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A Novel Chiral Bisphosphine-Thiourea Ligand for Asymmetric Hydrogenation of β,β-Disubstituted Nitroalkenes

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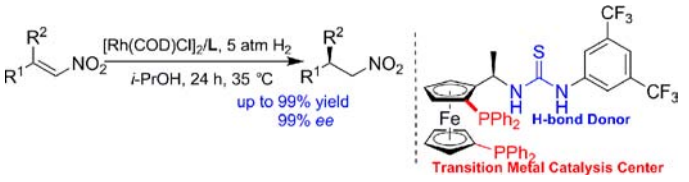
ABSTRACT



A novel chiral bisphosphine-thiourea ligand was developed and applied in the highly enantioselective hydrogenation of β,β-disubstituted nitroalkenes (up to 99% yield and 99% *ee*). With low catalytic loading (0.25 mol %), 98% *ee* and 98% conversion were obtained. The thiourea group takes on an important role in this catalytic system.

The concept of combining metal catalysis with organocatalysis has been developed as a powerful tool to promote unprecedented transformations in recent years.[1,2] Some effective strategies, such as cooperative catalysis,[3] synergistic catalysis,[4] and sequential/relay catalysis,[5] have been established. However, the incompatibility of catalysts, substrates, intermediates, and solvents is the main challenge. To solve this problem, a different strategy has been developed, wherein a single functional molecule combines

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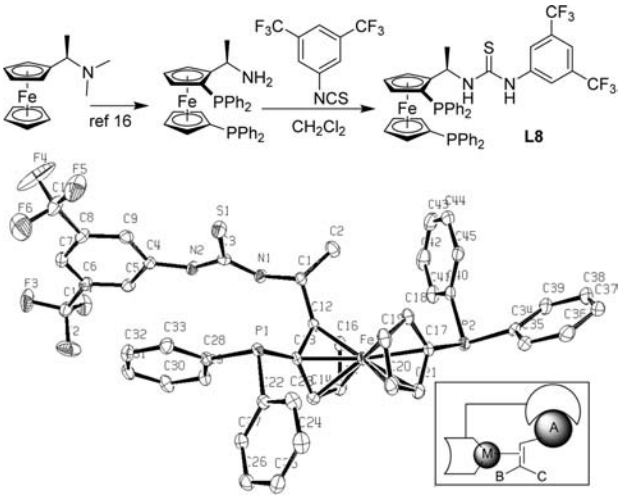
activation modes of metal catalysis and organocatalysis.[6−11] These catalysts could be easily tuned by modifying or replacing the metal complex and the organocatalyst unit.

Hydrogen bonding of (thio)urea derivatives has been widely applied in the catalyst design as one of the important noncovalent interactions.[12] Although (thio)ureaphosphine ligands have been reported as metal-P,O(S)-type catalysts and self-assembling supramolecular catalysts in asymmetric catalysis, there are no effective metal/bisphosphine-thiourea catalytic systems with thiourea as an activating and directing group in asymmetric hydrogenation.[2j,13,14] Thus, we designed a novel catalyst involving a metal species coordinated by a chiral ferrocenyl bisphosphine[15] as the scaffold and a tunable thiourea[12] as the hydrogen bond donor (Scheme 1). Based on previous reports,[6−15] we envisioned that the incorporation of the thiourea group could activate substrates and provide an excellent chiral environment in catalysis. The ligand was easily prepared from readily accessible Ugi's amine (Scheme 1).[16]

Rhodium catalyzed asymmetric hydrogenation of olefins is a powerful method to construct versatile chiral molecules.[17] However, highly enantioselective hydrogenation of nitroalkenes remains a challenge. Compared with biocatalytic reduction,[18] transfer hydrogenation,[19,20] and conjugate addition,[21] direct hydrogenation is potentially more practical if high enantioselectivities and turnovers could be achieved. Only recently we reported the first example catalyzed by Rh-Josiphos with modest to good enantioselectivities (82−96% *ee*) at a 1.5−3 mol % catalyst loading under 50 atm of H_2.[22] Since thioureas have been approved for the activation of the nitro group in organocatalysis, we reasoned that asymmetric hydrogenation of nitroalkenes should be ideal to test our new catalysts. Indeed, this novel strategy proved to be efficient in this transformation: up to 98% *ee* and 98% conversion were obtained with a 0.25 mol % catalyst loading under 5 atm of H_2.

Scheme 1. Ligand **L8** Design, Synthesis, and X-ray Structure (All hydrogen atoms are omitted for clarity)



At the beginning of our study, we examined the catalytic activity of **L8** with different metal sources (Table 1, entries

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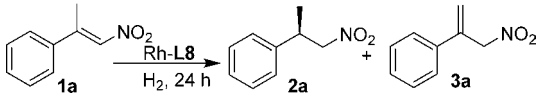
Table 1. Metal Source and Solvent Screening[a]



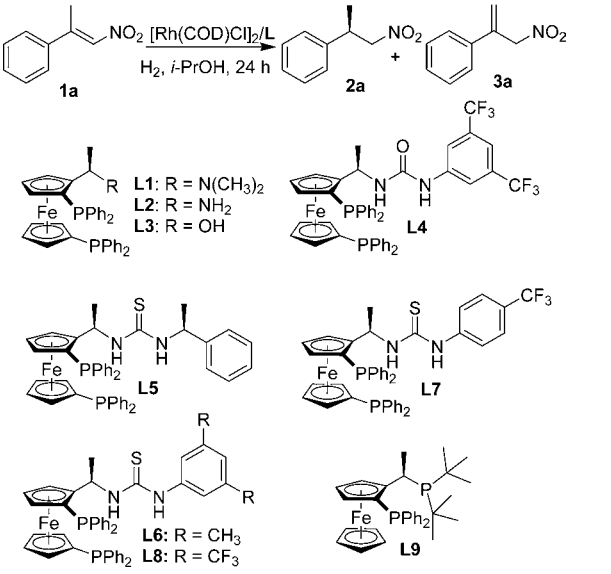
entry	solvent	metal source	distribution (%)[b] **1a**:**2a**:**3a**	**2**, *ee* (%)[c]
1	MeOH	$[Rh(COD)_2]BF_4$	0:100:0	55
2	MeOH	$[Rh(COD)_2]SbF_6$	48:48:4	63
3	MeOH	$[Rh(COD)_2]BARF$	23:75:2	83
4	MeOH	$[Ir(COD)Cl]_2$	83:15:2	55
5	MeOH	$[Rh(COD)Cl]_2$	0:100:0	94
6	CH_2Cl_2	$[Rh(COD)Cl]_2$	24:74:2	90
7	toluene	$[Rh(COD)Cl]_2$	24:74:2	93
8	THF	$[Rh(COD)Cl]_2$	34:66:0	63
9	*i*-PrOH	$[Rh(COD)Cl]_2$	0:100:0	99
10	CF_3CH_2OH	$[Rh(COD)Cl]_2$	1:99:0	98
11	*t*-BuOH	$[Rh(COD)Cl]_2$	1:99:0	97
12[d]	*i*-PrOH	$[Rh(COD)Cl]_2$	0:100:0	99
13[e]	*i*-PrOH	$[Rh(COD)Cl]_2$	3:97:0	98
14[f]	*i*-PrOH	$[Rh(COD)Cl]_2$	0:100:0	98
15[g]	*i*-PrOH	$[Rh(COD)Cl]_2$	2:98:0	98

[a] Unless ortherwise mentioned, reactions were performed with **1a** (0.05 mmol) and a Rh/L/**1a** ratio of 1/1.1/50 in 1.0 mL of solvent at 35 °C under 20 atm of H_2. [b] Determined by ^1H NMR. [c] Determined by chiral HPLC analysis. [d] a Rh/L/**1a** ratio of 1/1.1/100 in 0.25 mL of solvent at 35 °C under 5 atm of H_2. [e] a Rh/L/**1a** ratio of 1/1.1/200 in 0.25 mL of solvent at 35 °C under 5 atm of H_2. [f] a Rh/L/**1a** ratio of 1/1.1/200 in 0.25 mL of solvent at 35 °C under 20 atm of H_2. [g] a Rh/L/**1a** ratio of 1/1.1/400 in 0.25 mL of solvent at 35 °C under 30 atm of H_2. COD = 1,5-cyclooctadiene, NBD = 2,5-norbornadiene, BARF = $B[3,5\text{-}(CF_3)_2C_6H_3]_4$.

1−5). $[Rh(COD)Cl]_2$ afforded the best result with full conversion and high enantioselectivity (Table 1, entry 5). We noticed that this new catalytic system was solvent dependent. Poor enantioselectivities and conversions were obtained in nonprotic solvents (Table 1, entries 6−8), while excellent results were observed in protic solvents (Table 1, entries 5, 9−11). In particular, full conversion and 99% *ee* were obtained in *i*-PrOH. In addition, pressures, temperatures, and concentrations were changed to optimize the reaction (see Supplementary Table S1). The best result was observed at 35 °C under 5 atm of H_2 with 1 mol % catalyst (Table 1, entry 12). Increasing the H_2 pressure accelerated the reaction (Table 1, entries 13 and 14). With a low catalytic loading (0.25 mol %), 98% *ee* and 98% conversion were obtained (Table 1, entry 15).

To obtain insight into this catalytic system, a series of chiral ligands were prepared and some control experiments were undertaken (Table 2). The Rh-ferrocenylbisphosphine complex without a (thio)urea group (**L1**, **L2**, and **L3**) showed very low activity, although the single hydrogen bond possibly formed between the OH/NH and the nitro group[23] (Table 2, entries 1−3 vs 4−8). A dramatic difference was observed between the urea **L4** and the more acidic

Table 2. Ligand Study and Control Experiments[a]



entry	ligands	distribution (%)[b] **1a**:**2a**:**3a**	**2**, *ee* (%)[c]
1	**L1**	61:15:24	8
2	**L2**	78:3:19	ND
3	**L3**	70:8:22	ND
4	**L4**	56:33:11	75
5[d]	**L5**	22:78:0	85
6[d]	**L6**	5:95:0	96
7[d]	**L7**	8:92:0	98
8[d]	**L8**	0:100:0	99
9[e]	**L1**	64:5:31	ND
10[f]	**L9**	97:1:2	ND
11[g]	**L9**	98:0:2	ND
12[h]	**L9**	97:0:3	ND

[a] Unless ortherwise mentioned, reactions were performed with **1a** (0.1 mmol) and a Rh/L/**1a** ratio of 1/1.1/50 in 0.5 mL of *i*-PrOH at 25 °C under 5 atm of H_2. [b] Determined by ^1H NMR. [c] Determined by chrial HPLC analysis. [d] a Rh/L/**1a** ratio of 1/1.1/100 in 0.25 mL of *i*-PrOH at 35 °C under 5 atm of H_2. [e] a Rh/L/thiourea/**1a** ratio of 1/1.1/1.1/100 in 0.25 mL of *i*-PrOH at 35 °C under 5 atm of H_2. [f] a $Rh(COD)BF_4$/**L9**/**1a** ratio of 1/1.1/100 in 0.5 mL of CH_2Cl_2 at 35 °C under 5 atm of H_2. [g] a $Rh(COD)BF_4$/**L9**/thiourea/**1a** ratio of 1/1.1/1.1/100 in 0.5 mL of CH_2Cl_2 at 35 °C under 5 atm of H_2. [h] a $[Rh(COD)Cl]_2$/**L9**/thiourea/**1a** ratio of 1/1.1/1.1/100 in 0.5 mL of CH_2Cl_2 at 35 °C under 5 atm of H_2. ND = not determined.

and less self-assembling thiourea **L8**.[12b] In addition, low conversions and enantioselectivities were obtained by employing ligands **L5**, **L6**, and **L7** (Table 2, entry 8 vs entries 5−7). Consistent with previous reports,[12,24] this finding suggested that the CF_3 group on the 3,5-(trifluoromethyl)-phenyl moiety played an important role in the catalytic system. Meanwhile, combining chiral phosphine ligands together with the simple thiourea did not improve the

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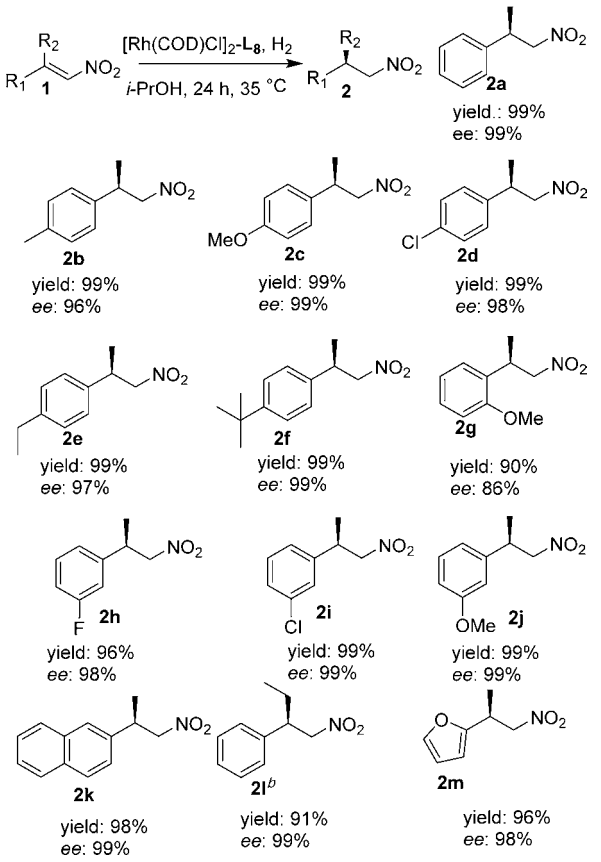
Scheme 2. Substrate Scope Screening[a]



[a] **1** (0.1 mmol) and a Rh/L/**1** ratio of 1/1.1/100 in 0.25 mLof solvent at 35 °C under 5 atmof H_2. Yield was determined by ^{1}H NMR; **3** was not observed. *ee* was determined by chiral HPLC analysis. [b] Rh/L/**1a** = 1/1.1/50.

activity under the optimized conditions (Table 2, entry 1 vs 9, entry 11 vs 12), which implied that the covalent linker was important. When the simple olefin was used, there was no hydrogenation product.[25] On the basis of previous mechanism studies of bisphosphine-metal catalysts and hydrogen-bond catalysts, together with our control experiments, we proposed that the thiourea activated the substrate efficiently and acted as an excellent directing role.

Under the optimized conditions, a variety of nitroalkenes examined (Scheme 2). *Meta* and *para* substitutions on the phenyl ring led to excellent results (96−99% yield and 96−99% *ee*) regardless if they were electron-withdrawing or -donating groups (**2b**−**2f**, **2h**−**2j**). However, the *ortho*-methoxy group on the phenyl ring resulted in lower conversion and enantioselectivity (**2g**). When R^2 was an ethyl group, high conversion and excellent enantioselectivity were observed (**2l**). In addition, the heteroaromatic product (**2m**) was obtained with excellent conversion and enantioselectivity.

In conclusion, a novel chiral bisphosphine-thiourea ligand has been developed based on the concept of combining metal catalysis with organocatalysis. This new Rh-bisphosphine-thiourea catalytic system was applied in the asymmetric hydrogenation of challenging β, β-disubstituted nitroalkenes, and excellent results were obtained. The thiourea group played an important role in the transformation. Further studies on the application and reaction mechanism of this methodology are currently underway.

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Supporting Information Available. General procedure and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

(25) We examined the simple olefin (*E*)-but-2-en-2-ylbenzene under optimized conditions. There was no hydrogenation product.

The authors declare no competing financial interest.