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DFT 研究 Schrock 钼催化剂催化的丙烯和丙烯腈复分解反应机理

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摘要:使用密度泛函理论方法研究了 Schrock 钼催化剂催化的丙烯和丙烯腈复分解反应机理。研究结果表明:所有金属环丁烷中间体都是三角双锥结构,配体 OCF_3 和 NMe 占据三角双锥结构的 2 个顶点。大部分过渡态具有与金属环丁烷中间体相似的结构特征。Schrock 钼催化剂催化的丙烯和丙烯腈的复分解反应包含了 3 个反应步骤。基于不同通道过渡态结构的相对能量,我们预测顺式和反式产物的产率为 9:1,这个结果与实验事实吻合得很好。

关键词:复分解反应; Schrock 钼催化剂; 反应机理
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DFT Study on the Mechanism of Cross-Metathesis between Acrylonitrile and Propene Catalyzed by Schrock's Molybdenum Catalyst

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Abstract: Density functional theory calculations have been carried out to explore the mechanism of the cross-metathesis between acrylonitrile and propene molecules catalyzed by the Schrock's molybdenum catalyst. All intermediate metallacyclobutanes are in the trigonal bipyramidal geometry with axial OCF_3 and NMe ligands. The transition states leading to the four-membered ring intermediate or decomposing this four-membered ring intermediate have most of the features of intermediate except the entering or leaving group even further away from metal alkylidene. Three independent steps are involved in the cross-metathesis. Based on the relative energies of the transition state structures leading to the cis and trans products, the equilibrium condensation ratio of the cis to trans products is predicted to be about 9:1, which is in good agreement with the experiment results.

Key words: cross-metathesis; Schrock's molybdenum catalyst; mechanism

0 Introduction

Transition-metal catalyzed olefin metathesis has had a tremendous impact on polymer chemistry, basic and fine chemical synthesis[1-4]. Olefin metathesis can be carried out in the presence of both homogeneous and heterogeneous catalytic systems. The reaction proceeds according to the carbene mechanism and active carbene complexes are present in the reaction environment. Metal carbene reacts with olefin, thus forming the metallacyclobutane complex. Subsequent decomposition of the metallacyclobutane leads to formation of a new olefin and a carbene.

There are many theoretical investigations of the structures and reactivity of the olefin metathesis catalysts. Most of the efforts have been concentrated on

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the Ru-carbene catalysts[5,6]. In the case of d^0 Mo imido complexes, computational studies have been focused on the electronic structure of starting alkylidenes and the molybdacyclobutane intermediates[7,8].

Functionalized olefin metathesis has been a goal in transition metal catalysis. This goal has driven the search for milder, more selective catalysts and the move toward the more electronegative transition metals lying further to the right in the periodic table. Acrylonitrile is a functional olefin that has eluded all previous attempts at productive olefin metathesis until Crowe reported the first examples of productive acrylonitrile metathesis reactions [9]. Crowe mixed acrylonitrile and a second olefin with Schrock′s catalyst Mo(=CHCMe$_2$Ph)(=NAr)[OCMe(CF$_3$)$_2$]$_2$ (5mol%)[10~12]. The following features were observed: (1) acrylonitrile is unable to undergo productive self-metathesis; (2) the production of the second olefin′s self-metathesis is usually very low; (3) the main product is the cross-metathesis product of acrylonitrile and a second olefin; (4) the cis-isomers of the cross-metathesis are much more favor than the trans-isomers and the ratio of the cis to trans is ranging from 3:1 to 9:1 depending the different substituents of the second olefin.

Since acrylonitrile cross-metathesis is a valuable reaction for functionalization of terminal olefins, understanding the mechanistic origin for the predominance of cis olefin product is useful. This is the purpose of this study.

1　Thermodynamic analysis

For a system mixing an acrylonitrile and a second olefin, there are three kinds of metathesis that maybe take place in the reaction system: the self metathesis between two acrylonitrile molecules, the self metathesis between two second olefin molecules, and the cross metathesis between acrylonitrile and olefin molecules (Fig.1).

When the second olefin is propene, we carry out simple calculations to estimate the differences of the standard Gibbs free energies $\Delta G^{\ominus}$ at B3LYP/6-311g* level of theory at 298.15 K. The following conclusion can easily be obtained from these calculations: (a)

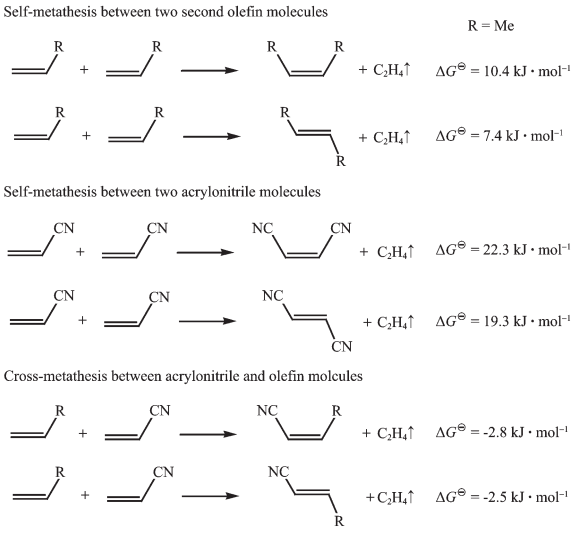


Fig.1　Three possible metatheses

Thermodynamically the self-metathesis of acrylonitrile is very unfavored. The equilibrium constant is predicted to be only 4.1×10^{-4} for the trans product and 1.2×10^{-4} for the cis product according to $\Delta G^{\ominus}=-RT\ln K^{\ominus}$. (b) The self-metathesis of the propene is unfavored either. (c) The cross-metathesis is thermodynamically favored. The equilibrium constant is predicted to be 2.74 for the trans product and 3.10 for the cis product. For the cross-metathesis reactions, $K_{cis}^{\ominus}/K_{trans}^{\ominus}=1.13$ is obtained thermodynamically, indicating that the equilibrium yields of the *cis*- and *trans*- products should almost be same.

Therefore, the first, the second and the third features of acrylonitrile cross-metathesis are origin from thermodynamical reason. But the fourth feature cannot be explained thermodynamically. There must be some other reasons for it.

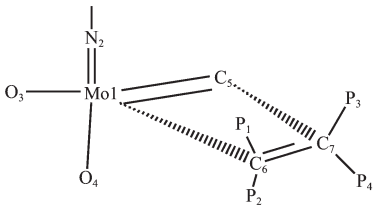
2　Model and computation method

Calculations are carried out with B3LYP method as implemented in the Gaussian 03 package[13] on the model systems. Mo(=CH$_2$)(=NMe)(OCF$_3$)$_2$ is used to represent the Schrock′s catalyst Mo(=CHCMe$_2$Ph)(=NAr)[OCMe(CF$_3$)$_2$]$_2$. CH$_2$CHMe is used to stand for the second olefin. The Mo atom is represented with LanL2DZ basis set[14]. The remaining atoms are represented with 6-31G(d) basis sets. Geometry optimizations are performed without any symmetry constraints, and the nature of the extrema is checked by frequency

calculations. Energies are further evaluated using B3LYP method, SDDAll basis set and ECP for Mo and 6-311++G(d,p) for other atoms. *f* orbital is also included for Mo[15]. The energies given throughout the paper are electronic energies E with ZPE corrections.

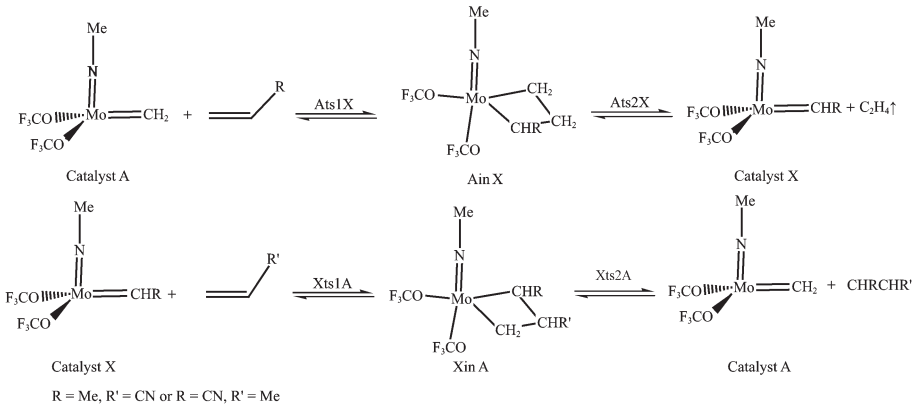
3 Results and discussion

In olefin metathesis, the alkene can potentially approach to the alkylidene ligand from three (front and back CNO faces, and bottom COO face) of the four triangular faces of the tetrahedron. Note that the bottom approach (COO face) requires rotation of the alkylidene group, in contrast to the approach to the two other faces. We have therefore studied the reaction pathways for the front approach (the front and the back approach are identical). Scheme 1 shows the definition of the position number. In the intermediate structure, Mo(1), C(5), C(6) and C(7) form a four-member ring according to the well-established Chauvin mechanism. As shown in Scheme 1, P1 or P3 is up this four-member ring and syn to the imido group (=NMe), P2 or P4 is down this four-member ring and trans to the imido group (=NMe), P1 or P2 is much closer to the metal center than P3 or P4. When the substituted ethylene interacts with catalyst the substituted group can occupy one of these four positions.



Scheme 1

Scheme 2 shows the possible reaction approach. According to Chauvin mechanism, the substituted ethylene attacks the CNO face of the catalyst A leading to formation of the four-member ring intermediate AinX, the decomposition of AinX results a new catalyst X. When R=Me, we denote the new catalyst X as B when Me is syn to the imido group and as C when Me anti to the imido group. When R=CN, the new catalyst X is denoted as D when CN is syn to the imido group and as E when CN anti to the imido group.



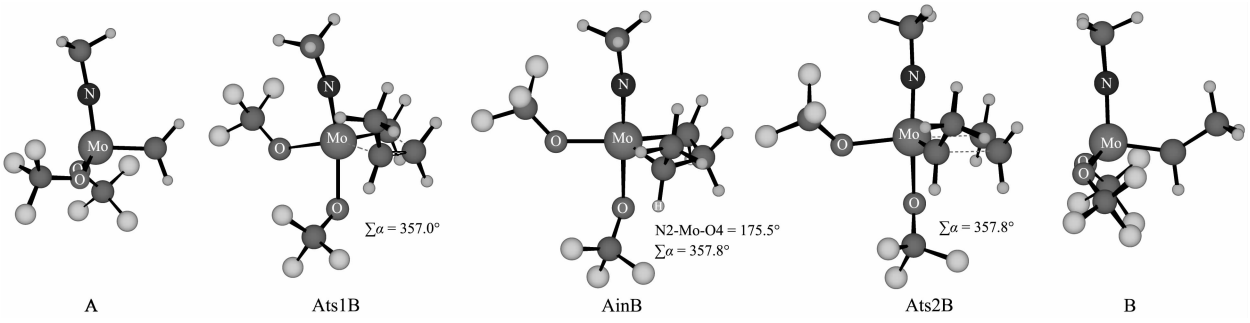
Scheme 2

3.1 First step: the formation of the catalyst B or C

It can be seen from Schemes 1 and 2 that only the substituted ethylene in which Me or CN occupies P1 or P2 can interact with catalyst A leading to a new catalyst X (catalysts B, C, D, or E). The optimized geometries of the extrema located along the reaction pathway leading to catalyst B are shown in Fig.2.

Fig.2 shows that the intermediate AinB has the trigonal bipyramidal (TBP) geometry with axial OCF_3 and NMe ligands. The angle between the OCF_3 and NMe ligands, N(2)-Mo-O(4), is 175.5°. The sum $\sum\alpha$ of the angles between the equatorial ligands is equal to 357.8° showing that these ligands are nearly co-planar. The transition state Ats1B and Ats2B have most of the features of intermediate AinB but with the entering propene or leaving ethylene much further away from metal alkylidene. The one of OCF_3 ligands, the alkylidene ligand, and the one of the carbon atoms of propene or ethylene are near co-planar too, as shown by the sum $\sum\alpha$ of the angles between these equatorial ligands 357.0° and 357.8°.

The reaction of catalyst A with propene leads to



Atom numbering is shown in Scheme 1; ∑α=O(3)-Mo-C(5)+O(3)-Mo-C(6)+C(5)-Mo-C(6); Angles are in degree

Fig.2　Optimized geometries of the extrema located along the reaction pathway for metathesis of the catalyst A with propene leading to the catalysts B

catalyst C via one intermediate AinC and two transition states Ats1C and Ats2C. The reaction of catalyst A with acrylonitrile leads to catalyst D via one intermediate AinD and two transition states Ats1D and Ats2D, leads to catalyst E via one intermediate AinE and two transition states Ats1E and Ats2E. The character of the extrema located along each of these three reaction pathways is very similar to that of the extrema located along the reaction pathway leading to the catalyst B.

Fig.3 shows that catalyst B can be produced with a barrier only 2.5 kJ·mol^{-1}, catalyst C with a barrier only 2.9 kJ·mol^{-1}, catalyst D with a barrier 21.7 kJ·mol^{-1}, and catalyst E with a barrier 35.1 kJ·mol^{-1}. Therefore, catalysts B and C are much easier to be produced kinetically whereas the reactions producing D or E can be ruled out at this step.

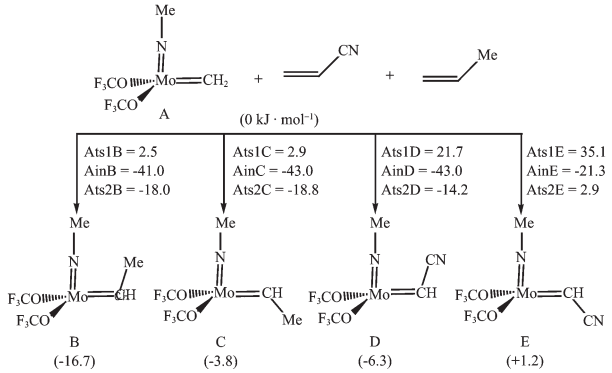


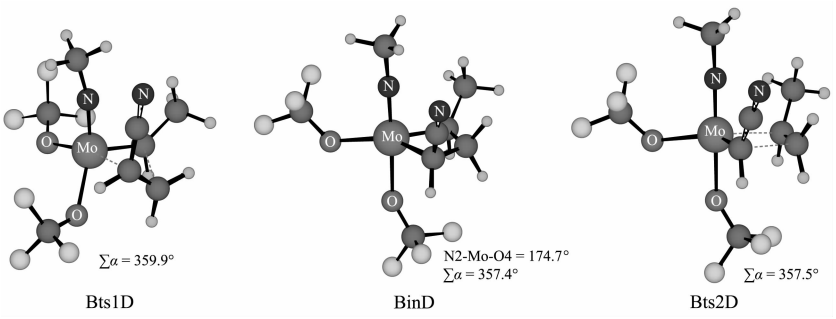
Fig.3　Relative energies for the extrema located along the metathesis pathways for metathesis of the catalyst A with propene leading to the catalysts B and C or with acrylonitrile leading to the catalysts D and E

3.2　Second step: the formation of the catalyst D from the catalyst B or C

As soon as the catalyst B is yielded, it can further interact with the methyl or cyano substituted ethylene. We have shown that the cross-metathesis is much more favored than the self-metathesis, therefore here only the cross-metathesis will be considered. The reaction of catalyst B with acrylonitrile leads to catalyst D via one intermediate BinD and two transition states Bts1D and Bts2D. It can be seen from Fig.4 that the intermediate BinD has the TBP geometry with axial OCF_3 and NMe ligands. The angle between the OCF_3 and NMe ligands, N(2)-Mo-O(4), is 174.7°. The sum $\sum\alpha$ of the angles between the equatorial ligands is equal to 357.4° showing that these ligands are nearly co-planar. The transition state Bts1D and Bts2D have most of the features of intermediate BinD but with the entering acrylnitrile or leaving propene much further away from metal alkylidene. The one of OCF_3 ligands, the alkylidene ligand, and the one of the carbon atoms of acrylonitrile are near co-planar too, as shown by the sum $\sum\alpha$ of the angles between these equatorial ligands (359.9° and 357.5°).

The catalyst B interacts with acrylonitrile leads to catalyst D with a barrier 9.6 kJ·mol^{-1}, leads to catalyst E with a barrier 17.6 kJ·mol^{-1}, leads to cis product with a barrier 22.6 kJ·mol^{-1}, leads to the trans-product with a barrier 38.9 kJ·mol^{-1} (Fig.5). Therefore, catalyst D is much easier to be produced kinetically whereas the reactions that produce catalyst E, *cis*- and *trans*-product can be ruled out at this step.

As mentioned above, Catalyst C is also easy to be produced kinetically in the first step. As soon as Catalyst C is yielded, it may further interact with acrylonitrile molecule. Our calculations indicate that



Atom numbering is shown in Scheme 1; ∑α=O(3)-Mo-C(5)+O(3)-Mo-C(6)+C(5)-Mo-C(6); Angles are in degree

Fig.4 Optimized geometries of the extrema located along the reaction pathway for metathesis of the catalyst B with acrylnitrile leading to the catalysts D

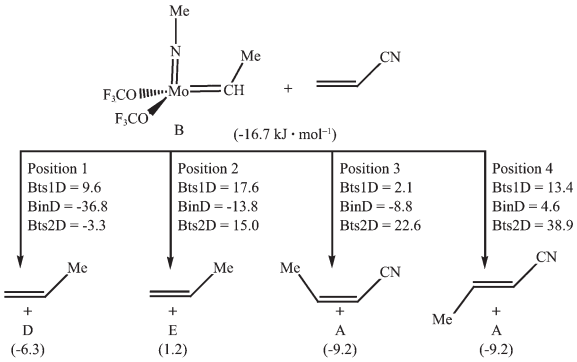


Fig.5 Relative energies for the extrema located along the metathesis pathways starting with the catalyst B

the reaction barriers leading to catalyst D, E, the cross-metathesis *trans*- and *cis*- product from the catalyst C are 13.0, 35.9, 29.3, and 38.0 kJ·mol^{-1}, respectively. The reaction that produces the catalyst D has the smallest barrier 13.0 kJ·mol^{-1}. So among all the four reaction channels only the one that produces the catalyst D would take place most possibly.

3.3 Third step: the formation of the *cis*- or *trans*-product from the catalyst D

As soon as the catalyst D is yielded, it can further interact with propene in system to complete the cycle of the cross-metathesis reaction. When Me group of the propene is in position 1 the catalyst B is produced. The catalyst C is produced when Me is in position 2. When Me is in position 3 or 4, the *cis*- or *trans*- product is yielded, and at the same time the catalyst A is reproduced. The optimized geometries of the extrema located along these reaction pathways starting from the catalyst D with propene are located and the relative energies are evaluated. Our calculation results show that the barriers that produce catalyst B and C are 9.6 and 13.0 kJ·mol^{-1}, respectively, whereas the barriers leading to *cis*- and *trans*- products are 13.0 and 18.4 kJ·mol^{-1}, respectively.

3.4 Overall reaction mechanism

The overall calculation results are summarized in Fig.6, where the bold lines show the most favored pathways from the reactants (Catalyst A+CH_2CHCN+CH_2CHMe) to the products (*cis* or *trans* MeCHCHCN), the plain lines denote the less favored pathways, and the dash lines indicate that these pathways can be ruled out. The data above the lines are the reaction barriers of the corresponding steps. For the cross-metathesis between acrylonitrile and propene catalyzed by the Schrock′s catalyst, three independent steps are involved. The first step corresponds to the formation of catalysts B and C. The barrier is only 2.5 or 2.9 kJ·mol^{-1}. The second step is the formation of catalyst D from catalyst B or C. The barrier for this step is 9.6 or 13.0 kJ·mol^{-1}, respectively. The third step is the formation of

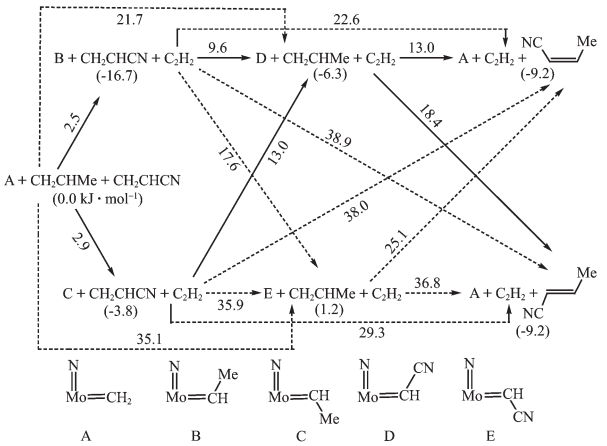


Fig.6 Overall calculation results of the cross-metathesis between propene and acrylonitrile catalyzed by Shrock catalyst Mo(=CH_2)(=NMe)(OCF_3)$_2$, A

the cross-metathesis products. The barrier for the third step is 13.0 or 18.4 kJ·mol^{-1}. Fig.6 clearly shows that the highest barriers is 13.0 kJ·mol^{-1} for producing the *cis* product starting from acrylonitrile and propene catalyzed by the catalyst A while it is 18.4 kJ·mol^{-1} for yielding the *trans* product. The equilibrium condensation ratio of the cis to trans is therefore estimated about 9∶1 at room temperature according to $k=Ae^{-E/(RT)}$. This is in good agreement with the experimental results, that is, the ratio of the cis to trans is ranging from 3∶1 to 9∶1 depending the different substituents of the second olefin[9].

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