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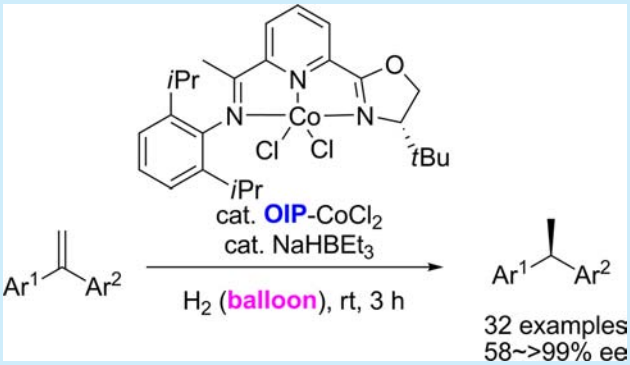
Cobalt-Catalyzed Asymmetric Hydrogenation of 1,1-Diarylethenes

Jianhui Chen, Chenhui Chen, Chonglei Ji, and Zhan Lu*

Department of Chemistry, Zhejiang University, 866 Yuhangtang Road, Hangzhou 310058, China

Supporting Information

ABSTRACT: Highly enantioselective cobalt-catalyzed hydrogenation of 1,1-diarylethenes was developed by using bench-stable chiral oxazoline iminopyridine−cobalt complexes as precatalysts. A unique *o*-chloride effect was observed to achieve high enantioselectivity. Easy removal as well as further transformations of the chloro group make this protocol a potentially useful alternative to synthesize various chiral 1,1-diarylethanes. This process can be successfully performed under 1 atm of hydrogen at room temperature on gram scale.



The 1,1-diarylalkane scaffold is an important motif in many biologically active molecules,[1] among which 1,1-diarylethanes show potential treatment of various diseases, such as inflammation, insomnia, cancer, and obesity (Figure 1).[2] On account of their potential applications in pharmaceuticals, the development of efficient methods for asymmetric synthesis of 1,1-diarylethanes has received much attention.[3−5] Among a variety of catalytic processes,[3,4] asymmetric hydrogenation of 1,1-diarylalkenes is one of the most efficient and useful methods.[5] Transition-metal-catalyzed highly enantioselective hydrogenation of 1,1-diarylethenes is challenging due to the difficulty in differentiating two enantiotopic faces in prochiral substrates.

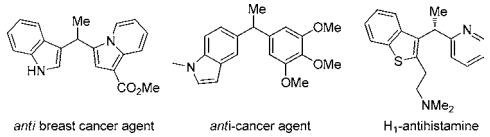
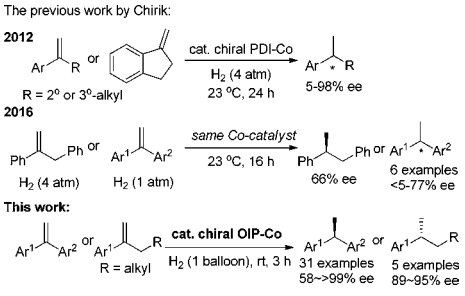


Figure 1. Bioactive 1,1-diarylethanes.

Although precious metal catalysts including rhodium, iridium, and ruthenium have been used for hydrogenation of 1,1-disubstituted alkenes to achieve high enantioselectivities,[6] the high cost of removing trace amounts of precious metals for pharmaceutical utility and potential depletion of precious metals make the development of green, sustainable base-metal catalysts for hydrogenation highly desirable. Furthermore, the distinct electronic structures and unique redox ability of base-metals provide numerous opportunities for exploring new reactivity.

Because of the lower costs and toxicity of cobalt catalysts, rapid progress has been made in cobalt-mediated or -catalyzed transformations during the last two decades.[7] However, cobalt-catalyzed enantioselective hydrogenation of alkenes were rare.[8] Ohgo et al have investigated the asymmetric hydrogenation of alkenes using dimethylglyoximatocobalt(II) complexes to afford the products in 7−49% ee.[8a] Pfaltz employed chiral semicorrin cobalt complex-catalyzed asymmetric hydrogenation of α,β-unsaturated esters to raise the ee value to 96%.[8b] Very recently, Chirik and co-workers successfully utilized rapid evaluation of libraries of chiral diphosphine ligands for asymmetric hydrogenation of alkenes under 34 atm of hydrogen gas, but only limited substrates have been investigated.[9] By using moisture- and air-sensitive C1-asymmetric bisiminopridine cobalt complexes, the same group studied the asymmetric hydrogenation of α-2°-alkyl styrene with high levels of enantioselectivity.[10] After our revised manuscipt was submitted, Co-catalyzed enantioselective hydrogenation of 1,1-diarylalkenes was reported by Chirik group, however, the enantioselectivities were less than idea (<5−77% ee). To the best of our knowledge, chiral base metal-catalyzed highly enantioselective hydrogenation of 1,1-diarylalkenes has not previously been described (Scheme 1).

Scheme 1. Cobalt-Catalyzed Asymmetric Hydrogenation of 1,1-Disubstituted Alkenes



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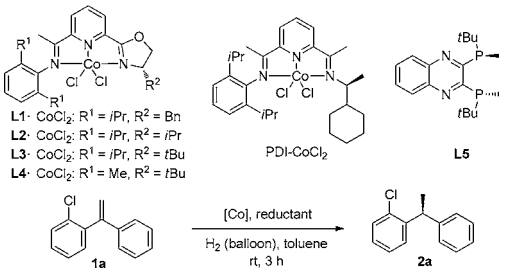
Recently, we have independently synthesized the enantiopure oxazoline iminopridine ligands[11,12] and their bench-stable iron and cobalt complexes that could catalyze highly enantioselective hydroboration and hydrosilylation of 1,1-disubstituted alkenes. These results led us to consider that hydrogen as a mild and clean reagent may also act as a selective hydrogen donor for asymmetric hydrogenation. Herein, we reported a highly enantioselective cobalt-catalyzed hydrogenation reaction of 1,1-diarylethenes.

To benefit from further transformations, we chose 1-(2′-chlorophenyl)-1-phenylethene (**1a**) as the substrate in which the *o*-chloro group can be easily removed or further transferred via cross-coupling reactions. Mixing 5 mol % of a cobalt complex **L1**·$CoCl_2$ with a reductant and **1a** in a solution of toluene at room temperature under 1 atm of hydrogen resulted in formation of the hydrogenation product **2a** in 77% conversion and 68% ee without any dechlorination product (Table 1).

Table 1. Optimization Studies for Asymmetric Hydrogenation of Alkenes[a]



entry	[Co]	reductant	yield[b] (%)	ee[c] (%)
1	**L1**·$CoCl_2$	$NaBHEt_3$	77	68
2	**L2**·$CoCl_2$	$NaBHEt_3$	99	81
3	**L3**·$CoCl_2$	$NaBHEt_3$	99	90
4	**L4**·$CoCl_2$	$NaBHEt_3$	16	82
5	**L3**·$CoCl_2$	$NaBHsBu_3$	87	89
6	**L3**·$CoCl_2$	$LiBHEt_3$	79	89
7	**L3**·$CoCl_2$		0	
8		$NaBHEt_3$	0	
9	$CoCl_2$	$NaBHEt_3$	0	
10	**L3**	$NaBHEt_3$	0	
11	**PDI**·$CoCl_2$	$NaBHEt_3$	37	77
12	**L5** + $CoCl_2$	$NaBHEt_3$	<5	

[a]Using **1a** (0.5 mmol), cat. (5 mol %), reductant (15 mol %), and toluene (1 mL) with a hydrogen balloon. [b]Yields determined by ^1H NMR analysis. [c]Ee values were determined by chiral HPLC analysis.

Sterically bulky substituents on oxazoline increased both reactivity and enantioselectivity (entries 1−3). Although the less sterically hindered imine precatalyst could also catalyze the reaction, either the reactivity or enantioselectivity was compromised. Different reductants, such as $NaBHsBu_3$ or $LiBHEt_3$, were tested instead of $NaBHEt_3$, affording the hydrogenation product with good levels of enantioselectivity, albeit with slightly low yields. Control reactions were conducted and did not occur without ligands, $CoCl_2$, cobalt precatalysts, or reductants, which implied that all these components were necessary for this transformation. The chiral cobalt catalysts used in the previous literature[9,10] were not efficient for this asymmetric transformation (entries 11 and 12).

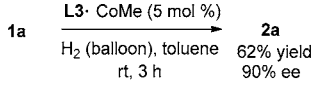
The scope of the cobalt-catalyzed asymmetric hydrogenation of 1,1-diarylethenes is illustrated in Scheme 2. Additional chloro substitution at the 3-, 4-, or 5-position on 2-chlorobenzene (**1b−d**) was tolerated, in which 1-(2,4-dichlorophenyl)-1-phenylethene (**1c**) gave the best enantioselectivity and 1-(2,5-dichlorophenyl)-1-phenylethene (**1d**) afforded **2d** with a slightly lower reactivity and enantioselectivity. 1,1-Diarylethenes containing 2-chlorobenzene with both electron-donating and electron-withdrawing properties all participated to give the corresponding 1,1-diarylethanes **2e−g** in 89−95% ee. Additionally, the reaction of **1h** containing a pyrrolic group on the 5-position of 2-chlorobenzene could also afford **2h** smoothly in 92% ee.

Substitutions on the phenyl ring were also investigated. The *p*- and *m*-methoxy groups on the phenyl rings yielded the hydrogenation products in 90% ee (**2i**) and 95% ee (**2j**), respectively. To our delight, the catalytic system distinguished between the chloro and methoxy group to afford **2k** in 85% ee. Although free alcohols inhibited the reactivity, TBS-protected phenols (**2n**) and alcohols (**2o**) were well compatible under the reaction conditions. Interestingly, the reaction of electron-deficient 3-CF_3 substrate afforded **2p** in >99% yield and >99% ee. 3-Phenyl or 4-phenyl substitutions were suitable for the reaction to give **2q** or **2r** with 89% ee, respectively. A dimethylamino group at the 4-position (**1s**) was also tolerated. The substrates with disubstitutions are good partners to give **2t−v** in 89−95% ee. The chiral indolyl derivatives (**2w** and **2x**) could be obtained in 93% yield with 96% ee, 97% yield, and 93% ee, respectively.

Various *ortho*-substitutions were also examined. 1,1-Diarylethenes with *o*-fluoro (**3a**) and methoxy (**3b**) substitutions participated to give the hydrogenation products in >99% yield, albeit, with a slightly low ee. To our delight, the simple alkyl groups such as methyl (**3c**) and ethyl (**3d**) could give **4c** and **4d** with good enantioselectivities. The reaction of 1-(2-bromophenyl)-1-phenylethene showed poor reactivity (<5% yield). 1-(1′-Naphthyl)-1-phenylethane can also be accessed using this method with 77% ee.[13] The *o*- and *m*-methylphenyl group could easily be deffiantiated through this method to afford **4f** with 86% ee. The reaction of **3g** and **3h** gave the hydrogenation product with 91% ee and 89% ee, respectively. The reaction of **3h** using 1 mol % of **L3**·$CoCl_2$ could afford **4h** in 80% yield and 88% ee.[14] The steric effect on the enantioselectivity is presented in the SI as a function of Charton steric parameters. There were no solid rules to determine the high enantioselectivity; however, more steric bulky groups seemed to promote the enantioselectivity, and the chloro group showed a unique property.

To prove the broad scope of this protocol, the asymmetric hydrogenation reactions of α-alkylstyrenes were also conducted smoothly to afford **4i−m** with 89−95% ee (Scheme 3). These transformations could be efficiently completed in 1 h without alkene-isomerization products.

To propose the initiation step of the reaction, the active cobalt species **L3**·CoMe[10a,12a] was synthesized to catalyze the reaction of **1a**, which afforded **2a** with 90% ee (eq 1).[15]



(1)

To showcase the utility of this transformation, a gram-scale reaction was easily conducted using a hydrogen balloon. The chloro group could also undergo further palladium-catalyzed transformations to afford the corresponding dechlorination,[16] phenylation, vinylation, and boronation products in excellent

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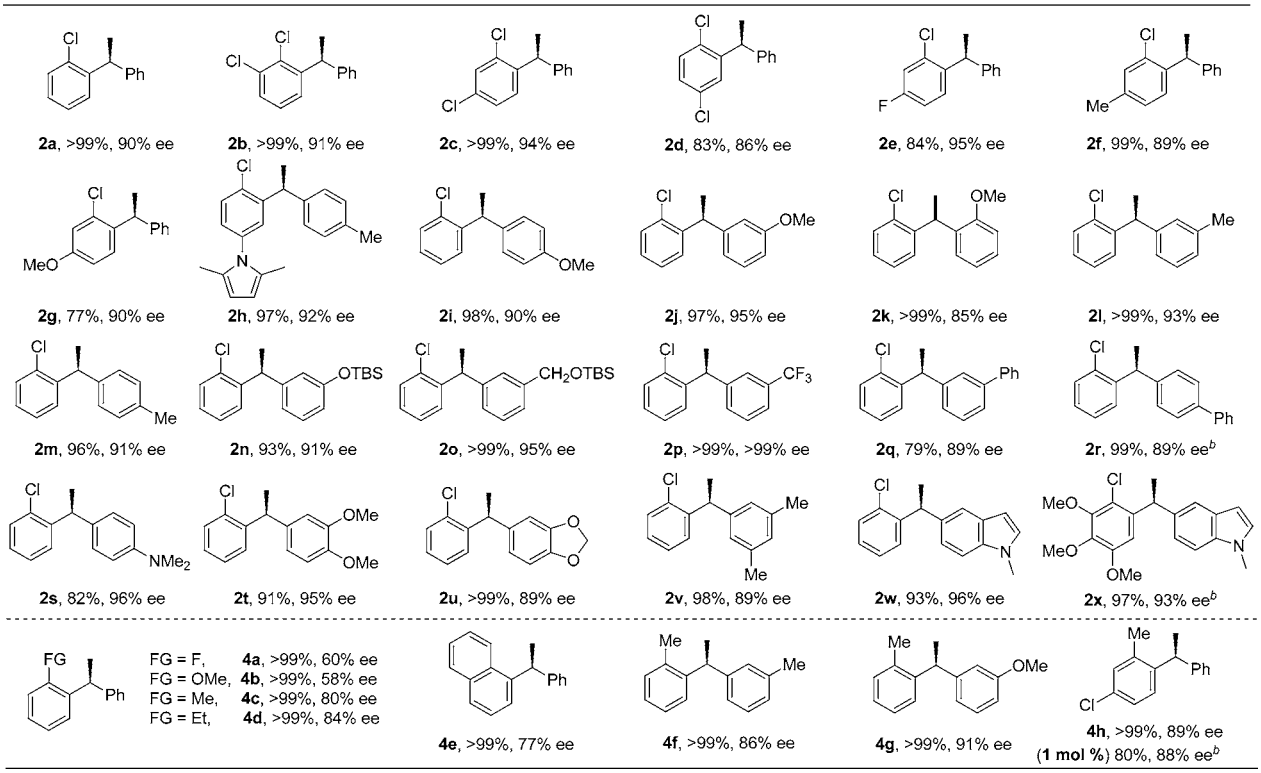
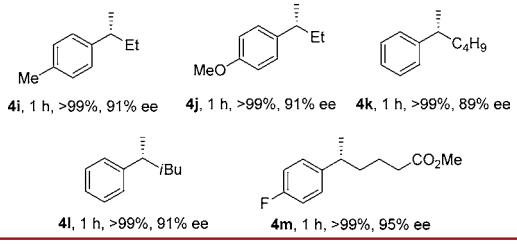
Scheme 2. Asymmetric Hydrogenation of 1,1-Diarylethenes[a]



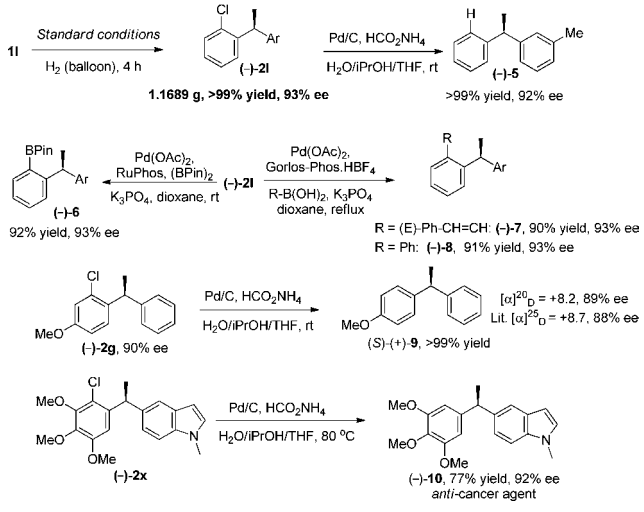
[a]Standard conditions: alkenes (0.5 mmol), **L3**·$CoCl_2$ (0.025 mmol), $NaBHEt_3$ (0.075 mmol) in 1 mL of toluene at rt with a hydrogen balloon for 3 h. [b]12 h.

Scheme 3. Asymmetric Hydrogenation of α-Alkylstyrenes



yields (Scheme 4).[17] We determined the absolute configuration of hydrogenation products by comparison of optical rotation after dechlorination with the known compound **9**.[18]

Scheme 4. Further Derivatizations



Additionally, the *anti*-cancer agent **10** could be obtained from **2x** via a dechlorination process.

In summary, we have successfully developed a cobalt-catalyzed highly enantioselective hydrogenation reaction of 1,1-diarylethenes using bench-stable chiral oxazoline iminopyridine ligands. A unique *o*-chloride effect was observed to achieve high enantioselectivity. Since the removal and further transformation of the chloro group are easily realized, this method provides a potetially useful alternative to synthesize various chiral 1,1-diarylethanes. Mechanistic studies and further applications of asymmetric base-metal catalysis are ongoing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00453.

Experimental procedures and characterization data for all new compounds (PDF)

X-ray crystallographic data for **4h** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: luzhan@zju.edu.cn.

Notes

The authors declare no competing financial interest.

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(13) The absolute configuration of hydrogenation product can be determined by the optical rotation through comparison with the literature data; see ref 3g.

(14) CCDC no. 1457562.

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