Kinetic Investigations of the Hydrogenation of Diolefin Ligands in Catalyst Precursors for the Asymmetric Reduction of Prochiral Olefins, II[1]

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Asymmetric hydrogenations of prochiral olefines by means of chiral rhodium(I) complexes of the type [Rh(L)(PP*)]A (L = COD, [(Z,Z)-cycloocta-1,5-diene], or NBD (norborna-2,5-diene), PP* = chiral bisphosphane forming seven-membered chelate rings, A = anion like BF_4^-) are often associated with induction periods caused by partial blocking of the catalyst. NBD complexes are hydrogenated faster than the corresponding COD complexes. Catalytic hydrogenation of COD/NBD mixtures and the determination of the ratio of the Michaelis constants showed that the steady-state concentration of the COD complex under hydrogen is higher than that of the NBD complex. However, under argon the NBD complex predominates owing to its higher thermodynamic stability compared with that of the COD complex as determined by ^{31}P-NMR spectoscopy. This complete reversion of the thermodynamically determined ratios of COD to NBD complex concentration under hydrogenation conditions was proven by means of UV/Vis spectroscopy.

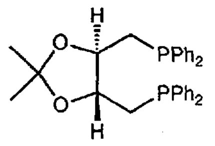
The asymmetric hydrogenation of olefins by seven-membered ring chelates of the type [Rh(bisolefin)(PP*)]BF_4 is often accompanied by an induction period. In ref.[1] we could show that this is the result of the concomitant hydrogenation of the bisolefin [usually (*Z*,*Z*)-cycloocta-1,5-diene (COD) or norborna-2,5-diene (NBD)][2].

The bisolefins partly block the active catalyst by coordination to rhodium. This was demonstrated experimentally by prehydrogenation of the precatalyst (in the absense of the prochiral olefin) and subsequent addition of prochiral substrate, or by using COD-free complexes. Only after complete hydrogenation of the bisolefin ligand does the full amount of catalyst become accessible for asymmetric hydrogenation. On the basis of the experimentally confirmed Michaelis-Menten kinetics the rate constants of the hydrogenation of COD and NBD by different chiral catalysts were determined (Table 1).

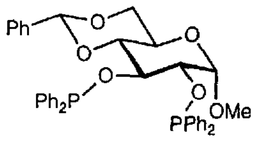
All investigated catalysts hydrogenated NBD faster than COD, in some cases considerably faster. Additionally, rate constants which differ by up to a factor of 50, were obtained for the hydrogenation of a bisolefin with different catalysts. Generally, methanol was used as solvent, however, similar results were obtained in other solvents, e.g. THF (ligands **1** and **7** in Table 1).

The induction period, observed for several catalysts (ligands **3**, **4**, **5**), which accompanies the catalytic hydrogenation of NBD with COD complexes (Figure 1) indicates that the Michaelis constant (K_M) for the COD hydrogenation is smaller than for the NBD hydrogenation.

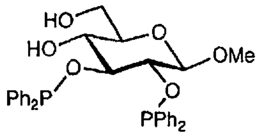
Rates of the hydrogenation of COD/NBD ≅ 1:1 mixtures are lower than expected. Product analysis after



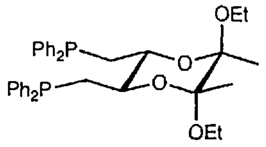
(*R*,*R*)-DIOP **1**



Me-α-glup **2**



Ph-β-glup-OH **3**



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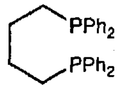
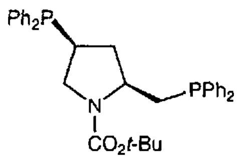
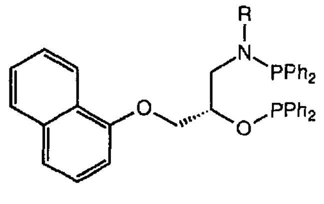


DPPB **5**



BPPM **6**



	R
7	c-C_6H_{11}
8	Et_2CH
9	i-Pr
10	c-C_5H_9
11	Me

(*S*)-Propraphos and derivatives **7** - **11**

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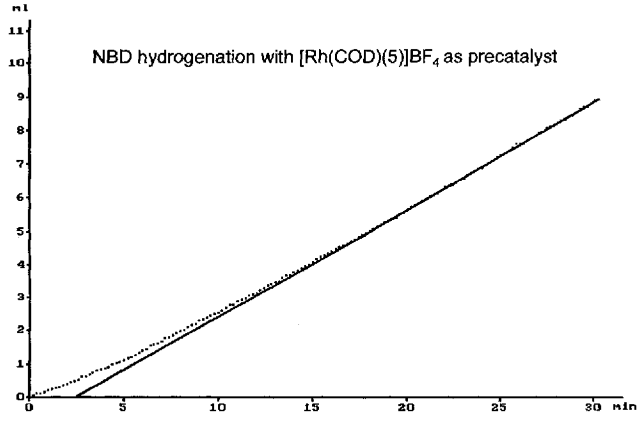
Table 1. Constants for the hydrogenation of COD and NBD with cationic Rh complexes of the type [Rh(L)PP*]A (L: cyclic bisolefin; PP* = chiral bisphosphane and A = anion like BF_4^-) at 25 °C, 1.0 atm total pressure in MeOH

Ligand	Ref.	$k_{2_{COD}}$ [1 / min]	$k_{2_{NBD}}$ [b] [1 / min]	$\frac{k_{2_{NBD}}}{k_{2_{COD}}}$	const. [d, e]	$\frac{K_{M_{NBD}}}{K_{M_{COD}}}$ [f]
1	[3]	0.23	1.29	5.6	0.55	3.1
		(0.22)[a]	(1.27)[c]	–	–	–
		THF: 0.25	–	–	–	–
2	[4]	0.37	13.40	36.2	0.07	2.5
3	[5]	0.20	9.52	47.6	0.14	6.6
		(0.19)[a]	(11.1)[c]	–	–	–
4	[6]	0.14	1.11	7.9	0.56	4.4
5	[7]	0.16	1.25	7.8	0.57	4.5
6	[8]	0.22	1.20	5.5	0.59	3.2
7	[9]	5.44	20.17	3.7	0.62	2.3
		THF: 2.63	–	–	–	–
8	[9]	4.09	21.48	5.3	–	–
9	[9]	3.77	21.96	5.8	0.54	3.1
10	[9]	2.94	18.40	6.3	–	–
11	[9]	0.53	8.20	15.5	–	–

[a] Calculated from initial rate of stoichiometric hydrogenations. – [b] With COD complexes (induction period). – [c] With NBD complexes (without induction period). – [d] See eqn. (3). – [e] Standard deviation: ±5–8%. – [f] See eqs. (1) and (2).

Figure 1. Part of the hydrogen absorption curve of the catalytic NBD hydrogenation with [Rh(COD)(5)]BF_4 (0.01 mmol of precatalyst, 1.0 mmol of NBD, 15.0 ml of MeOH, 25.0 °C, total pressure 1.0 atm)



quenching shows a higher amount of products of COD hydrogenation despite the smaller COD hydrogenation rate constant. Obviously, the faster hydrogenation of the NBD complex is partly compensated for by the preequilibria (Scheme 1) which favour the coordination of COD, and not of NBD, at rhodium. That means, in the presence of COD the catalyst discriminates NBD hydrogenation. This discovery allows the conclusion that the higher rate of hydrogenation of NBD as sole substrate does not guarantee that the initial disturbance caused by partial blockage of the catalyst by diolefines in the hydrogenation of prochiral olefines will be overcome by application of NBD instead of COD carrying precatalysts.

Results and Discussion

To obtain quantitative data about the ratio of both Michaelis constants, mixtures of COD and NBD were hydrogenated. In ref.[1] it was shown that the hydrogenation of COD as well as of NBD follows a simple Michaelis-Menten kinetic. Under steady-state conditions equations (1) and (2) (Scheme 1) describe the competitive hydrogenation of COD and NBD.

Equation (3), which is valid at any time *t*, results from the ratio of product formation rates after integration[10].

Application of this equation to the catalytic hydrogenation of COD/NBD mixtures yields a relation well-known in the literature[11]. Samples of the reaction mixtures were taken continuously as described in ref.[12] and analyzed by gas chromatography. Values for "const." were thus obtained as the slopes of the zero-point lines according to eq. (3) and are listed in Table 1. Within experimental error the slopes are independent of the initial ratios COD/NBD. Figure 2 shows the results for selected catalysts.

The values of "const." as listed in Table 1 for different catalysts show that $k_{2_{COD}} \cdot K_{COD}/k_{2_{NBD}} \cdot K_{NBD}$ is smaller than one. Also the corresponding hydrogen absorption graphs of the substrate mixtures and their characteristic bend (Figure 3), which is independent of the composition of the substrate mixture, verify values for "const." in that range[13].

Since the ratios of the rate constants are known, the ratios of the Michaelis constants for NBD and COD also may be determined (see final column in Table 1). It is obvious that in all investigated cases this ratio is greater than one; if preequiblibria have become established, it is the ratio of reciprocal stability constants. The Michaelis constant for the hydrogenation of COD is consequently smaller than that for the hydrogenation of NBD.

It may be shown that the ratio of the reciprocal Michaelis constants under hydrogenation conditions is related to the steady-state concentration of the bisolefin complex by eq. (4).

It follows from eq. (4) that by starting from equal NBD und COD concentrations under hydrogenation conditions the concentration of the COD complex becomes higher than that of the corresponding NBD complex, and this is in good agreement with the orienting experiments outlined above, whereby it is irrelevant if preequilibria are established or disturbed.

In order to investigate the ratios of the thermodynamic stabilities of two competing bisolefin complexes[14], we converted different catalyst (ligands **1**, **3**, **5** and **7**) into the corresponding solvent complexes by complete hydrogenation in methanol. Addition of an excess mixture of NBD/COD (composition determined by ^1H- and ^{13}C-NMR analysis; see Experimental) gave a mixture of bisolefin complexes which was subsequently analyzed by ^{31}P-NMR spectroscopy. The spectra show the signals of the NBD com-

Scheme 1

$$\mathrm{E + COD} \underset{k_{-1_{\mathrm{COD}}}}{\overset{k_{1_{\mathrm{COD}}}}{\rightleftharpoons}} \mathrm{ECOD} \xrightarrow{k_{2\,\mathrm{COD}}} \mathrm{COE + (E)}$$

$$\mathrm{E + NBD} \underset{k_{-1_{\mathrm{NBD}}}}{\overset{k_{1_{\mathrm{NBD}}}}{\rightleftharpoons}} \mathrm{ENBD} \xrightarrow{k_{2\,\mathrm{NBD}}} \mathrm{NBE + (E)}$$

$$r_{\mathrm{COE}} = \frac{k_{2_{\mathrm{COD}}} \bullet K_{\mathrm{COD}} \bullet [\mathrm{COD}] \bullet [\mathrm{E_0}]}{1 + K_{\mathrm{NBD}} \bullet [\mathrm{NBD}] + K_{\mathrm{COD}} \bullet [\mathrm{COD}]} \quad \text{with } K_{\mathrm{COD}} = \frac{k_{1_{\mathrm{COD}}}}{(k_{-1_{\mathrm{COD}}} + k_{2_{\mathrm{COD}}})} = \frac{1}{K_{\mathrm{M_{COD}}}} \quad (1)$$

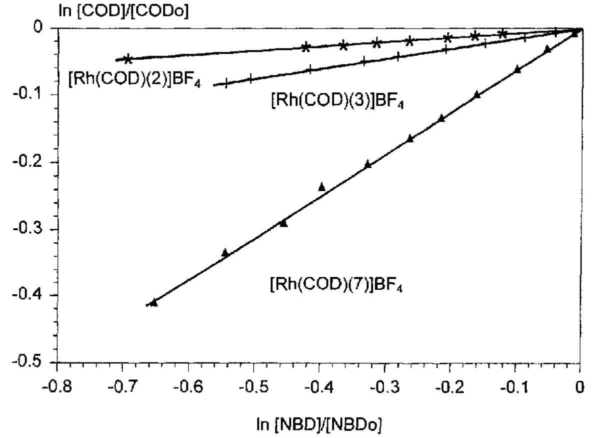
$$r_{\mathrm{NBE}} = \frac{k_{2_{\mathrm{NBD}}} \bullet K_{\mathrm{NBD}} \bullet [\mathrm{NBD}] \bullet [\mathrm{E_0}]}{1 + K_{\mathrm{NBD}} \bullet [\mathrm{NBD}] + K_{\mathrm{COD}} \bullet [\mathrm{COD}]} \quad \text{with } K_{\mathrm{NBD}} = \frac{k_{1_{\mathrm{NBD}}}}{(k_{-1_{\mathrm{NBD}}} + k_{2_{\mathrm{NBD}}})} = \frac{1}{K_{\mathrm{M_{NBD}}}} \quad (2)$$

(r_i = rate of product formation, k_i = rate constant, $k_{2j} = k_{2j}^{*} \bullet [\mathrm{H_2}]$ respectively, E = solvent complex, COE = cyclooctene, NBE = norbornene).

$$\ln\frac{[\mathrm{COD}]}{[\mathrm{COD_0}]} = \left(\frac{k_{2_{\mathrm{COD}}} \bullet K_{\mathrm{COD}}}{k_{2_{\mathrm{NBD}}} \bullet K_{\mathrm{NBD}}}\right) \bullet \ln\frac{[\mathrm{NBD}]}{[\mathrm{NBD_0}]} = \mathrm{const} \bullet \ln\frac{[\mathrm{NBD}]}{[\mathrm{NBD_0}]} \quad (3)$$

$$\frac{[\mathrm{ECOD}]}{[\mathrm{ENBD}]} = \frac{K_{\mathrm{COD}} \bullet [\mathrm{COD}]}{K_{\mathrm{NBD}} \bullet [\mathrm{NBD}]} \quad (4)$$

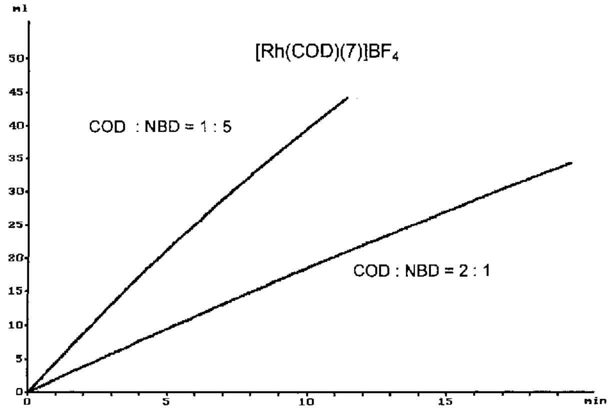
Figure 2. Hydrogenation of COD/NBD – mixtures with different catalysts and plot according to equation (3) $[\mathrm{Rh(COD)(\mathbf{2})]BF_4}$: 0.01 mmol, 1.21 mmol of COD, 2.88 mmol of NBD; $[\mathrm{Rh(COD)(\mathbf{3})]BF_4}$: 0.02 mmol, 2.45 mmol of COD, 1.66 mmol of NBD; $[\mathrm{Rh(COD)(\mathbf{7})]BF_4}$: 0.01 mmol, 3.19 mmol of COD, 1.46 mmol of NBD; 15.0 ml of MeOH, 25.0 °C, total pressure 1.0 atm)



plexes to be predominant (see Fig. 4) and allow the ratios of the stability constants K_i^* to be determined.

NMR experiments also showed that NBD displaces coordinated COD upon addition of a COD/NBD mixture to the COD complex. In some cases the considerably larger formation constants of the NBD complexes allow a simple synthesis of the NBD complexes from COD complexes which are sometimes more easily prepared[15].

Figure 3. Hydrogen absorption curves for the hydrogenation of COD/NBD mixtures with 0.01 mmol of $[\mathrm{Rh(COD)(\mathbf{7})]BF_4}$ in MeOH at 25.0 °C and 1.0 atm total pressure



Whereas in all investigated cases the NBD complex shows higher stability under argon (Table 2), the COD complexes predominate under hydrogen [Table 1 column 7; eq. (4)][16].

This could easily be proven by means of UV/Vis spectroscopy (see Figure 5). A short while (1–2 min) after the exchange of argon by hydrogen, the lower spectrum in Figure 5 was obtained. A gas chromatographic analysis of the reaction mixture indicates that 96% of the NBD substrate remained unchanged.

Our results indicate that the thermodynamically determined ratios of the bisolefin complex concentrations

Figure 4. ^{31}P NMR spectra of $[Rh(NBD)(3)]BF_4$ and $[Rh(COD)(3)]BF_4$ (a) and spectrum after reaction of the solvent complex with an excess of COD/NBD mixture (b)

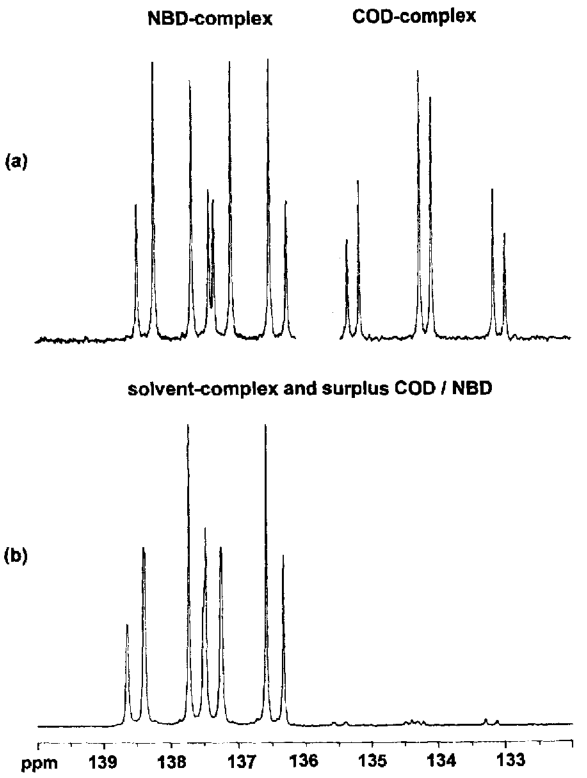


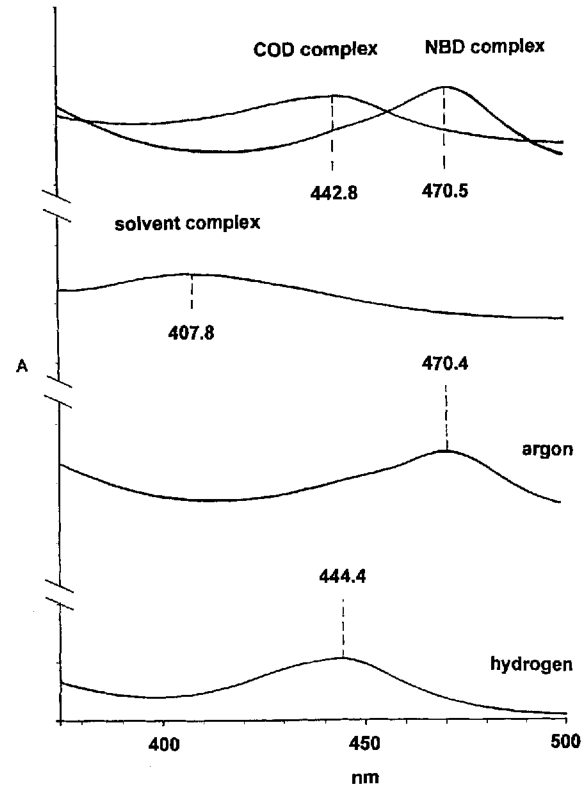
Table 2. Ratios of NBD/COD formation constants K_f^* for different complexes $[Rh(bisolefin)(PP^*)]BF_4$

$$\left(K^*_{\mathrm{NBD}} = \frac{[\mathrm{ENBD}]}{[\mathrm{E}]\bullet[\mathrm{NBD}]} = \frac{k_{1_{\mathrm{NBD}}}}{k_{-1_{\mathrm{NBD}}}} \quad \text{and} \quad K^*_{\mathrm{COD}} = \frac{[\mathrm{ECOD}]}{[\mathrm{E}]\bullet[\mathrm{COD}]} = \frac{k_{1_{\mathrm{COD}}}}{k_{-1_{\mathrm{COD}}}}\right)$$

Ligand (PP*)	$K^*_{\mathrm{NBD}} / K^*_{\mathrm{COD}}$
(1)	2.3
(3)	33.3
(5)	1.7
(7)	> 100

$[Rh(COD)(PP^*)]BF_4$ and $[Rh(NBD)(PP^*)]BF_4$ invert during the hydrogenation of COD/NBD mixtures by cationic chiral Rh(I) complexes. Eventually, such effects have to be considered in asymmetric hydrogenation, e. g. concerning the interpretation of pressure dependence of stereoselection[17] (k_2, rises under isobaric conditions with increasing partial pressure). Concerning the change of ratios of thermodynamically determined major-minor diastereoisomers in asymmetric hydrogenation of prochiral substrates, it must be taken into account that these diastereomers are derived from only one substrate. It has recently been pointed out on seven-membered ring chelates[18] that the diastereomers may interchange the substrate predominantly through intramolecular equilibria, that means under rotation of the partly bound substrate.

Figure 5. UV/Vis spectra of $[Rh(COD)(3)]BF_4$ and $[Rh(NBD)(3)]BF_4$, respectively, and the corresponding solvent complex. The two bottom spectra show the solvent complex treated with an excess of COD/NBD mixture under argon or hydrogen (0.02 mmol of precatalyst in 40.0 ml of MeOH, 25.0 °C)



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Experimental

All anaerobic procedures were carried out as usual. Hydrogen (AGA 6.0) was used as received.

Hydrogenations: All experiments were performed under isobaric conditions using an automatic gas-measuring apparatus. For setup and performance of hydrogenation experiments see ref.[1]. Substrates were introduced into the reaction vessel anaerobically as defined solutions. Experiments were carried out at 25.0 °C and standard pressure. Atmospheric pressure was taken as reference and corrected to 1.0 atm in the evaluation.

Substrates: (*Z*,*Z*)-cycloocta-1,5-diene (COD) and norborna-2,5-diene (NBD) were purchased commercially, dried and distilled under argon.

Analysis: COD, NBD, and its hydrogenation products were detected directly from the reaction mixture by gas chromatography: HP 5890 series 2; FID, carrier gas argon: 1 ml/min: fused silica, 50 m HP 1; ID 0.2 mm; furnace temperature 90 °C.

NMR: Bruker ARX 400 (^1H at 400.13 MHz, ^{31}P at 161.98 MHz, ^{13}C at 100.61 MHz), ambient temperature (25 °C), solvent $[D_4]$-methanol. ^{31}P-NMR data of the complexes $[Rh(L)(PP^*)]BF_4$:

PP* = **1**, L = COD: δ = 12.9, ^{1}J(P,Rh) = 144 Hz. – PP* = **1**, L = NBD: δ = 16.9, ^{1}J(P,Rh) = 154 Hz. – PP* = **3**, L = COD: δ_A = 134.7, δ_B = 133.6, ^{2}J(P,P) = 29 Hz, $^{1}J(P_A$,Rh) = 177 Hz, $^{1}J(P_B$,Rh) = 178 Hz. – PP* = **3**, L = NBD; δ_A = 137.8, δ_B = 137.0, ^{2}J(P,P) = 41 Hz, $^{1}J(P_A$,Rh) = 184 Hz, $^{1}J(P_B$,Rh) = 185 Hz. – PP* = **5**, L = COD: δ = 24.5, ^{1}J(P,Rh) = 143 Hz. – PP* = **5**, L = NBD: δ = 27.6, ^{1}J(P,Rh) = 153 Hz. – PP* = **7**, L = COD: δ_A = 124.8, δ_B = 81.0, ^{2}J(P,P) = 27 Hz, $^{1}J(P_A$,Rh) = 173 Hz, $^{1}J(P_B$,Rh) = 158 Hz. – PP* = **7**, L = NBD: δ_A = 126.8, δ_B = 88.6; ^{2}J(P,P) = 38 Hz, $^{1}J(P_A$,Rh) = 181 Hz, $^{1}J(P_B$,Rh) = 169 Hz.

Quantitative Measurements: The composition of the NBD/COD mixture used for the determination of ratios of formation constants[14] was determined by NMR spectroscopy. 5 mg $Cr(acac)_3$ was added to the sample to ensure complete relaxation. ^{1}H and ^{13}C measurements revealed a molar ratio of [NBD]/[COD] = 1.08 : 1.00. The ratio of [ENBD]/[ECOD] was determined by ^{31}P-NMR analysis. Complexes $[Rh(L)(PP^*)]BF_4$ were converted into the corresponding solvent complexes by hydrogenation in methanol. Subsequently a surplus mixture of NBD/COD was added (molar ratio complex/sum of dienes = 1 : 100). For quantitative evaluation ^{31}P-NMR spectra were recorded with 30° pulses at intervals of 10 s with "inverse gated" ^{1}H decoupling. (For L = **3** and **7** the T_1 times of phosphorus were estimated by the inversion-recovery method to be about 1 s). The following molar ratios [ENBD]/[ECOD] were determined: PP* = **1**: 2.5; PP* = **3**; 36.0; PP* = **5**: 1.8; PP* = **7**: no COD complex could be detected by ^{31}P-NMR, [ENBD]/[ECOD] is presumably larger than 100.

Ligand **3** was shown to establish the same ratio [ENBD]/[ECOD] irrespective of the addition of the COD/NBD mixture to the diene complex $[Rh(COD)(\mathbf{3})]BF_4$ or to the solvent complex $[Rh(\mathbf{3})(CD_3OD)_2]Bf_4$.

UV/Vis: Perkin Elmer lambda 19. For on-line measurement an optical fibre light guide connected to a submersible optrode (Hellma) was used (Suprasil; path length 0.5 cm). An integrated standard ground glass joint allows a simple handling in thermostated glass vessels under anaerobic conditions or hydrogen. Spectra were thus recorded with a slit width of 1.0 nm and registration speed of 60 nm/min.

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[10] Provided that at t = 0 cyclooctene (COE) and norbornene (NBE) are absent, and by taking into account the relation COD_0 = COD + COE, integration is feasible.

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[14] From the definition of the thermodynamic stability constants (Table 2) their ratio may be described by: $\frac{K^*_{COD}}{K^*_{NBD}} = \frac{[NBD]\cdot[ECOD]}{[COD]\cdot[ENBD]}$. The ratio **[ECOD]/[ENBD]** may be determined by ^{31}P-NMR analysis (see Experimental). Bacause of the high excess of bisolefin to the rhodium complex, the ratio of the free ligands [NBD]/[COD] is nearly equivalent to the known ratio $[NBD_0]/[COD_0]$ (^{1}H, ^{13}C-NMR respectively). (The error is less than 2% for a concentration ratio of bisolefin to rhodium = 100).

[15] Typical preparation of a NBD complex: to a suspension of 300 mg (0.333 mmol) of $[Rh(COD)(\mathbf{7})]BF_4$ in 40 ml of MeOH 3.37 ml (33.3 mmol) of NBD was added. After stirring for 2 min a dark orange solution was obtained. Removal of the solvent under vacuum yielded the pure NBD complex as revealed by NMR spectroscopy. Even better is the precipitation of the NBD complex from the methanolic solution by diethyl ether.

[16] Reasons for this experimental observation are not yet clear; in addition to the disturbance of the equilibrium by the relative fast hydrogenation of the NBD complex, different formation rates of the bisolefin complexes might be important.

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