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# Theoretical Studies of the Relative Stabilities of Transition Metal Alkylidyne $(CH_3)_2M(\equiv CH)(X)$ and Bis(alkylidene) $(CH_3)M(=CH_2)_2(X)$ Complexes

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Density functional molecular orbital calculations at the B3LYP level were performed to investigate the relative stabilities of the tautomeric pairs of transition metal alkylidyne $(CH_3)_2M(\equiv CH)(X)$ and bis(alkylidene) $(CH_3)M(=CH_2)_2(X)$ complexes (M = W, Mo, Os, and Ru; X = Cl, $CH_3$, $CF_3$, $SiH_3$, and $SiF_3$). Calculation results indicate that the relative stabilities of the bis(alkylidene) tautomers increase with the increasing $\pi$-accepting ability of X for the W and Mo complexes. When X is a silyl ligand, it is found that the tautomeric pair for W or Mo have similar stabilities. These results have been explained in terms of $\pi$ interaction between ligand X and the electron density in the metal−alkylidyne/alkylidene bonds. For the Os and Ru complexes, the bis(alkylidene) tautomers are found more stable no matter what X is. The stabilities of the bis(alkylidene) tautomers for these $d^2$ metal complexes have been related to the bonding characteristic of the orbital that accommodates the two metal d electrons.

## Introduction

High oxidation state transition metal alkylidyne ($L_nM\equiv CR$) and alkylidene ($L_nM=CR_2$) complexes have been of great interest, not only because of their unique structure and bonding properties but also because of their relevance to organic synthesis and catalysis.[1−7] The α-hydrogen atoms in a number of alkylidyne and alkylidene complexes have been found to undergo exchanges among the α-carbon atoms. For example, direct exchange of α-hydrogen atoms is observed for $d^0$ alkylidyne complexes $(Bu^tCH_2)_3W\equiv CSiMe_3$[8−10] and $(Bu^tCH_2)_3W\equiv {}^{13}CBu^t$[9b] and $d^2$ bis(alkylidene) complex $Os(=CHBu^t)_2(CD_2Bu^t)_2$.[10] The related W bis(alkylidene) and Os alkylidyne complexes, respectively, are proposed to be the reactive intermediates. Here, the assignment of the $d^0$ and $d^2$ configurations for the two metal centers is based on the commonly accepted assumption of $[CR_3]^-$, $[CR_2]^{2-}$, and $[CR]^{3-}$ moieties in the metal complexes. The relative energies of the corresponding alkylidyne and bis(alkylidene) complexes in both cases are assumed to be large. As a result, only one of the structural forms can be observed,[11] and there had been no report of direct observation of coexistence of the alkylidyne and bis(alkylidene) tautomeric pair.

Recently, Xue and co-workers reported the direct observation of an equilibrium between a $d^0$ alkylidyne complex $(Bu^tCH_2)_2W(\equiv CBu^t)(SiBu^tPh_2)$ and its bis(alkylidene) tautomer $(Bu^tCH_2)W(=CHBu^t)_2(SiBu^tPh_2)$ (Scheme 1).[12] Thermodynamically, these two tautomers are found to be close in energy, although the alkylidyne tautomer is slightly more stable. It is surprising that such an equilibrium is only observed for complexes with a $-SiBu^tPh_2$ substituent, but not for alkyl, chloro, or even the $-Si(SiMe_3)_3$ substituents.[13] This is an example of substituted ligands with different electronic properties having an influence on the relative stabilities of a

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(11) For example, alkylidynes were the structural forms observed for $(Bu^tCH_2)_3Mo\equiv CBu^t$ (McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5987) and $(Me_3SiCH_2)_3M\equiv CSiMe_3$ (M = Mo, W) (Andersen, R. A.; Chisholm, M. H.; Gibson, J. F.; Reichert, W. W.; Rothwell, I. P.; Wilkinson, G. *Inorg. Chem.* **1981**, *20*, 3934), and $(Me_3SiCH_2)_3W\equiv CBu^t$ (Chisholm, M. H.; Huffman, J. C.; Klang, J. A. *Polyhedron* **1990**, *9*, 1271).

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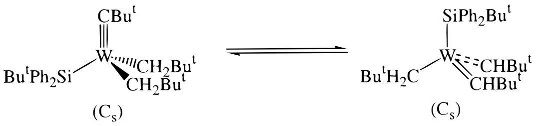
**Scheme 1**



tautomeric pair. Moreover, only the bis(alkylidene) tautomer is observed when the metal center is Os with alkyl substituents.[10] In other words, the energy of the bis(alkylidene) tautomer is comparatively lower than the alkylidyne tautomer for a d$^2$ metal center. It is not clear how metal centers and substituted ligands influence the stabilities of these tautomers. Theoretical studies are needed to understand these phenomena and explain the influence of these factors on the relative stabilities of the transition metal alkylidyne and bis(alkylidene) complexes. In this work, we examine the effect of metal centers and substituted ligands on the relative stabilities of transition metal alkylidyne and bis(alkylidene) complexes using density functional molecular orbital calculations.

## Computational Details

Model complexes $(CH_3)_2M(\equiv CH)(X)$ **1** and $(CH_3)M(=CH_2)_2(X)$ **2** (M = W, Mo, Os, Ru; X = Cl, CH$_3$, CF$_3$, SiH$_3$, SiF$_3$) were used to mimic the tautomeric structures of transition metal alkylidyne and bis(alkylidene) complexes, respectively. To examine the effect of the metal center on the relative stability of the corresponding alkylidyne and bis(alkylidene) tautomers, density functional molecular orbital calculations were performed for model complexes with both group 6 and 8 metal centers. The ligand effect was also demonstrated by using ligand X with different electronic properties. Such ligands include $\pi$-donor (Cl$^-$), $\sigma$-donor (CH$_3{}^-$ and CF$_3{}^-$), and $\pi$-acceptor ligands (SiH$_3{}^-$ and SiF$_3{}^-$).

Full geometry optimizations for all model complexes were performed at the Becke3LYP (B3LYP) level.[14] Transition metal atoms and silicon were described by effective core potentials (ECPs) of Wadt and Hay[15] with a double-$\zeta$ valence basis set, and the standard 6-31G basis sets were used for hydrogen, carbon, and fluorine atoms.[16] The effect of polarization functions was also examined for the alkylidyne/bis(alkylidene) pair of $(CH_3)_2W(\equiv CH)(SiF_3)$ and $(CH_3)W(=CH_2)_2(SiF_3)$ with the use of 6-31G** basis sets on carbon, hydrogen, and fluorine atoms, while polarization functions were added for silicon ($\zeta$ = 0.282).[17] The result of calculations revealed that the inclusion of extra polarization functions does not substantially affect the relative energy and the geometries of the tautomeric pair. The change in the relative energy is within 1.6 kcal/mol (from −6.72 to −5.11 kcal/mol), while the differences in bond lengths and bond angles are within 0.02 Å and 2°, respectively. To examine the effect of electron correlation, CCSD(T)//B3LYP calculations were also performed for the above tautomeric pair. The change in the relative energy is also small (from −6.72 to −5.08 kcal/mol). The CCSD(T)[18] level of theory has been popularly used to test the accuracy of calculations.[19] Further examination of $(CH_3)_2Mo(\equiv CH)(SiF_3)$ and $(CH_3)Mo(=CH_2)_2(SiF_3)$ once again gives a small change in the relative energy (from −3.75 to −2.27 kcal/mol). Geometry optimizations were all performed using the Gaussian 98 package[20] on a Silicon Graphics Indigo$^2$ workstation. The molecular orbitals (Figures 3 and 7) obtained from B3LYP results were plotted using the Molden v3.5 program written by G. Schaftenaar.[21]

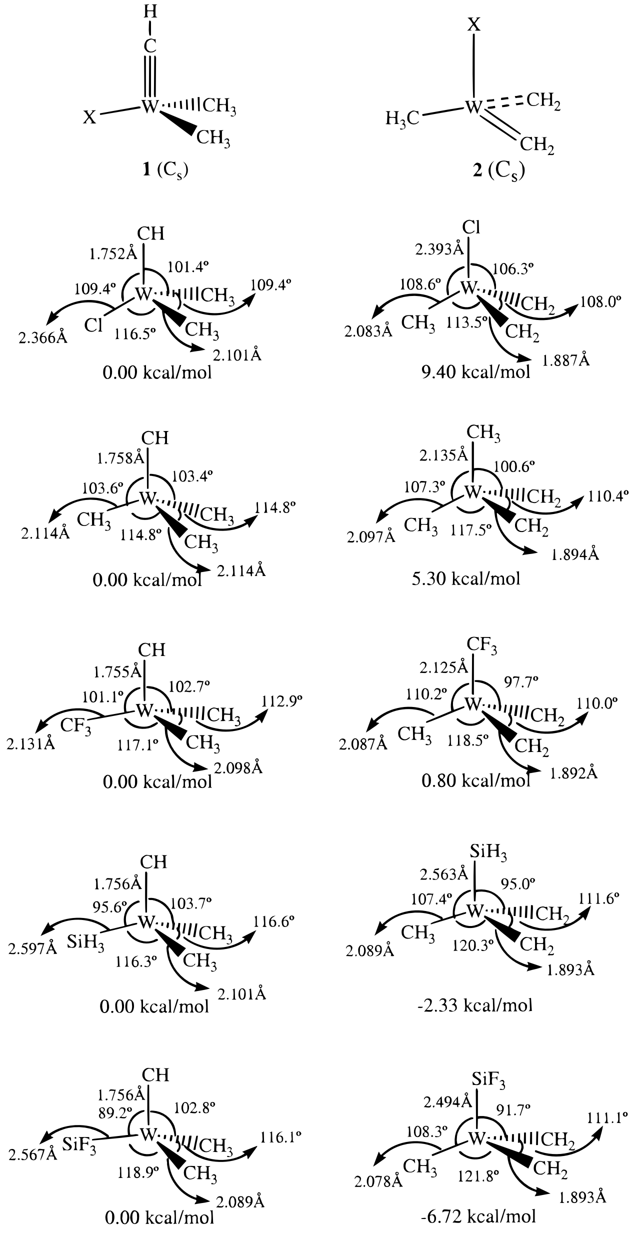


**Figure 1.** Calculated geometries and relative energies of model complexes $[(CH_3)_2W(\equiv CH)(X)]$ and $[(CH_3)W(=CH_2)_2(X)]$ with different substituents X.

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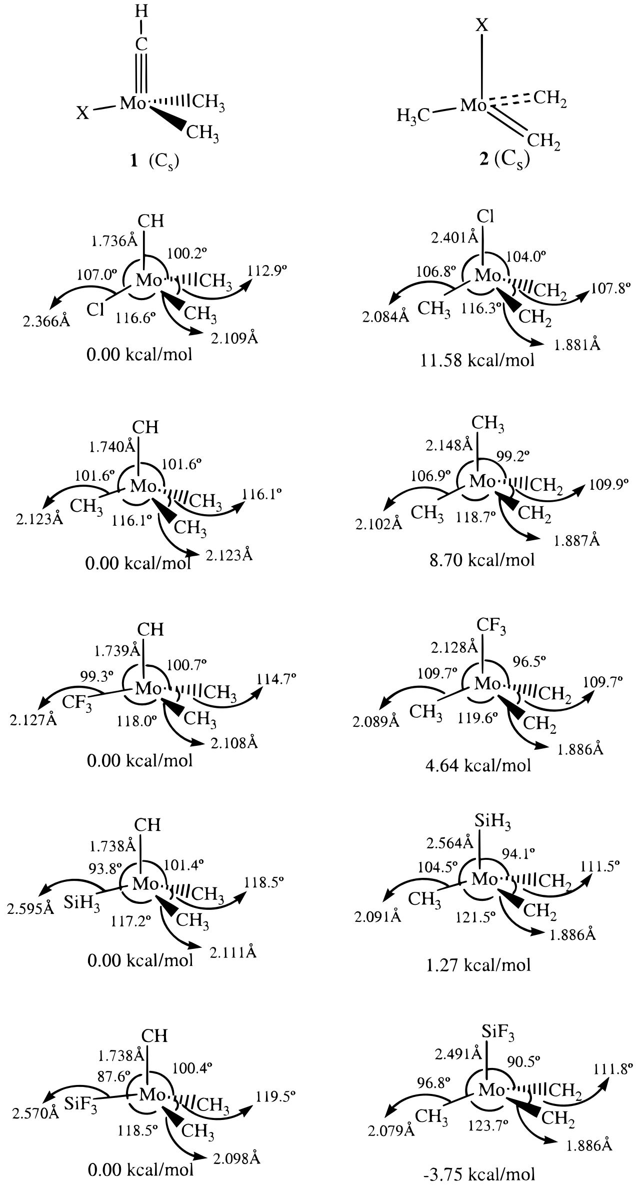

**Figure 2.** Calculated geometries and relative energies of model complexes [$(CH_3)Mo(\equiv CH)(X)$] and [$(CH_3)Mo(=CH_2)_2(X)$] with different substituents X.

## Results and Discussion

**d$^0$ Transition Metal Alkylidyne and Bis(alkylidene) Complexes.** Model complexes $(CH_3)_2M(\equiv CH)(X)$ **1** and $(CH_3)M(=CH_2)_2(X)$ **2** (M = W, Mo; X = Cl, $CH_3$, $CF_3$, $SiH_3$, $SiF_3$) are used to simulate the tautomeric pairs, alkylidyne and bis(alkylidene), with a four-coordinated d$^0$ metal center. The relative energies and structural parameters for the W and Mo alkylidyne/bis(alkylidene) tautomers with different ligands X are illustrated in Figures 1 and 2. All optimized structures of the model complexes adopt a distorted trigonal-pyramidal geometry with approximately $C_s$ symmetry, no matter what X is. For each of the alkylidyne tautomeric structures **1** (see the left column in Figure 1 or 2), the two methyl ligands and X form the base triangle. The pyramidal position is occupied by the alkylidyne ligand ($\equiv$CH). In contrast to **1**, for each of the bis(alkylidene) tautomeric structures **2** (see the right column in Figure 1 or 2), ligand X occupies the pyramidal position, while the methyl group and the two alkylidene ligands take the positions in the base triangle.

**1** ($C_s$) **2** ($C_s$)

Figures 1 and 2 show that the alkylidyne tautomers **1** with different X adopt similar structures. This is also the case for bis(alkylidene) tautomers **2**. Significant structural changes are in the bond angles related to X and alkylidyne/alkylidene ligands, i.e., $HC\equiv M-X$ for tautomers **1** and $H_2C=M-X$ for tautomers **2**. The $HC\equiv M-X$ bond angles (see the left column in Figure 1 or 2) decrease drastically, by a maximum of 20°, from X = Cl to $CH_3$, $CF_3$, $SiH_3$ and then to $SiF_3$; so do the $H_2C=M-X$ bond angles (see the right column in Figure 1 or 2).

Figures 1 and 2 also show the relative energies between alkylidyne tautomers **1** and bis(alkylidene) tautomers **2** with different ligands X. The relative energies decrease along the series of X for both W and Mo complexes. For the W complexes, the alkylidyne tautomers are more stable when X = Cl, $CH_3$, and $CF_3$, while the bis(alkylidene) tautomers become more stable when X = $SiH_3$ and $SiF_3$. For the Mo complexes, the bis(alkylidene) tautomers are more stable only when X = $SiF_3$. These results are consistent with the experimental observation that only the alkylidyne tautomer **1** is observed when X is an alkyl group. Substitution of X with a silyl ligand allows both the alkylidyne and bis(alkylidene) tautomers to have similar stabilities so that an equilibrium between them can be experimentally observed.[12] The phenyl groups in the $-SiBu^tPh_2$ ligand used experimentally perhaps enhance the $\pi$-accepting abilities of the silyl ligand, thus further enhancing the bis(alkylidene) tautomer.

As mentioned above, the angles between ligand X and alkylidyne/alkylidene ligands decrease significantly along the series of X (see Figures 1 and 2). In other words, there is a strong tendency for ligand X in both structures to move toward the alkylidyne/alkylidene ligands. Electronically, along the series, there is an increasing ability for the coordinated atom of X to accommodate more electron density beyond the octet. This increasing electron-deficient property along the series is the driving force for ligand X moving toward the electron-rich region of metal$-$alkylidyne/alkylidene multiple bonds.

To understand this structural behavior, we plotted the two metal$-$alkylidyne $\pi$-bonding molecular orbitals which correspond to the HOMO (highest occupied molecular orbital) and SHOMO (second HOMO) for the alkylidyne tautomer **1** when M = W and X = $CH_3$, shown in Figure 3a. These two d$-$p $\pi$-bonding molecular orbitals, which are almost degenerate because of the $C_{3v}$ symmetry when X = $CH_3$, are assigned as $\pi_x$ and $\pi_y$ depending on their spatial orientations.

When X is not $CH_3$, the two corresponding metal$-$alkylidyne $\pi$-bonding molecular orbitals no longer have similar energies. One can expect the $\pi_y$ component to have a stronger $\pi$ interaction with ligand X because of

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**Table 1. Calculated Orbital Energies of the Two $\pi$-Bonding Molecular Orbitals (HOMO and SHOMO) for Alkylidyne [$(CH_3)_2M(\equiv CH)(X)$] 1 and Bis(alkylidene) [$(CH_3)M(=CH_2)_2(X)$] 2 of the Model Complexes**[a]

| | | alkylidyne **1** | | | bis(alkylidene) **2** | | |
|---|---|---|---|---|---|---|---|
| M | X | $e(\pi_x)$ | $e(\pi_y)$ | $\Delta$ | $e(\pi_-)$ | $e(\pi_+)$ | $\Delta$ |
| W | Cl | −0.25828 | −0.25333 | −0.00495 | −0.24215 | −0.24995 | −0.00780 |
| | $CH_3$ | −0.22979 | −0.22984 | 0.00005 | −0.22459 | −0.22608 | −0.00149 |
| | $CF_3$ | −0.25979 | −0.26850 | 0.00871 | −0.26320 | −0.25960 | 0.00360 |
| | $SiH_3$ | −0.24403 | −0.25339 | 0.00936 | −0.25085 | −0.24119 | 0.00966 |
| | $SiF_3$ | −0.27528 | −0.29198 | 0.01670 | −0.29224 | −0.27356 | 0.01868 |
| Mo | Cl | −0.26923 | −0.26200 | −0.00723 | −0.24081 | −0.25226 | −0.01145 |
| | $CH_3$ | −0.23965 | −0.23965 | 0.00000 | −0.22810 | −0.22976 | −0.00166 |
| | $CF_3$ | −0.26905 | −0.27748 | 0.00843 | −0.26609 | −0.26190 | 0.00419 |
| | $SiH_3$ | −0.25296 | −0.26016 | 0.00720 | −0.25525 | −0.24159 | 0.01366 |
| | $SiF_3$ | −0.28448 | −0.29666 | 0.01218 | −0.29781 | −0.27165 | 0.02616 |

[a] Abbreviation used: $\Delta = e(\pi_x) - e(\pi_y)$ or $\Delta = e(\pi_+) - e(\pi_-)$; $e(\pi_x)$, $e(\pi_y)$, $e(\pi_+)$, and $e(\pi_-)$ are the orbital energies of $\pi_x$, $\pi_y$, $\pi_+$, and $\pi_-$, respectively. The labels of these $\pi$ orbitals are shown in Figure 3.

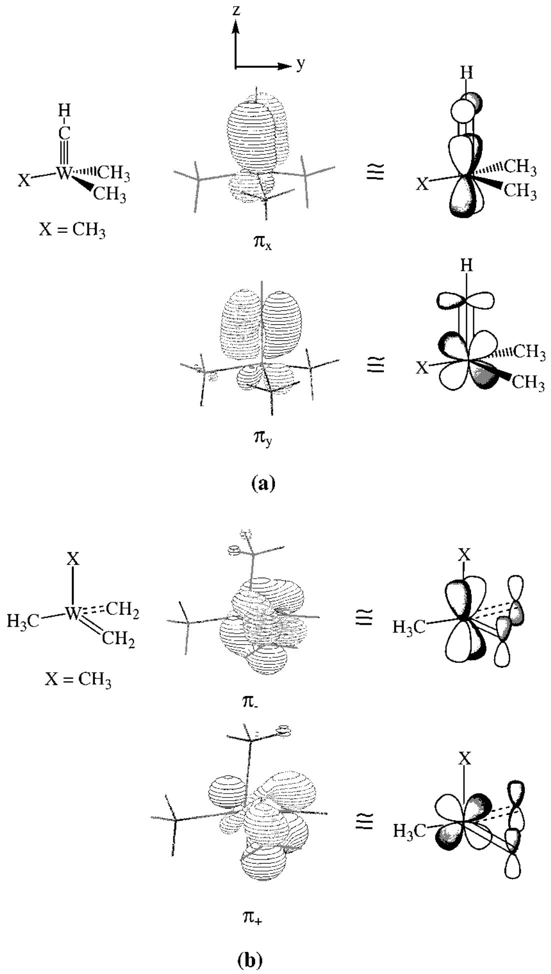

**Figure 3.** (a) Spatial plots of the two highest occupied molecular orbitals ($\pi_x$ and $\pi_y$) for the alkylidyne tautomer **1**, [$(CH_3)_3W(\equiv CH)$]. (b) Spatial plots of the two highest occupied molecular orbitals ($\pi_-$ and $\pi_+$) for the bis(alkylidene) tautomer **2**, [$(CH_3)_2W(=CH_2)_2$]. The molecular orbitals were obtained from the B3LYP calculations.

better $\pi-\pi$ overlap. When X is a $\pi$-donor ligand, the interaction is destabilizing. When X is a $\pi$-acceptor ligand, the interaction, however, is stabilizing. The molecular orbital calculations show that the $Cl^-$ ligand destabilizes the $\pi_y$ orbital while the $SiF_3^-$ ligand stabilizes it the most (see Table 1). Experimentally, the chloro alkylidyne complex $(Bu^tCH_2)_2(Cl)W\equiv CBu^t$ was found to be less thermally stable than its alkyl analogue $(Bu^tCH_2)_3W\equiv CBu^t$.[13]

Figure 3b shows the HOMO and SHOMO for the bis(alkylidene) tautomer **2** when M = W and X = $CH_3$. These two orbitals correspond to the in-phase and out-of-phase linear combinations of the two metal−alkylidene $\pi$-bonding orbitals in **2**. They are assigned as $\pi_-$ and $\pi_+$ depending on their combination characteristics. The $\pi_-$ and $\pi_+$ orbitals are close in energy (see Table 1) when X = $CH_3$. From Figure 3b, we expect a stronger $\pi$ interaction between $\pi_-$ and ligand X because X is now located at the pyramidal position. The $\pi$-donor ligand ($Cl^-$) destabilizes $\pi_-$, while $\pi$-accepting ligands ($CF_3^-$, $SiH_3^-$, and $SiF_3^-$) stabilize it. The trend of $\Delta = [e(\pi_+) - e(\pi_-)]$ values in Table 1 clearly supports the argument above. Here, $e(\pi_+)$ and $e(\pi_-)$ are the orbital energies of $\pi_+$ and $\pi_-$, respectively.

The energy separation of the two $\pi$-bonding orbitals ($\Delta$) for each alkylidyne or bis(alkylidene) structure discussed above can be well understood by considering the increasing trend in the $\pi$-accepting ability of X along the series. The increasing energy separation ($\Delta$) is also well correlated with the decrease in the $HC\equiv M-X$ or $H_2C=M-X$ bond angles.

Clearly, the $\Delta$ values can be used as a measurement of the $\pi$ stabilization effect of a $\pi$-acceptor ligand derived from the structural distortion (decreasing $HC\equiv M-X$ or $H_2C=M-X$ angles) discussed above. The $\Delta$ values in Table 1 show that the extent of stabilization derived from the structural distortion is more significant for the bis(alkylidene) tautomers **2** than that for the alkylidyne tautomers **1**. This observation is consistent with the results of our energetic calculations; that is, the relative stability of the bis(alkylidene) tautomers **2** increases along the series. The greater stabilization for a bis(alkylidene) tautomer **2** containing a better $\pi$-acceptor ligand X, when compared with its corresponding alkylidyne tautomer **1**, can be related to the more electron-rich property of the M=C double bonds (relative to the M≡C triple bond). A metal alkylidyne triple bond is analogous to an alkyne bond,[22] while a metal alkylidene double bond is similar to an alkene bond.[6] In organic chemistry, an alkene double bond is considered to be more electron-rich for electrophilic addition reaction when compared to an alkyne triple bond.[23]

**$d^2$ Transition Metal Alkylidyne and Bis(alkylidene) Complexes.** Model complexes $(CH_3)_2M(\equiv CH)$-

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[22] Cotton, F.; Wilkinson, G.; Gaus, P. L. A. *Basic Inorganic Chemistry*, 3rd ed.; John Wiley: New York, 1995; p 698.

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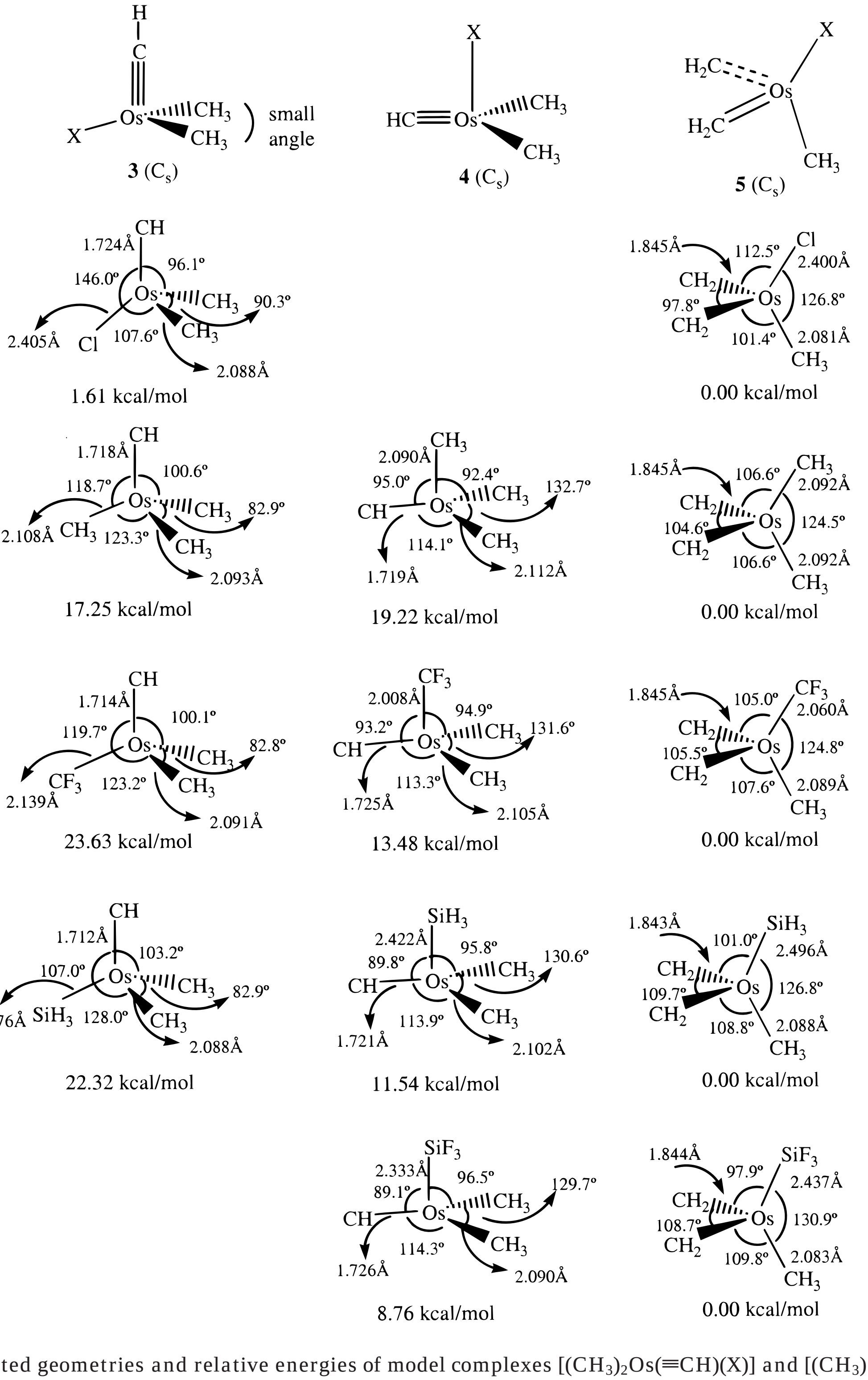


**Figure 4.** Calculated geometries and relative energies of model complexes [$(CH_3)_2Os(\equiv CH)(X)$] and [$(CH_3)Os(=CH_2)_2(X)$] with different substituents X.

(X) and $(CH_3)M(=CH_2)_2(X)$ (M = Os, Ru; X = Cl, $CH_3$, $CF_3$, $SiH_3$, $SiF_3$) are used to simulate the alkylidyne/bis(alkylidene) tautomeric pairs with a four-coordinated $d^2$ metal center. All optimized geometries for these model complexes with different X ligands have approximately $C_s$ symmetry, illustrated in Figures 4 and 5. Interestingly, for some complexes, the alkylidyne tautomer can have two structures (**3** and **4**, the first two columns in the figures), while the bis(alkylidene) tautomer has only one structure (**5**, the third column in the figures). Similar to **1**, **3** has a structure in which the alkylidyne ligand is in the pyramidal position. However, it has one very small $CH_3-M-CH_3$ angle ($<90°$) and two large $X-M-CH_3$ angles ($>120°$). This distortion is not observed for the analogous $d^0$ W and Mo alkylidyne complexes **1** in which the three angles are rather close to each other. Structure **4** has the ligand X in the pyramidal position and the alkylidyne ligand is in the base triangle. The angle between the two methyl groups becomes extremely large (~135°). The

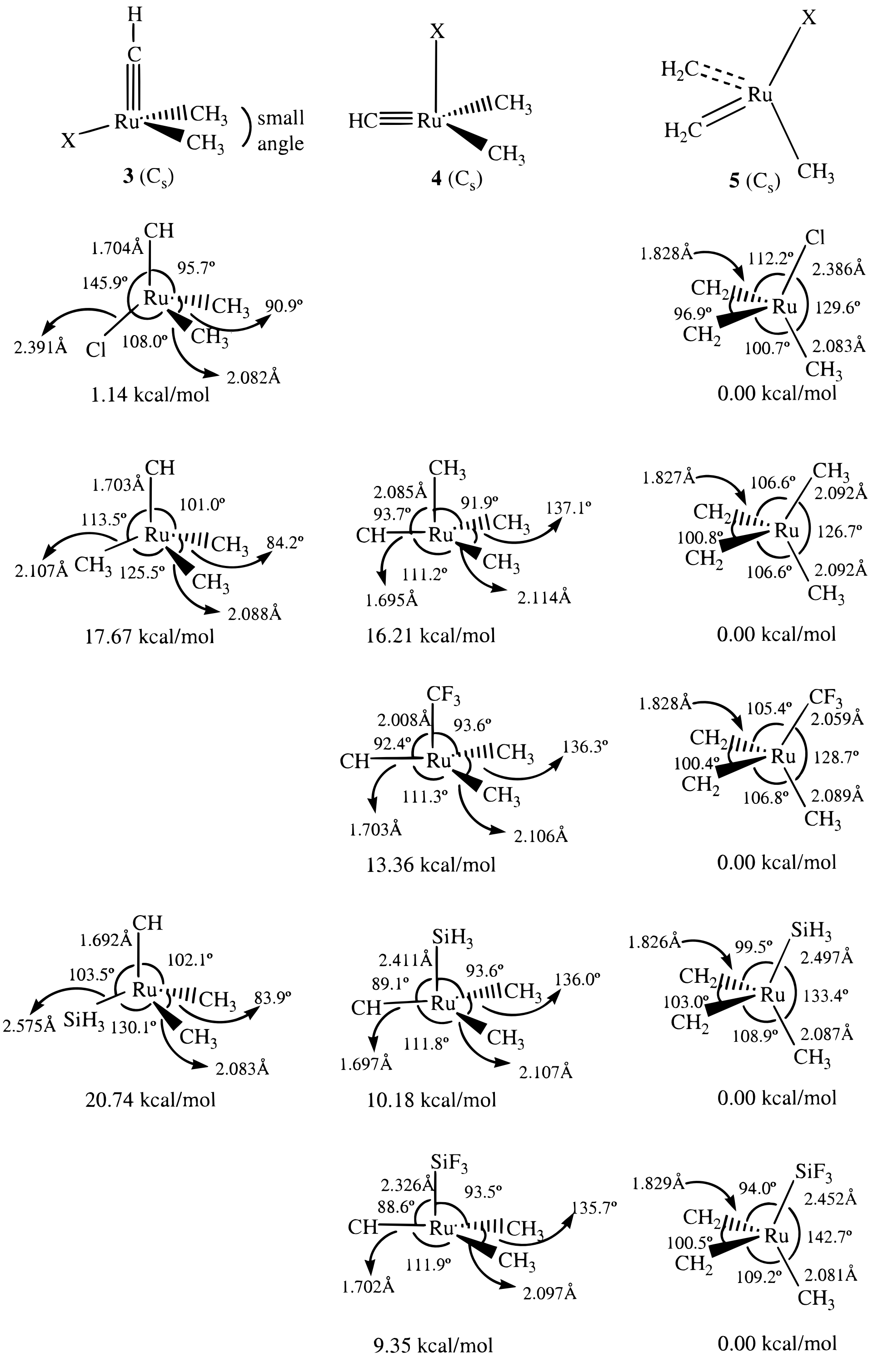
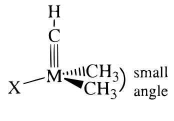
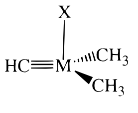


**Figure 5.** Calculated geometries and relative energies of model complexes [$(CH_3)_2Ru(\equiv CH)(X)$] and [$(CH_3)Ru(=CH_2)_2(X)$] with different substituents X.

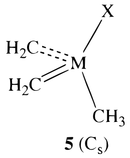
optimized bis(alkylidene) structures **5** adopt a $C_s$ geometry in which all atoms of the two alkylidene ligands lie in the same plane.



**3** ($C_s$)



**4** ($C_s$)



**5** ($C_s$)

To understand why there are two structures for each of the Os and Ru alkylidyne tautomers, it is helpful to start with an idealized $C_{3v}$ trigonal-pyramidal structure, which is adopted by the $d^0$ W and Mo alkylidyne complexes. Figure 6a shows schematically the splitting of d orbitals for a $C_{3v}$ trigonal-pyramidal $L_3M(\equiv CH)$ complex in which the alkylidyne ligand occupies the pyramidal position. The $d_{xz}$ and $d_{yz}$ orbitals are the highest in energy because they are involved in the metal−alkylidyne $\pi$ interactions.[2] The $d_{z^2}$ orbital is also

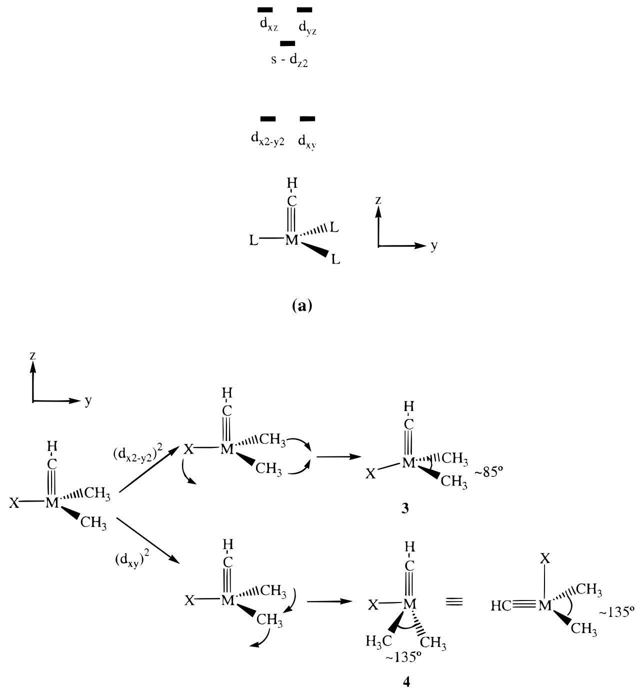


**Figure 6.** (a) Splitting of d orbitals in an idealized $C_{3v}$ $L_3M{\equiv}CH$ metal complex. (b) Schematic diagram showing how the geometries of the two $d^2$ alkylidyne structures **3** and **4** are derived from a trigonal-pyramidal geometry. The occupation of $d_{x^2-y^2}$ leads to **3**, while the occupation of $d_{xy}$ gives **4**.

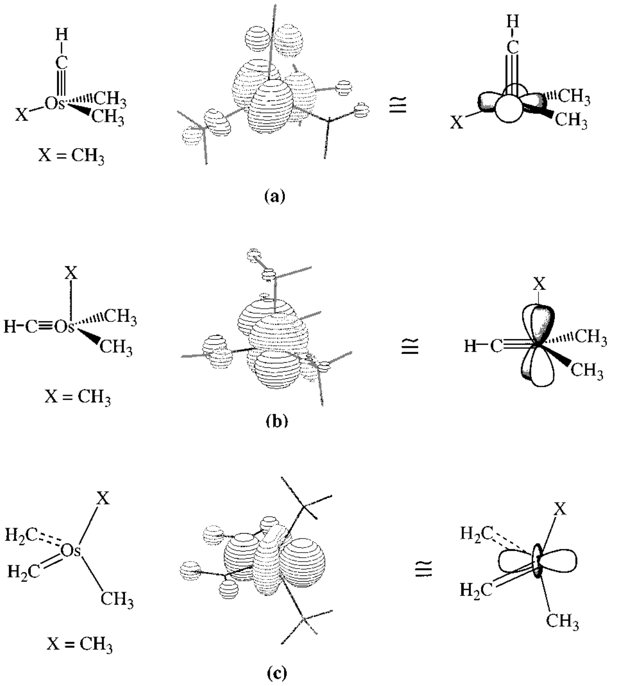


**Figure 7.** (a) Spatial plots of the HOMO for the alkylidyne **3**, $[(CH_3)_3Os({\equiv}CH)$. (b) Spatial plots of the HOMO for the alkylidyne **4**, $[(CH_3)_3Os({\equiv}CH)]$. (c) Spatial plots of the HOMO for the bis(alkylidene) **5**, $[(CH_3)_2Os({=}CH_2)_2]$. The molecular orbitals were obtained from the B3LYP calculations.

$\sigma^*$ antibonding with respect to the alkylidyne ligand. For a $d^2$ complex, the two d electrons are supposed to occupy one of the two degenerate orbitals ($d_{x^2-y^2}$, $d_{xy}$). In such a situation, first-order Jahn–Teller distortions[24] are expected. Based on the structures (see the left and central columns in Figure 4 or 5) obtained from the molecular orbital calculations, the relevant structural distortions are illustrated in Figure 6b to show how each structure is derived from the occupation of either the $d_{x^2-y^2}$ or $d_{xy}$ orbital. Occupation of the $d_{x^2-y^2}$ orbital gives structure **3**, while occupation of $d_{xy}$ leads to structure **4**.

A detailed analysis of bond lengths and bond angles of the two alkylidyne structures in Figures 4 and 5 indicates that there is a slight tendency for ligands X to be ca. 90° with respect to the alkylidyne ligands for structures **4** (see the central column in Figure 4 or 5). However, the tendency of X moving itself toward the electron-rich region of the alkylidyne ligand cannot be observed for structures **3** (see the left column in Figure 4 or 5). For structures **5** (see the right column in Figure 4 or 5), however, ligand X shows again the preference of moving itself toward the electron-rich region of the metal–alkylidene bonds along the series. Compared to the structural distortions observed for the $d^0$ W and Mo complexes, the relevant distortions are less significant. It is expected that these different behaviors in the structural changes are related to the two additional d electrons in the Os and Ru alkylidyne/bis(alkylidene) complexes. To have a thorough understanding of these behaviors, it is helpful to have the spatial plots of the HOMO that accommodates the two d electrons for each of these structures. The spatial plots of the HOMOs for structures **3**, **4**, and **5** when M = Os and X = $CH_3$ are illustrated in Figure 7. The HOMOs of **3**–**5** with other X ligands are similar. In contrast to complexes with a $d^0$ metal center, the HOMO orbitals do not involve p interactions with the alkylidyne or alkylidene ligands.

Figure 7a shows the HOMO, which is a $d_{x^2-y^2}$ orbital, for the alkylidyne tautomer with structure **3** when X = $CH_3$. In the HOMO, except ligand X, all other ligands avoid $\sigma$ overlapping with the d orbital. Indeed, the dihedral angles between the two $HC{\equiv}M{-}CH_3$ planes for all calculated structures **3** are close to 90°. As ligand X is $\sigma^*$ antibonding with the d orbital, the movement of the ligand X toward the more electron-rich region in the metal–alkylidyne multiple bond is prevented. The calculation results indeed show a compromise in which the $HC{\equiv}M{-}X$ angles in **3** are ca. 110–120° (see the left column in Figure 4 or 5). For X = Cl, the angles are ca. 146° for both Os and Ru complexes. The extremely large angles are due to the $\pi$-donor property of the $Cl^-$ ligand. Both the $\pi$-donor property and $\sigma^*$-antibonding character with the $d_{x^2-y^2}$ orbital favor a large angle between the $Cl^-$ ligand and the electron-rich alkylidyne ligand. When X = $SiF_3$, the alkylidyne structure **3** cannot be located from the molecular orbital calculations for both Os and Ru. The strong electrophilic property of $SiF_3^-$ would make a small $HC{\equiv}M{-}SiF_3$ angle (~90°). However, such a small angle is extremely unfavorable because the HOMO would become very antibonding (see Figure 7a). A compromise cannot be made for such a situation. Similar arguments might be applied for the Ru case when X = $CF_3$, although some other factors might also be involved.

Figure 7b shows the HOMO for the alkylidyne structure **4** when X = $CH_3$. All ligands are located in the

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[24] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 99.

nodal regions of the HOMO and no $\sigma^*$-antibonding character exists with the alkylidyne ligand. The HC≡M−X angles are all close to 90° (see the central column in Figure 4 or 5). Therefore, energetically structures **4** are preferred over structures **3**. The spatial orientation of the HOMO allows a maximum d−p $\pi$ interaction with ligand X, which is stabilizing for $\pi$-acceptor ligands and destabilizing for $\pi$-donor ligands. Consequently, the relative stabilities of structures **4** increase with the increasing $\pi$-accepting ability of X along the series. When X = Cl, structure **4** cannot be obtained. Figure 7b shows that the HOMO would experience a very strong $\pi^*$-antibonding interaction. In addition, $\pi$-donor ligand $Cl^-$ tends to have a larger angle with the electron-rich alkylidyne ligand.

Figure 7c shows the HOMO for the bis(alkylidene) tautomer **5** when X = $CH_3$. Again, all the ligands avoid $\sigma^*$-antibonding interaction with the d orbital. The $H_2C$=M−X angles decrease with the increasing $\pi$-accepting ability of ligand X (see the right column in Figure 4 or 5). These structural changes indicate the increasing electrophilicity of ligand X toward the electron-rich region of the alkylidene ligands along the series. Figures 4 and 5 show that the Os and Ru bis(alkylidene) tautomers are more stable than their alkylidyne tautomers. These results agree well with the experimental observation that the energy of the bis(alkylidene) tautomer is generally lower than that of its alkylidyne tautomer for a $d^2$ metal center. The relative stabilities of the bis(alkylidene) tautomers **5** with respect to the alkylidyne structures **4** decrease with the increasing $\pi$-accepting ability of X. This stability trend is opposite of that observed for the W and Mo complexes. The observation here suggests that the stabilization of the HOMO by a stronger $\pi$-acceptor X for an alkylidyne tautomer with structure **4** is more significant.

It is now clear that alkylidyne structures **3** are the least stable because of the $\sigma^*$-antibonding character in the orbital (HOMO, see Figure 7a) occupied by the two d electrons. An increase in the HC≡M−X angles could alleviate the $\sigma^*$-antibonding character at the cost of destabilizing metal−alkylidyne $\pi$-bonding orbitals. When X = Cl, the HC≡M−X angles are close to the tetrahedral angle for the $d^0$ W and Mo alkylidyne complexes and are normally much greater than the tetrahedral angle for other structures in the $d^2$ Os and Ru complexes. Therefore, the alkylidyne tautomer with structure **3** is particularly stable for $(CH_3)_2M(\equiv CH)Cl$ (M = Os and Ru). The alkylidyne structures **4** do not have the $\sigma^*$-antibonding character for the HOMO (see Figure 7b). However, they are expected to experience significant ligand−ligand repulsion because the ligands are not evenly distributed on the coordination sphere. In terms of ligand−ligand arrangements and the bonding feature of the orbital (Figure 7c) occupied by the two d electrons, the bis(alkylidene) structures **5** provide the optimal situation.

## Conclusion

The relative stabilities of four-coordinated transition metal alkylidyne $(CH_3)_2M(\equiv CH)(X)$ and bis(alkylidene) $(CH_3)M(=CH_2)_2(X)$ complexes with $d^0$ (M = W and Mo) and $d^2$ (M = Os and Ru) metal centers (X = Cl, $CH_3$, $CF_3$, $SiH_3$, and $SiF_3$) are examined using density functional molecular orbital theory. For the W and Mo complexes, the relative stabilities of the bis(alkylidene) tautomers with respect to their alkylidyne tautomers increase with the increasing $\pi$-accepting ability of the substituted ligand X (from Cl to $CH_3$, $CF_3$, $SiH_3$ and then to $SiF_3$). The increasing stabilities of the bis(alkylidene) tautomers along the series of X are related to the increasing electrophilic interaction between ligand X and the more electron-rich metal−alkylidene $\pi$ bonds. When X = Cl and $CH_3$, the alkylidyne tautomers are found to be more stable. The bis(alkylidene) tautomers become more stable when X = $SiF_3$. When X = $SiH_3$, the tautomeric pair have similar stabilities. However, the alkylidyne tautomer is slightly more stable when X = $CF_3$.

For the $d^2$ Os and Ru complexes, two alkylidyne structures exist because of the first-order Jahn−Teller effect. The results of calculations indicate that the bis(alkylidene) tautomers are more stable. For the case when X = Cl, the tautomeric pair are predicted to have similar stabilities. The higher stability of the bis(alkylidene) tautomers is related to the optimal ligand arrangement and the nonbonding feature of the HOMO which is occupied by the two d electrons.

The current work deals with the thermodynamic aspect of the alkylidyne and bis(alkylidene) exchanges and explains the relative stabilities of the tautomeric pairs. Studies are underway to probe the kinetic/mechanistic aspect of the exchanges.[25]

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(25) Preliminary calculations show that the transition state of the interconversion between the tautomeric pair of $(CH_3)_2W(\equiv CH)(SiH_3)$ and $(CH_3)W(=CH_2)_2(SiH_3)$ adopts a rhombic structure in which the transferring H is bound to W and the two C atoms involved in the process. The long W- - -H distance (1.826 Å) indicates that the transition state cannot be considered as a normal tungsten hydride.