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Agostic Interaction in the Methylidene Metal Dihydride Complexes H_2MCH_2 (M = Y, Zr, Nb, Mo, Ru, Th, or U)

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Multiconfigurational quantum chemical methods (complete active space self-consistent field (CASSCF)/second-order perturbation theory (CASPT2)) have been used to study the agostic interaction between the metal atom and H(C) in the methylidene metal dihydride complexes H_2MCH_2, where M is a second row transition metal or the actinide atoms Th or U. The geometry of some of these complexes is highly irregular due to the formation of a three center bond CH···M, where the electrons in the CH bond are delocalized onto empty or half empty orbitals of d- or f-type on the metal. No agostic interaction is expected when M = Y, where only a single bond with methylene can be formed, or when M = Ru, because of the lack of empty electron accepting metal valence orbitals. The largest agostic interaction is found in the Zr and U complexes.

1. Introduction

Agostic (Greek for *hold on to oneself*) interactions are usually defined as an interaction between a CH group on a ligand and the metal in a metal complex. The first synthesis of an Mo complex showing such an interaction between the metal and CH bond in an alkyl group was made in 1974.[1] A recent, slightly different example is the interaction between a Cr(I) ion and a phenyl group in the bimetallic complex ArCrCrAr.[2] The CH group acts as an electron donor in an interaction with an electron-deficient metal center. One condition for the interaction to be effective is that the hydrogen and the metal can be brought into contact without straining the system too much. Typical agostic metal−hydrogen distances are 1.9−2.4 Å. An interesting discussion of the difference between agostic bonding and normal hydrogen bonds can be found in ref 4.

The early theoretical investigations of simple group 4 H_2MCH_2 complexes used small basis sets and described planar symmetrical structures.[9,10] More recent configuration interaction calculations employed a small basis for carbon, assumed C_{2v} structures, and found them to be stable.[11] Recently, density functional theory (DFT) calculations have been used to investigate a large number of complexes, including the simple H_2MCH_2 model complexes.[12−20] Numerous theoretical methods from Hartree−Fock (HF) to coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) have been employed to evaluate the agostic bond in the simple CH_2TiHF complex first prepared in the laboratory.[21,22] This work demonstrated that higher levels of theory are needed to more fully characterize the agostic bonding interaction. Hence, we have performed state-of-the-art complete active space self-consistent field (CASSCF)/second-order perturbation theory (CASPT2) calculations to investigate the agostic interaction in the title series of simple H_2MCH_2 complexes.

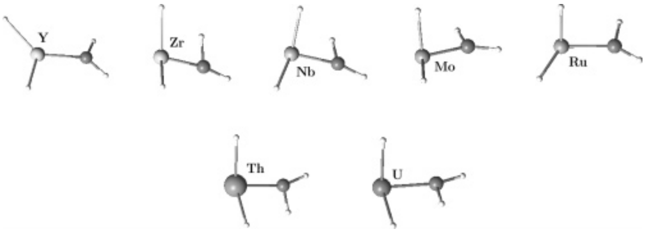

Figure 1. The geometries of the CASPT2 optimized molecules.

Here we shall study the agostic interaction between the metal and a CH_2 hydrogen in the methylidene metal dihydride complex H_2MCH_2, where M is a second row transition metal or an actinide (Th and U). These simple methylidene metal dihydride complexes serve as model complexes for larger ligand stabilized group 4−6 transition metal complexes that are important in synthetic organometallic chemistry. Such complexes have been extensively investigated for more than three decades, and it is of interest that many of these complexes reveal agostic bonding interactions.[3] This work has produced considerable information on metal coordination chemistry and on important new compounds to serve as metathesis and polymerization catalysts for alkenes and alkynes.[3,5−8]

2. Theoretical Approach

The results presented in this report have been obtained using multiconfigurational quantum chemical methods. The CASSCF method[23] has been used to generate reference wave functions for the ground state of the H_2MCH_2 complexes. These wave functions are used as reference functions for the calculation of dynamic correlation energy effects using CASPT2.[24,25] Relativistic effects are included based on the Douglas−Kroll−Hess (DKH) Hamiltonian.[26,27] The scalar part of this Hamiltonian is used in the generation of the CASSCF/CASPT2 wave functions. Spin−orbit (SO) effects are not included in the present work because they are expected to have only minor effects on computed geometries and relative energies, except for the

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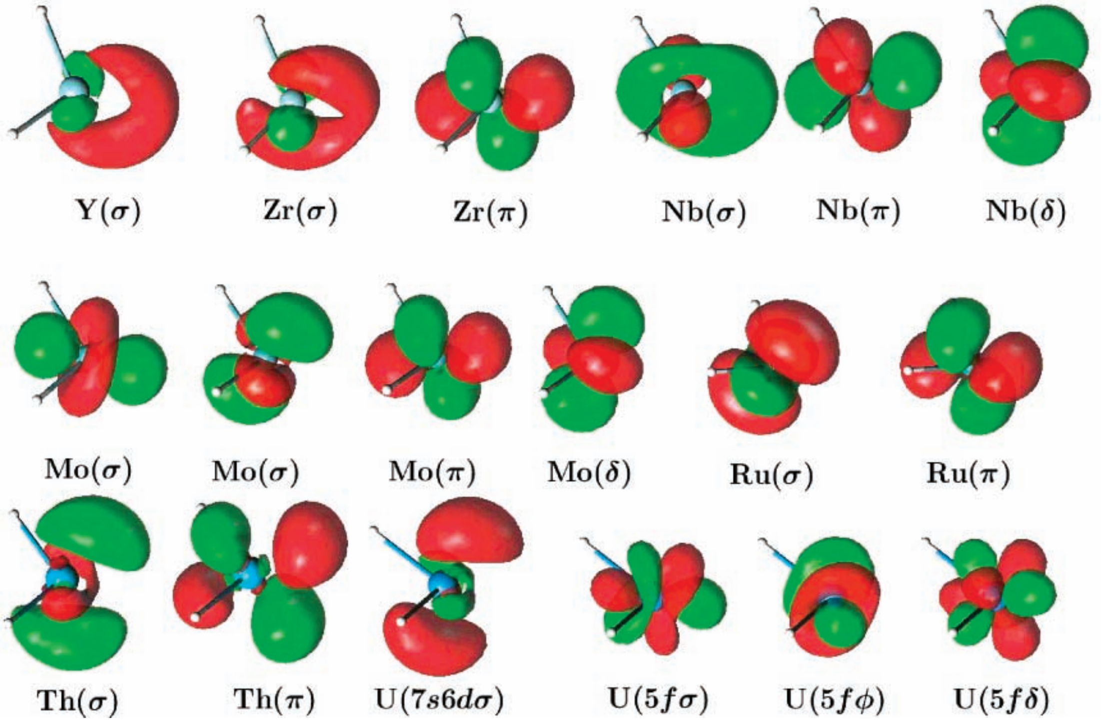

Figure 2. The singly occupied orbitals in the MH_2 moieties (the iso density level is 0.05 e/au^3).

actinide complexes where they are computed using an effective one-electron SO Hamiltonian based on an atomic mean field approximation of the two-electron part.[28] The approach has been described in detail in ref 29.

The atomic orbital (AO) basis set used is of the atomic natural orbital type and has been especially designed to include the effects of the scalar relativistic terms of the DKH Hamiltonian.[30−32] All basis sets were of triple-ζ quality (TZP), which corresponds to the following contracted basis sets: H/3s2p; C/4s3p2d1f; Y,Zr,Nb,Mo,Ru/7s6p4d2f1g; and Th,U/9s8p6d4f2g.

The geometries of all complexes were optimized at the CASPT2 level of theory using numerical gradients. No symmetry constraints were used in the structure optimization of the H_2MCH_2 complexes, whereas the MH_2 moieties were optimized assuming C_{2v} symmetry. Drawings of the optimized molecules are presented in Figure 1. All calculations have been performed with the computer software MOLCAS-6.[33]

3. Results

We discuss the bonding between the MH_2 group and the methylene, starting from the electronic structure of MH_2 in its lowest electronic state. The geometry of the complex is determined to a large extent by the nature of the open shell orbitals on the metal moiety. Roughly, the structure of H_2MCH_2 can be described as follows: the methylene group and the MC bond form a plane (see the angle β in Table 2). This is the optimum arrangement for the open shell $\sigma-$ and $\pi-$orbitals to form a double bond with the metal. The situation is more complicated on the metal side. The 4d orbitals (6d and 5f in the case of Th and U) are not necessarily in an optimal bonding condition for a planar conformation. Therefore the MH_2 group will be tilted, and the out-of-plane angle (the angle between the plane and the MC bond) is larger than 0°.

The nature of the MC bond will thus depend on the character of the MH_2 orbitals that are available for bonding. In Figure 2 we have plotted all singly occupied CASSCF orbitals for MH_2, which were obtained after a CASPT2 optimization of the structure. The structural data and the ground state symmetry are presented in Table 1. All of the molecules have C_{2v} symmetry and have a high-spin ground state, which varies between doublet for Y and quintet for Mo and U. Thus, the MH_2 group can form a double bond to CH_2 in all cases except Y, which has a doublet ground state with a single open shell electron. How is this bond formed and how do the properties of the open shell electrons in the MH_2 group affect the structure and properties of the complex? This will be analyzed below for the different cases. An interesting feature of the structure is the almost linearly decreasing value for the HMH bond angle as a function of the atomic number in the series Zr−Ru, which must be the result of a decreasing 5s population in the MH bonds (see Table 1).

TABLE 1: Calculated Geometries and Ground State[a] for the MH_2 Moieties

	ground state	R(MH) (Å)	∠HMH
C[b]	$^3B_1$	1.080	133.6
Y	$^2A_1$	1.967	120.4
Zr	$^3B_1$	1.863	121.9
Nb	$^4B_2$	1.762	115.8
Mo	$^5B_2$	1.695	104.7
Ru	$^3B_1$	1.569	94.6
Th	$^3B_1$	2.084	119.1
U	$^5B_1$	2.062	105.3

[a] C_{2v} geometry. [b] Experimental values: CH, 1.085; ∠HCH, 135.5.

A note concerning the character of the electronic structure: The CASSCF calculations, in all cases, give wave functions that are essentially single configurational. The weights of the leading configuration vary between 86 and 94% (see Table 2). Thus, all bonds are well developed, with only a small occupation of the antibonding orbitals. Single configurational based methods such as coupled cluster or DFT should thus also work well for these compounds, at least from the near degeneracy point of view.

3.1. The Transition Metals from Y to Ru. Only one open shell electron is available to form the MC bond when M = Y. The two other valence electrons are used to form the YH bonds

TABLE 2: CASPT2 Geometries and Spin State[a] for the H_2MCH_2 Complexes[b]

metal	C[c]	Y	Zr	Nb	Mo	Ru	Th	U
spin	0	1/2	0	1/2	1	0	0	1
weight[d]	0.92	0.94	0.90	0.90	0.86	0.89	0.94	0.93
CH	1.08	1.09	1.13, 1.08	1.12, 1.08	1.10, 1.08	1.09	1.12, 1.08	1.14, 1.08
MH	1.08	2.00	1.87, 1.89	1.77, 1.79	1.68, 1.71	1.55	2.10, 2.11	2.01, 2.02
MC	1.34	2.31	1.94	1.87	1.86	1.79	2.13	2.02
M···H′[e]	2.12	3.08	2.10	2.11	2.34	2.55	2.36	2.25
∠HCH	117.3	107.8	112.9	115.2	116.9	115.6	111.0	111.3
∠HMH	117.3	121.3	117.0	117.7	101.3	95.6	107.6	97.0
∠MCH	121.4	125.6	81.9, 163.7	85.7, 159.1	101.8, 141.2	122.2	87.5, 160.1	82.0, 166.4
∠CMH	121.4	119.3	105.1, 108.6	98.8, 112.6	92.9, 119.7	89.1	100.0, 103.6	95.7, 96.8
α[f]	0.0	0.0	56.1	57.6	58.8	88.7	69.7	80.5
β[g]	0.0	0.0	7.0	0.4	2.6	1.7	7.4	2.8
dE (kcal/mol)[h]	183.2	84.6	113.9	111.2	93.0	97.7	114.3	98.5

[a] C_1 geometry. [b] Distances are in Å, and angles are in degrees. When two geometry parameters are equal, only one is given. [c] Experimental values: CH, 1.08, CC, 1.34, ∠HCH, 117.8. [d] Weight of the leading configuration in the CASSCF wave function. [e] The agostic M···H′ distance. [f] α is the angle between the HMH plane and the MC axis. [g] β is the angle between the HCH plane and the MC axis. [h] The bond energy for $H_2MCH_2 \rightarrow MH_2+CH_2$.

Figure 3. Three occupied orbitals in H_2ZrCH_2 showing the agostic interaction (the iso density level is 0.05 e/au^3).

using sd hybrid orbitals. Thus, only a single YC bond is formed. The shape of the orbital (see Figure 2) shows that the preferred geometry for the complex is planar. The YC bond distance is long, 2.31 Å, and the geometry is planar with C_{2v} symmetry. No agostic interaction is possible due to the long Y···H′ distance, 3.08 Å, where H′ is the agostic hydrogen atom. More details about the structure are given in Table 2.

The situation is different for the other atoms (Zr−Ru). The ZrH_2 complex has two unpaired electrons and a triplet ground state; therefore, a double bond can be formed. It can be seen from Figure 2 that a tilted configuration is preferred. This is also the outcome of the geometry optimization, which gives a tilt angle of 56° and a ZrC distance of 1.94 Å (also see Figure 1). The Zr···H′ distance is now only 2.10 Å. Typical agostic M···H′ distances are in the range 1.85−2.40 Å. How is this interaction formed? Charge transfer is possible from the CH bond to the empty 4d orbitals on ZrH_2. Three of them are involved in the ZrH and ZrC bonds, but two are empty and can be used as electron acceptors from the CH′ bond. We show in Figure 3 three of the strongly occupied natural orbitals (NOs) that illustrate this interaction. They are mixed into the ZrH and ZrC bonding orbitals, but the delocalization of charge from CH′ to the metal is nicely illustrated. The effect on the geometry is substantial. The CH′ distance is elongated from the normal 1.08 Å to 1.13 Å, and the MCH′ angle is only 81.9°. The agostic interaction computed here is close to that obtained in an earlier CCSD(T) study, which gave a Zr···H′ distance of 2.14 Å[20] which is only slightly longer than the present value.

The agostic interaction decreases for the next two atoms, Nb and Mo. This is most clearly seen for the MCH′ angle, which increases to 85.7° (Nb) and 101.8° (Mo), respectively. The CH′ distance decreases to 1.12 and 1.10 Å, respectively. The natural explanation for this trend is the increased occupation of the metal 4d orbitals. For Mo they are all occupied, two of them singly, which leads to a triplet ground state for the H_2MoCH_2 complex. The tilt angle (α) also slowly increases along the series but is less affected because it mainly depends on the structure of the orbitals responsible for the MC bond. We can extrapolate these findings to complexes with heavier transition metals (Tc and later metals). There will be less and less agostic interaction due to the increased population of the 4d orbitals. The results obtained for the Ru complex nicely illustrates this. Here, all 4d orbitals are filled, and there are no empty valence orbitals on the metal that can act as electron acceptors. As a result, there is no agostic interaction, and the molecule has C_s symmetry with equal MH and CH distances (see Table 2 for details). The agostic Ru···H′ distance is long, 2.55 Å. The RuH_2 open shell orbitals shown in Figure 2 indicate that the optimal double bond is obtained with a large tilt angle. This is also the outcome of the calculations that yields $\alpha = 88.7°$, the largest angle found for any of the compounds studied here. A strong, short double bond is formed with an RuC distance as short as 1.79 Å. This molecule is thus an illustration of the fact that the agostic interaction and the tilting of the MH_2 group are two separate effects with different origins.

Table 2 also includes bond energies, computed at the CASPT2 level of theory as the energy difference between H_2MCH_2 and $MH_2 + CH_2$. The computed values are only approximate because no vibrational zeroth-order energy correction has been added, which would decrease all of them, but they give a nice illustration of the trends; the largest bond energy in the TM series is obtained for the Zr complex, which is where we also see the largest agostic interaction. Finally, one should note that all structures presented in Figure 1 and in Table 2 represent energy minima. For the unsymmetrical molecules there are two equivalent minima connected with a transition state with C_s symmetry.

3.2. The Actinides Th and U. The actinide complexes H_2ThCH_2 and H_2UCH_2 have also been studied. One might have expected to find the same trends here as for the transition metal complexes. However, although the Th complex shows an agostic interaction that is smaller than the corresponding transition metal complex (Zr), the opposite is true for uranium. Before attempting to address that issue, we shall study how the MC bond is formed. The picture of the orbitals of the MH_2 moiety shows that the preferred α is large for both Th and U. The computed values are 69.7° and 80.5°, which are larger than those of any of the transition metal complexes except Ru. For Th, the bonding is dominated by the 6d orbitals, whereas the 5f orbital is the most important for the U complex.

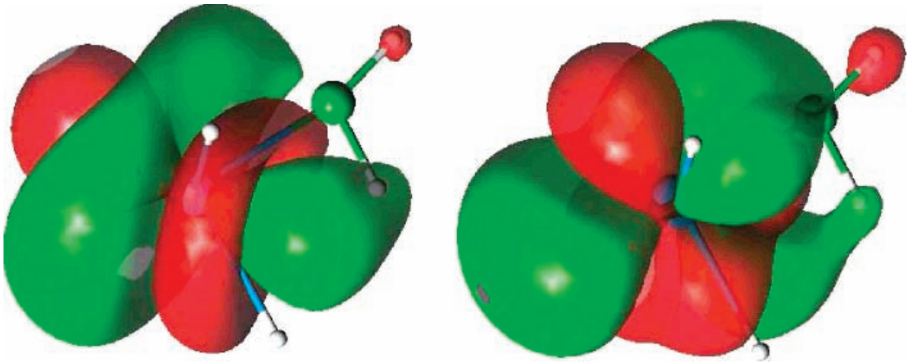

Figure 4. The two singly occupied orbitals in H_2UCH_2 showing the agostic interaction (the iso density level is 0.01 e/au^3).

TABLE 3: DFT Geometries and Spin State[a] for the H_2MCH_2 Complexes[b,c]

Transition Metal Compounds

metal	C	Y	Zr	Nb	Mo	Tc	Ru[d]
spin	0	1/2	0	1/2	1	3/2	0
CH	1.08	1.10	1.12, 1.08	1.11, 1.08	1.10, 1.09	1.090, 1.088	1.10
MH	1.08	2.00	1.87, 1.88	1.79, 1.80	1.70, 1.71	1.70	1.57
MC	1.33	2.33	1.96	1.90	1.87	1.83	1.79
M···H′[e]	2.11	3.10	2.30	2.35	2.51	2.56	2.56
∠HCH	116.5	107.8	112.5	115.1	115.3	117.9	114.6
∠HMH	116.5	121.0	116.4	120.9	107.6	133.9	96.1
∠MCH	121.7	126.1	92.9, 153.5	99.7, 145.0	113.0, 131.6	120.3, 121.7	122.7
∠CMH	121.7	119.5	105.9, 110.2	109.8, 118.9	95.6, 116.0	103.5	92.1
freq[f]		3.2, 3.4	5.1, 6.6	4.9, 4.0	5.5, 5.4	not observed	2.1

Actinide Compounds

metal	Th[g]	U
spin	0	1
CH	1.12, 1.09	1.12, 1.09
MH	2.09, 2.10	2.02, 2.04
MC	2.12	2.06
M···H′[e]	2.49	2.37
∠HCH	111.4	112.2
∠HMH	106.6	102.9
∠MCH	95.6, 151.9	91.9, 155.1
∠CMH	101.5, 106.0	98.9, 106.8
freq[f]	0.1, 0.2	1.2, 0.8

[a] C_1 geometry. [b] Distances are in Å, angles are in degrees. When two geometry parameters are equal, only one is given. [c] Calculated at the B3LYP/6-311++G(3df,3pd) level of theory. [d] Ru observation from unpublished results. [e] The agostic M···H′ distance. [f] Calculated M−H stretching frequencies are given in % higher than the argon matrix observed values. [g] The Th−H distances are incorrectly reversed in ref 18.

Still, the agostic interaction in the Th complex is small, with a M···H′ distance as large as 2.36 Å. A possible explanation for this behavior is the energy difference between the CH bonding orbitals and the empty 6d orbitals of the metal. These orbitals are less stable than in the corresponding TM complexes, which makes the electron-transfer less effective. DFT/B3LYP calculations using the same basis set and including scalar relativity give the following energies for the two most stable virtual orbitals: Zr = −2.76 and −2.18 eV; Th = −2.35 and −1.62 eV. Another contributing factor is the longer MC distances of 1.94 Å in the Zr complex and 2.13 Å in Th.

The MC distance in the U complex decreased to 2.02 Å, and the M···H′ distance decreased to 2.25 Å. The agostic UCH′ angle is as small as 82.0°. This complex also has the longest CH′ distance of all the studied compounds, 1.14 Å. The more stable singly occupied 5f orbitals of uranium lead to an increased possibility for an effective charge transfer. We show the two singly occupied orbitals in the U complex in Figure 4. A low iso density level of 0.01 e/au^3 has been used so that the electron-transfer from the CH′ bond becomes visible. The reason for the need of a lower density is the compact nature of the 5f orbitals as compared to the 4d orbitals of the TM complexes. The interaction results in a small positive spin population (0.004 electrons) on the agostic hydrogen instead of the expected negative density.

3.3. Comparison with DFT and Experiment. The structures computed by the B3LYP density functional using large Gaussian basis sets have been presented in our original papers[14−19] and have been discussed in our review article.[20] The main structural features are presented in Table 3. It is interesting to compare here the results of the hybrid density functional with the more rigorous quantum chemical methods used here. One can see that the results are essentially the same for ethene and the symmetrical Y complex, but for the Zr, Nb, and Mo complexes, the MC bond is slightly shorter, the CH′ bond is slightly longer, the agostic M···H′ distance is slightly shorter, and the agostic MCH′ angle is slightly smaller for the CASSCF/CASPT2 calculations. This means that a stronger agostic interaction is described by the higher level of theory. Nevertheless, the vibrational frequencies are accurately predicted by the harmonic DFT frequency calculation within the limits expected. The B3LYP calculated frequencies for the very strong M−H stretching mode are 2−6% higher than the observed argon matrix values for the transition metal methylidene dihydrides and are 0.1−1.2% higher for the actinide species. This is slightly higher than that which is usually found for the B3LYP functional for normal chemical compounds, but it is typical for a wide range of methylidene complexes.[20] The CH_2 wagging mode and M═C stretching modes are observed for some of these complexes, and those modes are predicted with the same level of accuracy by the DFT frequency calculations. In general, one can conclude that both the CASPT2 and the DFT methods give the same description of the agostic effects in these compounds, even if they differ in the details. The table also contains results for the Tc compound for which no CASPT2 calculations have been performed. The trend is, however, the expected one, with a small agostic interaction because only one open shell orbital is available on Tc to accept the electron.

4. Summary and Conclusions

We have demonstrated through a series of quantum chemical calculations how the agostic interaction in methylidene metal dihydride complexes varies with the character of the metal. The largest interaction is found when a well-developed double bond is formed between the metal and the carbon atoms and when the metal contains empty or half empty valence orbitals that can act as electron acceptors. As a result, the most effective agostic interaction among the transition metal complexes occurs for Zr, whereas no interaction is shown for Y, because no double bond is formed, and for Ru, because there are no electron acceptor orbitals. The Th complex essentially follows the same trend, but uranium is different. The 5f orbitals are effective electron acceptors even if they are already half filled. This increased ability to form agostic bonds in the uranium compound is an interesting observation, which could have consequences for uranium complexes to act as catalyzing agents in a more effective way than the corresponding transition metal complexes.

The calculations thus show the transfer of C−H bonding electron density to the transition metal center, as was originally suggested by Brookhart and Green[5] to characterize the agostic interaction, which results in M═C bond stabilization and CH_2 distortion. In addition, they show that the agostic interaction and distortion in the model H_2MCH_2 methylidene complexes is even more pronounced than predicted by simple DFT.[14−20]

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