



Metathesis of carbonyl containing olefins by 2nd generation Ru alkylidene catalysts: A computational study

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ABSTRACT

The metathesis reaction of *cis*-1,4-diacetoxy-2-butene (**2**) mediated by a second generation ruthenium alkylidene catalyst (IMesH₂)Cl₂Ru=CHPh (**1**) where IMesH₂ is 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene group has been modeled at PBE0/LACV3P*//PBE0/LACVP* level of theory. The calculations demonstrate that the driving force of the metathesis reaction is the formation of a Ru–O coordination bond in the corresponding Ru acetoxyethylidene complex **8a-II**. The free activation energy of metathesis by **8a-II** complex is higher than that of the metathesis reaction mediated by the conventional ruthenium alkylidene catalyst (**8b**), due to the additional stabilization of the Ru center by a carbonyl oxygen revealing lower reactivity of carbonyl containing ruthenium carbene species. It has been shown that conjugation between carbonyl and olefin double bonds decreases the reactivity of olefins due to stabilization of nonproductive complex between Ru center and carbonyl group of the olefin.

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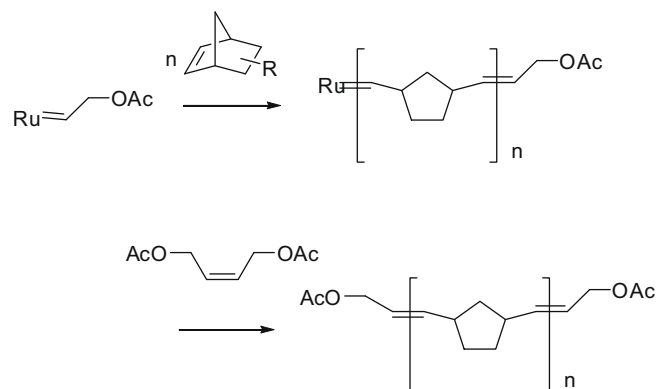
1. Introduction

The ruthenium alkylidene catalysts coordinated with N-heterocyclic carbene ligands provide opportunities to metathize challenging olefins with sterically hindered or deactivating functional groups [1]. For example, ester-containing olefins are challenging object due to the presence of the electron-withdrawing groups [2]. Recently, we have reported a density functional study of ruthenium alkylidene mediated metathesis of dimethyl maleate [3] and other challenging substrates [4]. The mechanism of enyne metathesis mediated by 2nd generation Ru alkylidene has been recently studied too by Lippstreu and Straub [5].

The computational modeling shows that the low reactivity of dimethyl maleate in the metathesis reaction by Ru-alkylidene catalysts is not only caused by significant steric hindrances of two carbonyl groups of olefin, but also due to nonproductive complex formation between a carbonyl oxygen and a Ru active center that impedes the metathesis [3] (Scheme 1).

It is worth noting, that the complex formation between a carbonyl oxygen and a Ru center in metathesis of ester and amide containing olefins by Ru-alkylidene catalysts has already been discussed [1b,1c,2c]. Thus, the low metathesis activity of olefins with electron-rich amides was explained by a complex formation between carbonyl oxygen and a Ru active center [1b]. On the other hand, it is well known, that *cis*-1,4-diacetoxy-2-butene is widely used as a cross-metathesis partner. Thus, acetoxy (hydroxy)-termi-

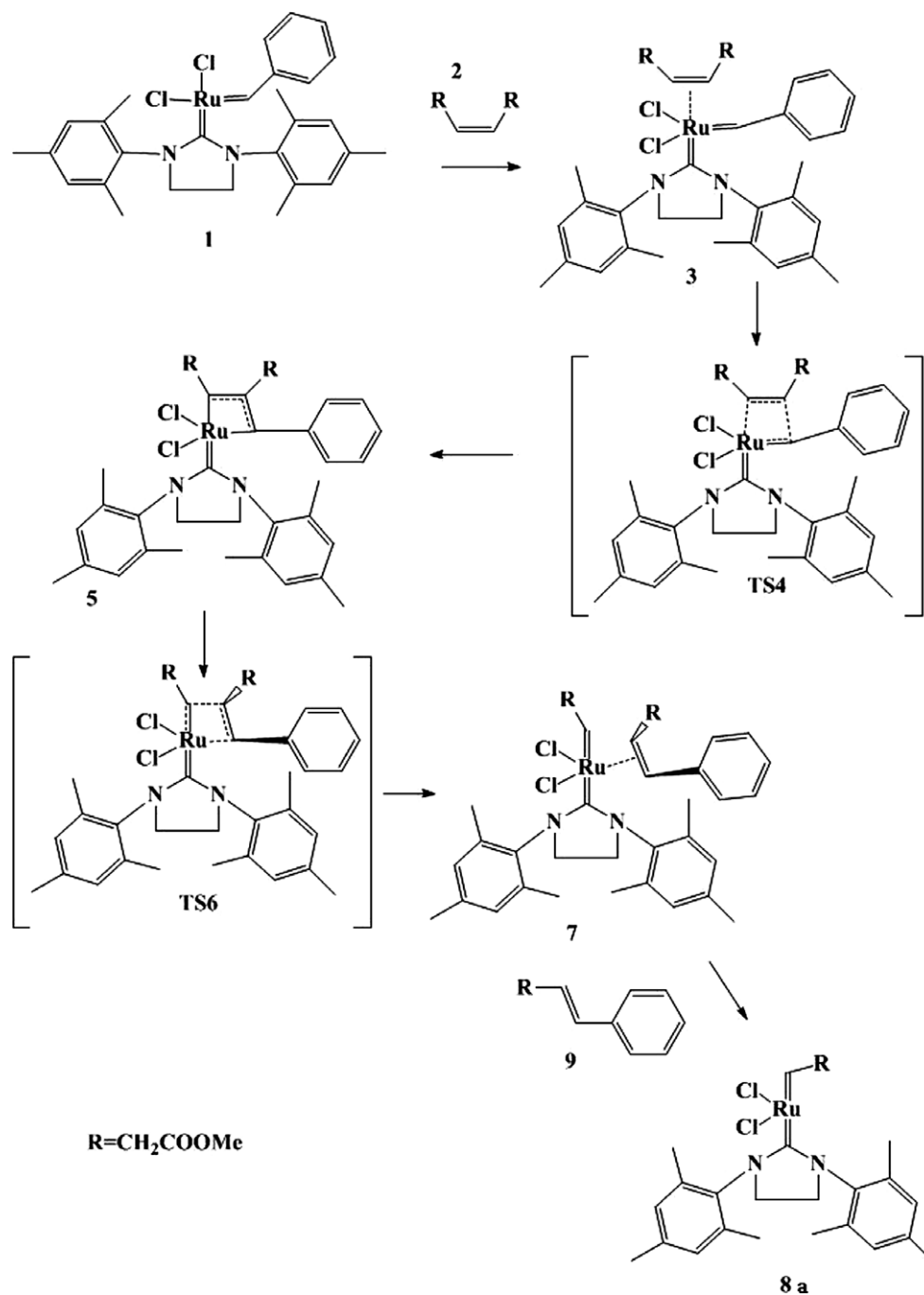
nated telechelic polybutadiene and polynorbornene have been synthesized by the metathesis degradation of corresponding polymers or ring-opening metathesis polymerization (ROMP) of *cis,cis*-1,5-cyclooctadiene and norbornene using *cis*-1,4-diacetoxy-2-butene as a chain transfer agent [6]. It is assumed that, this reaction proceeded via the formation of a ruthenium acetoxyethylidene complex which is different from a conventional alkylidene complex due to the presence of electron-withdrawing acetoxy group.



The carbonyls of acetoxy groups may coordinate with the 14 electron Ru-alkylidene catalyst and slow down the formation of

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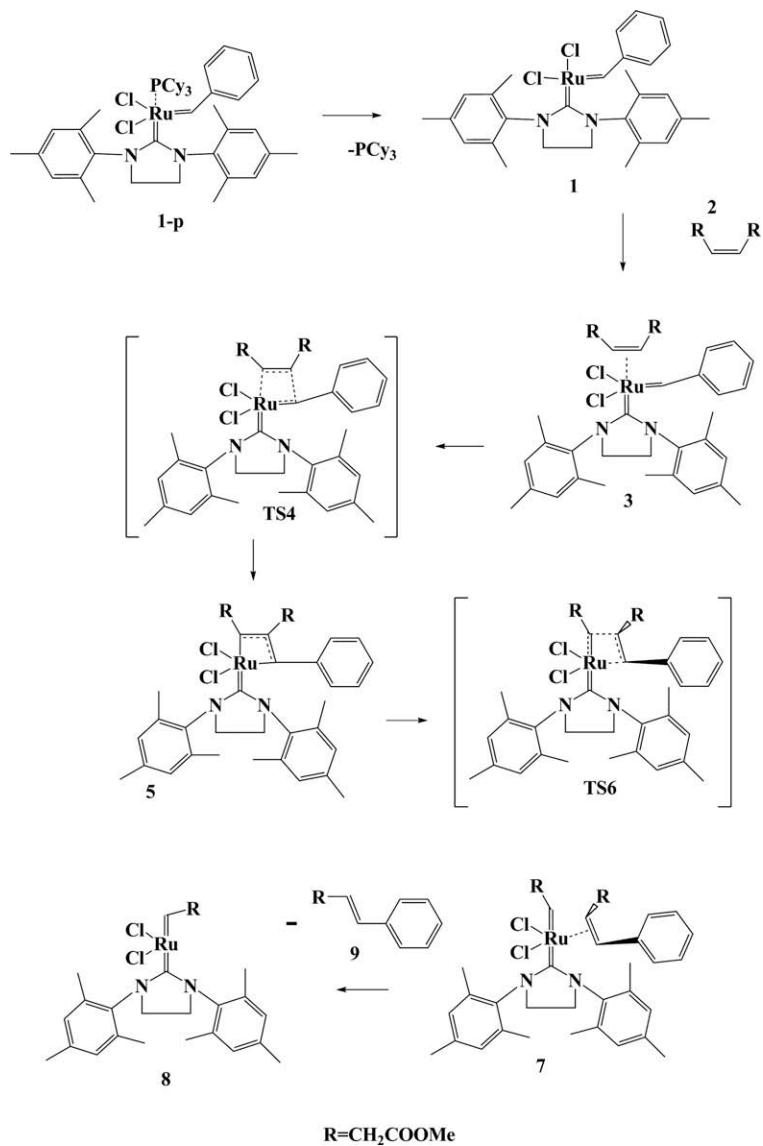
Scheme 1. The metathesis reaction scheme of dimethylmaleate.

corresponding ruthenium–carbene active species. Thus, our experiments show that the cross-metathesis degradation of natural rubber and *cis*-polybutadiene with *cis*-1,4-diacetoxy-2-butene as a chain transfer agent (CTA) proceeded slower compared to the same reaction using *cis*-1,4-dichloro-2-butene as a CTA. It has also been reported that α,β -carbonyl containing olefins require high catalyst loadings and extending reaction times [1b,2d].

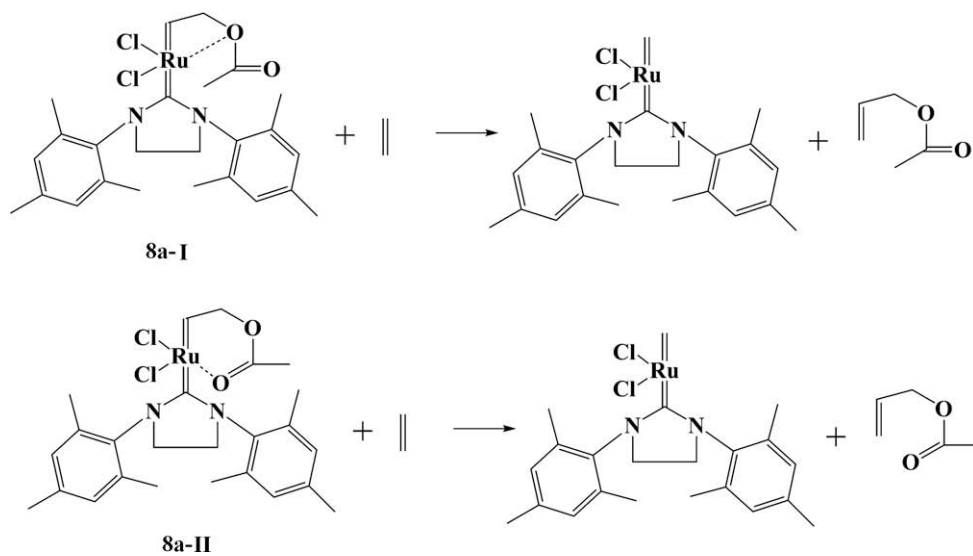
The goal of this study is to model the reaction pathways and chelation effects of carbonyl groups on the metathesis activity of *cis*-1,4-diacetoxy-2-butene (2) using the second generation Grubbs catalyst (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (IMesH_2) $\text{Cl}_2\text{Ru}=\text{CHPh}$ (1).

2. Computational details

All calculations were carried out using JAGUAR 7.0 suite of programs [7]. Test calculations were carried out to establish the most appropriate theoretical model. Four different functionals B3LYP, MPW1K, M05 and PBE0 were tested to compare the optimized and experimental structures of recently synthesized ruthenium–alkylidene complex [8] using double and triple ζ basis sets (LACVP* and LACV3P*, respectively) as defined in JAGUAR 7.0 suite of programs. Test calculations demonstrated that MPW1K and PBE0 reproduced best the experimental geometry (the largest deviation from experiment was found to be of 0.04 Å for Ru–Cl and Ru–P



Scheme 2. The reaction of **2** metathesis by Ru catalyst **1**.



Scheme 3. Homodesmotic reaction for the determination of Ru–O binding energy in intermediate **8a**.

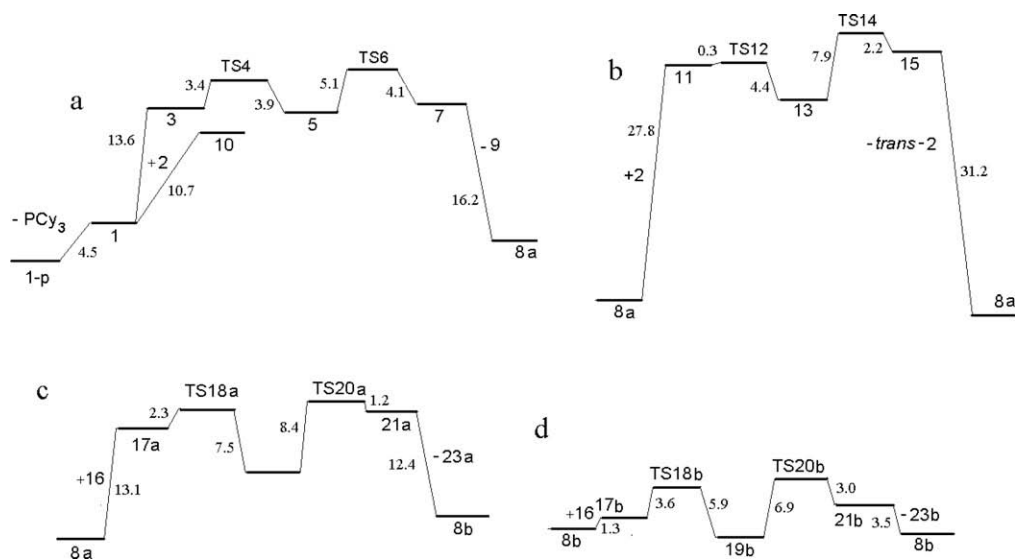


Fig. 1. The free Gibbs reaction energy profile for 2 metathesis (a), self-metathesis (b), the metathesis of *cis*-butene (16) by 8a (c) and 8b (d) catalysts, respectively, (kcal/mol).

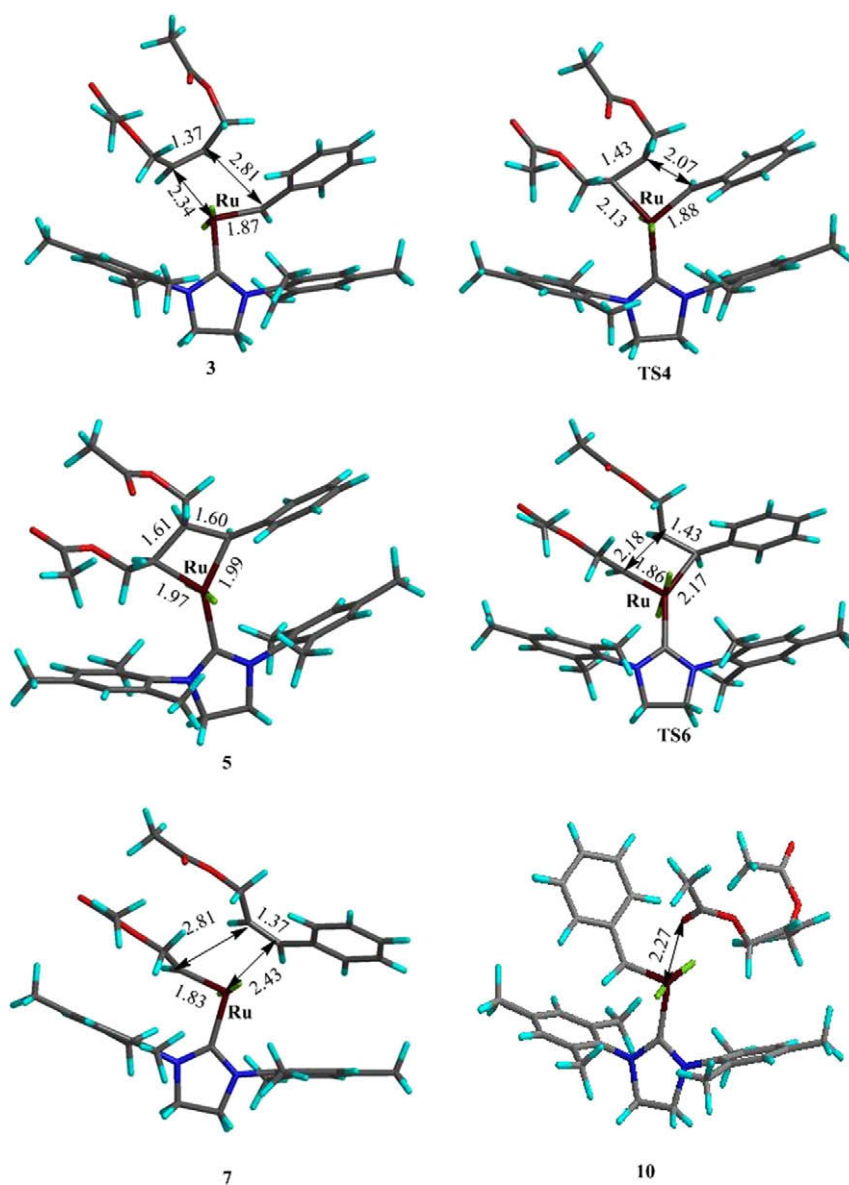


Fig. 2. Optimized geometries of the reaction intermediates for 2 metathesis.

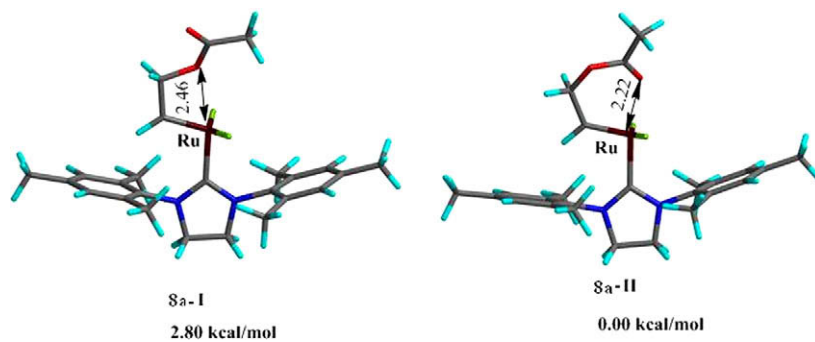
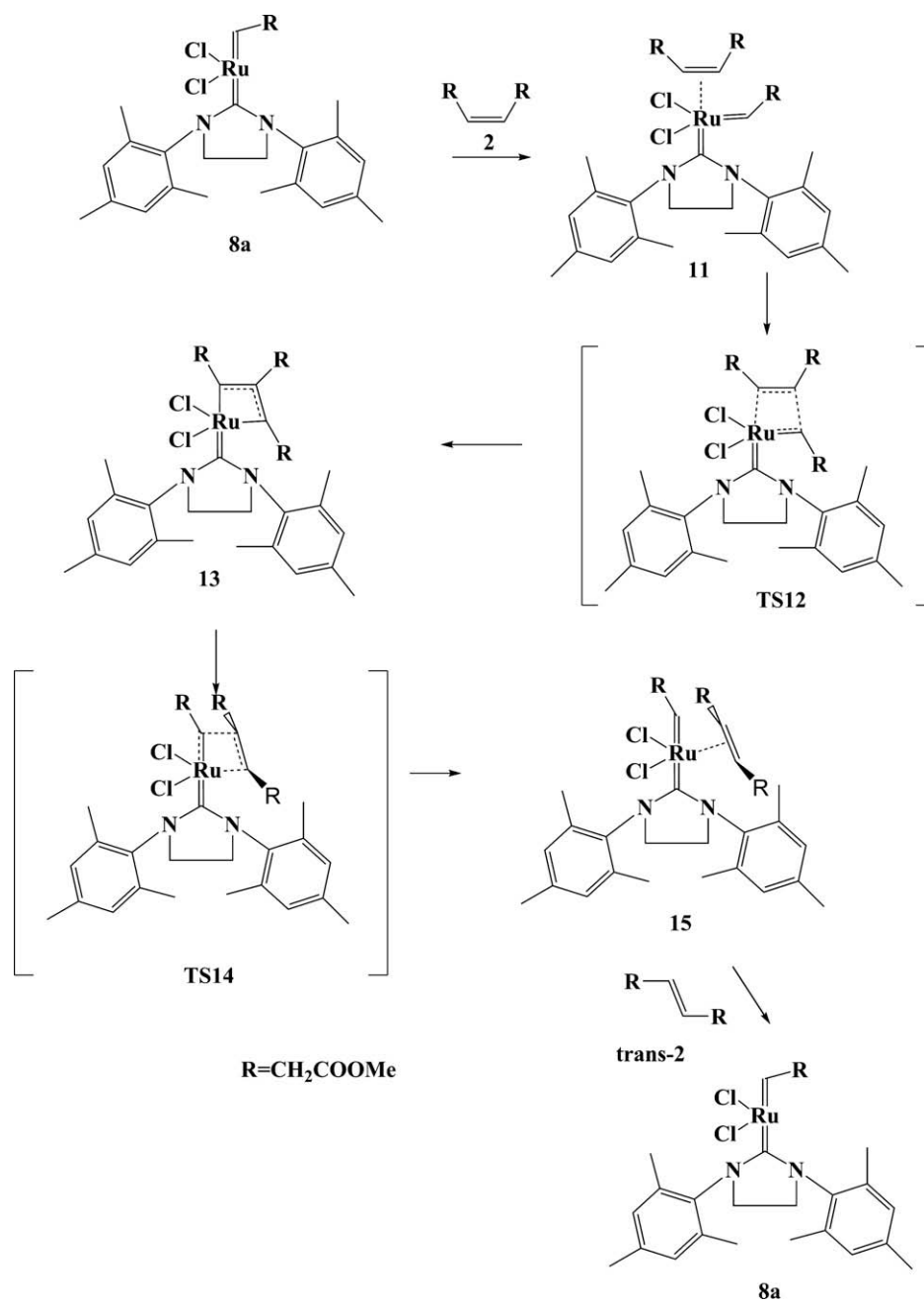


Fig. 3. Optimized geometries of different conformations of acetoxyethylidene complexes of **8a** (**8a-I** and **8a-II**) and their relative free Gibbs energies.



Scheme 4. The reaction of **2** self-metathesis by Ru catalyst **8a**.

bonds for LACVP* basis set). The use of LACV3P* basis set does not lead to substantial improvement of optimized geometries. Thus, the bond lengths differences between LACV3P* and LACVP* optimized geometries do not exceed 0.005 Å for PBE0 and MPW1K functionals). To verify the effect of the triple and double ζ basis sets on the reaction energetic the binding energies for complex **3** (Scheme 2) were calculated at PBE0/LACVP*, PBE0/LACV3P* and PBE0/LACV3P**/PBE0/LACVP* levels of theory giving of 3.68, 8.15 and 7.90 kcal/mol, respectively. As seen, the use of LACVP* optimized geometry for the single point calculation with LACV3P* basis set produces the binding energy within 0.25 kcal/mol compared with that using LACV3P* optimized geometries.

Considering the fact that PBE0/LACV3P**/PBE0/LACVP* model reproduces very well the experimental enthalpy of the phosphine ligand dissociation in (IMesH₂)(PCy₃)Cl₂Ru=CHPh (23.8 (theory) and 25 ± 4 kcal/mol (experiment), respectively [9]), this model was adopted for all calculations.

The total Gibbs energies of all molecules (*G*) were calculated as follows: $G = E_t + \Delta G$, where E_t is the total electronic energy calculated at the PBE0/LACV3P* level using PBE0/LACVP* optimized geometry and ΔG is the Gibbs energy correction calculated as the

difference between the total electronic energy and the Gibbs energy estimated at the PBE0/LACVP* level using PBE0/LACVP* optimized geometry.

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.

The initial structures for calculations were obtained using the Titan builder [10].

A few test run were carried out to take into account solvent effect (1,2-dichloroethane) using a Poisson–Boltzman solver [11,12] implemented in the JAGUAR v 7.0 suite of programs. The difference between the gas and solution state free Gibbs energies was found to be within 1.5 kcal/mol. It has been shown earlier [13] that solvation energies of similar molecules in nonpolar solvents introduce smaller error than the method itself. Therefore, all calculations were carried out in gas phase.

The binding energies between a Ru center and oxygen atoms in **8a-I** and **8a-II** complexes (ΔE_{int}) were estimated at PBE0/LACV3P**/PBE0/LACVP* level as the reaction energy of a homodesmotic reaction shown in Scheme 3.

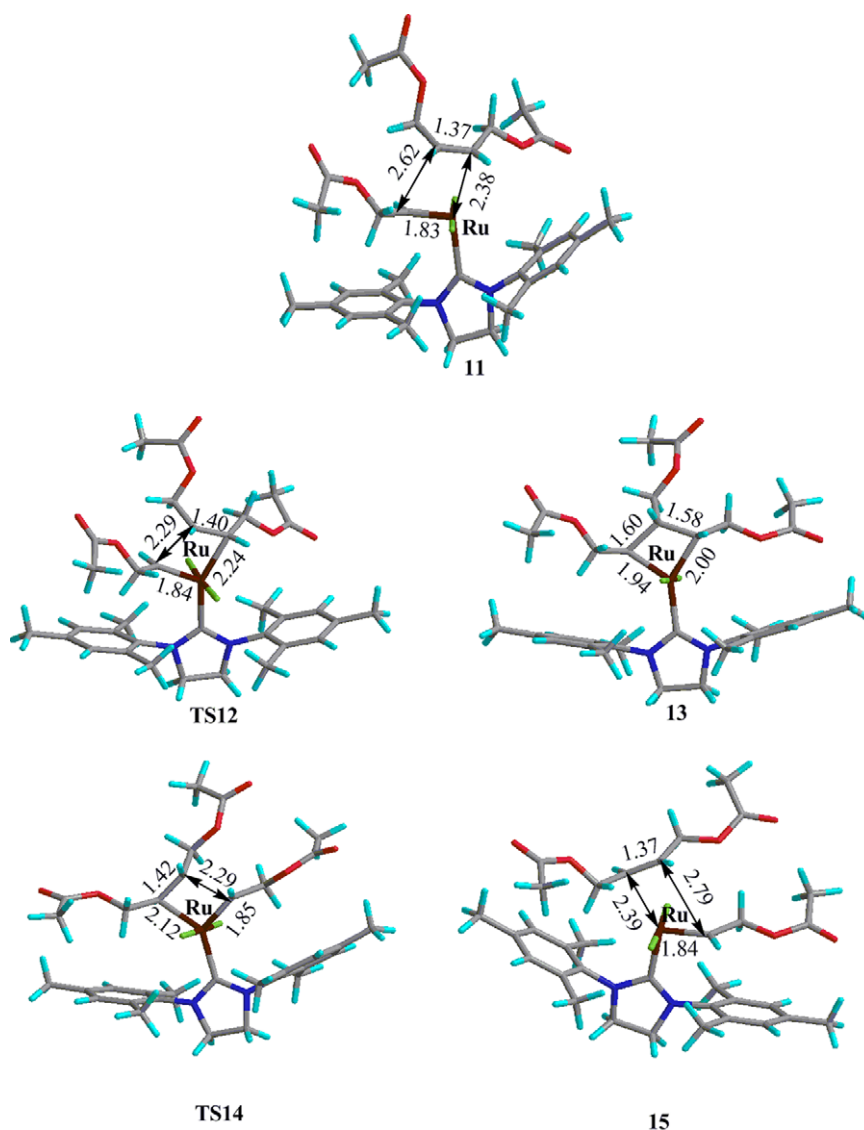
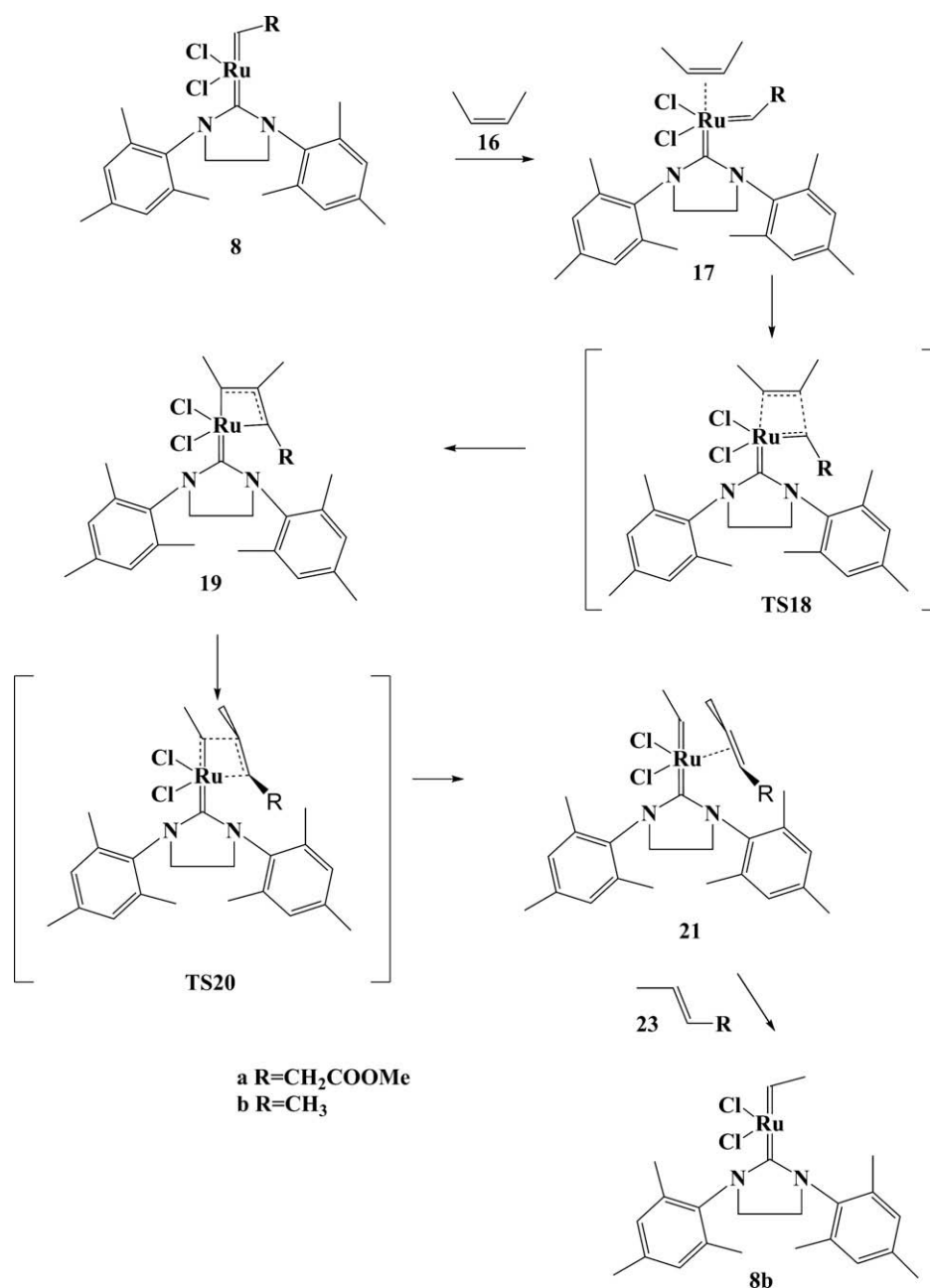


Fig. 4. Optimized geometries of reaction intermediates for **2** self-metathesis.

3. Results and discussion

Scheme 2 shows the reaction route of *cis*-1,4-diacetoxy-2-butene (**2**) metathesis. Fig. 1a depicts the Gibbs free energy profile for the metathesis reaction corresponding to the Scheme 2. The first step is the dissociation of a phosphine ligand followed by the formation of π -complex **3** and a transition state **TS4** formation. The reaction is endergonic (13.6 kcal/mol for the formation of **3** from **1**). According to the Curtin–Hammett principle [14] the total Gibbs free activation energy of the process can be estimated as a sum of the free Gibbs energy formation of complex **3** and the Gibbs free activation energy of the reaction **3** \rightarrow **5**. As seen from the Fig. 1a the total activation energy of the formation for metallacyclobutane **5** is of 17.0 kcal/mol. The dissociation of **5** leads to the formation of final complex **7** through transition state **TS6**. The dissociation of the complex **7** giving the corresponding ester car-

bene **8a** and the corresponding olefin **9** is strongly exergonic (Fig. 1a) with ΔG of -16.2 kcal/mol, manifesting unusual stability of the 14 electron carbene **8a-II**. The total Gibbs free activation energy for **1** + **2** \rightarrow **8a** + **9** reaction is of 18.2 kcal/mol (Fig. 1a), while the free Gibbs reaction energy is of -2.1 kcal/mol. However, if the dissociation of phosphine ligand is taken into account (4.5 kcal/mol) the free Gibbs reaction energy is slightly positive (2.2 kcal/mol). The driving force of this reaction should be related to unusual stability of metallacarbene **8a**. The stability of the ruthenium based ester carbene complex **8a** could be due to additional stabilization of a Ru center by the carbonyl group. Fig. 2 depicts optimized geometries of the reaction intermediates for **2** metathesis while Fig. 3 shows conformations of **8a** where different oxygen atoms interact with the Ru center. O–Ru distances are well within of the sum of van der Waals radii for Ru (2.1 Å) and O (1.3 Å) for both conformers. According to calculations the binding energy



Scheme 5. The metathesis of *cis*-butene (**16**) by **8a** and **8b** catalysts.

between Ru and carbonyl oxygen atoms for the most stable conformer of **8a** (**8a-II**) is of 12.0 kcal/mol, while in conformer **8a-I** 8.3 kcal/mol. Conformer **8a-II** is more stable than **8a-I**, showing shorter Ru–O distance for conformer **8a-II** compared to that for **8a-I**. The interaction of Ru with the carbonyl oxygen allows to form a six-membered cycle for conformer **8a-II**. As seen Ru–O interaction is the reason for negative ΔG of $1 + 2 \rightarrow 8a + 9$ reaction. It is noteworthy that ruthenium based ester carbene complex similar to **8a** formed by the reaction **1** and dimethyl maleate (**DM**) also manifests Ru–O interaction [3]. However, in the case of **DM** the nonproductive complex of the carbonyl oxygen with a Ru active center is 10.5 kcal/mol more stable than productive complex [3], thus inhibiting the metathesis reaction. Recalculation of **DM** productive and nonproductive complexes at PBE0/LACV3P*//PBE0/LACVP* level gave the difference of 7.7 kcal/mol. The situation drastically changes for **2** when the difference reduces to only 2.9 kcal/mol (Fig. 1a). This phenomenon can be understood comparing HOMO of olefins **2** and **DM**. In case of **DM** the most important contribution to the HOMO comes from *p* orbital of a carbonyl oxygen while an olefin double bond contributes little. In case of **2**, π -orbitals of the olefin contribute mostly to HOMO. As a result, the

electron density is located predominantly at the olefin double bond in **2**, while in **DM** the electron density is shifted from the olefin double bond to the carbonyl group. The recalculation of **DM** metathesis reaction described in [3] at PBE0/LACV3P*//PBE0/LACVP* level for the comparison purpose reveals that the total free Gibbs activation energy of **2** metathesis is 3.3 kcal/mol lower, in accordance with the fact that the substituents directly linked to the double bond of the olefin contribute to the increase of the activation energy [4a].

It has also been studied the self-metathesis reaction of **2** initiated by Ru carbene complex **8a** (Scheme 4). Fig. 1b shows the free energy profile for the self-metathesis. As seen the free activation energy of self-metathesis is much higher than that using a Ru=CHPh catalyst. Such high free Gibbs activation energy of the reaction is due to the fact that in this case breaking Ru–O coordination bond is required as seen from the Scheme 4. As it can be noted from the Fig. 1 that the difference between the effective activation energies for **2** metathesis and isomerization (the complex formation plus activation energies) for the formation of intermediates **5** and **13**, respectively is of 11.1 kcal/mol, close to 12 kcal/mol estimated as binding the energy in intramolecular complex **8a-II**.

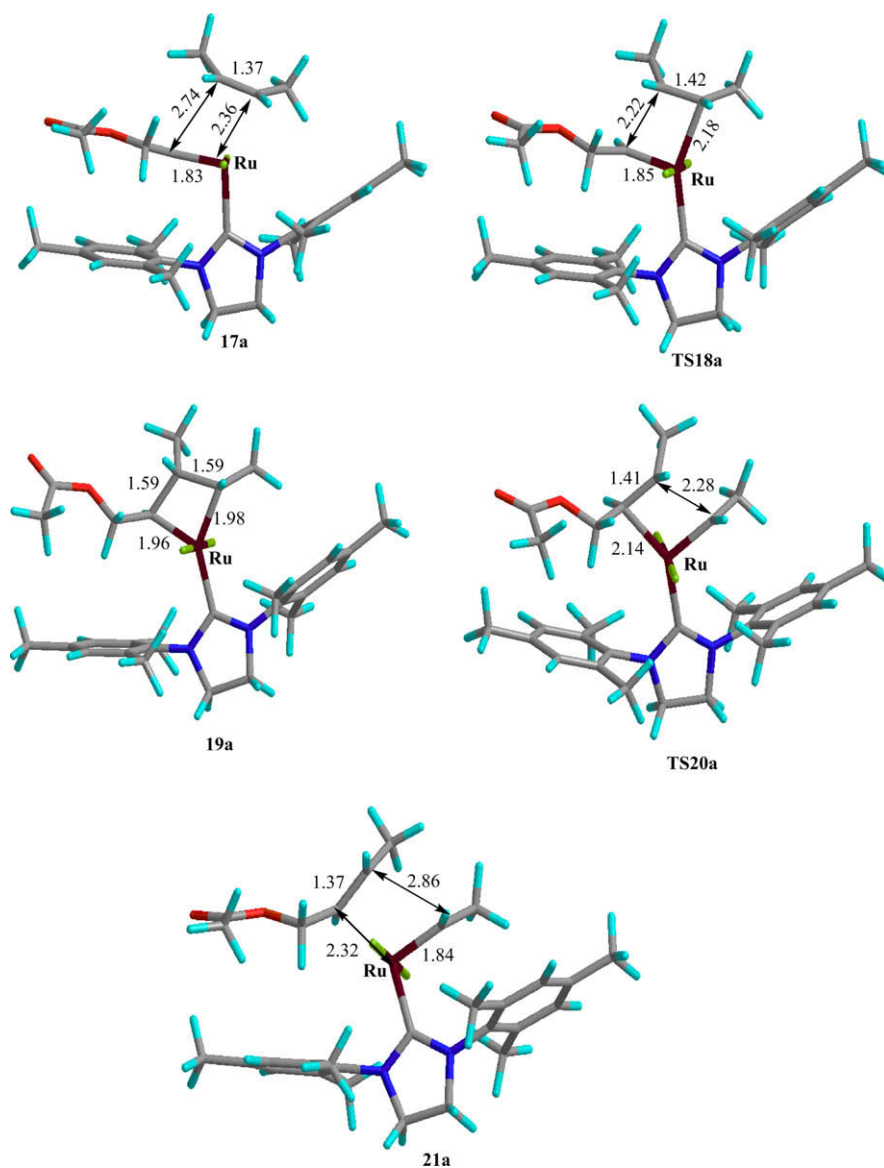


Fig. 5. Optimized geometries of reaction intermediates for **16** metathesis by **8a**.

Therefore, the high free Gibbs activation energy of **2** isomerization is due to intramolecular Ru–O complex formation. This bond is being broken when the metathesis reaction occurs.

Fig. 4 shows the optimized geometries of the reaction intermediates for **2** self-metathesis. Since the metathesis of **2** will proceed via the formation of a ruthenium acetoxyethylidene complex which is more stable than a ruthenium alkylidene one, this transformation may slow down the metathesis reaction. In fact, the behavior of metallacarbene **8a-II** should resemble that of metathesis precatalysts before the dissociation of phosphine ligands. Thus, the calculated energy of a Ru–O coordination bond in **8a-II** is of 12.0 kcal/mol; about half of that measured experimentally [9] for phosphine ligand elimination in ruthenium complexes of the general formula $L(PR_3)(X)_2Ru=CHR_1$.

For the comparison purposes, the reaction paths for *cis*-butene (**16**) metathesis mediated by ruthenium complexes **8a** and **8b** (Scheme 5) have been calculated. Fig. 1 shows the corresponding free energy profiles for the reactions (c and d, respectively).

As seen the activity of the complex **8a** is significantly lower compared to **8b**. The presence of the carbonyl group in **8a** increases both; the effective free Gibbs activation (16.3 vs. 5.9 kcal/mol) and the free Gibbs reaction energies (2.7 vs. -0.6 kcal/mol). The most important contribution to the activation energy for **16** metathesis mediated by **8a** is the formation of π -complex **17a**, since this step

implies breaking the Ru–O coordination bond in complex **8a**. Again, the difference between **17a** and **17b** formation (11.8 kcal/mol) is close to 12.0 kcal/mol, estimated binding energy between ruthenium and oxygen atoms in **8a** complex, supporting the hypothesis that the difference in activation energies of the metathesis **16** by **8a** and **8b** is due to dissociation of Ru–O coordination bond in **8a-II**. The endergonic character of **16** metathesis mediated by **8a** is also related to the additional stability of **8a** compared to **8b** due to stabilization of a Ru center by carbonyl oxygen.

Figs. 5 and 6 show the optimized geometries of the reaction intermediates involved in the reactions shown in Scheme 5. As seen, the geometry of the reaction intermediates participating in **16** metathesis is very similar for all molecules except for complexes **21a** and **21b** due to strong difference in the olefin nature. Similarly, the reaction and activation energies in paths **17** \rightarrow **21** are similar for paths **a** and **b**, signifying that the difference between path **a** and path **b** is due to the presence of carbonyl group in **8a**.

4. Conclusions

The calculations unravels that the reactivity difference between **DM** and **2** is related to the charge transfer from double bond to carbonyl group in **DM**, stabilizing nonproductive and destabilizing

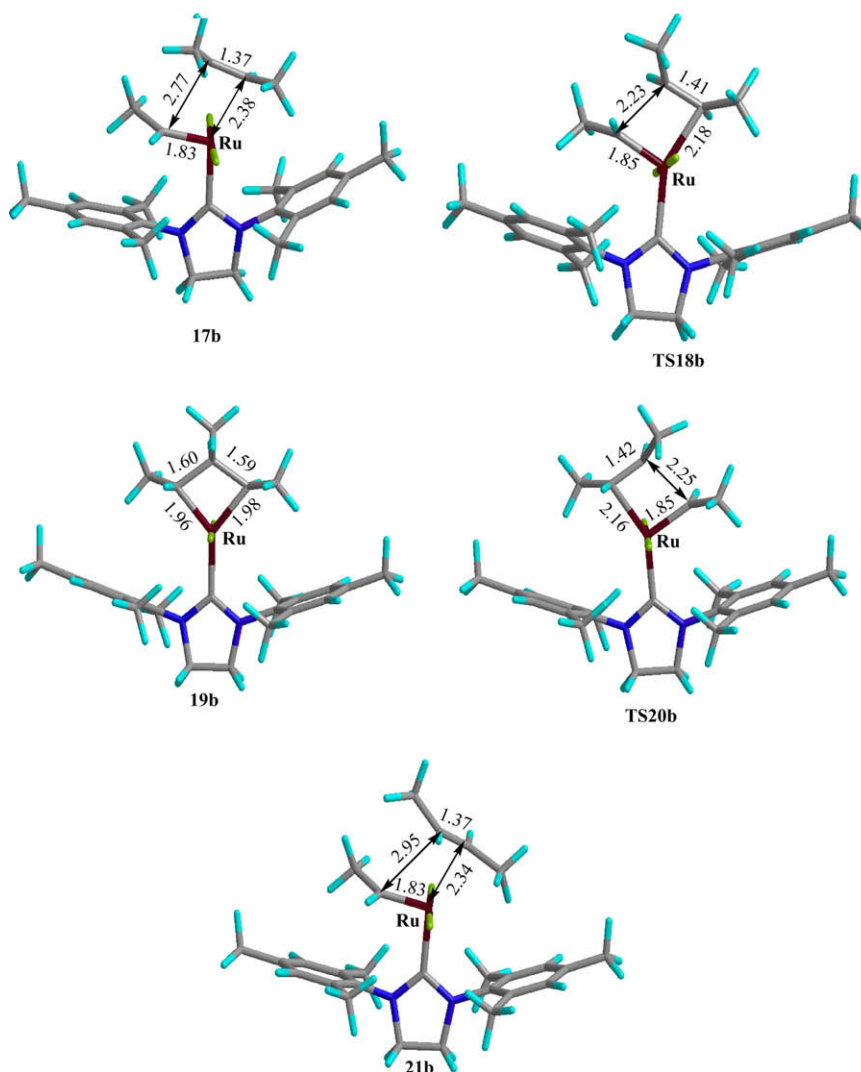


Fig. 6. Optimized geometries of reaction intermediates for **16** metathesis by **8b**.

productive complexes. This process is not possible for **2** where there is no conjugation between carbonyl and the double bond. This effect can have important implications for the reactivity in the metathesis reaction of different carbonyl containing olefins since the conjugation between the carbonyl group and the olefin double bond leads to the decrease of the olefin reactivity.

The driving force of the metathesis reaction of **2** using ruthenium alkylidene catalysts is the formation of an internal Ru–O coordination bond in metallacarbene complex **8a**. Since any metathesis reaction mediated by metallocarbene **8a** requires breaking of the Ru–O coordination bond the free Gibbs activation energy of metathesis initiated by acetoxyethylidene Ru complex **8a** is higher than this using a conventional alkylidene catalyst (**8b**).

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.010.

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