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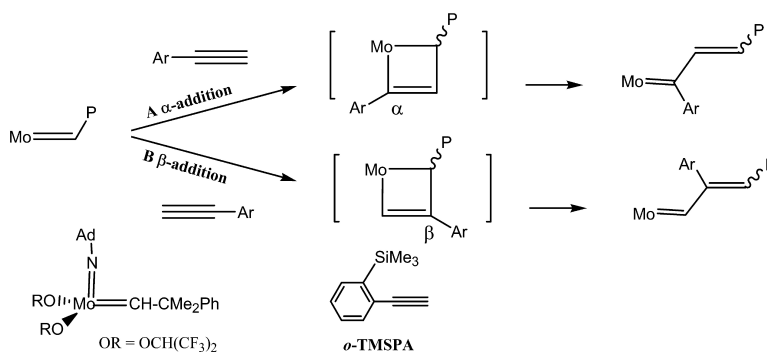
A Theoretical Study of the Ring-Opening of Metallacyclobutene Derived from the Addition of Acetylene to Molybdenum Alkylidenes

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A Theoretical Study of the Ring-Opening of Metallacyclobutene Derived from the Addition of Acetylene to Molybdenum Alkylidenes

Yinghong Sheng,[†,‡] Yun-Dong Wu,[*,†] and Jerzy Leszczynski[*,‡]

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China, and The Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, P.O. Box 17910, 1400 J. R. Lynch Street, Jackson, Mississippi 39217

The ring-opening reaction of metallacyclobutenes derived from the addition of alkyne ($HC \equiv CR$, R = H, Me) to molybdenum alkylidene $Mo(NH)(OR')_2(=CHR'')$ (R' = Me, CF_3, R'' = H, Me) has been studied using quantum mechanics methods. Two ring-opening paths, NH outward and NH inward ring-openings, have been found for metallacyclobutene intermediates $Mo(NH)(OR')_2(CH_2)(HCCH)$ (R' = Me, CF_3) and α- and β-addition metallacyclobutene intermediates $Mo(NH)(OMe)_2(CH_2)(C_2HMe)$. The NH outward ring-opening is found to be favored over the NH inward ring-opening. The electron-withdrawing group (OCF_3) in molybdenum alkylidene and α-methyl group further enhance the preference for the NH outward ring-opening pattern. Four ring-opening paths have been found for $Mo(NH)(OMe)_2$-$(CHMe)(C_2H_2)$, an intermediate in the addition of acetylene to $Mo(NH)(OMe)_2(CHMe)$. The conformation of the product is found to be dependent upon the conformation of the molybdenum alkylidene. That is, when *trans*-molybdenum alkylidene is used as the catalyst, an *anti*-polymer is generated, while using *cis*-molybdenum alkylidene may lead to the polymer in different conformations. The *anti/syn*-isomerization of the electron-withdrawing group substituted molybdalkylidene is calculated to be much slower than the polymerization steps; therefore, an all-*trans*-polymer can be obtained.

Introduction

Molybdenum alkylidene complexes $Mo(NR^1)(CHR')$-$(OR'')_2$ and their tungsten analogues have been widely used as the catalysts for olefin metathesis.[1−16] Progress

* To whom correspondence should be addressed. E-mail: chydwu@ust.hk; jerzy@ccmsi.us.
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‡ Jackson State University.
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has also been made in the application of these metal-alkylidenes as catalysts for alkyne polymerization.[17−23] For example, Schrock et al. have found that substituted phenylacetylenes can undergo living polymerization. In particular, (*o*-(trimethylsilyl)phenyl)acetylene (*o*-TMSPA) has been found to polymerize to give soluble and highly conjugated polyenes.[1,4,11,24−28] Such synthesis allows questions concerning the correlation of the nonlinear optical property with the chain length and structure to be addressed.[29,30]

Two alternative paths are possible for the addition of *o*-TMSPA to alkylidene, path A (α-addition) and path

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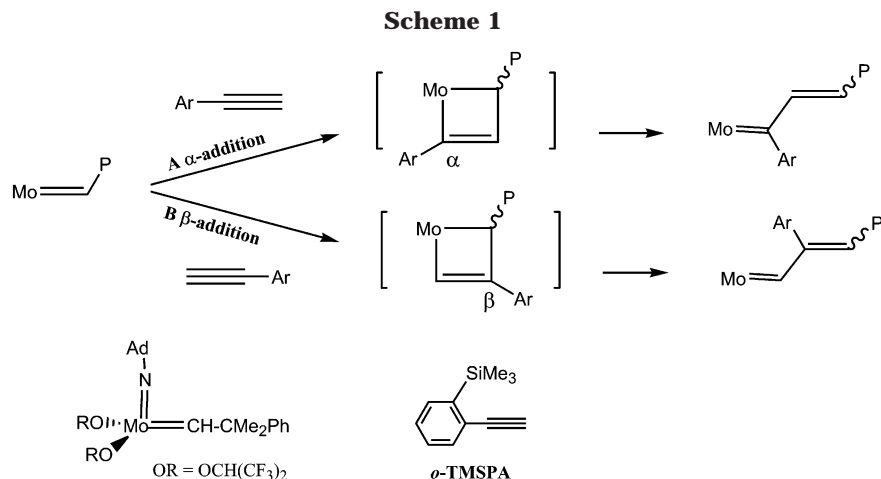(24) Schrock, R. R.; Luo, S.; Lee, J. C.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996,** *118,* 3883.
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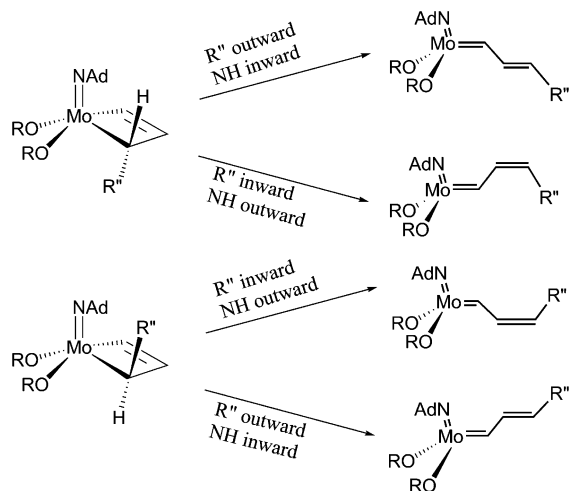(26) Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975,** *8,* 717.
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Scheme 1

Scheme 2. Conrotatory Ring-Opening

B (β-addition), as shown in Scheme 1. Our recent theoretical studies[31] indicated that the α-addition proceeds more easily than the β-addition; these results are in good agreement with experimental results.[18,24,32,33] The alkyne polymerization using molybdenum alkylidene as the catalyst is a multistep reaction; the pattern of ring-opening of the formed metallacyclobutene after addition of *o*-TMSPA to molybdenum alkylidene is expected to have impact on the resultant polymers. Therefore a detailed investigation of the ring-opening mechanism of the Mo intermediate is needed.

The ring-opening of molybdacyclobutene should be similar to cyclobutene ring-opening.[34] Therefore, conrotatory rotation should proceed. As shown in Scheme 2, the R″ group can be either *cis* or *trans* to the Mo=N ligand. Since both R″ and Mo=N fragments can rotate

outward or inward, four products are possible. In the case of cyclobutene ring-opening, extensive experimental and theoretical studies have established that an alkyl group prefers to rotate outward.[34] Thus, it is vital to know the preference of the Mo=N fragment rotation. In this paper, we present the results of theoretical studies of the ring-opening patterns of the molybdacyclobutene intermediate obtained from the HC≡CR (R = H, Me) addition to molybdenum alkylidene complexes $Mo(NH)(CHR'')(OR')_2$ (R″ = H, Me; R′ = Me, CF₃). The purposes of our study are (1) to investigate the geometrical features of the ring-opening transition structures and polymeric products; (2) to study the difference in the ring-opening mechanism for the molybdacyclobutene intermediate from either the α- or β-addition of alkyne to molybdenum alkylidene; (3) to evaluate the preference of the inward and outward ring-opening of molybdacyclobutenes; and (4) to discuss the effect of *cis*- and *trans*-molybdenum alkylidene on the configuration of the polymer.

Calculation Methods

Theoretical calculations were carried out using the GAUSSIAN 94 program.[35] Initially, the geometries were optimized with the closed-shell Hartree−Fock method and the all-electron 3-21G basis set.[36] Harmonic vibrational frequencies were calculated for each structure to characterize whether it is a minimum or transition state (one imaginary vibrational frequency). Thermal energy and reaction entropy were also calculated. The geometries were further optimized with the HW3 basis set according to Frenking's definition,[37,38] which was constructed by the contraction scheme [3311/2111/311] + ECP[39] on a 28-electron core for the molybdenum atom and the 6-31G(d) basis set for the other atoms. Density functional

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Table 1. Calculated Changes of Energies (ΔE, kcal/mol), Thermal Energies (ΔH^0_{298}, kcal/mol), and Entropies (ΔS_{298}, cal/mol·K) of the Species Involved in the Ring-Opening Reactions of Molybdacyclobutene

			ΔE		
entry	reaction		HF/3-21G	HF/HW3	B3LYP/HW3
		$Mo(NH)(CH_2)(C_2H_2)(OCH_3)_2$			
1	**1 → 5**	outward RO-TS[a]	7.9	5.9	2.0
2	**1 → 6**	inward RO-TS	12.9	8.6	5.4
3	**1 → 7**	*anti*-product	−18.4	−18.7	−12.9
4	**1 → 8**	*syn*-product	−19.6	−20.7	−14.9
		$Mo(NH)(CH_2)(C_2H_2)(OCF_3)_2$			
5	**2 → 9**	α-outward RO-TS	5.2	3.0	0.3
6	**2 → 10**	α-inward RO-TS	/	7.8	6.5
7	**2 → 11**	*anti*-product	−28.5	−26.5	−15.0
8	**2 → 12**	*syn*-product	−29.1	−28.9	−18.2
		α-$Mo(NH)(CH_2)(C_2HMe)(OCH_3)_2$			
9	**3 → 13**	α-outward RO-TS	7.0	4.8	0.5
10	**3 → 14**	α-inward RO-TS	11.8	8.5	4.7
11	**3 → 17**	α-*anti*-product	−18.4	−17.0	−11.4
12	**3 → 18**	α-*syn*-product	−19.2	−18.1	−12.0
		β-$Mo(NH)(CH_2)C_2HMe)(CH_3)_2$			
13	**4 → 15**	β-outward RO-TS	8.1	6.3	2.4
14	**4 → 16**	β-inward RO-TS	14.3	11.1	7.9
15	**4 → 19**	β-*anti*-product	−15.1	−13.5	−8.5
16	**4 → 20**	β-*syn*-product	−15.5	−15.9	−10.9
		trans-$Mo(NH)(CHMe)OCH_3)_2$			
17	**21 → 23**	*trans*-outward RO-TS	6.2	5.5	1.7
18	**21 → 24**	*trans*-inward RO-TS	16.3	12.5	9.3
		cis-$Mo(NH)(CHMe)OCH_3)_2$			
19	**22 → 25**	*cis*-outward RO-TS	12.1	10.3	0.3
20	**22 → 26**	*cis*-inward RO-TS	7.5	6.9	−2.1

[a] Outward RO-TS: outward ring-opening transition state.

Scheme 3
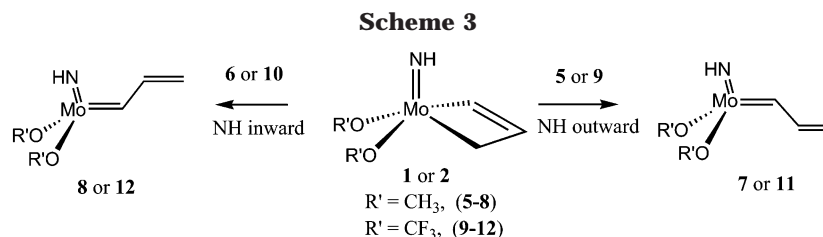
theory calculations were also carried out using the density functional approximation of B3LYP.[40-43] Similar methods have been shown to give quite good results for many systems including transition structures.[44]

Results and Discussion

The calculated energies of the stationary points on the potential energy surface of the ring-opening of molybdacyclobutene at the HF/3-21G, HF/HW3, and B3LYP/HW3 levels are tabulated in Table S1 of the Supporting Information. The HF/3-21G computed zero-point energy, thermal energy, and entropy of the species involved in the ring-opening reactions of molybdacyclobutene are also listed. The relative energies with respect to the molybdacyclobutene intermediates and the ring-opening activation energies are listed in Table 1.

A. Structures of Metallacyclobutene. Figure 1 shows the optimized structures of intermediates Mo-$(NH)(CH_2)(OR')_2(C_2HR)$ **1**, **2** (R = H, R' = Me, CF₃), **3**,

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and **4** (R = Me, R′ = Me). These structures are similar to each other, except that the CF₃ groups cause some changes in the orientations of the alkoxyl groups.

In the case of the addition of alkenes (C=C double bond) to molybdenum alkylidene, both experiments and theoretical calculations indicate that the geometry of metallacyclobutane is highly dependent upon the nature of the alkoxyl groups;[45,46] that is, the electron-donating groups favor square-pyramidal geometries, while the electron-withdrawing groups lead to trigonal-bipyramidal conformations. However, all molybdacyclobutenes (**1−4**) are found to be in square-pyramidal geometries. This is due to the significant repulsive interaction of the nonreacting π-orbital of acetylene (C≡C triple bond) with the two axial ligands, as discussed in our previous study.[31]

B. Ring-Opening of $Mo(NH)(CH_2)(OR')_2(C_2H_2)$ (R′ = CH₃ and CF₃). First, we studied the ring-opening mechanism of metallacyclobutene $Mo(NH)(CH_2)(OMe)_2$-(C_2H_2), which is derived from the addition of parent acetylene HC≡CH to the molybdenum alkylidene $Mo(NH)(CH_2)(OMe)_2$. Two ring-opening pathways are shown in Scheme 3; the NH group can rotate either outward (NH outward) to generate an *anti* alkylidene (**7**) or inward (NH inward) to yield a *syn* alkylidene (**8**).

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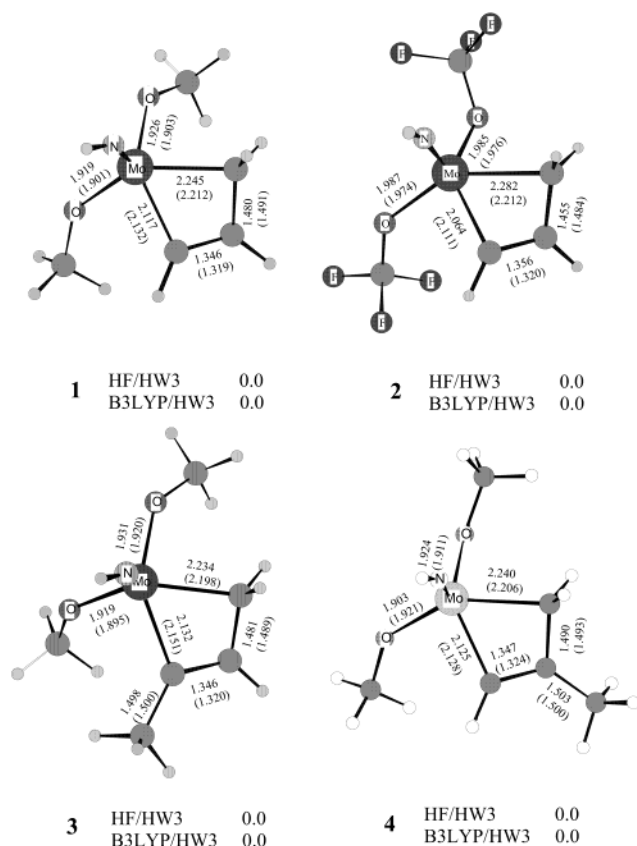
Figure 1. Calculated geometries for Mo(NH)(CH$_2$)(OR')$_2$-(HCCH) (**1**, R' = CH$_3$ and **2**, R' = CF$_3$) and Mo(NH)(CH$_2$)-(OCH$_3$)$_2$(HCCR'') (R'' = Me) (**3** and **4**). Selected geometrical parameters are from the B3LYP/HW3 and HF/HW3 (in parentheses) methods. For ring-opening reactions, the energies of the structures are set as the zero energy reference, units in kcal/mol.

Two ring-opening transition structures (**5** and **6**) have been located; see Figure 2. In the NH outward ring-opening transition structure **5**, the β-carbon of acetylene lies under the Mo–C(alkylidene)–C(α) plane, with the dihedral angle Mo–C(α)–C(β)–C(alkylidene) being about 38.6°. The Mo–C(alkylidene) bond length is slightly elongated to 2.343 Å from 2.245 Å in molybda-cyclobutene **1**. In the NH inward ring-opening transition structure **6**, the β-carbon of acetylene lies above the Mo–C(alkylidene)–C(α) plane with the dihedral angle Mo–C(α)–C(β)–C(alkylidene) being about −54.8°. The Mo–C(alkylidene) bond is significantly broken, being 2.692 Å. In addition, C(α)–C(β) and C(β)–C(alkylidene) have more pronounced single-bond (1.428 Å) and double-bond (1.375 Å) characteristics, respectively, than in the intermediates.

We also located two ring-opening transition structures (see structures **9** and **10** in Figure 2) for Mo(NH)(CH$_2$)-(OCF$_3$)$_2$(C$_2$H$_2$) with electron-withdrawing OCF$_3$ ligands (**2**). The geometrical features of the outward ring-opening transition structure (**9**) are similar to those of transition structure **5**, except for the changes in the orientation of the alkoxyl groups. The dihedral angle Mo–C(α)–C(β)–C(alkylidene) is calculated to be about 44.1°. The Mo–C(alkylidene) bond length is elongated to 2.479 Å from 2.282 Å in molybdacyclobutene **2**. However, in the NH inward ring-opening transition structure (**10**), the Mo–C(alkylidene) bond length is only
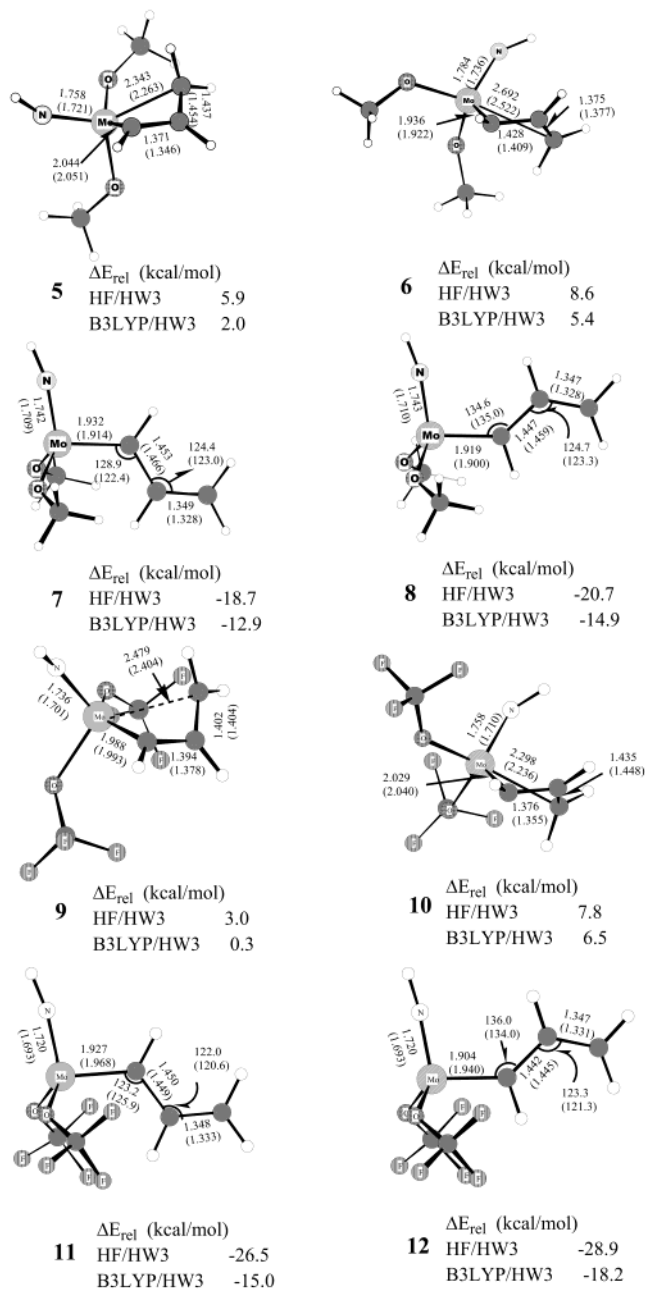
Figure 2. Calculated geometries and relative energies (kcal/mol) for the ring-opening transition states and first insertion products of Mo(NH)(CH$_2$)(OCH$_3$)$_2$(HCCH) (**5**, **6** and **7**, **8**) and Mo(NH)(CH$_2$)(OCF$_3$)$_2$(HCCH) (**9**, **10** and **11**, **12**). Selected geometrical parameters are from the B3LYP/HW3 and HF/HW3 (in parentheses) methods.

enlogated to 2.298 Å, 0.016 Å longer than that in structure **2**. This indicates the formation of a very early NH inward ring-opening transition state for Mo-alkylidene with electron-withdrawing alkoxyl ligands.

The calculated activation energies for the NH outward and NH inward ring-opening pathways of Mo(NH)-(CH$_2$)(OMe)$_2$(C$_2$H$_2$) (**1**) are 2.0 and 5.4 kcal/mol, respectively. The calculated activation energies for the NH outward and NH inward ring-opening pathways for Mo(NH)(CH$_2$)(OCF$_3$)$_2$(C$_2$H$_2$) (**2**) with electron-withdrawing alkoxy ligands are 0.3 and 6.5 kcal/mol, respectively. The electron-withdrawing OCF$_3$ ligands lower the activation barriers of the NH outward ring-opening by about 2 kcal/mol. Both cases indicate that the NH

5

6
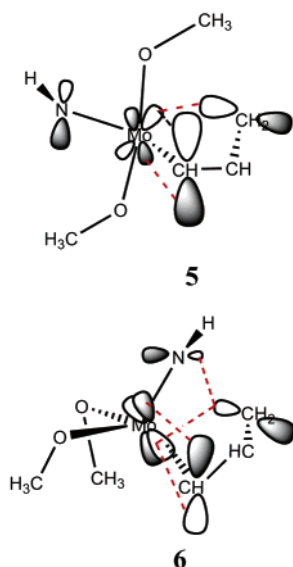
Figure 3. Orbital interactions in transition structures **5** and **6**.

outward ring-opening of metallacyclobutene proceeds more readily. Thus, the NH outward rotation preference is about 3.4 kcal/mol for **1** and is increased to about 6 kcal/mol for **2**.

The substituent effect on inward/outward rotation of cyclobutene ring-opening has been extensively studied. In particular, Houk et al. have developed an elegant frontier molecular orbital model to rationalize the substituent effect. They have also been able to make many predictions based on theoretical calculations.[34] However, we are not aware of any theoretical study on the ring-opening of metallacyclobutene.

The preference for the NH outward rotation is very interesting, because it leads to a less stable *anti* Mo-alkylidene product, as structures **7** and **11** are calculated to be less stable than **8** and **12** (by 2.0 and 2.8 kcal/mol, respectively). Thus, the NH outward rotation preference should be rationalized on the basis of the kinetic argument. A detailed analysis of orbital interactions is necessary to develop a solid understanding of the stereochemistry. Here we can present only a simplified model. Figure 3 shows the HOMO of transition states **5** and **6**. In transition state **5**, the d-orbitals of the Mo center have maximum $\pi_d-\pi_p$ interactions with the π-orbital of the α-carbon. In addition, the π-orbital of the alkylidene carbon atom points to the Mo center, facilitating the $\pi_d-\pi_p$ interaction. Therefore the NH outward ring-opening transition structure **5** is largely stabilized.

In the NH inward ring-opening transition structure **6**, the π-orbital of the alkylidene carbon atom points to the imido group instead of the Mo center. Therefore only a fractional overlap exists between the d-orbital of the Mo center and the π-orbital of the alkylidene carbon atom. It is also noticed that the N$-$Mo$-$C(alkylidene) angle is about 85° and the N/C(alkylidene) distance is about 3.1 Å in the transition state **6**, much smaller than the corresponding values of 140° and 3.9 Å in transition state **5**. This causes a strong repulsion between the π-orbital of alkylidene carbon with the imido lone pair, destabilizing transition state **6**; as a result a higher activation energy is predicted.
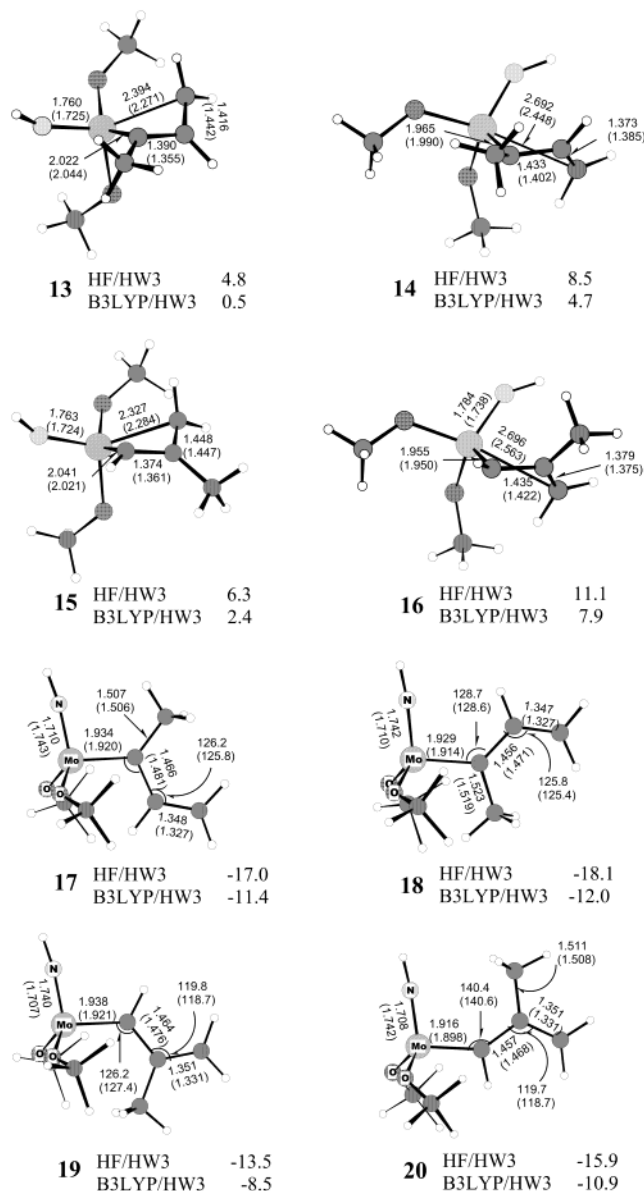
Scheme 4

α-**metallacyclobutene**

β-**metallacyclobutene**
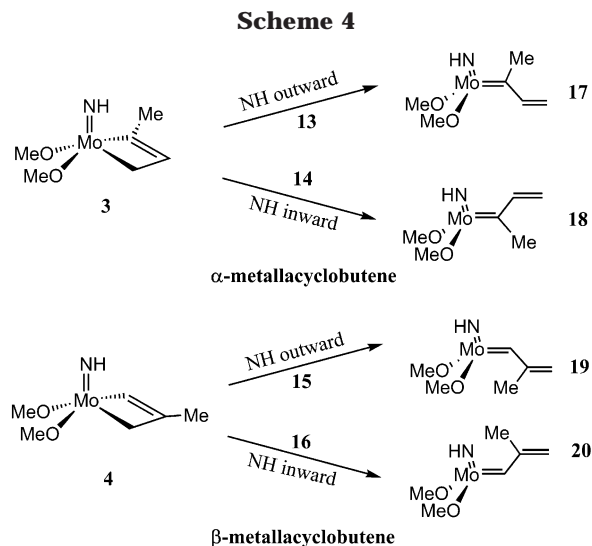
C. Ring-Openings of α- and β-Addition Mo(NH)-(CH$_2$)(OMe)$_2$(C$_2$HMe) Intermediates. The ring-opening patterns of the α- and β-addition intermediates Mo(NH)(CH$_2$)(OMe)$_2$(C$_2$HMe) were also studied. Scheme 4 shows the NH outward and NH inward ring-openings for both α-addition metallacyclobutene (**3**) and β-addition metallacyclobutene (**4**). The NH outward ring-opening of **3** and **4** leads to *anti*-products **17** and **19**, respectively, while the *syn*-products **18** and **20** are formed via NH inward ring-opening.

The optimized NH outward (**13** and **15**) and NH inward ring-opening transition structures (**14** and **16**) for the α-insertion and β-addition intermediates (**3** and **4**) are shown in Figure 4. Their activation energies are summarized in Table 2. For comparison, the ring-opening activation energies for the NH outward and NH inward ring-opening transition states of the metallacyclobutenes Mo(NH)(CH$_2$)(OR′)$_2$(C$_2$H$_2$) (R′ = CH$_3$ and CF$_3$) (**1** and **2**) are also listed in Table 2.

Compared to the ring-opening of the Mo intermediate **1**, one can conclude that the α-methyl group lowers the activation energy of the NH outward and inward ring-openings by about 1.5 and 0.7 kcal/mol, respectively. The β-methyl group, on the other hand, is found to increase the activation energies of the NH outward and inward ring-openings by about 0.4 and 2.5 kcal/mol, respectively. In the case of cyclobutene ring opening, substituents such as Cl, Br, and CN on the double bond are found to increase the activation barrier of ring opening by about 1 kcal/mol.[34] An analysis of calculated atomic charges (see Table 3) indicates that the C=C moiety carries less negative charge and the Mo center carries less positive charge in the NH outward rotation trantition structures (**5**, **9**, **13**, and **15**) than the NH inward rotation transition structures (**6**, **10**, **14**, and **16**). Therefore, the C=C in the outward rotation transition structures behave as a better π-donor and has a stronger interaction with the metal center, resulting in a greater stabilization.

The optimized geometries of the ring-opening products Mo(NH)(OMe)$_2$(C$_3$H$_3$Me) (**17**–**20**) are also shown in Figure 4. Comparing molecules **7** and **8** and the initial alkylidenes, one can conclude that all orientations of the OR and NH groups are similar. The two Mo$-$C$-$H angles in alkylidenes are about 130° and 114°, respec-

13 HF/HW3   4.8
       B3LYP/HW3   0.5

14 HF/HW3   8.5
       B3LYP/HW3   4.7

15 HF/HW3   6.3
       B3LYP/HW3   2.4

16 HF/HW3   11.1
       B3LYP/HW3   7.9

17 HF/HW3   -17.0
       B3LYP/HW3   -11.4

18 HF/HW3   -18.1
       B3LYP/HW3   -12.0

19 HF/HW3   -13.5
       B3LYP/HW3   -8.5

20 HF/HW3   -15.9
       B3LYP/HW3   -10.9

Figure 4. Calculated geometries and relative energies (kcal/mol) for the ring-opening transition structures and first insertion products of α-Mo(NH)(CH$_2$)(OCH$_3$)$_2$(HCCMe) (**13**, **14** and **17**, **18**) and β-Mo(NH)(CH$_2$)OCH$_3$)$_2$(HCCMe) (**15**, **16** and **19**, **20**). Selected geometrical parameters are from the B3LYP/HW3 and HF/HW3 (in parentheses) methods.

Table 2. B3LYP/HW3 Calculated Activation Energies (kcal/mol) for the NH-Outward and NH-Inward Ring-Openings of Metallacyclobutenes 1−4, 21, and 22

	$\Delta E^{\ddagger}_{\text{NH−outward}}$	$\Delta E^{\ddagger}_{\text{NH−inward}}$	$\Delta E^{\ddagger}_{\text{out−in}}$
OCH$_3$-substituted (**1**)	2.0	5.4	3.4
OCF$_3$-substituted (**2**)	0.3	6.5	6.2
α-addition (**3**)	0.5	4.7	4.2
β-addition (**4**)	2.4	7.9	5.5
anti (**21**)	1.7	9.3	7.6
syn (**22**)	4.7	2.2	-2.5

tively, with the one involving the *anti*-H atom being much smaller. The difference in the angle values becomes larger when one H atom is replaced by the −HC=CH$_2$ group (structures **17** and **18**).[18] The relative energy for the *anti* α-insertion product (**17**) is −11.4 kcal/mol; the relative energy for the *syn*-product (**18**) is

Table 3. B3LYP/HW3 Calculated Atomic Charge Distributions on Mo, C(α), C(β), and C(alkylidene) of the NH-Outward Transition Structures 5, 9, 13, and 15 and the NH-Inward Transition Structures 6, 10, 14, and 16

|	Mo	C(α)	C(β)	C(alkylidene)
NH-outward				
OCH$_3$-substituted (**5**)	1.218	−0.191	0.096	−0.119
OCF$_3$-substituted (**9**)	1.139	−0.159	0.125	0.004
α-addition (**13**)	1.134	−0.088	0.083	−0.021
β-addition (**15**)	1.219	−0.243	−0.200	−0.166
NH-inward				
OCH$_3$-substituted (**6**)	1.131	−0.229	0.061	−0.018
OCF$_3$-substituted (**10**)	1.117	−0.133	0.108	−0.023
α-addition (**14**)	1.097	−0.141	0.034	0.018
β-addition (**16**)	1.151	−0.271	0.162	−0.047

Scheme 5
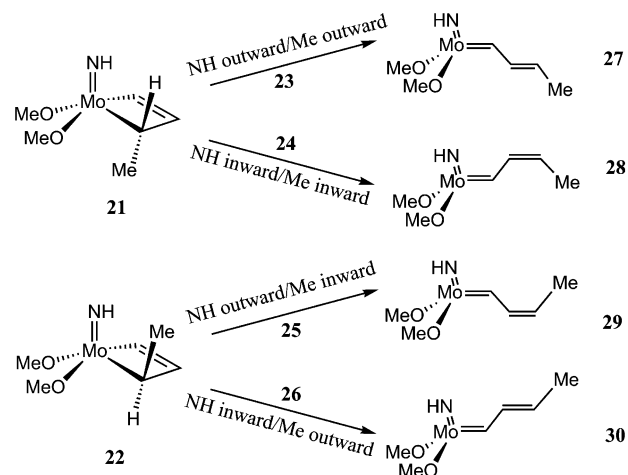
−12.0 kcal/mol. The small energy difference between **17** and **18** is expected because both substituents at the alkylidene carbon should have a *syn* preference. The relative energies for the *anti* β-insertion product (**19**) and the *syn*-product (**20**) are −8.5 and −10.9 kcal/mol, respectively.

D. Ring-Opening of *cis*- and *trans*-Mo(NH)-(CHMe)(OMe)$_2$(C$_2$H$_2$). In experiments, Mo(NAd)(CH−CMe$_2$Ph)(OCF$_3$)$_2$ was used as the initial catalyst. The conformation of the CH−CMe$_2$Ph group, either in the *cis*-conformation or in the *trans*-conformation with respect to the imido group, is expected to affect the conformation of yielded polyene. Therefore in this section we will discuss how *cis*- and *trans*-molybdenum alkylidenes affect the conformations of the first insertion products using the model compounds shown in Scheme 5.

Structure **21** is the *anti*-intermediate from the addition of acetylene to *trans*-Mo(NH)(CHMe)(OMe)$_2$, while structure **22** is *syn*-Mo(NH)(CHMe)(OMe)$_2$(C$_2$H$_2$), obtained using *cis*-Mo(NH)(CHMe)(OMe)$_2$ as the catalyst. We used MeO ligands instead of electron-withdrawing OCF$_3$ ligands because we were unable to locate some of the transition structures (too reactive to have a measurable activation barrier).

In structure **21**, the molybdenum alkylidene methyl group is *anti* to the NH group. Two transition structures (**23** and **24**) are derived. In transition structure **23**, both the methyl group and the NH group rotate outward, while in transition structure **24** both groups rotate inward. The calculated activation energies for the two transition structures are about 1.7 and 9.3 kcal/mol,

Scheme 6

R = CH(CF$_3$)$_2$
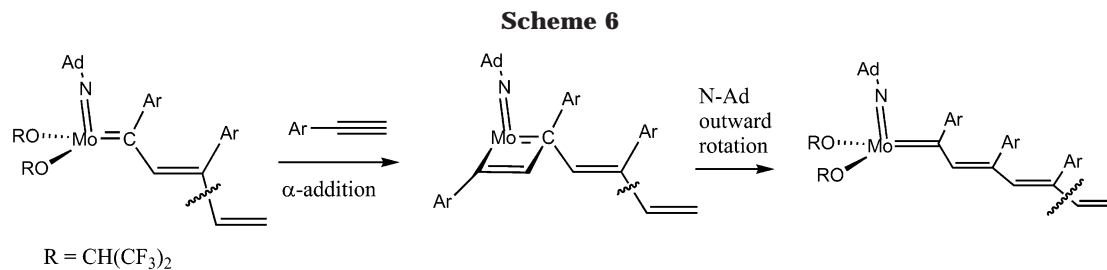
Table 4. Calculated Activation Energies for the Isomerization of Mo(NH)(CH$_2$)(OCH$_3$)$_2$, Addition of Acetylene to Mo(NH)(CH$_2$)(OCH$_3$)$_2$, and Ring-Opening of Mo(NH)(CH$_2$)(OCH$_3$)$_2$(HC≡CH) at the B3LYP/HW3 Level

Mo(NH)(CH$_2$)(OR)$_2$ + HC≡CH	isomerization	acetylene addition	ring-opening
OR=OCH$_3$	9.6	9.3	2.3
OR=OCF$_3$	18.1	0.6	0.3

respectively. If we assume that the preference for NH outward rotation is similar to that of systems **1** (3.4 kcal/mol between structures **5** and **6**), we estimate that there is also a preference of about 4.2 kcal/mol for the methyl group rotating outward.

In structure **22**, the molybdenum alkylidene methyl group is *syn* to the NH group. There are also two types of conrotatory transition structures. In transition structure **25**, the NH group rotates outward but the methyl group rotates inward. In transition structure **26**, the situation is the opposite; the NH group rotates inward and the methyl group rotates outward. On the basis of the calculated activation energies with the two transition structures, one can roughly estimate that the methyl group has a preference of about 5.9 kcal/mol for outward rotation. Thus, we can qualitatively conclude that the methyl group has a preference of about 4−6 kcal/mol for outward rotation in the ring-opening of molybdacyclobutenes. This is comparable to the outward rotation preference for 3-methyl cyclobutene ring-opening, which is about 6−7 kcal/mol.[34]

Therefore, it can be concluded that the pattern of ring-opening is dependent upon the conformation of the initial molybdenum alkylidene catalyst. That is, if the imido and the molybdenum alkylidene methyl groups are in the *trans* position, NH outward/Me outward ring-opening proceeds readily, as a result yielding *anti*-product (**28**). On the contrary, when the imido NH and the methyl groups are in the *syn*-conformation, *cis*-product (**30**) is generated via the NH inward/Me outward ring-opening.

E. Polymerization Rate versus Isomerization Rate of Alkylidene. Up to now we have studied the ring-opening of Mo intermediates derived from the addition of alkyne to molybdenum alkylidene and the relationship between the conformation of the intermediate and the conformation of the first insertion product. Associated with our previous study,[31] the first insertion product is formed via α-addition of acetylene to molybdenum alkylidene, followed by the NH outward/Me outward ring-opening of the formed four-membered ring Mo intermediate. This first insertion product is in *anti*-conformation; however, it is less stable than its *syn*-isomer. For example, the relative energy of the *anti* first insertion product **7** is higher than **8** by about 2.0 kcal/
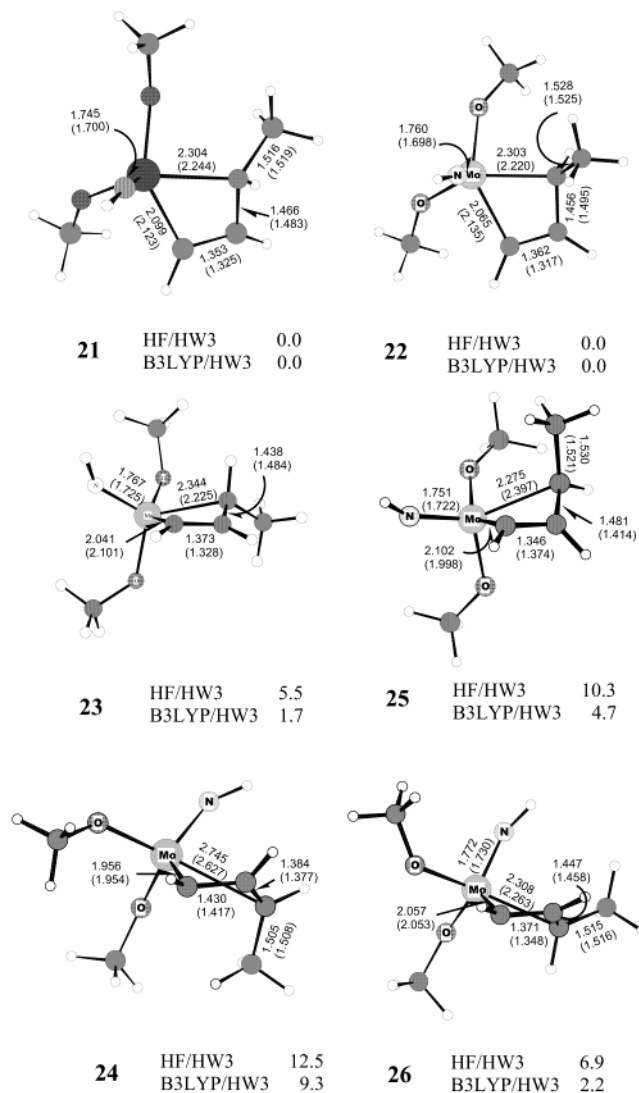
Figure 5. Calculated geometries and relative energies (kcal/mol) for the ring-opening transition states (**23**, **24**) of *trans*-Mo(NH)(CHMe)(OCH$_3$)$_2$(HCCH) (**21**) and ring-opening transition states (**25**, **26**) of *cis*-Mo(NH)(CH$_2$)(OCF$_3$)$_2$-(HCCH) (**22**). Selected geometrical parameters are from the B3LYP/HW3 and HF/HW3 (in parentheses) methods.

mol. This indicates that the *anti*-product is kinetically favored, while the *syn*-product is thermodynamically favored. This is also supported by Schrock's experiment[24] where the ratio of the *syn* and *anti* first insertion products obtained from a reaction between *o*-TMSPA and Mo(NAd)(CHCMe$_2$Ph)[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine) changes with time to an equilibrium value of 5−7 at 24 °C in favor of the *syn*-product, while the ratio is approximately 1 when the reaction time was shortened to 5 min and the reaction solution was kept below 0 °C. To obtain a polymer of high stereospecificity and tac-

ticity, it is necessary for the *anti*/*syn*-isomerization to proceed much slower than the alkyne addition to molybdenum alkylidene and the ring-opening of the Mo intermediate. Therefore the *anti*/*syn*-isomerization of the first insertion products is also investigated.

Table 4 shows the calculated activation energies for the addition of parent acetylene to alkylidene Mo(NH)-$(CH_2)(OR')_2$[31] and the ring-opening of molybdacyclobutene Mo(NH)$(CH_2)(OR')_2(C_2H_2)$ and the *anti*/*syn*-isomerization activation energy for Mo(NH)(CH_2)-$(OR')_2$ (R' = Me, CF_3). When Mo(NH)$(CH_2)(OMe)_2$ is used as the catalyst for alkyne polymerization, the calculated activation energies for the *anti*/*syn*-isomerization and polymerization are similar. Since the polymerization reaction is associated with a large loss of enthopy (bimolecular reaction),[16,31] the *anti*/*syn*-isomerization should be faster than polymerization. This would lead to polymers with nonuniformity, because each polymerization step would involve two equilibrium rotamers.

On the other hand, the activation energy for the addition of acetylene to Mo(NH)$(CH_2)(OCF_3)_2$ is rather small, about 0.6 kcal/mol. The *anti*/*syn*-isomerization of Mo(NH)$(CH_2)(OCF_3)_2$ needs to overcome a barrier height of about 18.1 kcal/mol. This indicates that *anti*/*syn*-isomerization is expected to be much slower than the addition of alkyne to the molybdenum alkylidene and its ring-opening. This guarantees that only one rotamer is involved in each step of polymerization, and the polymer can grow in a uniform fashion. Since each step generates a disubstituted alkylidene, both alkylidene substituents (one vinyl and one arenyl) should have similar preferences of outward/inward rotation. Therefore, it is expected that the direction of ring-opening is determined by the imido group. As shown in Scheme 6, each step of polymerization would generate a Mo-alkylidene with the arenyl group *syn* to the Mo=N bond, resulting from N–Ad outward rotation and Ar group inward rotation.

Summary

The ring-opening mechanisms of metallacyclobutenes derived from the addition of alkyne (HC≡CR, R = H, Me) to molybdenum alkylidene Mo(NH)$(OR')_2(CHR'')$ (R' = Me, CF_3, R'' = H, Me) have been studied using quantum mechanical methods. The results are summarized as follows.

(1) Two ring-opening patterns have been found for metallacyclobutene intermediates. One is the NH outward ring-opening which leads to *anti*-product, and the other is through the NH inward ring-opening pattern to form *syn*-product. The NH outward ring-opening is more favorable than the NH inward ring-opening. The electron-withdrawing OCF_3 ligands on molybdenum alkylidene further enhance the preference of the NH outward ring-opening.

(2) The effect of substituents at the C=C bond of molybdacyclobutene has been studied. A C_α-methyl substituent is found to reduce the activation energy of both NH outward and inward rotations. A C_β-methyl group, on the other hand, increases the action energy for both NH outward and inward rotations. Both substituents also increase the preference for NH outward rotation over inward rotation.

(3) Four ring-opening paths have been found for Mo(NH)$(OMe)_2(CHMe)(C_2H_2)$, the intermediate of the addition of acetylene to Mo(NH)$(OMe)_2(CHMe)$. The molybdenum alkylidene methyl group also has a preference of about 4−6 kcal/mol for outward rotation, which is comparable to that in cyclobutene ring-opening. If the molybdenum alkylidene methyl is in *trans* position to the NH, the ring-opening will strongly favor NH outward/methyl outward rotation, leading to a *trans*-alkylidene; if the molybdenum alkylidene methyl is *cis* to the NH, NH inward/methyl outward rotation would be favorable, resulting in a *syn*-alkylidene.

As a result, the final polymer is expected to be highly *trans* and isotactic.

Supporting Information Available: Calculated energies of the stationary points on the potential energy surface of the ring-opening of molybdacyclobutene at the HF/3-21G, HF/HW3, and B3LYP/HW3 levels. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0342614