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Part III. COD versus NBD precatalysts. Dramatic difference in the asymmetric hydrogenation of prochiral olefins with five-membered diphosphine Rh-hydrogenation catalysts☆

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

Induction periods in the asymmetric hydrogenation of prochiral olefins with five-membered chelates of the type $[Rh(PP)(diolefin)]BF_4$ originate from the parallel-running hydrogenation of the prochiral substrate and the diolefin that enters the system as a constituent of the precatalyst. Reactivities towards the most commonly used diolefins COD or NBD can differ by three powers of ten. X-ray crystal structure analyses of $[Rh((S,S)$-Et-DuPHOS)(NBD)]BF_4 and of $[Rh((R,R)$-Et-DuPHOS)(COD)]BF_4 imply that a recently discussed relation between the sense of rotation of the diolefin in the precatalyst (*clockwise* or *anticlockwise twist*) is not very likely.

Complexes of rhodium, ruthenium, and more recently of iridium, have been successfully employed for the catalytic asymmetric hydrogenation of prochiral substrates [1]. The use of these complexes is in no way limited to academia, as is powerfully demonstrated by the large scale preparation of the grass herbicide 'Metolachlor', where hydrogenation catalysed by an iridium complex forms the key synthetic step [2]. Catalyst precursors are usually employed in organometallic chemistry since it is seldom possible to add the actual active species of a catalytic cycle directly into the reaction. These precursors normally contain stabilising ligands, such as COD ((*Z*,*Z*)-cycloocta-1,5-diene), which allow the complexes to be easily handled. The precatalyst is usually formed in situ, for example through the reaction of a chiral bisphosphine with $[Rh(COD)_2]BF_4$. In about half of the asymmetric hydrogenations of the model substrate (*Z*)-*N*-acetylaminocinnamic acid reported, the catalyst was formed in situ, according to Brunner et al. [1d].

In the literature it was generally accepted that the well known hydrogenation of the diolefins COD or NBD (norborna-2,5-diene) with cationic rhodium(I) complexes [3] takes place before the more interesting asymmetric hydrogenation of the prochiral olefin. However, quantitative investigations of diolefin hydrogenation with seven-membered chelate complexes of the type $[Rh(PP)(diolefin)]BF_4$ (PP is a chelating bisphosphine) [4] showed that the hydrogenation of the diolefins usually employed (i.e. COD) took considerably longer than generally presumed. In Fig. 1 the hydrogen uptake and the COD conversion (determined by gas chromatography, in parallel experiments) are plotted as a function of time for various catalyst systems [5]. The investigations confirm that the hydrogenation of the prochiral olefin takes place parallel to that of the diolefin. In particular, when DIOP (2,3-*O*-isopropyliden-2,3-dihydroxy-1,4-bis(diphenylphosphino)butan) is used as the ligand, it was shown that COD is still present in the solution under normal reaction condi-

☆ Part II: Kinetic investigations of the hydrogenation of diolefin ligands in catalyst precursors for the asymmetric reduction of prochiral olefins [4b].

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tions, after the hydrogenation of the prochiral olefin is complete (precatalyst:substrate 1:100). According to NMR investigations under stationary conditions this COD quantity remains unchanged as precatalyst [6].

The parallel hydrogenation of the diolefin and the prochiral olefin leads to a time dependent 'blocking' of part of the catalyst. The rate of the asymmetric hydrogenation increases as more catalyst becomes available due to the advancing hydrogenation of the diolefin. This results in a typical induction period [7], which is clearly visible as a maximum in the rate profile (see Fig. 4). The induction period itself depends on many factors, which are discussed at length in Ref. [4a]. As well as the relationship between the hydrogenation rates for the diolefin and the prochiral olefin, the relationship between the stability constants of the corresponding substrate complexes is also of considerable importance, with the latter being largely determined by the solvent.

This induction period, which has been mentioned qualitatively by other authors [8], prevents a kinetic evaluation of the hydrogenation [9] and is also reputedly the cause of non-linear effects [10].

Five-membered rhodium chelates induce a high enantioselectivity in asymmetric hydrogenations due to their conformationally rigid ligand backbone. Although the low activity of these five-ring chelates is a disadvantage, this can be compensated for by raising the pressure of hydrogen used during the hydrogenation. In addition, due to this lower activity of the five-membered chelate complexes, the diolefins should be reduced before the prochiral olefin and thus an induction period does not play a role [1b].

Recently the mechanism of the hydrogenation of NBD with $[Rh(NBD)(PPh_3)_2]BF_4$ in CH_2Cl_2 has been investigated extensively [11]. The rate constants for the hydrogenation of the diolefins COD and NBD with the five-membered rhodium complexes have not been described previously in the literature; first results are presented in this paper.

The difficulties described in the literature concerning the hydrogenation of COD from the [Rh(DIPAMP)-(COD)]BF_4 complex (DIPAMP: 1,2-bis-(*o*-methoxyphenyl-phenyl-phosphino)ethane) in MeOH [12], are confirmed by corresponding in situ NMR investigations under stationary conditions [6]. Induction periods also pose a problem for the five-membered chelates of Rh(I).

In the case of the hydrogenation of (*Z*)-*N*-acetylaminocinnamic acid with the COD precatalyst, which contains the NORPHOS ligand (bis-(diphenylphosphino)-bicyclo[2,2,1]hept-5-ene) [13], gas chromatographic analysis proves that 22% COD remains after *two* consecutive hydrogenations, each of which was conducted in the presence of a hundred-fold excess of the prochiral olefin (Fig. 2). Thus the COD contained in the precatalyst is not fully hydrogenated after 205 min.

Analogous induction periods are seen with other rhodium catalysts which have typical five-membered chelating ligands, such as CHIRAPHOS (2,3-bis-(diphenylphosphino)butane) [14] or PROPHOS (1,2-bis(diphenylphosphino)propane) [14b,15] (Fig. 3).

In the case of the hydrogenation of a hundred-fold excess of methyl *N*-acetylaminoacrylate with the [Rh-(PROPHOS)(COD)]BF_4 complex, the solution still contains over 80% COD! Appropriate induction periods

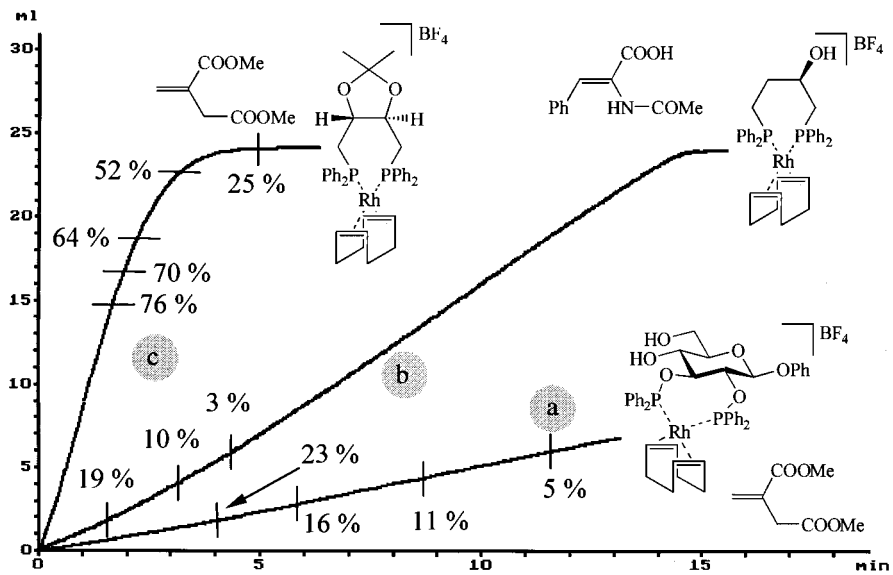


Fig. 1. Hydrogenation curves as well as the proportion of non-hydrogenated COD present in the precatalyst, COD in %. (a) [Rh(Ph-β-glup-OH)(COD)]BF_4/dimethyl itaconate; 78% ee (*R*) (Ph-β-glup-OH = phenyl-2,3-bis-(*O*-diphenylphosphino)-β-D-glycopyranosid). (b) [Rh((*R*)-2-MHOP)(COD)]BF_4/(*Z*)-methyl-*N*-acetylaminocinnamate; 41% ee (*R*) (2-MHOP = 1,4-bis(diphenylphosphino)-2-hydroxy-butane). (c) [Rh((*R*,*R*)-DIOP)(COD)]BF_4/dimethyl itaconate; 30% ee (*S*)). (a) 0.02 mmol precatalyst, otherwise standard conditions, see Section 1).

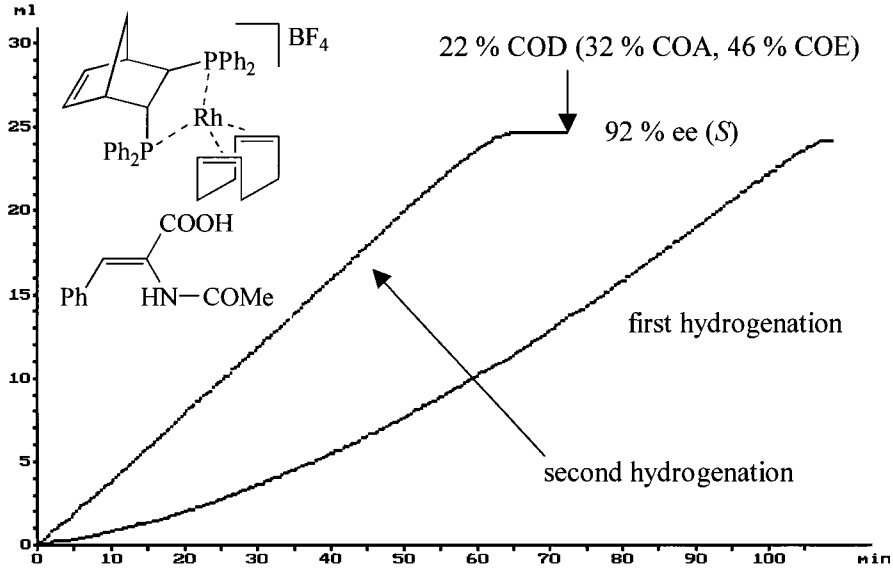


Fig. 2. Hydrogenation of (*Z*)-*N*-acetylaminocinnamic acid with [Rh((*R*,*R*)-NORPHOS)(COD)]BF_4 (standard conditions; a new charge of substrate was added after the first hydrogenation was complete).

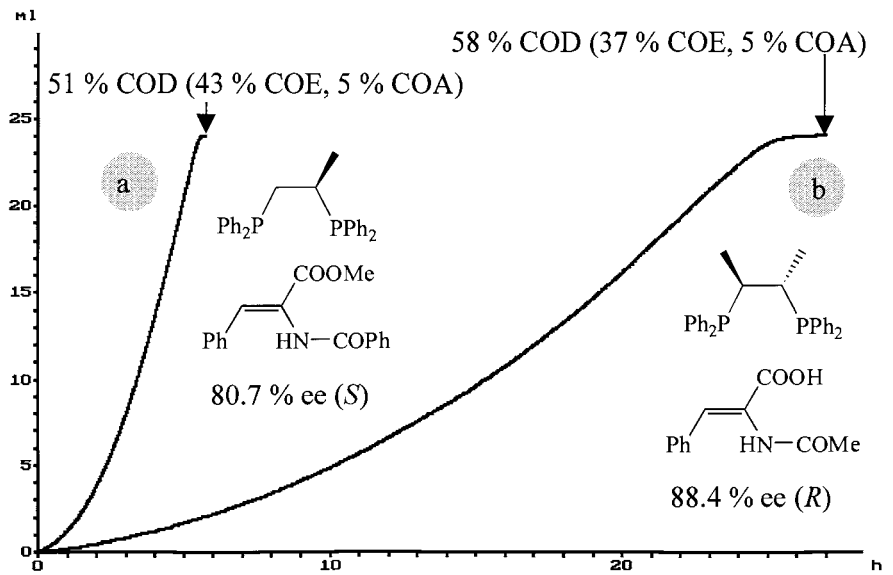


Fig. 3. Induction periods for asymmetric hydrogenations: (a) [Rh((*R*)-PROPHOS)(COD)]BF_4/(*Z*)-methyl-*N*-benzoylaminocinnamate; (b) [Rh((*S*,*S*)-CHIRAPHOS)(COD)]BF_4/(*Z*)-*N*-acetylaminocinnamic acid; standard conditions.

are observed naturally also in other solvents as for example THF or *iso*-PrOH.

A whole series of extremely active catalyst systems containing chiral five-ring chelating ligands are known in the literature for asymmetric hydrogenation. Examples are the bis-phospholane ligands of the BPE/DuPHOS type [16], or the BASPHOS/ROPHOS type [17], which are particularly notable since they can be synthesised easily from cheap starting materials. Similar ligands are based on phosphetanes (CnrPHOS), phospholenes and phosphorous analogues of norbornane (PennPHOS) [18–20]. Also worthy of mention are ligands of the BIPNOR type as well as BisP and its relevant derivatives [21,22]. Due to the higher activity of these systems, one would predict that the COD introduced with the precatalyst could not be removed completely before the asymmetric hydrogenation, and indeed typical induction periods are observed, as is expected.

In Fig. 4 various ways of conducting the hydrogenation of (*Z*)-methyl-*N*-benzoylaminocinnamate using a catalyst containing the Me-Duphos (1,2-bis(2,5-dimethyl-phospholanyl)benzene) ligand are compared. In the first case the catalyst is prepared in situ by the

reaction of $[Rh(COD)_2]BF_4$ with one equivalent of Me-DuPHOS. In the second case the precatalyst is used directly, in the form of [Rh(Me-DuPHOS)(COD)]BF_4, and in the final example the solvent complex [Rh(Me-DuPHOS)$(MeOH)_2$]BF_4 is used (ca. 90 min pre-hydrogenation of the precatalyst, NMR control). The hydrogen uptake was recorded next to the characteristic rate profile for the case of the catalyst prepared in situ. The results from this experiment show that with equal enantioselectivities in the first two cases, there was still free COD present after completion of the asymmetric hydrogenation.

Logically, there is more COD left after the completion of asymmetric hydrogenation in the case where the catalyst was prepared in situ. The example in Fig. 4 demonstrates very clearly that for asymmetric hydrogenation under the usual reaction conditions only a part of the usually expensive catalyst is required. It should be stressed that the amounts of COD given in Fig. 4 are the amounts left after the whole hydrogenation process. That means during the asymmetric hydrogenation the concentration of the COD complex is (time dependent) much higher, and therefore the concentration of the active catalyst is still lower as at the end. In addition the problem of characterising the catalyst activity by means of the 'half-life' also becomes clear. Using the same catalysts, the time for 'half conversion' of the substrate under optimal conditions in the example is only about a quarter of that for the reaction where the catalyst is formed in situ.

In order to prove that the hydrogenation of the diolefin and the prochiral olefin also run parallel in the case of the five-membered chelates, the asymmetric hydrogenation of (*Z*)-methyl-*N*-benzoylaminocinnamate with [Rh((*S*,*S*)-Et-DuPHOS)(COD)]BF_4 (Et-DuPHOS = 1,2-bis(2,5-diethyl-phospholanyl)benzene) was studied in situ under stationary conditions using NMR spectroscopic methods. Since the reaction takes place too quickly at 25°C for the use of the method described in Ref. [6] (through improvements it is possible to follow hydrogenation using a gas uptake rate of ca. 1 ml min^{-1}, without diffusion having an appreciable influence), a reaction temperature of ca. 13°C was chosen. The ^{31}P-NMR spectrum registered before exposure to hydrogen (Fig. 5, bottom trace) exhibits besides the complex [Rh(Et-DuPHOS)(COD)]BF_4 (70.3 ppm, J(P,Rh) = 148 Hz) minor amounts (less than 10%) of further, not unambiguously identified (substrate complex) species. The asymmetric hydrogenation starts with the introduction of hydrogen. The new signals showing up on increasing conversion from substrate to product are not due to the *major* substrate complex (86.9 ppm, J(P,Rh) = 163 Hz, J(P,P) = 34 Hz; 81.7 ppm, J(P,Rh) = 153 Hz), and in the end there are more species than the only expected solvent complex [Rh(Et-DuPHOS)$(CD_3OD)_2$]BF_4 (95.7 ppm, J(P,Rh) = 205 Hz) present. A stringent explanation for these findings is not available at the moment [23]. Besides dynamic (exchange) processes, the streaming hy -drogen (gas bubbles) leads to a considerable broadening of the resonance lines. Despite these difficulties it is clearly visible that the concentration of the COD complex decreases only slowly with the progress of the hydrogenation, and after its completion (63 min reaction time with an enantioselectivity of 99.4% ee (*S*)) more than half of the rhodium is still present as COD complex [24]. This parallel-occurring hydrogenation of the prochiral olefin and the diolefin corresponds qualitatively to the results presented in Figs. 2–4.

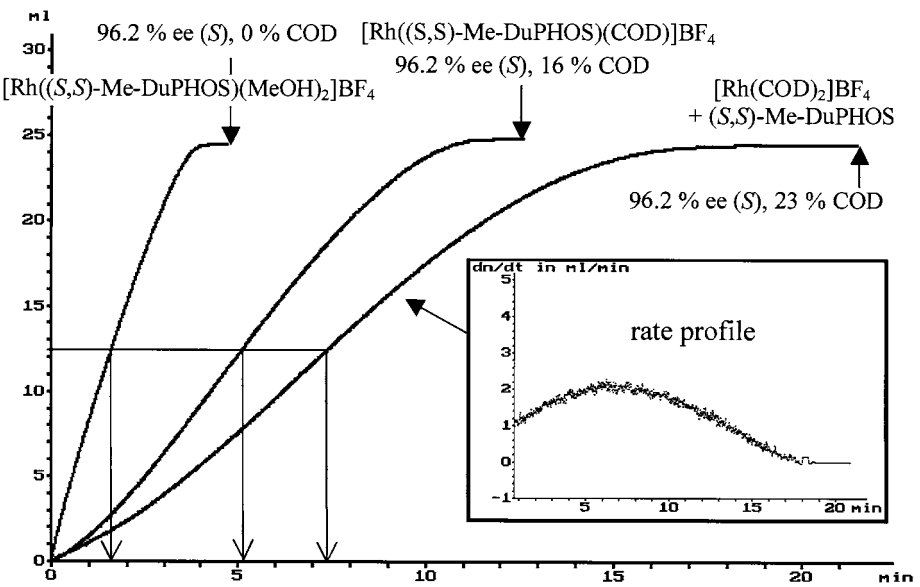


Fig. 4. Different methods for the asymmetric hydrogenation of (*Z*)-methyl-*N*-benzoylaminocinnamate with a catalyst containing the Me-DuPHOS ligand; standard conditions for each experiment.

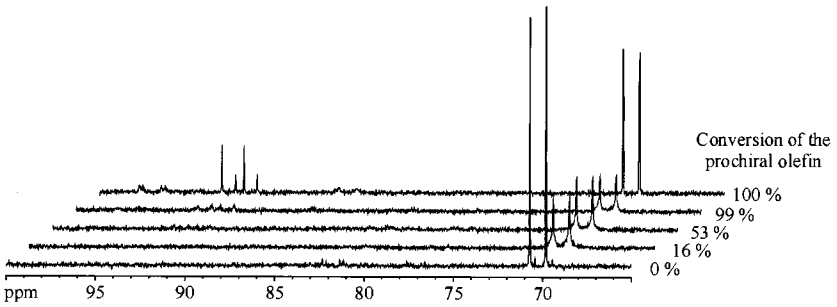


Fig. 5. ^{31}P-NMR spectroscopically monitored hydrogenation of (*Z*)-methyl-*N*-benzoylaminocinnamate with [Rh((*S*,*S*)-Et-DuPHOS)(COD)]BF_4 at ca. 13°C and continuous hydrogen supply (0.01 mmol precatalyst, 1.0 mmol prochiral olefin). The first and the last spectrum were recorded without streaming hydrogen, which leads to a smaller half-width and hence a larger signal amplitude. The conversion of the prochiral olefin was determined from the methyl singlet (3.83 ppm) in the ^{1}H-NMR spectra.

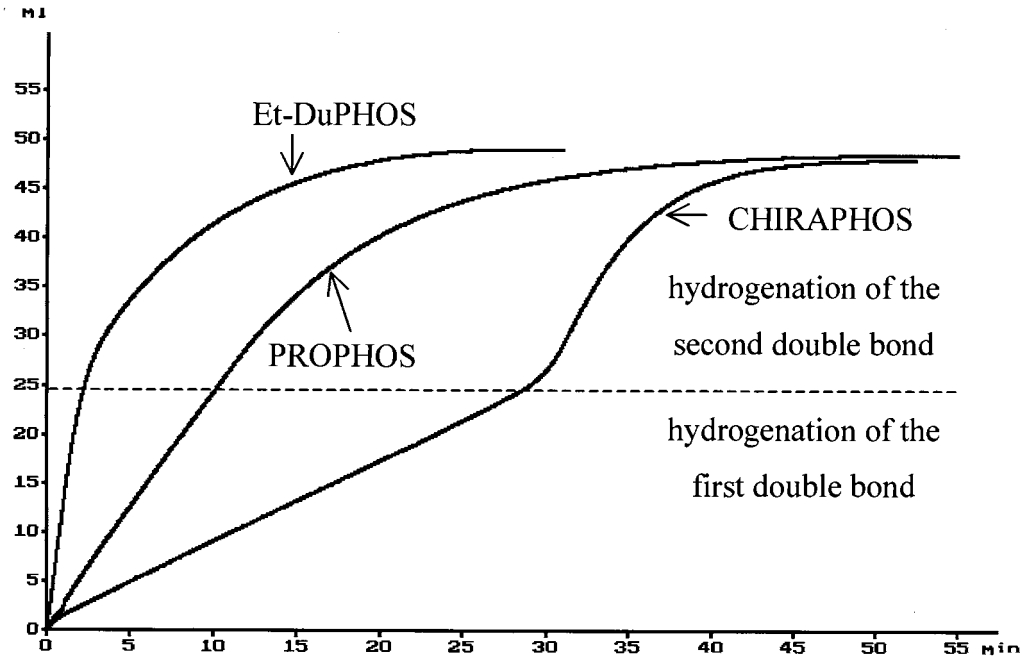


Fig. 6. Catalytic hydrogenations of NBD with five-membered chelates of the type [Rh(PP)(NBD)]BF_4; because of the high rate only 0.00875 mmol of catalyst with PP = Et-DuPHOS was employed, otherwise standard conditions.

In order to compare different precatalysts with respect to the size of the induction periods or the time required for quantitative removal of the diolefin, the rate constants for the hydrogenation of the diolefins ($k_{2\text{diolefin}} = k'_{2\text{diolefin}}[H_2]$) according to the following reaction sequence were determined:

$$[Rh(PP)(MeOH)_2]^+ + \text{diolefin} \overset{k_{1\text{diolefin}}}{\underset{k_{-1\text{diolefin}}}{\rightleftharpoons}} [Rh(PP)\text{diolefin}] + \xrightarrow{k_{2\text{diolefin}}[H_2]} \text{monoolefin} + ([Rh(PP)(MeOH)_2]^+)$$

Therefore, the catalytic hydrogenations of the diolefins were followed in the saturation region of the underlying Michaelis–Menten kinetics, as described in detail earlier [4a,b]. Dividing the slope of the linear curves of hydrogen uptake by the initial catalyst concentration yields the desired rate constant. Because of the isobaric conditions, the thus determined values still contain the hydrogen concentration in solution at a partial pressure of 0.84 atm H_2 (total pressure of 1.0 atm reduced by the solvent's vapour pressure, 0.16 atm for MeOH according to Ref. [25]).

Examples for the catalytic NBD hydrogenation with several catalysts are collected in Fig. 6. As observed with seven-membered chelates [4a,b], the hydrogenation of NBD proceeds very selectively and in the saturation region of Michaelis–Menten kinetics.

Regarding the complex with the ligand CHIRAPHOS, the well known phenomenon is observed that the hydrogenation of the monoolefin to the alkane is faster than the hydrogenation of the diolefin to the monoolefin. The reason of this uncommon behaviour (cf. Ref. [4a] for seven-membered chelates) is obviously

the great stability of the diolefin complex. The monoolefin is not being hydrogenated before complete consumption of the diolefin.

Hydrogenations of COD with five-membered chelates are distinctively slower. Results from such reactions, employing catalysts with the ligand Et-DuPHOS or with the achiral DCPE (1,2-bis(dicyclohexylphosphino)ethane) are presented in Fig. 7. It is remarkable here that the selectivity of the COD hydrogenation with the Et-DuPHOS catalyst is possibly lower than for the other examples. Because of the very slow reaction at normal pressure, experimental causes for the deviation cannot completely be excluded. The determination of the constant $k_{2\text{diolefin}}$ is, however, possible without problems from the initial part of the curve (up to 10 h).

The catalytic hydrogenations of COD for typical five-membered chelates such as CHIRAPHOS or PROPHOS can no longer be measured meaningfully under normal pressure, because they run even slower. The respective reactions were performed under elevated pressure in an autoclave (isochoric conditions) to obtain at least tentative values for the rate of diolefin hydrogenation. The kinetics of product formation for the above-mentioned reaction sequence is described as follows:

$$\frac{\mathrm{d[monoolefin]}}{\mathrm{d}t} = k'_{2\text{diolefin}}[[\mathrm{Rh(PP)(diolefin)}]\mathrm{BF_4}][\mathrm{H_2}]$$
$$(k_{2\text{diolefin}} = k'_{2\text{diolefin}}[\mathrm{H_2}]) \quad (1)$$

The assumption of a very large stability constant for the diolefin complexes of five-membered chelates [3d] leads to the conclusion that the stationary concentration of $[\mathrm{Rh(PP)(diolefin)}]\mathrm{BF_4}$ equals the weight-in of catalyst. Pseudo-stationary conditions with respect to hydrogen concentration can be approximated by a sufficiently large volume of the gas phase. Under these conditions, straight lines are obtained for the hydrogenation of the first double bond, like under normal pressure. Taking into account the initial catalyst concentration, the slopes of these lines deliver the desired rated constants. Fig. 8 presents typical pressure–time curves for such experiments. The upper trace provides a reference, the autoclave was charged exclusively with hydrogen to probe the tightness of the system.

But an exact statement on the rate constant $k'_{2\text{diolefin}}$ is difficult, because there are different values for the solubility of hydrogen in MeOH at 25.0°C in the literature. At a partial pressure of 1.0 atm, the solubility is 0.00331 mol l^{-1} according to Ref. [26], 0.00288 mol l^{-1} according to Ref. [27]. To make the data obtained at different pressures comparable, the values determined from autoclave experiments were converted to normal pressure. Additionally, some rate constants already known from normal-pressure experiments were determined under elevated pressure to check the method. Results obtained for hydrogenations of COD, catalysed by complexes of the ligands DIOP or DPPB (1,4-bis-(diphenylphosphino)butane), coincide very well with published results [4a,b].

The results are collected in Table 1 which lists, besides the rate constants for the diolefin hydrogenation, the chemical shifts of the diolefin-rhodium com-

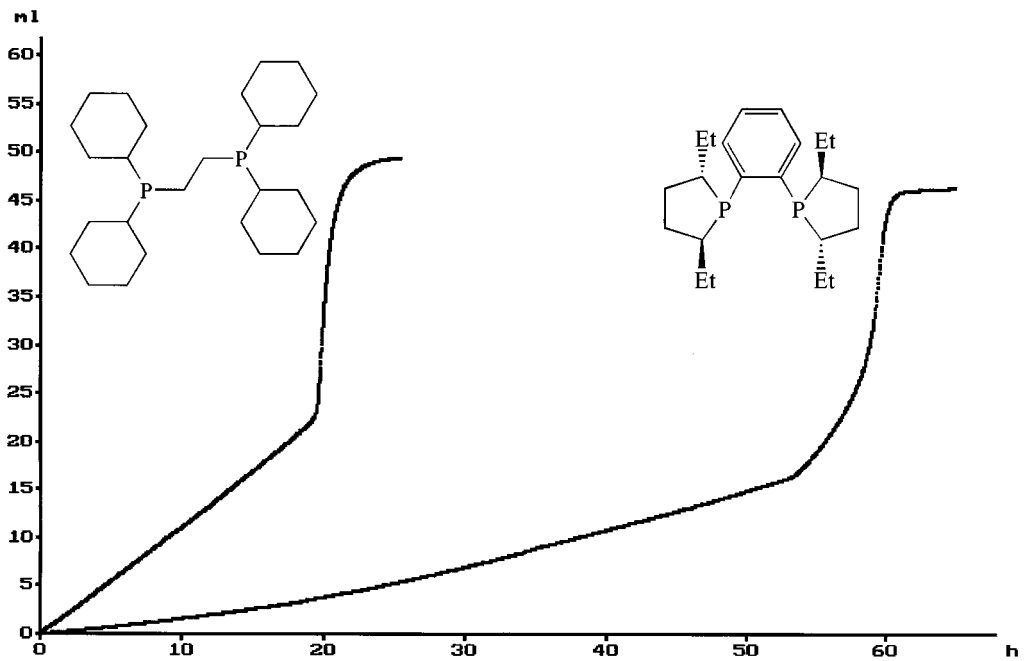


Fig. 7. Hydrogenations of COD with five-membered rhodium chelates containing the ligands Et-DuPHOS or DCPE; standard conditions.

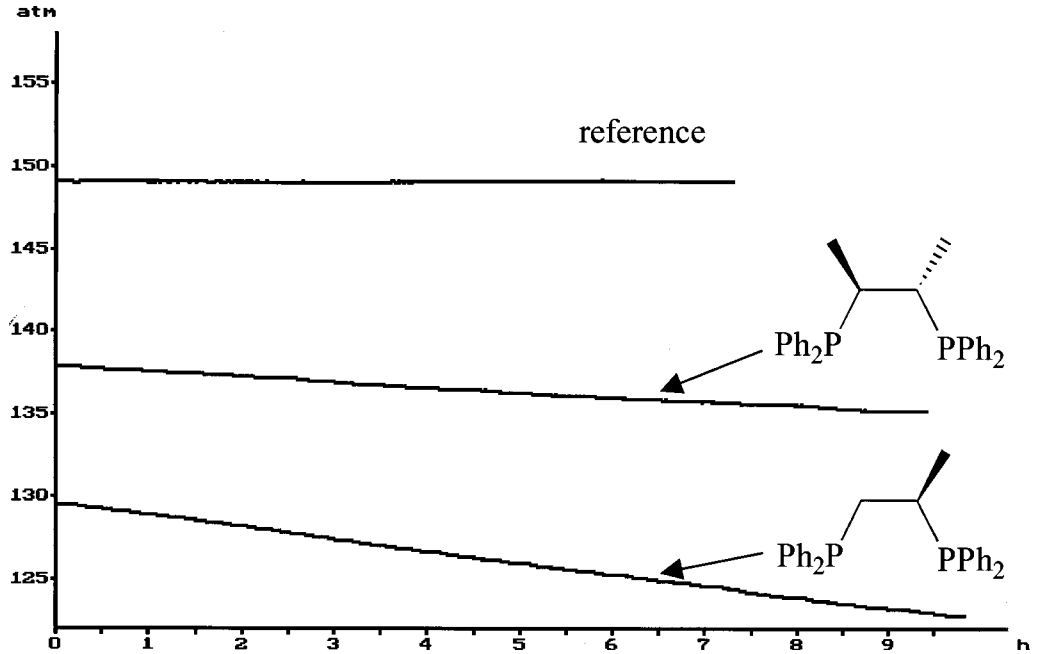


Fig. 8. Decay of pressure for [Rh(PP)(COD)]BF_4-catalysed hydrogenations of COD in an autoclave at 25.0°C plotted over time; isochoric conditions, see text.

plexes in the ^{31}P-NMR spectra and their absorption maxima in the UV–Vis spectra. Some achiral diphosphane ligands forming differently sized chelates are included for comparison.

All results may be summarised in the following way: Regardless of chelate ring size and of the diolefin, the stepwise hydrogenation of the double bonds is characteristic. The diolefin is hydrogenated first, with a high selectivity, and after its consumption, the monoolefin.

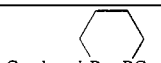
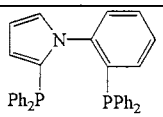
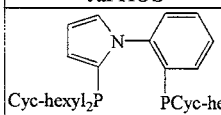
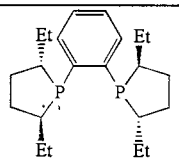
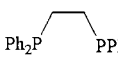
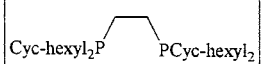
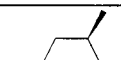
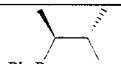
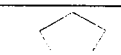
The largest differences between COD and NBD hydrogenation for the formerly studied seven-membered chelates were found for bis-phosphinite ligands (Me-α-glup or Ph-β-glup-OH [4b]). The achiral bis-phosphinite DPOE fits this pattern.

A comparison of the seven-membered chelates DPPB [4b] and DCPB shows that replacing the phenyl by cyclohexyl groups (which increases the steric requirements of the substituents as well as the electron density at rhodium) increases the ratio of the rate constants k_{2NBD}/k_{2COD}. The same effect is observed when comparing JaPHOS to Cyc-JaPHOS, a new and interesting ligand type investigated by Beller et al. [28]. The latter exhibits furthermore a significantly greater difference for the hydrogenation rates of COD and NBD than known so far for seven-membered chelates. The difference in reactivity between the COD and the NBD complex with the Cyc-JaPHOS ligand already approaches the difference in reactivity between the diastereomeric substrate complexes in the hydrogenation of (*Z*)-methyl-*N*-acetylaminocinnamate with [Rh(DIPAMP)$(MeOH)_2$]BF_4 catalyst [29]. This makes such complexes ideal model systems for systematic investigations of factors governing the selectivity such as the ratio of intermediates and the ratio of their reactivities [30].

Comparing the reactivites of the respective NBD and COD complexes of five-membered chelates in diolefin hydrogenation reveals clearly greater differences than found for the seven-membered chelates. Introducing the cyclohexyl residue instead of the phenyl group (DCPE versus DPPE) obviously has the opposite effect, compared to seven-membered chelates.

The influence of the diolefin ligand on the induction period is more pronounced with five-membered than with seven-membered chelates, because of the clear differences in reactivity for the diolefin hydrogenation. The choice of the diolefin within the precatalyst and the manner of conducting the experiment (Fig. 4) allow us to 'play' with the macroscopically observable activity. This is illustrated in Fig. 9 by the hydrogenation of (*Z*)-methyl-*N*-acetylaminocinnamate with an Et-DuPHOS catalyst, either with a COD or NBD complex or with the solvent complex. As expected, one still finds unchanged COD at the end of the asymmetric hydrogenation, therefore only a fraction of the catalyst has been used to generate the chiral product. NBD and solvent complex exhibit similar activities due to the fast NBD hydrogenation in the precatalyst. Whereas the same enantioselectivity is observed in all cases, the apparent activity is clearly different, see Fig. 9. The time required for conversion of half of the substrate with the COD complex is six times as long as that required with the NDB complex, and if we consider the

Table 1
Rate constants $k_{2diolefin}$ for the hydrogenation of the complexes [Rh(PP)(diolefin)]BF_4 in MeOH at 25.0°C and 1.0 atm total pressure, chemical shifts and absorption maxima from UV–Vis spectra ($k_{2diolefin}$ values as peudo-constants still contain the hydrogen solubility!)

chelate-ligands (7-rings)	k_{2COD} (1/s)	k_{2NBD} (1/s)	$\frac{k_{2NBD}}{k_{2COD}}$	^{31}P-NMR δ(ppm)	maxima UV/Vis (nm)
 DPOE [a]	$4.2\cdot10^{-3}$	$2.8\cdot10^{-1}$	66	COD: 125.7 NBD:131.5	COD: 444 NBD: 471
 DCPB [a]	$1.2\cdot10^{-1}$	3.8	32	COD: 24.5 NBD: 27.4	COD: 452 NBD: 470
 JaPHOS [a]	$5.6\cdot10^{-3}$	$5.6\cdot10^{-1}$	100	COD: 18.1; 21.4 NBD: 18.6; 22.6	COD: 450 NBD: 477
 Cyc-JaPHOS [a]	$1.8\cdot10^{-3}$	≥ 11.7 [b]	≥ 630	COD: 4.9; 24.4 NBD: 10.6; 25.5	COD: 452 NBD: 470
(5-rings)					
 (*S*,*S*)-Et-DuPHOS	ca. $2.3\cdot10^{-4}$	$8.7\cdot10^{-1}$	ca. 3800	COD: 69.5 NBD: 69.2	COD: 453 NBD: 479
 DPPE [a]	(autoclav) [c] ≈ $3\text{-}6\cdot10^{-5}$	$2.9\cdot10^{-1}$	≥ 4800 [d]	COD: 56.9 NBD: 56.5	COD: 447 NBD: 473
 DCPE	$1.3\cdot10^{-3}$	$8.1\cdot10^{-1}$	634	COD: 68.5 NBD: 70.5	COD: 452 NBD: 478
 (*R*)-PROPHOS	(autoclav) [c] ≈ $5\cdot10^{-5}$	$1.5\cdot10^{-1}$	≥ 3000 [d]	COD: 43.6; 59.4 NBD: 43.2; 61.2	COD: 448 NBD: 473
 (*S*,*S*)-CHIRAPHOS	(autoclav) [c] ≈ $3\cdot10^{-5}$	$5.0\cdot10^{-2}$	≥ 1700 [d]	COD: 56.4 NBD: 58.0	COD: 448 NBD: 474
(6-rings)					
 DPPP [a]	$4.0\cdot10^{-4}$	$2.6\cdot10^{-2}$	65	COD: 10.2 NBD: 15.8	COD: 455 NBD: 473

[a]: DPOE = 1,2-bis(diphenylphosphinoxy)ethane
DCPB = 1,4-bis(dicyclohexylphosphino)butane
JaPHOS = 1-(2-diphenylphosphinophenyl)pyrol-2-diphenylphosphine
Cyc-JaPHOS = 1-(2-dicyclohexylphosphinophenyl)pyrol-2-dicyclohexylphosphine
DPPE = 1,2-bis(diphenylphosphino)ethane
DPPP = 1,3-bis(diphenylphosphino)propane

[b]: The activity is so great that an influence of diffusion (hydrogen transfer from the gaseous to the liquid phase) cannot be completely excluded.

[c]: Data are scaled to 1.0 atm total gas pressure.

[d]: Values might be even larger because data for COD hydrogenation are less accurate and of only tentative character.

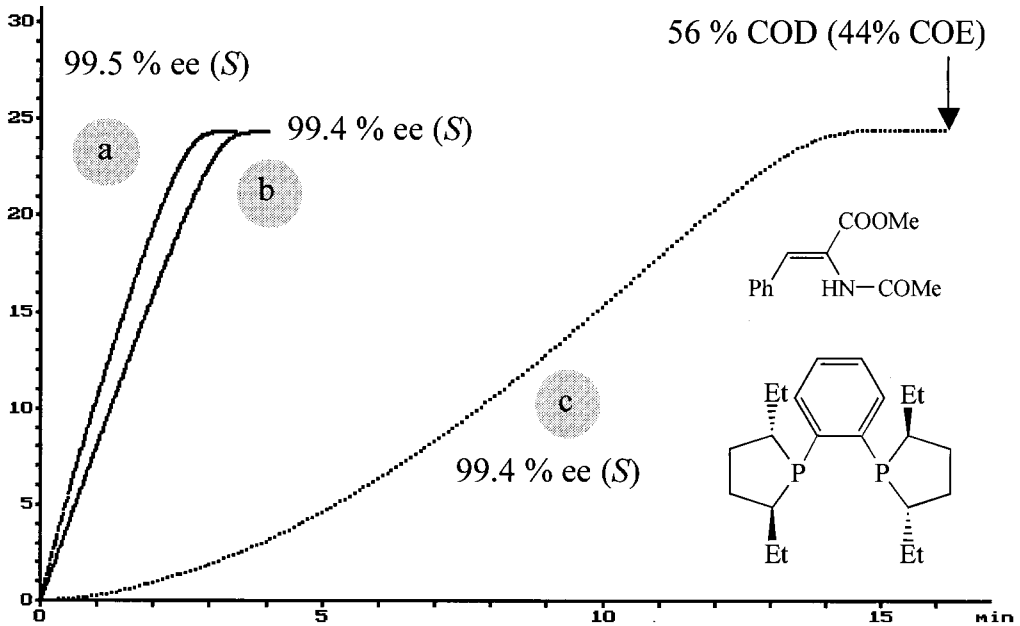


Fig. 9. Asymmetric hydrogenations of (*Z*)-methyl-*N*-acetylaminocinnamate with catalysts bearing the (*S*,*S*)-Et-DuPHOS ligand (standard conditions): (a) [Rh((*S*,*S*)-Et-DuPHOS)$(MeOH)_2$]BF_4, (b) [Rh((*S*,*S*)-Et-DuPHOS)(NBD)]BF_4, (c) [Rh((*S*,*S*)-Et-DuPHOS)(COD)]BF_4.

system (*Z*)-*N*-acetylaminocinnamic acid/PROPHOS catalyst, the analogous factor is about 20!

The reasons for these drastic differences in reactivity, especially with five-membered chelates, are unclear, just as they are unknown for the diastereomeric substrate complexes involved in asymmetric hydrogenation. According to the *major/minor* concept developed by Halpern–Landis and Brown, the *minor* substrate complex dominates the selectivity, despite its lower concentration, by its extraordinary reactivity. There are no X-ray crystallographic studies on *minor* substrate complexes, so we decided to take a closer look at the structures of the diolefin complexes, which differ in reactivity in a similar manner.

An important feature of all published X-ray crystallogaphic data of diolefin complexes is that they do not have an ideal square-planar coordination geometry [16a,c,o,31]. Analogous investigations of seven-membered chelates revealed that the more reactive NBD complexes show generally a less pronounced distortion from the square-planar towards a tetrahedral ligand sphere than the corresponding COD complexes do [32]. A detailed discussion is in preparation.

The following discussion concerns X-ray crystal structure analyses of the complexes [Rh((*R*,*R*)-Et-DuPHOS)(COD)]BF_4 and [Rh((*S*,*S*)-Et-DuPHOS)-(NBD)]BF_4, whose reactivity in diolefin hydrogenation differs by three powers of ten. Relevant parameters are given in Table 2, graphic representations in Figs. 10 and 11. The unit cell of the NBD complex contains two independent molecules, the unit cell of the COD complex only one.

Bond lengths and angles are similar to those of the already published structure of [Rh((*S*,*S*)-Me-DuPHOS)(COD)]SbF_6 [16c]. The deviation from the square-planar towards a tetrahedral coordination sphere is characteristic. The dihedral angles between the planes defined by P, Rh, P and C=C, Rh, C=C (the centroids of the double bonds are used) are 6.1° and 15.0° for the NBD complex, thus they are clearly smaller than for the COD complex (21.1°, Fig. 12). An angle of 18° has been described for the analogous complex [Rh((*S*,*S*)-Me-DuPHOS)(COD)]SbF_6, and 15.6° for [Ir((*R*,*R*)-Me-DuPHOS)(COD)]BF_4 [16c,33]; a further discussion is given in Ref. [16o]. This is the most prominent difference in the solid-state structure of the complexes, whose hydrogenation activity towards COD and NBD is distinguished by about three orders of magnitude. This shows that, at least for the diolefins under consideration, a higher reactivity in hydrogenation for five-membered chelates is also associated with a smaller deviation from the square-planar ligand sphere [34].

The distortion of the expected square-planar structure towards a tetrahedron has the consequence that the diolefin may be oriented either *clockwise twist* or *anticlockwise twist* (in this way chiral complexes may result even with an achiral bisphosphane). Recently, the question was raised whether a *clockwise twist* or an *anticlockwise twist* arrangement of the diolefins COD or NBD in the precatalyst would result in the formation of *S* or *R* enantiomers, respectively, in asymmetric hydrogenations [31f,33]. Regarding the structures of the complexes [Rh(Et-DuPHOS)(diolefin)]BF_4 one finds (Fig. 12) that the direction of the twist is formally the same, for both

the NBD and the COD complex. But the complexes differ in the chirality of the Et-DuPHOS ligand (*S*,*S* with NBD, *R*,*R* with COD), so it is to be expected that the twist would be opposite if the bisphosphine with the same chirality were present.

Another example showing that the direction of the twist depends on the diolefin itself is the precatalyst formed with the ligand SKEWPHOS (2,4-bis-(diphenylphosphino)pentane, Fig. 13) [35]. Also in the case of the complex with the ligand (*S*)-Cyc-PRO-PRAPHOS ((*S*)-2,3-*O*,*N*-bis(diphenylphosphino)-1-(naphthoxy)-2-hydroxy-3-cyclohexylaminopropane) the NBD complex shows a *clockwise twist* (2.2°), the COD complex shows a *anticlockwise twist* (5.2°) [36].

All of these examples confirm that the chirality found in the product of an asymmetric hydrogenation is hardly to be correlated with the direction of the diolefin twist. Instead, the macroscopically observed selectivity results from a complex interdependence of single factors. The enantioselectivity, as a kinetic phenomenon, is governed by the ratio of the reactivites of the diastereomeric substrate complexes and by the concentration ratio of these intermediates.

Summing up, it has to be stated that induction periods are of relevance to the asymmetric hydrogenation of prochiral olefins with five-membered chelates of the type $[Rh(PP)(diolefin)]BF_4$ as well [37]. These induction periods are recognised by a distinct increase in activity during the asymmetric hydrogenation and originate from the parallel-running hydrogenation of the prochiral substrate and the diolefin that enters the system as a constituent of the precatalyst, as was already described for seven-membered chelates. A certain amount of the expensive catalyst is thus unavailable for the intended asymmetric hydrogenation, because it is blocked by the diolefin. This characteristic feature could be proven by in situ NMR spectroscopy under stationary conditions for some examples. Surprisingly it turned out that reactivities towards the most commonly used diolefins COD or NBD might differ by three powers of ten. This is primarily due to the very slow hydrogenation of COD. The reason for these great differences in reactivity remains unclear. The herein presented X-ray crystal structure analyses of $[Rh((S,S)$-Et-DuPHOS)(NBD)$]BF_4$ and of $[Rh((R,R)$-Et-DuPHOS)(COD)$]BF_4$ reveal a significantly greater deviation from square-planar coordination for the less reactive COD complex. Whether it is possible to generalise this trend remains yet unanswered. The crystal structures now solved imply further that a recently discussed relation between the sense of rotation of the diolefin in the precatalyst (*clockwise* or *anticlockwise twist*) is not very likely, for this direction may depend on the diolefin itself, if the same chiral ligand backbone is considered.

An important practical consequence of the induction periods is that the frequently used COD complexes do not imply optimal activity in the catalysis, at least for five-membered chelates, and cannot therefore be regarded very economically.

Table 2
Crystallographic and refinement data for $[Rh((S,S)$-Et-DuPHOS)(NBD)$]BF_4$ and $[Rh((R,R)$-Et-DuPHOS)(COD)$]BF_4$

	$[Rh((S,S)$-Et-DuPHOS)(NBD)$]^+BF_4^-$	$[Rh((R,R)$-Et-DuPHOS)(COD)$]^+BF_4^-$
Empirical formula	$C_{29}H_{44}BF_4P_2Rh$	$C_{30}H_{48}BF_4P_2Rh$
Formula weight	644.30	660.34
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	8.957(2)	10.620(2)
b (Å)	19.566(4)	16.882(3)
c (Å)	17.449(3)	17.362(3)
α (°)	90	90
β (°)	101.96(3)	90
γ (°)	90	90
V (Å^3)	2991.6(10)	3112.8(10)
D_{calc} (Mg m^{-3})	1.431	1.409
Z	4	4
μ(Mo–K$_\alpha$) (mm^{-1})	0.72	0.69
F(000)	1336	1376
Crystal size (mm)	$0.2\times0.4\times0.4$	$0.2\times0.4\times0.6$
Temperature (K)	200	200
θ Range for data collection (°)	1.58–22.42	1.68–22.50
Index range (h,k,l)	−9/9, −20/18, −18/18	−11/11, −18/18, −18/7
Reflections collected	12973	11146
Independent reflections	7285	4079
Observed reflections	4565	3295
Refined parameters	667	343
R_1 ($2\sigma(I)$)	0.0452	0.0428
R_1 (all data)	0.0772	0.0549
wR_2 (all data)	0.0877	0.0967
Goodness of fit	0.799	0.966
Flack x parameter (esd)	−0.0846 (0.0373)	0.0023 (0.0543)
Largest difference peak and hole (e Å^{-1})	0.65/−0.53	0.64/−0.46

1. Experimental

1.1. General

Reactions were performed under argon using standard Schlenk techniques.

1.2. Hydrogenations

The experiments under normal pressure and isobaric conditions were carried out with an automatically registrating gas measuring device described in Ref. [4c].

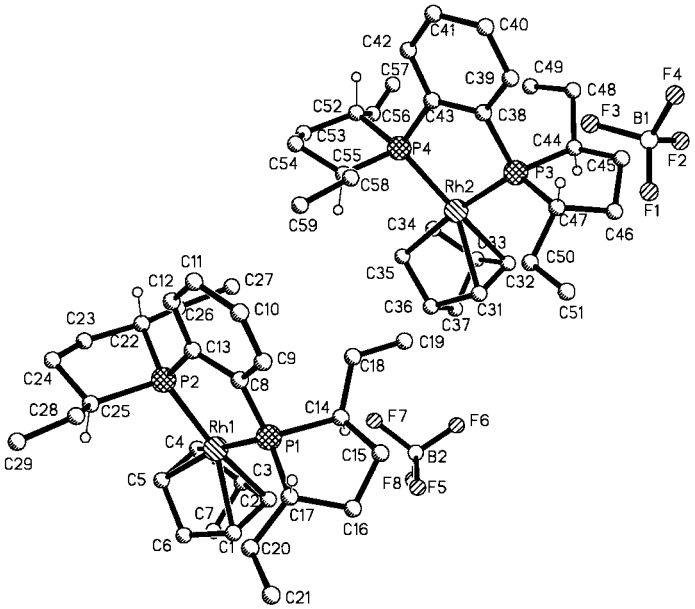


Fig. 10. Perspective view and numbering scheme of the two complexes [Rh((*S*,*S*)-Et-DuPHOS)(NBD)]BF_4 in the asymmetric unit. All hydrogens except for the asymmetric carbon atoms have been omitted for clarity. Interatomic distances (Å): Rh1–C1 = 2.243(10), Rh1–C2 = 2.250(11), Rh1–C4 = 2.211(11), Rh1–C5 = 2.198(11), Rh1–P1 = 2.297(3), Rh1–P2 = 2.276(3), Rh2–C31 = 2.254(11), Rh2–C32 = 2.222(12), Rh2–C34 = 2.145(17), Rh2–C35 = 2.230(10), Rh2–P3 = 2.288(3), Rh2–P4 = 2.277(3). Intramolecular angles (°): P1–Rh1–P2 = 84.53(10), C1–Rh1–C2 = 35.5(4), C4–Rh1–C5 = 35.7(4), P3–Rh2–P4 = 84.74(11), C31–Rh2–C32 = 35.6(4), C34–Rh2–C35 = 35.3(4).

Hydrogen (AGA 6.0) was used as received. The experiments were carried out under standard conditions with 0.01 mmol catalyst, 1.0 mmol of substrate in 15.0 ml solvent at 25.0°C. If it was necessary to hydrogenate the precatalysts, the prochiral olefin in 1.0 ml of solvent was fused in a glass ampulla under strictly anaerobic conditions. To start the hydrogenation after completion of the diolefin hydrogenation and thermic equilibration (vapour pressure and H_2 solubility), the ampulla was destroyed by the magnetic stirrer.

1.3. Substrates

(*Z*)-*N*-acetylaminocinnamic acid, methyl-*N*-acetylaminoacrylate and dimethyl itaconate are commercially available. (*Z*)-methyl-*N*-acetylaminocinnamate and (*Z*)-methyl-*N*-benzoylaminocinnamate where prepared by published procedures. (*Z*,*Z*)-Cycloocta-1,5-diene (COD) and norborna-2,5-diene (NBD) were dried with CaH_2 and distilled under Ar.

1.4. Catalysts

The rhodium complexes of the commercially available ligands CHIRAPHOS, PROPHOS, Me-Duphos, Et-Duphos, DPPE, DCPE, DCPB and DPPP, and of the new ligands JaPHOS and Cyc-JaPHOS provided by Professor M. Beller [28], were prepared by usual procedures [38]. The other used complexes were kindly donated by Professor R. Selke {[Rh(Ph-β-glup-OH)-(COD)]BF_4} and Professor A. Börner {[Rh(2-MHOP)(COD]BF_4, [Rh(DIOP)(COD]BF_4, [Rh(NOR-PHOS)(COD]BF_4, [Rh(DPOE)(COD]BF_4}.

1.5. Analysis

GC was performed with a GC 5890 Serie II equipped with FID, carrier gas argon (1 ml min^{-1}). HPLC was

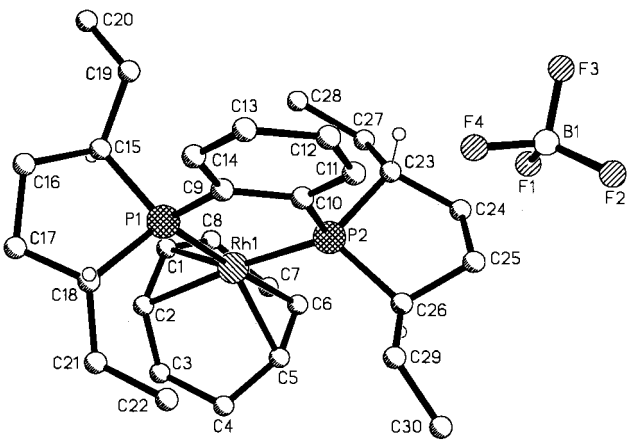


Fig. 11. Perspective view and numbering scheme of the complex [Rh((*R*,*R*)-Et-DuPHOS)(COD)]BF_4. All hydrogens except for the asymmetric carbon atoms have been omitted for clarity. Interatomic distances (Å): Rh1–C1 = 2.236(7), Rh1–C2 = 2.297(6), Rh1–C5 = 2.190(6), Rh1–C6 = 2.224(7), Rh1–P1 = 2.291(2), Rh1–P2 = 2.262(2). Intramolecular angles (°): P1–Rh1–P2 = 85.32(6), C1–Rh1–C2 = 34.3(3), C5–Rh1–C6 = 36.2(2).

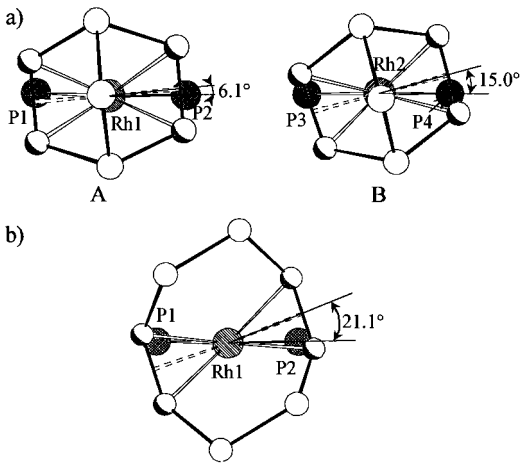


Fig. 12. Elevation views of the X-ray crystal structures of the diolefin-RhPP fragment of the [Rh(Et-DuPHOS)(diolefin)]BF_4 complexes, showing the dihedral angle between the P–Rh–P plane and the centroid–Rh–centroid plane: (a) [Rh((*S*,*S*)-Et-DuPHOS)(NBD)]BF_4 with the molecules A and B, *anticlockwise twist*; (b) [Rh((*R*,*R*)-Et-DuPHOS)(COD)]BF_4, *anticlockwise twist*.

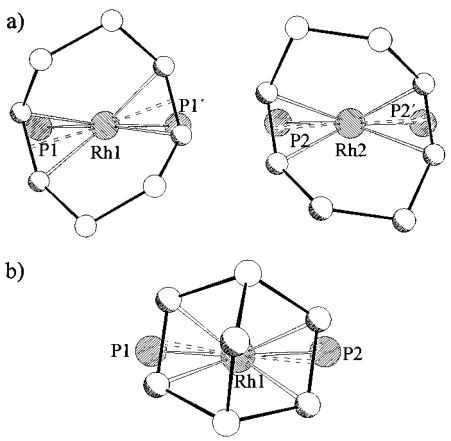


Fig. 13. Parts of the structure of (a) [Rh((*S*,*S*)-SKEWPHOS)-(COD)]ClO_4, *anticlockwise twist* 17.6° and 3.4°, and (b) [Rh((*S*,*S*)-SKEWPHOS)(NBD)]ClO_4, *clockwise twist* 8.7° [35]. Crystallographic data are from the Cambridge Crystallographic Data Centre (JEBRAJ or JEBREN).

performed with a Liquid Chromatograph 1090 series II equipped with DAD (Hewlett–Packard).

The conversion of COD and NBD was determined by GC (HP 1, 50 m × 0.2 mm ID, 85°C). (*Z*)-*N*-acetylaminocinnamic acid was esterified with trimethylsilyldiazomethane before the GC measurements. Determination of ee were carried out by GC or HPLC on chiral stationary phases. GC: (*Z*)-methyl-*N*-acetylaminocinnamate (165°C, XE-60-L-valin-tert-butylamide, 10 m × 0.2 mm ID); *N*-methyl-acetylaminoacrylate (120°C, Chirasil-Val, 25 m × 0.25 mm ID, Alltech); dimethyl itaconate (120°C, FS-Lipodex E, 25 m × 0.25 mm ID, Machery-Nagel). HPLC: (*Z*)-methyl-*N*-benzoylaminocinnamate (column Chiralcel OD-H, 4.6 × 250 mm ID (Merck), eluent *n*-hexane–ethanol 90:10).

NMR spectra were recorded with a Bruker ARX 400 instrument ($B_0 = 9.4$ T) in methanol-d_4 solutions at 297 K, unless indicated otherwise. ^{31}P chemical shifts are given in ppm relative to 85% H_3PO_4 (ext.).

1.6. Crystal structure determinations for [Rh((S,S)-Et-DuPHOS)(NBD)]BF_4 and [Rh((R,R)-Et-DuPHOS)(COD)]BF_4

Crystals for the X-ray analyses were obtained by slow diffusion of diethyl ether (NBD complex), tert-butyl-methyl ether (COD complex), respectively, into a concentrated MeOH, THF, respectively, solution of the respective rhodium complex. Crystal data and details of the structure solution are summarised in Table 2.

For both compounds data were collected on a STOE-IPDS diffractometer using graphite monochromated Mo–K_α radiation. The structures were solved by direct methods (SHELXS-97) [39] and refined by full-matrix least-square techniques against F^2 (SHELXL-97) [40]. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in theoretical positions and were refined by using the riding model. The weighting schemes are $\omega = 1/[\sigma^2(F_o^2) + (0.0290P)^2 + 0.0000P]$ for [Rh((*S*,*S*)-Et-DuPHOS)-(NBD)]BF_4 and $\omega = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.0000P]$ for [Rh((*R*,*R*)-Et-DuPHOS)(COD)]BF_4 with $P = (F_o^2 + 2F_c^2)/3$.

2. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication CCDC No. 147960 for [Rh((*S*,*S*)-Et-DuPHOS)(NBD)]BF_4 and CCDC No. 147961 for [Rh((*R*,*R*)-Et-DuPHOS)(COD)]BF_4. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) J.M. Brown, Hydrogenation of functionalized carbon–carbon double bonds. In: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Springer, Berlin, 1999, Chapter 5.1, pp. 121–182. (b) U. Nagel, J. Albrecht, Topics Catal. 5 (1998) 3. (c) M.J. Burk, F. Bienewald, Unnatural α-amino acids, via asymmetric hydrogenation of enamides. In: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. I, Wiley-VCH, Weinheim, 1998, Chapter 1.1.2, pp. 13–25. (d) H. Brunner, Hydrogenation. In: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vols. I and II, VCH, Weinheim, 1996, Chapter 2.2, pp. 201–219. (e) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994, Chapter 2, pp. 16–94. (f) P.A. Chaloner, M.E. Esteruelas, F. Joo, L.A. Oro, Homogeneous Hydrogenation, Kluwer Academic Publishers, Dordrecht, 1994. (g) H. Takaya, T. Ohta, R. Noyori, Asymmetric hydrogenation. In: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, Chapter 1, pp. 1–39.

[2] (a) F. Spindler, H.U. Blaser, Enantiomer 4 (1999) 557. (b) H.U. Blaser, M. Studer, Appl. Catal. A 189 (1999) 191. (c) H.U. Blaser, H.P. Buser, H.P. Jalett, B. Pugin, F. Spindler, Synlett. S1 (1999) 867. (d) H.U. Blaser, H.P. Buser, K. Coers, R. Hanreich, H.P. Jalett, E. Jelsch, B. Pugin, H.D. Schneider, F. Spindler, A. Wegmann, Chimia 53 (1999) 275. (e) H.-U. Blaser, F. Spindler, Topics Catal. 4 (1997) 275.

[3] (a) J.R. Shapley, R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 91 (1969) 2816. (b) R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 93 (1971) 3089. (c) R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 98 (1976) 2134. (d) R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 98 (1976) 4450.

[4] (a) D. Heller, K. Kortus, R. Selke, Liebigs Ann. (1995) 575. (b) D. Heller, S. Borns, W. Baumann, R. Selke, Chem. Ber. 129 (1996) 85. (c) D. Heller, J. Holz, S. Borns, A. Spannenberg, R. Kempe, U. Schmidt, A. Borner, Tetrahedron: Asymm. 8 (1997) 213.

[5] *cis*-Cyclo-octene (COE) and/or cyclo-octane (COA) as well as norbornene (NBE) and/or norbornane (NBA) resulted as hydrogenation product when COD or NBD was used.

[6] W. Baumann, S. Mansel, D. Heller, S. Borns, Magn. Reson. Chem. 35 (1997) 701.

[7] Substrate inhibition as the cause for the observed induction period can be ruled out. The induction periods also cannot be caused by neglecting to add additional hydrogen. For a substrate/precatalyst ratio of 100, there is an error of 2% expected for the complete hydrogenation of the olefin to the saturated product distributed over the entire gas uptake curve.

[8] (a) U. Nagel, T. Krink, Angew. Chem. 105 (1993) 1099; Angew. Chem. Int. Ed. Engl. 32 (1993) 1052. (b) U. Nagel, A. Bublewitz, Chem. Ber. 125 (1992) 1061. (c) U. Nagel, E. Kinzel, J. Andrade, G. Prescher, Chem. Ber. 119 (1986) 3326.

[9] D. Heller, R. Thede, D. Haberland, J. Mol. Catal. A 115 (1996) 273.

[10] D.G. Blackmond, T. Rosner, T. Neugebauer, M. Reetz, Angew. Chem. 111 (1999) 2333; Angew. Chem. Int. Ed. Engl. 38 (1999) 2196. 1:1 mixtures of the diastereomeric catalysts led to unexpectedly high enantioselectivities for the hydrogenation of dimethyl itaconate. These are the results of the various induction periods for the diastereomeric COD employed catalysts, so that the end effect is that the hydrogenation at first runs via a diastereomeric catalyst.

[11] M.E. Esterulas, J. Herrero, M. Martin, L.A. Oro, V.M. Real, J. Organomet. Chem. 599 (2000) 178.

[12] (a) J.M. Brown, R.A. Chaloner, Tetrahedron Lett. 21 (1978) 1877. (b) J.M. Brown, P.A. Chaloner, J. Am. Chem. Soc. 102 (1980) 3040.

[13] (a) H. Brunner, W. Pieronczyk, Angew. Chem. 91 (1979) 655; Angew. Chem. Int. Ed. Engl. 18 (1979) 620. (b) H. Brunner, W. Pieronczyk, B. Schonhammer, K. Streng, I. Bernal, J. Korp, Chem. Ber. 114 (1981) 1137. For problems encountered with RENORHOS refer to [31b]. A hydroxy derivative of NORPHOS is described in J. Ward, A. Börner, H.B. Kagan, Tetrahedron: Asymm. 3 (1992) 849.

[14] (a) M.D. Fryzuk, B. Bosnich, J. Am. Chem. Soc. 99 (1977) 6262. (b) M.D. Fryzuk, B. Bosnich, J. Am. Chem. Soc. 100 (1978) 5491.

[15] Since the partial reaction order for hydrogen, for the asymmetric reaction as well as for the diolefin hydrogenation, is one [4c] analogous results will also be obtained with other pressures.

[16] (a) M.J. Burk, J.E. Feaster, R.L. Harlow, Organometallics 9 (1990) 2653. (b) M.J. Burk, J. Am. Chem. Soc. 113 (1991) 8518. (c) M.J. Burk, J.E. Feaster, W.A. Nugent, R.L. Harlow, J. Am. Chem. Soc. 115 (1993) 10125. (d) M.J. Burk, S. Feng, M.F. Gross, W. Tumas, J. Am. Chem. Soc. 117 (1995) 8277. (e) M.J. Burk, M.F. Gross, J.P. Martinez, J. Am. Chem. Soc. 117 (1995) 9375. (f) M.J. Burk, Y.M. Wang, J.R. Lee, J. Am. Chem. Soc. 118 (1996) 5142. (g) M.J. Burk, M.F. Gross, T.G.P. Harper, C.S. Kalberg, J.R. Lee, J.P. Martinez, Pure Appl. Chem. 68 (1996) 37. (h) M.J. Burk, J.G. Allen, W.F. Kiesmann, J. Am. Chem. Soc. 120 (1998) 657. (i) J. Albrecht, U. Nagel, Angew. Chem. 108 (1996) 444; Angew. Chem. Int. Ed. Engl. 35 (1996) 407. (j) M.J. Burk, C.S. Kalberg, A. Pizzano, J. Am. Chem. Soc. 120 (1998) 4345. (k) S.D. Debenham, J. Cossrow, E.J. Toone, J. Org. Chem. 64 (1999) 9153. (l) M.J. Burk, K.M. Bedingfield, W.F. Kiesman, J.G. Allen, Tetrahedron Lett. 40 (1999) 3093. (m) T.A. Stammers, M.J. Burk, Tetrahedron Lett. 40 (1999) 3325. (n) M.J. Burk, N.B. Johnson, J.R. Lee, Tetrahedron Lett. 40 (1999) 6685. (o) M.J. Burk, A. Pizzano, J.A. Martin, Organometallics 19 (2000) 250.

[17] (a) J. Holz, D. Heller, R. Stiirmer, A. Börner, Tetrahedron Lett. 40 (1999) 7059. (b) J. Holz, M. Quirmbach, U. Schmidt, D. Heller, R. Stürmer, A. Börner, J. Org. Chem. 63 (1998) 8031. (c) W. Li, Z. Zhang, D. Xiao, X. Zhang, Tetrahedron Lett. 40 (1999) 6701. (d) Y.-Y. Yan, T.V. RajanBabu, J. Org. Chem. 65 (2000) 900. (e) W. Li, Z. Zhang, D. Xiao, X. Zhang, J. Org. Chem. 65 (2000) 3489. (f) Y.-Y. Yan, T.V. RajanBabu, Org. Lett. 2 (2000) 199.

[18] (a) A. Marinetti, J.P. Genêt, S. Jus, D. Blanc, V. Ratovelomanana-Vidal, Chem. Eur. J. 5 (1999) 1160. (b) A. Marinetti, F. Labrue, J.P. Genêt, Synlett. 12 (1999) 1975. (c) A. Marinetti, S. Jus, J.P. Genêt, Tetrahedron Lett. 40 (1999) 8365. (d) A. Marinetti, S. Jus, J.P. Genêt, L. Ricard, Tetrahedron 56 (2000) 95.

[19] F. Bienewald, L. Ricard, F. Mercier, F. Mathey, Tetrahedron: Asymm. 10 (1999) 4701.

[20] Q. Jiang, Y. Jiang, D. Xiao, P. Cao, X. Zhang, Angew. Chem. 110 (1998) 1203; Angew. Chem. Int. Ed. Engl. 37 (1998) 1100.

[21] (a) F. Robin, F. Mercier, L. Ricard, F. Mathey, M. Spagnol, Chem. Eur. J. 3 (1997) 1365. (b) F. Mathey, F. Mercier, F. Robin, L. Ricard, J. Organomet. Chem. 577 (1998) 117.

[22] (a) T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, J. Am. Chem. Soc. 120 (1998) 1635. (b) T. Miura, T. Imamoto, Tetrahedron Lett. 40 (1999) 4833.

[23] Very recently Gridnev and Imamoto have described product complexes for similar systems. I.D. Gridnev, N. Higashi, K. Asakura, T. Imamoto, J. Am. Chem. Soc. 122 (2000) 7183.

[24] The results obtained in the NMR tube correspond approximately to those determined in the standard hydrogenation vessel at 15.0°C (total reaction time 45 min, 99.5% ee (**5**) 48% COD).

[25] T.E. Jordan, Vapor Pressure of Organic Compounds, Interscience, New York, 1954.

[26] P.G.T. Fogg, W. Gerrard, Solubility of Gases in Liquids, Wiley, Chichester, 1991.

[27] P. Lühring, A. Schumpe, J. Chem. Eng. Data (1989) 250.
[28] M. Beller, R. Jackstell, unpublished results.
[29] C.R. Landis, J. Halpern, J. Am. Chem. Soc. 109 (1987) 1746.
[30] H. Neumann, K. Wannowius, W. Baumann, R. Thede, D. Heller, submitted for publication.
[31] (a) R.G. Ball, N.C. Payne, Inorg. Chem. 16 (1977) 1187. (b) E.P. Kyba, R.E. Davis, P.N. Juri, K.R. Shirley, Inorg. Chem. 20 (1981) 3616. (c) M.P. Anderson, L.H. Pignolet, Inorg. Chem. 20 (1981) 4101. (d) J. Oliver, D.P. Riley, Organometallics 2 (1983) 1032. (e) M.J. Burk, J.E. Feaster, R.L. Harlow, Tetrahedron: Asymm. 2 (1991) 569. (f) S.K. Armstrong, J.M. Brown, M.J. Burk, Tetrahedron Lett. 34 (1993) 879. Reviews on structures of chiral rhodium complexes are found in J.M. Brown, P.L. Evans, Tetrahedron 44 (1988) 4905 or H. Brunner, A. Winter, J. Breu, J. Organomet. Chem. 553 (1998) 285.
[32] D. Heller, Habilitationsschrift, Emst-Moritz-Arndt-Universität, Greifswald, 1998.
[33] B.F.M. Kimmich, E. Somsook, C.R. Landis, J. Am. Chem. Soc. 120 (1998) 10115.
[34] It must be mentioned here that the NBD complexes of ligands with cyclohexyl instead of phenyl residues (DCPB 1,4-bis(dicyclohexylphosphino)butane, DCPE 1,2 bis(dicyclohexylphosphino)ethane) are still the more reactive species but also exhibit greater distortions from the square-planar arrangement (R. Kempe, A. Spannenberg, D. Heller, Z. Kristallogr. (in press). R. Kempe, A. Spannenberg, H.-J. Drexler, D. Heller, Z. Kristallogr. (in press)). The role of the cyclohexyl ligand in such situations is still unexplored.
[35] J. Bakos, I. Toth, B. Heil, G. Szalontai, L. Parkanyi, V. Fülüp, J. Organomet. Chem. 370 (1989) 263.
[36] (a) R. Kempe, A. Spannenberg, D. Heller, Z. Kristallogr. 213 (1998) 636. (b) A. Spannenberg, H.-J. Drexler, D. Heller, Z. Kristallogr. (in press).
[37] The problem of induction periods is by no means restricted to asymmetric hydrogenation, but is a general phenomenon in homogeneous catalysis whenever precatalysts are used. This has been shown for the photocatalysed [2 + 2 + 2] cycloaddition of alkynes with nitriles, for instance: B. Heller, D. Heller, G. Oehme, J. Mol. Catal. A 110 (1996) 211.
[38] R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 93 (1971) 2397.
[39] G.M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997.
[40] G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.