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# Preparation and Selective Cleavage Reactions of Boron-Zirconium 1,1-Bimetalloalkanes

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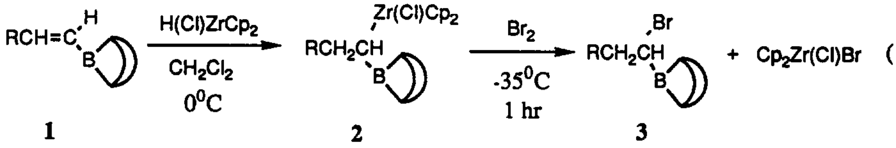
*Abstract: Hydrozirconation of various vinyl-9-BBN derivatives with Schwartz's reagent, H(Cl)ZrCp$_2$, provides 1,1-dimetalloalkanes of boron and zirconium. By selective cleavage of carbon-zirconium bond in these 1,1-dimetallics with bromine, a convenient method for preparation of α-bromoboranes was achieved.*

Hydrozirconation is one of the most promising organometallic techniques used in organic synthesis. Schwartz and co-workers have developed this reaction in a series of papers.[1-5] These organozirconium intermediates are useful for organic synthesis by utilizing the reactivity of zirconium-carbon bond with a variety of electrophilic reagents to give desired organic products.

Transition metal alkylidene complexes are undergoing active study for various applications toward organic synthesis.[6-12] 1,1-Dimetallic compounds containing zirconium as well as aluminium,[13-15] zinc[11,14] have been investigated for olefination with a ketone. We wish to report here the preparation and selective reaction of new substituted and highly functionalized zirconium and boron 1,1-dimetallic reagents. Unfortunately these 1,1-dimetallic reagents showed no olefination with a ketone under mild condition, even in the presence of zinc chloride. This may be due to the less active carbon-boron bond. The study of olefination of these reagents with a ketone is under investigation in the presence of other catalysts. But it was found that these reagents selectively react with bromine to afford α-bromoboranes which represent a useful class of boron intermediates for organic synthesis.[16]

In this study, we have now found that hydrozirconation of various B-alkenyl borabicyclo[3.3.1] nonanes[17] **1** (B-alkenyl-9-BBN) by Schwartz's reagent, H(Cl)ZrCp$_2$,[1-5,18] proceeds smoothly in dichloromethane, affording 1,1-bimetallics of boron and zirconium depicted as **2** (eq 1).



(1)

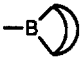
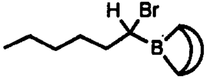
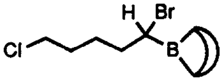
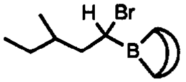
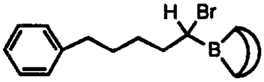
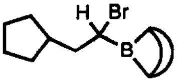
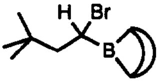
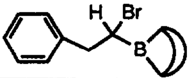
 = B-borabicyclo[3.3.1]nonyl

**Table I. Preparation of α-Bromoboranes 3 by Bromination of 1,1-bimetallic compounds 2.**

| Entry | R in Vinyl-9-BBN, 1 | Hydrozirconation Time, hr | Bromination Product, 3 | $^1$H NMR δ (ppm) of α-H(dd) | Yield$^a$ % |
|---|---|---|---|---|---|
| 1 | n-butyl | 1 |  | 4.13 | 97 |
| 2 | 3-chloropropyl | 1 |  | 4.08 | 99 |
| 3 | 1-methylpropyl | 1.5 |  | 4.10 | 95 |
| 4 | 3-phenylpropyl | 1.5 |  | 4.26 | 99 |
| 5 | cyclopentyl | 2 |  | 4.19 | 91 |
| 6 | t-butyl | 6 |  | 4.24 | 87 |
| 7 | phenyl | 6 |  | 4.27 | 83 |

$^a$ crude yields, percent based on vinyl -9-BBN

A solvent study showed that there was no hydrozirconation of alkenylboranes with Schwartz's reagent in both diethyl ether and hexanes. In benzene, the reaction was rather slow. Hydrozirconation, however, can be completed in dichloromethane and THF, and took 1 hr and 1.5 hrs respectively at 0 $^0$C for B-hexenyl-9-BBN. The study of solvent effect suggested that the electronic donor ability of a solvent favors the hydrozirconation process. This is different from the solvent effect observed in hydroboration where both diethyl ether and THF are suitable solvents.

We have also found that cyclic alkenylboronic esters, such as hexenyl-1,3,2-benzodioxaborole, ethylene glycol hexenylboronate and pinacol hexenylboronate, underwent partial hydrozirconation with one equivalent of Schwartz's reagent slowly. Alternatively, groups substituted on boron atom larger than 9-BBN also inhibited the rate of hydrozirconation. Thus diisopinocamphenyl hexenylborane and diisocaranyl hexenylborane were incompletely hydrozirconated at reduced rate. Obviously both electronic and steric factors greatly influence the course of hydrozirconation of B-alkenylboranes.

Addition of bromine in dichloromethane in situ at -35 °C resulted in the immediate discharge of color and yielded the slow formation of a white precipitate within 1 hr. The proton NMR of this isolated solid material is consistent with a zirconocene dihalide. After pumping of dichloromethane, extraction with hexanes from the reaction mixture provided the crude oily $\alpha$-bromoboranes[19] in high yields. The results are summarized in Table I. This reaction serves two purposes. It provides confirmation of the regioselectivity of the hydrozirconation step,[20] and secondly generates the useful $\alpha$-bromoboranes which can be converted into a multitude of organic products[16,21,22] conveniently.

In addition to these results, the hydrozirconation of B-(-3-methoxy-1-propenyl)-9-BBN was carried out. By comparison with B-hexenyl-9-BBN, the required time for hydrozirconation was shortened by half. This interesting result hints that the coordination of zirconium in Schwartz's reagent to electronegative atom , oxygen, in the alkenylboranes would speed up the hydrozirconation. Unfortunately the formed dimetallics and the product of bromination were complex. Further study is in progress.

In conclusion, we have prepared 1,1-bimetalloalkanes of zirconium and boron by hydrozirconation of alkenylboranes with Schwartz's reagent. A selective cleavage of carbon-zirconium bond in these 1,1-bimetallics provides a convenient method to obtain $\alpha$-bromoboranes. The further synthetic scope of these 1,1-bimetallic reagents is underway in our laboratories.

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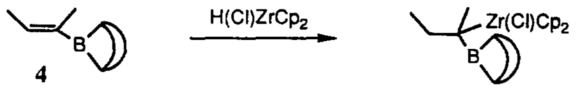
19. Typical procedure. **Preparation of B-(-1-bromohexyl)-9-borabicyclo[3.3.1]nonane:** All reactions and operations were under argon. To a stirred ice-cooled suspension of Schwartz's reagent (0.26g, 1mmol) in dry $CH_2Cl_2$ (1ml) was added a solution of B-hexenyl-9-BBN (0.20g, 1 mmol) in dry $CH_2Cl_2$ (1 ml).The cloudy suspension of the mixture became clear yellow solution in 1 hr at 0 $^0$C (or 10 min at ambient temperature). After cooling to -35 $^0$C, bromine (0.16g, 1mmol) in 1ml of $CH_2Cl_2$ was added dropwise. As the reaction mixture became colorless, a white precititate slowly formed. The resulting mixture was stirred 1 hr, and warmed to ambient temperature. After pumping off $CH_2Cl_2$, dry hexanes (2x2ml) was added, and the reaction mixture extracted. Filtration of this hexanes solution and evaporation of the solvent from the filtrate afforded the crude product, α-bromohexyl-9-BBN, as a clear colorless oil (0.27g, 97%). Organic products were identified by $^1$H NMR.

20. Zheng, B.; Srebnik, M. unpublished result. Schwartz and co-workers demonstrated that hydrozirconation of olefins proceeded to place the zirconium moiety at the sterically least hindered position of the olefin chain.[1] We found that hydrozirconation of disubstituted B-alkenyl-9-BBN, such



as 2-butenyl-9-BBN **4,** did not necessarily place zirconium moiety on the least hindered terminal carbon. Therefore this regioselectivity of hydrozirconation step was further proved.

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