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Regioselective homogeneous hydrogenation of quinoline by use of pyrazolyl borate ligand and transition metal complexes as a precatalyst

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Abstract

In situ regioselective quinoline hydrogenation with transition metal complexes, such as $[Rh(COD)Cl]_2$, $[Ir(COD)Cl]_2$, $[Ir(COE)_2Cl]_2$ and $RuCl_2(CH_3CN)_4$ stabilized with the ligands tris-pyrazolyl borates Tp = $NaHB(pz)_3$ and Tp* = $KHB(pz^*)_3$ (pz* = 3,5-dimethylpyrazolyl), via one pot reaction is described. The results are compared to those carried out with the complex $TpIr(Ethylene)_2$. The system formed by the complex $[Rh(COD)Cl]_2$ with the ligand Tp is the most efficient and regioselective catalyst precursor for this reaction. Influence of the type of Tp ligand in the activity of this system was observed. The complex $TpIr(Ethylene)_2$ shows catalytic activity in the hydrogenation, with strong influence of temperature, H_2 pressure and a polar solvent such as MeOH favors the formation of the active species.

Keywords: Homogeneous catalyst; Quinoline hydrogenation; Tris-pyrazolyl borates ligands

1. Introduction

The hydrogenation of polynuclear heteroaromatic nitrogen compounds is an important area because it is related to commercial hydrodenitrogenation (HDN) process in which the nitrogen content of the different fuel products derived from the coal is minimized. Studies of the HDN process showed that selective hydrogenation of the nitrogen ring occurs previous to the carbon–nitrogen bond cleavage [1]. A few examples of the hydrogenation of these types of compounds using homogeneous catalysts are found in the literature. Several homogeneous Rh, Ir, Ru and Os systems have been published by Fish and coworkers [2–6], Sánchez-Delgado and coworkers [7,8] and recently by Rosales et al. [9,10]. Much of this work has been carried out using a triphenylphosphine (PPh_3) and pentamethylcyclopentadienyl (Me_5C_5) as ligands. In this communication new results are presented on the hydrogenation of quinoline (Q) using the tris-pyrazolyl borates Tp = $NaHB(pz)_3$ and Tp* = $KHB(pz^*)_3$ (pz* = 3,5-dimethylpyrazolyl) introduced by Trofimenko [11] as a stabilizing ligand with different transition metal complexes as precursor catalyst.

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2. Experimental

All manipulations were carried out under nitrogen atmosphere using Schlenck techniques. Quinoline was purified by distillation under reduced pressure. Solvents were dried and distillated by known procedure, and were stored under inert atmosphere. The ligands Tp = Na[$HB(pz)_3$], Tp* = K[$HB(pz^*)_3$], (pz^* = 3,5-dimethylpyrazolyl) and the complexes [M(COD)Cl]$_2$ (M = Rh, Ir), [$Ir(COE)_2Cl]_2$, TpIr(Ethylene)$_2$, $RuCl_2(CH_3CN)_4$ were prepared following procedure from the literature [12–18]. The IR spectra of the complexes (in KBr) were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. ^{1}H NMR spectra were measured in CD_2Cl_2, D_2O solutions at room temperature on a Bruker AMX 300 spectrometer. GC analyses were performed on a Varian 3400 with FI detector Megabore types capillary column, 15 m; DB-5 phase; 1.5 u FT (J and W Scientific). Quantification was achieved by using the internal standard (2-methylnaphthalene) method.

2.1. Catalytic tests

In a typical experiment, a toluene solution (50 ml) of the catalyst or the catalytic mixture [e.g., metal complex (0.15 mmol) + Na[$HB(pz)_3$] (0.30 mmol) and the substrate (7.45 mmol), were introduced into a glass-lined stainless steel autoclave (300 ml) from PARR instrument equipped with internal stirring, temperature control unit and a sampling valve. Air was removed by flushing three times with hydrogen; then, the reactor was charged to the required pressure and heated to the study temperature with stirring at 630 rpm. During the catalytic test, samples of the reaction were periodically extracted via the sampling valve, and the total pressure of the system was continuously adjusted to a constant value by make up from a high-pressure reservoir. The samples were analyzed by gas chromatography.

3. Results and discussion

Catalyst selection: five catalyst precursors were evaluated for the hydrogenation of quinoline. Four of them, [Rh(COD)Cl]$_2$ **(1)**, [Ir(COD)Cl]$_2$ **(2)**, [$Ir(COE)_2Cl]_2$ **(3)** and $RuCl_2(CH_3CN)_4$ **(4)**, were stabilized with Na[$HB(pz)_3$] ligand via one pot reaction. TpIr(Ethylene)$_2$ **(5)** was used without any excess of Tp. The quinoline reduction was carried out at 373 K and 500 psi of H_2, with molar ratio catalyst/substrate = 50. The results are summarized in Table 1.

According to these results, the catalytic systems [Rh(COD)Cl]$_2$ **(1)** and [Ir(COD)Cl]$_2$ **(2)** (entries 1 and 2, Table 1), stabilized with Na[$HB(pz)_3$], showed the best activity under the reaction conditions. This feature can be an attribute, if it is considered that the Tp ligand reacts immediately with this type of precursors to give the corresponding TpRh(COD) [19,20] and TpIr(COD) [21] under the reaction condition and these can react with H_2 transforming in the catalysts precursor for the hydrogenation. However, both systems decomposed at the end of the reaction and presumably it can be a consequence of the role induced by the substrate as a participant during the formation and of the active species. This kind of peculiarity was reported by Sánchez-Delgado et al. [8] in the homogeneous quinoline hydrogenation using the rhodium complex $[Rh(COD)(PPh_3)_2]^+$ where they found that the substrate replaces the phosphine ligands to give $[Rh(COD)(Quinoline)_2]^+$

Table 1
Quinoline hydrogenation by Ru, Rh, Ir complexes using TP = Na[$HB(pz)_3$] as a ligand

Entry	Catalyst	t (h)	Conversion (%)
1	[Rh(COD)Cl]$_2$	2	100
2	[Ir(COD)Cl]$_2$	3	100
3	$[Ir(COE)_2Cl]_2$	6	68
4	$RuCl_2(CH_3CN)_4$	6	56
5	TpIr(Ethylene)$_2$	6	28

Conditions: [catalyst] = 3×10^{-3} M, [substrate] = 1.5×10^{-1} M, $P(H_2)$ = 500 psi, T = 100°C, solvent toluene (50 ml).

and it was identified as the catalytically active species during the catalysis. In our case, we suspect that the quinoline replaces the COD ligand to lead the complex $TpRh(Quinoline)_2$ and can be presumed as the catalytically active species. Experiments needed to identify the nature of this type of complex are currently going on and will be published in a future communication.

After we found the high activity of the Rh system, we decided to investigate with more details the effect of the type of Tp ligand in the catalysis. Thus, the same reaction was carried out using the $Tp^* = K[HB(pz^*)_3]$, a ligand with methyl group's substitute in the pyrazol ring. The result can be observed in Fig. 1.

The initial reaction rate for the system with Tp^* is slightly higher than the one for normal Tp and this result suggests that the formation of the $Tp^*Rh(COD)$ [20] is faster compared with the normal Tp and it is more reactive toward the quinoline hydrogenation. Another point to clear is related to the presence of the methyl substitutes in the pyrazole ring which definitely has a special role in the formation and reactivity of the catalytically active specie during the reaction.

After determining that the type of Tp ligand has an influence on the activity, experiments needed to confirm the nature of the catalyst

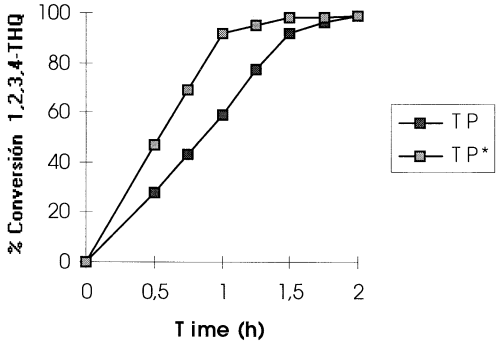

Fig. 1. Quinoline hydrogenation with $[Rh(COD)Cl]_2$ stabilized with $Tp = Na[HB(pz)_3]$ and $Tp^* = K[HB(pz^*)_3]$ ($pz^* = 3,5$-dimethylpyrazolyl). $T = 100°C$; $P(H_2)$: 500 psi; mmol [substrate]/mmol [cat] = 50; solvent: toluene (50 ml).

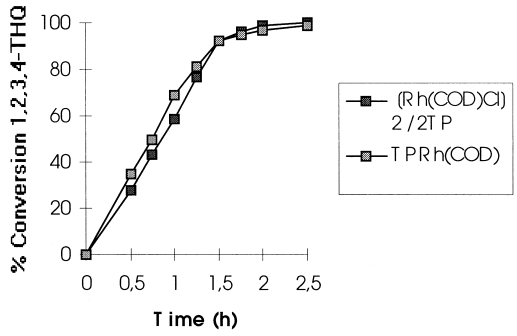

Fig. 2. Quinoline hydrogenation with $[Rh(COD)Cl]_2$ stabilized with $Tp = Na[HB(pz)_3]$ and TpRh(COD). $T = 100°C$; $P(H_2) =$ 500 psi; mmol [substrate]/mmol [cat] = 50; solvent: toluene (50 ml).

precursor were carried out. In this sense the TpRh(COD) [19,20] was prepared and a hydrogenation experiment was performed.

As shown in Fig. 2, the initial reaction rates for both complexes are very close. The above results confirm that the immediate reaction between the $[Rh(COD)Cl]_2$ and the Tp ligand under the reactions conditions leads to the formation of the complex TpRh(COD) [20,22,23], which reacts with H_2 to form the active specie responsible for the catalysis.

Another system studied, the $[Ir(COE)_2Cl]_2$ **(3)** with Tp as a ligand (entry 3, Table 1) catalyzes the quinoline hydrogenation under mild conditions without any decomposition with lower activity compared with the previous systems. It can be associated with some reaction between $[Ir(COE)_2Cl]_2$ and MTp ligand under the reaction condition [16,24]. It is noteworthy to emphasize that this kind of chemistry has been extensively studied by Carmona et al. where they showed that the initial reaction between the $[Ir(COE)_2Cl]_2$ and MTp under mild condition in the absence of coordinating substrate conduces to several unsaturated species derived from irreversible dissociation of cyclooctene ligand [16] which upon high temperature goes to an unsaturated hydrido–allyl complex by β-H elimination [24]. This unsaturated complex can react with a coordinating ligand like quinoline in the presence of H_2 to promote the hydrogenation, Concerning the Ru system, a

few examples of catalytic hydrogenation using derivatives of tris-pyrazolyl borates complexes have been reported in the literature [22,23]. In fact, a very interesting result was found using $RuCl_2(CH_3CN)_4$ **(4)** (entry 4, Table 1) as a catalyst precursor where it catalyzes the quinoline hydrogenation with a 56% conversion. The result at the beginning was unexpected, because we were expecting to get the dimer $[TpRu]_2$ previously isolated by using the same ruthenium complex under mild conditions, which showed inactivity toward olefin hydrogenation [22]. However, the result above suggests that under stronger conditions, monomeric 'Ru-Tp' can be formed and this specie react with H_2 and quinoline leading the hydrogenation. The TpIr(Ethylene)$_2$ (entry 5, Table 1) catalyzes this reaction with a lower conversion. It is possible that the C–H activation of ethylene moiety that gives hydride–allyl complex or hydride–alkene–vinyl complexes, reactions that are reported in the literature for this kind of complex [24–26], has an effect on the catalytic properties. In this sense, we carried out an experiment to study the behavior of this complex under different reaction conditions. For this reason, the effect of the H_2 pressure (see Fig. 3) on the hydrogenation of quinoline was studied.

As can be seen in Fig. 3, a high conversion is reached at 500 psi while when the H_2 pressure decreases to 250 or 100 psi, the percentage conversion was lower. Probably under high concentrations of H_2 the formation of the active specie is favored, increasing the catalytic activity of this complex.

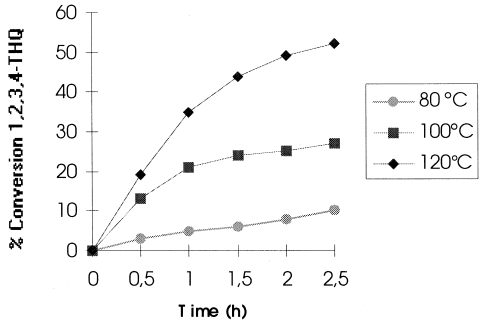

Fig. 4. Quinoline hydrogenation with TpIr(Ethylene)$_2$: $P(H_2) =$ 500 psi, [catalyst] $= 3\times10^{3}$ M, [substrate] $= 1.5\times10^{-1}$ M, toluene: 50 ml.

Fig. 4 shows the effect of the temperature. At high temperatures, the catalytic activity is increased almost twice with respect to the preceding temperature. Formation of the active specie is also favorable at high temperatures.

Finally, the effects of the solvent on the catalytic activity were determined. Fig. 5 shows the results of the quinoline hydrogenation using solvents with different degrees of polarity.

There is a remarkable enhancement of the activity when the polarity of the solvent is increased; the use of MeOH as solvent implies higher conversion than toluene and THF. This result indicates that polar medium favors the formation of the active specie.

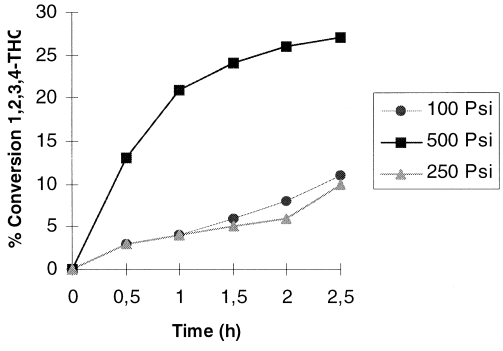

Fig. 3. Quinoline hydrogenation with TpIr(Ethylene)$_2$: $T = 100$°C, [catalyst] $= 3\times10^{-3}$ M, [substrate] $= 1.5\times10^{-1}$ M, toluene: 50 ml.

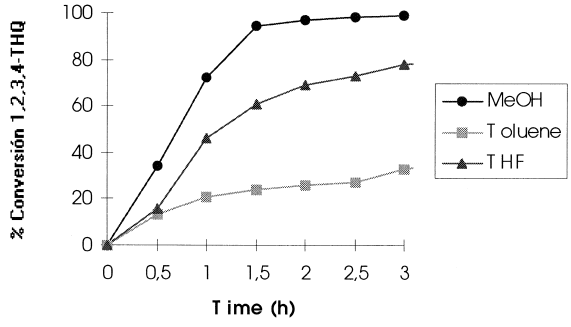

Fig. 5. Quinoline hydrogenation with TpIr(Ethylene)$_2$: $P(H_2) =$ 500 psi, $T = 100$°C, [catalyst] $= 3\times10^{3}$ M, [substrate] $= 1.5\times10^{-1}$ M, solvent: 50 ml.

4. Conclusions

The ligands tris-pyrazolyl borates Tp = $NaHB(pz)_3$ and Tp* = $KHB(pz^*)_3$ (pz* = 3,5-dimethylpyrazolyl) are useful compounds for the stabilization of different transition metal complexes in the homogeneous hydrogenation of quinoline.

The system formed by the complex $[Rh(COD)Cl]_2$ with the ligand Tp showed the highest activity for hydrogenation of quinoline. The influence of the type of Tp ligand in this catalysis has also been demonstrated.

The complex $TpIr(Ethylene)_2$ showed lower catalytic activity in the hydrogenation of quinoline, with strong influence of the reaction conditions and remarkable dependence with the polarity of the solvent used in the reaction.

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