

# Metathesis of halogenated olefins A computational study of ruthenium alkylidene mediated reaction pathways

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## Abstract

The cross-metathesis reaction pathways of norbornene (NB) with ethylene (**2a**), *trans*-1,2-difluoro-ethylene (**2b**) and *trans*-1,2-dichloro-ethylene (**2c**) using (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy<sub>3</sub>)Cl<sub>2</sub>Ru=CHPh (**I**) have been studied at B3LYP/LACVP\* level of theory. The calculations show that the Gibbs free activation energy of the metathesis reaction is strongly dependent on the volume of halogene substituents. The calculated Gibbs free activation energies for cross-metathesis of NB with **2a**, **2b** and **2c** are of 10.2, 17.3 and 25.1 kcal/mol, respectively. Strong binding in transition states results in large deformation energies increasing energy barrier. Calculation shows that steric hindrance caused by the atoms directly linked to the olefin double bond is the most important factor influencing the activation energy of the metathesis reaction.

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## 1. Introduction

The ruthenium alkylidene catalysts coordinated with *N*-heterocyclic carbene ligands open vast opportunities to metathesize challenging olefins with sterically hindered or electronically deactivating ester and amide groups [1]. For example, halogenated olefins are challenging due to the presence of the electron-withdrawing groups and few examples of their metathesis exist. Thus, to the best of our knowledge the metathesis of allyl chloride and allyl bromide using the heterogeneous Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub>/SnMe<sub>4</sub> catalyst [2], cross-metathesis of allyl halides [2f] and nonafluoro-1-hexene with terminal olefin [1a] and metathesis of vinyl-*gem*-difluorocyclopropane derivatives [3] by (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (PCy<sub>3</sub>)Cl<sub>2</sub>Ru=CHPh (**I**) are the only known publications on the topic. Recently, we reported a density functional study of ruthenium alkylidene mediated metathesis of chlorinated olefins [4]. It is worth noting, that particularly interesting substrates for the olefin metathesis are those where halogen atom is

directly linked to olefin carbon. In this case, the metathesis will proceed via the formation of ruthenium-halo carbene complex which is different from usual alkylidene complex. Cross-metathesis of 1-chloro- and 1-bromoethylene with propylene using Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub>/SnMe<sub>4</sub> [2a], ring-closing metathesis of vinyl chlorides [2g] and metathesis of 1,1-difluoroethylene [5] by catalyst (**I**) are the reports on the metathesis of directly halogenated olefins.

Ring-opening metathesis polymerization of cycloolefins in the presence of functionalized olefins as chain transfer agents (CTAs) is widely used for the synthesis of telechelic polymers [6]. Telechelics have found a wide demand as intermediates in the synthesis of block copolymers, polymeric networks and as cross-linking agents to enhance thermal and mechanical properties of materials [7]. For instance, hydroxyl-terminated telechelic polybutadiene has been used as cross-linking agent in the polyurethane industry [8].

The mechanism of ruthenium alkylidene catalyzed olefin metathesis has recently been a subject of intense experimental [9,10] and theoretical [11] investigations. These results clearly indicate that for ruthenium complexes with general formula L(PR<sub>3</sub>)(X)<sub>2</sub>Ru=CHR<sup>1</sup> (R = Cy, Cp and Ph, X = Cl, Br and I, L = *N*-heterocyclic carbene ligand, NHC) initiation occurs by

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dissociative substitution of a phosphine ligand ( $\text{PR}_3$ ) with olefin substrate, giving a monoligand complex.

The goal of this study is to model reaction pathways for the cross-metathesis of norbornene (NB) with ethylene (**2a**) and directly halogenated olefins; *trans*-1,2-difluoro-ethylene (**2b**) and *trans*-1,2-dichloro-ethylene (**2c**) using (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) ( $\text{PCy}_3$ ) $\text{Cl}_2\text{Ru}=\text{CHPh}$  (**1**).

## 2. Computational methods

All calculations were carried out with the Jaguar v 6.0 program [12]. The lowest energy conformers were located using a conformational search method as implemented in the Titan package version 1.0.5 [13] using PM3(tm) method. A systematic search algorithm was applied thus exploring totally conformational space. The total number of possible conformers was found to be between 80 and 100 for different molecules. The lowest energy conformers were used as initial structures for further optimization using Becke's three parameter functional (B3) [14] in combination with the Lee, Yang and Parr (LYP) correlation function [15] and LACVP\* basis set. The molecular geometries of all calculated molecules were optimized to a global minimum at B3LYP/LACVP\* level of theory. The LACVP series of basis sets is a combination of the successful 6-31G basis set with the LANL2DZ [16] effective core basis set. Specifically the atoms H–Ar are described with the 6-31G (or 6-31G\*, 6-31+G\*\*, etc.) basis set while heavier atoms are modeled using the LANL2DZ basis set. For Ru atom LACVP basis set includes valence and outermost core orbitals (4s, 4p, 5s, 4d, 5p).

Frequency calculations at 298.15 K were run for all structures to make sure that a transition state (one imaginary mode) or minimum (zero imaginary modes) is located and to reach zero point energy (ZPE) correction and thermodynamic properties. Corrections to  $\Delta H$  and  $\Delta G$  are taken from vibrational calculations and include ZPE. All calculations were carried out in gas phase since as it has been shown that solvation energies of similar molecules in non-polar solvents introduce smaller error than the method itself [4a]. However, to verify how solvation affects the reaction energies Poisson–Boltzmann solver implemented in Jaguar v 6.0 was used to calculate solvation effect in 1,2-dichloroethane for **3c**  $\rightarrow$  **4c** reaction at B3LYP/LACVP\* level of theory. The solvation effect change the activation energy by only 0.53 kcal/mol that is well inside of the method error.

In the SCRF method that Jaguar uses, Jaguar first calculates the usual gas phase wave function and from that the electrostatic potential, and fits that potential to a set of atomic charges. These charges are passed to the Poisson–Boltzmann solver, which then determines the reaction field by numerical solution of the Poisson–Boltzmann equations and represents the solvent as a layer of charges at the molecular surface (which serves as a dielectric continuum boundary). These solvent point charges are returned to Jaguar's SCF program, which performs another quantum mechanical wave function calculation, incorporating the solvent charges. This process is repeated until self-consistency is obtained.

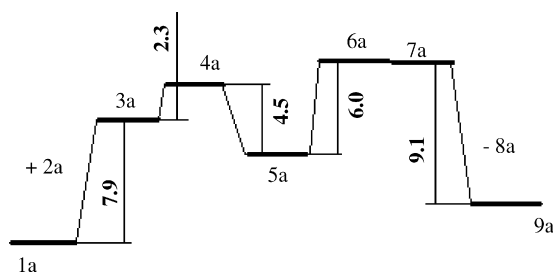


Fig. 1. The Gibbs free energy profile for cross-metathesis of NB with **2a** by (**1**).

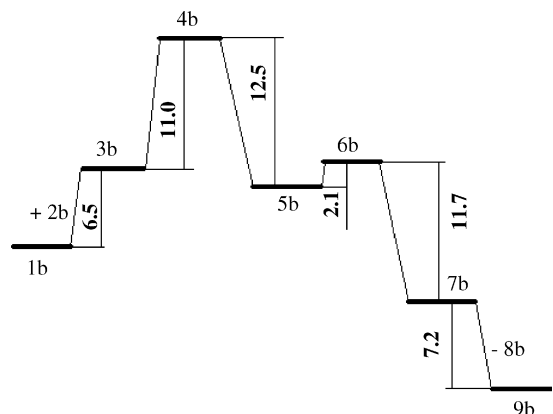


Fig. 2. The Gibbs free energy profile for cross-metathesis of NB with **2b** by (**1**).

## 3. Results and discussion

Scheme 1 shows the chain transfer to **2a**, **2b** and **2c** during the cross-metathesis of NB by Ru-alkylidene catalyst (**1**). Figs. 1–3 present the energetic profiles for these reactions. There are marked differences between **2a** and **2b** (**2c**) in the metathesis reaction. However, when inspecting geometry and the binding energies of complexes **3a–c** one can observe that  $\pi$ -complex **3a** is the tightest one less positive Gibbs free binding energy. On the other hand **3c** is not a  $\pi$ -complex at all, the binding in this complex is due to the interaction of hydrogen of **2c** with chlorine atom of Ru complex. This suggestion is confirmed by the analysis of the charge distribution in complex **3c** and its geometry. Thus, in free complex **1c** and **2c** natural charge at Cl and H atoms are of  $-0.53$  and  $+0.26$  e, respectively, while in complex **3c** the corresponding natural charges are of  $-0.54$  and  $+0.28$  e,

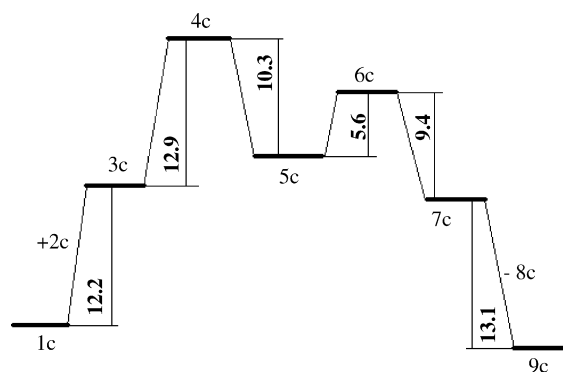
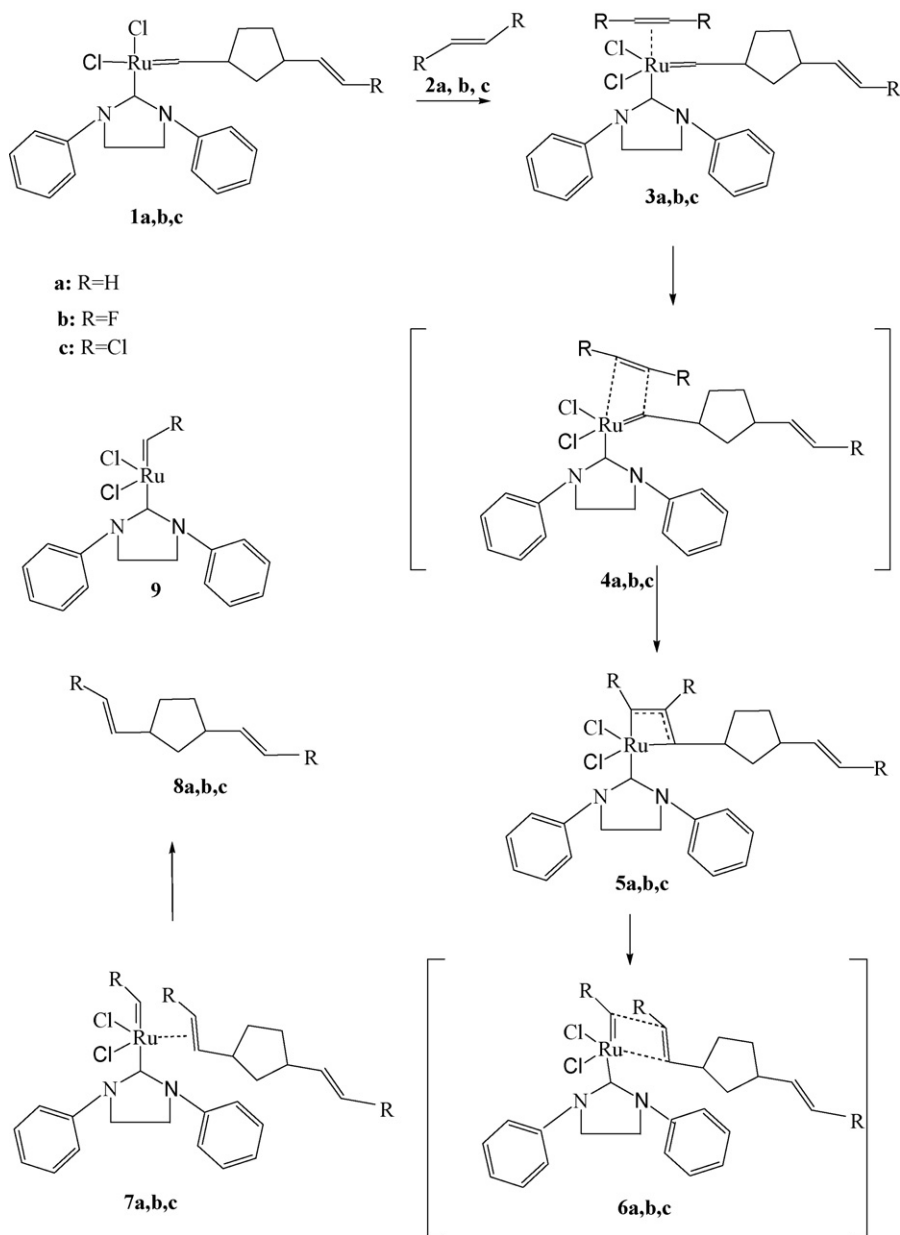


Fig. 3. The Gibbs free energy profile for cross-metathesis of NB with **2c** by (**1**).

Scheme 1. Chain transfer to **2a**, **2b** and **2c** during the cross-metathesis of NB by (**1**).

therefore, there is a slight charge transfer from hydrogen of **2c** to chlorine atom in **3c**. Moreover, the distance between Cl and H atoms is 2.71 Å that is less than a sum of the Van der Waals radii of H and Cl atoms (3.01 Å).

Complex **3a** is tighter compared to **3b**, however, its geometry is similar to **3a** suggesting interaction between  $\pi$ -electron of **2b** and empty d-orbitals of Ru atom. This could be explained by steric hindrances. In spite of favourable electronic properties bulky chlorine atoms directly attached to the double bond impedes interactions between **2c** and Ru. Less bulky fluorine atoms of **2b** allow better fitting between  $\pi$ -orbitals of olefin and d-orbitals of Ru atom and in case of ethylene (**2a**) the absence of steric hindrances allows the formation of tight complex. Therefore, steric factors are of primary importance for the complex formation in the metathesis reaction.

The located transition states **4a–c** and **6a–c** (Figs. 4–6) correspond to the rotation of carbene groups. As seen from energy profiles transition states **4a–c** determine the reaction kinetics. The kinetic control of the reactions under the study follows from the fact that the metathesis of **2b** and **2c** shows negative  $\Delta G$  ( $\Delta G = -11.9$  and  $-2.0$  kcal/mol for **2b** and **2c**, respectively) while ethylene metathesis presents slightly positive energy ( $\Delta G = 2.5$  kcal/mol). On the other hand the Gibbs free activation energy (as a sum of the complex Gibbs free energy formation and the Gibbs free activation energies) is highest for **2c** metathesis (25.1 kcal/mol) as compared to **2b** (17.3 kcal/mol) and ethylene (10.2 kcal/mol). It is worth noting that ROMP of cycloolefins in the presence of **2c** as a CTA does not result in control over molecular weight and end functionality of the polymer whereas the same reaction in the presence of **2a** yields  $\alpha,\omega'$ -

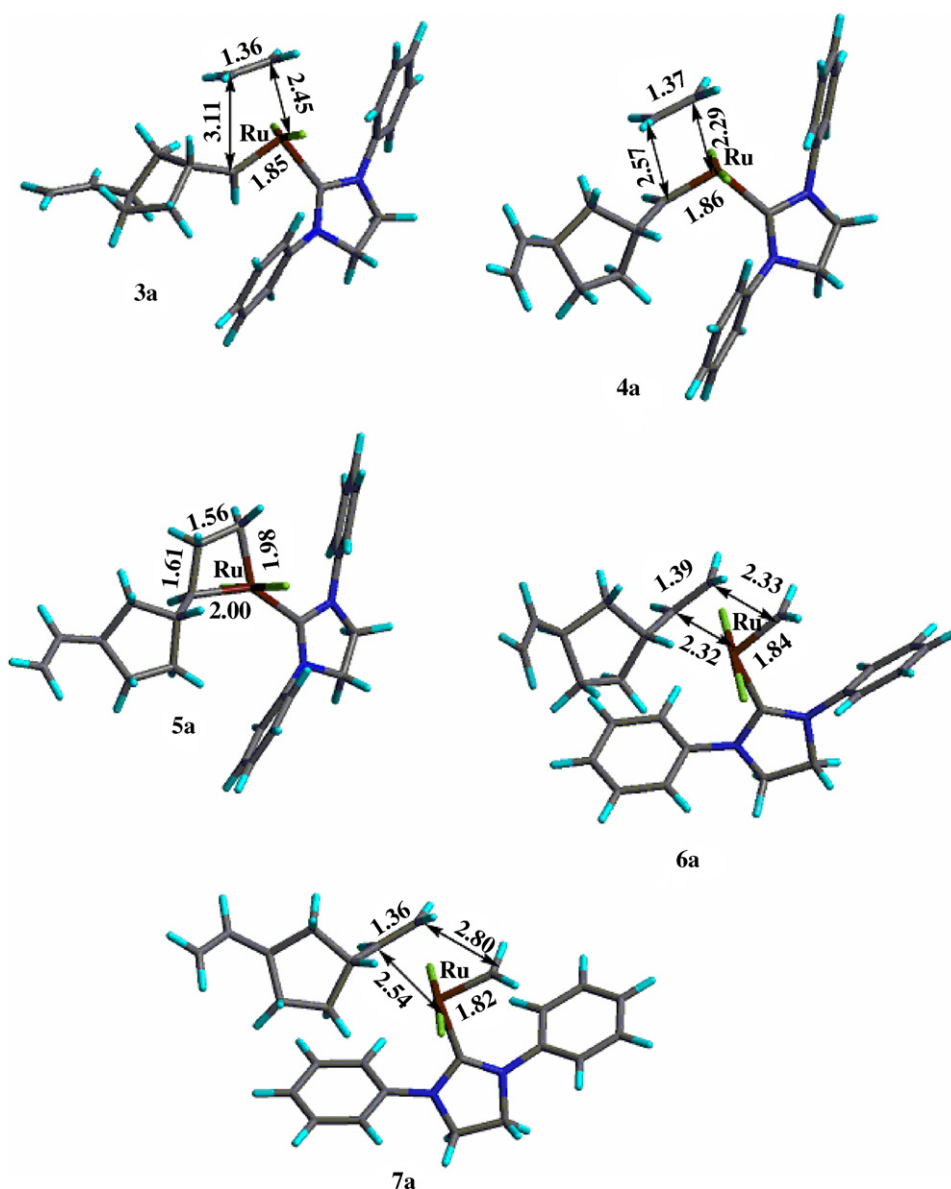


Fig. 4. B3LYP/LACVP\* optimized geometries of reaction intermediates for cross-metathesis of NB with **2a** by (1).

diolefins which can be used as cross-linking agents and starting compounds in the production of fine chemicals [6].

The  $\Delta G$  of the studied metathesis reaction can be understood in terms of ruthenium complex stability. Thus, the difference in  $\Delta G$  of **2b** metathesis ( $-10.0$  kcal/mol) and **2c** ( $-2.0$  kcal/mol) is easy to understand taking into account strong +M effect of fluorine in complex **9b** compared to chlorine and hydrogen which dominates in stabilizing carbene complex compared to  $-I$  effect of fluorine.

HOMO energies for **2a**, **2b** and **2c**, calculated at B3LYP/6-31G\* level are of  $-0.2666$ ,  $-0.2535$  and  $-0.2597$  a.u., therefore **2b** is the most donor one. On the other hand LUMO energies calculated at the same theoretical level give  $0.0188$ ,  $0.0188$  and  $0.0192$  a.u. showing that the back donation interaction is the weakest in **2c**. The theoretical data are confirmed by the experimentally determined ionization potentials for **2a** ( $10.52$  eV), **2b**

( $10.3$  eV) and **2c** ( $9.66$  eV), which are in line with calculated HOMO energies [17].

It has been shown that there is no correlation between global electrophilicity index ( $\omega$ ) of olefins and the Gibbs free activation energy ( $G^\ddagger$ ) of the metathesis reaction, while a clear correlation between molecular volume of olefin (only atoms linked directly to the double bond are taken into account) and  $G^\ddagger$  is observed [4a]. Thus, the calculated molecular volumes of **2a**, **2b** and **2c** were of  $31.6$ ,  $38.8$  and  $58.5$  Å<sup>3</sup>, respectively. It is seen that metathesis of **2c** with highest molecular volume shows highest Gibbs free activation energy. Therefore, steric effect caused by atoms closest to double bond is the determining factor for the activation energy, while the electronic factor at least is not as important [4a].

One can try to estimate the relative importance of electronic and steric contributions to the activation energy using the follow-

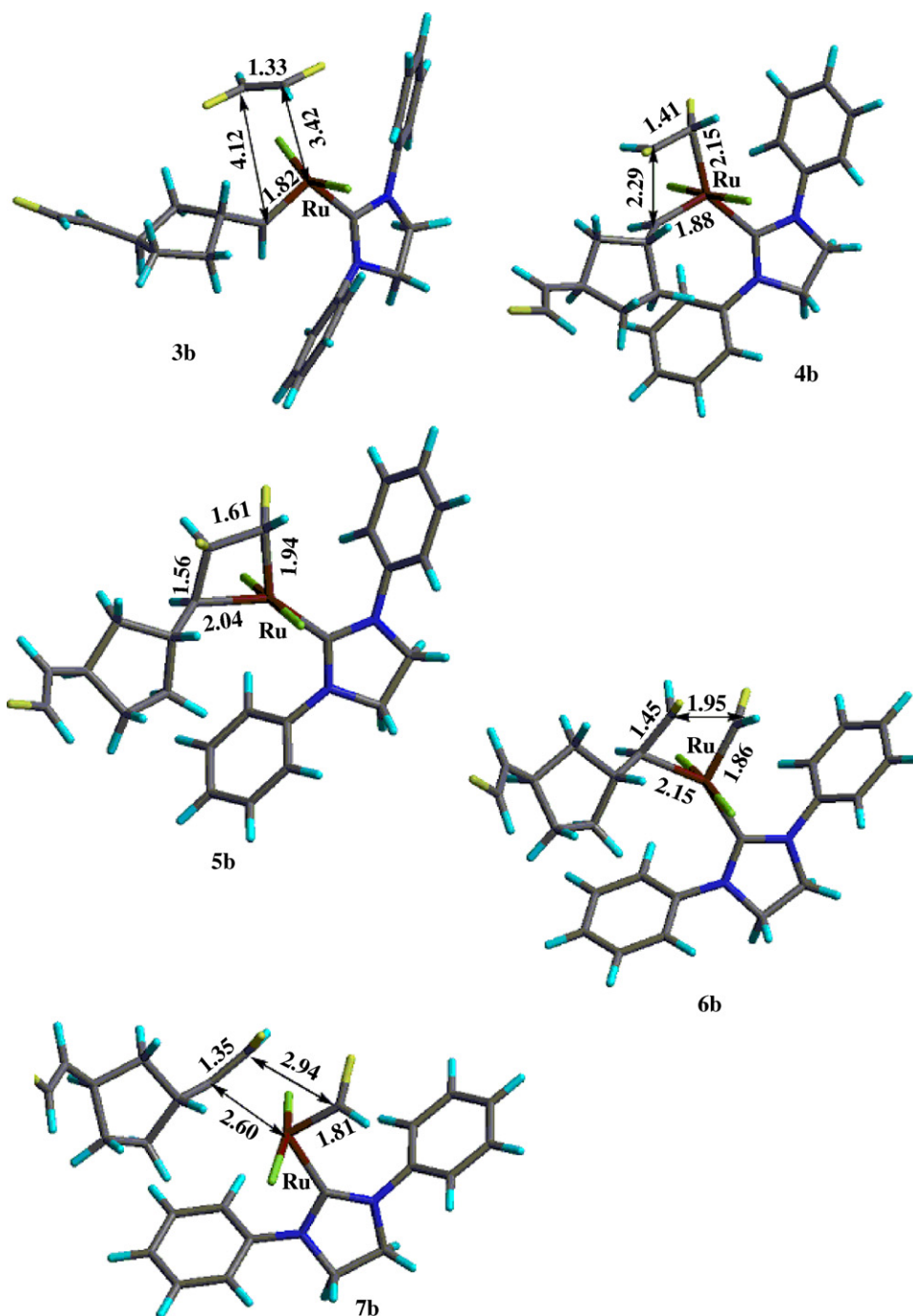


Fig. 5. B3LYP/LACVP\* optimized geometries of reaction intermediates for cross-metathesis of NB with **2b** by (1).

ing scheme. The formation of transition states can be represented as a two step process. The first step is the deformation of olefin **2** and catalytical complex **1** to the geometry corresponding geometry in transition state **4**. Second step is the connection of two deformed fragments to form transition state **4**. Table 1 shows the results of such energy partition for the transition states **4a–c**. As seen from Table 1 molecular volume of olefin plays an important role in building-up of molecular strain. Thus, ethylene contributes only with 2.9 kcal/mol, while in case of **2b** and **2c** the deformation energy of olefins in transition states **4** approaches 20 kcal/mol. The same situation holds for the defor-

mation energy of catalytic complex **1**; the deformation energy is lowest in the case of **2a** and increases for bulky olefins **2b** and **2c**. As a result, total deformation energies are lowest for **4a** in accordance with the lowest olefin molecular volume for **2a**. However, there is apparent contradiction when comparing deformation energies for **2b** and **2c**. In spite of larger molecular volume of **2c** ( $58.5 \text{ \AA}^3$ ) compared to **2b** ( $38.8 \text{ \AA}^3$ ) the deformation energy of **4b** is higher compared to **4c** (Table 1). This can be understood revising the geometry and the binding energies of **4b** and **4c**. The fact that **4b** has higher deformation energy than **4c** is explained by tighter structure of **4b** compared to **4c**

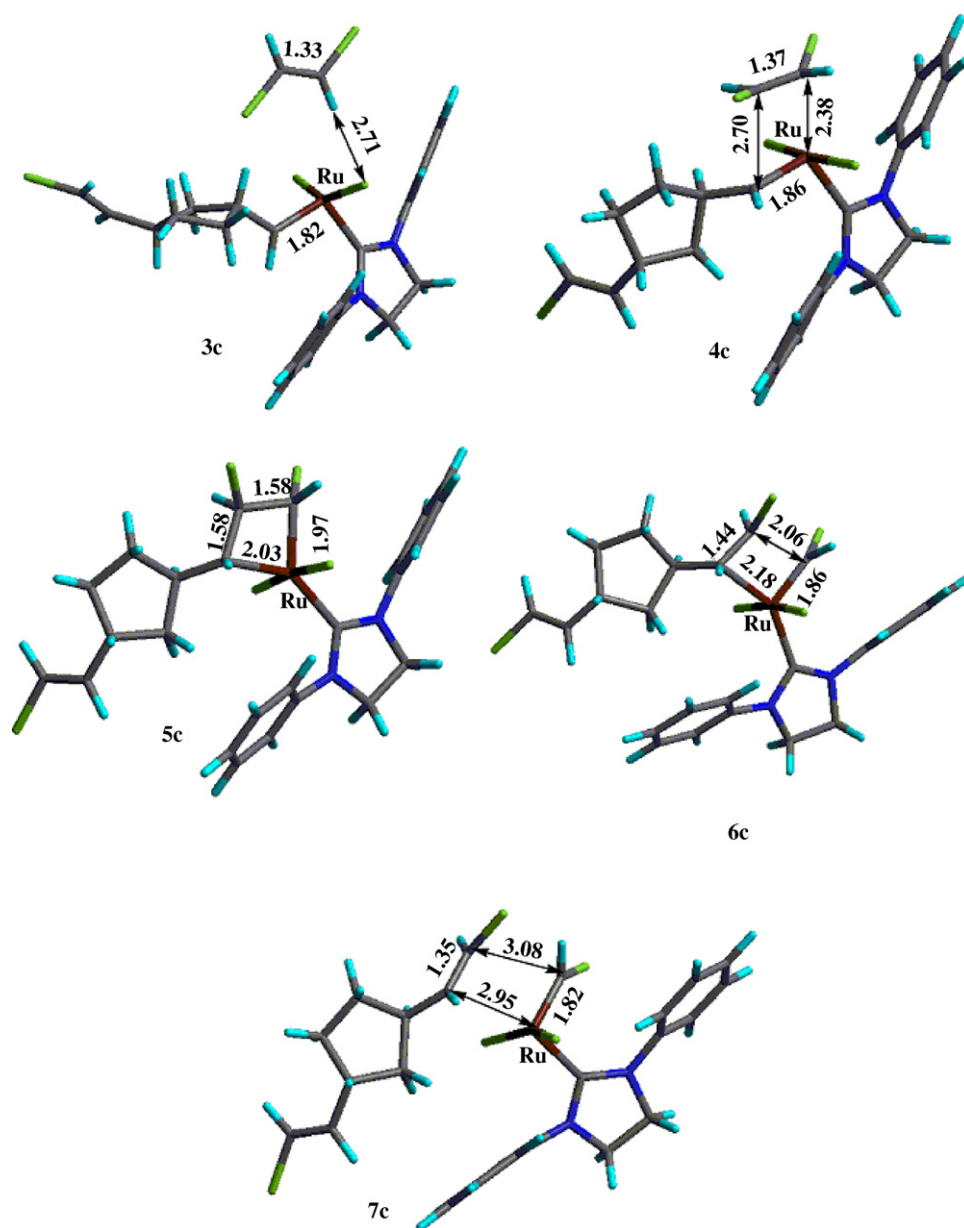


Fig. 6. B3LYP/LACVP\* optimized geometries of reaction intermediates for cross-metathesis of NB with **2c** by (**1**).

Table 1  
Deformation and binding energies (kcal/mol) calculated at B3LYP/LACVP\* level

	<b>4a</b>	<b>4b</b>	<b>4c</b>
$\Delta E_{\text{def}}^{\text{a}}$	21.2	44.3	42.2
$\Delta E_{\text{bind}}^{\text{b}}$	-24.6	-41.8	-32.1
$\Delta E_1$	18.3	24.0	23.8
$\Delta E_2$	2.9	20.3	18.4

<sup>a</sup> Calculated as  $\Delta E_1 + \Delta E_2$ , where  $\Delta E_1$  is the difference between electronic energies of **1** having equilibrium geometry and that with geometry in **4**.  $\Delta E_2$  is the difference between electronic energies of **2** having equilibrium geometry and that with geometry in **4**.

<sup>b</sup> Calculated as  $E - (E_3 + E_4)$ , where  $E$  is total electronic energy of molecules **4**,  $E_3$  and  $E_4$  are the total electronic energies of fragments **2** and **1** possessing geometries as in **4**.

and even to **4a** (Figs. 5 and 6). On the other hand, tighter geometry of **4b** is due to higher binding energy (Table 1). As the matter of fact the binding energy of **4b** is highest of all three transition states which can be understood in terms of orbital interactions. All other things being equal, the highest binding energy of an olefin to metal center is for olefin with highest HOMO and lowest LUMO to maximize donation and back donation interactions with metal. This is the case of **2b**. Together with **2a**, **2b** shares the lowest LUMO energy (0.0188 a.u.) and has highest HOMO energy (-0.2535 a.u.) which corresponds to highest binding energy (Table 1). Therefore, steric factor make the most important contribution to the activation energy of the metathesis. It is noteworthy, that strong binding results in large deformation energies increasing energy barrier as seen for **4b**. Lowest activation energies will be observed for olefins

with small molecular volume weakly interacting with metal center.

#### 4. Conclusions

The metathesis of directly halogenated olefins **2b** and **2c** by Ru-alkylidene catalyst is definitely kinetically controlled process. Thus, the low efficiency of **2c** is due to high activation energy of the process and not thermodynamics. The calculations show that the highest binding energy of an olefin to metal center is for olefin with highest HOMO and lowest LUMO to maximize donation and back donation interactions with metal. Lowest activation energy is observed for **2a** with small molecular volume weakly interacting with metal center.

#### Acknowledgment

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