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Regioselective hydrogenation of olefinic or carbonyl functional group of α,β-unsaturated substrates by iridium cycloocta-1,5-diene precursor stabilized with hydro(pyrazolyl)borate ligands

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Abstract

The in situ regioselective hydrogenation of α,β-unsaturated aldehydes using $[Ir(COD)Cl]_2$ stabilized by hydro(pyrazolyl)borate ligands such as: hydrotris(pyrazolyl)borate (Tp), hydrotris(3,5-dimethylpyrazolyl)borate (Tp*), hydrotris(3,4,5-trimethylpyrazolyl)borate (Tp^{3Me}) and dihydrobis(3,4,5-trimethylpyrazolyl)borate (Bp*) is described. When using *trans*-cinnamaldehyde (CNA) as a model substrate, the results show that selectivity towards the saturated aldehydes and the unsaturated alcohol depends on the reaction conditions and becomes more pronounced with the type of stabilizing ligands employed. As an example, when the Tp and Bp* ligands are used, the selectivity shifts to the saturated aldehydes, while for Tp* and Tp^{3Me}, the selectivity changes dramatically to the corresponding allylic alcohol. The foregoing observation was extended to another α,β-unsaturated aldehyde such as α-methyl-*trans*-cinnamaldehyde, where the corresponding allylic alcohol was obtained when Tp* was employed as a stabilizing ligand.

Keywords: Hydrogenation; α,β-Unsaturated substrates; Hydro(pyrazolyl)borate; Iridium

1. Introduction

During the last decades, the chemistry of poly(pyrazolyl) borate metal complexes has been extensively developed due to the fact that the pyrazolyl ring can contain different substituents. This allows to prepare different ligands with specific steric and electronic properties, a fact which has contributed to the development of the coordination chemistry related of those ligands [1–5]. However, much less work has been done regarding their application in catalysis, although some examples in homogeneous catalysis [6–11] and in olefin polymerization can be found [12–21].

As an example of catalytic applications, the potentiality of poly(pyrazolyl)borate metal complexes for the C–H bond activation of different substrates such as alkenes, aromatic aldehydes, ethers and amines has been reported [22–26]. However, their extension in the hydrogenation of different substrates has received little attention. In this context, initial work in olefins hydrogenation was performed by Onishi et al. using poly(1-pyrazolyl)borate ruthenium complexes containing nitrile ligands [27]. The authors established that solutions of $[RuCl(BPz_4)(PhCN)_2]$ and $[RuCl(BHPz_3)(PhCN)_2]$ in methanol under a hydrogen pressure of 50 kg/cm^2, with a catalyst:substrate molar ratio of 1:200 in the presence of Et_3N, were able to hydrogenate carbon–carbon double bonds of methyl acrylate as well as of 3-phenylpropene showing a conversion around 100%.

A very important contribution to understand the mechanism of the catalytic olefin hydrogenation carried out by poly(pyrazolyl)borate complexes was disclosed by Jia and co-workers employing some ruthenium complexes as catalyst precursors [28]. When $[Ru(HBPz_3)(PPh_3)_2(CH_3CN)]BF_4$ and $[Ru(HBPz_3)(PPh_3)(CH_3CN)_2]BF_4$ were used in THF solutions (either anhydrous or with the addition of H_2O or Et_3N) at 110 °C, under 40 atm of dihydrogen, both complexes were capable of hydrogenating sterically hindered olefins in the company of polar groups like carbonyl, showing from low to moderate activities. Two mechanisms were proposed, one in an anhydrous reaction medium and the other in the presence of H_2O or Et_3N, which showed a promoting effect. In both cases, a dihydrogen complex

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($[Ru(HBPz_3)(PPh_3)(L)(H_2)]BF_4$; L = PPh_3, CH_3CN) was involved. The catalytic activity of both complexes was discussed for a wide range of olefins. Particularly for those olefins with polar groups like benzylideneacetone, it was found that the $[Ru(HBPz_3)(PPh_3)_2(CH_3CN)]BF_4$ complex hydrogenates *only* the C=C bond showing a low yield (8%), while the $[Ru(HBPz_3)(PPh_3)(CH_3CN)_2]BF_4$ complex hydrogenates preferentially the C=C bond (48%) with a minor amount of the corresponding product of C=O bond hydrogenation (4%).

Another interesting application is the reduction of ketones in the presence of dihydrogen or a hydrogen transfer agent, catalyzed by $[Tp^*RuH(H_2)_2]$ and [Tp*RuH(COD)] under mild conditions (50–80 °C, 3 bar H_2) [29]. These complexes showed good turnovers, ca. 50 h^{-1} under H_2 and 400 h^{-1} in hydrogen transfer conditions, but their hydrogenation catalytic responses were affected by steric hindrance of the different ketones and by the dihydrogen pressure. Further, the [Tp*RuH(COD)] complex was able to reduce preferentially cyclohexanone in the presence of olefins, whereas the olefins had a promoting effect.

A different way to achieve hydrogenation of unsaturated substrates was reported by Alvarado et al. [30]. In this case, a heteroaromatic nitrogen compound like quinoline was regioselectively hydrogenated with a high conversion, using $[Rh(COD)Cl]_2$, $[Ir(COD)Cl]_2$, $[Ir(COE)_2Cl]_2$ and $RuCl_2(CH_3CN)_4$ as catalyst precursors, stabilized with hydro(pyrazolyl)borate ligands (Tp, Tp*), via one pot reaction. $[Rh(COD)Cl]_2$ and $[Ir(COD)Cl]_2$ stabilized with Tp($Na[HB(Pz)_3]$) showed the best activity under the reaction conditions used (100 °C, 35 atm H_2, precursor: substrate molar ratio 1:50). The catalytic hydrogenation responses of these systems were affected by the substitutes on the pyrazolyl rings (cone angle; Tp*: 276°, Tp: 199°), dihydrogen pressure (under low H_2 pressure, the conversion decreased), temperature (at high temperature, the catalytic activity is increased) and the polarity of the solvent (at high polarity, the conversion is increased).

Continuing with the search for new catalytic applications for hydro(pyrazolyl)borate complexes, in this article we reported the first example of regioselective hydrogenation of the olefinic or carbonyl function of α,β-unsaturated substrates such as *trans*-cinnamaldehyde (CNA) (3-phenyl-2-propenal), 2-methyl-*trans*-cinnamaldehyde (Me-CNA) by $[Ir(COD)Cl]_2$ precursor stabilized with hydro(pyrazolyl) borate ligands, via one pot reaction. The effect of the reaction conditions and the role of the hydro(pyrazolyl)borate ligands during the regioselective hydrogenation of α,β-unsaturated substrates are discussed.

2. Experimental

2.1. General

All manipulations were carried out under nitrogen atmosphere using standard Schlenck and vacuum-line techniques [31]. Solvents were dried and distilled by known procedures and stored under inert atmosphere. The α,β-unsaturated substrates *trans*-cinnamaldehyde, 2-methyl-*trans* cinnamaldehyde were purified by distillation under reduced pressure. The ligands $K[HB(pz)_3]$ (Tp), $K[HB(pz^*)_3]$ (Tp*), $K[HB(pz^{3Me})_3]$ (Tp^{3Me}), $K[H_2B(pz^{3Me})_2]$ (Bp*), and the complexes $[Ir(COD)Cl]_2$ and Tp*Ir(COD) were prepared following procedures from the literature [1,2,32,33]. GC analyses were performed in a Varian 3400 with FI detector and a Megabore type capillary column, 15 m (DB-5 phase; 1.5 u FT, J and W Scientific) was used. Quantification was achieved using the internal standard (2-methyl-naphtalene) method.

2.2. Catalytic tests

In a typical experiment, a precatalytic mixture (metal complex (0.15 mmol) and hydro(pyrazolyl)borate ligand (0.30 mmol) in toluene (50 ml) and the substrate (7.45 mmol)) were introduced into a glass-lined stainless steel autoclave (300 ml) from a PARR instrument equipped with internal stirring, temperature control unit and a sampling valve. Air was removed by pressurizing three times with hydrogen and the reactor was charged to the required pressure (34.02 atm), heated to the reaction temperature (100 °C) under constant stirring at 630 rpm. During the catalytic test, the total pressure of the system was continuously adjusted to a constant value by making up from a high-pressure reservoir and reaction mixture samples were periodically taken through the sampling valve. The reaction was stopped after 6 h and the reaction mixture was analyzed by gas chromatography. All catalytic results are the average of three consecutive experiments. The definition of conversion is the following: conversion = (moles of product/moles of *trans*-cinnamaldehyde used) × 100%. The C=C/C=O ratio was calculated as the resulting product amount obtained in each reaction averaging three consecutive analyses.

3. Results and discussion

The common hydrogenation route for the α,β-unsaturated substrates exemplified by *trans*-cinnamaldehyde with the corresponding products like the saturated aldehyde, hydrocinnamaldehyde (HCNA) (**2**), the allylic alcohol, cinnamol (**3**) and the saturated alcohol 3-phenyl-1-propanol (**4**) is displayed in Fig. 1.

Initially, it was necessary to determine the stabilization role of the hydro(pyrazolyl)borate ligands (shown in Fig. 2) during the catalysis. For that reason, one experiment was carried out *in absence* of the ligand at 100 °C, 34.02 atm of H_2 and a substrate/$[Ir(COD)Cl]_2$ molar ratio of 50.

When the iridium complex was used in absence of the ligand the result obtained showed that the substrate was converted into different products due to the presence of metallic particles formed in the reaction medium. According to

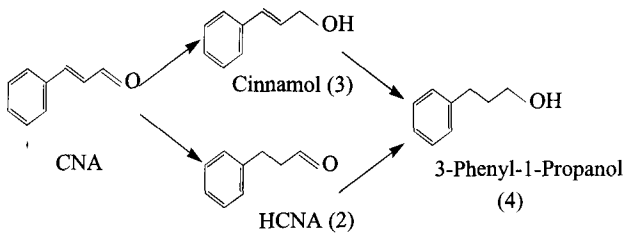


Fig. 1. Hydrogenation pathway for *trans*-cinnamaldehyde.

Table 1
trans-Cinnamaldehyde hydrogenation by $[Ir(COD)Cl]_2$/hydrotris(pyrazolyl)borate ligands

Ligand	Conversion (%)	Product distribution (%)	
		HCNA (2)	Cinammol (3)
Tp	65	62	3
Tp*	80	4	76

Conditions: [precatalyst] = 3×10^{-3} M, [substrate] = 1.5×10^{-1} M, pH_2 = 34.02 atm, T = 100 °C, [ligand]/[metal]: 2, solvent: toluene (50 ml), time: 6 h.

this, when the CNA hydrogenation was carried out through two independent experiments in the presence of the hydro(pyrazolyl)borate ligands such as Tp and Tp*, prepared in situ by mixing the metal complex and the ligand, with a ligand/metal ratio = 2, and maintaining the same reaction conditions, the results indicated, in each case that the reaction is merely carried out by molecular species, the results of which are summarized in Table 1.

As can be seen therein, the resulting catalyst precursors transformed the CNA with moderate and high activity without indication of decomposition of the catalyst system. It was observed that the type of ligand had an influence on the catalytic activity, obtaining higher conversions when the more sterically hindered ligand Tp* was used. An interesting fact was detected when the product distribution was analyzed. Thus, only two main products were identified by GC: hydrocinnamaldehyde (**2**) and cinnamyl alcohol, cinnamol (**3**). The fully-saturated alcohol, 3-phenyl-1-propanol (**4**) and other possible decarbonylation product like allylbenzene was not detected, indicating that both catalyst systems act as selective hydrogenating reagents.

A more interesting aspect was the one regarding the possibility to change the selectivity towards the unsaturated alcohol by using a more sterically hindered and electron donor ligand like Tp* [4]. As shown in Table 1, by a remarkable effect on the selectivity is observed when varying the type of ligand. The C=C/C=O ratio of 20 observed for the Tp ligand changed to 0.05 for the Tp*.

After this promising results, it was necessary to confirm if the reaction proceeded in a homogeneous phase. The mercury test was carried out in two independent experiments using Tp or Tp* and the results showed no interference at all with the evolution of the reaction [34,35].

Once that the type of hydro(pyrazolyl)borate ligands was determined to have an influence on the activity, selectivity and that it was also confirmed that the reaction was carried out purely by molecular species, another experiment to prove the nature of the catalyst precursor was carried out. In this

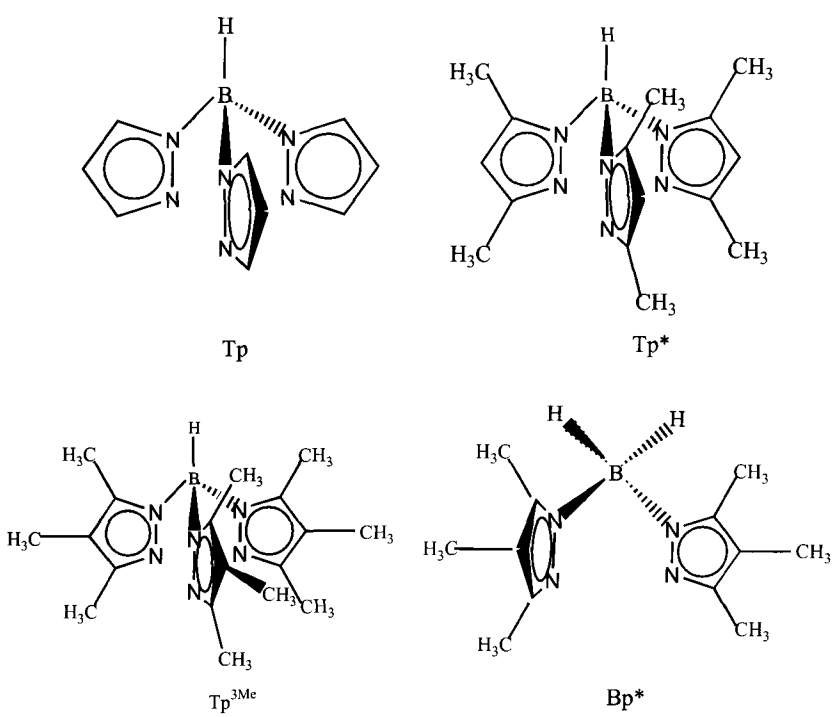
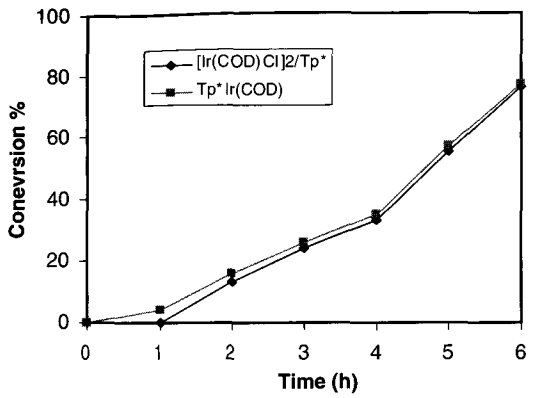


Fig. 2. Hydro(pyrazolyl)borates used as stabilizing ligands.



Conditions: [precatalyst] =3 x10^{-3}M, [substrate] =1.5 x10^{-1} M, pH_2=34.02 atm, T=100°C, [ligand]/[metal]: 2, solvent: toluene (50 ml) , time : 6 hrs

Fig. 3. *trans*-Cinnamaldehyde hydrogenation with $[Ir(COD)Cl]_2$/Tp* and the Tp*Ir(COD) complex.

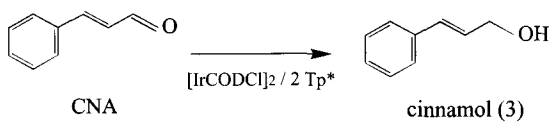


Fig. 4. Selectivity towards cinnamol (**3**).

sense, Tp*Ir(COD) [36] was prepared and a hydrogenation experiment was performed. The result thereof was compared with the reaction done by the in situ preparation. As shown in Fig. 3, the reaction profile describing the production of cinnamol (**3**) in each case is very close.

The above shown results suggest that the reaction between the $[Ir(COD)Cl]_2$ and the Tp* ligand under this reaction condition leads to the formation of the Tp*Ir(COD) complex [36,37], which reacts with H_2 accompanied with cyclooctane elimination[2] to form the plausible active species responsible for this selectivity. This fact was also observed during the hydrogenation of quinoline when using the system comprising with $[Rh(COD)Cl]_2$ and the ligand Tp as a catalyst precursor [30].

The result above prompted us to investigate with more details if the influence of the reaction conditions and the nature of the hydro(pyrazolyl)borate ligands could enhance the selectivity of the unsaturated alcohol, cinnamol (**3**), according to Fig. 4.

In order to study the effect of the reaction temperature, reactions were performed between 80 and 120 °C. These results are summarized in Table 2.

As can be observed therein, the reaction temperature contributes to the enhancement of the selectivity towards the unsaturated alcohol, which reached a maximum value at 100 °C. At 120 °C, the selectivity decreased by the decomposition of the catalyst system, presumably as a result of the high reaction temperature used during the experiment.

[2] Cyclooctane was detected in both cases as a product in the reaction medium.

Table 2
Effect of the reaction temperature on the selectivity towards cinnamol (**3**)

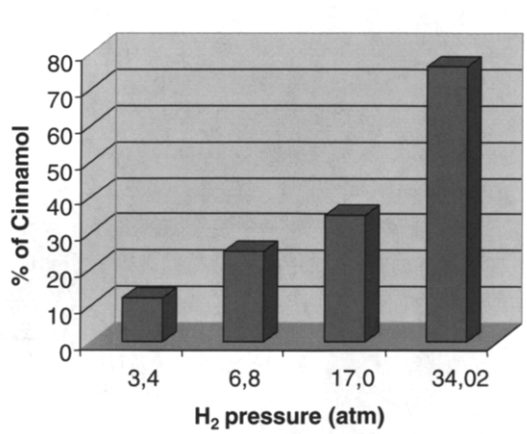
Temperature (°C)	Percentage of cinnamol (**3**)
60	15
80	40
100	76
120	43

Conditions: [precatalyst] = 3×10^{-3} M, [substrate] = 1.5×10^{-1} M, pH_2 = 34.02 atm, T = 100 °C, [ligand]/[metal]: 2, solvent: toluene (50 ml), time: 6 h.

The effect of the hydrogen pressure was also studied. Thus, hydrogenation reactions were performed at lower H_2 pressure, maintaining the other operation variables constant. The result obtained are presented in Fig. 5.

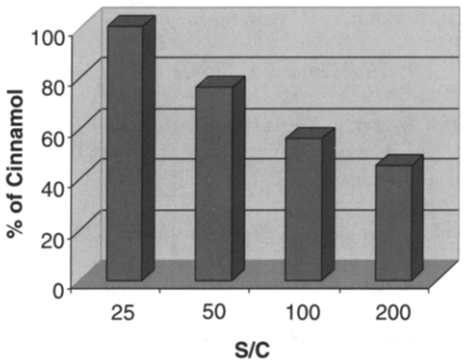
As can be seen, the highest conversion towards cinnamol was achieved at 500 psi, while at low H_2 pressures, the cinnamol production decreased considerably. This result can be related to a previous observation reported by Jia and co-workers during the styrene hydrogenation, using the $[Ru(HB(pz)_3(PPh_3)_2CH_3CN]BF_4$ and $[Ru(HB(pz)_3(PPh_3)(CH_3CN)_2]BF_4$ complexes [29]. The authors described that both complexes showed very little activity at low hydrogen pressure (3–5 atm). However, at high H_2 pressure (40 atm), the corresponding dihydrogen $[Ru(HB(pz)_3(PPh_3)(H_2)]BF_4$ and $[Ru(HB(pz)_3(CH_3CN)(H_2)]BF_4$ complexes were identified in the reaction medium and the authors concluded that both species were responsible for the enhancement of the catalytic activity.

In the same context, the formation of hydro(pyrazolyl) borate iridium complexes with dihydrogen ligands has been revised by Heinekey and co-workers [38]. They pointed out that one way to obtain such complexes was starting from $Tp^*Ir(PMe_3)H_2$ with 1 eq. of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at room temperature or below leading the, $[Tp^*Ir(PMe_3)(H_2)H]BF_4$ cationic species without H_2 elimination [38b,c]. Another possibility disclosed is through the



Conditions: [precatalyst] =3 X10^{-3} M, [substrate] =1,5 X10^{-1} M, T =100 °C,[ligand]/[metal]: 2, solvent: toluene (50 ml), time : 6 hrs.

Fig. 5. Effect of the pressure on the selectivity towards cinnamol (**3**).



Conditions: [precatalyst] =3 x10^{-3} M, [substrate] =1.5 x10^{-1} M, pH_2= 34.02 atm, T=100°C, [ligand]/[metal]: 2, solvent: toluene (50 ml), time : 6 hrs.

Fig. 6. Effect of the substrate/catalyst ratio on the selectivity towards cinnamol (**3**).

interaction of $TpIr(PMe_3)(C_2H_4)$ with H_2 under relative hydrogen pressure. Based on those reports, we suspect that a dihydrogen complex of the [Tp*Ir(H_2)] type, similar to the above-mentioned complexes, which can be formed under relative hydrogen pressure, is probably responsible for the catalytic activity during the CNA hydrogenation.

Another aspect evaluated in this work was the effect of the substrate/catalyst ratio on the selectivity of cinnamol (results presented in Fig. 6). The results show that the selectivity of cinnamol has a strong dependence with the concentration of the catalyst precursor. In fact, 100% of this product is achieved at a substrate/catalyst ratio of 25; while when this ratio decreased, still the selectivity towards the cinnamol product is conserved. These results indicate that the catalyst system can operate with good selectivity in a certain range of substrate/catalyst ratio.

After the examination of the three fundamental parameters governing the selective hydrogenation of CNA, we conclude that the conversion of cinnamol (**3**) to 100% is maximized at $T = 100\,°C$, $pH_2 = 500$ psi and S/C = 25. However, for a good comparison of the ligand effect, it is better to use a reaction condition where the cinnamol production is below 100%. For this reason, we decided to use $T = 100\,°C$, $pH_2 = 34.02$ atm, S/C = 50 where the cinnamol yield is about 76%.

Another point necessary to be covered in this study was the type of hydro(pyrazolyl)borate ligand. In this sense, different ligands with a more pronounced steric effect and better electron donating properties were tested, maintaining the same reaction conditions. Table 3 shows the results obtained for all the pyrazolyl ligands tested.

As can be seen, the iridium systems comprised by the ligands with none and two methyl groups (3, 5 positions) in each pyrazolyl ring (entry 1 versus 3) showed a different behavior regarding the product selectivity. As can be observed, HCNA (**2**) was produced mainly by the normal Tp (62%),

Table 3
Effect of the type of pyrazolyl ligand on the CNA hydrogenation

Entry	Ligand	HCNA (**2**), (%)	Cinnamol (**3**), (%)
1	Tp	62	3
2	Bp*	60	4
3	Tp*	4	76
4	Tp^{3Me}	0	90

Conditions: [precatalyst] = 3×10^{-3} M, [substrate] = 1.5×10^{-1} M, pH_2 = 34.02 atm, $T = 100\,°C$, [ligand]/[metal]: 2, solvent: toluene (50 ml), time: 6 h.

while the introduction of two methyl groups in each ring, promoted the formation of cinnamol (**3**) in 76%.

Furthermore, when a ligand with two methyl groups is replaced with the corresponding fully methylated like Tp^{3Me}, the selectivity changes from 76 to 90% of the cinnamol (**3**) with *no* production of HCNA (**2**) (entry 3 versus 4). The above-mentioned results let us conclude that the selectivity can be tuned depending on the ligand used; it can be interpreted that depending on the hydrogenation requirements, the C=C bond can be hydrogenated in the presence of the C=O bond, by using the Tp and Bp* ligands; otherwise, the Tp* and Tp^{3Me} are better candidates for the selective hydrogenation of the C=O bond.

The results above encouraged us to investigate if the number of pyrazolyl rings had a special effect on the selectivity towards cinnamol (**3**). Thus, another ligand, namely Bp*, having two pyrazolyl rings, while maintaining the same number of methyl groups as Tp^{3Me} in each ring, was used. The results showed that HCNA (**2**) was produced with a 60% yield, while only 4% of cinnamol (**3**) was obtained (see entry 2 versus 4). This result clearly illustrates that *not only* the methyl groups are responsible for the selectivity towards cinnamol (**3**). Probably another effect that could be related with the possible species involved during the reaction pathway is operating.

Finally, in order to corroborate if this selectivity could be extended to other α,β-unsaturated substrates, another set of experiments using the $[Ir(COD)Cl]_2$/Tp* catalyst precursor and maintaining the same reaction conditions, was carried out, using α-methyl-*trans*-cinnamaldehyde as the substrate. For this substrate, a 76% yield and a 72% selectivity towards cinnamol were obtained.

These results demonstrate that α-methyl-*trans*-cinnamaldehyde can be selectively hydrogenated and the presence of the methyl group in the α position, does not create any disturbance for the catalyst precursor to coordinate the substrate preferentially to the C=O bond, leading concomitantly to a higher production to the corresponding unsaturated alcohol.

This work shows that it is possible to tune the C=C/C=O selectivity modifying the type of the hydro(pyrazolyl)borate ligand with the iridium center and it opens a possible application in organic synthesis where the selective reduction of one functional group in the presence of the other is necessary in many cases to obtain an intermediate or a final product with multiple applications.

Studies concerning the determination of the possible species responsible of the selectivity as well as the extension of this study to other α,β-unsaturated substrates with another set of hydro(pyrazolyl)borate ligand are currently under investigation and the results will be published in a future article.

4. Conclusions

In summary, we report a new catalytic system for the selective hydrogenation of α,β-unsaturated aldehydes exemplified by *trans*-cinnamaldehyde, by using the [Ir(COD)Cl]$_2$ iridium complex stabilized with different hydro(pyrazolyl)borate ligands as catalyst precursors. The influence of the nature of pyrazolyl-borate ligand on this catalytic reaction was illustrated when the selectivity changed dramatically depending on the ligand employed. The presence of different degrees of methyl substitution on the pyrazolyl ring in the tridentate form leads to the effective tune of the selectivity towards the unsaturated alcohol cinnamol (**3**) and illustrates the potential use of such systems for different applications in organic synthesis like the selective reduction of C=O bonds in the presence of different functional groups or in mixtures of substrates with this kind of groups.

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