

Addition of boranes to $(E)-(\eta^5-C_5H_5)_2Zr(CH=CHPh)Cl$

Research Article

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Abstract: In this study, the addition of boranes to $(E)-(\eta^5-C_5H_5)_2Zr(CH=CHPh)Cl$ (**3**) has been examined in order to investigate the regioselectivity of these 'hydroboration' reactions. We have found that these additions proceed with remarkable selectivity to give exclusive formation of a saturated organic molecule where one carbon atom has both the boron and the zirconium fragments. These reactions do not proceed via a conventional hydroboration reaction, but instead go through an initial transmetalation step to generate $(E)-(\eta^5-C_5H_5)_2Zr(H)Cl$ (**1**) and the corresponding alkenyl boron intermediate, whereupon subsequent hydrozirconation of this latter species gives the geminal products. An x-ray diffraction study has been conducted on $gem-(\eta^5-C_5H_5)_2Zr(CH(Bpin)CH_2Ph)Cl$ (pin = 1,2- $O_2C_2Me_4$) (**2**). Crystals of **2** were orthorhombic with $a = 18.545(3)$ Å, $b = 15.713(3)$ Å, $c = 16.157(3)$ Å in the space group *Pccn*. An x-ray diffraction study has also been conducted on the trinuclear zirconium oxide species $(\eta^5-C_5H_5)_2ZrO_2[ZrCl(\eta^5-C_5H_5)_2]_2$ (**4**). Crystals of **4** were orthorhombic with $a = 13.6000(8)$ Å, $b = 14.2252(8)$ Å, $c = 17.6500(10)$ Å in the space group *P2(1)2(1)2(1)*.

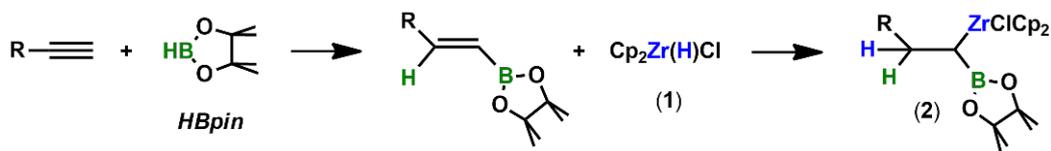
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1. Introduction

The ability to make organoboron compounds has had a tremendous impact in organic synthesis the past few decades, especially in light of the remarkable utility of the Suzuki-Miyaura cross-coupling reaction [1,2]. While several methodologies exist for the synthesis of organoboranes, one of the most elegant is the hydroboration reaction, which was developed by H.C. Brown in the late 1950's [3]. Hydroboration involves the addition of a B-H bond to an unsaturated organic molecule, usually an alkene or alkyne, and generates a new B-C bond, which can be subsequently transformed into a wide array of functional groups. Srebnik and

co-workers have found that hydroboration of an alkyne using pinacolborane (HBpin, pin = 1,2- $O_2C_2Me_4$) followed by hydrozirconation of the resulting alkenylboronate ester gave regioselective formation of the corresponding *gem*-borazirconocene alkanes (Scheme 1) [4-8]. Pinacolborate derivatives have been used in these studies as the resulting products are stable to air, water and chromatography. Hydrozirconation is the addition of a Zr-H bond to an unsaturated molecule, conventionally using Schwartz's reagent, $(\eta^5-C_5H_5)_2Zr(H)Cl$ (**1**) [9,10]. In essence, the methodology developed by Srebnik essentially generates saturated products that contain one carbon atom bearing both a boryl (BR_2) group and a zirconium fragment, both of which can be transformed

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Scheme 1. The regioselective formation of *gem*-borazirconocene alkanes.

independently into a wide variety of functional groups [4]. Our interest in designing new boranes [11,12] and catalyst systems for the hydroboration reaction [13] led us to investigate the reverse reaction, involving the addition of boranes to $(E)-(\eta^5-C_5H_5)_2Zr(CH=CHPh)Cl$ (**3**), to see if we could generate alternate products, the results of which are presented herein.

2. Experimental Procedure

2.1. General methods and materials

Reagents and solvents used were obtained from Aldrich Chemicals. $(E)-(\eta^5-C_5H_5)_2Zr(CH=CHPh)Cl$ [14], 4,4,5,5-tetraphenyl-1,3,2-dioxaborolane [11], 4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaborocine [12], dicyclohexylborane [15], dimesitylborane [16], $Rh(\eta^6\text{-catBcat})(dppb)$ [17], were all prepared by previously reported methods. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR spectrometer. 1H NMR chemical shifts are reported in ppm and are referenced to residual protons in deuterated solvent at 270 MHz. ^{11}B NMR chemical shifts are reported in ppm and are referenced to external $BF_3 \cdot OEt_2$ at 87 MHz. Microwave reactions were performed using a CEM Discover SP system in standard closed vessels with the reaction temperature monitored by an internal IR pyrometer.

2.2. Typical addition of a borane to $(E)-(\eta^5-C_5H_5)_2Zr(CH=CHPh)Cl$ (**3**)

To a stirred C_6D_6 (0.5 mL) solution of $(E)-(\eta^5-C_5H_5)_2Zr(CH=CHPh)Cl$ (50 mg, 0.15 mmol) was added a C_6D_6 (0.5 mL) solution of the appropriate borane (1 equivalent). Catalyzed reactions were conducted in a similar fashion except the catalyst (5 mol%) was added to the solution of $(E)-(\eta^5-C_5H_5)_2Zr(CH=CHPh)Cl$ and stirred for 30 minutes prior to addition of the borane. Reactions were allowed to proceed for 18 h at RT at which point the reaction was analyzed by multinuclear NMR spectroscopy.

2.3. X-ray crystallography

Crystals of **2** and **4** were grown from saturated solutions of benzene at RT. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer.

A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT) [18] and corrected for absorption (SADABS) [19]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL) [20]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model. Both of the cyclopentadienyl groups coordinated to the Zr3 atom are disordered into two positions. Restraints of SAME are applied to fix the geometry of the second part of these Cp groups. Each SAME command generates 10 restraints (5 for bond length and 5 for bond angle), so the total number of restraints is 20. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC 901259 (**2**) and 902373 (**4**)). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

3. Results and discussion

Compound $(E)-(\eta^5-C_5H_5)_2ZrCl(CH=CHPh)$ (**3**) is readily prepared in quantitative yield from the room temperature addition of $(\eta^5-C_5H_5)_2Zr(H)Cl$ (**1**) to $PhC\equiv CH$ [9,10]. Remarkably, we have found that addition of HBpin to **3** proceeded at room temperature over several hours (12–18 h) to give selective formation of *gem*- $Cp_2ZrCl(CH(Bpin)CH_2Ph)$ (**2**) as the only new boron-containing product. This result is unusual as elevated temperatures or catalytic amounts of transition metals are usually required to facilitate the addition of this sluggish borane to alkynes and alkenes, even to monosubstituted sterically unhindered alkynes and alkenes such as 1-octene [21]. Multinuclear NMR data for **2** are consistent with those reported previously [4–8]. A single crystal X-ray diffraction study was conducted to confirm the regioselectivity of this reaction, the molecular structure of **2** is shown in Fig. 1 and crystallographic data provided in Table 1. Bond distances and angles

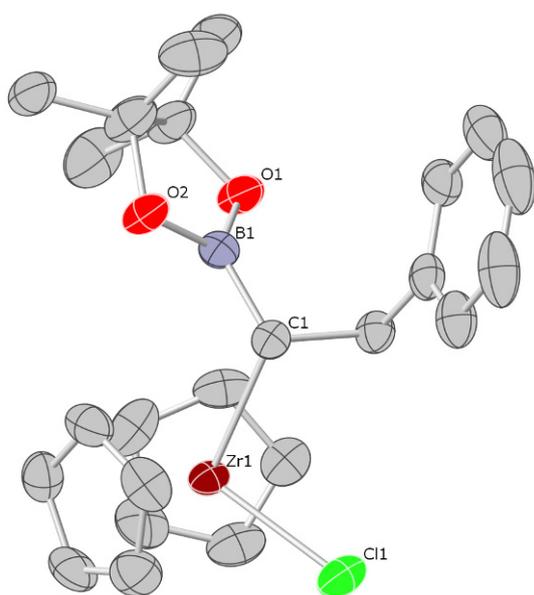


Figure 1. The molecular structure of **2** with ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å): Zr(1)-C(1) 2.306(4), Zr(1)-Cl(1) 2.4610(11), B(1)-O(2) 1.371(5), B(1)-O(1) 1.382(5), B(1)-C(1) 1.534(5). Selected bond angles (°): C(1)-Zr(1)-Cl(1) 97.42(9), O(2)-B(1)-O(1) 111.1(3), O(2)-B(1)-C(1) 126.6(4), O(1)-B(1)-C(1) 122.3(4), B(1)-C(1)-C(2) 111.2(3), B(1)-C(1)-Zr(1) 119.1(3).

are typical for analogous systems. Indeed, the Zr(1)-C(1) bond of 2.306(4) Å is close to those found in related systems, such as $\text{Cp}_2\text{Zr}[\eta^3\text{-CH}(\text{C}_6\text{H}_5)](\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_2$ [22]. The boron-oxygen bonds of B(1)-O(2) 1.371(5) Å and B(1)-O(1) 1.382(5) Å are well within the range of other Bpin species [23]. The sum of the angles around the boron atom is 360.0(4)°, signifying a three coordinate environment.

To gain a further understanding of the nature of this reaction, we investigated whether a transition metal complex could be used to catalyse this addition. Although reactions using 5 mol% $\text{RhCl}(\text{PPh}_3)_3$ [24] did not seem to improve reaction times significantly, it is interesting to note that compound **2** was only generated in 80% yield, as ascertained by ^1H NMR spectroscopy, along with minor amounts of $\text{PhCH}_2\text{CH}_2\text{Bpin}$ (10%) and decomposition product B_2pin_3 (10%). Attempts to use $\text{Rh}(\eta^6\text{-catBcat})(\text{dppb})$, an active and selective precatalyst for a wide range of substituted vinyl arenes [17], gave a number of boron compounds including $\text{PhCH}_2\text{CH}_2\text{Bpin}$, B_2pin_3 , and significant amounts (>50%) of the alkenyl borate (*E*)- $\text{PhCH}=\text{CHBpin}$. It is interesting to note that this catalyst system did not afford any of the desired addition product **2**, or its isomer. Other catalyst systems, however, such as $[\text{Ir}(\text{cod})\text{Cl}]_2/2$ dppb (cod = 1,5-cyclooctadiene, dppb = 1,4-bis(diphenylphosphino)butane) and $[\text{Cp}^*\text{IrCl}_2]_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), could be

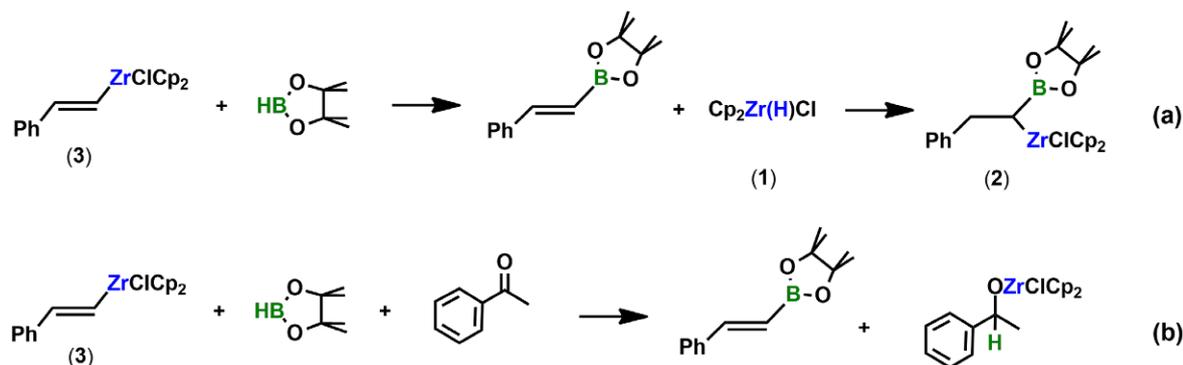
Table 1. Crystallographic data-collection parameters for **2** and **4**.

Complex	2	4
Formula	$\text{C}_{24}\text{H}_{30}\text{BClO}_2\text{Zr}$	$\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{O}_2\text{Zr}_3$
Molecular weight	487.96	563.47
Crystal system	Orthorhombic	Orthorhombic
Space group	Pccn	P2(1)2(1)2(1)
a/Å	18.545(3)	13.6000(8)
b/Å	15.713(3)	14.2252(8)
c/Å	16.157(3)	17.6500(10)
V/Å³	4708.0(15)	3414.6(3)
Z	8	6
$\rho_{\text{calc.}}/\text{Mg m}^{-3}$	1.377	1.644
Crystal size/mm³	0.55 × 0.20 × 0.17	0.29 × 0.28 × 0.23
Temp/K	198(1)	200(2)
Radiation	Mo-K α ($\lambda = 0.71073$ Å)	Mo-K α ($\lambda = 0.71073$ Å)
μ/mm^{-1}	0.597	1.086
Total reflections	30162	8253
Total unique reflections	5316	8043
No. of variables	266	478
θ Range/°	1.70 to 27.50	1.84 to 28.09
S (GoF) on F²	1.193	1.048
R1^a ($I > 2\sigma(I)$)	0.0477	0.0168
wR2^b (all data)	0.1384	0.0378

^a) $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b) $wR2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^4)])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0316 P)^2 + (5.487 P)]$ (2) and $1/[\sigma^2(F_o^2) + (0.0202 P)^2 + (5.375 P)]$ (4), where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

used to generate **2**, yet all reactions also gave various amounts of $\text{PhCH}_2\text{CH}_2\text{Bpin}$, (*E*)- $\text{PhCH}=\text{CHBpin}$, and B_2pin_3 .

The formation of alkenyl borate (*E*)- $\text{PhCH}=\text{CHBpin}$ is interesting as it suggests a competing pathway to the traditional hydroboration addition is occurring in these reactions. For instance, an initial transmetalation step with HBpin and **3** presumably generates (*E*)- $\text{PhCH}=\text{CHBpin}$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{H})\text{Cl}$ (**1**) (Scheme 2a). Transmetalation of boron reagents with main group compounds has been reported previously [25]. Once generated in solution, Schwartz's reagent **1** can then either react with the alkenyl borate, as shown by Srebnik and co-workers, to give **2**, or it can react with the active metal catalyst and decompose to generate dihydrogen. Hydrogenation of (*E*)- $\text{PhCH}=\text{CHBpin}$ would then afford the saturated species $\text{PhCH}_2\text{CH}_2\text{Bpin}$, which is also observed in solution. To confirm that transmetalation was occurring in these reactions, we then did a competition experiment by adding HBpin to **3** in the presence of acetophenone, as hydroborations of this ketone with



Scheme 2. A possible transmetalation/hydrozirconation pathway.

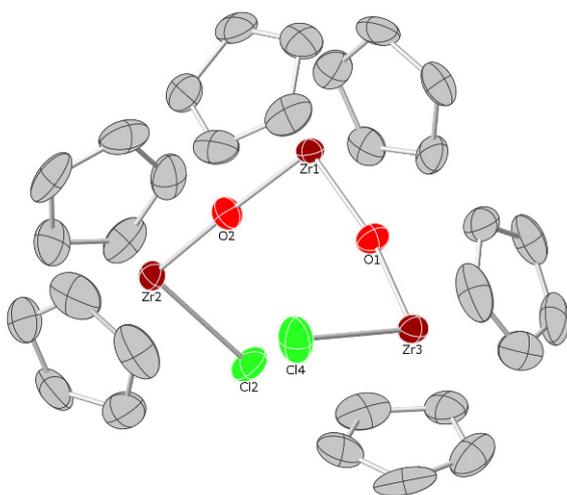
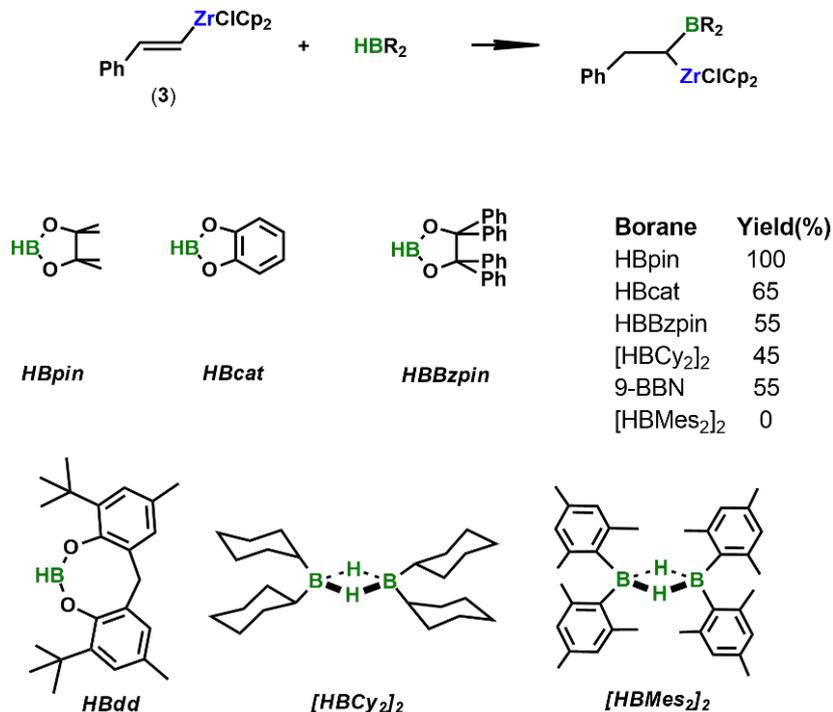


Figure 2. The molecular structure of **4** with ellipsoids drawn at the 50% probability level and hydrogen atoms and solvent benzene molecules omitted for clarity. Selected bond distances (Å): Zr(1)-O(1) 1.9747(11), Zr(1)-O(2) 1.9761(12), Zr(2)-O(2) 1.9259(12), Zr(2)-Cl(2) 2.4719(5), Zr(3)-O(1) 1.9285(11), Zr(3)-Cl(4) 2.4837(5). Selected bond angles (°): O(1)-Zr(1)-O(2) 101.48(5), O(2)-Zr(2)-Cl(2) 97.50(4), O(1)-Zr(3)-Cl(4) 95.26(4).

HBpin are remarkably slow and take up to 48 hours to reach completion. Conversely, hydrozirconations are facile and take place within minutes so if Schwartz' reagent **1** was being generated in these reactions, we would expect to see the corresponding alkenyl borate along with equimolar amounts of hydrozirconated ketone product. Indeed, reactions proceeded smoothly to give both products as observed by multinuclear NMR spectroscopy and GC-mass spectrometry. Aqueous workup of this reaction allowed for isolation of the alkenyl borate, which is stable to chromatography, and the generation of 1-phenylethanol. Interestingly, we were also able to examine the fate of one of the zirconium by-products upon aqueous workup and a single crystal X-ray diffraction study has been

carried out on the trinuclear zirconium oxide species (η⁵-C₅H₅)₂ZrO₂[ZrCl(η⁵-C₅H₅)₂]₂ (**4**). The molecular structure of **4** is shown in Fig. 2 and bond distances and angles are typical of other organozirconium oxide species [26-29]. The two zirconium atoms with the terminal chloride ligands have somewhat shorter metal oxygen bonds of Zr(2)-O(2) 1.9259(12) Å and Zr(3)-O(1) 1.9285(11) Å than the central zirconium atom without a chloride ligand, Zr(1)-O(1) 1.9747(11) Å and Zr(1)-O(2) 1.9761(12) Å. Slight differences in the chloride ligand distances are also observed with Zr(2)-Cl(2) 2.4719(5) Å and Zr(3)-Cl(4) 2.4837(5) Å, presumably arising due to packing effects in the solid state. Similar disparities are common in oxo zirconium clusters, as seen in the unusual cyclooctatetraene species [Zr₄(μ-O)₄(μ-Cl)₂(C₈H₈)]²⁻ [28].

Reactions of **3** with a wide variety of different boranes (with various steric and electronic requirements such as 9-borobicyclo[3.3.1]nonane, dimesitylborane, catecholborane, dicyclohexylborane, bulky dialkoxyboranes 4,4,5,5-tetraphenyl-1,3,2-dioxaborolane [11] and 4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaborocine [12], etc) were investigated and *all* proceeded to give the corresponding products derived from initial transmetalation (Table 2). Hydrozirconation of the bulkier alkenyl boron species, not surprisingly, proved increasingly difficult and less of the reduced products were observed in solution. Indeed, no reaction was observed at room temperature or in the presence of a catalyst upon addition of the bulky diarylborane [HBMes₂]₂ to **3**. Although reduction of the alkene was observed under microwave irradiation, product distributions were complicated by degradation and redistribution of the starting borane. This present zirconium transmetalation route therefore provides an alternate method of generating these alkenylboron compounds, the selective synthesis of which is currently an area of considerable interest [30].

Table 2. Addition of boranes to **3**. (E) - $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}=\text{CHPh})\text{Cl}$ + 1 equiv. borane in C_6D_6 , 18 h, RT. Yields determined by integration of ^1H NMR spectroscopy data.

4. Conclusions

We have examined the addition of a variety of boranes (HBR_2), containing various steric and electronic properties, to the sterically-encumbered alkene (E)- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}=\text{CHPh})\text{Cl}$ (**3**). Hydroboration of these metal-containing substrates does not seem to occur as reactions proceed at room temperature *via* a transmetalation pathway to give the corresponding alkenyl boron species [$(E)\text{-PhCH}=\text{CHBR}_2$] along with one equivalent of Schwartz's reagent $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{H})\text{Cl}$ (**1**). A subsequent hydrozirconation reaction occurs with the less hindered alkenyl boranes. The presence of an active rhodium or iridium catalyst can facilitate the degradation of **1** and inhibit this second hydrozirconation step. Further studies are underway to generate and

isolate a number of synthetically useful alkenyl borate species that are difficult to obtain using conventional methods, the results of which will be published in due course.

Acknowledgements

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