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A New Class of C_2-Symmetric Chiral Cp Ligand Derived from Ferrocene Scaffold: Design, Synthesis and Application

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Abstract: A new class of C_2-symmetric, chiral cyclopentadienyl ligand based on planar chiral ferrocene backbone was developed. A series of its corresponding rhodium(I), iridium(I), and ruthenium(II) complexes were prepared as well. In addition, the rhodium(I) complexes were evaluated in the asymmetric catalytic intramolecular amidoarylation of olefin-tethered benzamides via C-H activation.

Transition-metal catalyzed asymmetric C-H activation constitutes one of the most important and challenging research frontiers in modern organic chemistry.[1] In 2012, Cramer et al.[2] and Rovis, Ward et al.[3] independently realized an asymmetric C-H activation by respectively using the mannitol derived chiral cyclopentadienyl (Cp) rhodium catalyst and the artificial enzyme bound Cp rhodium catalyst. Remarkably, it is the first time to show that chiral cyclopentadienylmetal (CpM)[4] catalyst is highly potential to realize asymmetric C-H activation reactions[5] characterized by involving inert C-H bond cleavage and simultaneous C-M bond formation, which is of milestone significance. The universal applicability of this strategy was subsequently well demonstrated by numerous follow-up studies.[6] As three free coordination sites are demanded by the CpM catalyzed C-H activation reactions, the effective chiral Cp metal catalysts should be those generated from chiral Cp ligands with noncoordinating substituents.[6] Whereas the ones derived from chiral Cp ligands with coordinating substituents[7] or from the complexation of both achiral Cp ligands and chiral ligands[8] are inapplicable, though they have been found useful in other types of asymmetric reactions.

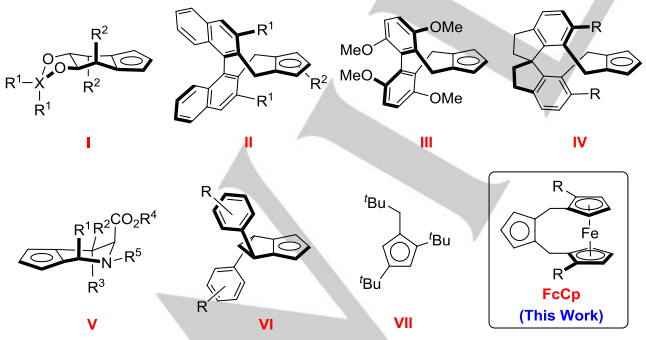
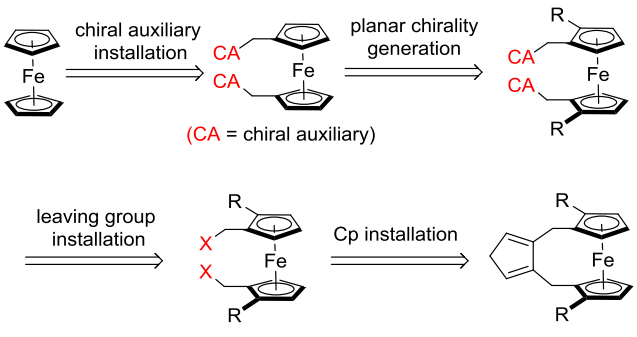


Figure 1. Cp ligands studied in asymmetric C-H activation reactions

Therefore, it is crucial to develop suitable chiral Cp ligands with noncoordinating substituents. However, in the past eight years, merely few classes of chiral Cp ligands were developed for the study of asymmetric C-H activation reactions (Figure 1), including the chiral Cp ligands **I**,[9] **II**,[10] **III** and **VI** respectively derived from mannitol,[2, 11] binaphthol[12, 13], biphenol[13z], and cinnamaldehyde[14, 15] by Cramer et al., the binaphthol derived Cp ligand **II** with multisubstituents on the Cp ring[16] as well as the chiral spirobiindane Cp ligand **IV**[17, 18] by You et al., the chiral piperidine fused Cp ligand **V** by Antonchick, Waldmann and et al.[19, 20] Interestingly, a planar chiral Cp rhodium catalyst bearing a prochiral Cp ligand **VII** was also developed by Perekalin et al.[21] Nevertheless, these limited families of Cp ligands can hardly meet the ever-growing needs of the rapid development of asymmetric C-H activation. Therefore, exploring new chiral Cp ligands must continue being a key and urgent task for chemists. Herein, we present a new class of C_2-symmetric chiral Cp ligands FcCp containing a planar chiral ferrocene[22] backbone. It is noteworthy that previously reported chiral Cp ligands are all based on centrally (**I**, **V**, **VI**) or axially (**II**, **III**, **IV**) chiral skeletons, whereas examples based on planar chiral scaffold have never been reported so far. In addition, preparation and characterization of a series of corresponding rhodium(I), iridium(I), and ruthenium(II) complexes are reported. Application of rhodium(I) complexes in the asymmetric catalytic C-H activation to synthesize various chiral fused tricyclic compounds is demonstrated as well.

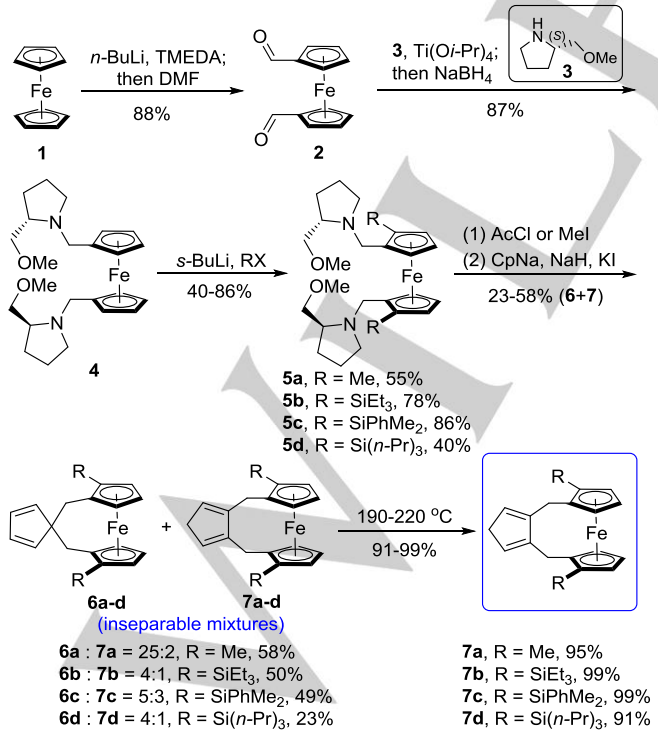
As depicted in Scheme 1, our designed synthetic route for the new Cp ligand FcCp includes initial installation of two chiral auxiliaries on each Cp ring of ferrocene, generation of the planar chiral 1,1',2,2'-tetrasubstituted ferrocene by diastereoselective di-*ortho*-functionalization, conversion of chiral auxiliaries to suitable leaving groups, and finally installation of Cp motif by twofold nucleophilic substitutions.



Scheme 1. Design of Cp ligands with planar chiral ferrocene scaffolds

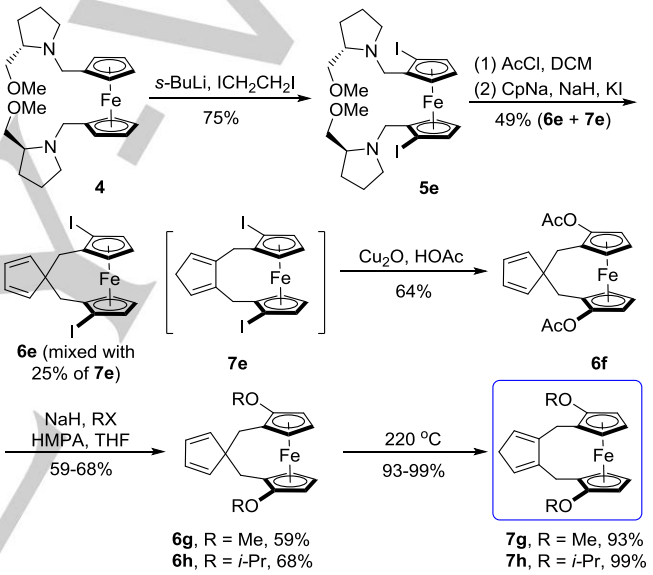
As shown in Scheme 2, to commence our synthesis, 1,1'-diformylferrocene **2** was prepared from ferrocene **1** in 88% yield by a dilithiation-diformylation sequence.[23] It was then allowed to react with (*S*)-2-(methoxymethyl)pyrrolidine **3** to form the chiral ferrocenyl diamine **4** in 87% yield via reductive amination with $Ti(Oi\text{-}Pr)_4$ and $NaBH_4$.[24] Highly diastereoselective difunctionalization of **4** was achieved by di-*ortho*-lithiation with *s*-

BuLi and subsequent quenching with various electrophiles (RX) according to Marinetti's protocol (>95:5 dr),[25] affording diverse planar chiral 1,1',2,2'-tetrasubstituted ferrocenes **5a-d** in 40-86% yields as pure single diastereomers. As quaternary ammonium group at the α-position of ferrocene could act as a leaving group,[26] we first attempted the Cp installation by using ferrocene quaternary ammonium as intermediate. Delightedly, it was found the ferrocene ammonium iodide prepared from **5a** and MeI reacted smoothly with CpNa in the presence of NaH, KI in DMF, affording the desired Cp derivatives as an inseparable mixture of **6a** and **7a** (**6a**:**7a** = 25:2) in 58% yield over two steps. Alternatively, inspired by the chemistry that dimethylamino group in the α-position of the ferrocene could be facilely substituted by chlorine upon treatment with methylchloroformate via a α-ferrocenyl carbocation intermediate,[27] we envisioned that the chiral pyrrolidine moieties in ferrocenyl diamine **5** might be cleaved and replaced by chlorines too under similar reaction conditions. Given the potential instability of ferrocenyl dichloride,[28] it would be better to generate and use it directly into the following Cp installation step without purification operations. Along this line, we decided to attempt the low-boiling acyl chloride (b.p. 51 °C) instead of chloroformate as the chlorination reagent and dichloromethane as the solvent, which could all be removed readily and thoroughly after reaction, simply by rotary evaporation under reduced pressure. In addition, the acetyl pyrrolidine byproduct produced in the chlorination step may not affect the Cp installation reaction. Gladly, this protocol proved feasible. The ferrocenyl dichloride crude product prepared from **5b-d** and AcCl reacted well with CpNa in the presence of NaH, providing the desired Cp derivatives as inseparable mixtures of isomers **6b-d** and **7b-d** in 23-50% yield over two steps. Subsequently, heating the mixture of isomers **6** and **7** at 190-220 °C exclusively gave the targeted product FcCp **7a-d** in 91-99% yield via thermal rearrangement of the spiro isomers **6a-d** to **7a-d**.



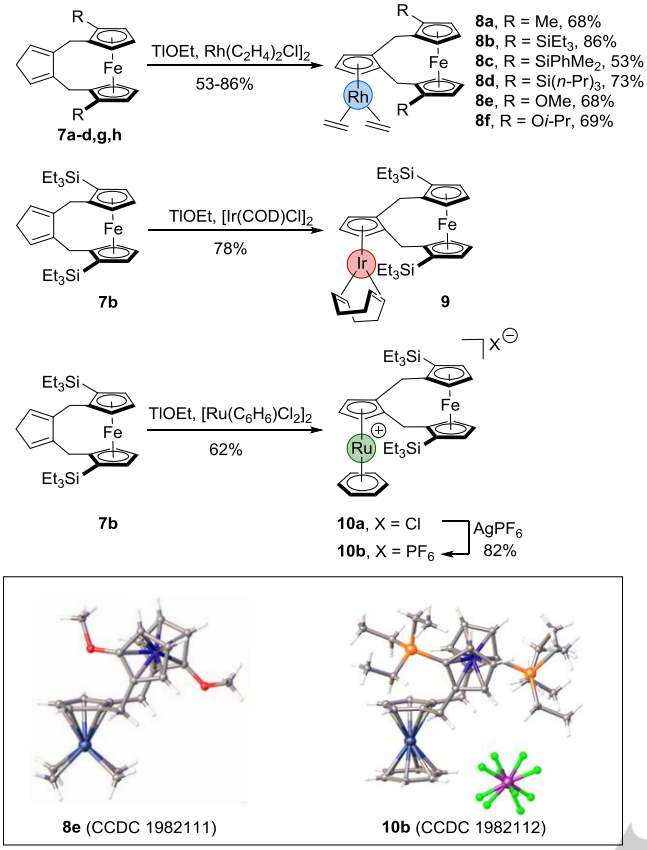
Scheme 2. Synthesis of 2,2'-dimethyl and disilyl ferrocenyl Cp ligands **7a-d**

Besides the above 2,2'-dimethyl and disilyl ferrocenyl Cp ligands **7a-d**, we also successfully synthesized 2,2'-dialkoxyferrocenyl Cp ligands **7g-h**. As illustrated in Scheme 3, according to our sequential chlorination and Cp installation protocol, the diiodoferrocene **5e** obtained from the highly diastereoselective iodination[29] of diaminoferrocene **4** could be conveniently transformed to the ferrocenyl Cp product as an inseparable mixture of **6e** and **7e** (**6e**:**7e** = 3:1) in 49% yield over two steps. By treating this mixture with HOAc and cupric oxide, the di-acetoxylated product **6f** was obtained in 64% yield (based on the amount of **6e**).[30] Delightedly, converting acetoxy to alkoxy could be facilely achieved by a one-pot two-step procedure involving de-acylation with NaH-HMPA and in-situ quenching with alkylhalide.[31] For instance, upon quenching with MeI and *i*-PrI, the dialkoxy ferrocenes **6g** and **6h** were respectively obtained in 59% and 68% yield. Finally, thermal rearrangement of **6g** and **6h** at 220 °C led to the desired dialkoxyferrocenyl Cp ligands **7g** and **7h** in 93% and 99% yield, respectively.



Scheme 3. Synthesis of 2,2'- dialkoxyferrocenyl Cp ligands **7g-h**

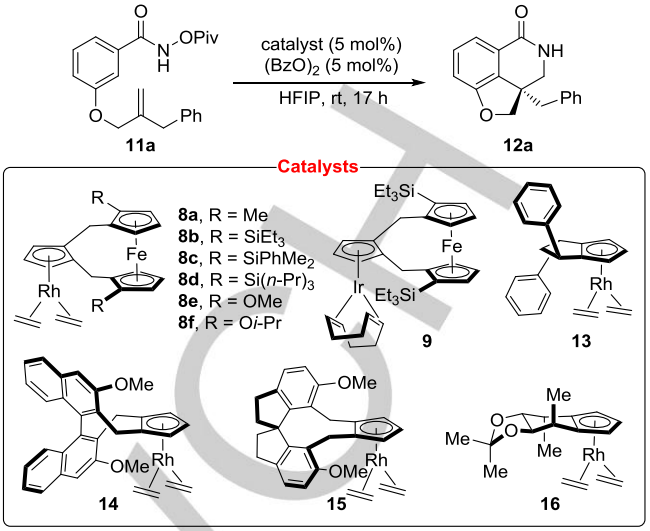
As shown in Scheme 4, with various chiral ferrocenyl Cp ligands **7** in hand, the corresponding CpM (M = Rh, Ir, Ru) metal complexes were prepared according to typical procedures,[12, 14] including the $CpRh^{I}$ complexes **8a-f** (53-86% yield), the $CpIr^{I}$ complex **9** (78% yield) and the $CpRu^{II}$ complexes **10a-b** (62-82% yield). Notably, the structures and absolute configurations of chiral Cp ligands were unambiguously confirmed by X-ray crystallographic analysis of the $CpRh^{I}$ complex **8e** and the $CpRu^{II}$ complex **10b**. Interestingly, it was found from these crystal structures that the chiral ferrocenyl moieties fold somewhat away from the metal centres, which could be attributed to the high flexibility of the ferrocenyl Cp rings. However, it is hard to predict to what extent the ferrocenyl moiety will continue keeping this favoured conformation in solution. It was envisioned that this new class of chiral CpM catalysts might perform differently from the existing ones in the asymmetric C-H activation.



Scheme 4. Synthesis of chiral ferrocenyl CpM (M = Rh, Ir, Ru) complexes

Then, the potential utility of these new CpM^{I} complexes in asymmetric catalysis was examined with the intramolecular amidoarylation of the olefin-tethered benzamide **11a** as the model reaction, which was previously reported by Rovis et al.[32] and Glorius et al.,[33] but in a non-asymmetric fashion. In addition, during the exploration of asymmetric intramolecular hydroarylation of alkenes, **12d** was once observed as the side product by Cramer et al.[13c] Among the rhodium precatalysts **8a-f**, it was found that **8b** bearing $SiEt_3$ substituents was optimal, furnishing the tricyclic product **12a** in >99% yield with 67% ee (Table 1, entries 1-6). In contrast, the CpIr^{I} complex **9** was unable to catalyze this reaction (entry 7). Moreover, for the sake of comparisons, some widely used chiral CpRh^{I} precatalysts **13-16** reported by Cramer et al. and You et al. were evaluated in this reaction. However, the cinnamaldehyde derived chiral CpRh^{I} **13** gave >99%yield whereas with poor enantioselectivity of 14% ee (entry 8). The atropchiral binaphthyl CpRh^{I} **14** gave comparable enantioselectivity of 70% ee in contrast to **8b**, but in an inferior yield of 50% (entry 9). Employing chiral spirobiindane CpRh^{I} **15** only led to trace amount of product with moderate enantioselectivity of 52% ee (entry 10). Lastly, the mannitol derived chiral CpRh^{I} **16** provided a good yield of 82% but with low enantioselectivity of 37% ee (entry 11). These results explicitly indicated that the ferrocene based Cp catalysts well complemented the existing chiral Cp catalysts in terms of the catalytic property.

Table 1. Evaluation of various Cp complexes in asymmetric C-H activation

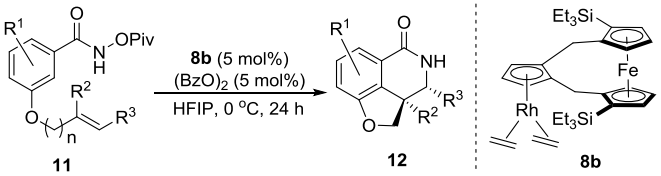


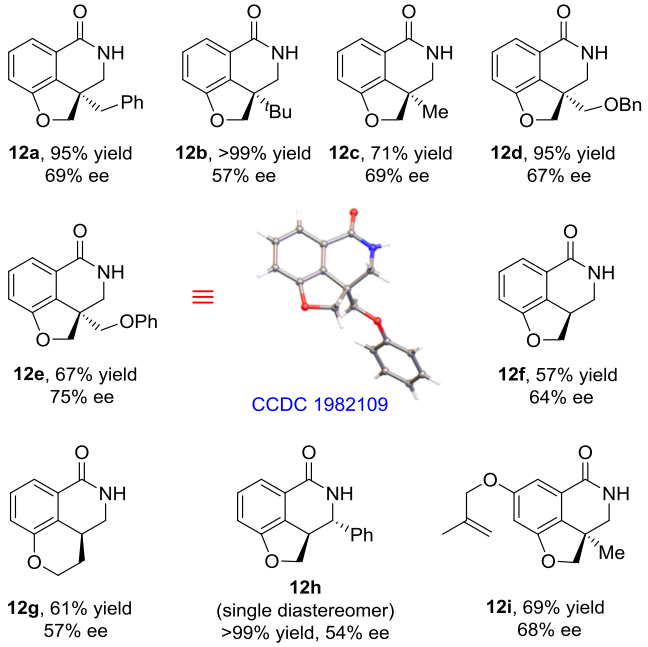
entry[a]	catalyst	yield (%)[b]	ee (%)[c]
1	**8a**	>99	19
2	**8b**	>99	67
3	**8c**	92	49
4	**8d**	76	66
5	**8e**	82	18
6	**8f**	>99	28
7	**9**	n.r.	-
8	**13**	>99	14
9	**14**	50	70
10	**15**	4	52
11	**16**	82	37

[a]**11a** (0.05 mmol, 1.0 equiv), catalyst (5 mol%), $(BzO)_2$ (5 mol%), hexafluoroisopropanol (HFIP, 0.2 mL), rt, 17 h. [b]Determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard. [c]Determined by HPLC.

Further studies revealed that, in the presence of precatalyst **8b** and $(BzO)_2$ at 0 ℃, diverse alkene-tethered benzamides, such as those bearing 1,1-disubstituted alkenes (**11a-e, i**), monosubstituted alkenes with varied chain length (**11f-g**), and 1,2-disubstituted alkene (**11h**), could all be smoothly converted into the corresponding tricyclic lactams in moderate to good yields and enantioselectivities (Table 2). Notably, the enantiopure lactam **12e** was facilely obtained via recrystallization from dichloromethane/methanol (6:1), and the absolute configuration of the major enantiomer of **12e** was determined to be *S* by X-ray crystallographic analysis.

Table 2. Substrate scope[a]





[a]**11** (0.1 mmol, 1.0 equiv), catalyst **8b** (5 mol%), $(BzO)_2$ (5 mol%), HFIP (0.4 mL, 0.25 M), 0 °C, 24 h. Isolated yields were reported.

In conclusion, a new class of C_2-symmetric, chiral Cp ligands based on planar chiral ferrocene scaffolds has been developed. A series of corresponding chiral $CpRh^{I}$, $CpIr^{I}$, and $CpRu^{II}$ complexes have been prepared. The potential use of these metal complexes as catalysts has been demonstrated by a chiral $CpRh^{III}$ catalyzed asymmetric intramolecular amidoarylation of olefin-tethered benzamides via C-H activation. Further applications of these chiral ferrocenyl Cp metal complexes and relatives into other asymmetric reactions are still under exploration.

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Keywords: chiral cyclopentadiene • asymmetric C-H activation • planar chiral • ferrocene • rhodium

[1] a) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861; b) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704; c) K. M. Engle, J. Q. Yu, *J. Org. Chem.* **2013**, *78*, 8927; d) C. Zheng, S.-L. You, *RSC Adv.* **2014**, *4*, 6173; e) F. Colobert, J. Wencel-Delord, *Synlett* **2015**, *26*, 2644; f) S.-L. You, *Asymmetric Functionalization of C-H Bonds*, The Royal Society of Chemistry, **2015**; g) J. He, M. Wasa, K. S. L. Chan, Q. Shao, J. Q. Yu, *Chem. Rev.* **2017**, *117*, 8754; h) C. G. Newton, S.-G. Wang, C. C. Oliveira, N. Cramer, *Chem. Rev.* **2017**, *117*, 8908; i) Y. F. Yang, X. Hong, J. Q. Yu, K. N. Houk, *Acc. Chem. Res.* **2017**, *50*, 2853; j) T. G. Saint-Denis, R. Y. Zhu, G. Chen, Q. F. Wu, J. Q. Yu, *Science* **2018**, *359*; k) J. Diesel, N. Cramer, *ACS Catal.* **2019**, *9*, 9164; l) G. Liao, T. Zhou, Q. J. Yao, B. F. Shi, *Chem. Commun.* **2019**, *55*, 8514; m) J. Loup, U. Dhawa, F. Pesciaioli, J. Wencel-Delord, L. Ackermann, *Angew. Chem. Int. Ed.* **2019**, *58*, 12803; n) Ł. Woźniak, N. Cramer, *Trends Chem.* **2019**, *1*, 471.

[2] B. Ye, N. Cramer, *Science* **2012**, *338*, 504.

[3] T. K. Hyster, L. Knörr, T. R. Ward, T. Rovis, *Science* **2012**, *338*, 500.

[4] For a relevant review, see: R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965.

[5] Selected examples for chiral CpM catalyzed other types of asymmetric reactions: a) G. Erker, A. A. H. van der Zeijden, *Angew. Chem. Int. Ed.* **1990**, *29*, 512; b) A. Gutnov, B. Heller, C. Fischer, H. J. Drexler, A. Spannenberg, B. Sundermann, C. Sundermann, *Angew. Chem. Int. Ed.* **2004**, *43*, 3795; c) B. Heller, A. Gutnov, C. Fischer, H. J. Drexler, A. Spannenberg, D. Redkin, C. Sundermann, B. Sundermann, *Chem. Eur. J.* **2007**, *13*, 1117; d) M. Hapke, K. Kral, C. Fischer, A. Spannenberg, A. Gutnov, D. Redkin, B. Heller, *J. Org. Chem.* **2010**, *75*, 3993.

[6] a) B. Ye, N. Cramer, *Acc. Chem. Res.* **2015**, *48*, 1308; b) C. G. Newton, D. Kossler, N. Cramer, *J. Am. Chem. Soc.* **2016**, *138*, 3935; c) T. Yoshino, S. Satake, S. Matsunaga, *Chem. Eur. J.* **2020**, doi: 10.1002/chem.201905417.

[7] a) U. Siemeling, *Chem. Rev.* **2000**, *100*, 1495; b) Y. Matsushima, K. Onitsuka, T. Kondo, T. Mitsudo, S. Takahashi, *J. Am. Chem. Soc.* **2001**, *123*, 10405; c) B. M. Trost, M. Rao, A. P. Dieskau, *J. Am. Chem. Soc.* **2013**, *135*, 18697.

[8] a) A. Hafner, R. O. Duthaler, R. Marti, G. Rihs, P. Rothe-Streit, F. Schwarzenbach, *J. Am. Chem. Soc.* **1992**, *114*, 2321; b) K. Murata, T. Ikariya, R. Noyori, *J. Org. Chem.* **1999**, *64*, 2186; c) E. P. Kündig, C. M. Saudan, F. Viton, *Adv. Synth. Catal.* **2001**, *343*, 51.

[9] The earliest example of chiral Cp ligand **I** was repoted by Halterman and Vollhardt: a) R. L. Halterman, K. P. C. Vollhardt, *Tetrahedron Lett.* **1986**, *27*, 1461; b) R. L. Halterman, K. P. C. Vollhardt, *Organometallics* **1988**, *7*, 883.

[10] The earliest example of chiral Cp ligand **II** was repoted by Halterman: a) S. L. Colletti, R. L. Halterman, *Tetrahedron Lett.* **1989**, *30*, 3513; b) S. L. Colletti, R. L. Halterman, *Organometallics* **1991**, *10*, 3438.

[11] For other applications of chiral Cp ligand **I**, see: C. Duchemin, N. Cramer, *Chem. Sci.* **2019**, *10*, 2773.

[12] B. Ye, N. Cramer, *J. Am. Chem. Soc.* **2013**, *135*, 636.

[13] For other applications of chiral Cp ligand **II**, see: a) G. Song, W. N. O. Wylie, Z. Hou, *J. Am. Chem. Soc.* **2014**, *136*, 12209; b) B. Ye, N. Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 7896; c) B. Ye, P. A. Donets, N. Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 507; d) J. Zheng, S. L. You, *Angew. Chem. Int. Ed.* **2014**, *53*, 13244; e) N. Cramer, B. Ye, *Synlett* **2015**, *26*, 1490; f) M. Dieckmann, Y. S. Jang, N. Cramer, *Angew. Chem. Int. Ed.* **2015**, *54*, 12149; g) D. Kossler, N. Cramer, *J. Am. Chem. Soc.* **2015**, *137*, 12478; h) S. Reddy Chidipudi, D. J. Burns, I. Khan, H. W. Lam, *Angew. Chem. Int. Ed.* **2015**, *54*, 13975; i) J. Zheng, S.-B. Wang, C. Zheng, S.-L. You, *J. Am. Chem. Soc.* **2015**, *137*, 4880; j) M. V. Pham, N. Cramer, *Chem. Eur. J.* **2016**, *22*, 2270; k) H. L. Teng, Y. Luo, B. Wang, L. Zhang, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2016**, *55*, 15406; l) C. Zheng, J. Zheng, S.-L. You, *ACS Catal.* **2016**, *6*, 262; m) Y.-S. Jang, M. Dieckmann, N. Cramer, *Angew. Chem. Int. Ed.* **2017**, *56*, 15088; n) D. Kossler, N. Cramer, *Chem. Sci.* **2017**, *8*, 1862; o) D. Kossler, F. G. Perrin, A. A. Suleymanov, G. Kiefer, R. Scopelliti, K. Severin, N. Cramer, *Angew. Chem. Int. Ed.* **2017**, *56*, 11490; p) Y. Luo, H. L. Teng, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2017**, *56*, 9207; q) Y. Sun, N. Cramer, *Angew. Chem. Int. Ed.* **2017**, *56*, 364; r) H. L. Teng, Y. Luo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2017**, *139*, 16506; s) Y. S. Jang, L. Wozniak, J. Pedroni, N. Cramer, *Angew. Chem. Int. Ed.* **2018**, *57*, 12901; t) B. Shen, B. Wan, X. Li, *Angew. Chem. Int. Ed.* **2018**, *57*, 15534; u) Y. Sun, N. Cramer, *Angew. Chem. Int. Ed.* **2018**, *57*, 15539; v) Y. Sun, N. Cramer, *Chem. Sci.* **2018**, *9*, 2981; w) H.-L. Teng, Y. Ma, G. Zhan, M. Nishiura, Z. Hou, *ACS Catal.* **2018**, *8*, 4705; x) G. Zhan, H. L. Teng, Y. Luo, S. J. Lou, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2018**, *57*, 12342; y) M. Brauns, N. Cramer, *Angew. Chem. Int. Ed.* **2019**, *58*, 8902; z) C. Duchemin, G. Smits, N. Cramer, *Organometallics* **2019**, *38*, 3939; aa) R. Mi, G. Zheng, Z. Qi, X. Li, *Angew. Chem. Int. Ed.* **2019**, *58*, 17666; ab) K. Ozols, Y. S. Jang, N. Cramer, *J. Am. Chem. Soc.* **2019**, *141*, 5675; ac) M. Tian, D. Bai, G. Zheng, J. Chang, X. Li, *J. Am. Chem. Soc.* **2019**, *141*, 9527; ad) S. G. Wang, N. Cramer, *Angew. Chem. Int. Ed.* **2019**, *58*, 2514; ae) S. G. Wang, Y. Liu, N. Cramer, *Angew. Chem. Int. Ed.* **2019**, *58*, 18136; af) X. Yang, G. Zheng, X. Li, *Angew. Chem. Int. Ed.* **2019**, *58*, 322; ag) W. Chen, J. Li, H. Xie, J. Wang, *Org. Lett.* **2020**, *22*, 3586; ah) L. Kong, X. Han, S. Liu, Y. Zou, Y. Lan, X. Li, *Angew. Chem. Int. Ed.* **2020**, *59*,

7188; ai) S. J. Lou, Z. Mo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2020**, *142*, 1200; aj) F. Wang, Z. Qi, Y. Zhao, S. Zhai, G. Zheng, R. Mi, Z. Huang, X. Zhu, X. He, X. Li, *Angew. Chem. Int. Ed.* **2020**, doi: 10.1002/anie.202002208; ak) G. Zheng, Z. Zhou, G. Zhu, S. Zhai, H. Xu, X. Duan, W. Yi, X. Li, *Angew. Chem. Int. Ed.* **2020**, *59*, 2890.

[14] S. G. Wang, S. H. Park, N. Cramer, *Angew. Chem. Int. Ed.* **2018**, *57*, 5459.

[15] For other applications of chiral Cp ligand **VI**, see: S. H. Park, S.-G. Wang, N. Cramer, *ACS Catal.* **2019**, *9*, 10226.

[16] W. J. Cui, Z. J. Wu, Q. Gu, S. L. You, *J. Am. Chem. Soc.* **2020**, *142*, 7379.

[17] J. Zheng, W. J. Cui, C. Zheng, S. L. You, *J. Am. Chem. Soc.* **2016**, *138*, 5242.

[18] For other applications of chiral Cp ligand **IV**, see: a) J. Zheng, S. B. Wang, C. Zheng, S. L. You, *Angew. Chem. Int. Ed.* **2017**, *56*, 4540; b) T. Li, C. Zhou, X. Yan, J. Wang, *Angew. Chem. Int. Ed.* **2018**, *57*, 4048; c) H. Li, X. Yan, J. Zhang, W. Guo, J. Jiang, J. Wang, *Angew. Chem. Int. Ed.* **2019**, *58*, 6732; d) X. Yan, P. Zhao, H. Liang, H. Xie, J. Jiang, S. Gou, J. Wang, *Org. Lett.* **2020**, *22*, 3219.

[19] Z. J. Jia, C. Merten, R. Gontla, C. G. Daniliuc, A. P. Antonchick, H. Waldmann, *Angew. Chem. Int. Ed.* **2017**, *56*, 2429.

[20] For other applications of chiral Cp ligand **V**, see: a) G. Shan, J. Flegel, H. Li, C. Merten, S. Ziegler, A. P. Antonchick, H. Waldmann, *Angew. Chem. Int. Ed.* **2018**, *57*, 14250; b) H. Li, R. Gontla, J. Flegel, C. Merten, S. Ziegler, A. P. Antonchick, H. Waldmann, *Angew. Chem. Int. Ed.* **2019**, *58*, 307.

[21] E. A. Trifonova, N. M. Ankudinov, A. A. Mikhaylov, D. A. Chusov, Y. V. Nelyubina, D. S. Perekalin, *Angew. Chem. Int. Ed.* **2018**, *57*, 7714.

[22] For a relevant book, see: L. X. Dai, X. L. Hou, *Chiral Ferrocenes in Asymmetric Catalysis*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, **2010**.

[23] U. T. Mueller-Westerhoff, Y. Zheng, G. Ingram, *J. Organomet. Chem.* **1993**, *463*, 163.

[24] S. Bhattacharyya, *Tetrahedron Lett.* **1994**, *35*, 2401.

[25] a) A. Voituriez, A. Panossian, N. Fleury-Brégeot, P. Retailleau, A. Marinetti, *J. Am. Chem. Soc.* **2008**, *130*, 14030; b) A. Voituriez, A. Panossian, N. Fleury-Brégeot, P. Retailleau, A. Marinetti, *Adv. Synth. Catal.* **2009**, *351*, 1968.

[26] a) G. W. Gokel, D. Marquarding, I. K. Ugi, *J. Org. Chem.* **1972**, *37*, 3052; b) L. Xiao, K. Mereiter, W. Weissensteiner, M. Widhalm, *Synthesis* **1999**, *1999*, 1354.

[27] a) L. Tebben, M. Neumann, G. Kehr, R. Fröhlich, G. Erker, S. Losi, P. Zanello, *Dalton Trans.* **2006**, *2006*, 1715; b) C. Usener, G. Kehr, R. Fröhlich, B. Wibbeling, C. Mück-Lichtenfeld, G. Erker, *Organometallics* **2010**, *29*, 3852.

[28] M. Hisatome, M. Yoshihashi, K. Masuzoe, K. Yamakawa, Y. Iitaka, *Organometallics* **1987**, *6*, 1498.

[29] M. Neel, A. Panossian, A. Voituriez, A. Marinetti, *J. Organomet. Chem.* **2012**, *716*, 187.

[30] G. Werner, H. Butenschön, *Organometallics* **2013**, *32*, 5798.

[31] A. Yamashita, A. Toy, *Synth. Commun.* **1989**, *19*, 755.

[32] T. A. Davis, T. K. Hyster, T. Rovis, *Angew. Chem. Int. Ed.* **2013**, *52*, 14181.

[33] Z. Shi, M. Boultadakis-Arapinis, D. C. Koester, F. Glorius, *Chem. Commun.* **2014**, *50*, 2650.

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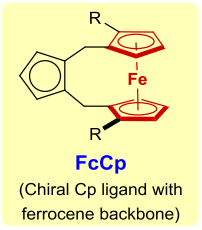

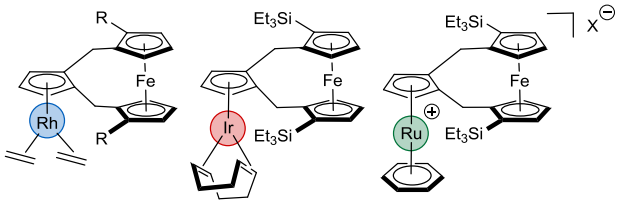

A new class of C_2-symmetric, chiral cyclopentadienyl ligand based on planar chiral ferrocene backbone was developed. A series of its corresponding rhodium(I), iridium(I), and ruthenium(II) complexes were prepared as well. In addition, the rhodium(I) complexes were evaluated in the asymmetric catalytic intramolecular amidoarylation of olefin-tethered benzamides via C-H activation.

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