Metathesis of fluorinated olefins by ruthenium alkylidene catalysts. Fluorine substituent effects on a Ru-carbene (alkylidene) complex stability: A computational study

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ABSTRACT

Cross-metathesis reaction pathways of ethylene (**2a**), *trans*-1,2-dichloro-ethylene (**2b**) and fluorinated olefins *trans*-1,2-difluoro-ethylene (**2c**) and tetrafluoro-ethylene (**2d**), with norbornene (NB) using a (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy_3)Cl_2Ru = CHPh (**I**) have been studied at B3LYP/LACVP* level of theory. The calculated ΔG of reactions for olefins **2a**, **2b**, **2c** and **2d** were of 2.5, −2.0, −11.9 and −31.6 kcal/mol, respectively. The calculations show that the natural charge at a Ru center is strongly dependent on substituent nature and can be a measure of the carbene stability. The stabilization of a metallacarbene is due to the stabilization of the metal center and not a carbene carbon itself.

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1. Introduction

Alkenyl halides where a halogen atom is directly linked to an olefin carbon remain challenging substrates for the olefin metathesis. Metathesis of halogenated olefins by a Ru-alkylidene catalyst will proceed via the formation of the ruthenium-halo carbene complex with their activity different from usual alkylidene complex [1]. The study of the metathesis mechanism of challenging substrates such as halogenated olefins is of important for the design of new catalysts tolerant to different functional groups.

Cross-metathesis of 1-chloro- and 1-bromoethylene with propylene using Re_2O_7/Al_2O_3/$SnMe_4$ [2a], ring-closing metathesis of α-halogenated dienes [2b–2f] and metathesis of 1,1-difluoroethylene [1] and β-fluorostyrene [2g] by (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)(PCy_3)Cl_2Ru = CHPh (**Ia**) are the studies on the metathesis reaction of directly halogenated olefins. Recently, we reported a computational study of ruthenium alkylidene mediated metathesis reaction pathways of chlorinated olefins where it has been shown that the steric factor is of primary importance for the metathesis reaction strongly affecting the activation energy being more important than an electronic factor [3].

Cross-metathesis of cycloolefins and their polymers (polyalkenamers) with linear olefins as chain transfer agents (CTAs) is widely used in the synthesis of products with controlled molecular weight and end functionalities (telechelics) [4]. Thus, cross-metathesis of *cis,cis*-1,5-ciclooctadiene with ethylene (ethenolysis) yields diolefins which can be used as cross-linking agents and starting compounds in the production of fine chemicals [4]. The use of halogenated olefins for the cross-metathesis would allow obtaining a great variety of novel chemicals inaccessible by other methods.

The goal of this study is to model cross-metathesis of ethylene (**2a**) and directly halogenated olefins; *trans*-1,2-dichloro-ethylene (**2b**), *trans*-1,2-difluoro-ethylene (**2c**) and tetrafluoro-ethylene (**2d**), with NB using (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy_3)Cl_2Ru = CHPh (**1**) catalyst and to evaluate the effect of halogen substituents on the Ru-alkylidene stability.

2. Computational details

All calculations were carried out with the Jaguar v 7.0 program [5]. The lowest energy conformers were located using a Monte-Carlo method as implemented in the Titan package version 1.0.5 [6] using PM3(tm) model. The lowest energy conformers were used as initial structures for the geometry optimization using Becke's three parameter functional (B3) [7] in combination with the Lee, Yang and Parr (LYP) correlation function [8] and LACVP* basis set. LACVP* basis set uses standard 6-31G* basis set for light elements and LAC pseudopotential [9] for third row and heavier elements. The molecular geometries of all calculated molecules were optimized to the global minimum at B3LYP/LACVP* level of theory. Frequency calculations were carried out to estimate the free Gibbs energy at 298.15 K and 1 atm.

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All calculations were carried out in gas phase since as it has been shown that solvation energies of similar molecules in nonpolar solvents introduce smaller error than the method itself [3]. However, to verify how salvation affects the reaction energies Poisson–Boltzman solver implemented in Jaguar v 7.0 was used to calculate solvation effect in 1,2-dichloroethane for **3b → 4b** reaction at B3LYP/LACVP* level of theory. The solvation effect changes the activation energy by only 0.53 kcal/mol that is well inside of the method error.

3. Results and discussion

Scheme 1 shows the chain transfer to **2a**, **2b**, **2c** and **2d** during the cross-metathesis of NB by Ru-alkylidene catalyst (**1**). Figs. 1–4 present the energetic profiles for these reactions and Figs. 5–8 the geometries of the intermediates. There are marked differences between these monomers in the metathesis reaction. However,

when inspecting the geometry and the binding energies of complexes **3a–d** one can observe that π-complex **3a** is the tightest one with less positive the Gibbs free binding energy. On the other hand **3b** is not a π-complex at all, the binding in this complex is due to the interaction of hydrogen of **2b** with chlorine atom of Ru-complex. This suggestion is confirmed by the analysis of the charge distribution in complex **3b** and its geometry. Thus, in **1b** and **2b** the natural charge at Cl and H atoms are of −0.53 and +0.26 e, respectively, while in complex **3b** the corresponding natural charges are of −0.54 and +0.28 e, therefore, there is a slight charge transfer from hydrogen of **2b** to chlorine atom in **3b**. 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). The distances between Ru center and olefins in **3c** and **3d** exceed 3.5 Å. Therefore, it is unlikely that an olefin will have any orbital overlap with the metal. It seems that there is effectively no interaction between olefin and metal for **3b–d**, apart from a weak electrostatic

a: R$_1$=R$_2$=H
b: R$_1$=Cl R$_2$=H
c: R$_1$=F R$_2$=H
d: R$_1$=R$_2$=F
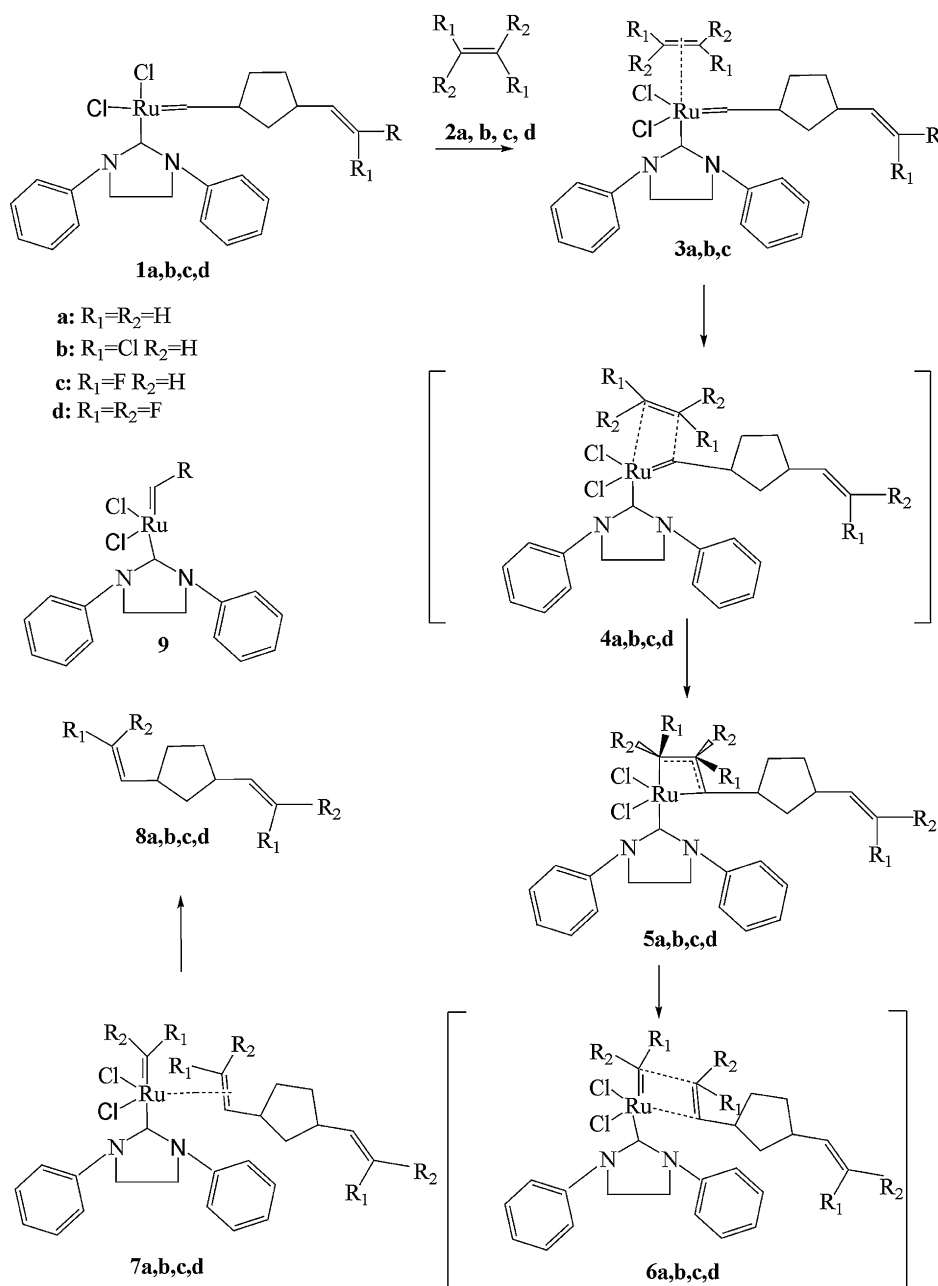
Scheme 1. Chain transfer to **2a**, **2b**, **2c** and **2d** during the cross-metathesis of NB by (**1**).
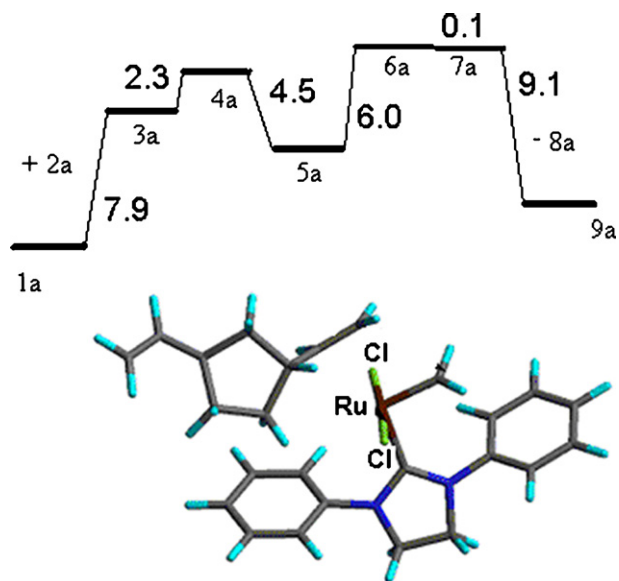
Fig. 1. The Gibbs free energy (kcal/mol) for cross-metathesis of norbornene (NB) with ethylene (**2a**) with **1** at 298.15 K and 1 atm. Structure of **7a** complex.

interaction. This electrostatic interaction can be quantifiable from the electronic binding energy (ΔE) for olefin coordination. Thus, ΔE for the olefin coordination for complexes **3b–d** are of −3.9, −1.9 and −2.9 kcal/mol, characteristic of weak interaction. Large and positive ΔG of complex formation comes from entropy loss (both translational and rotational). Thus, the translational entropies of **3b–d** complex formation are of −39.1, −38.1 and −39.2 cal/mol while for the rotational entropy −22.7, −21.7 and −22.9 cal/mol.

The located transition states **4a–d** and **6a–d** (Figs. 5–8) correspond to formation of C–C bonds. As seen from the energy profiles the transition states **6a** and **4b–d** determine the reaction kinetics. The kinetic control of the reactions under the study follows from the fact that the metathesis of **2b**, **2c** and **2d** shows negative ΔG (ΔG = −2.0, −11.9 and −31.9 kcal/mol for **2b**, **2c** and **2d**, respectively) while ethylene metathesis presents slightly positive energy (ΔG = 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
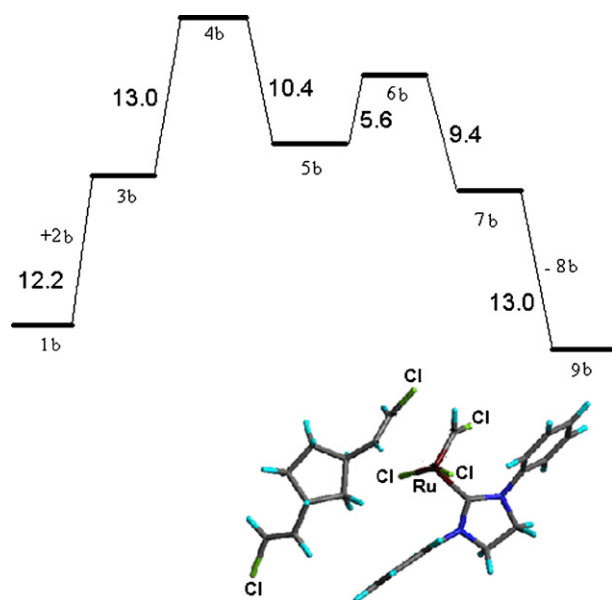

Fig. 2. The Gibbs free energy (kcal/mol) for cross-metathesis of norbornene (NB) with trans-dichloroethylene (**2b**) with **1** at 298.15 K and 1 atm. Structure of **7b** complex.
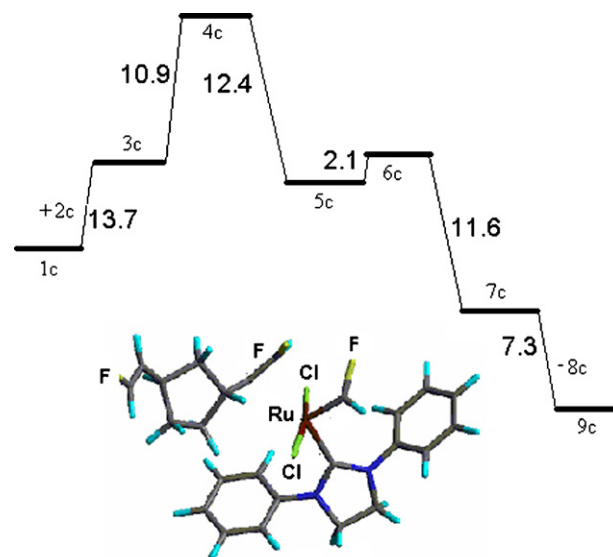

Fig. 3. The Gibbs free energy (kcal/mol) for cross-metathesis of norbornene (NB) with trans-difluorethylene (**2c**) with **1** at 298.15 K and 1 atm. Structure of **7c** complex.

Gibbs free activation energies) is highest for **2b** metathesis (25.1 kcal/mol) as compared to **2c** (17.3 kcal/mol), **2d** (19.8 kcal/mol) and **2a** (10.2 kcal/mol). The activation energies reflect the steric hindrances related to the molecular volume of the olefin. Thus, molecular volumes of **2a**, **2b**, **2c** and **2d** are of 32.8, 61.5, 39.4 and 45.6 Å3, correlating with calculated the free Gibbs activation energies. It is noteworthy that in the case of transition states **6a–d** (Figs. 5–8) the most negative ΔG of the reaction corresponds to the earliest transition state. This phenomenon is reflecting the relative stability of carbene complexes **9a–d** that increases significantly from **9a** to **9d**. The relative stability of carbene complex **9a–d** also affects the activation energy of $5 \rightarrow 7$ transformation (Figs. 1–4). Thus, in case of the metathesis **2a**, the transition state **6a** is the highest stationary point on the potential energy surface, while in the case of olefin **2d** the transition state **6d** is barely detectable laying only 0.3 kcal/mol above the metallacyclobutene complex **5d**.

It is worth noting that ROMP of cycloolefins in the presence of **2b** as a charge transfer agent (CTA) does not result in control over molecular weight of the polymer whereas the same reaction yields α, ω-diolefins in the presence of **2a** which can be used as cross-linking agents and starting compounds in the production of fine chemicals [6]. High activation energy found for **2b** metathesis compared to **2a** results in prevent **2b** to be a good chain transfer agent.

Table 1 presents the ΔG of the studied metathesis reactions. Thus, the difference in ΔG of metathesis of **2a** (ΔG = 2.5 kcal/mol), **2b** (ΔG = −2.0 kcal/mol), **2c** (ΔG = −11.9 kcal/mol) and **2d** (ΔG = −31.6 kcal/mol) is easy to understand taking into account strong +M effect of fluorine atoms in complexes **9c** and **9d** compared to chlorine in **9b**.

Table 1
Natural charges at carbene carbon (Q_1), Ru center (Q_2), occupations of $2p_z$ orbital of carbene carbon (P_1), $4d_{xz}$ and $4d_{yz}$ orbitals of Ru center (P_2 and P_3) of metallacarbene complexes **9a–d** and **1Ph**. The free Gibbs transformation energies for $1 + 2 \rightarrow 8 + 9$ reactions (ΔG) (kcal/mol).

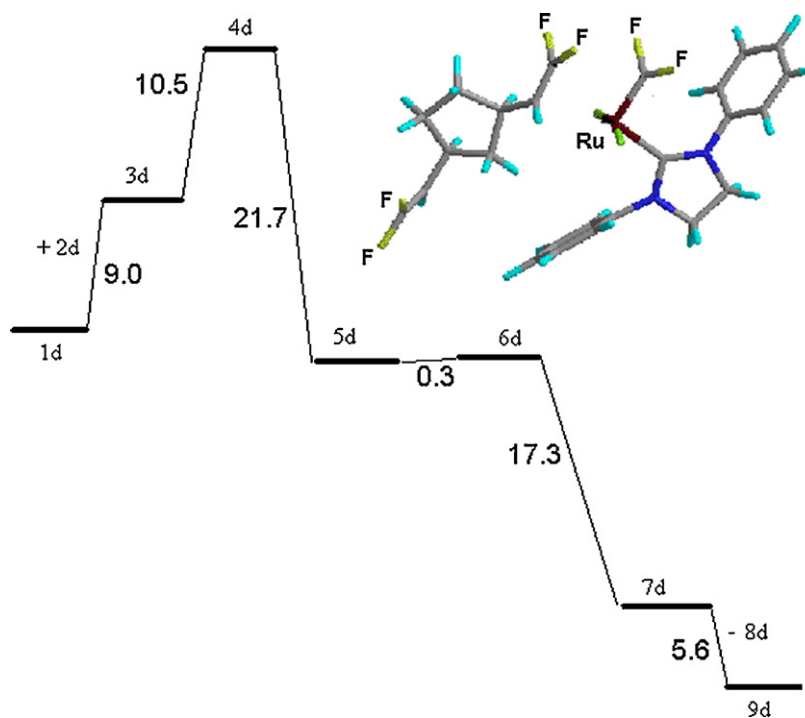| Complex	Q_1	Q_2	P_1	P_2	P_3	ΔG
9a	−0.25	0.40	0.83	1.53	1.26	2.5
9b	−0.15	0.41	0.86	1.81	1.52	−2.0
9c	0.35	0.34	0.95	1.16	1.71	−11.9
9d	0.86	0.30	0.66	1.83	1.68	−31.6
1Ph	−0.04	0.39	0.93	1.58	1.35	0.24

Fig. 4. The Gibbs free energy (kcal/mol) for cross-metathesis of norbornene (NB) with tetrafluorethylene (**2d**) with **1** at 298.15 K and 1 atm. Structure of **7d** complex.
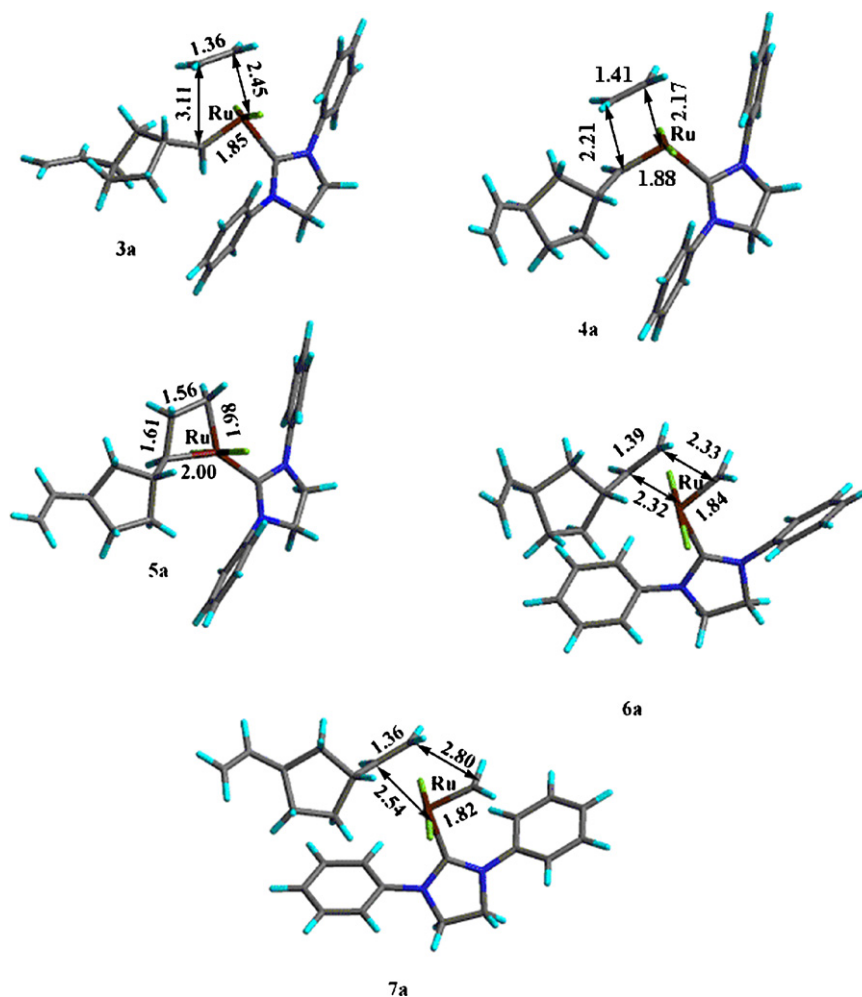

Fig. 5. B3LYP/LACVP* optimized geometries of reaction intermediates for cross-metathesis of NB with ethylene (**2a**) by (**1**). The distances are in Å.

Fig. 9 shows the interaction scheme of atomic orbitals in carbene complexes **9b–d**. Since fluorine and chlorine atoms have lone pairs they can interact with orbitals of the complex having appropriate symmetry in **9b**, **9c** and **9d**. This kind of interaction is not impossible for **9a**. As seen from Table 1 the ΔG of the metathesis reactions become more negative from **a** to **d** reflecting the increasing stability of ruthenium complexes **9**. At the first sight there is a contradiction between natural charges calculated for carbene carbon and the ability of sharing p-electron density by substituents. The most negative charge is observed for **9a** and the most positive is for **9d**. This contradiction is due to the fact that halogens manifest both positive mesomeric (+M) and negative inductive (−I) effects. Thus, strong −I effect of fluorine decreases the total electron density at a carbene atom in spite of the fact that fluorine is the best p-donor due to effective 2p–2p interaction between p_z orbitals of fluorine and carbon atom. Chlorine shows both weaker +M and −I effects. As a result, the natural charge at a carbene carbon in **9b** is more negative compared to **9c**. This conclusion can be verified examining natural occupations of the correspond-

ing atomic orbitals. As seen from Table 1 the occupation of p_z orbital of carbene atom (Fig. 9) is highest for **9c** and lowest for **9a** in accordance with p-donating ability of substituents. $2p_z$ orbital of carbene is overlapped with $4d_{yz}$ orbital of Ru center as seen from the Fig. 9. Natural occupation of $4d_{yz}$ orbital of a Ru depends strongly on the nature of substituent at carbene center. As seen, the highest occupation is for **9c** while the lowest is for **9a**. Therefore, one can conclude that there is p-electron density transfer from halogen atoms to a Ru center through $2p_z$ orbital of a carbene, thus stabilizing the positively charged Ru atom. As seen from Table 1 the natural charge at Ru atom is less positive for **9d** proving the hypothesis. Therefore, the stability of the fluorine containing metallacarbene complexes can be explained by the stabilization of $4d_{yz}$ Ru center by 2p electrons of fluorine through $2p_z$ orbital of carbene. This process is schematically shown in Fig. 9. The effective stabilization is only possible when p-electrons are located at 2p orbital when strong overlapping with 2p orbital of carbine carbon takes place. In case of **9b** p-electrons are located at 3p orbital of chlorine atom which drastically decreases the importance of this mechanism.
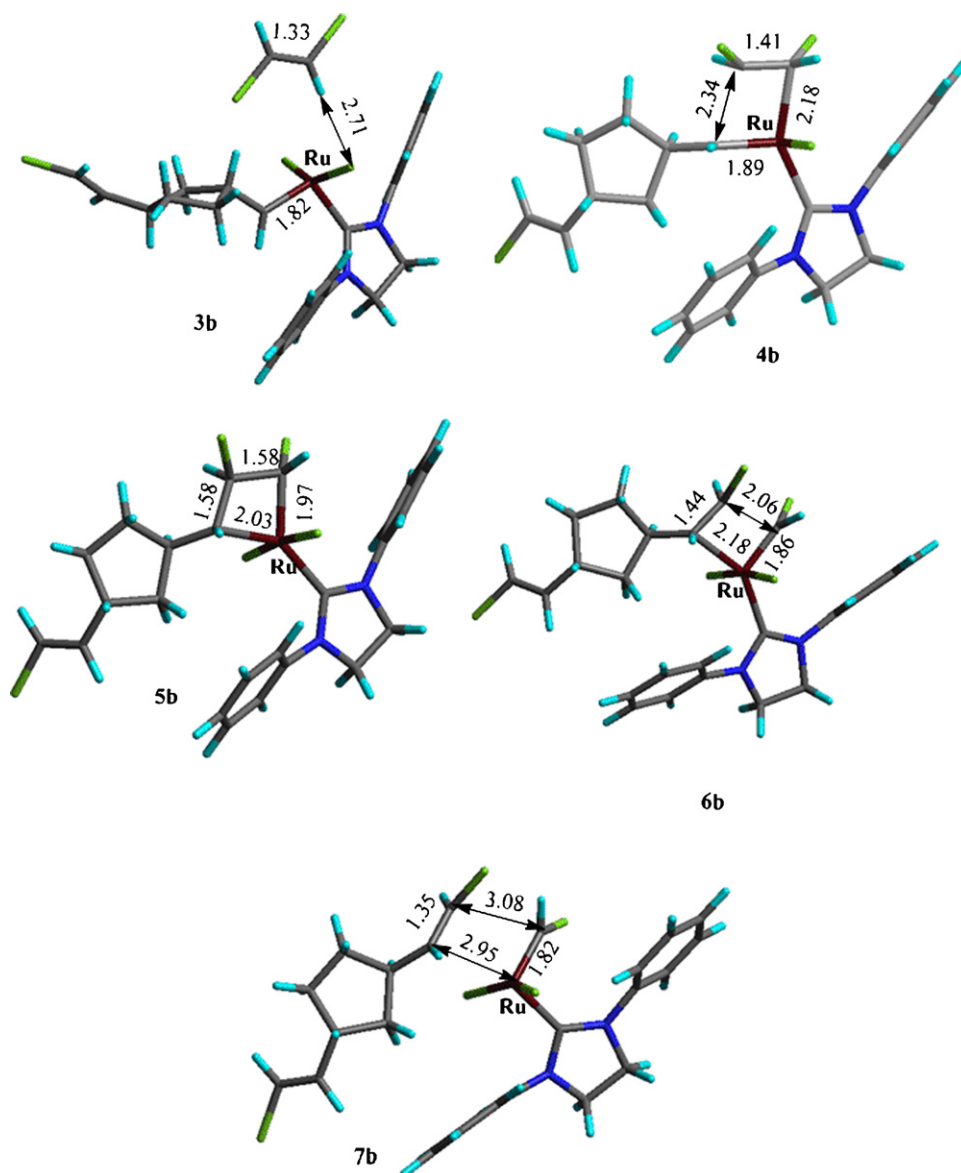

Fig. 6. B3LYP/LACVP* optimized geometries of reaction intermediates for cross-metathesis of NB with *trans*-dichloroethylene (**2b**) by (**1**). The distances are in Å.
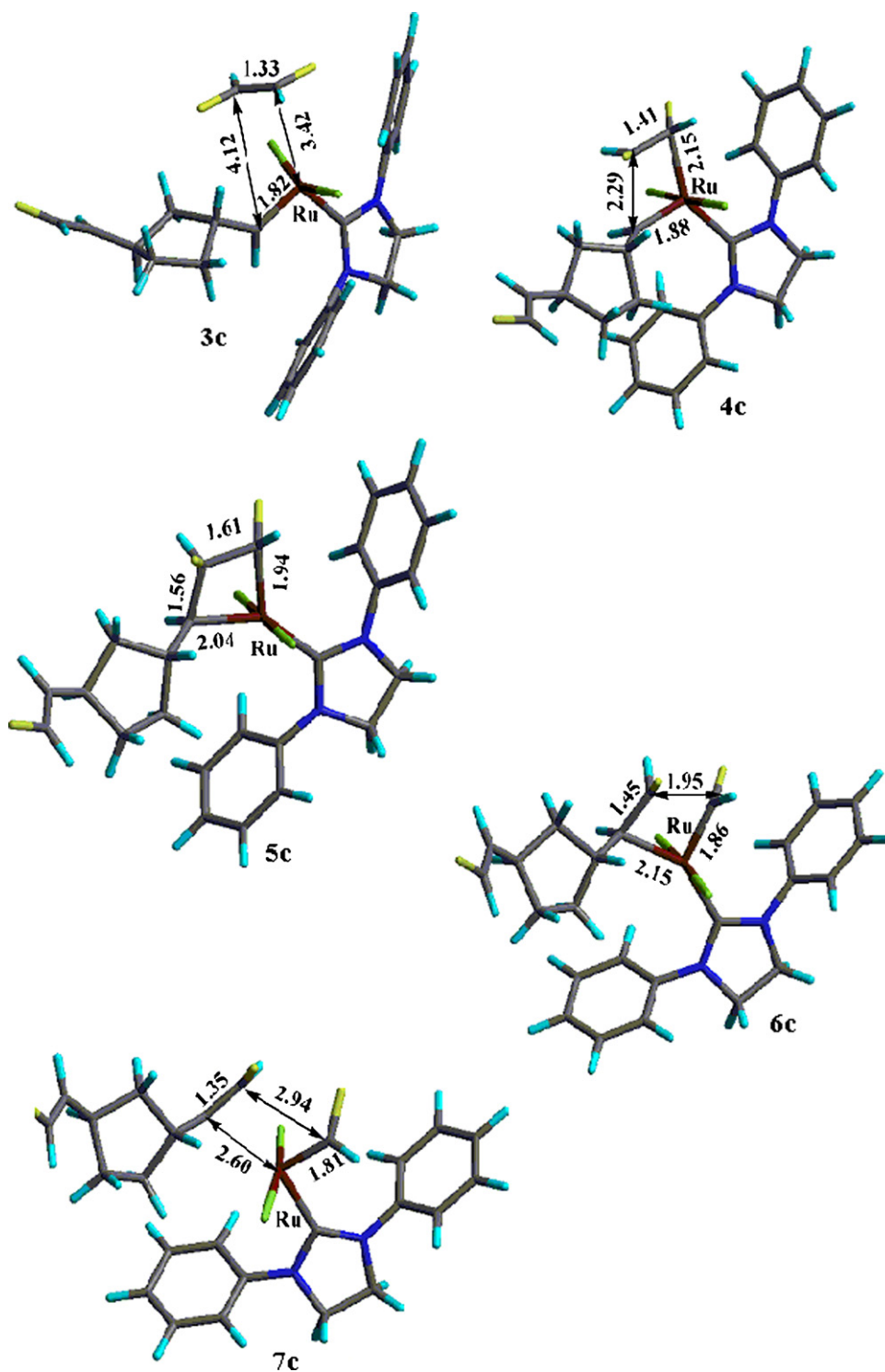
Fig. 7. B3LYP/LACVP* optimized geometries of reaction intermediates for cross-metathesis of NB with *trans*-difluorethylene (**2c**) by (**1**). The distances are in Å.

Ruthenium difluorocarbene complex **9d** following the trend found for **9c** has the lowest positive charge at Ru (+0.30) thus, being the most stable out all studied carbenes (Table 1). The stable ruthenium difluorocarbene complex has been synthesized via metathesis of 1,1-difluoroethylene using catalyst (**Ia**) [2]. However, the mechanism of stabilization must be different from that of **9c**, since the occupation of $4d_{yz}$ of Ru atom is similar for **9c** and **9d** complexes. We believe that additional stabilization of **9d** takes place through the direct interaction of p_z orbital of second fluorine

and $4d_{xz}$ orbital of a Ru as shown in Fig. 9. The viability of the proposed mechanism is confirmed by the fact that the occupation of $4d_{xz}$ orbital increases from 1.16 for **9c** to 1.83 to **9d**. It is noteworthy that apart from electronic factors, steric factors are of importance for the stabilization of a Ru-carbene. Thus, in case of phenylcarbene complex (**1Ph**) 2p orbitals of benzene ring are effective donors to stabilize the Ru center, however, as seen from Table 1 the charge at a Ru center is similar to that of a non-stabilized methylidene **9a**. The explanation of this phenomenon is
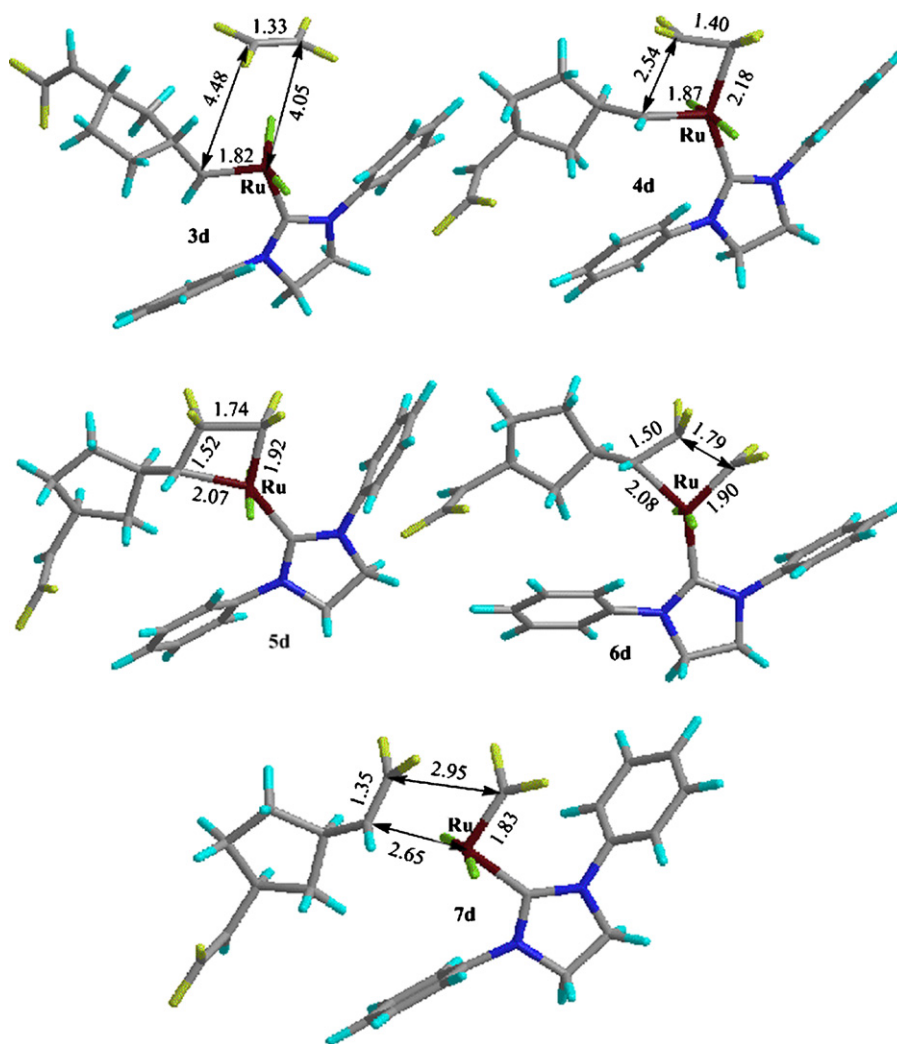
Fig. 8. B3LYP/LACVP* optimized geometries of reaction intermediates for cross-metathesis of NB with tetrafluorethylene (**2d**) by (**1**). The distances are in Å.
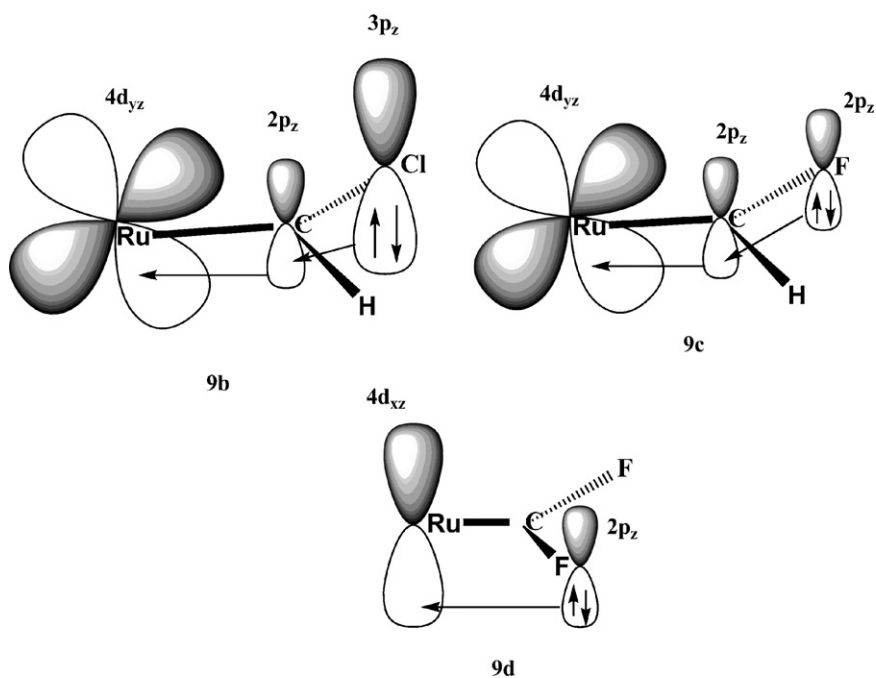

Fig. 9. The interaction scheme of atomic orbitals in carbene complexes **9b–d**.

that due to the fact that transfer of p-electron density from phenyl ring of **1Ph** destroys the aromaticity. Additional point to the mention is that the steric hindrances impede the parallel alignment of 2p orbital of carbene and 2p orbitals of a benzene ring (dihedral between Ph and CH_2 is of $15°$ decreasing the efficiency of the orbital overlap).

As seen from Table 1 the natural charge at a Ru center can be a measure of carbene stability. The stabilization of metallacarbene is due to the stabilization of a metal center and not a carbene carbon. As can be seen from the data presented above the matathesis of halogenated olefins leads to the formation of stable ruthenium-halo carbene complex slowing down the reaction with participation of these complexes. This effect is moderate for chlorine atoms but becomes very strong for fluorine substituents.

4. Conclusions

The metathesis of halogenated olefins is kinetically controlled process where steric factor contributes the most to the reaction barrier as follows from the found correlation between the molecular volume of an olefin and the free activation energy of the metathesis. The stability of carbene complexes **9a–d** affects not only the reaction but also the activation energy. The free Gibbs activation energy of the transformation of metallacarbene complexes **5a–d** to π-complexes **7a–d** decreases with stability of carbene complex **9**. The extraordinary stability of carbene complexes **9c** and **9d** and somewhat **9b** is related to the stabilization of Ru center by lone electron pairs of halogen atoms.

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