A Regio- and Stereoselective Platinum(0)-Catalyzed Hydroboration of Allenes Controlled by Phosphine Ligands

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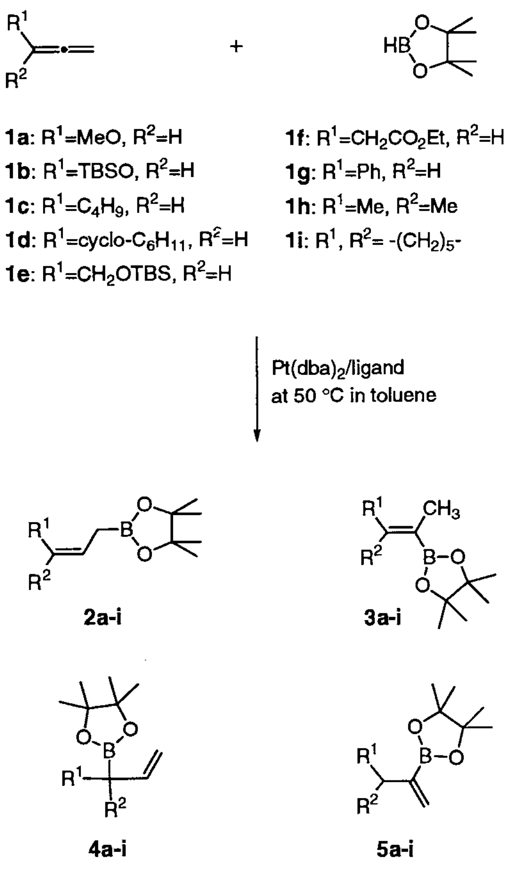
(Received July 8, 1999; CL-990605)

The hydroboration of terminal allenes with pinacolborane was carried out at 50 ℃ in the presence of a $Pt(dba)_2/2PR_3$ catalyst. The formation of one of three possible monohydroboration products was regioselectively synthesized by choosing an appropriate phosphine ligand.

The transition-metal complex-catalyzed hydroboration of alkenes and alkynes with di(alkoxy)boranes has been intensively studied as a method for the synthesis of alkyl- and 1-alkenylboronic esters.[1] The hydroboration with BH_3 or R_2BH usually needs no catalyst, but the transition metal-catalyzed hydroboration has various advantages over an uncatalyzed reaction in the reaction of di(alkoxy)boranes. The presence of a catalyst allows a very fast reaction under mild conditions for catecholborane and pinacolborane whereas the uncatalyzed reaction requires elevated temperature. It is also interesting that different chemo-, regio- and stereoselectivities are often realized between catalytic and non-catalytic conditions.[1] The regio- and stereoselectivities including their mechanistic aspects have been studied in detail for alkynes and alkenes, but the reaction has not yet been studied for allenes. In this paper, we detail a platinum(0)-catalyzed hydroboration of terminal allenes with pinacolborane (Scheme 1). The uncatalyzed hydroboration[2] of allenes gives a mixture of monohydroboration and dihydroboration products or a mixture of four possible regioisomers (**2**-**5**), but the phosphine ligand on the platinum(0) catalyst controlled the regio- and stereoselectivity so as to provide **2** or **3** from alkoxyallenes (**1a**,**b**), and **3** or **5** from aliphatic and aromatic allenes (**1c**-**i**).



Scheme 1.

Table 1. Effects of catalysts and ligands[a]

Entry	Catalyst	Ligand	Yield/%	(**2c** / **3c** / **5c**)[b]
1	$[RhCl(cod)]_2$	2 PPh_3	25	(0 / 62 / 38)
2		4 PPh_3	26	(0 / 32 / 68)
3		2 PCy_3	20	(0 / 65 / 45)
4		2 $P(t\text{-Bu})_3$	28	(0 / 50 / 50)
5	$Pt(dba)_2$	2 $P(n\text{-Bu})_3$	35	(0 / 0 / 100)
6		2 $P(i\text{-Pr})_3$	70	(0 / 0 / 100)
7		2 PCy_3	79	(0 / 0 / 100)
8		2 $P(t\text{-Bu})_3$	79	(0 / 0 / 100)
9		2 PPh_3	68	(0 / 0 / 100)
10		4 PPh_3	22	(0 / 0 / 100)
11		2 TTMPP	58	(0 / 100 / 0)

[a]A mixture of **1c** (1.0 mmol), pinacholborane (1.5 mmol), $Pd(dba)_2$ (0.03 mmol) and a ligand (0.06 or 0.12 mmol) in toluene (5 ml) was stirred at 50 °C for 2 h. [b]Isolated yields by Kugelrhor distillation or chromatography over silica gel. The composition of products was determined by ^1H NMR and GC analyses.

The effect of ligand is summarized in Table 1. For all reactions, a mixture of 1,2-heptadiene **1c** and pinacolborane (1.5 equivs) in toluene was stirred at 50 ℃ in the presence of 3 mol% of rhodium(I) or platinum(0) catalyst generated *in situ* from $[RhCl(cod)]_2$ or $Pt(dba)_2$ and a two equivalents of a phosphine ligand.[3] The rhodium catalyst resulted in the formation of a mixture of terminal and internal hydroboration products, **3c** and **5c** (entries 1-4), but the platinum complex selectively provided one of two products without formation of other regioisomers or dihydroboration products (entries 5-11). Various phosphines including alkyl- and arylphosphines were effective for the hydroboration of the internal double bond giving **5c**, but the high yields were achieved in bulky phosphines such as PCy_3 (Cy=cyclohexyl) and P^tBu_3 (entries 7 and 8). On the other hand, the regioselective hydroboration of terminal double bond occurred

Table 2. Hydroboration of allenes[a]

Entry	Allene	Ligand	Yield/%	(**2** / **3** / **5**)[b]
1	**1a**	PCy_3	65	(100 / 0 / 0)[c]
2	**1b**	PCy_3	77	(100 / 0 / 0)[d]
3		P(*t*-Bu)$_3$	86	(100 / 0 / 0)[e]
4		TTMPP	76	(0 / 100 / 0)
5	**1d**	P(*t*-Bu)$_3$	91	(0 / 0 / 100)
6		TTMPP	76	(0 / 91 / 9)
7	**1e**	P(*t*-Bu)$_3$	76	(0 / 0 / 100)
8		TTMPP	76	(0 / 39 / 61)
9	**1f**	P(*t*-Bu)$_3$	60	(0 / 0 / 100)
10		TTMPP	49	(0 / 0 / 100)
11	**1g**	P(*t*-Bu)$_3$	97	(0 / 0 / 100)
12		TTMPP	63[f]	(0 / 57 / 43)
13	**1h**	PCy_3	63	(33 / 0 / 67)
14		P(*t*-Bu)$_3$	53	(6 / 0 / 94)
15		TTMPP	76	(0 / 95 / 5)
16	**1i**	PCy_3	70	(56 / 0 / 44)
17		P(*t*-Bu)$_3$	96	(1 / 0 / 99)
18		TTMPP	76	(0 / 100 / 0)

[a]A mixture of **1** (1.0 mmol), pinacholborane (1.5 mmol), Pd(dba)$_2$ (0.03 mmol) and a ligand (0.06 mmol) in toluene (5 ml) was stirred at 50 °C for 2 h. [b]Isolated yields by Kugelrhor distillation or chromatography over silica gel. [c]*E/Z* = 16/84. [d]*E/Z* = 9/91. [e]*E/Z* = 10/90. [f]16 h.

when using a very bulky and basic tris(2,4,6-trimethoxyphenyl)phosphine[4] (TTMPP). The presence of NOE (2%) between CH_3 and allylic CH_2 in R^1 established the stereochemistry of (*Z*)-configuration of **3c**.[5]

The platinum-catalyzed hydroboration of the representative allenes are summarized in Table 2. The steric and electronic effects of MeO orTBSO (TBS=*t*-butyldimethylsilyl) play a major role in influencing the course of the reaction as evidenced by the preferential formation of the *cis*-isomer by way of attack from the less-hindered side of **1a,b** *via anti*-Markovnikov addition of borane to the terminal double bond (entries 1-3). Thus, the reaction allows the stereoselective synthesis of (*Z*)-γ-alkoxyallyboronic esters which are an excellent reagent for the diastereoselective preparation of *syn*-1,2-alkandiols *via* the allylboration of aldehydes.[6,7]

In contrast to the hydroboration of alkoxyallenes, the addition of pinacolborane to aliphatic and aromatic allenes (**1d-i**) with Pt(dba)$_2$/2P^{t}Bu$_3$ occurred at the internal double bond to selectively provide **5d-i**, which are not available by the uncatalyzed hydroboration of terminal allenes[2] or terminal alkynes[8] (entries 5, 7, 9, 11, 14 and 17). Both the P(*t*-Bu)$_3$ complex and the PCy_3 complex revealed similar catalyst activity for various allenes, but high regioselectivity can be obtained from the P(*t*-Bu)$_3$ complex (entries 13 and 16).[9]

Similarly to the hydroboration of **1c** (Table 1), TTMPP exhibited a quite unusual regioselectivity in the hydroboration of various allenes. Although the hydroboration of functionalized allenes resulted in poor regioselectivity (entries 8 and 12) or no formation of **3f** (entry 10), the platinum-TTMPP catalyst predominantly provided Markovnikov addition products for **1b**, **1c**, **1d**, **1h**, and **1i** by way of attack at the terminus of the allene linkage (entries 4, 6, 15 and 18).

The catalytic cycle may involve the oxidative addition of pinacolborane to platinum(0) to give an H-Pt-BX$_2$ intermediate, the insertion of allene, and finally the reductive elimination of hydroboration product, similarly to the nickel-, rhodium- and iridium-catalyzed hydroboration[1] or the related catalyzed hydrometalation reactions of alkenes and alkynes with silanes or stannanes.[10] TTMPP exhibited a characteristic effect, which dramatically changed the regioselectivity to the Markovnikov addition from the *anti*-Markovnikov addition of other ligands in the addition to the terminal double bond of allenes. The orientation and stereochemical outcome give some insight into the insertion process whereby the TTMPP ligand induces the insertion of allene into the Pt-BX$_2$ bond rather than the H-Pt bond;[1] however, further investigation is needed to discuss the mechanism in detail.

References and Notes

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