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Regiospecific solvent-free transfer hydrogenation of α,β-unsaturated carbonyl compounds catalyzed by a cationic ruthenium(II) compound

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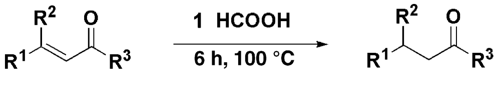
Abstract—$[(PPh_3)_2Ru(CH_3CN)_3Cl][BPh_4]$ has been found to catalyze the selective reduction of double bonds in α,β-unsaturated ketones with high conversions when formic acid is the hydrogen donor.

Transition metal catalyzed transfer hydrogenation of ketones and aldehydes has attracted attention due to the relatively benign nature of the reagents and mild reaction conditions employed.[1–4] In contrast to conventional hydrogenation using dihydrogen and metal catalysts, which frequently require a high hydrogen pressure and hazardous reducing reagents,[5,6] transfer hydrogenation has unique advantages in its simplicity and avoidance of cumbersome reducing agents. Regioselective transfer hydrogenation of unsaturated carbonyl compounds has attracted a great deal of attention in recent years.[7–10] Although, the reduction of α,β-unsaturated carbonyl compounds to allylic alcohols has been reported, the selective reduction of double bonds in enones are relatively less explored. Ruthenium compounds have been used as catalysts for the transfer hydrogenation of carbonyl compounds in general.[11,12] However, the selective reduction of double bonds in unsaturated carbonyl compounds using ruthenium catalysts is found to give mixtures of reduced products.[9] Recently, it was shown that, $[RuHCl(CO)(PPh_3)_3]$ is an effective catalyst for the selective reduction of enones to ketones in benzene using isopropanol as the hydrogen donor.[9] Similarly, palladium chloride has been found to be an effective catalyst for the regioselective reduction of α,β-unsaturated ketones to saturated ketones using formic acid as the hydrogen source.[7] Organic transformations in water or under solvent-free conditions are important due to environmental reasons.[13] Recently, we reported the synthesis and structure of the cationic ruthenium compounds, $[Ru(PPh_3)_2(CH_3CN)_3Cl]^+A^-\{A = BPh_4$ and $ClO_4\}$, which were found to be effective catalysts for the transfer hydrogenation of aldehydes and ketones.[14] We were interested in exploring further the catalytic activity of these compounds for the transfer hydrogenation of α,β-unsaturated ketones using formic acid as the hydrogen donor. We report herein $[Ru(PPh_3)_2(CH_3CN)_3Cl]^+[BPh_4]^-$ (**1**) catalyzed selective reduction of the double bonds in α,β-unsaturated ketones with formic acid.

The carbonyl compound (1 mmol) was mixed with **1** (0.02 mmol) and to this was added formic acid (98%; 3 cm^3). The reaction mixture was then refluxed for 6 h at 100 °C (Scheme 1).

The reaction mixture was cooled to room temperature, diluted with water (50 cm^3) and extracted with ether and after the usual work-up, the products were isolated and purified by column chromatography. The reactions



R^1 = Ph, R^2 = H, R^3 = Ph
R^1 = Ph, R^2 = H, R^3 = CH_3
R^1 = Ph, R^2 = H, R^3 = CH=CH-Ph
R^1 = R^2 = R^3 = Me

Scheme 1.

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Table 1. Transfer hydrogenation of α,β-unsaturated carbonyl compounds catalyzed by **1**[a]

Substrate	Hydrogen donor	Product(s)	Yield (%)	Conversion	Turnover number[c]
Benzylidene acetophenone	Formic acid	1,3-Diphenylpropan-1-one	75	77	38.5
Benzylidene acetone	Formic acid	4-Phenylbutan-2-one	84	85	42.5
4-Methylpent-3-en-2-one	Formic acid	4-Methylpentan-2-one	65	70	35.0
Dibenzylidene acetone	Formic acid	1,5-Diphenylpentan-3-one	64	85	42.5
		1,5-Diphenylpentan-3-ol	18		
Benzylidene acetophenone	2-Propanol[b]	1,3-Diphenylpropan-1-ol	20	37	18.5
		1,3-Diphenylpropan-1-one	15		
Benzylidene acetone	2-Propanol[b]	4-Phenylbutan-2-ol	30	48	24.0
		4-Phenylbutan-2-one	15		

[a] Reaction conditions: substrate, 1 mmol; **1**, 0.02 mmol; formic acid, 3 cm^3; reaction time, 6 h; temperature 100 °C.

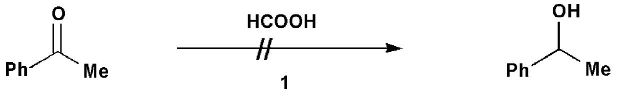
[b] K_2CO_3 (1 mmol) and 10 cm^3 2-propanol were used.

[c] Mol of product/mol of catalyst.

were monitored by TLC and the products were isolated in low to high yields (Table 1). The products were characterized by elemental analyses and ^{1}H NMR spectroscopy.

We also studied the effect of the hydrogen donor on the reactions. It was shown in our earlier work that **1** catalyzes the transfer hydrogenation of saturated aldehydes and ketones using 2-propanol as the hydrogen donor in the presence of K_2CO_3. Thus, we also used 2-propanol as a hydrogen source. In the present reactions, 2-propanol was found to be not only less effective, but also, its use resulted in a mixture of products, saturated ketones as well as saturated alcohols (Scheme 2). The conversions were very poor as compared to the reactions with formic acid as the hydrogen donor.

The specificity of formic acid as a hydrogen donor for the hydrogenation of double bonds was further tested by the reaction of styrene with formic acid in the presence of **1**. It was found that **1** catalyzed the hydrogenation of styrene with formic acid as the hydrogen donor.

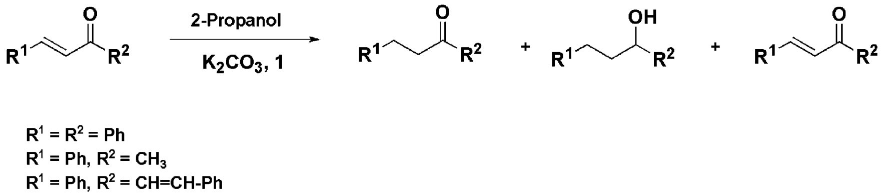


Scheme 3.

Similarly, formic acid was effective in the reduction of double bonds in cinnamic acids (Table 2).

In order to test the efficacy of formic acid in the transfer hydrogenation of carbonyl groups, the reaction of acetophenone catalyzed by **1** with formic acid as the hydrogen donor was carried out under similar reaction conditions (Scheme 3). However, we did not observe any reduced product in this case. Thus it is clear that formic acid is ineffective as a hydrogen donor in the reduction of carbonyl groups catalyzed by Ru(II) complex **1**.

The reactions of unsaturated ketones with formic acid in the absence of **1** failed to give any product and unre-



Scheme 2.

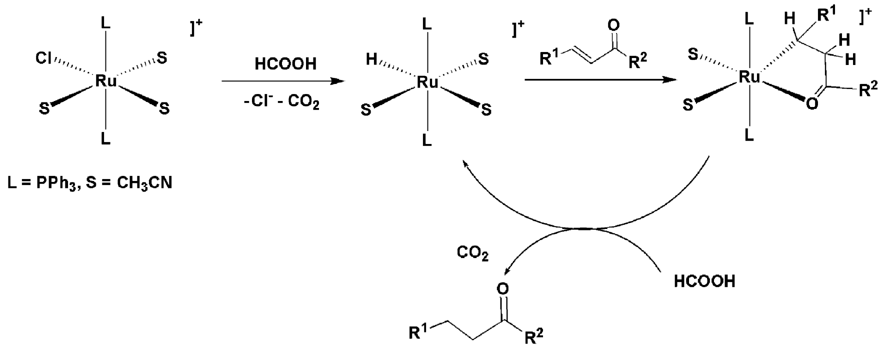
Table 2. Transfer hydrogenation of unsaturated compounds catalyzed by **1**[a]

Substrate	Hydrogen donor	Product(s)	Yield (%)	Conversion	Turnover number[c]
Styrene	2-Propanol[b]	—	—	—	—
Cinnamic acid	2-Propanol[b]	—	—	—	—
2-Chloro-cinnamic acid	2-Propanol[b]	—	—	—	—
Styrene	Formic acid	Ethylbenzene	65	68	34.0
Cinnamic acid	Formic acid	3-Phenylpropionic acid	72	75	37.5
2-Chloro-cinnamic acid	Formic acid	3-(2-Chlorophenyl)propionic acid	80	83	41.5

[a] Reaction conditions: substrate, 1 mmol; **1**, 0.02 mmol; formic acid, 3 cm^3; reaction time, 6 h; temperature 100 °C.

[b] K_2CO_3 (1 mmol) and 10 cm^3 2-propanol were used.

[c] Mol of product/mol of catalyst.



Scheme 4.

acted substrates were recovered. Thus, all the control reactions confirmed that, **1** catalyzes the regiospecific transfer hydrogenation of unsaturated ketones and formic acid is a specific hydrogen donor in the reduction of double bonds. Also it is clear that 2-propanol is a more effective hydrogen donor in the reduction of carbonyl groups. A similar observation was made by Selvam et al.[15] in the PdMCM-41 catalyzed hydrogenation of α,β-unsaturated ketones and it has been suggested that, when 2-propanol is used as the hydrogen donor, a metal alkoxide is formed and this has an affinity for the carbonyl groups.

However, it was reported that, $[Ru(PPh_3)_3Cl_2]$ can selectively reduce α,β-unsaturated ketones when heated with various high boiling alcohols such as benzyl alcohol.[16] It may be noted that, except in the case of dibenzylidene acetone, we did not observe any saturated alcohol formation, when formic acid was used as the hydrogen donor. Thus it is clear that the catalytic behaviour of **1** is different to the parent compound from which it is generated.[14]

Our repeated attempts to identify the catalytically active species and the reaction intermediates by NMR spectroscopy failed. However, there were striking similarities in reactivity and stereoselectivity in rhodium catalyzed enantioselective reduction of C=C double bonds by both molecular hydrogen and the transfer hydrogenation protocol.[17] Based on reported mechanisms[17,18] on rhodium catalyzed transfer hydrogenation of C=C double bonds, a possible reaction pathway is proposed and is shown in Scheme 4.

In summary, the cationic ruthenium compound, $[Ru(PPh_3)_2(CH_3CN)_3Cl]^+[BPh_4]^-$ has been found to be an effective catalyst for regiospecific reduction of double bonds in α,β-unsaturated ketones when formic acid is used as the hydrogen donor. However, when 2-propanol is used as the hydrogen donor, the conversions were found to be poor and non-specific.

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