About the Crystal Structure of [Rh((*S*,*S*)-DIPAMP)-((*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl Acrylate)]BF_4: Major or Minor Catalyst−Substrate Complex?†

Thomas Schmidt, Wolfgang Baumann,* Hans-Joachim Drexler, Antonio Arrieta, and Detlef Heller*

Leibniz-Institut für Organische Katalyse an der Universität Rostock e.V., Albert-Einstein-Strasse 29a, Rostock 18059, Germany

Helmut Buschmann

ESTEVE, Av. Mare de Deu de Montserrat 221, ES-08041 Barcelona, Spain

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Asymmetric hydrogenation of (*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate with [Rh((*S*,*S*)-DIPAMP)$(MeOH)_2$]BF_4 was investigated. Low temperature NMR measurements prove the recently published X-ray structure of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]BF_4 to be the major substrate complex. The asymmetric hydrogenation of the prochiral DOPA precursor with the cationic Rh-DIPAMP catalyst therefore follows the "anti-lock-and-key" motif analogue to similar substrate complexes already known from literature.

Introduction

The asymmetric hydrogenation supported by cationic Rh(I) complexes is both one of the most intensively investigated and best understood selection processes. According to Halpern and Landis[1] as well as Brown,[2] the asymmetric hydrogenation proceeds as shown in the general reaction sequence of Scheme 1.

In pre-equilibria diastereomeric substrate complexes are formed by coordination of a prochiral olefin to the catalyst−solvent complex as the active species. These intermediates react in a sequence of elementary steps (oxidative addition of hydrogen, insertion, and reductive elimination) to the enantiomeric products.

Halpern and Brown were able to show for hydrogenation of different α-dehydroamino acid derivatives that the main source of selectivity seems to be the ratio of the rate constants for oxidative addition of hydrogen (k_{2min}/k_{2maj}). Relative stability of the intermediates obviously does not play an important role.[1f] The result, that the less stable intermediate dominates the enantioselectivity by its high reactivity, which was not expected in those days, entered the literature as the so-called *major−minor concept* or, according to Landis, *anti lock-and-key motif*.

Since it has been experimentally proven in several examples of asymmetric hydrogenation,[1a,d,e] it has to all intents and purposes been developed to a basic concept of homogeneous catalysis. The concept is, for example, reflected in the ligand accelerated catalysis.[3]

Detailed investigations concerning mechanism[4] or rather activation of hydrogen as well as insertion under use of isotope effects,[5] detection of dihydrido-catalyst−substrate complexes,[6] reversibility of product formation,[7] extended models,[8] influence of electronic effects,[9] and interconversion of the diastereomeric substrate complexes[10] have been published.

† Dedicated to Günther Wilke on the occasion of his 80th birthday.

* To whom correspondence should be adressed. E-mail: detlef.heller@ifok-rostock.de. Phone: +49 381 1281183; Fax: +49 381 12815000. E-mail: wolfgang.baumann@ifok-rostock.de.

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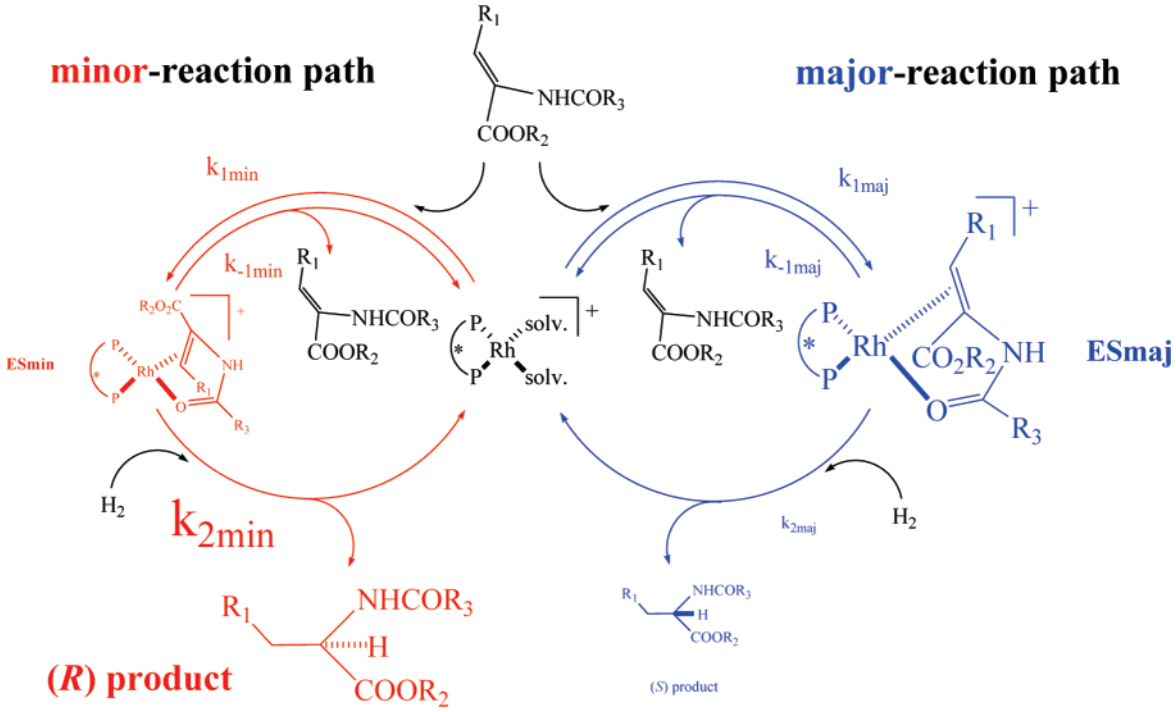
Scheme 1. Selection Model of Rh(I) Complex-catalyzed Asymmetric Hydrogenation to the (*R*)-amino Acid Derivative According to Halpern, Landis and Brown. (ES_{Maj} and ES_{min}, Respectively, Are the Diastereomeric Catalyst−Substrate Complexes)



Recently, Gridnev and Imamoto were able to detect rhodium alkyl complexes in solution at temperatures below −50 °C in rhodium BisP*-catalyzed asymmetric hydrogenation of α-dehydroamino acid derivatives.[11] They also described a dihydrido complex with the mentioned catalyst at −95 °C. Therefore, the hydrogenation of α-acetylamino acrylates seems to be alternatively imaginable according to the so-called "hydride route".[12] Nevertheless, the question remains if this reaction sequence is also possible at room temperature (i.e., under common hydrogenation conditions).

Very recently it has been discussed for a chiral P/S-ligand that a catalyst−substrate complex of an α-dehydroamino acid derivative characterized by X-ray analysis obviously leads to the main enantiomer in asymmetric hydrogenation.[13] We were able to publish an analogue result for the asymmetric hydrogenation of different *β*-dehydroamino acid derivatives.[14] Three of five isolated catalyst−substrate complexes characterized by X-ray were proven to be the major substrate complex, which leads, unlike as predicted by the major−minor concept, to the main hydrogenation product.

Furthermore, the X-ray structure of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoyl-amino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]BF_4 (Figure 1) has been published.[15]

In analogy to the substrate complexes described by Halpern et al., the C−C double bond and the oxygen of the amide group are both coordinated to the rhodium. Following the generally accepted mechanism of hydrogen transfer from the rhodium site, this intermediate leads to the (*S*)-enantiomer. Nevertheless, experimentally 99% (*R*)- but only 1% (*S*)-product have been found. In conclusion, the substrate complex shown in Figure 1 leads to the byproduct. This result corresponds to the

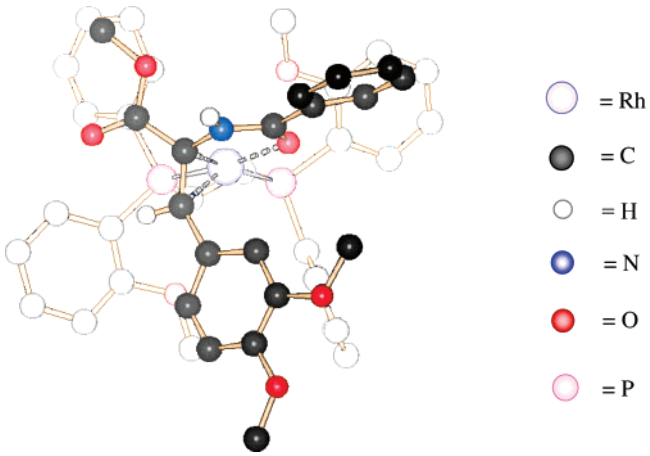


Figure 1. Solid-state molecular structure of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]BF_4.[15] (The anion and the hydrogen atoms (except at the α-carbon and at the amide-nitrogen) are omitted for clarity.)

A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869−9882. (e) Kadyrov, R.; Freier, T.; Heller, D.; Michalik, M.; Selke, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1745−1746. (f) Ramsden, J. A.; Claridge, T. D. W.; Brown, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 2469−2471. (g) Heller, D.; Kadyrov, R.; Michalik, M.; Freier, T.; Schmidt, U.; Krause, H. W. *Tetrahedron: Asymmetry* **1996**, *7*, 3025−3035. (h) Kless, A.; Börner, A.; Heller, D.; Selke, R. *Organometallics* **1997**, *19*, 2096−2100.

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(13) Evans, D.; Michael, F. E.; Tedrow, J. S.; Campos, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3534−3543. Unfortunately, it could not be proven that the only visible signal in NMR is identical to the isolated substrate complex.

(14) Drexler, H.-J.; Baumann, W.; Zhang, S.; Schmidt, T.; Sun, A.; Spannenberg, A.; Fischer, C.; Buschmann, H.; Heller, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 1184−1188.

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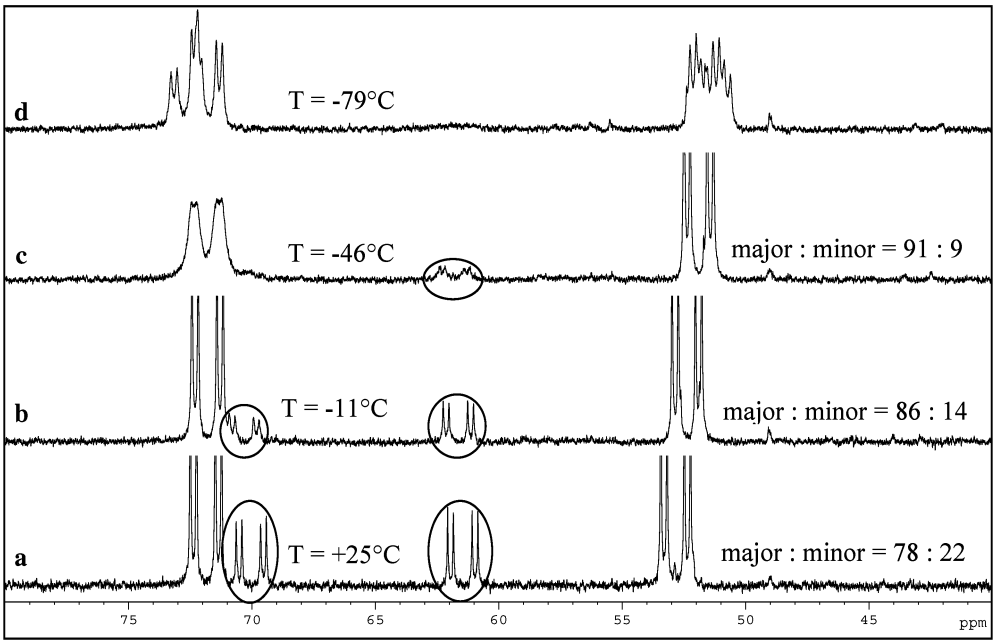


Figure 2. Temperature dependent ^{31}P NMR spectra of a solution of [Rh((*S*,*S*)-DIPAMP)−((*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]BF_4. The minor signals are encircled.

classical major−minor concept. This simple conclusion relies on the assumption that the isolated crystals are equal to the major substrate complex. Nonetheless, in principle it cannot be excluded that the minor complex was crystallized, referring to the classical discussion of Halpern et al.[1a]

To clarify this problem Halpern, Bosnich, and coworkers used a correlation of solid-state CD spectroscopy and CD spectroscopy of dissolved catalyst−substrate complexes.[16] However, according to the authors, this method is only conclusive if the coordination of the prochiral olefin has a remarkable effect on the circular dichroism.

One aim of this work was to find out whether the isolated substrate complex [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoyl-amino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]-BF_4 corresponds to the major or to the minor substrate complex. Moreover, it was proven for the first time that the two detected catalyst−substrate complexes in solution surely are diastereomeric complexes and not complexes with isomerized substrate.

Results and Discussion

Identification of the Major Substrate Complex. In addition to CD spectroscopy, useful methods to clarify the discussed problem are NOE measurements, solid-state NMR, and prevention of interconversion while dissolving the diastereopure catalyst−substrate complexes.

To apply NOE measurements successfully, all signals of the complicated proton spectra must be assigned beforehand. For the alternative use of solid-state NMR, large amounts of diastereopure substrate complex have to be available. Furthermore, measurements have to occur under inert conditions.

For that reason, we looked for an appropriate method to prevent interconversion between the two diastereomeric substrate complexes, which can in principle occur inter- or rather intramolecularly,[10] to correlate the X-ray structure with one of the respective signal sets. Freezing out interconversion while dissolving the single crystals at the lowest temperature applicable[17] followed by ^{31}P NMR spectroscopy at low temperature as well seemed to be suitable.

Successful performance of this method is only possible under the following preconditions:

1. The single crystals must be dissolved at the lowest possible temperature at which the interconversion cannot occur.

2. At both room temperature and the chosen low temperature, each substrate complex, especially the minor complex, must be detectable.

The simplest way to check the second condition is to measure ^{31}P NMR spectra of a solution of the substrate complex at room temperature as well as at low temperature.

At first a solution of the substrate complex in methanol-d_4 was generated from the solvent complex[18] by adding an excess of substrate. As a handicap, it turned out that both the substrate and the resulting complex have a poor solubility in methanol.[19] Figure 2a shows the resulting phosphorus NMR spectrum. The minor complex is easily detectable with a share of 22%. Corresponding NMR data can be found in Table 1. They are comparable with ^{31}P NMR data from the literature of a similar complex.[20]

To check whether the minor substrate complex can also be detected at low temperatures, the same solution

(16) Chua, P. S.; Roberts, N. K.; Bosnich, B.; Okrasinsky, S. J.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1981**, 1278−1280.

(17) The temperature decrease is only limited by the solubility of the single crystals and the melting point of the solvent.

(18) Starting from [Rh(DIPAMP)NBD]BF_4 as precatalyst it is prehydrogenated for 20 min. Thus, all rhodium is present in the form of a solvent complex. (See also: Drexler, H.-J.; Baumann, W.; Spannenberg, A.; Fischer, C.; Heller, D. *J. Organomet. Chem.* **2001**, *621*, 89−102.)

(19) A part of the catalyst−substrate complex was recrystallized in the NMR tube after 24 h. This is a further hint for its low solubility in methanol.

(20) Bender, B. R.; Koller, M.; Nanz, D.; Philipsborn, W. v. *J. Am. Chem. Soc.* **1993**, *115*, 5889−5890. (Supporting Information.)

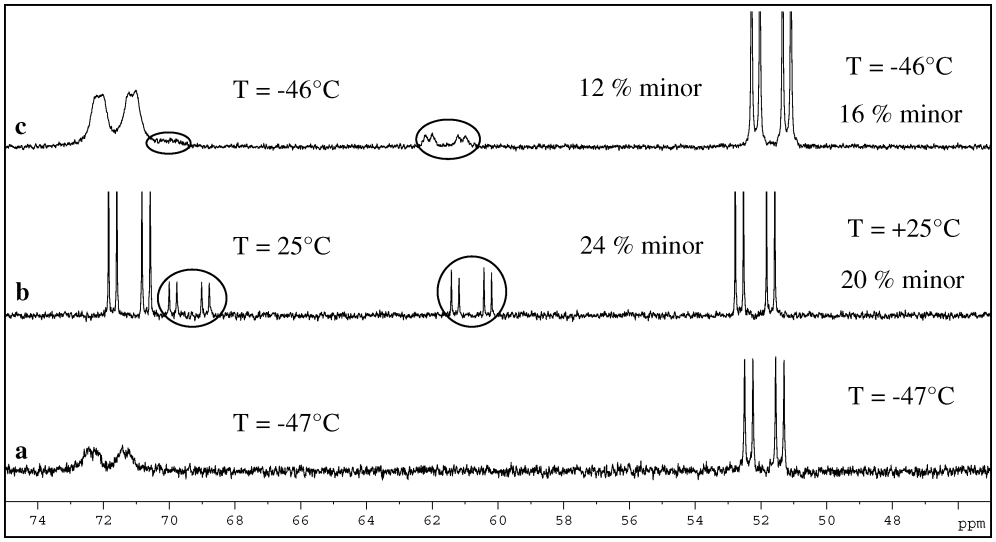
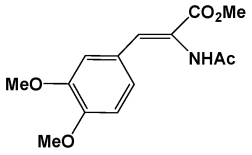
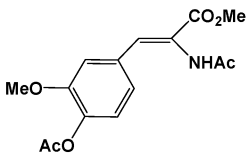


Figure 3. ^{31}P NMR spectra of the dissolved diastereopure crystals of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]BF_4 under temperature variation from −47 °C (a) to +25 °C (b) and cooling again to −46 °C (c). The minor signals are encircled.

Table 1. ^{31}P NMR Data of Catalyst−Substrate Complexes of the Type [Rh(DIPAMP)-((*Z*)-3-(aryl-substituted)-2-acylamino-methyl Acrylates)]BF_4 in Methanol-d_4 at 25 °C

substrate	diastereomer	δ (ppm)	^{1}J(P-Rh) (Hz)	^{2}J(P-P) (Hz)	share (%)
	major:	52.8 / 71.9	154.2 / 164.0	40.9	78
	minor:	61.5 / 70.0	160.2 / 159.7	37.3	22
	major: [20]	48.2 / 70.8	151.4 / 161.7	39.4	-
	minor: [20]	56.6 / 69.4	161.0 / 155.9	36.9	-

was cooled stepwise, measuring the ^{31}P NMR spectrum at each temperature. The corresponding spectra are represented in Figure 2b−d.

Lowering the temperature to −11 °C decreases the share of the minor complex (14%). Moreover, a change in chemical shifts can be observed. A further decrease in temperature to −46 °C leads to a signal broadening. Nonetheless, the minor complex is still detectable with a share of 9%. Cooling the solution to −79 °C causes a particularly strong broadening of the minor signals. Under this condition they are hardly visible. In addition to the change in chemical shift and peak broadening peak splitting of the major signals was observed.

We were able to show that at a temperature above −46 °C the minor diastereomer can be detected without difficulties. Lower temperatures are not suitable for working on this objective.

Correlation of the NMR signals to the crystal structure was realized by dissolving single crystals of the catalyst−substrate complex at −75 °C followed by measuring ^{31}P and ^{1}H spectra at −47 °C (Figures 3a and 4a). The same solution was heated to +25 °C. The resulting spectra can be found in Figures 3b and 4b). In a last experiment, the sample was cooled again to −46 °C (Figures 3c and 4c).

In the spectrum taken directly after dissolving the single crystals, no signal of the minor complex could be detected (Figure 3a). Hence, the major complex must have been dissolved at a temperature at which the equilibrium between the two diastereomers is not established. The NMR spectrum taken after warming the very same solution up to room temperature represents the thermodynamic equilibrium between the major and minor substrate complex (Figure 3b). Cooling the equilibrated solution again to nearly the temperature of the first measurement (Figure 3c) did not lead to a vanishing of the minor signals but to the expected spectrum with both the diastereomers. The shares of the minor complex are comparable in Figures 2a (22%) and 3b (24%) as well as in Figures 2c (9%) and 3c (12%), respectively, within experimental error. Thus, we could show that after warming to room temperature the solution was in equilibrium, which can still be found after reducing the temperature once again.

Furthermore, the proton spectra, which have a significantly lower limit of detection, corroborate these findings.

Because of the complexity of the ^{1}H NMR spectra we chose the most characteristic parts for analysis. Figure 4 shows the area of the methoxy peaks. (A figure showing the aromatic signals can be found in the Supporting Information.) The marked minor signals are again at first undoubtedly detectable after heating the solution to room temperature (Figure 4b, 20%).

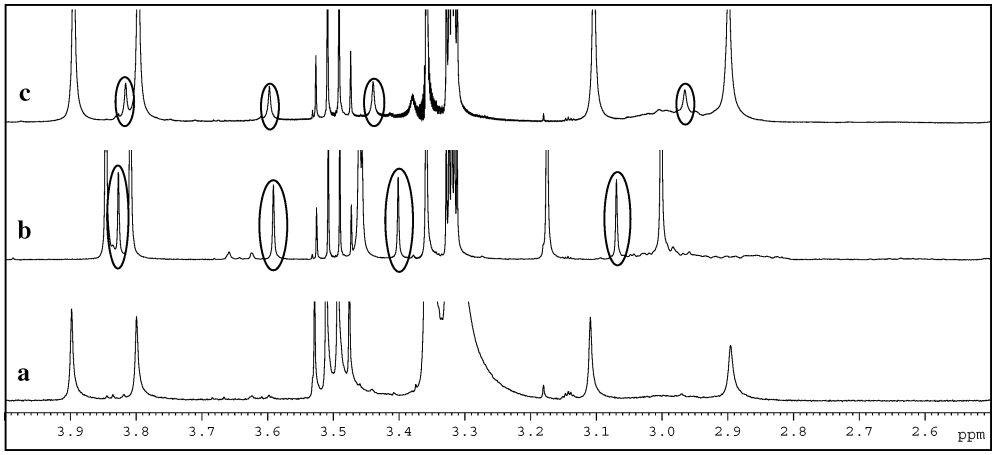


Figure 4. ^{1}H NMR spectra (4−2.5 ppm) of the dissolved single crystals of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]BF_4 at different temperatures. The minor signals are encircled.

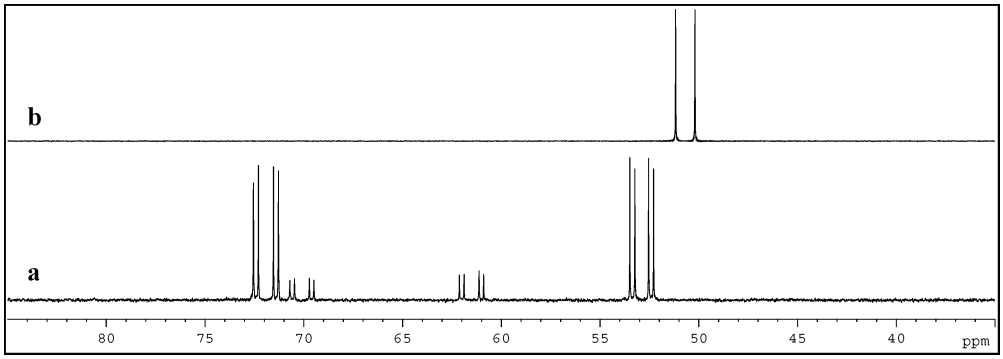


Figure 5. Phosphorus spectra to check substrate displacement by NBD. a) diastereomeric substrate complexes of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoylamino-3-(3,4-dimethoxy-phenyl)-methyl acrylate)]BF_4; b) spectrum of [Rh((*S*,*S*)-DIPAMP)(NBD)]BF_4 after displacement of the prochiral olefin by NBD.

The share correlates with the one determined from the ^{31}P NMR spectrum (24%) within experimental error. The ^{1}H NMR signals of the minor diastereomer are still detectable after cooling to the temperature of the first measurement (Figure 4c,16%). The share is likewise comparable with the ^{31}P NMR spectrum (12%).

Both phosphorus and proton NMR spectroscopy prove that interconversion between the major and minor catalyst−substrate complex was prevented by dissolving the crystals of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoylamino-3-(3,4-dimethoxy-phenyl)-methyl acrylate)]BF_4 and afterward operating at a temperature of ca. −45 °C. Hence, the crystal structure must be equal to the *major* substrate complex.

Exclusion of *E*/*Z*-Isomerization. To verify that the signals in Figure 2 exclusively correspond to substrate complexes of the *Z*-isomer of 2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate (in the literature one can find publications of *E*/*Z*-isomerization of similar substrates at rhodium catalysts[21]), we displaced the substrate starting from the already described single crystals by NBD as complexation agent (10-fold excess) followed by ^{1}H NMR spectroscopy to investigate the displaced prochiral olefin.

At first the characterized single crystals of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoylamino-3-(3,4-dimethoxy-phenyl)-methyl acrylate)]BF_4 were dissolved in methanol-d_4. At room temperature equilibrium between the diastereomers was rapidly reached. Figure 5a exhibits the ^{31}P NMR spectrum. The analogue proton spectrum in Figure 6a (area of methoxy groups; aryl group area can be found in the Supporting Information) shows the signals of coordinated substrate beside signals of the (*S*,*S*)-DIPAMP ligand and the solvent.

In a second step, NBD was added in approximately 10-fold excess followed by ^{1}H and ^{31}P NMR spectroscopy. In the ^{31}P NMR spectrum (Figure 5b) exclusively signals of the NBD complex are visible.[22] Thus, the substrate must have completely been displaced from the rhodium. In the corresponding ^{1}H spectrum (Figure 6b), several signals of the meanwhile free *Z*-substrate are detectable (compare with the NMR spectrum of pure (*Z*)-2-benzoylamino-3-(3,4-dimethoxy-phenyl)-methyl acrylate in methanol-d_4, Figure 6d).

To make sure no *E*-isomer was set free, a solution of (*E*)-2-benzoylamino-3-(3,4-dimethoxy-phenyl)-methyl acrylate, roughly equimolar to the rhodium amount, in methanol-d_4 was added (Figure 6c). As expected, the proton NMR spectrum shows additional signals that can be allocated to the *E*-isomer. Since we could show that the substrate was exclusively coordinated as *Z*-isomer to the rhodium the observed signals in the ^{31}P NMR spectrum undoubtedly have to represent the diastereomeric substrate complexes.

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(22) The chemical shift of the solvent complex is 80.5 ppm. The shift of the oxidized ligand can be found at 37.2 ppm.

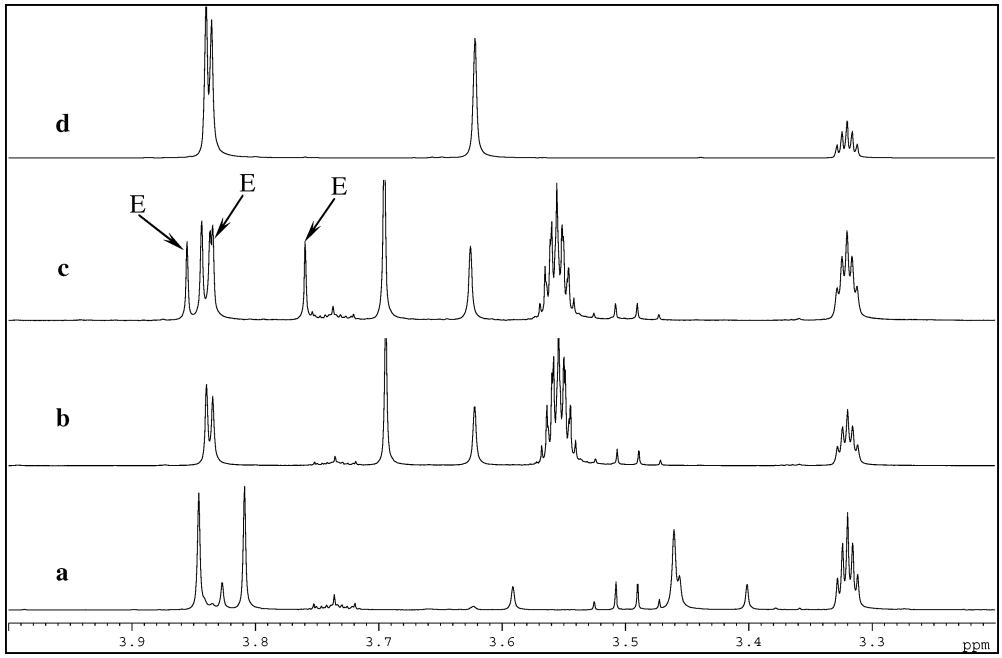


Figure 6. Methoxy group area of the proton spectra to exclude *Z*/*E*-isomerization. (a) Dissolved single crystals. (b) Addition of NBD to solution of (a). (c) Addition of (*E*)-2-benzoylamino-3-(3,4-dimethoxy-phenyl)-methyl acrylate. (d) (*Z*)-2-Benzoylamino-3-(3,4-dimethoxy-phenyl)-methyl acrylate. The signals of the *E*-isomer are marked.

Reactivity Ratio as Level of Selection. The selectivity expressed by the ratio of the enantiomeric products corresponds to Scheme 1 (eq 1):[23]

$$\frac{[R]}{[S]} = \frac{[ES_{min}]}{[ES_{maj}]} \cdot \frac{k_{2min}}{k_{2maj}} = \left(\frac{\dfrac{k_{1min}}{k_{-1min} + (k_{2min} \cdot [H_2])}}{\dfrac{k_{1maj}}{k_{-1maj} + (k_{2maj} \cdot [H_2])}} \right) \cdot \frac{k_{2min}}{k_{2maj}} \quad (1)$$

Due to eq 1 the selectivity is a result of two factors: The ratio of the intermediate concentrations $[ES_{min}]$ and $[ES_{min}]$ as the first selection level as well as their ratio of reactivity (k_{2maj}/k_{2min}) as the second level of selection.[24]

At room temperature, the ratio of the diastereomeric substrate complexes of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoyl-amino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]-BF_4 equals 78:22 (Figure 2). This is a further example for reactivity as the main source of enantioselectivity in analogy to reports already described in the literature. Under consideration of the experimental product ratio of 99 (98% ee in methanol at normal pressure) and eq 1, the minor complex is approximately 350 times more reactive than the corresponding major substrate complex.[25]

This result corresponds to known reactivity ratios of diastereomeric catalyst−substrate complexes with α-acylamino acrylates as prochiral olefins. Kinetic investigations on the hydrogenation of (*Z*)-*N*-acetylamino methyl cinnamate with $[Rh(DIPAMP)(MeOH)_2]^+$ resulted in a rate constant for the minor complex 580-fold higher than that for the major diastereomer at 25 °C.[1d] In the case of CHIRAPHOS as chiral ligand, the reactivity difference of the analogue ethyl ester was estimated to be even more than 1000.[16]

Conclusions

By freezing out interconversion between the two diastereomeric substrate complexes, we were able to prove the X-ray structure shown in Figure 2 to be undoubtedly the major substrate complex. Nonetheless, hydrogenation of this diastereomer leads to the product that was found in HPLC analysis only in traces with 1%. Therefore, the hydrogenation of [Rh((*S*,*S*)-DIPAMP)-((*Z*)-2-benzoyl-amino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]BF_4 corresponds to the major−minor concept in agreement with reports already stated in the literature for α-dehydroamino acid derivatives. Despite its relatively low concentration in solution, the minor substrate complex dominates the enantioselectivity in the hydrogenation because of its approximately 350-fold higher reactivity compared to that of the corresponding major diastereomer. Additionally, it could be proven for the first time that the observed complexes in solution are really diastereomeric substrate complexes, which was hitherto assumed but never shown.

Experimental Section

Preparation of (*Z*)-2-benzoylamino-3-(3,4-dimethoxy-phenyl)-methyl acrylate (2). Preparation of **2** was carried out as described in ref 26 (Scheme 2).[26] From 3.8 g, 2.7 g of white crystals was isolated (yield = 68% of the theroretical

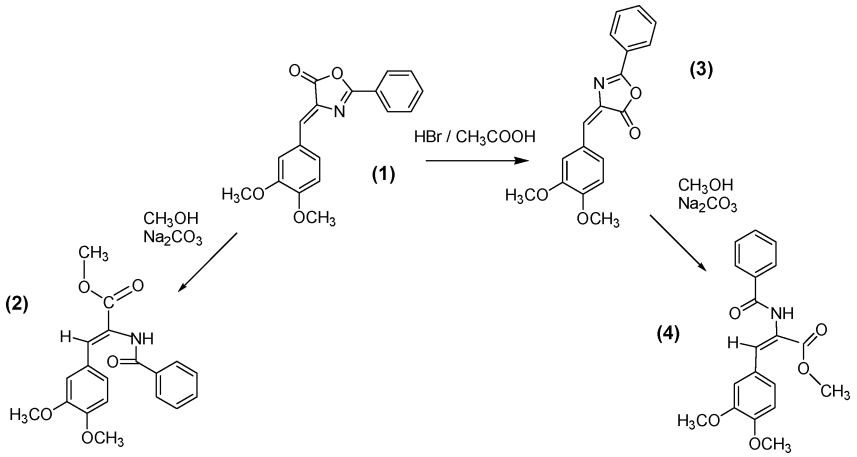
(23) An analogue equation with the stability constants resulting from the *equilibrium approximation* is already described by Halpern and Landis.[1d] For the used equation resulting from the *steady state* approach the ratio of the stability constants has to be replaced by the reciprocal values of the corresponding *Michaelis* constants.

(24) Heller, D.; Buschmann, H.; Scharf, H.-D. *Angew. Chem., Int. Ed.* **1996**, *35*, 1852−1854.

(25) These considerations only apply if the ratio of the diastereomeric substrate complexes determined under argon corresponds to the one under hydrogen atmosphere. For the example of hydrogenation of (*Z*)-*N*-acetylamino methyl cinnamate with the DIPAMP catalyst it seems to be roughly the case: Heller, D.; Buschmann, H. *Top. Catal.* **1998**, *5*, 159−176.

(26) O'Reilly, N. J.; Derwin, W. S.; Lin, H. C. *Synthesis* **1990**, 550−556.

Scheme 2. Preparation of (*Z*)- 2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl Acrylate (2) and (*E*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl Acrylate (4) Starting from (*Z*)-4-(3,4-dimethoxy-benzylidene)-2-phenyl-4H-oxazol-5-one (1)



value). mp 126−127 °C (methanol); literature:[26] 135−137 °C. $C_{19}H_{19}NO_5$ (fw 341.18 g/mol). Analysis (calcd/exptl): C: 66.83/66.66, H: 5.61/5.50, N: 4.12/4.06. TLC: R_f = 0.31 (ethyl acetate/*n*-hexane, 1:1). ^{1}H NMR (400.13 MHz, DMSO-d_6): 3.33 (s, 3H), 3.72 (s, 3H), 3.76 (s, 3H), 7.28 (dd, 1H), 7.35 (d, 1H), 7.45 (s, 1H), 7.50−7.65 (m, 3H), 8.00 (d, 1H), 8.02 (s, 1H), 10.02 (s, 1H). ^{1}H NMR (400.13 MHz, MeOH-d_4): 3.62 (s, 3H), 3.84 (d, 6H), 6.97 (d, 1H), 7.23 (m, 1H), 7.33 (d, 1H), 7.53 (m, 2H), 7.60 (s, 1H), 7.62 (m, 1H), 7.99 (d, 2H). ^{13}C NMR (100.63 MHz, DMSO-d_6): 31.7, 52.0, 55.0, 55.4, 78.1, 111.4, 112.8, 124.0, 125.9, 127.5 128.4, 131.8, 135.2, 148.2, 150.0, 165.6, 169.4, 192.2.

Preparation of (*E*)-4-(3,4-Dimethoxy-benzylidene)-2-phenyl-4H-oxazol-5-one (3). Preparation of **3** was accomplished in analogy to ref 27. *Z*-Azlactone (**1**) (3,1 g) was dissolved in 200 mL of glacial acetic acid. In the course of 30 min, 10 mL of a HBr solution (77% in acetic acid) was added. Afterward, stirring at room temperature was continued for a further 45 min. The deep red solution was added to 1 L of water. The raw product was filtered and washed at least three times with water at room temperature. The yellow azlactone was dried for 24 h in the exsiccator and afterward for 10 h under vacuum (10^{-2} mbar). $C_{18}H_{15}NO_4$ (fw 309.32). mp 136−137 °C (water).

Preparation of (*E*)-2-Benzoylamino-3-(3,4-dimethoxyphenyl)-methyl Acrylate (4). The procedure and the molar ratios are equal to the ones of the preparation of the *Z*-isomer. Unlike the *Z*-compound, the desired *E*-product precipitates spontaneously and is filtered together with the excess sodium carbonate. The recrystallization from methanol gives moderate yields due to its low solubility but a clean product according to HPLC analysis. This procedure is eased by using a mixture of methanol/methyl acetate 1:1 for recrystallization. From 4.8 g of *E*-azlactone, 2.6 g of pure product was obtained (yield = 50% of the theoretical value). $C_{19}H_{19}NO_5$ (fw 341.18). mp 177−178 °C (methanol), colorless crystals. Analysis (calcd/exptl): C: 66.83/66.86, H: 5.61/5.62, N: 4.12/4.04. TLC: R_f = 0.38 (ethyl acetate/*n*-hexane, 1:1). ^{1}H NMR (400 MHz, DMSO-d_6): 3.66 (s, 3H), 3.74 (s, 3H), 3.76 (s, 3H), 6.69 (s, 1H), 6.83 (m, 1H), 6.88 (d, 1H), 6.92 (d, 1H), 7.4−7.7 (m, 3H), 7.93 (d, 1H), 7.95 (s, 1H), 10.47(s, 1H). ^{1}H NMR (400.13 MHz, MeOH-d_4): 3.76 (s, 3H), 3.84 (s, 3H), 3.86 (s, 3H), 6.80 (s, 1H), 6.91 (m, 1H), 6.93 (m, 1H), 6.99 (d, 1H), 7.52 (m, 2H), 7.61 (m, 1H), 7.92 (m, 2H). ^{13}C NMR (100.63 MHz, DMSO-d_6): 51.7, 55.3, 55.4, 55.3, 55.4, 111.4, 111.5, 121.1, 122.2, 126.5, 127.2, 127.6, 128.4, 132.0, 132.7, 148.2, 148.6, 164.8, 165.5. Additionally, the solid-phase molecular structures of the *Z*-isomer (**2**) (left) as well as the *E*-isomer (**4**) (right) were carried out (Figure 7, see also Supporting Information).[28]

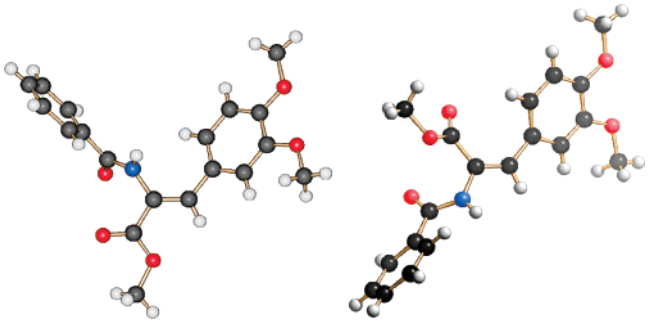


Figure 7. Solid-state molecular structure of (*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate (left) (ORTEP, 50% probability ellipsoids) and of (*E*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate (right) (ORTEP, 50% probability ellipsoids).

Accomplishment of the Low-Temperature NMR Experiments. Degassed methanol-d_4 (0.7 mL) in a secured NMR tube was frozen at −98 °C. Circa 10 mg of single crystals of [Rh((*S*,*S*)-DIPAMP)-((*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl acrylate)]BF_4 was added, and the tube was sealed under argon. Afterward, the temperature was raised until −75 °C, and the single crystals were dissolved as much as possible.

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Supporting Information Available: Additional NMR spectra concerning low-temperature NMR investigations and detailed information on the solid-state molecular structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0490536

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(28) Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-251115 for the *Z*-isomer and CCDC-251116 for the *E*-isomer. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK. Fax: Int. code + (1223) 336−033. E-mail: deposit@ccdc.cam.ac.uk. Web: www: http://www.ccdc.cam.ac.uk.