Mechanism of the Ta⁺-Mediated Activation of the C−H Bond in Methane

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The mechanistic details of the C−H bond activation brought about by a Ta⁺ ion, which was observed in the gas phase, have been computationally investigated using approximate density functional theory. In accord with the experimental information, the overall reaction sequence $Ta^+ + CH_4 \rightarrow TaCH_2^+ + H_2$ is computed to be exothermic by *ca.* 14 kcal mol⁻¹ and the Ta−C binding energy in the tantalum carbene cation is computed as 119 kcal mol⁻¹, in satisfying agreement with the experimental lower bound for this quantity of 111 kcal mol⁻¹. The bond activation process itself consists of several steps, commencing with the formation of an electrostatically bound encounter complex, followed by the insertion of the Ta⁺ into a C−H bond and the generation of a $H_2TaCH_2^+$ dihydrido species. Finally, this latter intermediate rearranges into a productlike complex between molecular hydrogen and a tantalum carbene cation, which concludes the sequence by subsequent loss of H_2. Interestingly, the reaction does not proceed adiabatically on one potential energy surface; rather, there are several changes in multiplicity along the reaction coordinate. The structures of singlet $TaCH_2^+$ and related intermediates where a carbene substructure is involved show several peculiarities, which are rationalized by an analysis of the relevant molecular orbital and the electron density.

Introduction

The activation of C−H bonds by catalysts is of paramount interest in experimental and theoretical chemistry due to its decisive role in e.g. catalytic processes. Already in 1979 Allison, Freas, and Ridge discovered that atomic transition metal cations are capable of activating such bonds.[1] In the years to follow many such ion−molecule reactions were investigated experimentally in the gas phase, mainly by mass spectrometric methods. Thus, any interfering effects of ligating groups or a solvent could be avoided.[2−5] Using this experimental strategy, it was possible to establish many elementary steps of organometallic reactions, but usually experiments alone were not able to characterize the whole reaction sequence.

A possible solution to this problem can be contributed by the interplay between computational strategies and experimental studies. In main-group-element chemistry, it is nowadays usually a routine task to reliably locate minima and saddle points on a potential energy surface using quantum-chemical methods. The situation is unfortunately not quite as satisfying when it comes to open-shell transition-metal-containing compounds. The capability of a balanced treatment of near-degeneracy and dynamic electron correlation effects is a prerequisite for the application of a particular quantum-chemical method to such problems. Using conventional, wave-function-based multireference CI (or similar) approaches, such calculations are inevitably constrained to small systems by computing resources.[6] It is there-fore necessary to identify a quantum-chemical method which can describe the complicated electronic situation of those molecules sufficiently accurately at reasonable computational costs. An alternative to Hartree−Fock (HF)−based methods is provided by approximate den-sity−functional theory (DFT). A number of recent studies have proven that DFT, in particular HF/DFT hybrid functionals such as B3LYP, is a valuable tool which affords at least qualitatively correct results at moderate computational costs, even for describing com-plicated electronic structures as they are common in open−shell transition-metal chemistry.[7,8] The B3LYP functional was also successfully employed in a recent investigation of the related reaction between Pt⁺ and methane.[9]

The motivation for the present theoretical study was the recent experimental work of Wesendrup and Schwarz.[10] These authors were investigating the pos-sibility of using a transition-metal ion to activate carbon dioxide by generating a C−C bond link with methane. While the cations Ta⁺, W⁺, Os⁺, Ir⁺, and Pt⁺ of the third transition-metal row react exothermically with meth-ane, forming the respective carbene complex MCH_2^+ and molecular hydrogen,[9] only the metal−oxygen bonds M⁺−O of Ta⁺ and W⁺ are strong enough to reduce carbon dioxide exothermically. With both cations the monoxide MO^+ is generated in a first step, and subse-

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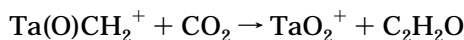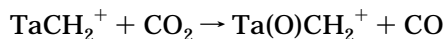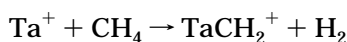(2) Armentrout, P. B. *Annu. Rev. Phys. Chem.* **1990,** *41,* 313.
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quently the dioxide MO_2^+ is formed. The formation of a C−C bond is, however, only possible by using Ta^+. The overall reaction sequence is shown in Scheme 1 and consists of three individual steps: first, the tantalum carbene is formed, which in a second step reacts with a carbon dioxide molecule to generate a $Ta(O)CH_2^+$ species. Finally, this intermediate reacts with a second CO_2 to yield C_2H_2O with release of TaO_2^+. The actual connectivities of the compounds $Ta(O)CH_2^+$ and C_2H_2O are still unknown; however, on the basis of thermodynamic data the experimentalists suggested that C_2H_2O corresponds to ketene.

Scheme 1

$$Ta^+ + CH_4 \rightarrow TaCH_2^+ + H_2$$

$$TaCH_2^+ + CO_2 \rightarrow Ta(O)CH_2^+ + CO$$

$$Ta(O)CH_2^+ + CO_2 \rightarrow TaO_2^+ + C_2H_2O$$

$$Ta^+ + CH_4 + 2CO_2 \rightarrow TaO_2^+ + H_2 + CO + C_2H_2O$$

The detailed reaction mechanisms of the elementary steps of this reaction are not known so far, which calls for a comprehensive theoretical investigation. In the following we will concentrate on the first part of this sequence: the activation of a C−H bond in methane brought about by a tantalum cation.

Methods

We used the Becke3LYP functional (B3LYP) as implemented in Gaussian94 combined with two one-particle descriptions. In both cases the chemically inert 60 core electrons ([Kr], $4d^{10}$, $4f^{14}$) of the tantalum cation were replaced by a relativistic effective core potential (RECP). The first approach, termed BS1, employs the standard basis set lanl2dz as available in Gaussian94, whose RECP for Ta was developed by Hay and Wadt.[11−13] The description of the valence electrons of Ta^+ are according to a $(8s6p3d) \rightarrow (3s3p2d)/[341|321|21]$ contraction. Carbon and hydrogen were described by the standard split valence D95 basis set.[14] In a second set of calculations a more flexible description consisting of an RECP determined by Dolg *et al.*[15] was used in combination with a valence basis set augmented by an additional, uncontracted f-function (α_f = 0.790). The final contraction for the remaining 12 electrons of Ta^+ is of $(8s7p6d1f) \rightarrow (6s5p3d1f)/[311111|22111|411|1]$ quality. The polarized, standard 6-31G** basis set[16] was chosen for C and H. This RECP/basis combination will be designated as BS2.

Using BS1 all geometries were optimized using analytical gradient procedures. The analytically calculated force constant matrices were evaluated for the characterization of the stationary points (minima or transition states) and zero-point vibrational energy (ZPVE) and thermal corrections. On several occasions it was necessary to reduce the actual point group symmetry to slightly symmetry broken C_1-symmetric structures, since unexpected negative eigenvalues for minima appeared.[17] All structures reported correspond to fully converged geometries with gradients as well as displacements below the standard thresholds implemented in Gaussian 94.

Table 1. Theoretical Thermochemistry (in kcal mol^{-1}) for the Reaction $Ta^+ + CH_4 \rightarrow TaCH_2^+$ ($^3A_2$) $+ H_2$

$\Delta H_{0\,K}$	9.4	$T\Delta S_{298\,K}$	−13.5
$\Delta H_{0\,K}$ + ZPVE	−0.3	$\Delta G_{298\,K}$	−14.2
$\Delta H_{298\,K}$	−0.7		

The application of BS2 led to severe complications in the optimization processes, since no analytical gradient procedures for RECP with f-functions in the valence basis set are available in Gaussian 94. Therefore, we had to fall back to the Fletcher−Powell optimization scheme,[18] which is based on a numerical evaluation of the gradients. Transition structures were localized utilizing the Gaussian 94 options *EnOnly* (numerical procreation of the gradients by displacement of geometrical parameters) and *EF* (eigenvector following).[19−21] No force constant matrices were computed using BS2, due to the extremely high computational costs of the required fully numerical scheme.

All relative energies are corrected for ZPVE, entropic, and thermal contributions and correspond to free energies at 298 K, $\Delta G_{298\,K}$. Thus, the calculated results are directly comparable to the experimental data. The Gibbs free energy change, $\Delta G_{298\,K}$, was computed using

$$\Delta G_{298\,K} = \Delta H_{298\,K} - T\Delta S_{298\,K} \tag{1}$$

The thermal corrections to ΔH and absolute entropies have been determined using standard statistical mechanics formulas. Due to the lack of frequencies at the BS2 level, the corrections obtained from the harmonic frequency calculations using BS1 were used throughout. The volume−pressure term ($p\Delta V$) amounts to ΔnRT if ideal gas behavior is assumed.[22] To provide an idea of the magnitudes of the various corrections, they are explicitly listed in Table 1 for the energetics of the overall reaction, based on total energies obtained with BS2.

Thus, in terms of total energies alone, the reactants are more stable than the products by 9.4 kcal mol^{-1}. After inclusion of ZPVE a theoretically predicted reaction exothermicity of 0.3 kcal mol^{-1} is obtained for 0 K. At 298 K the exothermicity changes only slightly to 0.7 kcal mol^{-1}. Taking into account also the difference of $T\Delta S$ of −13.5 kcal mol^{-1} between Ta^+/CH_4 and $TaCH_2^+/H_2$, the final value for $\Delta G_{298\,K}$ of this reaction amounts to −14.2 kcal mol^{-1} at 298 K.

Partial charges and orbital occupations are based on the natural bond analysis (NBO) scheme.[23] All bond lengths and angles are specified in angstroms (Å) and degrees (deg), respectively. While spin-free, kinematic relativistic effects are covered through the RECP, no corrections for spin/orbit coupling have been included (see discussion below). In the following, all energetic data will refer to the B3LYP/BS2 results with ZPVE and thermal corrections obtained at the B3LYP/BS1 level of approximation. All calculations were performed with Gaussian 94[24] installed on our own IBM RS/6000

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workstations and Cray J90 computers at the Konrad-Zuse Zentrum für Informationstechnik, Berlin.

Experimental Background for the [Ta,C,H$_4$]$^+$ System

The gas-phase reaction Ta$^+$ + CH$_4$ → TaCH$_2$ + H$_2$ was first observed by Freiser and co-workers,[5,25] and investigated in detail using FT-ICR mass spectrometry by Wesendrup and Schwarz.[10] Since the reaction was observed under thermochemical conditions, it has to be exothermic or nearly thermoneutral. Thus, it can be inferred that the binding energy of the product Ta=CH$_2^+$ has to be ≥111 kcal mol^{-1}.[25,26] In agreement with this lower bound, Irikura and Goddard[27] recommend a binding energy for Ta=CH$_2^+$ of 115 ± 5 kcal mol^{-1}, on the basis of sophisticated multireference configuration interaction calculations. Consequently, the reverse process, TaCH$_2^+$ + H$_2$ → Ta$^+$ + CH$_4$, could not be observed in these experiments, confirming that there is a kinetic barrier or the reaction is endothermic. The activation barrier or endothermicity should exceed 5 kcal mol^{-1}, because otherwise the reaction would have been observed in the experimental setup. However, a single and a double exchange of hydrogen for deuterium occurs during the reaction of tantalum carbene cations with molecular deuterium:[28]

$$TaCH_2^+ + D_2 \rightarrow TaCHD^+ + HD$$
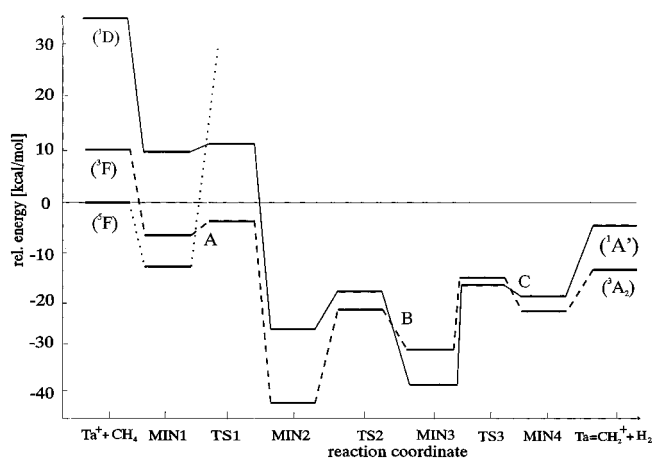
$$TaCH_2^+ + D_2 \rightarrow TaCD_2^+ + H_2$$
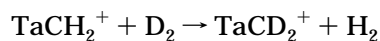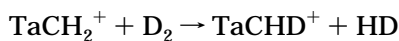
This H/D scrambling reaction can only proceed *via* an intermediate in which the hydrogen and deuterium atoms have lost their individuality as belonging to D$_2$ or TaCH$_2^+$, respectively. The most plausible candidate is a hydrido methyl intermediate, HTaCH$_3^+$ (see below). Thus, all elementary steps between the channel TaCH$_2^+$ + H$_2$ and the HTaCH$_3^+$ intermediate lie below this asymptote, while the saddle point connecting HTaCH$_3^+$ with the next species *en route* to the Ta$^+$ + CH$_4$ asymptote has to be energetically more demanding than the energy of TaCH$_2^+$ + H$_2$. Finally, TaCH$_2^+$ is bound with respect to ground-state Ta$^+$ and CH$_2$ by at least 111 kcal mol^{-1}.

Results and Discussion

We will start by considering the interaction of a ground-state tantalum cation with the carbon–hydrogen bond in methane. The geometries of the relevant stationary points are given in Figure 2. Figure 1 summarizes the C–H bond activation branch of the [Ta, C, H$_4$]$^+$ potential energy surface (PES). The relative energies, ZPVE data, and resulting relative Gibbs free energies obtained with BS1 and BS2 are collected in Table 2.

It should be noted that the structures of the energetically higher lying spin states are very similar to the ones shown, except for MIN3, TS4, MIN4, and the TaCH$_2^+$ ion (see discussion below). However, the rela-

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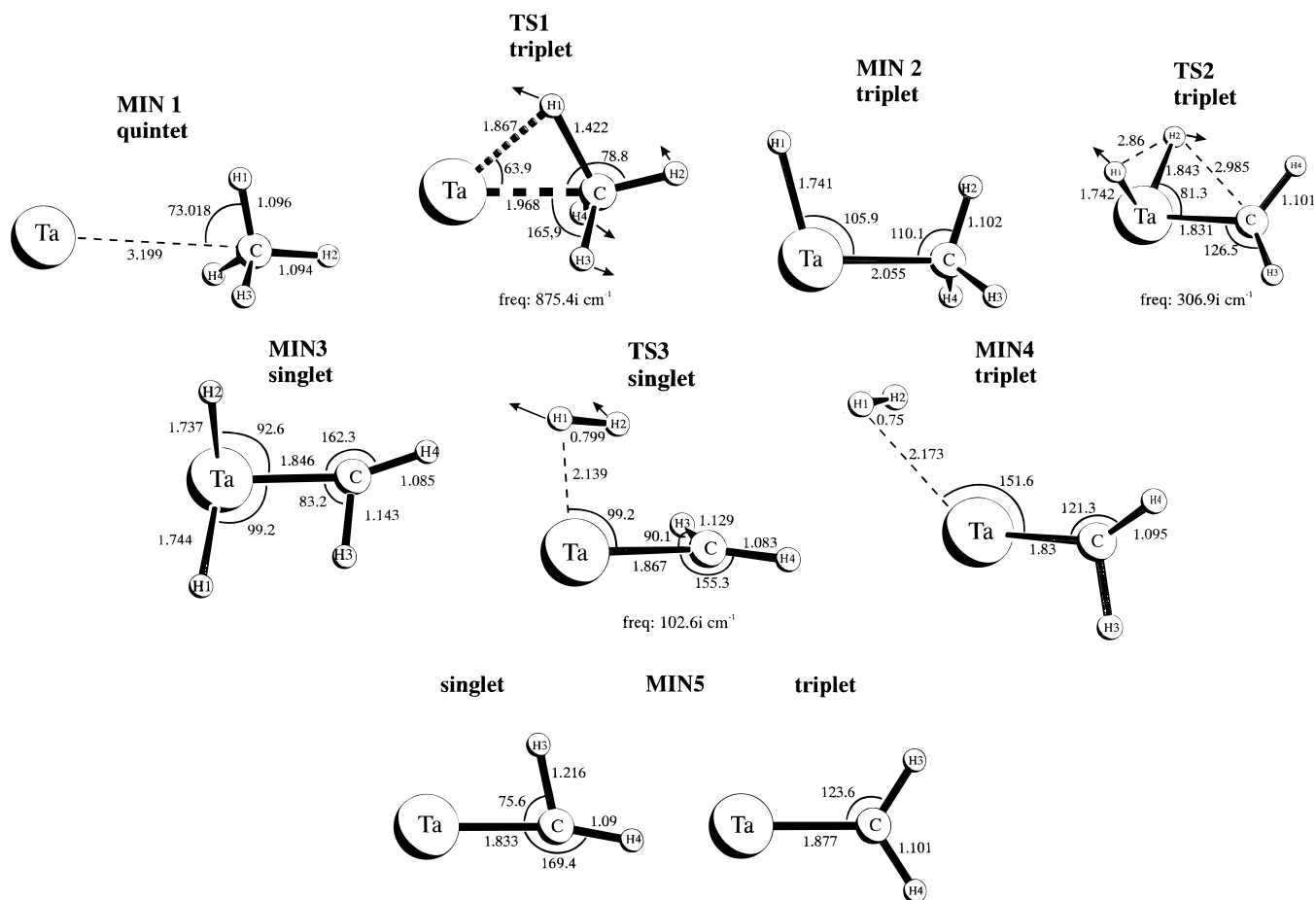(26) Irikura, K. K.; Beauchamp, J. L. *J. Phys. Chem.* **1991**, *95*, 8344.
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Figure 1. C–H bond activation branch of the [Ta, C, H$_4$]$^+$ potential energy surface.

tive energies obtained with the two basis sets frequently differ significantly. For instance, the barrier height connected with TS3 on the triplet potential energy surface between MIN3 and MIN4 is very low (2.6 and 3.5 kcal mol^{-1} relative to MIN3 and MIN4, respectively) if the smaller one-particle description, BS1, is used. In contrast, this barrier raises considerably if BS2 is employed; the difference in Gibbs free energies amounts to 9.9 and 6.8 kcal mol^{-1} with respect to MIN3 and MIN4, respectively. If not otherwise noted, all energies given in the following discussion will refer to $\Delta G_{298\ K}$ values obtained with the more flexible BS2 (corrected for the thermal contributions based on the harmonic frequencies predicted with BS1).

The entrance channel for the reaction is given by Ta$^+$ and CH$_4$. The atomic ground term of Ta$^+$ is computationally predicted as ^{5}F (5d^{3}6s^1). At the B3LYP/BS2 level, this atomic term is 10.1 kcal mol^{-1} or 0.44 eV more stable than the triplet term (^{3}F, 5d^{2}6s^2) and 36.9 kcal mol^{-1} or 1.60 eV below the singlet (^{1}D, 5d^{2}6s^2). At this point it is important to realize that for the Ta$^+$ cation the LS coupling scheme is no longer appropriate. Rather, the spin/orbit interaction is already significant and the spectroscopic ground state of Ta$^+$ is the $J = 1$ level of the ^{5}F multiplet.[29] Thus, in order to compare the computed term splittings with the experimentally derived excitation energies, the latter have to be averaged over their various J levels (assuming that the spin/orbit interaction between levels of the same J but originating from different LS terms is small). In comparison to the experimental $^5F_1$ ground state, the J-averaged ^{5}F term is 3755 cm^{-1} or 10.7 kcal mol^{-1} higher in energy, while for the ^{3}F term, the lowest level, $J = 2$, is 4031 cm^{-1} or 11.5 kcal mol^{-1} below the J average. The ^{1}D term does of course consist of only the $J = 2$ level.[29] Thus, the J-averaged separations of the ^{3}F and ^{1}D terms from the ^{5}F ground term are 0.43 and 1.22 eV, respectively. The agreement with the computationally predicted numbers given above is good and similar to the accuracy found for atomic excitations for the 3d elements.[8,30] Since in our computational approach spin/orbit effects are not accounted for, we need to discuss how the complete neglect of these effects will

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MIN 1 quintet · **TS1 triplet** · **MIN 2 triplet** · **TS2 triplet** · **MIN3 singlet** · **TS3 singlet** · **MIN4 triplet** · **MIN5 singlet / triplet**

Figure 2. Optimized geometries (bond lengths in Å and angles in deg). For the transition structures, the transition vectors, i.e., the normal modes corresponding to the imaginary frequencies, are also shown.

Table 2. Theoretical Thermochemistry (in kcal mol⁻¹) for the Species Relevant to the Reaction Ta⁺ + CH₄ → TaCH₂⁺ (³A₂) + H₂ with the Basis Sets BS1 and BS2

compd	BS1 ΔE_{rel}	ΔE_{ZPVE}	$\Delta G_{298 K}$	BS2 ΔE_{rel}	ΔE_{ZPVE}	$\Delta G_{298 K}$
Ta (⁵F) + CH₄	0.0ᵃ	0.0	0.0	0.0ᵇ	0.0	0.0
Ta (³F) + CH₄	18.6	18.6	18.6	18.5	18.5	18.5
Ta (¹D) + CH₄	40.2	40.2	40.2	45.2	45.2	45.2
MIN1quintet	−19.6	−19.3	−17.8	−13.8	−13.5	−12.0
MIN1triplet	−12.6	−12.1	−11.7	−10.3	−9.8	−9.4
MIN1singlet	14.5	15.0	14.7	12.9	13.3	13.1
TS1triplet	−1.3	−3.5	−10.1	8.2	3.4	−3.1
TS1singlet	22.2	22.6	20.8	13.6	13.4	15.4
MIN2triplet	−37.5	−41.2	−49.5	−31.4	−35.0	−43.4
MIN2singlet	−18.3	−22.2	−32.3	−12.8	−16.8	−24.6
TS2triplet	4.5	−0.5	−6.8	−10.9	−14.8	−21.7
TS2singlet	−6.9	−14.3	−20.4	−5.3	−12.1	−18.3
MIN3triplet	−6.0	−13.1	−22.4	−8.2	−15.4	−24.9
MIN3singlet	−27.7	−34.3	−45.2	−22.8	−30.0	−39.6
TS3triplet	−3.1	−10.4	−25.0	7.1	−2.9	−15.0
TS3singlet	8.8	1.4	−8.0	0.1	−7.2	−16.2
MIN4triplet	−4.0	−10.6	−28.5	2.9	−7.5	−21.8
MIN4singlet	8.6	1.1	−9.8	−0.9	−8.0	−19.3
TaCH₂⁺ (³A₂) + H₂	3.9	−4.7	−27.3	9.4	−0.3	−14.2
TaCH₂⁺ (¹A′) + H₂	15.1	6.3	−7.8	18.9	10.9	−3.9

ᵃ E_{tot} = −97.866 44. ᵇ E_{tot} = −97.115 41.

qualitatively influence our computed results. It is probably safe to assume that the spin/orbit stabilization of some 11 kcal mol⁻¹ in the Ta⁺ atom provides an upper bound to the spin/orbit stabilization in any Ta⁺-containing compound, because the electron distribution in a molecule is much more delocalized than in the atom and there will be considerable quenching of the spin/orbit stabilization. Because the atomic ion will benefit much more from the spin/orbit stabilization than the molecule, the most obvious effect of the neglect of any spin/orbit interaction will be an overestimation of binding energies, in particular if the bare Ta⁺ ion is involved.

Table 3. Experimental (D_0) and Calculated (D_0) Binding Energies (kcal mol^{-1})

species	exptl	calcd	
Ta$^+$=CH$_2$	$\geq 111^a$	115 ± 5^b	119.4
Ta=O	199 ± 15^c		204.5
Ta$^+$−H		54^d	60.3

^{a} D_0 values taken from refs 25 and 26. ^{b} D_0 values taken from ref 27. ^{c} Chase, M. W., Jr.; Davies, C. A., Jr.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Synernd, A. N. JANAF Thermochemical Tables (3rd ed.) Supplement 1. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1655. ^{d} Ohanessian, G.; Brusich, M. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1990**, *112*, 7179.

Furthermore, since the different states of a particular species will not profit equally from spin/orbit interactions, there will also be an impact on the relative energetics of the various multiplicities discussed below. The stabilization will be smallest for states with $S = 0$ and will probably increase with the number of unpaired electrons. However, this differential stabilization will certainly be significantly smaller than the effect on the binding energies. An estimate on the quantitative role of spin/orbit effects can be extracted from an explicit four-component Dirac−Fock MP2 treatment of the closely related PtCH$_2^+$ molecule. Here, the spin/orbit stabilization in the molecule was about half as large as in the Pt$^+$ ion.[31] If in the present case a similar quenching occurs, the uncertainty in our computed binding energies produced by the neglect of spin/orbit effects should be on the order of 5 kcal mol^{-1} and will certainly not exceed 10−11 kcal mol^{-1}. The error for the relative stabilities of different spin states will be much smaller. To conclude, the neglect of spin/orbit effects does of course introduce a certain error margin in our computed results; however, we are confident that its neglect does not change the qualitative features of the reaction mechanism.

To calibrate the quality of our B3LYP/BS2 approach and to estimate the accuracy for energetic data that can be expected from this level of theory, we checked the bond dissociation energies of molecules that are of importance for a description of the Ta$^+$ + CH$_4$ interaction. Unfortunately, there is only very limited information available on such compounds. Table 3 compares the binding energies for TaCH$_2^+$, TaO, and TaH$^+$ (obtained either from experiments or from highly correlated, wave function based ab initio calculations) with our corresponding theoretical predictions, which represent the only data suitable for a critical assessment of our computational approach that we could locate in the literature.

First of all, we note that the B3LYP functional without exception predicts binding energies that are slightly too high. There are probably two reasons for this. First, this is another manifestation of the well-known tendency of DFT to overestimate binding energies.[32] Even though the admixture of "exact" Hartree−Fock exchange in the B3LYP functional alleviates this problem to some extent,[33−35] it is still visible in the

present data. Second, in comparison to experimental data, the neglect of spin/orbit stabilization, which will be more pronounced in the atom than in the molecule,[31] will also contribute to a potential overestimation of the computed binding energies. An additional source of error is provided by the basis set superposition error (BSSE), which will also tend to artificially increase the binding energies. For the TaCH$_2^+$ system we estimated the BSSE as 5.7 or 5.6 kcal mol^{-1} for the triplet and singlet, respectively, using the standard Boys/Bernardi counterpoise scheme.[36] However, we do not simply correct the interaction energies by this amount, since it is well-known that the BSSE is always interwoven with the error induced by the incompleteness of the one-particle description. The latter effect will lower the binding energy and to a certain (but usually unknown) extent, these two effects cancel.[37,38] Thus, we merely give here the magnitude of the BSSE but do not use it for correcting our data. For a detailed account of this subject, see the discussion in ref 39.

The C_s-symmetric 5A″ ground state of the cationic tantalum−methane complex (MIN1) lies 12 kcal mol^{-1} below the entrance channel Ta$^+$ + CH$_4$. The corresponding C_1-symmetric triplet and singlet complexes are less stable by 2.6 and 25.1 kcal mol^{-1}, respectively. Thus, the triplet is 9.4 kcal mol^{-1} lower than the entrance channel, while the singlet species is 13.1 kcal mol^{-1} above this asymptote. In MIN1 the methane moiety retains the tetrahedral geometry of isolated methane. The tantalum cation interacts with the carbon atom and one of the hydrogen atoms, H1. The metal center is not on the C−H2 axis but is slightly shifted to H1. The interaction between Ta$^+$ and methane is principally of electrostatic nature; there is hardly any charge transfer with a partial charge on the metal of +0.98. The minimal covalent contribution is visible in the small expansion of the C−H1 bond of 0.003 Å. If there is a covalent bond, then it is a η^2-bond.

As a second genuine Ta(CH$_4$)$^+$ minimum, the C−H1-inserted species MIN2 was identified. The ground state of this compound is now a triplet. It is 31.4 kcal mol^{-1} more stable than the ^{5}A″ state of MIN1. The corresponding singlet lies 18.8 kcal mol^{-1} above the triplet. The metal ion inserts into the C−H1 bond and breaks this bond, while the hydrogen atom H1 is migrating to the metal center. Now there are bonds between Ta$^+$ and H1 as well as between the tantalum cation and the carbon atom of the remaining methyl group. In this triplet structure the tantalum cation employs two electrons from the now hybridized 5d and 6s orbitals for the bonds. The remaining two unpaired electrons are uncoupled and form the triplet state. Thus, an intersystem crossing from the quintet to the triplet surface has to take place *en route* from the electrostatic complex MIN1 to the intermediate MIN2. However, it can be safely assumed that the spin/orbit interaction is

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large enough to allow for an efficient conversion to the energetically most favorable surface along the reaction coordinate. It is a known phenomenon by now that transition-metal-mediated reactions very often occur on more than one adiabatic potential energy surface. The efficient switch from one surface to another brought about by spin/orbit coupling in such systems has been observed already for the lighter 3d transition metals and has in some instances been shown to have decisive consequences on the reaction mechanisms.[40,41]

MIN1 and MIN2 are connected by the transition structure TS1. This represents the first stationary point along the reaction path which assumes a triplet ground state. Hence, the triplet surface crosses the quintet surface somewhere between MIN1 and TS1. The C_1-symmetric saddle point TS1 is situated 3.1 kcal mol^{-1} below the entrance channel. The activation barrier with respect to MIN1 amounts to 6.3 (triplet) and 8.9 (quintet) kcal mol^{-1}. The corresponding singlet species is 18.5 kcal mol^{-1} less stable than the triplet. TS1 is clearly characterized as a transition structure by an imaginary frequency of 875.4i cm^{-1}. The transition vector shows unequivocally the expected components: The cleavage of the C−H1 bond is accompanied by a reorientation of the methyl group. The structure of TS1 shows an elongation of the C−H1 bond ($\Delta r_{\text{C−H1}}$ = 0.326 Å) and a shortening of the Ta−C distance ($\Delta r_{\text{Ta−C}}$ = 1.231 Å). That TS1 directly connects minima MIN1 and MIN2 was explicitly shown by calculating the intrinsic reaction coordinates (IRC; on the triplet potential energy surface, no change of multiplicity is possible in these strictly non-spin/orbit-coupled calculations).

As one proceeds along the C−H bond activation reaction coordinate, MIN2 is converted into MIN3, the dihydrido complex [H$_2$TaCH$_2$]$^+$. It is interesting to note that in our previous studies on the C−C and C−H bond activation reactions in alkanes mediated by Fe$^+$ [17,42] or Co$^+$ [43] no such dihydrido species could be localized. The multiplicity of the ground state is now a singlet, while the corresponding triplet structure lies 14.7 kcal mol^{-1} higher in energy. MIN3 is localized 39.6 kcal mol^{-1} below the entrance channel. MIN3 prefers a singlet ground state, since the originally unpaired electrons of the tantalum atom are utilized to form a covalent bond to the second hydrogen atom H2 and a second bond to the carbon atom, resulting in a formal Ta=C double bond to the carbon atom. There is a certain amount of charge transfer from the H$_2$Ta moiety onto the CH$_2$ group, as indicated by the partial charge of +1.2 for the dihydrido metal group. The NBO analysis also shows that the binding in Ta=CH$_2$$^+$ displays the typical characteristics of a classical donation−back-donation situation, which is well-known for transition-metal carbenes.[44] The σ-bond is built by electron donation from sp^2-hybridized orbitals on the carbon atom into the appropriate empty d orbitals on Ta$^+$, while the π-bond is formed by a transfer of electrons from the tantalum into the single occupied p$_z$ orbital of the carbon atom.

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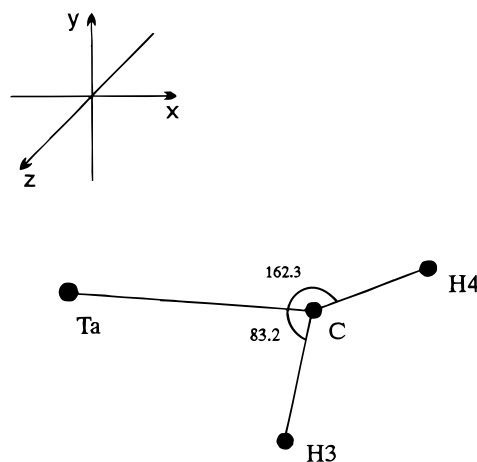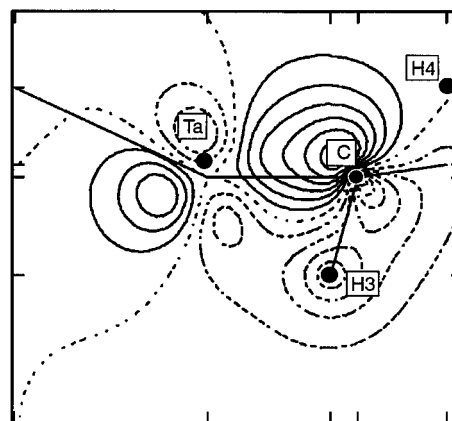
Chart 1. Orientation of the Ta−C−H3−H4 Fragment

Chart 2. Orbital Plot of MO9 in the *xy* Plane

xy-plane

The structure of the singlet state of MIN3 has a special feature: as shown in Chart 1 (Ta, C, H3, and H4 in the *xy* plane), the two hydrogen atoms of the TaCH$_2$ unit (H3 and H4) are not symmetrically arranged.

The bond between H3 and the carbon atom is lengthened by 0.08 Å, and the angle Ta−C−H3 differs considerably from the expected value around 120°, amounting to merely 83.2°. On the other hand, the C−H4 bond does not show any irregularities and is similar to the C−H bonds in comparable structures. However, the angle Ta−C−H4 is widened up to 162.3°. In order to understand this unusual arrangement, we carefully analyzed the wave function of singlet MIN3. First, when we look at the molecular orbitals,[45] there is one orbital in particular (MO 9, Chart 2), which seems to be responsible for this peculiarity.

The d orbitals of the tantalum and the carbon hybrid orbital (consisting of 2s, 2p$_x$, and 2p$_y$ AO contributions) responsible for the Ta−C σ-bond are easily recognized in the *xy* plane. This σ-bond, which is shifted off the bonding axes, seems to be slightly bent. Besides, there is also a bonding, albeit very weak, interaction of the Ta atom with the σ-orbital of the C−H3 bond. In addition, MO 9 also contributes a destabilizing orbital

(45) We note that this analysis is based on Kohn−Sham orbitals, which in principle do not have the same physical significance as Hartree−Fock orbitals. Nevertheless, in most cases both sets of orbitals are very similar and yield the same qualitative conclusions.

Chart 3. AIM Analysis of MIN3 (Singlet)
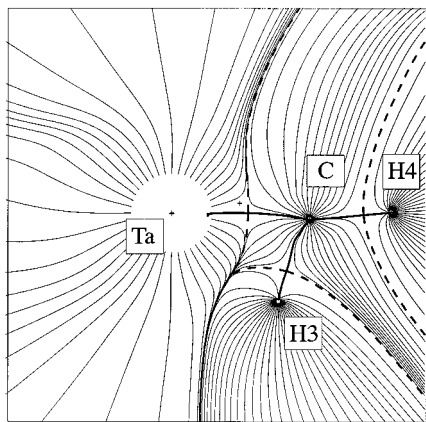
interaction between H3 and the carbon atom, which might explain the elongation of this C−H bond.

To gain further insight into the bonding situation of this species, an Atoms-in-Molecules (AIM) analysis by the method of Bader[46] and coworkers was carried out.

Chart 3 displays the gradient vector field of the electronic charge density for the singlet MIN3 and provides information about the bonding characteristics in this molecule. First, there are no indications for a bond critical point and a bond path which would characterize a covalent bond between tantalum and H3. The bond between the metal and the carbon atom is bent slightly outward, as already seen in MO 9 (Chart 2). Finally, H4 is linked by a regular σ-bond to the carbon atom and no interactions between H4 and the metal center are indicated. In conclusion, this analysis indicates a stabilizing interaction between the tantalum and H3, resulting in a shorter Ta−H3 bond and a small Ta−C−H3 bond angle. In contrast, there seems to be no significant interaction between Ta and H4 and the large Ta−C−H4 angle is simply a consequence of the regular H−C−H angle of some 120° in a carbon sp^2-hybridized environment.

The two minima MIN2 and MIN3 are connected through TS2 with an activation barrier of 21.7 kcal mol^{-1} relative to MIN2. TS2 is situated on the triplet surface; hence, the intersystem crossing takes place along the reaction coordinate between the transition state TS2 and MIN3. TS2 is characterized as a genuine saddle point by an imaginary frequency of 306.9i cm^{-1}. The components of the transition mode correspond to the direction which represents the reorientation in MIN3. In addition, that TS2 indeed connects MIN2 and MIN3 (triplet) has been confirmed by IRC calculations. From a structural point of view, the C−H2 bond in TS2 is very long and has to be considered as already being broken. At the same time, the carbenoid structure is formed to a considerable extent, as documented by the rather short Ta−C distance.

In contrast to the minimum MIN3, where both hydrogen atoms are connected to the tantalum center by σ-bonds without any interaction between these two hydrogen atoms, the next minimum along the reaction coordinate, MIN4, is formed as a cationic complex between a cationic tantalum carbene and a hydrogen molecule. The ground state of this complex is charac-

terized by two unpaired electrons; i.e., it corresponds to a triplet and is located 21.8 kcal mol^{-1} below the entrance channel. The corresponding singlet species is energetically very close, lying merely 2.5 kcal mol^{-1} above the triplet.

Transition state TS3 connects minima MIN3 and MIN4. The activation barrier amounts to 23.4 kcal mol^{-1} relative to MIN3. The ground state of TS3 has only paired electrons and lies on the singlet surface. The triplet state is slightly (1.2 kcal mol^{-1}) less stable than the singlet. Even though these small energy differences do not allow for an unequivocal conclusion, there seems to be again a change of the spin multiplicity between TS3 and MIN4. This saddle point is characterized by an imaginary frequency of 102.6i cm^{-1}. The components of the transition mode are indicative of the breaking of the Ta−H σ-bond. In comparison to those in the dihydrido minimum MIN3, the bonds between the tantalum atom and the hydrogen atoms are already significantly lengthened ($\Delta r_{\text{Ta}-\text{H1}} = 0.46$ Å), while the distance between the hydrogen atoms is in the typical range for an H−H bond ($r_{\text{H1}-\text{H2}} = 0.80$ Å). The calculated intrinsic reaction coordinates show that TS3 directly connects the minima MIN3 and MIN4.

The last minimum along the reaction coordinate, MIN4, is composed of molecular hydrogen, which is bound to the tantalum carbene moiety merely by electrostatic interactions. The next step is the loss of this molecular hydrogen molecule. The energetically most favored exit channel lies on the triplet surface and is given by the molecules Ta=CH$_2^+$ (^{3}A$_2$) and H$_2$ ($^1\Sigma_g^+$), while the singlet exit channel (Ta=CH$_2^+$ (^{1}A′) + H$_2$ ($^1\Sigma_g^+$)) is 10.3 kcal mol^{-1} higher in energy. The optimized structures of the singlet and triplet states of Ta=CH$_2^+$ are summarized in Figure 2. The triplet geometry adopts C_{2v} symmetry and has the electronic structure typical for a Schrock type carbene species: The σ-bond is due to donation from C to Ta, and the π-bond is due to the corresponding Ta−C back-donation.[44] We have also localized a $S = 2$ state (^{5}A$_2$) of TaCH$_2^+$, but it is energetically much less favored (22 and 11.7 kcal mol^{-1} higher than the triplet and singlet states, respectively). The triplet state lies 14.2 kcal mol^{-1} below the entrance channel, confirming the experimentally deduced overall exothermicity of the reaction. A lower bound for the binding energy of Ta=CH$_2^+$ is estimated experimentally as 111 kcal mol^{-1}.[25,26] As mentioned already above, our calculations yield a Ta−C binding energy of 119.4 kcal mol^{-1}, obtained from the ZPVE-corrected data of the fragments Ta$^+$ (^{5}F) and CH$_2$ (^{3}B$_1$) and from the ZPVE-corrected ground-state energy (^{3}A$_2$) of the molecule Ta=CH$_2^+$. This result is in good agreement with the experimental estimate as well as with the computationally predicted binding energy of 115 ± 5 kcal mol^{-1} reported by Irikura and Goddard,[27] who also identified a ^{3}A$_2$ ground state for cationic tantalum carbene. For the reasons discussed above, it is likely that the binding energy predicted from the current B3LYP calculations is slightly too high, due to the known tendency of DFT methods to overestimate binding energies[47] and the complete neglect of spin/orbit effects. The whole reaction proceeds below the energy of the Ta$^+$ + CH$_4$ entrance channel. TS1 represents the highest barrier but is still

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3.1 kcal mol^{-1} more stable than the Ta$^+$ + CH$_4$ asymptote. However, this saddle point is significantly (11.1 kcal mol^{-1}) above the TaCH$_2^+$ + H$_2$ asymptote, in complete harmony with the experimental fact that the back-reaction is not observed and the results from the deuterium exchange experiments described above. Finally, it should be noted that the sequence of steps identified in the present theoretical study for the Ta$^+$-mediated activation of methane bears many similarities to the reaction mechanism proposed empirically for this process by Buckner *et al.*[25]

Conclusions

Density functional calculations employing the B3LYP hybrid functional combined with an adequate one-particle description were carried out in order to identify the mechanism of the experimentally observed Ta$^+$-mediated methane activation. The reaction sequence consists of several steps, commencing with the formation of an electrostatically bound encounter complex, followed by the insertion of the Ta$^+$ into a C$-$H bond and the generation of a H$_2$TaCH$_2^+$ dihydrido species. Finally, this latter species rearranges into a productlike complex between molecular H$_2$ and a tantalum carbene cation, which ends the sequence by subsequent loss of H$_2$. The overall reaction is exothermic by 14 kcal mol^{-1} and proceeds completely below the energy of the entrance channel. The energetically most demanding saddle point connects the initial encounter complex with the C$-$H inserted species but is still 3.1 kcal mol^{-1} below the Ta$^+$ + CH$_4$ asymptote.

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