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Asymmetric Hydrogenation of Dimethyl Itaconate Catalysed by Rhodium Chelates of Aminophosphine Phosphinites : A Kinetic and NMR Spectroscopical Study[1)]

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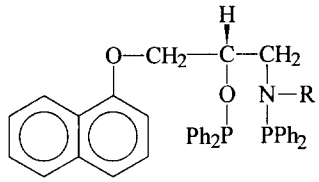
Abstract: The asymmetric hydrogenation of dimethyl itaconate in the presence of cationic seven-membered ring aminophosphine phosphinite rhodium(I)-cyclooctadiene complexes derived from Propranolol (PROPRAPHOS-Rh derivatives) can be described by the Michaelis-Menten kinetics. Variation of the nitrogen substituent in the aminophosphine phosphinite moiety of the rhodium catalyst causes a change in the concentration of the catalyst-substrate complexes. This is especially high in the case of the N-cyclohexyl derivative as follows from the Michaelis constants. ^{31}P NMR spectra of this compound gave signals of three catalyst-substrate complexes due to the different phosphorus donors: one minor- and two major-complexes. A second minor-complex could not be observed. Line-shape analysis indicates the intramolecular interconversion between diastereomeric catalyst-substrate complexes, being in favour of the intermolecular processes as found already for bis(phosphinite) chelates.

Introduction

A series of rhodium(I) complexes with aminophosphine phosphinites derived from Propranolol - PROPRAPHOS analogues of the type **1** (Scheme 1) - have been studied[1c] to find relationships between electronic as well as steric factors and the activity and stereoselectivity for the asymmetric hydrogenation reaction of amino acid precursors.

Recently,[2a] by kinetic measurements in the presence of cationic seven-membered ring chelates of rhodium(I), we have shown that the actual catalyst concentrations remain indefinitely and the initial rate of reaction is based on the parallel hydrogenation of the diolefin (COD, NBD) bound in the precatalyst and the prochiral

[1)] 4 th paper "NMR investigations on chiral catalyst complexes"; parts 1-3 see Ref. 1.

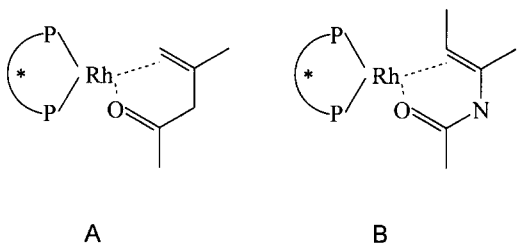


	1a	1b	1c	1d	1e	1f
R	H	methyl	2-propyl	3-pentyl	cyclopentyl	cyclohexyl

Scheme 1

olefin. The higher stability constant of the Rh-diolefin compared to the prochiral olefin complexes causes a partial blocking of the catalyst concentration for the asymmetric hydrogenation, which can be overcome only after the complete hydrogenation of the diolefin.

The rhodium complexes of the type **1** have been proven as very suitable for kinetic measurements due to the relatively fast hydrogenation of the COD,[2b] but low reaction rate against dimethyl itaconate ($ItMe_2$). The dehydroamino acid precursors turned out to be too reactive and, therefore, unsuitable for such measurements. Catalyst-substrate complexes formed by five- or seven-membered ring chelate catalysts with derivatives of itaconic acid are well studied.[3] Dimethyl itaconate (**A**) turns out a similar binding mode with respect to the formation of rhodium complexes as α-acetamidocinnamic acid (**B**) (Scheme 2) and is, therefore, convenient as model substance for such investigations.



A B

Scheme 2

In the system Rh-DIOP/methyl β-itaconate, diastereomers have been found.[3a] In contrast to the well studied five-membered ring chelate-substrate complexes,[4a-4i] fewer results are known regarding the corresponding seven-membered ring systems.[1b, 4i-4k]

Results and Discussion

Fig. 1 shows the product-proportional plots of turnover and the enantiomeric excess values for the hydrogenation reactions under standard conditions using the catalysts Rh-**1b** - Rh-**1f.**

Corresponding to the mechanistic ideas of Halpern and Brown the catalyst-substrate complexes (major-minor) are formed by a fast pre-equilibrium and hydrogenated in the rate-determining step to the reaction product.

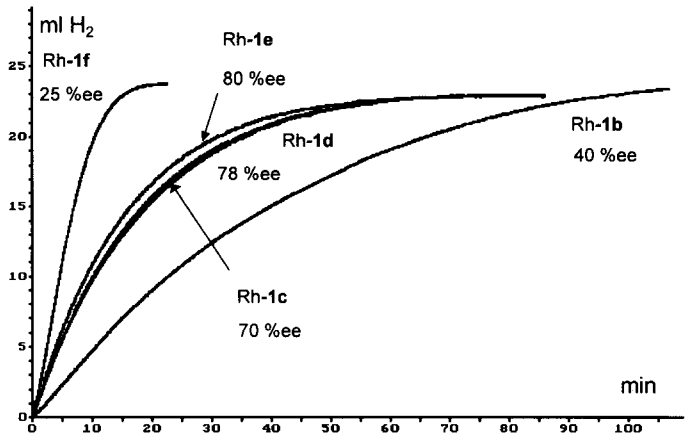
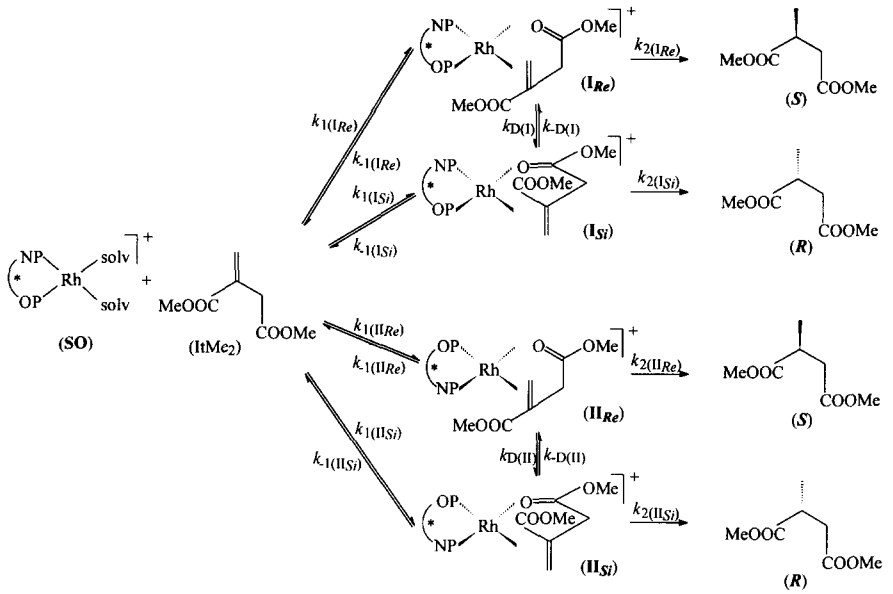


Figure 1 Asymmetric hydrogenation of $ItMe_2$ under standard conditions (15.0 ml of MeOH, 25°C, 0.1 MPa total pressure, 0.01 mmol of precatalyst, 1.0 mmol substrate)

According to the mode of complexation for the intermediates the hydrogenation follows Scheme 3. In contrast to the C_2-symmetric complexes causing the formation of only two catalyst-substrate species (major-minor) four different stereoisomeric species have to be taken into consideration in the case of the corresponding complexes of Rh-**1a** - Rh-**1f** with the prochiral substrate. The NMR experiments described below show that three stereoisomers can be observed. These Rh-substrate complexes are coupled by intramolecular equilibria. The existence of such intramolecular exchange processes has recently been reinforced by EXSY studies on rhodium complexes derived from (S,S)-bis(2,3-diphenylphosphino)butane[4g] and (2-methoxyphenyl)-P-phenyl-P-(2'-diphenylphosphino)ethylphosphine[5] and could also be confirmed for another seven-membered chelate-substrate complex.[1b] Among these and assuming regioselection of **I** and **II** based on the more basic N-P compared with O-P the hydrogenation path $k_{2(I_{Re})}$ and $k_{2(I_{Si})}$ should be favoured.

With the assumption of steady state conditions, for the hydrogenation rate an equation follows analogously to the Michaelis-Menten kinetics.[6]



Scheme 3

$$\frac{d(S)}{dt} + \frac{d(R)}{dt} = \frac{(k_{2(I_{Re})} \bullet K_{I_{Re}} + k_{2(II_{Re})} \bullet K_{II_{Re}}) \bullet E_0 \bullet S + (k_{2(I_{Si})} \bullet K_{I_{Si}} + k_{2(II_{Si})} \bullet K_{II_{Si}}) \bullet E_0 \bullet S}{1 + S \bullet (K_{I_{Re}} + K_{I_{Si}} + K_{II_{Re}} + K_{II_{Si}})} =$$

$$-\frac{d H_2}{dt} = \frac{k_{obs.} \bullet E_0 \bullet S}{K_M + S} \qquad (1)$$

(E_0 = initial precatalyst concentration, S = free substrate concentration (S = S_0 - P); K_M = Michaelis constant ($K_M = \frac{1}{(K_{I_{Re}} + K_{I_{Si}} + K_{II_{Re}} + K_{II_{Si}})}$; for the values of $K_{i,j}$ see Ref. 7a); $k_{obs.}$ = brutto-rate constant ($k_{obs.} = \frac{(k_{2(I_{Re})} \bullet K_{I_{Re}} + k_{2(II_{Re})} \bullet K_{II_{Re}} + k_{2(I_{Si})} \bullet K_{I_{Si}} + k_{2(II_{Si})} \bullet K_{II_{Si}})}{(K_{I_{Re}} + K_{I_{Si}} + K_{II_{Re}} + K_{II_{Si}})}$)).

The $1/K_M$ value has to be considered as sum of the concentration ratios of all catalyst-substrate complexes to the product of E • S, independent whether the preequilibria are established or disturbed. The value of $k_{obs.}$ is the sum of the products of the rate constants multiplied by the mole fraction of the corresponding catalyst-substrate concentration.[7b] Since all ligands used in precatalysts are C_1-symmetrical, the formation of the respective enantiomeric hydrogenation products takes place, in principle, from two stereoisomeric substrate complexes. For the enantiomeric ratio the following relation (2) results from Eq. (1):

$$\frac{(S)}{(R)} = \frac{(k_{2(\mathrm{I}_{Re})} \bullet K_{\mathrm{I}_{Re}} + k_{2(\mathrm{II}_{Re})} \bullet K_{\mathrm{II}_{Re}})}{(k_{2(\mathrm{I}_{Si})} \bullet K_{\mathrm{I}_{Si}} + k_{2(\mathrm{II}_{Si})} \bullet K_{\mathrm{II}_{Si}})} \qquad (2)$$

Therefore, for the plot of ln (*S*/*R*) versus 1/T (Eyring-plot) a nonlinear behaviour is to be expected corresponding to the so-called „isoinversion principle" discussed in Ref. 8* and 9.

The interpretation of the hydrogenation curves for the complexes with the ligands **1c** - **1e** shows that they can be described as first-order reaction up to the 90 % turnover (Guggenheim- plot[10]). On the other hand, with catalysts Rh-**1b** and especially Rh-**1f**, a greater region than the initial part of Equation (1) can be described. For linearisation of Equation (1) the Hanes plot[11] was used. The determination of the interesting constants was accomplished by nonlinear regression with the initial values obtained by the linearisation. Results are given in Table 1.

The description as first-order reactions of the catalysts with ligands **1c** - **1e** means, provided the same kinetic model holds as for **1b** and **1f**, that the values of the Michaelis constants must be very large (or the reciprocal values must be very small). To test this conclusion, we have measured for Rh-**1c** the dependence of hydrogenation rate on the substrate concentration (Fig. 2). A gas burette as described in Ref. 12 was used to measure the high gas consumptions.

Table 1 Results of kinetic analysis of asymmetric hydrogenations of $ItMe_2$ with Rh-**1b** - Rh-**1f**

ligand	% ee (*S*)	*k* (first order) 1/sec	$1/K_M$ L/mol	$k_{obs.}$ 1/sec
1f (cyclohexyl)	25	$7.27*10^{-3}$ [a]	**35**	$\mathbf{3.12*10^{-1}}$
1b (methyl)	40	$8.17*10^{-4}$ [a]	**18**	$\mathbf{7.27*10^{-3}}$
1c (2-propyl)	70	$\mathbf{8.67*10^{-4}}$	-	-
1d (3-pentyl)	78	$\mathbf{8.50*10^{-4}}$	-	-
1e (cyclopentyl)	80	$\mathbf{1.07*10^{-3}}$	-	-

[a] Calculated according $k = \frac{k_{obs.} \bullet E_0}{K_M}$.

* Corresponding to common model concepts as indicated above, the following three reasons might cause a nonlinear temperature dependence of enantiomeric ratio in asymmetric hydrogenation: (i) disturbed pre-(inter-molecular)equilibria, (ii) intramolecular exchange processes between diastereomeric catalyst-substrate complexes, (iii) use of C_1 -symmetrical ligands.

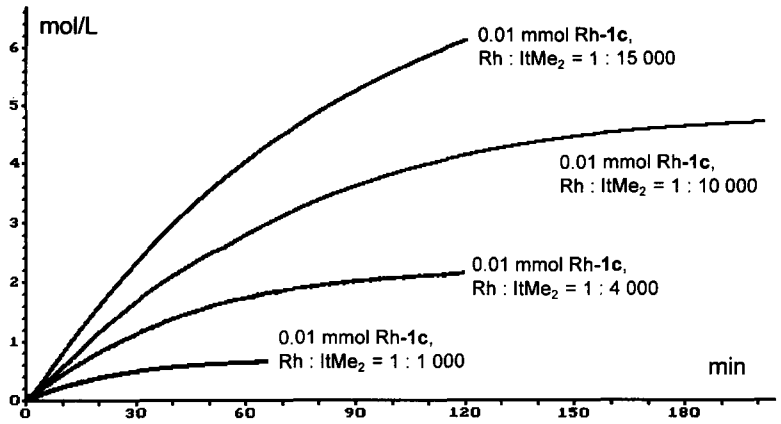


Figure 2 Variation of the $ItMe_2$ concentration for Rh-**1c**

The results show that, even at very high substrate concentrations, the concentration-independent rate of the Michaelis-Menten kinetics (saturation kinetics) will not be reached in agreement with the very small $1/K_M$ values mentioned above. For comparison with the $1/K_M$ values determined, some literature data of formation constants for other seven-ring chelate complexes of dehydroamino acids are summarized in Table 2. But it should be noticed that $1/K_M$ values are not always equal to the formation constants of the catalyst-substrate complexes, they represent, at best, the lower limits.

Comparing Tables 1 and 2, it can be seen that the $1/K_M$ values are essentially lower than the formation constants given in Table 2. Regarding the fact that the determined constants correspond to the sum of our possible substrate complexes, the conclusion can be drawn that under normal hydrogenation conditions considerable concentrations of the solvent complex are to be expected in addition to only small concentrations

Table 2 Stability constants for different 7-membered ring Rh(I) chelate complexes with dehydroamino acids

ligand	solvent	substrate	stability (L/mol)	T (K)	Ref.
DIOP	MeOH	AMe[a]	about 120	230	[4k]
DIOP	MeOH	AMe	100	298	[13]
DIOP	MeOH	BH[b]	about 90	270	[4k]
DIPHOS-4	MeOH	AMe	360	298	[13]
DIPHOS-2[c]	MeOH	AMe	5300	298	[14]

[a] AMe = methyl (*Z*)-2-acetamido-cinnamate. [b] BH = (*Z*)-2-benzamido-cinnamic acid.

[c] 5-Membered ring chelate.

of the substrate complexes. For this reason, so-called „brutto-activity comparisons" (e.g. half-lifes) of different catalysts are to be excluded or, at best, highly questionable.

From Table 1 and from the interpretation of the $1/K_M$ values for Rh-**1c** to Rh-**1e**, respectively, follows that the highest concentrations of catalyst-substrate complexes should be expected in the case of Rh-**1f**. Therefore, and owing to the finding of Brown et al.[4j,k] that the concentrations of the catalyst-substrate complex raise with lowered temperature, dynamical ^{31}P NMR measurements on the system Rh-**1f**/ItMe$_2$ were carried out. On lowering the temperature characteristical line-shape alterations were found in the $^{31}P\{^1H\}$ spectra of Rh-**1f**/ItMe$_2$ in methanol-d$_4$ solution, which can be assigned to the exchange processes specified in Scheme 3. Some selected $^{31}P\{^1H\}$ spectra recorded at different temperatures are given in Fig. 3 and 3a, respectively.

An eight-lines spectrum (AM part of an AMX system) appears above 303 K, which can be assigned to the solvate complex (**SO**) because of the coupling constant $^1J(^{103}Rh,^{31}P)$ in the range of 220 - 230 Hz.[15] For substrate complexes lower values of couplings are to be expected[3a] (see Table 3).

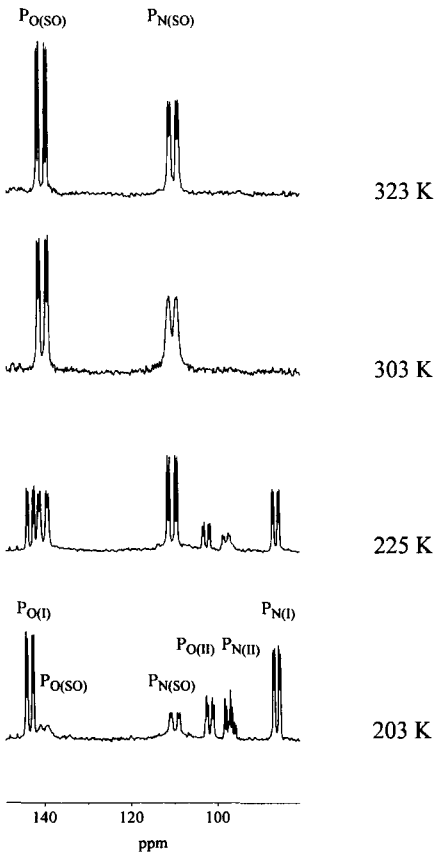


Figure 3 Experimental $^{31}P\{^1H\}$ NMR spectra of Rh-**1f**/ItMe$_2$ in methanol-d$_4$ solution.

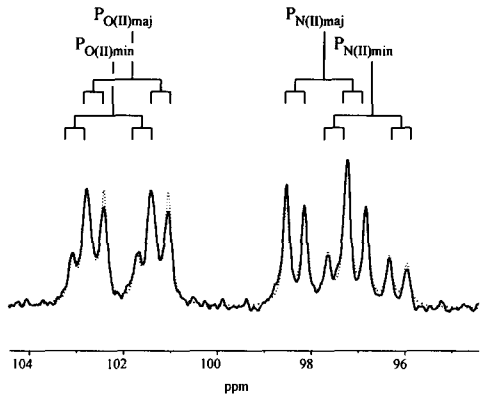


Figure 3a Experimental and calculated (dots) $^{31}P\{^{1}H\}$ NMR spectrum of Rh-**1f**/ItMe$_2$ at 203K (expanded plot of $P_{O(II)}$ and $P_{N(II)}$ signals).

On decreasing the temperature it was observed, at first, a broadening of the high-field signal (P_N) and afterwards a new splitting of the signals for P_N and P_O. In the spectrum at 225 K we find the averaged signals for P_N and P_O of the substrate complexes $\mathbf{I}_{Re}$ and $\mathbf{I}_{Si}$ as well as the corresponding averaged signals for the substrate complexes $\mathbf{II}_{Re}$ and $\mathbf{II}_{Si}$.

Further cooling below 220 K causes a new splitting of the signal multipletts at $\delta \approx 103$ and $\delta \approx 98$, respectively. Separate signals for the substrate complexes $\mathbf{II}_{Re}$ and $\mathbf{II}_{Si}$ result. For the exchange $\mathbf{I}_{Re}$ $\rightleftharpoons$ $\mathbf{I}_{Si}$ under the given conditions up to 187 K only the signals for one species were observed for both the P_O and the P_N. It must be pointed out that it is questionable, whether the signals for **I** are averaged or indicate exclusively the major product of **I**. The obtained ^{31}P NMR data and equilibrium ratios in dependence on temperature are listed in Table 3.

Table 3 ^{31}P NMR data (δ, rel. 85% H_3PO_4 ext., J/Hz [a]) and ratios (%) of the solvate complex **SO** and the substrate complexes **I** and **II** of the system Rh-**1f**/ItMe$_2$ in methanol-d_4.

	SO			**I**			**II** major[b]		**II** minor[b]		
T(K)	δP_O	δP_N	%	δP_O	δP_N	%	δP_O	δP_N	δP_O	δP_N	%
323	141.6	110.7									
303	141.4	110.7									
225	140.4	110.6	54	143.4	86.6	32	102.6	98.1	102.9	97.1	14
214	140.3	110.4	38	143.5	86.5	43	102.3	97.9	102.5	97.0	19
203	140.2	110.2	21	143.6	86.4	55	101.9	97.7	102.2	96.8	24

[a] **SO** (323 K): $^{1}J(Rh,P_O)$ = 228Hz, $^{1}J(Rh,P_N)$ = 222Hz, $^{2}J(P_O,P_N)$ = 59Hz, **I** (203K): $^{1}J(Rh,P_O)$ = 175Hz, $^{1}J(Rh,P_N)$ = 158Hz, $^{2}J(P_O,P_N)$ = 43Hz, **II** (203K): $^{1}J(Rh,P_O)$maj,min = 167Hz, $^{1}J(Rh,P_N)$maj,min = 159Hz, $^{2}J(P_O,P_N)$maj = 47Hz, $^{2}J(P_O,P_N)$min = 45Hz. [b] 225-203K maj:min = 69:31%.

The signal assignment to complexes **I** and **II** was done on the basis of the signal intensities as well as coupling constants and chemical shifts regarding the coordination of the substrate via the olefinic double bond and the β-ester carbonyl group, respectively.[3a] However, the assignment of the signals of complex **II** to $\mathbf{II}_{Re}$ and $\mathbf{II}_{Si}$, respectively, is not possible. Therefore, in Tables 3 and 4 only the major-minor notation is used. By means of the program DNMR5[16] we carried out a quantitative calculation of the exchange processes. The kinetic data are given in Table 4.

Table 4 Kinetic data of the complexation reaction **SO** + $ItMe_2$ ⇌ **I** + **II** and the major-minor complex isomerisation $\mathbf{II}_{maj}$ ⇌ $\mathbf{II}_{min}$.

	SO + $ItMe_2$ ⇌ **I** + **II**		$\mathbf{II}_{maj}$ ⇌ $\mathbf{II}_{min}$	
T (K)	$k_{1(obs.)}$[a] (s^{-1})	$k_{D(II)(obs.)}$ (s^{-1})	$k_{+D(II)}$ (s^{-1})	$k_{-D(II)}$ (s^{-1})
225	<5[b]	72	22	50
214		18	6	12
203		<5[b]		

[a] $k_{1(obs.)} = k_{1(IRe)(obs.)} + k_{1(ISi)(obs.)} + k_{1(IIRe)(obs.)} + k_{1(IISi)(obs.)}$
[b] At k <5 s^{-1} the line-shape alterations were too low to determine exactly the rate constants by CLSA.

The dynamic NMR results show that the intermolecular exchange processes **SO** + $ItMe_2$ ⇌ $\mathbf{I}_{Re}$ + $\mathbf{I}_{Si}$ and **SO** + $ItMe_2$ ⇌ $\mathbf{II}_{Re}$ + $\mathbf{II}_{Si}$, respectively, are essentially slower than the intramolecular exchange between the substrate complexes $\mathbf{II}_{Re}$ ⇌ $\mathbf{II}_{Si}$ (and also $\mathbf{I}_{Re}$ ⇌ $\mathbf{I}_{Si}$, but this process was not observable at the given temperature range). This means that the major-minor isomerisation of the diastereomeric complexes proceeds preferable by the intramolecular than by the intermolecular processes. This finding is in agreement with the results of Brown et al.[5] obtained for five-membered chelate complexes.

The $\Delta G^{\neq}$ values of the process $\mathbf{II}_{maj}$ ⇌ $\mathbf{II}_{min}$ (corresponding to isomerisation $\mathbf{II}_{Re}$ ⇌ $\mathbf{II}_{Si}$) are between 47-49 KJ mol^{-1} and they are in a range comparable with the value of 40 kJ mol^{-1} we found for another seven-membered ring chelate of rhodium(I), the *trans*-1,2-*O*-bis(diphenylphosphino)cyclohexane-1,2-diol-rhodium(I) dimethyl itaconate.[1b **]

This is a further example for the energy barrier of the intramolecular isomerisation to be, obviously, considerably lower in the case of seven-membered chelate complexes with ligands of low basicity compared to the five-membered bis(phosphine) chelates (ca. 80 kJ mol^{-1} for $[Rh(DIPAMP)(BMe)]^+$ [18 ***]). But in contrast

** The possibility that the intramolecular conversion between the diastereomeric substrate complexes could proceed via intermediates was currently investigated by ab-initio methods.[17]
*** BMe = methyl (*Z*)-2-benzamido-cinnamate

to the above mentioned bisphosphinite complex with a C_2-symmetrical ligand causing, therefore, only two possible substrate complexes (major and minor), in case of the C_1-symmetrical aminophosphine phosphinite rhodium chelates (Rh-**1**) studied here four different substrate complexes are to be expected, $\mathbf{I}_{Re}$, $\mathbf{I}_{Si}$, $\mathbf{II}_{Re}$, $\mathbf{II}_{Si}$ corresponding to Scheme 3. The signals of three of them could be observed under the experimental conditions given in the present case, the major and minor products of **II** ($\mathbf{II}_{Re}$ and $\mathbf{II}_{Si}$) and the signals of **I**.

Experimental

Preparation of the itaconate complex: An orange suspension of the [Rh(**1f**)(COD)]BF_4 complex (0.05 mmol) in 0.8 ml degassed CD_3OD was stirred under hydrogen for 1 h. After replacing of hydrogen by argon the yellow-brown solution of solvent complex was filtered to 0.25 mmol of the dimethyl itaconate in a 5 ml NMR tube, which was then sealed under vacuum.

Hydrogenations: Hydrogen (AGA 6.0) was used as received. All experiments were performed under isobaric conditions using an automatic gas-measuring apparatus. For set-up and performance of hydrogenation experiments see Ref. 2. Experiments were carried out at 25.0°C and normal pressure. Atmospheric pressure was taken as reference and corrected to 1.0 atm in the evaluation.

The temperature dependent ^{31}P NMR spectra were recorded with a BRUKER ARX-300 spectrometer (121.5 MHz). The temperature was controlled using ethanediol and methanol, respectively.

Acknowledgement

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7. (a) The complete equation for $K_{I_{Re}}$ is (as example):

$$K_{I_{Re}} = \frac{\left[k_{1(I_{Re})} \bullet (k_{2(I_{Si})} + k_{-1(I_{Si})} + k_{-D(I)}) + (k_{-D(I)} \bullet k_{1(I_{Si})})\right]}{\left[(k_{2(I_{Re})} + k_{-1(I_{Re})} + k_{D(I)}) \bullet (k_{2(I_{Si})} + k_{-1(I_{Si})} + k_{-D(I)}) - (k_{-D(I)} \bullet k_{D(I)})\right]} = \frac{[I_{Re}]}{[E] \bullet [S]}$$

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