Highly Enantioselective Hydrogenation of Enamides and Itaconic Acid in Water in the Presence of Water-Soluble Rhodium(I) Catalyst and Sodium Dodecyl Sulfate

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The water-soluble cationic Rh complexes, such as [Rh(α-D-glucopyranosyl-(1,1)-2,3-di-*O*-(diphenylphosphino)-α-D-glucopyranoside)(cod)]BF_4 (**1**) and [Rh(*β*-D-glucopyranosyl-(1,1)-2,3-di-*O*-(diphenylphosphino)-*β*-D-glucopyranoside)(cod)]BF_4 (**2**) bearing free hydroxy groups, are effective catalysts in the asymmetric hydrogenation of various enamides and itaconic acid (up to 99.9% ee) in water in the presence of sodium dodecyl sulfate (SDS) (7.5×10^{-3} to 1.0×10^{-1} M). The hydrogenation of methyl (*Z*)-α-acetamidocinnamate in water using the corresponding Rh complexes of triflate (**6**) and D-camphor-10-sulfonate (**7**), prepared separately, results in a formation of the product of the same enantioselectivity (48% ee), but the use of SDS can reduce the amount of the catalyst and improve the enantioselectivity to 81% ee. These results show that the counteranions do not directly influence the enantioselectivity. Although the effect of SDS on the enhancement of enantioselectivity remains speculative, the formation of micelle seems to play an important role in improving the enantioselectivity.

Introduction

Recently, asymmetric catalytic reactions in water have attracted a great deal of attention, mainly due to the economical and environmental concerns.[1] In general, the low solubility of a catalyst and a substrate in water causes the deceleration of the reaction rate. One approach to address the solubility of the catalyst in water is to incorporate the water-soluble ligands into the catalyst.[1,2] The use of a surfactant provides another approach to make both a substrate and a catalyst soluble in an aqueous medium. Oehme, Selke, and co-workers introduced the various surfactants to the rhodium-catalyzed asymmetric reactions in water and obtained a good enantioselectivity as well as a high reactivity in the hydrogenation of enamides, α-aminophosphinic acids, and their esters.[3] Recently, we have succeeded in the enantioselective hydrogenation of dehydroamino acids

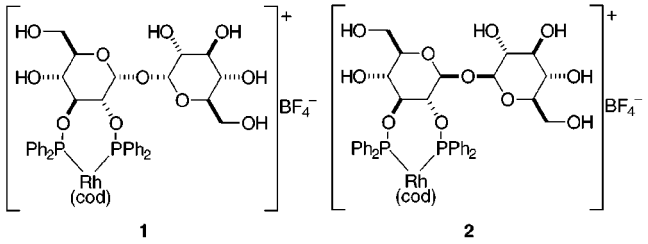

Figure 1. Water-soluble chiral rhodium complexes derived from α,α- and *β*,*β*-trehalose.

(1) (a) Cornils, B.; Herrmann, W. A. *Aqueous-Phase Organometallic Catalysis*; Wiley-VCH: New York, 1998. (b) Cornils, B.; Herrmann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: New York, 1996. (c) Joó, F.; Kathó, Á. *J. Mol. Catal. A: Chem.* **1997**, *116*, 3. (d) Papadogianakis, G.; Sheldon, R. A. *New. J. Chem.* **1996**, *20*, 175. (e) Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1575. (f) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A: Chem.* **1995**, *104*, 17. (g) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.

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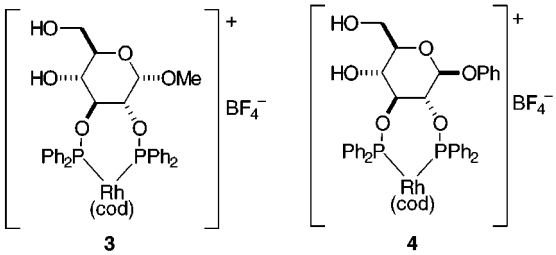

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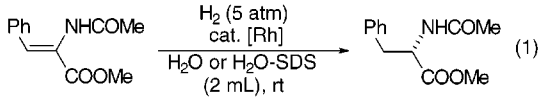
and their esters in an aqueous/organic biphasic medium using water-soluble rhodium complexes **1** and **2** prepared from α,α- and *β*,*β*-trehalose as ligand sources,[4] respectively (Figure 1).[5a] In a previous study, we also found that sodium dodecyl sulfate (SDS) works as a surfactant to enhance the enantioselectivity up to 99.9% ee in the hydrogenation of methyl (*Z*)-α-acetamidocinnamate in water.[5a] This success stimulated us to investigate the asymmetric hydrogenation of other substrates in the presence of a water-soluble rhodium catalyst and a surfactant in water. In this paper we report the scope and limitations of water-soluble rhodium complexes as catalysts in the hydrogenation of various enamides and itaconic acid under micellar conditions.

Results and Discussion

We previously reported the hydrogenation of methyl (*Z*)-α-acetamidocinnamate in water under H_2 pressure (5 atm) using water-soluble rhodium catalysts **1** and **2** (Figure 1), where the enantioselectivities of the product were in 55% and 88% ee, respectively (eq 1).[5a] On the



(1)

cat. [Rh]	time (h)	%ee
1 (5 mol%)	6	55
1 (1 mol%) + SDS (7.5×10^{-3} M)	1	90
2 (5 mol%)	6	88
2 (1 mol%) + SDS (7.5×10^{-3} M)	1	>99

other hand, the reactions in the presence of sodium dodecyl sulfate (SDS) (7.5×10^{-3} M) as a surfactant gave higher selectivity of 90% and 99.9% ee, respectively. The use of SDS also accelerated each reaction to be complete within 1 h. Oehme, Selke, and co-workers have already reported similar effects of the SDS in the hydrogenation of enamides in water using rhodium catalysts **3** and **4**.[3e,f,h] Then we applied the combination of the catalyst **2** and SDS to the hydrogenation of several enamides in water. The results are summarized in Table 1. The hydrogenation of enamides was carried out under H_2 pressure (5 atm) at room temperature using 1 mol % of **2** in the presence of SDS. (*Z*)-α-*N*-Acetamidocinnamic acid was hydrogenated in the presence of SDS (7.5×10^{-3} M) to give the *N*-acetylphenylalanine in >99% ee (entry 1). The reaction of methyl (*Z*)-α-*N*-benzamidocinnamate required a higher concentration of SDS (1.5×10^{-2} M), its selectivity being 93% ee (entry 2). The introduction of chloro and nitro groups on the phenyl ring caused the decrease of solubility of substrates in water, and therefore, a higher concentration of SDS (9.0×10^{-2} M) was required to attain the good selectivities (94% ee) and shorter reaction times (entries 3−6). The hydrogenation of methyl (*Z*)-α-acetamido-*β*-(1-naphthyl)acrylate and methyl (*Z*)-α-acetamido-*β*-(2-naphthyl)acrylate required much higher concentration of SDS (1.0×10^{-1} M) to give an almost complete selectivity (entries 7 and 8). The use of a lesser amount of SDS (7.5×10^{-3} M) frustrated the conversion of the substrate at most to 20%, possibly due to poor solubility of the substrate in water. Methoxy groups on a phenyl ring decreased the amount of SDS required to 7.5×10^{-3} M, the induction of chirality being over 99% ee (entries 9 and 10). The addition of SDS (7.5×10^{-3} M) also affected the enantioselectivity in the hydrogenation of methyl α-*N*-acetamidoacrylate, leading to 96% ee (entry 11). We also attempted the hydrogenation of simple enamides, resulting in the formation of chiral amines, because, despite their potential importance, few successful results have so far been reported.[6] A highly enantioselective hydrogenation (83% ee) proceeded with *N*-acetyl-α-phenylethenamine in water in the presence of the catalyst **2** and SDS (7.5×10^{-3} M) (entry 12). To the best of our knowledge, this is the most successful result in the hydrogenation of this substrate in water. This catalytic system, however, is only marginally effective in the hydrogenation of α-(*N*-acetylamido)-indene to give 33% ee (entry 13). Itaconic acid was also hydrogenated under the same condition to give the corresponding product with moderate selectivity (71% ee) (entry 14).

As mentioned above, the combination of the water-soluble chiral catalyst **2** and SDS is most effective in the enantioselective hydrogenation of enamides and itaconic acid in water. More interestingly, the catalyst **2** showed amphiphilic nature in solubility; i.e., it was soluble in less polar solvent such as 1,2-dichloroethane as well as in water.[5a] Therefore, the hydrogenation of methyl (*Z*)-α-acetamidocinnamate in 1,2-dichloroethane using the catalyst **2** smoothly occurred to give the product with high enantioselectivity (94% ee) (eq 2). On the contrary, the complex **5**[7] with cyclohexylidene protections of hydroxy groups at 4,6:2′,3′:4′,6′ positions of **2** was fairly soluble in 1,2-dichloroethane, but less in water. Thus, the hydrogenation of methyl (*Z*)-α-acetamidocinnamate using the catalyst **5** took place in 1,2-dichloroethane with high enantioselectivity of 95% ee, while the same reaction scarcely occurred in water. However, the addition of SDS

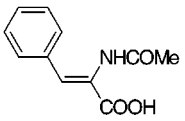
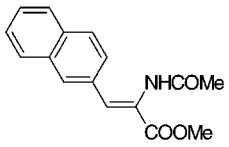
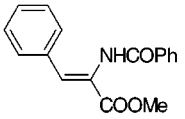
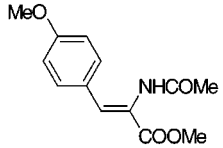
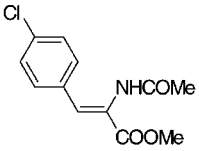
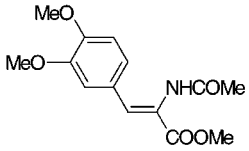
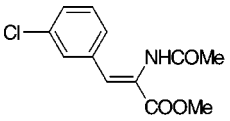
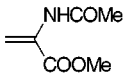
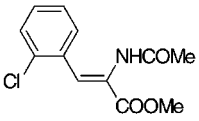
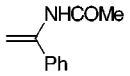
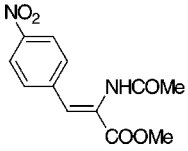
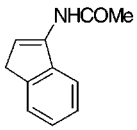
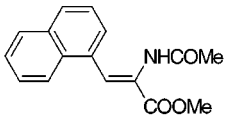
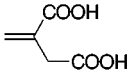
(4) The derivatization of monosaccharide and α,α-trehalose for the synthesis of chiral ligands and their application to asymmetric reactions have been reported. For examples, see: (a) RajanBabu, T. V.; Radetich, B.; You, K. K.; Ayers, T. A.; Casalnuovo, A. L.; Calabrese, J. C. *J. Org. Chem.* **1999**, *64*, 3429. (b) Yonehara, K.; Hashizume, T.; Ohe, K.; Uemura, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1967. (c) Boog-Wick, K.; Pregosin, P. S.; Wörle, M.; Albinati, A. *Helv. Chim. Acta* **1998**, *81*, 1622. (d) RajanBabu, T. V.; Ayers, T. A.; Halliday, G. A.; You, K. K.; Calabrese, J. C. *J. Org. Chem.* **1997**, *62*, 6012. (e) RajanBabu, T. V.; Casalnuovo, A. L.; Ayers, T. A. *Adv. Catal. Proc.* **1997**, *2*, 1. (f) Berens, U.; Selke, R. *Tetrahedron: Asymmetry* **1996**, *7*, 2055. (g) Gilbertson, S. R.; Chang, C.-W. T. *J. Org. Chem.* **1995**, *60*, 6226. (h) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869. (i) Selke, R.; Facklam, C.; Foken, H.; Heller, D. *Tetrahedron: Asymmetry* **1993**, *4*, 369. (j) RajanBabu, T. V.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6265. (k) Selke, R. *J. Organomet. Chem.* **1989**, *370*, 249. (l) Brown, J. M.; Cook, S. J.; Khan, R. *Tetrahedron* **1986**, *42*, 5105. (m) Selke, R.; Pracejus, H. *J. Mol. Catal.* **1986**, *37*, 213. (n) Jackson, R.; Thompson, D. J. *J. Organomet. Chem.* **1978**, *159*, C29. (o) Cullen, W. R.; Sugi, Y. *Tetrahedron Lett.* **1978**, 1635.

(5) (a) Yonehara, K.; Hashizume, T.; Mori, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 5593. (b) Recently, RajanBabu and co-worker have independently reported the synthesis of water-soluble chiral Rh complex from α,α-trehalose. See: Shin, S.; RajanBabu, T. V. *Org. Lett.* **1999**, *1*, 1229.

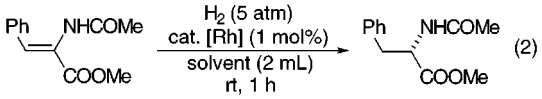
(6) (a) Zhang, Z.; Zhu, G.; Jiang, Q.; Xiao, D.; Zhang, X. *J. Org. Chem.* **1999**, *64*, 1774. (b) Hu, W.; Yan, M.; Lau, C.-P.; Yang, S. M.; Chan, A. S. C.; Jiang, Y.; Mi, A. *Tetrahedron Lett.* **1999**, *40*, 973. (c) Zhu, G.; Zhang, X. *J. Org. Chem.* **1998**, *63*, 9590. (d) Burk, M. J.; Casy, G.; Johnson, N. B. *J. Org. Chem.* **1998**, *63*, 6084. (e) Zhang, F.-Y.; Pai, C.-C.; Chan, A. S. C. *J. Am. Chem. Soc.* **1998**, *120*, 5808. (f) Burk, M. J.; Wang, Y. M.; Lee, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 5142. (g) Sinou, D.; Kagan, H. B. *J. Organomet. Chem.* **1976**, *114*, 325.

(7) The rhodium complex **5** was synthesized from 2,3:4,6-di-*O*-cyclohexylidene-*β*-D-glucopyranosyl-(1,1)-4,6-*O*-cyclohexylidene-2,3-di-*O*-(diphenylphosphino)-*β*-D-glucopyranoside[5a] and $[Rh(cod)_2]BF_4$ in degassed THF under Ar at room temperature for 1 h.

Table 1. Asymmetric Hydrogenation of Enamides and Itaconic Acid Using 2 (1 mol %) in Aqueous Micellar Medium[a]

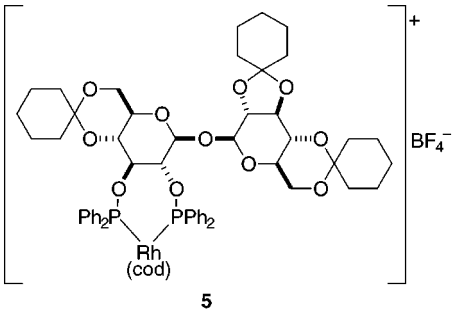
entry	substrate	surfactant (x 10^{-3} M)	%ee[b,c]	entry	substrate	surfactant (x 10^{-3} M)	%ee[b,c]
1		7.5	>99[d] (*S*)	8		100	>99 (*S*)
2		15	93 (*S*)	9		7.5	99 (*S*)
3		90	>99 (*S*)	10		7.5	>99 (*S*)
4		90	94 (*S*)	11		7.5	96 (*S*)
5		90	98 (*S*)	12		7.5	83 (*S*)
6		90	97 (*S*)	13		7.5	33 (*S*)
7		100	>99 (*S*)	14		17.5	71 (*R*)

[a] Reaction conditions: 0.15−0.35 mmol of substrate, 1.5×10^{-2} to 3.5×10^{-2} mmol of catalyst, SDS (7.5×10^{-3} to 1.0×10^{-1} M), 2.0−3.0 mL of H_2O, H_2 (5 atm), rt, 1 h. Complete conversion of substrate in all cases. [b] The enantiomeric excess was determined by HPLC. [c] Absolute configuration was determined by its optical rotation. [d] The ee (%) value of its methyl ester was determined by HPLC.



(2)

cat. [Rh]	solvent	%ee
2	$ClCH_2CH_2Cl$	94
5	$ClCH_2CH_2Cl$	95
5 + SDS (7.5×10^{-2} M)	H_2O	94

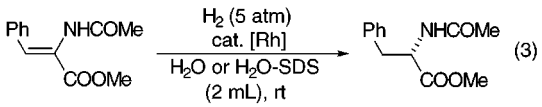


5

(7.5×10^{-2} M) could promote the hydrogenation using **5** in water to give the product with high enantioselectivity (94% ee). These results show that the assembly of a catalyst and a surfactant, namely the micelle formation, plays an important role to influence the efficiency and the enantioselectivity of the hydrogenation irrespective of the solubility of catalysts in water.

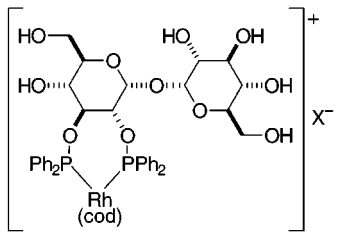
To obtain some evidence regarding the micelle formation, we examined the ^{31}P NMR spectra of the catalyst **1** in D_2O in the presence of SDS. The resonances of two phosphorus nuclei of **1** were observed at δ 132.0 and 139.5 ppm as a doublet [^1J(Rh,P) = 189 Hz] in D_2O, respectively. After an excess amount of SDS was added to this solution, the resonances of two phosphorus nuclei in ^{31}P NMR spectrum were observed at δ 127.5 and 136.1 ppm as a doublet of doublet [^1J(Rh,P) = 177 Hz, ^2J(P,P) = 24 Hz], respectively. The high field shift of the resonance peaks implies that the phosphorus atoms become more electrically negative or they are not deshielded by the proximal structure. One plausible explanation of this might be made by assuming an anion exchange of the complex with dodecyl sulfate. To elucidate an

exchange of the anion we prepared two types of rhodium complexes, such as **6** and **7**,[8] and carried out the hydrogenation of methyl (*Z*)-α-acetamidocinnamate using them (5 mol %) under H_2 pressure (5 atm) in water (eq 3). Both



(3)

cat. [Rh]	time (h)	%ee
6 (X^- = $^-$OTf) (5 mol%)	6	48
7 (X^- = D-camphor-10-sulfonate) (5 mol%)	6	48
6 (1 mol%) + SDS (7.5×10^{-3} M)	1	81



6 or **7**

complexes **6** and **7** did not show any difference in the enantioselectivity of the hydrogenation (48% ee) in water. However, the use of SDS (7.5×10^{-3} M) in the presence of the catalyst **6** could reduce the catalyst amount to 1 mol % and improve the enantioselectivity to 81% ee. These results suggest that the counteranions do not have much affect on the enantioselectivity. Although the effect of SDS on the enhancement of enantioselectivity remains speculative, the formation of larger micelle seems to play an important role to improve the enantioselectivity. The complexes **1** and **2** contain both hydrophilic and hydrophobic parts. When SDS was added, the hydrophobic metal centers of catalysts and hydrophobic tails of surfactants form spherical aqueous micelles which have larger hydrophobic cores with the polar headgroups outside. The reaction might take place in such larger hydrophobic cores, although the formation and dissociation of micelles are very fast processes.[9] The acceleration of the reaction can be attributed to permeation of the hydrophobic reactants into the hydrophobic cores. Although the exact reason for the enhancement of the selectivity in a micellar system is not yet clear at present, the micelle core representing the lower dielectric constant in comparison with water might provide a better coordination sphere around the metal. The high field shifts of phosphorus nuclei in ^{31}P NMR in the presence of SDS suggest that the phosphorus atom becomes electrically more negative than in the absence of SDS, probably due to the decrease of charge separation between the central rhodium and the counteranion. Thereby, the proximal ligand can strongly coordinate to an active center to give a higher enantioselectivity under the micellar conditions.

(8) The rhodium complex [Rh(2,3:4,6-di-*O*-isopropylidene-α-D-glucopyranosyl-(1,1)-4,6-*O*-isopropylidene-2,3-di-*O*-(diphenylphosphino)-α-D-glucopyranoside)(acac)] formed in situ by the reaction of [Rh(acac)(cod)] with the chiral ligand 2,3:4,6-di-*O*-isopropylidene-α-D-glucopyranosyl-(1,1)-4,6-*O*-isopropylidene-2,3-di-*O*-(diphenylphosphino)-α-D-glucopyranoside[5a] in degassed THF under Ar was treated with 80% aqueous TfOH or D-camphor-10-sulfonic acid at room temperature for 1 h to give a cationic water-soluble rhodium complex [Rh(α-D-glucopyranosyl-(1,1)-2,3-di-*O*-(diphenylphosphino)-α-D-glucopyranoside)(cod)]OTf (**6**) or [Rh(*β*-D-glucopyranosyl-(1,1)-2,3-di-*O*-(diphenylphosphino)-*β*-D-glucopyranoside)(cod)]-D-camphor-10-sulfonate (**7**).

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Summary

We succeeded in the highly enantioselective hydrogenation of enamides and itaconic acid using water-soluble rhodium complexes **1** and **2** in an aqueous micellar media (>99% ee). Although the precise mechanism of the surfactant improving the enantioselectivity is not known at this stage, the micelle formation is very important to influence the ee values.

Experimental Section

General. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under argon. Dichloromethane, *N*,*N*-dimethylformamide (DMF), and triethylamine were distilled from calcium hydride. ^{31}P NMR spectra were measured for solutions in $CDCl_3$, MeOH-d_4, THF-d_8, or D_2O with $P(OMe)_3$ as an external standard. α,α-Trehalose dihydrate was purchased from Hayashibara Corp. [Rh(α-D-glucopyranosyl-(1,1)-2,3-di-*O*-(diphenylphosphino)-α-D-glucopyranoside)(cod)]BF_4 (**1**) and [Rh(*β*-D-glucopyranosyl-(1,1)-2,3-di-*O*-(diphenylphosphino)-*β*-D-glucopyranoside)(cod)]BF_4 (**2**) were synthesized according to the procedure of our previous report.[5a]

[Rh(2,3:4,6-di-*O*-cyclohexylidene-*β*-D-glucopyranosyl-(1,1)-4,6-*O*-cyclohexylidene-2,3-di-*O*-(diphenylphosphino)-*β*-D-glucopyranoside)(cod)]BF_4 (5). $[Rh(cod)_2]BF_4$ (16.2 mg, 0.04 mmol) and 2,3:4,6-di-*O*-cyclohexylidene-*β*-D-glucopyranosyl-(1,1)-4,6-*O*-cyclohexylidene-2,3-di-*O*-(diphenylphosphino)-*β*-D-glucopyranoside (38.0 mg, 0.04 mmol) were dissolved in degassed THF (1.5 mL) under Ar, and the solution was stirred at room temperature for 1 h. Degassed Et_2O (5.0 mL) was added, and the yellow precipitates were filtered and washed with Et_2O to give pure **5** (36.9 mg, 0.03 mmol, 76%): mp 235.0−236.1 °C; ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 136.5 (dd, ^1J(Rh,P) = 183 Hz, ^2J(P,P) = 24 Hz), 139.2 (dd, ^1J(Rh,P) = 183 Hz, ^2J(P,P) = 24 Hz) ppm; LRMS (FAB) *m*/*z* ($M^+ - BF_4$) = 1161.

A Typical Procedure for Synthesis of a Water-Soluble Rh Complex. [Rh(acac)(cod)] (15.5 mg, 0.05 mmol) and 2,3:4,6-di-*O*-isopropylidene-*β*-D-glucopyranosyl-(1,1)-4,6-*O*-isopropylidene-2,3-di-*O*-(diphenylphosphino)-*β*-D-glucopyranoside (41.5 mg, 0.05 mmol) were dissolved in degassed dry THF (1.0 mL), and the mixture was stirred under Ar. After 20 min, 60% aqueous trifluoromethanesulfonic acid was added to the solution and the mixture was stirred at room temperature for 1 h. Degassed dry Et_2O (5.0 mL) was added, and the complex was separated out as an orange syrup. The supernatant solution was decanted, and degassed, dry Et_2O (5.0 mL) was again added to the obtained syrup. The product, [Rh(α-D-glucopyranosyl-(1,1)-2,3-di-*O*-(diphenylphosphino)-α-D-glucopyranoside)(cod)]OTf (**6**) (42.8 mg, 0.04 mmol, 79%), was obtained as an orange powder; mp (dec) 160.2−161.0 °C; ^{31}P NMR (161.9 MHz, THF-d_8) δ 131.5 (dd, ^1J(Rh,P) = 183 Hz, ^2J(P,P) = 25 Hz), 138.3 (dd, ^1J(Rh,P) = 183 Hz, ^2J (P, P) = 25 Hz) ppm.

[Rh(*β*-D-glucopyranosyl-(1,1)-2,3-di-*O*-(diphenylphosphino)-*β*-D-glucopyranoside)(cod)]-D-camphor-10-sulfonate (7): 63% yield, an orange powder; mp 147.0−147.5 °C; ^{31}P NMR (161.9 MHz, MeOH-d_4) δ 131.0 (dd, ^1J(Rh,P) = 180 Hz, ^2J(P,P) = 28 Hz), 138.6 (dd, ^1J(Rh,P) = 180 Hz, ^2J(P,P) = 28 Hz) ppm.

A Typical Procedure for the Hydrogenation of Enamides in an Aqueous Micellar Medium. To the Rh complex **1** or **2** (1.5 mg, 0.15×10^{-2} mmol), sodium dodecyl sulfate (10−200 mol %) and substrate (0.15 mmol) in a stainless steel autoclave with a glass container was added H_2O (2.0−3.0 mL) by a syringe under Ar, and the mixture was stirred vigorously under H_2 pressure (5 atm) at room temperature. After the end of the reaction was confirmed by GLC, TLC, or ^{1}H NMR, the solvent was evaporated under vacuum and the residue was

subjected to column chromatography on SiO_2 to give the hydrogenation product (85−93% yield). The enantiomeric excess was determined by HPLC using either Daicel Chiralcel OB or OJ column (4.6 × 250 mm) at 40 °C except for an *N*-acetylalanine methyl ester, the ee value of which being determined by optical rotation.[10] The separation of racemic mixtures under HPLC conditions is as follows: ***N*-acetylphenylalanine methyl ester** (OJ, 1.0 mL/min, 10% 2-PrOH/hexane), (*R*) t_1 = 10.0 min, (*S*) t_2 = 13.1 min; ***N*-benzoylphenylalanine methyl ester** (OJ, 1.0 mL/min, 10% 2-PrOH/hexane), (*R*) t_1 = 10.5 min, (*S*) t_2 = 13.4 min; ***N*-acetyl-3-(1-naphthyl)alanine methyl ester** (OJ, 0.5 mL/min, 10% 2-PrOH/hexane), (*S*) t_1 = 27.8 min, (*R*) t_2 = 32.5 min; ***N*-acetyl-3-(2-naphthyl)alanine methyl ester** (OJ, 0.5 mL/min, 10% 2-PrOH/hexane), (*R*) t_1 = 43.4 min, (*S*) t_2 = 51.7 min; ***N*-acetyl-3-(2-chlorophenyl)alanine methyl ester** (OJ, 1.0 mL/min, 10% 2-PrOH/hexane), (*R*) t_1 = 10.1 min, (*S*) t_2 = 12.2 min; ***N*-acetyl-3-(3-chlorophenyl)alanine methyl ester** (OJ, 1.0 mL/min, 10% 2-PrOH/hexane), (*R*) t_1 = 10.2 min, (*S*) t_2 = 12.5 min; ***N*-acetyl-3-(4-chlorophenyl)alanine methyl ester** (OJ, 1.0 mL/min, 10% 2-PrOH/hexane), (*R*) t_1 = 10.2 min, (*S*) t_2 = 13.6 min; ***N*-acetyl-3-(4-nitrophenyl)alanine methyl ester** (OJ, 1.5 mL/min, 10% 2-PrOH/hexane), (*R*) t_1 = 21.1 min, (*S*) t_2 = 37.0 min; ***N*-acetyl-3-(4-methoxyphenyl)alanine methyl ester** (OJ, 1.0 mL/min, 10% 2-PrOH/hexane), (*R*) t_1 = 16.0 min, (*S*) t_2 = 27.5 min; ***N*-acetyl-3-(3,4-dimethoxyphenyl)alanine methyl ester** (OJ, 1.0 mL/min, 10% 2-PrOH/hexane), (*R*) t_1 = 26.0 min, (*S*) t_2 = 37.4 min; ***N*-acetyl-1-(4-methylphenyl)ethenamine** (OB, 1.0 mL/min, 10% 2-PrOH/hexane), (*S*) t_1 = 10.3 min, (*R*) t_2 = 14.3 min; **1-(*N*-acetylamido)Indane** (OB, 1.0 mL/min, 10% 2-PrOH/hexane), (*S*) t_1 = 11.2 min, (*R*) t_2 = 14.1 min.

Hydrogenation of Itaconic Acid in an Aqueous Micellar Medium. To a mixture of the Rh complex **2** (3.5 mg, 0.35 × 10^{-2} mmol), sodium dodecyl sulfate (10.1 mg, 0.35 × 10^{-1} mmol), and itaconic acid (46 mg, 0.35 mmol) in a stainless steel autoclave with a glass container was added H_2O (2.0 mL) by a syringe under Ar, and the mixture was stirred vigorously under H_2 pressure (5 atm) at room temperature for 2 h. After the reaction was complete, 2 N HCl aqueous solution (10 mL) was added and the mixture was extracted with Et_2O (10 mL × 3). The organic layer was dried over $MgSO_4$ and the solvent was evaporated to give methylsuccinic acid (40.7 mg, 88%). The enantiomeric excess was determined by its optical rotation.[11]

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