C–H Activation

[$H_2C{=}ZrH_2$]: The Simplest Carbene Hydride Complex, Agostic Bonding, and C–H Activation of CH_4 to Form [$(CH_3)_2ZrH_2$]**

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High oxidation state transition-metal complexes with a carbon–metal double bond have proven important for understanding the nature of metal coordination and for catalysts in alkene-metathesis and alkane-activation reactions.[1–3] Several early transition-metal alkylidenes are agostic,[1] and these compounds provide the opportunity to characterize the agostic interaction of hydrogen to a transition-metal center in a simple carbene complex (most agostic interactions involve much more complicated systems) and to help understand the important alkane C–H bond-activation process (a key step in many transition-metal catalyzed reactions).[4–8]

The simplest compound of this type is the methylidene complex, [$H_2C{=}MH_2$], which is an ideal model system to examine substituent effects and the agostic interaction. Such Group 4 compounds have been investigated by electronic-structure calculations using small basis sets and shown to have symmetrical structures without agostic interactions.[9–11] Recently we have treated laser-ablated Ti, Zr, and Hf atoms with CH_3F and prepared the fluorine substituted [$H_2C{=}MHF$] derivatives.[12–14] These methylidene species result from α-hydrogen migration in the initial [CH_3MF] intermediate. Our electronic-structure calculations using basis sets with polarization functions reveal a tilted CH_2 group and provide evidence for agostic interaction in the [$H_2C{=}MHF$] molecules.

The simple [$H_2C{=}MH_2$] analogues contain two intense infrared chromophores, namely the CH_2 and MH_2 groups, which are sensitive to the distortion associated with intramolecular agostic bonding. Hence the IR spectrum of [$H_2C{=}ZrH_2$] can provide evidence for agostic interaction through symmetry lowering in the molecule, as can computations using large basis sets. In particular, a simple count of [$CHD{=}ZrHD$] isotopomers provides a ready method to confirm agostic interactions in this simplest possible carbene complex, as only two isotopomers (*cis* and *trans*) will be formed if there is no agostic interaction (C_{2v} or C_s symmetry), but four isotopomers (*cis* and *trans* for H and for D in the agostic position) if there is agostic interaction (C_1 symmetry). We report herein the first experimental characterization of [$H_2C{=}ZrH_2$] and demonstrate the agostic C–H···Zr interaction from the IR spectrum in solid neon and from density functional structure and frequency calculations.

The laser-ablation matrix-IR experiment has been described elsewhere.[15,16] Briefly, laser-ablated zirconium atoms (Johnson–Matthey) reacted with CH_4 (Matheson), $^{13}CH_4$, CD_4, CH_2D_2 (Cambridge Isotopic Laboratories) in excess neon (Spectra Gases) during condensation on a CsI window at 5 K. IR spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 750 spectrometer with HgCdTe detector. Samples were irradiated by a mercury arc lamp (175 W, globe removed), were annealed, and more spectra were recorded.

Complementary density functional theory (DFT) calculations were performed using the Gaussian 98 package,[17] B3LYP density functional, 6-311++G(2d,p) basis sets for C and H atoms, and SDD pseudopotential and basis set for the Zr atom to provide a consistent set of vibrational frequencies for the reaction products. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed via vibrational analysis. All the vibrational frequencies were calculated analytically.

IR spectra are illustrated in Figure 1 in the Zr–H stretching region for laser-ablated Zr and CH_4 (0.4 % in neon). Four new product absorptions are observed at 1546.2 and 1581.0 cm^{-1} (labeled **1**) and at 1587.5 and 1617.2 cm^{-1} (labeled **di**). The bands increased on $\lambda > 530$ nm and 240–380 nm irradiations. Annealing to 10 K sharpened and slightly increased these absorptions, and produced a new 1551.0 cm^{-1} satellite feature (labeled **1′**). Further annealing to 11 K increased the 1587.5, 1617.2 cm^{-1} set, decreased the 1546.2, 1581.0 cm^{-1} pair (**1**), and increased the satellite (**1′**). Continued annealing to 12 K increased the high-wavenumber set (**di**) another 10 %, almost destroyed the low-wavenumber pair (**1**), markedly increased the 1551.0 cm^{-1} satellite and an associ-

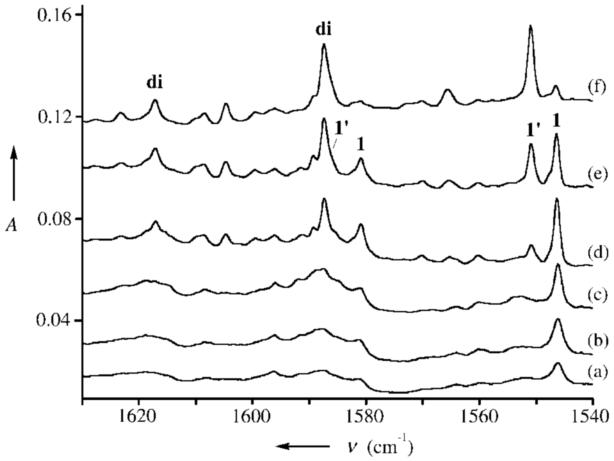

Figure 1. IR spectra in the 1630–1540 cm^{-1} region for laser-ablated zirconium co-deposited with CH_4 in excess neon at 5 K. a) 0.4 % CH_4 in neon deposited for 45 min, b) after $\lambda > 530$ nm irradiation for 20 min, c) after 240–380 nm irradiation for 20 min, d) after annealing to 10 K, e) after annealing to 11 K, and f) after annealing to 12 K. For a discussion of the bands **1** (assigned to [$H_2C{=}ZrH_2$]), **1′**, and **di** (assigned to [$(CH_3)_2ZrH_2$]) see the text.

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ated 1586 cm^{-1} shoulder absorption (also labeled **1'**). Subsequent visible and UV irradiation (not shown) decreased the 1586, 1551.0 cm^{-1} (**1'**) features in favor of the original 1581.0 and 1546.2 cm^{-1} bands (**1**) and slightly decreased the 1617.2 and 1587.5 cm^{-1} absorptions (**di**).

Table 1 lists these frequencies, their unshifted $^{13}CH_4$ counterparts, and analogous displaced CD_4 reaction product bands. These absorptions have H/D frequency ratios of 1.389–1.396, which characterize Zr–H stretching vibrations. Figure 2 shows spectra in the Zr–H and Zr–D stretching regions for reactions with CH_4, CH_2D_2, and CD_4 after UV irradiation. The important new information is that two new mixed H, D absorptions (marked **4**,**6** and **3**,**5**) appear between the low-wavenumber pair (**1**) in each region and one new mixed H, D band (marked **di**) appears between the high-wavenumber pair (**di**) in each region. Finally, all the **di** bands increase markedly on annealing.

Table 1: IR bands [cm^{-1}] observed for laser-ablated zirconium atom reactions with methane in excess neon.

CH_4	$^{13}CH_4$	CD_4	CH_2D_2	CH_2D_2	Identity
1617.2	1617.2	1158.1	1616.2	–	$[(CH_3)_2ZrH_2]$
			1602.2	1150.5	$[(CH_3)_2ZrHD]$
1587.5	1587.5	1142.6	1587.5	1142.5	$[(CH_3)_2ZrH_2]$
1586 sh	1586 sh	1136.9			$[H_2C{=}ZrH_2]$[a]
1581.0	1581.0	1133.1	1580.7	1132.7	$[H_2C{=}ZrH_2]$
1551.0	1551.0	1115.2	1550.1	1115.5	$[H_2C{=}ZrH_2]$[a]
1546.2	1546.2	1112.3	1545.5[b]	1112.5[c]	$[H_2C{=}ZrH_2]$
1375.1	1372.0	1009.0			$[(CH_3)_2ZrH_2]$
1125.0	1114.8	895.9	949.4		$[(CH_3)_2ZrH_2]$
757.0	737.4	687.0	750	718	$[H_2C{=}ZrH_2]$
634.5	629.8	499.4			$[H_2C{=}ZrH_2]$
593.4	592.2	–			$[(CH_3)_2ZrH_2]$
564.2	559.2	469.7			$[(CH_3)_2ZrH_2]$

[a] Bands owing to different neon packing configuration. [b] Additional bands at 1554.4 and 1571.0 cm^{-1} with annealing counterparts at 1558.7 and 1573.3 cm^{-1} for $[CHD{=}ZrHD]$ isotopomers. [c] Additional bands at 1116.2 and 1129.2 cm^{-1} with annealing counterparts at 1118.9 and 1133.0 cm^{-1} for $[CHD{=}ZrHD]$ isotopomers.

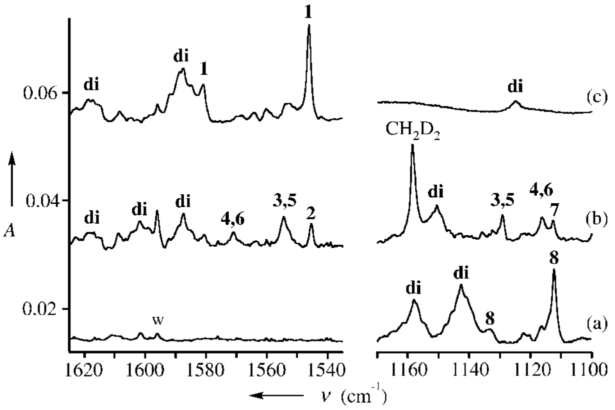


Figure 2. IR spectra in the 1620–1540 cm^{-1} Zr–H stretching and 1170–1100 cm^{-1} Zr–D stretching regions for laser-ablated Zr co-deposited with CH_4, CH_2D_2, and CD_4 in excess neon at 5 K for 45 min and subjected to $\lambda > 530$ and 240–380 nm irradiations. a) 0.4% CD_4 in neon, b) 0.6% CH_2D_2 in neon, and c) 0.4% CH_4 in neon. For discussion of the spectra see text; **1**–**8** indicate bands from the correspondingly numbered isotopmers in Scheme 1 **di** = isotopomers of $[(CH_3)_2ZrH_2]$, w = water.

The lower frequency region contains four associated weaker absorptions at 757.0, 634.5, 593.4, and 564.4 cm^{-1} (not shown). On photolysis and annealing the 757.0, 634.5 cm^{-1} bands track with the low-wavenumber pair in the Zr–H stretching region (1581.0 and 1546.2 cm^{-1} (**1**)), and the 593.4 and 564.4 cm^{-1} absorptions follow the 1617.2, 1587.5 cm^{-1} pair (**di**). A weak 1375.1 cm^{-1} band and the 1125.0 cm^{-1} absorption (Figure 2c, **di**) also track with the **di** bands. The $^{13}CH_4$ and CD_4 isotopic counterparts are given in Table 1.

Calculations were performed for $[H_2C{=}ZrH_2]$ using the B3LYP density functional, and the global minimum energy C_1 structure with no symmetry is illustrated in Figure 3. The CH_2 group is tilted owing to the agostic C–H···Zr interaction. Additional calculations using the BPW91 functional and the MP2 method[17] gave similar skewed structures. When C_{2v} symmetry was imposed, the resulting planar structure which gives two imaginary frequencies is 0.8 kcal mol^{-1} higher in energy. Clearly, the planar form is unstable and relaxes along the imaginary CH_2 rocking and ZrH_2 wagging motions to the stable C_1 structure.

The C–H···Zr separation computed for the C_1 structure, 2.345 Å, is slightly longer

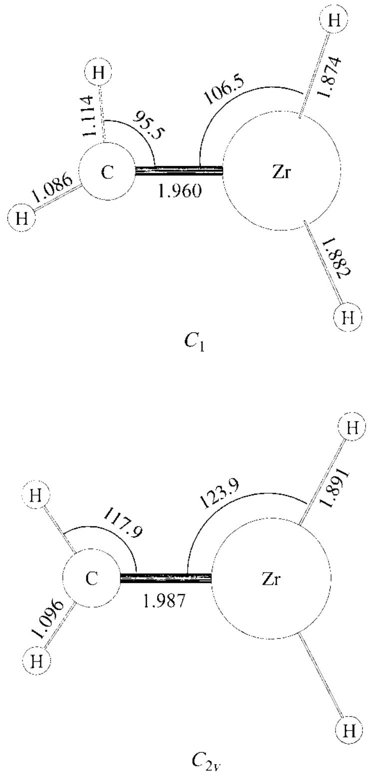


Figure 3. Minimum energy C_1 and C_{2v} symmetry structures computed for $[H_2C{=}ZrH_2]$ at the B3LYP/6-311++G(2d,p)/SDD level of theory.

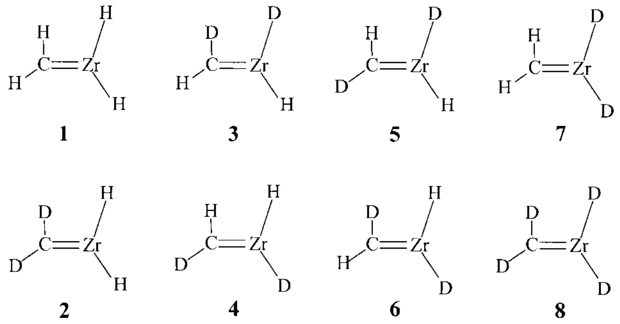
than agostic bonds measured for Cr and W complexes in crystals (2.24 and 2.27 Å),[6] but shorter than the agostic bond length computed (2.379 Å) for a model Ir complex using basis sets with polarization functions.[7] Since agostic bond energies in the 10–15 kcal mol^{-1} range have been determined for the Group 6 complexes,[6] our slightly longer agostic bond in [$H_2C{=}ZrH_2$] is probably almost as strong.

Computed frequencies listed in Table 2 provide the basis to identify agostic [$H_2C{=}ZrH_2$] from four observed frequencies and [CHD=ZrHD] isotopic modifications. The 1581.0 and 1546.2 cm^{-1} absorptions are due to symmetric and antisymmetric stretching modes of a ZrH_2 group: [ZrH_2] itself has been observed at 1519 cm^{-1} in solid argon and at 1530 cm^{-1} in solid neon.[18,19] The related satellite features at 1586 and 1551.0 cm^{-1} are due to a different neon packing configuration around the Zr center that is formed on annealing and destroyed on photolysis. The observed ZrH_2 modes are just below computed ZrH_2 modes for both structures, and these discrepancies are in line with that expected for the B3LYP density functional,[20] but structural assignment cannot be made on this basis. However, a definitive choice can be made from the [CHD=ZrHD] isotopomers since the symmetrical form has two and the agostic form has four such variants. Our calculations for *cis* and *trans* planar [CHD=ZrHD] predict the same ZrHD stretching modes (± 0.1 cm^{-1}) for each isomer so only one DZr–H and one HZr–D mode would be observed in each region. However four such bands are found (Figure 2b **3**,**4**,**5**,**6**). Our calculations describe four distinct [CHD=ZrHD] isotopmers (**3**, **4**, **5**, and **6** in Scheme 1), and two of these isotopmers have Zr–H and Zr–D stretching modes that are different from those of the other two isotopmers. Our calculations predict **3** and **5** to have a Zr–H stretching mode 9.2 cm^{-1} above the strong antisymmetric stretching mode of **1** and a Zr–D stretching mode 13.3 cm^{-1} above the strong antisymmetric stretching mode of **8** (compare Figure 2 a–c). These bands are observed 8.3 and 17.0 cm^{-1} higher, respectively. In like manner our calculations find **4** and **6** to have strong Zr–H and Zr–D stretching modes 21.6 cm^{-1} above **1** and 4.2 cm^{-1} above **8**, and these bands are observed 24.8 and 4.0 cm^{-1} higher, respectively. The bands labeled **2** and **7** in Figure 2 arising from [$D_2C{=}ZrH_2$] and [$H_2C{=}ZrD_2$] are predicted to be shifted 0.1 cm^{-1} from **1** and **8**, and 0.7 and 0.2 cm^{-1} differences are found.

Table 2: Harmonic vibrational frequencies [cm^{-1}] computed for the C_1 and C_{2v} structures of [$H_2C{=}ZrH_2$] shown in Figure 3.

Mode Description	C_1 Freq.	Int.[a]	C_{2v} Freq.	Int.[a]
CH_2 str	3172	(1)	3096	(8)
CH_2 str	2876	(6)	3014	(1)
ZrH_2 str	1640	(303)	1625	(379)
ZrH_2 str	1610	(574)	1582	(755)
CH_2 s*cis*	1316	(17)	1314	(9)
C=Zr str	762	(134)	742	(130)
CH_2 wag	661	(151)	720	(206)
ZrH_2 s*cis*	643	(91)	561	(16)
ZrH_2 rock	520	(9)	643	(0)
CH_2 twist	415	(22)	524	(0)
CH_2 rock	278	(131)	131 i	(0)
ZrH_2 wag	227	(95)	196 i	(471)

[a] IR intensities [km mol^{-1}]; i = imaginary frequencies.



Scheme 1. Isotopmers of [$H_2C{=}ZrH_2$].

The excellent agreement between experiment and theory for Zr–H and Zr–D stretching modes in four different CHD=ZrHD isotopomers (**3**, **4**, **5**, and **6**) with H or D in the agostic bonding position confirms the identification and the C_1 symmetry agostic structure for [$H_2C{=}ZrH_2$]. Although [$H_2C{=}ZrH_2$] is isoelectronic in the valence shell with the fundamentally and industrially important symmetrical, planar ethylene molecule, $H_2C{=}CH_2$, the d orbitals on zirconium support agostic bonding to one methylene hydrogen and reduce the symmetry in the [$H_2C{=}ZrH_2$] molecule.

Additional spectroscopic evidence for the C_1 structure is found in the lower frequency C–Zr stretching and CH_2 wagging modes, whose vibrational character and thus isotopic shifts depend heavily on molecular symmetry. The C_{2v} structure has a strong mixed C–Zr stretching, CH_2 bending mode computed at 742 cm^{-1} with an 8.9 cm^{-1} ^{13}C shift, whereas the C_1 structure has a strong mostly C–Zr stretching mode computed at 762 cm^{-1} with a 17.4 cm^{-1} ^{13}C shift. A pure ^{12}C–Zr diatomic oscillator would shift 26 cm^{-1} for ^{13}C–Zr in this region. Hence the observed 757.0 cm^{-1} absorption with 19.6 cm^{-1} ^{13}C shift fits the C_1 frequency prediction very well and the C_{2v} prediction very poorly. Our calculation for the C_1 structure slightly under estimates the ^{13}C shift and over estimates the D shift for this mode. The C_{2v} structure has a strong CH_2 wagging mode computed at 720 cm^{-1} whereas for the C_1 structure this mode is computed at 661 cm^{-1}. The associated absorption observed at 634.5 cm^{-1} is clearly in line with the C_1 and not the C_{2v} results, and the isotopic shifts are appropriate for this assignment.

The 1617.2 and 1587.5 cm^{-1} absorptions (labeled **di** in Figure 1) are assigned to dimethyl zirconium dihydride, [$(CH_3)_2ZrH_2$]. These frequencies may be compared to the antisymmetric stretching mode for [ZrH_4] observed at 1623 cm^{-1} in solid argon and at 1648 cm^{-1} in solid neon.[18,19] Our calculations predict a very stable molecule with effectively C_{2v} symmetry and strong Zr–H_2 stretching modes at 1673 and 1642 cm^{-1}, which are only 3.4 % higher than the observed values, which is slightly better agreement than found above for [$CH_2{=}ZrH_2$]. The [$(CD_3)_2ZrD_2$] counterparts at 1158.1 and 1142.6 cm^{-1} and single intermediate -ZrHD species bands at 1602.2 and 1150.5 cm^{-1} confirm this assignment (Figure 2b). The next strongest lower frequency ZrH_2 bending and deformation modes predicted at 612 and 569 cm^{-1} are observed at 593.4 and 564.2 cm^{-1}, and weaker CH_3 bending and deformation modes computed at 1419 and 1166 cm^{-1} are found at 1375.1 and 1125.0 cm^{-1}. This is the first report of a Group 4 dimethyl dihydride. The $[(CH_3)_2TiF_2]$ analogue has been observed in similar Ti reactions with CH_3F.[12]

The zirconium atom reaction with methane apparently proceeds with excited zirconium atoms produced in the laser ablation process[16] or by irradiation,[21] this is because the C–H activation to form the $[CH_3ZrH]$ intermediate requires activation energy.[22] Then α-hydrogen transfer[23] gives $[H_2C{=}ZrH_2]$, Equation (1).

$$Zr^* + CH_4 \rightarrow [CH_3ZrH]^* \rightarrow [H_2C{=}ZrH_2] \tag{1}$$

Our calculations show that $[CH_3ZrH]$ ($^3A''$) and $[H_2C{=}ZrH_2]$ (^1A) have comparable energies.[24] However, the reaction with a second CH_4 molecule to form $[(CH_3)_2ZrH_2]$ appears to be spontaneous on annealing in solid neon. The $[(CH_3)_2ZrH_2]$ molecule is computed to be 65 kcal mol^{-1} more stable than $Zr(^3F)$ and two methane molecules, and the reaction in Equation (2) is exothermic by 44 kcal mol^{-1}. Alkylidene complexes are also known for their roles in C–H activation processes,[2] and the reaction in Equation (2) provides a simple example of the C–H activation process for methane.

$$[H_2C{=}ZrH_2] + CH_4 \rightarrow [(CH_3)_2ZrH_2] \tag{2}$$

Herein we have demonstrated how matrix IR spectroscopy and electronic structure calculations can work together to identify novel molecules with unique bonding interactions.

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[24] We find $[CH_3ZrH]$ bound by 25.0 kcal mol^{-1} and $[H_2C{=}ZrH_2]$ bound by 21.3 kcal mol^{-1} relative to $Zr(^3F_2) + CH_4$.