

# Structures and Reactivity of Neutral and Cationic Molybdenum Methylidene Complexes

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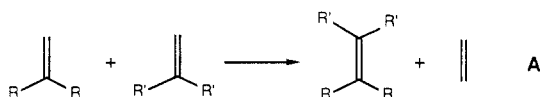
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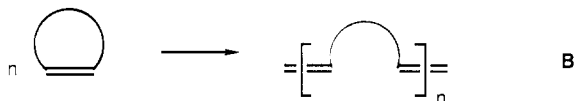
The reactivity of Mo alkylidene complexes with olefins was studied by generalized valence bond ab initio electronic structure calculations. We illustrate an approach using molecular fragments for predicting electronic structures for alkylidene and metallacycle complexes. The analysis is presented with an emphasis on understanding how the bonding influences reactivity. The reaction of the cationic complex  $\text{Cl}_3\text{MoCH}_2^+$  with ethylene was found to be endothermic by 3 kcal/mol. The geometry of the coordination sphere, however, is favorable for metathesis. The reaction of  $\text{Cl}_4\text{MoCH}_2$  with ethylene was found to be exothermic by 11 kcal/mol, but the coordination sphere is sterically crowded.

## I. Introduction

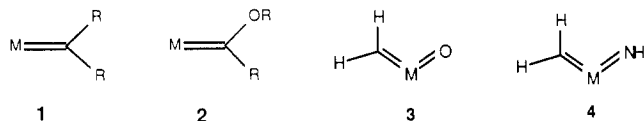
Transition-metal alkylidenes form a versatile set of catalysts with potential to perform both olefin metathesis<sup>1</sup> and ring-opening metathesis polymerizations.<sup>2</sup> Olefin metathesis involves the simultaneous cleavage of two olefin double bonds followed by the formation of alternate double bonds (A).



Ring-opening metathesis polymerization is essentially the same as olefin metathesis, except that the double bond is incorporated in a ring (B).



The carbene catalysts can either be of the alkylidene-type<sup>3</sup> (high-valent,  $d^0$ ) 1, Fischer-type<sup>4</sup> (low-valent,  $d^n$ ) 2, alkylidene-oxo type<sup>5</sup> (high-valent,  $d^0$ ) 3, or alkylidene-imido type<sup>6</sup> (high-valent,  $d^0$ ) 4.



The wide variety of these catalysts emphasize the importance of a metal-carbon double bond for catalytic activity, and yet, the catalytic activity strongly depends upon the metal and its ligands. Several metals spanning the d block elements from Ti to Ir catalyze the metathesis reaction. In fact, ring-opening metathesis polymerization can be catalyzed by the so-called classical systems<sup>7</sup> such as  $\text{RuCl}_2$  and  $\text{OsCl}_3$ . It is proposed that these compounds react with cyclic olefins to form very reactive alkylidenes. These catalysts, however, give high polydispersities<sup>8</sup> due to slow initiation rates relative to propagation rates.

The most effective metathesis catalysts known involve high-valent (generally  $d^0$ ) complexes of groups IVB and VIB. The group IVB catalysts are based on the titanocene metallacyclobutanes developed by Grubbs.<sup>9</sup> These catalysts have been extensively studied mechanistically<sup>10</sup> and theoretically.<sup>11</sup> The group VIB catalysts are based upon

tungsten alkylidenes developed by Osborn<sup>12</sup> and Basset<sup>13</sup> and imido alkylidenes developed by Schrock.<sup>14</sup> Due to their recent development, these catalysts have not been extensively studied either mechanistically or theoretically.

The Osborn catalyst 5 and the Basset catalyst 6 require the labilization of a halide ligand for high catalytic activity.<sup>12,13</sup> This is normally accomplished by the addition of a Lewis acid such as  $\text{AlCl}_3$  or  $\text{GaBr}_3$  (C and D). The essential difference in reactivities between 5 and 7 or 6 and 8 is not completely understood but most likely depends upon the oxidation state of the metal and its coordination environment. The electronics involved in the coordination sphere as well as the coordination geometry are probably responsible for the high activity of 7 and 8. Due to the recent interest in ring opening metathesis polymerizations

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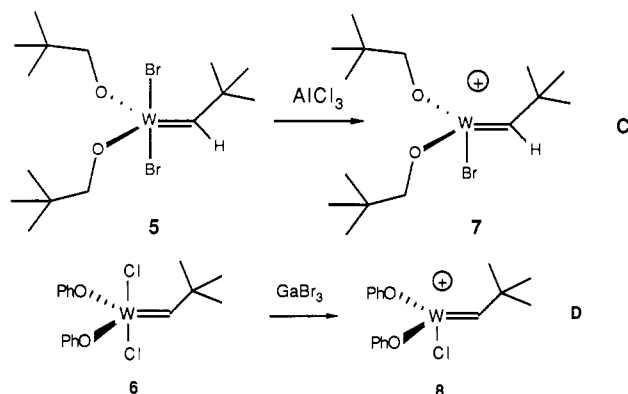
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for making industrially useful polymers (rubbers,<sup>15</sup> block copolymers,<sup>16</sup> conductive polymers<sup>17</sup>), an investigation of the activity of **5** and **7** by ab initio methods was undertaken to determine the essential differences and similarities between them.

Olefin metathesis has been studied previously by the extended Hückel,<sup>18</sup> ab initio Hartree-Fock (HF),<sup>19</sup> and generalized valence bond (GVB) methods.<sup>20</sup> In calculations to model the titanocenemetallacyclobutane catalytic systems, the extended Hückel method found a titanocene methylidene olefin adduct to be substantially more stable than a titanacyclobutane.<sup>18b</sup> Experimentally, however, the ground state for this catalytic system has been shown to be a titanacyclobutane.<sup>9,10</sup> The HF and GVB studies revealed that the reaction of Cl<sub>4</sub>MoCH<sub>2</sub> with ethylene was unfavorable. The reaction was found to be favorable, however, when Cl<sub>2</sub>Mo(O)CH<sub>2</sub> reacts with ethylene. The reactivity reversal was interpreted in terms of an increase in the Mo-O bond order upon formation of the metallacycle. This stabilizing "spectator oxo" effect was also found to play a role in hydrocarbon oxidation by high-valent group VI oxides.<sup>21</sup> In the present study, spectator effects are not involved and, instead, reactivity differences are related to bond strengths and coordination geometries.

## II. Computational Details

**A. Basis Sets and Effective Potentials.** In all the complexes studied, we explicitly considered all electrons for C and H, with ab initio effective potentials used to replace core electrons of Cl and Mo. For Cl, the Ne core was replaced with the SHC effective potential<sup>22</sup> (treating neutral Cl with seven explicit electrons), and for Mo, a relativistic effective potential<sup>23</sup> was used for the Zn core (treating neutral Mo with 12 explicit electrons). All calculations used Cartesian Gaussian basis sets. For carbon,<sup>24</sup> the (9s5p) primitive Gaussian basis was contracted to valence double  $\zeta$  [3s,2p]. For hydrogen,<sup>25</sup> the (3s) primitive basis was scaled ( $\zeta = 1.2$ ) and contracted to (2s). For Mo,<sup>23</sup>

the basis set was contracted to [3s,4p,2d] from the primitive (3s,5p,3d). For Cl,<sup>25</sup> the (3s,2p) primitive basis was contracted to [1s,1p] based on TiCl<sub>4</sub>.

**B. Wave Functions.** Two types of wave functions were utilized. 1. **Hartree-Fock (HF)**.<sup>26</sup> In this wave function, the singlet state has all orbitals doubly occupied and optimized self-consistently. This leads to a good description of bonds involving highly overlapping orbitals but a poor description of bonds involving low overlap, such as Mo-C  $\pi$  bonds (eq 1). 2. **GVB with Perfect-Pairing Restriction (GVBPP)**.<sup>27</sup> In this wave function doubly occupied orbitals of the HF wave function are replaced with correlated pairs of electrons described as a spin singlet state (eq 2). The GVB wave function introduces electron

$$\Psi_{\text{HF}} = (\psi_1\psi_1)(\alpha\beta - \beta\alpha) \quad (1)$$

$$\Psi_{\text{GVB}} = (\psi_r\psi_l + \psi_l\psi_r)(\alpha\beta - \beta\alpha) \quad (2)$$

correlation effects by allowing each electron to have its own orbital, which is then optimized self-consistently. GVB calculations can be carried out such that only a subset of the bond pairs are correlated. Typically, for  $\Delta E$  calculations, the GVB pairs are chosen to be the pairs that change significantly during a reaction sequence and which would otherwise have large correlation errors. To indicate the level of correlation, the GVB wave function is denoted as GVB( $n/m$ ), where  $n$  is the number of electron pairs being correlated and  $m$  is the number of orbitals used for the correlated pairs (generally  $2n$ ). In the energy calculations reported here, all Mo-C and C-C bonds were correlated. In addition, the C-H bonds in the methylidene complexes were correlated during geometry optimization. Thus, for Cl<sub>4</sub>MoCH<sub>2</sub>, Cl<sub>3</sub>MoCH<sub>2</sub><sup>+</sup>, Cl<sub>4</sub>MoC<sub>3</sub>H<sub>6</sub>, and Cl<sub>3</sub>MoC<sub>3</sub>H<sub>6</sub><sup>+</sup>, we correlated four bond pairs during geometry optimization, but for reaction  $\Delta E$ 's only two bond pairs for Cl<sub>4</sub>MoCH<sub>2</sub> and Cl<sub>3</sub>MoCH<sub>2</sub><sup>+</sup> were correlated.

**C. Geometry Optimizations and Energetic Comparisons.** Geometry optimizations were carried out with the GVB GRADIENT<sup>28</sup> program (developed by A. K. Rappé), which uses analytic gradients to optimize geometries for GVB-PP wave functions. All geometries containing Mo were fully optimized. As discussed in detail previously,<sup>29</sup> the following scheme for determining energetics for chemical processes was utilized. Using the GVB-PP method, we calculated the energy differences for reactions where the number and type of bonds are as similar as possible. To calculate enthalpy changes above 0 K for these processes, one must add the differential zero-point corrections to the calculated energy differences. The resulting  $\Delta H_{f,0}$  are combined with previously obtained  $\Delta H_{f,0}$  for the other species in the idealized reactions to calculate  $\Delta H_{f,0}$  for the molecule of interest. These  $\Delta H_{f,0}$  are combined with vibrational frequencies (experimental, calculated, or estimated) and moments of inertia to obtain  $\Delta H_{f,300}$  and  $\Delta S_{300}$ . Finally, the  $\Delta G_{f,300}$  for the reactions are calculated. The program FRCMAN<sup>28</sup> developed by Anthony Rappé was used to calculate these correction factors based on the JANAF Thermodynamic Tables.<sup>30</sup>

To determine the quantitative energy change between the alkylidene complexes and the metallacycle complexes,

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we needed the total energy of ethylene at a comparable geometry optimization level and correlation level. Therefore, ethylene was geometry optimized at the GVB(2/4) level where both the C-C  $\sigma$  and  $\pi$  bonds were correlated. The total energy for ethylene was then added to the total energy of an alkylidene complex. This sum was then compared with the corresponding metallacycle total energy to determine the free energy of reaction. The metallacycle complex and the corresponding alkylidene complex were correlated at comparable levels. Thus, if the alkylidene complex was described with GVB( $x/y$ ) and ethylene with GVB(2/4), then the metallacycle was always correlated at the GVB( $x+2, y+4$ ) level. This allows for a consistent energy evaluation between the alkylidene plus ethylene and the metallacycle. Thus, for  $\text{Cl}_4\text{MoCH}_2$  and  $\text{Cl}_3\text{MoCH}_2^+$ , we correlated two bond pairs (the Mo-C  $\sigma$  and Mo-C  $\pi$  bonds). For  $\text{Cl}_4\text{MoC}_3\text{H}_6$  and  $\text{Cl}_3\text{MoC}_3\text{H}_6^+$ , we correlated four bond pairs (the Mo-C  $\sigma$  and C-C  $\sigma$  bonds).

**D. Structural Simplifications.** Several simplifications of the experimental catalysts were made for calculational convenience. The studies presented are meant to probe the energetics of the bond-breaking and bond-forming reactions and are not meant to model the large steric interactions in the experimental catalysts. Therefore, the Osborn and Basset catalysts 5 and 6 are modeled by 9, and the cationic complexes 7 and 8 are modeled by 10. The alkyl groups are replaced by hydrogen, and the alkoxide or bromide ligands are replaced by chlorine. Mo was used in place of W for calculational convenience. It was felt that the close correspondence in the reactivities and structures of W and Mo alkylidenes<sup>31</sup> implied that this substitution would not significantly effect the reactivity trends calculated. Furthermore, the covalent and ionic radii for Mo and W are similar.<sup>32</sup>

### III. Results and Discussion

First, the GVB description of the bonding and charge distribution in the  $\text{H}_2\text{CMoCl}_4$  (9) complex will be contrasted with the  $\text{H}_2\text{CMoCl}_3^+$  (10) cationic complex. We find that the charge distribution and the coordination sphere of these two complexes control their relative reactivity toward ethylene and make the cationic complex  $\text{H}_2\text{CMoCl}_3^+$  more reactive kinetically, even though the reaction is more exothermic for  $\text{H}_2\text{CMoCl}_4$ . The discussions are presented with an emphasis on understanding the bonding and its relationship to reactivity.

**A. Bonding in  $\text{H}_2\text{CMoCl}_4$  and  $\text{H}_2\text{CMoCl}_3^+$  and the Corresponding Metallacycles  $\text{H}_6\text{C}_3\text{MoCl}_4$  and  $\text{H}_6\text{C}_3\text{MoCl}_3^+$ .** The goal of this study is to extract a quantitative and conceptual understanding of the bonding in 9 and 10 and a quantitative understanding of their reactivity with olefins. Thus, the geometries of 9 and 10 were fully optimized at the GVB(4/8) perfect-pairing level where both the C-H and the Mo-C bonds were correlated. The corresponding metallacycles 11 and 12 were also optimized at the GVB(4/8) perfect pairing level where both the C-Mo and the C-C bonds were correlated.

The fully optimized structures are presented schematically in Figure 1. Complexes 9 and 10 are models of the Osborn<sup>11</sup> and Basset<sup>13</sup> catalytic systems based on 5 and 6. For the alkylidenes (9 and 10) and metallacycles (11 and 12), the systems were constrained to have  $C_s$  symmetry.

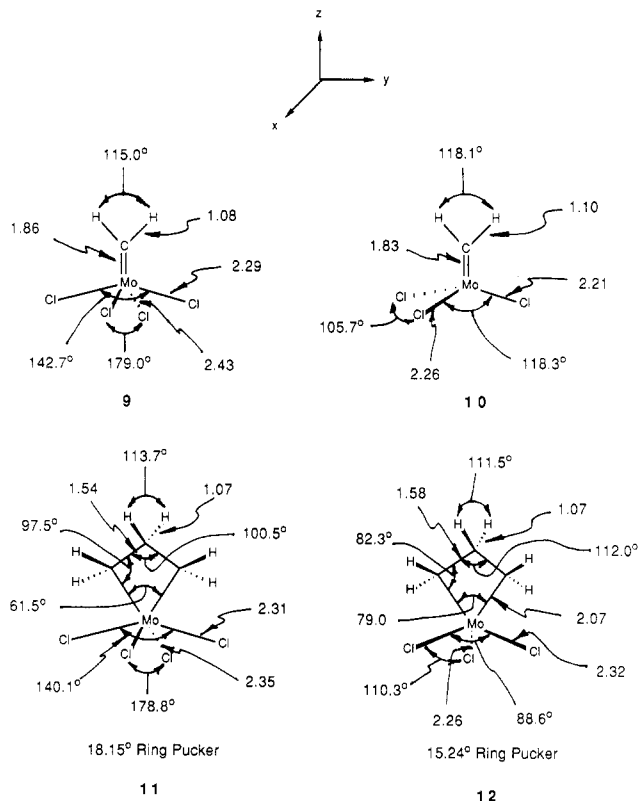


Figure 1. Fully optimized structures (bond lengths in angstroms).

This forced both the Mo-C and the C-C bonds of the metallacycle geometries to be identical across the  $xz$  plane in Figure 1. This constraint of  $C_s$  symmetry did not force the metallacycle ring to be planar and, in fact, both geometries displayed a puckered four-membered ring.

Comparisons of the geometries of 9 with 10 and 11 with 12 revealed that all the Mo-C and Mo-Cl bonds are significantly shorter in the cationic complexes. The Mo-C  $\sigma$  bonds are 0.24 Å shorter in the 12 than in the 11, while the Mo-Cl  $\sigma$  bonds are on an average 0.06 Å shorter in 12 than in 11. A similar trend is also observed in the methylidene complexes 9 and 10. In 10, however, the Mo-C double bond is only 0.03 Å shorter, while the Mo-Cl bond is 0.12 Å shorter than in 9. These shorter bonds are due to the ligands being drawn closer to the Mo in the cationic metallacycle and alkylidene due to their higher electrophilicity.

The metallacycles 11 and 12 are puckered by 15.24° and 18.15°, respectively. The puckering in the cationic complex is larger due to less steric interaction with the chlorines. Metallacycle ring puckering has been invoked to explain the stereochemistry of olefin metathesis.<sup>33</sup>

As a starting point for examining the bonding in the methylidene complexes and the metallacycle complexes, we chose to study the molybdenum chloride fragments. The spatial arrangement of the singly occupied orbitals of the triplet states of the molybdenum chloride fragments will dictate the lowest energy geometry of the alkylidenes and metallacycles. In  $\text{MoCl}_4$  and  $\text{MoCl}_3^+$ , four or three electrons on Mo, respectively, are used for partially ionic bonds to the chloride ligands. The chlorines remove  $s$  electron density from the metal due to the high electronegativity of the chlorines. The  $s$  electrons, not the  $d$  electrons, are preferentially removed due to their lower

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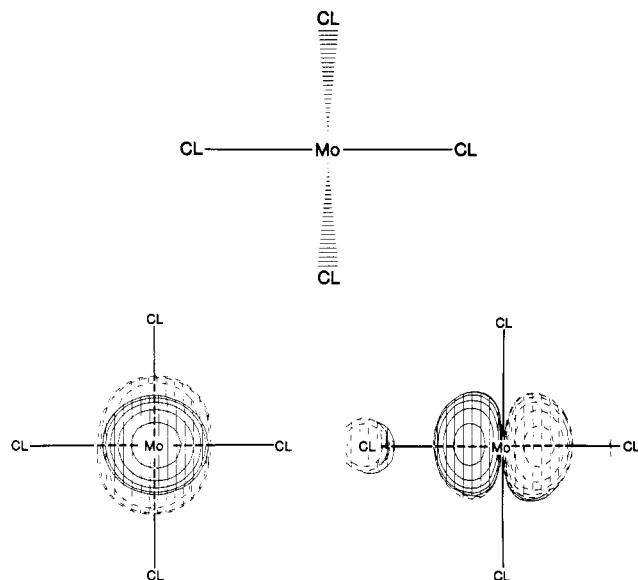


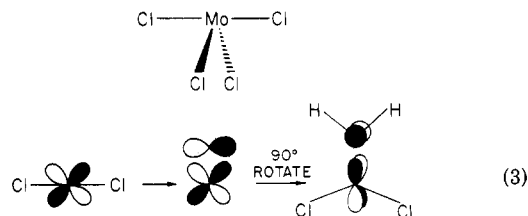
Figure 2. High-spin orbitals for the triplet state of  $\text{MoCl}_4$ .

ionization potential. This leaves two electrons on the Mo for bonding to the other ligands. There is the choice of  $d\sigma$ ,  $d\pi_y$ ,  $d\pi_x$ ,  $d\delta_{x^2-y^2}$ , and  $d\delta_{xy}$ .

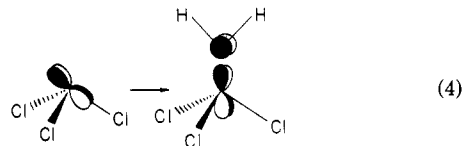
To determine which orbitals are used to bond to  $\text{CH}_2$ , the triplet states of  $\text{MoCl}_3^+$  and  $\text{MoCl}_4$  were calculated. For  $\text{MoCl}_4$ , trans chlorine angles of  $180^\circ$  and  $140^\circ$  were used since these correspond to the Cl-Mo-Cl angles in the final geometry 9. The high-spin orbitals are displayed in Figure 2. They are essentially pure Mo  $d\sigma$  and Mo  $d\pi$  orbitals.

In order for the high-spin orbitals to be orthogonal to the Mo-Cl bonds, one would predict that the lowest energy configuration would be the one in which the Mo-Cl bonds lie along the nodal planes of the singly occupied orbitals. In other words, the placement of the Mo-Cl bonds and the singly occupied orbitals are interrelated with both the singly occupied orbitals and the Mo-Cl bonding orbitals preferring to lie in each others angular nodes. The calculated configurations of the singly occupied orbitals are exactly those predicted by this reasoning. The chlorines at  $180^\circ$  from one another have their Mo-Cl bonds along a  $d\pi$  orbital angular node. This allows the Mo-Cl bonds to remain orthogonal to the high-spin  $d\pi$  orbital. The chlorines at  $140^\circ$  from one another have their Mo-Cl bonds along a  $d\pi$  orbital angular node also, but in addition, these Mo-Cl bonds lie in an angular node of the  $d\sigma$  orbital. The angular node in the  $d\sigma$  orbital dictates a bent Cl-Mo-Cl angle. When the high-spin  $^3B_2$  state<sup>34</sup> of  $\text{CH}_2$  bonds to  $\text{MoCl}_4$ , the high-spin orbitals of the  $\text{MoCl}_4$  fragment dictate that the H-C bonds are eclipsed with the chlorines that are  $140^\circ$  from one another (eq 3). Thus, the bending of the chlorines away from the alkylidene substituents in the  $yz$  plane (Figure 1) is not due to sterics between R groups on the alkylidene carbon and the chlorines but instead is rooted in the electronics of the  $\text{MoCl}_4$  fragment. In fact, we find the barrier to rotation of the methylene group to be 9 kcal/mol, favoring the predicted geometry (eq 3). This bonding arrangement yields three empty low-lying orbitals that are slightly antibonding with respect to the Mo-Cl bonds. The orbitals are basically Mo  $d\pi_y$ ,  $d\delta_{x^2-y^2}$ , and  $d\delta_{xy}$  in character.

To further develop the fragmental approach to predicting the lowest energy geometry of the alkylidenes, we



calculated the triplet state of  $\text{MoCl}_3^+$ . As previously shown, the high-spin orbitals of the quartet  $\text{MoCl}_3$  fragment also lie along the Mo-Cl bond's angular nodes.<sup>35</sup> Similarly, in triplet  $\text{MoCl}_3^+$ , the high-spin orbitals are  $d\sigma$  and  $d\pi + d\delta$  in character and lie along the Mo-Cl angular nodes. This consequently places the  $d\pi + d\delta$  orbital tilting over two Cl's (eq 4). Thus, this dictates that the  $\text{CH}_2$



group would bond with the plane formed by  $\text{CH}_2$  in the same plane as a Mo-Cl bond. There is a second degenerate  $d\pi$  orbital on Mo that the  $\text{CH}_2$  fragment could use to form a  $\pi$  bond. This orbital is rotated  $90^\circ$  from the  $d\pi$  orbital shown.<sup>35</sup> The geometry shown in eq 4, however, is the one that leads to the lowest energy metallacycle (vide infra).

The contour plots of the GVB orbitals of the methylidene complex 10 are presented in Figure 3. As discussed in the calculational details, each GVB orbital has one electron, but the two orbitals of a pair are allowed to overlap. The contour plots of the GVB orbitals of 9 appear approximately the same as those for 10.

As indicated in Figure 3, the methylidene complexes have covalent Mo-C  $\sigma$  and  $\pi$  bonds. The orbitals are typical for Mo-C double bonds and consist of a  $d\pi$  and  $d\sigma$  orbital on the Mo and a p and  $sp^2$  orbital on the carbon. The C-H bonds are also as expected. In the geometry optimization of 9 and 10, the Mo-C-H angles were allowed to vary freely, and thus any unusually small angles denoting an agostic interaction would have been allowed and detected. High-valent alkylidene complexes with electron counts of 10-14 electrons have been found to display agostic bonds.<sup>36</sup> Our calculations, however, do not support these bonds in complexes such as 9 and 10.

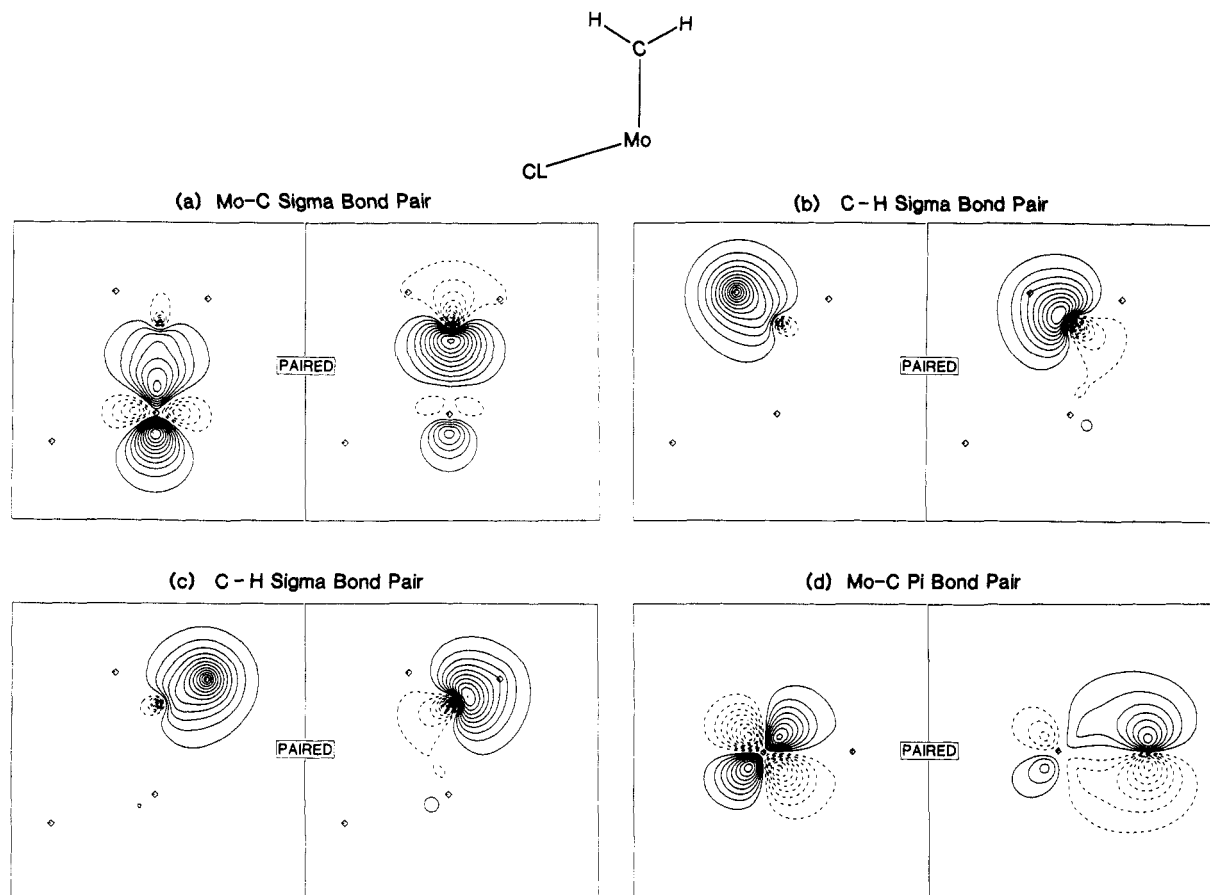
The lowest energy geometry of the metallacycles can also be predicted by examination of the Mo-C and Mo-Cl nodal planes. In addition, the lowest energy configuration of the  $\text{C}_3\text{H}_6$  fragment with respect to the Mo-Cl bonds can be predicted from the  $2 + 2$  reaction with ethylene without relaxation of the Mo-Cl bonds. The position of the Mo-Cl bonds with respect to the Mo-C bonds can then be adjusted by including steric effects. The steric interactions in the metallacycles are more pronounced than in the methylidenes due to the increase in coordination number.

The contour plots of the GVB orbitals of the metallacycles 11 and 12 are presented in Figure 4. The  $\text{C}_3\text{H}_6$  framework has central angles of  $100.5^\circ$  and  $112.0^\circ$  in 11 and 12, respectively, and the C-C bond pairs are unstrained and well directed along the bond axis. Only the C-C contour plots for 12 are displayed since those for 11 appear almost identical (Figure 4c,d). The carbon-centered Mo-C GVB pair orbitals have high p character (Figure

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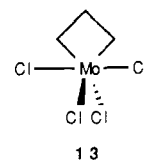
**Figure 3.** Contour plots of the GVB orbitals for  $\text{Cl}_3\text{MoCH}_2^+$ . Spacing between contours is 0.05 au; solid lines are positive and dashed lines are negative. Part d is plotted in a plane formed from a  $90^\circ$  rotation along the Mo-C bond vector.

4a,b,e,f). This is a reflection of the high positive charge on Mo due to the cationic charge of 12 or the influence of four electron-withdrawing chlorines on 11. The Mo consequently acts very electronegative. The C-Mo-C angles are  $61.5^\circ$  and  $79^\circ$  in 11 and 12, respectively. The much smaller angle of 11 relative to that of 12 is due to the much longer Mo-C bond distance in 11. In 11, the GVB orbitals that are centered on Mo are  $d\sigma$  in character and are directed  $4^\circ$  off of the Mo-C vector. The two d orbitals on Mo that bond to the carbons are  $55^\circ$  from one another. Rappé and Goddard<sup>37</sup> showed that for two pure d orbitals to be symmetric about their respective bond axes, they must be separated by either  $54.7^\circ$  or  $125.3^\circ$ . Therefore, 11 makes covalent  $\sigma$  bonds to the carbons at precisely the expected angle. On the other hand, electron repulsion effects favor a  $d\sigma$ ,  $d\delta$  ground-state configuration that favors a  $90^\circ$  bond angle. The competition between these effects usually results in metallacycles with a C-M-C angle between  $70^\circ$  and  $80^\circ$ .

The small C-Mo-C angle in  $\text{Cl}_4\text{MoC}_3\text{H}_6$  is due to the necessity of making four coplanar bonds to Mo. The metal must form two covalent bonds to C and two ionic bonds to Cl. There are only three d orbitals with density in the  $yz$  plane, and they are  $d\sigma$ ,  $d\pi_{yz}$ , and  $d\delta_{x^2-y^2}$  in character. If a linear combination of these  $d\pi$  and  $d\delta$  orbitals is taken, two additional  $d\sigma$  character orbitals are formed in the  $yz$  plane. All three  $d\sigma$  orbitals are shown in Figure 5.

These orbitals are the ones previously shown by Rappé and Goddard to be  $54.7^\circ$  from one another.<sup>37</sup> If two of these  $d\sigma$  orbitals (Figure 5a,b) are used to form the Mo-C

$\sigma$  bonds in 11, then the d orbital left over for bonding to the Cl's is c in Figure 5. This orbital mixes in s character and would tend to form two Mo-Cl bonds at an angle of  $180^\circ$  to each other. The optimized geometry, however, has a bond angle of  $140.1^\circ$ , and therefore these Mo-Cl bonds are slightly strained. A recalculation of the wave function with these Cl's at an angle of  $180^\circ$  (13) was performed on the  $\text{Cl}_4\text{MoC}_3\text{H}_6$  geometry. It was found to be 40 kcal/mol higher in energy than 11.

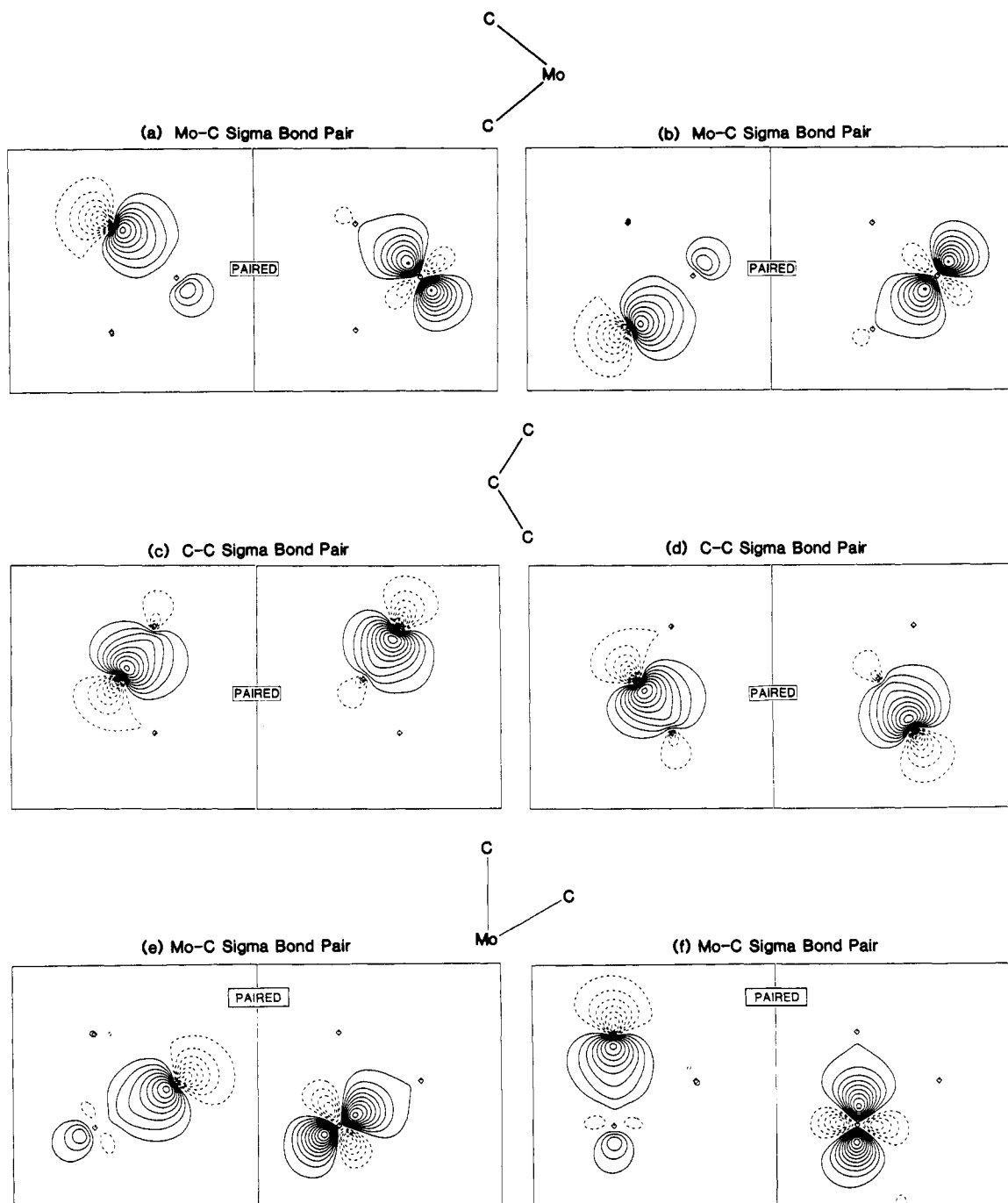


Complex 13 possesses the geometry predicted by a  $2 + 2$  reaction of 9 with ethylene if the chlorines did not change position. In addition, as just discussed, this geometry would be predicted by the angle that the d orbital (Figure 5c) makes with respect to the Mo-C bonds. This analysis, however, does not include the steric interaction between the coplanar chlorines and carbons. This steric interaction forces the Cl-Mo-Cl angle to be smaller than predicted and introduces strain into the Mo-Cl bonds.

Therefore, the small C-Mo-C bond angle of  $61^\circ$  is due to the constraint of forming four bonds from Mo to coplanar ligands. Since two of these bonds are to chlorine (which withdraws s electron density), the remaining bonds to C are forced to be high in d character and prefer an angle of  $54^\circ$ .

Complex 12, however, has a much wider C-Mo-C angle of  $79^\circ$ . This is due to the much shorter Mo-C bond distances. The two  $d\sigma$  orbitals that bond to the two carbons

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**Figure 4.** Contour plots of the GVB orbitals for  $\text{Cl}_3\text{MoC}_3\text{H}_6^+$  and  $\text{Cl}_4\text{MoC}_3\text{H}_6$ . Parts a, b, c, and d are for 12 and parts e and f are for 11. The C-C contour plots for 11 are not shown since they are almost identical with those for 12.

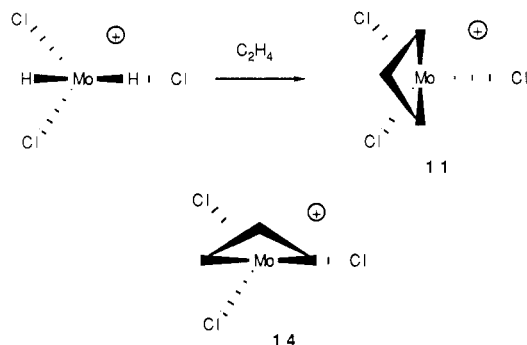
are at an angle of  $99^\circ$ . These orbitals are  $10^\circ$  off the Mo-C bond vectors (Figure 4a,b). The Mo in 12 is not as constrained to use pure d orbitals to bond to the carbons since the Mo only has to form the one Mo-Cl bonds in the same plane. Hence, the  $d\sigma$  orbitals have more s character because they do not have to compete with two Cl's in the same plane. This allows the orbital angle to open up to form the Mo-C bonds. Thus, the Mo-C bond distance is shorter in  $\text{Cl}_3\text{MoC}_3\text{H}_6^+$  than in  $\text{Cl}_4\text{MoC}_3\text{H}_6$  for two reasons. The first is the larger positive charge on Mo which draws the carbons closer in the cationic complex, and second, the Mo uses hybrids with more s character. In Table I, we tabulate the GVB bond overlaps for the complexes studied. The Mo-C  $\sigma$  bond overlaps for both 11 and 12 are the same. Thus these bonds are energetically similar.

The lowest energy configuration of the  $\text{C}_3\text{H}_6$  fragment with respect to the  $\text{MoCl}_3^+$  fragment can be predicted to

**Table I. GVB Bond Overlaps**

complex	bond	overlap
$\text{Cl}_4\text{MoCH}_2$	Mo-C $\sigma$	0.75
9	Mo-C $\pi$	0.52
$\text{Cl}_3\text{MoCH}_2^+$	Mo-C $\sigma$	0.76
10	Mo-C $\pi$	0.55
$\text{Cl}_4\text{MoC}_3\text{H}_6$	Mo-C $\sigma$	0.55
11	C-C $\sigma$	0.83
$\text{Cl}_3\text{MoC}_3\text{H}_6^+$	Mo-C $\sigma$	0.55
12	C-C $\sigma$	0.83

be the one formed by the 2 + 2 reaction of 10 with ethylene. This reaction forms a metallacycle with the  $\text{C}_3\text{H}_6$  fragment bisecting the Mo-Cl bonds (eq 5). The Mo-C bonds are neither eclipsed nor staggered with the Mo-Cl bonds. We find geometry 11 to be 27 kcal/mol lower in energy than the geometry with a Mo-C and Mo-Cl bond eclipsed, 14.



**B. Charge Distribution.** The Mulliken populations for compounds studied are shown in Figure 6. The charge distributions between the Mo and C atoms represent covalent interactions. The negative charges on the carbons are due to the positive charges on the hydrogens and are not due to electron withdrawal from the Mo. These covalent interactions are also supported by the GVB contour plots of the Mo-C bonds of all the complexes studied. There is no large charge polarization toward C in these contour plots. In the cation 12, the charge on Mo is +0.21 higher than in 11. The charge on Mo in the cation 10 is +0.23 higher than in 9. Thus in both geometries 10 and 12, the full positive charge is not completely isolated on the Mo center but is distributed among the chlorines and carbons. The chlorines are not as negatively charged in the cations since an s electron has been already removed due to the positive charge.

**C. Reactivity.** The 2 + 2 reaction of metal alkylidenes with ethylene was studied. This is the first step in the well-accepted Herrison-Chauvin mechanism for olefin metathesis.<sup>38</sup> The first catalyst studied was  $\text{Cl}_4\text{MoCH}_2$  (9). As indicated in Figure 7, this reaction is favorable, with  $\Delta G_{300} = -11$  kcal/mol.<sup>39</sup> The bonding in the metallacycle is strong enough to compensate for the loss of the  $\pi$  bonding in the metallacycle and the olefin. The analogous reaction for the cationic complex  $\text{Cl}_3\text{MoCH}_2^+$  was found to be unfavorable, with  $\Delta G_{300} = +3$  kcal/mol. In this case, the bonding in the metallacycle is not strong enough to compensate for the loss of the  $\pi$  bonding. The reactivity reversal is due to the stronger  $\pi$  bond in 10 than in 9. The  $\pi$  bond is stronger in the cationic complex due to the shorter Mo-C bond distance. The  $\pi$  bond overlap increases at a greater rate than  $\sigma$  bond overlap as the Mo-C bond distance decreases. In Table I, the GVB bond overlaps for 9 and 10 are tabulated. The overlap is 0.05 greater in 10 than in 9.

To further investigate the relative Mo-C double bond strengths in 9 and 10, the snap bond energies of the Mo-C double bonds were calculated. Snap-bond energies represent the energy of homolytic bond cleavage without allowing the detached molecular fragments to relax. The Mo-C double snap-bond strengths in 9 and 10 were found to be 53.8 and 75.2 kcal/mol, respectively. The bond strength of 10 is 21.4 kcal/mol greater than that in 9. This difference is similar to the 14 kcal/mol difference in free energies of reaction of 9 and 10 with ethylene. Therefore, the stronger Mo-C double bond of 10 considerably raises the energy of reaction of 10 with ethylene versus the same

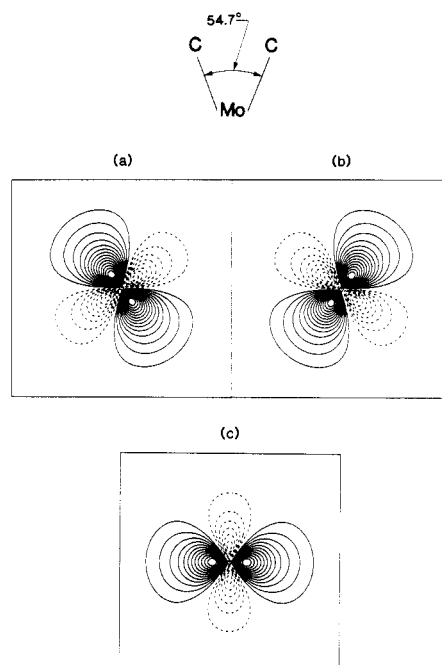


Figure 5. Three coplanar  $d\sigma$  orbitals at  $54.7^\circ$  from one another.

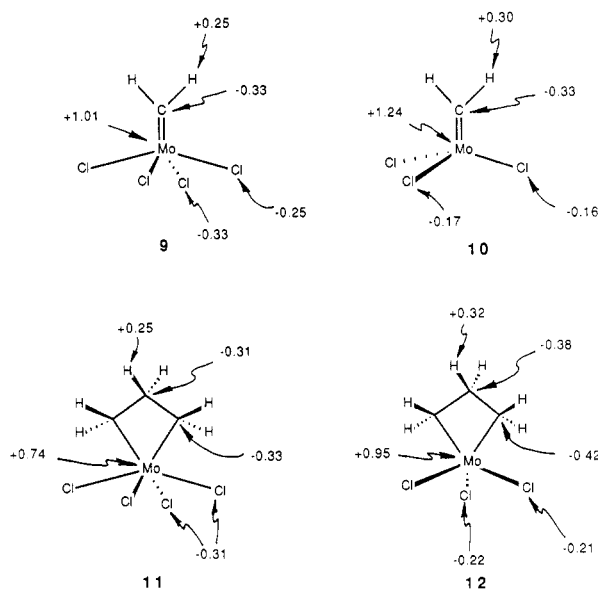


Figure 6. Mulliken populations.

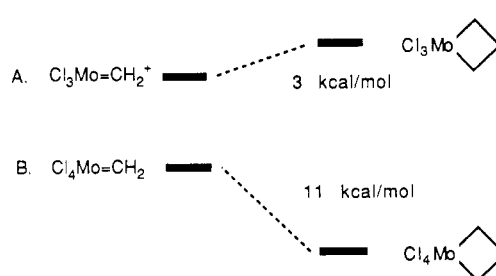


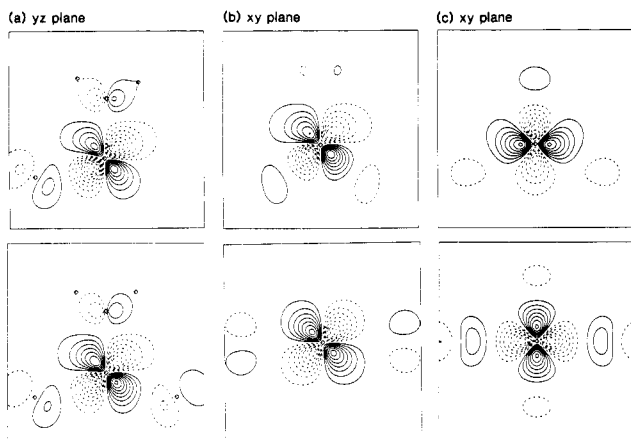
Figure 7. Schematic reaction coordinates for the metallacycle formation reactions.

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(39) This reaction has been previously found to be endothermic by +15 kcal/mol.<sup>19</sup> The discrepancy between the two results is probably due to different levels of electron correlation and the fact that complexes 10 and 15 are fully geometry optimized.

reaction for 9. Thus, the concept of the greater electrophilicity making 10 more reactive than 9 is only partially correct. The greater electrophilicity makes the Mo-C  $\pi$  bond stronger. The  $\sigma$  bond strength in 11 and 12 remains roughly the same since their overlaps are not significantly different (Table I). Consequently, the reactivity difference





**Figure 8.** Empty orbitals centered on Mo for  $\text{Cl}_3\text{MoCH}_2^+$  and  $\text{Cl}_4\text{MoCH}_2$ . The top row shows the empty orbitals for  $\text{Cl}_3\text{MoCH}_2^+$ , and the bottom row indicates the empty orbitals for  $\text{Cl}_4\text{MoCH}_2$ . The planes referred to are those given in Figure 1. Productive coordination would be along the horizontal axis in part c for both 9 and 10.

that favors 10 must be based on a kinetic preference. To probe the kinetic difference between the complexes, a calculation was performed to find the empty orbitals available for coordination of an olefin.

The empty orbitals for both 9 and 10 are shown in Figure 8. There are three empty orbitals as previously discussed for the  $\text{MoCl}_3^+$  and  $\text{MoCl}_4$  fragments (Figure 3). These orbitals are in the  $yz$  and  $xy$  planes. These orbitals can allow for olefin coordination along three different directions in both 9 and 10. The only productive coordination is along the  $+x$  or  $-x$  axis (Figure 8c). This coordination would lead to metallacycle formation.

In  $\text{Cl}_4\text{MoCH}_2$ , however, the empty orbital along the  $+x$  and  $-x$  direction is blocked by the trans chlorines which are  $180^\circ$  from one another. Therefore, olefin coordination along this axis is sterically encumbered and the reaction is predicted to be energetically unfeasible. In  $\text{Cl}_3\text{MoCH}_2^+$ , however, the coordination sites along the  $x$  and  $-x$  directions are open due to the wide  $\text{Cl-Mo-Cl}$  angle of  $118.3^\circ$ . This allows for olefin coordination and subsequent reaction. The reaction free energy of  $+3$  kcal/mol confirms that this reaction is feasible. In addition, due to the greater electrophilicity of the cationic  $\text{Cl}_3\text{MoCH}_2^+$  complex, the donor-acceptor olefin-methylidene complex should be lower in energy than the analogous olefin complex with  $\text{Cl}_4\text{MoCH}_2$ , further lowering the kinetic barrier to reaction. The reactivity difference between 9 and 10 lies primarily in the open coordination site in 10 and not solely in the greater electrophilicity of 10.

**D. Implications for Chemistry.** Several predictions can be formulated on the basis of the work presented. In the reaction between cationic molybdenum alkylidenes and alkenes, there are two opposing effects. When the electrophilicity of the molybdenum center increases, so does the  $\text{Mo-C}$  double-bond strength. This increased bond strength stabilizes the ground state and thus lowers reactivity. The greater electrophilicity, however, also stabilizes the transition state by increasing the donor-acceptor interaction in a hypothetical alkene-molybdenum alkylidene adduct. This would increase the reactivity of the molybdenum alkylidene with alkenes. An increased acceptor capability of the empty orbitals of the metal alkylidene promoting olefin metathesis has been predicted theoretically<sup>40</sup> and experimentally<sup>41</sup> for titanocene systems.

In the titanocene metallacyclobutanes, however, electron-withdrawing ligands were found to stabilize the ground state more than the transition state.<sup>41</sup>

In alkoxy molybdenum imido alkylidene complexes, electron-withdrawing alkoxides dramatically increase the reactivity.<sup>42</sup> Our calculations show that the increased electrophilicity at molybdenum should increase the  $\text{Mo-C}$  double bond strength and increase the thermodynamic barrier by stabilizing the ground state. Thus, in the alkoxy molybdenum imido alkylidene complexes, an increased electrophilicity at molybdenum must also stabilize the transition state (olefin complex) and make the reaction favorable kinetically.

In the future design of olefin metathesis catalysts, several features should be considered. If the chain-propagating species is a metallacycle, then electron-withdrawing groups should stabilize the transient metal alkylidene-olefin complex. If the chain-propagating species is a metal alkylidene, then electron-withdrawing groups should also stabilize both the metal alkylidene and the transient metal alkylidene-olefin complex. By inspection of the literature,<sup>12-14,40-42</sup> it appears that the predominant stabilization occurs in the metal alkylidene-olefin complex and not in the metal alkylidene complex. Therefore, the placement of electron-withdrawing ligands on the metal center should promote metathesis kinetically even though the thermodynamics of the reaction becomes more endothermic.

An increase in the reactivity of the catalyst is not necessarily desired for ring-opening metathesis polymerization of strained cyclic alkenes. Increased reactivity usually results in an increase in the atactic nature of the polymer and decreased preference for syn or anti addition. Furthermore, increased reactivity also usually results in high polydispersities.<sup>43</sup> The high polydispersities result from slow initiation rates compared with propagation rates<sup>44</sup> and increased chain transfer. The high reactivity of the electrophilic catalysts is usually tempered with large bulky alkoxide ligands. These ligands play two different roles. First, they increase a preference for syn or anti addition, and second, they hinder typical deactivation pathways such as catalyst oligomerization. Thus, one must balance an increase in electrophilicity of the metal center with increased steric hindrance to gain both fast turnover rates and selectivity.

#### IV. Summary

The geometry of bonding of triplet methylene to  $\text{MoCl}_3^+$  and  $\text{MoCl}_4$  is dictated by the geometry of the high-spin orbitals of  $\text{MoCl}_3^+$  and  $\text{MoCl}_4$ . The lowest energy configuration for the high-spin orbitals of the  $\text{MoCl}_3^+$  and  $\text{MoCl}_4$  fragments occurs when the angular nodes of the high-spin orbitals are placed along the  $\text{Mo-Cl}$  bonds. The bonds from Mo to C are essentially covalent, whereas those to Cl are polarized toward the Cl's and are of high  $s$  character on the Mo. The  $d$  orbitals not used to make bonds to the carbons are empty and are slightly antibonding with respect to the  $\text{Mo-Cl}$  bonds. These empty orbitals dictate the direction of coordination of olefins.

The metallacycle  $\text{C}_3\text{H}_6\text{MoCl}_4$  has an unusually small  $\text{C-Mo-C}$  bond angle and a long  $\text{Mo-C}$  bond length of  $2.31$  Å. The small angle is due to the necessity of making four coplanar bonds to Mo. Two of these bonds are to chlorine and are high in  $s$  character. Thus, the bonds to carbon are

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higher in d character than usual. This high d character induces a bond angle close to  $55^\circ$ , as previously shown by Rappé and Goddard.<sup>34</sup>

The reactivity of  $\text{Cl}_3\text{MoCH}_2^+$  with ethylene was found to be endothermic by 3 kcal/mol, but the empty d orbitals on Mo facilitate olefin coordination and metathesis. Conversely, the reaction of  $\text{Cl}_4\text{MoCH}_2$  with ethylene was found to be exothermic by 11 kcal/mol. The empty orbitals on Mo, however, are all blocked by the chlorine ligands, and thus coordination of an olefin is sterically encumbered. The thermodynamics of the reaction of

$\text{Cl}_3\text{MoCH}_2^+$  are less favorable than those of the reaction of  $\text{Cl}_4\text{MoCH}_2$  due to the stronger Mo-C bond strength in  $\text{Cl}_3\text{MoCH}_2^+$ .

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**Registry No.** 9, 119970-63-7; 10, 119970-64-8; 11, 83762-89-4; 12, 119970-65-9.

## Hydrogen Atom Transfer between $\mu_2$ -Ethyldiyne Radicals Generated by Electron Transfer: A Novel Disproportionation of a $\mu_2$ -Ethyldiyne Group to $\mu_2$ -Vinylidene and $\mu_2$ -Ethyldiene

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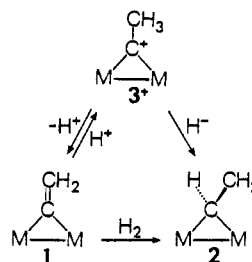
Received December 30, 1988

The bridging ethyldiyne complexes  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_3(\mu\text{-CCH}_3)]^+$  ( $4^+$ -M, M = Fe, Ru) are reduced electrochemically, or by cobaltocene, in one-electron, chemically irreversible electron-transfer reactions. The initially formed neutral  $\mu_2$ -ethyldiyne radicals undergo rapid decomposition reactions to provide mixtures of bridging vinylidene and ethyldiene complexes in good yields. The ratio of ethyldiene to vinylidene product yields is highest at high substrate concentrations. The decomposition of the radicals is proposed to take place via competing hydrogen atom loss to the medium and intermolecular hydrogen atom transfer processes between the radicals in a fashion reminiscent of the disproportionation of caged organic radicals.

### Introduction

During the last few years, the chemistry of dinuclear hydrocarbyl-bridged transition-metal complexes has received considerable attention.<sup>2,3</sup> Strong impetus for the study of such systems has come from the prospect that they may serve as models for species adsorbed on the surface of heterogeneous catalysts. The recent observation that, on a modified Ru(001) surface,  $\pi$ -bonded ethylene is converted to ethyldiyne which subsequently undergoes dehydrogenation to give surface-bonded vinylidene<sup>4</sup> has brought renewed actuality to the study of such model systems and also provides some support for the surface-cluster analogy.<sup>5</sup>

Scheme I



Some widely employed methods for achieving interconversions between  $\mu_2$ -vinylidene (1),  $\mu_2$ -ethyldiene (2), and cationic  $\mu_2$ -ethyldiyne ( $3^+$ ) complexes using stoichiometric reagents are depicted in Scheme I. Protonation of 1 yields  $3^+$ <sup>6</sup> in a reaction that may be reversed by the addition of a base (however, protonation may also take place at the  $\alpha$ -carbon to yield  $\mu_2$ -vinyl complexes<sup>7</sup>).

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