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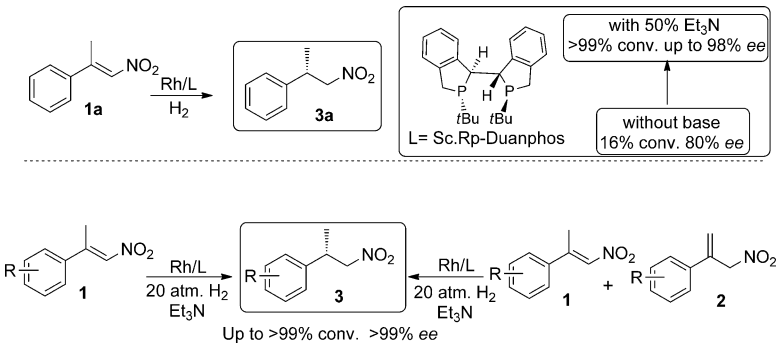
Rh-Catalyzed Highly Enantioselective Hydrogenation of Nitroalkenes under Basic Conditions

Shengkun Li,[a, b] Kexuan Huang,[b] Jiwen Zhang,[a] Wenjun Wu,*[a] and Xumu Zhang*[b]

Since the first report by Knowles, Horner et al. in 1968, catalytic asymmetric hydrogenation of alkenes has been one of the most powerful approaches to chiral compounds and great progress has been made.[1] Among the different alkenes, the hydrogenation of β,β-disubstituted nitroalkenes is a challenging problem. The resulting β-chiral nitroalkane from this "synthetic chameleon"[2] is a valuable synthetic scaffold. The nitro group serves as a masked functionality and can be easily transformed to amine, aldehyde, carboxylic acid, nitrile oxide, and denitrated compound.[3] A variety of asymmetric syntheses of the β-chiral nitroalkanes by starting from nitroalkenes have, therefore, been developed, such as biocatalytic reduction,[4] metal- or organocatalyzed transfer hydrogenations,[5] and enantioselective conjugate additions.[6] We envision that asymmetric hydrogenation will furnish an efficient and environmental benign approach to prepare these important chiral compounds. Recently, our group reported the first enantioselective hydrogenation of β,β-disubstituted nitroalkenes with a Rh/Josiphos catalytic system.[7] A number of chiral ligands were scanned and only a few promising results were achieved, and the enantioselectivity for most substrates was lower than 95% *ee* (*ee* = enantiomeric excess) It is highly desirable to develop a more convenient and highly enantioselective protocol. Herein, we would like to report a novel rhodium catalytic system under basic conditions for highly enantioselective hydrogenation of β,β-disubstituted nitroalkenes. We believe that a monohydride $Rh^{I}H$ is responsible for the high enantioselectivity under basic conditions and this new protocol is notable with several attractive features: 1) addition of base is necessary for achieving both high enantioselectivity and high activity, and up to >99% *ee* can be obtained (Scheme 1); 2) a number of chiral ligands (DuanPhos, TangPhos, Et-DuPhos, and Binapine) can be used in highly enantioselective hydrogenation, and this method is potentially practical for preparing chiral nitroalkanes; and 3) mixtures of nitroalkenes can also be used without erosion of either conversion or enantioselectivity.



Scheme 1. Hydrogenation of β,β-disubstituted nitroalkenes and nitroalkene mixtures.

Based on our previous work on the enantioselective hydrogenation of nitroalkenes,[7] the crucial role of additives[8] in the asymmetric hydrogenation of certain alkenes was examined. Our investigation into the asymmetric hydrogenation of nitoalkene **1a** demonstrated that the addition of base is necessary for improving the reactivity and enantioselectivity.

As shown in Table 1, the $[Rh(nbd)_2]SbF_6$/(Sc, Rp)-Duanphos catalyst (nbd = norbornadiene) barely can promote the hydrogenation in the absence of base, giving only 16% conversion (Table 1, entry 1). Addition of 50 mol% of NEt_3 brought a remarkable improvement of the enantioselectivity and catalytic activity to 95% *ee* and 100% conversion, respectively (entry 2). Fine-tuning of the amount of NEt_3 demonstrated that the conversion decreased sharply when the amount of NEt_3 is lower than 10 mol%, while no obvious

[a] S. Li, J. Zhang, Prof. Dr. W. Wu
College of Science
Northwest A&F University
Yangling, Shaanxi 712100 (P. R. China)
E-mail: wuwenjun@nwsuaf.edu.cn

[b] S. Li, K. Huang, Prof. Dr. X. Zhang
Department of Chemistry and Chemical Biology and
Department of Pharmaceutical Chemistry
Rutgers, the State University of New Jersey
Piscataway, New Jersey 08854 (USA)
Fax: (+1) 732-445-6312
E-mail: xumu@rci.rutgers.edu

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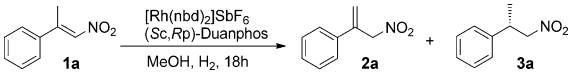
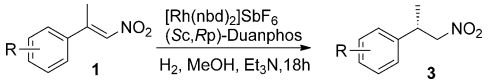
Table 1. Rh-catalyzed asymmetric hydrogenation of **1a** with different bases.[a]



Entry	Base [mol%]	H_2 [atm]	T [°C]	Conv. [%][b]	*ee* [%][c]
1	–	50	50	16	80
2	NEt_3 (50)	50	50	100	95
3	NEt_3 (20)	50	50	100	94
4	NEt_3 (10)	50	50	95	94
5	NEt_3 (5)	50	50	42	96
6	TMEDA (5)	50	50	40	96
7	urotropine (5)	50	50	40	96
8	NMP (5)	50	50	44	96
9	NMM (5)	50	50	38	97
10	piperidine (5)	50	50	63	92
11	diethylamine (5)	50	50	54	94
12[d]	NEt_3 (50)	20	40	100	98

[a] Unless otherwise mentioned, all reactions were carried out with a $[Rh(nbd)_2]SbF_6$/ligand/substrate ratio of 2:2:100, in MeOH, for 18 h. [b] The conversion of **1a** was determined by ^1H NMR spectroscopy and calculated with the formula, **3a**/(**1a**+**2a**+**3a**)×100%. [c] Enantiomeric excess was determined by HPLC analysis on a chiral phase. [d] [Rh-(nbd)$_2$]SbF_6/ligand/substrate ratio of 1:1.1:100.

Table 2. Rh/Duanphos-catalyzed asymmetric hydrogenation of β,β-disubstituted nitroalkenes.[a]



Entry	Substrate	Product	Conv. [%][b]	*ee* [%][c]
1[d]	R=H (**1a**)	**3a**	>99	97 (*S*) (−)
2	R=3,5-$(CF_3)_2$ (**1b**)	**3b**	>99	98 (−)
3	R=3-CF_3 (**1c**)	**3c**	>95	96 (−)
4	R=3-F (**1d**)	**3d**	>99	>99 (−)
5	R=3-Cl (**1e**)	**3e**	>99	97 (−)
6	R=3-Br (**1f**)	**3f**	>99	98 (−)
7	R=3-OMe (**1g**)	**3g**	>99	96 (*S*) (−)
8	R=4-CF_3 (**1h**)	**3h**	>99	99 (−)
9[e]	R=4-F (**1i**)	**3i**	65	95 (*S*) (−)
10[f]	R=4-Cl (**1j**)	**3j**	>99	96 (*S*)(−)
11	R=4-Br (**1k**)	**3k**	>99	>99 (*S*) (−)
12	R=4-Me (**1l**)	**3l**	>99	95 (−)
13	R=4-Et (**1m**)	**3m**	>99	98(−)
14	R=4-*t*Bu(**1n**)	**3n**	>99	97 (−)
15	R-Ph= 2-Naphthyl (**1o**)	**3o**	92	98 (−)
16[g]	R=2-F (**1p**)	**3p**	>99	96 (−)
17[g]	R=2-Cl (**1q**)	**3q**	88	91 (−)
18[h]	R=2-OMe (**1r**)	**3r**	68	96 (−)

[a] Unless otherwise mentioned, all reactions were carried out with 0.1 mmols of substrate, with a $[Rh(nbd)_2]SbF6$/ligand/substrate/NEt_3 ratio of 1:1.1:100:50, in MeOH, at 40°C, under 20 atm. of hydrogen for 18 h. [b] The conversion higher than 99% was determined by HPLC analysis, the others were detected based on ^1H NMR spectroscopy. [c] Enantiomeric excess was determined by HPLC analysis on a chiral phase. The absolute configuration was assigned by comparison of the observed optical rotation with reported data. [d] 1.63 g of **1a** was consumed. [e] 3% Rh, 400% NEt_3, 50°C, 50 atm. H_2. [f] 2% Rh, 200% NEt_3, 50°C, 20 atm. H_2. [g] 1.5% Rh. [h] 1.5% Rh, 50°C, 40 atm. H_2.

variation on enantioselectivity was detected (entries 3–5). To determine the effect of different bases on the catalytic activity and enantioselectivity, a number of organic base additives (5 mol%), including *N*,*N*,*N*',*N*'-tetramethyl-1,2-ethane (TMEDA), hexamethylenetetramine (urotropine), *N*-methylpyrrolidone (NMP), *N*-methylmorpholine (NMM), piperidine, and diethylamine, were tested under similar conditions, and comparable results have been achieved to that of NEt_3 (entries 6–11). The effect of inorganic base (K_2CO_3, Cs_2CO_3, K_3PO_4, see the Supporting Information) on this reaction was also investigated, and showed similar enhanced activity and enantioselectivity. It is remarkable that in the presence of 50 mol% of NEt_3, full conversion and up to 98% *ee* can be achieved when the original experimental parameters including catalyst loading, hydrogen pressure, and temperature were reduced to 1%, 20 atm., and 40°C, respectively (entry 12).

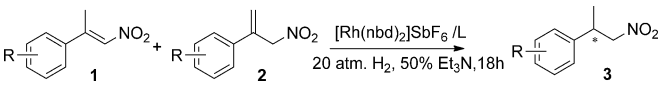
A variety of β-alkyl-β-aryl-nitroalkenes were hydrogenated to demonstrate the synthetic utilities of this methodology. As shown in Table 2, the *meta*-substituents at the aromatic ring of the substrates had a negligible effect on the activity, no matter if they were electron-donating or -withdrawing, and all the tested substrates were hydrogenated smoothly with full conversion (Table 2, entries 2–7). A slight enhancement of the ennatioselectivity was detected when electron-withdrawing substitutents were introduced to the *meta*-position, *meta*-fluoro-substituted substrate afforded the corresponding chiral nitroalkane with up to >99% *ee* (entry 4). The catalytic activity appears to be sensitive to the pattern and electronic properties when the substituents were switched to the *para*-position. Outstanding selectivities of ≥99% *ee* and full conversions were achieved in the hydrogenation of *para*-trifluoromethyl and bromo-substituted nitroalkenes (entries 8 and 11). While higher loading of catalyst or additive is necessary for fluoro- and chloro-substituted nitroalkenes to achieve comparable conversions (entries 9 and 10). Substrates with electron-donating substitutes at the *para*-position proceeded well under the standard conditions, and a small improvement of enantioselectivity with the increasing steric hindrance was detected (entries 12 vs. 13, 12 vs. 14). 2-Naphthyl nitroalkene showed similar reactivity, affording the corresponding β-chiral nitroalkane with up to 98% *ee* (entry 15). We were pleased to find that the some *ortho*-substituted nitroalkenes, such as fluoro, chloro, and methoxyl-substituted substrates, can also be hydrogenated in moderate to good conversion without a significant decrease in enantioselectivities (entries 16–18).

To explore the potential application of the [Rh-(nbd)$_2$]SbF6/DuanPhos/NEt_3 catalytic system in the practical asymmetric hydrogenation of nitroalkenes, further studies were carried out and some impressive results were obtained as follows: 1) This protocol can be easily implemented on a gram scale under the standard hydrogenation conditions. 1.63 g of **1a** were hydrogenated to the desired nitroalkane without obvious erosion of either conversion or enantioselectivity (Table 2, entry 1). 2) Study on the turnover number (TON) of the hydrogenation of **1a** showed that the transformation was complete with 1% catalyst at room temperature with 99% *ee*, and with 0.25% catalyst at 50°C (TON=400),

only a slight decrease in *ee* (96% *ee*) was detected. When the substrate to catalyst ratio was increased to 800, the enantioselectivity still remained unchanged with 72% conversion. This is the highest TON in either hydrogenation or conjugate reduction of β,β-disubstituted nitroalkenes. 3) A mixture of nitroalkenes are hydrogenated enantioselectively to the corresponding nitroalkanes with 94–99% *ee* (Table 3, entries 1–5). Compared with the pioneering work by Carreira[5c] on enantioselective conjugate reduction of isomeric mixtures of nitroalkenes, the positive effect of NEt_3 was detected in our novel catalytic system, and the highly enantioselective hydrogenation can be carried out in one pot through in situ equilibration. This will allow for a convenient application in a large-scale synthesis of β-chiral nitroalkanes. 4) A number of commercially available chiral bidentate phosphorus ligands, such as DuanPhos, TangPhos, Et-DuPhos, *f*-ketalPhos, and Binapine, can be used successfully in the current protocol, affording the β-chiral nitroalkanes with full conversion and good to excellent enantioselectivities (entries 6–8). Those features demonstrate that the current protocol holds a great potential for convenient synthesis of enantiopure nitroalkanes.

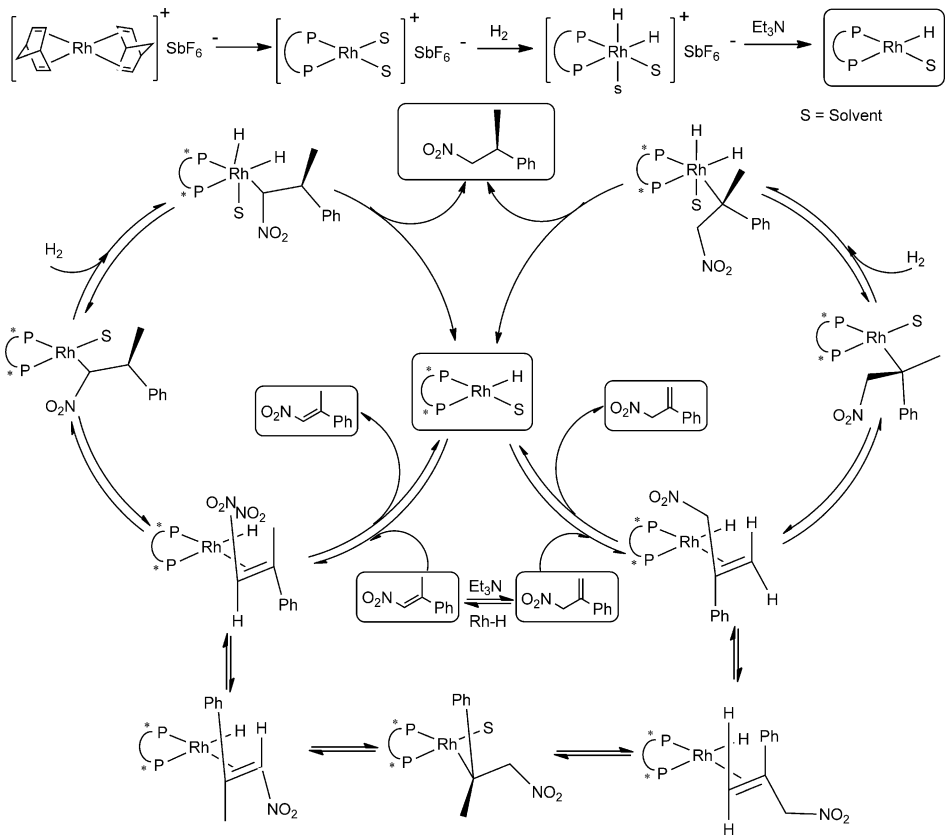
Consistent with earlier reports,[5c] our tests also showed immediate isomerization of β,β-disubstituted nitroalkenes in the presence of NEt_3. The rapid equilibrium was detected through ^1H NMR spectroscopy (see the Supporting Information). In our procedure, nitroalkenes were stirred with NEt_3 for 5–10 min before the catalyst was added and we envisioned that the substrate underwent isomerization before hydrogenation. The success in enantioselective hydrogenation of nitroalkenes mixtures demonstrated that tedious separation from isomers of nitroalkenes is unnecessary, making it a practical synthetic procedure. Variation of the amount of NEt_3 showed negligible effect on the equilibrium of the isomerization of nitroalkene **1a**, whereas significant influence was observed on the conversion (Table 1, entries 1–5). We deduced that the NEt_3 can result in not only isomerization of nitroalkenes but also alternation of the catalyst to a more active species. A reasonable explanation in the earlier report was that heterolytic activation of hydrogen was induced when the cationic Rh^I was used in conjunction with basic additives.[9] We assume that a monohydride Rh^IH complex is an active species and a proposed mechanism for the asymmetric hydrogenation of the nitroalkenes was shown in Scheme 2, in which the base additive possibly converts a cationic $Rh^{III}H_2$ species to a more active neutral Rh^IH complex and thus promotes the hydrogenation of nitroalkenes through a monohydride pathway.

Table 3. Rh-catalyzed asymmetric hydrogenation of nitroalkenes in presence of NEt_3.[a]



Entry	Ligand	Substrate	Product	*ee* [%][a]
1[b]	Duanphos	R = H(**1a**/**2a** = 3.4:1)	**3a**	98
2[b]	Duanphos	R = 3-Br (**1f**/**2f** = 1.9:1)	**3f**	96
3[b]	Duanphos	R = 3-OMe (**1g**/**2g** = 2.3:1)	**3g**	95
4[b]	Duanphos	R = 4-Br (**1k**/**2k** = 2:1)	**3k**	99
5[b]	Duanphos	R = 4-Me (**1l**/**2l** = 3.5:1)	**3l**	94
6	Tangphos	R = H (**1a**)	**3a**	95
7	Et-Duphos	R = H (**1a**)	**3a**	96
8	f-Ketalphos	R = H (**1a**)	**3a**	93
9	Binapine	R = H (**1a**)	**3a**	96
10[c]	Duanphos	R = H (**1a**)	**3a**	97
11[d]	Duanphos	R = H (**1a**)	**3a**	98
12[e]	Duanphos	R = H (**1a**)	**3a**	94
13[f]	Duanphos	R = H (**1a**)	**3a**	88

[a] See Table 2. [b] The ratio of isomers was determined by ^1H NMR spectroscopy. [c] In toluene. [d] In dichloromethane. [e] In ethyl actate. [f] In THF.



Scheme 2. Proposed pathway for highly enantioselective hydrogenation of nitroalkenes.

In conclusion, we have developed a highly enantioselective hydrogenation of β,β-disubstituted nitroalkenes and the isomeric mixtures of nitroalkenes by in situ equilibration. This novel Rh/DuanPhos catalytic system under basic conditions will furnish a convenient approach to β-chiral nitroalkanes, which are otherwise not so easy to make. This new method shows a great potential for a large-scale synthesis of enantiopure nitroalkanes. A further study is underway with the aim of exploring the mechanism of this novel catalytic system and expanding substrate scope.

Experimental Section

General: A stock solution was made by mixing $[Rh(nbd)_2]SbF_6$ with (Sc, Rp)-Duanphos in a 1:1.1 molar ratio in anhydrous methanol at room temperature for 30 min in a nitrogen-filled glovebox. NEt_3 solution in methanol (0.1 mL, 0.05 mmol) was added to a vial containing the substrate (0.1 mmol) and a stir bar in anhydrous methanol (1 mL). The resulting yellow solution was stirred for 5 min at room temperature, and then an aliquot of the catalyst solution (0.2 mL, 0.001 mmol) was transferred by syringe into the vial. The resulting vials were transferred to an autoclave, which then underwent three cycles of flushing with hydrogen gas by pressurizing to 20 atm. and then depressurizing. The reaction was then stirred under H_2 (20 atm.) at 40 °C for 18 h. The autoclave was cooled to room temperature and the hydrogen gas was released slowly and carefully. The solution was then concentrated and neutralized by addition of HCl aqueous solution (5 mL, 0.05 mmol). The aqueous layer was extracted by CH_2Cl_2 (2 mL × 3), The combined organic extracts were washed with a saturated solution of NaCl, dried over Na_2SO_4, and then concentrated and passed through a short column of silica gel (eluant: CH_2Cl_2). The *ee* values of all compounds were determined by HPLC analysis on a chiral stationary phase.

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Keywords: catalysis · hydrogenation · monohydride · nitroalkenes · rhodium

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