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Density Functional Study of Acetylene Metathesis Catalyzed by High Oxidation State Molybdenum and Tungsten Carbyne Complexes

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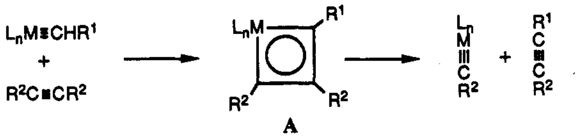
Nonlocal density functional theory has been used to study acetylene metathesis catalyzed by high oxidation state molybdenum alkylidyne complexes. The first part of this study discusses a dissociative mechanism in which a metallacyclobutadiene acts as an intermediate in the metathesis. In particular, the formation and decomposition of the metallacyclobutadiene $Cl_3MoC_3H_3$ was examined with the geometries, bonding, and energetics of the whole process given. The formation of the metallacyclobutadiene was found to be a formally symmetry allowed process with a calculated energy barrier of only 10 kJ mol^{-1}. The mechanism by which this process affords such a small reaction barrier was also examined in detail and found to be due to the ability of π and π^* type orbitals to interact throughout the course of the reaction. The metallacyclobutadiene was determined to be 70 kJ mol^{-1} more stable than the acetylene and molybdenum carbyne reactants. In the second part of this study, the formation of the metallatetrahedrane was examined. The direct formation of the metallatetetrahedrane from the acetylene and molybdenum carbyne fragments was determined to be a formally symmetry forbidden process and possesses a barrier of 40 kJ mol^{-1}. The formation of the metallatetrahedrane by the tautomerization of the metallacyclobutadiene was also examined in detail. The metallatetrahedrane was determined to be 52 kJ mol^{-1} more stable than the corresponding metallacyclobutadiene and 122 kJ mol^{-1} more stable than the free acetylene and molybdenum carbyne.

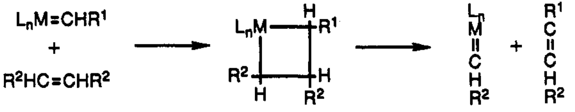
Introduction

High oxidation state tungsten(VI) and molybdenum(VI) alkylidyne complexes such as $(Me_3CO)_3W{\equiv}CCMe_3$[1] and $[(CF_3)_2MeCO](Mo{\equiv}CCH_3)$[2] have been shown to effectively metathesize acetylenes. The acetylene metathesis is believed to proceed through a dissociative mechanism in which a metallacyclobutadiene,[3,4] A, intermediate is formed as shown in eq 1. Evidence for this mechanism is provided by the role that metallacyclobutanes, B, play in olefin metathesis catalyzed by analogous alkylidene complexes, as shown in eq 2.



A

(1)

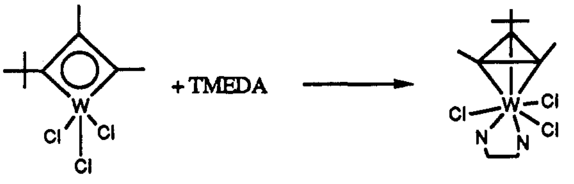


B

(2)

The rate-limiting step in the acetylene metathesis process (eq 1)[4,5] is expected to be the loss of acetylene from the metallacyclobutadiene. It is thus not surprising that the steric bulk of the ancillary ligands on the alkylidyne complex enhances the effectiveness of the catalyst.[3,4,6,7]

A potential side reaction in eq 1 is the formation of a metallatetrahedrane complex by tautomerization of the metallacyclobutadiene intermediate A. One such example[6,8] is the formation of $W[\eta^3\text{-}C(CMe_3)C(Me)C(Me)]Cl_3$ from the addition of tetramethylethylenediamine (TMEDA) to the metallacyclobutadiene $W[C(CMe_3)C(Me)C(Me)]Cl_3$, as shown in eq 3.[6] Metallatetrahedranes such as $W[\eta^3\text{-}C_3(CMe_3)Et_2](O_2CMe)_3$ can also form from the direct addition of acetylene to a metal alkylidyne complex.[9] The formation of stable metallatetrahedranes might inhibit the metathesis of acetylenes.[10]



(3)

Both the metallacyclobutadiene and the metallatetra-

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hedrane have been examined theoretically. Anslyn et al.[11a] and Bursten[11b] have studied the nature of the bonding in the metallacyclobutadiene and metallatetrahedrane. Jemmis and Hoffmann[11c] have treated the tautomerization of the metallacyclobutadiene and the metallatetrahedrane. A detailed study of the formation and decomposition of both the metallacyclobutadiene and the metallatetrahedrane have not been presented previously.

In the first part of this investigation, we shall study the formation and decomposition of the metallacyclobutadiene $Cl_3MoC_3H_3$ in detail. A similar study will be given in the second part for the formation of the corresponding metallatetrahedrane. Our analysis of the reaction pathways will be based on orbital symmetry considerations and quantitative density functional calculations.

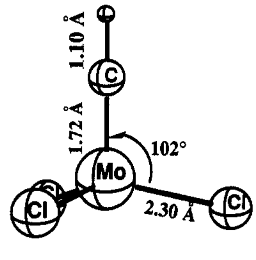
Although most acetylene metathesis systems involve tungsten carbyne catalysts with alkoxide ligands, molybdenum was used in place of tungsten and the alkoxide ligands were substituted by chlorine atoms. Both modifications were introduced in order to reduce the computational cost. There is usually a close correspondence between the second and third transition series metals of the same triad, especially for tungsten and molybdenum complexes, and it was felt that the substitution would not significantly effect the results. In fact, many molybdenum carbyne,[2,12] metallacyclobutadiene,[2] and metallatetrahedrane[11,13] systems have emerged including several molybdenum metathesis systems.[2,14]

Computational Details

The reported calculations were all carried out by utilizing the HFS-LCAO program system A-MOL, developed by Baerends et al.[15,16] and vectorized by Ravenek.[17] The numerical integration procedure applied for the calculations was developed by te Velde et al.[18] The geometry optimization procedure was based on the method developed by Versluis[19] and Ziegler. The electronic configurations of the molecular systems were described by an uncontracted triple-ζ STO basis set[20] on molybdenum for 4s, 4p, 4d, 5s, and 5p as well as a double-ζ STO basis set[19] on carbon (2s, 2p), chlorine (3s, 3p), and hydrogen (1s). Hydrogens and carbons were given an extra polarization function: $3d_C$ ($\zeta_{3d} = 2.5$); $2p_H$ ($\zeta_{2p} = 2.0$). The $1s^22s^22p^63s^23p^63d^{10}$ configuration on molybdenum, the $1s^2$ configuration on carbon, and $1s^22s^22p^6$ on chlorine were assigned to the core and treated by the frozen-core approximation. A set of auxiliary[21] s, p, d, f, and g STO functions, centered on all nuclei, was used in order to fit the molecular density and present Coulomb and exchange potentials accurately in each SCF cycle. Energy differences were calculated by including the local exchange-correlation potential by Vosko[22] et al. with Becke's[23] nonlocal exchange corrections and Perdew's[24] nonlocal correlation correction. Geometries were optimized without including nonlocal corrections. The application of approximate density functional theory to organometallic chemistry has been reviewed recently.[25]

Acetylene Metathesis through a Metallacyclobutadiene Intermediate

Metal Carbyne. Our discussion of the metathesis process will begin with a brief examination of the electronic and molecular structure of the metal carbyne. We have optimized the molybdenum carbyne complex Cl_3MoCH, 1, under C_{3v} constraints. Its structure is considerably different from the Cl_3MoCH framework in the metallacyclobutadiene, 2.



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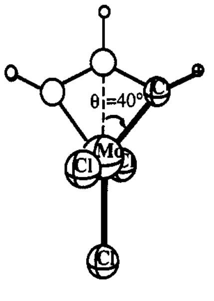

2

The most significant difference is in the positioning of the chlorine ligands. In the distorted carbyne, 2, the three chlorine ligands and the molybdenum center are coplanar, while in the free carbyne, 1, they are arranged in a pyramidal fashion. Also, the carbon atom in the metallacyclobutadiene is moved out of the coordination plane formed by the three chlorines and molybdenum center by $\theta = 40°$. As would be expected with these structural changes, the orbital makeup and energies are altered between the free and distorted carbyne fragments. Figure 1 displays a correlation diagram for the σ, π, and π^* orbitals of the free carbyne and distorted carbyne. C_s symmetry labels are used because the distortion and the reaction to form the metallacyclobutadiene both have a preserved C_s symmetry.

The σ, π, and π^* orbitals of the Cl_3MoCH molecule, Figure 1, are similar to the corresponding valence orbitals on acetylene, except that a $2p_\pi$ lobe has been replaced by a d hybrid with a more complicated nodal structure. The introduction of a d hybrid has subtle but important ramifications for the way in which Cl_3MoCH and acetylene interact to form the metallacyclobutadiene. The empty π^*-type orbital 3a′ on the distorted Cl_3MoCH framework is well suited for interactions with a π orbital on an incoming acetylene. The occupied π-type orbital 2a′ can at the same time overlap with an empty π^* orbital on

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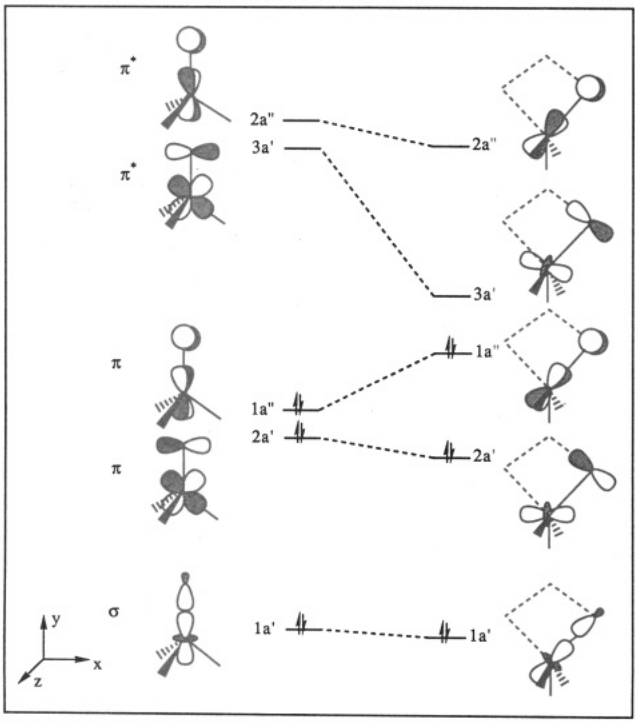
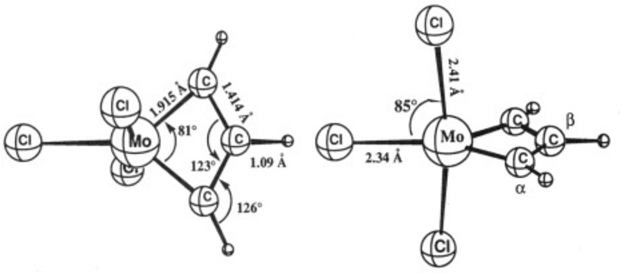


Figure 1. Free carbyne and distorted carbyne orbitals.

acetylene, Figure 1. Similar interactions between π* and π orbitals on two different acetylenes are not possible. We shall return to this point with more detail in a later section.

Structure and Bonding of Metallacyclobutadiene. In this study, the geometry and bonding of the metallacyclobutadiene $Cl_3MoC_3H_3$, **3**, was examined in detail. The structure of **3** was optimized within a C_{2v} symmetry constraint and later optimized with no symmetry constraints. The geometrical parameters of the two calculations showed no significant differences and both agreed well with experimental crystal structures of similar metallacyclobutadienes.[2,3,26,29b] **3** was calculated to have a Mo–C_α bond distance of 1.915 Å, which is slightly shorter than a typical molybdenum–carbon double bond, as well as a C_α–C_β bond length of 1.414 Å, which is somewhere between a typical carbon–carbon single and double bond. The C_α–Mo–C_α bond angle optimized to 81° while the C_α–C_β–C_α bond angle optimized to 123°.



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The six orbitals which make up the bonding of the ring are shown in Figure 2 with the hydrogen- and chlorine-centered orbitals not included. The metallacyclobutadiene ring system consists of two Mo–C_α σ bonds, $2a_1$ and $2b_1$, two C_α–C_β σ bonds, $1a_1$ and $1b_1$, and two delocalized π bonds, $1a_2$ and $1b_2$. The fact that only one π bonding orbital, $1b_2$, contributes to the C_α–C_β bond while both π bonding orbitals contribute to the Mo–C_α bonds can explain the rather short Mo–C_α bond length which is just shy of a typical Mo–C double bond.

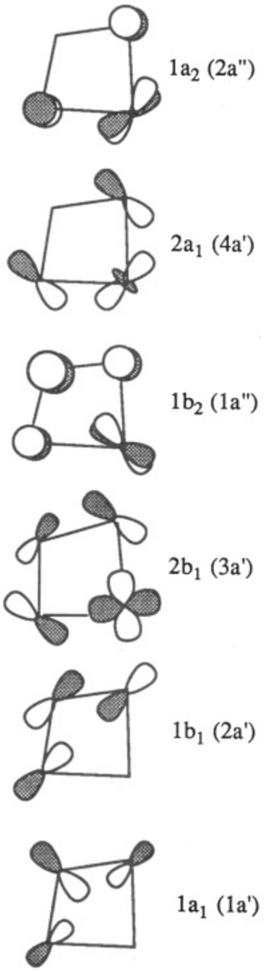

Figure 2. Bonding orbitals of the metallacyclobutadiene ring.

There has been some debate as to whether or not there is any significant bonding between molybdenum and the β carbon in view of the short M–C_β bond distance (~2.15 Å). Bursten found from a Fenske–Hall calculation that there was significant Mo–C_β bonding associated with the $1b_2$ orbital.[11b] On the other hand, Anslyn and Goddard concluded from GVB calculations, that no significant Mo–C_β bonding interaction[11a] was present. Our studies are in good agreement with Bursten's results. The overlap between the Mo(d_π) and C_β(p_π) components in $1b_2$ of Figure 2 is 0.17, clearly indicating that there is a significant bonding interaction between molybdenum and the β carbon.

The short Mo–C_β distance is not necessarily caused by the favorable Mo(d_π)–C_β(p_π) interaction in $1b_2$. Instead, the Mo–C_β distance is largely fixed by the Mo–C_α and C_α–C_β bond lengths relevant for a bond order of 2 and 1.5, respectively, as well as the C_α–C_β–C_α bond angle of ~120° around the sp^2-hybridized C_β carbon. It is interesting to note that several metallacyclobutanes of tungsten and molybdenum with a similar trigonal bipyramidal coordination around the metal also have been found to have short M–C_β distances although π-interactions are excluded for this type of system.[27]

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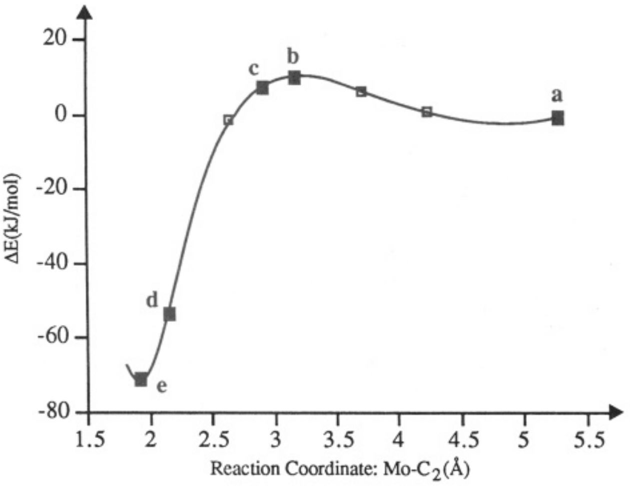
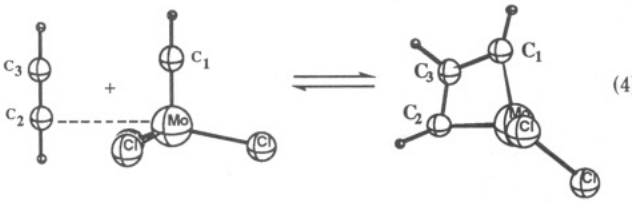


Figure 3. Energy profile for the formation of the metallacyclobutadiene.

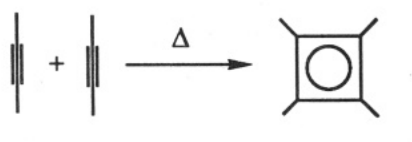
Formation of Metallacyclobutadiene. A detailed study on the formation of the metallacyclobutadiene was carried out in a postulated least motion pathway, as shown in eq 4. The molybdenum carbyne complex Cl_3MoCH, **1**,



(4)

was brought together with the acetylene molecule such that the three carbon atoms and the metal center remained coplanar throughout the course of the reaction. The Mo–C_2 distance was used as a reaction coordinate and varied between 5.29 Å, a distance where the two molecules are virtually noninteracting, to 1.92 Å, the distance of the Mo–C_2 bond length in the final metallacyclobutadiene, **3**. A total of eight steps along the reaction profile were calculated by fixing the Mo–C_2 distance and optimizing all other degrees of freedom within a C_s symmetry constraint. The energy profile for this reaction is shown in Figure 3. The labels on the plot will be discussed shortly.

The reaction profile reveals that the metallacyclobutadiene is 70 kJ mol^{-1} more stable than the two reacting species and that there is a small 10 kJ mol^{-1} reaction barrier with a maximum roughly occurring at a Mo–C_2 distance of 3.18 Å. The formation of metallacyclobutadiene is very similar to the $\pi^3 + \pi^3$ symmetry forbidden formation of cyclobutadiene from acetylene except that in the organometallic reaction one carbon is replaced by a metal center. We shall in the following try to understand how the organometallic reaction in eq 4 is able to circumvent the sizable barrier encountered in the direct formation of cyclobutadiene from two acetylene molecules in a least motion pathway, eq 5.



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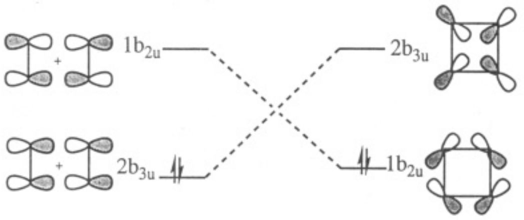


Figure 4. Correlation diagram for the formation of cyclobutadiene.

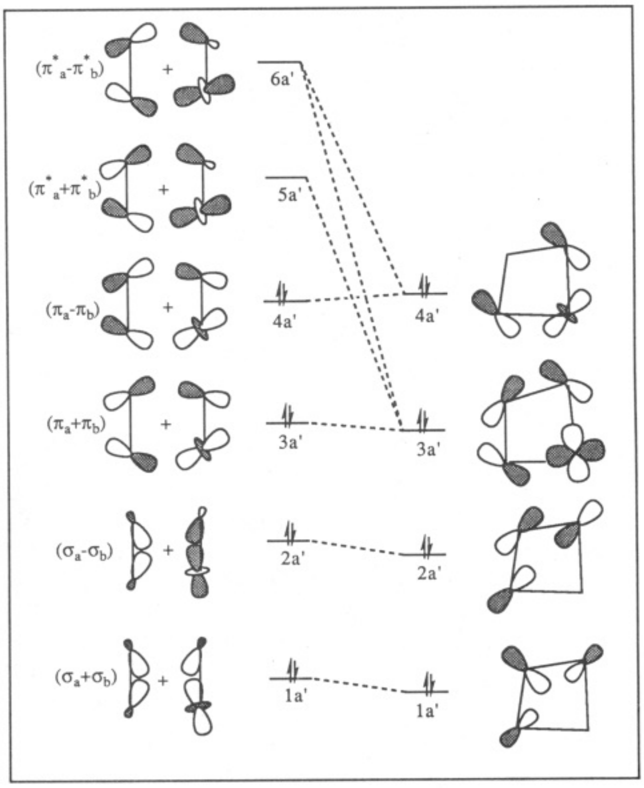
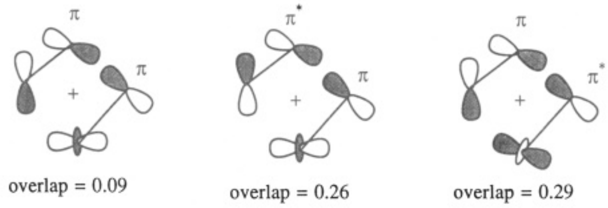


Figure 5. Correlation diagram for the formation of the σ-framework of the metallacyclobutadiene.

The reaction in eq 5 correlates an occupied π orbital, $2b_{3u}$, on the reactant side with an empty $2e_u$ orbital on the product side (Figure 4) as well as an empty π* orbital, $1b_{2u}$, on the reactant side with an occupied $1b_{2u}$ orbital on the product side. The net result is a transfer of charge (2 e) from π to π*. This transfer of charge can unfortunately not take place gradually since the π- and π*-type orbitals are of different symmetries and are thus noninteracting. The charge transfer must instead await the point where $2b_{3u}$ has been destabilized sufficiently to be of the same energy as $1b_{2u}$. However the destabilization of the fully occupied $2b_{3u}$, π–π, orbital translates into a sizable activation barrier.

Figure 5 provides a correlation diagram for the formation of σ bonds of the metallacyclobutadiene according to the least motion pathway of eq 4. This pathway has a preserved C_s symmetry, with the C_s plane being the plane of the ring in the resulting metallacycle. In this approach all orbitals in the σ-framework are of a′ symmetry and the orbitals are labeled accordingly. Orbitals 1a′ and 2a′ of the reactants are the plus and minus combinations, respectively, of the σ orbital of acetylene and the σ orbital of the metal carbyne. Similarly, the 3a′ and 4a′ orbitals of the reactants are the plus and minus combinations of the π orbitals of the acetylene and carbyne. Figure 5 shows that these four occupied orbitals of the reactants correlate smoothly with four product orbitals which form the σ bonding framework of the metallacycle. This is in contrast to the organic reaction in which the π–π orbital of the reacting acetylenes interacted repulsively and correlated with an excited state of the product, Figure 4.

In the organometallic reaction the repulsive interaction between the two π orbitals, 4a′ of Figure 5, is reduced by two factors. First, the π orbital on acetylene is 5 eV lower in energy than the π orbital on the metal carbyne. This gap will tend to reduce the repulsive interaction in 4a′ during the initial stages of the process in eq 6. Secondly, π and π^* orbitals can overlap throughout the process in eq 5, thus allowing for a gradual transfer of charge from π to π^*. Not only do the π and π^* orbitals interact with one another in the organometallic case, but also these interactions are actually stronger than the $\pi + \pi$ interactions. This can be illustrated by examining the overlaps between such orbitals, as shown in **4**. The rather large overlaps between the π and π^* combinations result from the odd π and π^* orbitals formed by the molybdenum carbyne, **2**, when it is distorted into the metallacyclobutadiene. The hybridization of the d orbitals of the molybdenum result in a π^* orbital, for example, resembling a π orbital to an incoming acetylene molecule, **4**. The protruding lobes of a π^* orbital on carbyne are of the same sign and resemble a π-type orbital to an incoming acetylene, allowing for the large overlaps between π and π^* orbitals. In a similar manner, a carbyne π orbital has protruding lobes of opposite sign and resembles a π^* orbital to an incoming acetylene.



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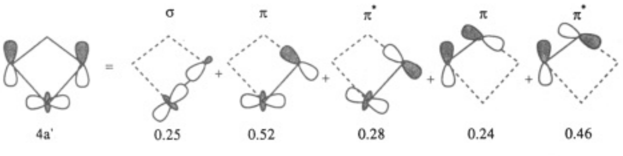
During the course of the reaction, the non-zero overlap between π and π^* orbitals allows for donation of electron density from the π orbital of the acetylene into the empty π^* orbital of the carbyne and back-donation from the π orbital of the carbyne into the empty π^* orbital of the acetylene, **5**. It is primarily this feature that distinguishes the organometallic reaction from the organic reaction and allows for stabilization of orbitals through donor–acceptor type interactions between π and π^* orbitals.



5

A correlation diagram for the change in the π system perpendicular to the C_s plane is given in Figure 6. The diagram in Figure 6 resembles in many ways that drawn[28] for the formation of the π system in cyclobutadiene. The most significant difference is that the 2a″ and 3a″ orbitals are degenerate and nonbonding in the square conformation of cyclobutadiene. This degeneracy will result in a Jahn-Teller distortion into a conformation with alternate bond lengths. In the metallacyclobutadiene 2a″ is bonding and of lower energy than 3a″. The bonding character in 2a″ is an attribute of the d-type orbitals on the metal center and enforces a conformation, **3**, with respectively equidistant C_α–C_β and M–C_α distances.

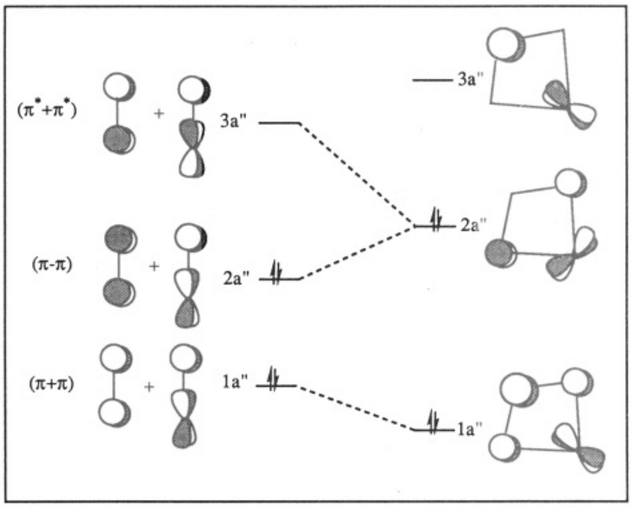
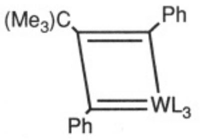


Figure 6. Correlation diagram for the formation of the π-framework of the metallacyclobutadiene.

Most metallacyclobutadienes have a planar, delocalized π system similar to that of **3**. However, some metallacyclobutadienes such as W(η^5-C_5H_5)[C(Ph)C(CMe$_3$)C(Ph)]Cl$_3$, **6**, have alternate double and single bonds despite being symmetrically substituted.[29] This type of distortion that is observed in **6** can result from mixing of the 2a″ orbital with the 3a″ LUMO, as shown in **7**. This results in a partial localization of the π system and an alternate double and single bond length pattern. The localization of the π bonding also allows for the ring puckering which is observed in these metallacycles.



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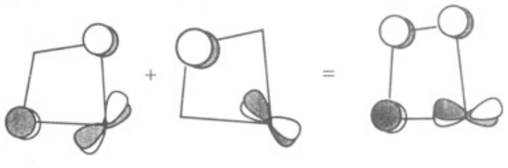

7

Detailed Study of the Path Leading to Metallacyclobutadiene. The discussion of the reaction in eq 4 has up to this point concentrated on why the formation of metallocyclobutadiene is feasible with a modest barrier whereas the corresponding $\pi^3 + \pi^3$ reaction between two acetylenes molecules is "symmetry forbidden" with an insurmountable activation barrier. We shall now turn to a more detailed account of the reaction in eq 4 based on

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[28] Albright, T. A.; Burdett, J. K.; Whangbo, M. H. In *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1984.

[29] (a) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046. (b) Churchill, M. R.; Ziller, J. W. *J. Organomet. Chem.* **1985**, *279*, 403.

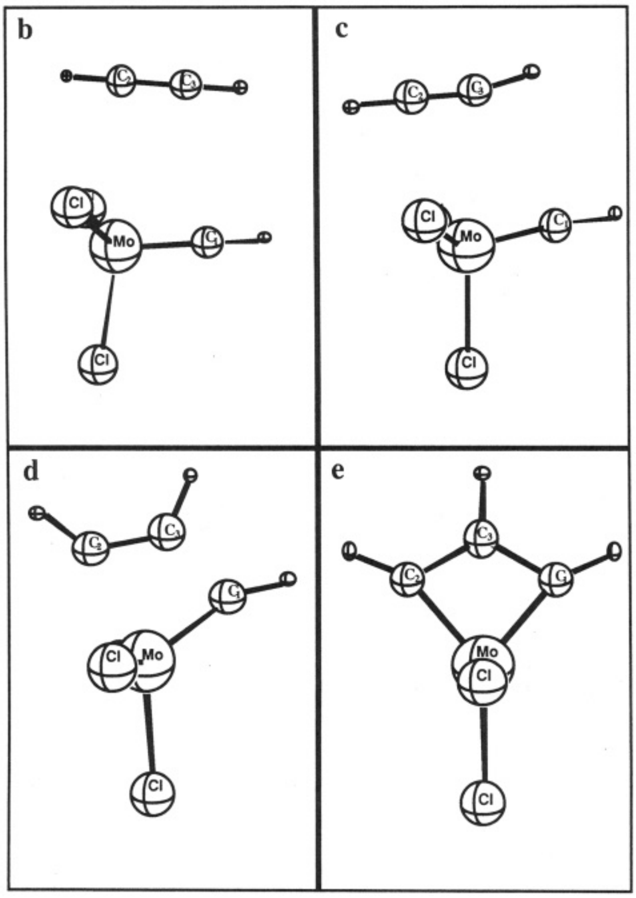
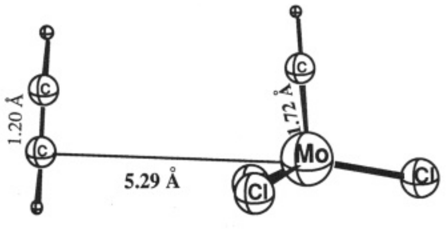
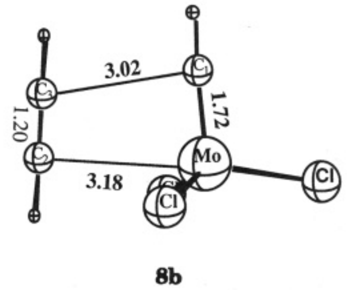


Figure 7. Formation of the metallacyclobutadiene $Cl_3MoC_3H_3$.

the profile presented in Figure 3. The labels **a**–**e** on the energy profile of Figure 3 refer to structures **8a** to **8e**, some of which are shown in Figure 7. Figure 7 illustrates exactly how the metallacyclobutadiene is formed in the least motion pathway from the acetylene and molybdenum carbyne fragments.

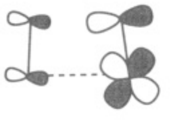


8a

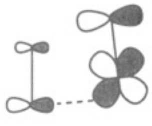


8b

Point **a** on Figure 7 corresponds to structure **8a** which has a Mo–C_1 distance of 5.29 Å. At this point in the process there is virtually no interaction between the reactants and both acetylene and carbyne are in their free undistorted states. As the Mo–C_1 distance is decreased from 5.29 Å the energy steadily rises until it reaches a maximum labeled **b** which is a total of 10 kJ mol^{-1} higher in energy than point **a**. This maximum occurs at a Mo–C_1 distance of 3.18 Å, and **8b** can be considered an approximate transition state. **8b** should only be considered an approximate transition state because no attempt has been made to verify whether or not it has a single normal mode with an imaginary frequency. An examination of the molecular orbitals of the transition state **8b** revealed that all but one of the σ, π, and π^* orbitals discussed earlier are localized on either the carbyne or acetylene fragments, as they would be in the free species. The one exception is the orbital, **9a**, which correlates to the carbyne π orbital on the reactant side, 4a′ in Figure 5. This orbital, although polarized toward the carbyne fragment, has a significant contribution from the π orbital of acetylene which mixes in an antibonding fashion, **9a**.

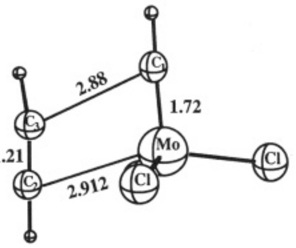


9a

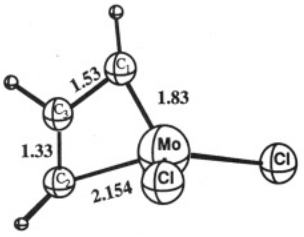


9b

In moving away from the transition state toward the final product, this π–π destabilizing interaction, **9a**, is relieved by electron donation into the π^* orbital of acetylene. The π^* acetylene orbital mixes in by decreasing the orbital lobe on C_3 which in turn results in a decreased π–π antibonding interaction between the two fragments, **9b**. This effect is readily apparent as early on as point **c** on the reaction profile, corresponding to **8c** where the Mo–C_2 distance is 2.91 Å. The mixing or the π^* orbital which polarizes the π–π orbital toward C_2 on the acetylene fragment also facilitates a nucleophilic attack of C_2 on the molybdenum center. It is evident from **9b** corresponding to the structure **8c** that the acetylene fragment has swung around toward the chlorine ligands, allowing the orbital lobe on C_2 to interact in a stabilizing fashion with another lobe on the molybdenum d_{xy} orbital. This type of stabilization involving the metal d orbital clearly cannot happen in the organic reaction between two acetylenes to form cyclobutadiene.



8c



8d

8c is primarily a weakly bonded Mo–C_2 complex, with the other σ and π bonds remaining completely localized on one of the two fragments. The Mo–C_1 bond length is unchanged from the free carbyne, while the mixing of the π^* orbital from the acetylene fragment has elongated the C_2–C_3 bond only slightly by 0.01 Å. The two chlorine ligands that were initially directed toward the incoming acetylene fragment have begun to swing around, moving toward their final axial positions in the metallacyclobutadiene.

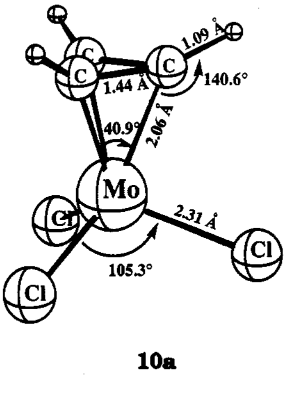
Following the formation of complex **8c** there is a steep decrease in energy. With this steep descent there is further mixing of the π^* orbital of the acetylene fragment, allowing for a stronger Mo–C_2 bond to form. This nucleophilic attack of the molybdenum is then followed by a polarization of the carbyne π orbital away from the metal center toward C_1. This is achieved by electron donation into the molybdenum carbyne π^* orbital. The polarization toward C_1 then facilitates the nucleophillic attack of C_3 by C_1, allowing for the ring closure. The electron donation into the π^* orbitals of both the carbyne fragment and the acetylene fragment allows for the three carbon atoms to undergo the sp to sp^2 rehybridization required to form the metallacyclobutadiene.

It is interesting to note that the ring closure and rehybridization does not occur until the late stages of the reaction, as shown in **8d**, which has Mo–C_2 bond distance of 2.15 Å (only 0.25 Å from the final bond distance in the metallacyclobutadiene). The donation and back-donation into the π^* orbitals of the metal carbyne and acetylene fragments are evident by the Mo–C_1 and C_2–C_3 bond distances which are roughly halfway between that found in the reactants and the final metallacycle. The structure of **8d** illustrates that the hydrogen substituents have bent back toward their final positions in the metallacyclobutadiene, showing the rehybridization that is taking place. Also, the two chlorine atoms have also assumed their axial positions in the final metallacyclobutadiene.

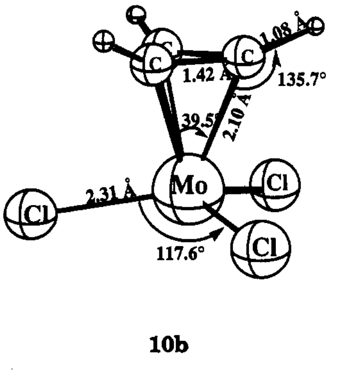
The picture developed here with an initial nucleophilic attack of the metal center followed by a subsequent nucleophilic attack of C_3 by C_1 is consistent with experimental results where the effectiveness of various X_3-W≡C—Y metal carbynes as metathesis catalyst was studied.[5] From these studies where the X ligand and the Y substituent were varied it was concluded that the W≡C bond of the carbyne behaved as if it were polarized, $W(\delta^+)\equiv C(\delta^-)$.

Metallatetrahedrane

Structure and Bonding of Metallatetrahedrane. A tautomeric form of the planar metallacyclobutadiene is the metallatetrahedrane or η^3-cyclopropenyl complex. Several tungsten and molybdenum metallatetrahedranes have been isolated and studied such as $W[\eta^3\text{-}C_3(CMe_3)Et_2](O_2CCH_3)_3$,[9] $Cl_3W[\eta^3\text{-}C_3Me_2(CMe_3)]$TMEDA,[6] and $MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(bpy)$[13]. We have studied the less coordinatively saturated metallatetrahedrane $Cl_3Mo(\eta^3\text{-}C_3H_3)$ in the two conformations **10a** and **10b**. The lowest energy conformation **10a** is one in which the chlorine ligands eclipse the carbons of the cyclopropenyl ring. **10a** was optimized under C_{3v} symmetry constraints and was found to have geometrical parameters in good agreement with similar tungsten and molybdenum metallatetrahedranes. The eclipsed structure **10a** was calculated to be 52 kJ mol^{-1} more stable in energy than the corresponding metallacyclobutadiene **3**. Our findings are consistent with the results of Anslyn and Goddard[11a] who determined the difference to be 34 kJ mol^{-1} without any geometry optimizations being performed.



10a



10b

The optimized structure of **10a** reveals that the ligands are tetrahedrally coordinated about the metal center with the C_3 axis passing through the center of the cyclopropenyl ring. The Mo–C bond distance of 2.06 Å is of the order of typical Mo–C single bonds, and the C–C bond distances of 1.44 Å in the cyclopropenyl ring are midway between a typical C–C single and double bond. The Cl–Mo–Cl bond angle was found to be 105°, which is close to the perfect tetrahedral bonding angle of 109°. It is interesting to note that the hydrogens of the metallatetrahedrane, **10a**, are bent 27° out of the plane of the cyclopropenyl ring. This out of plane bending is also observed experimentally in similar metallatetrahedranes where the hydrogen ring substituents of **10a** are replaced by alkyl groups. This bending was originally thought to be due to steric interactions between the ring substituents and the other ligands of the metal.[6] However, since the ring substituents of **10a** are hydrogens, the steric interactions with other ligands would be minimal. This suggests that the out of plane bending is not due to steric effects but rather bonding effects. This conclusion was also reached by Goddard who argued that the out of plane bending of the substituents was due to the hybridization at the carbons to form covalent bonds with the metal center.[11a] However Anslyn and Goddard were not able actually to optimize the structure of the eclipsed metallatetrahedrane **10a**.

The right side of Figure 8 displays the bonding orbitals for the metallatetrahedrane which consists of three Mo–C σ bonds and three C–C σ bonds. (The chlorine and hydrogen orbitals have been omitted for clarity.) The orbitals are labeled according to the C_{3v} point group symmetry with their orbital energies given in parentheses. The C–C bonding in the cyclopropenyl ring consists of the familiar $1a_1$ and 1e σ bonding orbitals found in three-membered rings of this type. The bonding between the molybdenum fragment and the cyclopropenyl ring also consists of three σ bonding orbitals of a_1 and e symmetry. The $2a_1$ orbital involves the interaction between the molybdenum d_{z^2} orbital and the C–C π bonding orbital of the cyclopropenyl ring. Since this orbital has a large C–C π bonding character, it significantly adds to the C–C bond order within the cyclopropenyl ring. The other two orbitals which form the σ bonding between the metal and the cyclopropenyl ring are the degenerate 2e orbitals. These orbitals primarily involve the interaction between the nonbonding π orbitals of the cyclopropenyl ring and the nonbonding d orbitals of the Cl_3Mo fragment.

This primarily σ type bonding description of the metallatetrahedrane **10a** is in agreement with the bonding picture presented by Goddard for the same compound.[11a] The out of plane bending of the hydrogen substituents in **10a** is consistent with the carbons hybridizing to form covalent bonds with the molybdenum. A Mulliken population analysis reveals that the cyclopropenyl ring possesses a total negative charge of 0.79. The fact that $C_3H_3^-$ is antiaromatic suggests that there has been some rehy-

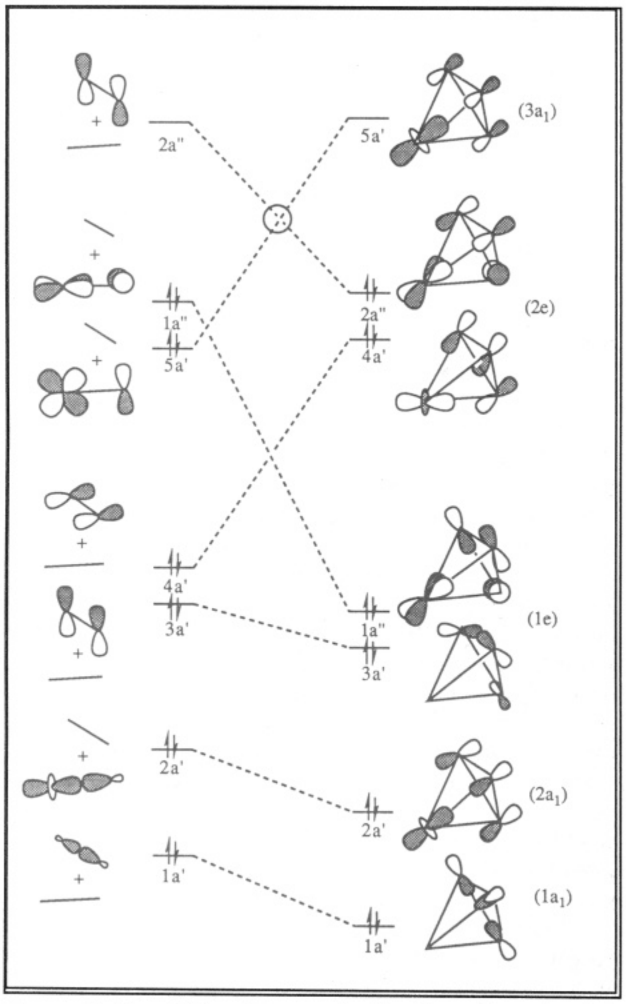
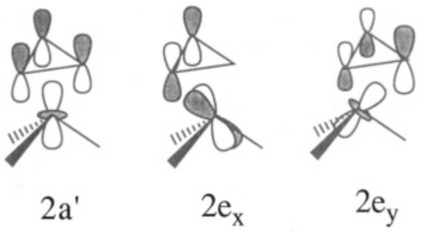


Figure 8. Correlation diagram for the formation of metallatetrahedrane from acetylene and metal carbyne.

bridization in the cyclopropenyl ring in order to avoid this. This effect has been confirmed by the fact that there is a charge transfer from the cyclopropenyl ring to the molybdenum when the ring is forced to be planar.[11a]

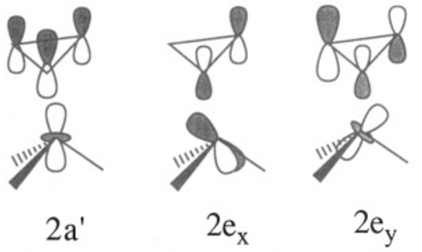
The staggered conformation **10b** of the metallatetrahedrane $Cl_3Mo(\eta^3\text{-}C_3H_3)$ was also optimized and found to be 38.6 kJ mol^{-1} higher in energy than the eclipsed conformation **10a**. This value is consistent with results obtained by Anslyn et al. who studied the same metallatetrahedrane, in the eclipsed and staggered conformations. They determined the eclipsed conformation, **10a**, to be 88 kJ mol^{-1} more stable than the staggered conformation, **10b**. The larger value obtained by Anslyn and Goddard can be accounted for by the fact that no geometry optimizations were performed on either structure and the Cl–Mo–Cl bond angle used for both conformations was closer to the bond angle found in the optimized structure **10a**.[30] The most distinguishable feature of **10b** is the large Cl–Mo–Cl bond angle of 117.6°. This large angle which is very close to 120° reveals that the three chlorines and the molybdenum center are very nearly coplanar. Some other notable features of **10b** are that the Mo–C bond distance is 2.10 Å, which is slightly more than that of the eclipsed formation. Further, the hydrogens are bent out of the plane of the cyclopropenyl ring by only 22.7°, as opposed to 27° in **10a**.

The three frontier orbitals of the trigonal pyramidal Cl_3Mo fragment have optimal interactions, **11a**, with the cyclopropenyl π system in the eclipsed conformation, **10a**.



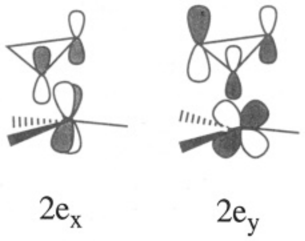
11a

A staggered conformation with the same trigonal pyramidal Cl_3Mo fragment but with the cyclopropenyl ring rotated 180° around the C_3 axis of Cl_3Mo would be sterically more favorable but have weaker interactions in the $2e_x$ and $2e_y$ orbitals, as shown in structure **11b**.



11b

The $2e_x$ and $2e_y$ interactions in the staggered conformation can be enhanced by changing the Cl–Mo–Cl angle from 109 to 120°, **11c**. The change in angle will induce a new hybridization of the two d orbitals which maximizes the $2e_x$ and $2e_y$ interactions in the staggered conformation.



11c

The analysis in **11a**–**11c** provides a rationale for why the sterically more congested eclipsed conformation **10a** is preferred over **10b**. In addition, the same analysis is able to account for the different geometries of the Cl_2Mo fragment in **10a** and **10b**.

Formation of Metallatetrahedrane from Metal Carbyne and Acetylene. Metallatetrahedranes are known to form from metallacyclobutadienes upon addition of donor ligands and from direct addition of acetylene to metal alkylidynes.[6,8,9] We shall in the following study the direct formation of the metallatetrahedrane $Cl_3Mo(\eta^3\text{-}C_3H_3)$, **10a**, in a least motion approach according to eq 6. We shall compare this reaction to the least motion

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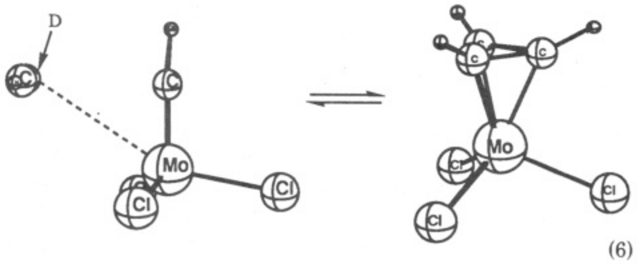
[30] A Cl–Mo–Cl angle of 109° was used for both the staggered and eclipsed conformations.



(6)

perpendicular approach of two acetylene molecules to form tetrahedrane, as in eq 7.

(7)

A correlation diagram for the process in eq 7 is given in Figure 9. The correlation diagram reveals that the occupied $2a_1$ ($\pi + \pi$) orbital of the reactants correlates to an empty product orbital. Similarly, the empty $1b_1$ ($\pi^*_\perp + \pi^*_\perp$) orbital of the reactant correlates to an occupied product orbital, thus making the reaction symmetry forbidden. The skew approach of the acetylenes affords the same basic nodal structure of the orbitals and would also be symmetry forbidden.

A correlation diagram for the formation of metallatetrahedrane according to eq 6 is given in Figure 8. The correlation diagram reveals that the direct formation of metallatetrahedrane by the perpendicular approach of the acetylene is forbidden by orbital symmetry just as the formation of the tetrahedrane is forbidden. The occupied 5a′ orbital which corresponds to a carbyne π bonding orbital correlates to an unoccupied σ^* orbital of the metallatetrahedrane. The empty acetylene π^* orbital of a″ symmetry correlates to an occupied Mo–C σ bonding orbital of the metallatetrahedrane. Consequently, for the metallatetrahedrane to form, the electron pair in the 5a′ orbital of the reactants must at some point during the course of the reaction jump into the 2a″ π^* orbital of acetylene. Since a change in occupancy of the orbitals of different symmetry can only occur when the two orbitals are of equal energy, the formation of the metallatetrahedrane by the perpendicular approach is expected to have at least a modest energy barrier. The magnitude of the energy barrier is dependent on where the crossing occurs. Thus, unlike the formation of the metallacyclobutadiene by the least motion pathway, the formation of the tetrahedrane is formally symmetry forbidden.

We have determined an energy barrier for the symmetry forbidden formation of the metallatetrahedrane as shown in eq 6. In this set of calculations the metallatetrahedrane is formed by the perpendicular approach of the reactants such that there is a preserved plane of symmetry (plane of the paper in eq 6). The distance between the molybdenum atom and the point D, the point colinear with and exactly midway between the two carbons of the acetylene molecule, is used as a reaction coordinate (this is shown in eq 6 as a dotted line). In this way, the molybdenum and point D remain on the preserved C_s plane. For all steps, the Mo–D distance was fixed, while all other degrees of freedom were optimized within the C_s symmetry constraint.

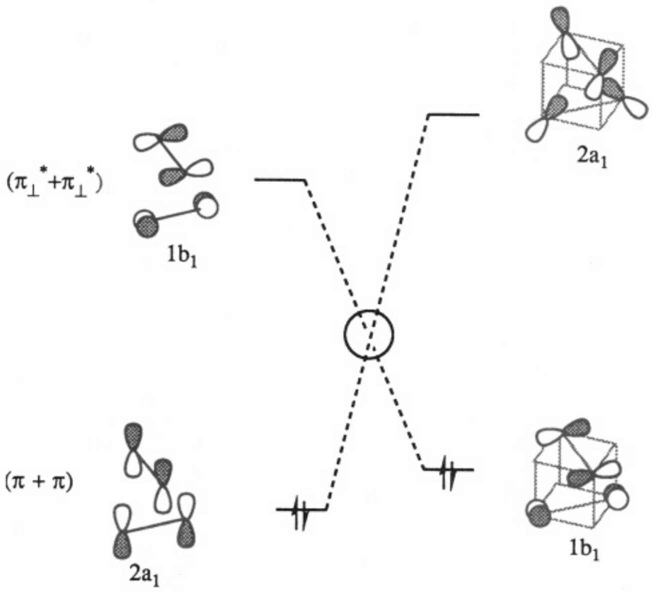


Figure 9. Correlation diagram for the formation of tetrahedrane.

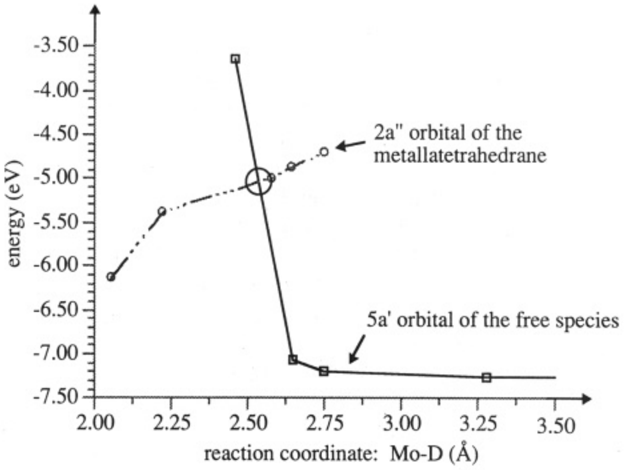


Figure 10. Correlation diagram of the 5a′ and 2a″ orbitals for the formation of metallatetrahedrane.

To represent the crossing that must occur in this forbidden reaction, two sets of calculations were performed, one in the electron configuration of the free species and the other in the electron configuration of the metallatetrahedrane. More specifically, for one set of calculations the metallatetrahedrane was formed by fixing the electron configuration to that of the free species (left side of Figure 8). In this way, the occupied 5a′ orbital of the free species is significantly raised in energy as the Mo–D distance is decreased. In the other set of calculations the metallatetrahedrane was decomposed by fixing its electron configuration to that of the right side of Figure 8. This caused the 2a″ orbital to increase in energy as the Mo–D distance was increased.

The energy of the 5a′ orbital of the free species and the 2a″ orbital of the metallatetrahedrane as the Mo–D distance is varied, as shown in Figure 10. The crossing is circled and occurs at a Mo–D distance of 2.55 Å. The total energy of the complex for both electron configurations relative to the free species is shown in Figure 11. The solid line represents the energy profile for the forbidden reaction. The energy profile traces the total energy of one configuration until the crossing distance of 2.55 Å, at which point it traces the total energy of the other electron configuration.

Figure 11 shows that there is only a modest 40 kJ mol^{-1} electronic barrier for the direct formation of the molyb-

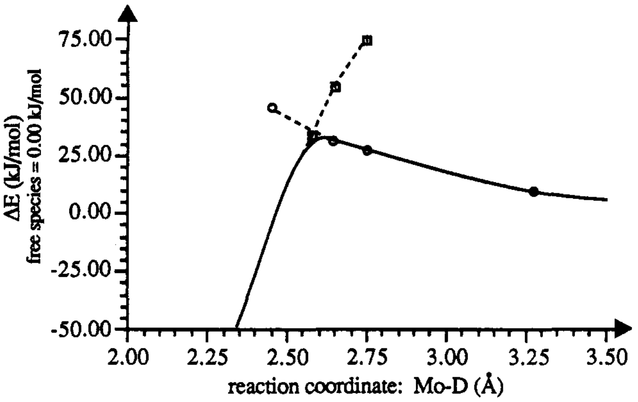


Figure 11. Energy profile for the formation of the metallatetrahedrane: (○) Total energy of the electron configuration of the free species; (▣) total energy of the electron configuration of the metallatetrahedrane.

denum tetrahedrane from the acetylene and molybdenum carbyne. Furthermore, although it is not shown in Figure 11, the metallatetrahedrane is 122 kJ mol^{-1} more stable than the free acetylene and molybdenum carbyne.

Conclusions

A density functional study of acetylene metathesis catalyzed by high oxidation state molybdenum and tungsten alkylidyne complexes was undertaken. In the first part of the study, the feasibility of a dissociative mechanism of metathesis was investigated where a metallacyclobutadiene acts as an intermediate. The geometries, bonding, and energetics of the formation and decomposition of the metallacyclobutadiene, $Cl_3MoC_3H_3$ (**3**), were determined. The formation of the metallacyclobutadiene was found to be fully symmetry allowed and possessed a small 10 kJ mol^{-1} electronic barrier. The formation of the metallacyclobutadiene has a small activation since the π- and π^*-type orbitals can interact throughout the course of the reaction. It was also found that the formation of the metallacyclobutadiene is initiated by the nucleophilic attack of the acetylene on the metal center. The metallacyclobutadiene was determined to be 70 kJ mol^{-1} more stable than the acetylene and molybdenum carbyne reactants, revealing that the rate determining step is the decomposition of the metallacyclobutadiene.

In the second part of this study we investigated the formation of metallatetrahedrane $Cl_3Mo(\eta^3\text{-}C_3H_3)$, **10a**, by the direct addition of the metathesis reactants. The direct formation of metallatetrahedrane was found to be forbidden by orbital symmetry and was determined to possess a 40 kJ mol^{-1} electronic barrier. The metallatetrahedrane, **10a**, was also found to be 52 kJ mol^{-1} more stable than its corresponding metallacyclobutadiene, **3**, and 122 kJ mol^{-1} more stable than the free acetylene and molybdenum carbyne. The modest 40 kJ mol^{-1} reaction barrier for the direct formation of the metallatetrahedrane reveals that the metallatetrahedrane is energetically accessible. It would be interesting to combine molecular mechanics and density functional calculations in an attempt to determine whether more bulky ligands on the metal center can influence the relative stability of metallatetrahedrane and metallacyclobutadiene. A theoretical study[27] of the analogous olefin metathesis reaction has recently appeared.

Acknowledgment. This investigation was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). Access to the IBM-6000 computing facilities at the University of Calgary is acknowledged.

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