

Stereospecific palladium-catalyzed borylation reaction of 1-alkenyl halides with diisopropylaminoborane

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Received 13 September 2004; revised 11 January 2005; accepted 11 January 2005

Available online 23 May 2005

Abstract

The palladium-catalyzed borylation reaction of 1-alkenyl halides with diisopropylaminoborane leads efficiently and stereospecifically to the corresponding *trans*-1-alkenyl(diisopropylamino)boranes in good yields.

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Keywords: Palladium; Borylation; Alkenes; Aminoboranes

1. Introduction

1-Alkenylboron derivatives have attracted considerable attention as versatile intermediates in synthetic organic chemistry [1–4]. They are involved in the synthesis of many natural products, bioactive compounds, and are often the milestone for novel π -conjugated organic photoactive materials and electronic devices [5].

These compounds have been mainly prepared by using the well-known alkyne hydroboration reaction [2] or by transmetalation of 1-alkenylmetal reagents by organoboranes [3]. Although efficient, these methods suffered from severe restrictions. Indeed (1) the transmetalation protocols require preliminary laborious peripheral functions protection steps, (2) hydroboration of internal alkynes takes place in number of cases only regioselectively [4] and (3) terminal alkynes often afford undesired *gem*-dihydroboration side-products [6]. The most recent syntheses of vinylboron derivatives by catalytic borylation either with pinacolborane (PinBH), catecholborane (CatBH) or bis(pinacolato)diboron

(Pin₂B₂) in the presence of alkenes [7], alkynes [8] or 1-alkenyl electrophiles [9] exclusively afford pinacol or catechol 1-alkenyl boronates (Fig. 1).

However, 1-alkenylboron compounds including in their framework a B_{sp²}–H moiety have to the best of our knowledge never been isolated nor spectroscopically characterized. They are only known as intermediates *in situ* generated by hydroboration reaction of alkynes with thexylborane [10] and monochloroborane [11], respectively (Fig. 1). In this paper, we wish to report an unprecedented one-step procedure synthesis of B_{sp²}–H containing 1-alkenyl boron derivatives as stable and isolable species.

2. Results and discussion

Recently, we demonstrated the excellent ability of monomeric aminoboranes to react as BH sources for C_{sp²}–B_{sp²} bond formation in a metal-catalyzed process [12]. For our purpose, we naturally envisaged applying our palladium-catalyzed borylation reaction to 1-alkenyl halides.

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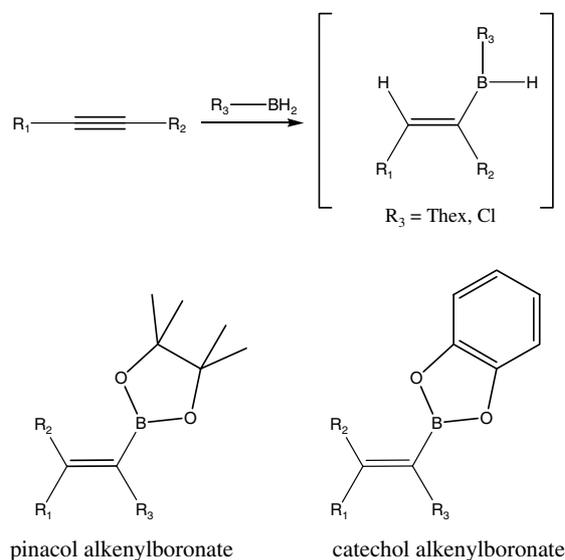


Fig. 1. Vinylboron derivatives.

The reaction was conducted in dioxane at 80 °C for 15 h, in the presence of a catalytic amount (5 mol%) of $(Ph_3P)_2PdCl_2$, triethylamine (5 eq.) as the base, diisopropylaminoborane (iPr_2N-BH_2 , 2 eq.) and 1-alkenyl halides (1 eq.) **1a–f** [13]. In all cases, the ^{11}B NMR spectroscopy revealed for isolated **2** a large singlet-like signal ($68 < \nu_{1/2} < 90$ Hz) contrarily to aryl(diisopropylamino)boranes [14], in a range of 34–37 ppm which is in agreement with the presence of the $iPr_2NB(H)-C_{sp^2}$ moiety. Notwithstanding the non-observable $^1J_{BH}$, the presence of the B–H bond in **2** was surprisingly confirmed by 1H NMR spectroscopy. The vinylic proton of the CH group adjacent to the boron atom exhibited an unexpected well-resolved doublet of doublet pattern for **2a** and **2d** and a doublet in the case of **2d**. The hypothesis of a through the boron $^3J_{HH}$ -coupling was then investigated by homonuclear decoupling experiments in the case of **2a** and **2b**. When irradiating in the zone corresponding to the more shielded but barely visible BH signal at 4.72 ppm (1416.6 Hz/300 MHz), the initially observed vinylic doublet of doublet collapsed to a doublet revealing a vinylic *trans*-coupling constant of 17.40 Hz in both cases (Fig. 2) [15]. Compounds **2** were obtained in medium to high yields (Table 1) and their spectroscopic data are fully in agreement with the proposed structures [16]. These features clearly indicates that whatever the stereochemistry of the starting styryl halide, the borylation reaction leads stereospecifically to the corresponding *trans*-styryl(diisopropylamino)boranes. These results are fully in accordance with Masuda's observations for the coupling of *cis*-1-iodo-3,3-dimethyl-but-1-ene with pinacolborane [9a].

trans Adducts **2** derive from the corresponding σ -vinylpalladium(II) intermediates resulting from the

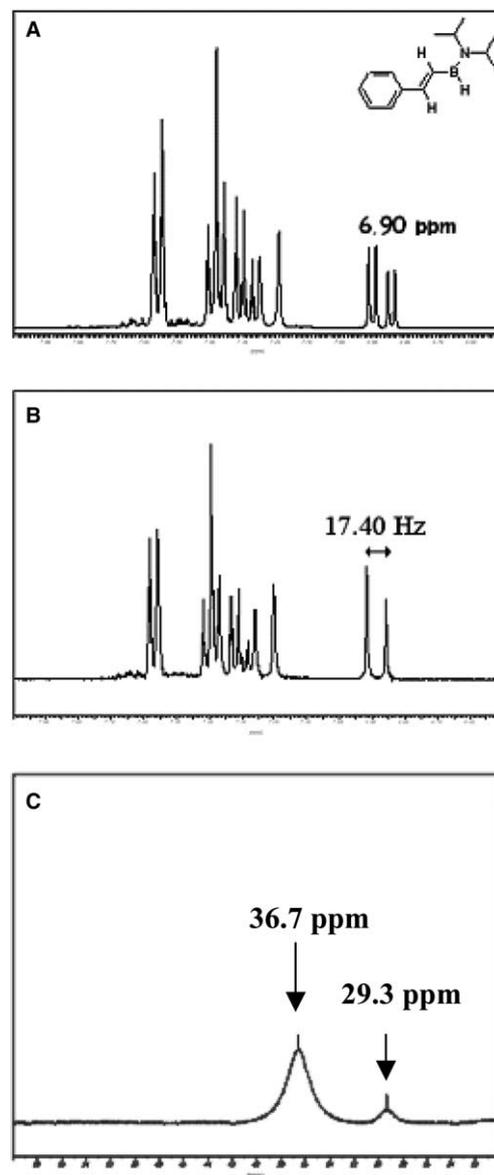
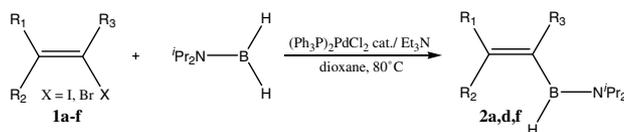


Fig. 2. Homodecoupling experiment: aromatic and vinylic protons zone of **2a** before (A) and after (B) irradiation. $^{11}B\{^1H\}$ NMR spectrum^a of **2a** (C). ^a**2a** is contaminated by traces of $[iPr_2NB(H)]_2O$ giving a more shielded signal at 29.3 ppm.

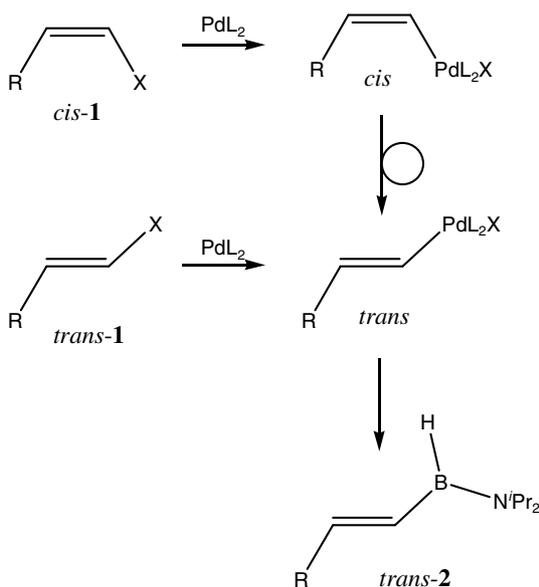
prior attack of the zerovalent palladium to the halogen substituted carbon of the 1-alkenyl halides in the oxidative addition step of the catalytic cycle [17]. The formation in all cases of *trans* adducts **2** would be dependent of this elementary step which generally takes place with retention of stereochemistry in the case of palladium, platinum or cobalt [18]. Now, *cis*- σ -vinylpalladium(II) complexes have been also reported to isomerize easily to the corresponding thermodynamically favoured *trans*- σ -vinylpalladium(II) specie [19]. Assuming the subsequent boron transfer step takes place as well with retention of stereochemistry, the hypothesis of the *cis* to *trans*-isomerization of the σ -vinylpalladium(II) intermediate vinylic bond under the reaction conditions

Table 1
Synthesis of 1-alkenyl(diisopropylamino)hydridoboranes



1	R ₁	R ₂	R ₃	X	Yield ^a (%)	δ ¹¹ B/ppm (CDCl ₃)
1a	Ph	H	H	I	2a : 33	36.7 (ν _{1/2} = 88 Hz)
1b	Ph	H	H	Br	2a : 94	36.7 (ν _{1/2} = 88 Hz)
1c	H	Ph	H	Br	2a : 72	36.7 (ν _{1/2} = 88 Hz)
1d	<i>p</i> -MeOC ₆ H ₄	H	H	Br	2d : 34	36.9 (ν _{1/2} = 68 Hz)
1e	H	<i>p</i> -MeOC ₆ H ₄	H	Br	2d : 84	36.9 (ν _{1/2} = 68 Hz)
1f	-CH ₂ -(CH ₂) ₃ -CH ₂ -	H	H	Br	2f : 81	33.9 (ν _{1/2} = 61 Hz)

^a Isolated yields.



Scheme 1.

could explain the stereospecificity of the borylation reaction as a whole (Scheme 1).

3. Conclusion

1-Alkenyl(diisopropylamino)boranes **2** are cleanly and stereospecifically produced by catalytic borylation reaction of 1-alkenyl halides involving (diisopropylamino)borane as new and efficient BH transferring agent. These compounds are the first examples of isolated and spectroscopically fully characterized B_{sp²}-H containing 1-alkenyl boron compounds. Spectroscopic evidence clearly confirm in these derivatives an unprecedented through the boron ³J_{HH}-coupling. However, the *trans*-stereospecificity of the reaction remains at the moment

not perfectly rationalized and is currently under investigation.

Acknowledgements

We thank D.S. Sinbandhit for homodecoupling experiments, the French ministry of research and the CNRS for their financial support.

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