

Studies on Catalytic Asymmetric Imine Hydrogenation in the Presence of Reverse Micelles: Enhanced Enantioselectivity due to Surfactant Head Group Coordination

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Asymmetric hydrogenation of the imines $\text{ArC}(\text{Me})=\text{NCH}_2\text{Ph}$ ($\text{Ar} = \text{C}_6\text{H}_5$ (**2**), 4-MeOC₆H₄ (**3**)) with $\text{Rh}[(\text{-})\text{bdpp}](\text{NBD})\text{ClO}_4$ (**1**) as the catalyst precursor in the presence of reverse AOT micelles results in enhanced enantioselectivity. For **2**, the ee in neat methanol is 59% (*R*), in neat benzene the value is 68% (*R*), and in benzene in the presence of 0.05 M AOT with $w = 5$ (5 equiv of water/AOT), the ee increases to 82% (*R*). For **3**, the ee increases from 68% (*R*) in neat methanol and 80% (*R*) in neat benzene to 87% (*R*) in the presence of 0.1 M AOT in benzene. The ee can be further increased to 92% (*R*) in 96% chemical yield if the reaction is carried out at 4 °C. Substitution of the water with a variety of coadditives such as anisole, 1,2-dimethoxyethane, methanol, and 15-crown-5 to the reverse AOT micelles in benzene also induces large increases in enantioselectivity and chemical yields in the presence of AOT; the highest ee achieved for hydrogenation of **2** with **1** is 87% (*R*) in quantitative yield in benzene with 0.1 M AOT and 15-crown-5. Since other nonsurfactant sulfonate salts also induce similar enhancements in enantioselectivity, the sulfonate anion, and not the reverse micellar structure, appears to be responsible for the observed increases in ee. ³¹P NMR and MS studies revealed that the sulfonate anion is bound to the Rh^I center in a bidentate fashion but is rapidly exchanging on and off the catalyst. The presence of halides, on the other hand, brings about an almost complete inversion of the enantioselectivity for the hydrogenation of **2** using **1**. We propose that a change of mechanism takes place, a dihydride pathway being operative when halide is present and a monohydride pathway in the presence of sulfonates in nonpolar solvents. The coordination of the sulfonate functionality during the enantioselective step(s) also appears to be necessary for the observed increases in enantioselectivity. The fact that sulfonate binding has been shown to play a role in the enantioselectivity of the catalytic hydrogenation has important implications for reactions involving sulfonated phosphine ligands.

Introduction

The field of homogeneous enantioselective catalysis has advanced tremendously in the last 30 years through the discovery of new molecular catalyst systems coupled with the synthesis and use of increasingly sophisticated chiral ligands.¹ The origins of the resultant enantioselectivities found for almost all reactions studied are, however, rarely explicable by any simple model and are often strongly dependent on more mundane effects such as the nature of the other achiral ligands on the metal or even the solvent used. Although plausible explanations can be offered for certain of these effects, the major problem in this area of research is that large changes in enantioselectivity result from small energy differences (≤ 5 kcal/mol) which can arise from apparently minor effects which are difficult to evaluate, such as solvation energies. We were therefore interested whether

placing a chiral catalyst in an organized surfactant medium such as micelle, lipid bilayer, or vesicle could affect the enantioselectivity of a given reaction. Although it is well-known that the use of an organized medium can induce profound effects on certain transition-metal-catalyzed reactions,² only recently has this concept been applied to chiral systems. Indeed, while this work was in progress, Oehme and co-workers reported that significant increases in enantioselectivity occur in the asymmetric hydrogenation of enamide substrates in water in presence of a variety of surfactants and polymerized micelles and concluded that the effects were induced by the micellar structure.³ Further, Takaya observed enhanced chemical yields for the

(2) For catalytic hydrogenation reactions, see for example: (a) Reger, D. L.; Habib, M. M. *J. Mol. Catal.* **1978**, *4*, 315. (b) Reger, D. L.; Habib, M. M. *J. Mol. Catal.* **1980**, *7*, 365. Dror, Y.; Manassen, J. *Stud. Surf. Sci. Catal.* **1981**, *7*, 887. (c) Larpent, C.; Bernard, E. *J. Chem. Soc., Chem. Commun.* **1992**, 535. For a recent review of microemulsions in chemistry see: Schwuger, M. J.; Stickdorn, K.; Schomäcker, R. *Chem. Rev.* **1995**, *95*, 849.

(3) (a) Oehme, G.; Paetzold, E.; Selke, R. *J. Mol. Catal.* **1992**, *71*, L5. (b) Grassert, I.; Paetzold, E.; Oehme, G. *Tetrahedron* **1993**, *49*, 6605. (c) Kumar, A.; Oehme, G.; Roque, J. P.; Schwarze, M.; Selke, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2197.

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(1) For an overview, see: Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.

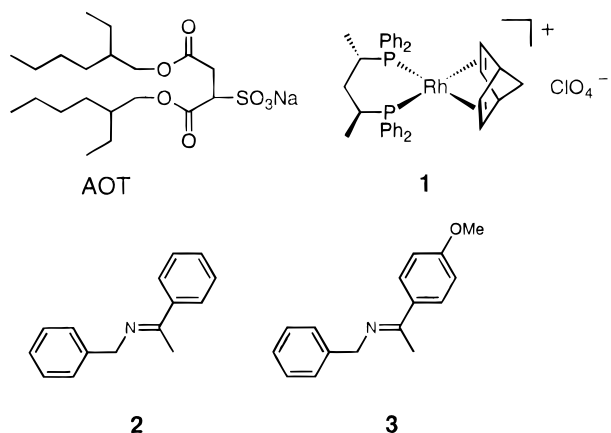


Figure 1. Surfactant, catalyst, and imines used in this study.

ruthenium-catalyzed transfer hydrogenation reactions in the presence of an anionic surfactant (SDS) but no increases in enantioselectivity were observed.⁴

We began our studies using the reverse micellar system formed by aggregation of sodium bis(2-ethylhexyl) sulfosuccinate (AOT), an extensively studied surfactant whose aggregates are well characterized (Figure 1).⁵ We surmised that this reverse micellar environment, although dynamic, could nevertheless influence catalyst–substrate orientations or conformational preferences and thereby affect the resultant enantioselectivity. Additionally, the unique properties of the water pool at the interior of these micelles could play an important role in catalysis. The size and characteristics of the reverse micelles are highly dependent upon the quantity of water dissolved in the micelle interior, normally defined by w , where $w = [\text{H}_2\text{O}]/[\text{AOT}]$. Examples of fascinating effects of reverse micelles on catalytic activity in transition-metal catalysis can be found in earlier work, for example, that of Sunamoto⁶ and Patin.⁷ In our initial studies we decided to investigate enantioselectivity changes occurring in the asymmetric hydrogenation of imines with chiral cationic rhodium complexes in the presence of reverse micelles of AOT. In spite of recent successes in asymmetric imine hydrogenation with rhodium-, iridium-, and titanium-based catalytic systems, a general methodology for effecting high ee's, similar to that of enamide hydrogenation, has not yet been described.⁸ Rh(NBD)-[(-)-bdpp]ClO₄ (**1**) was chosen as the catalyst precursor,⁹ since its reactivity for imine hydrogenation has been studied in detail.⁸ⁱ We anticipated that the water

Table 1. Results for Imine Hydrogenation in Reverse AOT Micelles in Benzene^a

imine	[AOT] (M)	additive	yield (%)	time (h)	ee (<i>R</i>) (%)
2 ^b	0				
2	0		86	23	68
2	0.05		72	11	69
2	0.05	H ₂ O ($w = 5$)	64	19	82
2	0.05	H ₂ O ($w = 5$)	33	23	87 ^c
3 ^b	0		95	21	80
3	0.1		>99	16	87
3	0.1		96	21	92 ^d
2	0.1	0.5 M anisole	96	70	79
2	0.1	0.1 M DME ^d	97	48	82
2	0.1	0.1 M MeOH	>99	25	78
2	0.1	0.1 M 15-crown-5	>99	69	87
2	0.1	0.1 M 15-crown-5	95	73	89 ^e
2	0	0.1 M 15-crown-5	96	45	64

^a Conditions: [**1**] = 5 mM; [imine]/[**1**] = 100; H₂ pressure 70 atm; $T = 25$ °C; solvent 10 mL C₆H₆; less than 2% hydrolysis observed in all cases; yields determined by ¹H NMR or GC; ee determined by ¹H NMR in CDCl₃ using L-(+)-mandelic acid as chiral shift reagent. ^b In neat methanol, ee = 68% (*R*). ^c $T = 6$ °C. ^d $T = 4$ °C. ^e $T = 8$ °C.

content of the reverse micelles might influence at least the rate of catalytic imine hydrogenation, since Wilkinson had proposed that protic solvents play an intimate role in the hydrogen transfer step for such rhodium-catalyzed hydrogenations.¹⁰ Indeed, we did observe significant enhancements of both chemical yield and enantioselectivity in these reactions, and we present here our detailed investigations on the origin of these effects.

Results and Discussion

Asymmetric Imine Hydrogenation in the Presence of Reverse AOT Micelles. The conditions for the hydrogenation of imines are described in the Experimental Section. Initially we chose to study imines **2** and **3**, which do not rapidly hydrolyze, and used cyclohexane as the bulk phase in which **1** is insoluble. Hence, any resultant activity when AOT is added would result from the presence of the surfactant. Although we found an increase in enantioselectivity for hydrogenation of **2** (ee = 70% (*R*) with 0.1 M AOT and $w = 10$) in comparison to the value obtained in methanol (ee = 59%), only partial dissolution of **1** occurred and the reaction was very slow. We then turned to benzene as the solvent, and the results obtained for the hydrogenation of imines **2** and **3** with **1** and AOT reverse micelles with varying values of w are presented in Table 1. First, we were surprised to find that the hydrogenation takes place quite satisfactorily in neat dry benzene and, further, that the ee for the amine product of hydrogenation of **2** (68% (*R*)) is greater than that obtained in methanol, although the reaction is somewhat slower. It had been previously assumed that an alcoholic cosolvent was required for hydrogenation of imines with rhodium–phosphine complexes.¹¹ Use of a protic solvent increases the rate, but it is not essential for reduction of these imines. When AOT (0.05 M) alone ($w = 0$) is added, the rate is similar to that found in benzene and the ee is unchanged at 69% (*R*). Incre-

(9) After exposure of this catalyst precursor to H₂, the active catalyst {Rh[(-)-bdpp]}⁺ is formed.

(10) Longley, C. J.; Goodwin, T. J.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1625.

(11) See refs 8f and 10.

(4) Nozaki, K.; Yoshida, M.; Takaya, H. *J. Organomet. Chem.* **1994**, *473*, 253.

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(6) Sunamoto, J. In *Solution Behavior of Surfactants*; Mittal, K. L., Fendler, J., Eds.; Plenum Press: New York, 1982; Vol. 2, p 767.

(7) (a) Briffaud, T.; Larpent, C.; Patin, H. *J. Chem. Soc., Chem. Commun.* **1990**, 1193. (b) Larpent, C.; Patin, H. *J. Mol. Catal.* **1992**, *72*, 315.

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(b) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952. (c) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562. (d) Lensink, C.; de Vries, J. G. *Tetrahedron: Asymmetry* **1992**, *3*, 235. (e) Bakos, J.; Orosz, A.; Heil, B.; Laghmani, M.; Lhoste, P.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1684. (f) Becalski, A. G.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kang, G.-J.; Rettig, S. J. *Inorg. Chem.* **1991**, *30*, 5002. (g) Ng Cheong Chan, Y. P.; Osborn, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9400. (h) Spindler, F.; Pugin, B.; Blaser, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 558. (i) Bakos, J.; Tóth, I.; Heil, B.; Szalontai, G.; Párkányi, L.; Fülöp, V. *J. Organomet. Chem.* **1989**, *370*, 263.

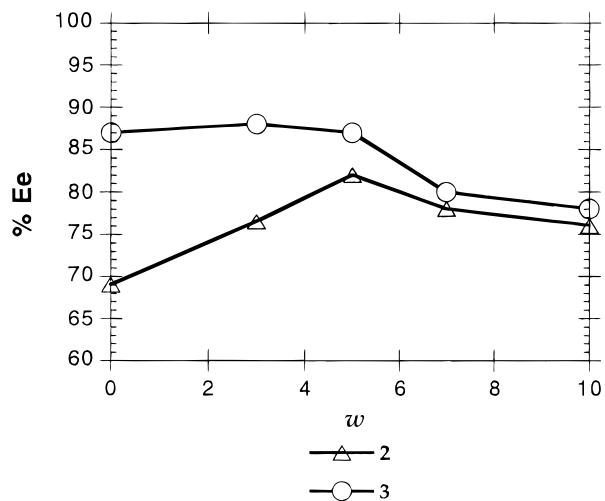


Figure 2. Dependence of the enantioselectivity of hydrogenation of imines **2** and **3** in the presence of inverse AOT micelles in benzene. Conditions: as in Table 1.

mental additions of water (Figure 2) cause an increase in ee, reaching 82% (*R*) with $w = 5$; however, when the w value is increased further to 10, the ee drops to 76% (*R*) and both the rate and yield diminish. Thus, there appears to be an optimum water concentration to obtain maximum enantioselectivity. We observe that at a high water content imine hydrolysis becomes significant, which lowers not only the product yield but also the efficiency of the catalyst, since the unreactive complex $\text{Rh}[(\text{-})\text{-bdpp}](\text{benzylamine})_2^+$ is formed (the benzylamine resulting from imine hydrolysis).¹²

A somewhat different behavior is found for the closely related substrate **3** (Figure 2). Although similar increases in ee are observed (68% (*R*) in MeOH, 80% (*R*) in neat C_6H_6 , 87% (*R*) in $\text{C}_6\text{H}_6/0.1$ M AOT), the addition of water ($w = 5$) causes no further change in this last value. At high values of w (10), both the rate and the ee (78%) are lowered. For **3** at 4 °C (with 0.1 M AOT and $w = 0$ in C_6H_6), a further increase in enantioselectivity to 92% (*R*) with 96% chemical yield is found after 1 h. This is the highest enantioselectivity achieved for this imine using nonsulfonated phosphines.¹³

The enantioselectivity for the hydrogenation of **2** and **3** is dependent upon the water content of the reverse micelles, as shown in Figure 2. In the case of **3**, however, water is not necessary to induce maximum enantioselectivity. Since these substrates have identical structures with the exception of the *p*-methoxy function on the phenyl group of **3**, the behavioral differences must be due to the presence of this ether group. Blank experiments showed that the addition of water to benzene solutions does not change the ee, and thus we surmised that during catalysis the ether group, being present in large excess, could play a similar role to that of water in these systems by modifying the structure of the AOT reverse micelles.

Effect of Additives on Imine Hydrogenation in AOT Micelles. In order to clarify the role of the

(12) ³¹P NMR data (at 121 MHz) for this complex in 4:1 $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$: δ 48.20 ppm ($^1J_{\text{Rh-P}} = 167$ Hz).

(13) Ee's of 92–95% have been reported using sulfonated (–)bdpp/ $[\text{Rh}(\text{COD})\text{Cl}]_2$ *in situ* catalysts: (a) Bakos, J.; Orosz, A.; Heil, B.; Laghmari, M.; Lhoste, P.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1684. (b) Lensink, C.; de Vries, J. G. *Tetrahedron: Asymmetry* **1992**, 3, 235.

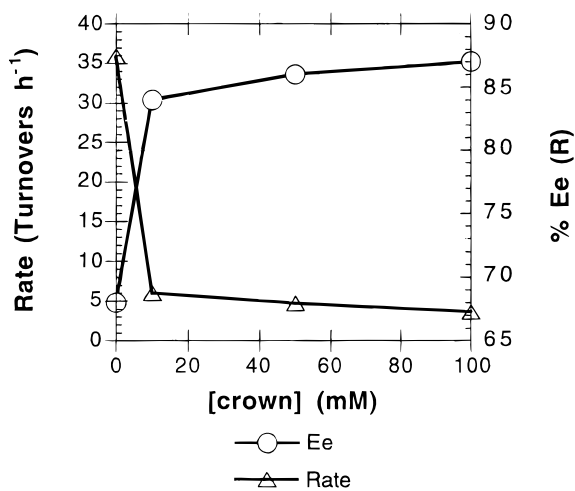


Figure 3. Dependence of enantioselectivity and rate on [15-crown-5] in the presence of 0.1 M AOT in benzene. Conditions: as in Table 1.

p-methoxy substituent, 0.5 M anisole (methoxybenzene) was added as a mimic of the ether functionality in **3** when **2** is hydrogenated with **1** in a 0.1 M AOT solution in benzene. No water was added. The presence of anisole caused the enantioselectivity to increase from 69% (*R*) to 79% (*R*), as shown in Table 1. The addition of anisole in the absence of AOT gave an ee of 63% (*R*). Therefore, an increase in ee in the hydrogenation of **2** is seen when AOT is combined with an additive, i.e. H_2O or anisole, or in the presence of the *p*-methoxy group of **3**, which explains the differences in behavior observed between the substrates **2** and **3**.

Previous studies have shown that addition of water to AOT reverse micelles causes the aggregate to take on a more open, extended structure.¹⁴ AOT micelles in the absence of water are compact structures with the alkyl chains arranged so tightly that even the organic solvent cannot penetrate into the micellar interior. The assembly becomes progressively more loose upon addition of water, due to loss of electrostatic interactions caused by solvation of the sodium counterions.¹⁴ In our case, in the absence of water or other additives, we suggest that the rhodium catalyst cannot interact readily with the reverse AOT micelles since the aggregate structure is so tightly arranged. Upon addition of H_2O , however, **1** permits an interaction of some type with the reverse micelles. Presumably the *p*-methoxy group of **3** or of anisole plays a similar role, thereby enhancing contact of the catalyst with the reverse micellar aggregates.

In order to gain support for this supposition, other additives which can solvate sodium ions were tested for hydrogenation of **2** in the presence of 0.1 M AOT in C_6H_6 . The additives examined include 1,2-dimethoxyethane (DME), methanol, and 15-crown-5. The results are summarized in Table 1. All of these additives result in enhancement of enantioselectivity over that in 0.1 M AOT, $w = 0$ (69% (*R*) ee), in benzene. One equivalent of 15-crown-5/AOT yields the highest ee, 87% (*R*), which can be increased to 89% (*R*) by carrying out the reaction at 8 °C. The effects of 15-crown-5 concentration on enantioselectivity and rates are shown in Figure 3. Only 10% 15-crown-5 with respect to AOT is necessary

(14) Martin, C. A.; Magid, L. J. *J. Phys. Chem.* **1981**, 85, 3938.

to induce a strong enhancement of enantioselectivity. Although the rate decreases, the overall chemical yields are greater in the presence of the AOT and 15-crown-5 combinations (see Table 1), since concomitant catalyst deactivation is slowed. We have found that up to 500 turnovers can be easily achieved with only a slight deterioration of ee.

The specificity of 15-crown-5 for sodium cation binding would indicate that complexation of the sodium cations is responsible, at least indirectly, for the increases in enantioselectivity observed. The other additives, i.e. anisole, DME, water, and methanol, complex the sodium ions less effectively and thus lead to smaller increases in enantioselectivity.

Physical Studies. A series of physical studies demonstrated that the presence of 1 equiv of 15-crown-5 per molecule of AOT induces a total breakdown of the reverse micellar structure. ^{23}Na NMR spectra of 0.1 M AOT in C_6D_6 reveal dramatic changes in line width upon addition of equimolar quantities of 15-crown-5.¹⁵ In the absence of crown ether, $\nu_{1/2} = 9200$ Hz ($\delta -9.2$ ppm), while with 1 equiv of 15-crown-5, the broad peak collapses, yielding a sharp singlet with $\nu_{1/2} = 185$ Hz ($\delta 5.66$ ppm). Static light scattering revealed that the aggregates formed by AOT in benzene over the range 0.01–0.5 M had an approximate mass of 5130, which corresponds to ca. 12 monomers/aggregate.¹⁶ Upon addition of 1 equiv of 15-crown-5 in benzene, however, aggregation disappears. These results indicate that monomeric AOT/15-crown-5 ion pairs, $[\text{Na}\cdot 15\text{-crown-5}]^+\text{-bis}(2\text{-ethylhexyl sulfosuccinate})^-$, are formed. Vapor pressure osmometry has shown that the aggregation number for AOT in benzene at 25 °C is ca. 13.¹⁷ Studies of a 1:1 AOT/15-crown-5 solution (0.1 M each) in benzene show the absence of large aggregates, the resultant data being interpreted in terms of only a strong association in the form of a tightly bound ion pair existing in solution.

These studies demonstrate that when the concentration of the crown ether is equal to that of AOT, the observed catalytic effects do not result from a reverse micellar effect. Since we observe the maximum enantioselectivity in the *absence* of reverse micelles, the increases in ee must be due in large part to the coordination of the anionic sulfonate group of AOT to the cationic rhodium catalyst (vide infra). The role of 15-crown-5 is to liberate the AOT monomers from the reverse micellar structure by weakening the sulfonate– Na^+ interaction, thus favoring binding of the sulfonate anion to the cationic rhodium catalyst in the nonpolar solvent (C_6H_6). For smaller ratios of 15-crown-5 to AOT, where micelles are certainly still present, however, we cannot exclude that this sulfonate–rhodium interaction may be taking place within the reverse micelle structure.

Effect of Other Sulfonate Salts on Imine Hydrogenation. If binding of the sulfonate group to the rhodium catalyst is the cause for the observed increases in enantioselectivity for imine hydrogenation, then other nonsurfactant sulfonate salts should show similar ef-

Table 2. Effect of Different RSO_3Na Salts on Hydrogenation of **2 with **1** in C_6H_6 ^a**

RSO_3Na	[15-crown-5] (M)	yield (%)	time (h)	ee (%)
none ^b	0	>99	4	59 (<i>R</i>)
none	0	86	23	68 (<i>R</i>)
0.1 M AOT	0	75	18	69 (<i>R</i>)
0.1 M AOT	0.1	>99	69	87 (<i>R</i>)
0.1 M EtSO ₃ Na ^c	0.1	98	55	81 (<i>R</i>)
0.005 M EtSO ₃ Na	0.005	87	45	73 (<i>R</i>)
0.1 M <i>p</i> -H ₃ CC ₆ H ₄ SO ₃ Na	0.1	92	69	81 (<i>R</i>)
0.1 M (<i>R</i>)-camphor-SO ₃ Na ^c	0.1	94	95	86 (<i>R</i>)
0.1 M (<i>S</i>)-camphor-SO ₃ Na ^c	0.1	96	95	86 (<i>R</i>)
0.1 M CF ₃ SO ₃ Na	0.1	93 ^d	4	81 (<i>R</i>)
0.1 M SDS	0.1	73	24	84 (<i>R</i>)
0.1 M CF ₃ CO ₂ Na	0.1	3	24	
0.1 CH ₃ (CH ₂) ₆ CO ₂ Na	0.1	3	48	
0.01 M N(ⁿ Bu) ₄ Cl	0	12	19	75 (<i>S</i>)
0.01 M N(ⁿ Bu) ₄ I	0	>99	19	80 (<i>S</i>)

^a Conditions are as in Table 1. ^b Solvent MeOH. ^c Some RSO_3Na salt remains undissolved. ^d No further reduction observed.

fects. As demonstrated in Table 2, this is indeed the case; in the presence of 1 equiv of 15-crown-5, all sodium sulfonate salts bring about increases in enantioselectivity: sodium ethanesulfonate, sodium *p*-toluenesulfonate, sodium (*R*)- and (*S*)-camphorsulfonate, and sodium triflate all result in ee's greater than 80% (*R*) in benzene. If enantiomerically pure (*R*)- or (*S*)-camphorsulfonate is used, no further chiral induction is observed, since both yield identical ee's of 86% (*R*) with superimposable reaction kinetics. Furthermore, hydrogenation of imine **2** with *achiral* Rh(NBD)(dppp)⁺ClO₄⁻ in the presence of chiral (*R*)-camphorsulfonate and 15-crown-5 (both 0.1 M) in benzene yields only the racemic product, revealing that the chirality of the sulfonate group has no effect on the enantioselectivity of the reaction.

Other types of anions with potential oxygen donor properties were also studied (see Table 2). A 0.1 M SDS (sodium dodecylsulfate) solution in benzene with 1 equiv of 15-crown-5 also induces an increase in the enantioselectivity of the reaction to 84% (*R*). Sodium trifluoroacetate and sodium octanoate with equimolar concentrations of 15-crown-5, however, inhibit all catalytic activity.

Evidence for Sulfonate Binding to the Rhodium Cation by ^{31}P NMR and Mass Spectrometry (FAB⁺) Studies. In a solution of AOT (0.1 M) in C_6D_6 , 5 mM **1** is treated with 1 atm of H₂. Two species (relative intensities ca. 2:1) are seen in the $^{31}\text{P}\{^1\text{H}\}$ NMR (Figure 4): a doublet at δ 41.48 ppm ($^1J_{\text{Rh-P}} = 194$ Hz) and a pair of doublets at δ 52.4 ppm ($^1J_{\text{Rh-P}} = 194$ Hz), separated by 11 Hz. The signal at δ 41.48 ppm was determined in a separate experiment to be the 18-electron benzene solvate $\text{Rh}[(\text{-})\text{bdpp}](\text{C}_6\text{D}_6)^+\text{X}^-$. We propose that the pair of doublets at δ 52.4 ppm result from the interaction of $\{\text{Rh}[(\text{-})\text{bdpp}]^+\}$ with the sulfonate group of AOT (used as a racemic mixture), leading to formation of two diastereomeric complexes. These are formed by nonstereospecific binding of enantiomerically pure $\{\text{Rh}[(\text{-})\text{bdpp}]^+\}$ with both enantiomers of the racemic bis(2-ethylhexyl) sulfosuccinate (the anionic portion of AOT), which possesses a chiral center α to the sulfonate group. This solution was then treated with the various additives previously discussed. On addition of 0.25 M H₂O ($w = 5$), the 11 Hz splitting collapses but the chemical shift and rhodium–phospho-

(15) For previous ^{23}Na NMR studies on reverse AOT micelles, see: Wong, M.; Thomas, J. K.; Nowak, T. *J. Am. Chem. Soc.* **1977**, *99*, 4730.

(16) For previous static light-scattering studies on reverse AOT reverse micelles, see: Kitahara, A.; Kobayashi, T.; Tachibana, T. *J. Phys. Chem.* **1962**, *66*, 363.

(17) Ueno, M.; Kishimoto, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1631.

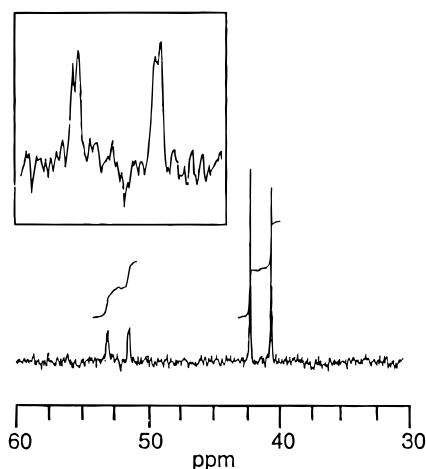


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complexes formed from hydrogenation of **1** in the presence of AOT. Conditions: $[\text{AOT}] = 0.1 \text{ M}$; $[\mathbf{1}] = 5 \text{ mM}$; solvent C_6D_6 ; $T = 298 \text{ K}$; H_2 pressure 1 atm. Inset: Closeup of the doublet at $\delta 52.40$.

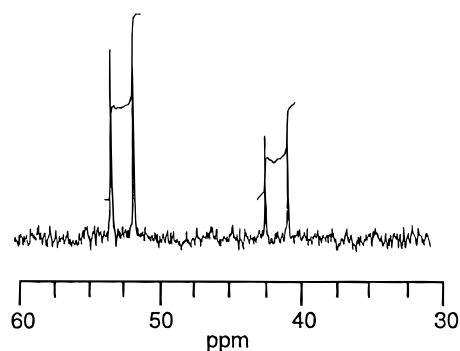


Figure 5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complexes formed from hydrogenation of **1** in the presence of 1:1 AOT and 15-crown-5. Conditions: 121 MHz; $[\mathbf{1}] = 5 \text{ mM}$; $T = 25 \text{ }^\circ\text{C}$; $p(\text{H}_2) = 1 \text{ atm}$; $[\text{AOT}] = [\text{15-crown-5}] = 0.1 \text{ M}$; solvent C_6D_6 .

Thus coupling constant remain unchanged. Rapid exchange of the sulfonate groups must now be occurring. When the solution is treated with 0.5 M anisole, no modification of the spectrum is observed and the 11 Hz splitting remains intact. In the presence of 0.1 M 15-crown-5, however, the relative concentrations of the two species in solution change (becoming ca. 1:2) and the 11 Hz splitting disappears (Figure 5). Thus, the apparent equilibrium involving the cationic benzene complex and the rhodium-sulfonate complex is displaced by the addition of 15-crown-5 in favor of the latter, along with the initiation of rapid sulfonate exchange. When a 5 mM solution of the complex $\text{Rh}(\text{NBD})[(-)\text{-bdpp}][\text{bis}(2\text{-ethylhexyl) sulfosuccinate}]$ (synthesized separately) is hydrogenated at 1 atm in C_6D_6 , a spectrum similar to that seen with 0.1 M AOT (no additives), including the 11 Hz splitting, is obtained. Positive FAB mass spectroscopy of this solution reveals peaks at m/z 543.0 (100% intensity), 627.1 (17% intensity), and 964.2 (35% intensity), corresponding to $[\text{Rh}((-)\text{-bdpp})]^+$, $[\text{Rh}((-)\text{-bdpp})(\text{C}_6\text{D}_6)]^+$, and $[\text{Rh}((-)\text{-bdpp})[\text{bis}(2\text{-ethylhexyl) sulfosuccinate}] - \text{H}]^+$, respectively. No peaks corresponding to dimers or species of higher nuclearity were observed. Overall, the evidence points strongly to the existence of a monomeric labile Rh^{I} complex bound to the oxygen(s) of the sulfonate.¹⁸ Indeed, complexes formed from $[\text{Rh}((-)\text{-bdpp})]^+$ and other sulfonate, sul-

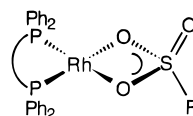


Figure 6. Proposed bidentate binding of RSO_3^- to the cationic rhodium catalyst.

fate, and carboxylate anions show ^{31}P NMR shifts in the same region with almost identical coupling constants.¹⁹ We propose that the sulfonate group binds to the rhodium center in a bidentate fashion, as shown in Figure 6.²⁰

The detection by ^{31}P NMR of only one pair of diastereomers with racemic AOT, coupled with the FAB data, would appear to be compelling evidence for the existence of predominantly monomer 1:1 complexes in solution. In order to affirm these conclusions, we studied the interaction of the catalyst with sodium camphorsulfonate salts. After hydrogenation of **1** under 1 atm of H_2 in the presence of 0.1 M sodium (*R*)-, (*S*)-, or (\pm)-camphorsulfonate in C_6D_6 with 0.1 M 15-crown-5, the ^{31}P NMR showed the doublet of the benzene solvate complex along with a signal of the corresponding $\text{Rh}[(-)\text{-bdpp}][\text{camphorsulfonate}]$ complex. The complex formed with the (*R*)-camphorsulfonate complex appears at $\delta 53.87 \text{ ppm}$ ($^1J_{\text{Rh-P}} = 195 \text{ Hz}$) with $\nu_{1/2} = 6 \text{ Hz}$, and the (*S*)-camphorsulfonate complex appears at $\delta 53.53 \text{ ppm}$ ($^1J_{\text{Rh-P}} = 195 \text{ Hz}$) with $\nu_{1/2} = 6 \text{ Hz}$, while with the racemic camphorsulfonate, the broad doublet appears at $\delta 53.67 \text{ ppm}$ ($^1J_{\text{Rh-P}} = 195 \text{ Hz}$) with $\nu_{1/2} = 30 \text{ Hz}$. The fact that the doublet associated with the racemic camphorsulfonate-rhodium complex is substantially broadened and has a chemical shift that is the average of those for the (*R*)- and (*S*)-camphorsulfonate complexes indicates that a rapid intermolecular exchange process is occurring involving the sulfonate anions. Low-temperature ^{31}P NMR in deuterated toluene was carried out to study the intermolecular camphorsulfonate exchange. As shown in Figure 7, the two diastereomers in the racemic camphorsulfonate solution can indeed be seen on lowering the temperature to 248 K. The ΔG^\ddagger value for the exchange can be calculated as ca. 14 kcal/mol at the coalescence temperature, 273 K.²¹ At even lower temperatures further broadening of the signals occurs, resulting from the freezing out of an additional dynamic process, a phenomenon also observed when

(18) The deuterated methanol-solvated complex $\text{Rh}[(-)\text{-bdpp}](\text{CD}_3\text{-OD})_x^+$ has a very similar chemical shift and rhodium-phosphorus coupling constant in ^{31}P NMR ($\delta 51.37 \text{ ppm}$ ($^1J_{\text{Rh-P}} = 194 \text{ Hz}$)) as compared to the bis(2-ethylhexyl) sulfosuccinate-rhodium complex ($\delta 52.40 \text{ ppm}$ ($^1J_{\text{Rh-P}} = 194 \text{ Hz}$)), which substantiates the assumption that the sulfonate coordination compound is a Rh^{I} complex bound to oxygen σ -donor ligands.

(19) For instance, the chemical shifts of other rhodium sulfonate/sulfate/carboxylate species in C_6D_6 with 0.1 M 15-crown-5 are as follows: 0.1 M EtSO_3Na , $\delta 54.26$ ($^1J_{\text{Rh-P}} = 195 \text{ Hz}$); 0.1 M sodium (*S*)-camphorsulfonate, $\delta 53.53$ ($^1J_{\text{Rh-P}} = 195 \text{ Hz}$); 0.1 M sodium dodecylsulfate, $\delta 53.90$ ($^1J_{\text{Rh-P}} = 196 \text{ Hz}$); 0.1 M sodium octanoate, $\delta 51.82$ ($^1J_{\text{Rh-P}} = 185 \text{ Hz}$); 0.1 M sodium trifluoroacetate, $\delta 50.72$ ($^1J_{\text{Rh-P}} = 185 \text{ Hz}$).

(20) Other examples of sulfonate groups binding in a bidentate fashion to a single transition-metal center include: (a) Stuhl, L. S.; Muetterties, E. L. *Inorg. Chem.* **1978**, *17*, 2148. (b) Pörschke, K. R.; Krause, J.; Haack, K.-J.; Nickel, T.; Proft, B. International Symposium on Homogeneous Catalysis by Transition Metals, Jerusalem, Israel, August 1994; Abstract C-8; For binding in a bridging fashion to two metal centers: Kilimann, U.; Schäfer, M.; Herbst-Irmer, R.; Edelmann, F. T. *J. Organomet. Chem.* **1994**, *469*, C10.

(21) ΔG^\ddagger values calculated using $\Delta G^\ddagger = 4.57T_c[9.97 + \log(T_c/\delta_\nu)]$, where T_c is the coalescence temperature and δ_ν the chemical shift separation in Hz just prior to coalescence. See: van Harald, G. *NMR-Spektroskopie*; George Thieme Verlag: Stuttgart, Germany, 1973.

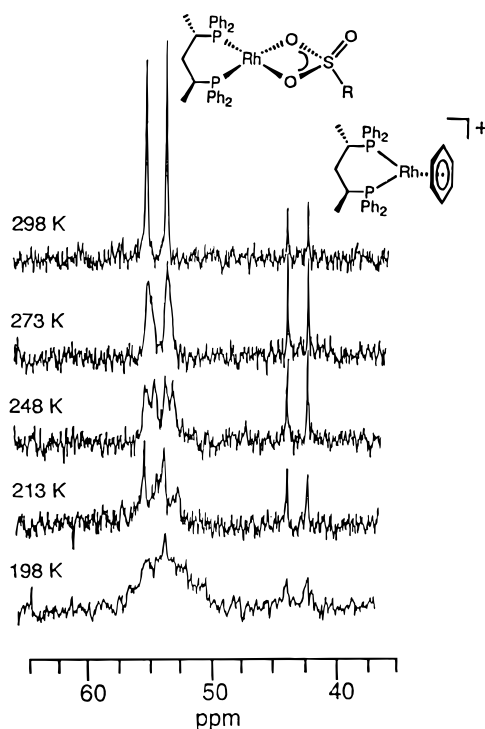


Figure 7. Variable-temperature ^{31}P NMR spectra of **1** under H_2 in the presence of 1:1 sodium (\pm)-camphorsulfonate and 15-crown-5. Conditions: 121 MHz; **1** = 5 mM; [sodium (\pm)-camphorsulfonate] = [15-crown-5] = 0.1 M; solvent d_6 -toluene; $p(\text{H}_2)$ = 1 atm; T = 298 K.

enantioselectively pure sodium (*R*)-camphorsulfonate is used. The most feasible interpretation is that if the sulfonate anion is behaving as a bidentate ligand, as shown in Figure 6, the phosphorus nuclei are non-equivalent (since the C_2 axis is lost), and at low temperatures the ^{31}P NMR spectrum would present a pair of overlapping ABX spectra. An intramolecular rearrangement of the sulfonate ligand on the complex as the temperature is raised (≥ 213 K) would then make the phosphorus nuclei equivalent on the NMR time scale, giving rise to the simplified spectra. This could occur by a pseudorotation process²² or, more probably, an arm-off mechanism as shown in Figure 8.²³ Again, the monomeric nature of the $\text{Rh}(-)\text{-bdpp}[\text{camphorsulfonate}]$ species is suggested by the observation that only two diastereomers are seen upon lowering the temperature, dimeric species being expected to give more complex spectra, e.g. as in the methanol-bridged dimers formed from $\text{Rh}[(\pm)\text{-phenphos}]^+$ ²⁴ and iodide-bridged dimers of the form $[\text{Ir}[(\pm)\text{-diphosphine}]\text{HI}_2]_2$.²⁵

In Figure 9 we summarize the role of 15-crown-5 on reverse micelles of AOT and subsequent binding of the

sulfonate group to the rhodium catalyst. We believe that the compact structure of the reverse AOT micelles in benzene does not allow the catalyst to interact strongly with the ordered aggregates. Upon addition of 15-crown-5, however, the sodium counterions of AOT are encapsulated, leading to a breakdown of the micellar structure and the formation of the monomeric ion pairs $[\text{Na}\cdot 15\text{-crown-5}]^+[\text{bis}(2\text{-ethylhexyl})\text{ sulfosuccinate}]^-$. The bis(2-ethylhexyl) sulfosuccinate anion is now free to bind to the cationic catalyst to form the neutral rhodium-sulfonate complex, thereby shifting the equilibrium away from the cationic benzene complex. The observed enhancement of enantioselectivity in imine hydrogenation must result at some stage from this sulfonate anion-catalyst interaction.

Anion Effects on the Enantioselectivity. The detailed mechanism for imine hydrogenation with cationic rhodium catalysts is still not clear.^{10,11,25} The influence of halides on this enantioselectivity with cationic rhodium catalysts has, however, been previously reported.^{8f,26} For instance, Fryzuk, James, and co-workers found that hydrogenation of **3** with an *in situ* $[\text{Rh}(\text{NBD})\text{Cl}]_2/(\text{R})\text{-cycphos}$ catalyst (1 equiv of Cl^-/Rh^+) in 1:1 MeOH/ C_6H_6 gave an ee of 60% (*S*).^{8f} Use of the preformed cationic complex $\text{Rh}(\text{NBD})[(\text{R})\text{-cycphos}]\text{PF}_6$ (no chloride present) resulted, under the same conditions, in an ee of 15% (*R*). It was proposed that the occupation of a coordination site on the rhodium by a halide ligand may limit the number of diastereomers in the enantioselective step^{8f} or that the mechanism of the reaction may be changed by the presence of anions.

In our studies, we note that the addition of halides (Table 2) to the cationic catalyst results in an almost complete *inversion of the enantioselectivity* of the reaction, the iodide-modified catalyst yielding 80% (*S*) product compared with 87% (*R*) obtained with sulfonate. This dramatic effect would seem to indicate that a change in mechanism has taken place. We have also found that anions have a profound effect on the hydrogenation of the olefinic substrate α -ethylstyrene using this same catalyst, bringing about even more dramatic increases in enantioselectivity. In this case, however, the sulfonate and halide catalysts both give the same product enantiomer.²⁷ We believe that these differences in behavior between the imine and α -ethylstyrene hydrogenations result from the possibility of deprotonation-protonation reactions occurring during the hydrogenation of imines, which necessarily is carried out under basic conditions. The presence of base (the imine itself) thus can deprotonate a cationic dihydride intermediate to form an active neutral monohydride species.²⁸ For ketone hydrogenation with cationic rhodium catalyst precursors, the presence of NEt_3 has been found to greatly improve the enantioselectivity,²⁹ and a monohydride catalyst was invoked to explain these observations.³⁰ Furthermore, it has been suggested that heterolytic H_2 activation may be imine assisted,^{8f} and a

(22) Similar fluxional behavior proposed to explain the dynamics of tridentate phosphine ligands on the $\text{M}(\text{COD})^+$ moiety ($\text{M} = \text{Rh}, \text{Ir}$) took place via associative binding of the fifth ligand to form either a trigonal-bipyramidal intermediate (drawn here) or a quasi-capped structure. See: El-Amouri, H.; Bahsoun, A. A.; Osborn, J. A. *Polyhedron* **1988**, *7*, 2035.

(23) Fourteen-electron intermediates have been shown repeatedly to be involved in rhodium-catalyzed processes. See for example: Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 2762.

(24) Brown, J. M.; Chaloner, P. A.; Kent, A. G.; Murrer, B. A.; Nicholson, P. N.; Parker, D.; Sidebottom, P. J. *J. Organomet. Chem.* **1981**, *216*, 263.

(25) (a) Sablong, R.; Osborn, J. A. Unpublished results. (b) Ng Cheong Chan, Y. P. Doctoral Thesis, Université Louis Pasteur, Strasbourg, France, 1990.

(26) (a) Vastag, S.; Bakos, J.; Törös, S.; Takach, N. E.; King, B. R.; Heil, B.; Markó, L. *J. Mol. Catal.* **1984**, *22*, 283. (b) Kang, G.-J.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1466.

(27) Buriak, J. M.; Osborn, J. A. Manuscript in preparation.

(28) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2134.

(29) See ref 8i. We have found that for hydrogenation of acetophenone with **1** in MeOH (using the conditions in ref 8i), an ee of 87% (*S*) results with 5 equiv of NEt_3/Rh^+ . In the absence of NEt_3 , the ee is only 24% (*S*).

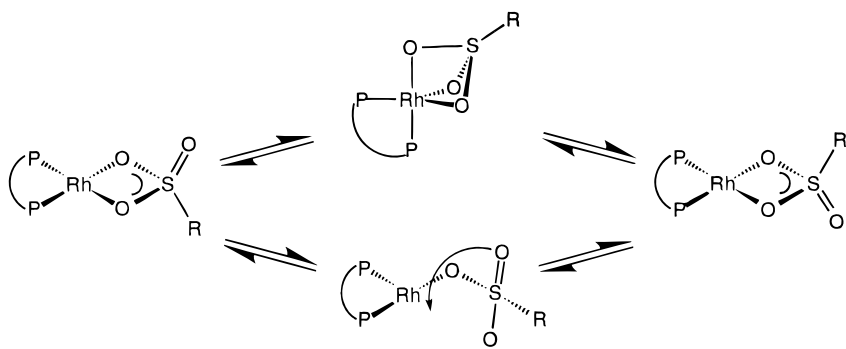


Figure 8. Proposed intramolecular rearrangement of the sulfonate group via either a five-coordinate trigonal-bipyramidal intermediate (top) or an unsaturated three-coordinate intermediate with the sulfonate bound in a monodentate fashion (bottom).

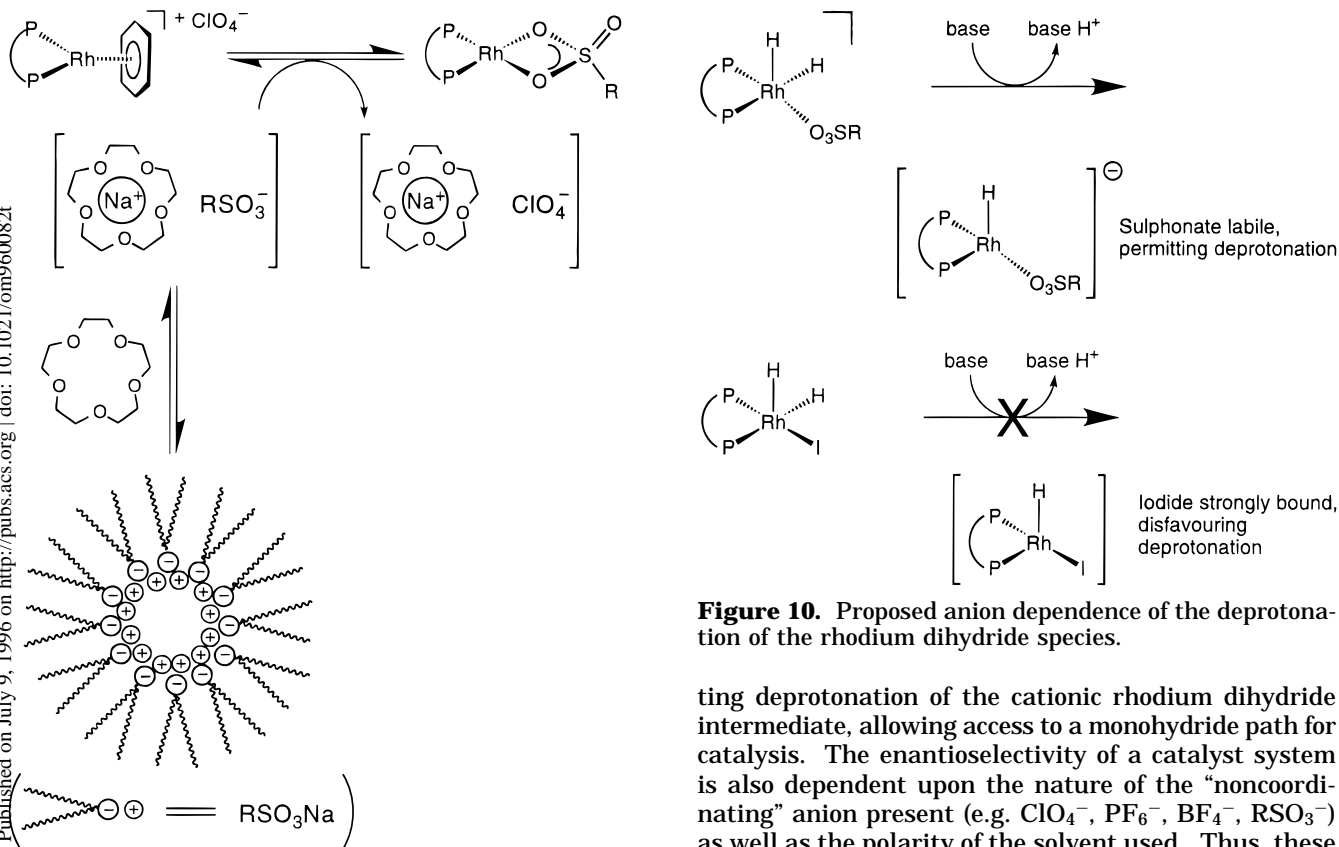


Figure 9. Proposed equilibria between the catalyst, AOT reverse micelles, and 15-crown-5 in benzene.

monohydride mechanism similar to that proposed for ketones could also be involved in imine hydrogenation.

We believe that, in the hydrogenation of α -ethylstyrene,²⁷ a dihydride route is operative. The coordination of a strongly bound halide ligand to the rhodium cation to form a neutral complex disfavors deprotonation of the eventually formed dihydride species (see Figure 10), even in the presence of base. Indeed, NMR experiments show that identical spectra are obtained with and without NEt_3 when **1** is treated with H_2 in the presence of 1 equiv of $\text{N}^t\text{Bu}_4\text{I}$. Thus, for both olefin and imine hydrogenation in the presence of halides, a dihydride route is followed. However, although the sulfonate anion also coordinates to the rhodium, its lability allows transient formation of cationic species, thereby permit-

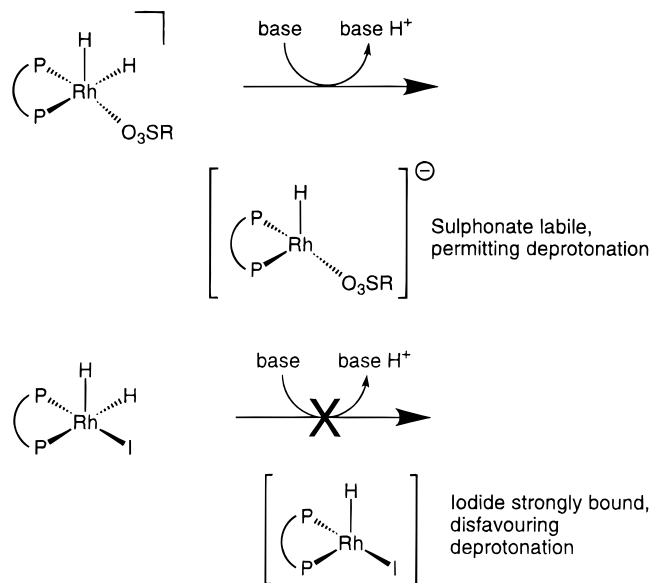


Figure 10. Proposed anion dependence of the deprotonation of the rhodium dihydride species.

ting deprotonation of the cationic rhodium dihydride intermediate, allowing access to a monohydride path for catalysis. The enantioselectivity of a catalyst system is also dependent upon the nature of the “noncoordinating” anion present (e.g. ClO_4^- , PF_6^- , BF_4^- , RSO_3^-) as well as the polarity of the solvent used. Thus, these labile anions must have a further role, later returning to bind to the catalyst and thereby influencing the enantioselectivity. For example, if coordination of RSO_3^- to $\text{Rh}(\text{diphosphine})\text{H}$ (Figure 10) takes place to form the anionic species $\text{Rh}(\text{diphosphine})\text{H}(\text{RSO}_3)^-$, transfer of the more nucleophilic hydride to a bound imine substrate may follow and, thus, the presence of the sulfonate ligand can thereby influence the enantioselectivity. The resultant anionic amido complex (perhaps stabilized by sulfonate chelation) can then receive a proton from the protonated imine, yielding the amine product. This proposal is largely speculative but serves to illustrate how a labile anion could play an important role in the resultant enantioselectivity.

Finally, it was observed that when monosulfonated ($-$)-bdpp was used as the ligand for rhodium-catalyzed hydrogenation of imines **2** and **3**, enantioselectivities greater than 92% were observed in ethyl acetate as solvent.¹³ Given our observations, these high enantioselectivities may be a result of intermolecular coordi-

(30) Bosnich, B. *Asymmetric Catalysis*; Martinus Nijhoff: Dordrecht, The Netherlands, 1986; p 31.

nation of a sulfonate group to the rhodium catalyst during the enantioselective step. We find that under our conditions using the nonsulfonated (–)-bdpp complex with 0.1 M AOT and 1 equiv of 15-crown-5 in ethyl acetate, hydrogenation of **2** gave an ee of 77% (*R*), which is an increase from 67% (*R*) found in neat ethyl acetate. While the enhancement is less than that observed using monosulfonated (–)-bdpp, it does suggest that intermolecular sulfonate binding to the rhodium center is, at least in part, responsible for the effects observed when monosulfonated (–)-bdpp is used. We note that dimeric complexes with bridging sulfonates, i.e. (Rh(1,5-cyclooctadiene)(triphenylphosphine-*m*-monosulfonate))₂, have been characterized, which adds credence to this proposition.³¹

Conclusions

In these studies concerning catalytic hydrogenation with chiral rhodium complexes in the presence of reverse micelles of AOT in benzene, we have shown that the significant increases in the enantiomeric excess of the product amine from imine reduction results predominately from an interaction of the rhodium catalyst with the anionic sulfonate groups on the AOT. We do not see any clear evidence for a reverse micellar effect in this case. The catalyst system does function, however, when micelles are present (low ratios of 15-crown-5/AOT) and appears to be somewhat more stable under these conditions, which indicates that the reverse micellar structure may offer some protection to the catalyst system by impeding dimerization or the like. The sulfonate anion effect, however, does not seem to result simply from occupation by the sulfonate group of a coordination site, since replacement of the sulfonate salt with halides (iodide and chloride) brings about a complete inversion of the enantioselectivity of the reaction. We propose that these observations may be related to the rapid on–off behavior of the sulfonate ligand on the catalyst, which can lead to a different catalytic pathway with a totally different enantioselectivity. Our results also provide at least, in part, an explanation for the observed enhancements of rhodium-catalyzed imine hydrogenation using monosulfonated (–)-bdpp as the chiral ligand.

Two further comments are to be noted. First, using the same chiral catalyst, *both product enantiomers* can be obtained with good enantioselectivity by simply changing the anion added to the medium as shown in Figure 10. Since one ligand antipode is often more expensive (as in the case of bdpp), or is obtainable only with difficulty, such behavior may be of interest for synthetic applications. This observation also serves as a reminder that models that attempt to correlate the resultant product chirality with catalyst–chiral ligand–substrate interactions should be used cautiously unless detailed mechanistic data are available. Second, the facile on–off behavior at the catalyst of such “noncoordinating” anions in nonpolar solvents may have significant effects on the catalytic process. Innocent anions are not necessarily innocent.

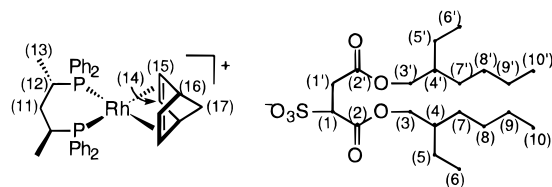
Experimental Section

Reagents and products were generally manipulated under nitrogen or argon atmospheres by standard Schlenk techniques

(31) Borowski, A. J.; Cole-Hamilton, D. J.; Wilkinson, G. *New J. Chem.* **1978**, *2*, 137.

or in a Vacuum Atmospheres glovebox. NMR spectra were acquired using Bruker spectrometers operating at 300, 400, or 500 MHz. Mass spectral data and elemental analyses were obtained at the Services for Mass Spectra and Microanalysis, respectively, at the Chemistry Research Center, ULP. Solvents were cyclically distilled under an inert atmosphere and dried over the usual drying agents. Imines **2** and **3** were prepared from benzylamine and acetophenone or 4-methoxyacetophenone, respectively, using a Dean–Stark apparatus to remove the water produced. The imines were crystallized three times from hot hexanes, yielding large pale yellow blocks whose elemental analyses were as expected. Rh[(–)-bdpp]-(NBD)ClO₄ (**1**) was prepared as previously described³² from Rh(NBD)(acac), 70% HClO₄, and (–)-bdpp (purchased enantiomerically pure from Strem Chemicals). The spectral data for **1** corresponded with those previously reported.⁸¹ Rh(NBD)-(dppp)ClO₄ was prepared in an identical fashion; its spectral data matched those in the literature.³³ AOT (99% stated purity, purchased from Aldrich) was purified by stirring for 12 h with activated charcoal in dry methanol, filtering repeatedly over Celite to remove charcoal and solids, and drying *in vacuo* for 48 h according to the method of Zulauf and Eicke.⁵ Static light-scattering experiments were carried out at 25 °C with a Sematech SEM-633 apparatus at λ = 632.8 nm. The refraction increment (*d_n/d_c*) was determined at 25 °C and λ = 632.8 nm using a Brice-Phoenix differential refractometer (Model BP-2000-K).

Preparation of Rh[(–)-bdpp](NBD)[bis(2-ethylhexyl) sulfosuccinate]. The acid form of bis(2-ethylhexyl) sulfosuccinate is prepared according to earlier published procedures by ion-exchanging a 1.0 M 1:1 H₂O/MeOH solution of AOT on a protonated strongly acidic Dowex column (Dowex 50X8 200).³⁴ To a solution of 100 mg of Rh(NBD)(acac) (3.4 × 10^{−4} mol) in 10 mL of dry degassed THF is added a solution of 186 mg of bis(2-ethylhexyl) sulfosuccinic acid (4.4 × 10^{−4} mol) in dry degassed THF via a cannula. The yellow solution instantly becomes paler. After it is stirred for 5 min, a solution containing 150 mg of (–)-bdpp (3.4 × 10^{−4} mol) in dry degassed THF is added via a cannula, upon which the solution immediately turns ruby red. After the mixture is stirred for 15 min, the THF is stripped off *in vacuo*. Degassed pentane is added in 20 mL portions, the mixture (under an argon atmosphere) is sonicated for 5 min, and the pale yellow pentane solution is taken off with a syringe and discarded; this procedure must be repeated at least five times to obtain pure material. After drying *in vacuo*, the deep red solid becomes flaky. This solid is then washed repeatedly (10 times) with 5 mL portions of pentane in a glass frit under an inert atmosphere to yield 270 mg (75% yield) of **13**. The deep red iridescent solid is hygroscopic and slightly air sensitive. The carbons of this complex are labeled as follows:³⁵



¹H NMR (300 MHz, CD₂Cl₂): δ 7.8–7.35 (4 C₆H₅, m, 20H), 4.85 (2 C₍₁₄₎H, m, 2H), 4.29 (2 C₍₁₅₎H, m, 2H), 4.1–3.9 (overlapping 2 C₍₁₆₎H, 2H; C₍₃₎H₂ and C_(3′)H₂, 4H; C₍₁₎H, 1H), 3.18 (C₍₁₇₎HH, dd, ²J = 18 Hz, ³J = 12 Hz, 1H), 3.02 (C₍₁₇₎HH, dd, ²J

(32) (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397. (b) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.

(33) Slack, D. A.; Baird, M. C. *J. Organomet. Chem.* **1977**, *142*, C69 (with BF₄[−] counterion).

(34) Eastoe, J.; Robinson, B. H.; Heenan, R. K. *Langmuir* **1993**, *9*, 2820.

(35) ¹³C NMR assignments and labelling of the bis(2-ethylhexyl) sulfosuccinate portion of the complex were based upon: Ueno, M.; Kishimoto, H.; Kyogoku, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1776.

= 18 Hz, $^3J = 4$ Hz, 1H), 2.81 (2, $C_{(12)}H$, m, 2H), 1.59 (2 $C_{(11)}H_2$, tt, $^3J = 20$ Hz, $\Sigma J = 7$ Hz, 2H), 1.58 ($C_{(17)}H_2$, s, 2H), 1.55–1.22 (overlapping $C_{(4)}H$, $C_{(4')}H$, $C_{(5)}H_2$, $C_{(5')}H_2$, $C_{(7)}H_2$, $C_{(7')}H_2$, $C_{(8)}H_2$, $C_{(8')}H_2$, $C_{(9)}H_2$, $C_{(9')}H_2$, m, 18H), 1.17 (2 $C_{(13)}H_3$, q, $\Sigma J = 7$ Hz, 6H), 0.95–0.8 (overlapping $C_{(6)}H_3$, $C_{(6')}H_3$, $C_{(10)}H_3$, $C_{(10')}H_3$, m, 12H).

$^{31}P\{^1H\}$ NMR (121 Hz, CD_2Cl_2): δ 27.90 (d, $^1J_{Rh-P} = 150$ Hz).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 172.33 ($C_{(2)}$, s), 169.76 ($C_{(2')}$, s), 136.10 (phenyl C, s), 133.2 (phenyl C), 132.39 (C_{ipso} , t, $\Sigma J = 22$ Hz), 132.10 (phenyl C, s), 130.78 (overlapping C_{ipso} , t; phenyl C, s), 130.01 (phenyl C, s), 72.44, 71.46, 67.44, 66.80, 65.44, 63.67 ($C_{(14)}$, s; $C_{(15)}$, s; $C_{(16)}$, s; $C_{(3)}$, s; $C_{(3')}$, s; $C_{(1)}$, s), 51.81 ($C_{(17)}$, s), 39.36 ($C_{(4)}$, s), 39.20 ($C_{(4')}$, s), 37.16 ($C_{(1)}$, s), 35.63 ($C_{(12)}$, m), 30.81 ($C_{(7)}$ and $C_{(7')}$, s), 29.32 ($C_{(8)}$ and $C_{(8')}$, s), 26.51 ($C_{(11)}$, t, $\Sigma J = 13$ Hz), 24.18 ($C_{(9)}$ and $C_{(9')}$, s), 23.46 ($C_{(5)}$ and $C_{(5')}$, s), 17.83 ($C_{(13)}$, s), 14.38 ($C_{(9)}$ and $C_{(9')}$, s), 11.29 ($C_{(10)}$ and $C_{(10')}$, s).

IR (solid, KBr wafer; cm^{-1}): 1732 (s, AOT C=O), 1434 (m, P– C_6H_5), 1237 (sb, AOT C–O), 1156 (m, AOT asym SO_3), 1032 (s, AOT sym SO_3), 998 (w, P–C).

MS FAB+ (m/z): 635.0, [M – bis(2-ethylhexyl) sulfosuccinate] $^+$; 542.7, [M – bis(2-ethylhexyl) sulfosuccinate – NBD] $^+$.

Hydrogenation Procedure. All hydrogenation experiments were carried out in high-pressure autoclaves (50 mL) in the absence of air. Conversions are measured by analysis (1H NMR or GC) of samples taken from the reaction mixture. For a series of experiments in the same solvent and same surfactant concentration, a standard solution is prepared and kept in the glovebox. A typical hydrogenation experiment is carried out as follows.

1 (37 mg, 5×10^{-5} mol) is loaded into a stainless steel autoclave with imine **2** (1.045 g, 5×10^{-3} mol). The entire autoclave is taken into a glovebox and the surfactant/solvent mixture (10 mL) added, along with any coadditives (15-crown-5, DME, etc.). The autoclave is closed and taken out of the box and attached to the high-pressure H_2 line. The line is purged of air and filled with H_2 and the autoclave pressurized to 70 atm H_2 pressure. The pressure is released to just above atmospheric level and the autoclave refilled with H_2 ; this procedure is repeated a total of three times. The autoclave is pressurized again to 70 atm and stirring begun. This moment is considered time zero for kinetic purposes. At the end of the reaction, the pressure is released and the amine purified by liquid chromatography (either column or preparative TLC) on silica using 1:1 hexane/ethyl acetate (R_f 0.33). The ee of the pure amine product is determined by 1H NMR using L-(+)-mandelic acid as a chiral shift reagent in $CDCl_3$. This reagent induces a $\Delta\delta$ value of 0.3 ppm in the methyl group α to the chiral center in the amine product. The hydrogenation product of **3** is purified and its enantiomeric excess determined in an identical fashion.

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