

MECHANISTIC STUDY OF A RUTHENIUM HYDRIDE COMPLEX OF TYPE $[\text{RuH}(\text{CO})(\text{N-N})(\text{PR}_3)_2]^+$ AS CATALYST PRECURSOR FOR THE HYDROFORMYLATION REACTION OF 1-HEXENE

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ABSTRACT

The catalytic activity of systems of type $[\text{RuH}(\text{CO})(\text{N-N})(\text{PR}_3)_2]^+$ was evaluated in the hydroformylation reaction of 1-hexene. The observed activity is explained through a reaction mechanism on the basis of the quantum theory. The mechanism included total energy calculations for each of the intermediaries of the elemental steps considered in the catalytic cycle. The deactivation of the catalyst precursors takes place via dissociation of the polypyridine ligand and the subsequent formation of thermodynamically stable species, such as $\text{RuH}(\text{CO})_3(\text{PPh}_3)_2$ and $\text{RuH}_3(\text{CO})(\text{PPh}_3)_2$, which interrupt the catalytic cycle. In addition, the theoretical study allows to explain the observed regioselectivity which is defined in two steps: (a) the hydride migration reaction with an anti-Markovnikov orientation to produce the alkyl-linear-complex (**3.1a**), which is more stable by 19.4 kJ/mol than the Markovnikov orientation (alkyl-branched-complex) (**3.1b**); (b) the carbon monoxide insertion step generates the carbonyl alkyl-linear specie (**4.1a**) which is more stable by 9.5 kJ/mol than the alternative species (**4.1b**), determining the preferred formation of heptanal in the hydroformylation of 1-hexene.

Key words: DFT, hydroformylation, ruthenium, homogeneous catalysis.

1. INTRODUCTION

The hydroformylation of olefins is a catalytic reaction of great industrial interest for preparing aldehydes and alcohols.^{1,2} The reaction allows the addition of a hydrogen atom and a formyl group (-CHO) to the double-bonded carbon atoms of an olefin, using CO and H₂ to generate an aldehyde with one more carbon than the initial alkene. The most widely used homogeneous catalysts in this reaction are usually mono- or polynuclear transition metal complexes, and hydride-carbonyls of type $\text{MH}(\text{CO})_x\text{L}_y$ or $\text{M}_y\text{H}_x(\text{CO})_z\text{L}_b$ with modified ligands (L), (M = Rh >> Co > Ir, Ru > Os > Pt > Pd > Fe > Ni)³.

Among these catalysts, organometallic rhodium compounds with different phosphorus-bearing ligands are the most active and selective.⁴⁻⁸ Furthermore, ruthenium(0) complexes with triphenylphosphine such as $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$, and others have been efficient catalysts in the hydroformylation of olefins.⁹⁻¹¹ On the other hand, Ru(II) complexes like dichlorotris(triphenylphosphine)ruthenium(II), and $\text{RuCl}_2(\text{PPh}_3)_3$ have been found to be effective catalysts in the hydroformylation of propen-1-ol.¹²

Haukka et al.¹³ have reported the catalytic activity of carbonylic ruthenium(II) complexes containing 2-substituted pyrazine ligands of the type $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{R-pz})]$ (R = Cl, OMe, SMe, CN, NH₂) in the hydroformylation of 1-hexene to produce aldehydes in 20-50% yields and alcohols in 12-30% yields. They determined that the electronic properties of the substituents in the pyrazine ligands improve the catalytic activity. Ruthenium polymers $[\text{Ru}(\text{CO})_4]_n$ have also been used in the hydroformylation of 1-hexene, showing greater levels of catalytic activity than the commonly used $\text{Ru}_3(\text{CO})_{12}$ cluster.¹⁴

The hydroformylation of α -olefins has also been reported using a catalytic system based on $\text{Ru}_3(\text{CO})_{12}/1,10$ -phenanthroline.¹⁵ In that work propylene was hydroformylated under 80 atm of synthesis gas (CO:H₂ = 1:1) in amide solvents to produce aldehydes (C_n) in high yields, with high regioselectivity in linear aldehyde (>95%). When using 1-octene, C₈ aldehydes were obtained in moderate yields (45-55%) with high regioselectivity in linear aldehyde (95%). Recently, Haukka reported the catalytic application of alkoxy-carbonyl systems of type $[\text{Ru}(\text{N-N})(\text{CO})_2\text{Cl}(\text{COOR})]$ and $[\text{Ru}(\text{N}_2)(\text{CO})_2\text{Cl}(\text{COOR})]$ derived from the $[\text{Ru}(\text{CO})_2\text{Cl}]_2$ dimer in the hydroformylation of 1-hexene.¹⁶ Ruthenium(II) complexes containing polypyridine ligands have been used in other reactions in a homogeneous phase, like the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$), and hydride species of the type $[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}]^+$ have been proposed as possible intermediaries in this reaction catalyzed by $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$ complex.¹⁷

Based on the knowledge of the stereo-electronic properties of the phosphorus- and nitrogen-bearing ligands in the activity and selectivity of catalytic systems, the objective of this paper is to study the catalytic activity of organometallic ruthenium hydride complexes of the type $[\text{RuH}(\text{CO})(\text{N-N})(\text{PR}_3)_2]^+$ containing monodentate phosphines like triphenylphosphine,

methyl(diphenyl)phosphine and nitrogen-bearing ligands of the polypyridine type like N-N=dipyrido[3,2-a:2,3-c]phenazine (dppz-R), where R = H, Me, Cl, 2,2'-biquinoline (biq), and pyrazine[2,3-f][1,10]-phenanthroline (ppl) (Figure 1).

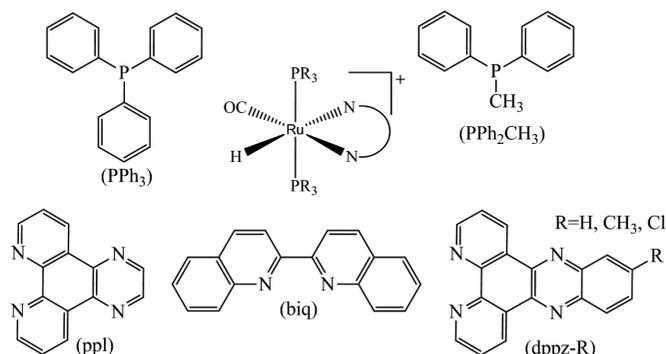


Figure 1. Molecular structure of the $[\text{RuH}(\text{CO})(\text{N-N})(\text{PR}_3)_2]^+$ complexes.

The synthesis and characterization of these complexes have been previously reported by our research group.¹⁸ Theoretical calculations were carried out using density functional theory (DFT) to elucidate the mechanism of the catalytic hydroformylation of 1-hexene with one of these systems and to interpret the observed catalytic activity.

2. EXPERIMENTAL

As we have mentioned above, the synthesis of the complexes used in this study were previously reported by us.¹⁸ For a comparison of catalytic activity of such systems with Ru(0) complexes, the complexes bis(triphenylphosphine) tricarbonyl ruthenium(0), $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, and trirutheniumdodecacarbonyl, $\text{Ru}_3(\text{CO})_{12}$ were prepared according to published procedures.¹⁹

2.1 Catalytic hydroformylation reactions. The hydroformylation of 1-hexene was carried out in a 100-mL stainless steel high pressure autoclave (Chemical Press) equipped with a PID temperature controller, thermocouple, gas feed valve, sampling valve, and safety valve. The CO and H₂ gases used in the hydroformylation reactions had 99% purity (Linde). The substrate 1-hexene and the internal standard n-decane were degassed before use. In

the hydroformylation experiments, a known quantity and ratio of substrate (1-hexene), catalyst and n-decane dissolved in toluene were loaded under vacuum into the autoclave, which had previously been purged with nitrogen. This mixture had been made previously in a Schlenk reactor connected to a vacuum line and in an inert atmosphere. After injecting the reaction system, the reactor was pressurized with carbon monoxide and hydrogen (between 50 and 100 bar) for the hydroformylation reactions. The reactor was heated to the desired temperature and the hydroformylation reaction was started with magnetic stirring for a period of 24 hours. After that time, the autoclave was cooled to room temperature, and after the gases were evacuated, and it was returned to atmospheric pressure. Finally, the reaction mixture was analyzed by gas chromatography.

2.2 Analysis of the products. The products of the catalytic reaction were analyzed in an Agilent Technologies Model 6890N gas chromatograph with a flame ionization detector (FID) and an HP-5 (5% phenylmethylsiloxane) capillary column (0.25 mm, 30 m) and nitrogen gas as carrier gas. The retention time of the different compounds were determined by injection of pure reference standards under identical GC conditions, with n-decane used as internal standard for the GC analysis. Those products that could not be analyzed by this technique were characterized by mass spectrometry. The heating program used to separate the products started at a temperature of 40 °C, increasing it to 120 °C at a rate of 5 °C/min (Ramp 1) during 17 minutes, and finally increasing it to 210 °C at a rate of 50 °C/min during a time of 19.8 min

2.3 Computational aspects.

In a first stage we investigate which ligand (PPh_3 , CO, H, N-N) of the catalyst precursors (1-6) could be dissociated. With this in mind, we determine the optimized molecular structures of 1-6 at the semiempirical level PM3(tm) (tm: transition metal). This approximated level of calculation was used by the high computational cost due to the large size of the complexes. Vibrational frequencies were obtained verifying that all the structures are minimum energy states.

Using the PM3(tm) total energies for the optimized molecular structures of

the complexes and the corresponding fragments, we calculated the interaction energy (E_{int}) for each ligand in the complex; $E_{\text{int}} = E_{\text{AB}} - (E_{\text{A}} + E_{\text{B}})$; where E_{AB} , E_{A} and E_{B} are the total energies of the complex AB, the fragment A and the ligand B that will be released (PPh_3 , CO, H, N-N).

According to the values obtained for E_{int} , we choose the two ligands with the higher values and propose a reaction mechanism in the gas phase for the hydroformylation for 1-hexene starting with the release of these ligands from the complex. For each species proposed in such mechanism, we carried out density functional theory (DFT) calculations with full molecular geometry optimization at the B3LYP/LACVP(d,p) level of theory. B3LYP is an exchange correlation functional that contains a Becke's three-parameter hybrid exchange functional: exact Hartree-Fock, local type Slater and nonlocal type Becke exchange^{20,21} and also contains the LYP correlation functional: a local Vosko, Wilk and Nusair (VWN) functional²² and a nonlocal Lee, Yang and Parr (LYP) functional.²³ For the LACVP(d,p) basis set²⁴, the LACVP effective core potential was considered to describe the metallic ruthenium atom and the 6-31G(d,p) basis set for describing the light atoms (C, N, O, P, H, Cl). The theoretical calculations were performed using the quantum packages Titan 1.0.8²⁵ (PM3(tm)) and Jaguar 6.5²⁶ (B3LYP/LACVP(d,p)).

Because to the large size of complexes and consequently the high computational cost associated we did not perform the study of the transition states. The set of the minimum energy states calculated at the density functional theory allowed to propose a potential energy surface associated to the possible mechanism that governs the catalytic cycle.

3. RESULTS AND DISCUSSION

3.1 Evaluation of the catalytic activity in homogeneous phase for the systems of the $[\text{RuH}(\text{CO})(\text{N-N})(\text{PR})_2]^+$ series. The catalytic activity was evaluated in the hydroformylation reaction of olefins, mainly with a substrate of industrial interest like 1-hexene. These reactions were carried out by a trial and error process. The reactions and the products expected in the hydroformylation of 1-hexene are summarized in the scheme shown in Figure 2.

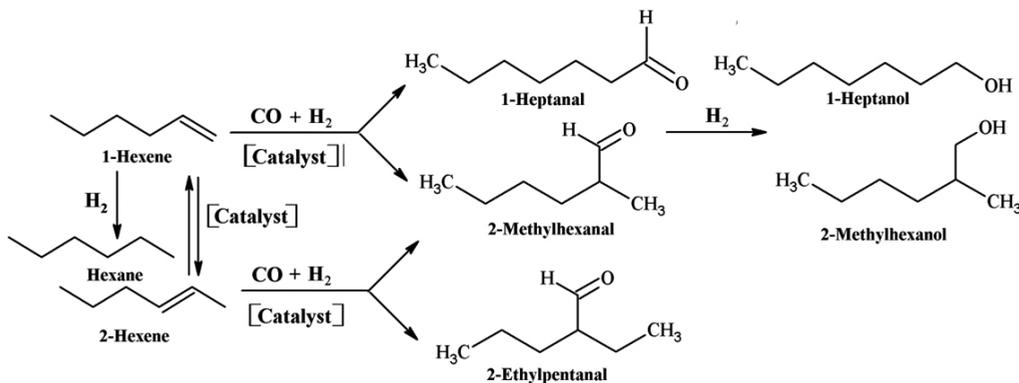


Figure 2. Catalytic hydroformylation of 1-hexene.

Analyzing the results of the conversion of substrate (1-hexene) to products, for the studied systems, it was found that the recorded activities are relatively low, with conversions going from 3 to 22% in 24 hours of reaction (see Table 1). However, it is seen that the chemoselectivity of the aldehydes is high for these systems and the regioselectivity in linear aldehyde (1-heptanal) is favorable under the conditions in which they were applied. Also, it can be seen that the system with the polypyridine ligand dppz-Cl (**3**) showed greater activity compared to systems (**1**) and (**2**). One reason can be attributed to the chlorine atom which has nonbonding electrons that can donate electron density through pi bonding of aromatic system (resonance donation) improving the performance of the metal center. The systems with ppl (**4**) and biq (**5**) ligands had less conversion of 1-hexene to aldehydes. The low activity of complex **5** could be explained by the high interaction energy calculated of the 2,2-biquinoline ligand in the complex (136 kJ/mol), compared to the other polypyridine ligands in the studied systems, as it will be shown below in Table 2, facilitating their breakage and later catalyst deactivation. However, this interpretation does not explain the low activity of complex **4**, since the interaction energy of the ppl ligand in the complex is 71.4 kJ/mol, of the same order of magnitude as the energy of the other polypyridine ligands in the series

of complexes with dppz-R.

On the other hand, the experimental determination of the vibrational frequencies of the carbonyl group by FT-IR spectroscopy of complexes **4** and **5**¹⁸ determined that both ligands (ppl and biq) present more acceptor characteristics than those of the dppz-R series. This can explain the lower catalytic activity seen in relation to the complexes of the dppz series. On the other hand, in the evaluation of the catalytic activity of complex **6** it was found that the inclusion of methylidiphenylphosphine instead of triphenylphosphine produces two differences in relation to complex **1**; it decreases the catalyst's activity from 10% to 5%. This is an expected effect because the quantum results show that methylidiphenylphosphine is a more basic phosphine that interacts more strongly with the metal, preventing the activation of the catalyst.¹² This was also confirmed by calculating the interaction energy (see Section 3.2.1) of the methylidiphenylphosphine ligand in the complex, -145.7 kJ/mol, lower by 14.5 kJ/mol than that of triphenylphosphine in complex **1**, and therefore more stable. The incorporation of the methylidiphenylphosphine ligand also changes the regioselectivity toward the formation of a branched aldehyde (2-methylhexanal). This same effect can be seen in the catalytic activity of complex $\text{RuHCl}(\text{CO})(\text{PPh}_2\text{CH}_2)_3$ (**7**), which favors the formation

of 2-methylhexanal.

Based on the results of the catalytic activity of complex **1**, and in order to determine how the catalyst's activation takes place, new catalytic experiments were carried out with the hydroformylation reaction of 1-hexene. Three new reaction conditions were applied. First, the catalytic test was established, providing an induction period for the reaction, and for this purpose a mixture of complex **1** (0.05 mmol) and toluene (20 mL) was injected into the reactor, which was immediately loaded with successive carbon monoxide and hydrogen pressures (40:40 bar). The system was allowed to react for 24 hours at a temperature of 120 °C. After that time, the reactor was rapidly cooled in an ice bath and the excess pressure was released. Then the substrate, 1-hexene (1.25 mL, 10 mmol), was injected and the reactor was loaded again with pressures of carbon monoxide and hydrogen, it was heated to 120 °C, and the system was allowed to react for 24 hours. Analysis of the reaction products showed a decrease in the percent conversion of the reaction (6%), indicating a loss of catalytic activity, possibly due to the formation of thermodynamically stable species that smother the catalytic process.

Second, with the purpose of establishing which is the ligand that dissociates to start the catalytic process, the reaction was run in the presence of an equimolar quantity of free dppz ligand (0.05 mmol). The chromatographic analysis showed loss of catalytic activity, evidenced by the percent conversion, which decreased to 6%, showing the absence of linear aldehyde (1-heptanal)

and an increase of the formation of 2-ethylpentanal. The latter corresponding to the product of the hydroformylation of the 2-hexene isomer. It means that the presence of the ligand in the reaction medium prevents the activation of the complex by breakage of the polypyridine ligand.

Third, with the purpose of determining if the breakage of the phosphorus bearing ligand (triphenylphosphine) has some effect on the activity of the catalyst, the reaction was also carried out in the presence of triphenylphosphine (0.1 mmol), showing, the same as in the previous attempt, a drop of the percentage conversion to 6%. Both experiments were the keys to determine that the activation of the catalyst occurs by the two ways, either by breakage of the nitrogen-bearing ligand or by breakage of the triphenylphosphine, a fact that is explained thermodynamically by theoretical calculations that are detailed in section 3.2.

In short, the activities recorded in the hydroformylation of 1-hexene by the proposed systems show a relatively low conversion of the substrate (1-hexene) to aldehydes. However, it is seen that the chemoselectivity to aldehydes is high and the regioselectivity to linear aldehydes is favorable under the applied conditions. On the other hand, the turnover frequency (TOF) analysis of complex **3** shows an activity comparable to ruthenium complexes such as $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**8**) and the $\text{Ru}_3(\text{CO})_{12}$ cluster in the presence of triphenylphosphine (**9**) (see Table 1).

Table 1. Results of the hydroformylation of 1-hexene for the series of $[\text{RuH}(\text{CO})(\text{N-N})(\text{PR}_3)_2]\text{PF}_6$ complexes.

Catalyst precursor	Conv. (%)	TOF (h^{-1})	1-Heptanal (%)	2-Methylhexanal (%)	2-Ethylpentanal (%)	Alcohols (%)	Chemo (%)	Regio (%)
(1)	10	0.8	6	3	1	0	100	55
(2)	10	0.9	5	3	0	2	82	59
(3)	22	1.8	15	6	0	0	98	72
(4)	3	0.2	2	1	0	0	100	71
(5)	3	0.1	0.5	1.5	1	0	100	83 ^a
(6)	5	0.4	1	4	0	0	100	77 ^a
(1) (IP)	6	0.5	1.5	1.5	1	2	70	38
(1)+ dppz	6	0	0	1.5	4.5	0	100	100 ^a
(2)+ 2PPh ₃	6	0.5	1	1	4	0	100	83 ^a
(7)	9	0.7	2	6	1	0	100	74 ^a
(8)	31	1.3	20	10	1	0	100	65
(9)	35	1.4	26	8	1	0	100	72

Conditions: T=120°C. Reaction time 24 h. Solvent: toluene (20 mL). Substrate: 1-hexene (10 mmol, 1.25 mL). Catalyst: (0.05 mmol). [Substrate]: [Catalyst] = 200, ligand dppz (0.05 mmol), CO pressure: 40 bar, H₂ pressure: 40 bar. Chemo = chemoselectivity in aldehydes. Regio = regioselectivity in linear aldehyde. Turnover frequency (TOF): (moles of reagent converted)/(moles of catalyst x time unit). IP= Induction period. Internal standard: n-decane. a = regioselectivity in branched aldehyde. Note: the hydrogenation product was not quantified. Complex (8) and (9) [Substrate]: [Catalyst] = 100.

3.2. Theoretical study of the mechanism of the hydroformylation of 1-hexene with the $[\text{RuH}(\text{CO})(\text{dppz})(\text{PPh}_3)_2]^+$ complex

3.2.1. Preliminary studies of bond dissociation energy

For the formulation of a reaction mechanism that gives account of the observed catalytic activity in the hydroformylation reaction of 1-hexene with the series of $[\text{RuH}(\text{CO})(\text{N-N})(\text{PR}_3)_2]^+$ complexes, it was necessary to carry out interaction energy calculations (E_{int}) for predicting which ligands in the catalyst precursors are dissociated more easily in such a way that it is activated, starting the catalytic process. Table 2 shows the E_{int} obtained.

For all the studied complexes, higher E_{int} values for the polypyridine (N-N) ligands compared to the other coordinated ligands (PPh₃, CO, H) are obtained. The positive value for E_{int} associated with the N-N ligands gives account of a weak bond and suggest that the precursors are activated by breaking

or dissociation of the nitrogen-bearing ligands. It is found that E_{int} is ≈ 48.2 - 67.5 kJ/mol for all the complexes with the exception in **5** that increases to 136.0 kJ/mol. It is interesting to mention that the complex **5** also shows the higher value of E_{int} for PPh₃ and CO ligands that suggests that the big ligand produces a destabilization degree. Table 2 also shows that the hydride is the stronger ligand because it has the lower interaction energy, and indicates that it would have the less possibility for dissociation. The ligands PPh₃ and CO have intermediate values of E_{int} .

Taking in consideration the preliminary E_{int} results, we propose a reaction mechanism for the hydroformylation of 1-hexene starting the catalytic cycle with the breaking of the polypyridine (N-N) ligand. As an alternative propose, we also choose the PPh₃ ligand because it presents the higher negative E_{int} value.

Table 2. Interaction energies (E_{int}) (kJ/mol) calculated at the semiempirical PM3(tm) level of theory for each of the ligands of the catalyst complexes.

Complex	Interaction energy (kJ/mol)			
	PPh ₃	CO	H	N-N
RuH(CO)(dppz)(PPh ₃) ₂ ⁺ (1)	-131.2	-276.0	-1350.8	73.3
RuH(CO)(dppz-CH ₃)(PPh ₃) ₂ ⁺ (2)	-137.0	-294.3	-1424.1	63.7
RuH(CO)(dppz-Cl)(PPh ₃) ₂ ⁺ (3)	-137.0	-294.3	-1427.0	68.5
RuH(CO)(ppl)(PPh ₃) ₂ ⁺ (4)	-138.0	-284.6	-1356.6	71.4
RuH(CO)(biq)(PPh ₃) ₂ ⁺ (5)	-120.6	-268.2	-1412.6	136
RuH(CO)(dppz)(PPh ₂ CH ₃) ₂ ⁺ (6)	-145.7	-293.3	-1424.1	53.1

3.2.2. DFT Computational Study of the 1-hexene hydroformylation catalytic cycle employing [RuH(CO)(dppz)(PPh₃)₂]⁺

In the quantum chemical proposal of the mechanism of the hydroformylation of 1-hexene with the active catalyst precursor [RuH(CO)(dppz)(PPh₃)₂]⁺, the study was made of two possible reaction pathways. They were established first by starting the formation of two catalytically active species that were formulated on the basis of the calculation of the interaction energy for the above mentioned complex. That is the reason of why the catalytic cycle was built from those two intermediary species, making a thermodynamic analysis at each of the stages involved. These are the coordination of substrate (1-hexene), migration of H ligand to a coordinated 1-hexeno, migratory insertion of monoxide, and reductive elimination to finally get the reaction products (aldehydes) and recover the active species (see Figure 3a y 3b).

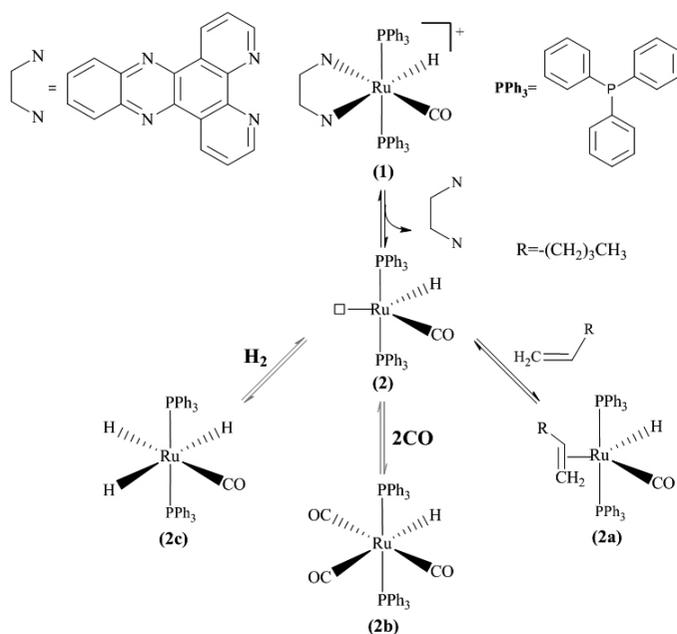


Figure 3a. Proposed mechanism for the hydroformylation of 1-hexene by RuH(CO)(dppz)(PPh₃)₂⁺.

For each of these stages the optimized molecular geometry and the total energy were determined at the DFT level using the B3LYP exchange and correlation functional and a pseudopotential LACVP (d,p) using the quantum chemical package JAGUAR 6.5²⁶ (see Figure 4). The study of the transition states associated with each of the stages was discarded by the high computational cost involved.

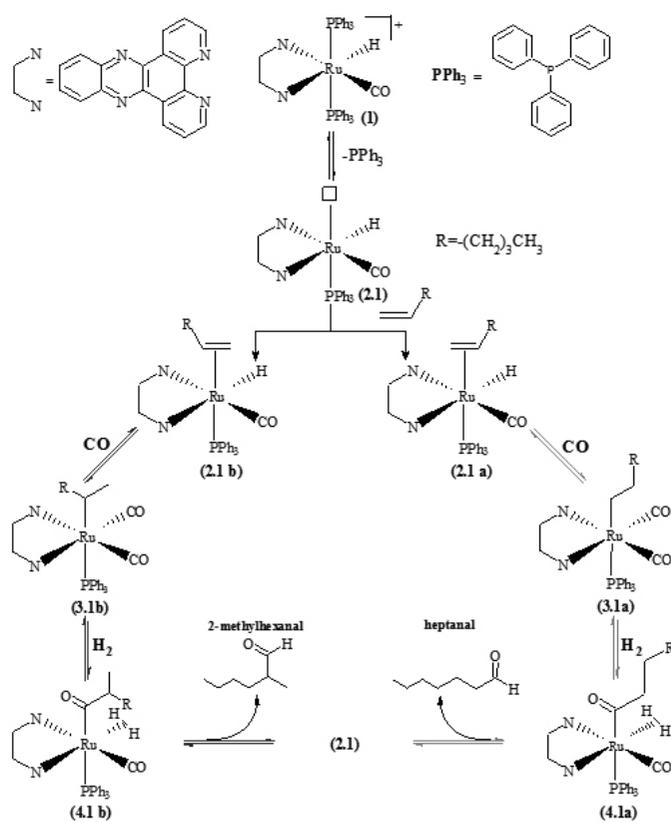
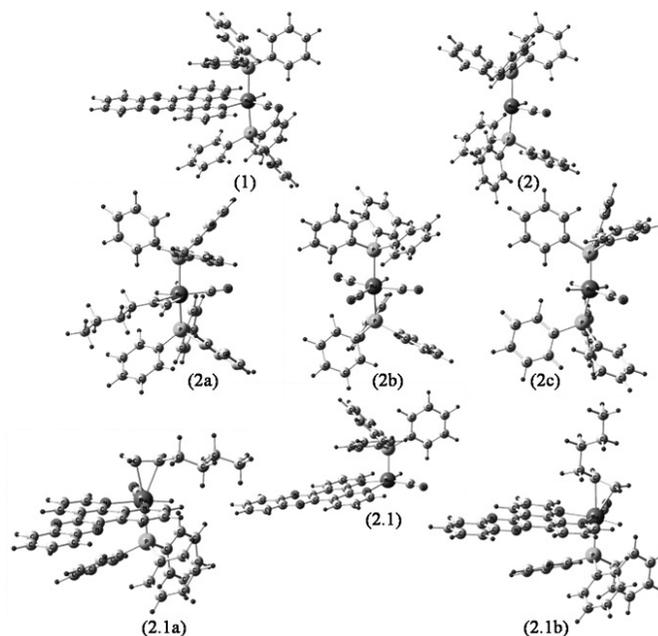


Figure 3b. Proposed mechanism for the hydroformylation of 1-hexene by RuH(CO)(dppz)(PPh₃)₂⁺.



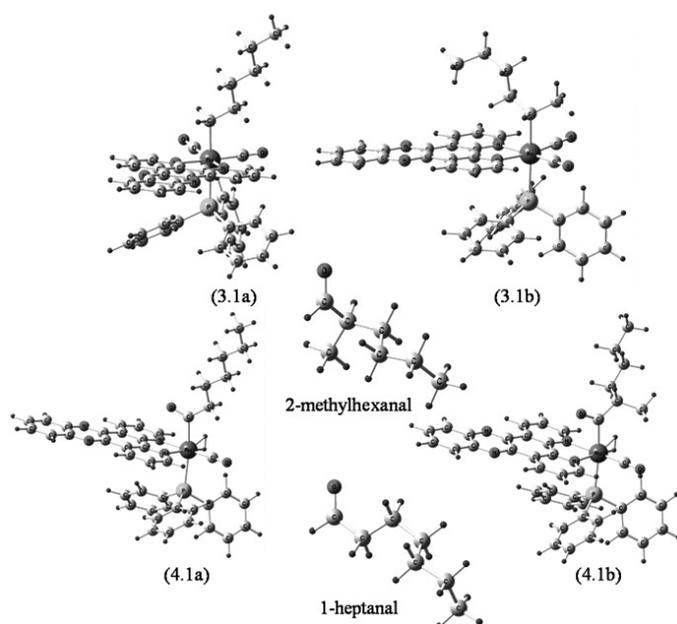


Figure 4. Optimized structures of intermediates of ruthenium complex (1) in the hydroformylation reaction of 1-hexene at the B3LYP/LACVP(d, p) level of theory.

In the first step, corresponding to the generation of the active species, the total energy of the dissociative process was determined, and it was in the order of 183 kJ/mol for **2.1**, and 186 kJ/mol for **2**, for the triphenylphosphine and polypyridine ligands, respectively, both processes being highly endothermic. However, the breakage of the triphenylphosphine ligand was favored with respect to the nitrogen-bearing ligand by 3 kJ/mol. The formation of species **2** and **2.1** can be explained experimentally, since when the catalytic reaction was performed in the presence of complex **1** and an equimolar (1:1) amount of the ligand that is assumed to dissociate (nitrogen- or phosphorus-bearing), a loss of catalytic activity is seen that is reflected in the percentage conversion of the reaction (see Table 1). This can be explained by the fact that the increase of ligand concentration would displace the equilibrium of the dissociative process and would prevent the breakage of the ligand and the later activation of the catalyst once species **2** is formed. The formation of two intermediaries is proposed, **2b** as the product of the coordination of carbon monoxide and **2c** as the product of the oxidative addition of hydrogen. Both processes were highly exothermic, with energies of -42.67 and -186.5 kJ/mol, respectively. This indicates high stability of both species, and it also predicts that under the reaction conditions (high CO and H₂ concentration), the catalytic reaction tends to form these two species, which may interrupt the cycle, because in an optimum cycle it is not convenient to have large energy wells or high activation energy maxima. Because in the catalytic reaction the substrate:catalyst ratio is high (200:1), the formation from species **2** of an intermediate species with which 1-hexene coordinates first to form species **2a** was also proposed. However, the reaction is not favored thermodynamically because it has an energy of 149.36 kJ/mol from **2** and an energy relative to the precursor of catalyst **1** of 335.45 kJ/mol. The total energy analysis mentioned in the previous paragraph indicates that the best reaction pathway for the hydroformylation of 1-hexene involves the formation of species **2.1**, where the coordination of 1-hexene occurs to form species **2.1a** and **2.1b**, which are favored thermodynamically with energies of -82 kJ/mol and -83 kJ/mol, respectively, involving species that do not show high thermodynamic stability. In relation to the coordination of the olefin (1-hexene), the two possible orientations **2.1a** and **2.1b** were studied, which would cause the migration of hydride by the anti-Markovnikov, **3.1a**, and Markovnikov, **3.1b**, mechanisms. The migration of hydride in the anti-Markovnikov orientation to give rise to the alkyl-linear-complex (**3.1a**) is favored from the coordination step of olefin (**2.1a**), since it involves the loss of 111.54 kJ/mol. Similarly, the insertion of hydride in the Markovnikov orientation (**3.1b**) with the concerted coordination of carbon monoxide, implies a loss of 91.1 kJ/mol with respect to the olefin coordination step. The greater stability of species **3.1a** compared to **3.1b** by 19.4 kJ/mol is a first indication that the formation of the linear aldehyde is more favored thermodynamically with respect to the branched aldehyde. The

coordination of hydrogen to form η^2 -dihydrogen species was proposed as a favorable step for the elimination of the aldehyde molecule and to recover the catalytically active species. Both reactions are exothermic, with the formation of 1-heptanal being less endothermic compared to 2-methylhexanal, indicating again the trend to greater formation of this product. Although this preliminary analysis of the reaction mechanism does not consider the kinetic aspect, it agrees with the experimental results (see Table 1) putting in evidence that getting the energy by DFT is a good approach to the study of the reaction mechanism in its thermodynamic aspect, (see energy profile, Figure 5).

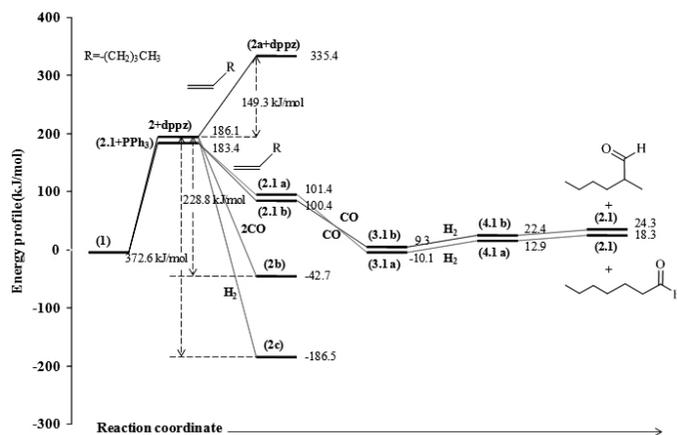


Figure 5. Potential energy profile for the hydroformylation reaction of 1-hexene. The green and blue lines represent the optimum reaction pathways for the production of linear and branched aldehydes. The red line represents the probable paths of catalyst deactivation.

4. CONCLUSIONS

The catalytic activity shown by the complexes in the hydroformylation of 1-hexene leads to the conclusion that they exhibit less activity in the conversion of 1-hexene to aldehydes compared to previously ruthenium(0) systems reported under the same reaction conditions.

The low activity is attributed to the deactivation of these catalyst precursors by breakage of the polypyridine ligand and the later formation of the thermodynamically stable species [RuH(CO)₃(PPh₃)₂] (**2b**) and RuH₃(CO)(PPh₃)₂ (**2c**), which interrupt the catalytic cycle. This fact was shown by the calculation of the interaction energies at the semiempirical level PM3(tm) level of theory and the later study of the catalytic cycle at the density functional theory level (B3LYP/LACVP(d,p)). The quantum-chemical study allowed the interpretation of the regioselectivity seen in the hydroformylation of 1-hexene, which is determined by two elemental steps of the catalytic cycle. One is the hydride migration reaction, in which the anti-Markovnikov orientation to produce the alkyl-linear complex (**3.1a**) is favored thermodynamically in relation to migration in the Markovnikov orientation (**3.1b**), with species **3a** as the more stable by 19.4 kJ/mol than **3.1b**. The other is the insertion of carbon monoxide, where species **4.1a** is more stable by 9.5 kJ/mol than species **4.1b**, a fact that determines the formation of more 1-heptanal than 2-methylhexanal. In relation to the initially proposed hypothesis, the incorporation of polypyridine ligands in the complexes was inadequate because under the reaction conditions in which these systems were tested, these ligands are dissociated, the active species loses its stability, and the charge transfer toward the metal is lost. The preliminary analysis of the reaction mechanism proposed theoretically, although not considering the kinetic aspect, agrees with the experimental results. It provided evidence that getting the energy profiles by density functional theory represents a good approach to the study of the reaction mechanism of hydroformylation of 1-hexene by a ruthenium hydride complex of the type [RuH(CO)(N-N)(PPh₃)₂]⁺.

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