Supporting Information

Major-minor concept revisited: Causes for the *reversal* of thermodynamically determined intermediate ratios under reaction conditions

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Experimental

General

All experiments were carried out using standard Schlenk techniques under oxygen- and moisture-free conditions. MeOH was dried on magnesia and freshly distilled under argon prior to use. Methanol-d_4, (*Z,Z*)-Cycloocta-1,5-diene (TCI, 98%) and norborna-2,5-diene (TCI, 97%) were dried on calcium hydride, distilled under argon and the oxygen removed in six freeze-pump-thaw cycles. [Rh(ACAC)(NBD)], [Rh(ACAC)(COD)] (Sigma-Aldrich, 99%), DIOP (Strem, 99.5%) and DPPB (Sigma-Aldrich, 98%) were used as received.

UV-vis spectroscopic measurements

All reactions were investigated under anaerobic conditions using a Perkin Elmer Lambda 19 connected to a fiber-optical sensor in a temperature-controlled vessel (298 K). Spectra were thus recorded with a slit width of 1.0 nm and registration speed of 60 nm·min^{-1}. Stopped-flow measurements were carried out using a Durrum, D-110 spectrometer.

Qualitative representation of intermediate reversal (Figure 1)
0.005 mmol **1a** was dissolved in 20 mL MeOH (25 °C) and 2.0 mmol NBD and 2.0 mmol COD were added. After equilibration (20 min) a spectrum was recorded (380-500 nm) under Ar. The atmosphere was exchanges to H_2 in the following and after 12 min and 16 min new spectra were recorded.

Reaction of **1b** in MeOH (Figure 2)
0.00505 mmol **1b** was dissolved in 20 mL MeOH (25 °C). The first spectrum was recorded, directly after the solvent addition. A spectrum (375-460 nm) was recorded every 38 s until equilibrium was reached (ca. 30 min).

Reaction of **1b** with a mixture of NBD and COD in MeOH (Figure 4)
0.01 mmol **1b** was dissolved in 20 mL MeOH (25 °C) and 1.0 mmol COD was added. After equilibration (30 min) a spectrum was recorded (350-500 nm). 0.87 mmol NBD was added and with the addition of NBD, spectra were recorded every 240 s until equilibrium was reached (ca. 60 min).

Reaction of **1b** with NBD (Figure 5)
0.0098 mmol **1b** was dissolved in 20 mL MeOH (25 °C) and after equilibration (30 min) a spectrum was recorded (350-550 nm). 1.0 mmol NBD was added and with the addition of NBD, spectra were recorded every 240 s until equilibrium was reached (ca. 60 min).

NMR Spectroscopy

^{1}H and ^{31}P NMR spectra were recorded on Bruker ARX 400 spectrometers or Magritek Spinsolve 80 at room temperature (297-298 K). Chemical shifts (δ) are internally referenced to the chosen deuterated solvent and externally referenced, respectively, to tetramethylsilane (TMS) for ^{1}H NMR or 85% H_3PO_4 solution for ^{31}P NMR.

Simulations

Simulations were performed using COPASI.[1] The following kinetic models, parameters and initial concentrations were used:
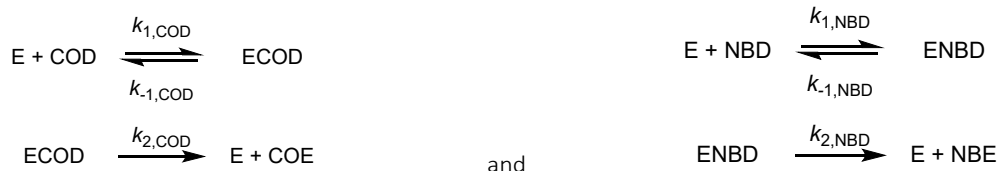
$$E + COD \underset{k_{-1,COD}}{\overset{k_{1,COD}}{\rightleftharpoons}} ECOD$$

$$ECOD \xrightarrow{k_{2,COD}} E + COE$$

and

$$E + NBD \underset{k_{-1,NBD}}{\overset{k_{1,NBD}}{\rightleftharpoons}} ENBD$$

$$ENBD \xrightarrow{k_{2,NBD}} E + NBE$$

Table S 1: Experimentally determined rate constants for the hydrogenation of a NBD/COD mixture with [Rh(**b**)(MeOH)$_2$]$^+$, used for the simulations.

Rate constants	a	b	c
k_{1COD}/ Lmol^{-1}s^{-1}	145	18	232
k_{1NBD}/ Lmol^{-1}s^{-1}	59	85	136
k_{-1COD}/ s^{-1}	1.2·10^{-5}	0.0011	3·10^{-5}
k_{-1NBD}/ s^{-1}	1.4·10^{-6}	0.00031	2.2·10^{-6}
k_{2COD}/ s^{-1}	3.8·10^{-3}	0.0033	2.7·10^{-3}
k_{2NBD}/ s^{-1}	2.1·10^{-2}	0.22	2.1·10^{-2}

Table S 2: Initial concentrations used for the simulations.

compound	c_0/L·mol^{-1}
[Rh(**a**)(MeOH)$_2$]$^+$	0.0005
[Rh(**b**)(MeOH)$_2$]$^+$	0.0005
[Rh(**c**)(MeOH)$_2$]$^+$	0.0005
1a	0
1b	0
1c	0
2a	0
2b	0
2c	0
COD	0.05
NBD	0.0435
COE	0
NBE	0

Synthesis of Diolefin Complexes

General Synthesis of [Rh(PP)(diolefin)]BF$_4$

All [Rh(PP)(diolefin)]BF$_4$ (PP = DPPB, DIOP, *β*-Ph-glup-OH; diolefin = COD, NBD) complexes were synthesized similar to the synthesis developed by Schrock and Osborn.[2] 0.1 mmol [Rh(ACAC)(diolefin)] was dissolved in 5 mL THF and cooled down to -78 °C. A solution of 0.1 mmol PP in THF was dropwise added to the cooled complex solution. After one hour, 100 µL HBF$_4$ were added and stirred at -78 °C for further 30 min. The solution was layered with Et$_2$O and the resulting crystals washed three times with Et$_2$O and dried in vacuum.

Data and Spectra of Diolefin Complexes

<u>**1a**</u> – [Rh(DIOP)(COD)]BF$_4$

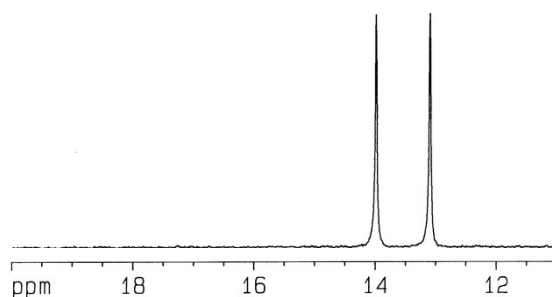Figure S 1: ^{31}P NMR spectrum of [Rh(**a**)(COD)]BF$_4$ (162 MHz, δ = 12.8 ppm (d, 144 in MeOD.

2a – [Rh(DIOP)(NBD)]BF$_4$
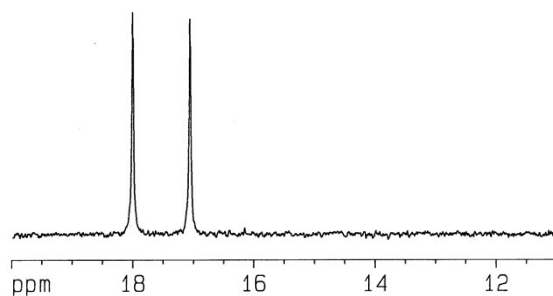
Figure S 2: ^{31}P NMR spectrum of [Rh(**a**)(NBD)]BF$_4$ (162 MHz, δ = 16.8 ppm (d, 153 in MeOD.

1b – [Rh(Ph-β-glup-OH)(COD)]BF$_4$ and **2b** – [Rh(Ph-β-glup-OH)(NBD)]BF$_4$
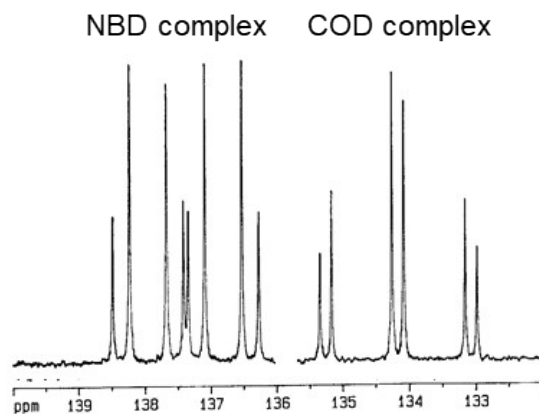

Figure S 3: ^{31}P NMR spectrum of [Rh(**b**)(COD)]BF$_4$ (162 MHz, δ = 133.6 ppm (dd, 178 Hz, 29 Hz); 134.7 ppm (dd, 177 Hz, 29 Hz))and [Rh(**b**)(NBD)]BF$_4$ (162 MHz, δ = 137.0 ppm (dd, 185 Hz, 41 Hz); 137.8 ppm (dd, 184 Hz, 41 Hz)) in MeOD.
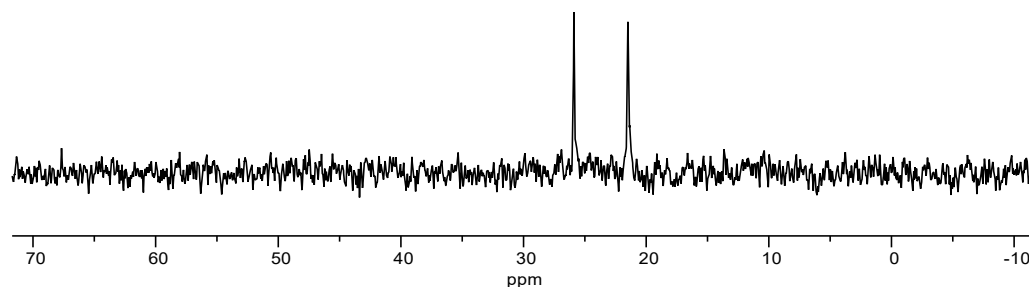
1c – [Rh(DPPB)(COD)]BF$_4$

Figure S 4: ^{31}P NMR spectrum of [Rh(**c**)(COD)]BF$_4$ (33 MHz, δ = 24.2 ppm (d, 143 in MeOD
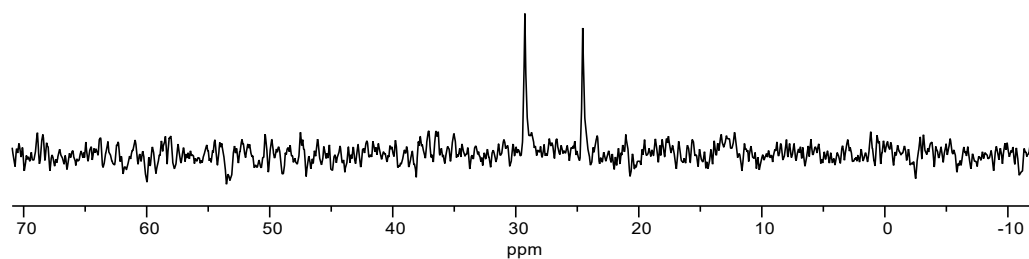
2c – [Rh(DPPB)(NBD)]BF$_4$

Figure S 5: ^{31}P NMR spectrum of [Rh(**c**)(NBD)]BF$_4$ (33 MHz, δ = 27.4 ppm (d, 154 in MeOD
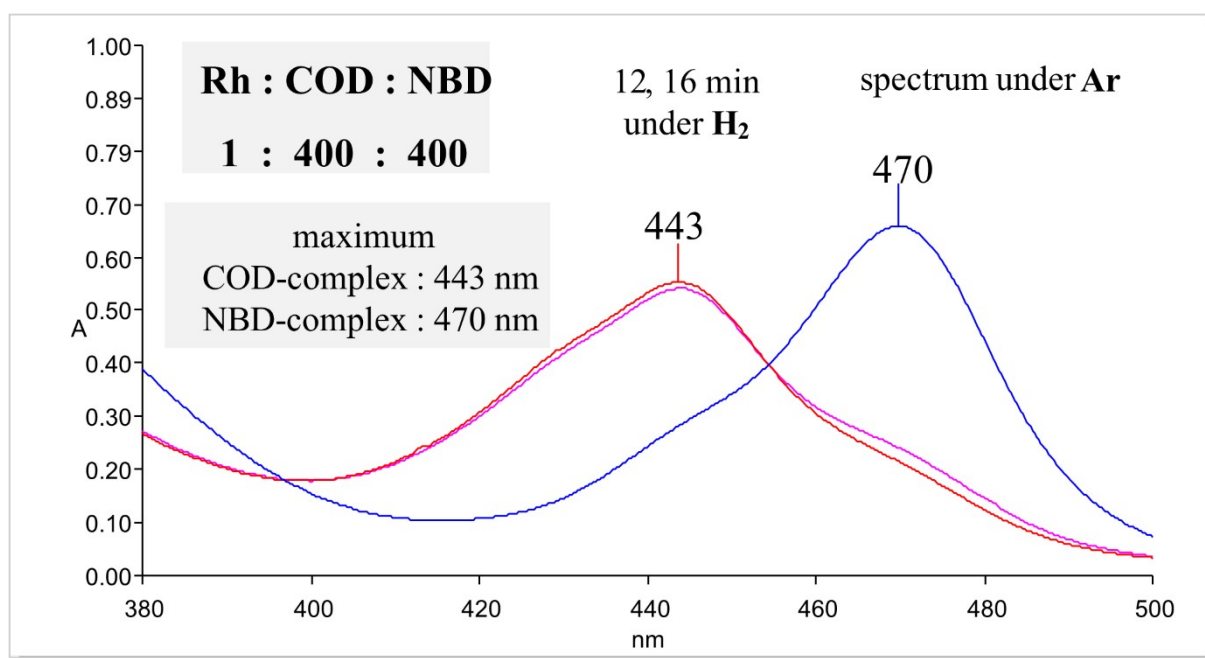
Additional Figures and Tables

Figure S 6: Reversal of thermodynamic determined intermediate ratios for **1b**, resp. **2b**. Composition of the reaction solution after quenching: 95% free NBD, 99.4% free COD (using 0.005 mmol **1b**, 2.0 mmol COD, 2.0 mmol NBD, 20 mL MeOH, T = 25 °C, scan rate 60 nm·min^{-1}).

$k_{-1COD} = 0.0011\ \mathrm{s}^{-1}$
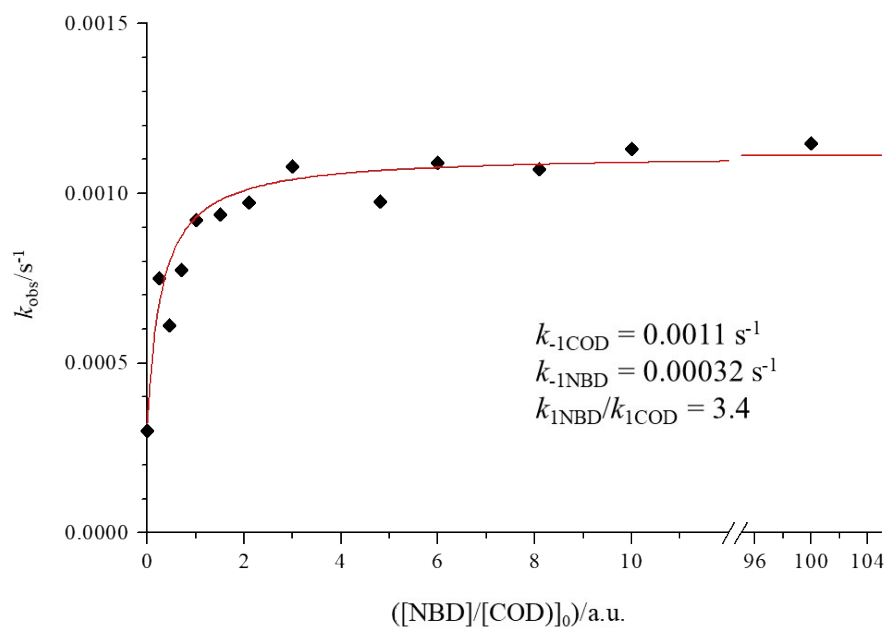
$k_{-1NBD} = 0.00032\ \mathrm{s}^{-1}$

$k_{1NBD}/k_{1COD} = 3.4$

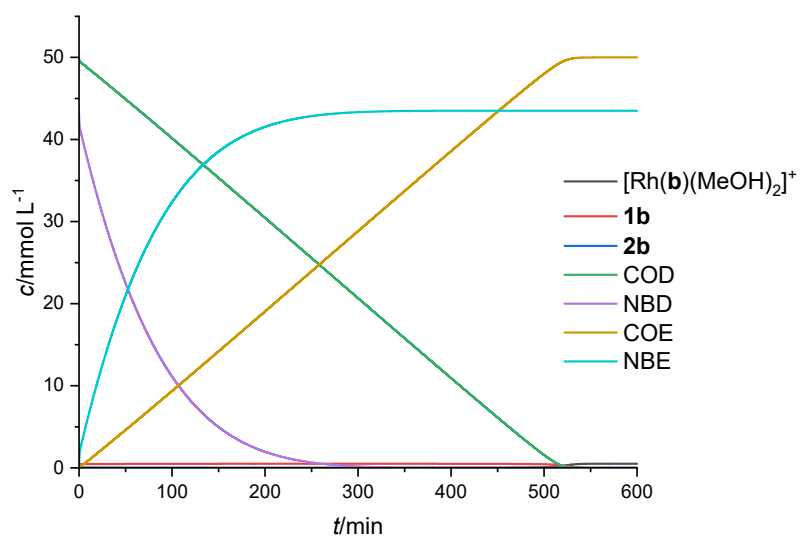Figure S 7: Plot of k_{obs}-values *vs*. concentration of $[NBD]_0/[COD]_0$ in excess (Eq. 5b) for **1b.**

Figure S 8: Simulated concentration-time plot for all species in the COD/NBD hydrogenation using $[Rh(\mathbf{b})(MeOH)_2]^+$ as catalyst. Initial concentrations: $[Rh]_0 = 0.5\ \mathrm{mmol \cdot L}^{-1}$, $[COD]_0 = 50.0\ \mathrm{mmol \cdot L}^{-1}$, $[NBD]_0 = 43.5\ \mathrm{mmol \cdot L}^{-1}$, $[\mathbf{1b}]_0 = [\mathbf{2b}]_0 = [COE]_0 = [NBE]_0 = 0\ \mathrm{mmol \cdot L}^{-1}$ (see Figure 4).

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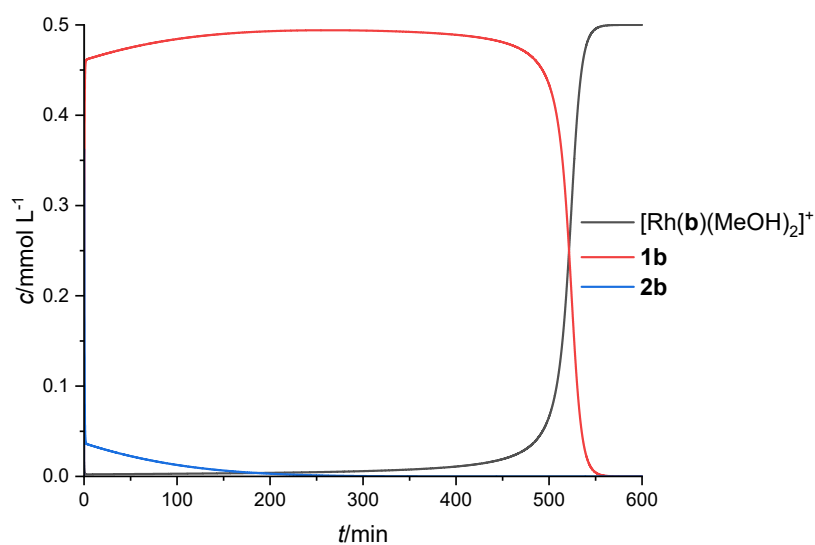
Figure S 9: Simulated concentration-time plot for $[Rh(\mathbf{b})(MeOH)_2]^+$, **1b** and **2b** in the COD/NBD hydrogenation using $[Rh(\mathbf{b})(MeOH)_2]^+$ as catalyst. Initial concentrations: $[Rh]_0 = 0.5$ mmol·L^{-1}, $[COD]_0 = 50.0$ mmol·L^{-1}, $[NBD]_0 = 43.5$ mmol·L^{-1}, $[\mathbf{1b}]_0 = [\mathbf{2b}]_0 = [COE]_0 = [NBE]_0 = 0$ mmol·L^{-1} (see Figure 4).
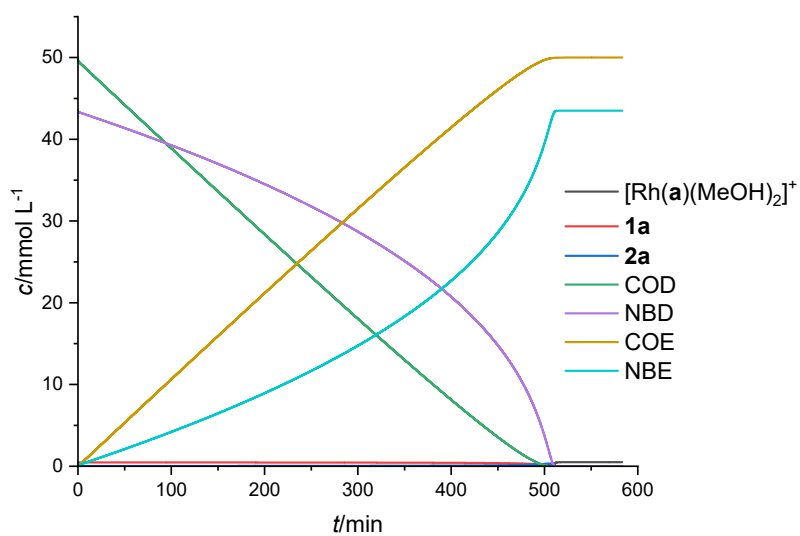

Figure S 10: Simulated concentration-time plot for all species in the COD/NBD hydrogenation using $[Rh(\mathbf{a})(MeOH)_2]^+$ as catalyst. Initial concentrations: $[Rh]_0 = 0.5$ mmol·L^{-1}, $[COD]_0 = 50.0$ mmol·L^{-1}, $[NBD]_0 = 43.5$ mmol·L^{-1}, $[\mathbf{1a}]_0 = [\mathbf{2a}]_0 = [COE]_0 = [NBE]_0 = 0$ mmol·L^{-1} (see Figure 4).
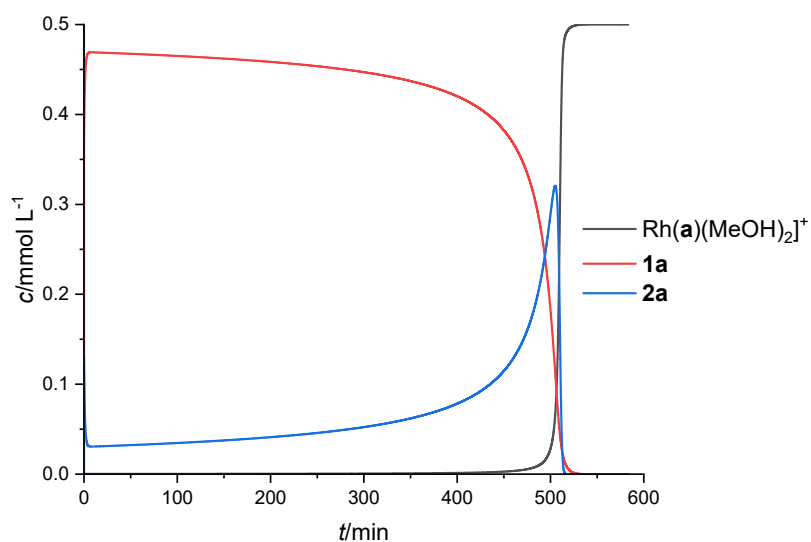
Figure S 11: Simulated concentration-time plot for $[Rh(\mathbf{a})(MeOH)_2]^+$, **1a** and **2a** in the COD/NBD hydrogenation using $[Rh(\mathbf{a})(MeOH)_2]^+$ as catalyst. Initial concentrations: $[Rh]_0 = 0.5$ mmol·L^{-1}, $[COD]_0 = 50.0$ mmol·L^{-1}, $[NBD]_0 = 43.5$ mmol·L^{-1}, $[\mathbf{1a}]_0 = [\mathbf{2a}]_0 = [COE]_0 = [NBE]_0 = 0$ mmol·L^{-1} (see Figure 4).
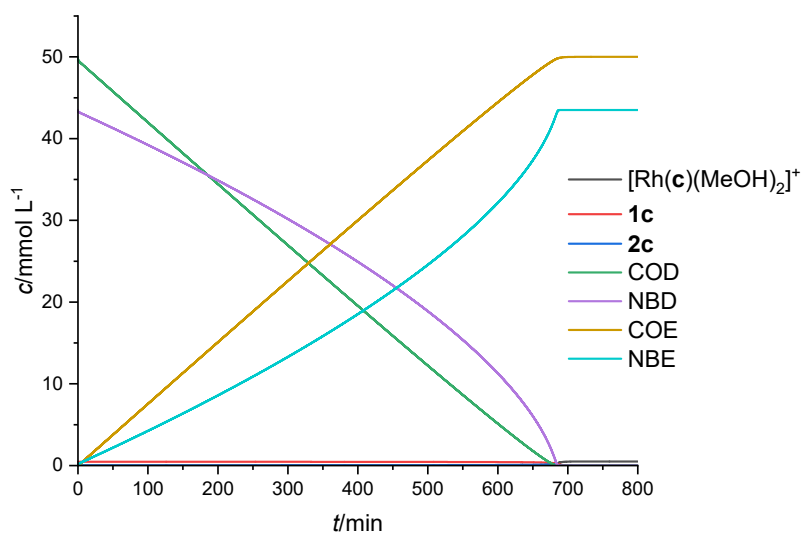

Figure S 12: Simulated concentration-time plot for all species in the COD/NBD hydrogenation using $[Rh(\mathbf{c})(MeOH)_2]^+$ as catalyst. Initial concentrations: $[Rh]_0 = 0.5$ mmol·L^{-1}, $[COD]_0 = 50.0$ mmol·L^{-1}, $[NBD]_0 = 43.5$ mmol·L^{-1}, $[\mathbf{1c}]_0 = [\mathbf{2c}]_0 = [COE]_0 = [NBE]_0 = 0$ mmol·L^{-1} (see Figure 4).
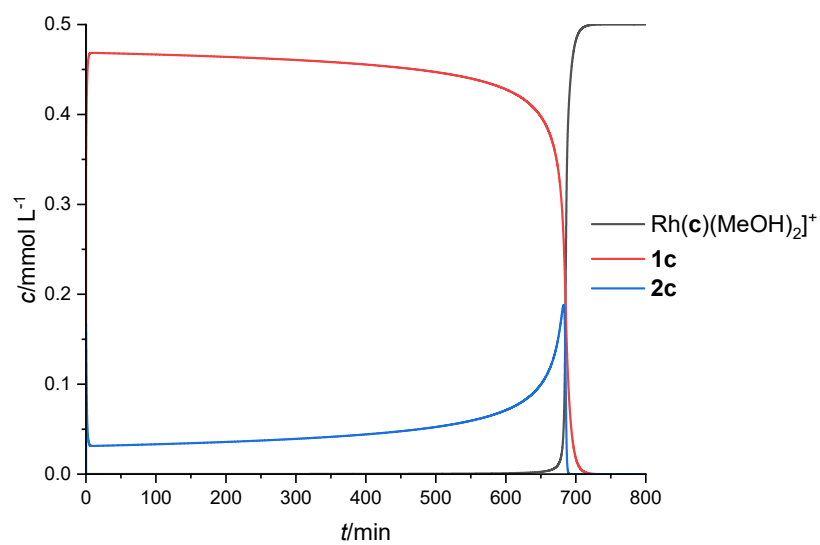
Figure S 13: Simulated concentration-time plot for $[Rh(\mathbf{c})(MeOH)_2]^+$, **1c** and **2c** in the COD/NBD hydrogenation using $[Rh(\mathbf{a})(MeOH)_2]^+$ as catalyst. Initial concentrations: $[Rh]_0 = 0.5$ mmol·L^{-1}, $[COD]_0 = 50.0$ mmol·L^{-1}, $[NBD]_0 = 43.5$ mmol·L^{-1}, $[\mathbf{1c}]_0 = [\mathbf{2c}]_0 = [COE]_0 = [NBE]_0 = 0$ mmol·L^{-1} (see Figure 4).

Derivation of Equations

Equation 4

$$\text{ECOD} \underset{k_{1COD}}{\overset{k_{-1COD}}{\rightleftharpoons}} \text{E + COD}$$

slow (above), fast (below)
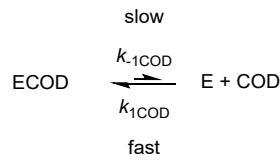
$$\frac{dX}{dt} = X = k_1([A]_0 - X) - k_{-1}X^2 = k_1[A]_0 - X(k_1 + k_{-1}X)$$

$$\Delta E_\lambda = E_{\lambda,t} - E_{\lambda,0} = l(\varepsilon_{\lambda,A}([A]-[A]_0) + \varepsilon_{\lambda,B}([B]-[B]_0) + \varepsilon_{\lambda,C}([C]-[C]_0))$$

$$= l(\varepsilon_{\lambda,A}(-X) + \varepsilon_{\lambda,B}(X) + \varepsilon_{\lambda,C}(X))$$

$$= l(X)(-\varepsilon_{\lambda,A} + \varepsilon_{\lambda,B} + \varepsilon_{\lambda,C})$$

$$X = \frac{E_{\lambda,t} - E_{\lambda,0}}{l(-\varepsilon_{\lambda,A} + \varepsilon_{\lambda,B} + \varepsilon_{\lambda,C})}$$

in which $Q_\lambda = l(-\varepsilon_{\lambda,A} + \varepsilon_{\lambda,B} + \varepsilon_{\lambda,C})$

$$\frac{d}{dt}\frac{E_{\lambda,t} - E_{\lambda,0}}{Q_\lambda} = k_{-1}[A]_0 - k_{-1}X - k_1 X^2 = k_{-1}[A]_0 - k_{-1}\left(\frac{E_{\lambda,t} - E_{\lambda,0}}{Q_\lambda}\right) - k_1\left(\frac{E_{\lambda,t} - E_{\lambda,0}}{Q_\lambda}\right)^2$$

$$\frac{d}{dt}(E_{\lambda,t} - E_{\lambda,0}) = k_{-1}[A]_0 Q_\lambda - k_{-1}(E_{\lambda,t} - E_{\lambda,0}) - \frac{k_1}{Q_\lambda}(E_{\lambda,t} - E_{\lambda,0})^2$$
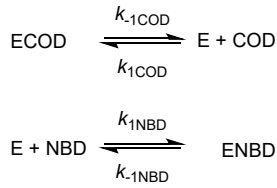
$$E_{\lambda,t} - E_{\lambda,0} = k_{-1}[A]_0 Q_\lambda(t-t_0) - \int_{t_0}^{t}(E_{\lambda,t} - E_{\lambda,0})dt - \frac{k_1}{Q_\lambda}\int_{t_0}^{t}(E_{\lambda,t} - E_{\lambda,0})^2 dt$$

with $\zeta = k_{-1}[A]_0 Q_\lambda$; $\zeta_1 = k_1$ and $\zeta_2 = k_1 Q_\lambda^{-1}$:

$$E_\lambda - E_{\lambda,0} = \zeta(t-t_0) - \zeta_1\int_0^t(E_\lambda - E_{\lambda,0})dt - \zeta_2\int_0^t(E_\lambda - E_{\lambda,0})^2 dt \quad \textbf{(4)}$$

X	extent of reaction
t	time
k	rate constant
$[A], [B], [C]$	concentration
E_λ	extinction
ε_λ	extinction coefficient
l	path length of the beam of light through the material sample

Equation 5

$$\text{ECOD} \underset{k_{1COD}}{\overset{k_{-1COD}}{\rightleftharpoons}} \text{E} + \text{COD}$$

$$\text{E} + \text{NBD} \underset{k_{-1NBD}}{\overset{k_{1NBD}}{\rightleftharpoons}} \text{ENBD}$$

$$\frac{d[\text{ECOD}]}{dt} = -k_{-1COD} + \frac{k^{*}_{1COD} \cdot (k_{-1COD} - k_{-1NBD})}{k^{*}_{1COD} + k^{*}_{1NBD}} \cdot [\text{ECOD}] + \frac{k^{*}_{1COD} \cdot k^{*}_{-1NBD} \cdot [\text{ECOD}]_0}{k^{*}_{1COD} + k^{*}_{1NBD}}$$

In equilibrium:

$$\frac{d[\text{ECOD}]_\infty}{dt} = 0 \Rightarrow \left(k_{-1COD} - \frac{k^{*}_{1COD} \cdot (k_{-1COD} - k_{-1NBD})}{k^{*}_{1COD} + k^{*}_{1NBD}} \right) \cdot [\text{ECOD}]_\infty = \frac{k^{*}_{1COD} \cdot k^{*}_{-1NBD} \cdot [\text{ECOD}]_0}{k^{*}_{1COD} + k^{*}_{1NBD}}$$

$[\text{ECOD}]_0$ can be described by $[\text{ECOD}]^\infty$

$$\frac{d[\text{ECOD}]}{dt} = \left(-k_{-1COD} - \frac{k^{*}_{1COD} \cdot (k_{-1COD} - k_{-1NBD})}{k^{*}_{1COD} + k^{*}_{1NBD}} \right) \cdot [\text{ECOD}] + \left(-k_{-1COD} - \frac{k^{*}_{1COD} \cdot (k_{-1COD} - k_{-1NBD})}{k^{*}_{1COD} + k^{*}_{1NBD}} \right) \cdot [\text{ECOD}]_\infty$$

$$-\frac{d[\text{ECOD}]}{dt} = \left(k_{-1COD} - \frac{k^{*}_{1COD} \cdot (k_{-1COD} - k_{-1NBD})}{k^{*}_{1COD} + k^{*}_{1NBD}} \right) \cdot ([\text{ECOD}] - [\text{ECOD}]_\infty)$$

$$\text{or } -\frac{d[\text{ECOD}]}{[\text{ECOD}] - [\text{ECOD}]_\infty} = \left(k_{-1COD} - \frac{k^{*}_{1COD} \cdot (k_{-1COD} - k_{-1NBD})}{k^{*}_{1COD} + k^{*}_{1NBD}} \right) \cdot dt$$

with substitution:

$$z = ([\text{ECOD}] - [\text{ECOD}]_\infty) \text{ or } \frac{dz}{d[\text{ECOD}]} = 1$$

it follows:

$$d[\text{ECOD}] = dz \text{ or } -\frac{dz}{z} = d\ln(z) \text{ ; } \int d\ln(z) = \ln(z)$$

The solution of this integration is Equation (5):

$$\ln\left(\frac{[\text{ECOD}] - [\text{ECOD}]_\infty}{[\text{ECOD}]_0 - [\text{ECOD}]_\infty} \right) = -\left(k_{-1COD} - \frac{k_{1COD} \cdot [\text{COD}]_0 \cdot (k_{-1COD} - k_{-1NBD})}{k_{1COD} \cdot [\text{COD}]_0 + k_{1NBD} \cdot [\text{NBD}]_0} \right) \cdot t = -k_{obs} \cdot t$$

(5a)

Examples for the calculation of K^{*}_{NBD}/K^{*}_{COD} and K_{MNBD}/K_{MCOD}

$$\frac{K_{2b}^{*}}{K_{1b}^{*}} = \frac{k_{1,2b}}{k_{-1,2b}} \cdot \frac{k_{-1,1b}}{k_{1,1b}} = \frac{85}{3.1 \cdot 10^{-4}} \cdot \frac{1.1 \cdot 10^{-3}}{18} = 12.1$$

$$\frac{K_{M,2b}}{K_{M,1b}} = \frac{k_{-1,2b} + k_{2,2b}}{k_{1,2b}} \cdot \frac{k_{1,1b}}{k_{-1,1b} + k_{2,1b}} = \frac{3.1 \cdot 10^{-4} + 2.2 \cdot 10^{-1}}{85} \cdot \frac{18}{1.1 \cdot 10^{-3} + 3.3 \cdot 10^{-3}} = 11.2$$

References

1. S. Hoops, S. Sahle, R. Gauges, C. Lee, J. Pahle, N. Simus, M. Singhal, L. Xu, P. Mendes and U. Kummer, *Bioinformatics*, 2006, **22**, 3067-3074.
2. J. A. Osborn and R. R. Schrock, *J. Am. Chem. Soc.*, 1971, **93**, 2397-2407.