C–H Activation

DOI: 10.1002/anie.201309207

Chiral Cp-Rhodium(III)-Catalyzed Asymmetric Hydroarylations of 1,1-Disubstituted Alkenes**

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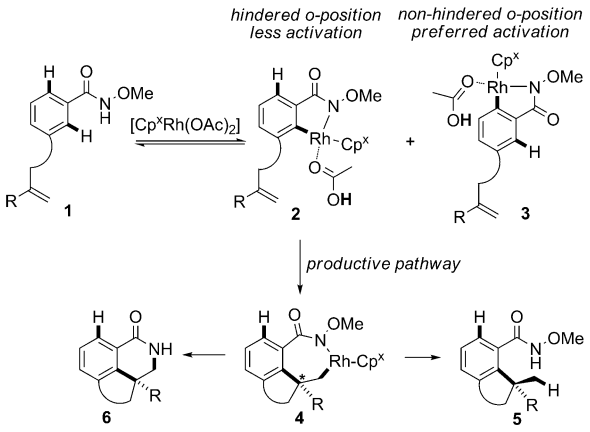
Abstract: *Metal-catalyzed functionalizations at the ortho position of a directing group have become an efficient bond-forming strategy. A wide range of transformations that employ Cp*Rh^{III} catalysts have been described, but despite their synthetic potential, enantioselective variants that use chiral versions of the Cp* ligand remain scarce (Cp* = pentamethyl cyclopentadienyl). Cyclopentadienyl compounds with an atropchiral biaryl backbone are shown to be suitable ligands for the efficient intramolecular enantioselective hydroarylation of aryl hydroxamates. Dihydrofurans that bear methyl-substituted quaternary stereocenters are thus obtained by C–H functionalization under mild conditions.*

Over the past decades, transition-metal-catalyzed C–H functionalizations have become a complementary synthetic tool to build molecular complexity from simple starting materials.[1] In stark contrast to the impressive number of new and powerful transformations, only few enantioselective versions have been reported.[2] A lack of suitable chiral ligands, in combination with the harsh conditions that are often required, is the main reason for this gap. A better mechanistic understanding is crucial for addressing these shortcomings. Within our longstanding interest in asymmetric C–H functionalizations, we seek to develop new ligand and catalyst systems that are able to overcome current reactivity boundaries.[3] Over the past years, the range of transformations that are triggered by the Cp*Rh^{III} fragment (Cp* = pentamethyl cyclopentadienyl) has proven to be particularly broad and synthetically versatile.[4] In this context, we[5] and Rovis, Ward et al.[6] have devised two complementary strategies for the development of chiral cyclopentadienyl ligands and reported their application in the Rh^{III}-catalyzed synthesis of dihydroquinolones. With this method, the products were provided in high yields and selectivities for terminal olefins, whereas only few examples on the use of cyclic olefins were reported. However, even for achiral reactions with Cp*Rh^{III}, more complex alkenes are often less reactive and therefore not suitable substrates.[7] With the exception of highly activated methylenecyclopropanes,[8] highly substituted alkenes (1,1-di- or trisubstituted) have failed to undergo any reaction with the rhodacyclic intermediate thus far. An additional issue is the poor regiocontrol that is observed for the insertion of unbiased alkenes. Recognizing these restrictions, we aimed for a strategy that entails the tethering of the olefin to the aryl group. This method would not only overcome the mentioned limitations, but also give access to valuable stereodefined cyclic building blocks, such as biologically important dihydrobenzofurans (Scheme 1).[9] However, the carboxylate-assisted concerted metalation–deprotonation



Scheme 1. Equilibrating C–H activations for hydroarylative enantioselective cyclizations with chiral Cp^{x}Rh^{III} complexes. Cp^x = chiral cyclopentadienyl.

(CMD) pathway[10] that leads from **1** to the cyclometalated key intermediates **2** and **3** is generally guided by steric factors that favor the least encumbered *ortho* position. In the process that we envisioned, only this more hindered and presumably less populated species **2** would be able to undergo a productive cyclization.[11] Taking advantage of the reversibility of the CMD pathway, we assumed that species **3** would be in equilibrium with **2** and could thus be fully converted into the product. Moreover, we previously observed that a *meta*-methoxy substituent causes poor regioselectivity control, which leads to a mixture of isomers.[5] The cyclometalated species **2** can undergo a productive migratory insertion that affords **4**. In the absence of β-hydrogen atoms, either a challenging reductive C(sp^3)–N bond formation would yield **6**, or proto-demetalation would be enforced to give **5**. Thus far, alkyl rhodium intermediates have only been shown to undergo reductive C(sp^3)–N bond formation with C(O)–NH–OC(O)R directing groups, but not with the

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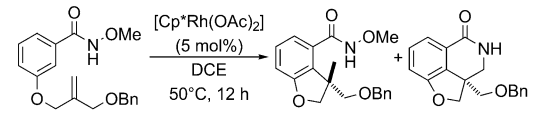
[**] This work is supported by the European Research Council under the European Community's Seventh Framework Program (FP7 2007–2013); ERC Grant agreement 257891). We thank Dr. R. Scopelliti for X-ray crystallographic analysis of **10**.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201309207.

C(O)–NHOMe directing group.[12,7] With this group,[13] Heck-type β eliminations are commonly reported for olefin incorporation with rhodium catalysts.[7b] Herein, we report the enantioselective construction of dihydrobenzofurans with quaternary stereogenic centers by intramolecular Rh^{III}-catalyzed enantioselective hydroarylation under mild conditions.

The general feasibility of the envisioned process was first explored on model substrate **1a** with an achiral Cp^*Rh^{III} complex [Eq. (1)]. Without any additive, cyclized products **5a** and **6a** were obtained in roughly equal amounts. We



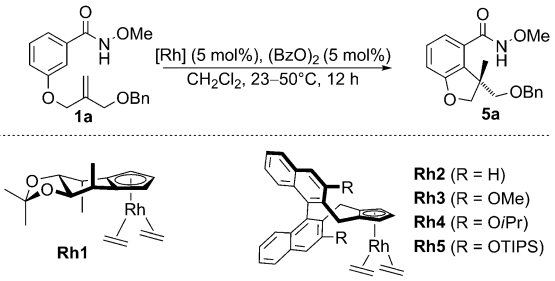
(1)

1a	additive	5a	6a
	none:	42%	47%
	PivOH (2 equiv):	65%	18%
	$AgSbF_6$ (10 mol%):	70%	18%
	$AgSbF_6$ (10 mol%), PivOH (2 equiv):	89%	4%

speculated that the addition of a carboxylic acid would enhance protonolysis. Indeed, when PivOH (2 equiv) was added, the hydroarylated compound **5a**, which bears a methyl-substituted quaternary stereogenic center, was formed as the major product, together with minor amounts of product **6a**. Moreover, we found that the ratio of these products could be further enhanced with silver additives, so that **5a** was almost exclusively obtained.

We next evaluated our chiral Cp ligand portfolio in the reaction.[5,14] Complex **Rh1**, which bears a dimethylcyclohexyl-derived ligand, provided exclusively **5a** in 66% yield and with a moderate enantiomeric ratio of 78:22 (Table 1, entry 1). In contrast to results obtained with the Cp* ligand system, traces of **6a** were not detected. The use of a complex with an unsubstituted biaryl scaffold as the ligand (**Rh2**) increased conversion and yield, while the modest enantioselectivity was not improved (entry 2). The selectivity could be significantly enhanced with methoxy substituents at the *ortho* positions of the biaryl scaffold (**Rh3**); this catalyst yielded **5a** in 83% with 95:5 e.r. (entry 3). Using ligands with larger substituents, such as isopropoxy (O*i*Pr; **Rh4**) or even triisopropylsilyloxy (OTIPS; **Rh5**) groups, resulted in diminished enantioselectivities (entries 4 and 5). Whereas the solvent had some influence on the enantioselectivity of the reaction, its impact on the reactivity was much greater. For instance, reactions in MeOH (60% conversion; entry 6) or THF (30% conversion, 19% yield; entry 8) did not go to completion. In this respect, dichloromethane was optimal and gave **5a** in 86% yield and 95.5:4.5 e.r. (entry 9). The influence of the carboxylic acid additive on the enantioselectivity is relatively small, but clearly measurable (entries 10 and 11). However, to our surprise, the addition of $AgSbF_6$ and PivOH completely abolished the enantioselectivity, giving racemic **5a** (entry 12). Furthermore, when **Rh3** and $AgSbF_6$ were used without the addition of carboxylic acid, a complex mixture of products was obtained (entry 13). Along the same lines, the use of $AgBF_4$ or $AgNO_3$ led to full conversion, but resulted in a 1:1 mixture of **5a** and the cyclized product **6a** (entries 14 and 15). There is a striking difference between the enantiomeric ratios of these two products, which points towards two different mechanistic pathways.[15]

Table 1: Optimization of the enantioselective hydroarylation.[a]

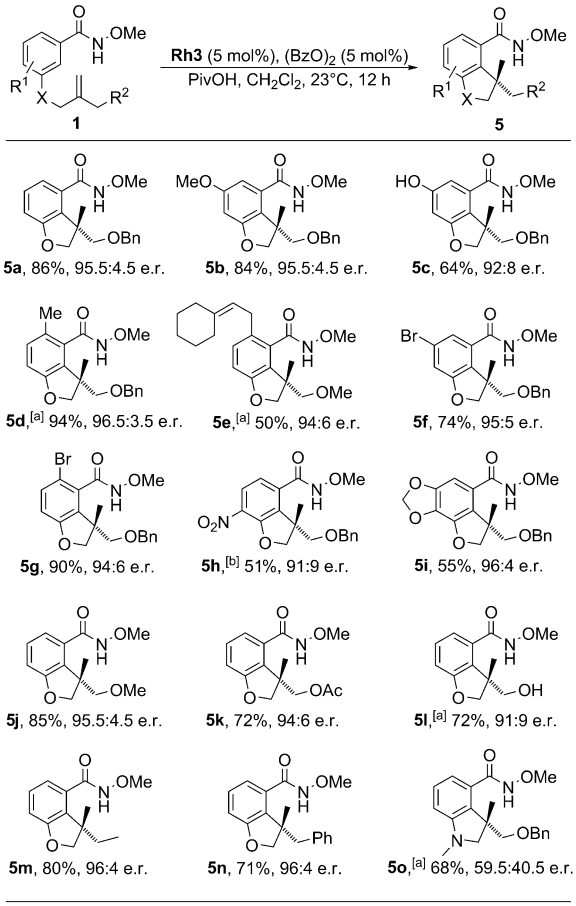


Entry	Rh	Additive	Solvent	T [°C]	Yield[b] [%]	e.r.[c]
1	**Rh1**	PivOH	DCE	50	66	78:22
2	**Rh2**	PivOH	DCE	50	80	69.5:30.5
3	**Rh3**	PivOH	DCE	50	83	95:5
4	**Rh4**	PivOH	DCE	50	83	90:10
5	**Rh5**	PivOH	DCE	50	84	88.5:11.5
6	**Rh3**	PivOH	MeOH	23	60	90.5:9.5
7	**Rh3**	PivOH	toluene	23	72	94:6
8	**Rh3**	PivOH	THF	23	19	89.5:10.5
9	**Rh3**	PivOH	CH_2Cl_2	23	87 (86)	95.5:4.5
10	**Rh3**	–	CH_2Cl_2	23	87	94.5:5.5
11	**Rh3**	AcOH	CH_2Cl_2	23	88	93.5:6.5
12	**Rh3**	PivOH, $AgSbF_6$	DCE	50	73	50:50
13	**Rh3**	$AgSbF_6$	DCE	50	20	67.5:32.5
14[d]	**Rh3**	$AgBF_4$	DCE	50	32	73:27
15[e]	**Rh3**	$AgNO_3$	DCE	50	20	92:8

[a] Reaction conditions: **1a** (0.05 mmol), RCO_2H (0.10 mmol), **Rh** (2.50 μmol), $(BzO)_2$ (2.50 μmol). [b] Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard; yields of isolated products are given in parentheses. [c] Determined by HPLC analysis on a chiral stationary phase. [d] **6a** was formed in 32% yield and 61:39 e.r. [e] **6a** was formed in 20% yield and 51:49 e.r. Bn = benzyl, Bz = benzoyl, DCE = 1,2-dichloroethane, Piv = pivaloyl.

With the optimized procedure in hand, we next explored the scope of the enantioselective hydroarylation. The reaction worked for both electron-rich and electron-poor arenes (Scheme 2). More delicate functional groups, such as a free phenol or a nitro substituent, were compatible with the reaction conditions. On the alkene moiety, a broad range of substituents were tolerated. For instance, different allylic ethers and even a free allylic alcohol were well tolerated. It is noteworthy that an allylic ester was a suitable substrate for this reaction and did not undergo ionization to the π-allyl species.[16] Moreover, hydrocarbon substituents on the olefin moiety, including ethyl and benzyl groups, did not interfere with the enantioselectivity. For some substrates,[17] the reaction had to be conducted at 50 °C because of lower reactivity or solubility. In these cases, we observed slightly reduced enantioselectivities. A substrate with a nitrogen tether (**1o**) displayed comparable reactivity for the cyclization, but the corresponding product was formed with poor enantioselectivity.

To shed light on the site selectivity and reversibility of the cyclometalation, the cyclization of **1m** was conducted in the presence of a large excess of deuterated acetic acid (20 equiv;



Scheme 2. Scope of the enantioselective cyclization. Reaction conditions: **1** (0.10 mmol), PivOH (0.10 mmol), **Rh3** (5.00 μmol), $(BzO)_2$ (5.00 μmol), CH_2Cl_2 (0.20 M), 23 °C, 12 h. Yields of isolated products are given. Enantiomeric ratios were determined by HPLC analysis on a chiral stationary phase. [a] At 50 °C. [b] At 80 °C.

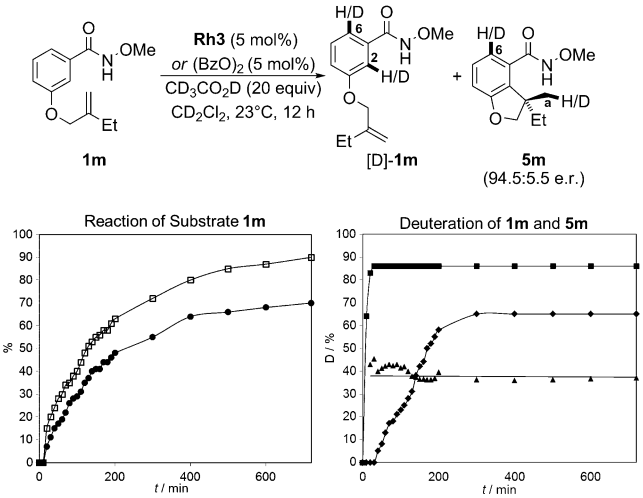


Figure 1. Kinetic profile (left) and deuteration studies (right) of **1m** and **5m** (conversion □; yield of **5m** ●; 2 position ◆; 6 position ■; *a* position ▲).

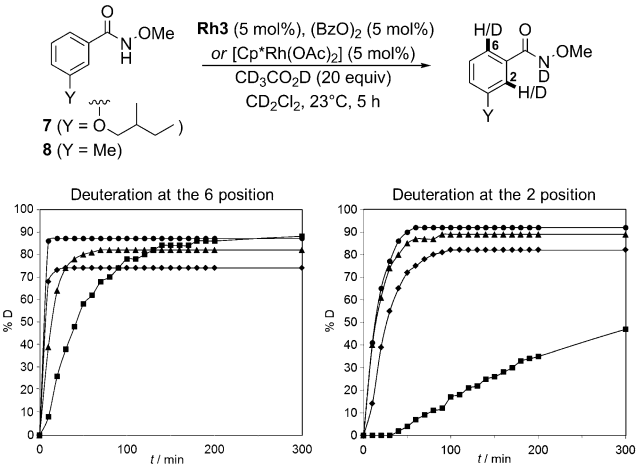
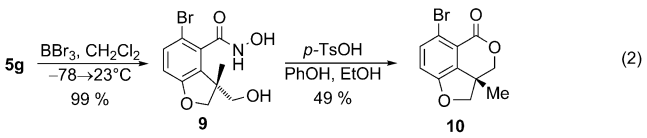


Figure 2. Kinetic deuteration profiles of **7** and **8** (**7** with $[Cp^*Rh(OAc)_2]$ ▲; **8** with $[Cp^*Rh(OAc)_2]$ ■; **8** with **Rh3** ◆; **7** with **Rh3** ●).

Figure 1). The reaction progressed steadily over twelve hours. In contrast to the reaction under optimized conditions, slightly lower reactivity and some decomposition of the substrate were observed, which are caused by the large excess of acetic acid. As expected, fast deuteration of the less hindered *ortho* position (C6) of **1m** occurs, reaching saturation within 20 minutes. During the course of the reaction, the ratio between **5m** and [D]-**5m** remains essentially constant. Despite the large excess of deuterated acid, significant quantities of **5m** with non-deuterated alkyl groups were formed. This finding suggests that the carboxylic acid that is generated during CMD and then bound to intermediate **2** remains at least partially in close proximity to the metal complex and then participates in the final protonation event. Furthermore, slow deuteration at the hindered *ortho* position (C2) of **1m** occurs, which indicates that migratory insertion of the olefin and protonation are competing events.

To investigate whether the olefin side chain plays the role of a secondary directing group, we used the hydrogenated congener **7**, which is not able to undergo a productive cyclization and *meta*-methyl-substituted derivative **8** as control substrates (Figure 2). With the chiral catalyst **Rh3**, the saturation levels for deuterium incorporation into substrate **7** were reached within ten minutes (Figure 2, left graph). The *meta*-methyl-substituted derivative **8** reacted more slowly, and saturation was observed after 30 minutes. For both substrates, the achiral complex with the more hindered Cp* ligand generally led to a slower reaction than the chiral complex with a 1,2-disubstituted cyclopentadienyl ligand.[18] As expected, cyclometalation was slower at the hindered *ortho* positions, and with both rhodium catalysts, longer times were required to reach saturation of the deuteration at the 2 position (Figure 2, right graph). Again, the chiral catalyst **Rh3** reacted faster. Furthermore, the differences between substrate **7** and **8** underline the importance of the alkoxy substituent as a secondary directing group for Rh-catalyzed reactions.[19]

To establish the absolute configuration of the cyclization products **5**, dihydrobenzofuran **5g** was deprotected with BBr_3 to furnish the free hydroxamic acid **9** [Eq. (2)]. Subsequent



(2)

cyclization under acidic conditions afforded lactone **10**. X-ray crystallographic analysis revealed that lactone **10** is *S*-configured.[20] The same configuration was attributed to the products **5** by analogy.

In summary, we have reported a mild enantioselective rhodium(III)-catalyzed hydroarylation to access functionalized dihydrobenzofurans that possess a quaternary stereocenter with very good enantioselectivities. Notably, the *meta*-alkoxy group acts as a secondary directing group, which allows for a selective reaction at the more hindered *ortho* position. Furthermore, we have shown that silver salts have a strong effect on the selectivity of the cyclization. Further studies will aim at improving our understanding of the selectivity-determining factors in reactions with chiral cyclopentadienyl ligands for enhancing their application in related synthetically versatile processes.

Received: October 22, 2013
Published online: December 6, 2013

Keywords: asymmetric catalysis · C—H activation · cyclopentadienyl ligands · hydroarylation · rhodium

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[19] A direct electronic influence or coordination to the rhodium complex can both be invoked.
[20] See the Supporting Information. CCDC 966109 (**10**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

