

DFT study of ethene metathesis proceeding on monomeric Mo^{VI} centres of $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst

The role of the molybdacyclobutane intermediate

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Abstract

Density functional theory (DFT) study of the pathway of ethene metathesis proceeding on monomeric Mo^{VI} centres of $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst is reported. Calculations were carried out with the GAUSSIAN 98 program using the hybrid B3LYP functional. Models of active Mo^{VI} sites including alumina cluster of formula $\text{Al}_2(\text{OH})_6$ were used. Ethene addition to molybdenamethylidene centre leading to the trigonal bipyramidal molybdacyclobutane as well as the conversion of the trigonal bipyramidal molybdacyclobutane to the square pyramidal structure were theoretically investigated. It was concluded that the last reaction competes with the decomposition of the trigonal bipyramidal molybdacyclobutane to molybdenamethylidene centre and ethene. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Molybdena–alumina catalyst; Ethene metathesis; DFT; Gaussian; Molybdacyclobutane

1. Introduction

Olefin metathesis proceeds according to the carbene mechanism [1] and active carbene species must be present in the reaction environment. In the case of heterogeneous catalysts, surface metal–alkylidene complexes are formed when the catalyst is brought into contact with alkene [2–4] or cycloalkane [5,6]. Metal–alkylidene compounds can also be immobilised on the carrier [7,8].

In Fig. 1 the generally accepted scheme of olefin metathesis is presented [1,3,4]. Cycloaddition of alkene to the metal–alkylidene complex is the first step of the catalytic cycle. Then, the metallacyclobutane

intermediate decomposes to a new alkene molecule and a second metal–alkylidene structure that can react with another reactant molecule. In the case of ethene metathesis only metal–methylidene complexes take part in the process and the only product is ethene.

Schrock and co-workers [9–15] have investigated olefin additions to four-coordinate $\text{W}(\text{CHR})(\text{NAr})(\text{OR}')_2$ and $\text{Mo}(\text{CHR})(\text{NAr})(\text{OR}')_2$ alkylidene complexes. They have isolated and characterised the metallacyclobutane complexes that have trigonal bipyramidal (TBP) or square pyramidal (SP) geometry depending on the electronic properties of the alkoxy ligands. It has been shown that olefin attack on the “CNO” face of the alkylidene complex is more favourable than the attack on the “COO” face and yields an initial TBP metallacyclobutane, which can rearrange by a Berry-type pseudo-rotation to the SP structure [14].

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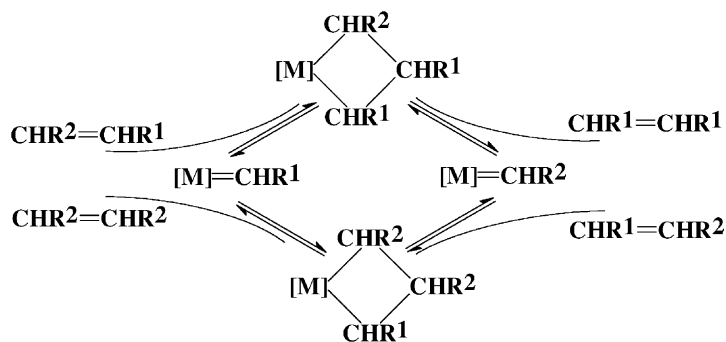


Fig. 1. Catalytic cycle of olefin metathesis.

Several theoretical studies on olefin metathesis proceeding in the presence of homogeneous catalysts [16–24] have been reported. Folga and Ziegler [20] have investigated $\text{Mo}(\text{CH}_2\text{CH}_2\text{CH}_2)(\text{X})(\text{L})_2$ ($\text{X} = \text{NH}, \text{O}$; $\text{L} = \text{Cl}, \text{OCH}_3, \text{OCF}_3$) molybdacyclobutanes and their role in olefin metathesis, applying density functional theory (DFT). They have predicted that TBP molybdacyclobutane is obtained if the alkylidene complex has electron-withdrawing ligands ($\text{L} = \text{OCF}_3$) that facilitate an early nucleophilic attack of an olefinic carbon atom on the metal centre. On the other hand, the electron-donating ligands ($\text{L} = \text{OCH}_3$) delay the nucleophilic attack and result in the direct formation of the SP molybdacyclobutane. The authors have also studied the pathway of the ethene addition to $\text{Mo}(\text{CH}_2)(\text{O})(\text{Cl})_2$ alkylidene complex. They have concluded that the reaction can proceed along one of the two possible routes, leading to TBP or SP molybdacyclobutane. In both cases the same path was predicted for the initial stage of ethene attack onto the carbene bond. However, the authors have not optimised the transition structures of the reactions studied. On the other hand, Wu and Peng [22], in their theoretical study on ethene addition to $\text{Mo}(\text{NH})(\text{CHR})(\text{L})_2$ alkylidene complexes ($\text{R} = \text{H}, \text{CH}_3$; $\text{L} = \text{OCH}_3, \text{OCF}_3$), have localised transition states leading to TBP molybdacyclobutanes but they have not found transition structures for SP molybdacyclobutanes formation. They proposed the initial formation of TBP molybdacyclobutane for both electron-withdrawing and electron-donating ligands, despite the fact that SP structure of the molybdacyclobutane complex with electron-donating ligands was predicted to be much more stable than the TBP structure.

In our previous works [25,26] we have theoretically investigated alkene metathesis proceeding on heterogeneous catalyst for the first time. We applied DFT and cluster model approach [27–29] to study the pathways of ethene addition to Mo^{VI} and Mo^{IV} methyldene centres of $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst. We localised transition states leading to the respective molybdacyclobutane complexes. In the case of the Mo^{VI} site, a transition structure leading to TBP molybdacyclobutane was found. We concluded that the active sites of ethene metathesis do not contain Mo^{IV} [26] because of high energy barriers of some elementary steps of the potential process involving Mo^{IV} centres. However in that study, simple active site models in which hydroxyl groups replaced the bonds between molybdenum and alumina were applied. More advanced active site models containing Mo^{VI} and Mo^{IV} centres mounted on $\text{Al}_2(\text{OH})_6$ cluster were used to study the thermodynamics of the elementary steps of ethene metathesis [25,26].

In the present work the pathway of ethene metathesis proceeding on Mo^{VI} centres of molybdena–alumina catalyst is theoretically investigated. Rearrangement of the TBP molybdacyclobutane intermediate to the SP structure is also studied. The active site models including alumina are applied in all the calculations.

2. Computational

Calculations were carried out with the GAUSSIAN 98 program [30] installed on SGI Origin2000 computer. The hybrid B3LYP functional [31] was used. All the structures were optimised by applying Berny

algorithm using redundant internal coordinates [32]. Harmonic vibration frequencies were calculated for each structure to confirm the potential energy minimum or the transition state involved and to obtain the enthalpy, entropy and Gibbs free energy. The obtained transition structures were additionally verified by the IRC calculations [33,34].

Two basis sets were employed parallel. The first one, LANL2DZ, includes the Hay–Wadt effective core potential plus double-zeta basis [35] (applied for Mo and Al) and Dunning–Huzinaga valence double-zeta basis (applied for C, H and O). The second one, denoted here as LANL2DZ(d), includes additionally d-polarisation functions for C and O.

3. Results and discussion

A cluster model of monomeric Mo^{VI} methylidene centre (**1**) that has been developed in the previous works [25,26] is shown in Fig. 2. The metal centre is mounted on a small cluster of alumina. Correctness of the alumina cluster model was previously verified [26]. The calculated pseudo-tetrahedral geometry of (**1**) is in very good agreement with both experimental data [14] and previous theoretical results [20,22,36,37] concerning molybdenaalkylidene complexes.

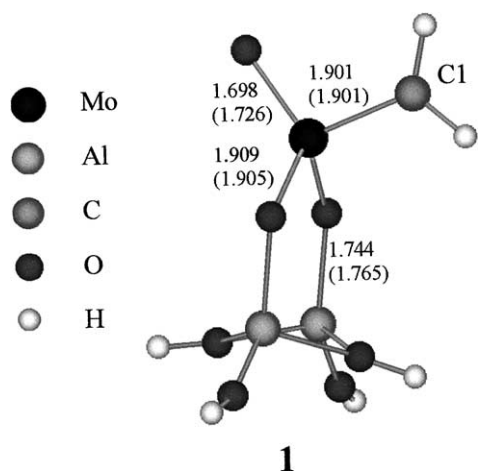


Fig. 2. Optimised structure of the cluster model of the Mo^{VI} methylidene centre. Bond lengths (Å) are calculated by applying LANL2DZ(d) and LANL2DZ (in parentheses) basis sets.

During the investigation of the pathway of ethene addition to molybdenamethylidene centre (**1**) we have localised a transition state (**2**) leading to a molybdacyclobutane complex (**3**) with TBP geometry (Fig. 3). In the current research we have not confirmed the existence of ethene–molybdenamethylidene π -complex. This is in contrast to our earlier calculations [25,26], in which, however, simpler active site models were applied.

The transition structure (**2**) has a pseudo-TBP geometry and a nearly flat ring with the predicted Mo–C1–C3–C2 dihedral angle of about 174°. The ring of the TBP molybdacyclobutane (**3**) is almost entirely flat. One can observe a significant Mo–C3 bond formation in the TS structure (**2**). The predicted Mo–C3 bond length in (**2**) is 2.34 Å, whereas the final Mo–C3 bond distance in the TBP molybdacyclobutane (**3**) is only 0.25 Å shorter (Fig. 3). However, the predicted difference between C1–C2 bond lengths in the structures (**2**) and (**3**) is much higher, of about 0.65 Å. Thus, the formation of the C1–C2 bond falls behind the Mo–C3 bond formation. This conclusion is in agreement with other reported results [20,22].

The TBP molybdacyclobutane can rearrange via transition state (**4**) to a molybdacyclobutane complex (**5**) with the SP geometry (Fig. 4). The TS structure (**4**) has the Mo–C1–C3–C2 dihedral angle of 156° (LANL2DZ(d) basis set). This value is very close to the final value of dihedral angle, which is 149°, in the SP molybdacyclobutane (**5**). Comparison between the bond lengths in the structures (**4**) and (**5**) is quite interesting. The Mo–C3 and C2–C3 bond distances (Fig. 4) are nearly the same as the respective final bond lengths in the SP molybdacyclobutane (**5**). On the other hand, the distances of the Mo–C1 and C1–C2 are hardly changed in comparison with their respective bond distances in the TBP molybdacyclobutane (**3**).

Because we have not localised a transition structure connecting directly the reactants (ethene and the structure (**1**)) with the SP molybdacyclobutane, we conclude that ethene addition to monomeric molybdenamethylidene centre of molybdena–alumina catalyst leads to initial formation of surface TBP molybdacyclobutane complex. Then, the initial TBP molybdacyclobutane can rearrange to the SP structure. Thus, the decomposition of the SP molybdacyclobutane to the molybdenamethylidene complex and ethene must occur via the TBP intermediate. This is consistent

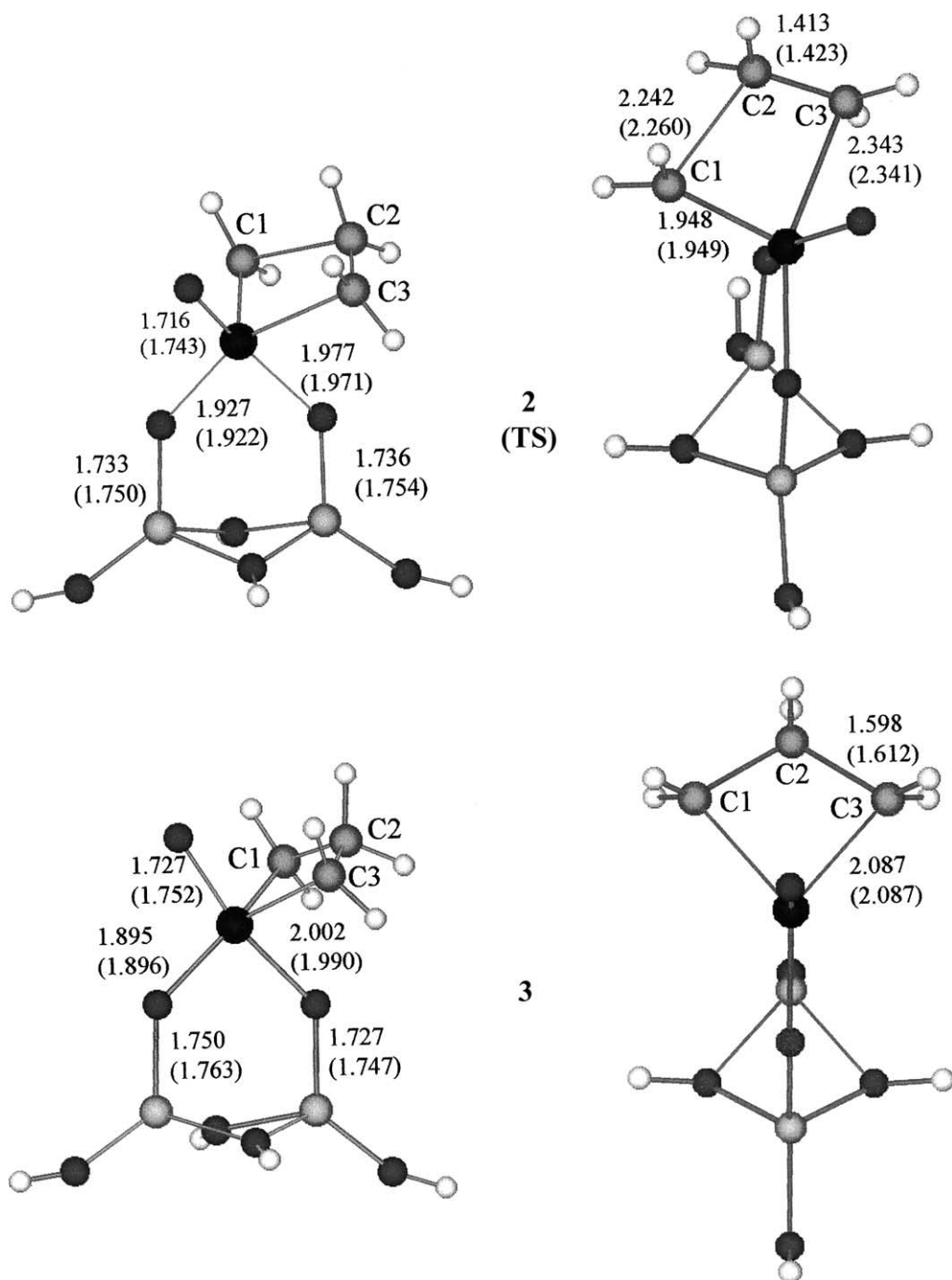


Fig. 3. Optimised structures of the transition state (2) and the TBP molybdacyclobutane (3). Bond lengths (Å) are calculated by applying LANL2DZ(d) and LANL2DZ (in parentheses) basis sets.

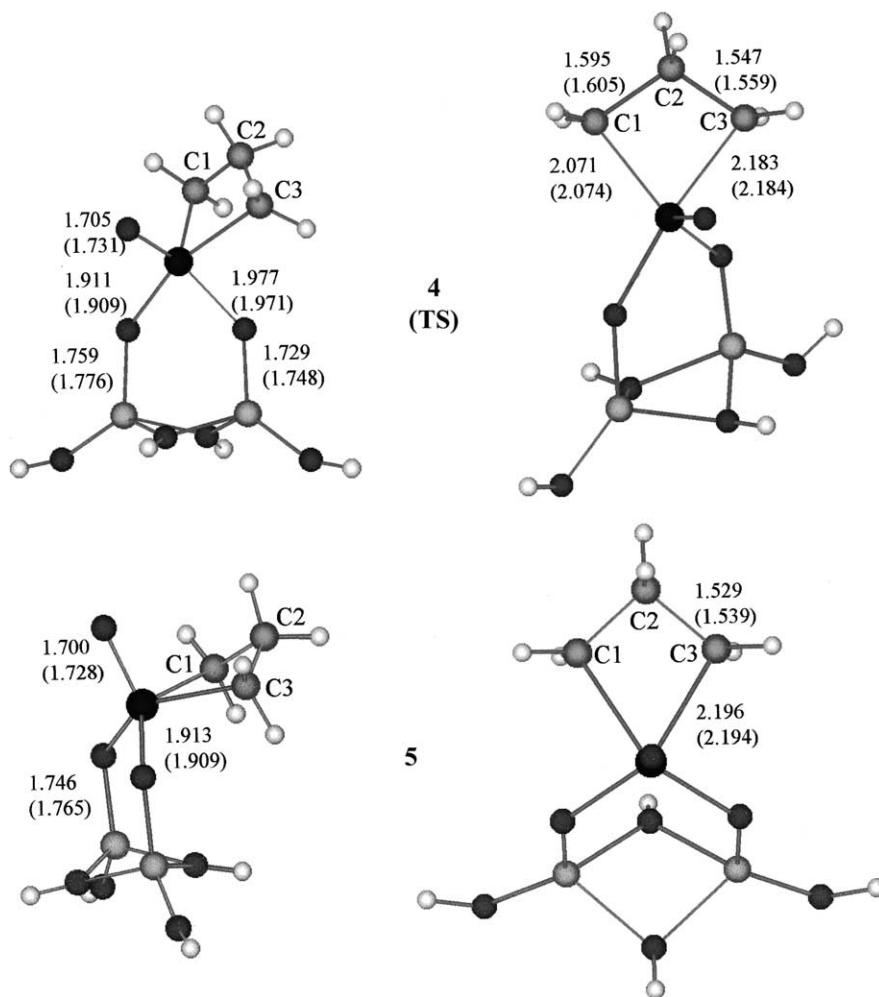


Fig. 4. Optimised structures of the transition state (**4**) and the SP molybdacyclobutane (**5**). Bond lengths (Å) are calculated by applying LANL2DZ(d) and LANL2DZ (in parentheses) basis sets.

with the propositions of Schrock and co-workers [12,14] and the theoretical results of Wu and Peng [22]. However in the latter's work, the rearrangement of the TBP molybdacyclobutane to the SP one has not been investigated.

In Fig. 5, enthalpy diagram of ethene metathesis is shown. The calculated changes of enthalpies, Gibbs free energies and entropies for the reaction studied are presented in Table 1. As we can see, the predicted activation enthalpy of ethene addition to molybdenamethylidene centre (**1**) is about 31 kJ mol^{-1} , according to the B3LYP/LANL2DZ(d)

calculations. The calculated activation Gibbs free energy of this step is high, because of the high negative value of the activation entropy (Table 1). The decomposition of the TBP molybdacyclobutane (**3**) to $[\text{Mo}]=\text{C}_3\text{H}_2$ molybdenamethylidene surface complex and $\text{C}_1\text{H}_2=\text{C}_2\text{H}_2$ is a necessary step to continue the catalytic cycle of ethene metathesis. Because of C_s symmetry of structure (**3**), in our discussion we need not distinguish between this step and the reverse decomposition (**3**) \rightarrow (**1**). The calculated activation enthalpy of this decomposition is about 37 kJ mol^{-1} (B3LYP/LANL2DZ(d)) and the activation Gibbs

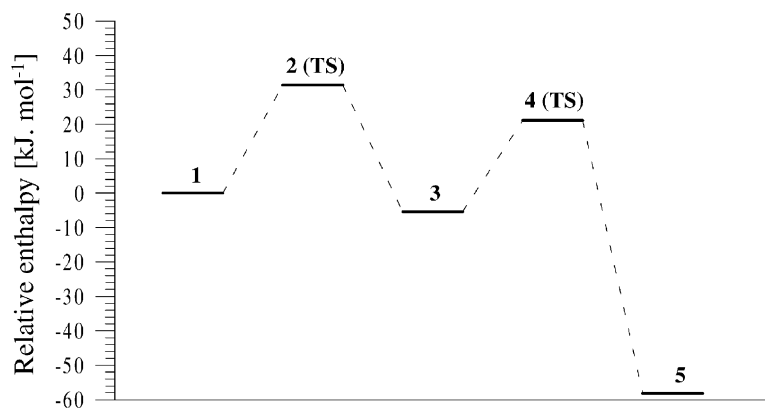


Fig. 5. Enthalpy diagram ($T = 298.15$ K) of ethene metathesis (B3LYP/LANL2DZ(d) calculations).

free energy is of the same range. However, the TBP molybdacyclobutane (**3**) can even more easily rearrange to the SP structure (**5**). It can be seen from Fig. 5 and Table 1 that this step has an activation barrier of about 27 kJ mol^{-1} and the similar value for the activation Gibbs free energy. The reverse conversion of the SP molybdacyclobutane (**5**) to the TBP one (**3**) has both a much higher activation enthalpy (79 kJ mol^{-1} , the B3LYP/LANL2DZ(d) calculations) and activation Gibbs free energy (83 kJ mol^{-1}), because the SP molybdacyclobutane (**5**) is predicted to be more stable than the TBP structure (**3**) (Table 1). Therefore, the possible rearrangement of the TBP molybdacyclobutane to the SP geometry decreases the overall rate of ethene metathesis because of the high energy barrier of the reverse rearrangement.

In the case of olefin metathesis involving Mo(CHR)(NAr)(OR')₂ alkylidene complexes, the relative sta-

bilities of the two possible structures of the molybdacyclobutane intermediate depend on the electronic properties of the alkoxy ligands [12,13,15,20,22]. For the surface Mo-alkylidene complexes, the carrier is the equivalent of the alkoxy ligands. Therefore, local electronic properties of the support can affect the relative stabilities of the TBP and the SP molybdacyclobutanes. When we developed the cluster models applied in the present calculations, we assumed that the molybdenum centre replaced basic hydroxyl groups connected with octahedral alumina [26]. If the metal centre replaced more acidic OH groups of alumina, the support would be a more electron-withdrawing "ligand" and the energy difference between the TBP and the SP intermediates could change. In any case, however, both possible structures of the molybdacyclobutane intermediate play role in the mechanism of ethene metathesis.

Table 1

Calculated changes of enthalpies (ΔH_{298}^0), Gibbs free energies (ΔG_{298}^0) and entropies (ΔS_{298}^0) for the reaction studied ($T = 298.15$ K)

Reaction	(ΔH_{298}^0) (kJ mol ⁻¹)		(ΔG_{298}^0) (kJ mol ⁻¹)		(ΔS_{298}^0) (J mol ⁻¹ K ⁻¹)	
	LANL2DZ	LANL2DZ(d)	LANL2DZ	LANL2DZ(d)	LANL2DZ	LANL2DZ(d)
1 + C ₂ H ₄ → 3 (TBP)	-7.3	-5.4	46.6	49.1	-181	-183
1 + C ₂ H ₄ → 2 (TS)	25.6	31.4	78.6	84.9	-178	-179
3 (TBP) → 2 (TS)	32.9	36.8	32.0	35.8	3	3
3 (TBP) → 5 (SP)	-41.3	-52.8	-43.6	-54.6	8	6
3 (TBP) → 4 (TS)	27.8	26.5	29.6	28.0	-6	-5
5 (SP) → 4 (TS)	69.0	79.3	73.2	82.6	-14	-11

4. Conclusions

Ethene addition to monomeric Mo^{VI} methylenide centre of molybdena–alumina catalyst leads to initial formation of the TBP molybdacyclobutane complex that can rearrange to the SP structure. Therefore, the decomposition of the SP molybdacyclobutane to the molybdenamethylenide complex and ethene must occur via the TBP intermediate.

The decomposition of the TBP molybdacyclobutane to molybdenamethylenide centre and ethene is a necessary step to continue the catalytic cycle of ethene metathesis. However, this process competes with the exothermic rearrangement of the TBP molybdacyclobutane to the SP intermediate. Thus, the proceeding of the latter reaction decreases the overall rate of ethene metathesis because of the high energy barrier of the back rearrangement of the SP molybdacyclobutane to the TBP one.

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