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Ruthenium Catalyzed Hydroboration of Terminal Alkynes to *Z*-Vinylboronates

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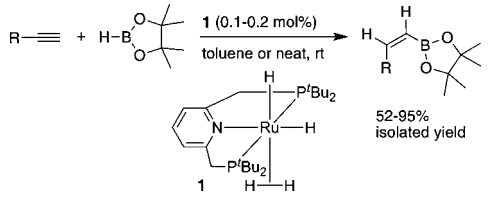
Supporting Information

ABSTRACT: The nonclassical ruthenium hydride pincer complex $[Ru(PNP)(H)_2(H_2)]$ **1** (PNP = 1,3-bis(di-*tert*-butyl-phosphinomethyl)pyridine) catalyzes the *anti*-Markovnikov addition of pinacolborane to terminal alkynes yielding *Z*-vinylboronates at mild conditions. The complex $[Ru(PNP)(H)_2(HBpin)]$ **2** (HBpin = pinacolborane), which was identified at the end of the reaction and prepared independently, is proposed as the direct precursor to the catalytic cycle involving rearrangement of coordinated alkyne to *Z*-vinylidene as a key step for the apparent *trans*-hydroboration.

Organoboron compounds are versatile building blocks in organic synthesis.[1] Among them, vinylboron reagents are finding wide application as stable vinyl anionic or cationic synthons,[2] as Michael donors,[3] in aldol reactions,[4] and in various coupling reactions. Several methods for the synthesis of vinylboron compounds have been developed.[5−8] Hydroboration of terminal alkynes is a straightforward method for the synthesis of vinylboranes, resulting in *E*-vinylboronates as the main product via *anti*-Markovnikov and *syn*-addition of the boron reagents.[5,6,9] Dehydrogenative borylation of alkenes also provides *E*-vinylboranes as the major products.[10] The synthesis of *Z*-vinylboron compounds is currently not possible by direct borylation but requires an elaborate two-step method.[11] Thus, while direct hydroboration of alkynes provides efficient access to vinylboron compounds, regio- and stereoselective control for *Z*-vinylboronates remains a challenge.[12]

In the present paper we describe the synthesis of *Z*-vinylboronates via a chemo-, regio-, and stereoselective borylation of terminal alkynes with pinacolborane catalyzed by the nonclassical ruthenium hydride pincer complex $[RuH_2(H_2)(PNP)]$ **1** (Scheme 1).[13] This selective hydroboration reaction proceeds for a broad scope of substrates under mild conditions. *Z*-Vinylboronate products are obtained in high yields and with high turnover numbers up to 970. X-ray diffraction data and NMR spectroscopy together with deuterium labeling studies suggest initial formation of a ruthenium borane complex and rearrangement of coordinated alkyne to vinylidene as key steps in the catalytic cycle.

Scheme 1. *Z*-Selective Borylation of Terminal Alkynes with Pinacolborane (HBpin) Using Catalyst 1



Complex **1** confines the structural motifs of a tridentate pincer ligand[14] at ruthenium with two classical hydrides and a nonclassical hydrogen ligand.[15] It is readily synthesized by hydrogenation of commercially available $[Ru(cod)(metallyl)_2]$ in the presence of the pincer ligand.[13] It has been shown to catalyze the H/D exchange of aromatic compounds[16] and the hydrogenation of nitriles to primary amines.[17]

When complex **1** (0.1 mol %) was dissolved in cold pinacolborane (3 mmol, −15 °C), the colorless solution turned yellow with concomitant gas evolution. Upon dropwise addition of phenylacetylene (2.5 mmol) to this solution at rt, the color turned reddish-brown immediately and an exothermic reaction was observed. After the reaction mixture was stirred for 24 h, GC analysis showed 99% conversion of alkyne and 96% selectivity to the *Z*-vinylboronate, which subsequently was isolated by column chromatography in 92% yield (Table 1, entry 1). Similar results were obtained when the reaction was performed in 3 mL of benzene or toluene for better temperature control. Reactions between phenylacetylene (1 mmol) and pinacolborane (1.5 mmol) without complex **1** under similar reaction conditions provided only 5% conversion after 24 h and exclusive formation of *E*-vinylboronate, confirming the efficient formation of the *Z*-vinylboronate to be the result of a metal complex catalyzed pathway.

Various terminal alkynes were subjected to the hydroboration reactions to explore the scope of the nonclassical ruthenium hydride complex **1** for the selective synthesis of *Z*-vinylboronates, and the results are summarized in Table 1. Quantitative conversion and high selectivities were observed consistently, providing excellent isolated yields above 80% for a wide variety of electronically and sterically different substituents at the triple bond (Table 1, entries 1−6, 9−11). Oxygen and nitrogen functionalities adjacent to the reactive sites were also tolerated (Table 1, entries 7−8).

The hydroboration reactions catalyzed by complex **1** are chemoselective for terminal alkynes. Terminal alkenes and internal[18] alkynes did not react. In an equimolar mixture of phenylacetylene and styrene, only the alkyne was converted to

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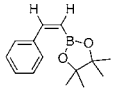
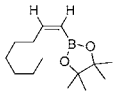
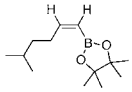
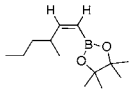
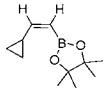
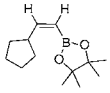
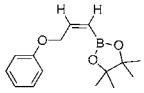
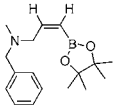
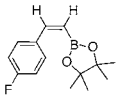
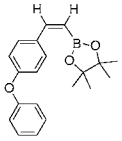
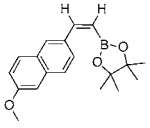
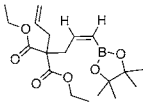
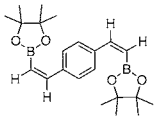
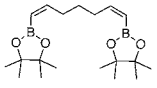
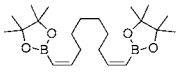
Table 1. Hydroboration of Terminal Alkynes Catalyzed by 1[a]

Entry	Z-vinylboranes	1 mol%	Selectivity[b]	Isolated Yield (%)[c]
1[d]		0.1	96	92
2[d]		0.1	97	89
3[d]		0.1	96	84
4		0.1	93	91
5		0.1	95	92
6		0.2	97	95
7[e]		0.2	95	67
8		0.2	98	68
9		0.2	90	82
10[f]		0.2	89	85
11		0.2	90	92
12[g]		0.2	66	52
13		0.2	89	85
14		0.2	93	82
15		0.2	87	86

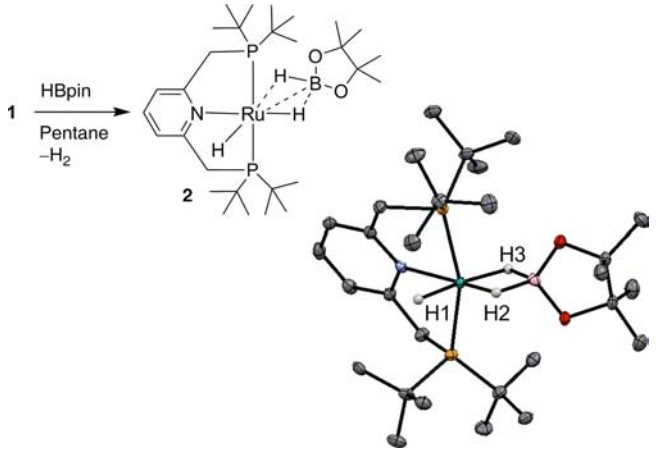
[a]Conditions: To a cold solution (−15 °C) of complex **1** and pinacolborane (3 mmol), in 3 mL of toluene, 2.5 mmol of precooled alkyne (1.25 mmol in cases of dialkyne) was added dropwise and the reaction mixture was stirred at rt for 24 h. [b]Selectivity for the *Z*-isomer based on GC analysis of crude reaction mixture; regioisomers are the main side products. [c]Isolated yields after column chromatography, based on alkynes. [d]Reactions carried out under neat conditions. [e]Conversion of alkyne is only 72%. [f]Reaction completed in 12 h. [g]*E*-Vinylboronates formed in 32%.

Z-vinylboronates according to GC and NMR analysis of the crude reaction mixture (85% isolated yields).[19] When 2-allyl-2-propargyl diethylmalonate was subjected to the hydroboration reaction, the reaction took place at the terminal alkyne functionality exclusively (Table 1, entry 12).[20] However, the *Z*/*E*-ratio of the reaction was significantly lower (*Z*/*E*, 66:32) than that for other substrates.

The hydroboration could also be carried out successfully on terminal dialkynes. Complete conversion of the C−C triple bonds was observed (GC), and very high *Z*-selectivities for the bis-vinylboronates were obtained in all reactions (Table 1, entries 13−15). When 1,4-diethynylbenzene was reacted with pinacolborane in the presence of **1**, the known styryl-bis-boronate, which was prepared earlier in 22% yield in two steps,[11a] was obtained directly in 85% isolated yields (Table 1, entry 13) with excellent stereocontrol (89% *Z*-selectivity; GC).[21] Similarly, 1,6-heptadiyne and 1,9-decadiyne gave the bis-boronate derivatives in very good isolated yields (Table 1, entries 14, 15).

Complex **1** reacts under pinacolborane with concomitant evolution of gas to complex **2** that was obtained in 96% yield in pentane (Scheme 2). Crystals of **2** suitable for single crystal X-ray diffraction studies could be obtained from toluene. The unit cell contains two independent molecules, which could be fully refined and show only minor structural differences.[22] The ruthenium atom occupies the center of a distorted octahedron.

Scheme 2. Synthesis and Single Crystal X-ray Structure of [Ru(PNP)(H){(μ-H)2Bpin}] 2[a]



[a]Selected bond lengths (Å) and angles (deg); values from DFT calculations in parentheses: Ru−H1 1.620 (1.619), Ru−H2 1.521 (1.623), Ru−H3 1.625 (1.781), Ru−B 2.125 (2.128), B−H2 1.458 (1.508), B−H3 1.403 (1.415); H1−Ru−H2 90.2 (82.3), H2−Ru−B 43.3 (44.9), H3−Ru−B 41.3 (41.3).

The PNP pincer ligand adopts a regular *mer*-coordination with two phosphines in axial positions and the pyridyl N at one of

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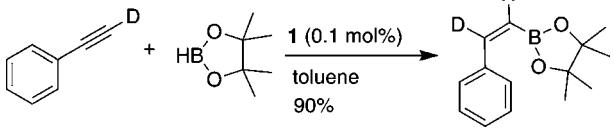
the four coordination sites in the equatorial plane. Electron densities consistent with three hydride ligands were located at the remaining sites. One is situated in a terminal position, whereas the other two are bridging to the boron center, resulting in a Ru−B distance of 2.125 Å.[15c,23]

DFT calculations on the molecular structure of **2** (B97-D/def2-TZVP(ECP); Scheme 2) are fully in line with the experimentally derived structure, supporting that the free refinement of the hydrogen centers reflects correct positions.[22] The calculated structure implies that the formulation as a ruthenium dihydride complex with a σ-bonded B−H group may also contribute to the overall bonding pattern. The structure of **2** as shown in Scheme 2 is also corroborated spectroscopically in solution. The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at 95.7 ppm, which is shifted downfield by 14 ppm relative to **1**.[13] In the ^1H NMR of **2** two broad singlets appeared at −11.72 and −5.02 ppm, attributed to the two bridging hydrides and one terminal hydride, respectively.[24]

NMR spectroscopic investigation of the reaction mixture revealed the presence of **2** as the only P-containing species after catalysis. Furthermore, when **2** (0.1 mol %) was used as the catalyst for the reaction of pinacolborane with phenylacetylene under standard conditions, the corresponding *Z*-vinylboronate was obtained in 93% (87% isolated) yield. These results indicate that **2** acts as the actual entry point into the catalytic cycle of the *Z*-selective hydroboration of terminal alkynes.[22]

Subjecting 1-deuterio-2-phenylacetylene and pinacolborane to the catalytic reaction lead to exclusive formation of the *Z*-vinylboronate with deuterium at the internal carbon (Scheme 3). The proton signal at a chemical shift of 7.2 ppm was absent

Scheme 3. Reaction with Deuterium Labeled Terminal Alkyne

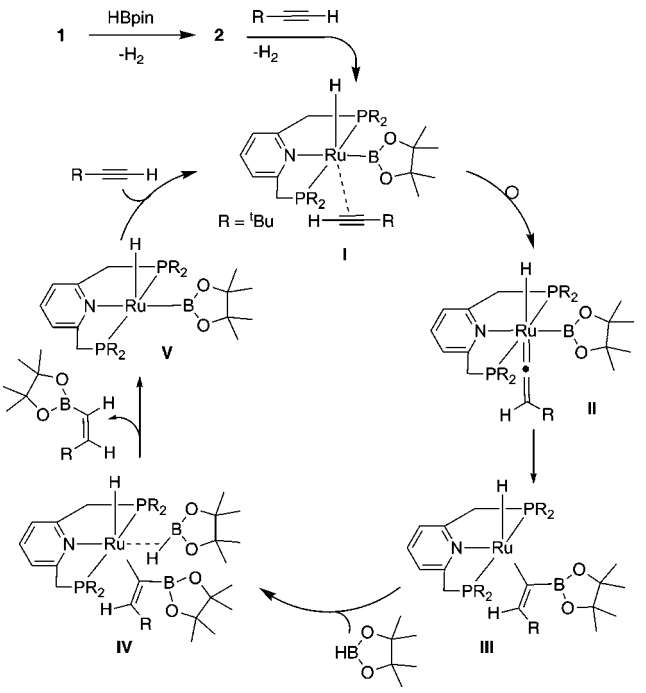


in the ^1H NMR spectrum while the ^{31}C NMR spectrum displayed a 1:1:1 triplet at 147.9 ppm (J_{DC} = 23.4 Hz) confirming the position of deuterium at the phenyl-substituted vinylic carbon (PhCD═).

On the basis of these data a catalytic cycle for the *Z*-selective hydroboration of terminal alkynes with pinacolborane is postulated (Scheme 4). The reaction of **1** with pinacolborane leads to the immediate formation of the ruthenium−borane complex **2**. This can undergo a σ-bond metathesis-type rearrangement to a ruthenium hydride with a covalent Ru−B bond and a nonclassically bonded dihydrogen molecule. The H_2 ligand is replaced with the alkyne to generate complex **I**. The η^2-coordinated terminal alkyne in **I** reacts under 1,2-hydrogen migration[25] to the η^1-vinylidene intermediate **II**. Coupling of the vinylidene and pinacolborate ligands generates the C−B bond in complex **III**. Coordination of pinacolborane in **IV** followed by σ-bond metathesis liberates the vinylboronate product and regenerates **V** to close the catalytic cycle.

The mechanism shown in Scheme 4 provides a rationale for the experimental observation that the apparent *trans*-addition of the borane results in fact from a 1,2-hydrogen shift at the alkyne and a geminal addition of the boron and hydrogen centers of the pinacol borane reagent. It also explains the very high

Scheme 4. Proposed Mechanism for *Z*-Selective *trans*-Hydroboration of Terminal Alkynes



chemoselectivity for the hydroboration of terminal alkynes with this system. The *Z*-stereochemistry in the product is determined in the reaction sequence from **I** to **III**, presumably reflecting steric interactions in the formation of complex **II**.

In conclusion, the ruthenium pincer complex **1** bearing a nonclassical hydride and its borane analog **2** catalyze the hydroboration of terminal alkynes to give selectively *Z*-vinylboronates in high yields under mild conditions. Mechanistic studies suggest a 1,2-hydrogen shift from an η^2-alkyne to a vinylidene complex as a key step prior to the C−B bond formation. Further work to elucidate the scope of this principle and the details of the stereochemical discrimination is currently underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral and X-ray data for intermediate complex **2**, and NMR data of *Z*-vinylboronates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) To the best of our knowledge, selective synthesis of *Z*-vinylboronates is limited to only one report and based on rhodium in the presence of excess phosphine ligands and a stoichiometrically excess amount of base. Ohmura, T.; Yamamoto, Y.; Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990−4991. Reaction with diynes and triynes under similar conditions gave predominantly *E*-vinylboronates. Lee, T.; Baik, C.; Jung, I,; Song, K. H.; Kim, S.; Kim, D.; Kang, S. O.; Ko, J. *Organometallics* **2004**, *23*, 4569−4575.

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