Halogenated Olefins as Chain Transfer Agents in the Synthesis of Telechelic Polynorbornenes Using Ruthenium Alkylidene Catalysts. Computational and Experimental Studies

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Abstract: Ring-opening metathesis polymerization (ROMP) of norbornene (NB) and its derivatives *N*-adamantyl-*exo-endo*-norbornene-5,6-dicarboximide (AdNDI) and *N*-cyclohexyl-*exo-endo*-norbornene-5,6-dicarboximide (CyNDI) in the presence of *cis*-1,4-dichloro-2-butene (**2a**) and *cis*-1,2-dichloro-ethylene (**2b**) as chain transfer agents (CTAs) using a [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolilydene] (PCy$_3$)Cl$_2$Ru=CHPh (**I**) has been studied. α Halogenated olefin **2b** shows no activity as a CTA when β halogenated olefin **2a** is readily cross-metathesized with NB and norbornene dicarboximides. The chain transfer reaction pathways during the ROMP of NB to **2b** using a (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy$_3$)Cl$_2$Ru=CHPh (**1**) have been studied at B3LYP/LACVP* level of theory. The calculations show that **2b** is a poor substrate for the metathesis reaction due to the steric effect produced by chlorine atoms directly linked to the double bond. The calculated Gibbs free activation energy of a chain transfer reaction from ring-opened NB to **2b** was 25.1 kcal/mol.

Keywords: Halogenated olefins, telechelic polynorbornene, ruthenium alkylidene, computational and experimental studies.

1. INTRODUCTION

Ring-opening metathesis polymerization (ROMP) of cycloolefins in the presence of difunctional acyclic olefins as chain transfer agents (CTAs) leads to linear products with controlled molecular weights and functionalities (telechelics) [1]. Telechelic polymers 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 [2]. For example, hydroxyl-terminated telechelic polybutadiene has been used as a cross-linking agent in the polyurethane industry [3].

The development of highly active metal-alkylidene catalysts opens vast opportunities in the design of well-defined products. Thus, using the ruthenium alkylidene complexes and *cis*-1,4-diacetoxy-2-butene as a CTA, norbornene polymers with controlled molecular weights and end groups have been obtained *via* ROMP of norbornene (NB) and metathesis degradation of polynorbornene (PNB**)** [4, 5].

It is worth noting, that NB and its derivatives have been the subject of interest due to facile preparation and high reactivity in the ROMP [1]. These strained cycloolefins are easily polymerized with approximate complete conversion to high molecular weight polymers with good mechanical properties and T_g's ranging from -34 to 270 °C [6, 7]. Polynorbornene derivatives have attracted much attention as membranes for gas separation. Thus, gas transport characteristics of membranes prepared from new polynorbornene dicarboximides with cyclohexyl, adamantyl and fluorine containing side chain groups have been reported [7-9].

The recent generation of ruthenium alkylidene catalysts coordinated with *N*-heterocyclic carbene ligands make it possible to metathesize the challenging cyclic and linear olefins with sterically hindered or electronically deactivating ester and amide groups [10, 11]. For example, halogenated olefins are challenging due to the presence of the electron-withdrawing groups [12, 13]. Recently, we reported a computational study of a ruthenium alkylidene mediated metathesis of olefins with electronically deactivating ester and halogen groups [14, 15].

The aim of this report is to study the ROMP of NB and its derivatives in the presence of halogenated olefins *cis*-1,4-dichloro-2-butene (**2a**) and *cis*-1,2-dichloro-ethylene (**2b**) as CTAs using a [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolilydene] (PCy$_3$)Cl$_2$Ru=CHPh (**I**) and to model the chain transfer reaction pathways from ring-opened NB to **2b** using a (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy$_3$)Cl$_2$Ru=CHPh (**1**).

2. SIMULATION METHOD

All calculations were carried out with the Jaguar v 6.0 program [16]. The lowest energy conformers were located using a Monte-Carlo method as implemented in the Titan package version 1.0.5 [17] using PM3(tm) method. Lowest energy conformers were used as initial structures for the geometry optimization using Becke's three parameter functional (B3) [18] in combination with the Lee, Yang and Parr (LYP) correlation function [19] and LACVP* basis set. LACVP* basis set uses standard 6-31G* basis set for light elements and LAC pseudopotential [20] 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 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 ΔH and ΔG 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 nonpolar solvents introduce smaller error than the method itself [14]. However, in order to verify how solvation affects the reaction energies Poisson-Boltzman solver implemented in Jaguar v 6.0 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. EXPERIMENTAL SECTION

3.1. Techniques

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian spectrometer at 300 and 75 MHz, respectively, in CDCl$_3$. Tetramethylsilane (TMS) was used as internal standard. Molecular weights and molecular weight distributions were determined with reference to polystyrene standards on a Varian 9012 GPC at 30 °C in chloroform using a universal column and a flow rate of 1 mL min^{-1}.

3.2. Reagents

N-Cyclohexyl-*exo-endo*-norbornene-5,6-dicarboximide (CyNDI) and *N*-adamantyl-*exo-endo*-norbornene-5,6-dicarboximide (AdNDI) were prepared according to the literature [7]. Halogenated olefins and other chemicals were purchased from Aldrich Chemical Co. 1,2-Dichloroethane was dried over anhydrous calcium chloride and distilled under nitrogen over CaH$_2$. The catalyst [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolilydene] (PCy$_3$)Cl$_2$Ru =CHPh (**I**) was purchased from Stream Chemicals, Inc. and used as received.

## 3.3. General Procedure of ROMP of Norbornenes with Olefins

A 25 mL glass vessel, under dry nitrogen atmosphere, was charged with NB (1.0 g, 10.6 mmol), 14.0 mL of anhydrous 1,2-dichloroethane and a stir bar. An amount of 0.11 mL (0.13g, 1.04 mmol) of *cis*-1,4-dichloro-2-butene was added *via* syringe to the stirred solution of NB. Catalyst **I** (0.01 g, 0.0117 mmol) was then added and the vessel was immersed in an oil bath thermostatted at 55 °C. After 12 hours, the reaction was inhibited by adding a small amount of ethyl vinyl ether and pouring into excess stirring methanol causing precipitation of a white semisolid (Scheme **1**). The material was collected by filtration and dried in a vacuum oven at 40 °C overnight. The obtained product was soluble, among others, in chloroform and dichloromethane. Yield=90%, M$_{w(theor)}$=2575 (theoretical MW based on complete monomer conversion and CTA incorporation), M$_{w(NMR)}$=2650 (MW determined by ^{1}H NMR end group analysis. An average of two functional groups per chain was assumed), M$_{n(GPC)}$=2800, PDI=1.9 (Table **1**). The ^{1}H NMR chemical shifts (Fig. **1**) were assigned as follows: ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 5.70-5.46 (2H, m), 5.28 (2H, s, *trans*), 5.14 (2H, s, *cis*), 4.11 (2H, m), 4.01 (2H, m), 2.71 (2H, s), 2.37 (2H, s), 1.94-1.70 (2H, m), 1.47-0.96 (4H, m).

^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 134.2, 132.9, 124.2, 124.0, 45.5, 43.4, 42.0, 38.7, 32.9.

4. RESULTS AND DISCUSSION

Scheme **1** shows ring-opening cross-metathesis of *N*-cycloalkyl-norbornene dicarboximide with **2a** using catalyst **I**. Table **1** presents the results of ROMP of NB, CyNDI and AdNDI in the presence of halogenated olefins as CTAs by **I**. As seen from Table **1**, experimental molecular weights of telechelics prepared *via* cross-metathesis of norbornene monomers with **2a** were in agreement with theoretical ones based on the initial NB/CTA ratio.

The ^{1}H and ^{13}C NMR spectroscopy of cross-metathesis products between NB monomers and **2a** were carried out to find evidence for the preparation of well-defined oligomers.
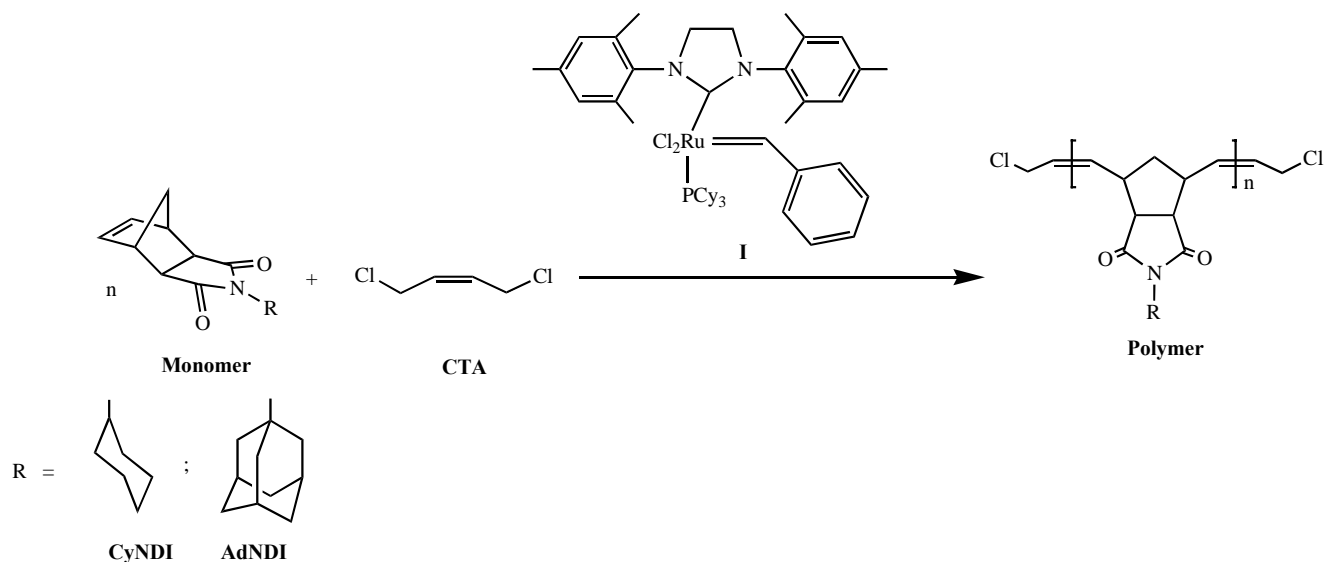
Scheme 1. Synthesis of diallyl chloride functionalized polynorbornene dicarboximide.

Table 1. ROMP of NB, *N*-adamantyl-*exo-endo*-norbornene-5,6-dicarboximide (AdNDI) and *N*-cyclohexyl-*exo-endo*-norbornene-5,6-dicarboximide (CyNDI) in the presence of *cis*-1,4-dichloro-2-butene (2a) and *cis*-1,2-dichloro ethylene (2b) as CTAs by a catalyst (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (PCy$_3$)Cl$_2$Ru=CHPh (I)[a]

Monomer	CTA	Mon/CTA[b]	Yield[c] (%)	MW[d] (theor)	MW[e] (NMR)	M$_n$[f] (GPC)	M$_w$/M$_n$[f] (%)	*trans*[g] (%)
CyNDI	**2a**	10	90	2575	2650	2800	1.9	62
CyNDI	**2a**	20	86	5025	5200	5250	2.2	64
CyNDI	**2b**	10	95	2547	---	1.5x10^5	1.5	61
AdNDI	**2a**	10	89	3095	3160	3215	2.1	63
AdNDI	**2b**	10	93	3067	---	2.1x10^5	1.6	62
NB	**2a**	20	80	2005	2250	2400	2.2	65
NB	**2a**	40	78	3885	4300	4350	2.2	64
NB	**2b**	20	70	2005	--	8.5x10^5	2.4	67

[a]Reaction conditions: 1,2-dichloroethane as solvent, initial monomer concentration = 1.0 M, room temperature, time 12 h, Ar atmosphere, monomer/catalyst = 1000; [b]Initial monomer/olefin ratio; [c]Isolated yield; [d]Theoretical MW based on complete monomer and olefin conversion; [e]MW determined by ^{1}H NMR CH$_2$Cl end group analysis. An average of two CH$_2$Cl groups per polymer chain was assumed; [f]Determined by gel permeation chromatography using THF as the eluent and results are reported relative to polystyrene standards; [g]Determined by ^{1}H and ^{13}C NMR.

Fig. (**1**) presents ^{1}H -NMR spectrum of telechelics prepared *via* ROMP of NB using **2a** as a CTA (Table **1**). The new peaks observed in the 5.70-5.46 ppm are attributed to an olefin proton in =CH-CH$_2$Cl bonds confirming the formation of diallyl- terminated polynorbornene. The peaks observed in the 4.11-4.01 ppm correspond to aliphatic protons in CH$_2$Cl of diallyl- terminated groups. The content of *trans*-isomers is about of 60%.

On the other hand, **2b** does not control the molecular weights of polynorbornenes (Table **1**). The computational modeling also shows that there are marked differences between these olefins in the metathesis reaction. Scheme **2** shows the chain transfer reaction pathways to **2b** during the

ROMP of NB or metathesis degradation of polynorbornene by catalyst **1**. It is seen the chain transfer involves the complex formation between the catalytic center with ring-opened NB and an 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 **9** and new diolefin **8** (telechelic). Fig. (**2**) presents the energetic profile for this reaction. The calculations show that there are marked differences between **2a** and **2b** in the metathesis reaction. Thus, the free Gibbs activation energy of **2a** metathesis reaction is of 18.6 kcal/mol [15] while the free Gibbs activation energy of **2b** metathesis is of 25.1 kcal/mol (as a sum of the complex Gibbs free energy
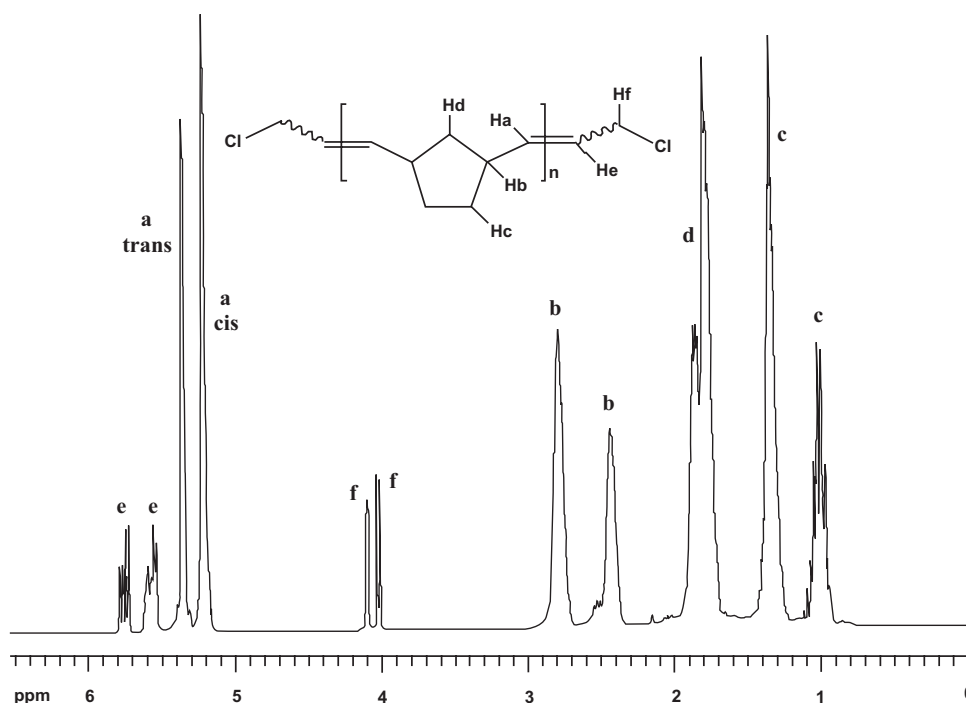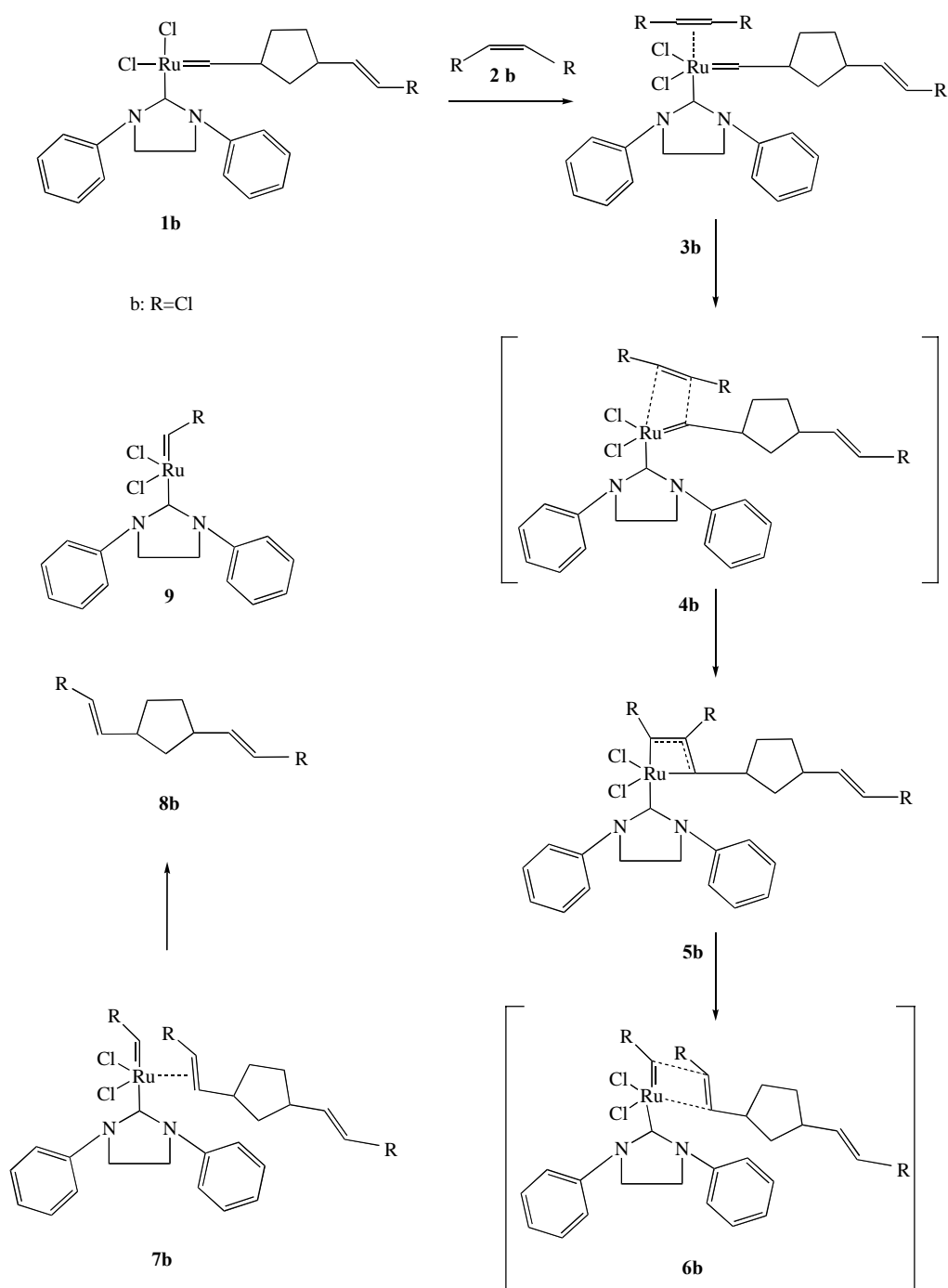

Fig. (1). ^{1}H NMR spectrum of diallyl chloride functionalized polynorbornene prepared during ROMP of NB in the presence of **2a** as a CTA by a (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (PCy$_3$)Cl$_2$Ru=CHPh (**I**).

Scheme 2. Chain transfer reaction pathways to **2b** during the cross-metathesis of NB by **1**.

formation and the Gibbs free activation energies). The difference is definitely related to the steric factor. As it has been shown earlier, the free Gibbs activation energy of the metathesis is directly related to the volume of the atoms linked to the olefin double bond [15]. The molecular volumes (only including carbons forming a double bond and the four atoms directly linked to them) are of 43.6, and 61.5 Å^3 for **2a** and **2b**, respectively. As seen the steric hindrances are more pronounced for **2b** resulting in increase of their free Gibbs activation energy. As seen from energy profile transition state **4b** determine the reaction kinetics. The kinetic control of the reaction under the study follows from the facts that while the chain transfer to **2b** shows slightly negative ΔG (ΔG= -2.0

kcal/mol) for **2a** ΔG is positive (4.9 kcal/mol). On the other hand **2a** participates in the metathesis while **2b** does not. The ΔG values of a chain transfer reaction can be explained in terms of a ruthenium complex stability (**9b**). When the chlorine atom is connected directly to the carbene, the effect of electron donating to the Ru complex through carbene carbon dominates thus stabilizing the carbene complex (**9b**). In the case of **2a** the effect of chlorine only is inductive, withdrawing electrons through σ-bonds, thus destabilizing the Ru active center resulting in positive ΔG (ΔG= 4.9 kcal/mol [15].

Fig. (**3**) shows the B3LYP/LACVP* optimised geometries of reaction intermediates for cross-metathesis of NB with **2b** by **1**. The important conclusion which can be made
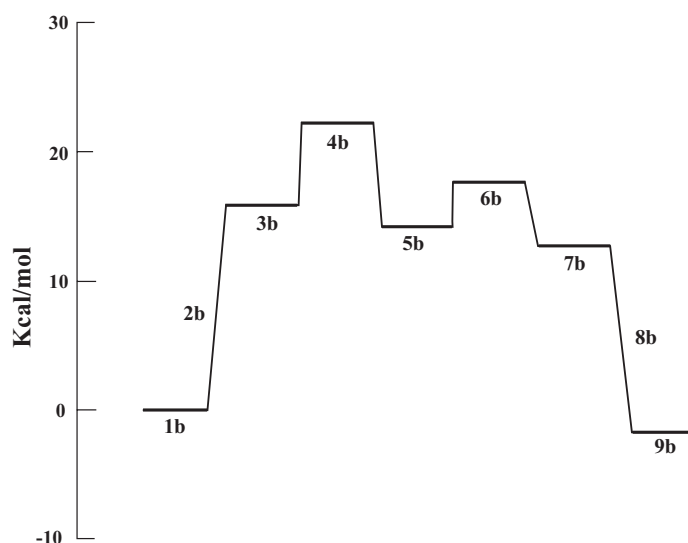
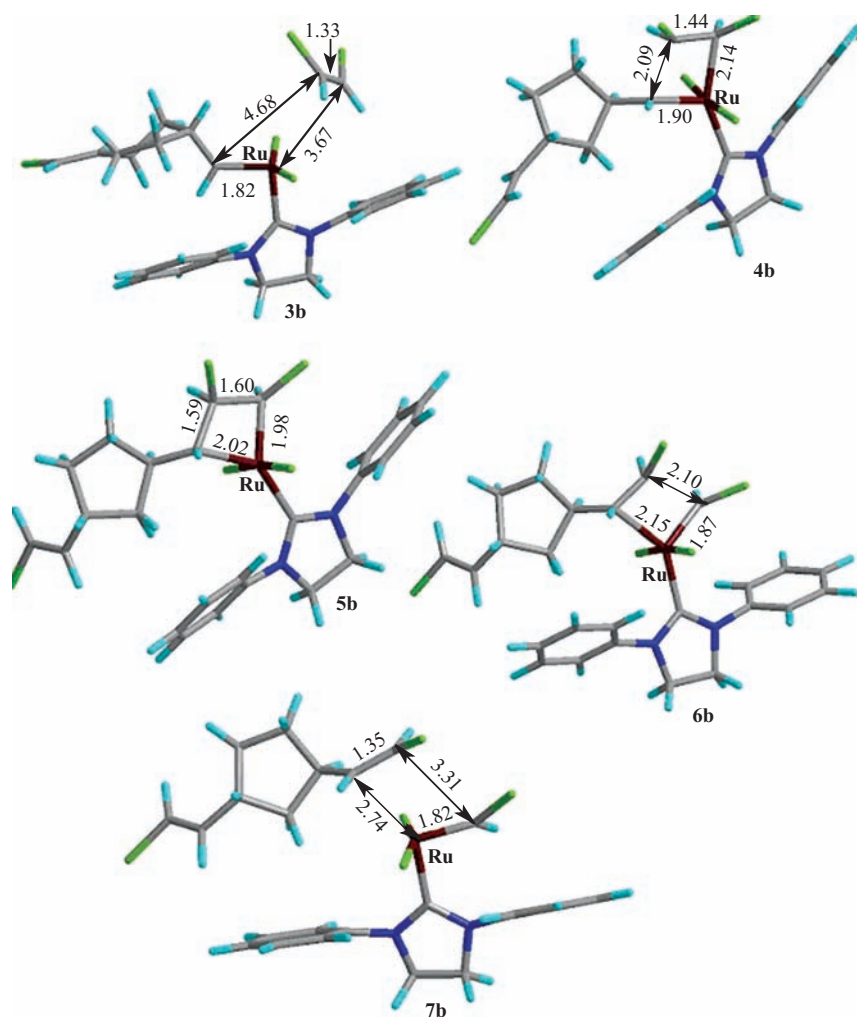**Fig. (2).** The Gibbs free energy profile for cross-metathesis of NB with **2b** by **1**.

Fig. (3). B3LYP/LACVP* optimised geometries of reaction intermediates for cross-metathesis of NB with **2b** by **1**.

revising the optimized geometries is that chlorine atoms directly linked to the double bond causes steric hindrances impeding the metathesis reaction. Therefore, steric factors are of primary importance for the activation energy in the metathesis reaction.

5. CONCLUSIONS

New bis(allylchloride) telechelic polynorbornene dicarboximides with perfectly controlled molecular weights were synthesized using **2a** as a CTA. The directly halogenated

olefin **2b** does not control the molecular weight of polynorbornenes. The computational modelling shows that the chain transfer reaction to **2b** during the Ru alkylidene mediated ROMP of NB is a definitely kinetically controlled reaction. The low efficiency of **2b** in the metathesis reaction is due to the high activation energy of the process and not thermodynamics. The steric effect caused by chlorine atoms directly linked to the double bond is the determining factor for the metathesis activity of halogenated olefin **2b**.

ACKNOWLEDGEMENTS

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