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Infrared Spectrum and Structure of $CH_2{=}ThH_2$

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The actinide methylidene $CH_2{=}ThH_2$ molecule is formed in the reaction of laser-ablated thorium atoms with CH_4 and trapped in a solid argon matrix. The five strongest infrared absorptions computed by density functional theory (two ThH_2 stretches, C═Th stretch, CH_2 wag, and ThH_2 bend) are observed in the infrared spectrum. The computed structure shows considerable agostic bonding distortion of the CH_2 and ThH_2 subunits in the simple actinide methylidene dihydride $CH_2{=}ThH_2$ molecule, which is similar to the transition metal analogue, $CH_2{=}HfH_2$.

Actinide chemistry is important because of its relevance to atomic energy, the nuclear industry, and environmental concerns. Thorium is the first actinide metal, but in many ways, its chemistry follows that of the group 4 transition metals with common ns^2nd^2 valence electron configurations and the group 14 carbon family with ns^2np^2 valence electron configurations.[1] The formation of the stable tetrahedral molecules ThH_4, HfH_4, and PbH_4 demonstrates this simple chemical principle.[2−5]

High oxidation state transition metal complexes with carbon−metal double bonds are significant for understanding metal coordination chemistry and for developing catalysts for use in alkene metathesis and alkane activation reactions.[6−8] Many early transition metal alkylidenes are agostic, and these compounds help to characterize the agostic interaction of hydrogen with a transition metal center.[8−12] The simplest compound of this type is the methylidene dihydride, $CH_2{=}MH_2$, which provides an ideal model system to examine substituent effects and the agostic interaction with different metals. Since agostic complexes usually involve the weak interaction between an electron-deficient metal center and hydrogen bonded to another element, thorium is a good partner. A large number of groups 4, 5, and 6 alkylidene complexes have been characterized,[8] but the corresponding actinide alkylidene complexes have remained elusive,[13] although closely related uranium−carbon multiple-bonded complexes and surface-stabilized actinide alkylidene species have been reported.[14,15] Unusual reactivity of actinide alkylidenes may render them difficult to isolate using conventional synthetic methods, but the solid argon matrix environment can preserve these compounds.

The reaction of laser-ablated Zr atoms and CH_4 first formed the $CH_3{-}ZrH$ insertion product, which rearranged by α-H transfer to the methylidene dihydride $CH_2{=}ZrH_2$.[16] This molecule was characterized from its matrix infrared spectrum and density functional theory (DFT) electronic structure calculations to exhibit CH_2 and ZrH_2 distortion, which are signatures of agostic bonding.[10,12] The so-called agostic H−C−Zr angle was computed as 92.9°.[16] A similar investigation with Hf and CH_4 found the analogous hafnium methylidene $CH_2{=}HfH_2$ with a 95.6° agostic H−C−Hf angle.[17] It is therefore of considerable interest to prepare the simple actinide methylidene dihydride $CH_2{=}ThH_2$ and to calculate its structure for possible agostic distortion.

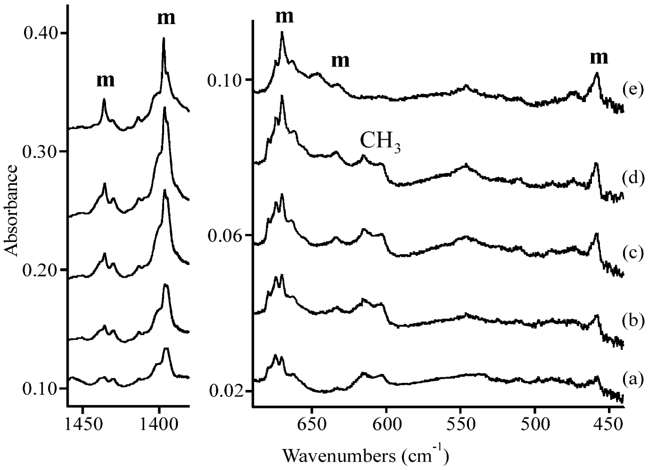

Figure 1. Infrared spectra in selected regions for the major product of the reaction between laser-ablated Th atoms and methane in excess argon. (a) Spectrum obtained from initial sample deposit at 8 K, (b) Spectrum after $\lambda > 420$ nm irradiation, (c) Spectrum after 240−380 nm irradiation, (d) Spectrum after $\lambda > 220$ nm irradiation, and (e) Spectrum after annealing to 26 K in sequence from the same sample.

Reactions of laser-ablated Th atoms with CH_4 in excess argon during condensation at 8 K, using methods described previously,[4,16,18] reveal one major new product. The infrared spectra in Figure 1 show new absorptions at 1435.7, 1397.1, 670.8, 634.6, and 458.7 cm^{-1} (labeled **m**). The CH_3 radical absorption[19] at 617−603 cm^{-1} arises from precursor dissociation by the ablation laser plume on the target surface. Visible ($\lambda > 420$ nm) irradiation increases the new absorptions by 50%, ultraviolet irradiation (240−380 nm) increases them another 50%, and full arc ($\lambda > 220$ nm) irradiation in sequence on the same sample

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TABLE 1: Observed and Calculated Fundamental Frequencies of $CH_2{=}ThH_2$[a]

approximate mode description	$CH_2{=}ThH_2$			$^{13}CH_2{=}ThH_2$			$CD_2{=}ThD_2$		
	obsd.	calcd.	int.	obsd.	calcd.	int.	obsd.	calcd.	int.
CH_2 stretch		3142.6	2		3132.2	2		2321.7	2
CH_2 stretch		2861.4	11		2854.9	11		2084.7	2
ThH_2 stretch	1435.7	1434.9	350	1435.7	1434.8	350	*b*	1023.5	110
ThH_2 stretch	1397.1	1394.2	698	1397.1	1394.2	698	*b*	1005.7	98
CH_2 bend		1327.5	11		1320.5	11		989.0	340
C=Th stretch	670.8	679.6	178	651.5	659.7	173	602.9	614.8	127
CH_2 wag	634.6	633.0	161	629.2	627.5	157	499.2	495.1	109
ThH_2 bend	458.7	492.8	110		492.3	108		355.8	34
ThH_2 rock		460.8	5		458.2	4		344.4	29
CH_2 twist		343.0	30		342.5	30		245.3	18
ThH_2 wag		321.9	65		321.6	66		230.2	30
CH_2 rock		248.4	62		248.1	62		177.5	30

[a] B3LYP/6-311++G(3df,3pd)/SDD level of theory. Frequencies and infrared intensities are in cm^{-1} and km/mol. Observed frequencies are from argon matrix. Intensities are calculated values. [b] Region covered by CD_4 precursor absorption.

increases these bands another 25%. A final annealing to 26 K sharpened and decreased the new absorptions about 10% and removed the CH_3 bands in favor of sharp C_2H_6 absorption.[20]

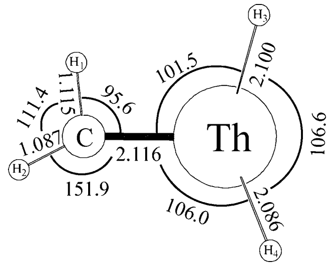

Figure 2. Structure calculated for singlet ground-state $CH_2{=}ThH_2$ using B3LYP/6-311++G(3df,3pd)/SDD methods. Bond lengths in angstroms and bond angles in degrees.

Isotopic substitution of the methane precursor was employed to characterize the product absorptions, which are listed in Table 1. Methane-^{13}C shifted the lower but not the higher wavenumber absorptions, which shows that carbon is involved in the vibrational modes responsible for the lower absorptions, but not the upper ones. Unfortunately, the strong CD_4 precursor absorption covered the higher-wavenumber band counterparts, but two lower bands were observed.

Electronic structure calculations were done for products expected from the Th + CH_4 reaction on the basis of our experience with Zr and Hf + CH_4 reactions.[16,17] We used the *Gaussian 98* program system, the B3LYP density functional, the energy-adjusted SDD relativistic pseudopotential for Th (30 valence electrons), and the large 6-311++G(3df,3pd) basis set for C and H.[21,22] This calculation predicted the strong mode for singlet-state ThH_4 only 5 cm^{-1} higher than observed in solid argon, which is a good calibration. The $CH_3{-}ThH$ triplet ground-state molecule, like $CH_3{-}ZrH$, has one strong infrared absorption, but this molecule is 10 kcal/mol higher in energy than the more stable α-H transfer product $CH_2{=}ThH_2$ singlet ground-state with C_1 symmetry. Finally, the $CH_2{-}ThH_2$ triplet state is 24 kcal/mol higher in energy with a C_s nonplanar structure, equivalent C—H (1.095 Å) and Th—H bonds (2.081 Å), and a longer (2.404 Å) C—Th bond.

The five new IR absorptions show unique photochemical and sample annealing behavior, and they can be assigned to the same new molecule. The two absorptions at 1435.7 and 1397.1 cm^{-1} in the Th—H stretching region and with no carbon-13 shift suggest strongly that this new molecule contains a ThH_2 subunit. The ThH_2 molecule has been observed with similar frequencies at 1480.1 and 1455.6 cm^{-1} in solid argon from reactions of laser-ablated Th atoms with H_2.[4] Furthermore, the 670.8 cm^{-1} band shifts 19.3 cm^{-1} upon carbon-13 substitution, and a C—Th diatomic harmonic oscillator would shift 25.0 cm^{-1}. Hence, the 670.8 cm^{-1} absorption has a substantial amount of C—Th stretching character, and it appears in the region expected and calculated for a C=Th double-bond stretching mode.[23] The computed vibrational frequencies and structure of $CH_2{=}ThH_2$ using density functional theory are listed in Table 1 and illustrated in Figure 2.

The vibrational frequencies calculated for the actinide methylidene $CH_2{=}ThH_2$ follow those computed for the analogous transition metal $CH_2{=}ZrH_2$ and $CH_2{=}HfH_2$ methylidenes.[16,17] Although the Hf—H stretching frequencies are higher than Zr—H frequencies owing to relativistic effects,[2,3] the Th—H stretching modes are lower owing to shell expansion. The close match between the five observed frequencies and the five calculated frequencies with the highest infrared intensities is striking. The calculated carbon-13 shifts are also in excellent agreement with the observed values: The two ThH_2 stretching modes have no $^{13}CH_2{=}ThH_2$ shift, but the mostly C=Th stretching mode is calculated to shift 19.9 cm^{-1} (observed 19.3 cm^{-1}) and the CH_2 wag is calculated to shift 5.5 cm^{-1} (observed 5.4 cm^{-1}). The latter two modes are calculated to shift 64.8 and 137.9 cm^{-1}, respectively, for $CD_2{=}ThD_2$ (observed 67.9 and 135.4 cm^{-1}). The excellent agreement between five observed and calculated frequencies and their isotopic modifications confirms our observation of the fundamentally important simple actinide methylidene hydride $CH_2{=}ThH_2$ molecule.[24]

The structure and bonding of $CH_2{=}ThH_2$ are of considerable interest in their own right. The $CH_2{=}Th$ subunit is essentially coplanar, and the H atoms on Th are out of this plane. The in-plane distortion of CH_2 and out-of-plane distortion of the ThH_2 group (unequal bond lengths and bond angles) are due to the agostic bonding interaction, which stabilizes the C=Th double bond.[12] Although this structure and agostic distortion (agostic H—C—Th angle 95.6°) are similar to that computed for $CH_2{=}HfH_2$ (95.6°), $CH_2{=}ZrH_2$ (92.9°), and $CH_2{=}TiH_2$ (91.6°),[16,17,25] this is the first observation and characterization of the simplest possible thorium methylidene hydride species, $CH_2{=}ThH_2$, which we may call "thora-ethylene," and thus, the simplest hydride containing a C=Th double bond. The C=Th bond length computed here for $CH_2{=}ThH_2$ is almost the same as that calculated for CThO (2.124 Å),[23] and the present 670.8 cm^{-1} C=Th stretching frequency is slightly higher than the 606.0 cm^{-1} argon matrix frequency for the CThO molecule.[26] The natural valence electron configuration[21] calculated for Th is dominated by 6d in the $CH_2{=}ThH_2$ molecule (natural valence electron configuration is Th: $7s^{0.40}\,5f^{0.23}\,6d^{0.83}\,7p^{0.03}$). As such, thorium behaves like a heavier group 4 transition metal d

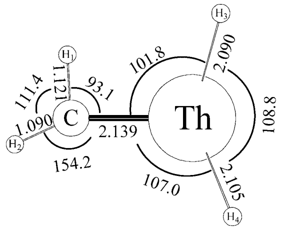

Figure 3. Structure calculated for singlet ground-state $\mathrm{CH_2{=}ThH_2}$ using CCSD/6-311++G(2d,p)/SDD methods. Bond lengths in angstroms and bond angles in degrees.

element.[27,28] There are two noteworthy differences: The natural charge computed for Th (2.57) is much higher than that for Hf (1.66),[17] and the C═Th bond length is 0.149 Å longer in these almost isostructural $\mathrm{CH_2{=}MH_2}$ methylidenes. Thus, the greater charge on Th compensates for the longer C═M bond length, as both methylidenes have the same B3LYP computed 95.6° agostic H—C—M angle.

To substantiate the agostic structure computed by DFT, we performed a coupled cluster with single and double excitation (CCSD) calculation[21] in C_1 symmetry at the CCSD/6-311++G-(2d,p)/SDD level, and the structure is shown in Figure 3. Notice that the B3LYP and CCSD computed structures are very similar: The agostic angle is 2.5° smaller but the C═Th bond is 0.023 Å longer at the CCSD level. This calculation provided a T1 diagnostic of 0.017, which suggests that multireference character is not a problem[29] in the ground singlet-state $\mathrm{CH_2{=}ThH_2}$ molecule. Earlier multiconfiguration/localized molecular orbital/configuration interaction calculations under C_{2v} symmetry found a stable structure for $\mathrm{CH_2{=}HfH_2}$.[30] Accordingly, the CCSD calculation was repeated under C_{2v} symmetry; the C═Th bond length increased (2.166 Å), the Th—H bond lengths increased (2.130 Å), and the CCSD energy increased (4.5 kcal/mol higher). The CCSD calculations were performed again with symmetry fixed at C_s, and there are two such structures. The structure with a vertical plane of symmetry has equivalent C—H (1.098 Å) and Th—H (2.097 Å) bonds, C═Th (2.157 Å), angle H—C—H(111.9°), angle H—Th—H (109.4°), angle H—C—Th (123.6°), angle C—Th—H (105.2°), and is 3.0 kcal/mol higher in energy than the C_1 structure. The distorted structure with a horizontal molecular plane (C—H, 1.118 Å, 1.092 Å; angle H—C—Th, 97.2°; angle H—C—H, 111.1°; C═Th, 2.155 Å; Th—H, 2.126 Å, 2.144 Å; angle C—Th—H, 112.9°; angle H—Th—H, 121.3°) is 3.9 kcal/mol higher in energy than the C_1 minimum-energy structure in Figure 3. It appears that $\mathrm{CH_2{=}ThH_2}$ enjoys considerable stabilization through agostic bonding interactions in the lower-symmetry structure, but more stabilization is gained from out-of-plane distortion of two Th—H bonds than in-plane $\mathrm{CH_2}$ distortion.

Similar Th atom reactions with methyl halides produce agostic methylidene thorium hydride halide complexes, which will be reported in a later paper.

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References and Notes

(1) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Adv. Inorg. Chem.*, 6th ed.; Wiley: New York, 1999.

(2) Pyykko, P. *Chem. Rev.* **1988**, *88*, 563.

(3) Chertihin, G. V.; Andrews, L. *J. Am. Chem. Soc.* **1995**, *117*, 6402.

(4) Souter, P. F.; Kushto, G. P.; Andrews, L.; Neurock, M. *J. Phys. Chem. A* **1997**, *101*, 1287.

(5) Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2003**, *125*, 9218.

(6) Tran, E.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 5071.

(7) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565.

(8) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.

(9) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(10) Ujaque, G.; Cooper, A. C.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 361.

(11) Wada, K.; Craig, B.; Pamplin, C. B.; Legzdins, P.; Patrick, B. O.; Tsyba, I.; Bau, R. *J. Am. Chem. Soc.* **2003**, *125*, 7035.

(12) Scherer, W.; McGrady, G. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1782.

(13) Pool, J. A.; Scott, B. L.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 1338.

(14) See, for example, Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 3589.

(15) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 641.

(16) Cho, H.-G.; Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2005**, *127*, 465.

(17) Cho, H.-G.; Wang, X.; Andrews, L. *Organometallics* **2005**, *24*, 2854.

(18) Liang, B.; Andrews, L.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **2002**, *124*, 6723.

(19) Jacox, M. E. *J. Mol. Spectrosc.* **1977**, *66*, 272.

(20) Davis, S. R.; Andrews, L. *J. Am. Chem. Soc.* **1987**, *109*, 4768.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.4; Gaussian, Inc.: Pittsburgh, PA, 2002, and references therein.

(22) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535.

(23) Zhou, M.; Andrews, L.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1999**, *121*, 12188.

(24) The BPW91 density functional gave almost the same structure (C═Th, 2.101 Å; Th—H, 2.077 Å, 2.091 Å, agostic H—C—Th angle 89.8°), slightly lower Th—H stretching and $\mathrm{CH_2}$ wagging frequencies, and a slightly higher C═Th stretching frequency.

(25) Andrews, L.; Cho, H.-G.; Wang, X. *Inorg. Chem.* **2005**, *44*, 4834.

(26) Andrews, L.; Liang, B.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **2003**, *125*, 3126.

(27) Pyykko, P.; Laakkonen, L. J.; Tatsumi, K. *Inorg. Chem.* **1989**, *28*, 1801.

(28) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719 and references therein.

(29) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.

(30) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 539.