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Chiral Bicyclo[2.2.2]octane-Fused CpRh Complexes: Synthesis and Potential Use in Asymmetric C−H Activation

Guozhu Li, Xiaoqiang Yan, Jijun Jiang, Hao Liang, Chao Zhou, and Jun Wang*

Dedicated to Zhaozheng Wang on the occasion of his 100th birthday and Furong Jiang on the occasion of her 98th birthday

Abstract: *A new class of chiral* cyclopentadienyl rhodium(I) *complexes (CpRh^{I}) bearing C_2-symmetric chiral bridged-ring-fused Cp ligands was prepared and successfully applied to the asymmetric C-H activation reaction of N-methoxybenzamides with quinones, affording a series of chiral hydrophenanthridinones in up to 82% yield with up to 99% ee. Interestingly, structure analysis reveals that the side wall of the optimal chiral CpRh^{I} catalyst is vertically more extended, horizontally less extended, and closer to the metal center in comparison with the classic binaphthyl and spirobiindanyl CpRh^{I} complexes, which may account for its superior catalytic performance.*

Asymmetric synthesis involving the process of transition-metal-catalyzed inert C-H bond cleavage to form C-M bond constitutes one of the most significant but highly challenging research frontiers in modern organic chemistry.[1] Notably, Group 9 cyclopentadienylmetal (CpM^{III}, M = Co, Rh and Ir)-catalyzed asymmetric C-H activation[2] has achieved great success by using chiral Cp ligands,[3] artificial metalloenzymes,[4] achiral CpM in combination with chiral carboxylic acids or chiral sulfonates,[5] or chiral transient directing groups.[6] So far, the use of CpM catalysts derived from chiral Cp ligands has become one of the most general and effective methods to realize asymmetric C-H activation.[3a] Since the pioneering work by Cramer,[7] diverse chiral Cp ligands have been revealed, including cyclohexane-fused Cp **I**,[7-8] binaphthyl Cp **II**,[9],[10] spirobiindanyl Cp **III**,[11],[12] biphenyl Cp **IV**,[13] piperidine-fused Cp **V**,[14],[15] cyclopentane-fused Cp **VI**,[16] and ferrocenyl Cp **VII**[17] (Figure 1). Besides, optically pure planar chiral CpM catalysts bearing achiral Cp ligands obtained by chiral resolution were also disclosed.[18] Despite these advances, it remains highly important to continuously develop new chiral Cp ligands and build a rich library of CpM catalysts in order to meet the diverse catalyst needs by various reactions to be studied.

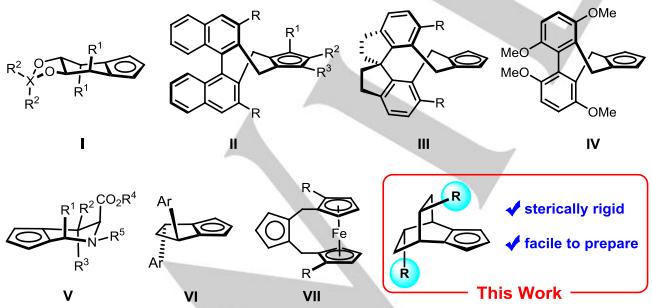
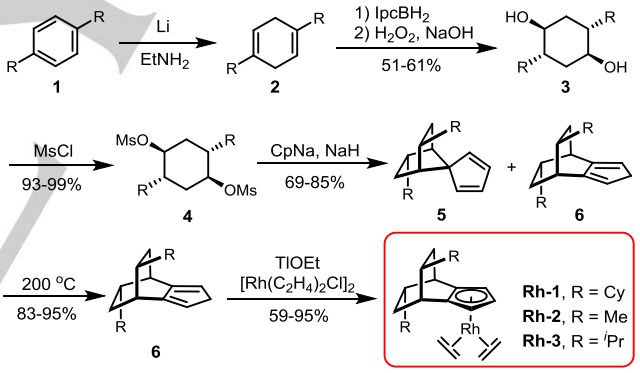


Figure 1. Chiral Cp ligands studied in asymmetric C-H activation.

Chiral bridged-ring-containing compounds play an important role in asymmetric synthesis. They are widely used as chiral auxiliary reagents, chiral reagents, chiral ligands and chiral catalysts. However, there are merely few studies on chiral bridged-ring-based Cp ligands.[19] The earliest example of chiral bridged-ring-based CpH was documented by Burgstahler et al. in 1976,[19i] which was derived from camphor. Later, from 1986 to 1991, some other relevant ligands were synthesized by Halterman,[19a, 19c, 19e, 19f, 19h] Vollhardt,[19e, 19f, 19h] Paquette,[19d, 19g] and Erker[19b] et al. However, surprisingly, during the past two decades these Cp ligands have not aroused much interest of chemists and been rarely studied. Driven by our continuous interest in exploring new chiral Cp catalysts[17] and new reactions[6, 12a, 12b, 20] for asymmetric C-H activation, recently we dedicated ourselves to developing chiral bridged-ring-based Cp catalysts for highly enantioselective C-H activation. As a result, we present herein the first synthesis and application of chiral bridged-ring-based CpRh catalyst in asymmetric C-H activation.



Scheme 1. Synthesis of chiral bridged-ring-containing CpRh(I) complexes.

Our study was commenced with the synthesis of C_2-symmetric bicyclo[2.2.2]octane fused cyclopentadienes that were initially reported by Vollhardt and Halterman in 1987.[19a, 19c, 19f] In comparison with other analogs derived from various chiral bridged-ring-containing natural products, such as camphor,[19b, 19e, 19g-i] nopol,[19g] and verbenone,[19d] its advantages include: 1) the starting materials don't rely on chiral pool, which makes the structure easier to tune; 2) the two faces of the Cp moiety are homotopic because of its C_2 symmetry, avoiding the formation of diastereomers when preparing CpM complexes. As depicted in Scheme 1, the 1,4-cyclohexadienes **2** prepared from Birch reduction of 1,4-dialkylbenzenes **1** were subjected to the asymmetric hydroboration-oxidation reaction with monoisopinocampheylborane ($IpcBH_2$, from (1*R*)-(+)-*α*-pinene) as the chiral reducing reagent to give the C_2-symmetric chiral *cis*-cyclohexane-1,4-diols **3**. Then, dimesylation of **3** with methanesulfonyl chloride gave the esters **4**, which were allowed to react with CpNa in the presence of NaH to provide a mixture

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of annulated cyclopentadienes **5** and **6**. After thermolysis at 200 °C, the desired chiral bridged-ring-fused cyclopentadienes **6** were obtained. Then the corresponding CpRh(I) complexes **Rh-1, Rh-2** and **Rh-3** were prepared by the classic thalliation/transmetallation procedure.[9b]

The structure of the complex **Rh-1** was confirmed by single crystal X-ray crystallographic analysis (Figure 2). Besides, the steric map of the binding pocket around the rhodium was generated with SambVca 2.1 tool.[21] For comparison, the single crystal structures and steric maps of the binaphthyl complex (*R*)-**Rh-4**[9b] and spirobiindanyl complex (*S*)-**Rh-5**[11] were also provided in Figure 2. In addition, the overlay of the crystal structures of **Rh-1** (red), (*R*)-**Rh-4** (blue) and (*S*)-**Rh-5** (green) were shown in Figure 3. According to the model proposed by Cramer and coworkers,[7] for **Rh-1** the cyclohexyl group in SW quadrant of the steric map acts as the side wall, which appears vertically more extended and horizontally less extended compared with the corresponding side walls in (*R*)-**Rh-4** and (*S*)-**Rh-5**. As a result, the metal center is more accessible for **Rh-1**, which may lead to some unique catalytic properties.

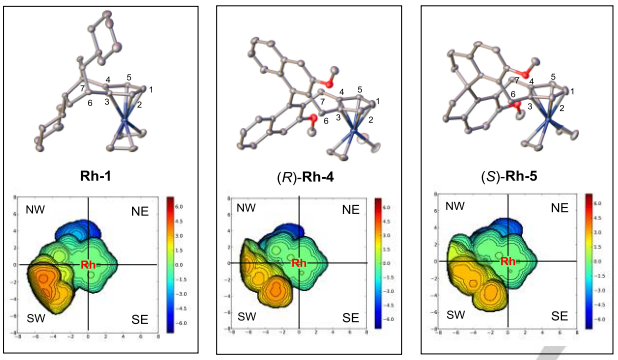

Figure 2. Crystal structures and steric maps of the chiral CpRh^{I} complexes **Rh-1**, (*R*)-**Rh-4** and (*S*)-**Rh-5**. The steric maps were generated by the SambVca 2.1 tool (Bondi radii scaled by 1.17, sphere radius 7.0 Å, mesh spacing 0.1 Å).

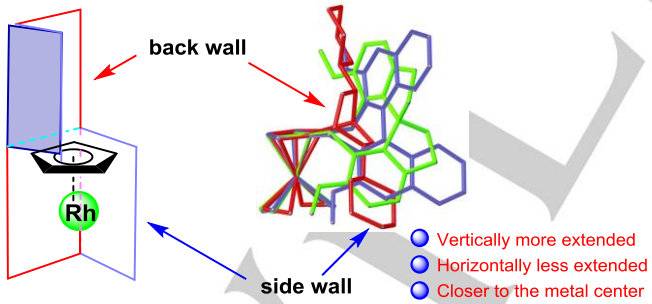

Figure 3. Overlay of the crystal structures of the chiral CpRh^{I} complexes **Rh-1** (red), (*R*)-**Rh-4** (blue) and (*S*)-**Rh-5** (green).

Additional interesting aspects were found by measuring some representative dihedral angles and Rh-C bond lenths of the above complexes (Table 1). On the one hand, the angle between the C3-C4-C5 plane and the C3-C4-C7 plane in **Rh-1** is significantly larger than those in (*R*)-**Rh-4** and (*S*)-**Rh-5** (entry 1). So is the angle between the C3-C4-C2 plane and the C3-C4-C6 plane (entry 2). It suggests the Cp plane of **Rh-1** bends the most significantly away from the metal, implying **Rh-1** experiences the strongest repulsion between its side wall and metal among all the three complexes. On the other hand, all the Rh-C bond lengths were measured (entries 3-7). Interestingly, the maximum difference between the Rh-C bond lengths in **Rh-1** is remarkably larger than those in (*R*)-**Rh-4** and (*S*)-**Rh-5** (entry 8). The extent of the geometry distortion of the halfsandwich CpRh complex can reflect the intensity of interaction between the side wall and the metal center. Thus, the side wall in **Rh-1** was expected to be closer to the metal center than those in (*R*)-**Rh-4** and (*S*)-**Rh-5**, which might great benefit stereocontrol for some reactions.

Table 1. Selected angles and bond lengths of the chiral CpRh^{I} complexes **Rh-1**, (*R*)-**Rh-4** and (*S*)-**Rh-5**.

entry	parameters	**Rh-1**[a]	(*R*)-**Rh-4**	(*S*)-**Rh-5**
1	the angle between the C3-C4-C5 plane and the C3-C4-C7 plane (°)	12.978 (14.013)	2.942	6.258
2	the angle between the C3-C4-C2 plane and the C3-C4-C6 plane (°)	13.041 (10.972)	7.811	8.082
3	Rh-C1 bond length (Å)	2.235 (2.247)	2.266	2.240
4	Rh-C2 bond length (Å)	2.241 (2.271)	2.263	2.239
5	Rh-C3 bond length (Å)	2.300 (2.312)	2.216	2.210
6	Rh-C4 bond length (Å)	2.335 (2.291)	2.263	2.282
7	Rh-C5 bond length (Å)	2.211 (2.183)	2.229	2.227
8	maximum difference between two Rh-C bond lengths (Å)	0.124 (0.129)	0.050	0.072

[a] As two independent molecules with slightly differed conformations were found in the lattice, the data in parentheses is for another molecule.

Then, the potential utility of these newly developed chiral bridged-ring-fused CpRh catalysts in the asymmetric C-H activation was explored. Recently, we reported an asymmetric C-H activation reaction of N-methoxybenzamides and quinones to prepare various synthetically important tricyclic hydrophenanthridinones.[20a, 22] Though the reaction conditions were intensively optimized, however, the highest enantioselectivity for the model reaction of N-methoxybenzamide **7a** and quinone **8a** can only reach 85% ee in the presence of the optimal catalyst (*R*)-**Rh-5** (5 mol%). In addition, the ee values for most of the examples in the substrate scope examination are lower than 90%. To our delight, when the newly developed chiral CpM catalyst **Rh-1** was employed in this reaction, the desired product **9a** was obtained in 54% yield with 91% ee (Table 2, entry 1). Solvent screening showed acetone was the best solvent, giving the product in 71% yield with 92% ee (entry 2). When the reaction was conducted at a lower temperature of 0 °C for 36 h, the product was obtained in 77% yield with 97% ee (entry 3). Further lowering the reaction temperature to -20 °C led to no improvement of enantioselectivity (entry 4). The catalyst loading could be reduced to 2.5 mol% without affecting the reaction outcome (entry 5). It should be noted that while the lactone **9a'** was observed as the major byproduct, the lactam **9a''** from

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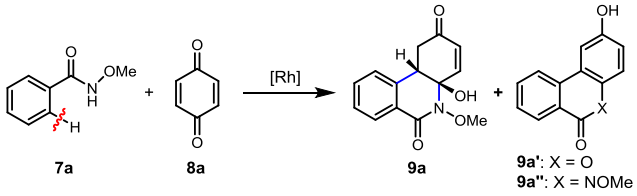
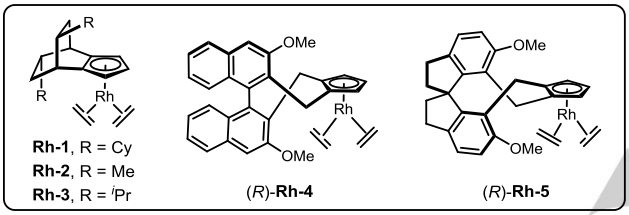
dehydration-aromatization of **9a** was not detected. When the chiral catalysts **Rh-2** and **Rh-3** were employed, inferior results were given (entries 6 and 7). For comparison, the binaphthyl catalyst (*R*)-**Rh-4** and the spirobiindanyl catalyst (*R*)-**Rh-5** were also tested under the same reaction conditions. The products were obtained in lower yields (54% and 62%), suggesting that the horizontally less extended feature of **Rh-1** might make the metal center more accessible by the reactants (entries 8 and 9). Moreover, lower enantioselectivities were observed (52% and 77% ee). The superior performance of the chiral bridged-ring-based CpRh catalyst in this reaction strongly indicates that it can well complement the existing chiral CpM catalysts. Finally, the optimal reaction conditions were identified as that shown in entry 5. For more details of optimization of reaction conditions, please see the Supporting Information.

Table 2. Optimization of reaction conditions.[a]



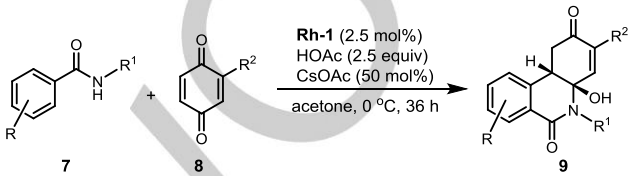


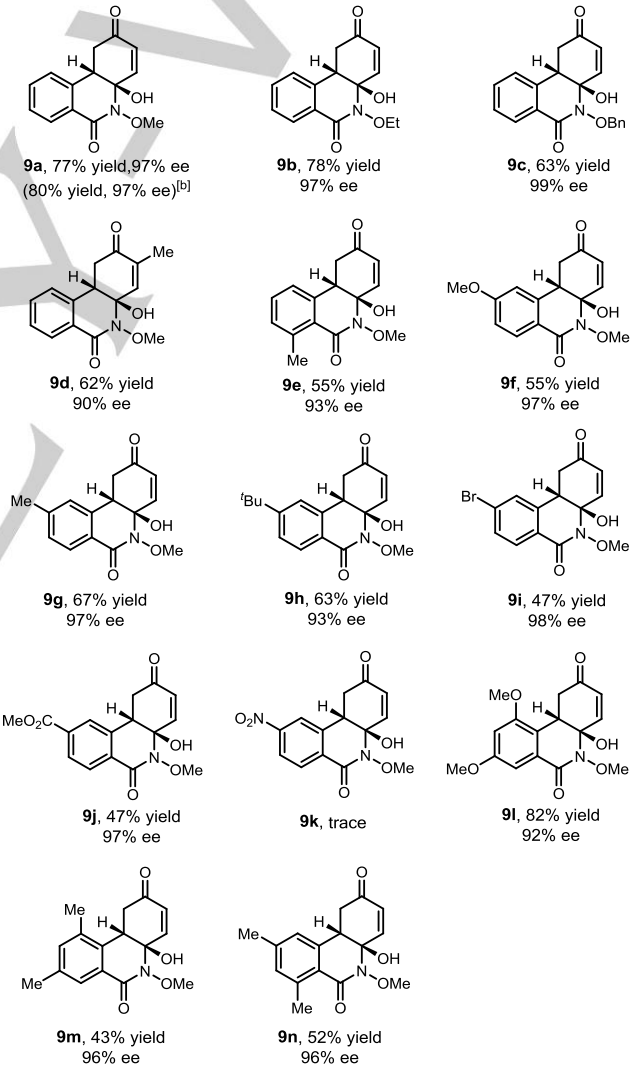
entry	[Rh] (mol%)	T (°C)	t (h)	yield (%)	ee (%)
1	**Rh-1** (5)	30	12	54	91
2	**Rh-1** (5)	30	12	71	92
3	**Rh-1** (5)	0	36	77	97
4	**Rh-1** (5)	-20	48	77	97
5	**Rh-1** (2.5)	0	36	**77**	**97**
6	**Rh-2** (2.5)	0	36	66	76
7	**Rh-3** (2.5)	0	36	81	62
8	(*R*)-**Rh-4** (2.5)	0	36	54	52
9	(*R*)-**Rh-5** (2.5)	0	36	62	77

[a] Under N_2 atmosphere, **7a** (0.1 mmol, 1.0 equiv), **8a** (2.0 equiv), [Rh], CsOAc (50 mol%), HOAc (2.5 equiv) in dichloroethane (DCE, 0.5 mL, for entry 1) or acetone (0.5 mL, for entries 2-9).

With the optimized reaction conditions in hand, the substrate scope was investigated (Table 3). When different N-alkoxy benzamide substrates were tested, high yields and high enantioselectivities were observed (**9a-c**). But the substrate N-methylbenzamide proved unreactive. When *p*-toluquinone was used to react with N-methoxy benzamide **7a**, the product **9d** was obtained in 62% yield with 90% ee. Then, various substituted N-methoxy benzamides were examined. The *ortho*-methyl substituted benzamide could be converted to the product **9e** in 55% yield with 93% ee. Then, several *para*-substituted benzamides were evaluated, providing the corresponding products **9f-9j** in good yields (47-67%) and high enantioselectivities (93-98% ee). But when *p*-nitrobenzamide was used, trace amount of product was obtained, which might be due to the strong electron-withdrawing property of nitro group. Moreover, some disubstituted amide substrates were also investigated, delivering the desired products **9l-9n** in 43-82% yield with 92-96% ee. It should be stressed that the outcomes achieved here are far superior to those in our previous studies. To check the practicality of this reaction, the model reaction was conducted on a large scale with 2.0 mmol of benzamide **7a**, affording the targeted product **9a** in 80% yield and 97% ee.

Table 3. Substrate scope.[a]





[a] Under N_2 atmosphere, **7** (0.1 mmol, 1.0 equiv), **8** (2.0 equiv), **Rh-1** (2.5 mol%), HOAc (2.5 equiv), CsOAc (50 mol%), acetone (0.5 mL), at 0 °C for 36 h. [b] Large scale reaction with **7a** (2.0 mmol, 1.0 equiv).

In summary, we have developed a new class of chiral CpRh catasts bearing C_2-symmetric chiral bridged-ring-fused Cp ligands for the asymmetric C-H activation. Structure analysis reveals that the side wall of the optimal catalyst **Rh-1** is vertically more extended, horizontally less extended, and closer to the metal center in comparison with the widely used binaphthyl based catalyst **Rh-4** and the spirobiindanyl based catalyst **Rh-5**. Moreover, **Rh-1** showed superior catalytic performance over **Rh-4** and **Rh-5** in the asymmetric C-H activation of N-methoxybenzamides and quinones, which may be ascribed to its unique structural features. A series of chiral tricyclic products were prepared in up to 82% yield with up to 99% ee. Further applications of these chiral bridged-ring-fused Cp metal complexes to other valuable asymmetric C−H activation are currently under exploration in our lab.

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Keywords: asymmetric catalysis • C-H activation • chiral bridged-ring-fused cyclopentadiene • rhodium • steric map

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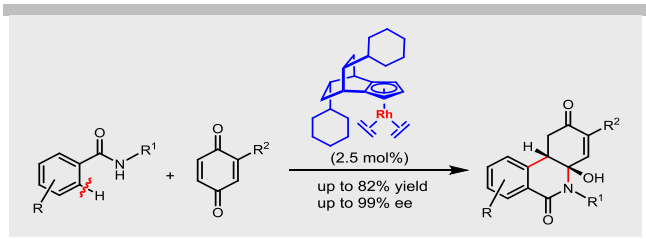

A new class of chiral cyclopentadienyl rhodium(I) *complexes bearing C_2-symmetric chiral bridged-ring-fused Cp ligands has been prepared and successfully applied to the asymmetric C-H activation reaction of N-methoxybenzamides with quinones, affording a series of chiral hydrophenanthridinones in up to 82% yield with up to 99% ee.*

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