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# Difluoroethylene as a chain transfer agent during ring-opening metathesis polymerization (ROMP) of norbornene by a ruthenium alkylidene complex: A computational study

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## Abstract

The polynorbornene chain transfer reaction pathways to ethylene (**2a**), *trans*-1,2-difluoroethylene (**2b**) and *trans*-1,4-dichloro-2-butene (**2c**) by (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy$_3$)Cl$_2$Ru=CHPh (**I**) have been studied at B3LYP/LACVP* level of theory. The calculations show that the free Gibbs activation energy of metathesis reaction is dependent on the volume of substituents directly linked to the double bond of an olefin. Highest activation energy is observed for **2c** with highest molecular volume. The activation energy is lower for **2a** with small molecular volume. Compared to **2a** and **2c**, fluorinated olefin **2b** binds more strongly to the 14 electron Ru-alkylidene catalyst to form tighter transition state. Therefore, sterical factor is the most important contribution to the activation energy for Ru-alkylidene mediated olefin metathesis.
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## 1. Introduction

The advent of highly active ruthenium alkylidene catalysts coordinated with N-heterocyclic carbene ligands opens 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$_2$O$_7$/Al$_2$O$_3$/SnMe$_4$ catalyst [2], the cross-metathesis of nonafluoro-1-hexene with terminal olefin [1a] and the metathesis of vinyl-*gem*-difluorocyclopropane derivatives [3] by (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (PCy$_3$)Cl$_2$Ru=CHPh (**I**) are the only known publications on the topic. Recently, we reported a density functional study of ruthenium alky-

lidene mediated metathesis of chlorinated olefins [4] where we show the importance of steric factor for Ru mediated metathesis of olefins. Computational studies of conformational preferences in the metathesis were also reported by other researches [5]. 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. To date, the cross-metathesis of 1-chloro- and 1-bromoethylene with propylene using Re$_2$O$_7$/Al$_2$O$_3$/SnMe$_4$ [2a] and metathesis of 1,1-difluoro-ethylene [6] by catalyst (**I**) are the only reports on the metathesis of directly halogenated olefins.

The ring-opening metathesis polymerization (ROMP) of cycloolefins in the presence of functionalized olefins as chain transfer agents (CTAs) is widely used for the synthesis of telechelic polymers [7]. Telechelics have found a wide demand as intermediates in the synthesis of block copolymers, polymeric networks and as cross-linking agents to

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enhance thermal and mechanical properties of materials [8].

The goal of this study is to model cross-metathesis reaction pathways of NB with ethylene (**2a**), *trans*-1,2-difluoro-ethylene (**2b**) and *trans*-1,4-dichloro-2-butene (**2c**) using (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy$_3$)-Cl$_2$Ru=CHPh (**I**).

## 2. Computational methods

All calculations were carried out with the JAGUAR v 6.0 program [9]. The lowest energy conformers were located using a Monte-Carlo method as implemented in the TITAN package version 1.0.5 [10] using PM3(tm) method. Monte-Carlo method is merged into a single simulated-annealing algorithm. This allows a uniform suite of tools to be used on systems with and without rings. For each structure conformational search was run several times until now new lowest energy structure had been located. The initial temperature was set to 5000 K. The number of Monte-Carlo steps is determined by program algorithm depending on number of atoms in molecule. The lowest energy conformers were used as initial structures for the geometry optimization using Becke's three parameter functional (B3) [11] in combination with the Lee, Yang and Parr (LYP) correlation functional [12] and LACVP* basis set. LACVP* basis set uses standard 6-31G* basis set for light elements and LAC pseudopotential [13] for third row and heavier elements. The molecular geometries of all calculated molecules were optimized to a global minimum at B3LYP/LACVP* level of theory. Frequency calculations were run for all structures to make sure that a transition state (one imaginary mode) or minimum (no imaginary modes) is located and to reach zero point energy (ZPE) correction and thermodynamic properties which were evaluated at 298.15 K. 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 [4]. Molecular volumes were calculated as solvent excluded volume using Conolly [14] scheme as implemented in Chem3D version 7.0 and the probe radio set to zero. VDW radii of 1.135 Å for hydrogen, 1.293 Å for fluorine, 1.688 Å for chlorine 1.431 Å for sp$^3$ and 1.462 Å for sp$^2$ carbons were employed. In case of olefin **2c** all atoms not linked directly to double bond were excluded from the calculations. B3LYP/LACVP* optimized structures were used for calculation of molecular volumes.

## 3. Results and discussion

A number of experimental [15,16] and theoretical [17] works show that for ruthenium complexes with general formula L(PR$_3$)(X)$_2$Ru=CHR$^1$ (R = Cy, Cp and Ph, X = Cl, Br and I, L = N-heterocyclic carbene ligand, NHC) the initiation occurs by dissociative substitution of a phosphine ligand (PR$_3$) with olefin substrate, giving a monoligand complex.

Scheme 1 shows chain transfer reaction pathways from ring-opened NB to **2a**, **2b** and **2c** by Ru-alkylidene catalyst (**1**). As seen the cross-metathesis involves the complex formation between the catalytic center and olefin (intermediate **3**) following by the formation of metallacyclobutane intermediate **5**. The last step of the process is the dissociation of complex **7** to produce new carbene complex and a new olefin (**9** and **8**). Figs. 1–3 present the energetic profiles for these reactions. There are marked differences between **2a** and **2b** (**2c**) in the metathesis reaction. When inspecting geometry (Figs. 4–6) and the binding energies of complexes **3a**–**c** one can observe that π-complex **3a** is the tightest one. Complex **3a** is tighter compared to **3b** and **3c**, however, the geometry of complexes **3b,c** is similar to **3a** suggesting interaction between π-electron of **2b** and **2c** and empty d-orbitals of Ru-atom. The π-complex **3c** is quite loose compared to **3a** and **3b**. This could be explained by steric hindrances of two chloromethyl groups. Less bulky fluorine atoms of **2b** allow better fitting between π 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.

The located transition states **4a**–**c** and **6a**–**c** (Figs. 4–6) correspond to the rotation of carbene groups. Interestingly, that the structure of **2b** in a transition state (**4b**) is tighter than that of **2a** and **2c** (Figs. 4–6). Tighter geometry of **4b** is due to higher binding energy. The calculated binding energies for **2a**, **2b** and **2c** in transition states were −24.6, −41.8 and −9.6 kcal/mol, respectively. The binding energy was calculated as the difference between total electronic energy of a transition state and the sum of energies of olefin **2** and catalytical complex **1** in geometry of transition state. As seen the binding energy of **4b** is highest of all three transition states which can be understood in terms of orbital interaction of olefins. 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. HOMO energies for **2a**, **2b** and **2c**, calculated at B3LYP/6-31G* level are of −0.2666, −0.2535 and −0.2772 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 −0.0379 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), and **2b** (10.3 eV), which are in line with calculated HOMO energies [18].

The metathesis of **2b** shows negative $\Delta G = -11.9$ kcal/mol while **2a** and **2c** metathesis presents positive energies ($\Delta G = 2.5$ and 4.5 kcal/mol for **2a** and **2c**, respectively). The $\Delta G$ of the studied metathesis reaction can be explained in terms of ruthenium complex stability (**9a**–**c**). When fluorine is connected directly to carbene, the effect of electron-donating of lonely pair to the catalytical complex through carbene carbon dominates thus stabilizing carbene complex

**a:** R=H
**b:** R=F
**c:** R=CH₂Cl
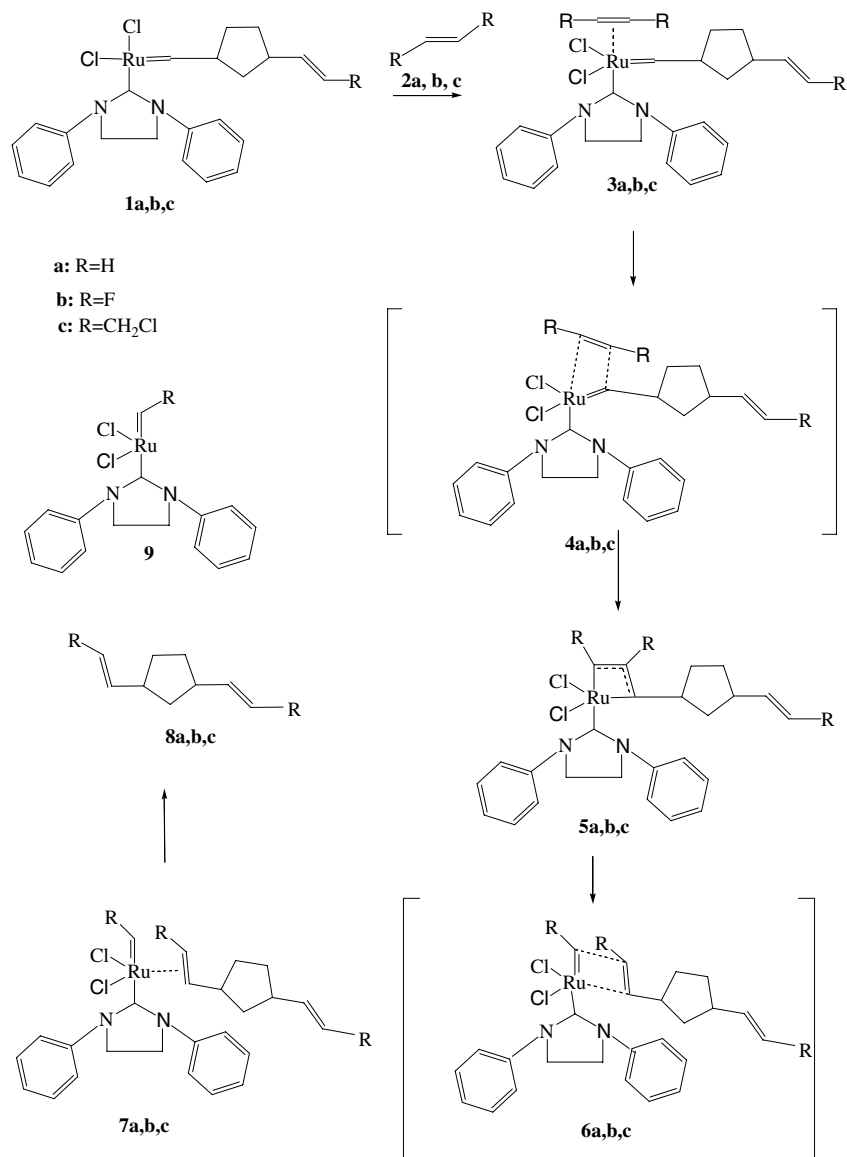
Scheme 1. Chain transfer to **2a**, **2b** and **2c** during the cross-metathesis of NB by **1**.
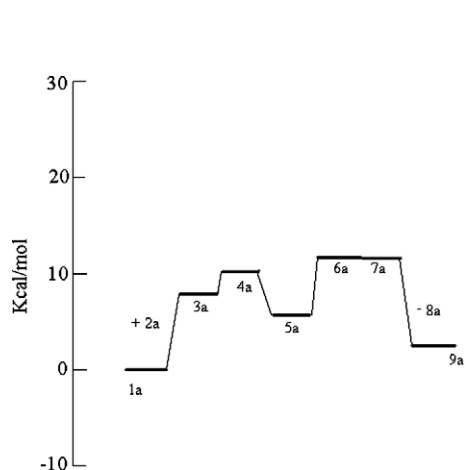


Fig. 1. The Gibbs free energy profile for cross-metathesis of NB with **2a** by **1**.
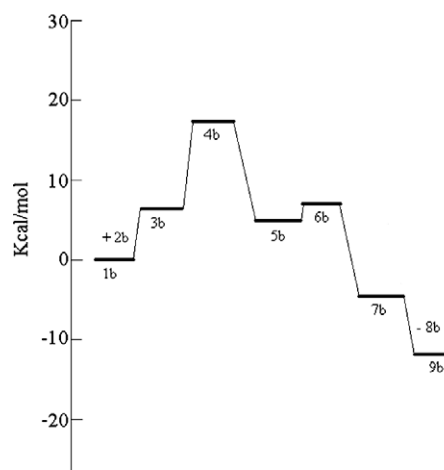
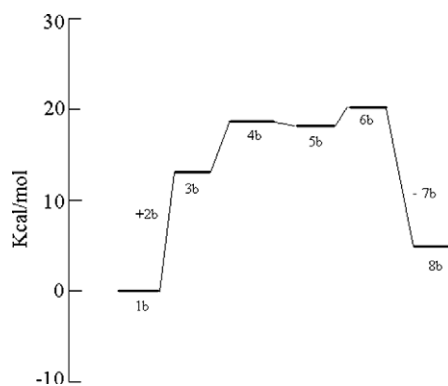Fig. 2. The Gibbs free energy profile for cross-metathesis of NB with **2b** by **1**.

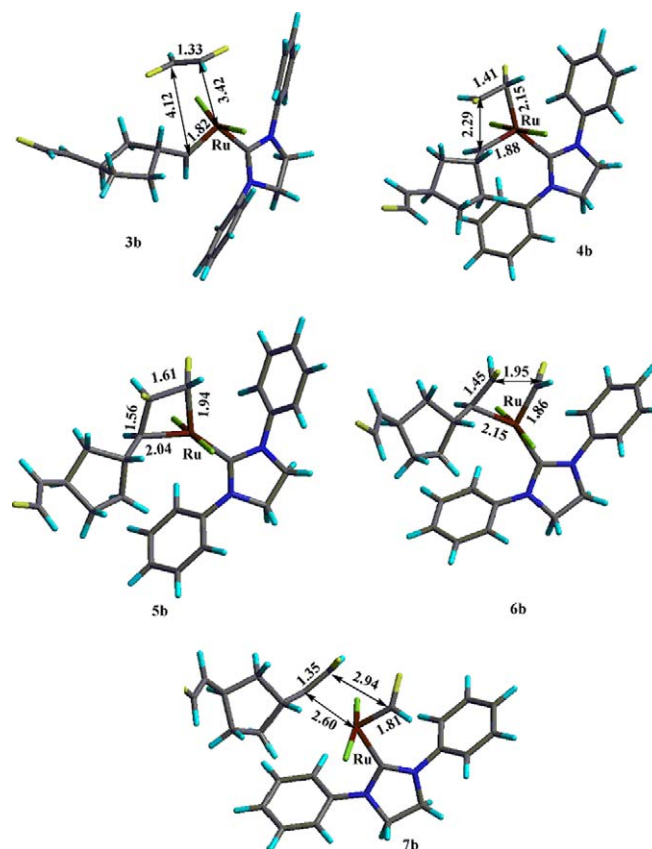Fig. 3. The Gibbs free energy profile for cross-metathesis of NB with **2c** by **1**.



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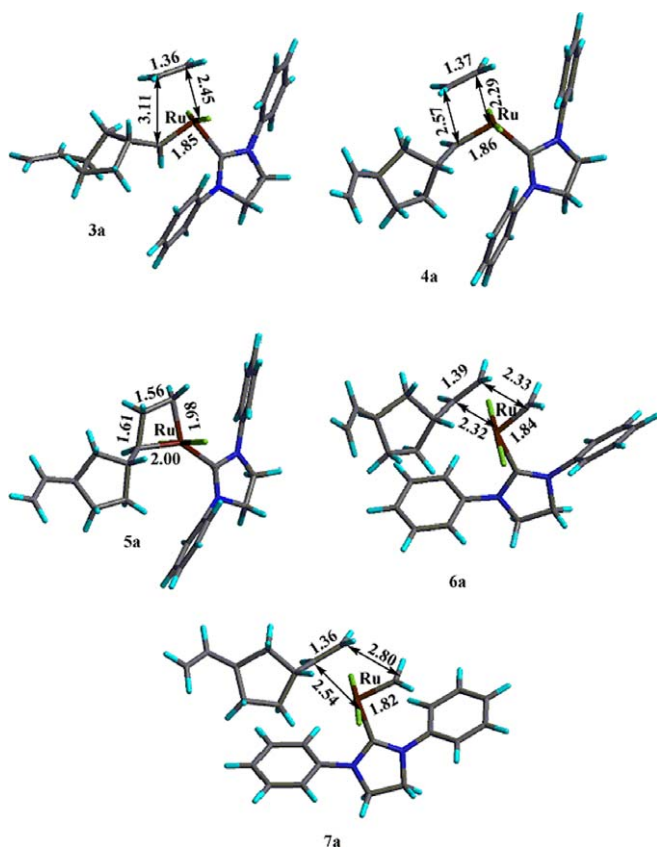


Fig. 5. B3LYP/LACVP* optimized geometries of reaction intermediates for cross-metathesis of NB with **2b** by **1**.

($\Delta G = -11.9$ kcal/mol for **2b**). It is worth noting that the stable ruthenium difluorocarbene complex has been synthesized via metathesis of 1,1-difluoroethylene by catalyst (**I**) [6]. In case of **9c** the only effect of chlorine is inductive, withdrawing electrons through σ-bonds, thus destabilizing carbene fragment since interaction of 3p electrons of chlorine with 2p orbital of carbon is far less effective compared to 2p–2p interactions in case of fluorine On the other hand, the total Gibbs activation free energy (as a sum of the complex Gibbs free energy formation and the free Gibbs activa-

tion energy) is highest for **2c** metathesis (18.7 kcal/mol) as compared to **2b** (17.3 kcal/mol) and ethylene (10.2 kcal/mol). As followed from Curtin–Hammett principle [19] when the relevant activation energy is one measured from the lowest preceding point on the potential energy surface, not necessarily the immediately preceding intermediate. It is important to note that ROMP of NB and other cycloolefins in the presence of **2a** and **2c** as CTAs yields polymers with controlled molecular weights and end functionalities (telechelics) [7,20].

As it has been shown earlier the rate limiting step for olefin metathesis reaction is the dissociation of π-complexes is not metathesis itself [21]. This statement agrees well with the dissociation energies of ethylene π-complexes for catalysts **1a** which is the lowest among $Cl_2(PCy_3)$-$(C_2H_4)Ru$=CHR (**II**) [17c] and $(CO)_4(C_2H_4)W$=CHR (**III**) [21]. Catalyst **1a**, the most active one has the lowest dissociation energy for ethylene π-complexes of (2–5 kcal/mol) while the catalyst **III** showing the lowest activity presents binding energies of (20 kcal/mol). Catalyst **II** showing intermediate activity has ethylene complexation energies of some 7–8 kcal/mol.

To obtain deeper insight into the difference in the reactivity between olefins the global electrophilicity indexes (ω) and molecular volumes of **2a**–**c** were estimated. The electrophilicity indexes (ω) were calculated according to [22]
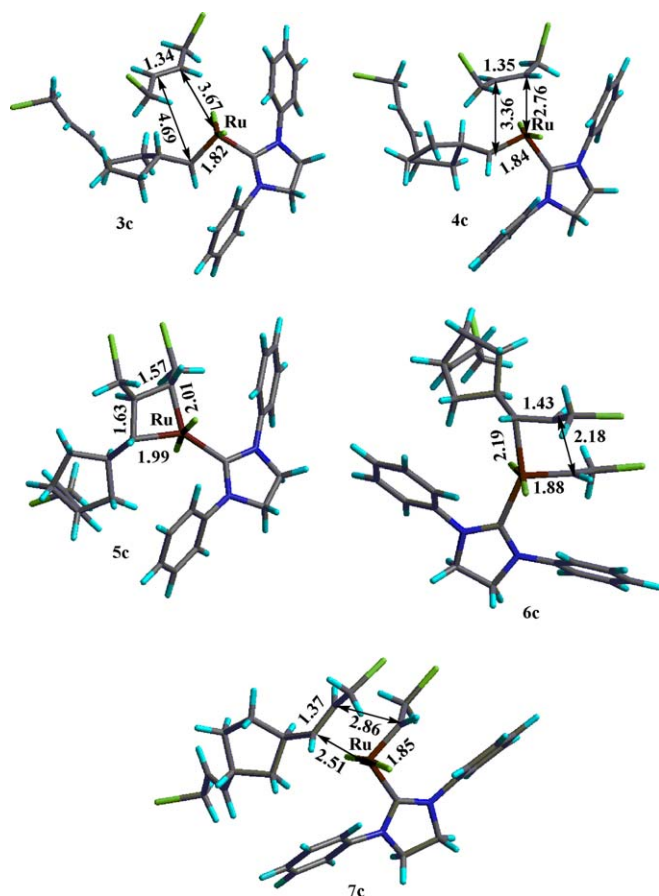
Fig. 6. B3LYP/LACVP* optimized geometries of reaction intermediates for cross-metathesis of NB with **2c** by **1**.

as $\mu^2/2\eta$, where $\mu$ is chemical potential approximated as $-(IP + EA)/2$ and $\eta$ is chemical hardness approached as $(IP - EA)$ where IP and EA are ionization potential and electron affinity, respectively. IP and EA were approximated as –HOMO and –LUMO energies, at B3LYP/LACVP* level of theory, respectively. Although, different functionals give different values of LUMO and HOMO; only absolute values of $\omega$ will change that does not affect the relative order of electrophilicity. Thus, **2a**, **2b** and **2c** show $\omega$ of 0.027, 0.025 and 0.052 a.u. Molecular volumes (only including carbons forming a double bond and the four atoms directly linked to them) were of 31.6, 37.5 and 43.6 Å$^3$ for **2a**, **2b** and **2c**, respectively. Therefore, the most electrophilic (electron deficient) olefin is **2c**, followed by **2a** and **2b**. The most nucleophilic olefin is **2b** due to strong $\pi$-electron-donating effect which is much stronger than $\sigma$-electron-withdrawing one. As seen from Figs. 1–3 there is no correlation between $\omega$ and the Gibbs free activation energy ($G^\#$) of the metathesis reaction is observed. On the other hand, there is a clear correlation between molecular volume of olefin and $G^\#$ (Figs. 1–3). 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.

## 4. Conclusions

The calculated Gibbs free activation energies for **2a**, **2b** and **2c** correlate with molecular their volumes when only atoms directly linked to the double bond are taken into account. Highest activation energy of **2c** is due to highest molecular volume. The steric factor is of primary importance for Ru-alkylidene mediated metathesis reaction strongly affecting activation energy. The extraordinary stability of fluorine-containing carbene complex is due to strong $\pi$-electron-donating effect of fluorine atom.

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