Theoretical Studies on Alkyne Addition to Molybdenum Alkylidenes: The Preference of α- and β-Additions

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Abstract: The addition of alkynes $HC\equiv CR$ to $Mo(NH)(CH_2)(OR')_2$ (R = H, Me, Ph; R′ = CH_3, CF_3) has been studied with both ab initio molecular orbital and density functional calculations. Geometry optimizations were carried out with the HF/3-21G, HF/HW3, and B3LYP/HW3 methods. The transition structures for these addition reactions are in distorted trigonal bipyramidal geometries, similar to those of alkene additions. The calculated activation enthalpy for $HC\equiv CH$ addition to $Mo(NH)(CH_2)(OR')_2$ is about 10.3 kcal/mol for R′ = CH_3 and about 2.3 kcal/mol for R′ = CF_3, indicating a significant preference for acetylene addition to $Mo(NH)(CH_2)(OCF_3)_2$ over $Mo(NH)(CH_2)(OCH_3)_2$. These barriers are higher than those of the corresponding ethylene addition by about 2−4 kcal/mol, even though the reaction of acetylene is much more exothermic. The α-addition of $HC\equiv CR$ (R = Me, Ph) is found to be considerably more favorable than the β-addition to $Mo(NH)(CH_2)(OR')_2$. Interestingly, the α-addition has a lower activation energy, while the β-addition has a higher activation energy, compared to that of the parent acetylene addition. Thus, α-addition is intrinsically favored over β-addition by over 4 kcal/mol. This preference is reduced by solvent effect. All these can be explained by a destabilizing interaction between the nonreacting π-orbital of alkyne and one of the lone pairs on the imido nitrogen. The steric effect of the bulky ligands in the real catalysts is also investigated qualitatively by the PM3 method. These studies give results in good accord with the experimentally observed regioselectivity.

Introduction

In recent years, significant progress has been made in the synthesis of a wide variety of molybdenum−alkylidene complexes of the type $Mo(NR)(CHR')(OR'')_2$, and to some extent their tungsten analogues,[1−3] and in the use of these complexes as olefin metathesis catalysts.[4−7] One of the most interesting applications of these alkylidene complexes is their use as initiators for the living polymerization of strained cyclic olefins such as norbornenes and substituted norbornadienes.[8−16]

Progress has also been made in the application of these metal−alkylidenes as catalysts for acetylene polymerization.[17−23] For example, Schrock et al. have found that certain 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, as shown in Scheme 1.[1,4,11,24−28] This makes it possible for head-to-tail low-polydispersity poly(*o*-TMSPA) to be prepared with predetermined absolute molecular weights, which allows for questions concerning the correlation of nonlinear optical property with chain length and structure to be addressed.[29,30] There are two alternative paths in the addition of *o*-TMSPA to alkylidene, path **A** (α-addition) and path **B** (β-addition), which are shown in Scheme 1. To get the narrowest

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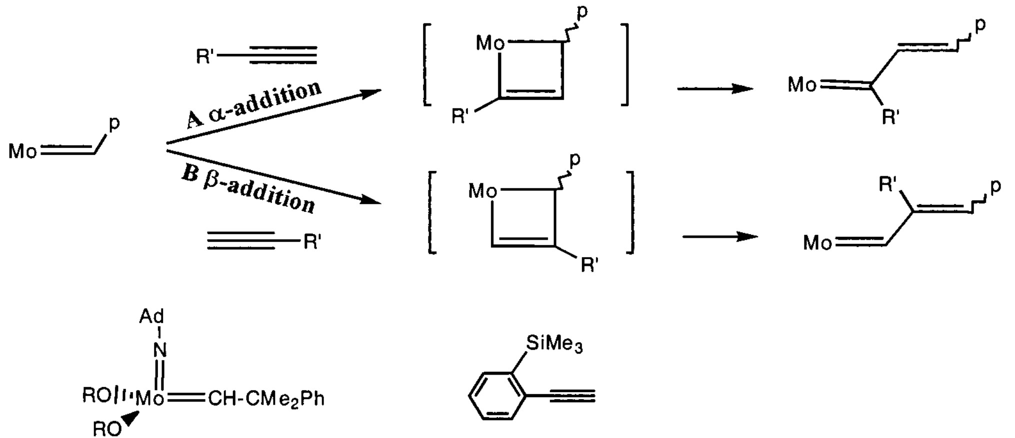
10.1021/ja0104756 CCC: $20.00

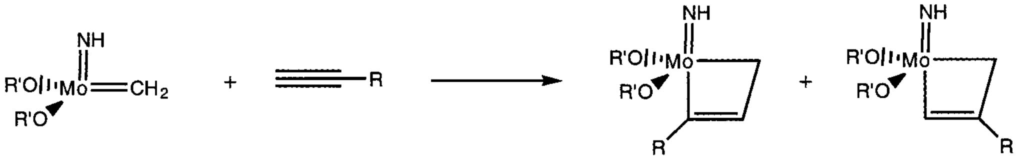
Scheme 1



OR = OCH(CCF$_3$)$_2$

***o*-TMSPA**

Scheme 2



1. R'= CH$_3$
2. R'= CF$_3$

3. R= H
4. R= CH$_3$
5. R= Ph

molecular weight distribution, it is required that α- and *β*-addition pathways should be of equal rate or either α- or *β*-addition takes place exclusively.[24] Otherwise, the resulting polyenes will possess high PDI which are not suitable for addressing the relationship between the nonlinear optic property and molecular structure.

It seems that *β*-addition of terminal alkynes will be most favorable, as the metal center is more crowded than the alkylidene center. Schrock's experiments have shown that the polymerization of *o*-TMSPA with alkylidenes is only that arising from α-addition when the alkoxyl ligand is not very bulky.[18−20] It is important to understand this preference for α-addition and the factors that influence the regiochemistry of acetylene metathesis. In addition, it is also valuable to understand the relative reactivities of alkyne and alkene additions, so that ene−yne cross-metathesis can be explored.[20]

We have studied the mechanism of molybdenum−alkylidene mediated alkene metathesis and stereochemistry of ring-opening metathesis polymerization of norbornadiene.[15,16] In the present paper, we present our ab initio and density functional studies on CH≡CR addition to the molybdenum alkylidene complexes Mo(NH)(CH$_2$)(OR′)$_2$, as shown in Scheme 2. The steric effect of the bulky ligands in the real catalysts is also investigated. The purposes of our study are (1) to investigate the geometrical features of the transition structure and metallacyclobutene product of alkyne addition, (2) to analyze the factors that cause the difference in the reactivity between alkyne and alkene addition to alkylidene, (3) to evaluate the preference of α-addition and *β*-addition of alkyne to alkylidene, and (4) to discuss the steric effect of the bulky ligands in the real catalysts on the reactivity of α-addition and *β*-addition of alkyne to alkylidene.

Calculation Methods

All calculations were carried out with the GAUSSIAN 94 program.[31] The geometries were optimized first with the closed-shell Hartree−Fock method and the all-electron 3-21G basis set.[32] For each structure of the reactions of acetylene and propyne, harmonic vibration frequencies were calculated to confirm minimum or transition state (zero and one imaginary vibration frequency, respectively), on the basis of which thermal energy and reaction entropy were calculated. The geometries were further optimized with the HW3 basis set according to Frenking's definition,[33,34] which was constructed by the contraction scheme [3311/2111/311] + ECP[35] on a 28-electron core for the molybdenum atom and the 6-31G* basis set for the other atoms. Density functional theory calculations were also carried out using the B3LYP nonlocal density functional approximation, which uses Becke's three-parameter nonlocal exchange function[36] and the Lee−Yang−Parr nonlocal correlation functional.[37,38] Geometry optimizations were carried out with the HW3 basis set.

The steric effect of the bulky ligands in the real catalysts on the reactivity of the α- and *β*-additions of substituted acetylenes to alkylidenes was investigated by using the semiempirical PM3 method,

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Table 1. Calculated Changes of Energies (ΔE, kcal/mol), Thermal Energies (ΔH°_{298}, kcal/mol), and Entropies (ΔS_{298}, cal/mol·K) of the Addition Reactions of Mo Alkylidenes with Ethyne and Ethane

			HF/3-21G			HF/HW3	B3LYP/HW3
entry	reaction		ΔE	$\Delta\Delta H^\circ_{298}$	ΔS_{298}	ΔH°_{298}	ΔH°_{298}
	$HC{\equiv}CH + Mo(NH)(CH_2)(OCH_3)_2$						
1	**1 + 3 → 6**	addition TS	23.8	1.0	−40.6	25.4	10.3
2	**1 + 3 → 8**	prod.	−23.4	3.5	−43.1	−21.6	−32.3
	$HC{\equiv}CH + Mo(NH)(CH_2)(OCF_3)_2$						
3	**2 + 3 → 7**	addition TS	12.2	1.6	-43.1	15.4	2.3
4	**2 + 3 → 9**	prod	−20.5	4.5	−44.6	−16.4	−29.5
	$HC{\equiv}CMe + Mo(NH)(CH_2)(OCH_3)_2$						
5	**1 + 4 → 10**	α-addition TS	19.1	1.5	−46.3	22.4	8.1
6	**1 + 4 → 11**	*β*-addition TS	26.6	1.4	−44.2	28.3	12.6
7	**1 + 4 → 14**	α-prod.	−19.5	3.9	−42.1	−16.6	−26.3
8	**1 + 4 → 16**	*β*-prod.	−21.8	3.7	−41.2	−19.7	−29.0
	$HC{\equiv}CMe + Mo(NH)(CH_2)(OCF_3)_2$						
9	**2 + 4 → 12**	α-addition TS	7.0	2.0	−47.5	11.9	0.1
10	**2 + 4 → 13**	*β*-addition TS	11.0	2.4	−52.0	17.7	4.9
11	**2 + 4 → 15**	α-prod.	−18.3	4.4	−45.8	−13.8	
12	**2 + 4 → 17**	*β*-prod.	−20.2	4.1	−47.4	−15.7	−28.3
	$H_2C{=}CH_2 + Mo(NH)(CH_2)(OCH_3)_2$						
13	**C_2H_4 + 1 → 24**	addition TS	10.9	2.6	−46.6	17.4	5.8
14	**C_2H_4 + 1 → 25**	prod.	−16.4	4.1	−40.7	−7.8	−14.0
	$H_2C{=}CH_2 + Mo(NH)(CH_2)(OCF_3)_2$						
15	**C_2H_4 + 2 → 26**	addition TS	−3.2	3.4	−51.7	8.7	0.3
16	**C_2H_4 + 2 → 27**	prod.	−16.6	4.6	−49.4	−5.0	−12.3

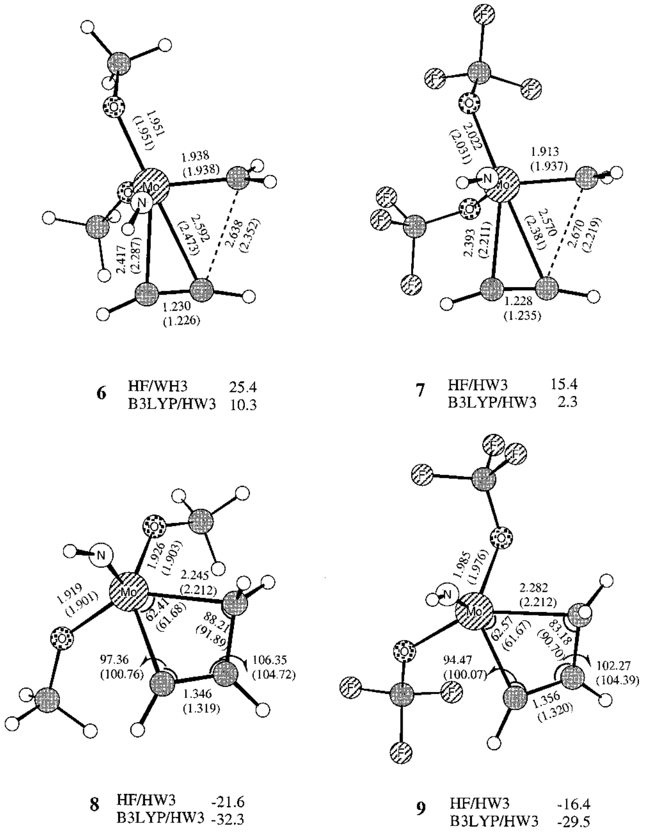
which is incorporated in the SPARTAN program.[39] Geometry-constrained optimization was carried out. That is, only the imido ligand, alkoxide ligands, and alkylidene substituent were optimized, and the rest were frozen in the HF/3-21G optimized geometries of $Mo(NH)(CH_2)(OR')_2$ ($R' = CMe_3$) with phenylacetylene.

Results and Discussion

The calculated total energies, thermal energies, and entropies of the reactants, transition structures, and the products that are involved in the reactions shown in Scheme 2 are given in Table S1 of the Supporting Information. Cartesian coordinates of the structures presented in the text are given in Table S2 of the Supporting Information. Table 1 gives the calculated reaction or activation energies, thermal energy ($T = 298$ K) corrections, and entropies of the reactions of acetylene and propyne with the HF/3-21G method and reaction or activation enthalpies with the HF/HW3 and B3LYP/HW3 methods. For comparison, the calculated energetics for the reaction of ethylene with **1** and **2** are also given in Table 1.

A. Reaction of Acetylene with Molybdenum−Alkylidene. Figure 1 shows the transition structures and metallacyclobutene product (intermediate for metathesis) of the addition reaction of acetylene with $Mo(NH)(CH_2)(OCH_3)_2$ (**6**) and $Mo(NH)(CH_2)(OCF_3)_2$ (**7**).

Structures **6** and **7** are similar with both the HF and B3LYP methods. Both structures are in a pseudo-trigonal bipyramidal (TBP) geometry with the NH and one of the OR groups taking the axial positions. The four-membered ring is formed in the equatorial plane, similar to the transition structures for ethylene addition to the corresponding molybdenum−alkylidenes.[16] Since the HF and B3LYP methods give similar geometrical parameters, the discussion of geometries will only be based on the B3LYP geometries.



6 HF/WH3 25.4
B3LYP/HW3 10.3

7 HF/HW3 15.4
B3LYP/HW3 2.3

8 HF/HW3 -21.6
B3LYP/HW3 -32.3

9 HF/HW3 -16.4
B3LYP/HW3 -29.5

Figure 1. The calculated geometries and activation enthalpies (kcal/mol) for the transition structures of the addition of HCCH to $Mo(NH)(CH_2)(OCH_3)_2$ (**6**) and to $Mo(NH)(CH_2)(OCF_3)_2$ (**7**) and the corresponding metallacyclobutenes (**8** and **9**). Selected geometrical parameters are from the B3LYP/HW3 and HF/HW3 (in parentheses) methods.

Transition structures **6** and **7** are characterized with the addition of acetylene to the molybdenum center. This is indicated by the following geometrical features: (1) In structures **6** and **7**, both Mo−C_1 and Mo−C_2 are significantly formed. With the B3LYP/HW3 method, the two distances are 2.42 and 2.59 Å in **6** and 2.39 and 2.57 Å in **7**. These are only about

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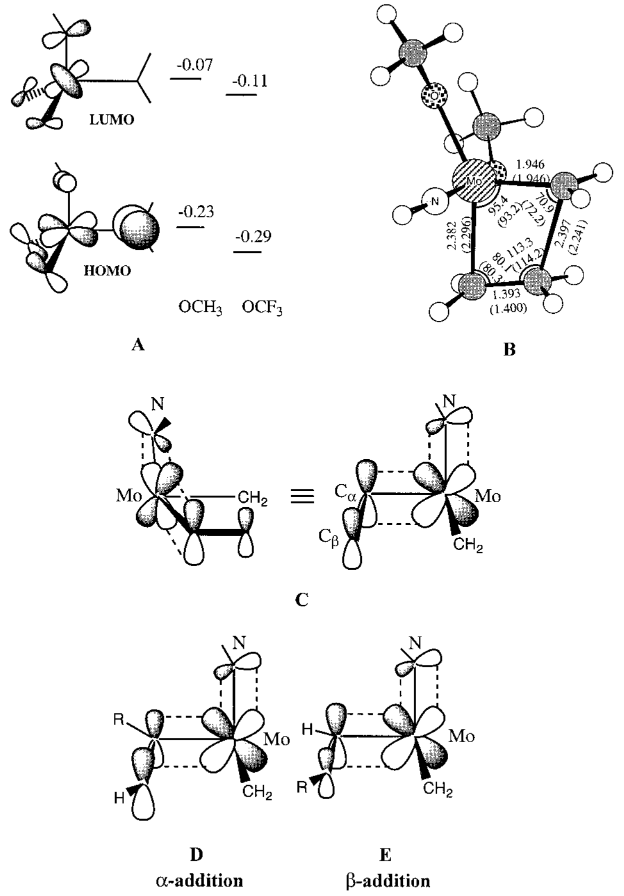
(39) *SPARTAN*, version 5.0; Wavefunction, Inc.: 18401 Von Karman Ave. #370, Ivrine, CA 92715.

Scheme 3



0.1–0.3 Å longer than the fully formed Mo–C single bonds. (2) The Mo–alkylidene (Mo═C) bond is only slightly elongated from the reactant with little pyramidalization at the alkylidene carbon center. (3) The C···C distance is quite long, about 2.6–2.7 Å, indicating little C···C bond formation. (4) Compared to the corresponding transition structures for ethylene addition, these transition structures occur somewhat earlier (compare with **B**). For the addition of olefin to Ti═C bond, Grubbs has proposed a slippery mechanism.[40] That is, the formation of the olefin–metal–alkylidene intermediate is followed by the slipping of the terminal carbon to form metallacyclobutane. Our calculations indicate that the LUMO of metal–alkylidene is a d-orbital of the metal with little participation of the alkylidene p-orbital (see **A** in Scheme 3). Thus, the reaction is best described as nucleophilic addition of the alkyne to the alkylidene. This is reflected by the above geometrical features of the transition structures. The calculated effect of alkoxyl ligands on the reactivity of alkylidene (next paragraph) and preference for α-addition (section B) further support this argument.

The calculated activation enthalpy for **6** is about 25.4 kcal by HF/HW3 and 10.3 kcal/mol by B3LYP/HW3 with respect to the separated reactants (with HF/3-21G thermal energy correction, see Table 1, entry 1). The calculated activation enthalpy for **7** is 15.4 kcal/mol by HF/HW3 and 2.3 kcal/mol by B3LYP/HW3 (see Table 1, entry 3), in agreement with the experimental result that the catalyst with stronger electron-withdrawing alkoxide ligands is more reactive.[4] The electron-withdrawing alkoxide (OCF_3) lowers the activation energy significantly. The calculations indicate large activation entropies of over 40 eu for these cyclization reactions (see Table 1, entries 1 and 3) because of the partial formation of two bonds in the transition structures.

The acetylene addition reaction is quite exothermic. The calculated reaction enthalpies for the reactions by the B3LYP/HW3 method are about −32 and −30 kcal/mol (Table 1, entries 2 and 4), respectively. These reaction enthalpies are about 15 kcal/mol more negative than those of the corresponding ethylene addition (compare entries 14 and 16 in Table 1). Despite the fact that the addition of acetylene is more exothermic than the addition of ethylene by about 15 kcal/mol, and **6** and **7** are indeed "earlier" than the corresponding transition structures of ethylene addition, the calculated activation enthalpies of acetylene addition to **1** and **2** are higher than those of ethylene addition to **1** and **2** by about 4.5 and 2.0 kcal/mol with the B3LYP/HW3 method, respectively. The energy difference is even larger with the HF/HW3 method.

The main difference between acetylene and ethylene additions is that acetylene has a nonreacting π-bond. As analyzed by Cundari and Ziegler before,[41,42] the five d-orbitals of the Mo center should have maximum π_d–π_p interactions with the ligands. Thus, the imido ligand contributes two lone pairs, and each of the other three ligands contributes one lone pair. In the transition state of acetylene addition, the nonreacting π-orbital of acetylene also behaves as a π_p donor (see Scheme 3). It competes with one of the imido lone pairs for a d-orbital of the metal center, as shown in **C**.[43] In addition, the nonreacting π-orbital also has some electrostatic repulsion with the axial alkoxy ligand. The involvement of this nonreacting π-orbital of acetylene in the interaction causes a destabilization to the transition structure and results in a higher activation energy than ethylene addition.

This interaction also explains some geometrical differences between the transition structures of acetylene and ethylene additions. In the transition structure (**B**) of ethylene addition to $Mo(NH)(CH_2)(OMe)_2$, the NH group is close to coplanar with the Mo–$C_{(alkylidene)}$ bond; the dihedral angle H–N–Mo–$C_{(alkylidene)}$ is about −163°. While in structure **6** the dihedral angle is about −121°, indicating that the hydrogen of the NH group bends slightly toward the C_α of acetylene. Moreover, the orientations of the two OR groups are different in the two cases; in structure **B**, the two $C_{(Me)}$–O–Mo–$C_{(alkylidene)}$ dihedral angles are about 75° and −113°, respectively, while they are 60°and 126°, respectively, in structure **6**.

Structures **8** and **9** are molybdacyclobutene products for the addition of acetylene. Both structures are in a square-pyramidal geometry. For the addition of alkenes, both experiment and calculations indicate that the geometry of the metallacyclobutane is highly dependent upon the nature of the alkoxyl groups.[42,44] Electron-donating groups favor square-pyramidal geometries, while trigonal-bipyramidal geometries are observed for electron-withdrawing groups. We are unable to locate a stable trigonal-bipyramidal structure for molybdacyclobutenes. This difference is also due to the nonreacting π-orbital of acetylene. In a trigonal-bipyramidal geometry, the C–Mo–C angle of the metallacyclobutene ring would be about 80°, and the π-orbital can have significant repulsive interaction with the two axial ligands just as schematically described in **C**. On the other hand, in a square-pyramidal geometry, this interaction is largely avoided.

B. Preferences of α- and *β*-Additions of Substituted Acetylenes to 1 and 2. From **C**, it is clear that the p-orbital of

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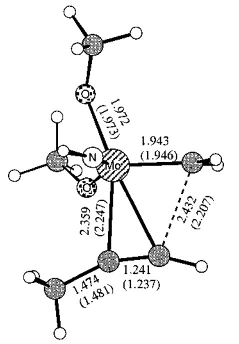
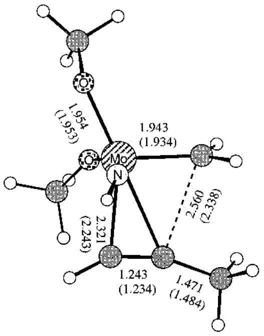
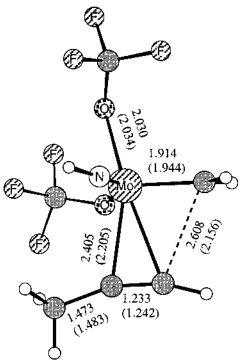


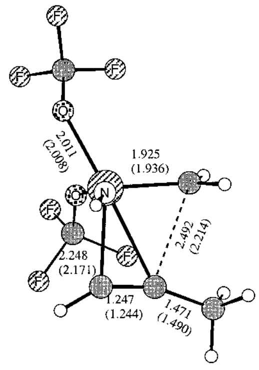
10 HF/HW3 22.4
B3LYP/HW3 8.1



11 HF/HW3 28.3
B3LYP/HW3 12.6



12 HF/HW3 11.9
B3LYP/HW3 0.1

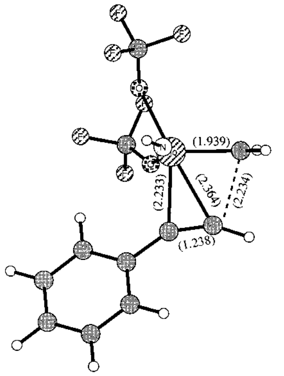


13 HF/HW3 17.7
B3LYP/HW3 4.9

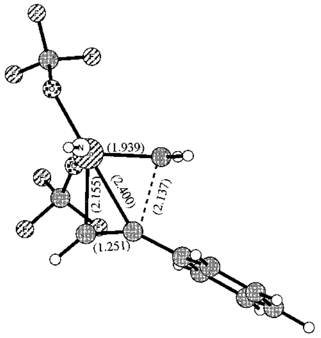
Figure 2. The calculated geometries and relative enthalpies with respect to reactants (kcal/mol) for the transition structures of α- and β-additions of HCCMe to $Mo(NH)(CH_2)(OCH_3)_2$ (**10** and **11**) and to $Mo(NH)(CH_2)(OCF_3)_2$ (**12** and **13**). Selected geometrical parameters are from the B3LYP/HW3 and HF/HW3 (in parentheses) methods.

the C_α of acetylene is most responsible for the destabilizing interaction. Therefore, it is expected that α-addition would be favored over β-addition for alkyl-substituted acetylenes. The alkyl group polarizes the π-orbital so that the C_α (note the difference from the normal nomenclature for alkynes) has a larger coefficient, as qualitatively shown in **D** and **E**. On the other hand, if a [2 + 2] scheme determines the regiochemistry, the β-addition would be favored, because it matches the charge distribution. Figure 2 shows two transition structures (**10**, **11**) of α- and β-additions of propyne to $Mo(NH)(CH_2)(OCH_3)_2$ (**1**). Compared with structure **6**, the methyl substitutent shortens the forming Mo−C and C−C bonds by about 0.06−0.08 and about 0.08−0.20 Å, respectively. The α-addition transition structure **10** is similar to the β-addition transition structure **11**. However, the axial OCH_3 group in **10** rotates in order to reduce its steric interaction with the methyl group of propyne. The calculated activation enthalpies for the α- and β-additions of propyne to $Mo(NH)(CH_2)(OCH_3)_2$ are about 8.1 and 12.6 kcal/mol, respectively, by the B3LYP/HW3 method (21.4 and 28.3 kcal/mol, respectively, by the HF/HW3).

Similar variations occur in the reactions of propyne addition to $Mo(NH)(CH_2)(OCF_3)_2$ (**12** and **13**). The calculated activation enthalpy for α-addition of propyne to $Mo(NH)(CH_2)(OCF_3)_2$ is about 11.9 kcal/mol with the HF/HW3 method and 0.1 kcal/mol with the B3LYP/HW3 method and that for β-addition is about 17.6 kcal/mol with the HF/HW3 method and 4.9 kcal/mol with the B3LYP/HW3 method.



18 HF/HW3 11.3



19 HF/HW3 16.2

Figure 3. The calculated geometries and activation enthalpies (kcal/mol) of the transition structures for HCCPh addition to $Mo(NH)(CH_2)(OCF_3)_2$ (**18**, α-addition and **19**, β-addition). Selected geometrical parameters are from the HF/HW3 (in parentheses) method.

The calculation results show that for both OCH_3- and OCF_3-substituted alkylidenes activation energy decreases when the methyl group is at the α-position, while it increases to some extent when the methyl group is at the β-position, compared to the parent acetylene case. This is in full agreement with the scenery shown in **C**−**E**. α-Addition has reduced activation energy because of reduced repulsion (smaller p lobe at C_α) while β-addition has increased repulsion (larger p lobe at C_α). On the other hand, the interaction between the π-orbital (HOMO) of alkyne with the LUMO of metal−alkylidene (d-orbital of MO) is not sensitive to the polarization of alkyne. Therefore, the regiochemistry is mainly determined by the repulsive interaction shown in **D**−**E**.

We also studied the preference of the α- and β-additions of phenylacetylene (**5**) to the catalyst model $Mo(NH)(CH_2)(OCF_3)_2$. To save CPU time, we only performed HF/3-21G and HF/HW3 calculations on these reactions (also no frequency calculation). Figure 3 shows the transition structures (**18** and **19**).

Compared with structures **12** and **13**, α-phenyl substitution elongates the forming Mo−C and C−C bonds by about 0.028 and 0.078 Å. The β-phenyl substitution shortens the Mo−C and C−C bonds by about 0.016 and 0.077 Å, respectively. Thus, β-addition has a later transition structure. A visible difference between structures **18** and **19** is the orientation of the phenyl group. In structure **18**, the phenyl group maintains conjugation with the nonreacting π-bond of acetylene, while in structure **19**, the phenyl group rotates by about 90°. This is necessary in order to avoid severe steric interaction with the alkylidene group. This rotation also minimizes the polarization of the nonreacting π-orbital but seriously destructs the conjugation between the phenyl group and acetylene. Therefore, the β-addition transition structure is still less stable. The activation energy for α-addition of phenylacetylene to $Mo(NH)(CH_2)(OCF_3)_2$ is calculated to be lower than that of β-addition by about 4.7 and 4.9 kcal/mol by the HF/3-21G and HF/HW3 methods, respectively.

C. Solvent Effect on Regiochemistry. To further test the electrostatic argument for the intrinsic preference of the α-addition, solvent effects on the stabilities of transition structures **10** and **11** were calculated both with the Onsager model[45−50] and the COSMO method.[51] As shown in Table 2, both methods give similar results. The preference for α-addition is reduced by solvent effect. More polar solvents (THF and acetonitrile) cause larger reduction in the α-addition preference. This is in accord with the concept that β-addition is destabilized by electrostatic interaction, and this destabilization is reduced in a more polar solvent.

Table 2. Calculated α-Preference for Propyne Addition to $(CH_3O)_2Mo(NH)(CH_2)$ with the B3LYP/HW3 Method in the Gas Phase and Solution

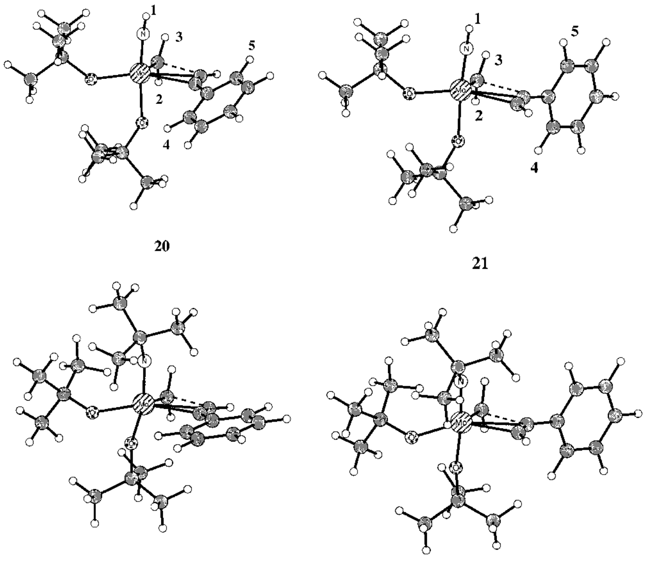
	$\Delta E^{\neq}_{\beta} - \Delta E^{\neq}_{\alpha}$	
	Onsager model	COSMO model
gas phase	4.6	4.6
toluene	3.9	3.2
THF	3.2	2.2
acetonitrile	2.8	1.6

For the polymerization of 1,6-heptadiyne derivatives, Schrock et al. noted that solvent plays a critical role in determining the rate of cyclization to give five- or six-membered rings.[18] For the polymerization of *o*-TMSPA, they also observed that the PDI value of poly(*o*-TMSPA) in toluene is smaller than that in THF.[24] This suggests that a less polar medium facilitates α-addition.

D. The Effect of Bulky Ligands on the Preferences of α- and *β*-Additions. The above model catalysts lack bulky ligands. It has been observed from experiments that the steric bulkiness of the ligands can have a key role in determining the fashion of alkyne polymerization.[24] Indeed, Schrock has realized that α-addition of terminal alkyne polymerization could be favored if a metal−alkylidene with relatively "small" alkoxyl ligands is used.[18,24] To ensure a *β*-addition, "larger" alkoxyl ligands are necessary. Thus, polymerization of 1,6-heptadiynes such as diethyldipropargyl malonate cyclopolymerizes to give mixed five-membered and six-membered ring compounds with initiators of the type $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCH(CF_3)_2]_2$ and homo six-membered ring compounds with initiators of type $Mo(CH\text{-}t\text{-}Bu)(NAr)[CO_2(CPh_3)]_2$.[18] Schrock et al. have also observed that the bulkiness of the alkyne substituent influences the regiochemistry of polymerization.[24] In this regard, they investigated the reactions between alkylidene and some ortho-substituted phenylacetylens $R^1C_6H_4C{\equiv}CH$ (R^1 = H, Me, *i*-Pr, *t*-Bu). They found that phenylacetylenes containing progressively larger ortho substituents react with alkylidene to give progressively more α-addition in the first insertion reaction.[24]

While the calculation result of significant preference for the α-addition of propyne and phenylacetylene with the model catalysts $Mo(NH)(CH_2)(OCX_3)_2$ (X = H, F) are in agreement with Schrock's observations, we would also like to gain a qualitative understanding of the effect of ligand bulkiness and alkyne bulkiness on the regiochemistry of alkyne polymerization. Thus, a series of model calculations have been carried out. All these calculations were performed with replacement of the imido hydrogen, the alkyl groups of the alkoxyl ligands, and one of the alkylidene hydrogens by a *t*-Bu group. Only the *t*-Bu groups and the phenyl substituent of the alkyne were optimized with the PM3 method, while the other atoms were constrained at the geometry of structure **18**.

To test the feasibility of the method, we first studied the preference of the α- and *β*-additions of phenylacetylene to catalyst model $Mo(NH)(CH_2)(O\text{-}t\text{-}Bu)_2$ with the HF/3-21G method, which predicts a regiochemistry similar to that calculated by higher levels for the reaction of phenylacetylene with catalyst model $Mo(NH)(CH_2)(OCF_3)_2$. Two transition structures (**20** and **21**) were obtained, as shown in Figure 4. Compared to the structures **18** and **19**, it is clear that replacement of the OCF_3 groups by O-*t*-Bu groups causes little geometrical change except that the two O-*t*-Bu groups bend apart from each other due to severe steric interactions between them. Structure **20** is calculated to be more stable than **21** by about 4.2 kcal/mol. Thus, the preference for α-addition is essentially not changed by the bulky alkoxyl groups alone.



20 **21** **22** **23**

Figure 4. Calculated geometries (HF/3-21G) of the transition structures for phenylacetylene addition to $Mo(NH)(CH_2)(O\text{-}t\text{-}Bu)_2$ (**20**, α-addition, and **19**, *β*-addition). Numbers 1−5 stand for t-Bu substitution positions (see Table 3) for PM3 transition structure modeling. Structures **22** (α-addition) and **23** (*β*-addition) have *t*-Bu substitution at position 1.

Table 3. The Substitution Patterns and the Corresponding Relative Energies for *t*-Bu-Substituted Phenylacetylene Addition to Molybdenum Alkylidene, $Mo(N{-}H)(O\text{-}t\text{-}Bu)_2CH_2$

entry	*tert*-butyl substitution position	α-addition	*β*-addition
1	none	0.0	2.9
2	1	0.0	−1.5
3	1, 2	0.0	3.0
4	1, 3	2.6	6.6
5	1, 2, 5	0.0	3.8
6	1, 3, 4		9.8
7	1, 3, 5	1.8	

When the PM3 calculations were carried out for the above two structures, a preference of about 3 kcal/mol for the α-addition was produced. This indicates that the PM3 calculation gives qualitatively correct regiochemistry.

When a *t*-Bu group is introduced to the imido group, a conformational change is introduced. As shown in structure **22**, the two *tert*-butoxyl groups have to rotate in order to avoid severe steric interaction with the imido *t*-Bu group. As a result, the α-addition transition structure is destabilized by the steric interaction between the phenyl group and the axial *tert*-butoxyl group. On the other hand, this geometrical change does not cause destabilization to the *β*-addition transition structure because the phenyl group is too far away. Therefore, the *β*-addition becomes somewhat favored (Table 3, entry 2).

Table 3 summarizes the calculation results on the preference of α- and *β*-additions with *tert*-butyl group substitution at various positions (refer to structures **20** and **21** for substitution

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positions). A *tert*-butyl group at the alkylidene center (entries 3 and 4) causes a significant destabilization to the β-addition transition structure. Thus, α-addition becomes favored. This result is expected, because the phenyl group in the β-addition transition structure is quite close to the *tert*-butyl group. When a *tert*-butyl group is introduced to the ortho position of the phenyl group, position 4 of the α-addition can be ruled out because it has severe steric interaction with the axial O-*t*-Bu group. For β-addition, the ortho *t*-Bu should avoid being on the same side as the alkylidene *t*-Bu group. Comparing entries 3 and 5, it is clear that the ortho *t*-Bu group disfavors β-addition, in agreement with Schrock's experimental observation.[18]

It should be noted that the above PM3 calculations have only qualitative value. A more detailed study is needed for a full understanding of the experimentally observed stereochemistry of alkyne polymerization.

E. Summary. We have studied transition structures and the regiochemistry of alkyne addition to metathesis catalyst models $Mo(NH)(CH_2)(OR')_2$ ($R' = CH_3$, CF_3) by ab initio and density functional theory calculations. The main results can be summarized as follows:

(1) The transition structure for alkyne addition to molybdenum–alkylidene is characterized with nucleophilic addition of the alkyne to the metal center with little formation of the C···C bond. Thus, in agreement with experimental observation, the catalytic activity of metal–alkylidenes is significantly increased by electron-withdrawing alkoxyl ligands.

(2) The calculated activation enthalpies for the addition of acetylene to $Mo(NH)(CH_2)(OR')_2$ are somewhat higher than those for the addition of ethylene. However, the former reaction is much more exothermic.

(3) The molybdacyclobutene formed by the addition of alkyne always has a square-pyramidal geometry, independent of whether the alkoxyl ligand of the molybdenum–alkylidene is electron-donating or electron-withdrawing. A trigonal-bipyramidal geometry is much higher in energy and is not a local minimum. This differs from molybdacyclobutane, which favors a square-pyramidal geometry with an electron-donating alkoxyl ligand but a trigonal-bipyramidal geometry with electron-withdrawing alkoxyl ligands.

(4) The calculated activation enthalpies for α- and β-additions of $HC{\equiv}CMe$ and $HC{\equiv}CPh$ to $Mo(NH)(CH_2)(OR')_2$ are higher and lower than that of parent acetylene addition, respectively, resulting in a considerable preference for α-addition over β-addition. This preference for α-addition is reduced by polar solvents.

(5) The above features (2–4) can be explained by a repulsive interaction between one of the lone pairs on the imido nitrogen with the nonreacting π-orbital of alkyne in a trigonal-bipyramidal transition structure or metallacyclobutene product. The repulsive interaction is reduced in the α-addition transition structure but is increased in the β-addition transition structure. A polar solvent reduces the preference for α-addition.

(6) α-Addition is disfavored by large alkoxyl ligands, while β-addition is disfavored by large alkylidene substituents, as observed experimentally.

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Supporting Information Available: Tables of calculated total energies for **1**–**21** and Cartesian coordinates for **6**–**13** and **18**–**23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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