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Selective two-phase-hydrogenation of sorbic acid with novel water soluble ruthenium complexes

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Abstract

Neutral and cationic water soluble Cp*-ruthenium-complexes of the type [Cp*Ru(CO)Cl(PR_3)] and [Cp*Ru(CO)(PR_3)]CF_3SO_3 (R = CH_2OH, $(CH_2)_3OH$, Ph-*m*-SO_3Na) have been synthesized for the first time and have been used as catalysts in two-phase-hydrogenations. The neutral complexes have been fully characterized. But the cationic complexes which have not been isolated are effective catalysts for the selective hydrogenation of sorbic acid in water/*n*-heptane leading to the formation of *cis*-3-hexenoic acid and *trans*-3-hexenoic acid. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Transition metal complex catalyzed reactions in two immiscible liquid phases can be industrially important alternatives to homogeneously catalyzed one-phase-reactions. The synthesis of butyric aldehyde by the Ruhrchemie/Rhône-Poulenc-process [1] serves as an example as well as the production of α-olefins in the SHOP-process [2]. After the catalytic reaction is completed one phase contains the products and the other phase contains the catalyst. After simply separating the two phases, the catalyst phase can be used again directly without any further treatment. A very suitable solvent for this phase is water since it is very cheap and immiscible with many organic solvents, which serve as solvents for the products [3]. The second innovative effect of two-phase-catalysis is the possibility to extract primary products during the catalytic reaction into the organic phase, resulting in novel possibilities of controlling the product selectivity [4].

Selective transformations of multifunctional substrates using two-phase-catalysis are of interest to the authors. The hydrogenation of sorbic acid **1**, which is produced industrially, can lead to many different products, some of which are shown in Scheme 1.

Generally, hexenoic acids like **2**–**5**, bearing one C=C-bond, are interesting as starting materials for the production of fine chemicals. Up to now it was not possible to hydrogenate **1** stereoselectively by means of homogeneous catalysis, although esters of sorbic acid were hydrogenated using catalytic one-phase-techniques [5].

Among others, chromium catalysts have being used to date for this reaction, which is questionable due to the toxicity of these compounds ([5]f, g). If a selective catalytic two-phase-hydrogenation with less toxic catalysts was successful, an alternative way of obtaining hexenoic acids industrially might be considered. We studied the hydrogenation of **1** to find out if it was possible to obtain *trans*-3-hexenoic acid **2** and *cis*-3-hexenoic acid **3** selectively and to avoid hydrogenation to hexanoic acid **6**. Prior to synthesizing new water soluble transition metal complexes, which serve as catalysts, it was necessary to develop a suitable purification

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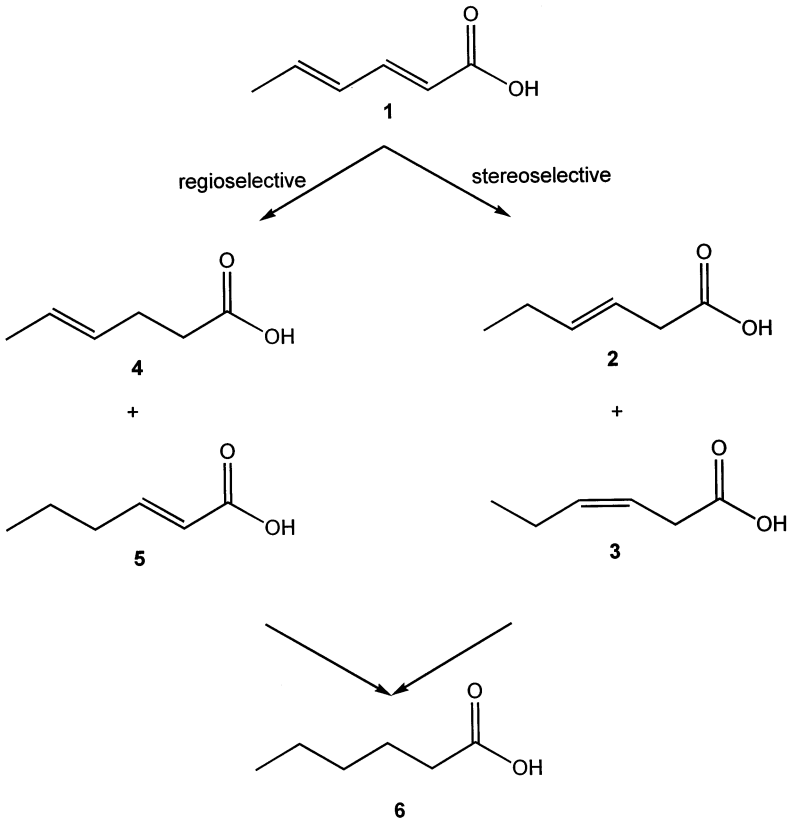


Scheme 1. Possible products in the hydrogenation of sorbic acid.

method for the ligand $P[(CH_2)_3OH]_3$ which was only known from patents as an additive for cosmetic products [6]. Using Tris(hydroxyalkyl)phosphane ligands and the well known tppts-ligand we synthesized for the first time water soluble Cp*-ruthenium-complexes of the general formula $[Cp^*Ru(CO)(PR_3)Cl]$.

2. Results and discussion

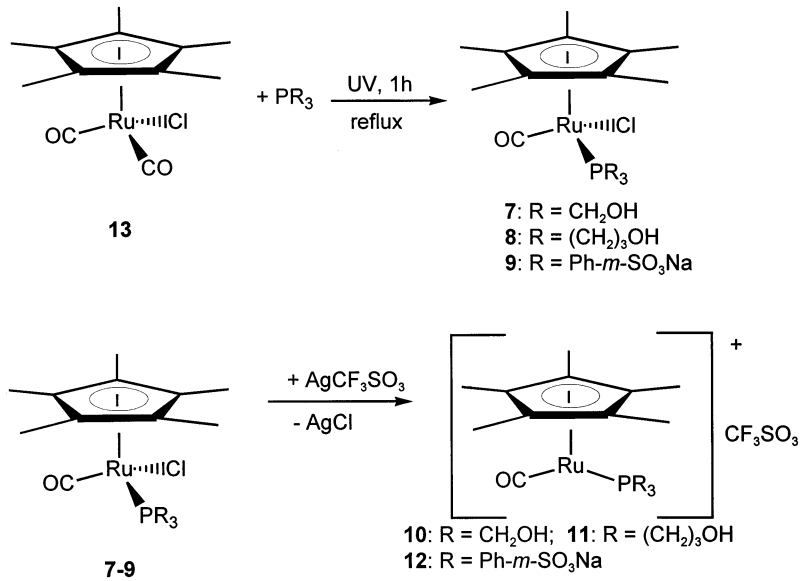
Tris(hydroxymethyl)phosphane **14** was synthesized following Pringle et al. [7]. The synthesis of Tris(3-hydroxypropyl)phosphane **15** is only described in a patent starting from PH_3 and allylacetate [6]. After hydrolysis of the acetate phosphane the product mixture contains about 70% of the desired phosphane and about 30% of the corresponding phosphane oxide. We developed an effective method to purify this ligand via column chromatography (see Section 4).

If $[Cp^*Ru(CO)_2Cl]$ **13** [8] is reacted with $P[CH_2OH]_3$ **14** and $P[(CH_2)_3OH]_3$ **15** in THF under irradiation with UV-light (Scheme 2), one obtains the complexes **7** (84%) and **8** (78%), respectively (for work up and purification see Section 4).

The same reaction with tppts **16** can be carried out using a solvent mixture of methanol/water and leads to the isolation of **9** (47%). All complexes could be characterized unambigously with IR- and NMR-spectroscopy as well as elemental analyses (see Section 4). The NMR data compare well with the structures shown in Scheme 2. The position of the IR band of the CO stretching vibration of terminal CO groups hints at the extent of the CO back donation. If there is a strong back donation the ν(CO) value is driven to lower wave numbers. The only difference in the neutral complexes **7**–**9** is the type of phosphane. Thus the electronic properties of the complexes can be directly compared. The CO stretching vibration has the lowest value ($\nu(CO) = 1921\ cm^{-1}$) in complex **8**, and in **9** and **7** the CO vibrations exhibit medium and maximum values of 1928 and 1935 cm^{-1}, respectively. These data also reflect the stability of the complexes. The elemental analyses of all complexes are in very good agreement with the values that were calculated for carbon and hydrogen.

We used these complexes as catalysts for the hydrogenation of sorbic acid **1**. The complexes were dissolved in water and the substrate in *n*-heptane. The two phases were then mixed thoroughly in the presence of hydrogen. Table 1 shows the results.

It emerged that hydrogenations using **7** and **8** as catalysts transformed **1** with acceptable conversions under the reaction conditions but the desired hexenoic acids were formed only with small to medium selectivities. While **6** was formed with 92% selectivity with **8**



Scheme 2. Reaction sequence for production of the neutral and cationic Cp*Ru-complexes.

being the catalyst but **3** and **2** only with 3% and in traces, respectively, **3** and **6** were both formed with 41% selectivity when **7** was used as catalyst. This reaction also yielded **2** with 10% selectivity. As far as the selectivities are concerned the results were similar with complex **9** as catalyst but the conversion only was 8%.

In order to find out if these results could be improved when the corresponding cationic ruthenium complexes were used, we studied the catalytic behaviour of complexes **10**–**12** which were generated in situ by reactions of **7**–**9** with $AgCF_3SO_3$. The results of the two-phase-hydrogenations of **1** are summarized in Table 2.

The cationic complexes **11** and **12** are seven and 4.3 times more active than the corresponding neutral complexes and the 3-hexenoic acids were formed with significantly higher selectivities. Complex **12** decomposes partly during the reaction, while **11** is stable. When **10** was used as catalyst the starting material did not react at all and a black precipitate was formed already during catalyst preformation, indicating the decomposition of the complex.

Hexanoic acid **6** was formed in the presence of **11** with a selectivity of 22% but it could not be detected using **12** as catalyst. It is interesting to note that the use of **11** yielded **3** with 66% and **2** with only 7% selectivity, whereas **12** led to nearly opposite results: **3** was formed with 1% and **2** with 85% selectivity. The selectivities obtained with **11** and **12** are good and do exceed the ones obtained in catalytic hydrogenations of sorbic acid esters with one phase reactions ([5]f, g). The higher activities of the cationic complexes relative to the neutral ones can be explained with an increased Lewis acidity. Through the loss of the chloride ion the cationic complexes have a vacant coordination site which makes the binding of the substrate easier, both from steric and electronic considerations. It should be noted that the 3-hexenoic acids are not only obtained with good selectivities but that it is also possible to

Table 1
Two-phase-hydrogenation of sorbic acid **1** with complexes **7**–**9** as catalyst precursor

Complex	**7**	**8**	**9**
Conversion (%)	40	52	8
TON	40	52	8
TOF (h^{-1})	2.6	3.5	0.5
$S_{\text{hexanoic acid}}$ **6** (%)	41	92	40
$S_{trans\text{-2-hexenoic acid}}$ **5** (%)	7	5	20
$S_{cis\text{-3-hexenoic acid}}$ **3** (%)	41	3	20
$S_{trans\text{-3-hexenoic acid}}$ **2** (%)	10	Traces	20
ν(CO) (cm^{-1})	1935	1921	1928

Reaction conditions: 80°C, 15 h, 50 bar H_2, 0.1 mmol Cat./30 ml H_2O, 10 mmol sorbic acid in 60 ml *n*-heptane.

Table 2
Catalysis results of the cationic in situ systems **10**, **11** and **12** in the biphasic hydrogenation of sorbic acid **1**

Complex	**10**	**11**	**12**
Conversion (%)	—	62	14
TON	—	62	14
TOF (h^{-1})	—	15.5	3.5
$S_{\text{hexanoic acid}}$ **6** (%)	—	22	—
$S_{\text{2-hexenoic acid}}$ **5** (%)	—	5	15
$S_{cis\text{-3-hexenoic acid}}$ **3** (%)	—	66	1
$S_{trans\text{-3-hexenoic acid}}$ **2** (%)	—	7	85
ν(CO) (cm^{-1})	—	1930	1959

Reaction conditions: 80°C, 4 h, 50 bar H_2, each 0.1 mmol Cat. and $AgCF_3SO_3$ in 30 ml H_2O, 10 mmol sorbic acid in 60 ml *n*-heptane.

control the stereochemical outcome of the reaction by the choice of the ligand.

The CO-band in the IR-spectrum of **8** (1921 cm^{-1}) is shifted by about nine wavenumbers in **11** to 1930 cm^{-1}. The same trend is observed for **9** (1928 cm^{-1}) and **12** (1959 cm^{-1}), the shifts being 31 wavenumbers, respectively. The shift to higher wavenumbers is assigned to stronger M–CO-bonds which is strongly indicative for the presence of cationic complexes. ^{31}P-NMR- and ^{13}C-NMR-spectra show that there are either no or only very small interactions between the oxygen atoms of the hydroxy groups of the phosphane ligand **15** and the ruthenium atom.

3. Conclusions

We have used $P[CH_2OH]_3$ as well as the phosphanes $P[(CH_2)_3OH]_3$ and tppts for the syntheses of water soluble ruthenium complexes. We were able to isolate and characterize the complexes **7**–**9** with the general formula [Cp*Ru(CO)Cl(PR_3)]. The corresponding cationic derivatives **10**–**12** having the formula [Cp*Ru(CO)(PR_3)]CF_3SO_3 have been synthesized in situ. Both types of complexes catalyze the two-phase-hydrogenation of sorbic acid **1** but it is the cationic complexes which give very good selectivities and good conversions to 3-hexenoic acids.

The choice of the ligand enables one to control the stereochemistry of the reaction and thus makes it possible to synthesize *cis*-3-hexenoic acid and *trans*-3-hexenoic acid selectively. Catalytic studies with other water soluble complexes containing new ligands of this kind should lead to a more profound understanding of the ligand effect with respect to the stereochemistry of this reaction. Studies of this kind as well as the syntheses of new water soluble catalysts are currently under investigation.

4. Experimental

4.1. General

All procedures were carried out under an atmosphere of dry argon using standard Schlenk techniques. The argon was deoxygenated by BASF catalyst R-3-11 and dried using molsieve Linde 4 A. Solvents were freshly distilled under an argon atmosphere and dried by standard procedures. Air and moisture sensitive solutions and reagents were handled using syringe techniques. Under pressure, hydrogenation experiments were carried out in 100 ml stainless steel autoclaves equipped with special stirrers for two-phase-catalysis. NMR spectra were acquired on Bruker AC-300 and Bruker DPX-300 spectrometers. Chemical shifts were referenced to internal or external TMS (^{1}H, ^{13}C) respectively external 85% H_3PO_4 (^{31}P). IR spectra were recorded on a Nicolet 505-FT-IR spectrometer. Sorbic acid was purchased from Aldrich. The hydrogen used had a purity of 99.9%. [Cp*Ru(CO)$_2$Cl] was prepared using literature procedures [8].

4.2. General procedure for preparation of the neutral complexes

[Cp*Ru(CO)$_2$Cl] **13** (0.03 mmol) and 0.3 mmol of the appropriate ligand (**14**–**16**) were dissolved separately, each in 20 ml THF or in MeOH/H_2O. The solutions were introduced in an autoclave (quartz glass) via syringes and under argon. The autoclave was fitted with a magnetic stirrer bar, a delivery tube for argon and a reflux condenser. At about 10 cm from the autoclave a UV-lamp was placed to irradiate the stirred reaction mixture for 1 h. After ca. 10 min the reaction mixture was under reflux and the color of the yellow solution became more intense. After the reaction, the solvent was removed in vacuo and the resulting yellow residue was dissolved in ether.

Complex **7** was purified as follows: The product mixture was separated by column chromatrography on silica with ether as solvent (column dimensions: 2 cm diameter, length 25 cm). As a first fraction unreacted **13** was recovered. The solvent was then changed to ethyl acetate or THF and a yellow solution was obtained. The solvent was removed in vacuo and the residue treated with pentane. The solution was decanted from the solid product **7** which was obtained in 85% yield after drying.

^{1}H-NMR (300 MHz, CD_3OD): $\delta = 1.71$ ppm (s, 15H, Cp*) 4.17 (s, CH_2, 6H). ^{13}C-NMR (75 MHz, CD_3OD): $\delta = 203.2$ (d, *C*O, J(PC) = 19.5 Hz), 95.4 (s, *C*p–Me_5), 58.16 (s, *C*H_2OH, J(PC = 27,4 Hz), 9.22 (s, Cp–*Me*$_5$). ^{31}P-NMR (121 MHz, CD_2Cl_2) $\delta = 37.91$ ppm, (free ligand: $\delta = -23.24$ ppm). IR (KBr): ν(CO) 1935 cm^{-1}. Elemental analysis: $C_{14}H_{24}PO_4ClRu$ (423.67 g mol^{-1}); C_{found}: 39.68% ($C_{calc.}$ 39.69%); H_{found} 5.66% ($H_{calc.}$ 5.68%).

Complex **8** was purified as follows: The first column chromatography was carried out as described above. After **13** was removed, the solvent system was changed to ethyl acetate/methanol (4:1), which yielded the product fraction. The solvents were removed in vacuo. The residue was washed with a small amount of water and then dried. Recrystallization from refluxing toluene yielded **8** in 78% as yellow microcrystals.

^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.79$ ppm (s, 15 H, Cp*), 1.95 (tr, 12 H, CH_2CH_2OH, $J = 12$ Hz), 3.61 (tr, 6 H, CH_2CH_2OH, $J = 12$ Hz), 4.87 (s, H_2O). ^{13}C-NMR (75 MHz, CD_3OD): $\delta = 205.5$ (d, *C*O, J(PC) = 20.6

Hz, 94.4 (s, *C*p–Me_5), 61.1 (s, CH_2OH, J(PC = 14 Hz), 25.5 (s, $CH_2CH_2CH_2OH$), 21.5 (d, $CH_2(CH_2)_2OH$, J(PC) = 27.2 Hz), 7.76 (s, Cp–*Me*$_5$). ^{31}P-NMR (121 MHz, d_6-acetone) $\delta = 30.43$ ppm, (free ligand: $\delta = -30$ ppm). IR (KBr): ν(CO) 1921 cm^{-1}. Elemental analysis: $C_{20}H_{36}PO_4ClRu$ (507.52 g mol^{-1}); C_{found}: 47.29% ($C_{calc.}$ 47.28%); H_{found} 7.11% ($H_{calc.}$ 7.09%).

Complex **9** was purified as follows: After the irradiation, the solvents were removed in vacuo. The residue was suspended twice in 5 ml portions of ether. After decantation, the solid was dried in vacuo and then dissolved in 2 ml water. This solution was used for chromatrography on Sephadex® (column dimensions: diameter 2.5 cm, 45 cm length). The first fraction was unreacted ligand and the corresponding oxide. Subsequently complex **9** was obtained as a deep yellow fraction. After removal of water the residue was recrystallized from ethanol (yield: 47%).

^{1}H-NMR (300 MHz, D_2O): $\delta = 1.33$ (s, 15 H, Cp*), 4.61 (s, ca. 6 H), 7.66 (m, 12 H, tppts). ^{13}C-NMR (75 MHz, D_2O): $\delta = 204.2$ (d, CO, J(PC, 20 Hz) 141.1 (d) 133.97 (s) 128.84 (s) 127.5 (d) u.127.73 (d) all tppts, 95.6 (s, *Cp*–Me_5), 6.79 (s, Cp–*Me*$_5$). ^{31}P-NMR (121 MHz, CD_3OD): $\delta = 50.69$ (s). IR(KBr): ν(CO): 1928 cm^{-1}. Elemental analysis: $C_{29}H_{33}RuClPO_{13}S_3Na_3$ (921.96 g mol^{-1}); C_{found} 37.18% ($C_{calc.}$ 37.78%); H_{found} 3.48% ($H_{calc.}$ 3.57%).

4.3. General procedure for preparation of the cationic complexes

Two millimoles of the appropriate neutral complex (**7**–**9**) were reacted with 2 mmol $AgCF_3SO_3$ in 40 ml CH_2Cl_2 in the dark. The suspension was filtered over celite. The solvent was removed from the filtrate in vacuo. The remaining residue was characterized spectroscopically and used for the hydrogenation of sorbic acid.

Characterization of **11**: ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta = 3.57$ (s, 6H, C*H*$_2$OH), 2.0–1.4 (m, br., 12 H, PC*H*$_2$CH$_2$ and Cp–*Me*$_5$). ^{31}P-NMR (121 MHz, CD_2Cl_2): $\delta = 30.05$ (s). ^{19}F-NMR (282 MHz, CD_2Cl_2): $\delta = -79.24$. IR(KBr): 1958 cm^{-1}.

4.4. General procedure for purification of ligand *15*

A chromatographic purification of **15** was found to be the best. The stationary phase was silica 60 (Merck) which was evacuated several times and set under argon. The glass column which can be handled under argon (∅3.5 cm, length 45 cm) was filled with 500 ml silica which was suspended in 160 ml methanol and 640 ml ethyl acetate. A 250 ml aliquot of the solvent mixture was run through the column to homogenate the column. The column was left to settle overnight. A solution of 5 g Tris(3-hydroxypropyl)phosphane **15** in 5 ml of methanol was deposited and eluted with a mixture of ethyl acetate/methanol 4:1. The phosphane oxide was obtained first and was detected with UV-light. The desired phosphane **15** could be detected with molybdatophosphoric acid solution in ethanol. The purification by column chromatography took about 12 h and gave the phosphane in a pure form.

4.5. Hydrogenation reaction

The cold catalyst solution was transferred into a 100 ml stainless steel autoclave via syringe with a PTFE cannula. The *n*-heptane phase containing the sorbic acid was added and the autoclave was pressurized with hydrogen. The autoclave was placed in an oil bath of 80°C. After the reaction the autoclave was cooled in an ice bath and was slowly vented. The two phases were separated. The products were in the *n*-heptane phase which was analyzed by GC [CP-Wax-58-(FFAP)-CB (50 m)].

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