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Reduction of ketones by dihydrogen or hydrogen transfer catalysed by a ruthenium complex of the hydridotris(3,5-dimethyl)pyrazolyl borate ligand

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Abstract

The hydride complexes $Tp^*RuH(H_2)_2$ (**1**) and $Tp^*RuH(COD)$ (**2**) (Tp^* = hydridotris(3,5-dimethyl)pyrazolyl borate) show good catalytic activity for the reduction of unactivated ketones either by dihydrogen or by hydrogen transfer from alcohols in basic media.

Keywords: Hydrogen; Ketones; Pyrazolyl derivative; Reduction; Ruthenium

1. Introduction

While the hydrogenation of carbon–carbon multiple bonds catalysed by transition metal complexes has been extensively studied for the past 30 years, relatively little attention has been devoted to the reduction of carbon oxygen double bonds. However, several systems are known to catalyse efficiently the reduction of ketones into alcohols either in the presence of dihydrogen [1] or by hydrogen transfer from alcohols, generally isopropanol [2]. Some systems are even able to reduce selectively ketone functions in molecules containing olefinic functions by hydrogen transfer [3] or to hydrogenate enantioselectively activated ketones [4].

We have recently prepared the complex $Tp^*RuH(H_2)_2$ (**1**; Tp^* = hydrido tris(3,5-dimethyl)pyrazolyl borate) [5]. This complex is a rare case both of a polyhydride in a nitrogen donor environment and of a bis(dihydrogen) complex. Furthermore, it displays an anomalous reactivity characterized by its ready reactions with D_2, C_6D_6 and nucleophiles but its absence of reactions with electrophiles such as CH_3I or CF_3COOH [6]. This suggests an acidic character for the hydrogen atoms linked to ruthenium. Since the efficient catalysts for ketone reduction were found to be electrophilic derivatives, in contrast to hydrogen transfer catalysts which require hydridic M–H bonds, we decided to evaluate the catalytic activity of **1** in hydrogenation of ketone by H_2 or by hydrogen transfer from alcohols in basic medium. We describe hereafter our preliminary results.

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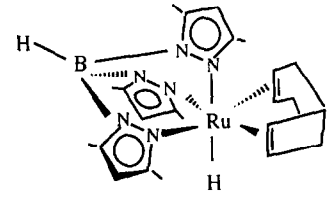
2. Results and discussion

Choice of the catalyst: 3 catalyst precursors were evaluated $Tp^*RuH(H_2)_2$ (**1**), $Tp^*RuH(COD)$ (**2**) and TpRuH(COD) (**3**) (Tp^* = hydridotris(3,5-dimethyl)pyrazolyl borate; Tp = hydridotrispyrazolyl borate; COD = 1,5-cyclooctadiene). Complex **1** being prepared by hydrogenation of **2**, this precursor complex was also studied. However the reaction between **3** and dihydrogen does not clearly lead to a complex analogous to **1**.

Hydrogenation reactions were carried out at 80°C under 3 bar of H_2 with a molar ratio catalyst:substrate of 1:100. Some significant results are shown on Table 1.

First there is no significant difference between **1** and **2** (see also Scheme 1) for the hydrogenation of cyclohexanone. This suggests that **2** is rapidly hydrogenated in the reaction conditions. By contrast much more forcing conditions are necessary when employing **3** as the catalyst precursor as a result of the reluctance of this compound to be hydrogenated. The differences observed for the hydrogenation of different ketones is probably due to steric factors: the bulky acetophenone molecule cannot have access to the active site. The case of i-butyraldehyde is different since the lack of conversion to alcohol could result from a reaction with the aldehyde shown independently to give an as yet unidentified product.



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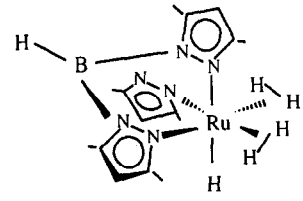

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Scheme 1. Proposed structures for $Tp^*RuH(H_2)_2$ (**1**) and $Tp^*RuH(COD)$ (**2**).

The pressure effect (entries 3 and 4, Table 1) is unexpected. Thus a high pressure of dihydrogen inhibits the catalytic reaction. This can be due to the stability and lack of reactivity of **1** which precipitates out of the solution in these conditions. **1** can be redissolved when the hydrogenation pressure is released thus indicating the need for a dihydrogen ligand to be dissociated during the catalytic process.

Finally, it was of interest to determine whether this system shows any selectivity for ketone reduction in the presence of olefins. Table 2 shows

Table 1
Reduction of ketones and aldehydes by ruthenium complexes of hydridotris(pyrazolyl) borate ligands

Entry	Catalyst	Substrate	*T* (°C)	*P* (bar)	*t* (h)	Conversion (%)
1	$Tp^*RuH(H_2)_2$	cyclohexanone	80	3	2	93
2	$Tp^*RuH(COD)$	cyclohexanone	80	3	2	92
3	$Tp^*RuH(COD)$	acetone	80	3	2	63
4	$Tp^*RuH(COD)$	acetone	85	32	2	6
5	$Tp^*RuH(COD)$	acetophenone	80	3	15	6
6	$Tp^*RuH(COD)$	i-butyraldehyde	80	3	2	0
7	TpRuH(COD)	cyclohexanone	80	3	2	0
8	TpRuH(COD)	cyclohexanone	120	4	15	98
9	TpRuH(COD)	acetophenone	120	4	15	29

Conditions: [cat.]: 1 mmol; [substrate]: 100 mmol; solvent: heptane (10 ml).

Table 2
Influence of the presence of an olefin promoter on the reduction of cyclohexanone to cyclohexanol by molecular hydrogen catalysed by Tp*RuH(COD)

Olefin added	Conversion of ketone (%)	Conversion of olefin (%)	Solvent
none	30	–	heptane
cyclohexene	73	38	octane
cyclohexene	63	15	heptane
cyclooctene (1:1)	54	13	heptane
cyclooctene (0.5:1)	65	28	heptane
styrene	74	18	heptane
styrene (no ketone)	–	30	heptane

Conditions: [cat.]: 1 mmol; [cat.]:[total substrate] = 1:100; [olefin]:[ketone] = 1:1; temperature: 50°C; dihydrogen pressure: 3 bar; duration: 4 h.

the result of cyclohexanone hydrogenation in the presence of various olefins. It is clear that the system shows a selectivity for cyclohexanone hydrogenation compared to the olefins employed but, furthermore, olefins show a promoting effect for the reaction. This could suggest that after the hydrogenation reaction cyclohexanol could remain in the coordination sphere of ruthenium and be a better ligand than cyclohexanone. The presence of an olefin, yet a better ligand, could help to regenerate the active species. However, the promoting effect remains limited.

These results show that **1** and **2** are good catalytic precursors for the hydrogenation of ketones. The reaction occurs in mild conditions (50–80°C, 3 bar H_2) and with good turnovers (ca. 50 h^{-1} at 80°C). In separate experiments we have shown that **2** reacts with H_2 in the presence of a ligand L (L = tetrahydrothiophene, pyridine) to give $Tp^*RuH(H_2)L$ (**4**) or $Tp^*RuH(L)_2$ (**5**) depending upon the reaction conditions [5]. It is therefore possible that a species such as **4** or **5** but containing a ligand L′ (L′ = alcohol or ketone) could be formed under the reaction conditions. However, it was not possible to isolate such species probably because of their lack of stability compared to **1** and of the ready hydrogenation of the C=O bond. The hydrogenation mechanism could involve protonation of the C=O bond followed by hydrogenolysis to regenerate the catalyst. The presence of a high pressure of H_2 could prevent the formation of species such as **4** or **5** and give only **1**. A similar type of behaviour is observed when **2** is reacted with $HNEt_2$ under H_2, which only leads to the formation of **1**. The substituted complex $Tp^*RuH(H_2)(HNEt_2)$ is obtained by substitution of H_2 on **1** in the absence of excess dihydrogen [6]. The selectivity for ketone hydrogenation could then be understood in terms of the easier protonation of the C=O bond compared to the C=C one.

To complete this preliminary study we have explored the potential of our system for transfer hydrogenation. As for relevant ruthenium systems, the reaction had to be carried out in a basic medium. The results depicted in Fig. 1 show that **1** and **2** have comparable activity but that the reaction works better in the absence of water. This can result either from the competition between the substrate and water for access to the active site or from the presence of a stronger basic medium in the absence of water.

The reaction rate is comparable to that of other ruthenium-based catalytic systems for cyclohexanone (three times slower than the polyhydride system used in Ref. [2]) but, as shown in Fig. 2, it is much more sensitive to the nature of the substrate. For example the hydrogenation of acetophenone is very slow compared to that of cyclohexanone whereas it is only approximately two times slower in systems involving $RuCl_2(PPh_3)_3$ as catalyst precursor. This suggests

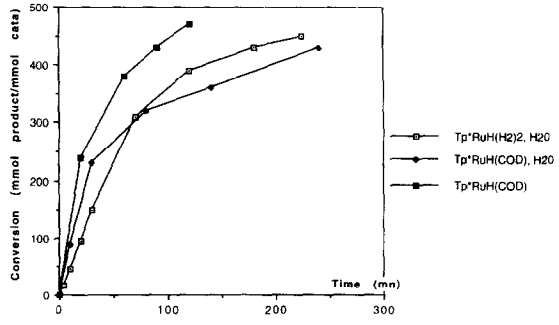

Fig. 1. Hydrogen transfer from isopropanol to cyclohexanone catalysed by Tp*Ru complexes. Conditions: temperature 70°C; [NaOH]: 500 mmol; [cat.]: 1 mmol.; [substrate]; 0.5 mol; solvent ^{i}PrOH (10 ml); H_2O (when present): 0.02 ml (0.2%).

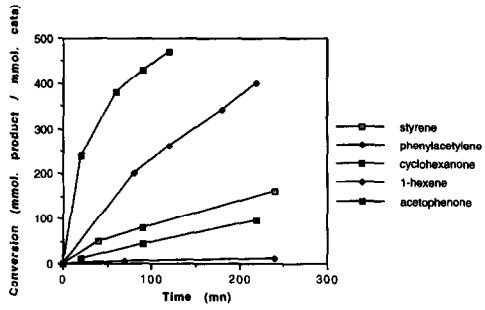

Fig. 2. Hydrogen transfer from isopropanol to various substrates catalysed by Tp*RuH(COD). Conditions: temperature 70°C; [NaOH] : 500 mmol; [cat.]: 1 mmol; [substrate]: 0.5 mol; solvent ^{i}PrOH (10 ml).

in our case a strong steric effect due to the fact that the Tp* ligand remains coordinated to ruthenium throughout the catalytic process. Furthermore, our system is able to hydrogenate olefins by hydrogen transfer which is relatively unusual. Interestingly, phenylacetylene reacted 10 times more slowly than styrene (Fig. 2). This reversed selectivity for olefin hydrogenation compared to acetylene hydrogenation [2] is attributed to steric effects.

3. Conclusion

In summary, we report in this communication a new stable system for the hydrogenation of ketones by molecular hydrogen or by hydrogen transfer in basic media. In both cases the reactions occur in mild conditions (50–80°C, 3 bar H_2) and with good turnover numbers (ca. 50 h^{-1} under H_2, 400 h^{-1} in hydrogen transfer conditions for ca. 95% conversion).

The originality of this system lies in its thermal stability and in the steric bulk of the substituted hydridotris(pyrazolyl) borate ligands which induce a steric selectivity in the hydrogenation of various substrates. This is exemplified by the easier hydrogenation of styrene compared to phenylacetylene in contrast to all other ruthenium based catalysts. This selectivity can be of importance when considering the potential use of such systems for the asymmetric hydrogenation of ketones.

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