

Density Functional Theory Study of Ruthenium Alkylidene Mediated Cross-Metathesis Reaction Pathways between Cycloolefins and Halogenated Olefins

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The reaction pathways for the ring-opening cross metathesis of norbornene (NB) with ethylene, *trans*-1,4-dichloro-2-butene (**2b**), and *trans*-1,2-dichloroethylene (**2c**) using (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy₃)Cl₂Ru=CHPh (**I**) have been studied at the B3LYP/LACVP* level of theory. It has been shown that the low efficiency of **2c** as a chain transfer agent (CTA) is due to the high activation energy of the process. The steric factor is of primary importance for Ru alkylidene mediated metathesis reactions, strongly affecting the activation energy, these being more important than electronic factors. Steric effects produced by the chlorine atom directly linked to the double bond contribute most to the overall steric effects.

Introduction

The development of highly active metal alkylidene catalysts opens vast opportunities in olefin metathesis and their application to well-defined product synthesis.¹ Thus, using the ruthenium alkylidene complexes and appropriate olefins as CTAs, norbornene oligomers with controlled molecular weights and end groups have been obtained via ring-opening metathesis polymerization (ROMP) of highly strained norbornene (NB) and metathesis degradation of polynorbornene (PNB).^{2,3} The recent generation of ruthenium alkylidene catalysts coordinated with N-heterocyclic carbene ligands makes it possible to metathesize challenging olefins with sterically hindered or electronically deactivating ester and amide groups.⁴ For example, halogenated olefins are challenging, due to the presence of the electron-withdrawing groups, and few examples of their metathesis exist. Thus, to our knowledge the metathesis of allyl chloride and allyl bromide using the heterogeneous Re₂O₇/Al₂O₃/SnMe₄ catalyst,⁵ the cross-metathesis of nonafluoro-1-hexene with terminal olefin,^{4a} and the metathesis of vinyl-*gem*-difluorocyclopropane derivatives⁶ by (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)-(PCy₃)Cl₂Ru=CHPh (**I**) are all of the known publications. It is worth noting that particularly interesting substrates for olefin metathesis are the directly halogenated olefins. In this case, the metathesis will proceed

via the formation of a ruthenium halo carbene complex which is different from the usual alkylidene complex. To date, the cross-metathesis of 1-chloro- and 1-bromoethylene with propylene using Re₂O₇/Al₂O₃/SnMe₄^{5a} and the metathesis of 1,1-difluoroethylene⁷ by catalyst **I** constitute all of the reports on the metathesis of directly halogenated olefins.

The mechanism of ruthenium alkylidene catalyzed olefin metathesis has recently been a subject of intense experimental^{8,9} and theoretical¹⁰ investigations. These results clearly indicate that for the ruthenium complexes with general formula L(PR₃)(X)₂Ru=CHR¹ (R = Cy, Cp, Ph, X = Cl, Br, I, L = N-heterocyclic carbene ligand (NHC)) initiation occurs by dissociative substitution of a phosphine ligand (PR₃) with olefin substrate, giving a monoligand complex (Scheme 1).

The goal of this study is to model chain transfer reaction pathways for the cross-metathesis of NB with ethylene and halogenated olefins *trans*-1,4-dichloro-2-butene (**2b**) and *trans*-1,2-dichloroethylene

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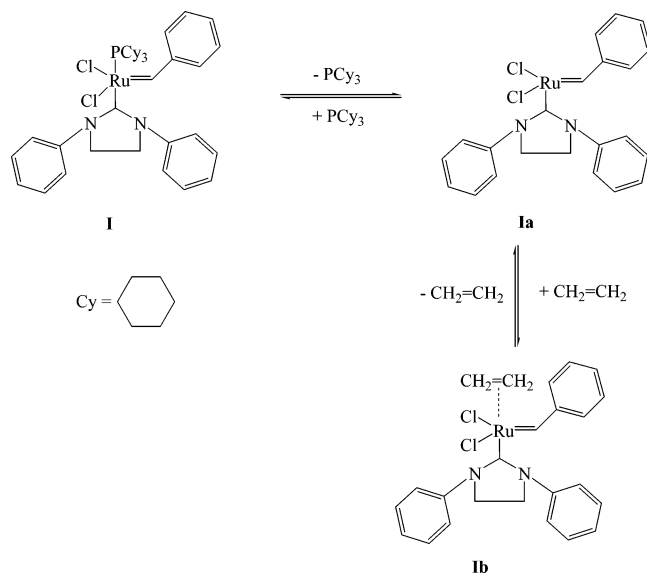
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Scheme 1. Dissociation Pathway of the Ru Alkylidene Catalyst 1

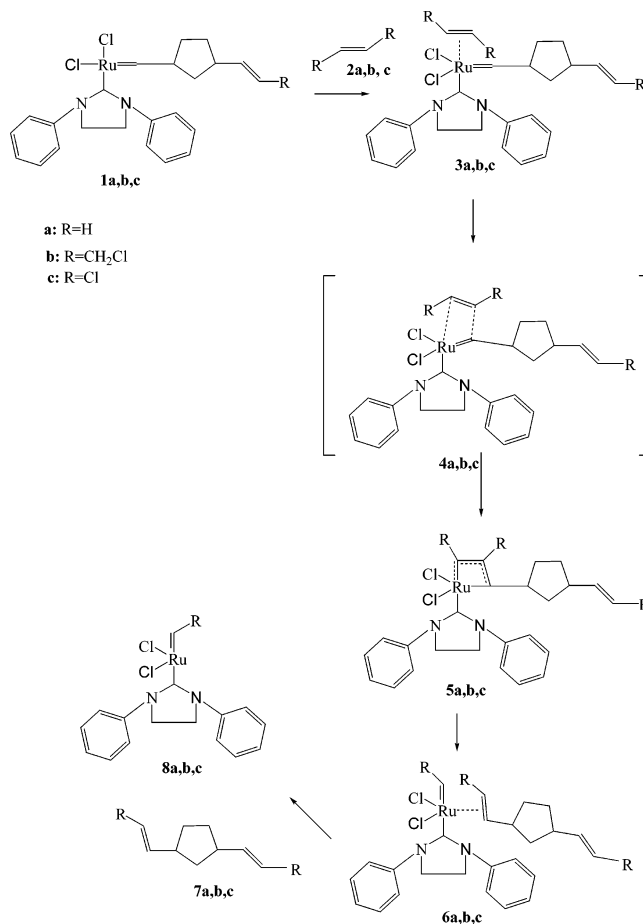
(**2c**) using (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene)-(PCy₃)Cl₂Ru=CHPh (**1**).

Computational Methods

All ab initio calculations were carried out with the Jaguar version 6.0 program.¹¹ The lowest energy conformers were located using a Monte Carlo method, as implemented in the Titan package version 1.0.5,¹² using the PM3(tm) method. The lowest energy conformers were used as initial structures for the geometry optimization using Becke's three-parameter functional (B3)¹³ in combination with the Lee, Yang, and Parr (LYP) correlation function¹⁴ and LACVP* basis set. The LACVP* basis set uses the standard 6-31G* basis set for light elements and the LAC pseudopotential¹⁵ for third-row and heavier elements. The molecular geometries of all calculated molecules were optimized to a global minimum at the B3LYP/LACVP* level of theory. Frequency calculations at 298.15 K were run for all structures at the same level of theory 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 ΔH and ΔG are taken from vibrational calculations and include ZPE. All calculations were carried out in the gas phase since, as has been shown before,¹⁰ solvation energies of similar molecules in nonpolar solvents introduce smaller errors than the method itself.¹⁰ However, to verify how solvation affects the reaction energies, the Poisson-Boltzmann method implemented in Jaguar version 6.0 was used to calculate solvation effects in 1,2-dichloroethane for the reaction **3c** → **4c** at the B3LYP/LACVP* level of theory. The solvation effect changes the activation energy by only 0.53 kcal/mol, which is well within the method error.

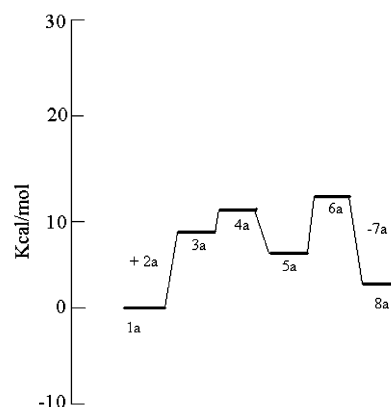
Results and Discussion

Scheme 2 shows a model adopted for the chain transfer to ethylene (**2a**), **2b**, and **2c** during the cross-metathesis of NB by the Ru alkylidene catalyst **1**. As can be seen, the chain transfer involves complex formation between the catalytic center and olefin (intermedi-

Scheme 2. Chain Transfer to Ethylene and DB during the Cross-Metathesis of NB by 1

ate **3**), followed by the formation of the metallacyclobutane intermediate **5**. The last step of the process is the dissociation of complex **6** to produce a new carbene complex and a new olefin (**8** and **7**).

The first step of the metathesis is complex formation between the transition-metal atom and olefin molecule. The interaction between the olefin and the transition metal is due to both π electron donation to unoccupied orbitals of a transition-metal atom and donation of d electrons to the LUMO of the olefin (back-donation mechanism). The geometries of metal-olefin complexes are shown in Figures 4 and 5. The binding enthalpies are shown in Table 1. HOMO energies for **2a-c**,

**Figure 1.** Gibbs free energy profile for chain transfer to ethylene during the cross-metathesis of NB by **1**.

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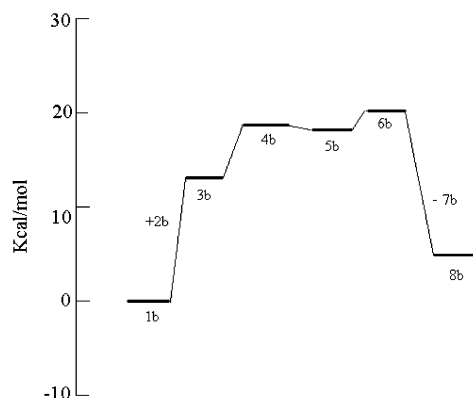


Figure 2. Gibbs free energy profile for chain transfer to DB during the cross-metathesis of NB by **1**.

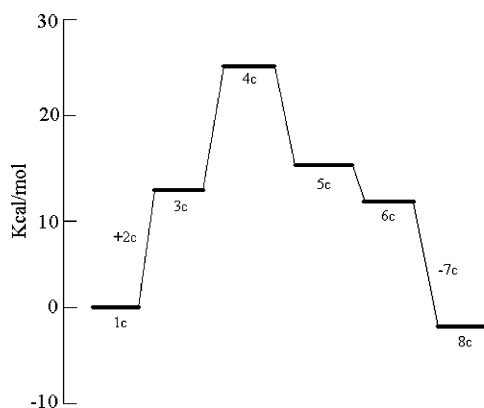


Figure 3. Gibbs free energy profile for chain transfer reaction to DE by **1**.

calculated at the B3LYP/6-31G* level, are $-0.266\ 57$, $-0.277\ 25$, and $-0.259\ 74$ au; therefore, **2c** is the most donating species. On the other hand, LUMO energies calculated at the same theoretical level give $-0.018\ 81$, $-0.037\ 94$, and $-0.019\ 21$ au, showing that the back-donation interaction is stronger in **2c** compared to that in ethylene. The theoretical data are confirmed by the experimentally determined ionization potentials for ethylene (10.52 eV) and **2c** (9.66 eV), which are in line with calculated HOMO energies.¹⁶ However, when inspecting the geometry and the binding energies of complexes **3a–c**, one can observe that the π complex **3a** is the tightest one with the most negative binding enthalpy. On the other hand, **3c** is not a π complex at all; the binding enthalpy of this complex is due to interaction of the hydrogen of **2c** with the chlorine atom of the 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 in **2c** the natural charges at the Cl and H atoms are -0.53 and $+0.26$ e, respectively, while in complex **3c** the corresponding natural charges are -0.54 and $+0.28$ e; therefore, there is a slight charge transfer from the hydrogen of **2c** to the chlorine atom in **3c**. Moreover, the distance between Cl and H atoms is $2.71\ \text{\AA}$, which is less than the sum of the van der Waals radii of H and Cl atoms ($3.01\ \text{\AA}$).

Complex **3b** is looser compared with **3a**; however, its geometry is similar to that of **3a**, suggesting interaction

between the π electrons of **2b** and empty d orbitals of the Ru atom. This apparent contradiction is explained by steric hindrance. Despite favorable electronic properties, bulky chlorine atoms directly attached to the double bond impede interactions between **2c** and Ru. The more flexible CH_2Cl groups of **2b** allow better fitting between the π orbitals of the olefin and the d orbitals of the Ru atom, and in the case of ethylene, the absence of steric hindrance allows the formation of a tight complex. Therefore, steric factors are of primary importance for complex formation in the metathesis reaction.

The located transition states **4a–c** (Figures 4 and 5) correspond to the rotation of the carbene group. Similar to the case for complexes **3b,c**, the transition states **4b,c** are less compact compared to **4a**, due to steric hindrance. Activation enthalpies for ethylene and **2b** are very low, reaching 2.0 and 2.3 kcal/mol, respectively, in the gas phase. However, in the case of **2c**, the activation enthalpy reaches 12.9 kcal/mol. When inspecting the geometry of transition states, one can easily understand the reason for high activation enthalpy in the reaction **3c** \rightarrow **5c**. The dihedral angles in the fragments $\text{HC}=\text{CH}$ (ethylene), $\text{CC}=\text{CC}$ (**2b**), and $\text{ClC}=\text{CCl}$ (**2c**) of transition states **4a–c** are 168 , 168 , and 148° , respectively, while the angle in free olefins is 180° . Therefore, it is the additional angular strain that contributes to the high activation enthalpy of the reaction **3c** \rightarrow **5c**.

Unlike Fisher type W(0) carbene complexes, where the metallacyclobutane intermediate represents a transition state,¹⁷ in case of the Ru catalysts **1a–c** the metallacyclobutane intermediate is a minimum on the potential energy surface (structures **5a–c**) with almost equal olefin C–C bond lengths (Figure 3). The dissociation of metallacyclobutanes leads to the stable π complexes **6a,b**. The dissociation energies are somewhat higher for the **2a** case. The activation energies of these processes, if any, are very low, and it was not possible to locate any transition states.

It is interesting to compare complexes **3c** and **6c** (Figures 4 and 5) to demonstrate the importance of steric factors on the metathesis reaction. As has been mentioned above, complex **3c** is formed by weak interactions between the **2c** hydrogen and chlorine atoms connected to the Ru complex. On the other hand, complex **6c** is a typical π complex, as judged by its geometry and olefin–carbene distance ($3.08\ \text{\AA}$), although the cyclopentane ring is more bulky compared to chlorine. Therefore, it can be concluded that steric hindrance caused by the chlorine atom directly linked to the double bond is the only important steric contribution.

As has been shown earlier,¹⁷ the rate-limiting step for the olefin metathesis reaction is the dissociation of π complexes, not metathesis itself. This statement agrees well with the dissociation energies of ethylene π complexes for catalyst **1a**, which is the lowest among $\text{Cl}_2(\text{PCy}_3)(\text{C}_2\text{H}_4)\text{Ru}=\text{CHR}$ (**II**)^{10c} and $(\text{CO})_4(\text{C}_2\text{H}_4)\text{W}=\text{CHR}$ (**III**).¹⁷ Catalyst **1a**, the most active catalyst, has the lowest dissociation energy for ethylene π complexes, 2–5 kcal/mol, while the catalyst **III** has the lowest activity, with a binding energy of 20 kcal/mol. Catalyst **II**, displaying intermediate activity, has ethylene complexation energies of some 7–8 kcal/mol.

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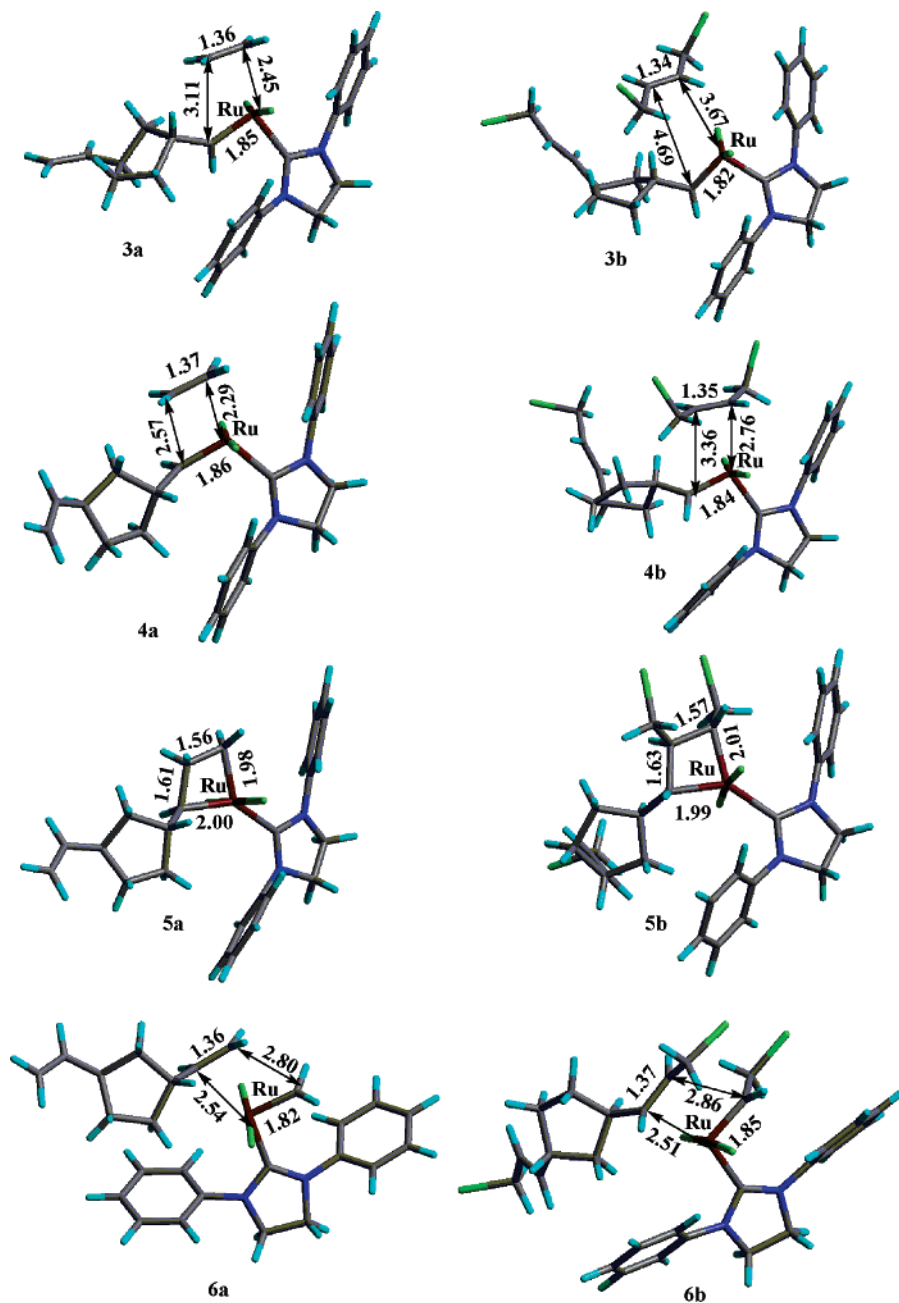


Figure 4. B3LYP/LACVP* optimized geometries of reaction intermediates in chain transfer to ethylene and DB during the cross-metathesis of NB by **1**.

It is worth noting that the ROMP of NB and its derivatives 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 **2b** resulted in bis(allyl chloride) functionalized telechelic PNB with controlled molecular weights.¹⁸

To obtain deeper insight into the differences in the reactivities of the olefins studied, the Gibbs free energy profiles were inspected (Figures 1–3). Two important conclusions can be made. The first is that the only metathesis reaction which shows a negative ΔG value is the metathesis of **2c** ($\Delta G = -2.0$ kcal/mol), while two other reactions (ethylene and **2b**) present slightly posi-

tive energies ($\Delta G = 2.5$ and 4.9 kcal/mol for **2a,b**, respectively). Second, the ΔG activation free energy is highest for **2c** metathesis (12.9 kcal/mol), as compared to **2b** and ethylene metathesis, suggesting that the chain transfer reaction is kinetically controlled. Taking into account the relatively large positive Gibbs free energy formation for complexes **3a–c**, one can estimate the Gibbs activation free energies of the processes as a sum of the complex Gibbs free energy formation and the Gibbs activation free energies. Therefore, for ethylene and **2b,c** the total Gibbs activation free energies (Figures 1–3) will be 10.2 , 18.7 , and 25.1 kcal/mol. As follows from the Curtin–Hammett principle,¹⁹ the relevant activation energy is one measured from the

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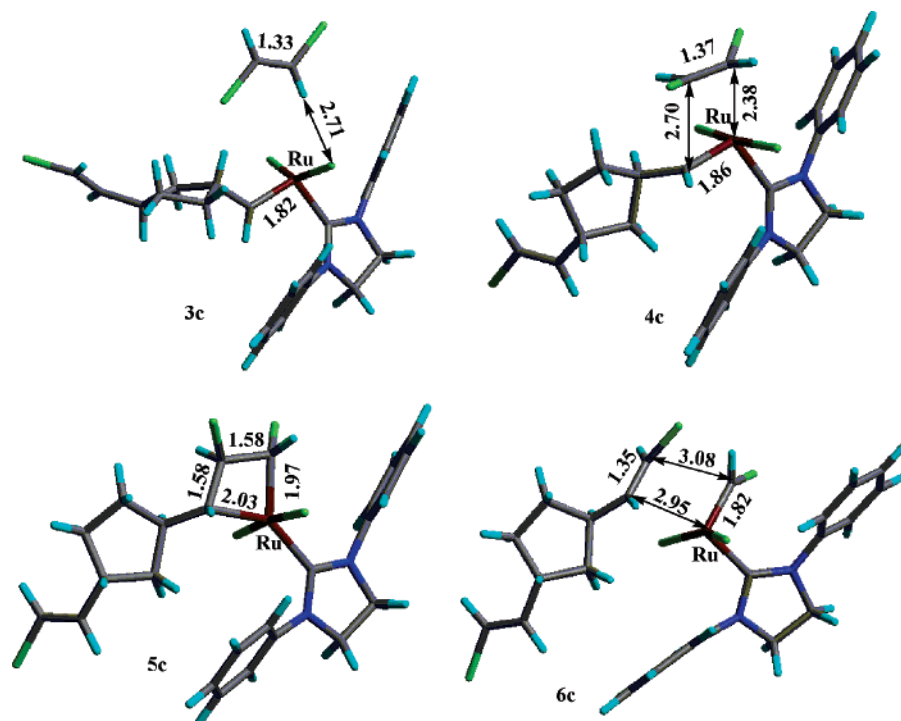


Figure 5. B3LYP/LACVP* optimized geometries of reaction intermediates in chain transfer to DE during the cross-metathesis of NB by 1.

Table 1. Reaction (ΔH) and Activation (H^\ddagger) Enthalpies, Gibbs Free Energies (ΔG) and the Gibbs Free Activation Energies (G^\ddagger) (kcal/mol) at 298.15 K Calculated at the B3LYP/LACVP* Level of Theory

run	reacn	ΔH	H^\ddagger	ΔG	G^\ddagger
1	1a + 2a \rightarrow 3a	-4.1		7.9	
2	3a \rightarrow 5a	-4.0	2.0	-2.2	2.3
3	5a \rightarrow 6a	8.5		5.9	
4	6a \rightarrow 7a + 8a	5.8		-9.1	
5	1b + 2b \rightarrow 3b	-3.1		7.5	
6	3b \rightarrow 5b	-0.1	2.3	5.1	5.6
7	5b \rightarrow 6b	6.5		2.0	
8	6b \rightarrow 7b + 8b	3.0		-15.3	
9	1c + 2c \rightarrow 3c	-2.5		12.2	
10	3c \rightarrow 5c	1.4	12.6	2.6	12.9
11	5c \rightarrow 6c	-1.1		-3.8	
12	6c \rightarrow 7c + 8c	2.8		-13.0	

lowest preceding point on the potential energy surface, not necessarily the immediately preceding intermediate.

One can estimate the relative importance of the entropy factors for the studied metathesis reactions by comparing their Gibbs free energies and the enthalpies. The smaller is difference, the lesser the contribution of the entropy factor. The formation of complexes **3a–c** is strongly affected by entropy factors, due to a decrease in the number of particles during the reaction (Table 1, runs 1, 5, and 9). The difference between ΔG and ΔH is minimal for the formation of the loose complex **3b**. The formation of metallacyclobutane intermediates **5a–c** (runs 2, 6, and 10) is less sensitive to the entropy. The formation of complexes **6a–c** (runs 3, 7, and 11) is moderately sensitive to the entropy factor, due to an increase in atomic molecular freedom in **6** compared to that in **5**. Similar to the formation of complexes **3a–c**, the dissociation of complexes **6a–c** is also strongly affected by the entropy, due to an increase in the number of particles during the reaction (runs 4, 8, and 12).

When H^\ddagger and G^\ddagger are compared for the reaction **3c** \rightarrow **5c**, one can see that the difference between them is just 0.3 kcal/mol, meaning that the entropy factor barely contributes to the high activation energies of this reaction and its origin is merely enthalpic. Another point to mention is that although in complex **3c** the olefin molecule is not properly oriented for the metathesis, the entropy penalty is not of importance for the reaction **3c** \rightarrow **5c**.

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 ref 20 as $\mu^2/2\eta$, where μ is the chemical potential approximated as $-(IP + EA)/2$ and η is chemical hardness defined as $IP - EA$, where IP and EA are the ionization potential and electron affinity, respectively. IP and EA were approximated as $-\text{HOMO}$ and $-\text{LUMO}$ energies, at the B3LYP/LACVP* level of theory, respectively. Thus, **2a–c** have ω values of 0.027, 0.052, and 0.040 au. Molecular volumes (only including carbons forming a double bond and the four atoms directly linked to them) were 31.6, 43.6, and 58.5 Å³ for **2a–c**, respectively. Therefore, the most electrophilic (electron-deficient) olefin is **2b**, where Cl atoms manifest a pure σ -acceptor effect, followed by **2c**, where competing σ -acceptor and π -donor effects prevail over the first effect. The most nucleophilic (electron-donating) olefin is ethylene. As can be seen in Table 1, no correlation between ω and G^\ddagger of the metathesis reaction is observed. On the other hand, there is a clear correlation between the molecular volume of the olefin (where only atoms linked directly to the double bond are taken into account) and G^\ddagger or H^\ddagger (Table 1). Therefore, steric effects caused by atoms closest to the double

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bond are the determining factors for the activation energy, while the electronic factors are at least not as important.

Conclusions

The chain transfer reaction to **2c** during Ru alkylidene mediated NB polymerization is definitely a kinetically controlled process. Thus, the low efficiency of **2c** as a CTA is due to the high activation energy of the process and not thermodynamics. Steric factors are of

primary importance for Ru alkylidene mediated metathesis reactions, strongly affecting the activation energies of the metathesis reactions, and are more important than electronic factors. The steric influence of the chlorine atom directly linked to the double bond contributes the most to the overall steric effect.

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