

Ruthenium Catalyzed Hydroboration of Terminal Alkynes to Z-Vinylboronates

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S Supporting Information

ABSTRACT: The nonclassical ruthenium hydride pincer complex $[\text{Ru}(\text{PNP})(\text{H})_2(\text{H}_2)]$ **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 $[\text{Ru}(\text{PNP})(\text{H})_2(\text{HBpin})]$ **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 $[\text{RuH}_2(\text{H}_2)(\text{PNP})]$ **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.

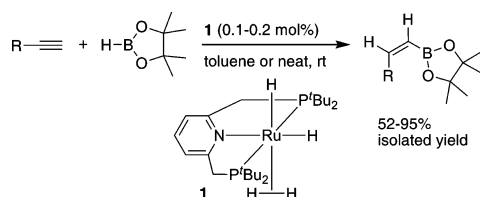
Complex **1** confines the structural motifs of a tridentate pincer ligand¹⁴ at ruthenium with two classical hydrides and a nonclassical hydrogen ligand.¹⁵ It is readily synthesized by hydrogenation of commercially available $[\text{Ru}(\text{cod})(\text{metallyl})_2]$ in the presence of the pincer ligand.¹³ It has been shown to catalyze the H/D exchange of aromatic compounds¹⁶ 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 internal¹⁸ alkynes did not react. In an equimolar mixture of phenylacetylene and styrene, only the alkyne was converted to

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



Received: July 27, 2012

Published: August 22, 2012

Table 1. Hydroboration of Terminal Alkynes Catalyzed by **1**^a

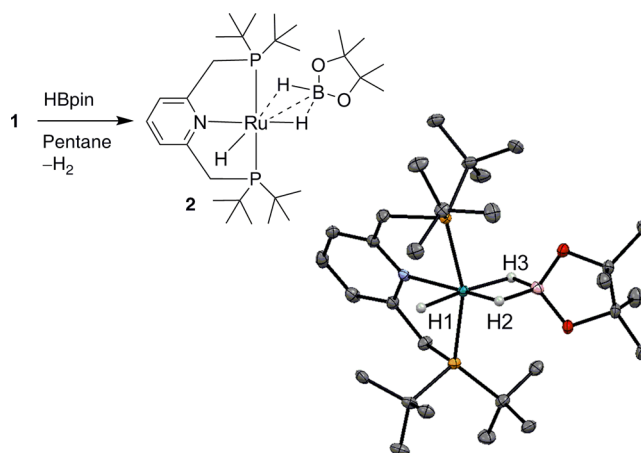
Entry	Z-vinylboranes	1 mol%	Selec- tivity ^b	Isolated Yield (%) ^c	Entry	Z-vinylboranes	1 mol%	Selec- tivity ^b	Isolated Yield (%) ^c
1 ^d		0.1	96	92	9		0.2	90	82
2 ^d		0.1	97	89	10 ^f		0.2	89	85
3 ^d		0.1	96	84	11		0.2	90	92
4		0.1	93	91	12 ^g		0.2	66	52
5		0.1	95	92	13		0.2	89	85
6		0.2	97	95	14		0.2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

^aConditions: 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. ^bSelectivity for the Z-isomer based on GC analysis of crude reaction mixture; regioisomers are the main side products. ^cIsolated yields after column chromatography, based on alkynes. ^dReactions carried out under neat conditions. ^eConversion of alkyne is only 72%. ^fReaction completed in 12 h. ^gE-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

^aSelected 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

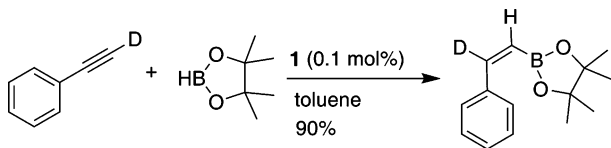
the four coordination sites in the equatorial plane. Electron densities consistent with three hydride ligands were located at the remaining sites. One is situated in a terminal position, whereas the other two are bridging to the boron center, resulting in a Ru–B distance of 2.125 Å.^{15c,23}

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 ³¹P {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

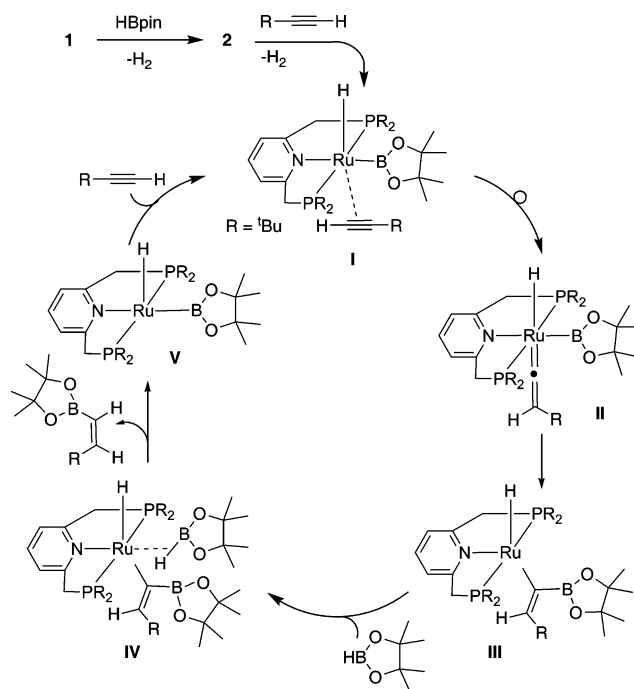


in the ¹H NMR spectrum while the ³¹C NMR spectrum displayed a 1:1:1 triplet at 147.9 ppm (*J*_{DC} = 23.4 Hz) confirming the position of deuterium at the phenyl-substituted vinylic carbon (PhCD=).

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 H₂ ligand is replaced with the alkyne to generate complex **I**. The η^2 -coordinated terminal alkyne in **I** reacts under 1,2-hydrogen migration²⁵ 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.

■ ACKNOWLEDGMENTS

C.G. is grateful to the AvH Foundation for the award of a Humboldt Research Fellowship. We thank J. Wurlitzer and H. Eschmann for the GC measurements and Prof. U. Englert for X-ray diffraction studies.

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