1,3-Metal–Carbon Bonding and Alkyne Metathesis: DFT Investigations on Model Complexes of Group 4, 5, and 6 Transition Metals

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ABSTRACT: The formation of metallacyclobutadienes (MCBs) from chloro-ligated alkylidyne complexes of group 4, 5, and 6 transition metals (MCl₄(C₃H₃)) has been studied at the BP86/def2-TZVP level. All the MCBs showed M–C₃ distances (~2.1 Å) very close to M–C₃ distances (1.8–2.0 Å), suggesting a bonding interaction between the metal and the β-carbon (1,3-MC bond). Energy decomposition analysis using C₃ symmetric structures revealed that a β₂ orbital composed of mainly metal d₉ and C₃p₂ overlap and an agostic a₁ orbital contributed to the orbital interaction of the 1,3-MC bond. The bond order of the 1,3-MC bond is a minimum of 0.26 for M = Cr and a maximum of 0.43 for M = Ta. Further, all the MCBs showed a characteristic δ orbital interaction through an a₂ orbital, which contributed to the double-bond character of M–C₃ bonds (bond order 1.27–1.44). Although the formation of β₂ and a₁ orbitals increased the M–C interactions, they significantly reduced the π interactions within the C₃H₃ fragment (C–C bond order 1.09–1.18). 1,3-MC bonding suggested a planar tetracoordinate configuration for C₃β as the C₃α–C₃β bonds possessed largely formal C₃σ₁–C₃σ₂ single-bond character. Electron density analysis showed a “catastrophic” character of the 1,3-MC bond. In groups 4 and 5, MCBs were more stable than the isomeric η³-structures (metallatetrahedranes). A mechanistic study on the reaction between acetylene and alkylidyne complex MCl₄CH showed that a nearly barrierless and exothermic pathway exists for MCB formation (exothermic value 75–102 kcal/mol for groups 4 and 5; 6–27 kcal/mol for group 6). The rich metathesis chemistry associated with Mo and W is attributed mainly to the moderate activation energy required for the alkyne disproportionation step of metathesis. A mechanistic possibility other than Katz’s is also proposed for alkyne metathesis that showed that the 1,3-MC bonded MCB complex can act as a metathesis catalyst by reacting with alkyne to form a bicyclic intermediate and subsequently disproportionating to yield the alkyne and the MCB. For this mechanism to be effective, rearrangement of the bicyclic intermediate to a more stable cyclopentadienyl complex has to be prevented.

INTRODUCTION

Alkyne metathesis provides an important homogeneous catalytic procedure for the creation of CC triple bonds.¹−¹¹ Although the first alkyne metathesis catalyst¹² was discovered in 1974, only a limited number of well-defined catalysts have been reported since then for the metathesis of CC triple bonds, and several of them were alkylidyne complexes of molybdenum and tungsten.¹³–²² Alkyne metathesis often passes through stable metallacyclobutadiene (MCB) intermediates, and in the Katz mechanism,²³–²⁵ a [2 + 2] cycloaddition step between alkyne and metal alkylidyne is responsible for the formation of the MCB intermediate. In 1982 Schrock et al. experimentally established this mechanism by isolating and characterizing the X-ray structure of the MCB intermediate Cl₃[W(C₃H₃)Me(MeCMe)] in the reaction between 2-butyne and the alkylidyne complex W(C₃H₃)(dme)Cl.²⁶,²⁷ Since then, a few more stable MCB structures are reported by both experiment and theory.²²,²⁷–³³ All the reported MCB intermediates of alkyne metathesis showed a characteristic short M–C₃ distance typically in the W–C single bond range 2.1–2.3 Å, and this was also very close to the value of the M–C₃ distance (1.8–2.0 Å). The short M–C₃ distance suggested significant bonding interaction between the metal and the C₃β. Fenske–Hall molecular orbital calculations on [W(C₃H₃)Cl]¹⁰ reported by Bursten in 1983 confirmed that the short M–C₃β distance is due to a strong orbital interaction between dₓz on the W and pₓ on the C₃β.³⁴ Later theoretical studies by Ziegler et al. and Lin and Hall have supported the dₓz–pₓ-type bonding for the short M–C₃β distance in MCB structures.³⁵,³⁶ Ziegler et al. also argued that the double-bond character of the M–C₃β bond as well as partial double-bond character of C₃α–C₃β bonds impacts...
structural restrictions within the four-membered ring of MCB to yield a short $\text{M} - \text{C}_\beta$ distance.\textsuperscript{35} Also a study by Goddard et al. based on generalized valence bond theory did not support the $\text{M} - \text{C}_\beta$ bonding in the molybdenum MCB complex.\textsuperscript{37} Very recently, we have made a thorough analysis of the nature of the $\text{M} - \text{C}$ bonding in the MCB complexes $(\text{Cl}_3\text{WC}_3\text{H}_3)$, $(\text{Cl}_3\text{MoC}_3\text{H}_3)$, and $(\text{Cl}_3\text{CrC}_3\text{H}_3)$ using energy decomposition analysis (EDA) and atoms-in-molecule analysis\textsuperscript{38} and showed that $\sigma$, $\pi$, and $\delta$ $\text{M} - \text{C}$ orbital interactions contribute to the overall $\text{M} - \text{C}$ bonding, and among them the $\pi$-type interaction from a $b_2$ orbital was mainly responsible for the $\text{M} - \text{C}_\beta$ bonding. Further, the Mayer bond order values 0.37, 0.31, and 0.26 calculated respectively for $(\text{Cl}_3\text{WC}_3\text{H}_3)$, $(\text{Cl}_3\text{MoC}_3\text{H}_3)$, and $(\text{Cl}_3\text{CrC}_3\text{H}_3)$ suggested the formation of an $\text{M} - \text{C}_\beta$ bond. We have named this bond as a 1,3-MC bond and also suggested that $\text{C}_\beta$ exists in the planar tetracoordinate state in the MCB complex.

The aim of this paper is to show that 1,3-MC bonding not only is unique to group 6 metals but also can be observed in other groups, particularly the earlier ones. To prove this, the metallacyclobutadienes of the group 4 and 5 transition metals are modeled and compared with complexes of group 6 metals. The 1,3-MC bonding has been examined with EDA and electron density analysis. Further, the importance of this bonding has been discussed in the context of alkyne metathesis by studying the potential energy surface for the $[2 + 2]$ type cycloaddition and cycloreversion processes. Moreover, the utilization of this bonding in designing realistic models of MCB complexes and a proposal to use them as potential catalysts for alkyne metathesis are discussed.

![Figure 1. Optimized structures of MCl$_n$(C$_3$H$_3$) systems at the BP86/def2-TZVPP level. (a) 1,3-MC bonded metallacyclobutadienes of group 4, 5, and 6 metals. (b) $\eta^3$-Complexes (metallatetrahedranes) of group 4, 5, and 6 metals. (c) Normal metallacyclobutadienes (without 1,3-MC bonding) of group 6 metals. Relative energy in kcal/mol, and bond lengths in Å.](image-url)
**METHODOLOGY**

Geometry optimizations were carried out with Gaussian03 at the gradient-corrected BP86/def2-TZVP level of theory as well as the BP86/TZVP level of theory using the ADF program version 2010.02. Essentially, both these levels of theory give almost identical results, and the later theory is chosen for doing the EDA analysis using ADF. The basis sets are triple-$\zeta$ quality, which are augmented by polarization functions $p$ and $d$ for hydrogen and $d$ and $f$ for other atoms. Scalar relativistic effects were considered by using the zero-order regular approximation (ZORA) in ADF calculations. EDA analysis implemented in ADF employs Morokuma's energy decomposition scheme to Kohn–Sham molecular orbitals as well as uses the extended transition state partitioning scheme of the orbital interactions as developed by Ziegler and Rauk. Vibrational frequencies were determined by calculating the Hessian matrix analytically. In all cases, the nature of the stationary points and transition states was verified.

In the EDA scheme, the complex is divided into two fragments, viz., the inorganic fragment consisting of the metal and the chloro ligands (fragment $A$) and the organic fragment consisting of the hydrocarbon part (fragment $B$). The bond dissociation energy ($D_b$) required for the fragmentation process can be partitioned into four contributions, viz., electrostatic interaction ($\Delta E_{el}$), Pauli repulsion ($\Delta E_{Pauli}$), orbital interaction ($\Delta E_{orb}$), and preparation energy ($\Delta E_{prep}$). $\Delta E_{el}$ is calculated with a frozen density distribution of the fragments in the geometry of the complex. $\Delta E_{corr}$ accounts for the energy change associated with the transformation from the superposition of the unperturbed electron densities of fragments $\rho_A + \rho_B$ to the wave function $\Psi = N(\Psi_A \Psi_B)$, which properly obeys the Pauli principle through explicit antisymmetrization ($A$) and renormalization ($N$) of the product wave function. $\Delta E_{orb}$ gives the stabilizing orbital interaction when the orbitals of the fragments relax to their final form. $\Delta E_{prep}$ is the energy that is necessary to promote the fragments $A$ and $B$ from their equilibrium geometry and electronic ground state to the geometry and electronic state that they have in the molecule. The sum of $\Delta E_{el} + \Delta E_{Pauli}$ and $\Delta E_{orb}$ gives the total interaction energy ($\Delta E_{int}$). The sum of $\Delta E_{int}$ and $\Delta E_{prep}$ gives the bond dissociation energy ($D_b$) by definition with opposite sign) given in eq 1.

$$D_b = \Delta E_{int} + \Delta E_{prep}$$

(1)

EDA provides one of the most robust methods for doing quantitative and systematic analysis on the nature of the chemical bonds. More accounts of the EDA method can be found in the literature.

We have also used the ETS-NOCV scheme, a recent extension of the EDA scheme that combines the extended transition state (ETS) approach with the natural orbitals for chemical valence (NOCV) method. This scheme decomposes the deformation density that is associated with the bond formation, $\Delta \rho$, into different components of the chemical bond and provides pairwise energy contributions for each pair of interacting orbitals to the total bond energy. The orbital interaction term, $\Delta E_{orb}$, in the ETS-NOCV scheme is given in eq 2.

$$\Delta E_{orb} = \sum_{k=1}^{N/2} \Delta E_{orb}^k = \sum_{k=1}^{N/2} \sum_{i=1}^{N/2} \nu_{i,k} [-F_{i,k}^TS_{i,k} - F_{k,i}^TS_{k,i} ]$$

(2)

where $F_{i,k}^TS$ and $F_{k,i}^TS$ are diagonal transition-state Kohn–Sham matrix elements corresponding to NOCVs with the eigenvalues $-\nu_{i,k}$ and $\nu_{i,k}$ respectively. More details of the ETS-NOCV method can be found in the recent literature.

Topological properties associated with the bond critical point and Laplacian distributions were obtained by using the AIMAll (version 12.06.03) program.

**RESULTS AND DISCUSSION**

Geometric Features of Metallacyclobutadienes. Optimized geometries of metallacyclobutadiene complexes selected for this study (CITi((C$_3$H$_3$)$_2$), ClZr((C$_3$H$_3$)$_2$), ClHf((C$_3$H$_3$)$_2$), ClV-(C$_3$H$_3$)$_2$, Cl$_2$Nb((C$_3$H$_3$)$_2$), Cl$_2$Ta((C$_3$H$_3$)$_2$, Cl$_2$Cr((C$_3$H$_3$)$_2$, Cl$_2$Mo-(C$_3$H$_3$)$_2$, and Cl$_2$W((C$_3$H$_3$)$_2$)) are presented in Figure 1a. Among the group 4 MCB complexes, TiCl((C$_3$H$_3$)$_2$) is planar and shows $C_2v$ symmetry, while ZrCl((C$_3$H$_3$)$_2$) and HfCl((C$_3$H$_3$)$_2$) are nonplanar and possess $C_4$ symmetry. All the MCl$_2$(C$_3$H$_3$) systems of group 5 showed $C_{2v}$ symmetry. The structure of CrCl$_2$(C$_3$H$_3$)$_2$ showed no symmetry, while both MoCl$_3$(C$_3$H$_3$) and WCl$_4$(C$_3$H$_3$)$_2$ have $C_2$ symmetry (Figure 1a). Optimization of ZrCl((C$_3$H$_3$)$_2$, HfCl((C$_3$H$_3$)$_2$, and CrCl$_2$(C$_3$H$_3$)$_2$ under $C_{2v}$ symmetry restriction gives structures that are only slightly higher in energy (0.5–0.9 kcal/mol) than the respective structures with lower symmetry. This indicates the effect of slight Jahn–Teller distortion in $C_{2v}$ structures. All the MCB complexes depicted in Figure 1a possess short M–C$_\beta$ bonds (1.80–2.03 Å), indicating strong double-bond character of the bonds. The most remarkable structural feature of these complexes is that they all show short M–C$_\beta$ distances (2.01 to 2.25 Å), which is unusual for atoms placed in 1 and 3 positions. A bonding interaction between the metal and the $\beta$-carbon (1,3-MC bond) can be suspected because the M–C$_\beta$ distance is shorter than the sum of the covalent radii of carbon and the metal (2.12–2.48 Å). The C$_\alpha$–C$_\beta$ bond distance is in the range 1.42–1.45 Å, which is close to a formal C$_\beta$–C$_\beta$ single-bond distance. The internal C$_\alpha$–C$_\beta$–C$_\beta$ angle is in the range 119–125°, while the external M–C$_\alpha$–H angles are in the range 154–164°. These structural features are in good agreement with the X-ray structural features reported by Schrock et al. for the MCB complex W(C$_3$Et$_3$)$_2$(0,2,6-C$_6$H$_3$(i-Pr)$_2$). Since the structural features suggest double-bond character for the M–C$_\beta$ bond, single-bond character between M and C$_\beta$, and formal C$_\beta$–C$_\beta$ single-bond character for both CC bonds, the drawing given in Scheme 1 is proposed for the
carbon atoms in the sp³-hybridized state, the angle defined by H, C, and M (163° for Ti, 168° for Zr, and 172° for Hf) supports mostly the sp-hybridized state of the carbon atoms. One of the sp orbitals will be directed toward the bonding direction of the metal and the other toward the bonding direction of the hydrogen, indicating in-plane overlap of p orbitals for C–C σ bonds. Unlike the group 4 η³-complexes, one of the C–C bonds of group 4 is significantly longer than a typical C–C single bond, whereas the other two C–C bonds show equal bond lengths in the range 1.42 to 1.44 Å. An X-ray structure showing very similar structural features was reported for the η³-vanadium complex.58 The C–C bond length of η²-complexes of group 6 is in the range 1.43 to 1.47 Å, which is typically observed in reported X-ray structures. Further, the angle defined by H, C, and M is 137° for Cr, 142° for Mo, and 146° for W.

The η²-TiCl(C3H3), η²-ZrCl(C3H3), η²-HfCl(C3H3), η²-VCl2(C3H3), η²-NbCl2(C3H3), and η²-TaCl2(C3H3) complexes are 24.0, 28.5, 32.6, 28.2, 37.0, and 41.7 kcal/mol less stable than the respective MCB complexes given in Figure 1a, indicating that the conventional η²-coordination of C3H3 with a metal center is much weaker than the unconventional 1,3-MC bonding. However, the η²-CrCl3(C3H3), η²-MoCl3(C3H3), and η²-WCl3(C3H3) complexes are 27.9, 11.1, and 0.8 kcal/mol more stable than the respective MCBs with a 1,3-MC interaction. Our result qualitatively agrees with a previous study by Goddard et al., who used GVB calculations to show that the metallatetrahedrane complex of Mo is 4.8 kcal/mol more stable than the metalacyclobutadiene complex.37 Our results are also consistent with the results of Ziegler et al., who using nonlocal DFT showed that the metallatetrahedrane complex of Mo is 12.4 kcal/mol more stable than the metalacyclobutadiene complex.38

Table 1. EDA Results (BP86/TZ2P+) of MCl(C3H3) Complexes (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W)° (all energies in kcal/mol)

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<th>energy</th>
<th>Ti</th>
<th>Zr</th>
<th>Hf</th>
<th>V</th>
<th>Nb</th>
<th>Ta</th>
<th>Cr</th>
<th>Mo</th>
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<td>ΔEa (kJ/mol)</td>
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<td>401.0</td>
<td>428.6</td>
<td>460.0</td>
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<td>−288.2</td>
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<td>−139.7</td>
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<td>−159.7</td>
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°Interacting fragments MCl₂ and C3H3 are in the quartet ground state.

One of the referees of this paper raised the following important question regarding the structure of the metalacyclobutadiene. How far can a C₂ atom in a four-membered ring get away from the metal? We may speculate that the structural restrictions within the unsaturated four-membered ring will always restrict the position of C₂ within the coordination sphere of the metal, and hence the observed short M–C₂ distance of MCBs is primarily structural and not electronic in nature. However, this argument is not fully correct because metallacyclobutadiene structures with a significant difference in the M–C₂ and M–C₃ distances are possible for group 6 MCl₃(C3H3) complexes (Figure 1c). In these minimum energy structures, the M–C₃ distance (2.519 to 2.611 Å) is significantly larger (0.549–0.696 Å) than the M–C₂ distance. Further, the M–C₃ distance is larger than the sum of the covalent radii of carbon and metal (2.12–2.48 Å). The C–C bond alternation is shorter that the C–C bond is double-bond localized and the longer one is a formal Csp² double bond. Unlike the group 4 MCB structures given in Figure 1c, structures showing a larger M–C₃ distance suggest that the p orbital of the C₂ has only a negligible interaction with the metal center for the complexes given in Figure 1c, and therefore a significant 1,3-MC interaction may not exist in such complexes. An intriguing observation is that M–C₃ bonds of MCB structures given in Figure 1a are shorter than the M–C₂ bonds designated as double bonds for the structures given in Figure 1c. Structures showing bond alternation at the C₃a–C₃b bonds or structures showing a larger M–C₃ distance than those reported in Figure 1a are not observed for group 4 and group 5 MCBs.

The 1,3-MC-bonded MCB structure of CrCl₃(C3H3) is 5.1 kcal/mol less stable than the structure showing C–C bond alternation, whereas 1,3-MC complexes of MoCl₃(C3H3) and WCl₃(C3H3) are 3.9 and 9.1 kcal/mol more stable than the corresponding structures having C–C bond alternation.

**Nature of Metal–Carbon Bonding.** For all the MCl₃(C3H3) metallacyclobutadiene complexes (Figure 1a), EDA is carried out with A and B fragments in singlet, doublet, triplet, and quartet electronic configurations. Always C₃a symmetry is used for the description of the MCl₃(C3H3) complexes and the fragments. In the doublet and quartet states A is MCl₂ and B is C₃H₅, while in the singlet and triplet cases, A and B are respectively MCl₃⁺ and C₃H₅⁻. The optimized structure and relative energy of C₃H₅ (doublet and quartet) and C₃H₅⁻ (singlet and triplet) are presented in Figure S1 of the Supporting Information. The ground state of C₃H₅ is doublet
and the quartet state is 38.8 kcal/mol higher in energy, whereas the ground state of C₂H₃⁻ is singlet and its triplet state is 6.1 kcal/mol higher in energy. The structure of the C₂H₃ fragment in the complex resembles more the optimized quartet structure. The MCl₃ fragment is more stable in the quartet state than the singlet (M = Hf is an exception), whereas the MCl₃⁺ fragment is more stable in the triplet state than the singlet (M = Hf is an exception; Table S1).

In the previous study, we have shown that in the case of group 6 complexes ΔEorb was the lowest for the quartet configuration, and hence this configuration was selected for the fragments in the complex. In the case of group 4 and 5 complexes, the neutral fragments in the quartet scheme are more suited for EDA analysis than those in the doublet scheme, whereas with charged fragments, the triplet scheme is slightly more preferred (5–8% on the orbital interaction) than the quartet scheme. In order to give a consistent description of the metal−carbon bonding using neutral fragments C₃H₃ and C₃H₃⁺, hereafter only the quartet EDA scheme will be discussed unless otherwise stated (EDA data for all other schemes are given in Table S1).

Table 1 reports the EDA data for the quartet states for all complexes. The ΔEpresp values suggest that the fragments of Ti, Zr, V, and Nb complexes require relatively lower ΔEpresp values (49–64 kcal/mol) than the rest. Among the three main components of ΔEorb, the destabilizing ΔEpnull is very high for all the cases (325–514 kcal/mol), which can be attributed to the compact ring structure of the complexes. In all the cases, the metal−ligand attraction is slightly dominated by ΔEorb (52–60%) than ΔEdep. Four types of molecular orbitals, which belong to irreducible representations a₁, a₂, b₁, and b₂ of the C₂ᵥ point group, contribute to the ΔEorb, which are designated as ΔEₐ₁, ΔEₐ₂, ΔEₐ₃, and ΔEₐ₄, respectively. These orbitals are given in Figure 2 for a representative case VCl₂(C₃H₃). The nature of the metal−ligand bonding is very similar for other metals. a₁ and a₂ are σ and δ orbitals, respectively. b₁ orbitals correspond to π orbitals that lie in the plane of the metallacycle, and the b₂ orbital corresponds to a π orbital orthogonal to the plane of the metallacycle.

The δ orbital a₂, the highest lying σ orbital a₁, and the in-plane π orbital b₁ contribute to the strength of M−Cσ bonds. The π orbital b₂ is mainly responsible for the M−Cπ bond, which is the same as the dₓ²−pₓ orbital reported by Bursten using Fenske–Hall molecular orbital calculations on the [W(C₃H₃)]³⁺ fragment. Ziegler and co-workers also reported qualitatively similar results on the δ- and π-bonding features of the metal−carbon bonds. Although the low-lying b₁ and a₁ orbitals are largely localized within the C₂H₃ fragment, they show some minor interactions with the d orbitals on the metal. Since the low-lying b₁ and a₁ orbitals largely define the C−C σ bonds, their interactions with the metal are agostic in nature. The EDA data reveal that ΔEorb contributions from a₁, a₂, b₁, and b₂ orbitals are respectively in the range 30–41%, 12–19%, 38–46%, and 5–9%. The largest contributions come from the in-plane a₁ and b₁ orbitals of the M−C₉ bonds, while the contribution of b₂ suggests the formation of a weak M−Cπ bond. The stabilizing δ orbital interaction is the highest for WCl₃(C₂H₃) (57.6 kcal/mol) and the lowest for CrCl₃(C₂H₃) (34.9 kcal/mol). Group 4 complexes show bond dissociation energies (Dₑ) of 134.1, 147.1, and 144.7 kcal/mol for M = Ti, Zr, and Hf, respectively. The vanadium complex in group 5 has a 26.7 kcal/mol lower Dₑ value than the titanium complex, whereas in the case of tantalum, Dₑ is increased by 15.0 kcal/mol compared to hafnium. Both zirconium and niobium complexes show comparable Dₑ values. In group 6, the chromium complex has the lowest Dₑ (32.0 kcal/mol) which is the same as the dₓ²−pₓ orbital reported by Bursten using Fenske–Hall molecular orbital calculations on the [W(C₃H₃)]³⁺ fragment. Ziegler and co-workers also reported qualitatively similar results on the δ- and π-bonding features of the metal−carbon bonds.

Figure 2. Plots of the highest occupied molecular orbitals responsible for metal−carbon bonding in VCl₂(C₃H₃). Eigenvalues of the orbitals are given in eV. Isosurface value is 0.08 for MO30 and 0.06 for all other MOs.
kcal/mol), while the $D_n$ of molybdenum and tungsten complexes are 82.4 and 108.8 kcal/mol, respectively.

We have also used the ETS-NOCV analysis to quantify the orbital interaction energy of the low-lying agostic $\alpha$- and $\beta$-orbitals given in Figure 2. This analysis showed that interaction due to $\beta$ is negligible ($-2$ to $-4$ kcal/mol), while that due to $\alpha$ is significant. The contribution of $\alpha_2$ in the quartet scheme of ETS-NOCV is $-10.4$, $-12.4$, $-13.9$, $-11.5$, $-17.2$, $-20.2$, $-16.7$, $-19.1$, and $-22.4$ kcal/mol for MCB complexes of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W, respectively. In Figure S2 in the Supporting Information, NOCV deformation density maps of all the MOs for the metal–carbon bonding are given for all the MCI(C,H)$_3$ complexes. They show that the 1,3-MC bond is largely defined by the sum of the $\Delta E_{\alpha \text{ag}}$ of the agostic $\alpha_2$ orbital and the $\pi$-type $b_1$ orbital, and this is estimated to be $-25.2$, $-29.6$, $-31.7$, $-27.9$, $-36.9$, $-41.5$, $-42.9$, $-47.9$, and $-54.5$ kcal/mol for MCB complexes of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W, respectively. It may be noted that these numbers cannot be exclusively used for $M$–C(r) interactions alone because the corresponding orbitals are delocalized to the $\alpha$-carbons too.

We have also analyzed the MCB complexes in Figure 1a on the basis of their Mayer bond order values given in Table 2.

### Table 2. Mayer Bond Order Values Calculated at the BP86/TZ2P+ Level for Metallacyclobutadiene Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>$M$–C$_{\alpha}$</th>
<th>$M$–C$_{\beta}$</th>
<th>C$<em>{\alpha}$–C$</em>{\beta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl(C,H)$_3$</td>
<td>1.33</td>
<td>0.31</td>
<td>1.14</td>
</tr>
<tr>
<td>ZrCl(C,H)$_3$</td>
<td>1.40</td>
<td>0.33</td>
<td>1.13</td>
</tr>
<tr>
<td>HfCl(C,H)$_3$</td>
<td>1.42</td>
<td>0.39</td>
<td>1.11</td>
</tr>
<tr>
<td>VCl$_2$(C,H)$_3$</td>
<td>1.30</td>
<td>0.31</td>
<td>1.16</td>
</tr>
<tr>
<td>NbCl$_2$(C,H)$_3$</td>
<td>1.40</td>
<td>0.35</td>
<td>1.12</td>
</tr>
<tr>
<td>TaCl$_2$(C,H)$_3$</td>
<td>1.44</td>
<td>0.43</td>
<td>1.09</td>
</tr>
<tr>
<td>CrCl$_3$(C,H)$_3$</td>
<td>1.27</td>
<td>0.26</td>
<td>1.18</td>
</tr>
<tr>
<td>MoCl$_3$(C,H)$_3$</td>
<td>1.34</td>
<td>0.32</td>
<td>1.15</td>
</tr>
<tr>
<td>WCl$_3$(C,H)$_3$</td>
<td>1.42</td>
<td>0.37</td>
<td>1.11</td>
</tr>
</tbody>
</table>

In all the cases, $M$–C$_{\alpha}$ bonds show double-bond character (bond order 1.27–1.44), which can be attributed to the $\delta$ interaction. The bond order for the 1,3-MC bond is a minimum of 0.26 for $M$ = Cr and a maximum of 0.43 for $M$ = Ta. The bond order of each C–C bond is in the range 1.09–1.18, which is rather small considering that three $\pi$-electrons are available for conjugation within the C$_2$H$_2$ fragment. This diminished double-bond character of the C–C bonds can be attributed to the involvement of the carbon $\pi$ orbitals in $\delta$ and 1,3-MC-bonded interactions. The bond order analysis strongly supports that the diagram given in Scheme 1 is appropriate for representing MCB complexes. The $\pi$ orbital interaction of the type $b_1$, which represents an interaction between atoms at the 1 and 3 positions, is rare in chemistry.

The nature of M–C bonding in MCB structures is also analyzed in terms of the topology of the electron density ($\rho(r)$). All the structures showed the expected (3, −1) bond critical points (bcp) for the M–C$_{\alpha}$ and C$_{\alpha}$–C$_{\beta}$ bonds. The $\rho(r)$ at the bcp of M–C$_{\alpha}$ bonds is in the range 0.126–0.176 e/Å$^3$, while that of C$_{\alpha}$–C$_{\beta}$ bonds is in the range 0.272–0.289 e/Å$^3$. The MCBs have not shown a (3, −1) bcp between M and C$_{\beta}$ whereas they showed a (3, +1) ring critical point (rcp) close to the midpoint region between M and C$_{\beta}$. The $\rho(r)$ at the rcp is the lowest (0.071 e/Å$^3$) for $M$ = Hf and the highest (0.090 e/Å$^3$) for $M$ = Mo (see also Table S3 in the Supporting Information). Figure 3a shows the contour line diagram of the Laplacian of electron density ($\nabla^2 \rho(r)$) in the plane of the metallacycle along with bond paths (dark green lines) and ring paths (pink lines) for the 1,3-MC-bonded vanadacyclobutadiene VCl$_4$(C,H)$_3$. This plot is a representative of other complexes, as they all show very similar Laplacian distributions. Areas of relative electronic charge concentration (dotted green lines) and areas of relative charge depletion (solid blue lines) are seen in the Laplacian plot. In the case of $\alpha$-carbon atoms of the metallacycle, the area of charge concentration is clearly aligned in the direction of the metal center, while in the case of the $\beta$-carbon, an appreciable amount of charge concentration in the direction of the metal is visible. All the ring paths show a flat curvature near the rcp, suggesting that the rcp point is a “catastrophe” point. The “catastrophic” character of the rcp emerges very clearly when the Laplacian distribution is plotted for a geometry of VCl$_4$(C,H)$_3$ with slight contraction (9%) of the V–C$_{\beta}$ distance from the equilibrium geometry (Figure 3b). The V–C$_{\beta}$ distance-restricted VCl$_4$(C,H)$_3$ is 8.5 kcal/mol higher in energy than the fully optimized geometry, and it showed a bcp near the ring center flanked by two very close lying rcps along with the bond path between the metal and C$_{\beta}$. The charge concentration in the direction of the metal from C$_{\beta}$ is more in the restricted geometry than the equilibrium geometry. Also depicted in Figure 3c is the Laplacian plot for the molybdenacyclobutadiene complex MoCl$_4$(C,H)$_3$, a representative example for a metallacyclobutadiene complex without a 1,3-MC bond (Mo–C$_{\beta}$ distance is 2.611 Å; Figure 1c). This plot is very helpful to further assess the 1,3-MC bond. In this plot, each ring path between the bcp and rcp appears as a straight line, and unlike MCB with a 1,3-MC bond, a flat curvature is not seen near the rcp. Most significantly, the charge concentration is aligned in the direction of the metal only from C$_{\alpha}$ atoms and not from C$_{\beta}$, which indicates that C$_{\beta}$ is not bonded with the metal.

**Alkylne Metathesis Reaction Models.** The MCB systems used in this study can be considered as formed from a [2 + 2] cycloaddition between acetylene and the alkylidyne complex MCl$_4$(CH). Hence, transition state modeling for the cycloaddition reaction can yield valuable insight into alkyn metathesis processes of group 4, 5, and 6 metals. The energy profiles of these reactions are presented in Figure 4. All of them are exothermic and give rise to the formation of 1,3-MC-bonded MCB complexes. All attempts to optimize a reactant van der Waals complex failed because the optimization always gave the MCB complex. Failure to detect van der Waals complexes may be due to a poor description of dispersion effects by the BP86 functional. Since van der Waals complexes are typically stabilized by 1–3 kcal/mol, the reactions can be described as nearly barrierless (Figure 4). The exothermic values of the reactions are very high for group 4 and 5 metals; the lowest is 75.2 kcal/mol for the Zr complex, and the highest is 101.7 kcal/mol for the Hf complex. The exothermic values of Cr, Mo, and W complexes are 6.4, 17.7, and 27.3 kcal/mol, respectively. In 1993, Ziegler and co-workers reported the energy profile for the formation of a molybdenacyclobutadiene complex from MoCl$_4$(CH) and acetylene using nonlocal DFT. They showed that the reaction was 16.7 kcal/mol exothermic, and the value obtained in the present study using more sophisticated DFT is only 1 kcal/mol higher. The high exothermic character of the reactions indicates that the loss of alkyne from the MCB (the cycloreversion reaction) will be very
difficult in the case of group 4 and 5 metals, while the reaction is feasible at room temperature for Cr and Mo. For W, cycloreversion could be achieved with slight tuning of the ligand environment. The low activation barrier observed for the cycloreversion step of the chromium MCB complex suggests the possibility of developing Cr-based systems for alkyne metathesis. Our results also firmly suggest a strong thermodynamic driving force for the formation of MCB complexes of group 4 and 5 metals, indicating that their alkylidyne complexes can be targeted for the development of alkyne metathesis catalysts. In fact, several good attempts have been made in the recent past to produce alkylidyne complexes capable of metathesis using group 4 and 5 metals.63−70

Proposal to Use Metallacyclobutadienes As Alkyne Metathesis Catalysts. A bottleneck in the development of alkyne metathesis catalysts is in synthesizing robust systems with M−C triple bonds. The inherent high reactivity of M−C triple bonds cannot be easily concealed by the modification of the stereoelectronic properties of the ligand environment. In this scenario, synthesis of catalysts without M−C triple bonds

Scheme 2. General Mechanistic Scheme for Alkyne Metathesis Using Metallacyclobutadiene I
could be considered for alkyne metathesis. The high amount of energy released in the formation of MCB systems in the case of groups 4 and 5 strongly suggests the possibility of the development of such stable complexes. We have considered the use of 1,3-MC-bonded MCBs as potential alkyne metathesis catalysts and propose a general mechanism given in Scheme 2, which is different from Katz’s mechanism for alkyne metathesis. At first the alkyne can be oxidatively added to the M–C₃ double bond of the MCB to produce a bicyclic intermediate (III). Reductive elimination of the new alkyne can be expected in the next step, which would liberate the catalyst.

Using the 1,3-MC-bonded dichloro derivatives of V, Nb, and Ta complexes, the mechanism given in Scheme 2 is explored using the BP86/def2-TZVPP method, and the results are summarized in Figure 5. In the case of vanadium, coordination metathesis was described on the basis of the loss of alkyne from the MCB to give an alkylidyne complex and regeneration of the MCB by further reaction of the alkylidyne and the alkyne. Essentially Katz’s mechanism was followed in that reaction. The theoretical study by Ziegler et al. was also on Katz’s mechanism, and through transition state modeling they reported an exothermic energy profile (16.7 kcal/mol) for the formation of molybdenacyclobutadiene. Schrock et al. also showed that the reactions of alkyne with allyloxy- and chloroligated tungstenacyclobutadienes were possible, but they yielded only Cp complexes and not alkyne metathesis. So far, alkyne metathesis is described via Katz’s mechanism, and the alternate possibility presented in Scheme 2 is far from reality. The strategy of using the MCB complex as a robust alkyne metathesis catalyst may become successful if the ring closing of the organic fragment leading to the Cp complex is prevented. This may be achieved by steric tuning of the substituents on the organic fragment as well as by steric and electronic tuning of other ligands on the metal center.

**CONCLUSIONS**

MCBs are intermediates of alkyne metathesis in the Katz mechanism, and they possess a characteristic M–C₃ bond distance, ~2.1 Å for group 4, 5, and 6 metals. The β-carbon of the MCB exists in a unique planar tetracoordinate geometry due to significant bonding interactions (1,3-MC bond) between the metal and the β-carbon. The dₓ₂–pₓ orbital interaction between the metal and the β-carbon (b₂ orbital) is mainly responsible for the 1,3-MC bond, and such a bond formed between atoms in the 1 and 3 positions is rare in chemistry. Very recently, Roy et al. have shown that 1,3-MC interactions can exist in metallacycloallene systems. The MCBs are also characterized by strong δ-bonding interactions (a₂ orbital) between a metal δ orbital and pₓ orbitals on the α-carbon atoms. The orbital interactions due to b₂ and a₂ orbitals significantly reduce the π-bonding interaction within the C₃H₃ fragment, and as a result, both the C₃–C bonded exist as formal C₃=Cₓ single bonds. Hence it can be assessed that metal–carbon δ- and π-bonding interactions have a direct influence on the activation of C–C bonds to induce cycloreversion leading to loss of alkyne from the MCB.

Formation of MCBs from metal alkylidyne complexes and alkynes through [2 + 2] cycloaddition reveals a barrierless and exothermic process. High exothermic values obtained for group 4 and group 5 MCBs suggest the possibility of isolating these complexes in an appropriate ligand environment. The disproportionation reaction or cycloreversion of the alkyne part from the MCB is very difficult to achieve for group 4 and group 5 complexes, and therefore the Katz mechanism of metathesis may not occur. Moderate exothermic values obtained for Cr, Mo, and W MCB complexes suggest the feasibility of metathesis through the Katz mechanism at ambient conditions, which also supports the rich metathesis chemistry associated with Mo and W alkylidyne complexes. Chromium is also an attractive choice for alkyne metathesis owing to the low activation energy required for both cycloaddition and cycloreversion steps.

The use of MCBs as C–C triple-bond metathesis catalysts is investigated by using a mechanistic scheme very different from that of Katz’s, and it reveals that a possible pathway exists for an MCB complex to carry out C–C triple-bond metathesis. However, this pathway becomes effective only if another dominant pathway leading to the formation of a cyclo-
pentadienyl complex is prevented. We hope that this can be achieved by proper tuning of the steric and electronic environment of the ligands.

**ASSOCIATED CONTENT**

Supporting Information

Optimized geometries and results of EDA and electron density analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Notes

The authors declare no competing financial interest.

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**REFERENCES**


(72) Bino, A.; Ardon, M; Shirman, E. Science 2005, 308, 234.