# Stereoselective catalytic hydrogenation of sorbic acid and sorbic alcohol with new Cp*Ru complexes†

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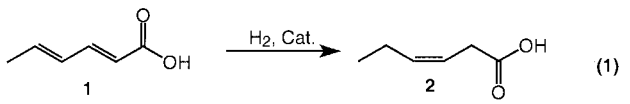
**The new Cp*Ru complexes [Cp*Ru(η⁴-MeCH=CHCH=CHCO$_2$H)]$^+$X$^-$ (X$^-$ = $CF_3SO_3^-$ or [B{C$_6$H$_3$(CF$_3$)$_2$-3,5}$_4$]$^-$) are very effective catalysts for the hydrogenation of sorbic acid to *cis*-hex-3-enoic acid and of sorbic alcohol to *cis*-hex-3-en-1-ol (leaf alcohol) under mild conditions in liquid two-phase systems.**

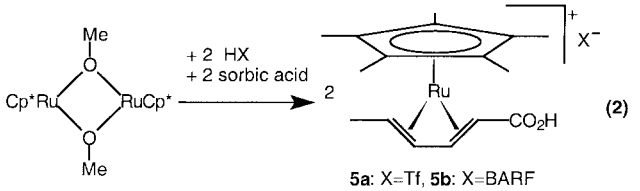
When sorbic acid **1**, a widely used preservative, or sorbic alcohol are hydrogenated, different products might occur. The mono-unsaturated products are of technical interest for the production of fragrances and vitamins.[1] This work focuses on the stereoselective preparation of *cis*-hex-3-enoic acid **2** [eqn. (1)] and of *cis*-hex-3-en-1-ol **3**, a fragrance commercialized as 'leaf alcohol'.



(1)

In early studies Frankel and coworkers showed that methylsorbate and sorbic alcohol can be catalytically hydrogenated by chromium(0) carbonyl compounds with high selectivities to methyl-*cis*-hex-3-enoate and to *cis*-hex-3-en-1-ol, respectively.[2a–d] Unfortunately the reaction only works with sorbic acid esters and sorbic alcohol but not with the cheaper sorbic acid **1**, and one must use toxic chromium catalysts and high catalyst/substrate ratios. Since the start of our studies on stereoselective hydrogenations of **1**[3,4] with complexes like [Cp*Ru(MeCN)$_3$]Tf **4**, we came to the conclusion that the [Cp*Ru]$^+$ fragment is essential for the stereoselectivity of the reaction. 'Naked' Cp*Ru complexes without inhibiting ligands should thus be more active and very selective.

We thus synthesized the model complexes [Cp*Ru(η⁴-MeCH=CHCH=CHCO$_2$H)]$^+$X$^-$ (X = Tf **5a**, X = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BARF) **5b**), in which the [Cp*Ru]$^+$ fragment is stabilized by a η⁴-bonded sorbic acid molecule. We assumed, that these complexes should have a similar structure as [Cp*Ru (η⁴-H$_2$C=CHCH=CH$_2$)I],[5] but should bear weakly coordinating ligands instead of an iodide ligand. The new complexes **5a**,**b** have been synthesized from [(Cp*Ru(μ-OMe))$_2$] [6] which was cleaved by 2 equivalents of trifluoromethanesulfonic acid or tetrakis[3,5-bis(trifluoromethyl)phenyl]boric acid (HBARF) in the presence of a slight excess of sorbic acid [eqn. (2)].



(2)

**5a**: X=Tf, **5b**: X=BARF

† Dedicated to Professor Wilhelm Keim on the occasion of his 65th birthday.

The complexes have been obtained as orange powders or crystals in 72% (**5a**) and 41% (**5b**) yield and have been characterized by $^1$H NMR, $^{13}$C NMR, secondary ion mass spectrometry and a crystal structure analysis.‡§ The η⁴-bonding mode of the sorbic acid in the complexes has been determined by a strong up-field shift of the olefinic proton signals in the $^1$H NMR spectrum in comparison to free sorbic acid and by the crystal structure. In solution, the complexes may exist as monomers whereas Fig. 1 shows that complex **5b** is a dimer in the crystalline state which is bridged by the carbonyl oxygens of the acid. The hydroxy groups form hydrogen bridges to a THF molecule, the BARF anions do not interact with the cationic ruthenium complex. **5a**,**b** are the first sorbic acid–ruthenium complexes.

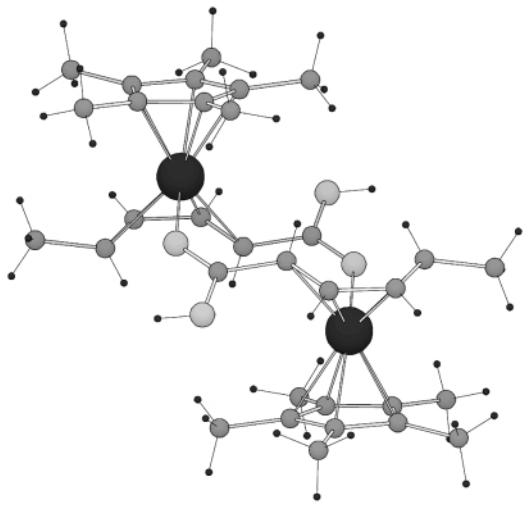


**Fig. 1** Crystal structure of the cationic part of **5b**.

Complex **5a** is soluble in polar organic solvents such as alcohols, nitromethane or sulfolane, but it is insoluble in water and nonpolar organic solvents like ethers or alkanes. **5a** can thus be used as catalyst in liquid two-phase systems such as nitromethane–dibutyl ether, ethylene glycol–MTBE (methyl tertiary butyl ether) or sulfolane–MTBE, in which the complex remains in the polar phase. After the reaction the complex can be separated easily by decantation. Table 1 presents the results of the hydrogenation of sorbic acid in different solvents at 60 °C. At 60 °C the solvents in the systems nitromethane–dibutyl ether and sulfolane–MTBE become miscible, and at room temperature the two solvents form two phases.

The results obtained with the nitromethane systems (Table 1, entries 1 and 2) show that **5a** is about 30 times more active than [Cp*Ru(MeCN)$_3$]Tf **4**, which shows, that a naked [Cp*Ru]$^+$ fragment is more active. **5a**,**b** are active at room temperature whereas **4** is active only above 60 °C. Nitromethane is normally used as a weakly coordinating, aprotic solvent, therefore we expected good catalytic results. However, in this case the hydrogenation activities and the selectivities to *cis*-hex-3-enoic acid are lower in comparison to the stronger coordinating sulfolane and in comparison to the protic ethylene glycol.

**Table 1** Stereoselective hydrogenation of **1** with **4** and **5a,b** as catalysts in various two-phase systems[a]

| Entry | Solvent system | Catalyst | $p(H_2)$/bar | Conv. **1** (%) | Selectivity (S) *cis*-hex-3-enoic acid **2** (%) | Selectivity (S) *trans*-hex-3-enoic acid (%) | TOF/$h^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | $MeNO_2$–$Bu^n{}_2O$ | **4** | 60 | 45 | 93 | 6 | 3.1 |
| 2 | $MeNO_2$–$Bu^n{}_2O$ | **5a** | 60 | 95 | 66 | 34 | 92 |
| 3[b] | Ethylene glycol–MTBE | **5a** | 60 | 94 | 86 | 7 | 300 |
| 4[b] | Ethylene glycol–MTBE | **5a** | 10 | 78 | 96 | 1 | 97 |
| 5 | Sulfolane–MTBE | **5a** | 60 | 68 | 71 | 29 | 580 |
| 6[c] | MTBE | **5b** | 16 | 85 | 96 | 3 | 1057 |

[a] *Reagents and conditions*: 60 °C; 20 mmol sorbic acid; 0.06 mmol catalyst; catalyst phase: 30 ml solvent; nonpolar product phase: 44 ml solvent; Conv. = conversion; selectivity (S) = (*n*(product)/$\sum n$ (all products)) × 100; TOF = turnover frequency = ($\sum n$ (all products))/(*n*(catalyst) h).; [b] Some *trans*-hex-2-enoic acid is formed: (3) S = 7%, (4) 3%. [c] 40 mmol sorbic acid, 75 ml MTBE, 50 °C.

**Table 2** Stereoselective hydrogenation of sorbic alcohol with **5a** as catalyst in ethylene glycol–MTBE[a]

| Entry | *T*/°C | $p(H_2)$/bar | *n* (**5a**)/mmol | *t*/h | Conv. sorbic alcohol (%) | Selectivity to leaf alcohol **3** (%) | TOF/$h^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | 21 | 20 | 0.0424 | 1.5 | 44 | 98.3 | 184 |
| 2 | 40 | 20 | 0.0426 | 0.42 | 70 | 98.9 | 1055 |
| 3 | 60 | 20 | 0.0219 | 0.40 | 88 | 98.6 | 2495 |
| 4 | 60 | 4 | 0.0428 | 0.77 | 86 | 97.8 | 714 |

[a] *Reagents and conditions*: 25–27 mmol sorbic alcohol; 25 ml ethylene glycol; 45 ml MTBE; in each experiment 1–2% *trans*-hex-3-en-1-ol is formed. Conv. = conversion; selectivity = (*n*(product) / $\sum n$ (all products)) × 100; TOF = turnover frequency = ($\sum n$ (all products))/(*n*(catalyst) h).

The highest selectivities (S) (S(*cis*-hex-3-enoic acid) = 96%) were obtained in ethylene glycol when the hydrogen pressure was reduced from 60 to 10 bar.

The highest activities with **5a** as catalyst (TOF = 580 $h^{-1}$) were obtained in sulfolane, but the selectivity was not as high as in ethylene glycol.

Since the BARF anion is much more lipophilic than the triflate anion, complex **5b** is more soluble in nonpolar solvents than **5a**. For this reason **5b** was used as catalyst in an MTBE solution instead of using it in a two-phase system. Experiments 5 and 6 in Table 1 can be compared because they both have been carried out in one-phase systems at the same reaction temperature. Evidently, **5b** is a more active catalyst than **5a** because the BARF anion has much weaker coordinating properties than the triflate anion.[7] Thus, the BARF anion does not compete with sorbic acid and hydrogen for free coordination sites at the ruthenium center in the catalytic steps of the reaction.

We also used hexa-2,4-diene-1-ol (sorbic alcohol) as substrate, which can be directly hydrogenated to *cis*-hex-3-ene-1-ol **3** (leaf alcohol). Preliminary results have shown that the catalytic hydrogenation is much faster with sorbic alcohol than with sorbic acid. It was thus possible to reduce the hydrogen pressure from 60 to 20 bar in the experiments shown in Table 2.

The best results were obtained with **5a**, which hydrogenates sorbic alcohol with a TOF of *ca*. 2500 $h^{-1}$ at 60 °C in the two-phase system ethylene glycol–MTBE. Even at low hydrogen pressures of 4 bar, which allows working in glassware reactors, the reaction rate stays fairly high (TOF = 714 $h^{-1}$). The very high selectivity (98–99%) to leaf alcohol is virtually independent of the reaction temperature, while the hydrogenation activity raises as expected with increasing temperature. Other than in hydrogenations of sorbic acid the selecivity depends negligibly on the conversion. While the selectivity to *cis*-hex-3-enoic acid often decreases at conversion rates of > 90%, the selectivity to *cis*-hex-3-enoic alcohol remains constant even at 100% conversion.

We have thus shown that the concept of using 'naked' Cp*Ru complexes for stereoselective hydrogenations of functionalized dienes to *cis*-olefins is successful. In further work we will try to elucidate the mechanism and the kinetics of the reaction.

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## Notes and references

‡ The complexes were synthesized in an argon atmosphere with dried solvents. Before the hydrogenation experiments the solutions of the complexes and the substrates were handled under argon.

*General procedure for the synthesis of* **5a**,**b**: 2.94 mmol [(Cp*Ru(μ-OMe))$_2$], which was prepared from 2.94 mmol [(Cp*$RuCl_2$)$_2$] according to the procedure described in the literature,[6b] were dissolved in 30 ml dichloromethane and 10 ml diethyl ether. A solution of 3.44 mmol sorbic acid and 3.15 mmol triflic acid (or HBARF) in 12 ml diethyl ether was added to the stirred solution of the complex at −78 °C. The reaction mixture changed immediately from deep red to brown. The reaction mixture was stirred for 10 min at −78 °C and was slowly brought to room temperature. After being stirred for a further 5 min at room temperature, the solvent was evaporated under reduced pressure. The residue was treated with 10 ml ethyl acetate to effect formation of an orange solid. For a better precipitation, 10 ml diethyl ether were added. The solid was filtered off washed twice with 10 ml diethyl ether and dried in high vacuum. 2.11 mmol **5a** were obtained (71.7% yield based on [(Cp*$RuCl_2$)$_2$]).

§ *Crystal data* for $C_{56}H_{51}BF_{24}O_4Ru$ **5b:** $M_r$ 1355.87, triclinic, $a$ = 12.648(6), $b$ = 14.323(3), $c$ = 16.711(6) Å, $\alpha$ = 78.23(2), $\beta$ = 80.09(3), $\gamma$ = 84.53(3)°, $V$ = 2914(2) Å$^3$, $T$ = 203 K, $Z$ = 2, space group $P\bar{1}$ (no. 2), $\mu$(Mo-Kα) = 3.80 $cm^{-1}$, 12258 independent reflections measured ($R_{int}$ = 0.032). The final $wR(F^2)$ = 0.1497 (all data). The structure was solved using direct methods and refined by full matrix least squares on $F^2$. Single crystals of [Cp*Ru(μ-O-(η:*s*-*cis*-2,3,4,5-Me(CH)$_4$CO(OH)))]$_2$[B(C$_6$H$_3$-(CF$_3$)$_2$-3,5)$_4$]$_2$·4THF **5b** were crystallized from THF–dibutyl ether and washed with pentane.

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