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Application of chiral tetrahydropentalene ligands in rhodium-catalyzed 1,4-addition of (*E*)-2-phenylethenyl- and (*Z*)-propenylboronic acids to enones

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ABSTRACT

Chiral tetrahydropentalenes (3a*R*,6a*R*)-**1** have been prepared and used as ligands in the Rh-catalyzed 1,4-addition of 1-alkenylboronic acids to cyclic enones **5**. It has been discovered that the stereochemistry of the reaction was controlled by the steric properties of the aryl groups in **1** rather than their electronic nature. In the vinylation with (*E*)-2-phenylethenylboronic acid **5**, ligands (3a*R*,6a*R*)-**1** provided enantioselectivity up to 87% ee and gave high yields of ethenylketones **6** in the presence of **1** (6.6 mol %). The configuration of all ketone products obtained with (3a*R*,6a*R*)-**1** is (*S*). Rh-catalyzed reaction of cyclopentenone **4a** and (*Z*)-propenylboronic acid **7** in the presence of ligands (3a*R*,6a*R*)-**1** yielded at 50 °C an inseparable mixture of (*Z*)- and (*E*)-ketones **8** with (*Z*)-**8** as the major product and both in only moderate enantiomeric excess.

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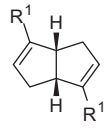
Since pioneering studies by Hayashi,[1] Carreira,[2] and Grützmacher,[3] chiral diene steering ligands proved to be very useful in Rh- and Ir-catalyzed reactions.[4] A broad variety of bicyclic diene ligands have been prepared and were utilized in 1,4-additions of aryl- and alkenylboronates to electron-poor alkenes,[5] 1,6-additions,[6] 1,2-additions to acylimines or hydrazones,[7] [4+2] cycloadditions,[8] aryl cross couplings,[9] cyclizations of alkynals,[10] cyclopropanations,[11] hydrogenation of dehydroamino acids,[12] and polymerizations.[13] Also some acyclic dienes were established as ligands in Rh-catalyzed asymmetric reactions.[14]

Bicyclo[3.3.0]octa-2,5-diene steering ligands **1** (Scheme 1), based on a tetrahydropentalene scaffold,[15] have been applied in asymmetric catalysis by our group[16] and, independently, by Xu, Lin, and co-workers[5p,17] These tetrahydropentalene-based ligands showed high stereoselectivity in Rh-catalyzed arylation of enones,[5n,5p,16,17] sulfonylimines,[5p,7c,7h,17,18] nitroalkenes,[5h] as well as in Pd-mediated aryl–aryl couplings.[9]

In order to expand the scope of olefinic steering ligands in asymmetric catalysis, we were interested to study the catalytic behavior of bicyclo[3.3.0]octa-2,5-diene derivatives **1**[16] in Rh-catalyzed conjugate addition of arylethenyl and alkylethenylboronic acids to enone substrates. For this purpose, electronic and steric properties of the substituents R^1 (Scheme 1) were varied, and their influence on stereoselectivity was investigated. The results are discussed below.



(3a*R*,6a*R*)-**1**

1	R^1
a	Ph
b	Bn
c	4-F-C_6H_4
d	4-MeO-C_6H_4

Scheme 1. Diene ligands **1a–d**.

For our experiments, a series of substituted tetrahydropentalenes **1** (Scheme 1) were synthesized. Ligands **1a** (R^1 = Ph) and **1b** (R^1 = Bn) have been earlier reported for both configurations, 3a*S*,6a[5p,16,17] and 3a*R*,6a*R*.[16] In contrast, only 3a*S*,6a*S*-isomers for structures **1c** (R^1 = *p*-F-C_6H_4) and **1d** (R^1 = *p*-MeO-C_6H_4) were described in the literature.[5n]

We focused on the synthesis of the enantiomers (3a*R*,6a*R*)-**1c** and (3a*R*,6a*R*)-**1d**. For this purpose we chose the well established cross coupling of organometallic reagents with bis(triflate) (3a*R*,6a*R*)-**3**[5p,16,17] (Scheme 2).[5n,16] Two different catalysts, Fe(acac)$_3$ and Pd(PPh)$_3$, were tested in order to suppress homo-coupling of the Grignard reagent and to optimize the reaction conditions. The best results were achieved using Pd(PPh)$_3$ (1.5 mol %) (for experimental details and conditions see Supplementary data).

Cyclic β-alkenyl ketones are widely used as building blocks in organic synthesis.[19] In our experiments, the conjugate 1,4-addition of (*E*)-2-phenylethenylboronic acid **5** to cyclic enones **4a–c** was investigated in the presence of tetrahydropentalene ligands

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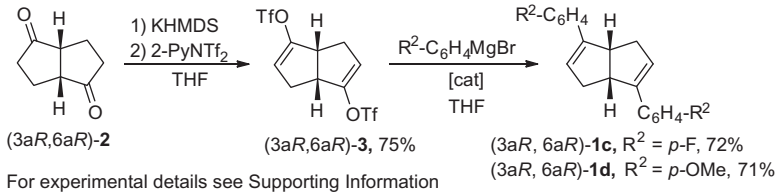
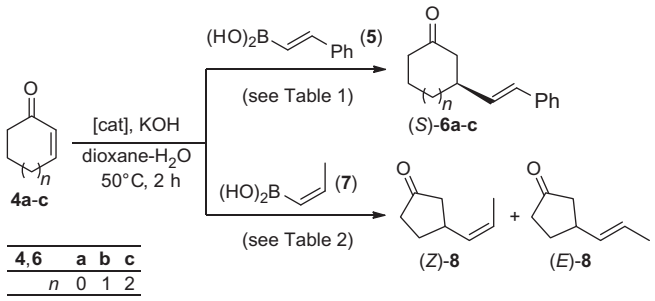


Scheme 2. Synthesis of diene ligands **1c,d**.



Scheme 3. Rh-catalyzed 1,4-addition of boronic acids **5**,**7** to cyclic enones **4a**–**c**.

Table 1
Enantioselective Rh-catalyzed 1,4-addition of (*E*)-2-phenylethenylboronic acid **5** to enones **4** in the presence of diene ligands (3a*R*,6a*R*)-**1**[a,b]

Entry	Enone	*n*	Ligand	Product[b]	Yield[c] (%)	ee (%)
1	**4a**	0	**1a**	**6a**	74	70
2	**4a**	0	**1b**	**6a**	51	32
3	**4a**	0	**1c**	**6a**	72	67
4	**4a**	0	**1d**	**6a**	66	76
5	**4b**	1	**1a**	**6b**	80	76
6	**4b**	1	**1b**	**6b**	63	48
7	**4b**	1	**1c**	**6b**	70	76
8	**4b**	1	**1d**	**6b**	65	77
9	**4c**	2	**1a**	**6c**	86	87
10	**4c**	2	**1b**	**6c**	71	58
11	**4c**	2	**1c**	**6c**	80	86
12	**4c**	2	**1d**	**6c**	76	85

[a] Reaction conditions according to Scheme 3. For experimental details see Supporting Information and Ref..[16]
[b] Configuration of the ligands is (3a*R*,6a*R*). Configuration of ligands and products was assigned by comparison of optical rotation with the literature data.[14b,16,23]
[c] Yields refer to isolated yields.

(3a*R*,6a*R*)-**1** (Scheme 3). Under reaction conditions typical for arylation,[16] for example 1.5 mol % of $[RhCl(C_2H_4)_2]_2$, 3.3 mol % of ligand **1** and KOH as a base, the reaction of (*E*)-2-phenylethenylboronic acid **5** with enones **4a–c** did not occur. Upon a two-fold increase of the catalyst loading, β-alkenylketones **6a–c** were produced with yields up to 86% and enantioselectivities up to 87% ee (Table 1). As compared to the arylated analogues **1a,c,d** (entries 1, 3–5, 7–9, 11, 12), the ligand **1b** bearing benzyl groups was much less efficient, giving lower yields and only moderate enantiomeric excess up to 58% ee (entries 2, 6, 10). Concerning the catalytic activity of the ligands **1a–d** with different electronic properties, the following trend was observed **1a** > **1c** > **1d** > **1b** regardless of the ring size of enone **4**. The structural influence of the enone substrate on the properties of the catalyst in the vinylation reaction was significant. An increase in the ring size of the cyclic enone substrate **4** led to an increase in both productivity and selectivity of the Rh-catalysts, derived from ligands **1a–d**.

Table 2
Enantioselective Rh-catalyzed 1,4-addition of (1*Z*)-prop-1-enylboronic acid **7** to cyclopentenone **4a** in the presence of diene ligands (3a*R*,6a*R*)-**1**[a,b]

Entry	Ligand[b]	Conversion (%)[c]	Product	*Z*:*E*	% ee (*Z*)[d,e]	% ee (*E*)[d]
1	**1a**	85	**8**	77:23	—	44
2	**1b**	87	**8**	75:25	(82)	50
3	**1c**	83	**8**	69:31	—	34
4	**1d**	81	**8**	69:31	(60)	42

[a] Reaction conditions according to Scheme 3. For experimental details see Supplementary data and Ref.[16]
[b] Configuration of the ligands is (3a*R*,6a*R*).
[c] Due to volatility of products **8**, yields could not be determined.
[d] Enantioselectivity was determined by capillary GC using a chiral stationary phase.
[e] No baseline separation of enantiomers by GC; therefore the ee-values were estimated.

Whereas 1,4-arylation of enones received an increased attention,[4a–c,5j,5o,5r,14b,20] studies dedicated to the conjugate addition of alkyl-[5k,5o,20j,21] and arylethenylboronic acids[5o,21,22] are scarce. In a series of experiments, the 1,4-addition of (*Z*)-prop-1-enylboronic acid **7** to cyclopentenone **4a** was investigated. (*Z*)-prop-1-enylboronic acid **7** was reacted with substrate **4a** in the presence of $[RhCl(C_2H_4)_2]_2$ (3 mol %) and ligands (3a*R*,6a*R*)-**1** (6.6 mol %), Table 2. In all cases, an inseparable mixture of 3-[(1*Z*)-prop-1-enyl]cyclopentanone (*Z*)-**8** and its (1*E*)-isomer (*E*)-**8** was obtained (Scheme 3). In comparison with (*E*)-2-phenylethenylboronic acid **5**, the boronic acid **7** was less reactive, and in the reaction with cyclopentenone **4a** complete conversion of the enone reagent could not be achieved (Table 2). The Rh-catalyzed *Z*/*E*-isomerization in **7** seems to occur faster than the addition of **7** to enone **4a**,[23] which leads to the appearance of the *E*-isomer (*E*)-**8**. Isomerization of the propenyl group and the slow rate of the addition reaction are possible reasons for low enantioselectivity of the process, with enantiomeric excess recorded for (*E*)-**8** between 34% ee and 50% ee and estimated for (*Z*)-**8** in a range of 60–82% ee.

In Rh-catalyzed addition reactions, mediated by a chiral olefinic ligand, it is assumed that a chiral olefin-Rh complex is formed.[24] These complexes possess molecular C_2-symmetry, defined by the ligand scaffold, which was illustrated by single crystal X-ray studies of isolated compounds.[25] The enone substrate coordinates with the Rh-center in a manner avoiding steric repulsion between the carbonyl group of the substrate and bulky substituents of the olefinic ligand.[5o,26] Intramolecular *syn*-addition of the aryl group to the enone in the chiral intermediate complex selectively leads to one enantiomer.[1]

The structures of free Ph-substituted tetrahydropentalene **1a** (3a*S*,6a*S*)-isomer[16] as well as (3a*R*,6a*R*)-isomer[5n] have been reported in the literature. Upon coordination of (3a*S*,6a*S*)-**1a** with the Rh-center, a C_2-symmetrical structure is formed, with Ph groups placed in opposite lateral sectors of the ligand core.[5n] By an analogy with earlier made assumptions (see above), the intermediate formation of corresponding chiral Rh complexes might be suggested for tetrahydropentalene-derived ligands (3a*R*,6a*R*)-**1a–d**. Subsequently, stereoselective coordination of an enone

substrate on the *si*-site to the Rh-center should lead to enantiomerically pure ketone products (*S*)-**6** (for a mechanistic proposal see Supplementary data). Flat aryl substituents in (3a*R*,6a*R*)-**1a,c,d** are presumably most suited to provide smooth coordination of the enone to the Rh-center. In contrast, the nonplanar benzyl group in ligand (3a*R*,6a*R*)-**1b** might shield the Rh-center from coordination with an enone substrate, which could be a reason for the low catalytic activity and enantioselectivity of the ligand.

Considering the size of the molecule and distribution of electron density, (*Z*)-prop-1-enylboronic acid **7** differs markedly from 2-phenylvinyl analogue **5**. The presence of the electron-donating Me-substituent seems to slow down the rate of reaction between boronic acid **7** and cyclopentenone **4a** (see above). In the same time, due to the small size of the propenyl moiety, the rate of *Z*/*E*-isomerization in the (*Z*)-prop-1-enyl group coordinated to the Rh-center is not affected by the bulky substituents of the chiral olefinic ligand. Consequently, appearance of the *E*-oriented ketone products could be expected in this situation, with a *Z*/*E* ratio controlled by the steric size of the boronic acid and almost independent from the bulkiness of the olefinic ligand. This was observed in our experiments. The reactions with rather bulky (*E*)-phenylethenylboronic acid **5** showed no sign of *E*/*Z*-isomerization. In the Rh-catalyzed addition of (*Z*)-propenylboronic acid **7** to cyclopentenone **4a**, mixtures of *Z*/*E*-products (*Z*)-**8** and (*E*)-**8** have been obtained in the presence of ligands **1a**–**d** (Table 2). The use of different substituted ligands **1a**–**1d**, led to only a small change in the content of *E*-isomer (between 23% and 31%).

In conclusion tetrahydropentalene-derived Rh catalysts showed high catalytic activity and stereoselectivity for 1,4-conjugate addition of (*E*)-2-phenylethenylboronic acid **5** to cyclic enone substrates **4a**–**c**. Several factors affect the selectivity and productivity of the process. The electronic nature of aryl substituents in the ligand framework has only little influence on the stereocontrol of the addition reaction. Conversely, steric factors have a considerable effect on enantiomeric purity and yield of the reaction. The ligand with nonplanar benzyl substituents was less efficient and selective than tetrahydropentalenes bearing planar aryl groups. Enantioselectivity and productivity of the Rh-catalyst are also dependent on the ring size of the cyclic substrate. The enantioselectivity also depends considerably on the nature of the used boronic acid. (*E*)-2-phenylethenylboronic acid **5** gave substituted ketones with quite high enantiomeric purity and yields. In contrast, the addition of (*Z*)-prop-1-enyl boronic acid **7** occurred with reduced enantioselectivity and was accompanied by *Z*/*E*-isomerization of the prop-1-enyl group. Based on the obtained knowledge, directed synthesis of β-substituted ketones could be performed with required selectivity by gentle tuning in the structure of the ligand, substrate, or used organoboronic acid. This should expand the applicability of the Rh-catalyzed 1,4-conjugate addition to the synthesis of chiral complex organic molecules.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet. 2012.04. 130.

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