

Cross-metathesis of dimethyl maleate and ethylene catalyzed by second generation ruthenium carbene complexes: B3LYP and MPW1K comparison study

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Abstract

The cross-metathesis of methyl maleate (**2**) and ethylene (**10**) using second generation Grubbs catalyst; (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (PCy₃)Cl₂Ru=CHPh has been modeled at B3LYP/LACVP* and MPW1K/LACVP* levels of theory. Both models predict the metathesis of **2** to be viable kinetically and thermodynamically. The low reactivity of **2** in the metathesis reaction can be explained by the non-productive complex formation between carbonyl oxygen and Ru center that impedes the metathesis. Calculations show that the metathesis of ethylene is slightly endothermic process reflecting the relative stability of (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)Cl₂Ru=CHCOOMe catalyst due to additional stabilization of Ru center by sp² or sp³ oxygen atoms. Although both models; B3LYP and MPW1K predict qualitatively similar picture of the metathesis; MPW1K functional seems to be superior to B3LYP in predicting the reaction energetics.

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Keywords: Metathesis; Ruthenium alkylidene; DFT study

1. Introduction

The recent generation of ruthenium alkylidene catalysts coordinated with N-heterocyclic carbene ligands opens vast opportunities to metathesize challenging olefins with sterically hindered or electronically deactivating groups [1]. For example, ester-containing olefins are challenging object due to the presence of electron-withdrawing groups and few examples of their metathesis exist [2]. Recently, we reported a density functional study of ruthenium alkylidene mediated metathesis of halogenated olefins [3] where the importance of steric factor for Ru mediated metathesis of olefins has been shown. It is worth noting, that the metathesis of ester-containing olefins should proceed via the formation

of a ruthenium ester carbene complex, which is different from usual alkylidene complex. The metathesis active ruthenium based ester carbene complex was first synthesized by the reaction of ethyl diazoacetate with RuCl₂(PPh₃)₃ [2a]. The first efficient generation of ruthenium ester carbene species *in situ* using the second generation Grubbs catalyst and successful catalytic cross-metathesis and ring-opening metathesis polymerization of previously inactive olefins have also been reported [2b].

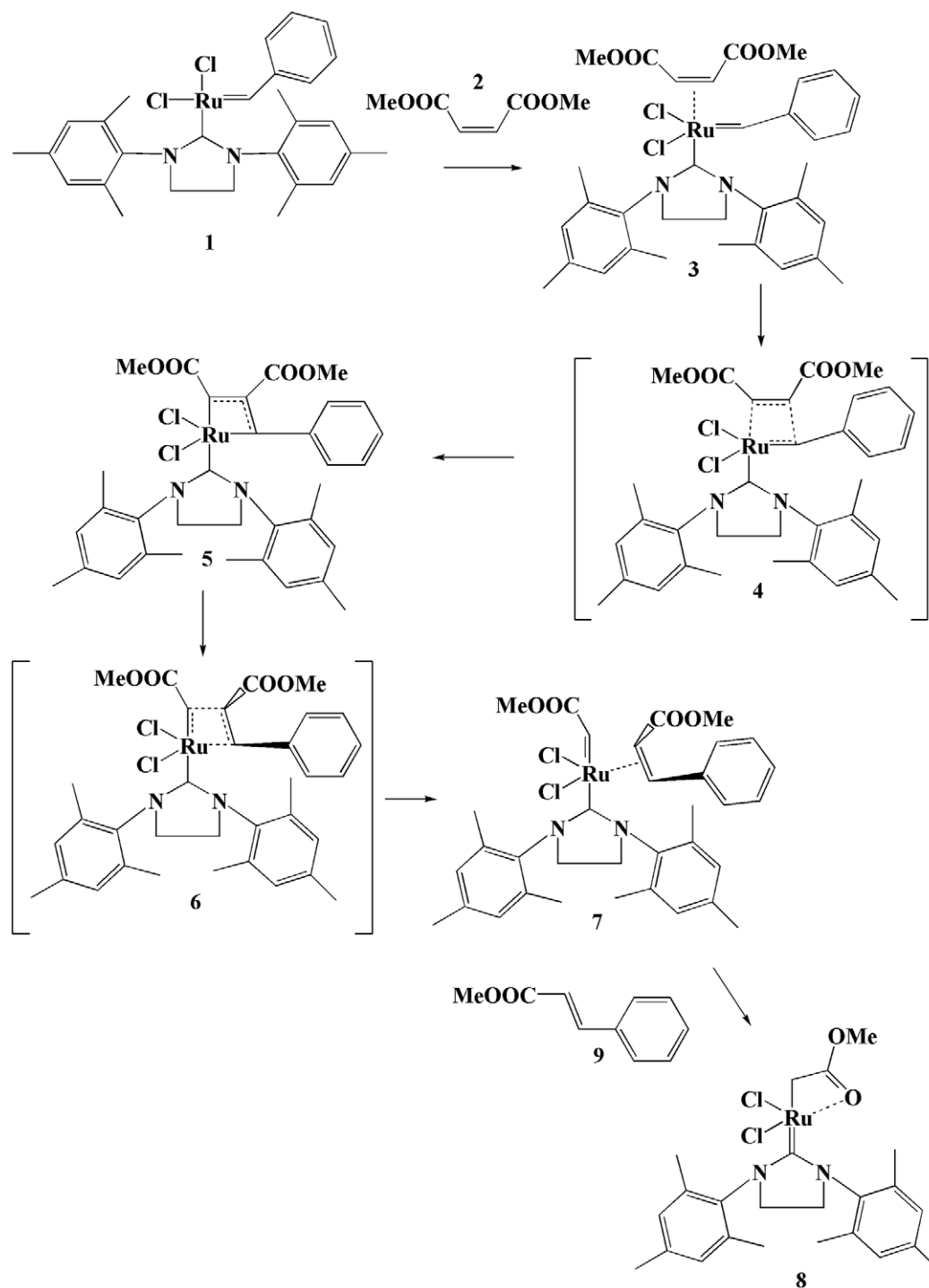
The mechanism of ruthenium alkylidene catalyzed olefin metathesis has recently been a subject of intense experimental [4,5] and theoretical [6] investigations. These results clearly indicate that for ruthenium complexes with general formula L(PR₃)(X)₂Ru=CHR¹ (R = Cy, Cp and Ph, X = Cl, Br and I, L = N-heterocyclic carbene ligand, NHC) initiation occurs via dissociative substitution of a phosphine ligand (PR₃) with olefin substrate, giving a monoligand complex.

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Methyl maleate (**2**) is a very poor chain transfer agent in the metathesis polymerization whereas acrylic acid derivatives do act as cross-metathesis partners [1d,2a,2c,7]. There are various possible reasons for such behavior. Some of them could be steric hindrances caused by two carbonyl groups resulting in high activation energy of a metathesis reaction or a non-productive complex formation between carbonyl and Ru

center impeding the productive complex formation between double C=C bond and Ru center of the catalyst.

The goal of this study is to clarify this problem studying the reaction pathways for the cross-metathesis of methyl maleate (**2**) and ethylene (**10**) using the second generation Grubbs catalyst (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) ($(PCy_3)_2Ru=CHPh$).

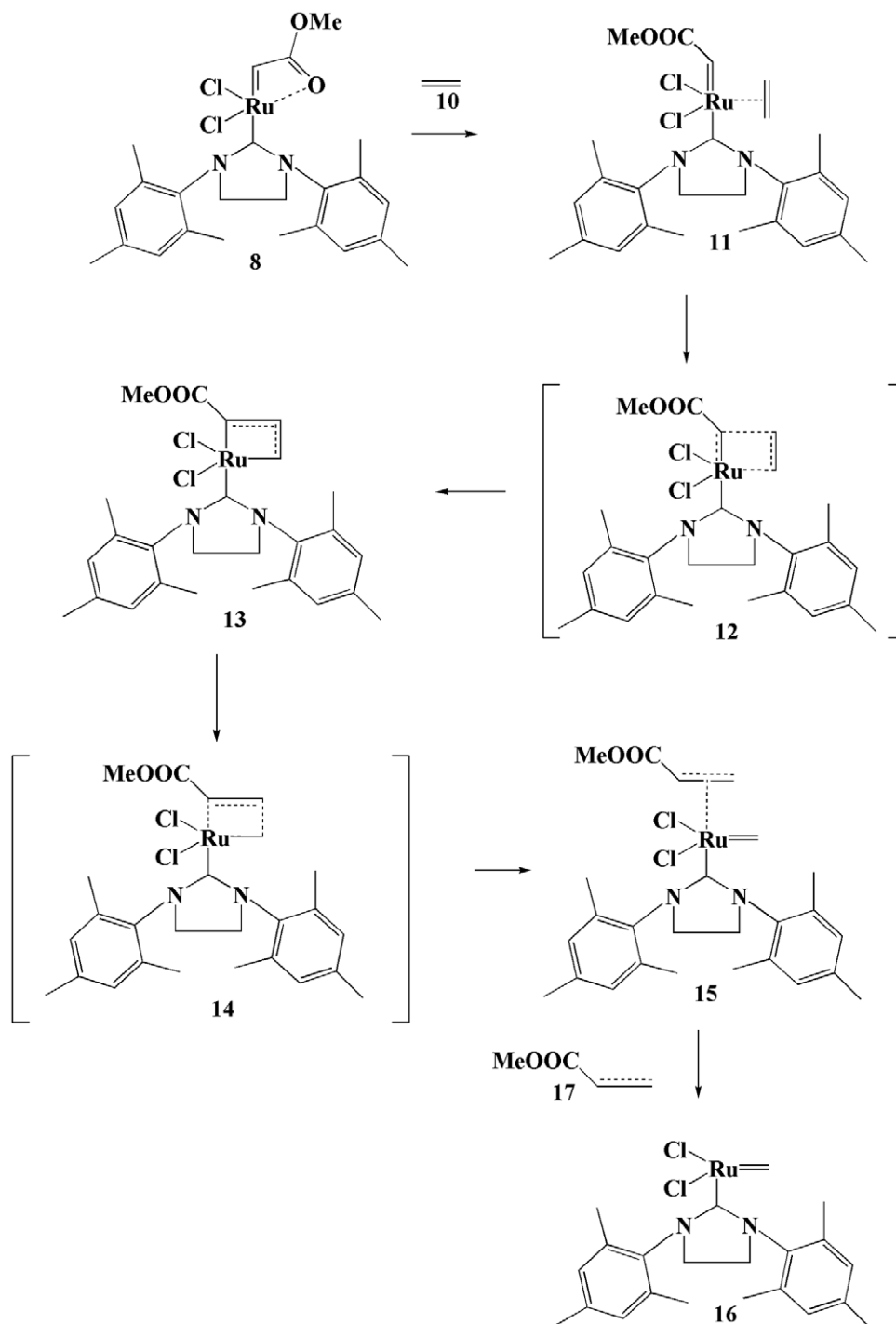


Scheme 1. Metathesis of dimethyl maleate (**2**) mediated by (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) $Cl_2Ru=CHPh$.

2. Computational details

All calculations were carried out with the JAGUAR v 6.0 program [8]. Becke's three parameter functional (B) [9] in combination with the Lee, Yang and Parr (LYP) correlation function [10] and LACVP* basis set was used for the geometry optimization. LACVP* basis set uses standard 6-31G* basis set for light elements and LAC pseudopotential [11] for third row and heavier elements. The molecular

geometries of all calculated molecules were optimized at 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 a minimum (zero imaginary modes) is located and to reach zero point energy (ZPE) correction and thermodynamic properties. All calculations were carried out in gas phase since as it has been shown before that solvation energies of similar molecules in non-polar sol-



Scheme 2. Metathesis of ethylene (**10**) mediated by (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) $\text{Cl}_2\text{Ru}=\text{CHCOOMe}$.

vents introduce smaller error than the method itself [3,6]. MPW1K functional [12] in combination with LACVP* basis set was used to perform all calculations done with B3LYP functional for comparison purpose.

3. Results and discussion

Schemes 1 and 2 show reaction routes for the cross-metathesis of dimethyl maleate (**2**) and ethylene (**10**). Figs. 1 and 2 depict the Gibbs free energy profiles for the metathesis reaction corresponding to Schemes 1 and 2, respectively. The first step; formation of π -complex **3** is detected by both models B3LYP and MPW1K, followed by a transition state **4** formation. Both methods predict positive the Gibbs free energy formations for complex **3** close to 7 kcal/mol, similar for two functionals. However, the geometries of complex **3** determined by two methods are rather different (Fig. 3). B3LYP predicts looser structure for complex **3** compared to MPW1K. Thus, carbene–olefin distance differs by 0.34 Å which is probably due to poor performance of B3LYP model for complexes where dispersion interactions are involved [13]. According to Curtin–Hammett principle [14] the total Gibbs free activation energy of the process can be estimated as a sum of complex **3** formations and the Gibbs free activation energy of the reaction **3** \rightarrow **5**. As seen from Fig. 1 the total activation energies of the formation of metalcyclobutane **5** are of 18.0 and 16.1 kcal/mol for B3LYP and MPW1K functional, respectively. The geometry of the transition state **4** is shown in Fig. 3. As seen, in this case two methods give similar results with the difference in interatomic distances not exceeding 0.03 Å. The formation of metalocyclobutane **5**, which is a minimum, is predicted by both models. Moreover, the geometries of intermediate **5** are quite similar for two methods (Fig. 3). However, MPW1K predicts **5** to be much more stable compared to B3LYP as seen from Fig. 1. The dissociation of metalocarbene **5** leads to the formation of final complex **7** through a transition state **6**. Two models predict rather different energetics for **5** \rightarrow **7** step. Thus, B3LYP predicts this transformation to be exothermic ($\Delta G = -3.7$ kcal/mol), while MPW1K calculations show that this process is endothermic with $\Delta G = 7.9$ kcal/mol. The Gibbs free activation energy of this transformation is different for two models as well. In accordance to various reports [15] B3LYP underestimates activation energies which is in line with higher the Gibbs free activation energy calculated with MPW1K functional, parameterized for kinetic applications (Fig. 1). Similar to complex **3** the geometry of complex **7** optimized using MPW1K functional is tighter compared to that using B3LYP model (Fig. 3). In case of transition state **6**, the difference between two methods is not so notorious. The most drastic difference between two models is manifested for the dissociation of the complex **7** to give metalocarbene **8** and olefin **9** where the difference for dissociation energies reaches 5.8 kcal/mol. As a result, the Gibbs free reaction energy

of the process can be estimated as a sum of complex **3** formations and the Gibbs free activation energy of the reaction **3** \rightarrow **5**. As seen from Fig. 1 the total activation energies of the formation of metalcyclobutane **5** are of 18.0 and 16.1 kcal/mol for B3LYP and MPW1K functional, respectively. The geometry of the transition state **4** is shown in Fig. 3. As seen, in this case two methods give similar results with the difference in interatomic distances not exceeding 0.03 Å. The formation of metalocyclobutane **5**, which is a minimum, is predicted by both models. Moreover, the geometries of intermediate **5** are quite similar for two methods (Fig. 3). However, MPW1K predicts **5** to be much more stable compared to B3LYP as seen from Fig. 1. The dissociation of metalocarbene **5** leads to the formation of final complex **7** through a transition state **6**. Two models predict rather different energetics for **5** \rightarrow **7** step. Thus, B3LYP predicts this transformation to be exothermic ($\Delta G = -3.7$ kcal/mol), while MPW1K calculations show that this process is endothermic with $\Delta G = 7.9$ kcal/mol. The Gibbs free activation energy of this transformation is different for two models as well. In accordance to various reports [15] B3LYP underestimates activation energies which is in line with higher the Gibbs free activation energy calculated with MPW1K functional, parameterized for kinetic applications (Fig. 1). Similar to complex **3** the geometry of complex **7** optimized using MPW1K functional is tighter compared to that using B3LYP model (Fig. 3). In case of transition state **6**, the difference between two methods is not so notorious. The most drastic difference between two models is manifested for the dissociation of the complex **7** to give metalocarbene **8** and olefin **9** where the difference for dissociation energies reaches 5.8 kcal/mol. As a result, the Gibbs free reaction energy

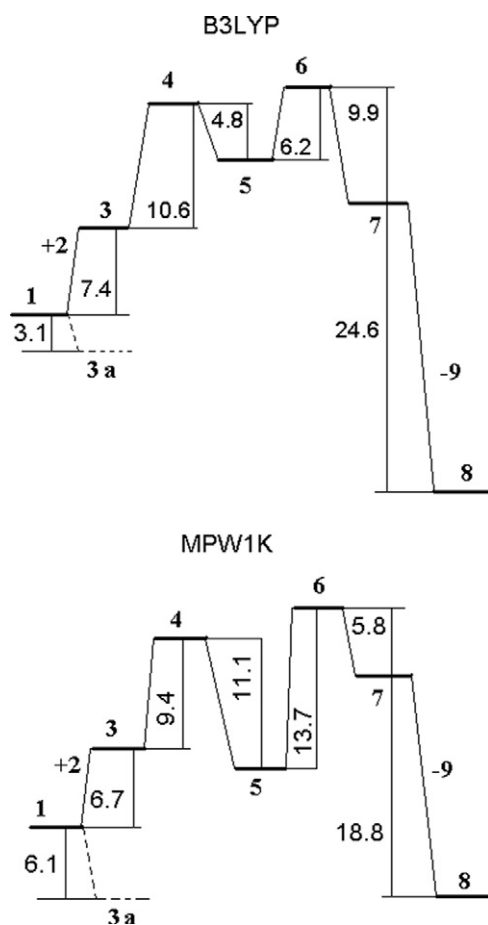


Fig. 1. The Gibbs free energy profile (kcal/mol) of the metathesis of dimethyl maleate (**2**) mediated by (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) $\text{Cl}_2\text{Ru}=\text{CHPh}$.

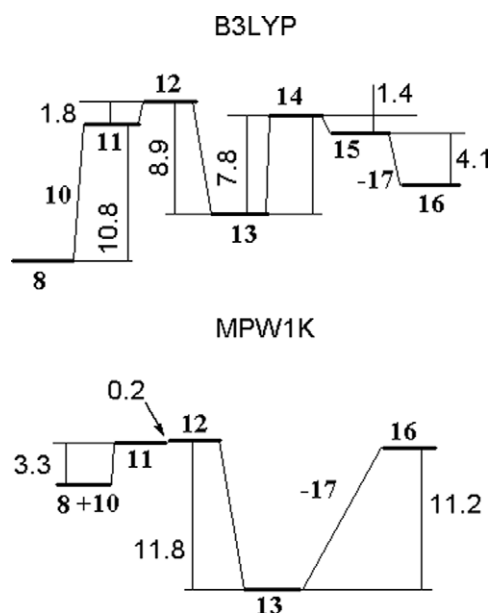


Fig. 2. The Gibbs free energy profile (kcal/mol) of the metathesis of ethylene (**10**) mediated by (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) $\text{Cl}_2\text{Ru}=\text{CHCOOMe}$.

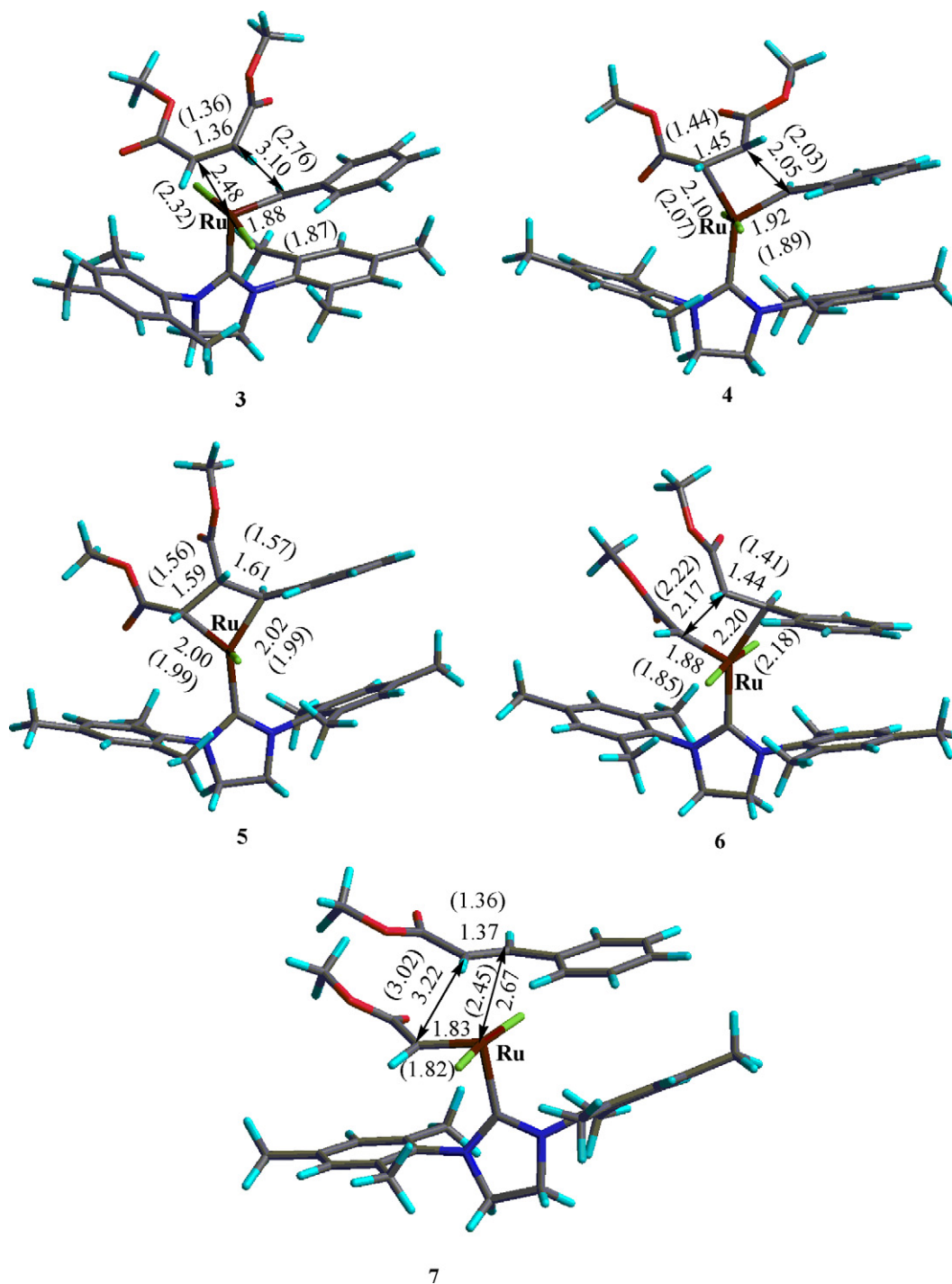


Fig. 3. Optimized geometries of the reaction intermediates participating in the metathesis of dimethyl maleate (**2**). Interatomic distances are for MPW1K (in baskets) and B3LYP models.

for the reaction $1 + 2 \rightarrow 8 + 9$ is of -15.1 and -5.9 kcal/mol for B3LYP and MPW1K model, respectively. The total Gibbs free activation energy for $1 + 2 \rightarrow 8 + 9$ reaction are of 19.4 and 18.7 kcal/mol for B3LYP and MPW1K models, respectively (Fig. 1). In spite of the differences in the reaction path description, both models; B3LYP and MPW1K give qualitatively similar picture. Two methods predict the reaction to be exothermic with similar activation energies close to 19 kcal/mol that is even

slightly less that calculated for the metathesis of 1,4-dichlorobutene at B3LYP/LACVP* level [3a], which is a good chain transfer agent. Therefore, according to the calculations the metathesis of **2** is viable kinetically and thermodynamically. The driving force of the reaction explaining rather negative ΔG is the *cis-trans* isomerization of the olefin during the transformation. Apparently, two carbonyl groups of maleate **2** do not causes excessive steric hindrances for the metathesis which is in accordance with

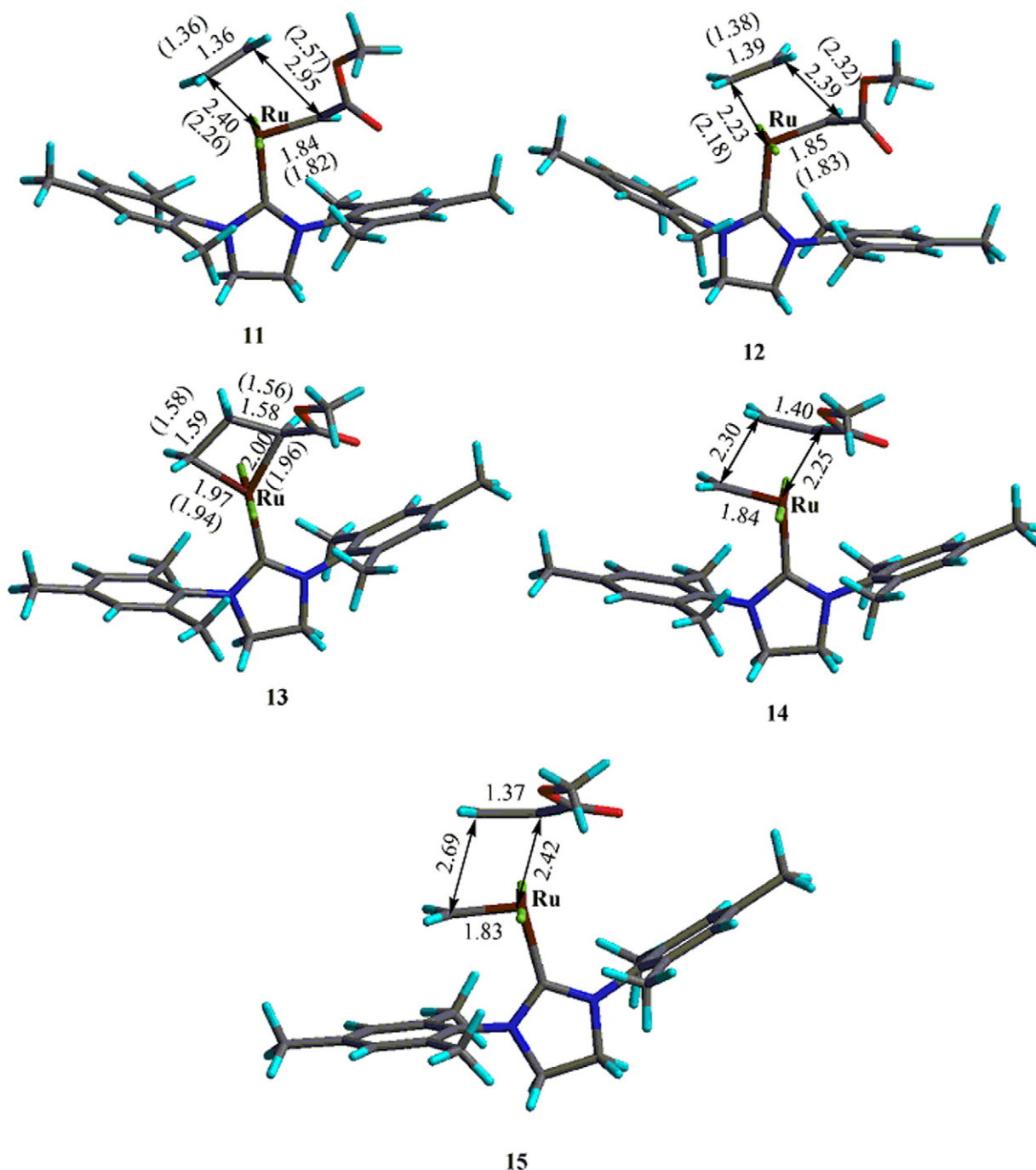


Fig. 4. Optimized geometries of the reaction intermediates participating in the metathesis of ethylene (10). Interatomic distances are for MPW1K (in baskets) and B3LYP models.

our statement [3a] that the most important steric hindrances are originated by the atom directly linked with olefin double bond. The molecular volume of **2** calculated using the methodology developed earlier [3a] (43.6 \AA^3) is similar to that of 1,4-dichlorobutene, which is good chain transfer agent.

The stability of ruthenium based ester carbene complex **8** could be explained by additional stabilization of Ru center by ester group. Fig. 5 shows two different conformations of **8**; **8a** and **8b** where there is apparent interaction

between sp^3 and sp^2 oxygen atoms with Ru center, respectively. O–Ru distances are well within of the sum of van der Waals radii of Ru (2.1 Å) and O (1.3 Å). Both functionals B3LYP and MPW1K predict conformer **8a** to be only slightly more stable compared to **8b** (0.8 and 0.9 kcal/mol, respectively). Therefore, in two conformers there is an interaction between oxygen atoms and ruthenium. Second, order perturbational analysis of Fock matrix in NBO basis reveals that in both conformers exists electron transfer of lone electron pair of oxygen atom to antibonding

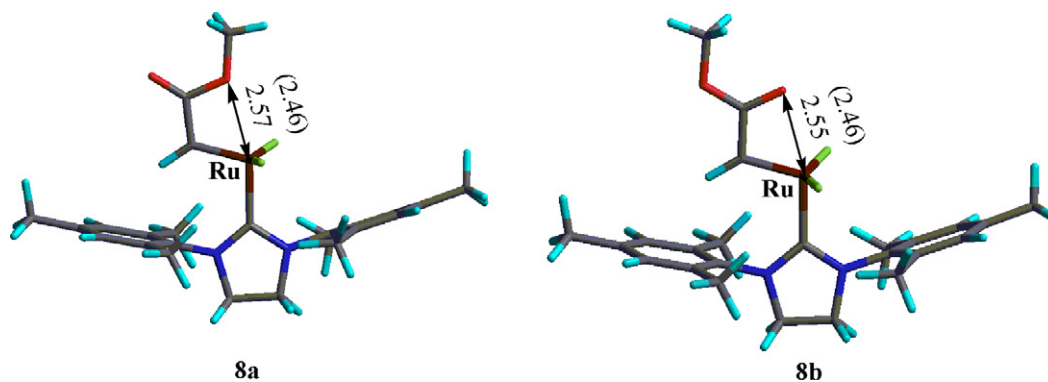


Fig. 5. Optimized geometries for two different conformers of metallocarbene **8**. Interatomic distances are for MPW1K (in baskets) and B3LYP models.

orbital of Ru–C(ligand) bond. Additionally, conformer **8a** is stabilized by the back donation of Ru electrons to the Rydberg orbitals of oxygen atom.

We studied the reactivity of carbomethoxy carbene **8** in the metathesis reaction with ethylene. Fig. 4 shows optimized geometries of reaction intermediates while Fig. 2 presents the Gibbs free energy profile for B3LYP and MPW1K models. The first step; the formation of π -complex **11** is detected by both models B3LYP and MPW1K, followed by the transition state **12**. Unlike the metathesis of **2**, these two functionals perform quite different for ethylene. According to B3LYP model (Fig. 2) the Gibbs free activation energy of the process is of 11.6 kcal/mol ($10.8 + 1.8$ kcal/mol) while MPW1K method predicts only 3.5 kcal/mol. This is quite unusual since it is known that B3LYP generally underestimates activation energies while MPW1K gives good account of activation energies. Moreover, MPW1K does not detect the transition state **14** and the final π -complex **15** located by B3LYP. On the other hand, both functional describe the metathesis of ethylene with **8** in a similar way as a slightly endothermic reaction with low activation energy. As in the case of dimethyl maleate **2** metathesis, MPW1K functional predicts more tight geometry for π -complex **11** and the transition state **12**, whereas the difference in interatomic distances in metallocyclobutane **13** does not exceeds 0.04 Å (Fig. 4).

Although, it is generally accepted that MPW1K functional performs better than B3LYP on organic molecules [16], it is not that evident for organometallic molecules. It has been shown that B3LYP is superior to MPW1K in predicting of geometrical parameters of selected transition metal compounds in combination with the split valence double ζ basis set [17]. On the other hand, B3LYP functional led to wrong conclusions for the reactivity of certain Pt complexes, while MPW1K model gave correct predictions [18].

In our case, the reaction profiles obtained with both functional predict the metathesis of **2** to be viable reaction pathway, which is not the case. The difference between calculations and experiment can be attributed to the ability of **2** to form alternative complex with active center of catalyst, thus impeding the metathesis reaction. Fig. 6 shows opti-

mized geometry of alternative complex **3a** where there is coordination between carbonyl oxygen and Ru-center. As seen, both functionals B3LYP and MPW1K predict negative ΔG formation for complex **3a** as seen from Fig. 1, being much more stable compared with **3**. The formation of the complex **3a** disables the active site of the catalyst due to complexation with carbonyl, thus impeding the metathesis. According to B3LYP and MPW1K the binding Gibbs free energies of **3a** complex are of -3.1 and -6.1 kcal/mol, respectively, corresponding to the equilibrium constants of 187 and 29700 for the complex formation. This means that in 1 to 1 mixture olefin-catalyst B3LYP predicts 93% of catalyst to be in the form of complex **3a**, while according to MPW1K 99.4% of Ru catalyst is deactivated by complex formation. Thus, MPW1K functional seems to give more reliable predictions compared to B3LYP one since according to B3LYP metathesis of **2** should occur, although slow, while MPW1K predicts practically all the catalyst to be deactivated by the complex for-

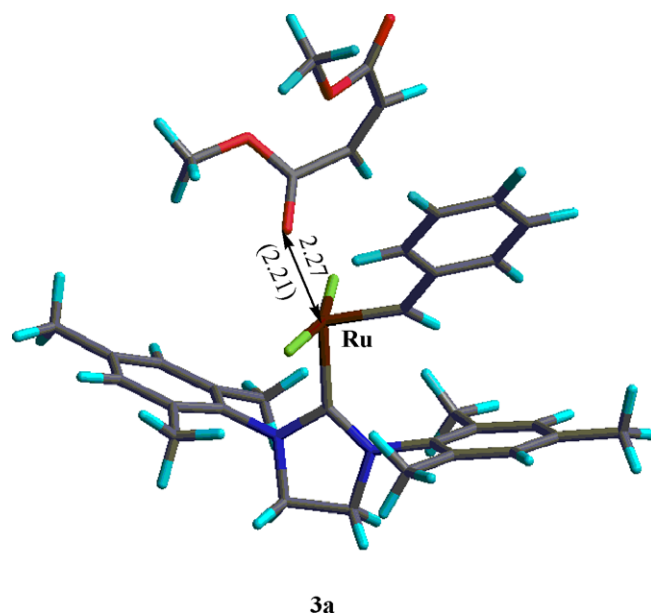


Fig. 6. Optimized geometry of non-productive complex **3a**. Interatomic distances are for MPW1K (in baskets) and B3LYP models.

mation with carbonyl group of dimethyl maleate with no reaction.

To be assured that salvation do not affect the conclusions we optimized geometries of complexes **3** and **3a** in 1,2-dichloroethane, a common solvent for the metathesis reaction using Poisson–Boltzman solver [19,20] implemented in JAGUAR v 6.0 suite of program [8]. In the gas phase ΔG between **3** and **3a** is of 10.5 kcal/mol. In solution this difference slightly increases to 12.2 (kcal/mol) supporting our suggestion that in this particular case the solvent effect is of little importance for the reaction energetics.

We also compared the complexation of ether oxygen with that of carbonyl for compounds with similar steric factor to separate electronic factor from steric one. The formation of stronger complex by carbonyl oxygen complex compared to ether one will favor our conclusions since this class of catalysts tolerate ether groups [21]. Thus, we calculated the free Gibbs binding energies **1** with diisopropyl ether to compare with the binding energy in complex **3a**. Olefin **2** and diisopropyl ether have very similar molecular volumes (102.7 and 101.8 Å³) and close ovality index (1.57 vs. 1.62) calculated using CHEM3D (v 7.0), implying similar steric factor for two ligands. Thus, the binding energy of complex **3a** between **2** and **1** at B3LYP/LACVP* level is –3.1 kcal/mol, while for the complex of **1** with diisopropyl ether is 6.1 kcal/mol. This test calculation agrees very well with the fact that this family of catalysts tolerates ether groups. We did not incorporate this part in manuscript considering that it is not essential for discussion.

4. Conclusions

The low reactivity of dimethyl maleate **2** in the metathesis catalyzed by second generation of ruthenium carbene complexes is the formation of non-productive complex between carbonyl oxygen and Ru center and not the low stability of carbomethoxy carbene complex **8**. Carbene **8** is stabilized due to interactions of sp³ or sp² oxygen with Ru center. MPW1K functional seems perform better than popular B3LYP model in predicting the energetics of studied metathesis reactions.

Acknowledgements

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