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# Probing the Mechanisms of Enantioselective Hydrogenation of Simple Olefins with Chiral Rhodium Catalysts in the Presence of Anions

Jillian M. Buriak,<sup>\*,[a]</sup> Jason C. Klein,<sup>[a]</sup> Deborah G. Herrington,<sup>[a]</sup> and John A. Osborn<sup>\*,[b]</sup>

**Abstract:** The strong influence of various anions upon the hydrogenation of 2-phenyl-1-butene, catalyzed by chiral rhodium catalysts was investigated. Both sulfonates and halides exert large increases in the enantioselectivity when  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{NBD})]\text{ClO}_4$  (bdpp = 2,4-bis(diphenylphosphino)pentane, NBD = 2,5-norbornadiene) is used as the catalyst precursor at high pressures (70 atm) of dihydrogen in nonpolar solvents. A dihydride mechanism similar to that for Wilkinson's catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$  was shown to be operat-

ing at both high- and low-pressure conditions through a combination of catalytic studies,  $^{31}\text{P}$ ,  $^1\text{H}$  and parahydrogen-induced polarization (PHIP) NMR experiments. With sulfonate and in neat methanol, however, a mechanistic switch takes place from a dihydride route (dihydrogen addition before olefin binding) at high pressure to an unsatu-

rate route (olefin binding before dihydrogen addition) at low pressures (< 30 atm). Olefin isomerization is inhibited by halide addition, but occurs with sulfonate and in neat methanol through what is most likely a  $\pi$ -allyl mechanism. A detailed understanding of the effects of addition of these anions is crucial for development of new classes of catalysts capable of efficient enantioselective reduction of prochiral olefins lacking a secondary polar binding group.

**Keywords:** alkenes • asymmetric catalysis • halides • rhodium • sulfonates

## Introduction

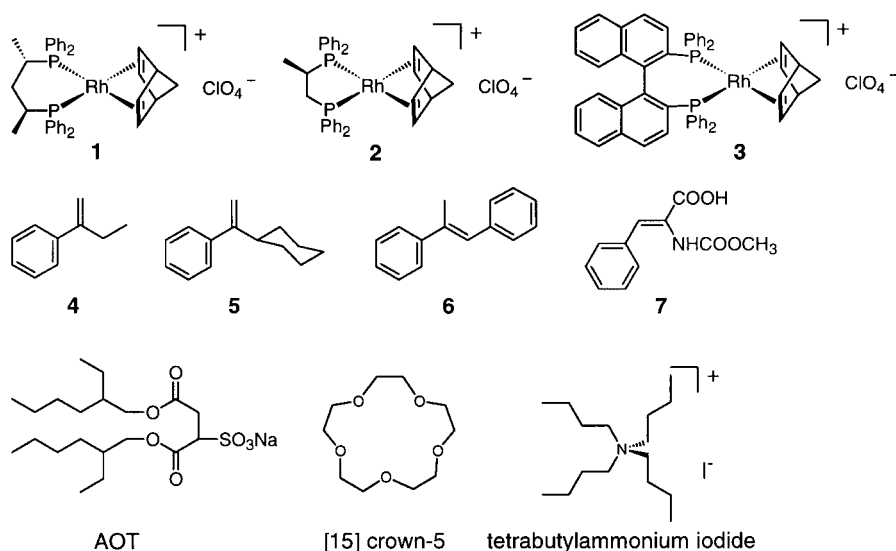
Asymmetric hydrogenation of prochiral olefins has for over 30 years been intensively investigated because of the utility of the chiral products for pharmaceutical and materials applications, to name a few.<sup>[1]</sup> The majority of catalysts tested have involved rhodium and ruthenium complexes rendered chiral through incorporation of optically active phosphane ligands.<sup>[2]</sup> Enantioselective olefin hydrogenation with late transition metal catalysts has been, however, essentially limited to specific classes of substrates capable of binding in a bidentate fashion to the metal center, like enamides,<sup>[3]</sup> unsaturated  $\alpha,\beta$ -carboxylic acids,<sup>[4]</sup> and allylic and homoallylic alcohols.<sup>[5]</sup> Much more difficult to reduce with good enantiomeric excesses are olefinic substrates lacking a polar secondary Lewis basic binding group in the correct position. Several groups have tackled the challenging class of di- and trisub-

stituted olefins capable of only monodentate coordination to the catalyst metal center with chiral titanium,<sup>[6]</sup> samarium<sup>[7]</sup> and late transition metal catalysts<sup>[8,9]</sup> and have achieved moderate to excellent enantioselectivities. These results are encouraging, and suggest that new approaches towards the design of catalysts may allow access to a wide range of reaction conditions and efficient metal complexes, extending the generality of enantioselective olefin hydrogenation reactions to broad classes of substrates.

Because catalysts based upon rhodium are extremely active for olefin hydrogenation,<sup>[10]</sup> we have been exploring the potential of chiral  $\text{Rh}^{\text{I}}$  catalyst precursors for hydrogenation of olefinic substrates lacking a secondary metal binding site. Recently we demonstrated that the binding of sulfonate groups to the metal center of the rhodium catalyst  $[\text{Rh}\{(-)\text{-bdpp}\}]^+$ , formed via hydrogenation of the precursor  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{NBD})]\text{ClO}_4$  (**1**; Scheme 1),<sup>[11]</sup> resulted in large increases in enantioselectivity for asymmetric imine hydrogenation.<sup>[12]</sup> In this work, we show that binding of anions such as sulfonates and halides in nonpolar solvents also induces strong enhancements for the enantioselective hydrogenation of the prochiral hydrocarbon substrate, 2-phenyl-1-butene (**4**) (also known as  $\alpha$ -ethylstyrene). We investigated **4** as a substrate because of its inherent difficulty to reduce with high enantioselectivity as compared to amide substrates.<sup>[13]</sup> With rhodium catalysts, it is hydrogenated with very poor to moderate enantioselectivities and thus any increases in *ee* due

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Scheme 1. Catalysts, olefins and additives used in this study.

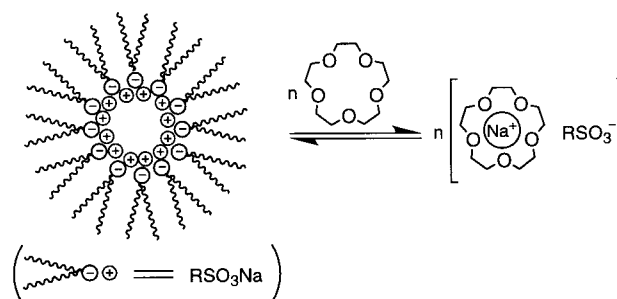
to anion binding would be easily observed and then further analyzed.<sup>[14]</sup> Takaya and co-workers recently investigated the influence of anions on the rate and enantioselectivity of hydrogenation of **4** and related cyclic hydrocarbon olefins with Rh<sup>I</sup>-binap complexes (binap = [1,1'-binaphthalene]-2,2'-diylbis(diphenylphosphane)) and observed strong effects.<sup>[9]</sup> A possible mechanistic explanation was proposed which we substantiate through detailed <sup>31</sup>P, <sup>1</sup>H and parahydrogen-induced polarization (PHIP) NMR studies. Additional insight into the problem of concomitant catalytic olefin isomerization is also provided. The seemingly disparate effects of non-dissociative and dissociative anions (halides and sulfonates, respectively) on hydrogenation can be rationalized through the two mechanistic schemes described here.

## Results and Discussion

**Catalytic results:** Applying the optimum conditions found for imine hydrogenation,<sup>[12]</sup> we examined the reactivity of **1** in the presence of 0.1M of the hydrocarbon-soluble surfactant AOT (see Scheme 1) and 0.1M [15]crown-5 in benzene. AOT is a commercially available surfactant with a sodium sulfonate head group and two branched aliphatic tails that forms reverse micelles in nonpolar solvents.<sup>[15]</sup> As demonstrated in earlier work, the role of [15]crown-5 is to complex the sodium cation of AOT, break up reverse micellar aggregates, and promote binding of the bis(2-ethylhexyl)sulfosuccinate anion of AOT to the cationic rhodium catalyst (Scheme 2).<sup>[12]</sup>

Control experiments were carried out in “regular” solvent systems—neat methanol, benzene, and 1:1 methanol/benzene—at varying temperatures and pressures without additives. The results are summarized in Table 1. Under no conditions were induction periods observed. Hydrogenation of **4** in benzene in the presence of AOT and [15]crown-5 results in a dramatic increase in enantioselectivity: with AOT and [15]crown-5, an *ee* of 63% (*S*) can be achieved (run 6), while in “regular” solvents, the highest enantioselectivity observed is 29% (*S*) in neat methanol (see runs 1–4).

Hydrogenation in benzene with 0.1M [15]crown-5 gave similar chemical and optical yields as in neat benzene (runs 4 and 8), demonstrating that the crown ether is not responsible for the improved enantioselectivity. The rates for the latter two runs in C<sub>6</sub>H<sub>6</sub> could not be accurately determined because of the heterogeneous nature of the catalytic mixture. Complex **1** is only slightly soluble in neat benzene, with or without addition of [15]crown-5, so only final yields could be determined with any accuracy. This lack of solubility explains the low chemical yields for these two cases.



Scheme 2. Schematic representation of the role of [15]crown-5 with AOT.

Not only is there a difference in the absolute enantioselectivity for hydrogenation in methanol and AOT/[15]crown-5 in benzene, but there is also a discrepancy in the effect of H<sub>2</sub> pressure on enantioselectivity in the two systems as shown in Figure 1. Catalysis in methanol and in the AOT/[15]crown-5/C<sub>6</sub>H<sub>6</sub> system show remarkably different dependencies on the hydrogen pressure. An increase in pressure for hydrogenation in MeOH results in a lowering of the enantioselectivity, while for the AOT/[15]crown-5 case the enantioselectivity increases and reaches a plateau at 30 atm of pressure. The enhancement of the *ee* value seen upon the increase of pressure may be due to a change in mechanism from an unsaturate route to a dihydride route at high pressures (vide infra).<sup>[16]</sup> Additionally, catalytic isomerization of **4** to the internal olefin (*E*)-2-phenyl-2-butene is observed at 1 atm pressure in both neat methanol and in the AOT/[15]crown-5/C<sub>6</sub>H<sub>6</sub> system as shown by GC and <sup>1</sup>H NMR spectroscopy.<sup>[17]</sup> Isomerization occurs only at atmospheric pressure and exclusively in the presence of **1**.

A comprehensive study of different salts was undertaken to determine the effect of other anions on the hydrogenation of **4** with **1**, including sulfates, carboxylates, and halides. The only other anions that resulted in strong increases in enantioselectivity were chloride and iodide (added in the form of the tetrabutylammonium salt) as shown in runs 9–16 of Table 1. Both of these halides induced large increases in enantioselectivity—up to 71% (*S*). The rate observed for catalysis in the presence of iodide in benzene was very rapid and was

Table 1. Results for hydrogenation using **1** as catalyst precursor.<sup>[a]</sup>

Run	Substrate	Solvent	Additives	$p_{\text{H}_2}$ [atm]	Rate <sup>[b]</sup>	$ee$ [%]
1	<b>4</b>	MeOH	-	70	$3.0 \times 10^2$	7 (S)
2	<b>4</b>	MeOH	-	1	81 <sup>[c]</sup>	29 (S)
3	<b>4</b>	1:1 C <sub>6</sub> H <sub>6</sub> /MeOH	-	70	33	12 (S)
4	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	-	70	<sup>[d]</sup>	29 (S)
5	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	0.1M AOT	70	33	54 (S)
6	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	0.1M AOT, 0.1M [15]crown-5	70	$3.8 \times 10^2$	63 (S)
7	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	0.1M AOT, 0.1M [15]crown-5	1	14 <sup>[e]</sup>	42 (S)
8	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	0.1M [15]crown-5	70	<sup>[e]</sup>	33 (S)
9	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	10mM N( <i>n</i> Bu) <sub>4</sub> Cl	70	$8.9 \times 10$	66 (S)
10	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	5 mM N( <i>n</i> Bu) <sub>4</sub> Cl	70	$1.7 \times 10^2$	65 (S)
11	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	5 mM Cl <sup>-</sup> (in situ) <sup>[f]</sup>	70	$1.6 \times 10^2$	68 (S)
12	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	10mM N( <i>n</i> Bu) <sub>4</sub> I	70	$4.8 \times 10^2$	68 (S)
13	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	5 mM N( <i>n</i> Bu) <sub>4</sub> I	70	$1.0 \times 10^3$	71 (S)
14	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	2.5 mM N( <i>n</i> Bu) <sub>4</sub> I	70	$1.2 \times 10^3$	70 (S)
15	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	1 mM N( <i>n</i> Bu) <sub>4</sub> I	70	$1.2 \times 10^3$	69 (S)
16	<b>4</b>	C <sub>6</sub> H <sub>6</sub>	2.5 mM N( <i>n</i> Bu) <sub>4</sub> I	1	$1.4 \times 10^2$	66 (S)
17	<b>5</b>	1:1 C <sub>6</sub> H <sub>6</sub> /MeOH	-	70	$1.0 \times 10^2$	17 (+)
18	<b>5</b>	C <sub>6</sub> H <sub>6</sub>	-	70	<sup>[g]</sup>	12 (+)
19	<b>5</b>	C <sub>6</sub> H <sub>6</sub>	0.1M AOT, 0.1M [15]crown-5	70	80	40 (+)
20	<b>5</b>	C <sub>6</sub> H <sub>6</sub>	5 mM N( <i>n</i> Bu) <sub>4</sub> I	70	<sup>[h]</sup>	7 (+)
21	<b>6</b>	1:1 C <sub>6</sub> H <sub>6</sub> /MeOH	-	70	<sup>[i]</sup>	<sup>[i]</sup>
22	<b>7</b>	MeOH	-	1	$1.4 \times 10^3$	74 (R)
23	<b>7</b>	4:6 CH <sub>2</sub> Cl <sub>2</sub> /C <sub>6</sub> H <sub>6</sub>	-	1	$4.8 \times 10^2$	72 (R)
24	<b>7</b>	4:6 CH <sub>2</sub> Cl <sub>2</sub> /C <sub>6</sub> H <sub>6</sub>	0.1M AOT, 0.1M [15]crown-5	1	$4.8 \times 10^2$	48 (R)
25	<b>7</b>	4:6 CH <sub>2</sub> Cl <sub>2</sub> /C <sub>6</sub> H <sub>6</sub>	10mM N( <i>n</i> Bu) <sub>4</sub> I	1	<sup>[j]</sup>	8 (S)

[a] Conditions: [**1**] = 5 mM; [substrate]/[**1**] = 100;  $T = 25^\circ\text{C}$ ; solvent volume = 10 mL; yields determined by GC or <sup>1</sup>H NMR spectroscopy; all chemical yields are 100% unless stated otherwise;  $ee$  values for hydrogenation product of **4** and **5** determined by <sup>31</sup>P NMR spectroscopy;<sup>[21]</sup>  $ee$  values for hydrogenation product of **7** determined by using optical rotation or by <sup>1</sup>H NMR spectroscopy with [Eu(hfc)<sub>3</sub>] (hfc = 3-(heptafluoropropylhydroxymethylene)-D-camphorate) in CDCl<sub>3</sub> as the chiral shift reagent. [b] Units of rate are turnovers h<sup>-1</sup> and correspond to the rate recorded for the first hour. Rates are accurate to within  $\pm 10\%$ . No induction periods were observed. [c] 10% isomerization to (*E*)-2-phenyl-2-butene. [d] Conversion after 21 h = 47%. [e] Conversion after 21 h = 46%. [f] Prepared in situ from 2.5 mM [(Rh(NBD))<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] and 5 mM (-)-bdpp. [g] Conversion after 20 h = 26%. [h] Conversion after 14 h = 92%. [i] Conversion after 19 h at 55 °C = 6%.  $ee$  value not determined because of the low yield. [j] Conversion after 24 h = 33%.

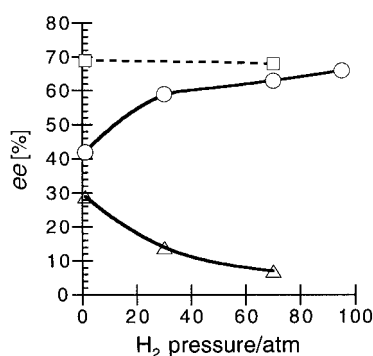


Figure 1. Effect of pressure on the enantioselectivity of hydrogenation of **4** with **1** in MeOH ( $\Delta$ ), in C<sub>6</sub>H<sub>6</sub> with 0.1M AOT/0.1M [15]crown-5 ( $\circ$ ), and with 2.5 mM N(*n*Bu)<sub>4</sub>I in C<sub>6</sub>H<sub>6</sub> ( $\square$ ). The conditions are as in Table 1.

substantially higher than in neat methanol or in the presence of AOT/[15]crown-5. Investigation of the effect of iodide concentration on the enantioselectivity and rate revealed that only one equivalent or less of iodide with respect to catalyst is required to bring about an increase in  $ee$  to 70% (S) (Figure 2 and Table 1, runs 13 and 14). Iodide is also responsible for large augmentations in rate; the fastest rates are four times higher than in neat methanol under the same conditions. Greater than one equivalent of either iodide or chloride per rhodium has an inhibiting effect on the rate of catalysis but is not detrimental to the enantioselectivity (Figure 2). The high reactivity of the iodide/Rh<sup>I</sup> catalyst can be demonstrated upon lowering the concentration of catalyst precursor [1:1 iodide/

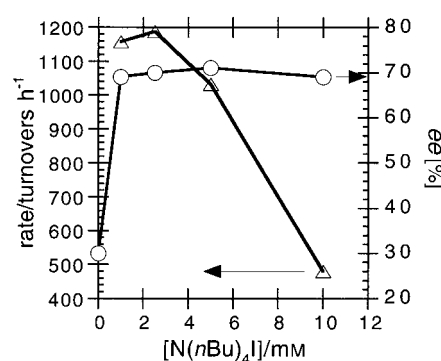


Figure 2. Enantiomeric excess [ $ee$  %] ( $\circ$ ) and rate ( $\Delta$ ) versus the concentration of N(*n*Bu)<sub>4</sub>I in C<sub>6</sub>H<sub>6</sub>. The hydrogen pressure is 70 atm. All other conditions as in Table 1. The rate with 0 mM N(*n*Bu)<sub>4</sub>I has been omitted because of the low solubility of **4** in neat benzene which made an accurate determination of initial rate impossible.

Rh<sup>I</sup>], and keeping the concentration of **4** identical. The rate at 0.25 mM of Rh<sup>I</sup> is over an order of magnitude faster than at 5 mM Rh<sup>I</sup>. The rate of the hydrogenation reaction increased with decreasing catalyst concentration, and the enantioselectivity was essentially unchanged (Figure 3).<sup>[18]</sup> In order to slow the rate of hydrogenation, the pressure was lowered to 1 atm. Two pertinent observations were made at this pressure:

- no significant isomerization of **4** was detected (< 1% by GC)
- the enantioselectivity did not depend on hydrogen pressure (compare runs 14 and 16 in Table 1).

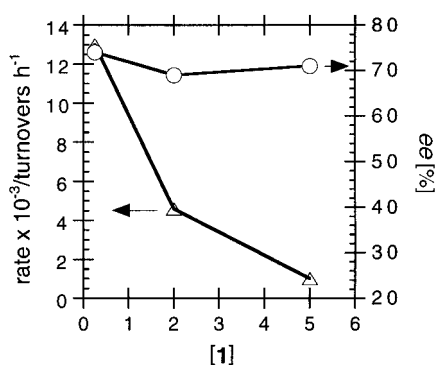


Figure 3. Enantiomeric excess [*ee* %] (○) and rate (Δ) versus the concentration of **1** (with one equivalent of N(*n*Bu)<sub>4</sub>I) in C<sub>6</sub>H<sub>6</sub> for the hydrogenation of **4**. The [**4**] is held constant at 0.5 M and the hydrogen pressure at 70 atm. All other conditions as in Table 1.

These observations are in stark contrast to hydrogenation in either neat methanol or with 1:1 AOT/[15]crown-5 in C<sub>6</sub>H<sub>6</sub> which did have a strong relationship between H<sub>2</sub> pressure and *ee*, and was accompanied by 10% isomerization to the internal *E* isomer at atmospheric pressure (Table 1, runs 6 and 7).

Other phosphanes and substrates were tested to further generalize the effect of anion binding on enantioselectivity. The addition of 0.1 M AOT and 0.1 M [15]crown-5 for hydrogenation of **4** with the catalyst precursors [Rh{(+)–prophos)(NBD)]ClO<sub>4</sub> (**2**) (prophos = 1-methyl-1,2-ethanediybis(diphenylphosphane)) and [Rh{(+)–binap)(NBD)]ClO<sub>4</sub> (**3**) brought about only small effects on the enantioselectivity. The effect of iodide on **2**, however, is dramatic as the *ee* inverts from 5% (*R*) in MeOH to 51% (*S*) in benzene with 10 mM N(*n*Bu)<sub>4</sub>I. This result parallels that of Takaya and co-workers who observed an increase in enantioselectivity for the hydrogenation of **4** with **3** in CH<sub>2</sub>Cl<sub>2</sub> in the presence of iodide.<sup>[9]</sup> Three other olefins, **5**, **6**, and **7** (see Scheme 1) were tested for hydrogenation with **1** as shown in Table 1, runs 17–25. The highest *ee* observed for hydrogenation of **5**, [40% (+)], was attained in the presence of 0.1 M AOT and 0.1 M [15]crown-5 in C<sub>6</sub>H<sub>6</sub>. This *ee* is more than double that observed in 1:1 MeOH/C<sub>6</sub>H<sub>6</sub> or neat C<sub>6</sub>H<sub>6</sub>. Surprisingly, iodide, however, causes a decrease in enantioselectivity for the reduction of **5**. Hydrogenation of *trans*- $\alpha$ -methylstilbene (**6**) was unsuccessful probably due to the steric hindrance of the internal, trisubstituted olefin. Reduction of the enamide, methyl-(*Z*)- $\alpha$ -acetamidocinnamate (**7**), was not improved in the presence of either AOT/[15]crown-5 or iodide (runs 22–25). The reasons for the observed decrease in *ee* with sulfonate are not clear since <sup>31</sup>P NMR studies revealed that the presence of 0.1 M AOT and 0.1 M [15]crown-5 does not prevent formation of the [Rh{(–)-bdpp}(enamide)]<sup>+</sup> complex (majority isomer) in 4:6 CH<sub>2</sub>Cl<sub>2</sub>/[D<sub>6</sub>]benzene.<sup>[19]</sup> Halides, on the other hand, are known to lower the enantioselectivity of enamide hydrogenation with chiral rhodium catalysts.<sup>[20]</sup>

**<sup>31</sup>P and <sup>1</sup>H NMR studies with halides:** It has been demonstrated previously that two rhodium complexes form in the presence of a sulfonate anion in [D<sub>6</sub>]benzene, [Rh{(–)-bdpp}( $\eta^6$ -C<sub>6</sub>D<sub>6</sub>)]<sup>+</sup> and [Rh{(–)-bdpp}](RSO<sub>3</sub>). In order to elucidate the species present under catalytic conditions in the

presence of halides, <sup>31</sup>P{<sup>1</sup>H} NMR studies were carried out. Using concentrations identical or similar to those of catalysis, we detected spectroscopically a total of three species after hydrogenation of **1** in [D<sub>6</sub>]benzene to form Rh{(–)-bdpp}<sup>+</sup>, upon addition of N(*n*Bu)<sub>4</sub>X (X = Cl, I). In absence of halide, the hydrogenated product of **1** (1 atm, 298 K) is only sparingly soluble but appears in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum as a doublet at  $\delta$  = 41.64 (<sup>1</sup>J<sub>Rh,P</sub> = 194 Hz). This species has a chemical shift and coupling constant indicative of the 18-electron complex [Rh{(–)-bdpp}( $\eta^6$ -C<sub>6</sub>D<sub>6</sub>)]<sup>+</sup> which forms readily in the presence of aromatic compounds.<sup>[21]</sup> When one equivalent of N(*n*Bu)<sub>4</sub>I is added to [Rh{(–)-bdpp}( $\eta^6$ -C<sub>6</sub>D<sub>6</sub>)]<sup>+</sup> in [D<sub>6</sub>]benzene, three distinct species are observed as doublets initially, two of which decrease in intensity after 1 h of equilibration. One of the species corresponds to [Rh{(–)-bdpp}( $\eta^6$ -C<sub>6</sub>D<sub>6</sub>)]<sup>+</sup>, and is still present in small concentrations after equilibration. The second and most intense doublet at  $\delta$  = 43.08 (<sup>1</sup>J<sub>Rh,P</sub> = 186 Hz) (Figure 4a) is most likely due to the iodide-bridged dimer [[Rh{(–)-bdpp}]<sub>2</sub>( $\mu$ -I)<sub>2</sub>] which would be expected to have a bent structure ( $\angle$  Rh-( $\mu$ -I)-Rh < 180°).<sup>[22]</sup> Similar iodide-bridged dimers have been observed with the diphosphanes chiraphos and 1,2-bis(diphenylphosphino)ethane (dppe).<sup>[23]</sup> Upon addition of a second equivalent of N(*n*Bu)<sub>4</sub>I (with respect to rhodium) to the dimeric [[Rh{(–)-bdpp}]<sub>2</sub>( $\mu$ -I)<sub>2</sub>], a new complex forms which corresponds to the third species seen before equilibration with a chemical shift of  $\delta$  = 42.35 (<sup>1</sup>J<sub>Rh,P</sub> = 179 Hz) (Figure 4b). Because of the clear

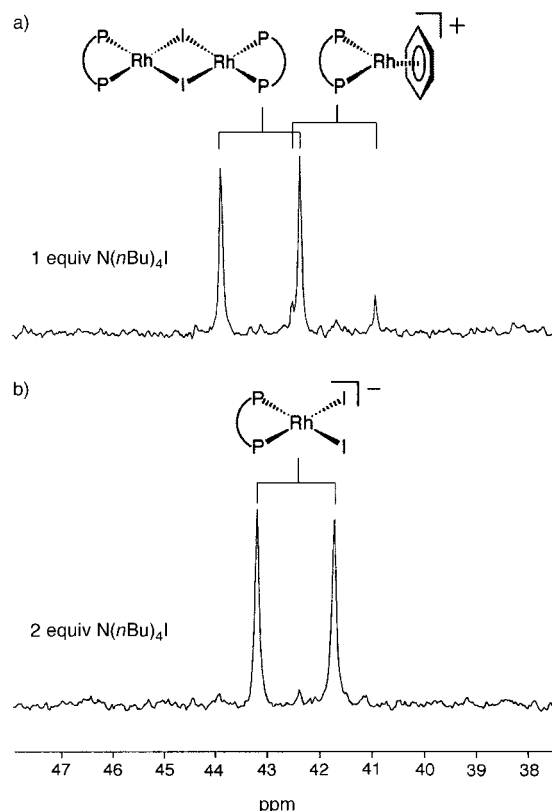


Figure 4. 121 MHz <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **1** (5 mM) in [D<sub>6</sub>]benzene in the presence of iodide under 1 atm of H<sub>2</sub> at 298 K after 2 h of equilibration under these conditions. [Rh{(–)-bdpp}( $\eta^6$ -C<sub>6</sub>D<sub>6</sub>)]<sup>+</sup> appears at  $\delta$  = 41.64 (<sup>1</sup>J<sub>Rh,P</sub> = 194 Hz), [[Rh{(–)-bdpp}]<sub>2</sub>( $\mu$ -I)<sub>2</sub>] at  $\delta$  = 43.08 (<sup>1</sup>J<sub>Rh,P</sub> = 186 Hz), and [[Rh{(–)-bdpp}( $\mu$ -I)]<sub>2</sub>] at  $\delta$  = 42.35 (<sup>1</sup>J<sub>Rh,P</sub> = 179 Hz).

dependence on iodide concentration, the smaller  $^1J_{\text{Rh,P}}$  coupling constant, and similarity of chemical shift, this complex is most likely the anionic diiodide complex  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})_2]^-$  with  $[\text{N}(n\text{Bu})_4]^+$  as the counterion. Similar monomeric anionic, square-planar  $\text{Rh}^{\text{I}}$  complexes previously characterized include *cis*- $[\text{Rh}(\text{PR}_3)_2(\text{NHPPh})_2]\text{Li}$  ( $\text{R} = \text{Ph}, \text{Et}$ ),<sup>[24]</sup> *cis*- $[\text{Rh}(\text{CO})_2(\text{I})_2]^-$ ,<sup>[25]</sup> and  $[\text{Rh}\{1,2\text{-bis}(\text{di-}i\text{-tert-butylphosphino})\text{ethane}\}(\text{C}_6\text{H}_5)_2]\text{Li}$ .<sup>[26]</sup> The *cis*- $[\text{Rh}(\text{PR}_3)(\text{NHPPh})_2]\text{Li}$  complex also involves an equilibrium between the amido-bridged dimer  $[\{\text{Rh}(\text{PR}_3)_2\}_2(\mu\text{-NHPPh})_2]$  and the monomeric anion, the relative ratios depending upon the equivalents of added lithium anilide. By analogy, a similar equilibrium between  $[\{\text{Rh}\{(-)\text{-bdpp}\}_2(\mu\text{-I})_2]$ ,  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})_2]^-$ , and  $[\text{Rh}\{(-)\text{-bdpp}\}(\eta^6\text{-C}_6\text{D}_6)]^+$  is proposed as shown in box I of Scheme 3. Similar equilibria could not be observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy for the related complexes  $[\text{Rh}(\text{NBD})(\text{dppe})]\text{ClO}_4$  and  $[\text{Rh}\{(+)\text{-binap}\}(\text{NBD})]\text{ClO}_4$  (5 mM concentrations) in  $[\text{D}_6]$ benzene with 5 mM  $\text{N}(n\text{Bu})_4\text{I}$  and 1 atm of  $\text{H}_2$  at 298 K. Presumably the neutral dimeric iodide-bridged complex formed so rapidly that the anion and benzene solvate were not spectroscopically observable under these conditions.<sup>[27]</sup>

With  $^1\text{H}$  NMR spectroscopy, stable hydride species can be detected within minutes after hydrogenation of 5 mM **1** in  $[\text{D}_6]$ benzene at 1 atm pressure in the presence of two equivalents of  $\text{N}(n\text{Bu})_4\text{Cl}$ , or one or two equivalents of  $\text{N}(n\text{Bu})_4\text{I}$  (Figure 5). With chloride, an apparent doublet of triplets centered around  $\delta = -15.5$  is rapidly produced (Figure 5a), and with iodide, a similar feature also resembling a doublet of triplets appears at  $\delta = -14.84$  (Figure 5b) but is, in addition, accompanied by a triplet of triplets of triplets at

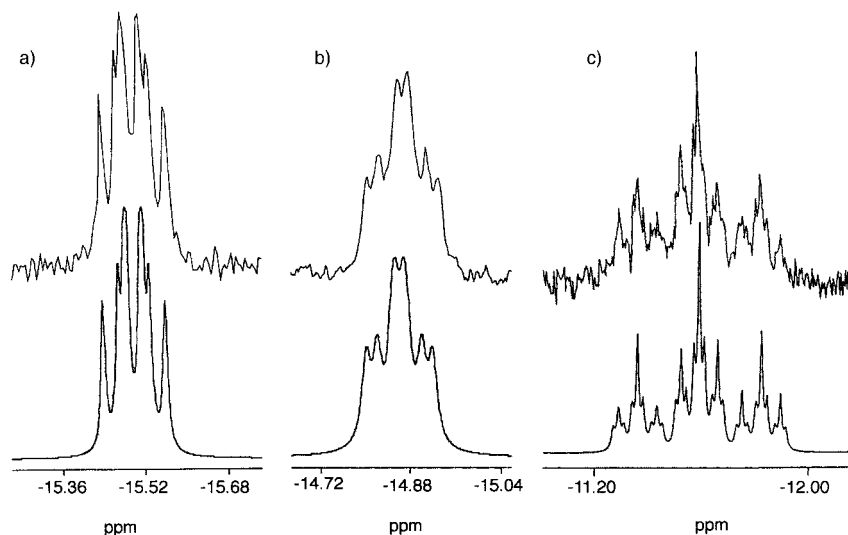
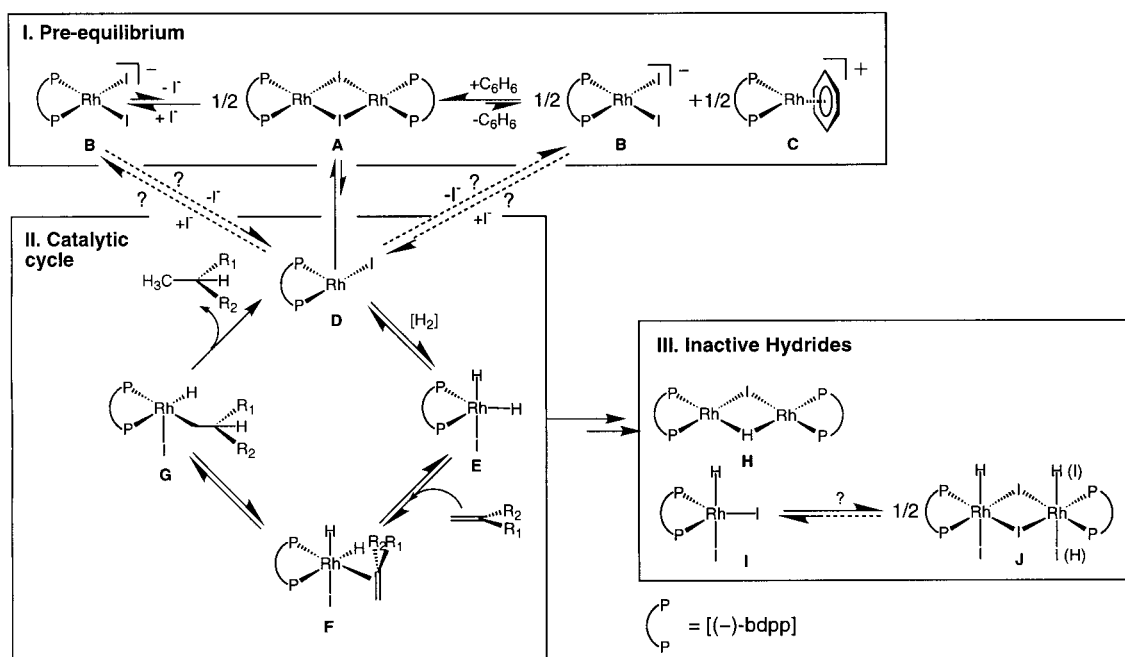


Figure 5. 300 MHz  $^1\text{H}$  NMR spectra of the hydride resonances observed after hydrogenation of **1** (5 mM) under 1 atm of  $\text{H}_2$  at 298 K. The top three spectra are observed experimentally and the bottom three simulated. a) 10 mM of  $\text{N}(n\text{Bu})_4\text{Cl}$  (equivalents of chloride anion) present. Observed and calculated coupling constants:  $^1J_{\text{Rh,H}} = 9.0$  Hz (observed),  $^2J_{\text{P}(\text{cis}),\text{H}} = 12.5$  Hz (observed),  $^2J_{\text{P}(\text{cis}),\text{H}} = 14.4$  Hz (calculated). Under the assumption of a monohydride species, this resonance represents about 0.05 of a proton as determined by integration. b) 5 mM (or 10 mM) of  $\text{N}(n\text{Bu})_4\text{I}$  (1 or 2 equivalents of iodide anion). Observed and calculated coupling constants:  $^1J_{\text{Rh,H}} = 5.9$  Hz (observed),  $^2J_{\text{P}(\text{cis}),\text{H}} = 15.9$  Hz (observed),  $^2J_{\text{P}(\text{cis}),\text{H}} = 13.8$  Hz (calculated). Under the assumption of a monohydride species, this resonance represents about 0.13 of a proton as determined by integration. c) 5 mM (or 10 mM) of  $\text{N}(n\text{Bu})_4\text{I}$  (1 or 2 equivalents of iodide anion) present. Observed and calculated coupling constants:  $^1J_{\text{Rh,H}} = 21.0$  Hz (observed),  $^2J_{\text{P}(\text{trans}),\text{H}} = 69.0$  Hz (observed),  $^2J_{\text{P}(\text{cis}),\text{H}} = 6.0$  Hz (observed). The assignment of  $^1J_{\text{Rh,H}}$  and  $^2J_{\text{P}(\text{cis}),\text{H}}$  is ambiguous but in related compounds,  $^2J_{\text{P}(\text{trans}),\text{H}} > ^1J_{\text{Rh,H}} > ^2J_{\text{P}(\text{cis}),\text{H}}$ .<sup>[23b, 33]</sup> Under the assumption of a monohydride species, this resonance represents about 0.10 of a proton as determined by integration.

$\delta = -11.62$  (Figure 5c). These hydride species are able to withstand stripping of the solvent in vacuo, followed by redissolution in  $\text{CD}_2\text{Cl}_2$  with no decrease in their relative concentrations, and thus probably represent stable species outside of the catalytic cycle. The proton spectra have been simulated and indicate that the features in Figures 5a and 5b are due coupling with two slightly chemically inequivalent phosphorus atoms and the rhodium center ( $^2J_{\text{P}(\text{cis}),\text{H}} = 12.5$  Hz (observed),  $^2J_{\text{P}(\text{cis}),\text{H}} = 14.4$  Hz (calculated),  $^1J_{\text{Rh,H}} = 9.0$  (observed)). Attempts to simulate the observed spectra with two equivalent *cis* phosphane ligands *cis* to the hydride ligand failed. The two phosphane ligands are chemically inequivalent due to loss of the  $\text{C}_2$  symmetry of the chiral phosphane.

The same hydrides observed in the presence of iodide at atmospheric pressure, form at high pressure as well.  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{NBD})]\text{ClO}_4$  and one equivalent of  $\text{N}(n\text{Bu})_4\text{I}$  were hydrogenated at 70 atm in an autoclave for 3 h at room temperature in  $\text{C}_6\text{H}_6$ , the pressure released, the benzene removed in vacuo, and the complexes dissolved in  $\text{CD}_2\text{Cl}_2$ , yielding a solution with a total  $[\text{Rh}]$  of 15 mM. The main species present is the  $[\{\text{Rh}\{(-)\text{-bdpp}\}_2(\mu\text{-I})_2]$  dimer as observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy and only the two hydrides shown in Figures 5b and 5c are observed. Assuming that the hydrides originate from dihydrogen, it appears that  $\text{H}_2$  is activated in a similar fashion at both low and high pressures since the same hydride products are observed in each case.

Possible structures for the species yielding the patterns observed in Figures 5a and 5b include a monomeric five-coordinate  $\text{Rh}^{\text{III}}$  trigonal-bipyramidal complex  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{H})\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{I}$ ) with H occupying an apical position, as represented by **I** in Scheme 3, but could be six-coordinate if a molecule of solvent is bound, as has been suggested in the case of the related complex  $[\text{Rh}(\text{PPh}_3)_2(\text{H})\text{Cl}_2]$  in  $\text{CH}_2\text{Cl}_2$ . A square-pyramidal structure with the hydride in the apical position is discounted since the hydride would be expected to resonate much farther up-field.<sup>[28]</sup> The chemical shift of the hydride (*trans* to Cl) in  $[\text{Rh}(\text{PPh}_3)_2(\text{H})\text{Cl}_2]$  is  $\delta = -16.1$  which compares very favorably with the  $\delta = -15.5$  feature observed for the  $(-)\text{-bdpp}$  complex with added chloride.<sup>[29]</sup> It was suggested that  $[\text{Rh}(\text{PPh}_3)_2(\text{H})\text{Cl}_2]$  may dimerize in solution through through bridging chlorides to give a formally octahedral coordination sphere around each rhodium. The species yielding the spectra of Figures 5a and 5b may thus be best interpreted as the dimeric

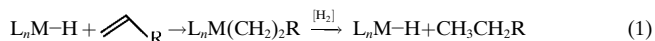


Scheme 3. Catalytic cycle, pre-equilibria and proposed monohydride species. Box I, the pre-equilibria, involves three rhodium species labeled **A**, **B**, and **C** whose relative concentrations depend upon the quantity of added iodide. Splitting of the dimer  $[\{\text{Rh}((-)\text{-bdpp})(\mu\text{-I})\}_2]$  results in formation of two identical 14-electron monomeric units,  $[\text{Rh}((-)\text{-bdpp})(\text{I})]$ , which are intermediates in the catalytic cycle for olefin hydrogenation (box II, the catalytic cycle). The possibility for the existence of equilibria between **B** and **D**, and **B** + **C** and **D** are postulated but not determined. Dihydrogen addition to form **E** (geometry unknown) is followed by olefin coordination, insertion, and then reductive elimination to yield the reduced, chiral product. Box III includes the proposed structures for the inactive, observed hydride complexes. The exact stereochemistry of the intermediates shown here is merely tentative.

complex  $[\{\text{Rh}((-)\text{-bdpp})(\text{H})(\text{X})\}_2(\mu\text{-X})_2]$  ( $\text{X} = \text{Cl}, \text{I}$ ) as shown in Scheme 3 (complex **J**) since it would lead to octahedral coordination about each rhodium center in the poorly coordinating benzene solvent. An identical compound based upon iridium,  $[\{\text{Ir}((-)\text{-bdpp})(\text{H})(\text{I})\}_2(\mu\text{-I})_2]$ ,<sup>[30]</sup> is known whose hydride is coupled (*cis*) to two chemically inequivalent phosphorus atoms as is the case with the rhodium complex. The  $C_2$  symmetry of the ligand broken by the apical H and I substituents oriented *trans* to each other.<sup>[31]</sup> Related dimeric species based upon rhodium have also been characterized, including  $[\{\text{Rh}(\text{PEtPPh}_2)_2(\text{Cl})_2(\mu\text{-Cl})_2\}]$ .<sup>[32]</sup> An exact determination of these hydride species remains to be seen but based upon literature precedent, a monomeric five-coordinate  $\text{Rh}^{\text{III}}$  trigonal-bipyramidal complex is possible which probably dimerizes in the nonpolar benzene solvent to yield  $[\{\text{Rh}((-)\text{-bdpp})(\text{H})(\text{X})\}_2(\mu\text{-X})_2]$  ( $\text{X} = \text{Cl}, \text{I}$ ). The compound producing the triplet of triplets pattern ( $^2J_{\text{P}(\text{trans}),\text{H}} = 69.0 \text{ Hz}$  (observed),  $^2J_{\text{P}(\text{cis}),\text{H}} = 6.0 \text{ Hz}$  (observed)) of Figure 5c is almost certainly the bridging monohydride dirhodium complex  $[\{\text{Rh}((-)\text{-bdpp})_2(\mu\text{-H})(\mu\text{-I})\}]$ , represented by **H** in Scheme 3, based upon the similarity of the  $^1\text{H}$  NMR spectrum with several closely related compounds that have been previously characterized by NMR<sup>[23b]</sup> spectroscopy and crystallographic analysis.<sup>[33]</sup> The routes leading to these hydride species remain elusive and are the subject of continuing investigation in our laboratory.

**Towards a mechanism in the presence of halide anions:** Because monohydride species were observed with halides, the possibility for a monohydride mechanism [Eq. (1)] needed to

be considered and contrasted with a dihydride Wilkinson's catalyst type mechanism [Eq. (2)].



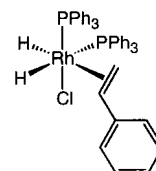
The observed monohydride species do not appear to be involved in catalysis due to their lack of observable reactivity with an excess of **4** in an argon-purged  $[\text{D}_6]$ benzene solution. In addition, no isomerization of the olefin is observed under catalytic conditions with the  $[\text{Rh}((-)\text{-bdpp})]$  iodide or chloride complexes. While rhodium monohydrides are known to be excellent isomerization catalysts,<sup>[10b, 34]</sup> these hydrides appear inert and unreactive with respect to alkenes. Because monohydride species may be formed through heterolytic dihydrogen activation, the addition of a strong, noncoordinating base would be expected to increase rates and effect enantioselectivity. Hydrogenation of **4** with **1** and one equivalent of  $\text{N}(n\text{Bu})_4\text{I}$  in  $\text{C}_6\text{H}_6$ , in the presence of a fivefold excess of the proton sponge *N,N,N',N'*-tetramethyl-1,8-naphthalenediamine, however, brought about little change in rate or enantioselectivity. Thus a mechanism based upon monohydride intermediates appears unlikely.

In order to ascertain definitively whether the hydrogenation mechanism proceeds through a mono or dihydride mechanism, PHIP  $^1\text{H}$  NMR spectroscopy was utilized.<sup>[35]</sup> Since PHIP can only be observed when both H atoms from a molecule of dihydrogen are transferred in a pairwise fashion to the same molecule of substrate, enhancement of peaks in a

hydrogenated product  $^1\text{H}$  NMR spectrum would clearly indicate a dihydride mechanism [Eq. (2)]. In a monohydride mechanism, the two hydrogen atoms transferred to the substrate would arise from different molecules of dihydrogen and thus polarization would not be observed [Eq. (1)].  $[\text{D}_8]\text{Styrene}$ , a perdeuterated model substrate studied previously with PHIP, was used in this study since it does not overlap with any of the hydrogenated product peaks.<sup>[36, 37]</sup> Upon addition of para-enriched hydrogen to 15 mM  $[\text{Rh}\{(-)\text{-bdpp}\}]^+$  (formed from hydrogenation of **1**) in  $[\text{D}_6]\text{benzene}$  with two equivalents of  $\text{N}(\text{nBu})_4\text{I}$  and 44 equivalents of  $[\text{D}_8]\text{styrene}$ , a net polarized spectrum can be observed (Figure 6a), which is enhanced by  $\approx 100$  fold as determined by integration. The polarized peaks correspond to the methylene and methyl hydrogens arising from incorporation of  $\text{H}_2$  in styrene to yield the expected ethyl benzene product. The polarization fades within 5 min (Figure 6b). That net polarization is observed reveals that the hydrogenation occurs before placement of the sample in the magnetic field and thus hydrogenation commences rapidly under these conditions.<sup>[38]</sup> Pairwise geminal C–H exchange in styrene catalyzed by  $[\text{Rh}\{\text{bis}(\text{diphenylphosphinobutane})\}]^+$  solvates in deuterated acetone has been observed in  $^1\text{H}$  PHIP NMR experiments, which leads to enhancement of those signals between  $\delta = 6$  and 5.<sup>[39]</sup> As can be seen from Figure 6a, no geminal C–H signal, corresponding to  $\text{C}_6\text{D}_5\text{CD}=\text{C}(\text{para}-\text{H})_2$ , is observed which suggests that this exchange process is slow under these conditions with added iodide.

All available evidence strongly points towards a dihydride Wilkinson's catalyst type mechanism. It is well known that rhodium–halide complexes form stable dimers in solution.<sup>[23b, 40]</sup> The faster rates at low  $\text{Rh}^{\text{I}}$  concentrations suggest a monomeric catalytically active species as represented by **D** in Scheme 3 whose formation is favored at the low concentrations, preventing self-inhibition through dimerization. The catalytically active monomeric complex is proposed to be the 14-electron  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})]$  which is spectroscopically unobservable. This coordinatively unsaturated  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})]$  species is similar to the monomeric intermediate  $[\text{Rh}(\text{PPh}_3)_2\text{Cl}]$  inferred for olefin hydrogenation with Wilkin-

son's catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$ .<sup>[41]</sup> Excess iodide inhibits the reaction rate through formation of  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})_2]^-$  which is probably not catalytically active. While the 14-electron monomeric intermediate  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})]$  has been implicated in this mechanism, Landis and Chan previously suggested that dihydrogen addition to one of the rhodium centers of the chloride-bridged dimer  $[\{\text{Rh}\{(+)\text{-diop}\}_2(\mu\text{-Cl})_2]$ , similar to **A** in Scheme 3, could occur which would result in  $[\text{Rh}\{(+)\text{-diop}\}(\text{Cl})\text{H}_2]$  after cleavage of the dimer.<sup>[42]</sup> In the case of the  $[\{\text{Rh}\{(-)\text{-bdpp}\}_2(\mu\text{-I})_2]$  dimer, dihydrogen addition would result in the same dihydride intermediate, **E**,  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})\text{H}_2]$ . Although this step could occur in parallel, it does not explain the increase in rate with decreasing  $[\text{Rh}]$  and is thus improbable in this particular system. Like the  $[\text{Rh}(\text{PPh}_3)_2\text{Cl}]$  complex in the Wilkinson mechanism, the  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})]$  complex then undergoes oxidative addition of dihydrogen to form **E** which then coordinates to the olefinic substrate. The geometry of the  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})\text{H}_2]$  species could be square-pyramidal or trigonal-bipyramidal, as shown. A recent study of olefin-catalyzed hydrogenation with  $[\text{RhCl}(\text{PPh}_3)_3]$  using parahydrogen-induced polarization indicates formation of the  $[\text{Rh}(\text{PPh}_3)_2\text{H}_2\text{Cl}(\text{olefin})]$  species with *cis* phosphane ligands;<sup>[43]</sup> one of the hydrides is forcibly *trans* to a phosphane ligand, a geometry previously believed to be highly unfavorable.<sup>[41]</sup>



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With the diphosphane  $(-)\text{-bdpp}$ , the phosphane ligands must coordinate in a *cis* fashion to the rhodium center because of the small bite angle of the ligand. Therefore, the complex  $[\text{Rh}\{(-)\text{-bdpp}\}(\text{I})\text{H}_2]$ , having a similar coordination sphere, is reasonable and could be the active species in our case. Because high pressures of  $\text{H}_2$  favor formation of dihydride species through oxidative addition of dihydrogen, the reaction mechanism at 70 atm is almost certainly a dihydride pathway (dihydrogen addition prior to olefin coordination). The catalytic results indicate that the enantioselectivity with halides is independent of pressure which suggests that the same mechanism is in operation at both 1 and 70 atm, explaining the lack of dependence of enantioselectivity on hydrogen pressure. Takaya and co-workers also noted that pressure had no bearing upon the enantioselectivity of hydrogenation of **4** with  $[\text{Rh}\{(+)\text{-binap}\}]$  complexes with halides, thus demonstrating the generality of this anion effect with monodentate olefinic substrates.<sup>[9]</sup>

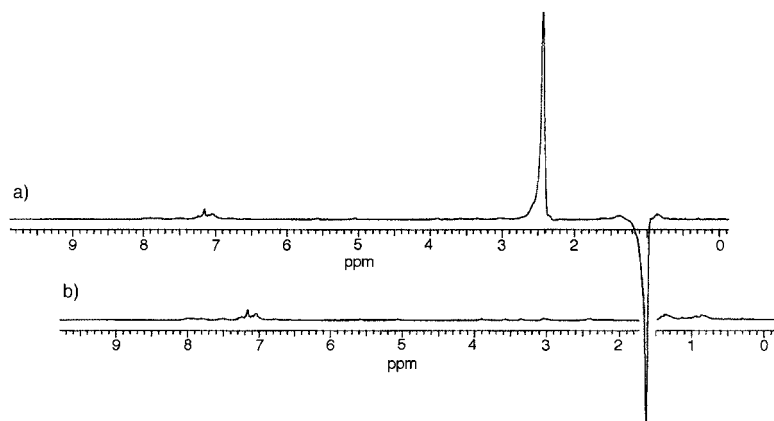
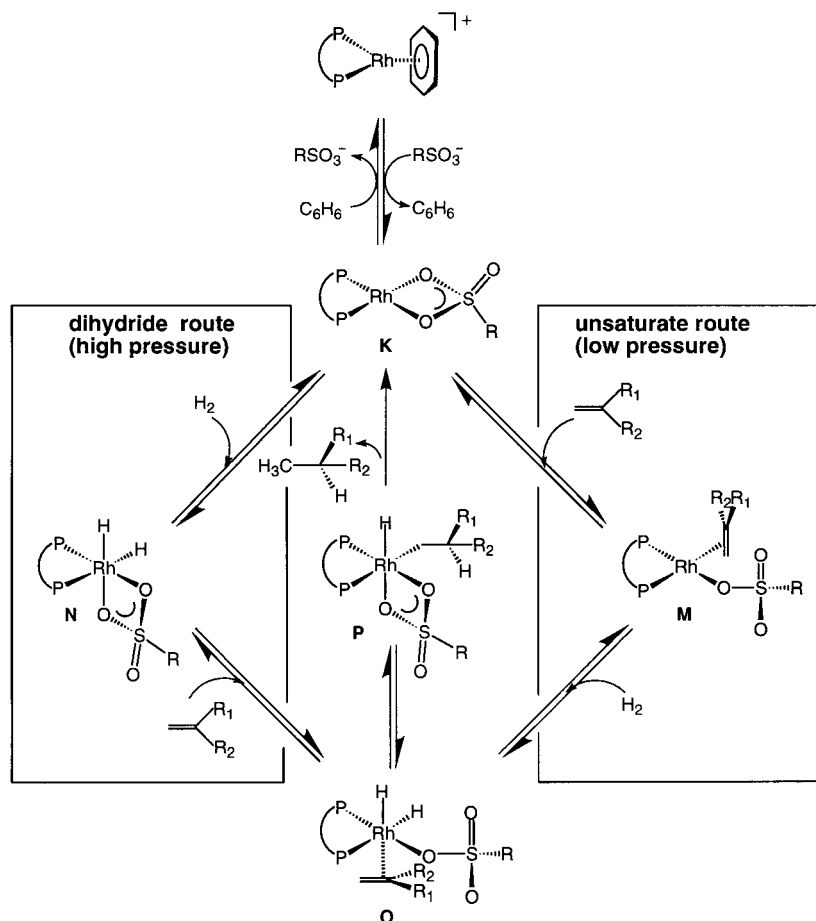


Figure 6.  $^1\text{H}$  NMR spectra of hydrogenation of  $[\text{D}_8]\text{styrene}$  carried out under PHIP conditions: 15 mM of **1** with two equivalents of  $\text{N}(\text{nBu})_4\text{I}$  in  $[\text{D}_6]\text{benzene}$  with one atmosphere of para-enriched hydrogen at 298 K. a) Two scans of the sample reveal a 100-fold increase in intensity of methylene and methyl peaks of the hydrogenated-ethylbenzene product due to net polarization. b) Two scans after allowing the sample to relax for 5 min, revealing complete disappearance of the polarization.



**Towards a mechanism in the presence of sulfonate anion:** The enantioselectivity does show pressure-dependent behavior with the AOT sulfonate anion in benzene and in neat methanol without additives (see Figure 1). With 0.1M AOT/0.1M [15]crown-5 in C<sub>6</sub>H<sub>6</sub>, the *ee* increases from 42% to 66% at 70 atm. The enhancement of enantioselectivity seen upon increased pressure can be explained by a change in mechanism from an unsaturate route (olefin binding prior to dihydrogen addition) at atmospheric pressure, to a dihydride route (dihydrogen addition before olefin binding) which is favored at higher pressures as outlined in Scheme 4. At high pressures of dihydrogen (>30 atm), the previously postulated neutral, four-coordinate Rh<sup>I</sup> complex, [Rh((-)-bdpp)(RSO<sub>3</sub>)] (**K** of Scheme 4) with a bidentate sulfonate ligand is hydrogenated, producing the six-coordinate dihydride species. Due to the strong *trans* effect of the hydride ligand, dissociation of one arm of the sulfonate ligand occurs, opening a binding site for the olefin (**O**). The olefin then inserts (**P**), and the product reductively eliminates. At low pressure, olefin binding occurs before dihydrogen addition, which explains the substantial (10%) isomerization of **4** to (*E*)-2-phenyl-2-butene, possibly

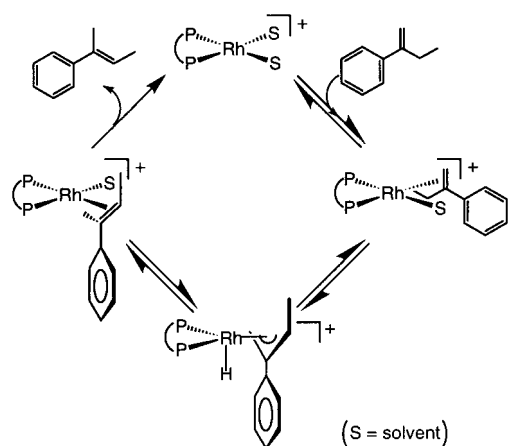


Scheme 4. Olefin hydrogenation in the presence of the sulfonate anion formed from 0.1M AOT and one equivalent of [15]crown-5. The neutral four-coordinate square-planar species [Rh((-)-bdpp)(RSO<sub>3</sub>)] (**K**) serves as the initial, common intermediate in the catalytic cycle. At low pressures (<30 atm of dihydrogen), an unsaturate route is followed whereby olefin binding (**M**) precedes dihydrogen addition (**O**). At high pressures (>30 atm), a dihydride route is operational and dihydrogen first oxidatively adds to **K**, producing the dihydride intermediate **N** which then coordinates a substrate molecule, forming **O**. Species **O** is common to both cycles and is followed by insertion of the olefin into the Rh–H bond to form the alkyl complex **P** which then reductively eliminates, producing the product alkane and the initial catalytic intermediate **K**. The exact stereochemistry of the intermediates shown here is merely tentative.

through a  $\pi$ -allyl mechanism (vide infra). At atmospheric pressure, the rate in neat MeOH is six times higher than in 0.1M AOT/0.1M [15]crown-5 in benzene, while at high pressure the latter is faster. The reason for the sluggishness of the AOT/[15]crown-5 system at 1 atm is due to the competition at the rhodium center for binding by the sulfonate, the benzene, and the olefin. The olefin must coordinate to enable dihydrogen addition so olefin binding becomes rate limiting. At higher pressures, the hydride mechanism becomes dominant and thus dihydrogen can add directly to the sulfonate complex (the major species present) to give the dihydride complex [Rh((-)-bdpp)(RSO<sub>3</sub>)H<sub>2</sub>]. The neutral sulfonate complex [Rh((-)-bdpp)(RSO<sub>3</sub>)] (**K**), being more electron rich than the cationic methanol solvate [Rh((-)-bdpp)(MeOH)<sub>x</sub>]<sup>+</sup>, would oxidatively add H<sub>2</sub> faster, also explaining at least partially the increase in rate. As a result, hydrogenation of **4** is not inhibited at high pressures by the large excess of bis(2-ethylhexyl)sulfosuccinate anion. The complex [Rh(cod)(dppe)(*p*-O<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)], which also contains a sulfonate counteranion, has been shown to be active for olefin isomerization at low pressures of hydrogen although details concerning hydrogen pressure effects were not stated.<sup>[44]</sup>

#### Effect of anion on isomerization:

A 10% isomerization (10 isomerization turnovers/molecule of catalyst) is observed in both neat methanol and in [D<sub>6</sub>]benzene with AOT/[15]crown-5. At high pressures, rhodium dihydride species are formed before olefin binding and thus a dihydride mechanism is taking place. Because rhodium dihydride complexes are generally not good isomerization catalysts,<sup>[10a, 34]</sup> isomerization is effectively blocked at high pressures. This explains the lack of isomerization in the all cases described here at high pressure, and with halides at low pressure as well since a dihydride mechanism dominates. At atmospheric pressure in neat MeOH and [D<sub>6</sub>]benzene with AOT/[15]crown-5, however, the olefin coordinates to the complex before dihydrogen addition, and is isomerized, possibly through a  $\pi$ -allyl mechanism as shown in Scheme 5. When a CD<sub>3</sub>OD solution of the methanol solvate, [Rh((-)-bdpp)(MeOH)<sub>x</sub>]<sup>+</sup>, is sparged extensively with Ar to remove residual H<sub>2</sub>, this complex rap-



Scheme 5. Isomerization of **4** via a  $\pi$ -allyl. The solvated, cationic species  $\text{Rh}(\text{P}-\text{P})^+$  forms in neat methanolic solvent, and when the less strongly binding sulfonate anion (as opposed to halide) dissociates.

idly isomerizes **4** in an NMR tube to give exclusively (*E*)-2-phenyl-2-butene. While trace, spectroscopically unobservable monohydrides may catalyze the isomerization, little evidence supporting active monohydrides has been obtained in this study.  $\pi$ -Allyl mechanisms have been invoked to explain the isomerization activity of rhodium hydrogenation catalysts<sup>[45]</sup> which operate through dihydride mechanisms.<sup>[46]</sup> The weakly bound anions like sulfonate and perchlorate (the counterion in **4**) dissociate readily, opening up coordination sites which enable the  $\pi$ -allyl mechanism to operate rapidly. The complex is also more Lewis acidic due to the positive charge of the complex which also encourages binding of the olefin to the metal center. Halide binding, renders the complex neutral and less Lewis acidic, and therefore olefin binding may occur less readily, leading to substantially less isomerization through a  $\pi$ -allyl mechanism under these conditions.

Because recent PHIP  $^1\text{H}$  NMR experiments by Bargon and co-workers revealed exchange of the geminal C–H hydrogens of styrene with parahydrogen mediated by cationic rhodium complexes under hydrogenation conditions, isomerization of **4** to the internal isomer (*E*)-2-phenyl-2-butene could occur through a similar route.<sup>[39]</sup> Insertion of the olefin into one of the Rh–H bonds of the dihydride complex can then undergo  $\beta$ -hydride elimination, reforming either **4** or (*E*)-2-phenyl-2-butene. The key to the mechanism is secondary coordination by the phenyl group of styrene.<sup>[39]</sup> Secondary phenyl coordination is much more likely in the case of cationic rhodium complexes because of their higher Lewis acidity and more open coordination sphere as compared to the neutral halide adducts. Takaya and co-workers proposed that reductive elimination of the alkane product from neutral  $[\text{Rh}(\text{binap})]$  complexes in the presence of halide was too rapid to allow for  $\beta$ -hydride elimination, explaining the lack of isomerization.<sup>[9]</sup> We observed, however, that hydrogenated **1**,  $[\text{Rh}(\text{--bdpp})]^+$ , in the absence of dihydrogen (in an argon-sparged solution of  $\text{CD}_3\text{OD}$ ), is capable of isomerization of **4** which supports a  $\pi$ -allyl type mechanism. Trace hydrogen may, however, remain in the solution and be responsible for the observed isomerization through the discussed mechanism involving dihydrides.

**Effect of anion on enantioselectivity:** Effects on enantioselectivity due to anion coordination have been observed previously upon addition of salts to rhodium-, iridium-, and ruthenium-catalyzed reductions.<sup>[47]</sup> The improvements in *ee* observed in this work for hydrogenation of **4** may be due to one or both of the following factors:

- The steric influence of the anionic ligand bound to the metal center could play an important role. It has been suggested repeatedly that the chirality of the phosphane backbone is transmitted to the substrate through the face–edge<sup>[48]</sup> or quasi-equatorial array<sup>[49]</sup> of phenyl groups. Certain quadrants around the metal center become more sterically hindered than others, forcing the prochiral substrate into a certain conformation leading to chiral induction. Therefore, an additional ligand would increase the steric bulk around the metal center and thus enhance one substrate binding mode over the other.
- Electronic effects could have large effects on catalyst reactivity. Because electronic effects have been shown to be important in asymmetric hydrogenation of enamides,<sup>[50]</sup> anion coordination could adjust the electronics of the metal center and favor certain diastereomeric intermediates or steps in the catalytic cycle.

As suggested earlier,<sup>[9]</sup> the formation of intermediate **E** in Scheme 3 and **N** in Scheme 4 could be the enantioselective step. If the anion is *trans* to the hydride, the *trans* effect of the anion could affect the stability of the hydride, modifying the difference of the free energy of activation of between the transition states of the diastereomeric complexes for olefin insertion, augmenting the enantioselectivity of the reaction. Because several possible isomers are possible, this interpretation remains plausible but speculative.

## Conclusions

The presence of anionic achiral additives has very strong effects on the enantioselectivity, hydrogen pressure dependence, and rate for the asymmetric hydrogenation of monodentate hydrocarbon olefins such as **4**. Strongly coordinating halides such as iodide bind to the cationic rhodium complex in nonpolar benzene to form neutral and anionic complexes, depending upon the relative ratio of anion/rhodium. Excess halide brings about a decrease in rate due to inhibition, but does not lower the enantioselectivity of the reaction. The NMR studies,  $^1\text{H}$ ,  $^{31}\text{P}$  and PHIP, indicate that a dihydride mechanism is in operation at both low and high pressures where dihydrogen addition occurs before olefin binding. Monohydride species observed by NMR spectroscopy with chloride and iodide are inactive, stable species not involved in the catalytic cycle. With the more dissociative sulfonate anion, however, catalytic data suggest that a dihydride mechanism occurs only at high pressure; an “unsaturate” route, that is olefin binding before  $\text{H}_2$  addition, occurs at atmospheric pressure. Olefin isomerization does not occur when halides are present at any pressure, but is seen with sulfonate at low pressure through what is probably mechanism involving a  $\pi$ -allyl. The effect of anion binding is clearly general and is the focus of continuing work. It is obvious that simple achiral

additives have a dramatic influence on catalytic mechanisms in late transition metal catalyzed reactions and a detailed understanding of their role is extremely useful, if not essential for the development of highly enantioselective catalysts capable of reducing new and broad classes of olefinic substrates.

## Experimental Section

The reagents and solutions were handled under nitrogen or argon atmosphere through standard Schlenk techniques or in a Vacuum Atmospheres glovebox. NMR spectra were obtained using either 300 MHz or 500 MHz Bruker spectrometers, or a 200 MHz 200 XLA Varian instrument. NMR spectra were simulated with NMR Version 1.0, 68881(2) Specific Code (developed by A. K. Rappé and C. J. Casewit). Gas chromatography (GC) was carried out with a Hewlett Packard Series II 5890 equipped with a semicapillary column (HP-1, methylsilicone gum, 10 m × 0.53 mm × 2.65 μm) and a flame ionization detector (FID). Optical rotations were performed by using a Perkin Elmer 241 polarimeter. Solution samples were taken in a 10 cm glass cell and neat samples in a 1 cm glass cell. High-pressure hydrogenation reactions were carried out in a 50 mL stainless steel autoclave (Autoclave Engineers). The temperature is held constant by a thermostated oil bath and the catalytic solution agitated by magnetic stirring. Hydrogenations carried out at 1 atm were performed on a dual manifold Schlenk line (Ace Glass) with H<sub>2</sub> fed directly into the manifold. Solvents were cyclically distilled under an inert atmosphere and dried over the usual drying agents or were purified by using a homemade Dow Chemical/Grubbs solvent purification system.<sup>[51]</sup> 2-phenyl-1-butene (**4**) and  $\alpha$ -cyclohexylstyrene (**5**) were synthesized by a Wittig reaction according to known procedures and their purities verified by NMR spectroscopy and GC.<sup>[52]</sup> *trans*- $\alpha$ -Methylstilbene and *N,N,N',N'*-tetramethyl-1,8-naphthalenediamine were purchased from Aldrich and used as received. [15]crown-5 was purchased from Aldrich and dried 12 h in vacuo over molecular sieves. N(*n*Bu)<sub>4</sub>I was purchased from Fluka as white crystals and used as received while N(*n*Bu)<sub>4</sub>Cl (Fluka) was dried 12 h in vacuo. AOT (Aldrich, 99% stated purity) was purified by stirring 12 h with activated charcoal in dry methanol, filtered repeatedly over celite to eliminate charcoal and insoluble solids, and dried in vacuo 48 h according to a literature procedure.<sup>[53]</sup> [D<sub>6</sub>]benzene was purchased from Cambridge Isotope Laboratories and used as received. Methyl-(*Z*)- $\alpha$ -acetamidocinnamate was a generous gift from Dr. Claire Newton. [[Rh(NBD)]<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] was prepared according to published procedures.<sup>[54]</sup> [Rh((-)-bdpp)(NBD)]ClO<sub>4</sub>, [Rh((+)-prophos)(NBD)]ClO<sub>4</sub> and [Rh((+)-binap)(NBD)]ClO<sub>4</sub> were prepared halide-free from [Rh(acac)(NBD)] (acac = acetylacetonate), 70% HClO<sub>4</sub>, and the enantiomerically pure phosphane purchased from Strem Chemicals, as previously described.<sup>[12]</sup>

**High-pressure hydrogenation procedure:** For a series of experiments in the same solvent and same surfactant concentration, a standard solution was prepared and kept in the glovebox. A typical hydrogenation experiment was carried out as follows. The entire autoclave was taken into the nitrogen-filled glovebox and filled with **1** (37 mg, 5 × 10<sup>-5</sup> mol), the olefinic substrate (5 × 10<sup>-3</sup> mol), the surfactant/solvent mixture (10 mL) and any co-additives (salts, [15]crown-5, etc.). The autoclave was sealed and removed from the glovebox and attached to a high-pressure stainless steel hydrogen line. The line was purged of air and the autoclave pressurized to 70 atm hydrogen pressure. The pressure was released and then refilled with hydrogen, repeating this procedure three times in total. The autoclave was refilled again to the desired pressure and the timing started with stirring of the solution. Periodic samples of the reaction solution were taken utilizing the dip/sample tube and analyzed. Hydrogenation of **4** and **5** could be monitored by <sup>1</sup>H NMR spectroscopy, or more conveniently, by GC; yields by these two methods correlate within 2%. Isomerized **4**, (*E*)-2-phenyl-2-butene, was identified by its <sup>1</sup>H NMR spectrum and was well separated from **4** and the hydrogenation product 2-phenylbutane by GC. Samples taken from hydrogenation reactions of **6** and **7** were analyzed by <sup>1</sup>H NMR spectroscopy. Following completion of the reaction, the pressure was released and the products separated from the catalyst and other additives by passing through a short (3 cm) plug of silica gel with a small excess of pentane. For hydrogenation of **4** in MeOH, the 2-phenylbutane product

was extracted with pentane. Previously, the *ee* of the 2-phenylbutane product had been determined in the literature through optical rotation, but in this work we utilize exclusively a quick and effective <sup>31</sup>P NMR method involving the catalyst itself, [Rh((-)-bdpp)]<sup>+</sup>, as an inorganic chiral shift reagent since it requires only small quantities of material and is easily performed.<sup>[21]</sup> Final yields for **6** and **7** were determined by <sup>1</sup>H NMR spectroscopy. Compound **7** was separated from its hydrogenation product by chromatography as previously reported.<sup>[55]</sup> The *ee* can be determined by optical rotation [[ $\alpha$ ]<sub>D</sub><sup>20</sup> = +16.4 (*c* = 2.0, MeOH)]<sup>[56]</sup> or using [Eu(hfc)<sub>3</sub>] in CDCl<sub>3</sub>.

For the *ee* determination of the 2-phenylbutane hydrogenation products of **4** and **6**, the <sup>31</sup>P NMR method previously described was utilized. For an accurate measurement of the hydrogenation product of **4**, the 2-phenylbutane had to be free of **4** and the isomerization product (*E*)-2-phenyl-2-butene; the following two methods could be used to purify the desired product. Reverse-phase HPLC using 85:15 H<sub>2</sub>O/MeOH with a Zarbox ODS semi-preparative reverse phase column (25 cm × 4.6 mm i.d.) cleanly separated the three compounds. Alternatively, "silvered" 2-mm thick preparative TLC silica plates could be used. Commercial TLC plates (Merck) were silvered by soaking in 80:20 EtOH/H<sub>2</sub>O with 10% AgNO<sub>3</sub> (by mass) for 2 min and then dried overnight in a dessicator in vacuo in absence of light. The plates are then heated in an oven in air for 1 h at 160 °C or until they become pale red/brown. Small quantities (25–50 mg) of pure 2-phenylbutane (sufficient for <sup>31</sup>P NMR *ee* determination) could be eluted with neat pentane. If, however, the total percentage of **4** and (*E*)-2-phenyl-2-butene in the sample was greater than 55%, obtaining a pure sample of 2-phenylbutane through this procedure was virtually impossible and HPLC had to be used. Compound **6** did not have to be separated from its hydrogenated product since it binds only weakly to [Rh((-)-bdpp)]<sup>+</sup> and is well separated in the <sup>31</sup>P NMR spectrum from the diastereomers formed.

**Hydrogenations in NMR tube:** The catalyst and additives were loaded into a 5 mm NMR tube and taken into the glovebox. The deuterated solvent was added and the tube sealed with a rubber septum and parafilm. The tube was removed from the box and then purged with H<sub>2</sub> through a stainless steel needle piercing the rubber septum. In the case of the halides, if the halide and catalyst were thoroughly mixed before hydrogen addition, the lemon-yellow five-coordinate complex [Rh(NBD)(P-P)X] (X = Cl, I) was formed. Since this complex reacts very slowly with dihydrogen, the following precautions were taken to avoid its formation: [Rh(NBD)(P-P)]ClO<sub>4</sub> and the halide salt were placed in the bottom of the NMR tube, and the [D<sub>6</sub>]benzene were added carefully without dissolution of the solids. The sealed tube was removed from the glovebox and purged with hydrogen through the rubber septum. Only at this point the tube was shaken to induce hydrogenation of [Rh(NBD)(P-P)]ClO<sub>4</sub> and then complexation of the resulting complex with halide. [Rh(NBD)(P-P)]ClO<sub>4</sub> reacts with dihydrogen almost immediately before formation of [Rh(NBD)(P-P)X] can take place, as demonstrated by NMR studies.

**Parahydrogen-induced polarization NMR procedure:** Parahydrogen was prepared according to the method of Bargon and co-workers.<sup>[58]</sup> [Rh((-)-bdpp)(NBD)]ClO<sub>4</sub> (6.7 mg, 9 × 10<sup>-6</sup> n) and N(*n*Bu)<sub>4</sub>I (6.6 mg, 1.8 × 10<sup>-5</sup> n, 2 equivalents) were weighed and placed into an NMR tube and brought into the dry box. [D<sub>6</sub>]benzene (0.6 mL) was then added to make the final [Rh] 15 mM, taking care not to disturb the solid on the bottom. The tube was then sealed and removed from the dry box. It was immersed in liquid nitrogen and purged with parahydrogen for 1 min. The tube was stored in liquid nitrogen, then thawed, shaken, and inserted into the NMR spectrometer. Two scans were immediately recorded; the process from thawing to accumulation taking no more than 30 s. The <sup>1</sup>H NMR spectrum failed to show any polarization due to metal hydride species. The tube was then brought back into the dry box and [D<sub>8</sub>]styrene (0.05 mL, 4 × 10<sup>-4</sup> n, 44 equivalents) added and the tube again sealed, removed from the glovebox, frozen in liquid nitrogen, and purged with parahydrogen. After the sample had been thawed, shaken, and immediately inserted into the NMR, two scans revealed a large enhancement of the alkyl signals at  $\delta$  = 2.45 and 1.05 of greater than 100 times. The two signals correspond to the H of the methylene and the methyl, respectively, of the ethylbenzene hydrogenation product. Repeated removal of the tube, shaking, and reinsertion in the instrument (8 times) renewed the observed polarization. A <sup>1</sup>H NMR spectrum taken 5 min after shaking with parahydrogen showed loss of all polarization.

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