

Computational modeling of ruthenium alkylidene mediated olefin metathesis

A DFT study of reaction pathways for the ring-opening cross-metathesis of norbornene with olefins

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Abstract

The chain transfer reaction pathways from ring-opened norbornene to ethylene and 1,4-dichloro-2-butene (DB) using (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy₃)Cl₂Ru=CHPh catalyst (**I**) have been studied at B3LYP/LACVP** level of theory. The calculations show that compared to ethylene, DB binds less strongly to the 14 electron Ru-alkylidene catalyst to form the metallacycle. The activation energies found for both chain transfer reactions, if any, are very low making the kinetic factor to be of little importance.

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1. Introduction

Ring-opening metathesis polymerization (ROMP) of cycloolefin in the presence of a difunctional acyclic olefin as a chain transfer agent (CTA) yields a telechelic polymer [1]. Telechelic polymers can be used 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 cross-linking agents in the polyurethane industry [3]. ROMP of cycloolefins in the presence of ethylene as a CTA (ethenolysis) yields α,ω -diolefins. This reaction has been exploited commercially for the preparation of high-purity hexa-1,5-diene from cycloocta-1,5-diene [1].

The development of highly active metal-alkylidene catalysts opens vast opportunities in olefin metathesis and its application to well-defined products synthesis [4]. Thus, using the ruthenium alkylidene complexes and appropriate olefins as CTAs, norbornene oligomers with controlled molecular weights and end groups have been obtained via ROMP of highly strain norbornene (NB) and metathesis degradation of polynorbornene (PNB) [5,6].

The recent generation of ruthenium alkylidene catalysts coordinated with *N*-heterocyclic carbene ligands make it possible to metathesize the challenging olefins with sterically hindered or electronically deactivating groups [4,7,8]. For example, halogenated olefins are challenging due to the presence of the electron-withdrawing groups.

The goal of this study is to model chain transfer reaction pathways for the ring-opening cross-metathesis of NB with 1,4-dichloro-2-butene (DB) and ethylene using (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy₃)Cl₂Ru=CHPh (**I**).

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2. Computational methods

All ab initio calculations were carried out with Jaguar v 4.2 program [9]. Lowest energy conformers were located using Monte–Carlo method as implemented in Titan package version 1.0.5 [10]. Lowest energy conformers found were used as initial structures for the geometry optimization using Becke's parameter functional (B) [11] in combination with Lee, Yang and Parr (LYP) correlation function [12] and LACVP** basis set. LACVP** basis set uses standard 6-31G** basis set for valence and outermost set of core electrons of third row and heavier elements and LAC pseudopotential [13] for inner core electrons. The elements of the first and second rows uses standard 6-31G** basis set. The molecular geometries of all calculated molecules were optimized to a global minimum at B3LYP/LACVP** level of theory.

3. Results and discussion

The mechanism of ruthenium alkylidene catalyzed olefin metathesis has recently been a subject of intense experimental [14,15] and theoretical [16] investigations. These results clearly indicate that for the ruthenium complexes with the general formula $L(PR_3)(X)_2Ru=CHR^1$ ($R = Cy, Cp$ and Ph ; $X = Cl, Br$ and I ; $L = N$ -heterocyclic carbene ligand, NHC)

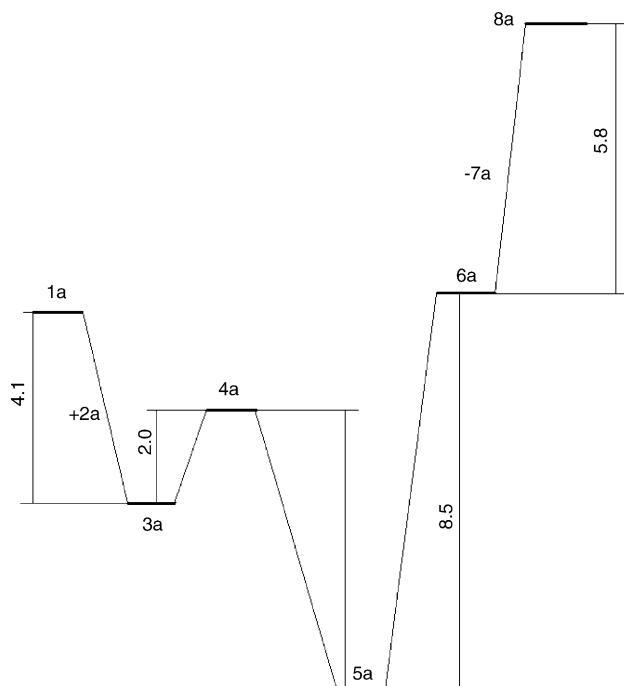
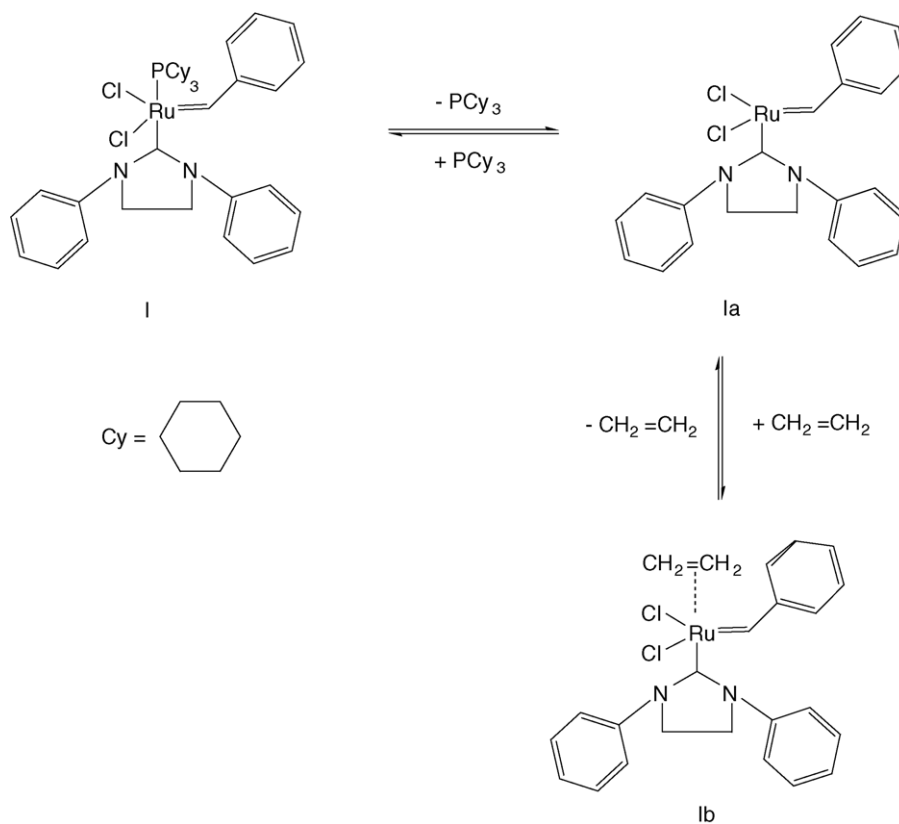
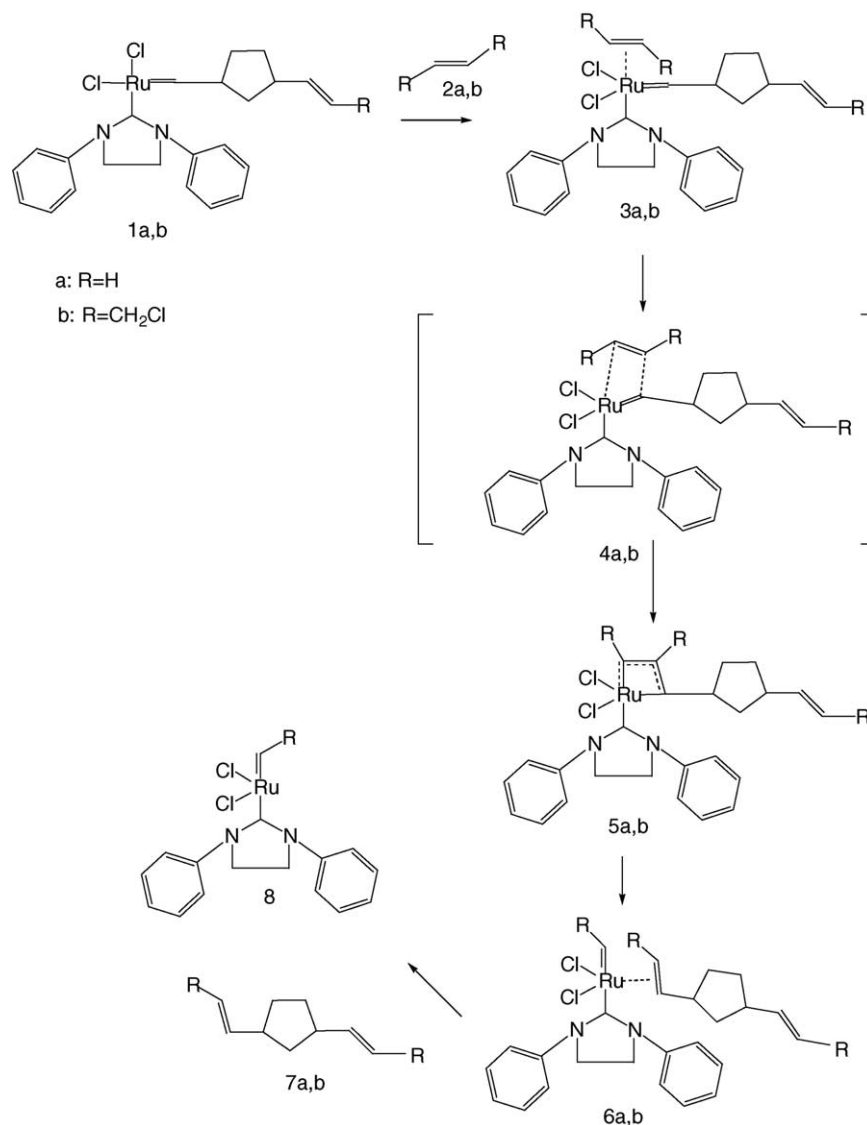


Fig. 1. Energy profile for chain transfer to ethylene during the cross-metathesis of NB by (I).



Scheme 1. Dissociation pathway of Ru-alkylidene catalyst (I).



Scheme 2. Chain transfer to ethylene and DB during the cross-metathesis of NB by (I).

initiation occurs by dissociative substitution of a phosphine ligand (PR₃) with olefin substrate, giving a monoligand complex (Scheme 1).

Scheme 2 shows the chain transfer to ethylene (**2a**) and DB (**2b**) during the ring-opening cross-metathesis of NB by Ru-alkylidene catalyst (I). Figs. 1 and 2 present the energetic profiles for these reactions. There are marked differences between DB and ethylene in the metathesis reaction. Thus, π-complex **3b** is quite loose compared to **3a** (Fig. 3) (the olefin–Ru separation distances are 4.69 and 3.11 Å, respectively), due to steric hindrances of two chloromethyl groups which is also reflected in lower binding energy of complex **3b**. In both cases, transition states were located corresponding to the rotation of carbene. Similar to complex **3b** transition state **4b** is less compact compared to **4a** due to steric hindrances. Both activation energies are very low reaching 2.0 and 2.3 kcal/mol for ethylene and DB, respectively in the gas phase. Unlike Fisher type W(0) carbene

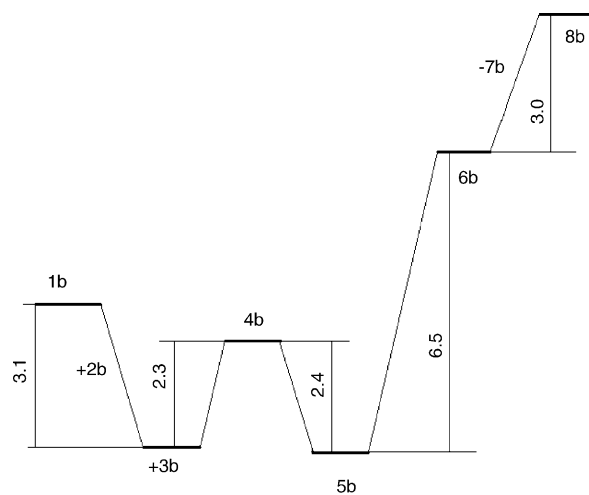
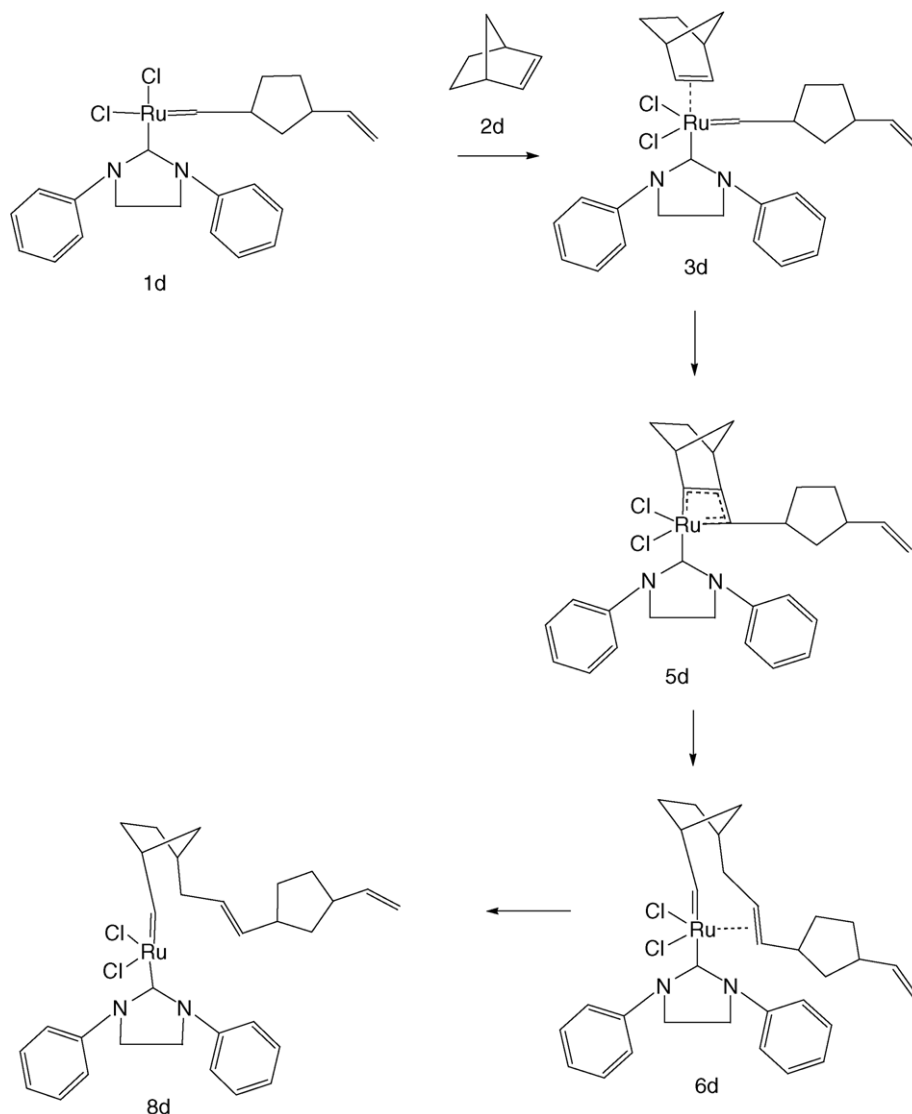


Fig. 2. Energy profile for chain transfer to DB during the cross-metathesis of NB by (I).



Scheme 3. ROMP of NB by (I).

complexes where metallocyclobutane intermediate represents a transition state [17] in case of Ru catalyst **1a and b** metallocyclobutane intermediate is a minimum (structures **5a and b**) with almost equal olefin C–C bond lengths. The dissociation of metallocyclobutanes leads to stable π -complexes **6a and b**. The dissociation energies are somewhat higher for ethylene case. The activation energies of those processes, if any, are very low and it was not possible to locate any transition states.

As can be seen from the energy profiles shown in Figs. 1 and 2, the reaction for DB favoured both kinetically and thermodynamically, however, low activation energies found for both reaction make the kinetic factor to be of little importance. It is worth noting that ROMP of NB and its derivatives in the presence of DB as a CTA resulted in bis(allyl chloride) functionalized telechelic PNB with controlled molecular weights [18,19].

As it has been shown earlier [17] the rate limiting step for the olefin metathesis reaction is the dissociation of π -complexes not the metathesis itself. This statement agrees well with the dissociation energies of ethylene π -complexes for catalysts **1a** which is the lowest among $\text{Cl}_2(\text{PCy}_3)(\text{C}_2\text{H}_4)\text{Ru}=\text{CHR}$ (**II**) [16c] and $(\text{CO})_4(\text{C}_2\text{H}_4)\text{W}=\text{CHR}$ (**III**) [17]. 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.

Since chain transfer competes with chain propagation, it is important to compare the chain propagation pathways with these of chain transfer (Scheme 3). The energy profile for the chain propagation is shown in Fig. 4. As seen this profile lack the transition state which we were not able to locate.

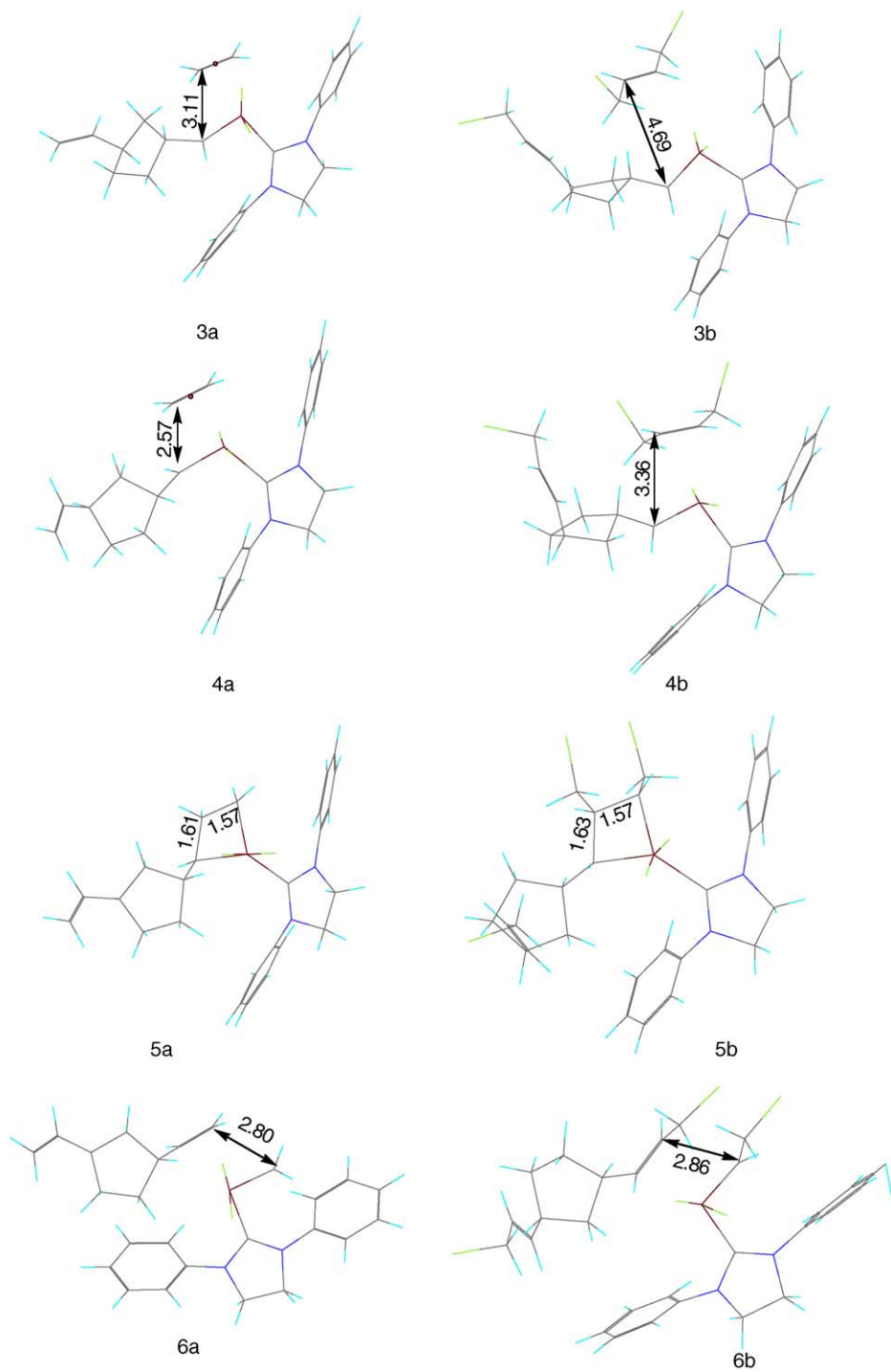


Fig. 3. B3LYP/LACVP** optimized geometries of reaction intermediates in chain transfer to ethylene and DB during the cross-metathesis of NB by (I).

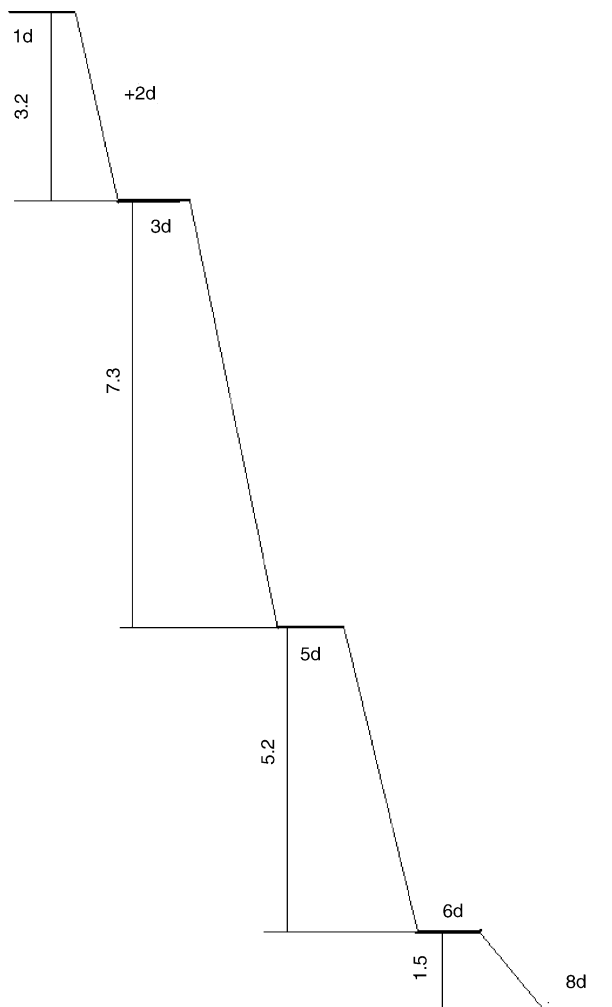


Fig. 4. Energy profile for chain propagation during ROMP of NB in the presence of ethylene by (I).

4. Conclusion

Computational modeling of chain transfer reaction pathways to ethylene and DB during the ROMP of norbornene by (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) $(PCy_3)_2Cl_2Ru=CHPh$ (**I**) demonstrated that compared to ethylene, DB is formed more loose π -complex with catalyst due to steric hindrances of two chloromethyl groups. In both cases, transition states were located corresponding to the rotation of carbene. The dissociation energies are somewhat higher for ethylene case. The activation energies of chain transfer reactions to olefins are very low reaching 2.0 and 2.3 kcal/mol for ethylene and DB, respectively.

Acknowledgments

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