A DFT Study of the Hexene Hydrogenation Catalysed by the Complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PCy}_3)$: Monophosphine vs Diphosphine Paths

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A DFT study of the hexene hydrogenation catalysed by the complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PCy}_3)$: monophosphine vs diphosphine paths

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Abstract

A DFT study of hexene hydrogenation catalysed by the $\text{RuH}(\text{CO})(\text{Cl})(\text{PCy}_3)_2$ complex is presented. The investigation explores the feasibility of two different mechanisms: the first exploits a single phosphine complex and the second uses a two phosphines complex. The energy barriers involving a hydrogen transfer have a ten kcal.mol^{-1} higher than the one obtained through the single-phosphine mechanism. These results confirm the experimental hypothesis claiming that the departure of a phosphine is favourable at the beginning of the reaction which is the substitution of the catalyst model $\text{RuHCl}(\text{CO})(\text{PMe}_3)_2$ by the real catalyst $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ shows no significant influence on the energetic barriers of hexene hydrogenation mechanism. The most important step of the mechanism is the kinetically determining step. The heterolytic cleavage of ruthenium-complexed H_2 molecule leads to the generation of two Ru-H bonds and the oxidation of the ruthenium from Ru(II) to Ru(IV). The energy profile of this step is not relative to an elementary reaction because a shouldering is observed after the transition state. This results in an unusual gradient norm profile with five extrema. This is a direct consequence of the asynchronous nature of the different processes taking place during this step. In the case of the model complex $\text{RuHCl}(\text{CO})(\text{IMes})(\text{PMe}_3)$ with $\text{IMes} = (\text{N}^-, \text{N}^+ \text{-bis(mesityl)imidazol-2-ylidene})$, an increase of the free enthalpy of activation is observed during the kinetically determining step, which is in agreement with the experimental work.

Keywords: Olefin hydrogenation, reaction mechanism, Energy profiles, DFT.

Introduction

Hydrogenation of alkenes is a useful and versatile chemical transformation. Hydrogenation reactions are carried out on a large scale in organic synthesis, fine chemical production and polymer chemistry [1-3]. These reactions use various heterogeneous and homogeneous catalysts. A typical process is the hydrogenation of vegetable oils into semi-solid fats for the production of margarine [4, 5]. The impressive development in organometallic chemistry has allowed the preparation of a wide variety of organometallic complexes which act as catalysts with a high selectivity for the hydrogenation of olefins [1, 2, 6]. Theoretical chemistry has increasingly gained an important role in understanding the reaction mechanisms [7, 8] and in some recent examples, new catalysts have been designed *in silico* before their synthesis,[9, 10]. Complexes containing a single Ru-H bond are important not only in organometallic chemistry, but also in organic synthesis [11]. Ruthenium complexes of the $\text{RuHCl(L)(PR}_3)_n$ class are particularly interesting because of their relatively low cost, versatility and efficiency in the reduction of certain substrates [12, 13], including unsaturated polymers [14, 15]. The Wilkinson complex $\text{RuHCl(P(C}_6\text{H}_5)_3)_3$ is the best-known example of a homogeneous hydrogenation catalyst [16]. The distinctive characteristics of the hydrogenation reaction catalysed by these monohydride metal complexes include high activity and selectivity towards terminal alkenes [17-20].

There is a wide variety of proposed mechanisms for hydrogenation reactions [21-23]. These mechanisms involve two phosphine complexes can be divided into two classes. The first class is the associative mechanism, where both phosphine ligands remain on the catalyst. The second one includes several dissociative mechanisms where a phosphine dissociates during catalysis before or after the coordination of the olefin.

We will focus in this work on studying this new ruthenium (II) catalyst $\text{RuH(CO)(Cl)(PCy}_3)_2$ which is distinguished by the fact that it belongs to the family of monohydride complexes of ruthenium. Thus, only one hydrogen atom of the catalyst is involved in the olefin hydrogenation process. The participation of a dihydrogen molecule allows the intervention of the second hydrogen atom. This catalyst is characterised by its high activity and selectivity for the hydrogenation of terminal and cyclic alkenes. In this case, kinetic studies [20] showed that the catalytic cycle begins with the dissociation of a phosphine from the metal. The authors showed also that the addition of H_2 to a cooled solution before adding an alkene substrate decreased the rate of the hydrogenation reaction. Since hydrogenation plays an important role in olefin reactions catalysed by transition metal complexes, we

describe in this work a theoretical study of the hydrogenation reaction mechanisms of hexene. This type of study can be very useful not only in understanding the mechanism of the reaction but also in understanding the selectivity (i.e. the comparison between two different catalysts).

Computational methods

Molecular geometries of reagents, intermediates, transition states (TS) and products were optimized using DFT/B3LYP method [24, 25]. Frequency calculations were performed on all optimized structures to ensure that the reactants and products have only positive frequencies and a single negative imaginary frequency in the case of the transition states. Thermochemical data and temperature corrections were calculated at 298.15 K for all optimized geometries. For ruthenium, the core electrons were represented by a relativistic small-core pseudopotential determined according to the Durand–Barthelat method [26]. The basis set 6-31G* was used for the other atoms [27]. To simplify the reaction, the catalyst was modeled by $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$. Previous theoretical studies confirmed the suitability of this catalyst model. [28-31]. All calculations were conducted using the Gaussian package 09 [32].

Results and discussion

1. Hydrogenation of hexene in the presence of complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$

The study of the reaction mechanism of hexene hydrogenation was explained by two different routes. The first one was with complexes that possess 14, 16 or 18 electrons including a single phosphine. The second one was carried out using complexes with 16 or 18 electrons retaining the two phosphines as indicated in Figure 1. For systems with multiple conformations, there is normally more than one possible structure for each compound and each transition state. It is impossible to explore the entire surface of potential energy. However, the most stable geometry and the structurally closest conformation to the crystal from the X-ray diffraction, was therefore examined in this study.

The geometry of the model complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$ was compared to the geometry obtained by a crystallographic study of $\text{RuH}(\text{CO})(\text{Cl})(\text{PCy}_3)_2$ [33]. The values of key geometric parameters were summarized in Table 1. Figure 2 illustrates the studied compound. The optimized structure of the complex was characterized by two phosphines in trans position. The angle P1-Ru-P2 was equal to 171.3°. In this type of structure, the phosphines are generally in the trans position and the angles P1-Ru-P2 are of the same order

of magnitude: 180° in $\text{RuHCl}(\text{CO})(\text{P}^i\text{Pr}_3)$ where ^iPr is an isopropyl group [34], 170.15° in $\text{RuCl}_2((\text{CO})(\text{P}^i\text{Pr}_3)_2)$ [35], 167.849° in $\text{Ru}(\text{CO})(\text{NO})(\text{BF}_4)(\text{P}^t\text{Bu}_2\text{Me})_2$ where ^tBu is a tertibutyl group [36], 169.0° in $\text{RuH}_2(\text{H}_2)(\text{GeH}_4)(\text{PH}_3)_2$ [37] and 159.17° in $\text{Ru}(\text{H})(\text{NO})(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$ [36].

The ligands Cl and C1O and H1 are in the equatorial plane with a dihedral angle Cl-H1-C1-Ru almost equal to 0.0° . Regarding the Ru-P1 linkage, the calculated value is approximately $0.05 \text{ \AA}$ weaker than the experimental value with a 2% error while the value calculated for the Ru-Cl bond is about $0.05 \text{ \AA}$ larger than the experimental value. The chlorine and the CO ligand are in the trans position with a Cl-Ru-C1 angle equal to 164.5° , which is lower than the experimental value of 13.4° corresponding to an error of 7%. The complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$ is then considered as a distorted octahedron where the six ligands were placed in its summit. We can estimate that the agreement between the calculated and experimental values is globally satisfactory. This validated the choice of the DFT/B3LYP method and the 6-31G * database in our work.

Figure 1: Proposed catalytic cycles for the hydrogenation of Hexene by the $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$ complex with pathways: **a)** one phosphine and **b)** two phosphines.

1. 1. Hydrogenation mechanism with a phosphine complex

The reaction mechanism of the hydrogenation of hexene complex was, initially, studied with a single phosphine as described in Figure 1a. The energy diagram of the reaction mechanism is shown in Figure 3. The optimised structures of all stationary points were

compiled in Figure 2 and the thermodynamic and kinetic descriptors were summarised in Table 2. The first step of the reaction corresponded to a π -complexation of hexene at $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$ to bring to the complex $n^\circ 2$ to 18 electrons with a free enthalpy of $24.4 \text{ kcal.mol}^{-1}$ greater than that of the starting complex. The complexation of hexene is very demanding in terms of energy. This could be explained by the steric hindrance of phosphines.

Figure 2: Optimised geometries compounds that intervene along the paths with one and two phosphines for the hydrogenation reaction of hexene in the presence of the complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$. (The hydrogens of the methyl groups are omitted for the sake of clarity).

The following step corresponded to the departure of a phosphine ligand PMe_3 which gave the complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)$ (A3) 16 electrons with a new site available for the coordination of reagents. This step was endothermic with an enthalpy ΔH^0 equal to $7.8 \text{ kcal.mol}^{-1}$ and it was favourable thermodynamically with a free enthalpy equal to -6.2

kcal.mol⁻¹. The reaction continued with the coordination of an H₂ molecule to obtain the ruthenium Ru(II) complex with 18 electrons. Its energy was higher than that of the intermediate (A3) of 8.6 kcal.mol⁻¹. The crucial step was the migration of the hydride H1 on hexene which was accompanied by the conversion of a Ru(II) complex to a Ru(IV) complex through a heterolytic cleavage of the H₂ molecule. This led to the formation of two hydrides. Its transition state corresponded to an activation barrier of 10.2 kcal.mol⁻¹.

TABLE 1 Geometric parameters selected for the test compounds 1, 2, A3, A4, A5, A6, B3, B4 and the transition states TSA1, TSA2, TSB1 and TSB2 optimised at DFT/B3LYP and those obtained by XRD for the complex RuH(CO)(Cl)(PCy₃)₂.

	1 _{Cal.}	1 _{Exp.}	2	A3	A4	TSA1	A5	TSA2	A6	B3	B4	TSB1	TSB2
Ru-P1	2.337	2.387	2.385	2.353	2.358	2.400	2.451	2.424	2.238	2.388	2.404	2.388	2.410
Ru-P2	2.377	-	2.398	-	-	-	-	-	-	2.402	2.422	2.412	2.393
Ru-Cl	2.450	2.397	2.508	2.440	2.487	2.492	2.476	2.474	2.339	2.488	2.588	2.553	2.528
Ru-C1	1.836	1.822	1.957	1.845	1.853	1.857	1.857	1.855	1.849	1.823	1.832	1.909	1.894
Ru-C2	-	-	2.220	2.337	2.320	2.307	2.477	2.492	-	2.944	3.160	2.268	3.449
Ru-C3	-	-	2.290	2.380	2.428	2.248	2.174	2.204	-	2.144	2.199	2.202	2.383
C2-C3	-	-	1.401	1.376	1.380	1.432	1.508	1.517	-	1.533	1.537	1.431	1.546
C2-H1	-	-	2.353	2.530	2.367	1.483	1.149	1.143	-	1.093	1.097	1.638	1.096
C3-H2	-	-	-	-	2.440	2.697	2.079	1.780	-	-	2.762	-	1.592
Ru-H1	1.570	-	1.646	1.561	1.586	1.666	2.009	2.034	-	3.015	3.276	1.691	3.487
Ru-H2	-	-	-	-	1.939	1.789	1.588	1.602	-	-	1.931	-	1.671
Ru-H3	-	-	-	-	1.929	1.805	1.579	1.577	1.565	-	1.929	-	1.747
H2-H3	-	-	-	-	0.788	0.836	1.698	1.845	-	-	0.780	-	1.068
C1-O	1.168	1.141	1.156	1.165	1.164	1.163	1.161	1.162	1.165	1.172	1.166	1.161	1.162
P1-Ru-C1	93.9	89	96.3	92.9	94.1	93.8	95.7	94.7	91.1	92.0	89.1	93.3	92.6
P1-Ru-Cl	86.8	88.1	83.5	85.0	83.8	82.8	82.8	83.4	101.9	86.0	83.1	81.9	82.3
Cl- Ru-C1	164.5	177.9	86.8	171.2	176.7	176.6	176.7	176.9	162.9	158.2	100.5	94.6	96.8
P1-Ru-P2	171.3	-	160.9	-	-	-	-	-	-	168.3	165.6	163.2	164.4

To ensure that the transition state connected well the two minima A4 and A5, the variation of the electronic energy during this step was calculated as a function of the intrinsic reaction coordinate (ξ) as shown in Figure 4-a. Two minima were found on both sides of the saddle point. Moreover, the electronic energy profile as a function of the intrinsic reaction coordinate (ξ) was of the same type as the universal profile for an elementary step [38].

Figure 3: Energy diagram in terms of free energy (kcal.mol⁻¹) for the hydrogenation reaction of hexene in the presence of the single-phosphine complex.

Figure 4: a) Variation of electronic energy and its first derivative b) Interatomic distances depending on the intrinsic reaction coordinate ξ during migration of the first hydrogen to hexene.

During the transition state TSA1 illustrated in Figure 2, the dihydrogen molecule was slightly activated since the distance between the two hydrogen atoms was 0.836 Å comparing to the distance in a free H₂. In addition, the transfer of the proton H1 from Ru to C2 was progressing since the distance between C2 and H1 was 1.483 Å. TSA1 was, thus, similar to

the product A5 but without breaking the molecule H₂ which did not cause any change in the degree of oxidation of ruthenium.

During the next step of the catalytic cycle, a hydride ligand was transferred to the carbon atom C3 of the olefin complexed with ruthenium. This led to the elimination of hexane and the formation of the intermediate (A6). This stage was almost free of enthalpy barrier (i.e. $\Delta G^\ddagger = 0.1 \text{ kcal.mol}^{-1}$). The final step corresponded to the addition of PMe₃ and the regeneration of the model catalyst RuH(CO)(Cl)(PMe₃)₂. The activation barrier was calculated by the energy difference between the transition state TSA1 and the complex (A3). It was equal to 18.8 kcal.mol⁻¹ (i.e. 37.0 kcal.mol⁻¹ - 18.2 kcal.mol⁻¹).

1.2. Hydrogenation mechanism with a complex with two phosphines

The catalytic cycle was proposed in Figure 1-b and the reaction mechanism was depicted in Figure 5. Thermodynamic and kinetic descriptors were summarized in Table 3. Both phosphines remained complexed to ruthenium during the entire studied process. The optimized structures of all stationary points were illustrated in Figure 6.

The first step of the reaction corresponded to a π -complexation of hexene on RuH(CO)(Cl)(PMe₃)₂. This complex possessed, thus, 18 electrons with a free enthalpy of 24.4 kcal.mol⁻¹ greater than that of the starting complex. The complexation of hexene required a lot of energy due to the steric hindrance of phosphines. The following step was the migration of the ruthenium-bonded hydride to hexene. The obtained complex B3 received again 16 electrons. It was, also, characterized by the formation of a Ru-C bond. The geometry of the transition state TS1 was optimized and was verified by a vibrational analysis (i.e. the presence of an imaginary frequency). The normal mode of vibration associated with the frequency of 7.30i cm⁻¹ corresponded to an intermediate structure where the hydrogen H1 moved away from ruthenium and approaches the carbon C2 of hexene.

Figure 5: Energy diagram of the hydrogenation of hexene in hexane in the presence of the ruthenium complex with two phosphines.

Figure 6: Optimised geometries of the compounds involved in the hydrogenation reaction of hexene in the presence of $\text{RuH(CO)(Cl)(PMe}_3)_2$ along the paths with one or two phosphines. (The hydrogens of the methyl groups are omitted for the sake of clarity).

To ensure that the transition state was linked to the two minima 2 and B3, the variation of the electronic energy was calculated as a function of the intrinsic reaction coordinate (ξ) at this step (Figure 7-a) and the two minima were spotted on both sides of the saddle point. The monitoring of the variation in the internuclear distances of the active atoms at the influence zone of the transition state is a technique that has been, increasingly, used to discuss the reaction mechanism of an elementary step [21, 38-40]. During this elementary step, H1 was transferred from Ru to C2 and a σ bond was created between Ru and C3. The variation of C2-H1, Ru-C3, Ru-H1 and C2-C3 distances were, also, evaluated and described in Figure 7-b.

Figure7: Variation of a) the electronic energy and its first derivative and b) the interatomic distances as a function of the intrinsic reaction coordinate during the migration of the first hydrogen through the diposphine path.

Before $\xi_1 = -0.77$, the distance C2-H1 decreased slightly while the distances Ru-C3 and C2-C3 remained substantially constant. Between $\xi_1 = -0.77$ and $\xi_2 = 0.91$, the distances C2-H1 and Ru-C3 decreased while the distance between C2 and C3 and Ru-H1 increased slightly. The transfer of H1 occurred almost in this zone (i.e. called activation zone). After $\xi_2 = 0.91$, the distances C2-H1 and Ru-C3 were stabilized. The C2-C3 distance increased before stabilization, reflecting the transformation of the double bond into a single bond. The electronic transfers responsible for the migration of H1 and the formation of the Ru-C3 bond occurred between these two zones. The addition of a molecule of dihydrogen to this complex led to the formation of the 18-electron complex B4. Its energy was $21.6 \text{ kcal mol}^{-1}$ greater than the one in B3. The final step of the catalytic cycle was the cleavage of the H_2 molecule by the migration of a hydrogen to the carbon atom of hexane that was already complexed with ruthenium. The second atom became a hydride. This allowed, on one side, the formation and the removal of the hexane and, on the other side the restoration of the catalyst in its initial structure. This step had an activation energy barrier of $13.2 \text{ kcal mol}^{-1}$.

Figure 8: Variation of a) the electronic energy and its first derivative and b) the interatomic distances as a function of the intrinsic reaction coordinate upon migration of the second hydrogen through the diphosphine path.

The reaction mechanism had two well-separated steps of migration of hydrogen atoms towards the double bond. The first hydrogen is the hydride, which was added to the double bond (i.e. π -complexed to Ru). Its energetic barrier, equal to 31.8. kcal mol^{-1} , was calculated by the energy difference between TSB1 and (1). The second atom was provided by the H_2 molecule once it was σ -complexed to Ru. The barrier that corresponded to the energy difference between TSB2 and B3 is equal to 31.4 kcal mol^{-1} (i.e. 43.6 kcal mol^{-1} - 12.2 kcal mol^{-1}). Each of these two barriers was about ten kcal mol^{-1} higher than the one obtained in the single-phosphine mechanism. The thermodynamic and kinetic descriptors were depicted in Table 3. The hydrogenation route by a single phosphine was, thus, more favourable. This is in agreement with the proposal of the experimental study, which is based on the departure of phosphine before the coordination of the olefin [20].

2. Ligands effect

2.1. Energetic study

In order to confirm whether the ligands affect the selectivity of the reaction and to validate our modeling of phosphine ligands by PMe_3 , the hydrogenation reaction of hexene was studied through a phosphine in the presence of $\text{RuHCl}(\text{CO})(\text{L1})(\text{L2})$ with (L1= L2= PCy_3) or (L1= IMes, L2 = PMe_3 with IMes = (N, N '-bis(mesityl)imidazol-2-ylidene)). The free energies were shown in table 2. In the case L1 = L2 = PCy_3 , we note that the complexation step of hexene in the case L1 = L2 = PCy_3 required more energy than in the case L1 = L2 = PMe_3 . This could be explained, on one hand, by the steric hindrance of the PCy_3 ligands since the Tolman cone angle for PCy_3 and PMe_3 are 170° and 118° , respectively

[41]. On the other hand, the step of dissociation of phosphine PCy_3 was more favourable thermodynamically than in the case PMe_3 .

From a kinetic point of view, the variation of the free activation enthalpy of the kinetically determining step was not affected by the nature of the ligands. It varied from $18.8 \text{ kcal.mol}^{-1}$ for PMe_3 to $21.2 \text{ kcal.mol}^{-1}$ for PCy_3 . The same trend was observed at the reductive elimination step. The activation enthalpy varied from $0.3 \text{ kcal.mol}^{-1}$ in the case of PMe_3 to $0.6 \text{ kcal.mol}^{-1}$ for PCy_3 . The steric effect of the chemical group carried by the phosphorus did not affect the activation barrier. Therefore, the model used previously for phosphine ligands appeared fully justified. In the case (L1=IMes , L2=PMe_3), the same trend was observed for the stability of the reaction intermediates. Moreover, we noticed a drastic increase of the activation-free enthalpy at the kinetically determining step (i.e. it increased from 18.8 to $23.7 \text{ kcal.mol}^{-1}$, which was in agreement with the experimental work) [42].

2.2. Structural study

The energy profile of the kinetically determining step in the presence of RuHCl(CO)(L1)(L2) with (L1=L2=PCy_3) was shown in Figure 9. It was not due to an elementary reaction because an energy increase was observed after the transition state. This led to an unusual reaction profile with five extrema: two minima during the activation phase and three maxima (i.e. the first two during the activation phase and the third during the relaxation phase).

Figure 9: Variation of a) the electronic energy and its first derivative and b) the interatomic distances as a function of the intrinsic reaction coordinate ξ during the migration of the first hydrogen to hexene in the presence of RuHCl(CO)(L1)(L2) with ($\text{L1} = \text{L2} = \text{PCy}_3$).

It is accompanied by a change from a Ru(II) complex to a Ru(IV) complex. Indeed, we noted a heterolytic cleavage of the molecule of H₂ leading to the formation of two hydrides H₂ and H₃.

Although the Ru (IV) dihydride complexes were, generally, considered less stable than the Ru (II) form[43], an increasing number of Ru(IV) dihydride complexes, possessing a dihydrogen ligand, have been identified [44-48]. The studied energetic profile was very different from the one considered universal for an elementary stage. This is a direct consequence of the asynchronous nature of the different processes taking place. This step had 5 extrema delimiting 6 zones spread over the reaction coordinate.

Table 2: Thermodynamic and kinetic descriptors (kcal.mol⁻¹) for studied steps of the hexene hydrogenation mechanism in the presence of RuH(CO)(Cl)(L1)(L2) complex by phosphine route

		L1=L2=PMe ₃	L1=L2=PCy ₃	L1=PMe ₃ , L2=IMes
Addition d'oléfine	$\Delta H(1-2)$	9.1	25.4	14.5
	$\Delta G(1-2)$	24.4	43.0	29.2
Départ du ligand L1	$\Delta H(2-A3)$	7.8	-14.0	0.9
	$\Delta G(2-A3)$	-6.2	-32.0	-13.3
Addition d'une molécule d'hydrogène	$\Delta H(A3-A4)$	-0.4	1.1	1.6
	$\Delta G(A3-A4)$	8.6	10.3	11.1
Transfert du premier atome d'hydrogène	$\Delta H(A4-A5)$	4.4	8.4	4.8
	$\Delta G(A4-A5)$	4.9	8.7	5.4
	$\Delta G^\#(A4-A5)$	10.2	10.9	12.6
	$\Delta G^\#(A3-A5)$	18.8	21.2	23.7
Transfert du deuxième atome d'hydrogène	$\Delta H(A5-A6)$	-22.6	-30.4	-25.6
	$\Delta G(A5-A6)$	-34.8	-44.4	-39.6
	$\Delta G^\#(A5-A6)$	0.1	1.1	0.1
Régénération du catalyseur	$\Delta H(A6-1)$	-29.9	-22.1	-27.8
	$\Delta G(A6-1)$	-19.7	-8.4	-15.6
Réaction totale	ΔH	-31.6	-31.6	-31.6
	ΔG	-22.8	-22.8	-22.8

Table 3: Thermodynamic quantities and kinetic parameters (kcal.mol⁻¹) for the studied stages of the catalytic cycle of hydrogenation of hexene with two phosphines

		Path with two phosphine
Addition of olefin	$\Delta H(1-2)$	9.2
	$\Delta G(1-2)$	24.4
Transfer of the first hydrogen atom	$\Delta H(2-B3)$	-11.4
	$\Delta G(2-B3)$	-12.2
	$\Delta G^\#(2-B3)$	7.4
	$\Delta G^\#(1-B3)$	31.8
Addition of dihydrogen	$\Delta H(B3-B4)$	12.1
	$\Delta G(B3-B4)$	21.6
Addition of the second hydrogen atom	$\Delta H(B4-1)$	-41.5
	$\Delta G(B4-1)$	-56.6
	$\Delta G^\#(B4-1)$	13.2
	$\Delta G^\#(B3-1)$	31.4
Total reaction	ΔH	-31.6
	ΔG	-22.8

As shown in Figure 9, the region where the reagents were approaching from each other was before the first maximum (zone 1) and the product of the relaxation zone was located after the third maximum (zone 6). The transfer of the proton H1 took place between the first and the second maximum (zone 2 and 3). In addition, the distance C2-H1 decreased from 1.949 Å to 1.275 Å, while the distance H2-H3 remained substantially constant. The formation of two hydrides H2 and H3, which accompanied the transformation of Ru (II) into Ru(IV), was between the second minimum and the third maximum (zone 5). The bond C2-C3 increased monotonically in zones 2, 3,4 and 5. It changed from a double bond (1.38 6 Å) to a single bond (1.509 Å). The transfer of the proton H1 and the formation of both hydrides were asynchronous. This was explained in Figure 9-b. The length of the C2-H1 bond was stabilized at 0.58 Å while the length of H2-H3 began to increase from 1.97 Å.

Conclusion

Two reaction mechanisms for the hydrogenation of hexene have been studied theoretically in the presence of the complex $\text{RuHCl(CO)(PMe}_3)_2$. The first mechanism consisted of a ruthenium complex with one phosphine (i.e. phosphine cleavage occurred at the beginning of the mechanism), which underwent a transformation upon five stages. The second mechanism was based on a similar complex with two phosphines undergoing 4-steps

transformation (i.e. the two phosphines remained coordinated to the ruthenium during the entire mechanism). The activation energy during the hydrogen transfer steps had about ten kcal.mol⁻¹ higher than the one obtained from the single-phosphine mechanism. These results confirmed the hypothesis stating that the departure of a phosphine is favourable at the beginning of the reaction mechanism. There was no significant difference between the real and the model catalysts (i.e. RuHCl(CO)(PMe₃)₂ and RuHCl(CO)(PCy₃)₂) in terms of the required activation barrier to reach the hexane (i.e. the product of the hydrogenation). From a kinetic point of view, the free enthalpy of activation was not affected by the nature of the phosphine ligands. Interestingly, the energetic profile of the kinetically determining step showed a shouldering after the transition state proving the asynchronous character of the different elementary steps occurring at this chemical transformation. In this step, the σ -complexed H₂ molecule with ruthenium was cleaved giving two hydrides, and ruthenium passed from the oxidation state II to IV. Through these two mechanisms, we have demonstrated the versatility of the ruthenium atom providing compounds at 18, 16 or 14 electrons.

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A DFT study of the hexene hydrogenation catalysed by the complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PCy}_3)$: monophosphine vs diphosphine paths

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Abstract

A DFT study of hexene hydrogenation catalysed by the $\text{RuH}(\text{CO})(\text{Cl})(\text{PCy}_3)_2$ complex is presented. The investigation explores the feasibility of two different mechanisms: the first exploits a single phosphine complex and the second uses a two phosphines complex. The energy barriers involving a hydrogen transfer have a ten kcal.mol^{-1} higher than the one obtained through the single-phosphine mechanism. These results confirm the experimental hypothesis claiming that the departure of a phosphine is favourable at the beginning of the reaction which is the substitution of the catalyst model $\text{RuHCl}(\text{CO})(\text{PMe}_3)_2$ by the real catalyst $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ shows no significant influence on the energetic barriers of hexene hydrogenation mechanism. The most important step of the mechanism is the kinetically determining step. The heterolytic cleavage of ruthenium-complexed H_2 molecule leads to the generation of two Ru-H bonds and the oxidation of the ruthenium from Ru(II) to Ru(IV). The energy profile of this step is not relative to an elementary reaction because a shouldering is observed after the transition state. This results in an unusual gradient norm profile with five extrema. This is a direct consequence of the asynchronous nature of the different processes taking place during this step. In the case of the model complex $\text{RuHCl}(\text{CO})(\text{IMes})(\text{PMe}_3)$ with $\text{IMes} = (\text{N}, \text{N}'\text{-bis}(\text{mesityl})\text{imidazol-2-ylidene})$, an increase of the free enthalpy of activation is observed during the kinetically determining step, which is in agreement with the experimental work.

Keywords: Olefin hydrogenation, reaction mechanism, Energy profiles, DFT.

Introduction

Hydrogenation of alkenes is a useful and versatile chemical transformation. Hydrogenation reactions are carried out on a large scale in organic synthesis, fine chemical production and polymer chemistry [1-3]. These reactions use various heterogeneous and homogeneous catalysts. A typical process is the hydrogenation of vegetable oils into semi-solid fats for the production of margarine [4, 5]. The impressive development in organometallic chemistry has allowed the preparation of a wide variety of organometallic complexes which act as catalysts with a high selectivity for the hydrogenation of olefins [1, 2, 6]. Theoretical chemistry has increasingly gained an important role in understanding the reaction mechanisms [7, 8] and in some recent examples, new catalysts have been designed *in silico* before their synthesis [9, 10]. Complexes containing a single Ru-H bond are important not only in organometallic chemistry, but also in organic synthesis [11]. Ruthenium complexes of the $\text{RuHCl(L)(PR}_3)_n$ class are particularly interesting because of their relatively low cost, versatility and efficiency in the reduction of certain substrates [12, 13], including unsaturated polymers [14, 15]. The Wilkinson complex $\text{RuHCl(P(C}_6\text{H}_5)_3)_3$ is the best-known example of a homogeneous hydrogenation catalyst [16]. The distinctive characteristics of the hydrogenation reaction catalysed by these monohydride metal complexes include high activity and selectivity towards terminal alkenes [17-20].

There is a wide variety of proposed mechanisms for hydrogenation reactions [21-23]. These mechanisms involve two phosphine complexes can be divided into two classes. The first class is the associative mechanism, where both phosphine ligands remain on the catalyst. The second one includes several dissociative mechanisms where a phosphine dissociates during catalysis before or after the coordination of the olefin.

We will focus in this work on studying this new ruthenium (II) catalyst $\text{RuH(CO)(Cl)(PCy}_3)_2$ which is distinguished by the fact that it belongs to the family of monohydride complexes of ruthenium. Thus, only one hydrogen atom of the catalyst is involved in the olefin hydrogenation process. The participation of a dihydrogen molecule allows the intervention of the second hydrogen atom. This catalyst is characterised by its high activity and selectivity for the hydrogenation of terminal and cyclic alkenes. In this case, kinetic studies [20] showed that the catalytic cycle begins with the dissociation of a phosphine from the metal. The authors showed also that the addition of H_2 to a cooled solution before adding an alkene substrate decreased the rate of the hydrogenation reaction. Since hydrogenation plays an important role in olefin reactions catalysed by transition metal complexes, we describe in this

work a theoretical study of the hydrogenation reaction mechanisms of hexene. This type of study can be very useful not only in understanding the mechanism of the reaction but also in understanding the selectivity (i.e. the comparison between two different catalysts).

Computational methods

Molecular geometries of reagents, intermediates, transition states (TS) and products were optimized using DFT/B3LYP method [24, 25]. Frequency calculations were performed on all optimized structures to ensure that the reactants and products have only positive frequencies and a single negative imaginary frequency in the case of the transition states. Thermochemical data and temperature corrections were calculated at 298.15 K for all optimized geometries. For ruthenium, the core electrons were represented by a relativistic small-core pseudopotential determined according to the Durand–Barthelat method [26]. The basis set 6-31G* was used for the other atoms [27]. To simplify the reaction, the catalyst was modeled by $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$. Previous theoretical studies confirmed the suitability of this catalyst model. [28-31]. All calculations were conducted using the Gaussian package 09 [32].

Results and discussion

1. Hydrogenation of hexene in the presence of complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$

The study of the reaction mechanism of hexene hydrogenation was explained by two different routes. The first one was with complexes that possess 14, 16 or 18 electrons including a single phosphine. The second one was carried out using complexes with 16 or 18 electrons retaining the two phosphines as indicated in Figure 1. For systems with multiple conformations, there is normally more than one possible structure for each compound and each transition state. It is impossible to explore the entire surface of potential energy. However, the most stable geometry and the structurally closest conformation to the crystal from the X-ray diffraction, was therefore examined in this study.

The geometry of the model complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$ was compared to the geometry obtained by a crystallographic study of $\text{RuH}(\text{CO})(\text{Cl})(\text{PCy}_3)_2$ [33]. The values of key geometric parameters were summarized in Table 1. Figure 2 illustrates the studied compound. The optimized structure of the complex was characterized by two phosphines in trans position. The angle P1-Ru-P2 was equal to 171.3° . In this type of structure, the phosphines are generally in the trans position and the angles P1-Ru-P2 are of the same order of magnitude: 180° in $\text{RuHCl}(\text{CO})(\text{P}^i\text{Pr}_3)$ where ^iPr is an isopropyl group [34], 170.15° $\text{RuCl}_2((\text{CO})(\text{P}^i\text{Pr}_3)_2$ [35],

167.849° in $\text{Ru}(\text{CO})(\text{NO})(\text{BF}_4)(\text{P}^t\text{Bu}_2\text{Me})_2$ where ^tBu is a tertibutyl group [36], 169.0° in $\text{RuH}_2(\text{H}_2)(\text{GeH}_4)(\text{PH}_3)_2$ [37] and 159.17° in $\text{Ru}(\text{H})(\text{NO})(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$ [36].

The ligands Cl and C1O and H1 are in the equatorial plane with a dihedral angle Cl-H1-C1-Ru almost equal to 0.0°. Regarding the Ru-P1 linkage, the calculated value is approximately 0.05 Å weaker than the experimental value with a 2% error while the value calculated for the Ru-Cl bond is about 0.05 Å larger than the experimental value. The chlorine and the CO ligand are in the trans position with a Cl-Ru-C1 angle equal to 164.5°, which is lower than the experimental value of 13.4° corresponding to an error of 7%. The complex $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$ is then considered as a distorted octahedron where the six ligands were placed in its summit. We can estimate that the agreement between the calculated and experimental values is globally satisfactory. This validated the choice of the DFT/B3LYP method and the 6-31G * database in our work.

Figure 1: Proposed catalytic cycles for the hydrogenation of Hexene by the $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$ complex with pathways: **a)** one phosphine and **b)** two phosphines.

1. 1. Hydrogenation mechanism with a phosphine complex

The reaction mechanism of the hydrogenation of hexene complex was, initially, studied with a single phosphine as described in Figure 1a. The energy diagram of the reaction mechanism is shown in Figure 3. The optimised structures of all stationary points were

compiled in Figure 2 and the thermodynamic and kinetic descriptors were summarised in Table 2. The first step of the reaction corresponded to a π -complexation of hexene at $\text{RuH(CO)(Cl)(PMe}_3)_2$ to bring the complex $n^\circ 2$ to 18 electrons with a free enthalpy of $24.4 \text{ kcal.mol}^{-1}$ greater than that of the starting complex. The complexation of hexene is very demanding in terms of energy. This could be explained by the steric hindrance of phosphines.

Figure 2: Optimised geometries compounds that intervene along the paths with one and two phosphines for the hydrogenation reaction of hexene in the presence of the complex $\text{RuH(CO)(Cl)(PMe}_3)_2$. (The hydrogens of the methyl groups are omitted for the sake of clarity).

The following step corresponded to the departure of a phosphine ligand PMe_3 which gave the complex $\text{RuH(CO)(Cl)(PMe}_3)$ (A3) 16 electrons with a new site available for the

coordination of reagents. This step was endothermic with an enthalpy ΔH^0 equal to 7.8 kcal.mol⁻¹ and it was favourable thermodynamically with a free enthalpy equal to -6.2 kcal.mol⁻¹. The reaction continued with the coordination of an H₂ molecule to obtain the ruthenium Ru(II) complex with 18 electrons. Its energy was higher than that of the intermediate (A3) of 8.6 kcal.mol⁻¹. The crucial step was the migration of the hydride H1 on hexene which was accompanied by the conversion of a Ru(II) complex to a Ru(IV) complex through a heterolytic cleavage of the H₂ molecule. This led to the formation of two hydrides. Its transition state corresponded to an activation barrier of 10.2 kcal.mol⁻¹.

TABLE 1 Geometric parameters selected for the test compounds 1, 2, A3, A4, A5, A6, B3, B4 and the transition states TSA1, TSA2, TSB1 and TSB2 optimised at DFT/B3LYP and those obtained by XRD for the complex RuH(CO)(Cl)(PCy₃)₂.

	l _{Cal.}	l _{Exp.}	2	A3	A4	TSA1	A5	TSA2	A6	B3	B4	TSB1	TSB2
Ru-P1	2.337	2.387	2.385	2.353	2.358	2.400	2.451	2.424	2.238	2.388	2.404	2.388	2.410
Ru-P2	2.377	-	2.398	-	-	-	-	-	-	2.402	2.422	2.412	2.393
Ru-Cl	2.450	2.397	2.508	2.440	2.487	2.492	2.476	2.474	2.339	2.488	2.588	2.553	2.528
Ru-C1	1.836	1.822	1.957	1.845	1.853	1.857	1.857	1.855	1.849	1.823	1.832	1.909	1.894
Ru-C2	-	-	2.220	2.337	2.320	2.307	2.477	2.492	-	2.944	3.160	2.268	3.449
Ru-C3	-	-	2.290	2.380	2.428	2.248	2.174	2.204	-	2.144	2.199	2.202	2.383
C2-C3	-	-	1.401	1.376	1.380	1.432	1.508	1.517	-	1.533	1.537	1.431	1.546
C2-H1	-	-	2.353	2.530	2.367	1.483	1.149	1.143	-	1.093	1.097	1.638	1.096
C3-H2	-	-	-	-	2.440	2.697	2.079	1.780	-	-	2.762	-	1.592
Ru-H1	1.570	-	1.646	1.561	1.586	1.666	2.009	2.034	-	3.015	3.276	1.691	3.487
Ru-H2	-	-	-	-	1.939	1.789	1.588	1.602	-	-	1.931	-	1.671
Ru-H3	-	-	-	-	1.929	1.805	1.579	1.577	1.565	-	1.929	-	1.747
H2-H3	-	-	-	-	0.788	0.836	1.698	1.845	-	-	0.780	-	1.068
C1-O	1.168	1.141	1.156	1.165	1.164	1.163	1.161	1.162	1.165	1.172	1.166	1.161	1.162
P1-Ru-C1	93.9	89	96.3	92.9	94.1	93.8	95.7	94.7	91.1	92.0	89.1	93.3	92.6
P1-Ru-Cl	86.8	88.1	83.5	85.0	83.8	82.8	82.8	83.4	101.9	86.0	83.1	81.9	82.3
Cl- Ru-C1	164.5	177.9	86.8	171.2	176.7	176.6	176.7	176.9	162.9	158.2	100.5	94.6	96.8
P1-Ru-P2	171.3	-	160.9	-	-	-	-	-	-	168.3	165.6	163.2	164.4

To ensure that the transition state connected well the two minima A4 and A5, the variation of the electronic energy during this step was calculated as a function of the intrinsic reaction coordinate (ξ) as shown in Figure 4-a. Two minima were found on both sides of the saddle point. Moreover, the electronic energy profile as a function of the intrinsic reaction coordinate (ξ) was of the same type as the universal profile for an elementary step [38].

Figure 3: Energy diagram in terms of free energy (kcal.mol^{-1}) for the hydrogenation reaction of hexene in the presence of the single-phosphine complex.

Figure 4: a) Variation of electronic energy and its first derivative b) Interatomic distances depending on the intrinsic reaction coordinate ξ during migration of the first hydrogen to hexene.

During the transition state TSA1 illustrated in Figure 2, the dihydrogen molecule was slightly activated since the distance between the two hydrogen atoms was $0.836 \text{ \AA}$ comparing to the distance in a free H_2 . In addition, the transfer of the proton H1 from Ru to C2 was progressing since the distance between C2 and H1 was $1.483 \text{ \AA}$. TSA1 was, thus, similar to the

product A5 but without breaking the molecule H₂ which did not cause any change in the degree of oxidation of ruthenium.

During the next step of the catalytic cycle, a hydride ligand was transferred to the carbon atom C3 of the olefin complexed with ruthenium. This led to the elimination of hexane and the formation of the intermediate (A6). This stage was almost free of enthalpy barrier (i.e. $\Delta G^\ddagger = 0.1 \text{ kcal.mol}^{-1}$). The final step corresponded to the addition of PMe₃ and the regeneration of the model catalyst RuH(CO)(Cl)(PMe₃)₂. The activation barrier was calculated by the energy difference between the transition state TSA1 and the complex (A3). It was equal to 18.8 kcal.mol⁻¹ (i.e. 37.0 kcal.mol⁻¹ - 18.2 kcal.mol⁻¹).

1.2. Hydrogenation mechanism with a complex with two phosphines

The catalytic cycle was proposed in Figure 1-b and the reaction mechanism was depicted in Figure 5. Thermodynamic and kinetic descriptors were summarized in Table 3. Both phosphines remained complexed to ruthenium during the entire studied process. The optimized structures of all stationary points were illustrated in Figure 6.

The first step of the reaction corresponded to a π -complexation of hexene on RuH(CO)(Cl)(PMe₃)₂. This complex possessed, thus, 18 electrons with a free enthalpy of 24.4 kcal.mol⁻¹ greater than that of the starting complex. The complexation of hexene required a lot of energy due to the steric hindrance of phosphines. The following step was the migration of the ruthenium-bonded hydride to hexene. The obtained complex B3 received again 16 electrons. It was, also, characterized by the formation of a Ru-C bond. The geometry of the transition state TS1 was optimized and was verified by a vibrational analysis (i.e. the presence of an imaginary frequency). The normal mode of vibration associated with the frequency of 7.30i cm⁻¹ corresponded to an intermediate structure where the hydrogen H1 moved away from ruthenium and approaches the carbon C2 of hexene.

Figure 5: Energy diagram of the hydrogenation of hexene in hexane in the presence of the ruthenium complex with two phosphines.

Figure 6: Optimised geometries of the compounds involved in the hydrogenation reaction of hexene in the presence of $\text{RuH}(\text{CO})(\text{Cl})(\text{PMe}_3)_2$ along the paths with one or two phosphines. (The hydrogens of the methyl groups are omitted for the sake of clarity).

To ensure that the transition state was linked to the two minima 2 and B3, the variation of the electronic energy was calculated as a function of the intrinsic reaction coordinate (ξ) at this step (Figure 7-a) and the two minima were spotted on both sides of the saddle point. The monitoring of the variation in the internuclear distances of the active atoms at the influence zone of the transition state is a technique that has been, increasingly, used to discuss the reaction mechanism of an elementary step [21, 38-40]. During this elementary step, H1 was transferred from Ru to C2 and a σ bond was created between Ru and C3. The variation of C2-H1, Ru-C3, Ru-H1 and C2-C3 distances were, also, evaluated and described in Figure 7-b.

Figure7: Variation of a) the electronic energy and its first derivative and b) the interatomic distances as a function of the intrinsic reaction coordinate during the migration of the first hydrogen through the diprophine path.

Before $\xi_1 = -0.77$, the distance C2-H1 decreased slightly while the distances Ru-C3 and C2-C3 remained substantially constant. Between $\xi_1 = -0.77$ and $\xi_2 = 0.91$, the distances C2-H1 and Ru-C3 decreased while the distance between C2 and C3 and Ru-H1 increased slightly. The transfer of H1 occurred almost in this zone (i.e. called activation zone). After $\xi_2 = 0.91$, the distances C2-H1 and Ru-C3 were stabilized. The C2-C3 distance increased before stabilization, reflecting the transformation of the double bond into a single bond. The electronic transfers responsible for the migration of H1 and the formation of the Ru-C3 bond occurred between these two zones. The addition of a molecule of dihydrogen to this complex led to the formation of the 18-electron complex B4. Its energy was $21.6 \text{ kcal mol}^{-1}$ greater than the one in B3. The final step of the catalytic cycle was the cleavage of the H_2 molecule by the migration of a hydrogen to the carbon atom of hexane that was already complexed with ruthenium. The second atom became a hydride. This allowed, on one side, the formation and the removal of the hexane and, on the other side the restoration of the catalyst in its initial structure. This step had an activation energy barrier of $13.2 \text{ kcal mol}^{-1}$.

Figure 8: Variation of a) the electronic energy and its first derivative and b) the interatomic distances as a function of the intrinsic reaction coordinate upon migration of the second hydrogen through the diposphine path.

The reaction mechanism had two well-separated steps of migration of hydrogen atoms towards the double bond. The first hydrogen is the hydride, which was added to the double bond (i.e. π -complexed to Ru). Its energetic barrier, equal to $31.8 \text{ kcal mol}^{-1}$, was calculated by the energy difference between TSB1 and (1). The second atom was provided by the H_2 molecule once it was σ -complexed to Ru. The barrier that corresponded to the energy difference between TSB2 and B3 is equal to $31.4 \text{ kcal mol}^{-1}$ (i.e. $43.6 \text{ kcal mol}^{-1} - 12.2 \text{ kcal mol}^{-1}$). Each of these two barriers was about ten kcal mol^{-1} higher than the one obtained in the single-phosphine mechanism. The thermodynamic and kinetic descriptors were depicted in Table 3. The hydrogenation route by a single phosphine was, thus, more favourable. This is in agreement with the proposal of the experimental study, which is based on the departure of phosphine before the coordination of the olefin [20].

2. Ligands effect

2.1. Energetic study

In order to confirm whether the ligands affect the selectivity of the reaction and to validate our modeling of phosphine ligands by PMe_3 , the hydrogenation reaction of hexene was studied through a phosphine in the presence of $\text{RuHCl}(\text{CO})(\text{L1})(\text{L2})$ with ($\text{L1} = \text{L2} = \text{PCy}_3$) or ($\text{L1} = \text{IMes}$, $\text{L2} = \text{PMe}_3$ with $\text{IMes} = (\text{N}, \text{N}'\text{-bis(mesityl)imidazol-2-ylidene})$). The free energies were shown in table 2. In the case $\text{L1} = \text{L2} = \text{PCy}_3$, we note that the complexation step of hexene in the case $\text{L1} = \text{L2} = \text{PCy}_3$ required more energy than in the case $\text{L1} = \text{L2} = \text{PMe}_3$. This could be explained, on one hand, by the steric hindrance of the PCy_3 ligands since the Tolman cone

angle for PCy_3 and PMe_3 are 170° and 118° , respectively [41]. On the other hand, the step of dissociation of phosphine PCy_3 was more favourable thermodynamically than in the case PMe_3 .

From a kinetic point of view, the variation of the free activation enthalpy of the kinetically determining step was not affected by the nature of the ligands. It varied from $18.8 \text{ kcal.mol}^{-1}$ for PMe_3 to $21.2 \text{ kcal.mol}^{-1}$ for PCy_3 . The same trend was observed at the reductive elimination step. The activation enthalpy varied from $0.3 \text{ kcal.mol}^{-1}$ in the case of PMe_3 to $0.6 \text{ kcal.mol}^{-1}$ for PCy_3 . The steric effect of the chemical group carried by the phosphorus did not affect the activation barrier. Therefore, the model used previously for phosphine ligands appeared fully justified. In the case (L1=IMes , L2=PMe_3), the same trend was observed for the stability of the reaction intermediates. Moreover, we noticed a drastic increase of the activation-free enthalpy at the kinetically determining step (i.e. it increased from 18.8 to $23.7 \text{ kcal.mol}^{-1}$, which was in agreement with the experimental work) [42].

2.2. Structural study

The energy profile of the kinetically determining step in the presence of RuHCl(CO)(L1)(L2) with (L1=L2=PCy_3) was shown in Figure 9. It was not due to an elementary reaction because an energy increase was observed after the transition state. This led to an unusual reaction profile with five extrema: two minima during the activation phase and three maxima (i.e. the first two during the activation phase and the third during the relaxation phase).

Figure 9: Variation of a) the electronic energy and its first derivative and b) the interatomic distances as a function of the intrinsic reaction coordinate ξ during the migration of the first hydrogen to hexene in the presence of RuHCl(CO)(L1)(L2) with ($\text{L1} = \text{L2} = \text{PCy}_3$).

It is accompanied by a change from a Ru(II) complex to a Ru(IV) complex. Indeed, we noted a heterolytic cleavage of the molecule of H₂ leading to the formation of two hydrides H₂ and H₃.

Although the Ru (IV) dihydride complexes were, generally, considered less stable than the Ru (II) form[43], an increasing number of Ru(IV) dihydride complexes, possessing a dihydrogen ligand, have been identified [44-48]. The studied energetic profile was very different from the one considered universal for an elementary stage. This is a direct consequence of the asynchronous nature of the different processes taking place. This step had 5 extrema delimiting 6 zones spread over the reaction coordinate.

Table 2: Thermodynamic and kinetic descriptors (kcal.mol⁻¹) for studied steps of the hexene hydrogenation mechanism in the presence of RuH(CO)(Cl)(L1)(L2) complex by phosphine route

		L1=L2=PMe ₃	L1=L2=PCy ₃	L1=PMe ₃ , L2=IMes
Addition d'oléfine	$\Delta H(1-2)$	9.1	25.4	14.5
	$\Delta G(1-2)$	24.4	43.0	29.2
Départ du ligand L1	$\Delta H(2-A3)$	7.8	-14.0	0.9
	$\Delta G(2-A3)$	-6.2	-32.0	-13.3
Addition d'une molécule d'hydrogène	$\Delta H(A3-A4)$	-0.4	1.1	1.6
	$\Delta G(A3-A4)$	8.6	10.3	11.1
Transfert du premier atome d'hydrogène	$\Delta H(A4-A5)$	4.4	8.4	4.8
	$\Delta G(A4-A5)$	4.9	8.7	5.4
	$\Delta G^\#(A4-A5)$	10.2	10.9	12.6
	$\Delta G^\#(A3-A5)$	18.8	21.2	23.7
Transfert du deuxième atome d'hydrogène	$\Delta H(A5-A6)$	-22.6	-30.4	-25.6
	$\Delta G(A5-A6)$	-34.8	-44.4	-39.6
	$\Delta G^\#(A5-A6)$	0.1	1.1	0.1
Régénération du catalyseur	$\Delta H(A6-1)$	-29.9	-22.1	-27.8
	$\Delta G(A6-1)$	-19.7	-8.4	-15.6
Réaction totale	ΔH	-31.6	-31.6	-31.6
	ΔG	-22.8	-22.8	-22.8

Table 3: Thermodynamic quantities and kinetic parameters (kcal.mol⁻¹) for the studied stages of the catalytic cycle of hydrogenation of hexene with two phosphines

		Path with two phosphine
Addition of olefin	$\Delta H(1-2)$	9.2
	$\Delta G(1-2)$	24.4
Transfer of the first hydrogen atom	$\Delta H(2-B3)$	-11.4
	$\Delta G(2-B3)$	-12.2
	$\Delta G^\#(2-B3)$	7.4
	$\Delta G^\#(1-B3)$	31.8
Addition of dihydrogen	$\Delta H(B3-B4)$	12.1
	$\Delta G(B3-B4)$	21.6
Addition of the second hydrogen atom	$\Delta H(B4-1)$	-41.5
	$\Delta G(B4-1)$	-56.6
	$\Delta G^\#(B4-1)$	13.2
	$\Delta G^\#(B3-1)$	31.4
Total reaction	ΔH	-31.6
	ΔG	-22.8

As shown in Figure 9, the region where the reagents were approaching from each other was before the first maximum (zone 1) and the product of the relaxation zone was located after the third maximum (zone 6). The transfer of the proton H1 took place between the first and the second maximum (zone 2 and 3). In addition, the distance C2-H1 decreased from 1.949 Å to 1.275 Å, while the distance H2-H3 remained substantially constant. The formation of two hydrides H2 and H3, which accompanied the transformation of Ru (II) into Ru(IV), was between the second minimum and the third maximum (zone 5). The bond C2-C3 increased monotonically in zones 2, 3,4 and 5. It changed from a double bond (1.38 6 Å) to a single bond (1.509 Å). The transfer of the proton H1 and the formation of both hydrides were asynchronous. This was explained in Figure 9-b. The length of the C2-H1 bond was stabilized at 0.58 Å while the length of H2-H3 began to increase from 1.97 Å.

Conclusion

Two reaction mechanisms for the hydrogenation of hexene have been studied theoretically in the presence of the complex $\text{RuHCl}(\text{CO})(\text{PMe}_3)_2$. The first mechanism consisted of a ruthenium complex with one phosphine (i.e. phosphine cleavage occurred at the beginning of the mechanism), which underwent a transformation upon five stages. The second mechanism was based on a similar complex with two phosphines undergoing 4-steps

transformation (i.e. the two phosphines remained coordinated to the ruthenium during the entire mechanism). The activation energy during the hydrogen transfer steps had about ten kcal.mol⁻¹ higher than the one obtained from the single-phosphine mechanism. These results confirmed the hypothesis stating that the departure of a phosphine is favourable at the beginning of the reaction mechanism. There was no significant difference between the real and the model catalysts (i.e. RuHCl(CO)(PMe₃)₂ and RuHCl(CO)(PCy₃)₂) in terms of the required activation barrier to reach the hexane (i.e. the product of the hydrogenation). From a kinetic point of view, the free enthalpy of activation was not affected by the nature of the phosphine ligands. Interestingly, the energetic profile of the kinetically determining step showed a shouldering after the transition state proving the asynchronous character of the different elementary steps occurring at this chemical transformation. In this step, the σ -complexed H₂ molecule with ruthenium was cleaved giving two hydrides, and ruthenium passed from the oxidation state II to IV. Through these two mechanisms, we have demonstrated the versatility of the ruthenium atom providing compounds at 18, 16 or 14 electrons.

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