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Rhodium-Complex-Catalyzed Asymmetric Hydrogenation: Transformation of Precatalysts into Active Species

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Abstract: The use of diolefin-containing rhodium precatalysts leads to induction periods in asymmetric hydrogenation of prochiral olefins. Consequently, the reaction rate increases in the beginning. The induction period is caused by the fact that some of the catalyst is blocked by the diolefin and thus not available for hydrogenation of the prochiral olefin. Therefore, the maximum reaction rate cannot be reached initially. Due to the relatively slow hydrogenation of cyclooctadiene (cod) the share of active catalysts increases at first, and this leads to typical induction periods. The aim of this work is to quantify the hydrogenation of the diolefins cyclooctadiene (cod) and norborna-2,5-diene (nbd) for cationic complexes of the type [Rh(ligand)(diolefin)]BF_4 for the ligands Binap (1,1′-binaphthalene-2,2′-diylbis(phenylphosphine)), Me-Duphos (1,2-bis(2,5-dimethylphospholano)benzene, and Catasium in the solvents methanol, THF, and propylene carbonate. Furthermore, an approach is presented to determine the desired rate constant and the resulting respective pre-hydrogenation time from stoichiometric hydrogenations of the diolefin complexes via UV/Vis spectroscopy. This method is especially useful for very slow diolefin hydrogenations (e.g., cod hydrogenation with the ligands Me-Duphos, Et-Duphos (1,2-bis(2,5-diethylphospholano)benzene), and dppe (1,2-bis(diphenylphosphino)ethane).

Keywords: asymmetric catalysis · hydrogenation · kinetics · rhodium · UV/Vis spectroscopy

Introduction

Asymmetric hydrogenations with cationic Rh complexes are often performed with commercially available precatalysts of the type [Rh(PP*)(diolefin)]anion (PP* = chelating chiral phosphine). The conventional "in situ" technique transforms [Rh(diolefin)$_2$]anion complexes into complexes of the above-mentioned type by adding one equivalent of chiral ligand under inert-gas conditions.[1]

Macroscopically, the hydrogenation curves show more or less pronounced characteristic induction periods that depend on diolefin, chiral ligand, and prochiral olefin (Michaelis constant and concentration),[2] that is, hydrogenation becomes faster in the beginning. The diolefin (*Z*,*Z*)-cycloocta-1,5-diene (cod) introduced with the Rh precatalyst is to some extent detectable after complete asymmetric hydrogenation of the prochiral olefin.

Simple experiments such as the monitoring of cod conversion in comparison to the conversion of prochiral olefin, hydrogenation of the precatalyst before the addition of substrate, and use of diolefin-free precatalysts show that induction periods in the hydrogen consumption of asymmetric hydrogenations are the result of simultaneous hydrogenation of the prochiral olefin and the diolefin introduced with the precatalyst, which is useful for increasing the stability in synthesis and for handling the precatalyst without difficulties.

This has unequivocally been proven by means of ^{31}P NMR spectroscopic measurements under hydrogenating conditions.[2c,3] Thus, the induction period is caused by the fact that part of the catalyst concentration is blocked for hydrogenation of the prochiral olefin, that is, inactive due to

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coordination of the diolefin ligand. Due to the relatively slow hydrogenation of cod, the fraction of active catalysts increases at first, and typical induction periods result. They complicate comparisons of activity of different catalysts systems, as well as kinetic interpretations of hydrogen-consumption curves.

To exclude such distracting induction periods and also to take advantage of the "intrinsic activity" of a catalyst, that is, the maximum possible catalytic activity for a given catalyst–substrate system, it is best to apply the respective solvate complexes [Rh(PP*)(solvent)$_2$]anion, as was proven earlier by Halpern and Landis.[4] Nevertheless, from a practical standpoint the question remains of how long the precatalysts must be pretreated under hydrogen to exclude any induction period.

As an example, Figure 1 shows the hydrogenation of methyl (*Z*)-(*N*)-benzoylamino cinnamate with the established Rh/Dipamp catalyst in MeOH at 25 °C under normal pressure with the solvate complex [Rh(dipamp)(MeOH)$_2$]BF$_4$ (Dipamp = 1,2-ethanediylbis[(2-methoxyphenyl)phenylphosphine]) and the commercially available [Rh(dipamp)(cod)]BF$_4$. Both catalysts give practically the same enantioselectivity of 96 % *ee*, but they differ considerably in their activity. After complete hydrogenation of a hundredfold excess of prochiral olefin with the cod complex, approximately 66 % of cod is still detectable by gas chromatography.[5] Further similar examples can be found.[2c,6]

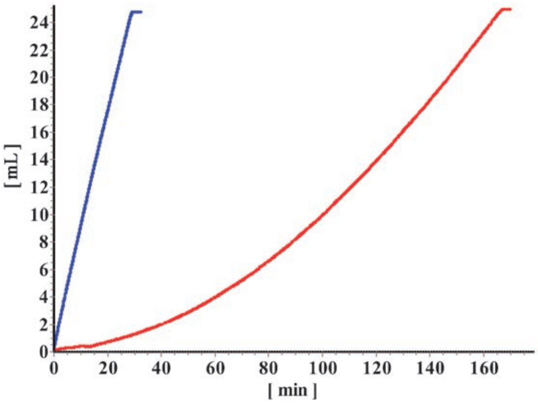


Figure 1. Comparison of the hydrogen consumption for the hydrogenation of methyl (*Z*)-*N*-benzoylamino cinnamate with the solvate complex (blue) and the cod precatalyst (red) of dipamp. (Both 0.01 mmol Rh complex; 1.0 mmol prochiral olefin; 15.0 mL MeOH; 25.0 °C; 1.0 bar.)

Hitherto published pseudo rate constants of diolefin hydrogenations (see ref. [2a] for a tabular summary) show that they can strongly depend on diolefin and ligand (ring size). As a consequence, it is not possible to generally predict prehydrogenation times of a precatalyst.[7] It is therefore necessary to experimentally determine the pretreatment time under hydrogen to complete elimination of the diolefin.

The aim of this work is to quantify the hydrogenation of diolefins cod and nbd for the ligands Binap,[8] Me-Duphos,[9] and Catasium[10] in different solvents. Beside the classical solvent methanol (protic, polar) also THF (aprotic, polar) and propylene carbonate (aprotic, dipolar), which has recently been successfully applied in asymmetric hydrogenations,[11] were investigated as solvents.

Furthermore, an approach is presented to determine the desired rate constant and the respective prehydrogenation time from stoichiometric hydrogenations by UV/Vis spectroscopy. This method is especially useful for very slow diolefin hydrogenations.

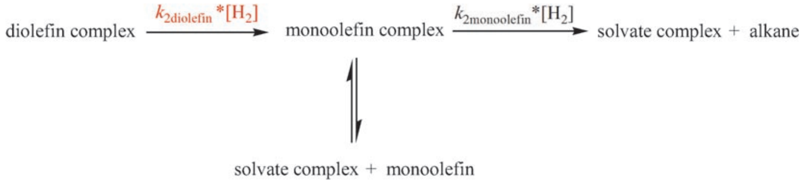
Results and Discussion

To compare several precatalysts in terms of the expected induction period and the time needed for quantitative elimination of the diolefin, pseudo rate constants $k'_{2\,\text{diolefin}}$[12] for diolefin hydrogenation were determined according to Scheme 1.

Under catalytic conditions in the presence of a very large excess of diolefin under isobaric conditions, saturation kinetics (Michaelis–Menten behavior) for the highly selective hydrogenation of the first double bond are expected due to the high stability of the diolefin complexes. This expectation could be confirmed experimentally.[2] Dividing the slope of the linear hydrogen-consumption curves (see also Figures 2 and 3) by the applied catalyst concentration results in the desired pseudo rate constants $k'_{2\,\text{diolefin}}$.[14]

Under stoichiometric conditions Scheme 1 corresponds in principle to a consecutive reaction. As method of choice for the quantitative monitoring of stoichiometric diolefin hydrogenations that are not too fast, ^{31}P NMR spectroscopy can be used.[2b]

For routine quantification of pseudo rate constants of diolefin hydrogenation, however, determination from catalytic hydrogenations of the respective diolefins with the corresponding diolefin complexes has proven to be a valuable tool. By using this methodology the values summarized in Table 1 for the investigated catalyst/solvent/diolefin systems of this work were obtained. Hydrogen-consumption curves for catalytic hydrogenation of cod and nbd at a diolefin/precatalyst ratio of 100 are shown in Figures 2 and 3, respectively.



Scheme 1. Reaction sequence for the hydrogenation of diolefin complexes to the corresponding solvate complexes and the alkanes.[13]

Table 1. Pseudo rate constants $k'_{2\,\text{diolefin}}$ [min^{-1}] from catalytic diolefin hydrogenations for several ligands and solvents.[15]

Ligand	Diolefin	Solvent		
		MeOH	THF	propylene carbonate
Me-Duphos	cod	0.115	0.16	0.14
	nbd	35.2	39.0	18.0
Binap	cod	0.23	0.28	0.14
	nbd	26.8	20.5	16.6
Catasium	cod	0.05	ca. 0.15	0.085
	nbd	24.9	11.8	9.4

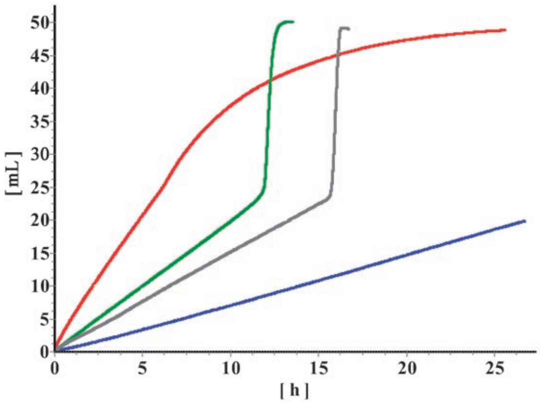


Figure 2. Hydrogen consumption for the catalytic hydrogenation of cod with the complexes [Rh(Binap)(cod)]BF_4 in THF (red), [Rh(Me-Duphos)(cod)]BF_4 in propylene carbonate (green), [Rh(Me-DuPhos)-(cod)]BF_4 in MeOH (gray), and [Rh(Catasium)(cod)]BF_4 in MeOH (blue). (All 0.01 mmol precatalyst; 1.0 mmol cod; 15.0 mL solvent; 25.0 °C; 1.0 bar.)

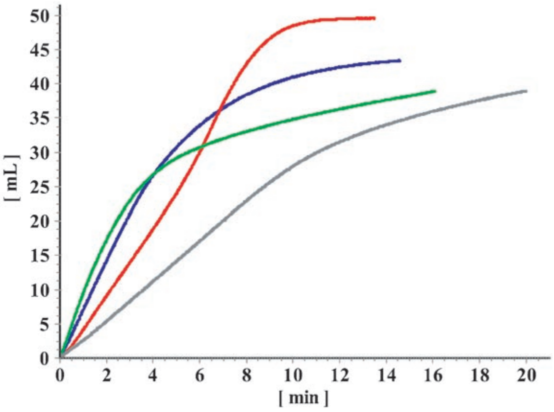


Figure 3. Hydrogen consumption for the catalytic hydrogenation of NBD with the complexes [Rh(Me-DuPhos)(nbd)]BF_4 in MeOH (blue) [Rh-(Binap)(nbd)]BF_4 in MeOH (green), [Rh(Binap)(nbd)]BF_4 in THF (red), [Rh(Catasium)(nbd)]BF_4 in propylene carbonate (gray). (All 0.01 mmol precatalyst; 1.0 mmol nbd; 15.0 mL solvent; 25.0 °C; 1.0 bar.)

The results can be summarized as follows:

1) As can be gathered from Figures 2 and 3, hydrogenations of both cod and nbd proceed very selectively, and in most cases distinct inflection points can be observed at half of the overall hydrogen uptake.[16]
2) For a given precatalyst/solvent system cod hydrogenation is always slower than nbd hydrogenation. This corresponds to published results, which, however, had practically only been obtained for MeOH.[2a] The ratios of rates lie between 75 and 450 for the investigated systems; the difference in pseudo rate constants is thus about two orders of magnitude. This experimental result is evidently independent of the solvent used.[17]
3) Table 1 shows that pseudo rate constants for a ligand/diolefin system maximally differ by a factor of about two or three, depending on the investigated solvents. It seems that the activity of diolefin hydrogenation is only slightly dependent on the polarity of the solvent and approximately independent of whether the solvent is protic or aprotic.
4) From some hydrogen-consumption curves in Figures 2 and 3, one can see that the second double bond is hydrogenated much faster than the first. A typical example is hydrogenation with the Me-Duphos/cod system, both in MeOH and in propylene carbonate. This known fact[2] must be interpreted as follows. Even though hydrogenation of the monoolefin is faster than the hydrogenation of the first double bond of the diolefin, due to the much higher stability constant of the diolefin (chelate effect) the hydrogenation of the monoolefin only occurs when practically no more diolefin is present in solution. The intrinsically higher activity of the monoolefin is virtually "blocked" by the thermodynamically much higher stability of the diolefin complex.

The cause of the known fact that cod hydrogenations are always slower than the corresponding nbd hydrogenations remains unclear. However, it seems that, independent of the ring size of the Rh/phosphane chelate, the less active cod complexes have a greater tetrahedral distortion of the expected square-planar arrangement than the corresponding nbd complexes, as derived from X-ray structures.[18,19]

Table 2 summarizes structural data (angle of tetrahedral distortion, that is, angle of the P-Rh-P plane to the centroid-Rh-centroid plane) and ratios of pseudo rate constants for the hydrogenation of cod and nbd.

Comparison of tetrahedral distortions of the complexes [Rh(Me-Duphos)(cod)]BF_4/[Rh(Me-Duphos)(cod)]SbF_6 and [Rh(Binap)(nbd)]BF_4/[Rh(Binap)(nbd)]ClO_4 clearly demonstrates that the tetrahedral distortion is hardly influenced by the counterion.

In case of Me-Duphos and Catasium it appears as expected that the nbd complex, which can be hydrogenated faster, deviates less from the ideal square-planar structure.

In contrast, the Binap complex is the first example in which the cod complexes are hydrogenated more than a hundred times slower but at the same time show much smaller tetrahedral distortion, independent of the solvent used. For the nbd complex an experimental torsion angle of about 14° is observed, while for the cod complex a torsion

Table 2. Angles between P-Rh-P and centroid-Rh-centroid planes (tetrahedral distortion) from X-ray crystal structures, and ratios of pseudo rate constants for diolefin hydrogenation.

	P-Rh-P/C_M-Rh-C_M angle [°]	$k'_{2\,NBD}/k'_{2\,COD}$		
		MeOH	THF	propylene carbonate
[Rh(Me-Duphos)(cod)]BF_4[18]	16.4	306	240	130
[Rh(Me-Duphos)(cod)]SbF_6[9c]	17.8			
[Rh(Me-Duphos)(nbd)]BF_4[20]	8.8			
[Rh(Catasium)(cod)]BF_4[10b]	25.4	469	ca. 79	111
[Rh(Catasium)(nbd)]BF_4[21]	8.8			
[Rh(Binap)(cod)]BF_4[22]	7.5	117	74	116
[Rh(Binap)(nbd)]ClO_4[8a,23]	14.9			
[Rh(Binap)(nbd)]BF_4[22]	13.2			

angle of only 7° is found.[24] The reasons for this unusual behavior are unclear.

The stoichiometric hydrogenation of diolefin complexes to solvate complexes basically corresponds to a consecutive reaction (see Scheme 1). A monoolefin complex, which could be expected as an intermediate, cannot be detected by ^{31}P NMR spectroscopy. After partial hydrogenation of the diolefin, only the solvate complex is visible in the ^{31}P NMR spectrum beside diolefin complex (see also Figure 4). Thus, the concentration of an intermediate monoolefin complex can only be very small.[25]

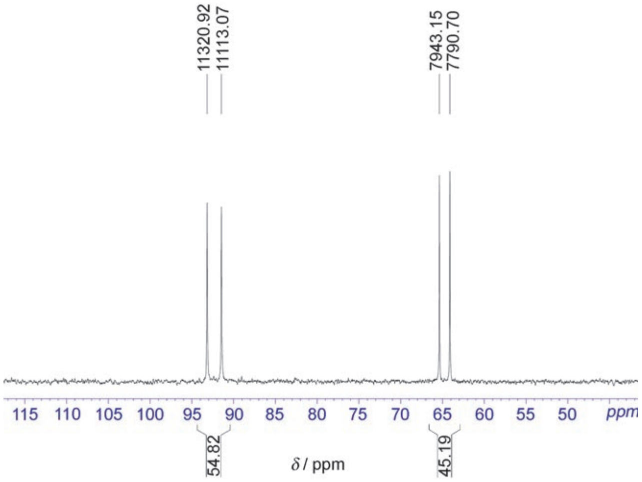


Figure 4. ^{31}P NMR spectrum of a solution of [Rh(Catasium)(cod)]BF_4 in propylene carbonate (not deuterated), partly hydrogenated (8.5 min).

The known high stability of the diolefin complexes and the finding that monoolefin hydrogenation is partly faster than diolefin hydrogenation (Figure 2) mean that diolefin hydrogenation to yield the saturated alkane under isobaric conditions can be reduced to a pseudo-first-order reaction. (A kinetic derivation can be found in the Supporting Information.)[26] Therefore the necessary prehydrogenation times for the formation of solvate complexes can be derived from the pseudo rate constants in Table 1.[27] For verification, some precatalysts were pretreated with hydrogen for a distinct period of time at normal pressure, after which the hydrogenation reactions were quenched and the solutions analyzed by ^{31}P NMR spectroscopy. The results (Table 3) prove that the pseudo rate constants calculated from Table 1 can be experimentally confirmed.

If pseudo rate constants of diolefin hydrogenation become very small, determination under catalytic conditions at normal pressure becomes more and more complicated due to rather long reaction times. Under pressure (the reaction order for hydrogen is unity), hydrogenation can be accelerated, but the quantitative measurement of relatively small hydrogen consumptions is difficult under such conditions.

Therefore, we sought further possibilities to determine the desired pseudo rate constants. A possibility to monitor stoichiometric hydrogenation is offered by UV/Vis spectroscopy. This methodology is presented for the example of cod hydrogenation by the Me-Duphos system, as well as for the dppe and Et-Duphos ligands.

As derived and experimentally confirmed, the consecutive reaction that is expected for the stoichiometric hydrogenation of a diolefin precatalyst can be reduced to a first-order reaction.[25,26] Furthermore, in the case of the Me-Duphos/cod/MeOH system $k'_{2\,\mathrm{diolefin}} \ll k'_{2\,\mathrm{monoolefin}}$ (see Figure 2).

By means of an immersion optrode, UV/Vis spectroscopy can be carried out in vessels of arbitrary dimensions. In our temperature-controlled vessel[28] the necessary exchange of gas (argon/hydrogen) is easily realized. Figure 5 shows the cyclically measured spectra for the hydrogenation of

Table 3. Half-lives $t_{1/2}$, experimental prehydrogenation times, ratio solvate complex/diolefin complex (expected and experimental from ^{31}P NMR spectrum), and coupling constants and chemical shifts of solvate and diolefin complexes.

System (ligand/diolefin/solvent)	$t_{1/2}$ (min)	Prehydrogenation time [min]	Solvate/diolefin complex (expected)	Solvate/diolefin complex (exptl)	δ [ppm], $J_{Rh\text{-}P}$ [Hz] (solvate complex/diolefin complex)
Me-Duphos/cod/MeOH	6.0	6.0	50/50	46.3/53.7	101, 204.5/76.4, 149
Me-Duphos/cod/MeOH	6.0	12.0	75/25	73.7/26.3	101, 204.5/76.4, 149
Catasium/cod/propylene carbonate	8.1	8.5	51.4/48.6	54.8/45.2[a]	92.3, 207.8/64.7, 152.9

[a] The spectrum is shown in Figure 4.

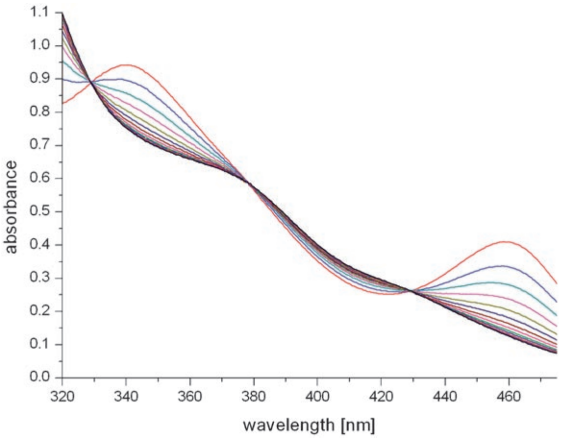


Figure 5. Reaction spectrum for the stoichiometric hydrogenation of [Rh(Me-Duphos)(cod)]BF_4 (0.02 mmol) in 40.0 mL MeOH at 25.0 °C and 1.0 bar overall pressure with a cycle time of 3 min.

[Rh(Me-Duphos)(cod)]BF_4 under stoichiometric conditions in MeOH at 25.0 °C.

The spectrum displays three isosbestic points in the shown range. They prove that only two (absorbing) species are present in solution: the cod complex and the formed solvate complex. Thus, it is a kinetically uniform reaction. A consecutive reaction with a detectable intermediate concentration could not be described in the same way.

Figure 6 shows the respective extinction diagrams for the reaction spectrum of Figure 5.[29] As expected for kinetically uniform reactions, straight lines result for the plot of arbitrary wavelengths.

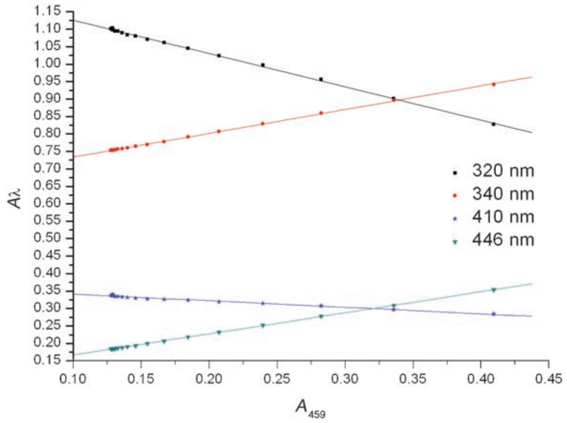


Figure 6. Extinction diagram with respect to Figure 5. 459 nm (maximum [Rh(Me-Duphos)(cod)]BF_4) as reference wavelength.

A plot of $(dA/dt)/A$ as linearization of a first-order reaction[28] shows the expected straight lines (the derivation of the linear equation can be found in the Supporting Information) with the desired pseudo rate constant (k'_{2COD}) as slope (Figure 7).

With the initial values from Figure 7 a nonlinear curve fit for the chosen wavelengths was processed for the pseudo-first-order reaction; a comparison of spectroscopic and fitted values is shown in Figure 8. These values (the average value for five different wavelength is 0.1177 min^{-1}) agree well with the result of the catalytic hydrogenation (Table 1; Me-Duphos/cod in MeOH: $k'_{2COD} = 0.115\ min^{-1}$).

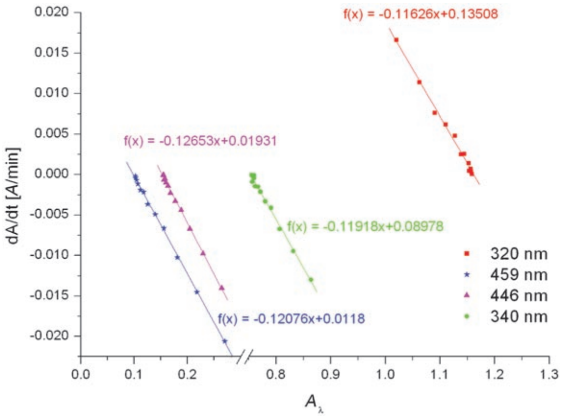


Figure 7. Linearization of a first-order reaction $(dA/dt)/A$ for several wavelengths from Figure 5.

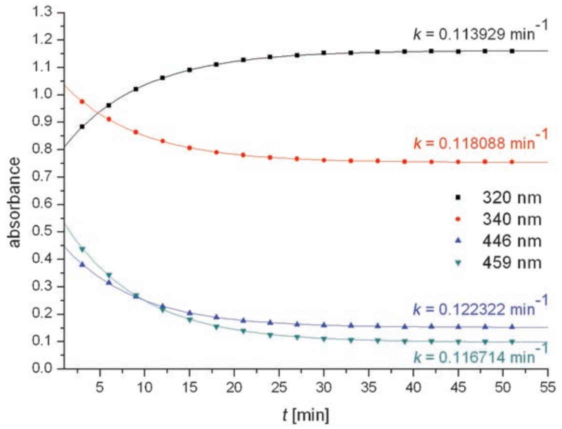


Figure 8. Comparison of spectroscopic values (points) and values fitted as pseudo-first-order (solid line) for several wavelengths from Figure 5.

Analogously, stoichiometric hydrogenation of cod complexes of Et-Duphos and dppe were investigated by UV/Vis spectroscopy. (The respective reaction spectra, extinction diagrams, linearizations, and nonlinear curve fits can be found in the Supporting Information.)

In the case of Et-Duphos a pseudo constant of 0.028 min^{-1} was observed. Even though this value is twice as high as the orienting value that was given in the literature,[2c] difficulties with the determination from catalytic measurements under normal pressure were indicated.

It is astonishing that the pseudo constants k'_{nbd}/k'_{cod} for Me-Duphos differ by only two orders of magnitude, while for Et-Duphos the difference is already three orders of magnitude.

For the ligand dppe one obtains a pseudo constant of 0.0033 min^{-1}. This value is exactly in the range (0.0018–0.0036) estimated from catalytic hydrogenations in an autoclave.[2c,30] The last examples prove that the UV/Vis spectroscopy is well suited to determine the desired pseudo rate constants for very slow diolefin hydrogenations.

Conclusion

The present study corroborates that induction periods observed for asymmetric hydrogenations of prochiral diolefins are caused by the fact that part of the catalyst concentration is blocked, that is, inactive due to coordination by the diolefin ligand. This blocking has its origin in the slow and simultaneously occurring hydrogenation of the diolefin introduced into the system with the precatalyst.

Quantification of the hydrogenation of the diolefins cod and nbd in the solvents methanol, THF, and propylene carbonate, which vary in proticity and polarity showed that the different solvents behave similarly with regard to the activity of diolefin hydrogenation. Independent of the solvent, the nbd complexes are always hydrogenated faster than the corresponding cod complexes; the hydrogenations proceed very selectively. The degree of conversion determined from pseudo rate constants as a function of prehydrogenation time was tested and verified by means of ^{31}P NMR spectroscopy for several examples.

For very slow diolefin hydrogenations UV/Vis spectroscopic monitoring of the stoichiometric hydrogenation is an appropriate method to determine the desired pseudo rate constants.

Experimental Section

All ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker 300 MHz spectrometer in [D$_4$]MeOH unless stated otherwise.

UV/Vis spectra were recorded by a Lambda 19; see also ref. [28].

Performance of hydrogenation reactions including the normal-pressure hydrogen device is extensively described in ref. [28].

Solvents were dried and purified by standard methods and distilled freshly prior to use.

Acknowledgements

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[12] Due to isobaric conditions the determined pseudo rate constants still contain the hydrogen concentration in solution, which is proportional to the overall pressure above the solution under consideration of the solvent vapor pressure; $k'_{2\,\mathrm{diolefin}} = \mathrm{k}^{*}_{2\,\mathrm{diolefin}}[\mathrm{H}_2]$.

[13] Because of the highly stable diolefin complexes, the corresponding equilibrium with the free diolefin and the solvate complex can be neglected.

[14] An extended derivation of the underlying equations can be found in refs. [2c,e].

[15] Each rate constant is the result of at least three measurements; reproducibility for several charges of precatalyst, solvent, and diolefin is approximately ±5–8 %.

[16] Of the investigated systems, only [Rh(Binap)(nbd)]BF$_4$ in propylene carbonate is an exception; the hydrogenation of the second double bond proceeds with approximately the same rate as the hydrogenation of the first. In the case of [Rh(Me-Duphos)(nbd)]BF$_4$ and [Rh(Catasium)(nbd)]BF$_4$ hydrogenation of the first double bond is linear up to a conversion of about 70 and 40 %, respectively.

[17] An interesting possibility to estimate how miscellaneous diolefins differ in their hydrogenation activity—and hence are more or less disturbing to asymmetric hydrogenation in the form of induction periods—has been proposed by McCague et al.: C. J. Cobley, I. C. Lennon, R. McCague, J. A. Ramsden, A. Zanotti-Gerosa, *Tetrahedron Lett.* **2001**, *42*, 7481–7483. The respective diolefin complexes are mixed in a ratio of 1:1, but the two complexes contain the selection-inducing ligand in opposite chirality. The higher the *ee* value of the corresponding hydrogenations the more the diolefins differ in their hydrogenation activity.

[18] H.-J. Drexler, S. Zhang, A. Sun, A. Spannenberg, A. Arrietta, A. Preetz, D. Heller, *Tetrahedron: Asymmetry* **2004**, *15*, 2139–2150. Obviously, the tetrahedral distortion in the observed structures represents an optimum between mutual steric evasion of the ligands and binding of these ligands to the central atom. The nbd complex must rotate less to achieve a similar steric relief than the cod complex. Thus, the tetrahedral distortion for nbd complexes should always be smaller than for the appropriate cod complexes.

[19] Kyba and Davis et al. developed the idea that "The forces which cause this nonideal diene orientation, be they steric or electronic, presumably would be those which would lead to enantioface differentiation in a prochiral olefin." E. P. Kyba, R. E. Davis, P. N. Juri, K. R. Shirley, *Inorg. Chem.* **1981**, *20*, 3616–3623.

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[24] In ref. [18] two examples of five-membered chelate rings are given in which the cod and the nbd complex practically have the same tetrahedral distortion.

[25] The addition of cyclooctene (coe) to the MeOH complex of Me-Duphos gives new signals in the range of 3% even at an excess of 150% of coe in comparison to Rh. Thus, it can be estimated that the equilibrium between cyclooctene and solvate complex (Scheme 1) surprisingly lies on the side of the solvate complex; the cyclooctene complex expected as an intermediate is apparently rather unstable.

[26] If the intermediate concentration of a simple stoichiometric consecutive reaction is sufficiently small, it switches to a first-order reaction. The intermediate concentration is very small if $k_2 \gg k_1$ and/or—as in the present case—if the intermediate concentration is decreased by an established equilibrium which does not lie on the side of the intermediate.

[27] For a first-order reaction the sevenfold half-life time corresponds to 99.2% conversion.

[28] H.-J. Drexler, A. Preetz, T. Schmidt, D. Heller, "Kinetics of Homogeneous Hydrogenation: Measurement and Interpretation" in *Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. Elsevier), Wiley-VCH, **2007**, Chap. 10, pp. 257–293.

[29] H. Mauser, *"Formale Kinetik"*, Bertelsmann Universitätsverlag, **1974**.

[30] This pseudo constant is so small that a catalytic hydrogenation of a hundredfold excess of cod with 0.01 mmol catalyst under normal pressure (cf. Figure 2) would take approximately 500 h.

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