Rhodium- or Iridium-Catalyzed *trans*-Hydroboration of Terminal Alkynes, Giving (*Z*)-1-Alkenylboron Compounds

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Received January 26, 2000

Hydroboration of alkynes is a practical route for the syntheses of 1-alkenylboron compounds which are a versatile reagent for organic synthesis.[1,2] Although much attention has been recently focused on the metal-catalyzed hydroboration with catecholborane (**1a**) or pinacolborane (**1b**), both the uncatalyzed[1,3] and the catalyzed reactions[4,5] yield (*E*)-1-alkenylboronates through the *anti*-Markovnikov and *syn*-addition of borane to terminal alkynes. Thus, (*Z*)-1-alkenylboron compounds have been synthesized by an alternative, two-step method.[6,7] We wish to report a formal *trans*-hydroboration of terminal alkynes with **1a** or **1b** to yield *cis*-1-alkenylboronates in the presence of a Rh(I)- or Ir(I)-P^{i}Pr$_3$ complex and Et$_3$N (Scheme 1). For convenience of the analyses, all products derived from **1a** were converted into the corresponding pinacol esters prior to isolation of **2**−**4**.

The selected results for the catalytic hydroboration of 1-octyne are shown in Table 1.

The catalyst in situ generated from [Rh(cod)Cl]$_2$ and P^{i}Pr$_3$ (4 equiv) completed the hydroboration of 1-octyne within 1 h at room temperature (entry 1).[8] The presence of more than 1 equiv of Et$_3$N was critical to achieve high yield and high *cis*-selectivity because a similar reaction resulted in a mixture of all isomers **2**−**4** in the absence of Et$_3$N (entry 2). Another dominant factor reversing the conventional *cis*-hydroboration to the *trans*-hydroboration was the use of alkyne in excess of the borane reagent because (*E*)-isomer **3** was predominated when using a slightly excess of **1a** (entry 3). The reaction initially yields (*Z*)-alkenylboronate **2**, but an addition/elimination sequence of Rh−H species isomerizes **2** to a more stable (*E*)-isomer **3**.[9a,b] The steric and electronic effects of P^{i}Pr$_3$ also play a major role in influencing the course of the reaction. The PCy$_3$ (Cy = cyclohexyl) complex revealed comparable selectivity (entry 5), but other complexes of PPh$_3$, PMePh$_2$, PMe$_3$, P^{n}Pr$_3$, P^{n}Bu$_3$ (entry 4), P^{i}Bu$_3$, and P^{t}Bu$_3$ (entry 6) yielded a mixture of three possible isomers. The Ir and Ru complexes are not effective for selective hydroboration (entries 7 and 8). The reaction of pinacolborane **1b** is shown in entries 9 and 10. The Ir-catalyzed reaction again resulted in a mixture of products, but high *cis*-selectivity was achieved by the Rh(I) complex in the presence of 2 equivalents of 1-octyne.

Both **1a** and **1b** hydroborate various terminal alkynes in the presence of a Rh(I)-P^{i}Pr$_3$ complex (Table 2).[10] There is no large difference in *cis*-selectivity for the representative terminal alkynes (entries 1−13), but the hydroboration with **1b**, in general, resulted in slightly lower selectivity than that of **1a**. However, it is interesting that pinacolborane **1b** exceptionally resulted in better stereoselectivities for *tert*-butyl acetylene in the presence of a Rh or Ir catalyst (entries 7−9). All attempts at the *trans*-hydroboration of internal alkynes were unsuccessful.

The hydroboration of 1-deuterio-1-octyne (96% d_1 incorporation) with **1a** gave mechanistic information for the *trans*-hydroboration (Scheme 2). The β-hydrogen in the *cis*-product unexpectedly does not derive from the borane reagents because the deuterium labeled at the terminal carbon selectively shifted to the β-carbon. Thus, the results do not fit the mechanisms previously proposed in the catalyzed *trans*-hydrometalation of terminal alkynes.[9,11] The mechanism isomerizing the *trans*-product

Scheme 1. Catalyzed Hydroboration of Alkynes

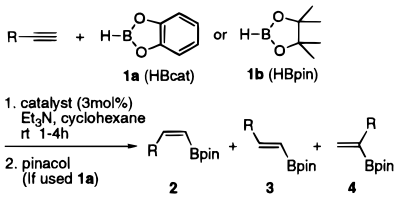

Table 1. Effect of Catalyst in the Hydroboration of 1-Octyne[a]

				isomeric ratio[c]		
entry	catalyst	borane	yield/%[b]	**2**	**3**	**4**
1	[Rh(cod)Cl]$_2$−4P^{i}Pr$_3$	**1a**	86(74)	99	1	0
2[d]		**1a**	60	18	65	17
3[e]		**1a**	94[f]	9	90	1
4	[Rh(cod)Cl]$_2$−4P^{n}Bu$_3$	**1a**	56	48	45	7
5	[Rh(cod)Cl]$_2$−4PCy$_3$	**1a**	86	98	2	0
6	[Rh(cod)Cl]$_2$−4P^{t}Bu$_3$	**1a**	34	21	64	15
7	[Ir(cod)Cl]$_2$−4P^{i}Pr$_3$	**1a**	43	58	32	10
8[g]	RuHCl(CO)(P^{i}Pr$_3$)$_2$	**1a**	7	55	45	0
9[h]	[Rh(cod)Cl]$_2$−4P^{i}Pr$_3$	**1b**	81(71)	91	7	2
10[h]	[Ir(cod)Cl]$_2$−4P^{i}Pr$_3$	**1b**	73	70	25	5

[a] To a solution of [M(cod)Cl]$_2$ (M = Rh or Ir, 0.015 mmol), a phosphine ligand (0.06 mmol), Et$_3$N (1 mmol), and a borane (1.0 mmol) in cyclohexane was added 1-octyne (1.2 mmol). The mixture was then stirred at rt for 1 h, unless otherwise noted. [b] GC yields based on a borane and isolated yields by chromatography over silica gel in parentheses. [c] Determined by ^{1}H NMR of crude product. [d] Reaction carried out in the absence of Et$_3$N. [e] alkyne/borane = 0.85/1. [f] Based on 1-octyne. [g] The reaction in CH$_2$Cl$_2$. [h] alkyne/borane/Et$_3$N = 2/1/5.

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(10) A typical procedure: To a solution of [Rh(cod)Cl]$_2$ (0.015 mmol), P^{i}Pr$_3$ (0.06 mmol), and Et$_3$N (1 mmol) in cyclohexane (3 mL) was added **1a** (1.0 mmol). After being stirred for 30 min, 1-decyne (1.2 mmol) was added and the mixture was stirred at room temperature for 1 h. A solution of pinacol (1.5 mmol) in cyclohexane (1 mL) was added and the resulting mixture was then stirred at rt for 12 h to convert the catechol ester to the pinacol ester. The chromatography over silica gel with hexane/ether = 40/1 afforded 2-[(*Z*)-1-octenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in 79% yield.

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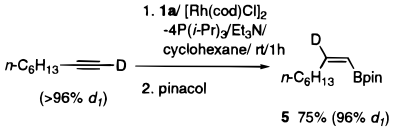
10.1021/ja0002823 CCC: $19.00
Published on Web 05/04/2000

Table 2. Hydroboration of Terminal Alkynes with **1a** or **1b**[a]

entry	alkyne	borane	yield/%[b]	isomeric ratio[c] 2	3	4
1	$CH_3(CH_2)_7C{\equiv}CH$	**1a**	79	99	1	0
2		**1b**	81	91	7	2
3	$TBDMSO(CH_2)_3C{\equiv}CH$	**1a**	72	98	2	0
4	$TBDMSOCH_2C{\equiv}CH$	**1a**	71	>99	<1	0
5	$CH_3(TBDMSO)CHC{\equiv}CH$	**1a**	70	98	2	0
6		**1b**	59	89	10	1
7	*t*-BuC≡CH	**1a**	62	89	11	0
8		**1b**	69	95	5	0
9[d]		**1b**	71	97	3	0
10[e]	$Me_3SiC{\equiv}CH$	**1a**	70	98	2	0
11[e]		**1b**	59	97	3	0
12	PhC≡CH	**1a**	60	99	1	0
13		**1b**	67	97	2	1

[a] To a solution of $[Rh(cod)Cl]_2$ (0.015 mmol), P(*i*-Pr)$_3$ (0.06 mmol), Et_3N (1 mmol for **1a** and 5 mmol for **1b**), and **1a** or **1b** (1.0 mmol) in cyclohexane was added an alkyne (1.2 mmol for **1a** and 2.0 mmol for **1b**) at rt. The mixture was then stirred for 1−2 h, unless otherwise noted. [b] Isolate yields based on a borane after chromatography over silica gel. [c] Determined by ^{1}H NMR of crude product. [d] $[Ir(cod)Cl]_2$ (0.015 mmol), P(*i*-Pr)$_3$ (0.06 mmol), Et_3N (5 mmol), **1b** (1.0 mmol), and *t*-BuC≡CH (1.2 mmol) were used. [e] At rt for 4 h.

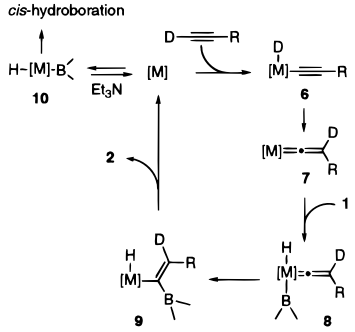
Scheme 2. Deuterium-Labeling Experiment



to a *cis*-isomer should be ruled out because the isomerization of (*Z*)-**2** selectively led to a thermally stable (*E*)-**3** (entry 3 in Table 1). The mechanism directly producing the *cis*-product via the *trans* to *cis* isomerization of a vinyl-metal intermediate[9] and the mechanism proceeding through the attack of metal hydride to the alkyne coordinated to a Lewis acid[11] do not result in the migration of an acetylenic hydrogen. A possible mechanism which might account for both the acetylenic hydrogen migration and the *anti*-addition of the B−H bond is one proceeding through a vinylidene complex **7** as shown in Scheme 3.[12]

The high electron-donating P^{i}Pr$_3$ favoring oxidative addition of the terminal C−H bond and stabilizing the vinylidene complex (**6**→**7**) has been amply demonstrated in the Rh,[13] Ru,[14] and Ir[13b] complexes and in the catalytic reactions induced by those

Scheme 3. Catalytic Cycle (M = RhCl, IrCl)



metals.[12,15] This process will be followed by oxidative addition of borane and the 1,2-migration of the boryl group to the α-carbon.[16] The key step leading to the *cis*-product is derived from the stereospecific formation of a thermodynamically stable (*E*)-**9** which is observed in the related migratory insertion of an alkynyl[14a] or a phenyl[17] group into the vinylidene complexes. Preliminary results suggested that the presence of Et_3N suppress the *cis*-hydroboration starting from **10** because the treatment of the key intermediate $[RhH(Cl)(Bcat)(P^iPr_3)_2]$ (**10**) with Et_3N led to the complete reductive elimination of **1a**/Et_3N complex.[18]

Acknowledgment. We are indebted to Professor F. Ozawa for many helpful discussions. The research is supported by JSPS Research Fellowship for Young Scientists.

Supporting Information Available: Experimental procedures and characterization data for of all compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0002823

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