Quantum chemical investigations of olefin addition on ruthenium II complexes

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ABSTRACT

Several stable isomers of the 16 electrons complex **1** $RuH_2(C_2H_4)(PH_3)_2$ which contains only one ethylene and its homologues 18 electrons complex **2** containing two ethylene molecules have been investigated by means of DFT/B3LYP technique. The discussion about the relative stability of various isomers of those complexes leads to understand the nature of the interactions between ethylene and the metal. The transition state relative to the intervention between the two most stable isomers of **2** series had been determined.

Key words: Ethylene hydrogenation – Ruthenium II complexes- isomerisation.

INTRODUCTION

Olefin metathesis or transalkylidenation (in some literature, a disproportionation) is an organic reaction which involves redistribution of olefinic (alkene) bonds.[1-2] Since its discovery, olefin metathesis has gained widespread use in research and industry for making products ranging from medicines and polymers to enhanced fuels. Its advantages include the creation of fewer sideproducts and hazardous wastes. Yves Chauvin, Robert H. Grubbs, Richard R. Schrock shared the 2005 Nobel Prize in Chemistry for "the development of the metathesis method in organic synthesis".

The complexes of transition metals in which the olefin is a ligand are of a large interest. In particular, the reduction of C=C double bonds is one of the most fundamental synthetic transformations and plays a key role in the manufacturing of a wide variety of bulk and fine chemicals. Hydrogenation of olefins can be achieved readily with molecular hydrogen in many cases and exhibit often chemo[3-6], regio[7] or enantioselectivity[8].

Complexes between metal salts and olefinic hydrocarbons are known since 1827. They take part in a variety of catalytic reactions including isomerization of olefin, hydrosilylation, hydrogenation, and hydroformylation[9]. The mechanism and the products of a specific reaction are dependent on the stability of the metal-olefin bond. Generally, the stoechiometric and catalytic reactions of organometallic complex imply the break and the formation of the metal-ligand bonds. Consequently, a thermodynamic evaluation of these reactions requires the knowledge of the metal-ligand binding energy. The experimental determination of these quantities in the organometallic complexes is still difficult[10]. However, it was shown that the functional density theory (DFT) leads to reliable results of binding energies in this type of complex[11-21].

The catalytic hydrogenation of the C=C bonds by ruthenium (**II**) complexes has been widely reported, and while the majority of catalysts operate under homogeneous conditions[9,22-25]. In 1985, the reactivity of the complex dihydrogene of ruthenium RuH_2 $(H_2)_2(PCy_3)_2$ (**I**) with respect to ethylene was

synthesised by Chaudret [26]. It has been used in a large variety of catalysed reactions. The complex (**II**) of our interest is $RuH_2(C_2H_4)_2(PCy_3)_2$ which is obtained by bubbling ethylene in a solution containing $RuH_2(H_2)_2(PCy_3)_2$. Such kind of complexes has been also observed more recently by Maienza, and all[27].

Curiously, the complex II has been detected in a reaction of ethylene hydrogenation in contradiction with the model of Dewar-Chatt-Duncancon[28,29] which is generally satisfactory to describe the interaction metal-ligand. It is usually supposed[30-31] that the process starts in a manner that would generate a 16-electron complex, which might be stabilized by solvent species, and leads to the formation of an alkyl hydride intermediate in which the olefin coordinates at the ruthenium. Reductive elimination of ethane would afford the 16-electron species that can re-enter the catalytic cycle.

In this work, we will study the complex **2** which models complex II by the replacement of cyclohexyl by hydrogen on the phosphines. We also will be interested by the 16 electrons complex **1** $RuH_2(C_2H_4)(PH_3)_2$ which contains only one ethylene in preoccupations of comparison and prediction because it was not detected. The aim of this study is to discuss the relative stability of various isomers of the complexes 1 and 2, and to try to understand the nature of the interactions between ethylene and the metal. In particular we will try to find similarities with carbon monoxide complexes where σ donation ligand-metal and π retrodonation metal-ligand were investigued.

A detailed attention will relate to the orientation of the ligands in the coordination sphere of ruthenium. Such phenomena has been invoked in order to interpret the gap between homogeneous and heterogeneous catalysis in hydrogenation of olefins by $Ir(CO)Cl(PPh_3)_2$ [8].

Computational details

The theoretical treatment of the different systems included in this work was performed by using the DFT/B3LYP approach implemented in the GAUSSIAN98 series of programs[32]. The B3LYP hybrid functional[33] has been found to be quite reliable in describing potential energy surfaces (PES) and binding energies in ruthenium complexes[34]. For ruthenium, the core electrons were represented by relativistic small-core pseudo-potential determined according to the Durand-Barthelat method[35]. The 16 electrons corresponding to the 4s, 4p, 4d, and 5s atomic orbitals were described by a (7s, 6p, 6d) primitive set of Gaussian functions contracted to (5s, 5p, 3d). Standard pseudo-potentials developed in Toulouse were used to describe the atomic cores of carbon and phosphorus [36]. A double-zeta plus polarization valence basis set was employed for each atom (d-type function exponents were 0.8 and 0.45, respectively). For hydrogen, a standard (4s) primitive basis contracted to (2s) was used. A p-type polarization function (exponent 0.90) was added for the hydrogen atoms directly bound to ruthenium. The geometries of the different species under consideration were optimized using analytic gradient.

RESULTS AND DISCUSSION

We chose the comparative study of several isomers resulting from the addition of one (**1a-1g**) or two ethylene molecules (**2a-2e**) on the 14 electrons complex $RuH_2(PH_3)_2$. They will be noted by increasing Latin alphabet according to their relative stability. These isomers are different by:

- The relative position of two phosphines, in position *cis* (**1c**, **1e**, **2b**, **2d** and **2e**) or trans (**1a**, **1b**, **1d**, **1f**, **1g**, **2a** and **2c**) one compared to the other.
- The position of the vacant site which can be opposite a hydride (**1a**, **1b**, **1d**, **1f** and **1g**), ethylene (**1c**) or of a phosphine (**1e**).

We optimized the geometry of the isomers **1a-g** by means of DFT/ B3LYP technique and we gathered the geometrical parameter values in Table 1. Fig. 1 depicts the studied compounds geometry. Compared to the length of calculated bond C=C (1.337Å) of free ethylene taken as reference, the distance C1-C2 of all isomers range from 1.349 Å to 1.530 Å. This lengthening varies between 1%. and 14.4%. In the isomers **1d** and **1g**, which are complexes of h[1] type, the bond length of C1-C2 (1.512Å and 1.530 Å) is characteristic of a simple bond. In the case of the compound **1f**, the

Table -1: Selected optimized geometrical parameters[a] and relative energies for the four isomers of *RuH₂(C₂H₄)(PH₃)₂* calculated at the DFT/B3LYP level of theory.

	1a	1b	1c	1d	1e	1f	1g
Ru-H1	1.638	1.637	1.613	1.582	1.612	1.783	1.736
Ru-H2	1.561	1.562	1.625	-	1.622	1.767	1.560
Ru-C1	2.253	2.296	2.276	2.061	2.159	2.064	1.923
Ru-C2	2.253	2.290	2.241	3.300	2.164	-	2.986
C1-C2	1.402	1.394	1.402	1.530	1.423	1.349	1.512
Ru-P1	2.298	2.348	2.377	2.310	2.375	2.317	2.296
Ru-P2	2.298	2.348	2.184	2.300	2.397	2.317	2.296
P1-Ru-P2	148.5	167.5	98.7	169.6	105.4	166.6	140.3
H1-Ru-H2	89.4	80.4	75.8	-	82.1	28.2	106.7
C1-Ru-C2	36.3	35.4	36.2	21.1	38.4	17.2	25.9
H1-Ru-P1	75.1	84.2	156.8	85.4	84.9	93.8	73.7
H1-Ru-P2	75.1	84.2	80.3	85.5	169.4	93.6	73.7
H2-Ru-P1	84.7	86.7	81.1	-	162.4	95.9	84.1
H2-Ru-P2	84.7	86.7	82.8	-	87.3	95.9	84.1
C1-Ru-P1	87.1	94.5	89.2	96.9	85.8	85.3	108.4
C2-Ru-P2	87.1	96.2	100.1	-	92.6	-	-
ΔE (kcal mol⁻¹)	0.0	2.0	5.8	6.9	16.0	19.0	28.0

[a] Distances are in angstrom (Å) and angles in degrees (°).

1a   1b   1c   1d

1e   1f   1g
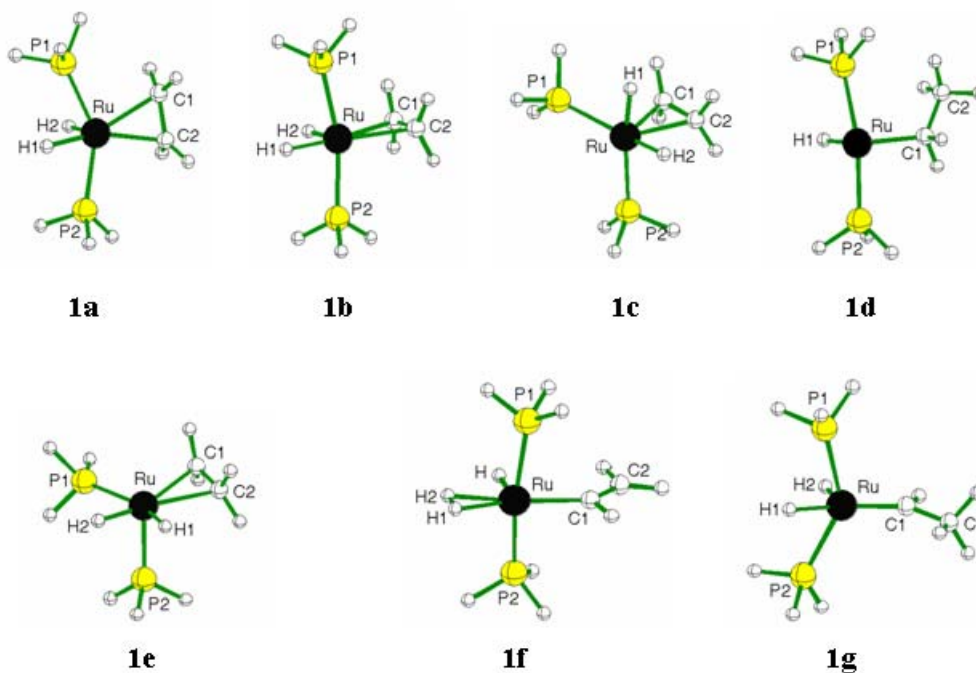
Fig. - 1: DFT/B3LYP-optimized geometries of RuH₂(C₂H₄)(PH₃)₂ isomers (1)

bond length of C1-C2 is 1.349Å and is very close to the value 1.337Å of free ethylene indicating that the formation of this isomer is an oxidizing addition of ethylene on $RuH_2(PH_3)_2$. A rearrangement of the two hydrides H1 and H2 is observed in the isomer **1f** to form a dihydrogene molecule σ-complexed on ruthenium as the value 0.866Å of the distance H-H testifies it.

The isomers **1a-c** and **1e** are of the η^2 complex type characterized by a bond length of C1-C2 about 1.4Å. This distance is intermediary between lengths of simple and double bonds. Observed lengthening is about 4.7% for the isomer **1a**. The most stable isomer, **1a**, is characterized by a position of ethylene perpendicular to the plan

formed by the two hydrides and the atom of ruthenium.

Relative energies of the seven studied isomers are gathered in Table 1. We remark that isomers for which phosphines are in trans position are more stable, and that the ethylene is in a position perpendicular to the equatorial plan formed by Ru, H1 and H2 (isomer **1a**).

We optimized also the five isomers of the 15 electrons complex $RuH_2(C_2H_4)_2(PH_3)_2$ (**2**). Their DFT/B3LYP optimized geometries are shown in Fig. 2 and the geometrical parameters are gathered in Table 2. Except for the isomer **2c** which admits the symmetry C_{2v}, other isomers are of C_1 symmetry.
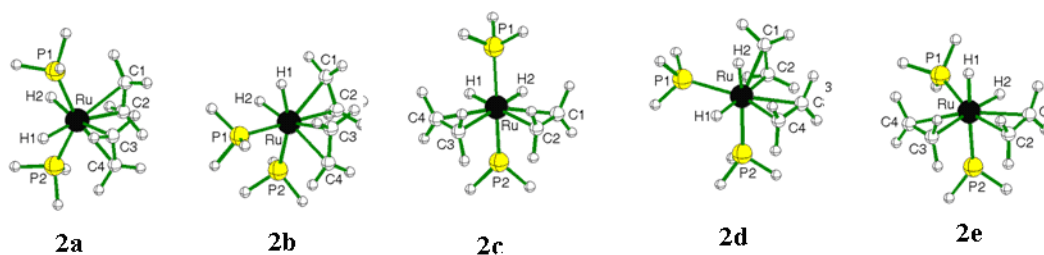

Fig. - 2: DFT/B3LYP-optimized geometries of $RuH_2(C_2H_4)_2(PH_3)_2$ isomers (2).

Compared with those isomers with their homologous complex $RuH_2(C_2H_4)(PH_3)_2$ [1], the lengths of the bonds are almost of the same order of magnitude. Addition of an ethylene on the complex **1** is done without a notable modification of the distances. In all the studied isomers, the distances Ru-C ranges from 2.256Å to 2.398Å, that is to say a variation of 6%. The longest distances Ru-C are found in the isomers **2c** and **2d** in which the two ethylenes are in the equatorial plan. We also notice that this distance is weaker in the isomer **2d** (2.256, 2.316, 2.264 and 2.281Å) in which the two ethylenes are in two almost orthogonal plans. Distance C-C varies slightly; it passes from 1.384 Å in **2c** to 1.399Å in **2d**, that is to say a variation of 1%. This distance is intermediate between simple. Lengthening is about 4% from the isomer **2a**, which is more important than that found in the complex $RuH_2(CO)_2(PH_3)_2$. We remark that the angles C1-Ru-C2 and C3-Ru-C4 are close to 35° in all studied isomers. The angle P1-Ru-P2 takes either a value close to 90° (*cis* form) or a value close to 180° (*trans*

form) except in the case to the isomer **2a** in which this angle is worth 138.1°, intermediate value between the form cis and the trans form. This is due to the steric effects caused by two ethylenes.

Relative energies of various isomers of $RuH_2(C_2H_4)_2(PH_3)_2$ are summarized in Table 2 . The four isomers **2a**, **2b**, **2c** and **2d** are close in energy. Similarly at the bahavior of complexes **1**, we remark that the two ethylene molecules are perpendicular to the plan containing the atom of ruthenium and the two hydrides. Phosphines are in trans position one compared to the other. The isomer **2d** is less stable than the isomer **2a** of 7.8 kcal mol^{-1}. This destabilization can have for origin the steric constraints in the plan which contains (P1, H2, C1, C2, C3 and C4).

Since isomers **2a** and **2b** are very close in energy (ΔE= 0.4 kcal mol^{-1}), we have calculated the energy of the isomerization barrier. We have optimized the geometry of the transition structure

Table - 2: Selected optimized geometrical parameters[a] and relative energies for the four isomers of *RuH₂(C₂H₄)(PH₃)₂* isomers and for TS$_{2a2b}$ calculated at the DFT/B3LYP level of theory.

	2a	**TS$_{2a2b}$**	**2b**	**2c**	**2d**	**2e**
Ru-H1	1.628	1.729	1.619	1.612	1.623	1.628
Ru-H2	1.628	1.727	1.622	1.612	1.614	1.616
Ru-C1	2.306	2.219	2.269	2.323	2.281	2.304
Ru-C2	2.309	2.246	2.288	2.398	2.316	2.349
Ru-C3	2.309	2.204	2.290	2.398	2.256	2.389
Ru-C4	2.306	2.209	2.325	2.323	2.264	2.344
C1-C2	1.392	1.405	1.396	1.388	1.399	1.390
C3-C4	1.392	1.434	1.395	1.388	1.397	1.384
Ru-P1	2.301	2.341	2.291	2.310	2.308	2.276
Ru-P2	2.301	2.422	2.360	2.310	2.391	2.380
P-Ru-P	138.1	126.5	94.8	166.5	96.8	99.7
H1-Ru-H2	95.2	28.8	78.3	72.4	79.2	90.4
C1-Ru-C2	35.1	367	35.7	34.2	35.4	34.7
C3-Ru-C4	35.1	37.9	35.2	34.2	36.0	34.0
C1-Ru-C3	87.6	81.4	87.0	106.5	84.0	106.5
C1-Ru-C4	94.7	84.4	105.5	140.7	116.2	140.3
C3-Ru-C2	101.1	113.3	89.4	72.4	85.2	72.1
C4-Ru-C2	87.6	98.7	87.8	106.5	120.7	106.0
ΔE(kcal mol⁻¹)	0.0	23.3	0.4	1.7	2.1	7.8

[a] Distances are in angstrom (Å) and angles in degrees (°).

denoted **TS$_{2a2b}$**. The optimization of geometry followed by the calculation of the frequencies gives us only one imaginary frequency which is 269i cm⁻¹. The geometrical parameters of **TS$_{2a2b}$** are shown in Table 2 and the energy diagram is represented in the Fig. 3. They are compatible with the formation of a complex containing the molecule H₂. Such complex formation has been observed in the case of the complex (I)-diazotizes[37].

The angle P1-Ru-P2 is equal to 126.7° in **TS$_{2a2b}$** which is comparable with its homologue in RuH₂(N₂)₂(PH₃)₂ [38]. Distance C-C in **TS$_{2a2b}$** takes a value lower than that in **2a** and **2b**, whereas the distance Ru-H is very stretched compared with the two corresponding minima. This transition state is 23 kcal mol⁻¹ above the energy of isomer **2a**. It means that the passage between these two isomers may be difficult at low temperature. This barrier is less important than that found for the complex carbonyl and the complex diazotizes[38].
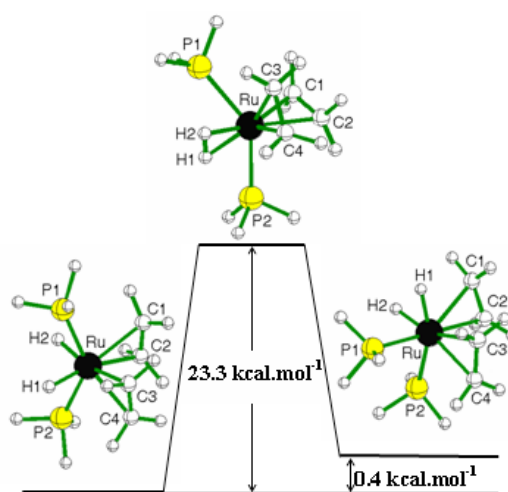
Fig. - 3: Schematic energy diagram for the isomerization process between the 2a and 2b isomers of RuH2(C₂H₄)₂(PH₃)₂ .

CONCLUSION

This work points out the fluxionality of ruthenium II complexes even if the passage of an isomer to another is sometimes difficult at ambient temperature. The value of the barrier of isomerization comparable with that is found in the case of the complexes of carbon monoxide and of diazotizes. We hope that this work helps in a best comprehension of metathesis reaction.

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