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Transmetalation of Organic Groups from Zirconacycles to Haloboranes: A New Route to Borolane Compounds

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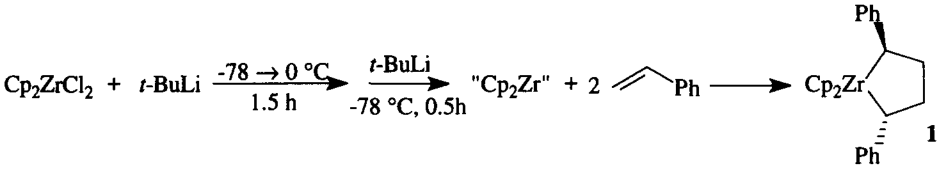
Abstract: *The reaction of styrene and "Cp_2Zr" forms the trans-2,5-diphenylzirconacycle. Transmetalation of this zirconacyle with an equivalent of boron trichloride forms the 1-chloro-trans-2,5-diphenylborolane with retention of stereochemistry. This B-chloroborolane is converted into other boranes and can be oxidized to the diol.* © 1997 Elsevier Science Ltd.

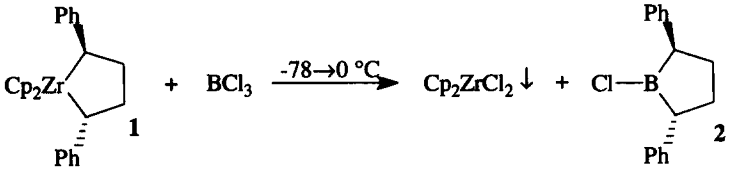
Organozirconium complexes have been developed into one of the most useful classes of organometallic reagents for use in organic synthesis.[1-3] Many of these complexes can readily be prepared in high regio- and stereoselectivity. Zirconium can activate unreactive unsaturated groups to undergo selective carbon-carbon bond forming reactions. Many of these reactions involve formation of a zirconacycle. These complexes are formed by the insertion of an alkene or alkyne into a zirconium complexed alkene, alkyne or arene. This is equivalent to the reaction of "Cp_2Zr" with enynes, diynes, or dienes yielding zirconacycles with new carbon-carbon bonds. The chemistry of these zirconium complexes has resulted in their established value in synthesis.[4-7] Unfortunately, there are relatively few reactions that can convert the organozirconium complex into the final product or other intermediates. This limitation was recognized by Schwartz, who explored transfer of organic groups from zirconium to other metals.[8] Transmetalation of organozirconocenes to aluminium, boron, copper, mercury, nickel, palladium, tin and zinc have been explored.[9] Transmetalation combines the best attributes of both metals, allowing conversions not possible using a single metal. We have been exploring the transfer of organic groups from zirconium to boron compounds.[10] The versatility of organoboranes, combined with the unique reactivity and selectivity of zirconacycles, dramatically expands the number and types of compounds that can be formed using either system alone. The alkenyl groups formed by hydrozirconation of alkynes represent a majority of the transferred groups. One of the few examples of a zirconacycle transmetalation was reported by Fagan.[11] A tetrasubstituted zirconacyclopentadiene transfered to a phenyldichloroborane to yield the borole, which rapidly dimerized with itself.

We chose the *trans*-2,5-diphenylzirconacyclopentane as our model system for the transmetalation of zirconacycles to boron. This complex is readily prepared by reacting two equivalents of styrene with "Cp_2Zr".[12,13] In contrast to alkyl substitutents, a phenyl group is preferentially placed α to the zirconium, although with slightly lower regioselectivity (90:10) than alkyl groups. The stereochemisty of the substitutents is predominantly trans (in the case of phenyl groups, $\geq 98\%$). The "Cp_2Zr" is prepared in situ using a modified

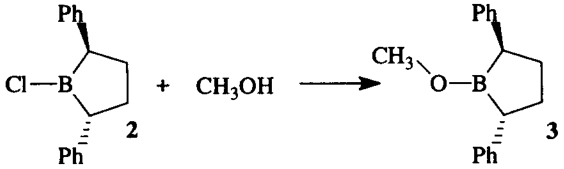
Negishi procedure, substituting toluene for Et_2O.[13] This is necessary since the ether forms a strong complex to BCl_3, which inhibits the transmetalation of the zirconacyclopentane to the haloborane. Cp_2ZrCl_2 (1.7 mmol) was alkylated with one equivalent of *tert*-butlyllithium at -78 °C for 0.5 h in toluene, then slowly warmed to room temperature over a period of 1 h for isomerization of the butyl group. The reaction mixture was again cooled to -78 °C and another equivalent of *tert*-butlyllithium was added. The reaction was stirred for an hour, followed by the addition of two equivalents of styrene. The mixture was stirred for 0.5 h before warming to 0 °C for 1 h. The formation of the metallocyclopentane, **1**, was confirmed by its protonation with two equivalents of hydrogen chloride in ether. Analysis by NMR and GC/MS showed 1,4-diphenylbutane as the major product (ca. 70%), and ca. 25% of the tert-butyl incorporated product, (3,3-dimethylbutyl)benzene. These results are in agreement with those reported by Negishi.[12]



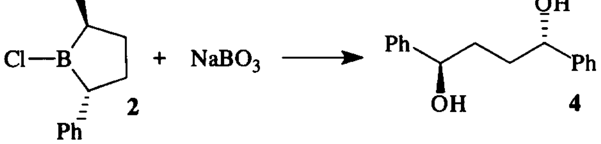
The reaction solution containing **1** was cooled to -78 °C, then rapidly transferred via large bore double-ended needle to one equivalent of boron trichloride in methylene chloride at -78 °C. The reaction mixture changed from a reddish-brown to a yellow color upon addition of the zirconium complex. The reaction mixture was stirred for 1 h at -78 °C before allowing it to warm to room temperature over a period of ca. 0.5 h. The ^{11}B NMR spectrum showed three principal signals. The largest (74%), observed at +77 ppm, corresponded to the expected *B*-chloroborolane product.[14] The other resonances seen at +86 (12%) and +60 ppm (15%), were consistent with R_3B and $RBCl_2$ type compounds, respectively.[15] The extent of conversion was very good, in excess of 85%, as measured by the ratio of boron species in the ^{11}B NMR spectrum. The yield of migration is in agreement with other zirconium to boron transmetalations.[16,17] In general, the purity of the formed organoboranes determined by the purity of the organozirconium complex. The reaction solution was decanted from the solid Cp_2ZrCl_2 and the volatiles were removed under reduced pressure. The ^{11}B NMR spectrum of the residual material showed a large, broad signal (89%) at +79 ppm. The boron spectrum showed two other small signals, R_3B at +86 (8%) and an almost complete loss of the $RBCl_2$ at +60 ppm. This species is a volatile alkyldichloroborane, probably containing a residual butyl group transferred from zirconium. The absence of significant amounts of a non-volatile $RBCl_2$ indicates that the second alkyl group migration for ring closure to the borolane is fast relative to the first group transfer. The ^1H and ^{13}C-NMR analysis of the reaction mixture gave values consistent with expected values for **2** and were in agreement with the data given by Reetz.[14,18] The trans stereochemistry of the diphenyl substitutents is consistent with the ^1H and NOESY spectra.



The boron chemical shifts of the trialkylboranes and dialkylchloroboranes are similar. To better distinguish between these boranes, one equivalent of lithium *tert*-butoxide in hexanes was added to the reaction mixture, converting the chloroborolane into the corresponding borinic ester. The boron NMR spectra showed the expected loss of signal at +79 ppm and the appearance of the borinic ester at +52.4 ppm (69%). In addition to the borinic ester, the trialkylborane remained unchanged at +86 ppm (ca. 12%) and small amounts of boronic ester (14%) and trialkoxyborane (5%) were formed. This suggests that a relatively small amount of trialkylborane formed along with the chloroborolane product. The boronic ester and trialkoxyborane are believed to be formed from entrained alkyldichloroborane and BCl_3 or by oxidation of the air-sensitive materials. More frequently, chloroboranes are converted to their corresponding esters by addition of methanol. The addition of excess methanol yielded the expected borinic ester, **3**, at +54.6 ppm (~57%), with smaller amounts of boronic and borate esters at +31.2 (~30%) and 18.0 ppm (~12%), respectively. Complete NMR analysis of this reaction mixture gave values consistent with expected values for compound **3**.[19] The amount of borinic ester did not change over a longer period of time (24 h) even with additional methanol, similar to results reported by Reetz.[14] In contrast, the boron-carbon bonds of the parent *B*-chloroborolane or *B*-phenylborolane were cleaved by alcohols.[20,21] Apparently, the 2,5-diphenyl substituted borolane is unreactive to alcohols and behaves like most organoboranes.



Oxidation of organozirconocenes gives the corresponding alcohols in modest yields. This is in part due to the competive protonation of the zirconium-carbon bonds along with their oxidation in the presence of protic oxidizing agents.[1] Perhaps the most widely recognized organoborane reaction is its stereoselective oxidation to the corresponding alcohol. Initial attempts of oxidizing **2** using the standard alkaline hydrogen peroxide gave unexpectedly very small amounts of the expected 1,4-diphenyl-1,4-butanediol, **4**. Recently, Kabalka, *et al.* reported difficulties in oxidizing benzylboranes, yielding instead the corresponding hydrocarbon.[22] Apparently the benzyl carbon-boron bond readily cleaves forming the relatively stable benzyl anion. They found that the milder oxidizing agent, sodium perborate, minimized the protonation of these benzylboranes. Oxidation with 3 equivalents of sodium perborate overnight, followed by saturation of the aqueous phase with sodium chloride and extraction using THF, gave the water soluble 1,4-diphenyl-1,4-butanediol, **4**, in a modest yield (~50-60%). Spectral analysis of this compound was consistent with the expected values of the diol product.[23]



Although the transmetalation of alkenyl and alkyl groups from organochlorozirconocenes has been demonstrated to have synthetic application, only a few examples have been reported for the zirconacycles. In the present study we report that the transfer of the *trans*-2,5-diphenylzirconacyclopentane to boron trichloride gives the *B*-chloroborolane in good yields. This transfer suggests that other zirconacycles may also behave similarly, giving a new route to these substituted borolane compounds.

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19. NMR assignments were based on HMQC, HMBC and COSY spectra. Compound **3**: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ= 7.20 (dd, *J*=7.5, 7.5, 4H), 7.10 (d, *J*=7.5Hz, 4H), 7.05 (d, *J*=7.5, 2H), 3.37 (s, 3H), 2.36 (dd, *J*= ~7, 9.2Hz, 2H), 2.29 (dd, *J*=9.2, 7.2 Hz, 2H), 1.71 (dd, *J*=9.75, ~7, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ= 144.13, 128.24, 128.05, 124.65, 50.21, 41.41 (b), 33.51.
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