic groups would migrate from zirconium to boron. Surprisingly, migration from organozirconium to boron was not actively investigated until recently.

There have a been a few examples of the transmetallation from zirconium to boron in the literature. Caulton first reported the migration of the methyl groups from the related dimethylzirconocene Cp_2ZrMe_2 to $BH_3{\cdot}THF$, forming a mixture of methylboranes.[51] More recently, two other groups have reported the migration of alkenyl groups from zirconium to boron. Fagan and co-workers published a novel synthesis of substituted boroles from the corresponding substituted zirconium metallacycles.[52] Fryzuk has used the selectivity of the hydrozirconation of 1,3-enynes followed by transmetallation to diphenylbromoborane to form substituted dienes.[53] However, no systematic investigation of the limitations of this potentially important route for the formation of organoboranes was undertaken.

We have been interested in the migration of organic groups between transition metals and boron, specifically from zirconium to boron.[54-56] We have found that transmetallation is facile with haloboranes,

producing high yields of organoboranes with complete retention of regio- and stereochemistry. We hereby summarize our findings and recent developments.

Results and Discussion

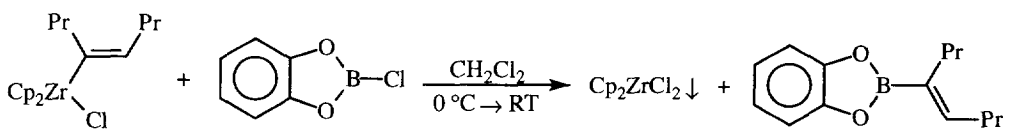
Our initial study concerned the migration of vinyl groups from zirconium to boron. We used the 1-hexenyl group as a representative 1-alkenyl system.[54] We also investigated the selective hydrozirconation of alkenes and disubstituted alkynes followed by migration to haloboranes. The organozirconium complexes were prepared from the hydrozirconation[48] of alkenes or alkynes by using freshly prepared Schwartz's reagent, $Cp_2ZrH(Cl)$.[57] The addition of 5 mmol of the 1-hexenylzirconium complex in methylene chloride to 5 mmol of boron trichloride, in hexane at 0 °C, rapidly formed an off-white precipitate. Analysis of the reaction mixture by ^{11}B NMR revealed a new signal at +52.7 ppm, which is consistent with the migration of the vinyl group. Since trivinylborane and all vinylchloroboranes have similar chemical shifts, ca. +55 ppm, the reaction mixture was methanolyzed with an excess of methanol, forming the readily distinguishable derivatives. In this reaction a new major peak was observed at +27.4 ppm, which corresponded to the vinyl boronic ester, and only small amounts of materials were detected at +18.4 ppm ($B(OMe)_3$ from unreacted BCl_3) and at +47.6 ppm (divinyl borinic ester). The ^{11}B NMR spectra indicated an approximately 90% conversion to 1-hexenyldichloroborane. This suggested selective migration of the 1-hexenyl group to form the monovinylborane. The 1-hexenyldimethoxyborane was isolated and analyzed by both ^1H and ^{13}C NMR. Analysis of the chemical shifts and coupling constants confirmed a pure trans stereochemical assignment of the 1-hexenyl group within the limits of detection by NMR (<3%).[58] In contrast, tribromoborane gave significant amounts of the divinylborane under the same conditions. However, boron trifluoride etherate did not produce any transmetallated products on reaction with the 1-hexenylzirconium complex, even after refluxing for 48 h. Because these transmetallations apparently proceed by electrophilic exchange[11] between the Lewis acidic haloboranes and alkenylzirconocene chlorides, the presence of a Lewis base may be expected to complex with the borane, inhibiting the exchange. Dimethylsulfide, tetrahydrofuran and diethyl ether are examples of Lewis acids that coordinate to boron.

Reaction of the 1-hexenylzirconium complex was carried out using other boranes. As above, equal molar solutions of *B*-chlorocatecholborane or *B*-bromocatecholborane yielded conversions of greater than 90%. Both reactions indicated clean formation of the *B*-1-hexenylcatecholborane. This boronic ester was isolated from the *B*-chlorocatecholborane in a 57% yield. Careful examination by ^1H and ^{13}C NMR did not result in detection of any (< 3%) regioisomeric or stereoisomeric products, indicating excellent product purity.[59,60] Although these vinyl boronic esters can be formed from the hydroboration of alkynes with catecholborane or dihaloboranes,[61,62] transmetallation may offer significant advantages over hydroboration. The hydrozirconation and transmetallation reaction offers a more rational route to 1-alkenyl and di-1-alkenyl boranes, avoiding potential limitations in the hydroboration of 1-alkynes.[63] Other *B*-halodialkoxyboranes did not undergo transmetallation of the 1-hexenyl group in high yields. 2-Chloro-1,3,2-dioxaborinane afforded approximately 70% conversion to the transmetallated vinyl boronic ester within 10 min at 0 °C. The reaction did not proceed further after extended periods of time and the product was isolated in a 41% yield. *B*-Chlorodiisopropoxyborane resulted in the formation of approximately 40% alkenyldiisopropoxyborane over 24 h. *B*-Chlorodimethoxyborane did not appear to form the expected vinyl boronic ester in any significant amounts within 24 h at room temperature.

The 1-hexenyl group can also be transferred to organohaloboranes. *B*-Bromo-9-BBN rapidly accepts the 1-hexenyl group within 5 min at 0 °C, forming the known *B*-1-hexenyl-9-BBN in 84% isolated yield. The sterically hindered dicyclohexylchloroborane also reacted cleanly to give, in a 64% isolated yield, the previously reported 1-hexenyldicyclohexylborane.[64] Though somewhat slower, *B*-chlorothexylhexylborane gave essentially quantitative yield of the thexylhexylhexenylborane after 2 h at room temperature. The more sterically hindered *B*-chlorodiisopinocampheylborane yields approximately 50% of the migrated vinyl product within 24 h at room temperature. Thus, it appears that almost any alkyl-substituted chloro- or bromoborane is capable of accepting a 1-hexenyl group from zirconium to give the 1-alkenylborane product.

Unlike the chloro- and bromoboranes, exchange of *B*-methoxy groups with the 1-hexenylzirconium complex does not proceed to completion even in the presence of 100% excess of the zirconium complex. Trimethoxyborane rapidly formed small amounts (less than 15%) of the exchanged product but did not proceed further over a period of 24 h. *B*-Methoxy-9-BBN was only slightly more effective, forming approximately 25% of the *B*-1-hexenyl-9-BBN after refluxing for 44 h. The more sterically hindered triisopropoxyborane did not form any detectable amounts of transmetallated product. Selected results of these transmetallation reactions and product ratios are summarized in Table 2.

We investigated the selective hydrozirconation of disubstituted alkynes followed by migration to chloro- and bromoboranes.[56] These migrations are slightly slower than the 1-alkenyl groups, with a slight reduction in corresponding yields. We used the 4-octenyl, 2hexenyl and the 4-methyl-2-pentenylzirconocene chlorides as representative disubstituted alkenyl systems. These reactions behaved very similarly to those reported with the 1-hexenyl zirconium system.[54] The 4-octenylzirconocene chloride, prepared via hydrozirconation of 4-octyne in methylene chloride, was transmetallated with one equiv of *B*-Chlorocatecholborane. The yield was 80% of the *B*-4-octenylcatecholborane, based on relative peak area by ^{11}B NMR. The transmetallation of this same disubstituted alkenyl zirconocene complex with one equiv of boron trichloride followed by methanolysis resulted in a 75% conversion to the expected 4-octenyldimethoxyborane.



The hydrozirconation of internal unsymmetrical alkynes in a ≤1:1 ratio gives low regioelectivities similar to most boranes.[7] However, if a slight excess of the zirconium hydride is added, there is a dramatic shift in the regiochemistry. This shift has been attributed to a second hydrozirconation of the vinylzirconium mixture, forming a 1,2 di-zirconium 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. This complex readily dehydrozirconates, leaving the zirconium on the least hindered carbon and 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. We found that the hydrozirconation of unsymmetrical internal alkynes, carried out in benzene with 3-5 mole % excess $Cp_2ZrH(Cl)$, initially at 0 °C and allowed to warm to room temperature overnight, worked as well as the method reported by Schwartz. The regioselectivity of the organozirconium can be determined from the ^1H NMR spectrum by comparing the integrals of the two types of methyl protons.[6] The regioselectivities of the vinylboranes were determined after the migration of 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 a 97:3 ratio of the 2-hexanone to 3-hexanone. The regioselectivity of the 4-methyl-2-pentenyl system gave 4-methyl-2-pentanone with ≥ 99.7% selectivity and no 2-methyl-3-pentanone. It is unknown whether the differences in regioselectivity 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 %.

The more sterically hindered *B*-chlorothexylalkylborane and *B*-chlorodiisopinocampheylborane did not undergo transmetallation to form the alkenylboranes. The vinyldihaloboranes can be prepared from boron trichloride or tribromide. However, tribromoborane does not selectively give the desired vinyldibromoboranes.

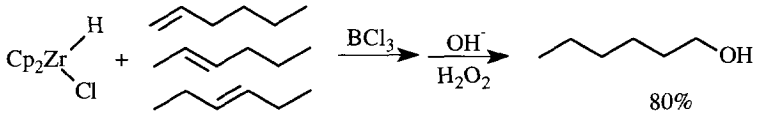
The transmetallation of these alkenylzirconiums to different boranes gives alkenylboranes in higher regioselectivity than can be readily attained by hydroboration. Selected results of these transmetallation reactions and product ratios are summarized in Table 2. This regioselective organometallic route 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 without formation of small amounts of unwanted dihydroborated byproducts.[41]

Alkyl groups also migrate from zirconium to haloboranes.[55] The dicyclopentadienyl-1-hexylzirconium chloride is readily prepared by the hydrozirconation of 1-hexene using Schwartz's reagent.[57] Cleavage of the hexyl group with an electrophilic reagent, such as N-bromosuccinimide, gave >99.8% regioisomeric purity of 1-bromohexane, as determined by gas chromatrographic analysis of the bromohexane.[65] As previously reported by Schwartz, alkyl group migration from zirconium to aluminum is significantly slower than the alkenyl groups. We therefore expected slower migration of the alkyl groups from zirconium to boron.[8] The transmetallation of the 1-hexyl group from 1-hexylzirconocene chloride to one equivalent of *B*-chlorocatecholborane, at room temperature, resulted in a >90% conversion to the 1-hexylboronic ester. *B*-bromocatecholborane also reacted in a similar fashion, but with lower conversion (70%). There was very little (<10%) or no exchange with other dialkoxyhaloboranes such as chlorodimethoxyborane, *B*-chlorodiisopropoxyborane and *B*-chloro-1,3,2-dioxoborinane.

Trihaloboranes readily react with the 1-hexylzirconocene chloride. Monoalkylation of both boron trichloride and boron tribromide to give the 1-hexyldihaloborane is achieved within 2 h after the addition of 1 equiv of the zirconium complex at 0 °C. Surprisingly, selectivity was not attained if 2 equiv of the organozirconium was added to the haloborane at this same temperature. However, lowering the reaction temperature to -78 °C, followed by slowly warming to 0 °C over a period of 2 h, gave 90% of the dihexylchloroborane and approximately 10% other boron containing materials. Tri-*n*-hexylborane can be cleanly formed by the addition of 3 or more equiv of 1-hexylzirconocene chloride to a trihaloborane. As previously mentioned, boron trifluoride etherate was found to be completely unreactive with the more reactive alkenylzirconium complexes.[54] Interestingly, reaction occurred, though not selectively, with 1 equiv of 1-hexylzirconocene chloride to give dihexylfluoroborane and starting material. Reaction with two and three equivalents of the organozirconocene gave exclusively the dialkylfluoroborane and trihexylborane, respectively. Basic oxidation of the dialkylfluoroborane yielded 73% 1-hexanol by GC analysis. Table 3 summarizes these results.

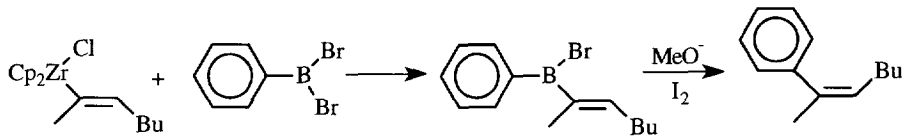
We also examined alkyldihaloboranes and dialkylhaloboranes for transmetallation with 1-hexylzirconocene chloride. These reactions work best at 0 °C. The reaction of *n*-octyldibromoborane[66] with 1 equiv of the 1-hexylzirconocene chloride yielded the dialkylbromoborane in an approximate 80% conversion within 2 h. This result was surprising since addition of 2 equiv of 1-hexylzirconocene chloride with BBr_3 formed a mixture of products under the same conditions. Essentially quantitative reaction was attained with phenyldibromoborane,[66] forming a mixture of phenyldihexylborane (14%), phenylhexylbromoborane (67%) and starting material (19%). Reactions with *B*-bromo-9-BBN, *B*-chloro-9-BBN and dicyclohexylbromoborane formed the trialkylboranes in yields of 63 to 74%. There was no indication of reaction with *B*-chlorodiisopinocampheylborane. The steric hindrance of the large isopinocampheyl groups presumably inhibits reaction. Table 4 summarizes these results.

As previously mentioned, a unique feature of the hydrozirconation of alkenes is facile isomerization. We pursued a few examples of this isomerization. Hydrozirconation, with Schwartz's reagent in THF, of an equal molar mixture of 1-, 2- and 3-hexene was followed by removal of the solvent under reduced pressure. Transmetallation to boron trichloride yielded the alkyldichloroborane, which was then oxidized with alkaline hydrogen peroxide. This afforded an 84% yield of 1-hexanol with a regiochemical purity >99.5%, as confirmed by gas chromatography and GC/MS. Hydrozirconation of 2-methyl-2-pentene, followed by migration to trichloroborane and subsequent oxidation of the organoborane, yielded 4-methyl-1-pentanol as the single product. This reaction illustrates another example of this facile migration as a potentially useful reaction.

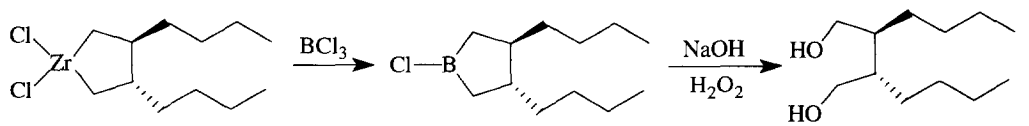


In the studies described above, we have demonstrated that the simple 1-hexenyl group, disubstituted alkenyl groups and alkyl groups readily migrate from zirconium to a variety of structurally different boron compounds. Hydrozirconation of unsymmetrical alkynes using 3-5 mole % excess of $Cp_2ZrH(Cl)$ forms the disubstituted alkenylzirconiums with regioselectivity equal to or, in most cases, better than hydroboration. This organometallic route gives disubstituted alkenylboranes with high regioselectivities and avoids formation of dihydroborated products. The facile isomerization of the hydrozirconation of alkenes is more selective than that of hydroboration. Importantly, these newly formed boranes can be further transformed into a variety organic substrates, using carbon-carbon bond forming reactions that have been established with organoborane chemistry.

We are currently investigating expanded synthetic aspects of transmetallation from zirconium to boron compounds. To demonstrate the utility of this facile transmetallation, we prepared 5,7-tetradecadiene from (1-bromo-1-hexenyl)-1-octenylbromoborane, using selective coupling to form the pure *trans, trans*-1,3-dienes. Hydrozirconation of 1-octyne was followed by migration to 1-bromo-1-hexenyl-dibromoborane to give the unsymmetrical divinylborane. The two vinyl groups were then coupled as reported previously, using sodium methoxide, followed by protonation with isobutyric acid.[67] The crude product was isolated after distillation in a 49% yield. Analytical data is in agreement with previously reported spectral data for this isomeric diene indicating pure isomeric product within the limits of detectability for the *trans, trans* product.[68] The high regioselectivity from hydrozirconation of internal alkynes has contributed to the synthesis of trisubstituted olefins.[69] Previous methods for synthesis of these olefins from boranes were based on hydroboration using a dialkylborane, which had some limitations. Generally, one of the alkyl groups on the boron was not utilized, which is undesirable if it came from an expensive olefin.[70] The hydroboration was also limited to the use of symmetrical alkynes.[71] Successive migration of alkyl groups and disubstituted vinyl groups from zirconium to a haloborane or selective migration of vinyl groups to organohaloboranes[66] gives the alkylvinylhaloborane. Reductive coupling with base and iodine gives the trisubstituted olefins with specific stereochemistry. The two groups that were *cis* to each other on the boron are now *trans* to each other. We have found that primary, secondary and aryl groups migrate to form these olefins.

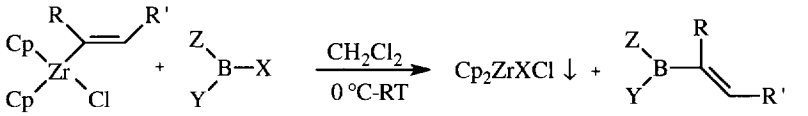


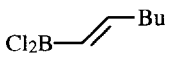
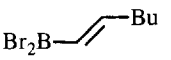
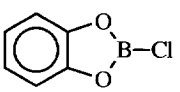
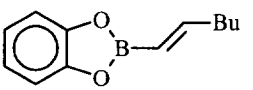
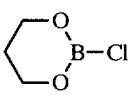
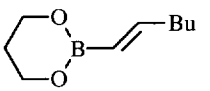
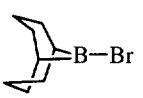
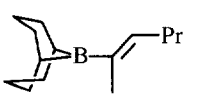
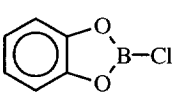
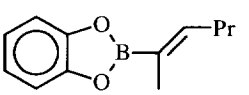
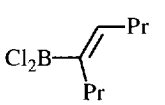
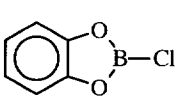
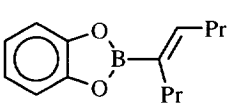
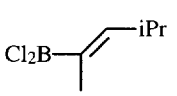
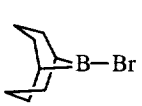
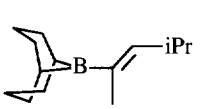
We have begun to investigate some aspects of migration from zirconacycles to boron. These unique intermediates may yield organoborane species that have not been previously prepared by hydroboration or organoborane chemistry. Our initial results indicate that these metallacycles migrate and retain stereochemistry, as evident by conversion of the formed borane to the diol.



Transmetallation from zirconium to boron and subsequent reactions that we are developing have the potential to expand the chemistries of zirconium and boron. The exploitation of facile reactions that are regio- and stereoselective is a powerful adjunct for the preparation of organic substrates.

Table 2. Migration of Alkenyl Groups from Zirconium to Various Boron Compounds



Borane	Chemical Shift	Product	Chemical Shift	Chemical Shift after Methanolysis	^{11}B NMR Product Ratios
BCl_3	46.0		53.0	27.4	>90%
BBr_3	38.5		52.1	27.4	53%
	28.5		30.9	27.2	>90%
	23.5		25.8	-	~70%
	6.8[a]		-	0.6[a]	71%
	28.5		31.6	31.5	67%
BCl_3	46.0		54.2	28.8	75%
	28.5		32.0	32.4	80%
BCl_3	46.0		54.3	28.2	67%
	6.8[a]		-	0.6[a]	84%

[a] Pyridine added in place of methanol to form the pyridine complex.

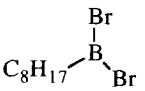
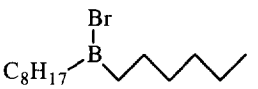
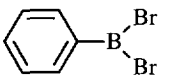
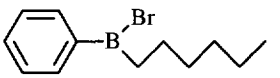
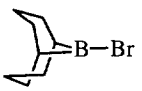
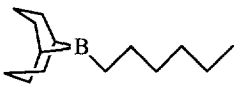
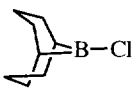
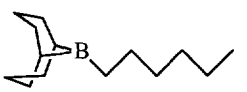
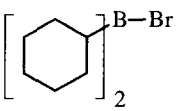
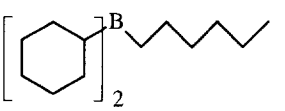
Table 3. Transmetallation of the 1-Hexyl Group to Trihaloboranes

$$BX_3 + y\ Cp_2Zr(Cl)C_6H_{13} \xrightarrow[2\ h]{CH_2Cl_2} (C_6H_{13})_yBX_{3-y} + y\ Cp_2Zr(Cl)X\downarrow$$

Borane	y	Temp, °C	Product	Yield, %
$BF_3{\cdot}OEt_2$	1	0	$(C_6H_{13})_2BF + BF_3{\cdot}OEt_2$	71[b]
$BF_3{\cdot}OEt_2$	2	0	$(C_6H_{13})_2BF$	73[b]
$BF_3{\cdot}OEt_2$	3.5	0	$(C_6H_{13})_3B$	100[a]
BCl_3	1	0	$(C_6H_{13})BCl_2$	77[b]
BCl_3	2	0	Mixture	77[b]
BCl_3	2	-78 to 0	$(C_6H_{13})_2BCl$	90[a]
BCl_3	3.8	0	$(C_6H_{13})_3B$	100[a]
BBr_3	1	0	$(C_6H_{13})BCl_2$	78[a]
BBr_3	2	0	Mixture	74[a]
BBr_3	3.5	0	$(C_6H_{13})_3B$	100[a]

[a] Yields determined by ^{11}B NMR integration.
[b] GC analysis of 1-hexanol from the oxidation of the organoborane, undecane used as internal standard.

Table 4. Transmetallation of the 1-Hexyl Group From Zirconium to Various Boranes

Borane	Product	Time, h	Temp, °C	Yield, %
		2	0	82[a], 79[b]
		2	0	>95[b]
		48	25	40[a]
		2	0	63[b]
		24	0	74[b]

[a] Yields determined by ^{11}B NMR integration.
[b] GC analysis of 1-hexanol from the oxidation of the organoborane, undecane used as internal standard.

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. Schwartz's reagent, $Cp_2ZrH(Cl)$, was prepared as previously reported by Buchwald.[57] The acetylenes, alkenes and boranes are available from commercial sources (Wiley, Aldrich). The following reagents were prepared according to literature procedures: *B*-methoxy-9-BBN,[72] *B*-chlorothexylhexylborane,[73] *B*-chlorodiisoproxyborane, *B*-chloro-1,3,2-dioxaborinane,[74] *B*-chlorodicylcohexylborane.[75,76] Solvents used were ACS grade and were dried prior to use. Manipulation of borane reagents was done under nitrogen atmosphere by using hypodermic and double ended needles, and solids were handled in a glove bag.[77] 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 the 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. GC/MS was performed on a Finnigan 3000 GC/MS + 6110 MS data system. 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 an internal standard. All yields reported as isolated materials had purities greater than 95% based on ^{11}B, ^1H and ^{13}C NMR spectroscopy. Major impurities are attributed to residual solvents. Microanalysis was performed by Desert Analytics, Tuscon, AZ.

Preparation of Bis(cyclopentadienyl)-1-hexenylzirconium Chloride.[6] A 50-mL flask with a septum-covered side arm was equipped with a magnetic stirring bar and adapter. Schwartz's reagent, 20 mmol (5.16 g), was added and suspended in 15 mL of methylene chloride. The mixture was cooled to 0 °C and 22 mmol 1-hexyne (1.81 g, 2.50 mL) was slowly added, followed by additional 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 6.80 (dt, 1 H, J = 18 Hz), 6.22 (s, 10 H), 5.76 (d, 1 H, J = 18 Hz), 1.93 (q, 2 H), 1.32 (m, 4 H), 0.89 (t, 3 H).

Preparation of Dicyclopentadienyl-(E)-2-hexenylzirconium Chloride.[6] In the glassware above, 6.5 mmol (3% excess) of $Cp_2ZrH(Cl)$ (1.68 g)was 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 and gave a dark orange solution. For NMR purposes, the liquid was decanted from the excess Schwartz's reagent, 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-pentenylzirconium Chloride.[6] As stated above, 13.43 mmol (3% excess) of Schwartz's reagent (3.46 g) was reacted with 13.0 mmol of 4-methyl-2-pentyne (1.071 g, 1.5 mL). As previously done, the benzene was replaced with $CDCl_3$, for NMR purposes: ^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).

Preparation of Bis(cyclopentadienyl)-1-hexylzirconium chloride from 1-Hexene. In the glassware above, 1.05 equiv of 1-hexene to a mixture of Schwartz's reagent in methylene chloride, under a nitrogen atmosphere at room temperature. After stirring for 5 min, the insoluble zirconium hydride completely dissolved to yield a yellow homogenous solution: ^1H NMR (CH_2Cl_2) δ 6.30 ppm (10H), 0.85-1.75 ppm (13H); ^{13}C-NMR (CH_2Cl_2) δ 14.04, 22.80, 31.50, 33.97, 56.33, 112.53

General Procedure for the Transmetallation from Zirconium to Boron. The borane (5 mmol) was dissolved in 5 mL of methylene chloride. It was added to a 25-mL flask, with a septum-covered side arm, equipped with a magnetic stirring bar and adapter. The solution was cooled to 0 °C and a stoichiometric amount of the dicyclopentadienyl-1-hexenylzirconium chloride solution was added. The reaction forms an off-white precipitate, generally within 15-30 min. The extent of reaction can be estimated by using the ratio of peak areas

in the ^{11}B NMR. This method appears to give satisfactory results for boron containing species with similar peak widths. The comparison of this method with weighted mixtures of the pure authentic boron products agreed within ± 3%. This procedure has also been used to estimate the concentration of organolithiums by reacting with trialkoxyboranes and analyzing by ^{11}B NMR.[78] Nöth and Wrackmeyer have also reported using this method to determine ratios of boron products in equilibrium mixtures.[79] To distinguish between borane products that have similar chemical shifts, the reaction mixtures were analyzed both before and after methanolysis or complexation with a suitable base, such as pyridine. Table 2 summarizes the results of selected reactions. 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 x 5 mL of pentane, followed by removal of the pentane from the combined extracts, to yield pure product, as indicated by NMR.

Preparation of *(E)*-1-Hexenyldichloroborane.[80] The preparation was conducted as in the general procedure. The dicyclopentadienyl-1-hexenylzirconium chloride solution was added to boron trichloride in methylene chloride (5 mmol, 5 mL): ^{11}B NMR (CH_2Cl_2) δ +53.0 ppm, after methanolysis +27.4 ppm, >90% product ratio. In order to assign the stereochemistry of the vinyl group, the *(E)*-1-hexenyldichloroborane was isolated from the reaction mixture and converted into the corresponding methyl ester. This was analyzed by NMR spectroscopy for retention of the *trans* stereochemistry, as reported by Brown.[81] Spectroscopic data are in agreement with reported values, indicating retention of the 1-alkenyl group: ^1H NMR ($CDCl_3$) δ 6.52 (dt, 1 H, *J* = 18 Hz), 5.42 (d, 1 H, *J* = 18 Hz), 2.13 (m, 2 H), 1.30 (m, 4 H), 0.90 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 152.00, 50.89, 35.30, 30.57, 22.30, 13.97.

Preparation of *(E)*-1-Hexenyl-9-BBN.[82] Ten mmol of the dicyclopentadienyl-1-hexenylzirconium chloride solution was added to *B*-bromo-9-BBN in methylene chloride (10 mmol, 10 mL). To distinguish between starting material and the vinyl-9-BBN product, 5 mmol of pyridine was added, forming the borane amine complexes: ^{11}B NMR (CH_2Cl_2) δ -1.70 ppm, >90% ratio of boron containing materials. Isolation of the compound afforded 1.71 g or 84% yield of *(E)*-1-hexenyl-9-BBN. Spectroscopic data are in agreement with expected and reported values[82]: ^{11}B NMR ($CDCl_3$) δ 77.4; ^1H NMR ($CDCl_3$) δ 6.84 (dt, 1 H, *J* = 6.4, 17.5 Hz), 6.22 (d, 1 H, *J* = 17.3 Hz), 2.26 (q, 2 H, *J* = 6.9 Hz), 2.00 - 1.65 (m, 12 H), 1.60 - 1.15 (m, 6 H), 0.95 (t, 3 H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 156.38, 36.12, 34.08, 31.02, 28.87, 22.69, 14.0; IR (neat) 2927, 1635, 1613, 1468, 1447, 1381, 1333, 999, cm^{-1}; EI mass spectrum: *m/z* (relative intensity) 206 (M^+, 27), 148 (22), 147 (20), 134 (43), 133 (37), 120 (72), 119 (52), 108 (26), 106 (41), 105 (40), 93 (54), 92 (89).

Preparation of (Z)-4-methyl-2-pentenyl-1,3,2-dioxaborazole. As in the general procedure for transmetallation, 5 mmol of the dicyclopentadienyl-4-methyl-2-pentenylzirconium chloride solution was added to 5 mmol *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) δ +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 methanolyzed starting material. In a similar reaction, methanolysis was not done but the solids were separated from the supernate and were washed with 4 x 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. An oil resulted which was distilled using short path distillation to afford 4-methyl-2-pentenyl-1,3,2-dioxaborazole. Isolated yield: 1.006 g (68%) of 4-methyl-2-pentenyl-1,3,2-dioxaborazole, bp 85-90° (0.1 mmHg). Spectroscopic data are in agreement with expected values: ^1H 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 5,7-tetradecadiene.[68] 1-Bromo-1-hexyne was hydroborated at 0 °C with 1.0 M dibromoborane-methyl sulfide in methylene chloride (24 mmol, 24 mL). Dicyclopentadienyl-1-octenylzirconium chloride (25 mmol) was prepared by hydrozirconation as previously reported. The zirconocene complex was added at 0 °C to the dibromoalkenylborane and after 15 min an off-white precipitate appeared. Following removal of the precipitate, the dialkenylbromoborane was isolated by evaporation of the solvent under reduced pressure. The borane was then dissolved in 50 mL of THF, and 3.89 g (72 mmol) of sodium methoxide in 72 mL of methanol was added at -25 °C. The cold bath was removed after 5 min and stirring was continued for 1 h at room temperature. The solvents were removed under reduced pressure. The flask was fitted with a reflux condenser and the vinylborane was protonated using 25 mL of isobutyric acid under reflux conditions for 3 h. The reaction was cooled and added to 100 mL of water and extracted with diethyl ether (6 x 25 mL). The ether extract was washed with a saturated aqueous solution of sodium carbonate to remove isobutyric acid and then oxidized with 8.5 mL of 3 M NaOH and 8.5 mL of 30% H_2O_2 to remove boron containing materials. The aqueous layer was extracted again with diethyl ether and the combined ether layers were dried over magnesium sulfate. The solvent was removed at reduced pressure and the product was distilled to give 2.27 g (49%) of the *trans-trans*-5,7-tetradecadiene, bp 65-70 °C (0.5 mmHg). Spectroscopic data are in agreement with expected and reported values:[68] ^{1}H NMR ($CDCl_3$) δ 6.0 (d, 2 H, J = 14.6 Hz), 5.56 (dt, 2 H, J = 14.6 Hz), 2.05 (q, 4 H), 1.30 (m, 12 H), 0.89 (t, 6 H); IR (neat) 3015, 2959, 2928, 2857, 1626, 1467, 990, 906 cm^{-1}. EI mass spectrum: *m/z* (relative intensity) 194 (M^+, 16), 123 (15), 110 (46), 109 (29), 96 (38), 95 (62), 82 (71), 81 (100).

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