

# Rhodium-catalysed synthesis of branched fatty compounds in temperature-dependent solvent systems

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## Abstract

For any industrial application of a homogeneously catalysed reaction a complete recycling of the—in general expensive—catalyst should be guaranteed. Also a highly efficient reaction without any mass transport problems is strongly desired. After examining the technically interesting rhodium-catalysed cooligomerization of diunsaturated fatty substances with ethylene, a solution of these requirements can be fulfilled by using some organic chlorides as promoting agents in combination with the new recycling concept of “temperature-dependent solvent systems.” Because of their physical properties the products **2 + 3**—internal branched fatty substances—are a very interesting class of new lubricants which are expected to be biodegradable. These branched fatty substances could be synthesised in high yields of up to 98% and the turn over frequency (TOF) could be increased from 2 up to 220 h<sup>-1</sup>.

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## 1. Introduction

The homogeneous transition metal catalysis is an important method of modern synthetic chemistry. About 10% of all catalytic reactions are carried out homogeneously [1]. The product line ranges from commodities like acetaldehyde or acetic acid to pharmaceuticals. In petrochemistry various commercial-scale processes have been established, e.g. the Ruhrchemie/Rhône-Poulenc oxo process (aqueous/organic biphasic hydroformylation of propene or butene) or the SHOP process (organic/organic biphasic oligomerization of ethene) [2]. A necessary recycling of the homogeneously dissolved, often expensive transition

metal catalysts can only be realised, if suitable recycling concepts are developed and applied. In commercial-scale applications multiphase systems are often used, especially the just mentioned liquid/liquid two-phase processes [3,4]. In these processes, the catalyst is dissolved in a polar, often aqueous phase thus forming the catalyst phase. By means of this immiscibility an easy separation of the catalyst and the product phase is possible by a simple decantation. But the efficiency of any reaction is strongly influenced by mass transport processes or can be inhibited by mass transport problems [5]. Therefore, we developed a new recycling concept, which is called “temperature-dependent solvent systems” [6]. These new solvent systems allow a single-phase reaction process by the repression of the miscibility gap at reaction temperature combined with an easy catalysts/product separation by the two-phase technique at room temperature. This new

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concept is especially suitable for reactions which have to be operated in single phase because of low solubilities of the reactants in the catalyst phase. The choice of the polar solvent is not limited to water. “Simple” salts of transition metals can be used as the catalyst because of the solubility in polar organic solvents.

In the past years, a lot of interesting new substances and syntheses, based on fats and oils as renewable raw materials, have been discovered [7]. Especially branched fatty substances can be seen as an interesting target product. Because of their excellent physical properties compared to their linear homologues (e.g. low melting points and viscosities), they might be used in lubricants or cosmetics [8,9]. At the end of the 1980s the rhodium-catalysed cooligomerization of derivatives of sunflower fatty acid and ethylene to internal branched fatty substances was examined by Behr and Laufenberg for the first time [10,11]. Using rhodium(III) chloride trihydrate ( $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ) as the catalyst and conjugated methyl linolate (**1**) as the fatty substance yields over 90% were achieved in single phase after 20 h with the solvent chloroform. This synthesis of branched fatty substances was carried out under mild conditions (100 °C/20 bar). Scheme 1 shows the reaction of the cooligomerization of conjugated methyl linolate (**1**) and ethylene yielding the branched adducts **2** and **3**. It was also possible to use the corresponding acid or alcohol to substitute the conjugated methyl linolate. However, the reaction showed only low reaction rates and an inactivation of the catalyst was observed. A recycling of the catalyst was not possible without any loss of activity.

Since the 1990s the Institut Français du Pétrole (IFP) has also examined the cooligomerization of derivatives of linoleic acid with ethylene to mono- and dibranched fatty substances. Using alternative catalyst complexes, e.g. ionic rhodium catalysts or nickel, cobalt and iron catalysts in presence of alkyl

aluminium chlorides as reducing agents and special phosphine ligands high yields could be achieved, but a solution of the catalyst recycling problem was not found [12–15].

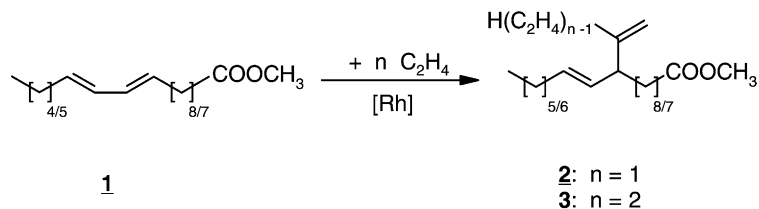
In the 1960s Cramer already examined the analogous codimerization of 1,3-butadiene with ethylene to 1,4-hexadiene. He discovered that rhodium(I) complexes were inactive, but could be activated by adding of HCl that is transformed in the active rhodium(III) species [16,17]. Based on these results, Su and Collette [18] used organic halides, e.g. allylic, aryl or acyl chlorides, instead of HCl for reactivation. Investigating the cooligomerization of 1,3-butadiene and 1-acetoxy-2,7-octadiene Bochmann and Thomas also observed a significant increase in the catalytic activity by adding organic halides [19,20]. Presumably the halides oxidise the rhodium(I) species to an active rhodium(III) complex possibly due to their labile C–Cl bonding.

In our present studies, we examined different possibilities to increase the catalytic activity and to recycle the catalyst. We studied the influence of organic chlorides containing labile C–Cl bonds as promoting agents and evaluated the new recycling concept of temperature-dependent solvent systems.

## 2. Experimental

### 2.1. Reagents

Conjugated sunflower fatty acid methyl ester (SFAME) (contains 60.5% methyl linolate, **1**) is synthesised by acid-catalysed esterification of conjugated sunflower fatty acid with methanol. Conjugated sunflower fatty acid was supplied as UKD 6010 by Cognis Deutschland GmbH. The catalysts were used as received from Degussa AG, i.e. without



Scheme 1. Rhodium-catalysed cooligomerization of conjugated linoleic acid methyl ester and ethylene to internal branched fatty substances.

any further purification. Ethylene 2.7 supplied from Messer-Griesheim was used. All reactions and the handling were done under argon using the standard Schlenk tube technique.

## 2.2. Homogeneous cooligomerization

Generally the catalyst rhodium(III) chloride trihydrate, the promoting agent, the different solvent components and the liquid reactant **1** were weighed in a Schlenk tube. In some experiments the catalyst could only be dissolved completely by heating it up to 50 °C or by an ultrasonic treatment for a short time. The reaction mixture was transferred into an evacuated 67 ml or a 300 ml stainless steel autoclave. The reaction mixture was saturated by 5 bar ethylene under stirring (750 rpm). The vessel was heated up to reaction temperature, pressurised to the desired ethylene pressure and then the reaction was started under isothermal conditions. For measuring the long-term experiments liquid samples were taken from the autoclave in regular intervals. Therefore, the reaction was carried out under isothermal and isobaric conditions, i.e. ethylene was fed continuously during the whole reaction time.

## 2.3. Analysis and product characterisation

All reaction mixtures were analysed by gas chromatography with methyl palmitate as an internal standard. After the total hydrogenation of the double bonds (heterogeneous palladium on charcoal (10% Pd) catalyst) the separation of both adducts **2** and **3** was realised by preparative gas chromatography. The

characterisation of the substances was done by standard NMR experiments (<sup>1</sup>H, <sup>13</sup>C, COSY, DEPT) and mass spectrometry.

## 3. Results and discussion

Screening different rhodium, palladium and nickel catalysts only rhodium(III) chloride trihydrate (RhCl<sub>3</sub>·3H<sub>2</sub>O) results in high yields over 90% if the solvents dioxane or hexane are used in single phase. Because rhodium(III) chloride trihydrate is soluble in polar organic solvents, a biphasic reaction process and thus an application of the liquid/liquid two-phase technique for the catalyst recycling seems to be possible.

### 3.1. Organic chlorides as promoting agents in biphasic systems

Although using the solvents propylene carbonate (PC) or short-chain diols like ethylene glycol yields of about 70% are achieved in biphasic systems (100 °C, 2.0 MPa, 24 h, 0.5 mol% rhodium). The yields as well as the catalytic activity might be increased considerably by using organic halides as promoters.

To apply this idea of reactivation to the synthesis of branched fatty substances, we used acetyl chloride (C<sub>2</sub>H<sub>3</sub>ClO), hexachloroacetone (C<sub>3</sub>Cl<sub>6</sub>O), cinnamoyl chloride (C<sub>9</sub>H<sub>7</sub>ClO) and cinnamyl chloride (C<sub>9</sub>H<sub>9</sub>Cl) (see Table 1). At first, the experiments were carried out in biphasic systems with propylene carbonate as the solvent for a possible application of the liquid/liquid two-phase technique. All experiments were carried out

Table 1  
Screening of organic chlorides as promoting agents in a mono- and biphasic system<sup>a</sup>

Promoting agent		Conversion of <b>1</b> (%)		Total yield of <b>2</b> + <b>3</b> (%)	
		Biphasic <sup>b</sup>	Single phase <sup>c</sup>	Biphasic <sup>b</sup>	Single phase <sup>c</sup>
Without agent	–	12	23	12	22
Acetyl chloride	C <sub>2</sub> H <sub>3</sub> ClO	65	75	32	42
Hexachloroacetone	C <sub>3</sub> Cl <sub>6</sub> O	41	54	32	43
Cinnamoyl chloride	C <sub>9</sub> H <sub>7</sub> ClO	44	73	35	72
Cinnamyl chloride	C <sub>9</sub> H <sub>9</sub> Cl	40	93	40	90

<sup>a</sup> Reaction conditions:  $T = 70\text{ }^{\circ}\text{C}$ ,  $P = 3.0\text{ MPa}$ , chloride/Rh = 25 (mol ratio),  $t = 2\text{ h}$ , conjugated methyl linolate **1**/Rh = 200 (mol ratio), 10 ml conjugated methyl linolate **1**, 60 ml propylene carbonate.

<sup>b</sup> Solvent propylene carbonate.

<sup>c</sup> Solvent system propylene carbonate/dioxane.

under the same mild conditions (70 °C, 3.0 MPa) and with a short reaction time of 2 h.

Related to the experiment without a promoting agent a significant increase in the yield is observed by adding organic chlorides with a labile C–Cl bond. At average of all experiments a three times higher yield can be achieved, but the selectivities differ strongly. In spite of this activating effect by the addition of promoting agents to the biphasic systems, the yields are still much too low seen from a technical point of view.

### 3.2. Organic chlorides as promoting agents in single-phase systems

Taking the same reaction conditions as before the organic chlorides were tested in single-phase systems for a further increase in the yields. A solvent system consisting of dioxane and propylene carbonate was used. Propylene carbonate was necessary as a co-solvent because the rhodium(III) catalyst is very well-soluble in this polar solvent. As shown in Table 1 strong differences between the single-phase experiments appeared in comparison to the experiments in two phases. An alarming increase in the yield was detected, for instance 90% with cinnamyl chloride.

Not only the use of cinnamyl chloride as the best promoting agent, but also a single-phase process are necessary to ensure high yields and high catalytic activity. The existing mass transport problems in biphasic systems can be verified by an examination of the influence of the stirring velocity using cinnamyl chloride (see Fig. 1). From 250 up to 800 rpm the yield increases linearly with the stirring velocity. At stirring velocities higher than 1000 rpm, nearly constant total yields of 60% are achieved. Under single-phase conditions with the solvent system propylene carbonate/dioxane, 1.5 times higher yields (90%) and a very high selectivity of 98% are observed, indicating that this reaction is not or hardly diffusion controlled.

The measurement of the concentration–time behaviour with and without the use of cinnamyl chloride in single phase discloses the influence and the necessity of the promoting agent (see Fig. 2). At the beginning, high reaction rates are detected in both cases. After about 30 min of maximum yields of only 36%, the slope of the curve is sharply reduced without cinnamyl chloride. Using cinnamyl chloride nearly quantitative yields of 96% are achieved which corresponds to an increase of more than 2.5 times.

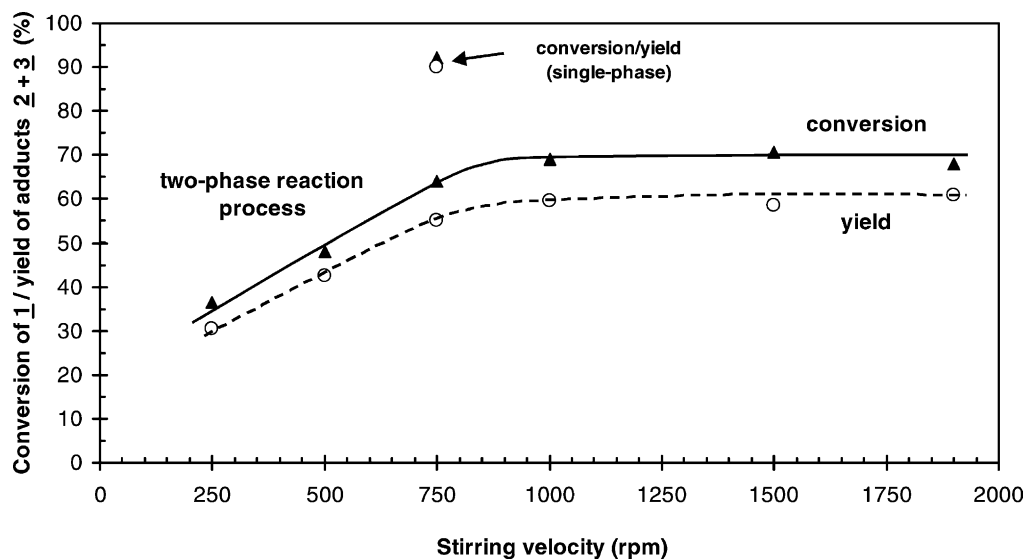


Fig. 1. Influence of the stirring velocity. Reaction conditions:  $T = 70\text{ }^{\circ}\text{C}$ ;  $P = 3.0\text{ MPa}$ ; cinnamyl chloride/Rh = 25 (mol ratio); conjugated methyl linolate 1/Rh = 200 (mol ratio);  $t = 2\text{ h}$ ; 17.5 ml conjugated methyl linolate 1; 17.5 ml propylene carbonate.

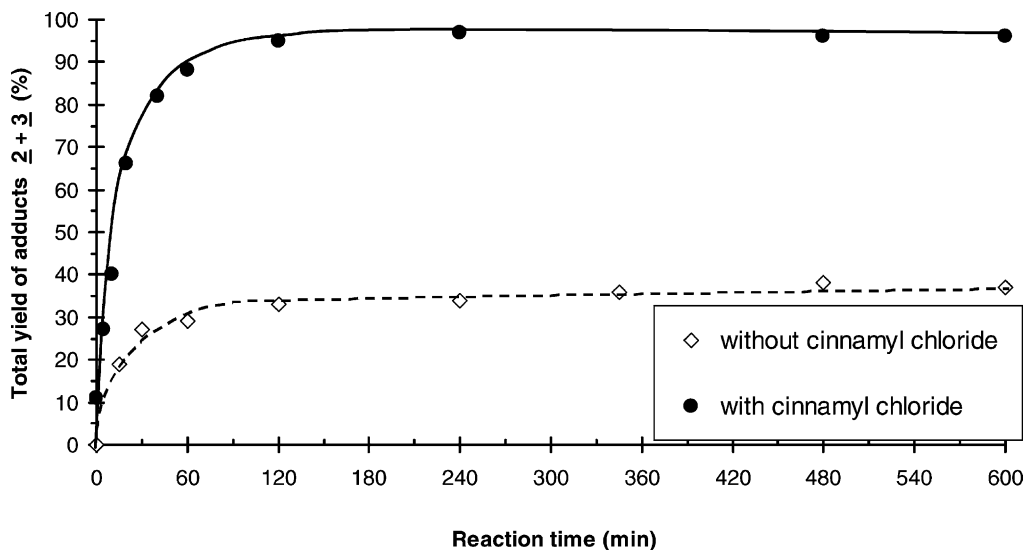


Fig. 2. Concentration–time behaviour with and without using cinnamyl chloride. Reaction conditions:  $T = 70^\circ\text{C}$ ;  $P = 3.0\text{ MPa}$ ; cinnamyl chloride/Rh = 25 (mol ratio); conjugated methyl linolate 1/Rh = 200 (mol ratio);  $t = 600\text{ min}$ ; PC/SFAME/dioxane = 1:1:0.4 (volume ratio); total reaction volume = 60 ml.

### 3.3. Mechanism

The reaction progress of the cooligomerization was examined in detail by measuring the concentration–time behaviour in a long-term experiment. Using cinnamyl chloride the 2:1 adduct (**3**) is formed in a consecutive reaction (see Fig. 3).

The catalytic active species of the cooligomerization is not rhodium(III) chloride trihydrate, but a rhodium(III) hydrido species  $\text{HRhCl}_2$ . This complex is formed during an induction period in presence of ethylene which was described by Cramer for the codimerization of 1,3-butadiene with ethylene [16,17].

Based on these studies the catalytic cycle in Fig. 4 (cycle A) explains the sequence of the cooligomerization reaction which can be described as follows.

- (I) The  $\text{HRhCl}_2$  complex (**A1**) adds one molecule of the conjugated methyl linolate **1** by the conjugated double bonds giving the  $\eta^3$ -complex **A2**.
- (II) After one molecule of ethylene is associated (**A3**), the insertion of ethylene into the rhodium allylic bond leads to the  $\sigma, \eta^2$ -complex (**A4**).

- (III) By the extrusion of the  $\sigma$ -alkyl ligand and  $\beta$ -hydride elimination the complex **A4** is converted to the  $\eta^2, \eta^2$ -1,4-complex (**A5**). After the dissociation of product **2** the catalytic active species **A1** is reformed again and able to start a new catalytic cycle.

There is not much difference in the description of the consecutive formation of product **3** (here adduct **2** acts as one reactant). Before the steps I–III will be passed through in the same way, a conjugation of the double bonds of adduct **2** (= 1,4-complex) is necessary. This “pre-step” is also catalysed by the rhodium catalyst. The conjugation is directly coupled with step I and both can be probably seen as one step.

Mass-spectrometric studies show a branching of the products mainly at the C9 carbon atom. Here the carboxylic group may act as an intramolecular donor ligand and causing a selective addition of ethylene to the  $\eta^3$ -complex.

A decay and inactivation of the catalytic system was observed by Behr and Laufenberg [10,11] when no promoting agent had been used. This effect is probably caused by the formation of the dimeric, chloro-bridged complex **B1**.

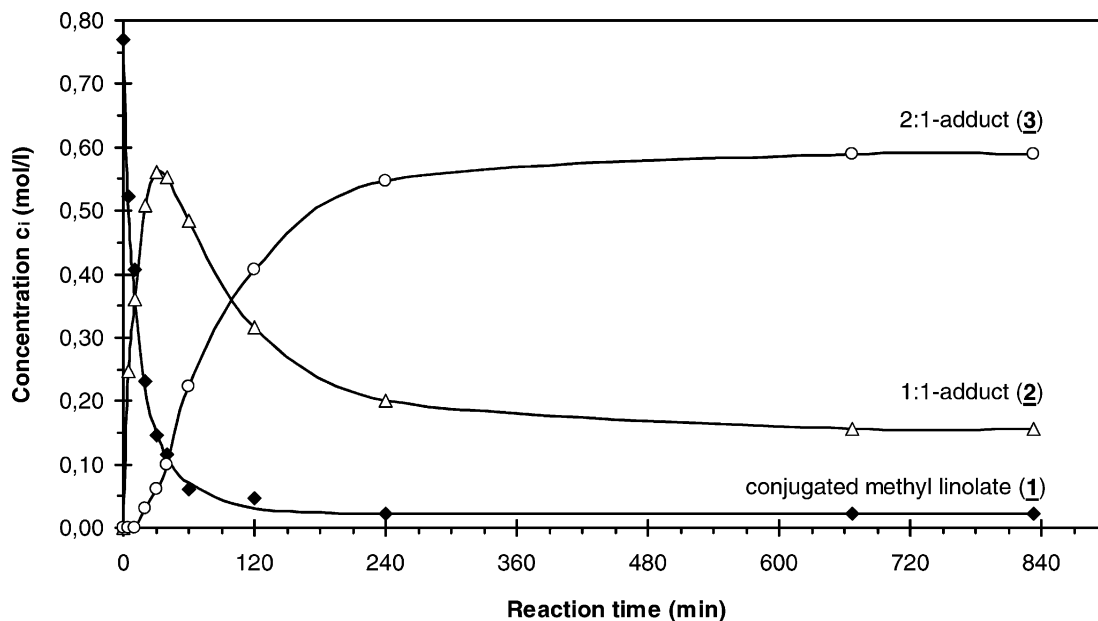


Fig. 3. Long-term experiment of the cooligomerization using cinnamyl chloride in single phase. Reaction conditions:  $T = 70^\circ\text{C}$ ;  $P = 3.0\text{MPa}$ ; cinnamyl chloride/Rh = 25 (mol ratio); conjugated methyl linolate **1**/Rh = 200 (mol ratio);  $t = 840\text{min}$ ; PC/SFAME/dioxane = 1:1:0.4 (volume ratio); total reaction volume = 100 ml.

If cinnamyl chloride with a labile C–Cl bond is added, a reactivation cycle B takes place in addition to the cooligomerization cycle A (see Fig. 4).

The  $\text{HRhCl}_2$  complex can either form an  $\eta^3$ -allylic complex (**A2**) with the conjugated methyl linolate **1** or can be reduced to the inactive rhodium(I) complex (**B1**) by the reductive elimination of HCl followed by adding ethylene.

Cramer proved that these rhodium(I) complexes are inactive for the codimerization [16,17]. By the oxidative addition of an organic chloride with a labile C–Cl bond like cinnamyl chloride the  $\sigma, \eta^2$ -complex **B2** is formed. After the insertion of ethylene into the rhodium–carbon bond and  $\beta$ -hydride elimination the active rhodium(III) hydrido species **A1** is formed again. However, it is assumed that the regeneration cycle B will only happen once in 100 cycles A. Thus, only traces of the product  $\text{RCH}=\text{CH}_2$ —the degradation product of the promoter—is formed in cycle B, which consequently could not be detected by GC analysis.

The prevailing of cycle A can be explained by the higher affinity, i.e. the higher co-ordination tendency of the functionalised diene (**1**) to the rhodium catalyst compared to ethylene.

### 3.4. New catalyst recycling method

After having solved the problem of catalyst decay the next aim was the recycling of the rhodium catalyst. The dilemma was that in biphasic systems the established liquid/liquid two-phase technique could be applied, but the reaction rates were too low because of the mass transport problems mentioned above. If the cooligomerization is carried out in single phase, high yields can be achieved, but without any chance of recycling the catalyst. Because of the high boiling points of products **2** + **3** and the thermal sensitivity of the catalyst/promoting agent system, a thermal recovery of the catalyst by the distillation of the products is not possible.

Therefore, the application of temperature-dependent solvent systems is an interesting recycling concept. Generally, these systems consist of a polar and a non-polar solvent  $s_1$  and  $s_2$ , which have to be immiscible for applying the two-phase technique. The third semi-polar solvent  $s_3$  must be miscible with both—the polar and non-polar—solvents and functions as a solubilizer. The general principle is shown in two-phase equilibria of a temperature-dependent

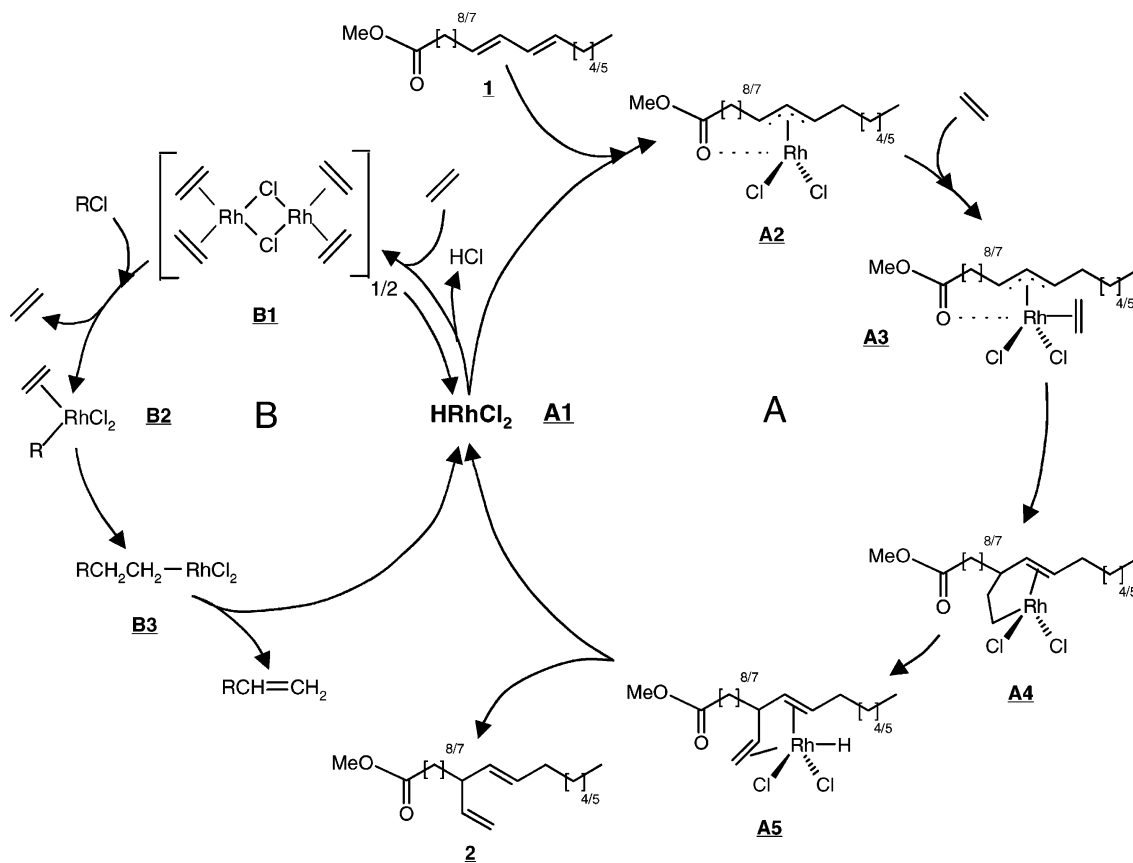


Fig. 4. Postulated mechanism of the rhodium(III)-catalysed cooligomerization (cycle A) and the reactivation of the inactive rhodium(I) catalyst (cycle B).

solvent system (see Fig. 5). At reaction temperature, the marked operation point is situated above the binodal curve, i.e. in the single-phase area. By reducing the temperature to room temperature, the two-phase area is enlarged, i.e. the operation point is then in the two-phase area. Depending on the phase equilibrium of the solvent systems, not only one operation point is possible, but various operation points can be used according to the reaction temperature, the composition and the different solvent components.

Propylene carbonate and ethylene glycol can be used as the polar solvent  $s_1$ . Because of the long alkyl chain, fatty substances have a similar solution behaviour as hydrocarbons and can therefore be used both as the reactant (**1**) and as the non-polar solvent  $s_2$ , which show a nearly complete miscibility gap with  $s_1$ . This alternative allows that the solvent excess

can be decisively decreased. As the third semi-polar solvent  $s_3$  ethers or short-chain alcohols can be used. In Table 2, the results of some ethylene glycol and propylene carbonate-based solvent systems are displayed. In addition, the results of the cooligomerization in the pure two-phase system are listed for comparison. In temperature-dependent solvent system, a high increase of the yields in single-phase systems can be obtained. Generally, in propylene carbonate-based systems, higher yields are achieved compared to ethylene glycol-based systems, especially concerning the 2:1 adduct (**3**). Above all, the propylene carbonate/SFAME/dioxane systems should be pointed out because of the extremely total yield of 96% and the high yield of the 2:1 adduct (**3**) of 64% after 2 h. If the reaction time is doubled to 4 h a nearly quantitative conversion rate (99%) can be observed.

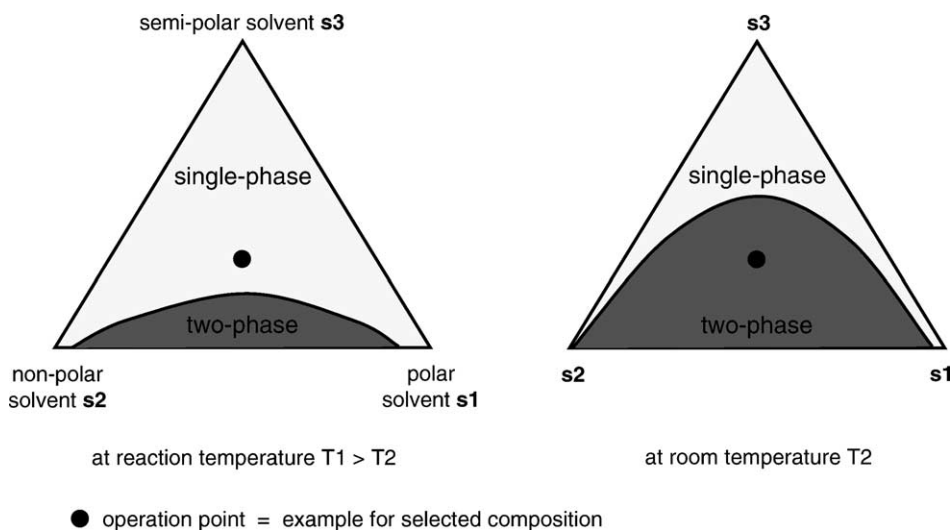


Fig. 5. General principle of temperature-dependent solvent systems.

Measuring the gas solubility of the system PC/SFAME/dioxane at pressures over 2.5 MPa the liquid phase contains ethylene in a molar excess compared to the second reactant—the conjugated methyl linolate **1**. Thus, the synthesis of branched fatty substances is not influenced by the gas–liquid mass transport and the reaction occurs in a pure liquid phase. This result can be verified by an investigation of the

influence of ethylene pressure (see Fig. 6). From 0.5 up to 1.5 MPa a linear increase of the total yield is observed. The curve approaches a nearly constant yield (96%) at pressures over 2.5 MPa. Especially the yield of the 2:1 adduct (**3**) indicates a strong influence of the gas–liquid mass transport at low pressures: After 4 h at 0.5 MPa only 2% of **3** is formed, whereas at 1.0 MPa already a yield of 20% of **3** can be achieved.

Table 2

Use of temperature-dependent solvent systems<sup>a</sup> with ethylene glycol or propylene carbonate as the catalyst dissolving solvent for the cooligomerization<sup>b</sup>

Solvent system (s1/s2/s3 single phase at $T \geq 50^\circ\text{C}$ )	Volume ratio	Conversion of <b>1</b> (%)	Yield (%)		
			<b>2</b>	<b>3</b>	Total ( <b>2</b> + <b>3</b> )
EG (two-phase process)		12	9	0	9
PC (two-phase process)		40	40	0	40
EG/SFAME/THF	1:1:2.8	79	72	4	76
EG/SFAME/dioxane	1:1:2.8	82	73	7	80
PC/SFAME/ethanol	1:1:1.5	85	60	19	79
PC/SFAME/anisole	1:1:0.4	86	61	14	75
PC/SFAME/toluene	1:1:0.4	91	65	18	83
PC/SFAME/THF	1:1:0.4	93	59	19	88
PC/SFAME/dioxane	1:1:0.4	96	31	64	95
PC/SFAME/dioxane	1:1:0.4	99	22	75	97 <sup>c</sup>

<sup>a</sup> EG: ethylene glycol; PC: propylene carbonate; SFAME: sunflower fatty acid methyl ester (containing 60.5 wt.% of **1**); THF: tetrahydrofuran.

<sup>b</sup> Reaction conditions:  $T = 70^\circ\text{C}$ ,  $P = 3.0\text{ MPa}$ , chloride/Rh = 25 (mol ratio), conjugated methyl linolate **1**/Rh = 200 (mol ratio),  $t = 2\text{ h}$ , total reaction volume = 60 ml.

<sup>c</sup> Enhanced reaction time of 4 h.



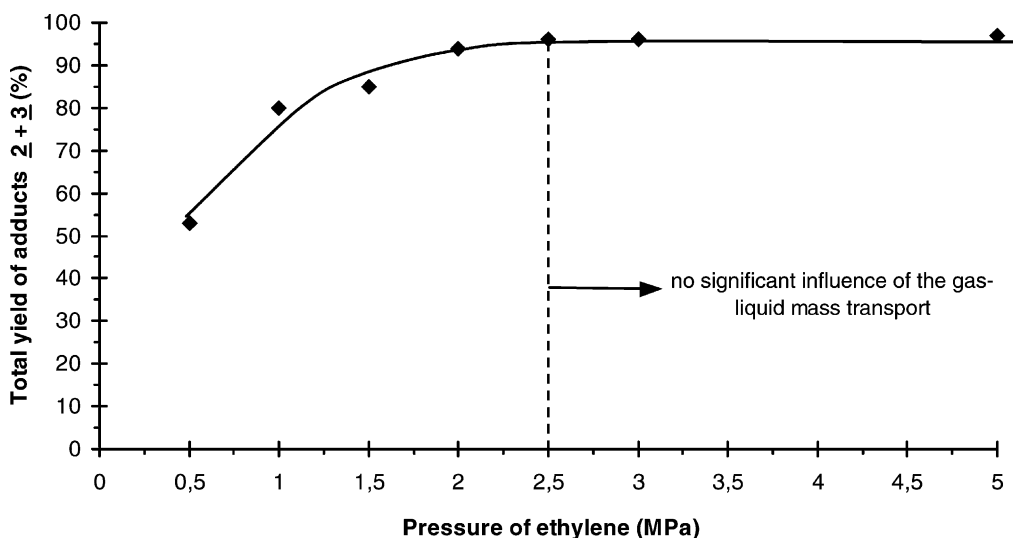


Fig. 6. Influence of the ethylene pressure. Reaction conditions:  $T = 70^\circ\text{C}$ ; cinnamyl chloride/Rh = 25 (mol ratio); conjugated methyl linolate 1/Rh = 200 (mol ratio);  $t = 2\text{ h}$ ; PC/SFAME/dioxane = 1:1:0.4 (volume ratio); total reaction volume = 60 ml.

### 3.5. Influence of cinnamyl chloride/rhodium ratio

The concentration of the catalyst as well as the concentration of the promoting agent have an important influence on the reaction progress, i.e. on the con-

version rate as well as on the activity. We investigated rhodium(III) chloride trihydrate and cinnamyl chloride in the temperature-dependent solvent system PC/SFAME/dioxane. Fig. 7 reflects the influence of the total yield related to the molar ratio of cinnamyl

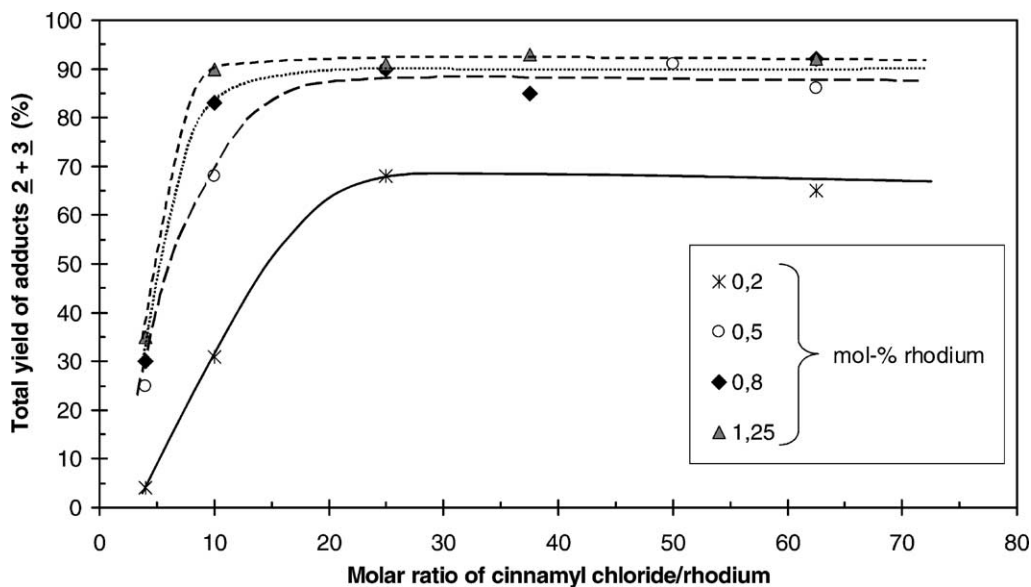


Fig. 7. Influence of the cinnamyl chloride/rhodium ratio. Reaction conditions:  $T = 70^\circ\text{C}$ ;  $P = 3.0\text{ MPa}$ ;  $t = 2\text{ h}$ ; PC/SFAME/dioxane = 1:1:0.4 (volume ratio); total reaction volume = 15 ml.

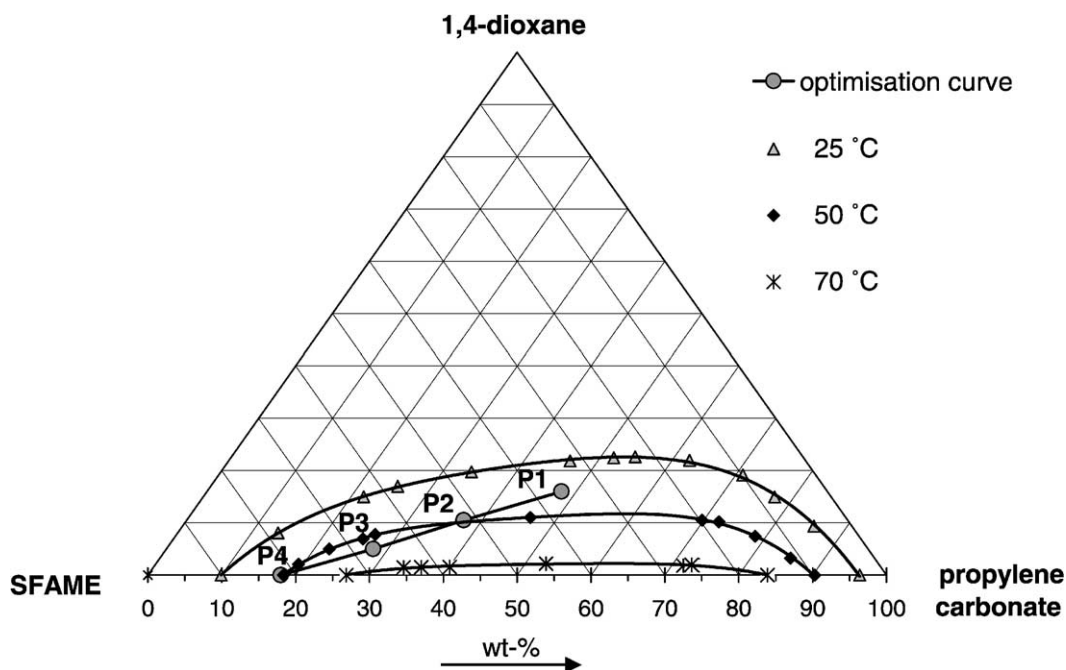


Fig. 8. Optimisation of the reactant **1**/solvent ratio. Reaction conditions:  $T = 70\text{ }^{\circ}\text{C}$ ;  $P = 3.0\text{ MPa}$ ; cinnamyl chloride/Rh = 25 (mol ratio); conjugated methyl linolate **1**/Rh = 200 (mol ratio);  $t = 2\text{ h}$ ; total reaction volume = 60 ml.

chloride to rhodium at different rhodium concentrations (related to **1**).

All curves form a similar line. In the lower range of concentration the total yield rises with increasing rhodium and cinnamyl chloride concentration. At molar ratios of cinnamyl chloride/rhodium higher than 25 no significant change of the yield can be observed. If the rhodium concentration is higher than 0.5 mol% a yield of about 90% is achieved.

An optimum yield of nearly 90% is obtained with a rhodium concentration of 0.5 up to 0.8 mol% at molar ratios of cinnamyl chloride to rhodium of 10 up to 25.

### 3.6. Optimisation of space–time yield

For the cooligomerization reaction the solvent/reactant ratio in the solvent system PC/SFAME/dioxane is optimised. Four possible operation points for the

Table 3  
Optimisation of the reactant SFAME (**1**)/solvent ratio<sup>a</sup>

Experiment <sup>b</sup>	PC/SFAME/dioxane ratio (wt.%)	SFAME/solvent ratio	Conversion (%) of <b>1</b>	Yield (%)		
				<b>2</b>	<b>3</b>	Total <sup>c</sup>
P1	45:36:16	0.6	96	31	65	96
P2	37.5:52:10.5	1.1	97	33	63	96
P3	28:67:5	2.0	95	38	57	95
P4	18:82:0	4.6	93	44	49	93

<sup>a</sup> Reaction conditions:  $T = 70\text{ }^{\circ}\text{C}$ ,  $P = 3.0\text{ MPa}$ , chloride/Rh = 25 (mol ratio), conjugated methyl linolate **1**/Rh = 200 (mol ratio),  $t = 2\text{ h}$ , total reaction volume = 60 ml.

<sup>b</sup> See Fig. 8.

<sup>c</sup> Total = **2** + **3**.

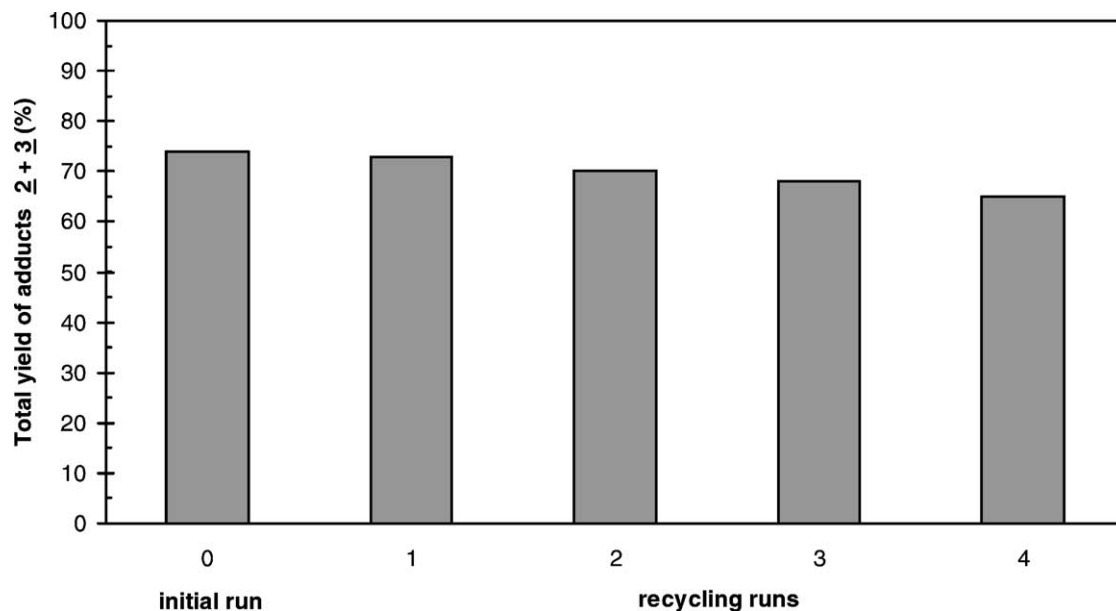


Fig. 9. Catalyst recycling experiments. Reaction conditions:  $T = 70\text{ }^{\circ}\text{C}$ ;  $P = 3.0\text{ MPa}$ ; cinnamyl chloride/Rh = 25 (mol ratio); conjugated methyl linolate 1/Rh = 200 (mol ratio);  $t = 40\text{ min}$ ; PC/SFAME = 1:4 (mass ratio); total reaction volume = 60 ml.

optimisation are drawn in the phase equilibrium of Fig. 8. For every operation point it must be ensured that at a temperature of  $70\text{ }^{\circ}\text{C}$  the reaction is carried out in single phase. The results, which are listed in Table 3, show high total yields of about 95%. A decrease in the yield of adduct 3 was only observed in experiment P4 where no dioxane was used. In a small range the semi-polar solvent dioxane is unnecessary. The reactant (SFAME)/solvent ratio can be increased from 0.6 up to 4.6.

### 3.7. Catalyst recycling investigations

Recycling experiments in the temperature-dependent solvent system PC/SFAME were all carried out with constant reaction conditions. After the reaction both phases were separated and the propylene carbonate phase, which contained the catalyst, was used again. The reactant SFAME as well as small amounts of propylene carbonate (containing the catalyst) were refreshed according to the phase equilibrium.

As seen in Fig. 9 a decrease of about 4% relatively of the total yield can be observed because of some leaching and decay mainly of the promoter cinnamyl chloride. Based on these recycling experiments, a to-

tal turn over number (TTON) of about 1500 can be extrapolated. The turn over frequency (TOF) in the initial run is  $220\text{ h}^{-1}$ .

## 4. Conclusion and outlook

The rhodium-catalysed cooligomerization of fatty acid derivatives with ethylene leads to internal branched fatty substances. By using organic chlorides with labile C–Cl bonds a significant increase in the catalytic activity can be seen and the inactivation of the rhodium(III) catalyst can also be prevented. Therefore, a combined catalytic cycle is postulated, which describes the cooligomerization as well as the regeneration by the promoter.

Although a biphasic cooligomerization seems to be interesting for the catalyst recycling via the liquid/liquid two-phase technique, only in single phase technically interesting yields can be achieved. Thus, cinnamyl chloride as the promoter and a single-phase reaction are necessary to solve the mass transport problems.

Temperature-dependent solvent systems as a new recycling concept can be applied successfully still

guaranteeing high yields and a not diffusion-controlled reaction as well as an easy catalyst recycling. The total yield can be increased to 98% using the solvent system propylene carbonate/SFAME/dioxane under very mild conditions (70 °C, 3.0 MPa) and the turn over frequency can be enhanced by factor 100 (2 versus 220 h<sup>-1</sup>). The sunflower fatty acid methyl ester can be used as the reactant as well as the non-polar solvent component whereby the reactant/solvent ratio can be increased to 4.6. Investigations of the catalyst recycling mirrored a slight decrease of the total yield in every recycling run, mainly due to the decay of cinnamyl chloride and its solubility in the product phase. The basis for the process development of the technical synthesis of branched fatty substances is provided.

First investigations of the application properties of a product mixture of adducts **2** + **3** show an excellent low-temperature performance, i.e. low pour points and a high oxidation resistance after hydrogenation of the double bounds.

If these interesting products also show a good biodegradability, they will be expected to be used as biolubricants. Thus, further properties as well as possibilities for a separation of the non-branched fatty components should be examined in more detail.

Furthermore, we are looking forward to applying the new recycling concept of temperature-dependent solvent systems to other technically interesting reactions, especially if the reactions are strongly influenced by mass transport processes.

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