

Theoretical Studies on Alkene Addition to Molybdenum Alkylidenes

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Abstract: The addition of ethene to Mo(NH)(CHR)(OR')₂ (R = H, Me; R' = CH₃, CF₃) has been studied with both *ab initio* molecular orbital and density functional theory calculations. Geometry optimizations were carried out with the HF/3-21G, HF/HW3, and B3LYP/HW3 methods. The energies were further evaluated with the MP2/HW3 and B3LYP/HWF (HWF basis set is equivalent to the 6-311G** basis set) methods. Ethene significantly favors attacking on the CNO face. The attack on the COO face by ethene is disfavored by 12.3 and 18.8 kcal/mol for R' = CH₃ and CF₃, respectively. The transition structure for the CNO face addition is in a distorted trigonal bipyramidal geometry, with the NH and one of the OR' groups axial. The calculated activation energy is low for R' = CH₃, and it is significantly lower for R' = CF₃. In agreement with the experiment, the syn alkylidene is calculated to be more stable than the anti rotamer (R = CH₃). This is apparently due to the stabilizing agostic interaction involving the anti-H of the syn rotamer on the COO face. However, the transition structures derived from the syn and anti rotamers have similar stabilities, due to the disappearance of the agostic interaction. Thus, the anti alkylidene is effectively a more reactive catalyst than the syn alkylidene. The molybdacyclobutane product significantly favors a square pyramidal geometry when R' = CH₃, but has a slight preference for a trigonal bipyramidal geometry when R' = CF₃.

Introduction

Olefin metathesis reactions play important roles both in industry and in the laboratory.^{1–4} Olefin metathesis polymerizations, now including ring-opening metathesis polymerization (ROMP),⁵ alkyne polymerization,⁶ and acyclic diene metathesis polymerization (ADMET),⁷ continue to be the focus of interest. Olefin metathesis reactions provide powerful methods for C–C bond formation. For example, ring-closing metathesis (RCM) has become a useful strategy for ring formation in organic synthesis in recent years.⁸

In the last decade, several d⁰ transition-metal alkylidene complexes with well-defined structures and reactivities have been synthesized^{9–13} and have served as initiators for ring-opening metathesis polymerizations (ROMP). Some of the most successful initiators are tungsten and molybdenum imido alkylidene complexes.^{10,11,14} These initiators catalyze polym-

erization of a variety of cyclic olefins, often in a living fashion, and high stereospecificity and tacticity for the outcoming polymer can be achieved.^{15–20} For example, when **A** is used

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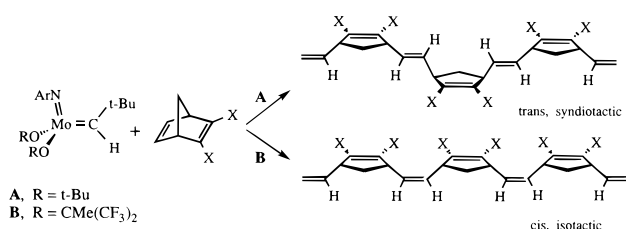
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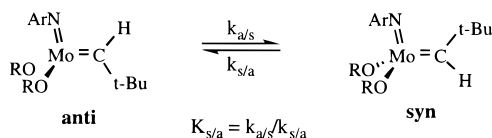
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as the catalyst and norbornadienes are the monomers, the polymers are highly trans, and highly syndiotactic.¹⁷ Cis polymers with high isotacticity are obtained if **B** is used as the catalyst.¹⁸



Understanding the mechanism and stereochemistry of the olefin metathesis reactions is the subject of interdisciplinary research.^{21–31} Schrock *et al.* have found that the reactivity of Mo-alkylidenes toward olefins is strongly influenced by the alkoxide ligands.^{14b,c} Reactivity is low when R' is electron donating, such as R' = *t*-Bu (**A**), and high when R' is electron withdrawing, such as R' = CMe(CF₃)₂ (**B**). Schrock *et al.* suggested that the syn/anti isomerization of Mo-alkylidene is critical to the observed stereochemistry.^{22,23} It has been found that in most cases syn alkylidene is much more stable than anti ($K_{s/a} > 10^3$). The syn/anti isomerization is relatively slow ($k_{s/a} = 10^{-5} \text{ s}^{-1}$ at 25 °C) for **A**, but it is significantly faster ($k_{s/a} = 1 \text{ s}^{-1}$ at 25 °C) for **B**.²² Kinetic study with **B** as the catalyst indicates that for the formation of a metallacyclobutane intermediate by olefin addition to the M=C bond (in a 2 + 2 fashion),²¹ the anti catalyst is much more reactive than the syn catalyst—reaction is at least 100 times more rapid.²² When **A** is used as the catalyst, the polymerization reaction is slow, and the syn/anti isomerization is faster. Thus, trans polymers are obtained, because the anti catalyst is more reactive. On the other hand, when **B** is used as the catalyst, the polymerization is faster than the syn/anti isomerization. Therefore, the syn catalyst is the active form and cis polymers are obtained.^{15b,22,23}



An important mechanistic aspect is the method of olefin addition to these four-coordinate pseudotetrahedral catalysts.

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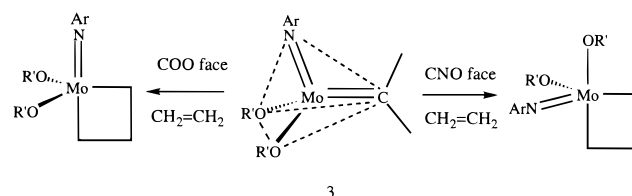
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Scheme 1



Two faces of addition are possible.^{15b} One is the “CNO” face and the other is the “COO” face if the alkylidene rotates by 90° before or during the process of olefin addition (Scheme 1). According to the structure of the base adduct of these catalysts²⁴ and other related reactions,²⁵ Schrock *et al.* proposed that attack on the CNO face is most favorable,^{10c,17} which yields an initial trigonal bipyramidal (TBP) metallacyclobutane complex in which the ring spans axial and equatorial sites with the nitrogen and one of the alkoxides taking the other two equatorial positions (Scheme 1). The initial metallacyclobutane complex can rearrange by a Berry-type pseudorotation to a square-pyramidal (SP) structure or other TBP structures. Several SP and TBP metallacyclobutanes have been isolated and characterized.²⁶

There have been several theoretical studies of olefin metathesis reactions and the electronic structures of these molybdenum and tungsten catalysts.^{27–31} Rappé and Goddard studied the catalytic cycle of olefin metathesis by the Cr, Mo, and W oxoalkylidene complexes.²⁸ Cundari and Gordon studied systematically the structures of metal alkylidene complexes, including Mo and W alkylidenes.^{29a,b} Schrock *et al.* analyzed the electronic structure of Mo alkylidene complexes and examined reactive intermediates in an effort to understand the insight of the reaction process.³⁰ Ziegler *et al.* recently reported a study on molybdacyclobutanes and their role in olefin metathesis by density functional theory.³¹ They analyzed the two geometries (SP vs TBP) of the molybdacyclobutanes and the reaction profile of ethene addition to a model catalyst Mo(O)(CH₂)Cl₂ and concluded that electron-withdrawing ligands lead to the formation of a TBP intermediate while electron-donating ligands result in the formation of a SP intermediate. But no actual transition structure was located in their study.

In this paper, we report our *ab initio* and density functional theory studies on ethene addition to the molybdenum alkylidene complexes Mo(NH)(CHR)(OR')₂ (R = H, CH₃; R' = CH₃, CF₃). The purposes of our study are (1) to find the influence of the electronic properties of the alkoxide ligands on the barrier to alkylidene rotation and the reactivity of the catalysts, (2) to evaluate the preference of the CNO and COO attacks by locating their transition structures, (3) to explore the relative stabilities of the syn and anti rotamers of the catalyst and their relative reactivities to olefin, and (4) to find the relative stabilities of the TBP and SP metallacyclobutane intermediates with different alkoxide ligands.

Calculation Methods

All calculations were carried out with the GAUSSIAN 94 program.³² The geometries were optimized first with the closed-shell Hartree–Fock method and the all-electron 3-21G basis set.³³ Harmonic vibration

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Table 1. Calculated Changes of Energies (ΔE , kcal/mol), Thermal Energies ($\Delta\Delta H^\circ_{298}$, kcal/mol), and Entropies (ΔS°_{298} , cal/(mol·K)) of the Metathesis Reactions of Mo Alkylidenes

entry	reaction	HF/3-21G			ΔE			
		ΔE	$\Delta\Delta H^\circ_{298}$	ΔS°_{298}	HF/HW3	MP2/HW3	B3LYP/HW3	B3LYP/HWF
1	1 \rightarrow 3	15.9	-0.3	-0.1	14.4	11.3	9.6	10.4
2	1 + C ₂ H ₄ \rightarrow 9	10.9	2.6	-46.6	14.8	-6.8	3.2	4.8
3	1 + C ₂ H ₄ \rightarrow 11	24.5	1.7	-46.0	28.3	13.6	15.5	18.0
4	1 + C ₂ H ₄ \rightarrow 17	-16.4	4.1	-40.7	-11.9	-23.9	-18.1	-15.4
5	1 + C ₂ H ₄ \rightarrow 18	3.1	4.4	-43.6	4.4	-21.6	-8.6	-6.3
6	2 \rightarrow 4	28.0	-1.1	-2.8	24.7	18.2	18.1	18.8
7	2 + C ₂ H ₄ \rightarrow 10	-3.2	3.4	-51.7	5.3	-21.1	-3.1	-2.6
8	2 + C ₂ H ₄ \rightarrow 12	19.5	0.9	-46.5	25.6	14.0	17.3	18.7
9	2 + C ₂ H ₄ \rightarrow 19	-16.6	4.6	-49.4	-9.6	-25.0	-16.9	-14.3
10	2 + C ₂ H ₄ \rightarrow 20	-6.9	4.7	-51.4	-2.3	-35.4	-15.2	-14.9
11	5 \rightarrow 6	0.7	0.2	1.5	1.5	2.0	2.0	2.1
12	5 + C ₂ H ₄ \rightarrow 13	11.0	2.7	-47.7	14.9	-10.7	2.7	4.0
13	6 + C ₂ H ₄ \rightarrow 14	9.6	2.7	-50.0	13.8	-12.4	1.0	2.2
14	7 \rightarrow 8	-0.6	0.2	0.0	1.5	4.0	2.2	1.9
15	7 + C ₂ H ₄ \rightarrow 15	1.2	3.7	-53.3	7.6	-29.6	-4.3	-3.3
16	8 + C ₂ H ₄ \rightarrow 16	1.9	3.7	-54.1	7.1	-32.6	-5.9	-4.4

frequencies were calculated for each structure to confirm a minimum or transition state (one imaginary vibrational frequency), 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,³⁴ which was constructed by the contraction scheme [3311/2111/311] + ECP³⁵ on a 28-electron core for the molybdenum atom and the 6-31G* basis set for the other atoms. The energy for each structure was further calculated by the MP2/HW3 method on the HF/HW3 geometries. Density functional theory calculations were also carried out by using the B3LYP nonlocal density functional approximation, which uses Becke's 3-parameter nonlocal exchange function³⁶ and the Lee–Yang–Parr nonlocal correlation functional.³⁷ Similar methods have been shown to give quite good results for many systems, including transition structures.³⁸ Geometry optimizations were carried out with the HW3 basis set. Then the energy of each structure was further calculated by the same method, but with a larger basis set, which adds a set of f-polarization functions to the HW3 for the molybdenum atom³⁹ and the 6-311G** basis set for the other atoms. This basis set is referred to as HWF in this paper.

Results and Discussion

The calculated total energies, thermal energies, and entropies of the reactants, transition structures, and products involved in the reactions are given in Table 1 of the Supporting Information. Table 1 gives the calculated reaction or activation energies, thermal energy ($T = 298$ K) corrections, and entropies of the reactions.

A. Alkylidene Rotational Barrier. Figure 1 shows the geometries of the molybdenum alkylidenes (**1** and **2**) and the transition structures (**3** and **4**) for Mo=C bond rotation of the two alkylidenes. The selected geometrical parameters from the B3LYP/HW3 and HF/HW3 (in parentheses) methods are also

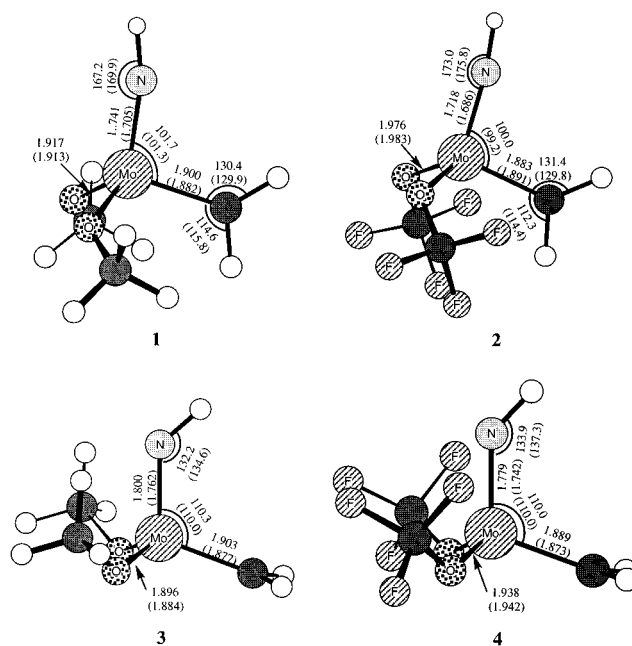


Figure 1. Calculated structures of coplanar Mo(NH)(CH₂)(OCH₃)₂ (**1**) and Mo(NH)(CH₂)(OCF₃)₂ (**2**) and perpendicular Mo(NH)(CH₂)(OCH₃)₂ (**3**) and Mo(NH)(CH₂)(OCF₃)₂ (**4**). Selected geometrical parameters from the B3LYP/HW3 and HF/HW3 (in parentheses) methods are given.

given in Figure 1. (The HF/3-21G geometries are very similar to those from the HF/HW3 method and are not discussed.)

The calculated bond lengths and bond angles of **1** and **2** are in excellent agreement with experimental¹⁷ and previous calculation results on similar compounds.^{29a,b,31} The B3LYP and HF results are also very similar, with the B3LYP bond lengths being slightly longer than the HF values for most of the bonds. The two Mo–N–H angles are about 170°, indicating that the Mo–N has the character of a triple bond; the two Mo–C–H angles are about 130° and 114°, respectively, with the one involving the anti-H atom being much smaller. The angle difference becomes even larger when the syn-H is replaced by a methyl group (see Figure 2). This may indicate that there exists an agostic interaction between the Mo and the anti C–H bond.^{40,41} As expected, R' = CF₃, which reduces the π -donating

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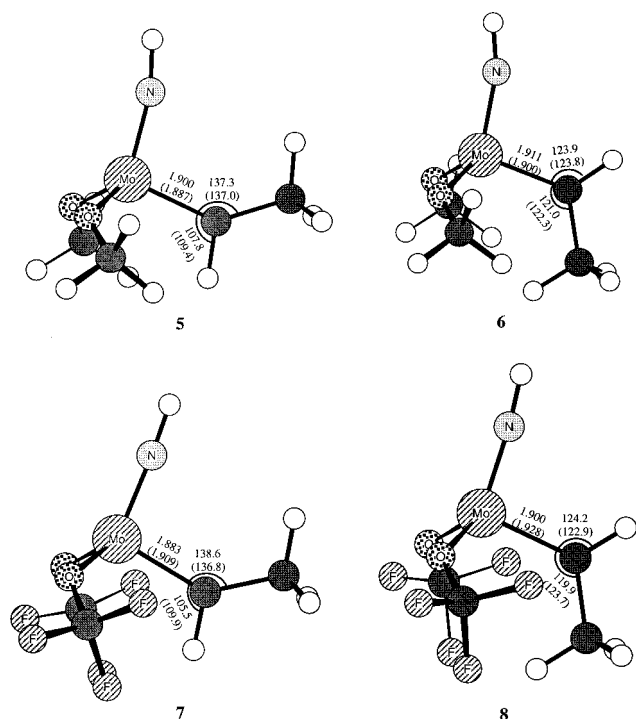


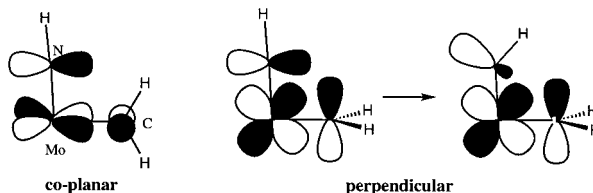
Figure 2. Calculated structures of syn (**5**) and anti (**6**) rotamers of Mo(NH)(CHMe)(OCH₃)₂ and syn (**7**) and anti (**8**) rotamers of Mo(NH)(CHMe)(OCF₃)₂ with selected geometrical parameters from the B3LYP/HW3 and HF/HW3 methods (in parentheses).

ability of the oxygen atom, increases the Mo–O bond length by about 0.06 Å, but reduces the Mo=C and Mo–N bond lengths by about 0.02 Å.

In transition structures **3** and **4**, the Mo=CH₂ plane is nearly perpendicular to the Mo=N bond. Some geometrical changes as a consequence of the M=C rotation are apparent: (1) While the M=C bond length is little changed, the bond length of Mo–N is lengthened by about 0.06 Å and the Mo–O bonds are shortened by 0.02–0.04 Å. (2) The Mo–N–H angle changes from nearly linear to significantly bent with values of 133–134° from the B3LYP calculations. (3) The orientation of the O–CH₃ and O–CF₃ groups changes from gauche with respect to the Mo=C bond to anti. These geometrical features have also been found in Cundari's studies for similar compounds,^{29b} and they attributed the changes to the competition between the multiply-bonded ligands for the dπ AOs (the t₂ set in these pseudotetrahedral complexes). Since the metal is formally d⁰, the orientation of the π-bonding ligands will be such as to maximize the dπ–π bonding.

The calculated barrier to the Mo=CH₂ bond rotation (see Table 1, entries 1 and 6) does not change very much at the MP2 and B3LYP levels; however, it is considerably higher at the HF level. For complex **1**, the calculated barrier (with HF/3-21G thermal energy correction) of 11.0 kcal/mol with the MP2/HW3 method and 10.1 kcal/mol with the B3LYP/HW3 method is somewhat lower than the value of 13.0 kcal/mol for Mo(NH)(CH₂)(OH)₂ calculated by Cundari with the MP2 method.^{29b} A barrier of about 13 kcal/mol is reported by Schrock *et al.* for the anti to syn isomerization of Mo(NAr)(CHCMe₂Ph)(OCMe₃)₂.²² The calculated barrier for complex **2** is about 17 kcal/mol (with the HF/3-21G thermal energy

Scheme 2



correction), thus, electron-withdrawing R' = CF₃ groups increase the barrier to Mo=CH₂ rotation, in agreement with the experimental observation that electron-withdrawing alkoxy groups increase significantly the barrier to alkylidene anti/syn isomerization.²²

The effect of the electron-withdrawing group on the Mo=C rotational barrier can be understood on the basis of the π-type orbital interactions. The π-donating abilities of the ligands are CH₂ > NH > OCH₃ > OCF₃. As analyzed by Cundari *et al.*,^{29b} in the coplanar structures (**1** and **2**), each nitrogen lone pair can overlap with one of the molybdenum t₂ d orbitals (not shown), but have no overlap with the d orbital that forms π-bonding with the carbene (CH₂). In the perpendicular structures, however, one of the nitrogen lone pairs has to compete with the carbene for π-bonding, resulting in less effective π-bonding (Scheme 2). In addition, electrostatic interaction between the nitrogen and the carbene p orbital is introduced in the perpendicular structures, and bending of the Mo–N–H toward the carbene carbon reduces the electrostatic repulsion, but further weakens the π-bonding involving the nitrogen. The loss in π-bonding involving the nitrogen in the perpendicular structures can be partially compensated by the gain in π-bonding involving the oxygen lone pairs, as indicated by the shortening of the Mo–O bonds. The OCF₃ group gives a higher barrier to Mo=C bond rotation because it is a much weaker π-donor than the OCH₃ group.

B. Alkylidene Syn/Anti Preference. Figure 2 shows the calculated structures of syn (**5**) and anti (**6**) rotamers of Mo(NH)(CHMe)(OCH₃)₂ and syn (**7**) and anti (**8**) rotamers of Mo(NH)(CHMe)(OCF₃)₂. The Mo=C bond lengths of both syn rotamers (**5**, **7**) are almost the same as those in the alkylidenes without the methyl substituent (**1**, **3**), but in the anti rotamers (**6**, **8**), Mo=C bond lengths are lengthened by about 0.01 and 0.02 Å with the HF and B3LYP methods, respectively. The Mo–C–C angle is about 137° and the Mo–C–H angle is about 106–108° in the syn rotamers, quite close to those observed in the X-ray crystal structures of molybdenum alkylidenes.¹⁷ On the other hand, the Mo–C–H and the Mo–C–C angles in the anti rotamers (**6**, **8**) are about 124° and 120°, respectively, which indicates the loss of agostic interaction.^{40,41} This is also reflected in the calculated relative energies: structure **6** is less stable than **5** by about 2.0 kcal/mol with both the MP2/HW3 and B3LYP/HWF methods (see Table 1, entry 11), while structure **8** is less stable than **7** by about 3.9 kcal/mol with the MP2/HW3 method and 1.9 kcal/mol with the B3LYP/HWF method (see Table 1, entry 14). This is in agreement with the experimental result of *K*_{eq} of about 10³.^{22,42}

C. Transition Structure of Ethene Addition to the CNO Face of the Catalyst. Figure 3 shows the transition structures of the ethene addition to the CNO face of Mo(NH)(CH₂)(OCH₃)₂ (**9**) and Mo(NH)(CH₂)(OCF₃)₂ (**10**) with the top view and side view being presented.

The structures **9** and **10** are very similar with both the HF and B3LYP methods. The general features of these transition

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(42) Experimental *K*_{eq} values were measured based on neophylidenes or neopentylidenes. Our calculations on neopentylidenes give preferences of over 3 kcal/mol for the syn rotamers over anti rotamers. Peng, Z.-H.; Wu, Y.-D. unpublished results.

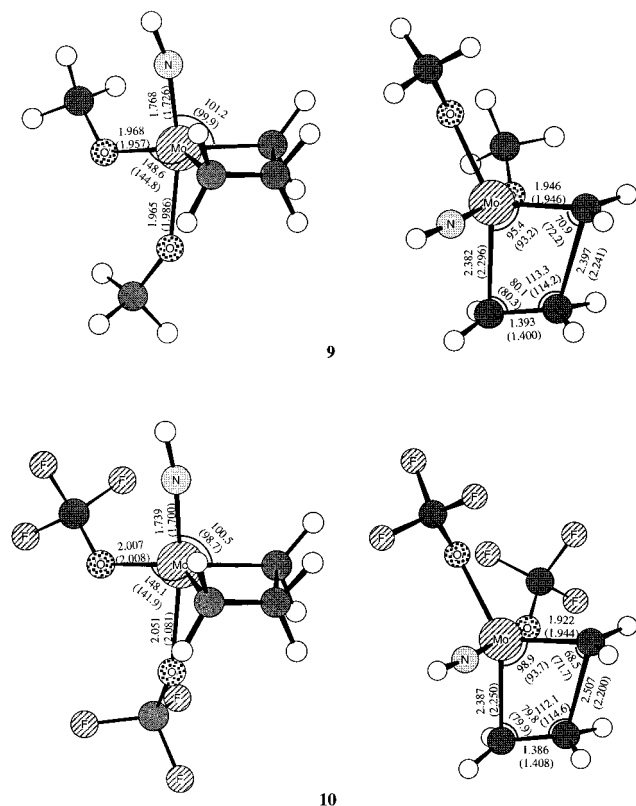


Figure 3. Calculated transition structures of cycloaddition reaction of C_2H_4 with $Mo(NH)(CH_2)(OCH_3)_2$ (**9**) and $Mo(NH)(CH_2)(OCF_3)_2$ (**10**) (left: side view; right: top view) with selected geometrical parameters from the B3LYP/HW3 and HF/HW3 (in parentheses) methods.

structures are different from those previously proposed. Both structures (**9** and **10**) are in a pseudo-TBP geometry with the NH and one of the OR' groups taking the axial positions, and the ring is formed in the equatorial plane, just like the structures of the TBP tungstacyclobutane intermediates which have been determined by X-ray crystal structure analysis.²⁶ While a TBP transition structure is generally accepted, Schrock *et al.* proposed^{10c,17} that one of the OR' groups and one of the M–C bonds take the axial positions which will give an initial “axial/equatorial” metallacycle. Ziegler *et al.*³¹ studied the reaction profile of the ethene addition to $Mo(O)(CH_2)Cl_2$ by varying the reaction coordinate $R_{(Mo-C)}$ in several steps from the reactant to the product, and proposed a very early TBP transition structure with one of the chlorine ligands and the forming Mo–C bond taking the axial positions, whereas the oxygen, the other chlorine, and the carbene carbon lie in the equatorial plane. This structure is similar to that proposed by Schrock *et al.*

In structures **9** and **10**, there is a significant Mo–C bond formation. The forming Mo–C bond lengths are about 2.38 Å with the B3LYP method, only about 0.3 Å longer than the Mo–C bond in the TBP structure of metallacyclobutanes (Figure 7). On the other hand, the Mo–C (alkylidene) bond is only slightly elongated in the transition structures. We are able to locate a weakly bound Mo–alkene complex for both systems, which is converted into the transition structure by the slippery mechanism as proposed by Grubbs.⁴³ However, the cyclobutane rings are formed asynchronously, that is, the formation of the C–C bond in the cyclobutane lags behind the Mo–C formation. Thus, the C–C distances are about 0.8–0.9 Å longer than those in the metallacyclobutane products. Although there is pyramidalization at the two olefin carbon centers, the carbene carbon

centers are still nearly planar in transition structures **9** and **10**. The C–Mo–C angles are 93–95°, about 10° larger than those in the products. The electron-withdrawing properties of the alkoxide ligands have little effect on the the geometry of the transition structure.

The calculated activation enthalpy with **9** is about –4.2 kcal from MP2/HW3 and 7.4 kcal/mol from B3LYP/HWF with respect to separated reactants (with HF/3-21G thermal energy correction, see Table 1, entry 2), which agrees with the general trend found by experiments that olefin metathesis reactions have low activation energies.² Bazan *et al.* reported an activation enthalpy of 6.6 kcal/mol for the reaction of $W(NAr)(CH-t-Bu)(O-t-Bu)_2$ with norbornadiene.¹⁸ Thus, the B3LYP/HW3 method gives quite similar activation energy to experimental observation. The electron-withdrawing alkoxide (OCF_3) lowers the activation energy further. Thus the calculated activation enthalpy for **10** is –17.7 kcal/mol with the MP2/HW3 method and 0.8 kcal/mol with the B3LYP/HWF method (with the HF/3-21G thermal energy correction, see Table 1, entry 7). The MP2 method appears to overestimate the correlation energy in the transition structures, and gives activation energies that are too low. The B3LYP method gives more reasonable activation energy. This situation is similar to the Diels–Alder cycloaddition reaction where the MP2 method also significantly underestimates the activation energy.⁴⁴ The large difference in the calculated activation energies by the two methods is also parallel to the large difference in the calculated reaction energies by the two methods. As shown in Table 1, the MP2/HW3 reaction energies with the TBP molybdacyclobutane are much more exothermic than the B3LYP/HWF values by about 15.3 and 20.5 kcal/mol for $R' = CH_3$ and $R' = CF_3$ (entries 5 and 10), respectively. However, both methods correctly calculate the trend of reactivity, that is, the activation energy with **10** is much lower than that with **9**, in agreement with the experimental result that the catalyst with stronger electron-withdrawing alkoxide ligands is more reactive. The calculations indicate large activation entropies for these cyclization reactions (see Table 1, entries 2 and 7) because of the partial formation of two bonds in the transition structures. The experimentally observed activation entropy for the reaction of $W(NAr)(CH-t-Bu)(O-t-Bu)_2$ with norbornadiene is about 40 eu.¹⁷

In the studies of the reaction process of $Mo(O)(CH_2)Cl_2$, Ziegler *et al.*³¹ found that electron-withdrawing ligands (OCF_3) facilitate an early nucleophilic attack of an olefin carbon on the metal center, leading to the formation of a TBP metallacyclobutane, while electron-donating ligands (OCH_3) delay the nucleophilic attack and result in the formation of a SP metallacyclobutane. Our calculations indicate that there is little difference in the two transition structures and that both are in a TBP geometry. Although we also found that the SP structure of the metallacyclobutane product with OCH_3 ligands is much more stable than the TBP structure, all efforts to find a SP transition structure have failed, presumably due to a more crowding environment in a SP transition structure. Such steric interaction is reduced in the SP product as we will discuss later. Therefore, we favor the initial formation of TBP metallacyclobutane for both electron-donating and electron-withdrawing alkoxy ligands.

D. Transition Structure of Ethene Addition to the COO Face. Figure 4 shows the two “transition structures” of the ethene addition to the COO face of $Mo(NH)(CH_2)(OCH_3)_2$ (**11**) and $Mo(NH)(CH_2)(OCF_3)_2$ (**12**). These structures are located

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(43) Anslny, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, 109, 4880.

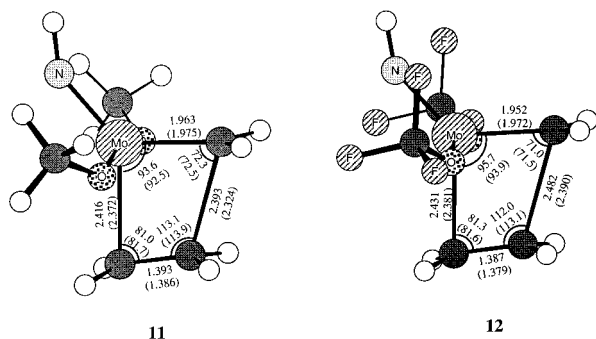


Figure 4. Calculated transition structures of C_2H_4 addition to the COO face of $Mo(NH)(CH_2)(OCH_3)_2$ (**11**) and $Mo(NH)(CH_2)(OCF_3)_2$ (**12**) with selected geometrical parameters from the B3LYP/HW3 and HF/HW3 (in parentheses) methods.

by a C_s symmetry constraint with the $Mo=CH_2$ plane perpendicular to the $Mo=N$ bond. Because the perpendicular alkylidene is the transition structure for the $Mo=C$ bond rotation, these "transition structures" both have two imaginary vibration frequencies, corresponding to the $Mo-C$ and $C-C$ bond formation and the $Mo=C$ bond rotation, respectively.

These structures differ from structures **9** and **10** in several aspects: (1) The two axial positions are occupied by the two alkoxy groups. (2) The two forming bonds, $Mo-C$ and $C-C$, are formed to less extent by about 0.1 Å than in **9** and **10**. (3) The $Mo-N-H$ angles are still significantly bent, as in structures **3** and **4**.

The calculated activation enthalpies for the ethene attack on the COO face are about 19.7 and 19.6 kcal/mol (with HF/3-21G thermal energy correction, see Table 1, entries 3 and 8) with the B3LYP/HWF method for the two Mo alkylidenes, respectively. Since all activation enthalpies are calculated with respect to the most stable planar alkylidene structures (**1** and **2**), the activation enthalpy for the ethene attack on the CNO face is about 12.3 and 18.8 kcal/mol more favorable than attack on the COO face for alkylidenes **1** and **2**, respectively. Apparently, the higher activation energy for the COO attack reflects the destabilization due to the 90° rotation of the $Mo=C$ bond in the perpendicular structures. Therefore, we conclude that olefin addition to metal alkylidene takes place on the CNO face, and it is highly unlikely that olefin attack will occur on the COO face.

E. Syn/Anti Preference in the Transition Structures of Ethene Addition to the CNO Face. Figure 5 shows the transition structures of the ethene addition to the CNO face of *syn*- $Mo(NH)(CHMe)(OCH_3)_2$ (**13**), *anti*- $Mo(NH)(CHMe)(OCH_3)_2$ (**14**), *syn*- $Mo(NH)(CHMe)(OCF_3)_2$ (**15**), and *anti*- $Mo(NH)(CHMe)(OCF_3)_2$ (**16**), respectively.

Compared with structure **9**, the methyl substituent in transition structures **13** and **14** shortens the forming $Mo-C$ and $C-C$ bonds by about 0.03–0.04 and about 0.01–0.02 Å, respectively, with both the HF/HW3 and the B3LYP/HW3 methods. A larger effect is found in transition structures **15** and **16**. Thus, compared with **10**, the forming $Mo-C$ and $C-C$ bonds are shortened by about 0.06–0.09 Å with the B3LYP method and about 0.15–0.2 Å with the HF/HW3 method.

The *syn* transition structures (**13** and **15**) are very similar to the *anti* transition structures (**14** and **16**) with almost the same forming $Mo-C$ and $C-C$ bond lengths. The calculations indicate almost the same stability for the *syn* and *anti* transition structures. This is not surprising because the differences in steric interactions are small, and the agostic interaction which is involved in the alkylidene reactant is largely absent from the transition structures. Since the *syn* alkylidene is more stable

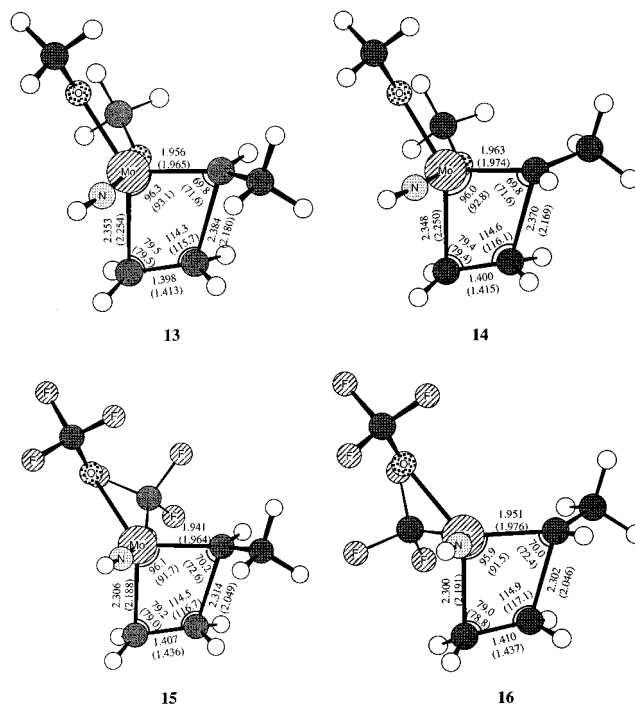


Figure 5. Calculated transition structures (top view) of cycloaddition reaction of C_2H_4 with *syn* (**13**) and *anti* (**14**) rotamers of $Mo(NH)(CHMe)(OCH_3)_2$ and *syn* (**15**) and *anti* (**16**) rotamers of $Mo(NH)(CHMe)(OCF_3)_2$ with selected geometrical parameters from the B3LYP/HW3 and HF/HW3 (in parentheses) methods.

than the *anti* alkylidene, the *anti* alkylidene is calculated to be more reactive than the *syn* alkylidene by about 1.8 kcal/mol with the B3LYP/HWF method for alkylidene with the electron-donating alkoxy (OCH_3) (see Table 1, entries 12 and 13) and by about 1.1 kcal/mol for the electron-withdrawing alkoxy (OCF_3) group (see Table 1, entries 15 and 16). This is in accord with the experimental result that the *anti* rotamer is more reactive than the *syn* rotamer. For example, Schrock *et al.* reported²² that *anti*- $Mo(NAr)(CHCMe_2)(OCMe(CF_3)_2)_2$ is at least 100 times more reactive than its *syn* rotamer at $-30^\circ C$.

The methyl substituent on the carbene carbon slightly reduces the activation energies for ethene addition (compare entry 2 with entries 12 and 13, entry 7 with entries 15 and 16). This can be attributed to the electron-donating property of the methyl group. The reaction can be considered as an electrophilic attack of the metal center to the olefin followed by a nucleophilic attack of the carbene carbon to the olefin, and the methyl group increases slightly the nucleophilicity of the carbene center.

F. Structures of the Metallacyclobutane. Figure 6 shows the calculated SP and TBP structures of $Mo(NH)(OCH_3)_2(C_3H_6)$ (**17**, **18**) and $Mo(NH)(OCF_3)_2(C_3H_6)$ (**19**, **20**). The core cyclobutane geometry is indicated on the top right of each structure.

The geometries of each structure compare favorably with the X-ray crystal structures of similar compounds²⁶ and previously calculated results of the same compounds by Ziegler *et al.*³¹ However, the relative stabilities of the two structures are quite different from those reported by Ziegler *et al.*³¹ The SP structure of $Mo(NH)(OCH_3)_2(C_3H_6)$ (**17**) is predicted to be more stable than the TBP structure (**18**) by about 9 kcal/mol with the B3LYP/HWF method and by about 12.3 kcal/mol with the MP2/HW3 method (see Table 1, entries 4 and 5), while Ziegler *et al.* found that **17** is only about 0.8 kcal/mol more stable than **18**. The relative stabilities of the SP (**19**) and TBP (**20**) structures of $Mo(NH)(OCF_3)_2(C_3H_6)$ are quite dependent on the method of calculation. While the HF method gives a significant

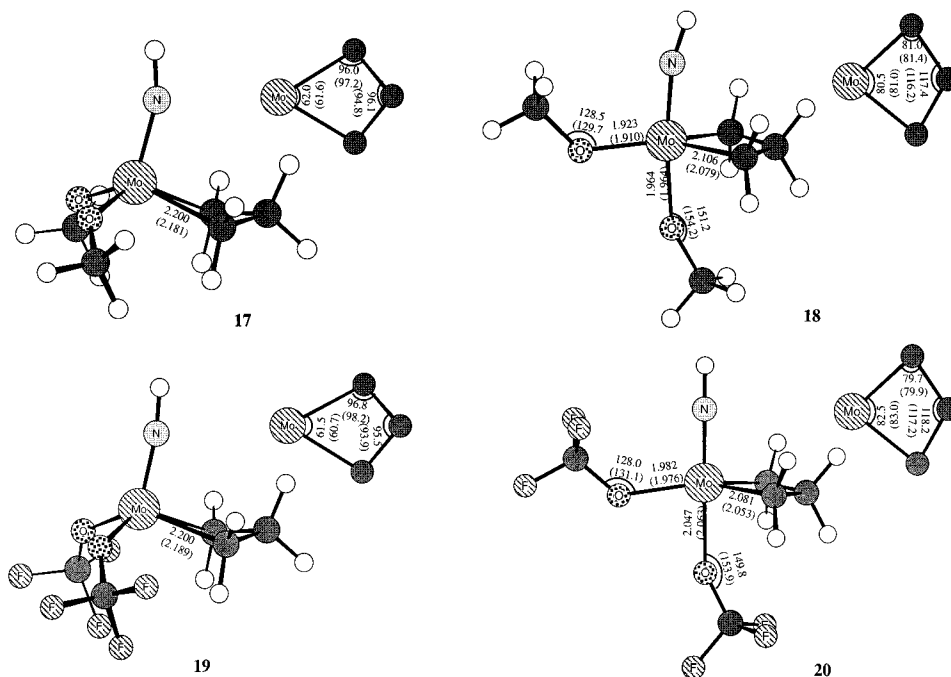


Figure 6. Calculated square pyramidal and trigonal bipyramidal structures of $\text{Mo}(\text{NH})(\text{C}_3\text{H}_6)(\text{OCH}_3)_2$ (**17**, **18**) and $\text{Mo}(\text{NH})(\text{C}_3\text{H}_6)(\text{OCF}_3)_2$ (**19**, **20**). Selected geometrical parameters are from the B3LYP/HW3 and HF/HW3 (in parentheses) methods.

preference for the SP structure, the MP2/HW3 calculation gives a 9.6 kcal/mol preference to the TBP structure. With the B3LYP method, the two structures are predicted to have similar stabilities. While the B3LYP/HW3 method gives a 1.7-kcal/mol preference to the SP structure, a 0.6-kcal/mol preference to the TBP structure is predicted with the B3LYP/HWF method. Ziegler's earlier calculations gave a 6.1-kcal/mol preference to the TBP structure.³¹ We feel that the B3LYP method gives more reliable energetics, and therefore suggest that for the electron-donating OCH_3 group, the SP structure is much more stable than the TBP structure, while for the electron-withdrawing OCF_3 group, the two structures have similar stabilities. It has been found that molybdacyclobutane has a higher preference for SP geometry than tungsten,^{11b} and this has been suggested as a factor accounting for the lower activity of molybdenum than tungsten catalysts in the metathesis of olefin. Furthermore, the substituents on the ring can also change the geometry of the metallacyclobutane.^{26b}

G. Summary. In this paper, we studied the metathesis catalysts of the type $\text{Mo}(\text{NH})(\text{CHR})(\text{OR}')_2$ ($\text{R} = \text{H}, \text{Me}$; $\text{R}' = \text{CH}_3, \text{CF}_3$) and their reactions with ethene by *ab initio* and density functional theory calculations. We found that the barrier to $\text{Mo}=\text{C}$ rotation is increased by the electron-withdrawing alkoxy ligands, in good agreement with experimental observations. The syn rotamers of the catalyst $\text{Mo}(\text{NH})(\text{CHMe})(\text{OR}')_2$ are about 2 kcal/mol more stable than the corresponding anti rotamers, and this may be due to the agostic interaction in the syn rotamer.

There is a significant preference for ethene to attack the CNO face over the COO face of the catalyst, which is 12.3 and 18.8 kcal/mol for $\text{R}' = \text{CH}_3$ and CF_3 , respectively. We conclude that the COO face attack is unlikely to happen during the addition process. The transition structure of the CNO face attack is in a distorted TBP geometry, with the NH and one of the

OR' groups being axial. There is significant $\text{Mo}-\text{C}$ and $\text{C}-\text{C}$ bond formation in the transition structures. The calculated activation enthalpy is low (about 7.4 kcal/mol) for $\text{R}' = \text{OCH}_3$ and much lower for $\text{R}' = \text{OCF}_3$ (about 0.8 kcal/mol). But there should be a large activation entropy. These are in agreement with the experimental results that such kinds of reactions are generally fast and the fact that the catalytic activity is increased significantly by the electron-withdrawing alkoxy ligands. The anti alkylidenes are found to be more reactive than the syn alkylidenes, which may be due to the disappearance of the agostic interaction in the transition structure. The methyl substituent on the carbene carbon slightly reduces the activation energy.

The SP geometry of the molybdacyclobutane is calculated to be much more stable than the TBP geometry for $\text{R}' = \text{CH}_3$, while the TBP geometry is slightly more stable than the SP structure for $\text{R}' = \text{CF}_3$. We predict that the initial product of the ethene addition is the TBP geometry of the molybdacyclobutane, with the imido and one of alkoxy groups being axial.

It is known that steric effects are important to the reactivity of these alkylidene catalysts as well as to the stability of the cycloaddition product and the stereochemistry and tacticity of the outcoming polymers. We are currently studying the steric effects and will report our results in due course.

Acknowledgment. We are grateful to the Research Grants Council of Hong Kong and the University Grants Council of Hong Kong for partial financial support.

Supporting Information Available: A listing of the calculated total energies, thermal energies, entropies, and Cartesian coordinates of structures **1**–**20** (10 pages). See any current masthead for ordering and Internet access instructions.

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