Agostic Interaction of the Smallest Zirconium Methylidene Hydride: Reproduction of the Distorted Structure Experimentally Observed in Matrix Infrared Spectra

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Many transition metals, including lanthanides and actinides, form C-H(X) insertion products and also high oxidation-state complexes with a carbon-metal multiple bond *via* following H(X) migration in reactions with small hydrocarbons and halomethanes.[1,2] These new breed of metal complexes, small cousins of metal complexes with large ligands, often show unique structures and photochemical properties. Particularly the methylidene complexes often show markedly distorted structures for one of the hydrogen atoms to position close to the metal atom (agostic structure).[2,3] These small complexes are more amenable to higher level of theoretical investigations and, therefore, considered as ideal systems to investigate the distinct structures and ligand effects of the transition-metal complexes with larger ligands.

While many transition-metal complexes with large ligands are often agostic, the experimental evidences are often elusive particularly in IR spectra.[1-3] Recently $CH_2=ZrH_2$, the smallest possible methylidene hydride complex, is generated from reactions of laser-ablated Zr atoms and methane isotopomers in excess neon and argon.[6] The strong symmetric and anti-symmetric stretching ZrH_2 absorptions, along with the deuterium counterparts, are observed along with other lower frequency absorptions. More importantly the two sets of Zr-H as well as Zr-D stretching absorptions of the half deuterated species are observed between the strong symmetric and anti-symmetric stretching bands, a strong IR evidence for the agostic structure.[6]

Normally the decoupled M-H stretching bands appear at the middle of the symmetric and anti-symmetric stretching bands if the two M-H bonds are identical. The two sets of strong absorptions observed between the symmetric and anti-symmetric ZrH_2 and ZrD_2 stretching absorptions, therefore, indicate that the molecule is markedly distorted such that the decoupled M-H stretching frequencies differ as large as 16.5 cm^{-1} in a Ne matrix.[6] Furthermore, electronic structure calculations show that $CH_2=ZrH_2$ has a highly distorted C_1 structure, where the methylene group is considerably distorted, and the Zr atom is located at the apex of the trigonal pyramid structure.[2,3,6] The 8 possible isotopomers with C_1 symmetry shown in Scheme 1 are grouped into four sets (**1-2**, **3-5**, **4-6**, and **7-8**), the two configurations in each set having essentially the same hydrogen stretching frequencies.[6] Calculations with the planar C_{2V} symmetry constraint generate two imaginary frequencies (the ZrH_2 wagging and CH_2 rocking modes).

In this study we have carried out a theoretical investigation at various levels in an effort to properly understand the details of the agostic interactions, which often play an important role for the structures of high oxidation-state transition-metal complexes. Density functional theory (DFT) calculations were carried out using the Gaussian 03 package,[7] the B3LYP density functional, 6-311++G(3df,3pd) basis sets for C, H, and SDD pseudopotential and basis for Zr (28 electron core). 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.[8]

Traditionally the agostic (meaning "toward") interaction has been explained as electron donation from the nearby C-H bond to the electron-deficient metal center.[4,5] 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.[3,4] Recently Sherer and McGrady have claimed that it is in fact a negative hyperconjugative delocalization of M-C bonding electrons in d^0 complexes to stabilize the carbon-metal bond.[5] More recently Berkaine et al. reported that the Group 4 metal methylidene systems, particularly $CH_2=TiH_2$, are essentially single configuration problems, and 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, suggesting strong electron delocalization of the agostic C-H bond to the metal-hydrogen anti-bond (σ^*(M-H)).[9]

The B3LYP/6-311++G(3df,3pd)/SDD structure of $CH_2=ZrH_2$ in its singlet ground state is shown in Figure 1 with the natural orbitals mostly involved in the agostic interaction. The methylene group is markedly rotated such that $\angle H_1CZr$ and $r(H_1\cdots Zr)$ are 92.9° and 2.300 Å, and the $C-H_1$ bond is elongated to 1.115 Å. The Zr atom is at the apex of the asymmetric trigonal pyramid formed by the C, Zr, and two hydrogen atoms (the $\angle CZrH_3$, $\angle CZrH_4$, and $\angle H_3ZrH_4$ are 105.9, 110.2, and 116.4°, respectively). The related geometric parameters at various levels of theory and the natural occupation numbers are listed in Table 1, which shows that the MP2 structure with the same basis is most agostic ($\angle H_1CZr$ = 80.1°) while the BPW91 structure is in between. The CCSD and CCSD(T) agostic angles are 86.1 and 83.8°, comparable to that of the BPW91 structure (85.5°).

The NBO occupation number of the agostic $C-H_1$ bond (1.924) estimated at the B3LYP/6-311++G(3df,3pd)/SDD level is considerably lower than the that for the $C-H_2$ bond

(1.993), whereas that of the Zr-H_4 anti-bonding orbital (σ^*(Zr-H_4)) is 0.037, in line with the recent results of Berkaine *et al.*[9] In addition, the occupation number for the Zr d-orbital is 0.060, showing the electron delocalization from the C-H bond occurs to the empty Zr d-orbital as well. Computation with the C_{2v} constraint and same basis set gives the C-H bonding, Zr-H anti-bonding, and Zr d-orbital occupation numbers of 1.988, 0.018, and 0.006 (not listed in Table 1), respectively. As a result, the electron delocalization of the Zr-H orbital in the C_{2v} structure is also far less important (only 1.64 kcal/mol).

Table 1 also shows that the more agostic BPW91 and MP2 structures are accompanied with the more electron delocalization. The B3LYP, BPW91, and MP2 delocalization energies (with B3LYP/6-311++G(3df,3pd)/SDD) to the σ^*(Zr-H_4) bond increase 4.9, 1.1, and 8.5 kcal/mol, respectively, from the C_{2v} (constrained) to C_1 structure, and those to the Zr d-orbital increase 13.3, 23.7, and 32.7 kcal/mol, respectively. Clearly the delocalization to the Zr d-orbital is substantially more important in most cases than to the Zr-H_4 anti-bond. While the increase in the sum of the B3LYP delocalization energies (~18 kcal/mol) is comparable to the previously estimated values,[4,5] the BPW91 and MP2 values are noticeably higher. The agostic distortion is also associated with the shorter C=Zr bond, in line with the recent report that the agostic interaction arises from negative hyperconjugation to stabilize the carbon-metal bond.[5]

While the details still need to be investigated further, these NBO results strongly indicate that the agostic structure, which is in fact counterintuitive, is a result of molecular distortion for more effective donation of the C-H bond electrons to the Zr-H_4 anti-bonding and empty Zr d-orbitals. The present results are also consistent with the previous investigations for the causes of the intra-molecular interaction, electron donation from the C-H bond in proximity to the empty metal d-orbital,[3,4] electron delocalization for stabilization of the carbon-metal bond,[5] and occupancy transfer to the σ^*(Zr-H) orbital.[9]

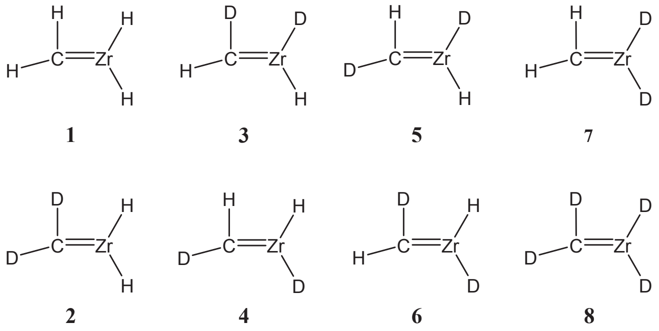
Interestingly enough, Table 1 also shows that removal of the diffusion functions from the basis set yields only negligible effects to the agostic structure, whereas the polarization functions play a major role for the agostic distortion at all levels of theory used in this study. Without the polarization functions, the geometry optimizations end up with a C_s structure with the two equal Zr-H bonds, in line with the recent matrix infrared study.[2] This clearly shows the importance the polarization function in reproducing electron delocalization in a transition-metal complex. Also shown in Table 1 is that the polarization functions for C is more important than for H. Inclusion of polarization functions for C but not for H leads to more agostic distortion and electron delocalization of the C-H bond than the reverse, reconfirming that the distinct inclination of the H atom is a result from the interaction of the C-H bond, not the H atom alone.[3-5,9]

Polarization functions (one or three sets of f-orbitals) are also added to the SDD effective core potential and basis.[10] Table 1 shows that addition of the polarization functions slightly increases the agostic distortion as well as the extent of the electron delocalization. Moreover, the observed Zr-H and Z-D stretching frequencies for the CH_2=ZrH_2 isotopomers[6] are best reproduced by the basis set with most polarization functions. For example, the Zr-H and Zr-D stretching modes of **3** and **5** are predicted 8.4 and 17.5 cm^{-1} above the ZrH_2 and ZrD_2 anti-symmetric stretching modes of **1** and **8**, respectively

Table 1. Geometrical Parameters, Occupation numbers, and Delocalization Energies Related to the Agostic Interaction of CH_2=ZrH_2 in Its Ground Singlet State[a]

Method	r(C-H_1)/ r(C-H_2)	<H_1CZr/ < H_2CZr	r(C=Zr)	<CZrH_3/ <CZrH_4	σ(C-H_1)/ σ(C-H_2)[b]	σ^*(Zr-H_4)[b]/ DE[c]	LP*(Zr)[b]/ DE[c]
B3LYP/6-311G/SDD	1.097/1.097	123.5/123.5	1.981	109.5/109.5	1.974/1.974	0.021/2.39	0.030/2.63
B3LYP/6-311++G/SDD	1.097/1.097	123.5/123.5	1.982	109.5/109.5	1.975/1.975	1.021/2.24	0.030/2.55
B3LYP/6-311++G(3df,3pd), 6-311++G/SDD[d]	1.111/1.083	96.3/150.0	1.968	106.2/110.7	1.935/1.985	0.035/5.69	0.051/10.81
B3LYP/6-311++G, 6-311++G(3df,3pd)/SDD[e]	1.117/1.086	94.0/152.7	1.955	106.5/111.0	1.928/1.986	0.038/6.84	0.056/13.14
B3LYP/6-311G(3df,3pd)/SDD	1.116/1.084	92.9/153.5	1.954	105.9/110.1	1.922/1.986	0.083/6.85	0.061/14.37
B3LYP/6-311++G(3df,3pd)/SDD	1.115/1.084	92.9/153.5	1.955	105.9/110.2	1.924/1.993	0.037/6.50	0.060/13.87
B3LYP/6-311++G(3df,3pd)/SDD(f)[f]	1.117/1.084	91.7/154.8	1.946	106.5/111.6	1.921/1.986	0.040/7.61	0.060/14.33
B3LYP/6-311++G(3df,3pd)/SDD(3f)[f]	1.118/1.084	91.2/155.4	1.943	106.8/112.3	1.919/1.986	0.041/8.13	0.059/14.49
B3LYP/6-311++G/SDD(3f)	1.098/1.098	123.6/123.6	1.969	111.3/111.3	1.975/1.975	0.021/2.64	0.027/2.43
BPW91/6-311++G/SDD	1.105/1.105	123.5/123.5	1.981	108.2/108.2	1.970/1.970	0.020/1.79	0.040/2.54
BPW91/6-311G(3df,3pd)/SDD	1.135/1.091	85.5/161.4	1.943	103.8/104.5	1.878/1.983	0.035/4.66	0.114/24.70
BPW91/6-311++G(3df,3pd)/SDD	1.135/1.091	85.5/161.4	1.943	103.8/104.5	1.879/1.984	0.034/4.26	0.113/24.22
MP2/6-311++G/SDD	1.103/1.103	122.7/122.7	1.995	111.3/111.3	1.984/1.984	0.023/3.81	0.012/2.17
MP2/6-311G(3df,3pd)/SDD	1.133/1.081	80.1/166.6	1.926	104.5/109.3	1.898/1.992	0.053/13.19	0.074/34.83
MP2/6-311++G(3df,3pd)/SDD	1.133/1.082	80.1/166.7	1.927	104.6/109.5	1.900/1.992	0.052/13.34	0.071/33.60
CCSD/6-311++G(3df,3pd)/SDD	1.124/1.082	86.1/162.2	1.942	108.1/117.9	1.928/1.992	0.055/20.40	0.029/11.82
CCSD(T)/6-311++G(3df,3pd)/SDD	1.130/1.084	83.8/164.1	1.947	106.7/115.0	1.919/1.992	0.054/18.10	0.043/18.48

[a] Bond lengths and angles are in Å and degree, and delocalization energies in kcal/mol. [b] Occupation number. [c] Delocalization energy. [d] H and C with and without polarization functions. [e] H and C without and with polarization functions. [f] Polarization functions (f-orbitals) added to the Zr basis.[10]



Scheme 1

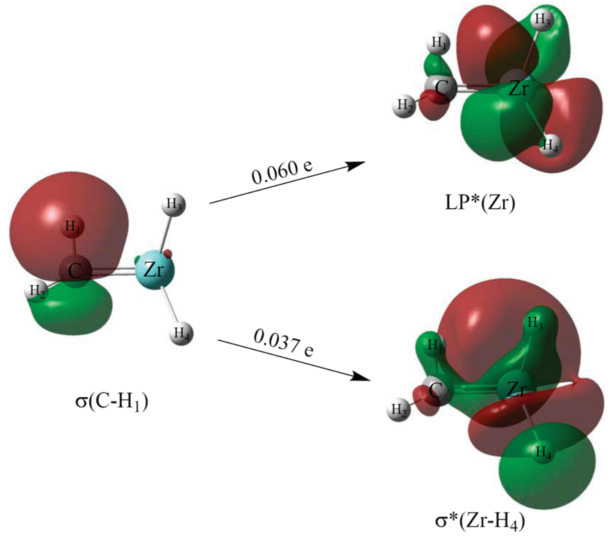


Figure 1. Delocalization of the natural C-H_1 bonding electrons to the Zr d- and Zr-H_4 anti-bonding orbitals.

(Scheme 1). They are observed 8.3 and 17.0 cm^{-1} above the strong ZrH_2 and ZrD_2 anti-symmetric stretching absorptions at 1546.2 and 1112.3 cm^{-1}.[6] Likewise the Zr-H and Zr-D stretching modes of **4** and **6** are predicted 27.3 and 3.6 cm^{-1} above the strong anti-symmetric modes, and they are observed 24.8 and 4.0 cm^{-1} above.

However, the polarization functions for C and H are still essential to reproduce the agostic structure even when the polarization functions are added to the Zr basis set; computation with polarization functions for Zr and none for C and H also leads to a C_s structure with two equal C-H bonds (no agostic distortion).

In conclusion, the NBO analyses show that the agostic-distortion of the smallest Zr methylidene hydride (CH_2=ZrH_2) is accompanied with electron delocalization to both the σ*(Zr-H_4) bond and Zr d-orbital. The increases in occupation number and delocalization energy of the Zr d-orbital are significantly higher than those of the σ*(Zr-H_4) bond. The BPW91, MP2, and CCSD methods produce more distorted structures and electron delocalization energies than the B3LYP method. The polarization functions for H and C are essential to reproduce the agostic distortion, of which the latter is more important than the former. Computations without the polarization functions lead to a C_s structure with two equal C-H bonds and insignificant delocalization energy. Addition of the polarization functions for Zr increases the agostic interaction and best reproduces the vibrational characteristics as well.

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