Theoretical Investigation of Alkyne Metathesis Catalyzed by W/Mo Alkylidyne Complexes

Jun Zhu, Guochen Jia,* and Zhenyang Lin*

Department of Chemistry and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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In this paper, the mechanism of alkyne metathesis catalyzed by W/Mo alkylidyne complexes has been theoretically investigated with the aid of density functional theory calculations. Calculations on various model alkylidyne complexes M(≡CMe)$(OR)_3$ (M = W, Mo; R = Me, CH_2F), W(≡CMe)$(NMe_2)_3$, and W(≡CMe)$(Cl)_3$ allow us to examine the factors that influence the reaction barriers. In the reaction mechanism, metallacyclobutadienes are initially formed from a ring-closing step between alkynes and alkylidyne complexes. A ring-opening step then gives the metathesis products. The factors that determine the metathesis reaction barriers have been examined. The reaction paths leading to the formation of Cp complexes, a possible path deactivating catalytic activity, were also studied.

Introduction

Catalytic alkene metathesis has become one of the primary tools in both organic synthesis and polymer chemistry, due to their extraordinary generality, chemoselectivity, and functional group tolerance.[1] In comparison, the analogous alkyne metathesis is relatively less developed. The situation appears to be changing, given the recent advances in the development of new alkyne metathesis catalysts.[2,3]

Several catalytic systems have been used so far for alkyne metathesis. The first effective catalytic system described in the literature consists of a heterogeneous mixture of tungsten oxide and silica that operates only at a very high temperature (ca. 200−450 °C).[4] The second active catalytic system, which was first introduced by Mortreux et al.[5] and recently improved by several other groups,[2b,6] consists of structurally not yet well-defined species formed in situ from $Mo(CO)_6$ and a phenolic additive (e.g., 4-chlorophenol). The simplicity and user-friendly nature of this catalyst system are offset somewhat by its rather limited tolerance of polar functional groups and the elevated temperature (ca. 140−150 °C) required to initiate and maintain the catalytic activity. A major breakthrough in rational catalyst design for alkyne metathesis came with the development of the well-defined and now widely used tungsten alkylidyne complexes $(RO)_3W{\equiv}CR'$ by the Schrock group.[7] Recently, the Fürstner group introduced a highly active monochloromolybdenum species which is conveniently prepared in situ by activation of the triamido complex Mo[N(t-Bu)Ar]$_3$ (Ar = 3,5-$C_6H_3Me_2$) with CH_2Cl_2 as a chlorine source.[8] Catalytically active molybdum(VI) alkylidynes Mo(≡CR)$(OAr)_3$ have been intro-

* Corresponding authors. E-mail: chjiag@ust.hk, chzlin@ust.hk.

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duced more recently by Cummins and Moore.[9,10] All these studies show that metal centers and ligands can have drastic effects on the catalytic performance. For example, W(≡C^{t}Bu)-(O^{t}Bu)$_3$ is astoundingly active for the metathesis of internal alkynes, while the corresponding Mo alkylidyne complexes Mo-(≡C^{t}Bu)(O^{t}Bu)$_3$ and the analogous W alkylidyne complexes containing amide ligands W(≡C^{t}Bu)(NR$_2$)$_3$ are almost metathesis inactive.[11,12] In addition, while Mo(≡C^{t}Bu)(O^{t}Bu)$_3$ does not react with internal alkynes and is catalytically inactive for alkyne metathesis, the analogous Mo alkylidyne complexes containing fluoroalkoxide (OC(Me)(CF$_3$)$_2$, OC(CF$_3$)$_3$) or phenoxide ligands do react with internal alkynes to give isolable metallacyclobutadiene complexes and are excellent catalysts for metathesis of alkynes.[11] For the monochloromolybdenum catalyst that was first developed by the Fürstner group and refined by the Moore group, α,α,α-trifluoro-*o*-cresol or perfluoro-*tert*-butyl alcohol or *p*-nitrophenol was sometimes added for alcoholysis to produce active species for alkyne metathesis.[10] All these observations show that the alkoxide ligands containing electron-withdrawing groups are likely to improve the activity of the catalysts for alkyne metathesis. The following questions deserve our attention. Why can W(≡C^{t}Bu)(O^{t}Bu)$_3$ catalyze the alkyne metathesis, but W(≡C^{t}Bu)(N^{t}Bu$_2$)$_3$ and Mo(≡C^{t}Bu)(O^t-Bu)$_3$ cannot? Why is Mo(≡C^{t}Bu)(O^{t}Bu)$_3$ almost metathesis inactive, whereas Mo(≡C^{t}Bu)(OR)$_3$ [OR = OC(Me)(CF$_3$)$_2$, OC-(CF$_3$)$_3$, or OAr] are excellent catalysts for alkyne metathesis? The main purpose of the project is to answer these questions by computational chemistry through studying the detailed mechanisms of alkyne metathesis. In the past, many theoretical studies on olefin metathesis have been pursued, and these studies have helped the understanding of the reaction mechanism of olefin metathesis and development of new catalysts.[13] Surprisingly, a detailed theoretical study on the alkyne metathesis has not been reported, despite the significance of alkyne methathesis. To the best of our knowledge, there was only one pioneer work done to date by the Ziegler group concerning the formation and decomposition of a metallacyclobutadiene using the model complex Mo(≡CH)Cl$_3$.[14a] The reaction profiles and the relevant transition states with the M(OR)$_3$ and M(NR$_2$)$_3$ fragments remain elusive. It is necessary to study the reactions in more detail to gain a deeper insight into the mechanisms of alkyne metathesis and to address the questions mentioned above. In this work, theoretical calculations based on the B3LYP density functional theory have been carried out to examine the structural and energetic aspects related to the possible reaction pathways. It should be pointed out here that there is another related theoretical work in the literature focusing on a metathesis-like reaction between W$_2$(OR)$_6$ (R = alkyl) and alkynes to give tungsten alkylidyne complexes.[14b]

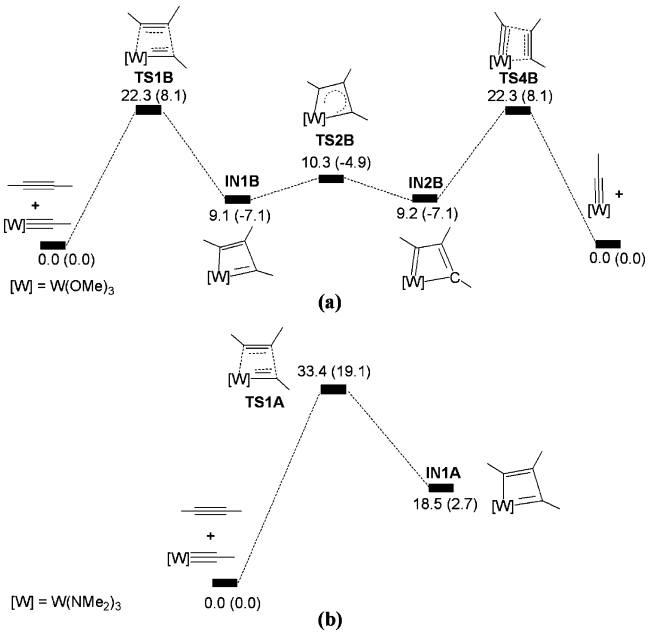

Figure 1. Energy profiles for the alkyne metathesis reactions catalyzed by W(≡CMe)R$_3$ (R = OMe (a), NMe$_2$ (b)). The free energies and relative energies (in parentheses) are given in kcal/mol.

Computational Details

Molecular geometries of all the model complexes in this work were optimized at the Becke3LYP (B3LYP) level of density functional theory.[15] Frequency calculations at the same level of theory have also been performed to confirm that all stationary points were minima (no imaginary frequency) or transition states (one imaginary frequency). Calculations of intrinsic reaction coordinates (IRC)[16] were also performed on transition states to confirm that such structures are indeed connecting two minima. The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ)[17] were used to describe W and Mo atoms, while the standard 6-31G basis set was used for C, N, F, O, and H atoms. Polarization functions were added for W (ζ(f) = 0.823) and Mo (ζ(f) = 1.043) and for O (ζ(d) = 0.8) and C (ζ(d) = 0.8) that are directly bonded to the metal centers.[18] Molecular orbitals obtained from the B3LYP calculations were plotted using the Molden 3.7 program written by Schaftenaar.[19] To examine the effect of basis sets, we also employed a larger basis set, which has SDDAll[20] for transition metals and 6-311g** for all other atoms, to perform single-point energy calculations for several selected structures. The additional calculations show that the basis set dependence is small. For example, using the smaller basis set, the relative energies of W(≡CMe)(OMe)$_3$ + MeC≡CMe, **TS1B**, **IN1B**, and **TS2B** (Figure 1a) are 0.0, 8.1, −7.1, and −4.9 kcal/mol, respectively. Using the larger basis set, the relative energies are

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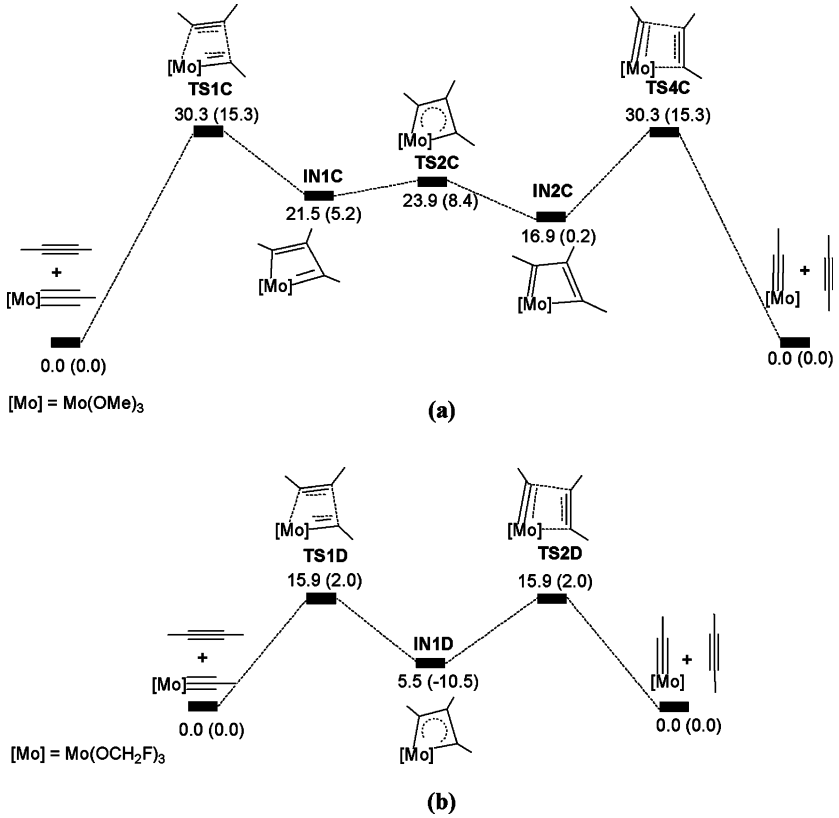


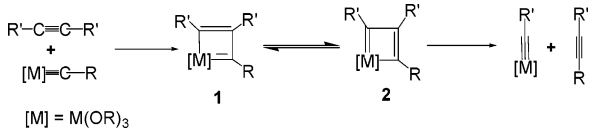
Figure 2. Energy profiles for the alkyne metathesis reactions catalyzed by Mo(≡CMe)(OR)$_3$ (R = CH_3 (a), CH_2F (b)). The free energies and relative energies (in parentheses) are given in kcal/mol.

0.0, 7.0, −7.1, and −3.2 kcal/mol, respectively. Similarly, using the smaller basis set, the relative energies of W(≡CMe)(NMe$_2$)$_3$ + MeC≡CMe, **TS1A**, and **IN1A** (Figure 1b) are 0.0, 19.1, and 2.7 kcal/mol, respectively. Using the larger basis set, the relative energies are 0.0, 18.3, and 2.8 kcal/mol, respectively. All calculations were performed with the Gaussian 03 software package.[21] The natural bond orbital (NBO) program,[22] as implemented in Gaussian 03, was also used to obtain Wiberg bond indices (bond orders),[23] which are a measure of bond strength.

Results and Discussion

It is now well accepted that alkyne metathesis catalyzed by group 6 metal alkylidyne complexes follows the mechanism shown in Scheme 1, which was initially proposed by Katz in 1975[24] and found support from the experiments carried out by Schrock et al. in the 1980s.[7] Metallacyclobutadienes (**1**) are

Scheme 1



initially formed from alkynes and alkylidyne complexes in much the same way as metallacyclobutanes formed from alkenes and metal alkylidene complexes. Through isomerization and a ring-opening step, metathesis products are formed.

Reaction Mechanisms of Alkyne Metathesis by Molybdenum and Tungsten Alkylidyne Complexes. The calculated potential energy profiles for the alkyne metathesis through the mechanism shown in Scheme 1 with the different model catalysts W(≡CMe)(OMe)$_3$, W(≡CMe)(NMe$_2$)$_3$, Mo(≡CMe)(OMe)$_3$, and Mo(≡CMe)(OCH$_2$F)$_3$ are shown in Figures 1 and 2. Selected structural parameters of the species involved in the ring-closing coupling step are illustrated in Figure 3.

In Figure 1a, the metathesis pathway starts with a ring-closing step between W(≡CMe)(OMe)$_3$ and MeC≡CMe, giving the metallacyclobutadiene intermediate **IN1B**. Along the reaction coordinate, no metal-alkyne intermediates can be located as minima on the potential energy surface, probably because the d^0 metal center cannot stabilize an alkyne complex due to lack of back-donation. The intermediate **IN1B** is then transformed to another metallacyclobutadiene intermediate **IN2B** through transition state **TS2B**. The interconversion of **IN1B** to **IN2B** has a very small barrier. The three stationary structures **IN1B**, **TS2B**, and **IN2B** have similar stability. The metallacyclobutadiene intermediates **IN1B** and **IN2B** are higher in the free energy than the reactants, W(≡CMe)(OMe)$_3$ + MeC≡CMe, by ca. 9.0 kcal/mol. We cannot overemphasize the existence of the three stationary structures (**IN1B**, **TS2B**, and **IN2B**) on the potential

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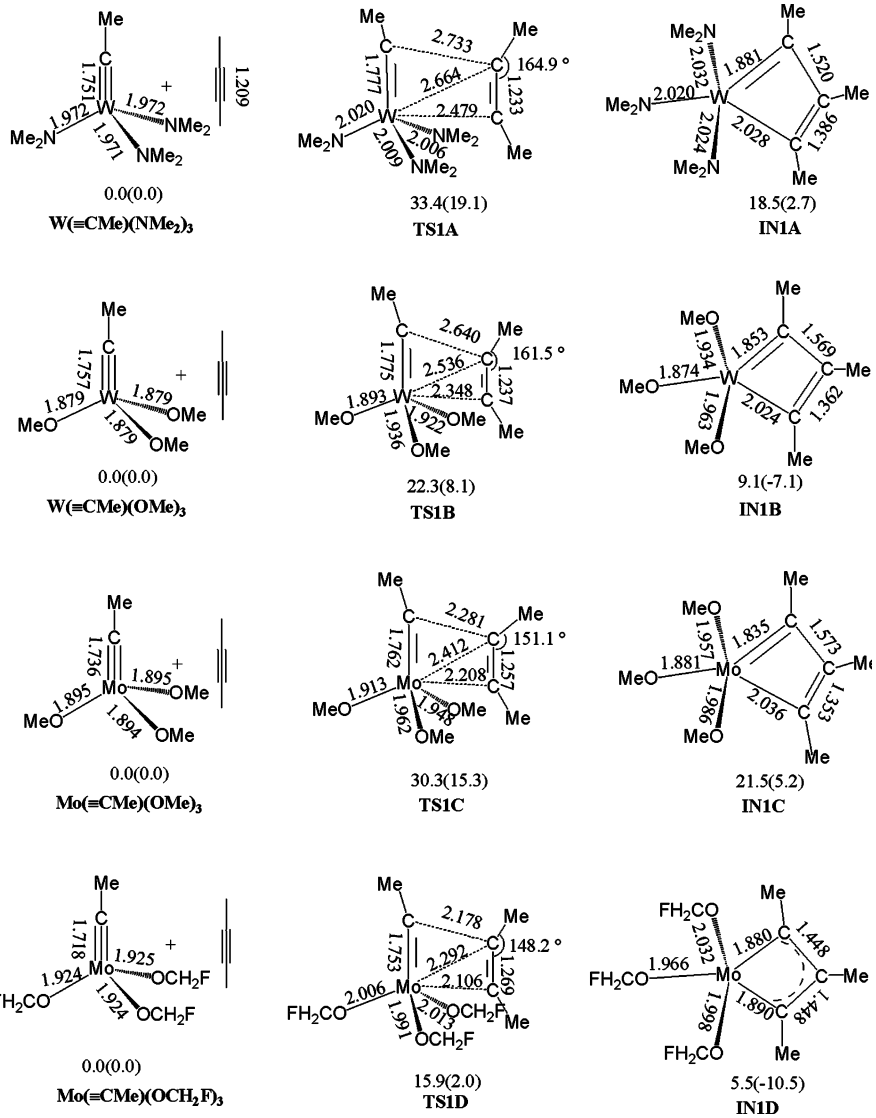

Figure 3. Selected structural parameters (Å), free energies (kcal/mol), and relative energies (kcal/mol, in parentheses) calculated for species involved in the ring-closing coupling steps catalyzed by W(≡CMe)$(OMe)_3$, W(≡CMe)$(NMe_2)_3$, W(≡CMe)Cl_3, and Mo(≡CMe)$(OR)_3$ (R = CH_3, CH_2F).

energy profile, as we shall see later that in the metathesis of Mo(≡CMe)$(OCH_2F)_3$ + MeC≡CMe (Figure 2b) we located only one intermediate in our calculations, which can be considered as an average structure of the three stationary structures. From the intermediate **IN2B**, a ring-opening step, which is the reverse step of the ring-closing step, completes the metathesis cycle.

In good agreement with the experimental observation that metathesis of alkynes catalyzed by W(≡CCMe_3)$(OCMe_3)_3$ occurs under mild conditions,[7b] a moderate free energy barrier (22.3 kcal/mol) to complete the ring-closing step with the formation of the metallacyclobutadiene **IN1B** was calculated. As mentioned in the Introduction, W(≡C^{t}Bu)$(N^tBu_2)_3$ cannot catalyze alkyne metathesis. To understand the inactivity, we also calculated the barrier of the ring-closing step for W(≡CMe)-$(NMe_2)_3$ + MeC≡CMe for comparison (Figure 1b). The geometries of the transition state and the metallacyclobutadiene intermediate are similar to those of the alkoxide analogoues. However, the barrier (33.4 kcal/mol) of the rate-determining step is significantly higher, as shown in Figure 1b, too high for alkyne metathesis to occur under mild conditions.

To probe the origin of the significant difference in the catalytic activity between the OR and NR_2 alkylidyne complexes, an energy-decomposition analysis of the reaction barriers, shown in Scheme 2, was carried out.[25] The deformation of tungsten alkylidyne complexes and alkyne leads to destablilization, while the binding of alkyne to the deformed metal complexes leads to stablization of the transition states. Scheme 2 shows that for the tungsten NR_2 and OR alkylidyne systems there is not much difference between the two tungsten alkylidyne deformation energies, $\Delta E_{\text{Deform(W carbyne)}}$, and between the two alkyne deformation energies, $\Delta E_{\text{Deform(alkyne)}}$. The difference between the two reaction barriers can be traced to the significant difference between the two binding energies of alkyne, ΔE_b. For the tungsten NR_2 alkylidyne system, ΔE_b is −11.6 kcal/mol, while for the tungsten OR alkylidyne system, the value becomes −24.4 kcal/mol. Clearly, it is the much greater alkyne binding energy of the tungsten OR alkylidyne versus the tungsten NR_2 alkylidyne that makes the reaction barrier relatively small for the tungsten OR system.

Interestingly, experiments showed that alkynes do not react with Mo(≡C^{t}Bu)$(O^tBu)_3$.[11] A particularly high barrier (30.3 kcal/mol) was calculated for the ring-closing rate-determining step with the formation of the metallacyclobutadiene **IN1C**

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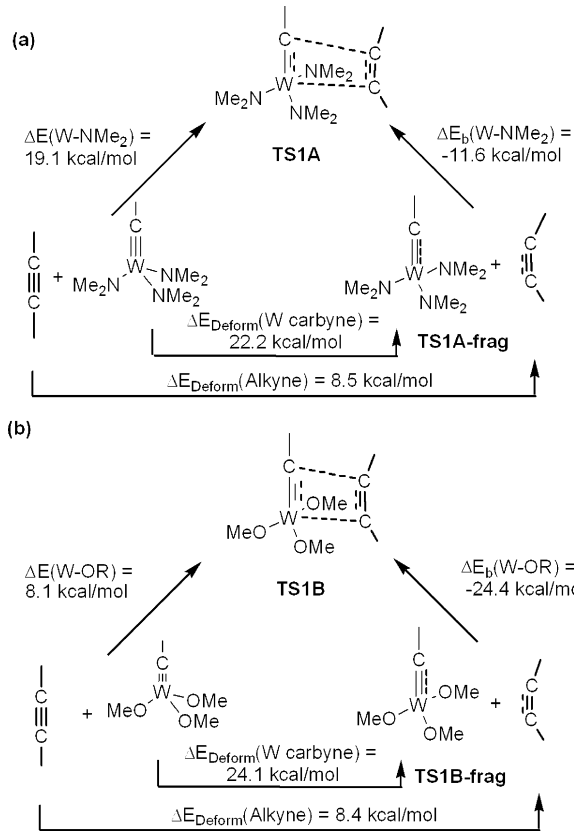
Scheme 2



(Figure 2a). The corresponding reaction barrier of the rate-determining ring-closing step for the alkyne metathesis catalyzed by Mo(≡CMe)$(OCH_2F)_3$ is only 15.9 kcal/mol (Figure 2b). The result is also consistent with the experimental observation that molybdenum fluoroalkoxide complexes are excellent catalysts for the metathesis of alkynes.[11] As mentioned earlier, only one intermediate, **IN1D**, was found in this case.

The significant difference in the catalytic activity between the OCH_3 and OCH_2F alkylidyne complexes can be again understood by an energy-decomposition analysis of the reaction barriers (Scheme 3).[25] For the molybdenum OCH_3 and OCH_2F alkylidyne systems, again, the differences between the two molybdenum alkylidyne deformation energies, $\Delta E_{\text{Deform(Mo carbyne)}}$, and between the two alkyne deformation energies, $\Delta E_{\text{Deform(alkyne)}}$, are not very significant. The two binding energies of alkyne, ΔE_b, are significantly different, giving rise to the difference between the two reaction barriers. For the molybdenum OCH_3 alkylidyne system, ΔE_b is -33.5 kcal/mol, while for the molybdenum OCH_2F alkylidyne system, the value is -50.8 kcal/mol. Clearly, it is the much greater alkyne binding energy of the molybdenum OCH_2F alkylidyne versus the molybdenum OCH_3 alkylidyne that makes the reaction barrier significantly small for the molybdenum OCH_2F system.

Examination of the transition structures (Figure 3) leads us to the following conclusion. In the transition states, the bonding interactions between the metal alkylidyne fragments and MeC≡CMe are mainly between the lowest unoccupied molecular orbitals (LUMOs) of the metal fragments and the HOMOs of the distorted MeC≡CMe structures. This is because the acetylenic bond of MeC≡CMe is closer to the metal center than to the alkylidyne carbon in each transition structure. Thus, the significant differences between these binding energies, ΔE_b (Schemes 2 and 3), can be related to the LUMOs of the four distorted metal alkylidyne fragments, **TS1A-frag**, **TS1B-frag**,

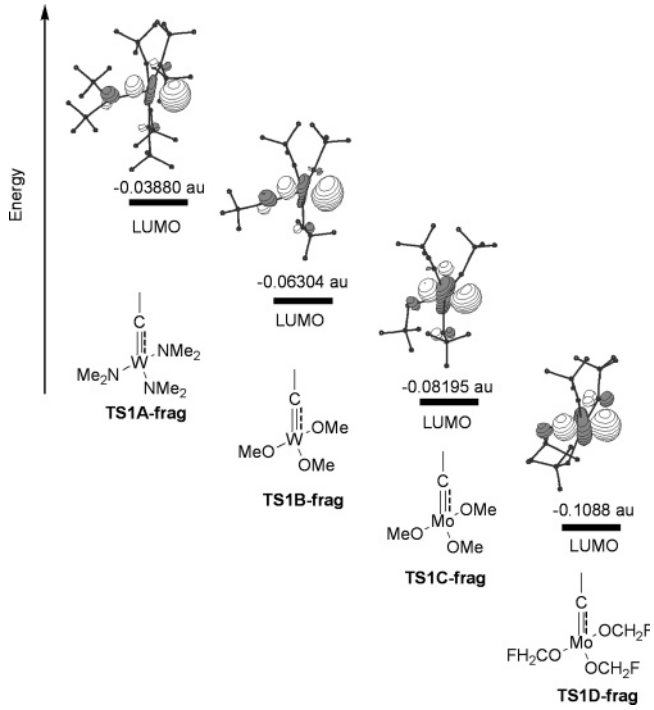
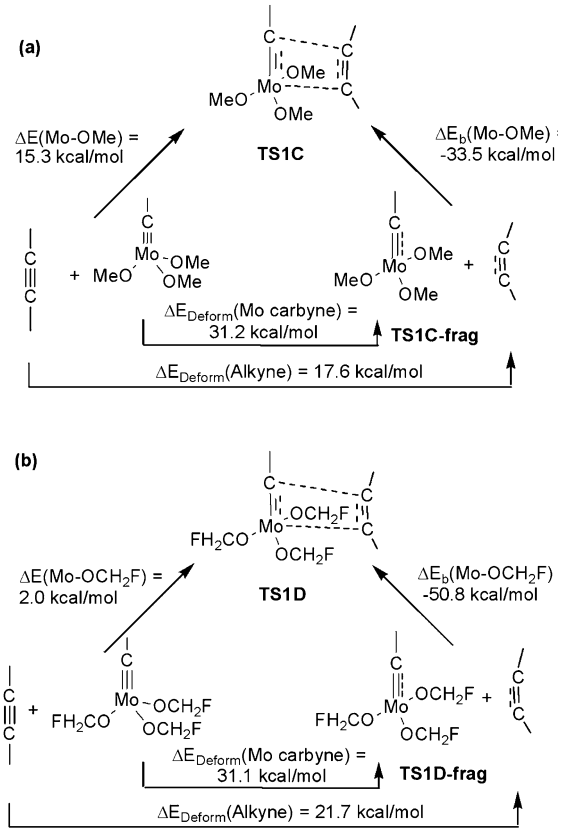


Figure 4. LUMOs of the metal fragments in the transition states of the ring-closing coupling steps. The orbital energies are given in atomic units (au).

Scheme 3



TS1C-frag, and **TS1D-frag** (Figure 4). The LUMOs are responsible for interaction with the distorted MeC≡CMe substrates in the transition states. On the basis of the orbital energies shown in Figure 4, the LUMO of the fragment **TS1A-frag** is significantly destabilized by the NMe_2 ligands due to their stronger electron-donating properties, compared with that

of the fragment **TS1B-frag**, lying 0.024 au (0.65 eV) higher in energy than that of **TS1B-frag**. It is expected that the attractive interaction between **TS1B-frag** and the distorted MeC≡CMe substrate is stronger than that between **TS1A-frag** and the distorted MeC≡CMe substrate, giving the larger binding energy ΔE_b. In addition to the electronic factor discussed above, sterically, the NMe_2 ligands in W(≡CMe)$(NMe_2)_3$ create a more crowded ligand environment, hindering the attack of the incoming MeC≡CMe substrate to the metal center.

Similarly, the LUMO of the fragment **TS1D-frag** is significantly stabilized by the electron-withdrawing CH_2F groups, compared with that of the fragment **TS1C-frag**, lying 0.027 au (0.73 eV) lower in energy than that of **TS1C-frag**. The greater attractive interaction between **TS1D-frag** and the distorted MeC≡CMe substrate gives the larger binding energy ΔE_b. The intermediate **INID** is relatively much more stable than the intermediate **IN1C** with respect to their reactants, indicating that the CH_2F groups also significantly stabilize the intermediate **IN1D**.

It is worth noting that although the LUMO of the deformed Mo(≡CMe)$(OMe)_3$ fragment **TS1C-frag** is lower in energy than that of W(≡CMe)$(OMe)_3$, **TS1B-frag** (Figure 4), Mo(≡CMe)-$(OMe)_3$ is metathesis inactive, but W(≡CMe)$(OMe)_3$ is active. We know that both the binding energies and the deformation energies affect the reaction barriers:

$$\Delta E(\text{barrier}) = \Delta E_{\text{Deform}}(\text{M carbyne}) + \Delta E_{\text{Deform}}(\text{Alkyne}) + \Delta E_b$$

The molybdenum alkylidyne deformation energy, ΔE_{Deform}(Mo carbyne) (31.2 kcal/mol), and the alkyne deformation energy, ΔE_{Deform}(alkyne) (17.6 kcal/mol), in Scheme 3a are greater than ΔE_{Deform}(W carbyne) (24.1 kcal/mol) and ΔE_{Deform}(alkyne) (8.4 kcal/mol) in Scheme 2b, respectively. These results indicate that the ring-closing coupling between Mo(≡CMe)$(OMe)_3$ and MeC≡CMe requires more significant distortions of the two reactants in order to reach the transition state when compared with that between W(≡CMe)$(OMe)_3$ and MeC≡CMe. A plausible explanation for these findings is as follows. Mo has less diffuse d orbitals than W. As a result, the molybdenum center requires shorter contact with the substrate, which leads to more significant distortion, to achieve effective activation of the substrate. In addition, a Mo−O bond is expected to be less ionic than a W−O bond. The less positive charge carried by the Mo center in the Mo(≡CMe)$(OMe)_3$ catalyst makes it less capable of polarizing the MeC≡CMe substrate. In **TS1C**, the C−C−C angle in the distorted alkyne is 151.1°, while in **TS1B**, the corresponding angle is 161.5°. In **TS1C**, the Mo≡C bond length is elongated by 1.5% with respect to the stable Mo(≡CMe)$(OMe)_3$, while in **TS1B**, the W≡C bond length is elongated by only 1.0%. In Mo(≡CMe)$(OMe)_3$, the NBO charge of the molybdenum center is +1.37, while in W(≡CMe)$(OMe)_3$, the charge of the tungsten center is +1.72.

Reactions Leading to the Formation of an η^5-C_5Me_5 Complex. Experimentally, it was found that metallacyclobutadienes **1** also react with excess alkyne to give cyclopentadienyl complexes, via a metallabenzene intermediate, although the reactions were found to be slow (in days).[26] Formation of cyclopentadienyl (Cp) complexes may deactivate the metathesis activity. Thus, the pathways to give Cp complexes were also studied for the model reactions of [M](≡CMe) + 2 MeC≡CMe → [M](η^5-C_5Me_5), where [M] = $W(OMe)_3$, $W(Cl)_3$, $Mo(OMe)_3$, and $Mo(OCH_2F)_3$. We understand that the cyclopentadienyl complexes obtained in the experiments are much more complex than the ideal model complexes (η^5-C_5Me_5)[M]. For example, the metallacyclobutadiene W[C_3(^{t}Bu)Et_2]$(Cl)_3$ reacts with excess EtC≡CEt to yield a mixture of reduced tungsten complexes that contain a peralkylated cyclopentadienyl ring, WCp′Cl_4 and WCp′Cl_2(EtC≡CEt) (Cp′ = η^5-$C_5Et_4{}^t$Bu).[27−28] It was speculated[27,28] that the two reduced tungsten complexes were formed via disproportionation of an intermediate tungsten(IV) complex, such as "WCp′$C1_3$", justifying us studying the model reactions in our calculations. The model calculations were for the purposes of providing qualitative insight into the formation of cyclopentadienyl ligands from metallacyclobutadiene intermediates and examining whether the formation is indeed via a metallabenzene intermediate.

Figure 5a shows the potential energy profile for the reaction of the metallacyclobutadiene intermediate **IN1B** with another MeC≡CMe molecule to give the metallabenzene intermediate **IN4B**, which can easily isomerize to the η^5-C_5Me_5 complex **PRCPB**. The barrier (28.2 kcal/mol) for the formation of **PRCPB** is relatively high, consistent with the experimental findings mentioned above that W(≡CMe)$(OR)_3$ are good catalysts for metathesis. For other catalysts, such as Mo(≡CMe)-$(OMe)_3$ and Mo(≡CMe)$(OCH_2F)_3$, the energy profiles for the formation of η^5-C_5Me_5 complexes were also calculated (Figure 6). From Figures 6, we can see that the Cp complexes' formation reactions have even higher barriers (45.3 and 37.8 kcal/mol, respectively).

As mentioned above, for the tungsten chloroalkylidyne complex, W(≡$CCMe_3$)(dme)Cl_3 (dme = 1,2-dimethoxyethane), although it is not a catalyst for metathesizing alkynes,[27] it can easily react with alkynes, giving tungstenacyclobutadiene, which readily reacts with another alkyne molecule to give Cp complexes.[28] The energy profile for the formation of the model Cp complex **PRCPE** is shown in Figure 5b. The formation of the tungstenacyclobutadiene intermediate **IN1E** was found to have a low barrier (12.6 kcal/mol) through a very early transition state, **TS1E**, the lowest one when compared with the ring-closing steps catalyzed by the other three catalysts, W(≡CMe)-$(OMe)_3$, Mo(≡CMe)$(OMe)_3$, and Mo(≡CMe)$(OCH_2F)_3$. Different from the other metallacyclobutadiene intermediates, **IN1E** is more stable than the reactants by ca. 8.5 kcal/mol in free energy. As shown in Figure 7, the newly formed W−C bond (1.907 Å) in **IN1E** is much shorter than that (2.024 Å) in **IN1B**, indicating that the Cl ligands can significantly stabilize the metallacyclobutadiene intermediate. The barrier leading to the formation of the metallabenzene **IN3E** is also moderate, explaining the formation of Cp complexes when W(≡CR)Cl_3 reacts with alkynes.

Examining the structures of W(≡CR)Cl_3 and W(≡CMe)-$(OMe)_3$, we can see that the W≡C bond (1.737 Å) in W(≡CR)Cl_3 is much shorter than that (1.757 Å) in W(≡CMe)-$(OMe)_3$. Therefore, we expect that an M−Cl bond is much weaker than an M−OR bond. Because of the weaker Cl bonds in comparison with the M−OR bonds, an MCl_3 fragment stabilizes the metallacyclobutadiene intermediate more significantly than an M$(OR)_3$ fragment does. Because of the high stability of the tungstenacyclobutadiene intermediate **IN1E**,

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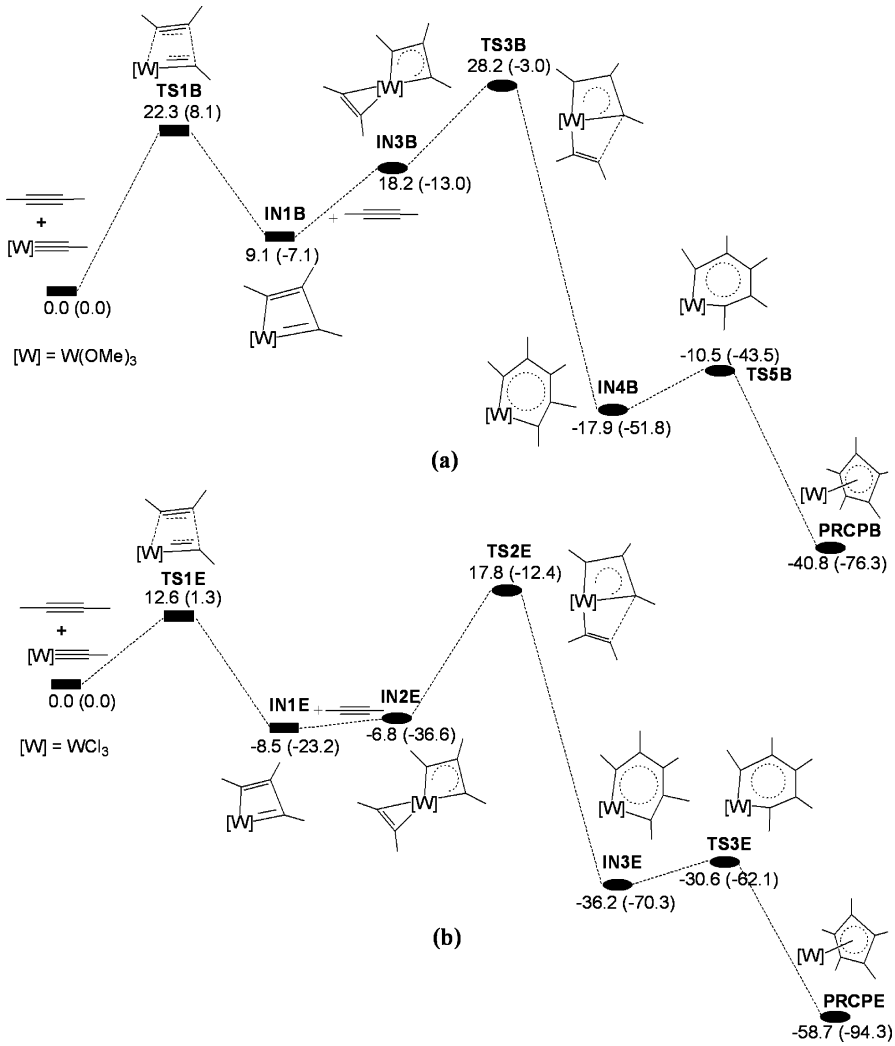

Figure 5. Energy profiles for the formation of η^5-C_5Me_5 complexes catalyzed by W(≡CMe)X_3 (X = OMe (a), Cl (b)). The free energies and relative energies (in parentheses) are given in kcal/mol.

which contains a WCl_3 fragment, the barrier (21.1 kcal/mol, Figure 5b) of the ring-opening step, i.e., the reverse step of the ring-closing step, is not low, making the alkyne metathesis not as easy as one might expect from the low barrier of the ring-closing step. The important factor to make W(≡CR)Cl_3 a poor catalyst is clearly related to the low barrier for the formation of a Cp ligand and the high stability of the Cp complex, again due to the weaker and more flexible W−Cl bonds. We note that the barrier (21.1 kcal/mol) for the alkyne metathesis is still lower than the barrier (26.3 kcal/mol) for the formation of a Cp complex (Figure 5b), although W(≡CR)Cl_3 is not a good catalyst for alkyne metathesis. We note that the chloride-containing tungsten alkylidyne in the experiments is W(≡CR)-Cl_3(dme) (dme = 1,2-dimethoxyethane), different from the model complex W(≡CR)Cl_3 we employed in the calculations. Neglecting the dme chelating ligand in the calculations, which is for the purposes of theoretical simplicity and easy comparison with other catalysts, is likely to underestimate the barrier for the ring-closing step.

Summary

The mechanism of alkyne metathesis catalyzed by W/Mo alkylidyne complexes has been theoretically investigated with the aid of density functional theory calculations. Metallacyclobutadienes are initially formed from a ring-closing step between alkynes and alkylidyne complexes. A ring-opening step then gives the metathesis products. The results of our calculations show that the alkyne binding capability of the metal alkylidyne complexes determines the stability of the transition states for the two important steps.

Compared with tungsten alkylidyne complexes containing alkoxide ligands, the analogues containing amide ligands have poorer binding capability because of the stronger W(VI)−NR_2 π-bonding interaction. Therefore, tungsten alkylidyne complexes containing alkoxide ligands are good catalysts for alkyne metathesis, but analogous complexes containing amide ligands are not. For Mo(≡CR)$(OR)_3$, the Mo metal center has less diffuse d orbitals when compared with W. As a result, significant deformation, which takes a lot of energy, is required in the catalyst and the alkyne substrate to achieve the transition state of the ring-closing step in the metathesis process, making the molybdenum alkylidyne complexes metathesis inactive. However, introduction of electron-withdrawing groups to the substituents R at O of the alkoxide ligands significantly increases the alkyne binding capability of the molybdenum alkylidyne complexes. Our calculations show that the alkyne metathesis catalyzed by the model complex Mo(≡CMe)$(OCH_2F)_3$ also has small barriers for the ring-closing and ring-opening steps, consistent with the experimental findings that Mo(≡C^{t}Bu)-$(OR)_3$ [OR = OC(Me)$(CF_3)_2$, OC$(CF_3)_3$, or OAr] are excellent catalysts.[11]

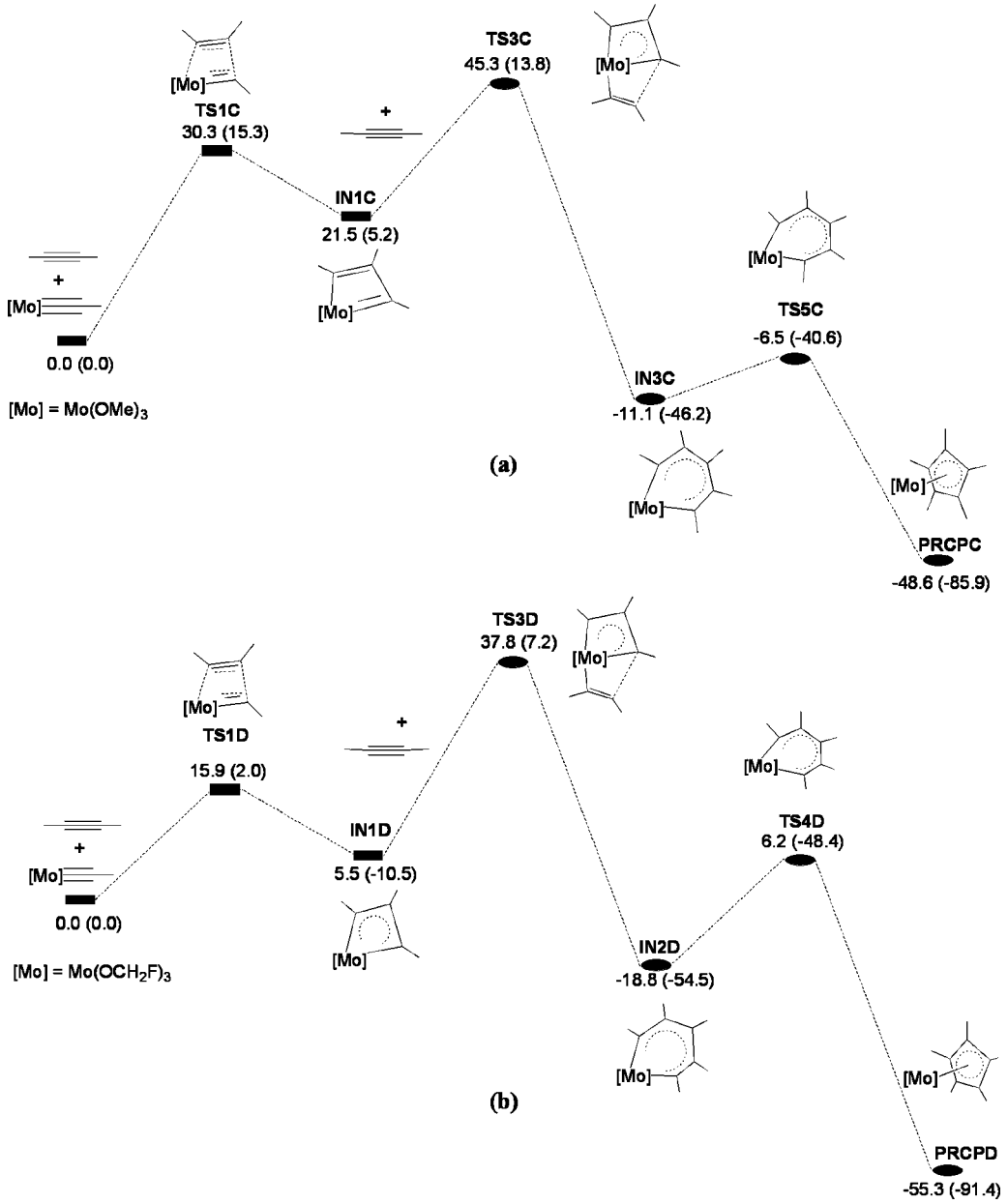

Figure 6. Energy profiles for the formation of η^5-C_5Me_5 complexes catalyzed by Mo(≡CMe)$(OR)_3$ (R = CH_3 (a), CH_2F (b)). The free energies and relative energies (in parentheses) are given in kcal/mol.

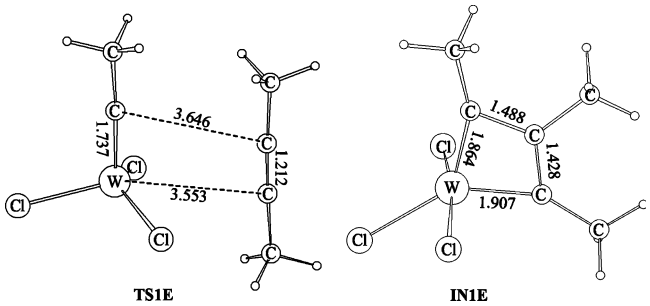

Figure 7. Selected structural parameters (Å) calculated for the ring-closing transition state **TS1E** and intermediate **IN1E** of the alkyne metathesis catalyzed by W(≡CMe)Cl_3.

Alkylidyne complexes containing chloride ligands are very capable of binding alkynes because of the relatively weaker, flexible M−Cl bonds in comparison with the M−OR or M−NR_2 bonds. However, the metallacyclobutadiene intermediates formed from the ring-closing step become so stable that the ring-opening step has a significantly high barrier. On the other hand, because of the weak, flexible M−Cl bonds, the barrier for the path leading to the formation of Cp complexes through interaction of the metallacyclobutadiene intermediate with a second alkyne molecule (Figure 5b) is relatively low. Therefore, alkylidyne complexes containing chloride ligands are not good catalysts for alkyne metathesis.

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Supporting Information Available: Cartesian coordinates for all the calculated structures are available free of charge via the Internet at http://pubs.acs.org.

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