

Supporting Information

Composition of rhodium carbonyl complexes in the absence of phosphorus ligands under hydroformylation conditions: an in-situ FTIR spectroscopic study

Benedict N. Leidecker^a, Dilver Peña Fuentes^a, Chunhong Wei^a, Mathias Sawall^b, Klaus Neymeyr^{a,b}, Robert Franke^{c,d}, Armin Börner^a and Christoph Kubis^{a*}

^a Leibniz-Institut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock (Germany)

^b Institut für Mathematik, Universität Rostock, Ulmenstr. 59, 18057 Rostock (Germany)

^c Evonik Oxeno GmbH & Co. KG., Paul-Baumann-Str. 1, 45772 Marl (Germany)

^d Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum (Germany)

E-Mail: christoph.kubis@catalysis.de

Phone: 0381/1281-233

Supporting Information -Table of Contents

	page
SI-A General	3
SI-B In-situ FTIR experiments	4
SI-C Additional information about performed experiments	5
SI-D DFT-calculations	13
SI-J References	16

SI-A General

All solutions were prepared under argon (5.0, Linde AG) or reactive gas using Schlenk techniques.

Commercial chemicals were purchased from Aldrich Chemical Co (neohexene (97 %), diphenylcarbonate (99 %), STREM Chemicals ($[\text{Rh}(\text{acac})(\text{CO})_2]$, 99 %) and Fluka Analytical (acacH, 99.5 %) as well as ABCR ($[\text{Rh}_4(\text{CO})_{12}]$, 98 %). Cyclohexane (99.5 %, extra pure) purchased from ACROS organics and *n*-dodecane (99 %) from ABCR.

Reactive gases used for the experiments were synthesis gas (50 vol% H_2 , 5.0 grade, 50 vol% CO 4.7, grade) H_2 (5.0 grade, Linde AG), D_2 (>99 %, Linde AG), Ethene (3.5 grade, Linde AG) and CO (4.7 grade, Linde AG).

SI-B: In-situ FTIR experiments

In-situ FTIR experiments with smaller volumes of reaction solutions (15 ml) were conducted using a stainless-steel Swagelok cylinder (25 ml) with magnetic stirrer bar.

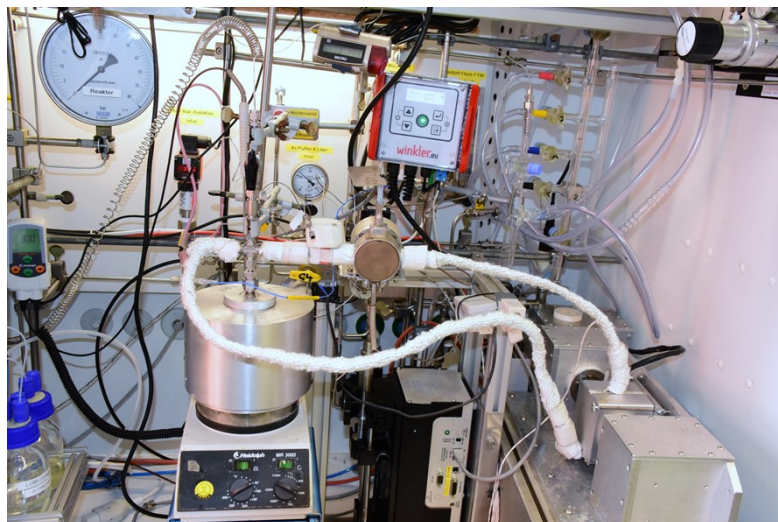


Figure SI-1: Experimental set-up with 25 ml cylinder (Swagelok) as reactor for in-situ FTIR monitoring.

Hydroformylation experiments with in-situ FTIR spectroscopic monitoring were conducted in a 200 mL stainless steel autoclave (Premex).



Figure SI-2: Experimental set-up with 200 ml reactor for in-situ FTIR monitoring during alkene hydroformylation.

Simultaneously to the IR-spectroscopy samples were taken under reaction conditions via an automated sampling devise (ASD) into GC-vials sealed with a rubber septum and filled with inert gas (nitrogen). The vials were purchased by Thermo Fisher scientific. The following GC-analysis was performed using an DB-Wax (60 m, 0.25 mm diameter, 0.25 μm film, temperature range: 20 – 250 $^{\circ}\text{C}$) column.

SI-C: Additional information about performed experiments

IR-Spectrum of acacH

In the Figure SI-3 infrared spectrum of acetylacetone (acacH) at 1 mM concentration dissolved in *n*-dodecane at $\vartheta = 30\text{ }^{\circ}\text{C}$ is displayed.

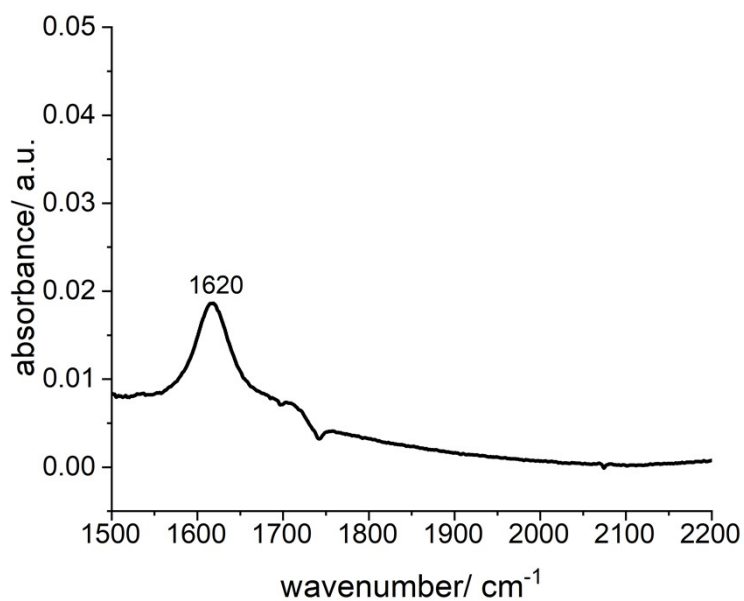


Figure SI-3: FTIR-spectrum of acetylacetone dissolved in *n*-dodecane. Conditions: [acacH] = 1 mM, $\vartheta = 30\text{ }^{\circ}\text{C}$.

Perturbation experiment

A stock solution (8 mL) of $[\text{Rh}(\text{acac})(\text{CO})_2]$ (83.9 mg 0.32 mmol) in *n*-dodecane has been prepared and transferred into an 8 mL syringe pump which has been used for the stepwise addition during the experiment.

Before the first addition of $[\text{Rh}(\text{acac})(\text{CO})_2]$ into the reactor 15 mL *n*-dodecane have been filled into the autoclave and were heated to 120 °C under syngas atmosphere (2.0 MPa). First addition of the rhodium solution consisted of 0.19 mL (0.008 mmol). Further details for the following steps are given in Table SI-1.

Table SI-1: Steps of the perturbation experiment (Figure 3 in the manuscript).

Step	$n(\text{Rh}(\text{acac})(\text{CO})_2)/$ mmol	$c(\text{Rh})/$ mmol L^{-1}	$V/$ mL
1	0.008	0.5	0.190
2	0.016	1.0	0.200
3	0.032	2.0	0.400
4	0.049	3.0	0.430
5	0.067	4.0	0.450
6	0.087	5.1	0.500
7	0.139	7.5	1.300
8	0.201	10.0	1.550

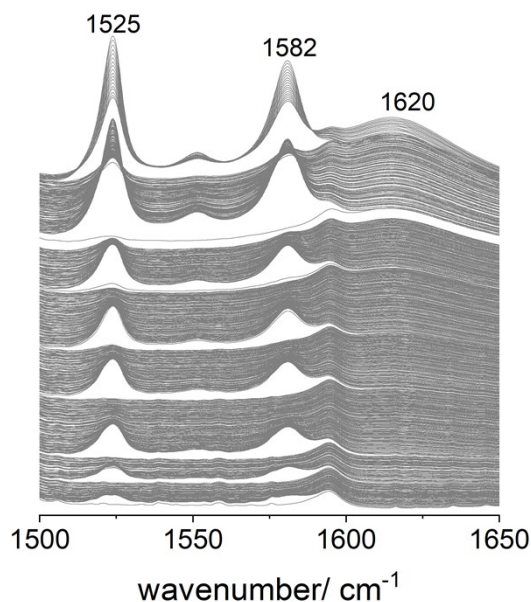


Figure SI-4: In-situ FTIR-spectra of $[\text{Rh}(\text{acac})(\text{CO})_2]$ decomposition in the spectral region between 1500-1650 cm^{-1} under syngas in context of the perturbation experiment. Assignments: $\nu = 1525, 1582 \text{ cm}^{-1}$ $[\text{Rh}(\text{acac})(\text{CO})_2]$, $\nu = 1620 \text{ cm}^{-1}$ acacH. Further conditions: $[\text{Rh}] = 0.5 - 10 \text{ mM}$, $[\text{DPC}] = 2 \text{ mM}$, $\vartheta = 120 \text{ }^\circ\text{C}$, $p(\text{CO}/\text{H}_2) = 2.0 \text{ MPa}$, solvent: *n*-dodecane.

Decomposition of $[\text{Rh}(\text{acac})(\text{CO})_2]$

$\vartheta = 120\text{ }^\circ\text{C}$, $[\text{Rh}] = 1\text{ mM}$, $p(\text{CO}) = 1.0\text{ MPa}$

$[\text{Rh}(\text{acac})(\text{CO})_2]$ (4 mg, 1.5×10^{-2} mmol) and diphenylcarbonate (6.8 mg, 3×10^{-2} mmol) have been dissolved in *n*-dodecane (15 mL) and transferred into the 25 mL autoclave connected with the in-situ infrared cell. Afterwards the system has been heated up to $120\text{ }^\circ\text{C}$ followed by the addition of carbon monoxide (1.0 MPa) which was the starting point of the in-situ FTIR spectroscopic reaction monitoring. The reaction has been investigated for four hours and resulted in significantly lower reaction rates (Figure SI-5) with respect to the decomposition of $[\text{Rh}(\text{acac})(\text{CO})_2]$ compared to the reaction with synthesis gas (CO/H₂).

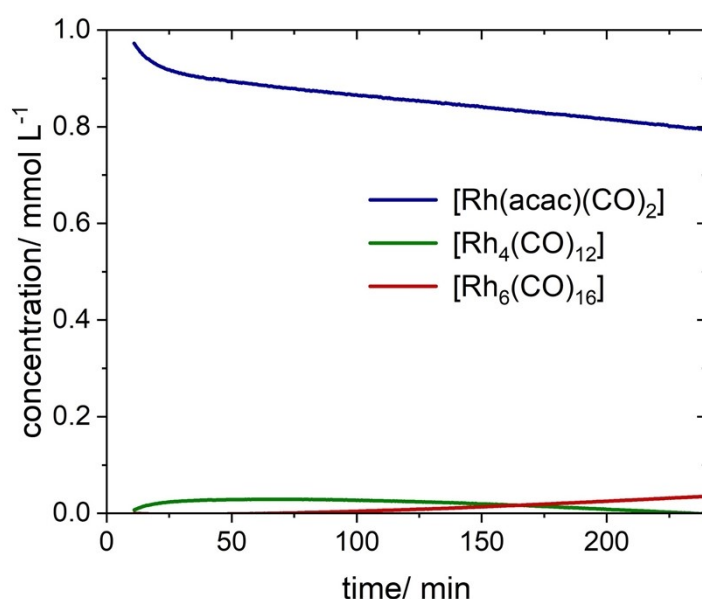


Figure SI-5: Concentration profile of $[\text{Rh}(\text{acac})(\text{CO})_2]$ decomposition under pure carbon monoxide atmosphere. Conditions: $[\text{Rh}] = 1\text{ mM}$, $[\text{DPC}] = 2\text{ mM}$, $\vartheta = 120\text{ }^\circ\text{C}$, $p(\text{CO}) = 1.0\text{ MPa}$, solvent = *n*-dodecane.

$\vartheta = 100\text{ }^\circ\text{C}$, $[\text{Rh}] = 1\text{ mM}$, $p(\text{CO}/\text{H}_2) = 2.0\text{ MPa}$

A solution containing $[\text{Rh}(\text{acac})(\text{CO})_2]$ (4 mg, 1.5×10^{-2} mmol) and diphenylcarbonate (6.8 mg, 3×10^{-2} mmol) has been prepared in *n*-dodecane (15 mL) and transferred into the 25 mL autoclave. Afterwards the solution has been circulated through the transmission IR-cell. The reaction mixture has been heated up to $100\text{ }^\circ\text{C}$ and pressurized with 2.0 MPa syngas (CO/H₂). Together with the addition of syngas the in-situ IR monitoring has been started.

$\vartheta = 100\text{ }^\circ\text{C}$, $[\text{Rh}] = 1\text{ mM}$, $[\text{acacH}] = 10\text{ mM}$, $p(\text{CO}/\text{H}_2) = 2.0\text{ MPa}$

In a separate experiment the investigation was repeated in the presence of 10 eq. acacH (10 mM) which has been added in to the reactor together with $[\text{Rh}(\text{acac})(\text{CO})_2]$ and diphenylcarbonate. The other conditions were not changed. The addition of acacH resulted in a lower rate for the conversion of the precursor $[\text{Rh}(\text{acac})(\text{CO})_2]$ towards polynuclear complexes. It seems that also a qualitative change in the observable

concentration profiles exists indicating alterations in the reaction kinetics. During the previous experiment the reaction were marked by the presence of $[\text{Rh}_4(\text{CO})_{12}]$ as an intermediate with a follow-up reaction to $[\text{Rh}_6(\text{CO})_{16}]$. But in this case the formation of $[\text{Rh}_4(\text{CO})_{12}]$ and $[\text{Rh}_6(\text{CO})_{16}]$ was detectable in parallel, see Figure SI-7.

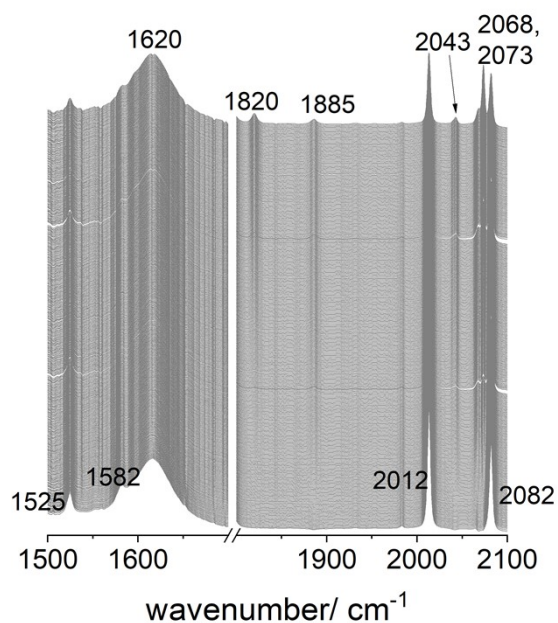


Figure SI-6: In-situ FTIR-spectra collected during $[\text{Rh}(\text{acac})(\text{CO})_2]$ decomposition under syngas in presence of acacH (10 eq.). Conditions: $[\text{Rh}] = 1 \text{ mM}$, $[\text{DPC}] = 2 \text{ mM}$, $[\text{acacH}] = 10 \text{ mM}$, $\vartheta = 100 \text{ }^\circ\text{C}$, $p(\text{syngas}) = 2.0 \text{ MPa}$, solvent = *n*-dodecane.

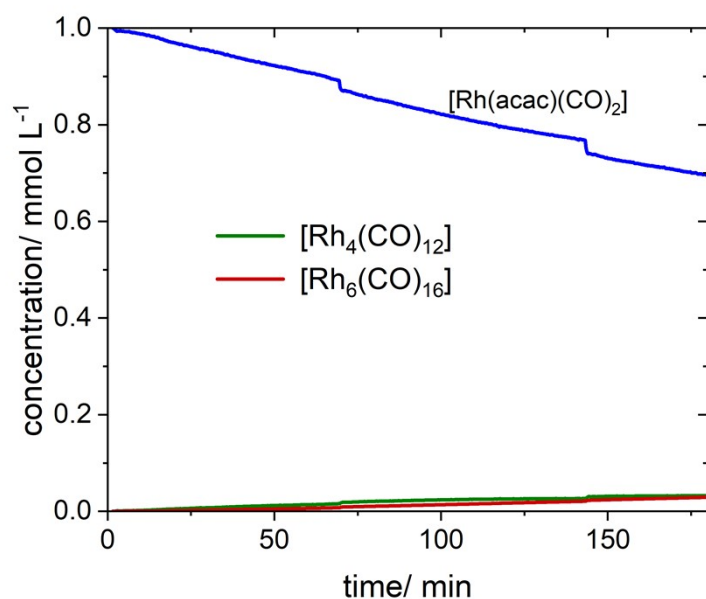


Figure SI-7: Concentration profiles of the $[\text{Rh}(\text{acac})(\text{CO})_2]$ decomposition under syngas atmosphere in the presence of 10 eq. of acacH. Conditions: $[\text{Rh}] = 1 \text{ mM}$, $[\text{DPC}] = 2 \text{ mM}$, $[\text{acacH}] = 10 \text{ mM}$, $\vartheta = 100 \text{ }^\circ\text{C}$, $p(\text{syngas}) = 2.0 \text{ MPa}$, solvent = *n*-dodecane. The steps in between in the concentration profiles resulted from re-additions of synthesis gas during the experiment.

$\vartheta = 50\text{ }^{\circ}\text{C}$, $[\text{Rh}] = 5\text{ mM}$, $p(\text{CO}/\text{H}_2) = 5.0\text{ MPa}$

A solution containing $[\text{Rh}(\text{acac})(\text{CO})_2]$ (20 mg, 7.5×10^{-2} mmol) and diphenylcarbonate (6.8 mg, 3×10^{-2} mmol) has been prepared in *n*-dodecane (15 mL) and transferred into the 25 mL autoclave connected with the in-situ IR-cell. After the temperature of $50\text{ }^{\circ}\text{C}$ was reached 5.0 MPa of syngas were added to the system together with the start of the in-situ FTIR monitoring. After approx. 5 hours full decomposition of $[\text{Rh}(\text{acac})(\text{CO})_2]$ was reached. In Figure SI-8 the FTIR-spectra in the spectral region between $1500\text{--}1650\text{ cm}^{-1}$ is displayed.

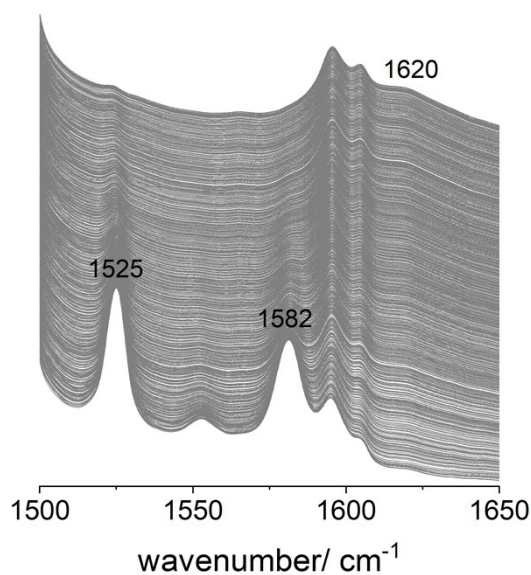


Figure SI-8: in-situ FTIR-spectra of $[\text{Rh}(\text{acac})(\text{CO})_2]$ decomposition under syngas. Assignments: $\nu = 1525, 1582\text{ cm}^{-1}$ $[\text{Rh}(\text{acac})(\text{CO})_2]$, $\nu = 1620\text{ cm}^{-1}$ acacH. Conditions: $[\text{Rh}] = 5\text{ mM}$, $[\text{DPC}] = 2\text{ mM}$, $\vartheta = 50\text{ }^{\circ}\text{C}$, $p(\text{syngas}) = 5.0\text{ MPa}$, solvent = *n*-dodecane.

$\vartheta = 30\text{ }^{\circ}\text{C}$, $[\text{Rh}] = 1\text{ mM}$, $p(\text{CO}/\text{H}_2) = 5.0\text{ MPa}$

A solution containing $[\text{Rh}(\text{acac})(\text{CO})_2]$ (4 mg, 1.5×10^{-2} mmol) and diphenylcarbonate (6.8 mg, 3×10^{-2} mmol) has been prepared in *n*-dodecane (15 mL) and transferred into the 25 mL autoclave connected with the in-situ IR-cell. The reaction start was initiated via the addition of syngas (2.0 MPa) combined with the start of the in-situ FTIR monitoring. Within ca. 26 hours full conversion towards $[\text{Rh}_4(\text{CO})_{12}]$ and small fractions of $[\text{Rh}_6(\text{CO})_{16}]$ has been reached and the gas atmosphere was changed to 4.0 MPa hydrogen and 1.0 MPa carbon monoxide which has been used for the detection of the hydrido complex.

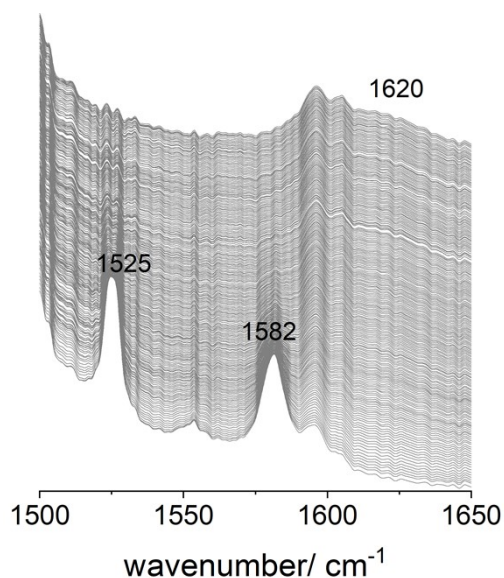


Figure SI-9: In-situ FTIR-spectra of the treatment of $[\text{Rh}(\text{acac})(\text{CO})_2]$ with syngas. Assignments: $\nu = 1525, 1582\text{ cm}^{-1}$ $[\text{Rh}(\text{acac})(\text{CO})_2]$, $\nu = 1620\text{ cm}^{-1}$ acacH (not clearly detectable). Further conditions: $[\text{Rh}] = 1\text{ mM}$, $[\text{DPC}] = 2\text{ mM}$, $\vartheta = 30\text{ }^{\circ}\text{C}$, $p(\text{syngas}) = 5.0\text{ MPa}$, solvent = *n*-dodecane.

$\vartheta = 30\text{ }^{\circ}\text{C}$, $[\text{Rh}] = 1\text{ mM}$, $p(\text{CO}/\text{D}_2) = 5.0\text{ MPa}$

In a separate experiment deuterium has been used instead of hydrogen for the detection of $[\text{DRh}(\text{CO})_4]$. All other conditions were unchanged. Interestingly showed the resulting complex lower reactivities which led to the absence of $[\text{Rh}_6(\text{CO})_{16}]$ within 48 hours at 5.0 MPa ($\text{D}_2:\text{CO} = 1:1$). Change of the gas atmosphere to 4.0 MPa deuterium and 1.0 MPa carbon monoxide has been used for a direct comparison of both complexes.

Formation of [HCo(CO)₄] and [DCo(CO)₄]

The starting complex [Co₂(CO)₈] ([Co] = 5 mM) dissolved in *n*-dodecane was treated under synthesis gas (5.0 MPa) at $\vartheta = 120$ °C to form [HCo(CO)₄] in significant molar fractions. The solution was then set to 2.0 MPa of synthesis gas. In the next step, the gas atmosphere was exchanged to carbon monoxide (1.0 MPa) and then deuterium (1.0 MPa) was added. The spectroscopic data collected during the H/D-exchange was analyzed by PGA.

Formation acyl complexes with ethene as alkene

$\vartheta = 30\text{ }^{\circ}\text{C}$, $[\text{Rh}] = 1\text{ mM}$, $p(\text{CO}) = 1.0\text{ MPa}$, $p(\text{C}_2\text{H}_4) = 1.0\text{ MPa}$, $p(\text{H}_2) = 1.0\text{ MPa}$ with prior-preformation of $[\text{Rh}_4(\text{CO})_{12}]$

Formation of the acyl complexes has been conducted using the solution which has been prepared in-situ for the identification of $[\text{DRh}(\text{CO})_4]$ after the re-exchange to normal synthesis gas (CO/H_2) and purging with CO . $[\text{Rh}_4(\text{CO})_{12}]$ was the dominant complex under the applied conditions. After pressurizing with 1.0 MPa of pure CO , 1.0 MPa of ethene was added. The formation of acyl complexes was started with the addition of 1.0 MPa of hydrogen. During the entire experiment in-situ FTIR spectra were registered for monitoring the reaction. After 24 hours a dominant fraction of the acyl complexes has been found which reached a mole fraction of ca. 0.78. Under these conditions $[\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{Rh}(\text{CO})_4]$ was only present in small relative amounts and $[\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{Rh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)]$ represented the dominant acyl complex.

$\vartheta = 30\text{ }^{\circ}\text{C}$, $[\text{Rh}] = 1\text{ mM}$, $p(\text{CO}/\text{H}_2) = 4.0\text{ MPa}$, $p(\text{C}_2\text{H}_4) = 1.0\text{ MPa}$ without prior-preformation of $[\text{Rh}_4(\text{CO})_{12}]$

The reaction was conducted with $[\text{Rh}(\text{acac})(\text{CO})_2]$ (4 mg, 1.5×10^{-2} mmol) as a precursor complex in the presence of diphenylcarbonate (6.8 mg, 3×10^{-2} mmol) dissolved in 15 ml *n*-dodecane. In the first step 2.0 MPa synthesis gas (CO/H_2) was used with 1.0 MPa of ethene. The conversion of $[\text{Rh}(\text{acac})(\text{CO})_2]$ was quite low with 12 % even after ca. 12 h. During this first step minor band contributions from the acyl complexes ($[\text{RC}(\text{O})\text{Rh}(\text{CO})_4]$, $[\text{RC}(\text{O})\text{Rh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)]$) were observed in the infrared spectra. No formation of $[\text{Rh}_4(\text{CO})_{12}]$ took place to any significant extent. Then, we decided to add further 2.0 MPa of synthesis gas. The bands of the acyl complexes increased in course of the reaction (Figure SI-10a). Interestingly, no significant formation of $[\text{Rh}_4(\text{CO})_{12}]$ was noticed also under these conditions. The PGA delivered only an averaged spectrum for an equilibrium mixture of $[\text{RC}(\text{O})\text{Rh}(\text{CO})_4]$ and $[\text{RC}(\text{O})\text{Rh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)]$ (Figure SI-10b). It seems that the tetra carbonyl complex is present at higher molar fractions compared to the experiment performed at 2.0 MPa synthesis gas and 1.0 MPa ethene starting from $[\text{Rh}_4(\text{CO})_{12}]$. This is plausible because of the higher partial pressure of carbon monoxide.

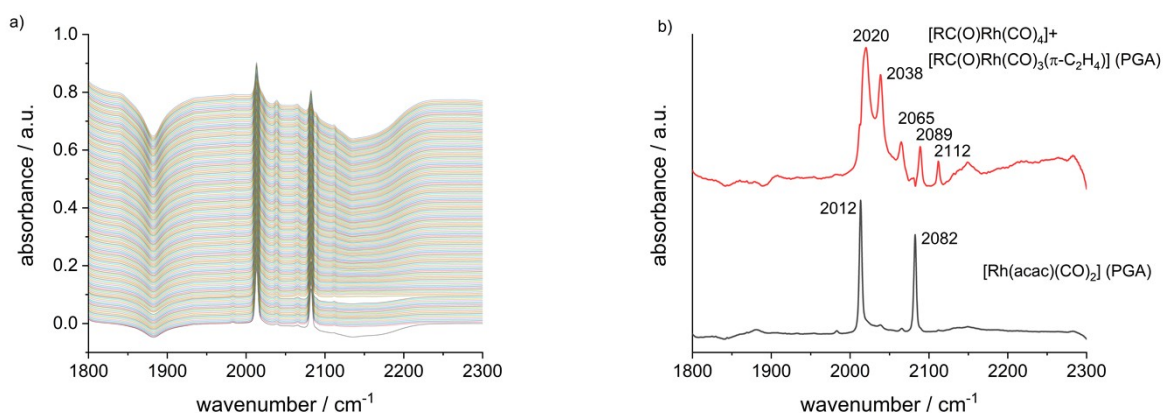


Figure SI-10: a) In-situ FTIR-spectra of the treatment of $[\text{Rh}(\text{acac})(\text{CO})_2]$ with syngas and ethene. Spectra represent the 2. step after increasing the CO/H_2 pressure from 2.0 to 4.0 MPa. Conditions: $[\text{Rh}] = 1\text{ mM}$, $[\text{DPC}] = 2\text{ mM}$, $\vartheta = 30\text{ }^{\circ}\text{C}$, $p(\text{syngas}) = 4.0\text{ MPa}$, $p(\text{ethene}) = 1.0\text{ MPa}$, solvent = *n*-dodecane, t_{Rx} : >48 h. b) PGA spectrum of $[\text{Rh}(\text{acac})(\text{CO})_2]$ and averaged PGA spectrum representing a mixture of $[\text{RC}(\text{O})\text{Rh}(\text{CO})_4]$ and $[\text{RC}(\text{O})\text{Rh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)]$.

Hydroformylation of neohexene

A solution containing $[\text{Rh}(\text{acac})(\text{CO})_2]$ (18.9 mg, 7×10^{-2} mmol) and diphenylcarbonate (31.5 mg, 1.4×10^{-2} mmol) has been prepared in cyclohexane (70 mL) and transferred into the 200 mL autoclave connected with the in-situ IR-cell. Heated up to 90 °C under Ar (0.5 MPa).

After the temperature of 90 °C was reached 2.0 MPa of syngas were added to the system together with the start of the in-situ FTIR monitoring.

SI-E: DFT-calculations

In the following Table SI-2, the cartesian coordinates and energies for rhodium complexes and acacH after geometry optimization (B3LYP, def2-SVP) using Gaussian 16 are given.¹

Table SI-2: Cartesian coordinates and energies for optimized molecular structures.

<p>[Rh(acac)(CO)₂] E= -682.036763</p> <p>O 1.19209 0.47041 -3.44549 O -1.66446 0.22521 -3.04137 C 0.8037 0.67861 -4.65107 C -1.67238 0.49496 -4.29755 C 1.93668 0.89606 -5.63891 H 1.57268 1.10718 -6.66532 H 2.57564 1.73918 -5.29512 H 2.58574 -0.00782 -5.66264 C -3.05612 0.57003 -4.91431 H -3.58082 -0.40055 -4.76905 H -3.65672 1.34016 -4.38149 H -3.02635 0.81449 -5.99597 C -0.53403 0.71516 -5.10437 H -0.70242 0.92531 -6.1712 Rh 0.13849 -0.23564 -1.85792 C 1.73953 -1.20941 -1.1037 C -0.7717 -0.33765 -0.05749 O 2.62359 -1.74711 -0.68724 O -1.27429 -0.39397 0.93666</p>	<p>acacH E= -345.463073</p> <p>O 0.63123 -1.20311 0.00025 C 1.95802 -1.24889 0.00006 C 2.6058 0.00001 -0.00019 C 1.95799 1.2489 -0.00023 O 0.69205 1.26164 -0.00012 C 2.77964 -2.51681 -0.00012 H 3.6955 0.00003 -0.00036 C 2.77957 2.51684 -0.00021 H 2.51826 3.11823 0.88543 H 3.86014 2.32326 -0.00208 H 2.51537 3.12023 -0.88359 H 3.8602 -2.3232 0.00095 H 2.51607 -3.1199 0.88366 H 2.51773 -3.11851 -0.88536 H 0.01525 0.0541 -0.00042</p>
<p>[HRh(CO)₄] E= -564.228900</p> <p>Rh -2.76585 0.38973 0. H -2.76585 0.38973 -1.55 C -0.74585 0.38973 0. O 0.57415 0.38973 0. C -3.77585 2.1391 0. O -4.43585 3.28226 0. C -3.77585 -1.35964 0. O -4.43585 -2.50279 0. C -2.76585 0.38973 2.02 O -2.76585 0.38973 3.34</p>	<p>[DRh(CO)₄] E= -564.231346</p> <p>Rh -2.76585 0.38973 0. H(Iso=2) -2.76585 0.38973 -1.55 C -0.74585 0.38973 0. O 0.57415 0.38973 0. C -3.77585 2.1391 0. O -4.43585 3.28226 0. C -3.77585 -1.35964 0. O -4.43585 -2.50279 0. C -2.76585 0.38973 2.02 O -2.76585 0.38973 3.34</p>
<p>[CH₃CH₂C(O)Rh(CO)₄] E= -755.976907</p> <p>Rh -2.76585 0.38973 0. C -0.74585 0.38973 0. O 0.57415 0.38973 0. C -3.77585 2.1391 0. O -4.43585 3.28226 0. C -3.77585 -1.35964 0. O -4.43585 -2.50279 0. C -2.76585 0.38973 2.02 O -2.76585 0.38973 3.34 C -2.76585 0.38973 -2.02 O -2.24673 1.2889 -2.67446 C -3.4605 -0.81355 -2.6842 H -4.48678 -0.84384 -2.38298 H -3.40382 -0.71544 -3.74819 C -2.75964 -2.11447 -2.2506 H -3.44393 -2.71964 -1.69346</p>	<p>[CH₃CH₂C(O)Rh(CO)₃-e-(C₂H₄)] E= -721.228255</p> <p>Rh 0.43503 0.02378 0.0004 C -0.06991 0.04034 1.9037 O -0.34404 0.06858 3.01311 C -0.0391 1.45316 -1.26412 O -0.257 2.30237 -1.99944 C 2.25917 0.79434 0.32002 O 3.29545 1.22125 0.5208 C -1.50908 -0.88199 -0.23341 O -1.63889 -2.04861 0.00649 C -2.7046 -0.02622 -0.66097 H -2.45803 0.46502 -1.61617 H -3.52909 -0.73359 -0.84699 C -3.12715 1.01832 0.37802 H -2.34045 1.76661 0.55546 H -4.02619 1.55067 0.03141 H -3.36972 0.54401 1.34205</p>

H	-2.43404	-2.65027	-3.11767	X	1.21382	-1.897	-0.87516
H	-1.91398	-1.87739	-1.63941	C	1.18524	-1.59557	-1.56185
				C	1.24239	-2.19844	-0.18846
				H	2.01671	-1.1275	-1.84913
				H	0.32184	-1.7269	-2.04171
				H	2.10579	-2.06711	0.2914
				H	0.41092	-2.66651	0.09882
[Rh₄(CO)₁₂] E= -1801.588032				[Rh₆(CO)₁₆] E= -2475.889849			
C	1.14674	3.18103	3.80542	C	-0.02668	-0.00967	0.57329
Rh	2.74031	3.26721	5.22483	Rh	0.01165	-0.01811	2.50015
Rh	3.54927	1.07321	3.79704	C	-0.31294	2.16185	2.84348
Rh	5.18807	3.26935	3.82959	Rh	-0.41408	1.40164	4.93812
C	6.87246	2.32324	3.81983	C	-0.99348	-0.02688	6.55082
Rh	2.75466	3.29474	2.40228	Rh	-2.86165	-0.0106	5.33227
C	1.91725	2.35979	0.93534	C	-4.05201	0.00298	3.44633
C	4.77541	3.19797	1.72975	Rh	-2.43638	-1.43234	2.89625
C	2.38794	5.11315	1.7965	C	-0.33977	-2.19547	2.82575
C	4.75689	3.15052	5.91849	Rh	-0.43184	-1.45059	4.92722
C	2.38828	5.07917	5.85446	C	1.42105	-1.69792	5.396
C	1.8813	2.31759	6.67125	C	1.93777	-0.03001	2.5694
C	5.90617	5.0813	3.85142	Rh	-2.41645	1.42134	2.90632
C	4.41216	0.148	5.29976	C	-2.86038	1.67024	1.04738
C	1.80572	0.16197	3.78223	C	-0.97435	-3.08778	5.7868
C	4.42996	0.17676	2.28505	C	-3.27725	3.06201	3.43785
O	0.80996	-0.40644	3.7769	C	-2.88624	-1.66712	1.03711
O	4.90989	-0.42729	6.15776	C	-3.31546	-3.06493	3.4211
O	4.93347	-0.382	1.41954	C	-0.94081	3.03879	5.80787
O	-0.01571	3.12896	3.79995	C	1.44082	1.62542	5.41088
O	5.33342	3.09636	6.92767	C	-3.81431	-1.40676	6.25792
O	5.3661	3.15365	0.72831	C	-3.79752	1.39107	6.2671
O	1.3754	1.74277	7.52549	O	-1.27447	-4.06439	6.30748
O	2.1913	6.15242	6.20523	O	-3.84733	-4.03864	3.71089
O	6.30444	6.15601	3.86341	O	-4.39147	-2.22048	6.82329
O	7.86653	1.75059	3.81404	O	2.51723	-1.86403	5.68883
O	1.42347	1.79226	0.06911	O	2.53926	1.7808	5.70108
O	2.172	6.18692	1.45898	O	-1.2318	4.01504	6.33436
				O	-4.36477	2.20819	6.83761
				O	-3.79243	4.04383	3.73038
				O	-3.13281	1.8405	-0.05342
				O	3.08433	-0.03343	2.58631
				O	-0.02517	-0.0077	-0.5734
				O	-3.16793	-1.82625	-0.06301
				O	-0.80435	-0.03217	7.70732
				O	-5.20534	0.01176	3.23901
				O	0.1735	3.11812	2.37201
				O	0.13515	-3.15382	2.34693
[CH₃CH₂C(O)Rh(CO)₃-a-(C₂H₄)] E= -721.220691				[Rh₂(CO)₈] C_{2v} E= -1127.278446			
Rh	0.43503	0.02378	0.0004	C	-0.00001	-1.30758	0.70129
C	-0.06991	0.04034	1.9037	C	-1.89786	-1.32642	-1.08925
O	-0.34404	0.06858	3.01311	C	1.89784	-1.32642	-1.08926
C	-0.0391	1.45316	-1.26412	C	1.89784	1.32644	-1.08923
O	-0.257	2.30237	-1.99944	C	0.00001	1.30755	0.70135
C	-1.50908	-0.88199	-0.23341	C	2.36736	-0.00003	1.44344
O	-1.63889	-2.04861	0.00649	C	-2.36736	0.00001	1.44344
C	-2.7046	-0.02622	-0.66097	C	-1.89781	1.32644	-1.08925
H	-2.45803	0.46502	-1.61617	O	-0.00001	-2.34134	1.24021
H	-3.52909	-0.73359	-0.84699	O	0.00001	2.34129	1.24032
C	-3.12715	1.01832	0.37802	O	3.11961	-0.00004	2.30207
H	-2.34045	1.76661	0.55546	O	2.3272	2.14889	-1.75379
H	-4.02619	1.55067	0.03141	O	-2.32727	-2.14885	-1.75378
H	-3.36972	0.54401	1.34205	O	-3.11961	0.00002	2.30206
X	2.48121	0.88813	0.35893	O	-2.32714	2.14891	-1.75381

C	2.47207	1.19401	-0.32634	O	2.32722	-2.14886	-1.75382
C	2.49035	0.58225	1.04419	Rh	-1.27096	0.	-0.00279
H	2.09115	2.11379	-0.3698	Rh	1.27097	0.	-0.00279
H	2.84277	0.61595	-1.04841				
H	2.11964	1.16031	1.76626				
H	2.87127	-0.33752	1.08765				
C	1.13421	-1.70066	-0.78565				
O	1.5911	-2.82752	-1.29931				
[Rh₂(CO)₈] D_{2d} E= -1127.268895				[Rh₂(CO)₈] D_{3d} E= -1127.264197			
C	1.48861	2.34355	0.	C	-1.1927	-1.70066	0.60912
O	2.37189	3.06851	0.	O	-1.14505	-2.77711	0.99445
C	-1.49488	2.33581	0.	C	-1.19325	0.32242	-1.77723
O	-2.3819	3.05616	0.	O	-1.14623	0.52736	-2.90207
C	0.00099	0.89926	1.7504	C	-1.19378	1.3782	1.16745
O	0.00175	0.74487	2.8862	O	-1.14713	2.2506	1.90652
C	-1.75074	-0.90246	0.	C	-3.13649	-0.00103	-0.00002
O	-2.88656	-0.74857	0.	O	-4.27832	-0.00129	-0.0002
C	0.00099	0.89926	-1.7504	C	3.13659	0.00093	0.0001
O	0.00175	0.74487	-2.8862	O	4.27842	0.00071	-0.00045
C	1.75013	-0.89621	0.	C	1.19387	-1.37822	-1.1674
O	2.88573	-0.74031	0.	O	1.14733	-2.25035	-1.90679
C	0.00231	-2.33993	1.49176	C	1.19341	-0.32246	1.77732
O	0.00359	-3.06266	2.37683	O	1.14557	-0.52678	2.90224
C	0.00231	-2.33993	-1.49176	C	1.19288	1.70065	-0.60904
O	0.00359	-3.06266	-2.37683	O	1.14466	2.77715	-0.99414
Rh	0.00043	-1.31482	0.	Rh	-1.35285	-0.00025	0.00003
Rh	-0.00031	1.31491	0.	Rh	1.35296	0.0002	0.00004

SI-F: References

- 1 Gaussian 16, Revision A.03, M. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016..