

## Agostic Structure of Titanium Methylidene Hydride ( $\text{CH}_2=\text{TiH}_2$ ): A Theoretical Investigation for the Elusive Intramolecular Interaction

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In metals complexes, the metal center often forms significant interaction with a C-H bond in vicinity, for the hydrogen atom to position close to the metal atom, called agostic (meaning "toward") interaction.<sup>1</sup> This intra-molecular interaction is in fact counterintuitive, considering the chemically inert nature of the C-H bond, and normally results in a substantial distortion in the ligand structure. While the agostic structures have been investigated by various methods, the experimental evidences are still elusive in many cases, particularly in IR region.<sup>1-4</sup> Moreover, the large ligands, which often contain conjugate systems for stabilization, prohibit application of high level theoretical approaches for exact reproduction of the distinct distortions.

High oxidation-state alkylidene complexes have been investigated extensively since the first discovery in early 1970's.<sup>5</sup> They have provided a wealth of information on the nature of metal coordination chemistry and important new applications, such as metathesis and polymerization catalysts for alkenes and cyclic compounds. In addition, recently a new breed of alkylidene complexes have been introduced from reactions of transition-metal atoms with small alkanes in excess Ar and Ne.<sup>6</sup> Particularly the methylidene hydride ( $\text{CH}_2=\text{MH}_2$ ) is the simplest possible cousin of the large transition-metal complexes. They are considered as model systems to study the ligand effects and electronic structures of the large complexes because they are much more amenable to the higher level of electronic structure calculations, and their photochemical behaviors and spectroscopic characteristics can be closely examined.

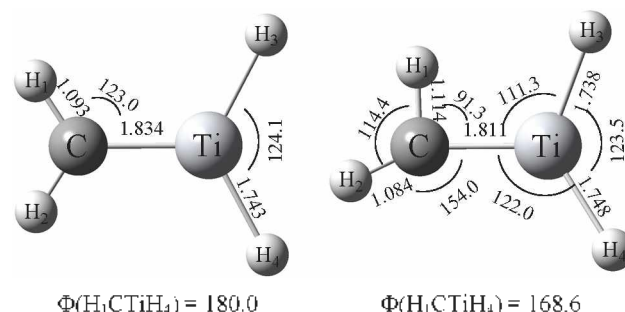
Interestingly enough, these small early transition-metal complexes also show markedly distorted structures, where one of the methylidene hydrogen atoms is significantly inclined to the metal atom (agostic structure).<sup>6-8</sup> The matrix IR spectra of the Group 4 metal methylidene hydrides, which are studied most among the recently introduced complexes, reveal that the two M-H bonds are different, showing two sets of M-H and M-D stretching absorptions between the  $\text{MH}_2$  and  $\text{MD}_2$  bands in the half deuterated isotopomer spectra.<sup>6-8</sup> The following theoretical studies have reproduced the distorted  $\text{C}_1$  structure of the methylidene hydride ( $\text{CH}_2=\text{MH}_2$ ) with two different M-H bonds.<sup>3,4</sup>

In this study, the agostic interaction of titanium methylidene hydride ( $\text{CH}_2=\text{TiH}_2$ ) has been examined at various levels of theory as a subsequent study of the previous report for the Zr analogue. Density functional theory (DFT) calculations were carried out using the Gaussian 03 package,<sup>9</sup>

B3LYP density functional, and 6-311++G(3df,3pd) basis sets for C, H, and Ti (all electron basis). HF, BPW91 functional, MP2, and more rigorous CCSD and CCSD(T) calculations were also done to complement the hybrid functional results. NBO analyses were also carried out to trace the extent of electron delocalization of the agostic C-H bond.<sup>10</sup>

Traditionally the agostic interaction has been explained as electron donation from the nearby C-H bond to the electron-deficient metal center.<sup>1</sup> The strength (typically estimated < 20 kcal/mol) and geometry of these bonds depend on the energy and disposition of the vacant metal orbitals relative to the C-H bonding orbitals and the steric effects imposed to the linkage.<sup>1-3</sup> Recently Scherer and McGrady have claimed that it is in fact a negative hyperconjugative delocalization of the C-M bonding electrons in  $d^0$  complexes to stabilize the carbon-metal bond.<sup>2</sup> More recently Berkaine et al. reported that in Group 4 metal methylidene systems, the occupation number of the M-H bond diagonal to the agostic C-H bond increases with the distortion while that of the C-H bond decreases.<sup>4</sup> However, the NBO results for  $\text{CH}_2=\text{ZrH}_2$  show that the electron delocalization of the agostic C-H bond to the empty Zr d-orbital is more important than to the metal-hydrogen anti-bond ( $\sigma^*$ (M-H)).<sup>11</sup>

Figure 1 shows the structures of  $\text{CH}_2=\text{TiH}_2$  computed at the level of B3LYP/6-311++G(3df,3pd) with planar  $\text{C}_{2v}$  and no constraints. Geometry optimization with planar  $\text{C}_{2v}$  constraint generates not only higher energy but two imaginary frequencies (the  $\text{TiH}_2$  wagging and  $\text{CH}_2$  rocking modes) as well. The



**Figure 1.** Structures of  $\text{CH}_2=\text{TiH}_2$  with planar  $\text{C}_{2v}$  ( $^1\text{A}_1$ ) and no constraint with B3LYP/6-311++G(3df,3pd). The  $\text{C}_{2v}$  structure is 0.5 kcal/mol more stable and generates two imaginary frequencies (the  $\text{TiH}_2$  wagging and  $\text{CH}_2$  rocking modes). Notice that the agostic distortion is accompanied with shortening of the C=Ti bond and elongation of the C-H<sub>1</sub> and Ti-H<sub>1</sub> bonds. The bondlengths and angles are in Å and deg. The  $\text{H}_1\text{CTiH}_2$  dihedral angles are also shown.

**Table 1.** Geometrical Parameters, Occupation numbers, and Delocalization Energies Related to the Agostic Interaction of  $\text{CH}_2=\text{TiH}_2$  in Its Ground Singlet State<sup>a</sup>

| Method                    | $r(\text{C-H}_1)/$<br>$r(\text{C-H}_2)$ | $\angle \text{H}_1\text{CTi}/$<br>$\angle \text{H}_2\text{CTi}$ | $r(\text{C=Ti})$ | $\angle \text{CTiH}_3/$<br>$\angle \text{CTiH}_4$ | $\sigma(\text{C-H}_1)/$<br>$\sigma(\text{C-H}_2)^b$ | $\sigma^*(\text{Ti-H}_1)^b/$<br>$\text{DE}^c$ | $\text{LP}^*(\text{Ti})^b/$<br>$\text{DE}^c$ |
|---------------------------|---|---|------------------|---|---|---|--|
| HF/6-311++G               | 1.086/1.086                             | 124.4/124.4   | 1.851            | 116.8/116.8                                       | 1.983/1.983   | 0.029/6.94                                    | 0.006/0.72                                   |
| HF/6-311++G(3df,3pd)      | 1.100/1.077                             | 100.2/147.5   | 1.818            | 114.4/120.8                                       | 1.960/1.989   | 0.046/17.57                                   | 0.003/1.25                                   |
| B3LYP/6-311++G            | 1.096/1.096                             | 123.0/123.0   | 1.840            | 115.5/115.5                                       | 1.972/1.972   | 0.030/4.61                                    | 0.019/2.10                                   |
| B3LYP/6-311++G(d)         | 1.115/1.089                             | 94.9/151.2  | 1.816            | 112.1/123.0                                       | 1.934/1.984   | 0.061/13.81                                   | 0.015/2.22                                   |
| B3LYP/6-311++G(2d,p)      | 1.116/1.086                             | 91.9/153.7  | 1.814            | 111.9/123.5                                       | 1.927/1.984   | 0.067/15.36                                   | 0.015/1.98                                   |
| B3LYP/6-311G(3df,3pd)     | 1.116/1.085                             | 90.2/155.6  | 1.803            | 111.6/123.3                                       | 1.930/1.981   | 0.066/15.85                                   | 0.004/1.38                                   |
| B3LYP/6-311++G(3df,3pd)   | 1.114/1.084                             | 91.3/154.0  | 1.811            | 111.3/122.0                                       | 1.924/1.984   | 0.068/15.20                                   | 0.021/3.67                                   |
| BPW91/6-311++G            | 1.105/1.105                             | 123.1/123.1   | 1.848            | 117.5/117.5                                       | 1.970/1.970   | 0.033/4.30                                    | 0.009/1.30                                   |
| BPW91/6-311++G(3df,3pd)   | 1.126/1.092                             | 88.7/157.1  | 1.816            | 110.5/125.4                                       | 1.912/1.982   | 0.079/15.48                                   | 0.014/2.11                                   |
| MP2/6-311++G              | 1.140/1.088                             | 84.5/155.6  | 1.811            | 110.5/120.3                                       | 1.926/1.990   | 0.074/28.73                                   | 0.014/3.34                                   |
| MP2/6-311G(3df,3pd)       | 1.134/1.081                             | 78.3/163.2  | 1.792            | 108.7/121.4                                       | 1.911/1.988   | 0.082/34.66                                   | 0.017/5.55                                   |
| MP2/6-311++G(3df,3pd)     | 1.134/1.081                             | 78.5/163.1  | 1.799            | 108.6/121.7                                       | 1.904/1.992   | 0.091/38.19                                   | 0.013/2.48                                   |
| CCSD/6-311++G             | 1.105/1.105                             | 124.3/124.3   | 1.926            | 115.7/115.7                                       | 1.987/1.987   | 0.029/5.26                                    | 0.005/<0.50                                  |
| CCSD/6-311++G(3df,3pd)    | 1.119/1.084                             | 87.3/160.2  | 1.839            | 111.2/122.2                                       | 1.937/1.992   | 0.062/26.06                                   | 0.004/1.73                                   |
| CCSD(T)/6-311++G(3df,3pd) | 1.127/1.086                             | 83.3/162.7  | 1.840            | 110.2/123.3                                       | 1.927/1.992   | 0.068/30.14                                   | 0.007/1.73                                   |

<sup>a</sup>Bond lengths and angles are in Å and degree, and delocalization energies in kcal/mol. <sup>b</sup>Occupation number. <sup>c</sup>Delocalization energy.

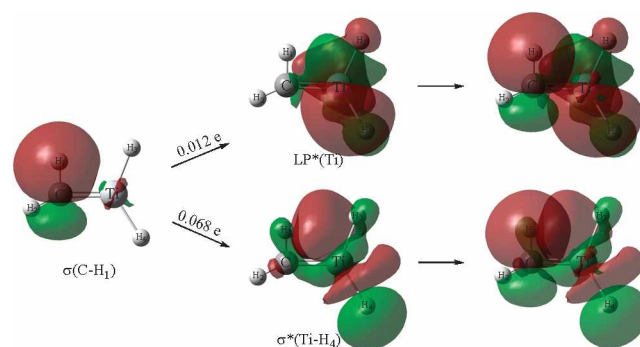
methylene group is markedly rotated ( $\angle \text{H}_1\text{CTi}$  and  $r(\text{H}_1\cdots\text{Ti}) = 91.3^\circ$  and 2.148 Å) in the  $\text{C}_1$  structure for one of the methylene hydrogen atom to locate close to the metal center, and the C-H<sub>1</sub> bond is elongated to 1.114 Å. The Ti atom is at the apex of the asymmetric trigonal pyramid formed by the C, Ti, and two hydrogen atoms (the  $\angle \text{CZrH}_3$ ,  $\angle \text{CZrH}_4$ , and  $\angle \text{H}_3\text{ZrH}_4$  are 111.3, 122.0, and 123.5°, respectively). The agostic angle ( $91.3^\circ$ ) is comparable to that of the Zr analogue ( $92.9^\circ$ ),<sup>11</sup> while the Ti complex is more planar. The geometric parameters related to the agostic distortion and the natural occupation numbers computed at various levels of theory are listed in Table 1.

Clearly the theoretical methods employed in this study with the 6-311++G(3df,3pd) basis set all generate an agostic structure for  $\text{CH}_2=\text{TiH}_2$  in its singlet ground state, parallel to the case of the Zr analogue.<sup>11</sup> Among them the MP2 and HF structures are most and least agostic ( $\angle \text{H}_1\text{CTi} = 78.5$  and  $100.2^\circ$ ), and the BPW91, CCSD and CCSD(T) agostic angles are 88.7, 87.3 and  $83.3^\circ$ . It is notable that parallel to the Zr case,<sup>11</sup> absence of the polarization functions leads to a  $\text{C}_s$  structure with two equal Ti-H bonds except for the case of MP2, which produces a less agostic structure instead. Table 1 also shows that the extent of distortion increases with the size of the polarization functions: from B3LYP/6-311++G (no polarization function) to B3LYP/6-311++G(3df,3pd), the agostic distortion gradually increases (from 123.0 (no distortion) to  $91.3^\circ$ ). On the other hand, the diffusion function only slightly changes the angle. The present results reconfirm the fact that the polarization functions are essential to reproduce the agostic interaction.<sup>7,11</sup>

The agostic distortion is also associated with the shorter C=Ti bond as shown in Table 1. The carbon-titanium bond lengths are 1.811 and 1.840 Å in the B3LYP  $\text{C}_1$  and  $\text{C}_s$  (no agostic distortion) structures from computations with and

without the polarization functions. The C-H<sub>1</sub> and Zr-H<sub>1</sub> bonds elongate from 1.096 to 1.114 Å and from 1.746 to 1.748 Å, respectively, as the C=Ti bond shortens. The extent of bond shortening varies substantially with the level of computation: the HF, B3LYP, BPW91, MP2, and CCSD methods lead to the decreases of 0.033, 0.029, 0.032, 0.019, and 0.087 Å, respectively. Strengthening of the C=Ti bond with the agostic distortion strongly suggests that the agostic interaction is correlated with attraction between the  $\text{CH}_2$  and  $\text{TiH}_2$  moieties while weakening the C-H<sub>1</sub> and Zr-H<sub>1</sub> bonds. This is also in line with the previous results for the origin of the agostic interaction, redistribution of the agostic C-H bond electrons to stabilize the carbon-metal bond.<sup>1-4</sup>

The NBO occupation numbers of the two C-H bonds are substantially different each other; those of the agostic C-H<sub>1</sub>



**Figure 2.** Illustration for delocalization of the natural C-H<sub>1</sub> bonding electrons using the natural orbitals. Unlike the case of  $\text{CH}_2=\text{ZrH}_2$ , the donation to the empty Ti d-orbitals is insignificant while the electron redistribution to  $\sigma^*(\text{Ti-H}_1)$  accounts for most of the electron delocalization energy. Notice that the overlap of  $\sigma(\text{C-H}_1)$  with  $\sigma^*(\text{Ti-H}_1)$  is far more effective than with a Ti d-orbital. The empty Ti d-orbital is grouped as  $\text{LP}^*$  in the NBO analysis.

and C-H<sub>2</sub> bonds are estimated 1.924 and 1.984 at the B3LYP/6-311++G(3df,3pd) level. It is noticeable that the occupation number of the Ti-H<sub>4</sub> anti-bonding orbital ( $\sigma^*(\text{Ti-H}_4)$ ) is 0.068, whereas electron donation to the empty Ti d-orbitals is almost negligible. In Figure 2, the natural orbitals mostly involved in the agostic interaction are illustrated on the C<sub>1</sub> structure. The present results contrast to the previous CH<sub>2</sub>=ZrH<sub>2</sub> case, where electron donation of the agostic C-H bond to the metal center is more important than electron delocalization to  $\sigma^*(\text{Zr-H}_4)$ .<sup>11</sup> The large delocalization energy from the C-H<sub>1</sub> bond to the Ti-H<sub>4</sub> anti-bond with various levels of theory (6.94-38.19 kcal/mol) is considered as the primary origin of the agostic interaction, being consistent with the recent results of Berkaine *et al.*<sup>4</sup>

Table 1 also shows that the larger agostic distortion is normally accompanied with a larger occupation number of  $\sigma^*(\text{Ti-H}_4)$  and electron delocalization energy. For example, the largest MP2  $\sigma^*(\text{Ti-H}_4)$  occupation number of 0.091 and delocalization energy of 38.19 kcal/mol lead to the largest agostic angle of 78.5°. In comparison, the smallest HF distortion ( $\angle \text{H}_1\text{CTi} = 124.4^\circ$ ) is correlated with the smallest delocalization (0.029 and 6.94 kcal/mol). In comparison with the previously reported values,<sup>1-4</sup> the HF methods evidently underestimate the agostic interaction, whereas the MP2 method overestimates. The increases in the B3LYP and BPW91 delocalization energies to  $\sigma^*(\text{Ti-H}_4)$  with the agostic distortion from the C<sub>s</sub> structures (10.59 and 11.18 kcal/mol with the 6-311++G(3df,3pd) basis set) are comparable to the previously estimated values,<sup>3,4</sup> whereas the increase in the CCSD value (20.8 kcal/mol) is somewhat too high.

Absence of the polarization functions not only gives a C<sub>s</sub> structure (no agostic distortion) with most methods (except MP2) but a much smaller occupation number for  $\sigma^*(\text{Ti-H}_4)$  and delocalization energy as well.<sup>7,11</sup> Evidently the polarization functions reshape the C-H bond orbital to effectively overlap with  $\sigma^*(\text{Ti-H}_4)$ , which carries a strong Ti d-character, and the effective overlap is expected to overcome the structural strain due to the distortion of the CH<sub>2</sub> group from the ethylene-like C<sub>s</sub> structure. This overlap between the C-H bonding and Ti-H<sub>4</sub> anti-bonding orbitals shortens the C=Ti bond and elongates the C-H and Ti-H bonds. The SDD core potential and basis set<sup>9</sup> for Ti (instead of all electron basis) also give similar results. This hyperconjugative  $\sigma(\text{C-H}_1) \rightarrow \sigma^*(\text{Ti-H}_4)$  delocalization also bears a resemblance to the  $\sigma(\text{C-H}) \rightarrow \sigma^*(\text{C}^+-\text{H}^+)$  interaction of ethane, which is sensitive to H-C-C'-H' dihedral angle, the torsional variation being the origin of the rotational barrier.<sup>12</sup>

In contrast, the electron coordination to the metal d-orbital is more important than to  $\sigma^*(\text{Zr-H}_4)$  in the Zr analogue, although the total electron delocalization energies of the two systems are comparable.<sup>11</sup> The origin of the difference is not clear at this point; however, it is noticeable that the Zr d-orbital in the methylene complex is close to the typical atomic d-orbital. The large deviation from the planar structure particularly at the metal center leads to the different lobe sizes

of the metal d-orbital, which most likely increases overlap with the C-H bond.<sup>11</sup> On the other hand, the more complicate Ti d-orbital of the methylene hydride suggests more contributions from other atomic orbitals. The NBO results also show that the Zr d-orbital in the complex is almost pure d-orbital, whereas large s- and p-characters (28.24 and 4.30%) are involved in the Ti d-orbital. While the details are yet to be investigated further, the electron donation from the C-H bond to the nearly pure d-orbital is apparently more favored.

In conclusion, the agostic structure of the first row transition-metal methylene hydride (CH<sub>2</sub>=TiH<sub>2</sub>) is reproduced at all levels of theory used in this study, but the extent of interaction varies widely with the methods. The NBO analyses show that the agostic distortion of CH<sub>2</sub>=TiH<sub>2</sub> is accompanied with electron delocalization of the C-H bond mostly to  $\sigma^*(\text{Ti-H}_4)$ , whereas delocalization to the empty Ti d-orbitals is estimated to be insignificant. While the total delocalization energies are comparable, the present result differs from the case of the Zr analogue, where donation to the d-orbital is the most important part of the electron delocalization.<sup>11</sup> The polarization functions are again essential for reproduction of the agostic interaction, suggesting that the polarization functions reshape the C-H bond orbital for a more effective overlap with the Ti-H anti-bonding orbital, which leads to the agostic distortion and shorter C=Ti bond due to extra attraction between the CH<sub>2</sub> and TiH<sub>2</sub> moieties.

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