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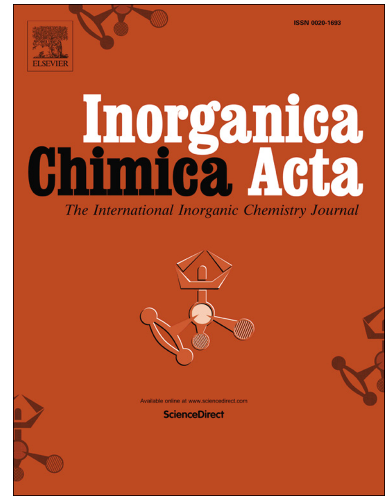

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Promoter effect of bicarbonate in hydrogenation of cinnamaldehyde catalyzed by a water-soluble Ru(II)-phosphine complex¶

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¶Dedicated to Professor Imre Sóvágó, our excellent teacher, esteemed colleague and longtime friend in recognition of his fundamental contributions to biocoordination chemistry, on the occasion of his 70th birthday.

Bullet points:

- $NaHCO_3$ strongly accelerates cinnamaldehyde hydrogenation with a water-soluble Ru(II)-phosphine catalyst

- The reaction is highly selective towards formation of the unsaturated alcohol

- A plausible reaction mechanism is suggested on basis of kinetic and NMR measurements

- Formate (from hydrogenation of bicarbonate) plays active role in catalysis

- *trans*-$[Ru(H)_2(H_2O)(m\text{tppms})_3]$ was identified as key catalytic species

Abstract

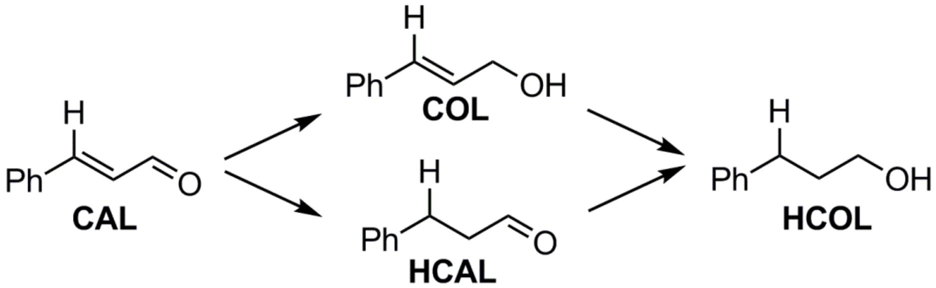
The highly selective formation of cinnamalcohol in hydrogenation of *trans*-cinnamaldehyde with [{$RuCl_2$(*m*tppms)$_2$}$_2$] + *m*tppms as catalyst (*m*tppms = monosulfonated triphenylphosphine) in aqueous solution was substantially accelerated by $NaHCO_3$ (in 20-50 mol% quantities relative to cinnamaldehyde). More than double conversion compared to bicarbonate-free systems was observed at n($NaHCO_3$)/n(Ru) = 20. Prehydrogenation of the reaction mixture before the addition of cinnamaldehyde resulted in further rate increase (45.3% conversion vs. 13.1% in water). ^{1}H-, ^{13}C- and ^{31}P-NMR studies revealed that formate produced in hydrogenation of bicarbonate facilitated formation of *trans*-[Ru(H)$_2$(H_2O)(*m*tppms)$_3$], a better catalyst than *cis*-*fac*-[Ru(H)$_2$(H_2O)(*m*tppms)$_3$] which is the product of the reaction of [{$RuCl_2$(*m*tppms)$_2$}$_2$] + *m*tppms with H_2 in the *absence* of formate (or bicarbonate). Accordingly, $NaHCO_2$ produced even higher rate increase than the same amount of $NaHCO_3$.

Keywords

Hydrogenation; Isomerization; Monosulfonated triphenylphosphine (*m*tppms); Ruthenium; Water-soluble.

1. Introduction

Selective reduction of unsaturated aldehydes (such as *trans*-cinnamaldehyde, CAL, Scheme 1) is a synthetically useful reaction and much research effort has been directed to selectively obtain from such substrates either saturated aldehydes or -and more importantly- unsaturated alcohols by catalytic hydrogenation or by hydrogen transfer from suitable H-donor compounds.[1-13] During our studies on hydrogenations in homogeneous aqueous solutions or in aqueous-organic biphasic systems we observed that [{$RuCl_2$(*m*tppms)$_2$}$_2$] (**1**; *m*tppms =diphenylphosphinobenzene-*m*-sulfonic acid Na-salt) in the presence of phosphine excess catalyzed exclusive formation of cinnamalcohol by catalytic hydrogen transfer from aqueous formate. [4, 14]



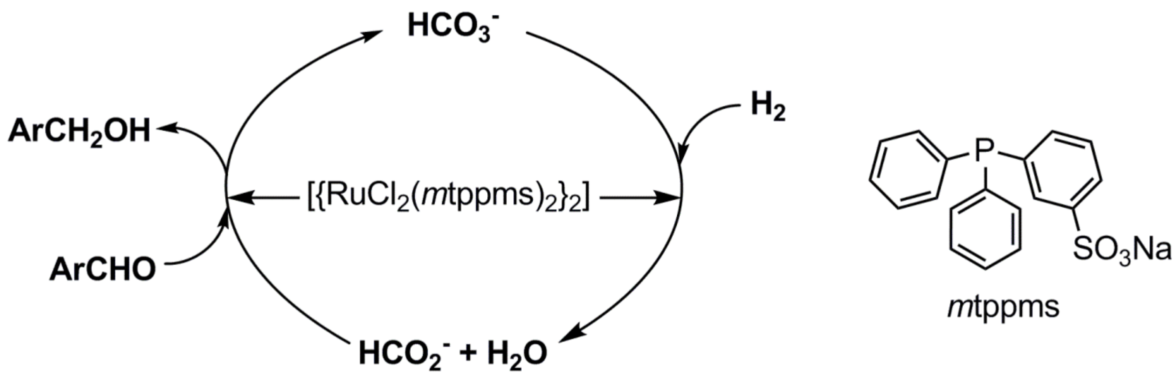
Scheme 1. Hydrogenation of *trans*-cinnamaldehyde.

Formation of unsaturated alcohols was also detected when unsaturated aldehydes were hydrogenated in an H_2 atmosphere (in the absence of formate) with the same Ru(II)-*m*tppms catalyst. In this case, a closer scrutiny of the effects of reaction parameters revealed that selectivity towards formation of either cinnamalcohol (COL) or 3-phenylpropanal (HCAL) critically depended on the pH of the aqueous phase (as well as on H_2 pressure[15]). At pH ≥ 8 hydrogenation yielded unsaturated alcohol while at pH ≤ 5 the exclusive product was saturated aldehyde – the pH even could be used as a selectivity switch.[16, 17] A detailed study later showed that depending on the pH and the hydrogen pressure in solutions of [{$RuCl_2$(*m*tppms)$_2$}$_2$] + n *m*tppms, altogether five hydrido-Ru(II) species could be formed, of which *trans*-[RuH_2(*m*tppms)$_4$], *cis*-*fac*-[RuH_2(H_2O)(*m*tppms)$_3$] and [RuH_2(η^2-H_2)(*m*tppms)$_3$] catalyzed the selective hydrogenation of the C=O function of aldehydes while [{RuHCl(*m*tppms)$_2$}$_2$] and [RuHCl(*m*tppms)$_3$] were active and selective in the saturation of the C=C bond.[18] It should be added here, that similar pH dependence of the rate and selectivity could not be studied in case of catalytic hydrogen transfer to unsaturated aldehydes from sodium formate since **1** is an active catalyst for decomposition of HCO_2H formed from HCO_2^- in acidic solutions.

It has been discovered recently that in aqueous solutions [{$RuCl_2$(*m*tppms)$_2$}$_2$] -in the presence of excess *m*tppms- actively catalyzed hydrogenation of bicarbonate to formate [19, 20] as well as the reverse reaction i.e. dehydrogenation of aqueous formate to bicarbonate.[21]

$$HCO_3^- + H_2 \rightleftharpoons HCO_2^- + H_2O$$

Considering the good H-donor properties of aqueous formate together with the high activity of [{$RuCl_2$(*m*tppms)$_2$}$_2$] + n *m*tppms in hydrogenation of bicarbonate to formate we reasoned that aqueous hydrogenation of aldehydes (with H_2) catalyzed by **1** + n *m*tppms, might be facilitated by addition of bicarbonate in sub-stoichiometric amounts relative the aldehyde. This possibility is shown schematically on Scheme 2.



Scheme 2. Selective catalytic hydrogenation of aldehydes in presence of bicarbonate.

Indeed, we have found a substantial promoter effect of HCO_3^- on hydrogenation of cinnamaldehyde catalyzed by **1**. Here we report the details of the reaction together with NMR studies on the possible Ru(II)-phosphine species participating in the catalytic cycles. A plausible reaction mechanism is also suggested.

2. Experimental Section

2.1. Materials and instruments

[{$RuCl_2$(*m*tppms)$_2$}$_2$] and *m*tppms were synthesized as described earlier [22] and their purities were checked by NMR spectroscopy. Cinnamaldehyde was purchased from Sigma-Aldrich and used as received. $RuCl_3 \times 3H_2O$ was obtained from Pressure Chemical Co., $NaHCO_3$ and $NaHCO_2$ were supplied by Sigma-Aldrich and Spectrum 3D. Argon and nitrogen (99.99% purity) were provided by Linde and used directly from cylinders. The pH of the solutions was adjusted to desired values using 0.2 M phosphate buffer solutions prepared from analytical grade $Na_2HPO_4 \times 12H_2O$ and $NaH_2PO_4 \times 2H_2O$. Deuterated solvents (99.9%) were purchased from Cambridge Isotope Laboratories Inc. and Sigma Aldrich.

NMR spectra were recorded on a BRUKER DRX 360 spectrometer and evaluated using the WinNMR program. ^1H, ^{13}C and ^{31}P NMR spectra were referenced to tetramethylsilane (TMS), 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), 85 % H_3PO_4 and residual solvent peaks, respectively. Gas chromatographic measurements were made on HP5890 Series II; Chrompack WCOT Fused Silica 30m*32mm CP WAX52CB; FID; carrier gas: argon; isothermal; temperatures: injector 250°C, oven 130°C, detector 250°C.

2.2. General experimental procedure for hydrogenation of cinnamaldehyde in the presence of $NaHCO_3$

In a Schlenk-flask, $NaHCO_3$ (16.8 mg, 0.2 mmol), [{$RuCl_2$(*m*tppms)$_2$}$_2$] (10.0 mg, 0.005 mmol) and *m*tppms (32.0 mg, 0.08 mmol) were dissolved in water (7.5 mL) under an argon atmosphere followed by addition of cinnamaldehyde (50 µL, 0.4 mmol). Argon was replaced by hydrogen and the solution was stirred at 50 °C for the desired reaction time. Samples (0.2 mL) were withdrawn periodically from the vigorously stirred solution and were diluted with 1.0 mL of water before extraction with 1.0 mL of chlorobenzene. The organic layer was dried ($MgSO_4$) and analyzed by gas chromatography. In experiments with prehydrogenation, the above solution of $NaHCO_3$, [{$RuCl_2$(*m*tppms)$_2$}$_2$] and *m*tppms was stirred in an H_2 atmosphere for 10 min at 50 °C before addition of cinnamaldehyde. Reactions with $P(H_2) > 1$ bar were carried out in home-made glass pressure tubes equipped with a needle valve, a pressure gauge and a septum inlet.

3. Results and discussion

When 0.4 mmol cinnamaldehyde was heated at 50°C in 7.5 mL 0.2M phosphate buffer of pH 8.3 under 1 bar H_2 for 1 hour in the presence of **1** and an excess of *m*tppms, a conversion of 13.1% was determined and the sole product of the reaction was cinnamalcohol. Addition of increasing amounts of $NaHCO_3$ resulted in a substantial increase of conversion which reached a maximum value of 29.9% with 0.2 mmol $NaHCO_3$ corresponding to $n(NaHCO_3)/n(Ru) = 20$. Note that this amount of $NaHCO_3$ is only 50 mol% of that of cinnamaldehyde (as can be seen later the effect can be conveniently studided in the 20-50 mol% range). Larger amounts of $NaHCO_3$ did not further increase the reaction rate, instead a small decrease of conversion was observed (Figure 1). In separate series of experiments the given amounts of $NaHCO_3$ were prehydrogenated under the same reaction conditions for 10 min at which time the substrate cinnamaldehyde was injected. In this experimental arrangement even larger increase of cinnamaldehyde conversion was observed (relative to bicarbonate-free conditions) with a maximum value of 45.3%. This conversion is more than three times higher than in the absence a HCO_3^- demonstrating a strong promoter effect of bicarbonate (Figure 1).

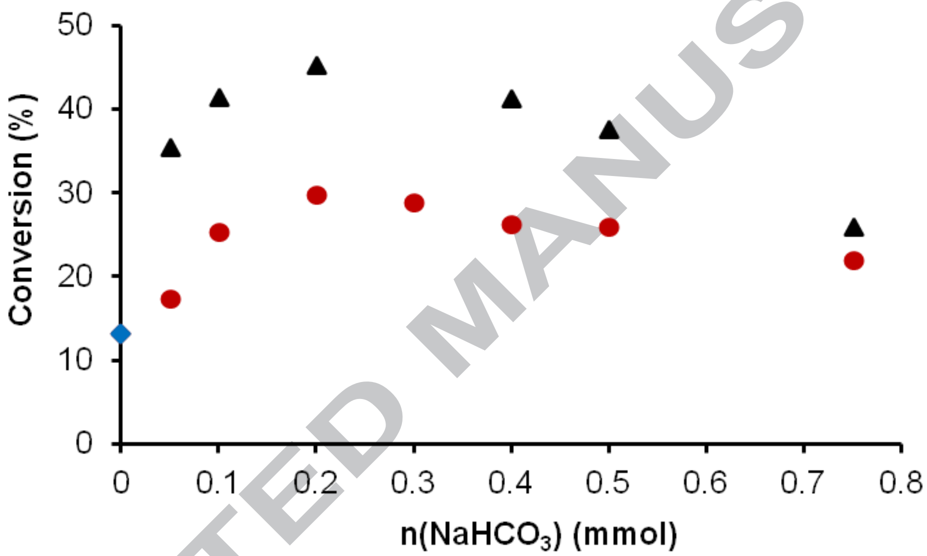


Figure 1. Conversions in hydrogenation of cinnamaldehyde catalyzed by **1** in the presence of $NaHCO_3$ and the effect of prehydrogenation of $NaHCO_3$. n(CAL) = 0.4 mmol, n(**1**) = 0.005 mmol, n(*m*tppms) = 0.08 mmol, V(H_2O) = 7.5 mL, P(H_2) = 1 bar, T = 50°C, t = 1 h. Symbols: ● no prehydrogenation; ▲ 10 min prehydrogenation of $NaHCO_3$; ♦ in the absence of $NaHCO_3$ the reaction was done in 0.2 M phosphate buffer, pH 8.30, V= 7.5 mL.

The major product at all $NaHCO_3$ concentrations, with or without prehydrogenation was the unsaturated alcohol (COL) and the maximum conversion to the saturated aldehyde (HCAL) never exceeded 2.5%.

Similar experiments were also conducted at 10 bar H_2 pressure (other conditions as on Figure 1). Again, $NaHCO_3$ had a pronounced positive effect on the hydrogenation rate of cinnamaldehyde resulting in a maximum turnover frequency of TOF =299 h^{-1} at n($NaHCO_3$)/n(Ru) = 40 as opposed to TOF = 102 h^{-1} in the absence of $NaHCO_3$ (TOF = mol converted substrate × (mol catalyst × time)$^{-1}$. In accordance with our earlier observation [15] at this H_2 pressure the reaction was completely selective to cinnamalcohol. Interestingly, the turnover frequencies of cinnamaldehyde hydrogenation as a function of hydrogen pressure showed a much steeper increase in the presence than in the absence of $NaHCO_3$ (Figure 2). For comparison, hydrogenations in the absence of $NaHCO_3$ were conducted in 0.2 M phosphate buffer solutions of pH=8.30 (corresponding to that of the $NaHCO_3$ solutions used in this comparative study).

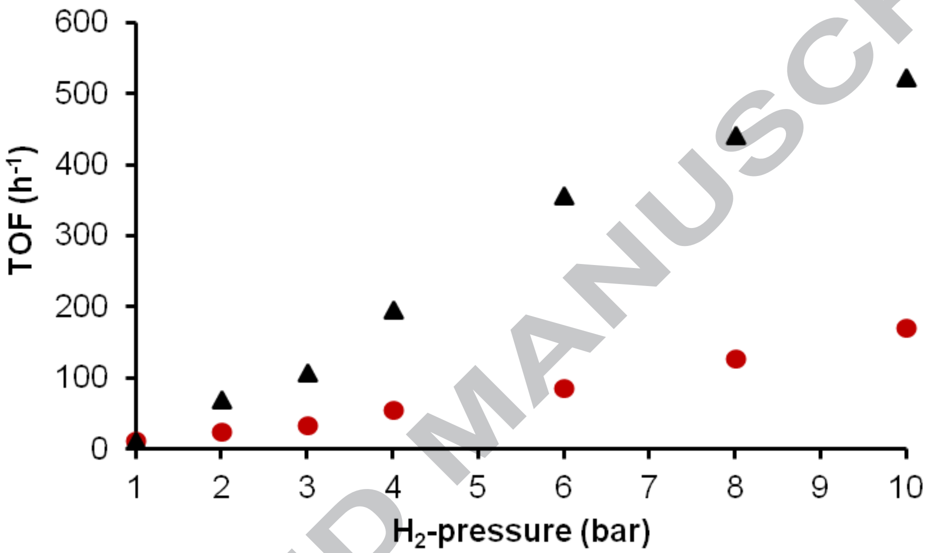


Figure 2. Turnover frequencies of cinnamaldehyde hydrogenation catalyzed by **1** as a function of H_2 pressure in the absence and presence of $NaHCO_3$. n(CAL) = 1.0 mmol, n(**1**) = 0.0025 mmol, n(*m*tppms) = 0.04 mmol, V(aqueous phase) = 7.5 mL, T = 50°C, t = 1 h. Aqueous phase: ● 0.2 M phosphate buffer, pH = 8.30, ▲ 13.3 mM $NaHCO_3$.

Table 1 shows the effect of added *m*tppms (ligand excess) on the conversion obtained in cinnamaldehyde hydrogenation at 10 bar H_2 pressure with [{$RuCl_2$(mtppms)$_2$}$_2$] catalyst as a function of the [*m*tppms]/[**1**] ratio (please note the dimeric nature of the complex). Increasing concentrations of *m*tppms result in substantially increased conversions which may refer to coordination of more than 2 phosphine ligands in the actual catalytically active Ru(II)-species.

Table 1. Effect of added phosphine on hydrogenation of cinnamaldehyde catalyzed by [{$RuCl_2$(*m*tppms)$_2$}$_2$] (**1**)

[mtppms]/[**1**]	TOF (h^1)	Conversion[a] (%)

0	68	8.5[b]
2	131	16.4
6	190	23.8
12	293	36.6
16	398	49.7

Conditions: n(CAL) = 1.0 mmol, n(**1**) = 0.0025 mmol, n($NaHCO_3$) = 0.2 mmol, V(H_2O) = 7.5 mL, P(H_2) = 10 bar, T = 50°C, t = 15 min. [a]Product is cinnamalcohol, except [b]5.4% cinnamalcohol + 3.1% 3-phenylpropanal.

Effect of temperature

The promoter effect of $NaHCO_3$ can be observed also in the temperature dependence of cinnamaldehyde hydrogenation (Figure 3). Under conditions of Figure 3, in the presence of $NaHCO_3$ conversion of cinnamaldehyde to hydrogenated products was as high as 65% in comparison to 30% determined in the bicarbonate-free system. Yield of cinnamalcohol was always predominant (maximum yield 55%) while those of 3-phenylpropanal and 3-phenylpropanol did not exceed 5.5 %, each (see Table 2 for details).

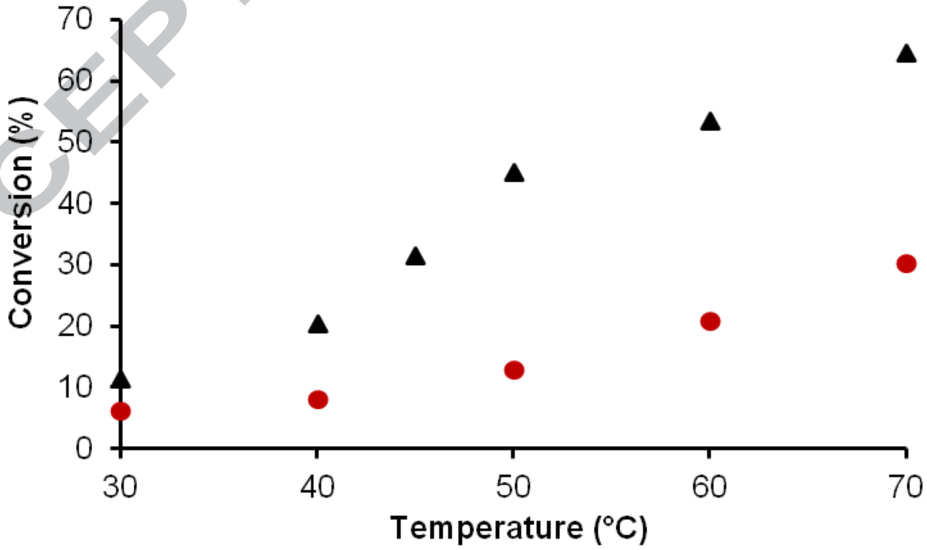


Figure 3. Conversions of cinnamaldehyde hydrogenation catalyzed by **1** in the absence and presence of $NaHCO_3$ as a function of the temperature. n(CAL) = 0.4 mmol, n(**1**) = 0.005

mmol, n(*m*tppms) = 0.08 mmol, V(aqueous phase) = 7.5 mL, P(H_2) = 1 bar, T = 50°C, t = 1 h. Aqueous phase: ● 0.2 M phosphate buffer, pH = 8.30, ▲ 26.7 mM $NaHCO_3$.

Similarly, at 10 bar H_2 pressures hydrogenation rates of cinnamaldehyde were consistently and substantially higher in presence of $NaHCO_3$ than in phosphate buffer solutions of the same pH (Figure 4).

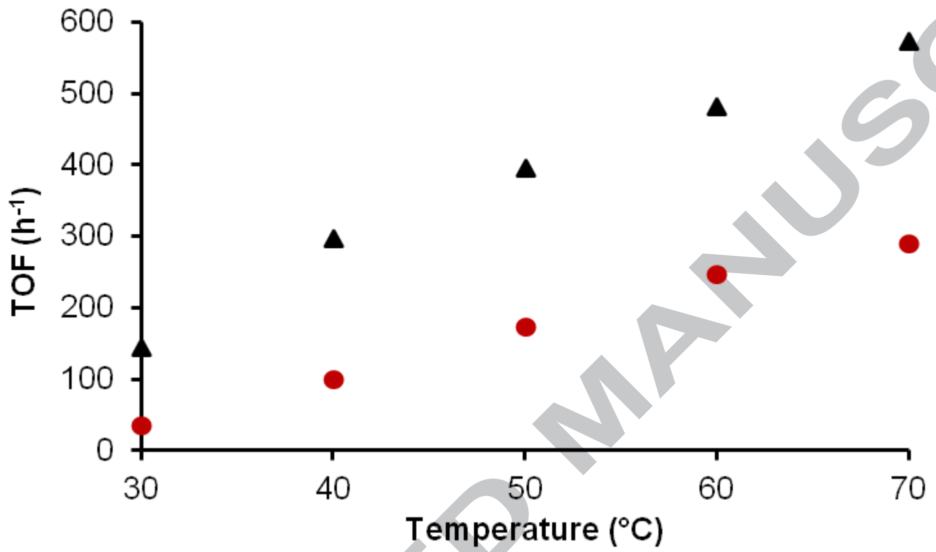
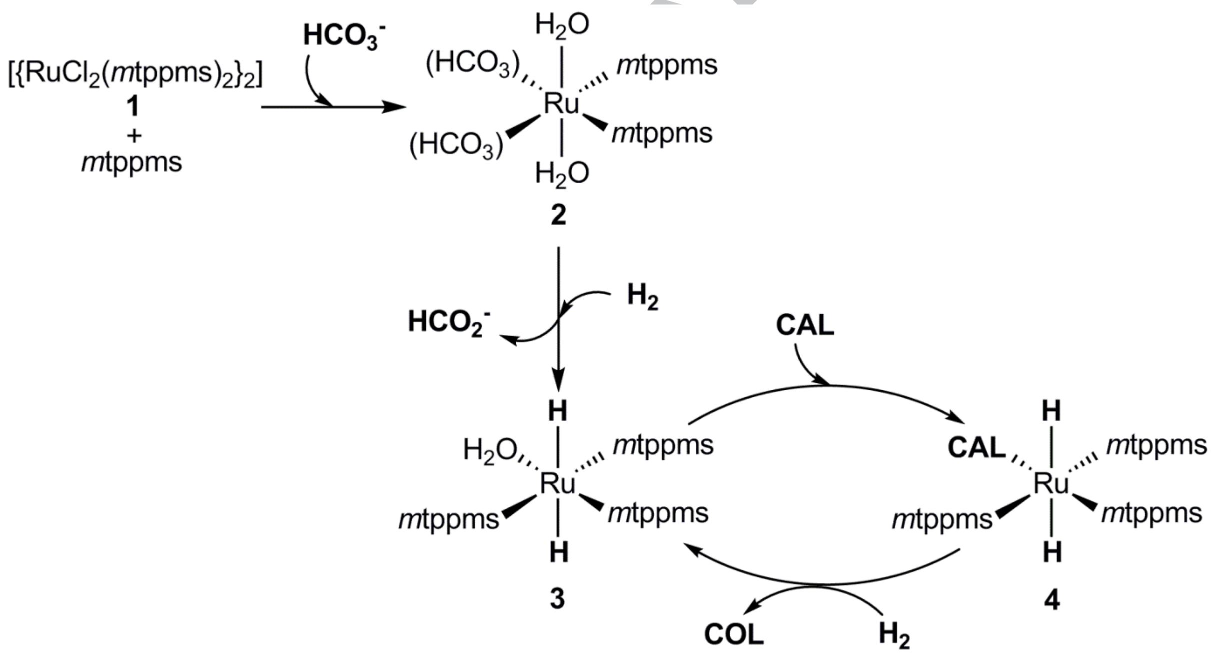


Figure 4. Effect of $NaHCO_3$ on the rate of cinnamaldehyde hydrogenation at 10 bar H_2 pressure. n(CAL) = 1.0 mmol, n(**1**) = 0.0025 mmol, n(*m*tppms) = 0.04 mmol, V(aqueous phase) = 7.5 mL, T = 50°C, t = 1 h. Aqueous phase: ● 0.2 M phosphate buffer, pH = 8.30, ▲ 26.7 mM $NaHCO_3$.

In addition to cinnamaldehyde hydrogenations, multinuclear NMR measurements were also made in order to follow the reactions of [{$RuCl_2$(*m*tppms)$_2$}$_2$] (**1**) under hydrogenation conditions (composition of the NMR sample: n(**1**) = 0.01 mmol, n(*m*tppms) = 0.042 mmol, n($NaHCO_3$) = 0.4 mmol, V(H_2O) = 0.5 mL, V(MeOD) = 0.1 mL, p(H_2) = 1 bar; room temperature). On the basis of kinetic and NMR data we suggest the following reaction mechanism (Scheme 3). In the first step [{$RuCl_2$(*m*tppms)$_2$}$_2$] (**1**) reacts with HCO_3^- yielding the known [20] monomeric [Ru(H_2O)$_2$(HCO_3)$_2$(*m*tppms)$_2$] (**2**). In this work, formation of **2** was investigated with the use of $NaH^{13}CO_3$ and was evidenced by the broad triplet ^{13}C-NMR signal of coordinated bicarbonate at δ=167.3 ppm (non-coordinated HCO_3^- resonates at δ=161.1 ppm). In addition, ^{31}P-NMR also showed the broad singlet signal of **2** at δ=51.0 ppm. Next, reaction of **2** and H_2 yields free formate (^{13}C-NMR: δ=170.7 ppm (s)) and *trans*-

$[Ru(H)_2(H_2O)(m\text{tppms})_3]$ (**3**). The *trans*-dihydrido-Ru(II) complex **3** has previously been obtained in reaction of $[\{RuCl_2(m\text{tppms})_2\}_2]$ + *m*tppms with $NaHCO_2$ in dilute aqueous solutions and was extensively characterized by its ^{1}H- and ^{31}P-NMR spectra [18]. Characteristic signals of **3**, such as ^{1}H-NMR: δ= -17.6 ppm (dt, $^2J_{HP}$=25 and 27 Hz), and ^{31}P-NMR: δ=44.0 ppm (br, d) and 77.3 ppm (br, t) were, indeed, observed in our hydrogenation system with added $NaHCO_3$. Addition of cinnamaldehyde to aqueous solution of **3** leads to a shift of the NMR signals with no change in the pattern and signal multiplicities, ^{1}H-NMR: δ= -18.7 ppm (br), and ^{31}P-NMR: δ=46.4 ppm (br, d) and 79.0 ppm (br, t). We suppose that cinnamaldehyde (CAL) replaces the H_2O ligand in **3** with formation of *trans*-$[Ru(H)_2(CAL)(m\text{tppms})_3]$ (**4**), however, this complex was not studied in more detail. Hydride migration in **4** and subsequent reactions with H_2 and H_2O yield cinnamalcohol (COL) as product and regenerate the catalytically active species, *trans*-$[Ru(H)_2(H_2O)(m\text{tppms})_3]$ (**3**).



Scheme 3. Suggested mechanism of cinnamaldehyde hydrogenation catalyzed by $[\{RuCl_2(m\text{tppms})_2\}_2]$ + *m*tppms in water in the presence of catalytic amounts of $NaHCO_3$.

It is important to mention here, that reaction of $[\{RuCl_2(m\text{tppms})_2\}_2]$ and *m*tppms with H_2 in the *absence* of HCO_2^- (or HCO_3^-) results in formation of a different hydride species, namely *cis-fac*-$[Ru(H)_2(H_2O)(m\text{tppms})_3]$ (**5**) with clearly distinct NMR spectra (^{1}H-NMR: δ= -10.4

ppm (dt, $^2J_{HP}$=39 and 34 Hz), and ^{31}P-NMR: δ=42.0 ppm (br) and 58.0 ppm (br) [18] – however, these signals were not detected in the presence of $NaHCO_3$.

The mechanism suggested above makes possible the rationalization of the experimental findings on cinnamaldehyde hydrogenation with added bicarbonate. $NaHCO_3$ is catalytically reduced to formate which directs the reaction of [{$RuCl_2$(*m*tppms)$_2$}$_2$] and *m*tppms with H_2 to yield *trans*-[Ru(H)$_2$(H_2O)(*m*tppms)$_3$] (**3**) rather than *cis-fac*-[Ru(H)$_2$(H_2O)(*m*tppms)$_3$] (**5**). **3** may be a better catalyst for aldehyde hydrogenation than **5** due to the strong strong *trans*-labilizing effect of a *trans*-hydride ligand which may facilitate hydride migration to coordinated CAL. Furthermore, it can also be conceived that in addition to H_2, formate also plays an important role in regeneration of **3** in the product forming step. This would be in accordance with the known easy formation of **3** in dilute formate solutions [18]. The advantageous effect of prehydrogenation of [{$RuCl_2$(*m*tppms)$_2$}$_2$] (**1**), *m*tppms and $NaHCO_3$ in the absence of cinnamaldehyde is also explained by the suggested mechanism, by that the reaction yields **3** and formate. Finally, the need for a ligand excess over **1** is rationalized by the fact that the species in the suggested catalytic cycle, **3** and **4** contain *three* *m*tppms ligands.

To obtain further evidence on the role of formate in speeding up the hydrogenation of cinnamaldehyde catalyzed by **1** + mtppms, we carried out reactions with added $NaHCO_2$ instead of $NaHCO_3$. The results are shown in Table 2.

Table 2. Effect of Na-formate in comparison to that of Na-bicarbonate on hydrogenation of cinnamaldehyde catalyzed by [{$RuCl_2$(*m*tppms)$_2$}$_2$] + *m*tppms.

Promoter	T (°C)	Products		
		COL (%)	HCAL (%)	HCOL (%)
$NaHCO_2$	60	70.0	2.6	2.6
$NaHCO_3$	60	49.0	3.3	0.0
none*	60	20.9	0.0	0.0
$NaHCO_2$	70	80.5	1.7	7.1
$NaHCO_3$	70	54.5	5.4	0.0
none*	70	30.3	2.4	1.9

Conditions: n(CAL) = 1.0 mmol, n(**1**) = 0.005 mmol, n(*m*tppms) = 8 mmol, n($NaHCO_2$) = n($NaHCO_3$) = 0.2 mmol, V(H_2O or *0.2 M phosphate buffer) = 7.5 mL, P(H_2) = 1 bar, t = 1 h, 10 min prehydrogenation before addition of CAL.

As can be seen, at both temperatures $NaHCO_2$ is more efficient in speeding up hydrogenation of cinnamaldehyde catalyzed with [{$RuCl_2$(*m*tppms)$_2$}$_2$] + *m*tppms (although the higher conversions are accompanied by a small loss in selectivity). This shows that in agreement with the suggested mechanism the most important species in the promoter effect of $NaHCO_3$ is in fact the formate, produced by hydrogenation of bicarbonate.

4. Conclusion

$NaHCO_3$ acts as promoter in hydrogenation of cinnamaldehyde to cinnamalcohol in aqueous systems with [{$RuCl_2$(*m*tppms)$_2$}$_2$] + *m*tppms catalyst. Study of the effects of reaction parameters together with multinuclear NMR measurements revealed that the origin of this promoter effect is in the formation of *trans*-[Ru(H)$_2$(H_2O)(*m*tppms)$_3$] (**3**) rather than *cis-fac*-[Ru(H)$_2$(H_2O)(*m*tppms)$_3$] (**5**) mediated by formate arising from hydrogenation of bicarbonate under reaction conditions. Formate can also accelerate regeneration of the real catalytic species, i.e. **3**. Accordingly, $NaHCO_2$ produces even higher rate increase than the same amount of $NaHCO_3$.

Acknowledgements

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Highlights:

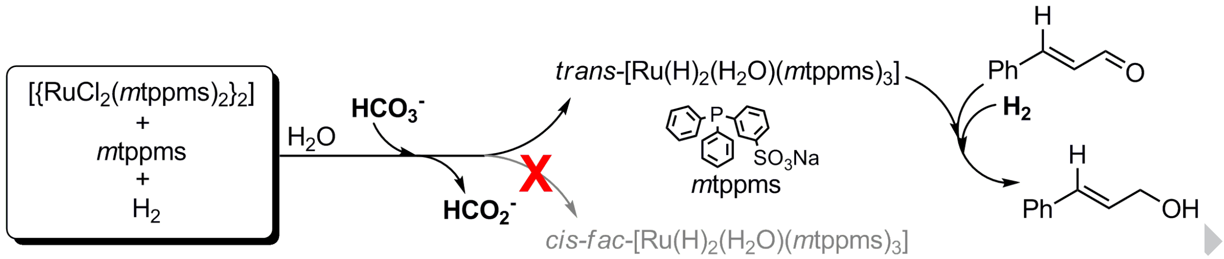
- $NaHCO_3$ strongly accelerates cinnamaldehyde hydrogenation with a water-soluble Ru(II)-phosphine catalyst

- The reaction is highly selective towards formation of the unsaturated alcohol

- A plausible reaction mechanism is suggested on basis of kinetic and NMR measurements

- Formate (from hydrogenation of bicarbonate) plays active role in catalysis

- *trans*-$[Ru(H)_2(H_2O)(m\text{tppms})_3]$ was identified as key catalytic species


[{RuCl2(mtppms)2}2]
+
mtppms
+
H2
H2O
HCO3-
HCO2-
trans-[Ru(H)2(H2O)(mtppms)3]
cis-fac-[Ru(H)2(H2O)(mtppms)3]
P
SO3Na
mtppms
H
Ph
O
H2
H
Ph
OH