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Quinoline transfer hydrogenation by a rhodium bipyridine catalyst

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Dedicated to celebrate Brian James's scientific career and 70th birthday.

Abstract

The catalytic activity of the rhodium complex *cis*-[Rh(bipy)$_2$Cl$_2$]Cl · 2H$_2$O in the transfer hydrogenation of different unsaturated substrates is reported. This complex, if pre-activated, is very active in the transfer hydrogenation of ketones (i.e., cyclohexanone is reduced with a 38.1% conversion at 283 K and 100% at 313 K) while in the case of hex-1-ene, a 36.8% conversion was reached at 293 K. A cyclic olefin (cyclohexene) was also reduced with a lower, but still significant, conversion.

It is interesting to note the catalytic activity of this complex in the transfer hydrogenation of a C=N double bond belonging to imides or nitrogen-containing heterocycles. For instance, *N*-benzylidenaniline was hydrogenated to *N*-benzylaniline at 303 K with a conversion of 27.3%. Increasing the temperature to 353 K, the conversion rised to 91.8%. A nitrogen containing heterocycle, quinoline, was also reduced by transfer hydrogenation at 353 K with a 11.7% conversion giving 1,2,3,4-tetrahydroquinoline (selectivity of 96.6%). The conversion rised up to 54.2% with a still high selectivity (84.5%) when the temperature was 383 K. Almost the same activity was shown in the reduction of pyridine to pyperidine (conversion, 51.1% at 383 K), while 2-methylpyridine was hydrogenated with a 24.7% conversion.

Keywords: Transfer hydrogenation; Rhodium; Quinoline; Pyridine; Ketone; Alkene

1. Introduction

Transfer hydrogenation is an useful tool to reduce organic substrates avoiding the use of molecular hydrogen and pressure apparatus. Several papers are reported on the use of rhodium complexes in the catalytic hydrogen transfer [1]. In a previous paper [2], we reported the transfer hydrogenation of organic substrates containing a functional group such as C=C, C=O, N=N or N–N. The catalysts were rhodium complexes with nitrogen containing ligands such as 2,2′-bipyridine (bipy), 1,10-phenantroline (phen) or 3,3′-dimethoxy-2,2′-bipyridine (dmo-bipy) while propan-2-ol was the hydrogen donor. These ligands show very important properties because they chelate the metal through two nitrogen atoms giving complexes having a higher stability than those containing monodentate ligands. The presence of an aromatic heterocycle improves the thermal and chemical stability of the ligand and the solubility of the metal complex in organic solvents.

The compounds *cis*-[Rh(bipy)$_2$Cl$_2$]Cl · 2H$_2$O (**1**), *cis*-[Rh(dmo-bipy)$_2$Cl$_2$]Cl · 2H$_2$O (**2**) and *cis*-[Rh(phen)$_2$Cl$_2$]Cl · 2H$_2$O (**3**) employed as catalytic precursors in the transfer hydrogenation from propan-2-ol to different organic substrates showed, after a pre-activation procedure, very good activity [2].

Taking into account these results, presently we have continued our investigation on the transfer hydrogenation of substrates such as alkenes, ketones, aldehydes, and imines using the catalyst *cis*-[Rh(bipy)$_2$Cl$_2$]Cl · 2H$_2$O (**1**), the more active among **1**–**3** [2]. The activation parameters of these hydrogenations have also been calculated. Furthermore, we have extended these studies to the transfer hydrogenation of aromatic nitrogen containing heterocycles such

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as quinoline, pyridine, and 2-methylpyridine. The regioselective hydrogenation of these substrates is involved in the manufacture of intermediates of considerable industrial interest such as petrochemicals, fine chemicals and pharmaceuticals. Furthermore, quinoline and its derivatives are commonly used as model substrates in hydrodenitrogenation (HDN), a reaction of relevant importance in petroleum refining.

The first paper on the catalytic activity of a rhodium complex in the reduction of nitrogen containing heterocycles with molecular hydrogen, was reported by Jardine and McQuillin in 1970 [3]. In the following years, several papers have been reported in this field [4] using ruthenium or rhodium complexes. Extensive studies on the homogeneous hydrogenation of nitrogen containing heterocycles using Rh(I) or Ru(II) complexes, such as $Rh(PPh_3)_3Cl$, $Ru(PPh_3)_3HCl$ and $[RhCp \cdot (MeCN)_3]^{2+}$, have been described by Fish and co-workers. These authors have also proposed a mechanism for these reactions [5].

Recently, some of us have reported a study on the hydrogenation of quinoline, and other nitrogen containing heterocycles, using the dihydride ruthenium complexes $RuH_2(CO)_2(P^nBu_3)_2$ (**4**), $RuH_2(CO)_2(PPh_3)_2$ (**5**) and $RuH_2(PPh_3)_4$ (**6**) [6]. These three complexes **4**–**6** are catalytically active in the hydrogenation of quinoline giving results comparable with those previously reported with other ruthenium systems like $RuCl_2(CO)_2(PPh_3)_2$ and $Ru_4H_4(CO)_{12}$, but operating under milder conditions and with a lower catalyst/substrate ratio [6,7]. The complex **6** is also catalytically active in the hydrogenation of pyridine and methylpyridine although to a lesser extent than quinoline, confirming a strong influence of the bonding mode of nitrogen containing heterocycles to the metal center on the conversion and selectivity of these reactions[1] [5,6,8,9].

2. Results and discussion

2.1. Synthesis of cis-[Rh(bipy)$_2$Cl$_2$]Cl (1)

$[Rh(bipy)_2Cl_2]Cl$ is a mononuclear complex reported as *cis*- or *trans*-dichloro isomers. The *cis* form was synthesised following the procedure reported by Gidney et al. [10], modified in order to obtain exclusively the pure *cis*-$[Rh(bipy)_2Cl_2]Cl$ (**1**): To an ethanol solution of $RhCl_3 \cdot 2H_2O$ and bipyridine, at room temperature, hydrazine monochloride was added as catalyst. The mixture was heated at reflux temperature for 90 min, then cooled to 277 K. A yellow solid was recovered that, after the usual work up, was obtained as the pure *cis* form of the Rh complex **1**.

2.2. Catalytic activity of cis-[Rh(bipy)$_2$Cl$_2$]Cl (1)

The catalytic activity of **1** was tested in the hydrogen transfer from propan-2-ol to substrates containing one of the following functional groups:

- a C=C double bond of a linear (hex-1-ene) or cyclic (cyclohexene) alkene;
- a C=O double bond of linear (butan-2-one) or cyclic (cyclohexanone) ketones and a linear aldehyde (butanal);
- a C=N double bond of an imine (*N*-benzylidenaniline) or nitrogen containing aromatic heterocycles (quinoline, pyridine, 2-methylpyridine).

As reported above, **1** was active in the transfer hydrogenation of acetophenone to 1-phenylethanol in the presence of propan-2-ol as hydrogen donor [2]. The catalyst **1** was active at a relatively high temperature (353 K) in the presence of a base (NaOH) as promoter, i.e., acetophenone was reduced to 1-phenylethanol with 95.5% conversion after 3 h at 353 K. Working at 333 K, a 5.1% conversion was reached after 5 h but, surprisingly, it was 95.7% after 6 h. However, if the same catalyst was pre-activated, heating a propan-2-ol solution of the complex in the presence of a base at 353 K, the transfer reduction of acetophenone was performed at 293 K with a 34.1% conversion: Working at 313 K, a 53.9% conversion was obtained while in the same conditions the catalysts **2** and **3** gave lower conversions: 26.7% and 20.8%, respectively. An almost total conversion was reached in the presence of **1** at 343 K after 3 h.

These evidences have suggested that during the reaction the catalytic precursor was transformed into a more active specie. In fact working in the presence of un-activated *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$ at 303 K, no transfer reaction was noticed even after 192 h. Mestroni et al. [1b] reported that Rh(I) catalysts are more active than Rh(III) in transfer hydrogenation and attribute this different behaviour to the oxidation state of the metal. They hypothesised that in the case of the $[Rh(4,7\text{-dimethyl-}1,10\text{-phen})_2Cl_2]Cl \cdot 2H_2O$, the Rh(III) complex was reduced to Rh(I) during the reaction. The reduction of Rh(III) to Rh(I) was suggested to be autocatalytic, and Rh(I) was hypothesised to be the catalyst of the Rh(III) reduction.

An analogous behaviour may be claimed in the presence of the complexes **1**–**3** working at 353 K. In the course of the reaction, the Rh(III) complex was slowly transformed into a Rh(I) compound. Once formed, this last complex catalyzes the complete reduction of the starting Rh(III) catalytic precursor. As a consequence a more active catalyst may be "in situ" prepared by heating a propan-2-ol solution of the Rh(III) complex/NaOH at 353 K for 3 h. Heating the complex **1** in a glass flask at this temperature, a color change of the solution from pale yellow to violet was observed. In this pre-activation process, the complex **1** is presumably reduced to a $Rh(bipy)_2^+$ cation and this specie is then transformed into a Rh–H compound. In agreement with this observation, Mulazzani et al. [11] have reported that $Rh(bipy)_2^+$ may be present in several forms depending on pH, and the Rh(I) complex is violet. Miller and Oliver [12] have also reported that a methanol solution of **1** is reduced to a $Rh(bipy)_2^+$ cation at 333 K in the presence of a base and a hydrogen atmosphere.

[1] The steric hindrance of the substrates is: PYR < MePYR ≅ Q.

This violet solution shows a very low stability and it is easily transformed into a black compound at high temperature, while it gives a yellow complex if cooled to 273 K. The violet complex may be obtained also by $NaBH_4$ reduction of **1** in propan-2-ol as solvent. In this case, the violet colour remains for a short time. An analogous behaviour was reported for the $[Rh(py)_2(HCONMe_2)Cl_2(BH_4)]$ complex (py = pyridine) employed as catalyst for the homogeneous hydrogenation of oct-1-ene [13].

If the reactions were carried out in a pressure vessel, under a low pressure of dinitrogen or argon the reaction were easily reproduced, probably due to the absence of sun-light or avoiding the accidental presence of air inside the reactor vessel.

The catalytic activity of *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$ (**1**) after its pre-activation, as described above, was investigated in the hydrogen transfer from propan-2-ol using a substrate/catalyst ratio of 100 or higher.

2.2.1. Transfer hydrogenation of a C=C group

Cyclohexene was reduced at 283 K even if with a low conversion after 3 h (4.1%), however, improving the temperature the conversion rises up to 13.0% at 293 K or 18.9% at 313 K (Table 1).

The activation parameters ΔG^{**}, ΔS^{**} and ΔH^{**}, evaluated using the Gibbs equation [14] in the temperature range among 283 and 313 K, gave a $\Delta S^{**} = -228$ J mol^{-1} K^{-1} and a $\Delta H^{**} = 33.28$ kJ mol^{-1}. The negative activation entropy suggests an associative rate determining step.

Linear hex-1-ene was easily reduced than cyclohexene with a conversion of 36.8% at 293 K.

This behaviour is in agreement with the data present in the literature. Zassinovich et al. [1e] described an analogous behaviour in the reduction with molecular hydrogen of the same olefins in the presence of $[Rh(NBD)(PPh_3)_2]PF_6$.

2.2.2. Transfer hydrogenation of a C=O group

Cyclohexanone was employed as reference ketone and the influence of temperature, catalyst concentration, and the presence of a different gas in the medium were evaluated. The ketone was just hydrogenated at 283 K with a 38.1% conversion that increases up to 100% when the reaction temperature raised to 313 K (Table 2). The catalyst gave good results also with a substrate/catalyst of 1000 or higher. When the temperature was increased from 300 to 333 K the conversion raised from 10.6% up to 76.6% working with a substrate/catalyst ratio of 1000 (Table 2).

Table 1
Transfer hydrogenation of alkenes to alkanes using propan-2-ol in the presence of pre-activated *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$

Alkene	T (K)	Conversion (%)	TON	TOF (h^{-1})
Hex-1-ene	293	36.8	36.8	12.3
Cyclohexene	283	4.1	4.1	1.4
Cyclohexene	293	13.0	13.0	4.3
Cyclohexene	313	18.9	18.9	6.3

cis-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$: 0.673 mM, alkene: 0.067 M, propan-2-ol: 10 ml, NaOH: 0.0125 M, pN_2: 1 MPa, reaction time: 3 h.
Catalyst pre-activation: T: 353 K, t: 3 h, pN_2: 1 MPa.

Table 2
Transfer hydrogenation of cyclohexanone to cyclohexanol uisng propan-2-ol in the presence of pre-activated *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$

T (K)	Catalyst/substrate ratio	[Catalyst] (mM)	Conversion (%)	TON	TOF (h^{-1})
283	1/100	0.673	38.1	38.1	12.7
293	1/100	0.673	52.7	52.7	17.6
303	1/100	0.673	53.2	53.2	17.7
313	1/100	0.673	100	100	33.3
313	1/500	0.647	50.9	254.5	84.8
300	1/1000	0.626	10.6	106.0	35.3
313	1/1000	0.626	27.5	275.0	91.7
323	1/1000	0.626	52.0	520.0	173.3
333	1/1000	0.626	76.6	766.0	255.3
313	1/3000	0.554	11.7	351.0	117.0
293	1/100[a]	0.673	100	100	33.3

Propan-2-ol: 10 ml, NaOH: 0.0125 M, pN_2: 1 MPa, reaction time: 3 h.
Catalyst pre-activation: T: 353 K, t: 3 h, pN_2: 1 MPa.
[a] Reaction performed in the presence of hydrogen (1 MPa).

The activation parameters ΔG^{**}, ΔS^{**} and ΔH^{**}, evaluated using the Gibbs equation [14] and the data reported in Table 2, gave $\Delta S^{**} = -278$ J mol^{-1} K^{-1} and $\Delta H^{**} = 13.76$ kJ mol^{-1}. The negative activation entropy is in agreement with an associative rate determining step.

Surprisingly, the Rh catalyst is more active in the reduction of a cyclic ketone than a cyclic alkene (conversions of 38.1% and 4.1%, respectively, at 283 K), however, an analogous behaviour was reported by Mestroni et al. [1f]. It should be noted that the transfer hydrogenation of a C=C double bond conjugated with a C=O group (cyclohex-2-en-1-one) gives selectively the saturated ketones at 313 K and *trans*-4-phenylbut-3-en-2-one (benzylidenacetone), at the same temperature, is converted into 4-phenylbutanone (71.6%), *trans*-4-phenylbut-3-en-2-ol (12.2%) and 4-phenylbutanol (15.0%) [15].

The cyclohexanone reduction was also performed in the presence of molecular hydrogen (1 MPa) reaching a complete conversion, while in the absence of hydrogen the conversion was 52.7%. These results show that molecular hydrogen increases the rate of the ketone reduction but it is not possible to evaluate if the reduction by molecular hydrogen is faster than the same reaction by transfer hydrogenation from propan-2-ol.

As previously reported, the transfer reduction of ketones decreases as the molecular weight of the ketone increases or the steric hindrance around the carbonyl group rises [15].

The transfer hydrogenation of an aldehyde (butanal) was also tested at 303 K, however, the rate of the aldol condensation of the substrate, due to the NaOH present in the medium, is faster than the hydrogenation obtaining a complete conversion but only a 11.8% of butan-1-ol.

2.2.3. Transfer hydrogenation of a C=N group

The transfer hydrogenation of a C=N group present in an imine (*N*-benzylidenaniline) or in nitrogen containing

aromatic heterocycles (quinoline, pyridine, methylpyridine) was tested.

2.2.3.1. N-Benzylidenaniline. The reduction of *N*-benzylidenaniline was performed in the temperature range among 303 and 373 K and the results are reported in Table 3.

The pre-activated Rh catalyst **1** was active at 303 K giving *N*-benzylaniline (conversion 27.3%) with a complete selectivity. Increasing the temperature up to 353 K, an almost complete conversion (91.8%) was reached. The reaction was always chemoselective, no hydrogenation of the aromatic ring or hydrogenolysis of the C–N single bond was noticed.

The reduction of a C=N double bond proceeded slowly than the corresponding C=O hydrogenation, but faster than the reduction of the C=C double bond present in cyclohexene. In fact at 303 K, the conversions were 53.2% for cyclohexanone, 27.3% for *N*-benzylidenaniline and 18.9% for cyclohexene. However, a C=C double bond present in a linear olefin (hex-1-ene) was easily reduced (36.8%) than a C=N group.

An unusual behaviour was shown in the transfer hydrogenation of *N*-benzylidenaniline at higher temperature (353–373 K): apparently the yield was not affected by an increase of the reaction temperature. We hypothesize that the benzylaniline formed competes with the imine to the coordination of the rhodium and consequently reduces the yield. To confirm this hypothesis, a transfer hydrogenation of benzylidenaniline was carried out in the presence of free aniline in the reaction medium. A lower conversion (37.4% instead of 51.1%) was obtained confirming the negative influence of the amine present in the medium on the conversion of the substrate. On the basis of these results, a total conversion of the substrate cannot be reached in one-step due to the presence of the amine formed in the course of the reaction itself. The amine, more basic than imine, reduces the possibility of the activation of the residual substrate by the catalyst, however, a complete conversion of the substrate may be reached through a recycle of the unreacted imine.

The activation parameters ΔG^{**}, ΔS^{**} and ΔH^{**}, evaluated using the Gibbs equation [14] and the data reported in Table 3, gave $\Delta S^{**} = -260\ \mathrm{J\ mol^{-1}\ K^{-1}}$ and $\Delta H^{**} = 20.14\ \mathrm{kJ\ mol^{-1}}$. The negative activation entropy is in agreement with an associative rate determining step.

Table 3
Transfer hydrogenation of *N*-benzylidenaniline to *N*-benzylaniline using propan-2-ol in the presence of pre-activated *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$

T (K)	Conversion (%)	TON	TOF (h^{-1})
303	27.3	27.3	9.1
313	51.7	51.7	17.2
323	87.2	87.2	29.1
353	91.8	91.8	30.6
363	91.2	91.2	30.4
373	90.9	90.9	30.3
313[a]	37.4	37.4	12.5

cis-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$: 0.67 mM, *N*-benzylidenaniline: 0.067 M, propan-2-ol: 10 ml, NaOH: 0.0125 M, pN_2: 1 MPa, reaction time: 3 h. Catalyst pre-activation: T: 353 K, t: 3 h, pN_2: 1 MPa.

[a] Reaction performed in the presence of aniline (0.335 M).

2.2.3.2. Quinoline. The hydrogenation of quinoline usually gives 1,2,3,4-tetrahydroquinoline (1,2,3,4-THQ) or 5,6,7,8-tetrahydroquinoline (5,6,7,8-THQ) in a first step and decahydroquinoline (DHQ) as the final product. The rhodium catalyst **1** was active in this reduction at 353 K with a conversion of 11.7% and a selectivity towards 1,2,3,4-THQ of 96.6%, 5,6,7,8-THQ was the other product. Other intermediates or DHQ were not formed in these conditions (Table 4). Increasing the temperature up to 383 K the conversion rises up to 54.2% but a slightly lower selectivity was obtained (84.5%). At 393 K the solution at the end of the reaction was not homogeneous even if the conversion of quinoline after 3 h was 92.5% (selectivity 80.0%).

The presence of a small amount of water in the reaction medium (up to 1.1% with respect to the amount of propan-2-ol) showed a beneficial effect improving the conversion, however, if a higher amount was present, it depressed the catalytic activity of **1**. The positive influence of small amount of water may be ascribed to an easier dissociation of the base, while the negative influence of an higher amount of water may be attributed to a reduction of the basicity of the solution.

The reaction is regioselective towards the formation of 1,2,3,4-THQ. The easy hydrogenation of the heterocyclic ring with respect to the carbocyclic one, may be connected with the presence of the nitrogen atom. It is more electronegative than carbon and reduces the electronic density on the heterocyclic ring and facilitates the attack of the reducing agent [16].

The transfer hydrogenation of quinoline was also carried out in the presence of a different additional gas at 373 K, after a reaction time of 3 h. In the presence of nitrogen, a conversion of 30.0% (25.9% 1,2,3,4-THQ, 4.6% 5,6,7,8-THQ) was obtained. Almost the same conversion (34.5%) was reached in the presence of helium (30.5% 1,2,3,4-THQ and 4.0% 5,6,7,8-THQ) while in the presence of molecular hydrogen a conversion of 81.1% was obtained (73.8% 1,2,3,4-THQ, 1.1% 5,6,7,8-THQ and 6.2% DHQ). This considerable improvement of the conversion in the presence of hydrogen suggests that the catalyst is more efficient in the hydrogenation with molecular hydrogen than in the transfer reduction. Furthermore, the formation of DHQ is an indication that this catalyst is also catalytically active in the total hydrogenation of quinoline. The presence of a small amount of 5,6,7,8-THQ suggests that it may be easily hydrogenated than 1,2,3,4-THQ to DHQ.

The activation parameters ΔG^{**}, ΔS^{**} and ΔH^{**} were evaluated using the Gibbs equation [14] and the data reported in Table 4. A negative activation entropy was obtained ($\Delta S^{\neq} = -160\ \mathrm{J\ mol^{-1}\ K^{-1}}$, $\Delta H^{\neq} = 62.86\ \mathrm{kJ\ mol^{-1}}$) and an associative rate determining step may be hypothesised also in this case.

Table 4
Transfer hydrogenation of quinoline using propan-2-ol in the presence of pre-activated *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$

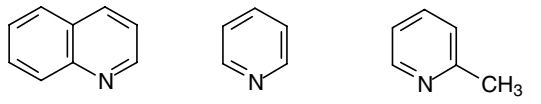
T (K)		Conversion (%)	Reaction products composition (%)				Selectivity (%)
			A	B	C	D	A/(A + B + C)
353	N_2	11.7	11.3	0.4	0.0	88.3	96.6
363	N_2	22.6	21.2	1.4	0.0	77.4	93.8
369	N_2	28.3	24.0	4.3	0.0	71.7	84.8
373	N_2	30.5	25.9	4.6	0.0	69.5	84.9
383	N_2	54.2	45.8	8.4	0.0	45.8	84.5
373[a]	He[a]	34.5	30.5	4.0	0.0	66.7	88.4
373[b]	H_2[a]	81.1	73.8	1.1	6.2	18.9	91.0
363	$N_2 + H_2O \leqslant 0.1\%$[b]	28.8	25.5	3.3	0.0	71.2	88.5
373	$N_2 + H_2O \leqslant 0.1\%$[b]	35.0	30.9	4.1	0.0	65.0	88.3
373	$N_2 + H_2O$ 1.1%[b]	37.1	32.3	4.8	0.0	62.9	87.1
373	$N_2 + H_2O$ 2.1%[b]	34.4	30.8	3.6	0.0	65.6	94.8
373	$N_2 + H_2O$ 5.1%[b]	22.2	20.3	1.9	0.0	77.8	97.6
373	$N_2 + H_2O$ 10.1%[b]	17.4	16.1	1.3	0.0	82.6	98.4
373	$N_2 + H_2O$ 50.1%[b]	0.8	0.8	0.0	0.0	99.2	100

A: 1,2,3,4-tetrahydroquinoline; B: 5,6,7,8-tetrahydroquinoline; C: decahydroquinoline; and D: quinoline.
cis-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$: 0.67 mM, quinoline: 0.067 M, propan-2-ol: 10 ml, NaOH: 0.0125 M, pN_2: 1 MPa, reaction time: 3 h.
Catalyst pre-activation: T: 353 K, t: 3 h, pN_2: 1 MPa.
[a] Nitrogen has been substituted by helium or hydrogen.
[b] Water was added (v/v with reference to the propan-2-ol).

2.2.3.3. Pyridine and 2-methylpyridine. The catalytic activity of the rhodium complex **1** has been also tested in the transfer reduction of pyridine and 2-methylpyridine at 373 K. The results are reported in Table 5.

Pyridine has been selectively reduced to pyperidine with a 51.1% conversion, while in the same conditions, 2-methylpyridine has been hydrogenated to 2-methylpyperidine with a 24.7% conversion.

These results are in agreement with those reported by Fish et al. [17] for the hydrogenation of the same substrates. A lower conversion was shown when the basicity and the steric hindrance around the nitrogen atom of the substrate were increased.



Quinoline pKa = 4.94 | Pyridine pKa =5.23 | 2-Methylpyridine pKa =5.97

2.3. Hypothesis on the transfer hydrogenation mechanism

In agreement with the data reported by Mestroni et al. [1a,1b] for the transfer hydrogenation of acetophenone using the catalytic precursor $[Rh(4,7\text{-dimethyl-}1,10\text{-phen})_2Cl_2]Cl \cdot 2H_2O$, we may assume that in our case too, the reaction evolves through an "hydridic route" (Scheme 1). We may assume that the catalytic precursor **1** in the course of the pre-treatment is reduced to a Rh(I) specie **7** that coordinates propan-2-ol giving **8**. In a following step, **8** is deprotonated by the base forming the alkoxy specie **9**. This last complex through a β-hydrogen shift and elimination of acetone forms the rhodium hydride **10** that has been assumed as the real catalyst.

Table 5
Transfer hydrogenation of nitrogen containing heterocycles using propan-2-ol in the presence of pre-activated *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$

Substrate	Conversion[a] (%)	TON	TOF (h^{-1})
Quinoline	54.2	54.2	18.0
Pyridine	51.1	51.1	17.0
2-Methylpyridine	24.7	24.7	8.2

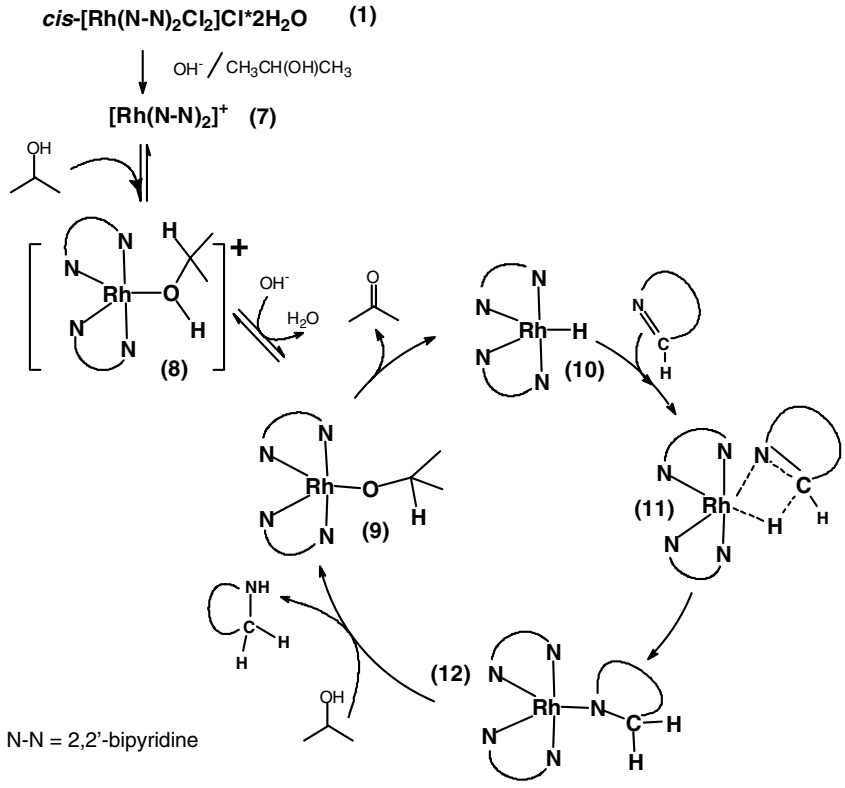
cis-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$: 0.67 mM, substrate: 0.067 M, propan-2-ol: 10 ml, NaOH: 0.0125 M, pN_2: 1 MPa, reaction time: 3 h, T: 383 K.
Catalyst pre-activation: T: 353 K, t: 3 h, pN_2: 1 MPa.
[a] Hydrogenated product: tetrahydroquinolines, pyperidine or 2-methylpyperidine, respectively.

Complex **10** reacts with the substrate forming the complex **11** that through a four center intermediate gives the specie **12**. As the final step, **12**, through an exchange reaction with propan-2-ol, forms the hydrogenated substrate and restores the alkoxy derivative **9**.

The formation of the complex **11** through addition of the nitrogen containing heterocycle to **10**, in agreement with the thermodynamic activation parameters, may be assumed as the associative rate determining step.

An hydrido specie $[Rh(bipy)_2H]$ has been reported in the literature [18], evidenced in the catalytic dehydrogenation of ethanol promoted by $[Rh(bipy)_2]Cl$ in the presence of NaOH. Morton et al. [19] also report $[Rh(bipy)_2H]$ as the prevailing specie formed by heating a methanol solution of $[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$ containing NaOH. Finally, Miller and Oliver [12] report that *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$ is reduced to a $[Rh(bipy)_2]^+$ specie when heated in an alkaline ethanol solution.

Taking into account that the thermodynamic activation parameters evaluated for the reductions tested are very close, an analogous mechanism may be involved in the transfer hydrogenation of the other substrates.



Scheme 1.

3. Conclusion

The preliminary results on the transfer hydrogenation using the pre-activated *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$ have been extended by evaluating the thermodynamic activation parameters in the reduction of ketones and the availability of this catalyst in the reduction of other substrates such as alkenes, aldehydes, imines and nitrogen containing aromatic heterocycles.

The cyclohexanone reduction has been performed in very mild conditions using a substrate/catalyst ratio up to 3000/1. Alkenes have also been reduced at low temperature.

The results show the strong influence of the steric hindrance of the substrate on the reduction of a C=N double bond as shown by the data on the reduction of pyridine and 2-methylpyridine. An analogous behaviour is reported in the reduction of a ketone: the conversion decreases in the order butan-2-one > 3-methylbutan-2-one > 3,3-dimethylbutan-2-one [15]. The length of the alkyl chain of a ketone also affects the catalytic activity of **1**: the conversion of butan-2-one is higher than that of pentan-2-one (Table 6) [2,15]. Moreover, the rate of hydrogenation of a cyclic ketone (cyclohexanone) is higher than that of linear or branched ketones and the conversion of acetophenone is slightly higher than butan-2-one.

The more interesting aspect is, however, the transfer hydrogenation of nitrogen containing aromatic heterocycles such as quinoline, pyridine and 2-methylpyridine. The *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$ catalyst is able to hydrogenate quinoline in the presence of propan-2-ol as hydrogen donor with a 54.2% conversion at 383 K after 3 h giving 1,2,3,4-THQ with a very high regioselectivity. To the best of our knowledge, only one paper has been reported up to now on the transfer hydrogenation of nitrogen containing heterocycles. An Ir catalyst after 17 h at 356 K reduces quinoline to 1,2,3,4-THQ with a 45.0% conversion [20].

Table 6
Transfer hydrogenation of ketones to the corresponding alcohols using propan-2-ol in the presence of pre-activated *cis*-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$ [2,15]

Ketone	Conversion (%)	TON	TOF (h^{-1})
Butanone	47.8	47.8	15.9
Pentan-2-one	20.4	20.4	6.8
3-Methylbutanone	42.1	42.1	14.0
3,3-Dimethylbutanone	7.4	7.4	2.5
Cyclohexanone	89.8	89.8	29.9
2-Phenylethanone	53.8	53.8	17.9

cis-$[Rh(bipy)_2Cl_2]Cl \cdot 2H_2O$: 0.67 mM, ketone: 0.067 M, propan-2-ol: 10 ml, NaOH: 0.0125 M, pN_2: 1 MPa, *T*: 313 K, reaction time: 3 h. Catalyst pre-activation: *T*: 353 K, *t*: 3 h, pN_2: 1 MPa.

By a perusal of the results reported in this paper with those previously discussed for the hydrogenation of the same nitrogen containing heterocycles using Ru catalysts [6], we may observe that in the presence of H_2 the rhodium complex is more active than ruthenium compounds. The rhodium complex **1** in the presence of propan-2-ol as hydrogen source, gives lower conversions than ruthenium

catalyst employed in the presence of molecular hydrogen, however, many advantages are connected with the use of a transfer hydrogenation process.

We may conclude that pre-activated *cis*-[$Rh(bipy)_2Cl_2$]-$Cl \cdot 2H_2O$/NaOH system is a versatile catalyst for the transfer hydrogenation of C=C, C=O, C=N, N=N double bonds and hydrogenolysis of a N–N [2] single bond using propan-2-ol as hydrogen donor.

4. Experimental

4.1. Instruments and materials

Quantitative analyses were performed using a Shimadzu GC14 chromatograph equipped with two FID detectors, using 2 m packed columns filled with the appropriate stationary phase. Quantitative GC analyses were performed using *p*-xylene as internal standard. The response factors of reagents and products versus *p*-xylene were detected. The identity of the products was confirmed by GC–MS using a Shimadzu apparatus (GCMS-QP5050A) equipped with a capillary column SP™-1 (length 30 m, diameter 0.25 mm, film thickness 0.1 μm).

Elemental analyses were performed with a Perkin–Elmer Analyzer Model 2400 Series II CHNS/O.

IR spectra were recorded with a Perkin–Elmer Model 1760 FT-IR spectrometer.

^1H, and ^{13}C NMR spectra were recorded using a Varian VXR300 spectrometer operating at 299.987 MHz for ^1H, and 75.429 MHz for ^{13}C, using solutions in deuterated solvents. $SiMe_4$ was used as external standard for ^1H and ^{13}C NMR. ^{13}C NMR spectra were acquired using a broad band decoupler.

All manipulations were routinely carried out under a nitrogen atmosphere using standard Schlenk technique.

Transfer hydrogenation experiments were carried out in a round bottomed flask or in a Parr Model 4759 stainless steel autoclave (150 ml) electrically heated and equipped with a magnetic drive stirrer or in a home made stainless steel high pressure vessel (150 ml) heated and rocked in a thermostated oil bath.

Hex-1-ene. The commercial reagent (99% pure) was eluted through activated Al_2O_3 (70–230 mesh) and distilled under nitrogen (b.p. 337 K).

Cyclohexene. The commercial reagent (99% pure) was eluted through activated Al_2O_3 (70–230 mesh) and distilled under nitrogen (b.p. 351 K).

Propan-2-ol. The commercial product (99 + % pure) was dried and deoxygenated by refluxing over calcium oxide for 4 h, then distilled under nitrogen (b.p. 355 K) and stored on activated molecular sieves 4 Å.

Pyridine. The commercial product (99.6% pure) was refluxed over KOH for 2 h, then distilled under nitrogen (b.p. 388 K).

All other products were provided by commercial suppliers and used without further purification.

4.1.1. Synthesis of *cis*-[$Rh(bipy)_2Cl_2$]$Cl \cdot 2H_2O$ (**1**)

In a 50 ml round bottomed flask, 144.7 mg (0.926 mmol) of 2,2′-bipyridine was dissolved in 2.1 ml of ethanol, then 103.0 mg (0.433 mmol) of $RhCl_3 \cdot 2H_2O$ in 2.1 ml of water was added. Finally, 8.6 mg (0.126 mmol) of hydrazine monochloride was introduced. The mixture was heated at reflux temperature for 90 min, then cooled to 277 K obtaining a yellow solid. It was separated, washed with ethanol, diethyl ether and dried under vacuum. The *cis*-[$Rh(bipy)_2Cl_2$]$Cl \cdot 2H_2O$ (**1**) was obtained with a 61.7% yield.

The IR spectrum (KBr pellet) showed bands at 3346 (vs), 3108 (sf), 3082 (s), 3025 (s), 1641 (m), 1603 (vs), 1564 (w), 1497 (s), 1468 (vs), 1445 (vs), 1422 (s), 1311 (s), 1283 (w), 1244 (s), 1215 (w), 1164 (ms), 1156 (s), 1123 (w), 1107 (ms), 1074 (ms), 1066 (m), 1037 (ms), 1027 (m), 1004 (w), 898 (ms), 803 (mw), 772 (vs), 725 (s), 668 (m), 653 (ms), 550 (m), 485 (mw), 467 (w), 459 (w), 421 (ms) cm^{-1}.

The ^1H NMR spectrum (CD_3OD) showed resonances at δ 9.85 (d, 1H, H6, $J_{6,5} = 5.6$ Hz), 8.78 (d, 1H, H3, $J_{3,4} = 8.0$ Hz), 8.68 (d, 1H, H3′, $J_{3',4'} = 8.2$ Hz), 8.51 (t, 1H, H4, $J_{4,3} = J_{4,5} = 7.9$ Hz), 8.24 (t, 1H, H4′, $J_{4',3'} = J_{4',5'} = 7.9$ Hz), 8.06 (t, 1H, H5, $J_{5,4} = J_{5,6} = 6.6$ Hz), 7.78 (d, 1H, H6′, $J_{6',5'} = 5.6$ Hz), 7.53 (t, 1H, H5′, $J_{5',6'} = J_{5',4'} = 6.7$ Hz) ppm [10a].

The ^{13}C NMR spectrum showed resonances at δ: 155.7 (s, 1C, C2), 155.5 (s, 1C, C2′), 151.4 (s, 1C, C6), 150.4 (s, 1C, C6′), 141.3 (s, 1C, C4), 140.9 (s, 1C, C4′), 128.7 (s, 1C, C5), 128.5 (s, 1C, C5′), 125.1 (s, 1C, C3), 125.0 (s, 1C, C3′) ppm.

Elemental *Anal*. Calc. for $CHCl_3NORu$: C, 43.08; H, 3.61; N, 10.05. Found: C, 43.15; H, 3.52; N, 9.78%.

4.2. Transfer hydrogenation experiments

In a pressure vessel or in a round bottomed flask, the catalyst was pre-activated heating a propan-2-ol solution (10 ml) of the complex **1** (0.674 mM) in the presence of NaOH (12.5 mM) at 353 K for 3 h, then cooled to room temperature. The substrate was added (0.067 M) and the transfer reaction was performed at the prefixed temperature for the selected time. At the end, the reactor was rapidly cooled and the solution analyzed as reported.

Every experiment was replicated three times and the medium values were reported.

4.3. Analysis of transfer hydrogenation mixtures

The reaction products composition was detected through GC analyses using the following conditions:

- hex-1-ene/hexane: a CW 20 M-KOH column was kept at 373 K for 2 min, then heated up to 423 K at a rate of 1 K/min, and kept at this temperature for 10 min;
- cyclohexene/cyclohexane: a PPG column was kept at 308 K for 15 min, then heated at a rate of 3 K/min up to 373 K, and kept at this temperature for 20 min;

- cyclohexanone/cyclohexanol: a FFAP column was kept at 358 K for 120 min;
- butanal/butanol: a CW 20 M column was kept at 323 K for 10 min, then heated up to 473 K at a rate of 10 K/min, and kept at this temperature for 20 min;
- quinoline/1,2,3,4-THQ, 5,6,7,8-THQ, DHQ: a CW 20 M-KOH column was heated at 473 K for 120 min;
- pyridine/pyperidine: a CW 20 M-KOH column was heated at 373 K for 120 min;
- 2-methylpyridine/2-methylpyperidine: a CW 20 M-KOH column was heated at 363 K for 120 min.

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