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Rhodium Catalysed Enantioselective Hydroboration of Alkenylboronic Esters with Catecholborane

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Abstract: Alkenylboronic esters such as (*E*)-2-(2-phenylethenyl)-1,3,2-dioxaborolane were subjected to catalytic hydroboration with catecholborane and with use of neutral and cationic rhodium complexes modified by various diphosphine ligands. The resulting 1,2-diboryl intermediate was oxidised with alkaline hydrogen peroxide to give the corresponding 1,2-diol with enantioselectivities up to 79 % e.e.

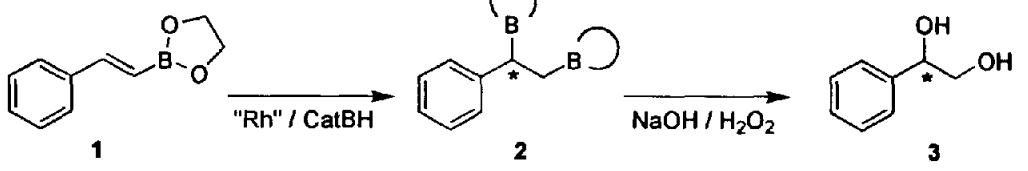
Introduction

The transition metal catalysed hydroborations, first reported by Männig und Nöth[1], further broadened the scope of the already widely used stoichiometric hydroboration reactions. It was found that especially the rhodium catalysed hydroboration of alkenes often proceeds with chemo-[1,2], regio-[3], enantio-[4] and diastereoselectivities[5] opposite to those of the uncatalysed processes. Much attention has been focused on the catalytic hydroboration of aromatic alkenes[6], allylic alcohol[7] and amine derivates[8]. Catalytic reaction of styrenes, e.g., proceeds with high regioselectivity in favour of the secondary boronate ester[9] while the primary adduct[10] is formed predominately in the uncatalysed hydroboration. Besides, there were also reported attempts in using transition metal catalysts with metals others than rhodium[11] as well as investigations on the reaction mechanism[12] describing details of the catalytic cycle. Recently, T. B. Marder, R. T. Baker and coworkers analysed several metal mediated degradation pathways of catecholborane which give rise to complex mixtures of highly active species responsible for a number of side-reactions in catalytic hydroborations.[13]

Results and discussion

The aim of this work is to extend the catalytic hydroboration reaction to functionalised alkenes such as vinylboronic esters which are easily accessible from the corresponding alkynes via hydroboration with catecholborane (CatBH), hydrolysis and reesterification with ethylene glycole.[14] If, e.g., **1** is subjected to catalytic hydroboration using Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, and CatBH the resulting crude 1,2-diboryl-intermediate **2** can be either isolated or oxidised with alkaline hydrogen peroxide to give 1-phenyl-1,2-ethanediol **3** in 75 % yield (Scheme 1). Furthermore, enantioselective hydroboration of **1** could be achieved with use of several neutral and cationic rhodium complexes modified with various enantiopure diphosphine ligands, leading - after oxidative workup - to optically active diol **3**.

Scheme 1



1 **2** **3**

Since both regio- and stereoselectivities of the hydroboration of simple styrenes and derivates highly depend on the structural features of the catalysts applied[6,15] it was of interest to search for a suitable catalytic system by using $[Rh(COD)_2]BF_4$, $[Rh(COD)Cl]_2$, $[Rh(NBD)_2]ClO_4$ and $[Rh(NBD)Cl]_2$ as rhodium sources and 1,2-bis-(diphenylphosphino)-ethane (DPPE), 1,3-bis-(diphenylphosphino)-propane (DPPP), 1,4-bis-(diphenylphosphino)-butane (DPPB) as diphosphine ligands as well as (2S,3S)-(-)-2,3-bis-(diphenylphosphino)-butane (Chiraphos), (2S,4S)-(-)-2,4-bis-(diphenylphosphino)-pentane (Skewphos), (2R,5R)-(+)-2,5-bis-(diphenylphosphino)-hexane (BPPH)[16] as their chiral analogues. Reaction conditions and results are summarised in Tables 1 and 2.

Table 1 : Hydroboration of vinylboronic ester **1** with catecholborane catalysed by rhodium-diphosphine complexes.[a]

entry	Rh complex	diphosphine	yield (%)[b]	entry	Rh complex	diphosphine	yield (%)[b]
1	$[Rh(COD)_2]BF_4$[c]	DPPE	7	7	$[Rh(NBD)_2]ClO_4$[d]	DPPE	13
2	$[Rh(COD)_2]BF_4$	DPPP	9	8	$[Rh(NBD)_2]ClO_4$	DPPP	5
3	$[Rh(COD)_2]BF_4$	DPPB	50	9	$[Rh(NBD)_2]ClO_4$	DPPB	46
4	Rh(COD)Cl-dimer	DPPE	15	10	Rh(NBD)Cl-dimer	DPPE	32
5	Rh(COD)Cl-dimer	DPPP	31	11	Rh(NBD)Cl-dimer	DPPP	30
6	Rh(COD)Cl-dimer	DPPB	53	12	Rh(NBD)Cl-dimer	DPPB	45

[a] All reactions were carried out in THF at -20 °C in the presence of 2 mol% rhodium catalyst (prepared in situ) and subjected to oxidative work up after 22 h. [b] Yield of isolated diol **3** after extraction and chromatography. [c] COD = 1,5-cyclooctadiene. [d] NBD = 2,5-norbornadiene.

Table 2 : Hydroboration of vinylboronic ester **1** with catecholborane catalysed by enantiopure rhodium-diphosphine complexes.[a]

entry	Rh complex	diphosphine	yield (%)[b]	ee (%)[c]	config.of **3**[d]
1	$[Rh(NBD)_2]ClO_4$	(S,S)-Chiraphos	13	72.6	(R)
2	$[Rh(NBD)_2]ClO_4$	(S,S)-Skewphos	17	40.6	(S)
3	$[Rh(NBD)_2]ClO_4$	(R,R)-BPPH	50	18.9	(S)
4	Rh(NBD)Cl-dimer	(S,S)-Chiraphos	12	72.1	(R)
5	Rh(NBD)Cl-dimer	(S,S)-Skewphos	20	40.4	(S)
6	Rh(NBD)Cl-dimer	(R,R)-BPPH	31	13.3	(S)

[a] All reactions were carried out in THF at -20 °C in the presence of 1 mol% rhodium catalyst and subjected to oxidative work up after 22 h. [b] Yield of isolated diol **3** after extraction and chromatography. [c] determined by HPLC (Chiracel OB). [d] The absolute configuration was determined by comparison of the signs of the specific rotation with literature values.[17]

The results shown in Table 1 clearly indicate that the formation of the desired product **3** highly depends on the length of the carbon backbone of the diphosphine ligand. DPPB gives rise to the highest yields quite independently of the diene ligand or the electronic state of the metal (Table 1, entries 3,6,9 and 12). In case of the smaller DPPE and DPPP ligands yields are in general very low but somewhat higher when neutral instead of cationic rhodium complexes are used. For DPPE, the size of the diene ligand seems to have some additional influence favouring the NBD over the COD ligand (entries 1,7 and 4,10). When the chiral diphosphine analogues are used (Table 2) a similar dependence of yield and length of the phosphine backbone is observed. Increasing length of backbone leads to higher yields of product but at the same time the enantioselectivity of the hydroboration reaction decreases. This might be due to the increasing size of the

rhodium - diphosphine chelate rings (five- to seven-membered ring when changing from Chiraphos to BPPH) thus allowing for higher conformational flexibility of the active rhodium complexes. Furthermore a change in the absolute configuration of product is observed on varying the length of the phosphine backbone, also indicating significant structural differences in the enantioselective step.

On further studies we selected (R)-(+)-2,2'-bis-(diphenylphosphino)-1,1'-binaphthyl (R-BINAP) and (4R,5R)-(-)-4,5-bis-(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane ((-)-DIOP) as the bidentate ligands both with a four carbon backbone and a rather stiffer structure compared to DPPB promissing higher enantioslectivities. As in similar cases, the reaction temperature also has a high influence on the chiral induction. At -20 °C the rhodium/R-BINAP catalyst system yielded diol **3** with optical purities of 34 % to 45 % ee depending on the rhodium precursor and the reaction conditions. The enantioselectivity was found to be somewhat higher for the neutral than for the cationic catalyst, whereas the latter gave better yields. On lowering the temperature to -40 °C the e.e.-values increase to a range of 47 % to 60 %. Finally, at -60 °C diole **3** was formed with 79 % e.e. using neutral and with 67 % to 72 % e.e. using cationic rhodium precursors, however with very low to moderate chemical yields (Table 3, entries 3 and 7). Although the reaction proceeds very slowly at -60 °C, after a reaction time of 9 days and with use of a cationic rhodium precursor the chemical yield reached 49 %. At minus 80 °C no detectable reaction took place within days.

With the rhodium/(-)-DIOP-system the rate of hydroboration at -60 °C is found to be much faster than with the BINAP modified catalysts giving **3** in 87 % yield but with only very low enantiomeric excess (entry 4).

A comparison of **1** with the related catechol ester (*E*)-2-(2-phenylethenyl)-1,3,2-benzodioxaborole as the hydroboration substrates showed almost identical results when the $[Rh(COD)_2]BF_4$/R-BINAP-system was used (entries 3 and 8). Double stereodifferentiation reactions using the enantiopure vinylboronic ester of (1S,2S,3R,5S)-(+)-pinan-2,3-diol as substrate did not remarkably improve the enantioselectivity as compared to the ethylene glycole ester **1**.

Table 3 : Selected data from the catalytic hydroborations of **1**.

entry	rhodium complex	added diphosphine	reaction temperature	isolated yield	enantiomeric excess	config. of product
1	$[Rh(COD)_2]BF_4$	R-BINAP	- 20 °C	20 %	34 %	(S)
2	$[Rh(COD)_2]BF_4$	R-BINAP	- 40 °C	28 %	47 %	(S)
3	$[Rh(COD)_2]BF_4$	R-BINAP	- 60 °C	49 %	72 %	(S)
4	$[Rh(COD)_2]BF_4$	(-)-DIOP	- 60 °C	87 %	6 -11 %	(R)
5	Rh(COD)Cl-dimer	R-BINAP	- 20 °C	18 %	45 %	(S)
6	Rh(COD)Cl-dimer	R-BINAP	- 40 °C	20 %	60 %	(S)
7	Rh(COD)Cl-dimer	R-BINAP	- 60 °C	≤ 9 %	79 %	(S)
8[a]	$[Rh(COD)_2]BF_4$	R-BINAP	- 60 °C	48 %	66 %	(S)

[a] (*E*)-2-(2-phenylethenyl)-1,3,2-benzodioxaborole was used as substrate.

In conclusion, we have shown that alkenylboronic esters can be subjected to catalytic hydroboration with Wilkinson's catalyst to give after oxidative workup diols in up to 75 % yield. By applying chiral diphosphine ligands enantioselective routes could be established. Although the reaction is quite sensible to the catalytic system and the yields are not satisfactory, as yet, the chiral 1,2-diboryl reaction products are expected to be very versatile intermediates due to the manifold of possible chemical transformations of boron substituents into a variety of other functional groups[10].

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References and Notes

1. Männig, D.; Nöth, H. *Angew. Chem.,Int. Ed. Engl.* **1985**, *24*, 878.
2. Lane, C.; Kabalka, G. W. *Tetrahedron* **1976**, *32*, 981.
3. a) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 6917. b) Zhang, J.; Lou, B.; Guo, G.; Dai, L. *J. Org. Chem.* **1991**, *56*, 1670.
4. a) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178. b) Brown, J. M.; Lloyd-Jones, G. C. *Tetrahedron Asymmetry* **1990**, *1*, 869. c) Sato, M.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1990**, *31*, 231. d) Burgess, K.; Donk, W. A. van der; Ohlmeyer, M. J. *Tetrahedron Asymmetry* **1991**, *2*, 613.
5. a) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 395. b) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 5861.
6. Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron Asymmetry* **1991**, *2*, 601.
7. a) Burgess, K.; Cassidy, J.; Ohlmeyer, M. J. *J. Org. Chem.* **1991**, *56*, 1020.
8. a) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1991**, *56*, 1027. b) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 5857.
9. Hayashi, T.;Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426.
10. Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*, Academic Press: New York, 1988.
11. a) Evans, D. A.; Muci, A. R.; Stürmer, R. *J. Org. Chem.* **1993**, *58*, 5307. b) Burgess, K.; Jaspers, M. *Organometallics* **1993**, *12*, 4197. c) Harrison, K. N.; Marks, T. J.; *J. Am. Chem. Soc.* **1992**, *114*, 9220. d) Evans, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1991**, *113*, 4042.
12. a) Brown, J. M.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866. b) Westcott S. A.; Marder, T. B.; Baker, R. T. *Organometallics* **1993**, *12*, 975. c) Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6679 d) Brown, J. M.; lloyd-Jones, G. C. *J. Chem. Soc., Chem. Commun.* **1992**, 710. e) Burgess, K.; Donk, W. A. van der; Kook, A. M. *J. Org. Chem.* **1991**, *56*, 2949 and 7360. f) Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 2280.
13. Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem.* **1993**, *32*, 2175.
14. Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249.
15. Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863.
16. Wiesauer, C.; Kratky, C.; Weissensteiner, W. to be published.
17. Dale, J. A.; Mosher, H. S. *J. Org. Chem.* **1970**, *35*, 4002.

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